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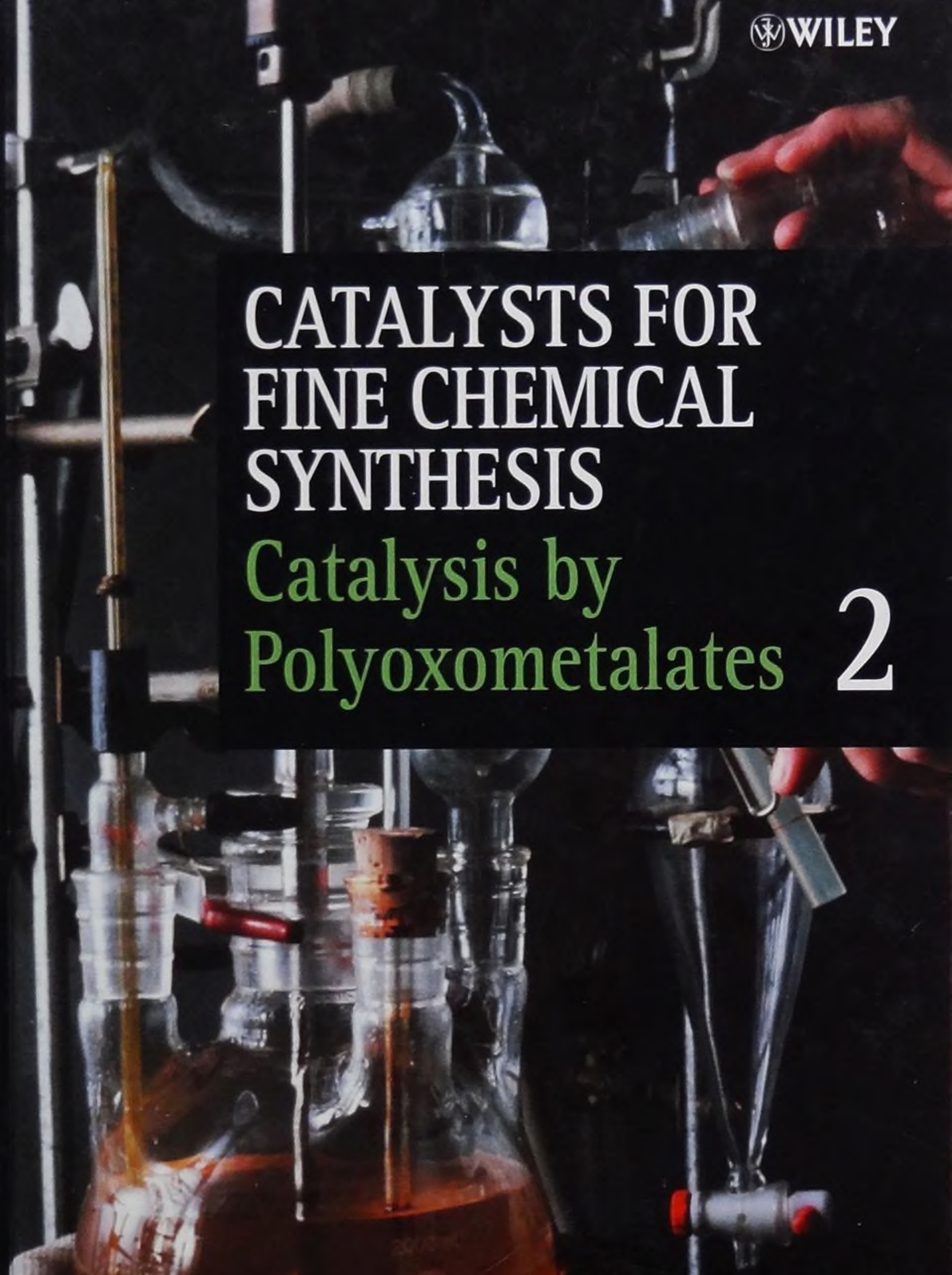

CATALYSTS FOR FINE CHEMICAL SYNTHESIS

Catalysis by Polyoxometalates

2

Ivan V. Kozhevnikov

Catalysts for Fine Chemical Synthesis

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Catalysts for Fine Chemical Synthesis

Volume 2

Catalysis by Polyoxometalates

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To Elena

Contents

Catalysts for Fine Chemical Synthesis Series Preface

During the early-to-mid 1990s we published a wide range of protocols, detailing the use of biotransformations in synthetic organic chemistry. The procedures were first published in the form of a loose-leaf laboratory manual and, recently, all the protocols have been collected together and published in book form (*Preparative Biotransformations*, Wiley-VCH, 1999).

Over the past few years the employment of enzymes and whole cells to carry out selected organic reactions has become much more commonplace. Very few research groups would now have any reservations about using commercially available biocatalysts such as lipases. Biotransformations have become accepted as powerful methodologies in synthetic organic chemistry.

Perhaps less clear to a newcomer to a particular area of chemistry is *when* to use biocatalysis as a key step in a synthesis, and when it is better to use one of the alternative non-natural catalysts that may be available. Therefore we set out to extend the objective of *Preparative Biotransformations*, so as to cover the whole panoply of catalytic methods available to the synthetic chemist, incorporating biocatalytic procedures where appropriate.

In keeping with the earlier format we aim to provide the readership with sufficient practical details for the preparation and successful use of the relevant catalyst. Coupled with these specific examples, a review of the products that may be obtained by a particular technology will be reviewed.

In the different volumes of this new series we will feature catalysts for oxidation and reduction reactions, hydrolysis protocols and catalytic systems for carbon–carbon bond formation *inter alia*. Many of the catalysts featured will be chiral, given the present day interest in the preparation of single-enantiomer fine chemicals. When appropriate, a catalyst type that is capable of a wide range of transformations will be featured. In these volumes the amount of practical data that is described will be proportionately less, and attention will be focused on the past uses of the system and its future potential.

Newcomers to a particular area of catalysis may use these volumes to validate their techniques, and, when a choice of methods is available, use the background information better to delineate the optimum strategy to try to accomplish a previously unknown conversion.

S.M. ROBERTS
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E. DEROUANE
LIVERPOOL, 2002

Preface for Volume 2: Catalysis by Polyoxometalates

The chemistry of polyoxometalates (heteropoly acids and heteropoly salts), started by Berzelius back in 1826, has now reached maturity. But it is still a rapidly developing field interconnected with many disciplines. Among numerous applications of polyoxometalates (Chapter 8), catalysis is by far the most important. Arguably, catalysis by polyoxometalates has been one of the most successful areas in fundamental and applied catalysis in the last few decades. Industry has now used polyoxometalates as catalysts for several large-scale chemical processes (Chapter 7). On the other hand, the enormous versatility of polyoxometalates offers significant opportunities for clean synthesis of fine and specialty chemicals. Consequently, much current research is focussed on various aspects of catalysis by polyoxometalates. Specific topics relevant to the field have been reviewed extensively (see references to Chapter 1).

This book presents a survey of recent developments in catalysis by polyoxometalates, both homogeneous and heterogeneous, focusing on its two major directions – acid catalysis and selective oxidation. The book is mainly addressed to academic and industrial chemists engaged with organic synthesis and catalysis who are concerned with research and development. The primary target is to facilitate a better understanding and promote a greater utilisation of catalysis by polyoxometalates in organic synthesis.

This book is written in the following sequence. Chapter 1 is an introduction, providing a brief historical overview of the field together with the scope, definitions and nomenclature of polyoxometalates. Chapter 2 gives a general review of the key physiochemical properties of polyoxometalates that underlie the catalysis by polyoxometalates. Knowledge of these properties is essential for understanding and practicing within the field. Chapter 3 briefly describes general methods of synthesis of polyoxometalates and provides the reader with a collection of laboratory procedures for the preparation of polyoxometalates that are most frequently used as catalysts for organic synthesis. The practical preparation of some specific acid and oxidation catalysts is also given. Most of information on catalysis by polyoxometalates is given in the following two chapters. Chapter 4 describes in detail the homogeneous and heterogeneous acid catalysis by heteropoly acids and salts. Likewise, Chapter 5 deals with the catalysis for selective oxidation. Miscellaneous catalytic applications as well as some new approaches to catalysis by polyoxometalates are described in Chapter 6. Use of polyoxometalates as catalysts in the chemical industry is highlighted in Chapter 7. Finally, Chapter 8 presents information on various applications of polyoxometalates other than catalysis.

Because this is an enormous field that crosses several disciplines, it has not been possible to describe every relevant work in detail. Consequently, I would recommend that the interested reader consult the references for further background. I have not attempted to provide a comprehensive bibliography, although I hope to have included most of important papers and reviews published by the mid-2001.

The author wishes to acknowledge several persons who directly or indirectly contributed to this book. I am especially grateful to Professor Klavdii I. Matveev who first introduced me, in the early 1970s, to the exciting chemistry and catalysis by polyoxometalates and who encouraged and supported our research in the 1970–80s in Boreskov Institute of Catalysis, Novosibirsk. I wish also to thank the late Professor Kirill Zamaraev for valuable discussions and support at that time. Sincere thanks are due to Professor Herman van Bekkum for his friendship and most enjoyable collaboration during my working in Delft in 1993–96. I wish to thank Professors Yusuke Izumi, Makoto Misono, and Yoshio Ono for their hospitality and most valuable discussions on catalysis by polyoxometalates during my visits to Japan. I should like to acknowledge Professor Michel Fournier for stimulating discussions and collaboration during my stay in Lille. Professors Eric Derouane and Stan Roberts of Liverpool University and Dr Martin Röthlisberger of John Wiley & Sons are thanked for their encouragement and support throughout this project.

I thank all my graduate students, postdoctoral fellows and colleagues, whose names appear in the bibliography, for their contribution to our research. I am grateful to Drs Geraldine Poignant and Rafiq Siddiqui who helped with the preparation of the manuscript. Finally, and most importantly, I thank my wife, Elena, for her patience and support.

Ivan Kozhevnikov
Liverpool, 2002

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1 Introduction

CONTENTS

1.1 SCOPE AND DEFINITIONS

Polyoxometalates belong to a large class of nanosized metal–oxygen cluster anions.[1,2] These form by a self-assembly process, typically in an acidic aqueous solution as illustrated by equations 1.1 and 1.2 and can be isolated as solids with an appropriate countercation, for example, H^+, alkali metal cation, NH_4^+, etc.

$$8\,H^+ + 7\,WO_4^{2-} \rightarrow [W_7O_{24}]^{6-} + 4\,H_2O \tag{1.1}$$

$$23\,H^+ + HPO_4^{2-} + 12\,MoO_4^{2-} \rightarrow [PMo_{12}O_{40}]^{3-} + 12\,H_2O \tag{1.2}$$

Generally, two types of polyoxometalates are distinguished as based on their chemical composition – isopoly anions and heteropoly anions. These anions may be represented by the general formulas:[1,2]

$[M_mO_y]^{p-}$	Isopoly anions
$[X_xM_mO_y]^{q-} (x \leq m)$	Heteropoly anions

where M is the addenda atom and X is the heteroatom also called the central atom when located in the centre of the polyanion. The distinction between the two groups is frequently artificial, especially in the case of mixed-addenda polyoxometalates.[2] Heteropoly compounds are by far more important for catalysis as well as for other applications; hence this book is mainly focused on them. Heteropoly acids – strong acids composed of heteropoly anions and protons as the countercations – constitute a special case of heteropoly compounds that is particularly important for catalytic applications.

The most common addenda atoms are molybdenum or tungsten, less frequently vanadium or niobium, or mixtures of these elements in their highest oxidation states (d^0, d^1). Much broader range of elements act as the heteroatoms; as such, almost all elements of the Periodic Table can be incorporated in heteropoly anions, most typical ones being P^{5+}, As^{5+}, Si^{4+}, Ge^{4+}, B^{3+}, etc. Molybdenum(VI) and tungsten(VI) are the best polyoxometalate formers as the result of a favourable combination of ionic radius and charge and of accessibility of empty d orbitals for metal–oxygen π bonding.[2]

1.2 NOMENCLATURE

A systematic nomenclature of polyoxometalates has been developed.[2,3] It uses a labelling system for the metal atoms and, in some cases, for the oxygen atoms to avoid ambiguity. The resulting names, however, are too long and complicated; these are practically never used for routine purposes.

In catalytic applications, only a relatively small number of well-known types of polyoxometalates have been involved so far, largely limited to the Keggin compounds and their derivatives. Usually, simplified conventional nomenclature, sometimes even trivial names, are sufficient for reporting and retrieving information in the field. Here we adopt the current nomenclature that treats polyoxometalates (also referred to as heteropoly anions, polyoxoanions, or polyanions) as quasi coordination complexes.[2] The heteroatom, if present, is considered as the central atom of a complex, and the addenda as the ligands. In the formulas of heteropoly anions, the heteroatoms are placed before the addenda, and the countercations before the heteroatoms; the heteropoly anion is placed in square brackets and thus separated from the countercations, as illustrated by the following examples:

$[SiW_{12}O_{40}]^{4-}$	12-tungstosilicate or dodecatungstosilicate
$H_3[PMo_{12}O_{40}]$	12-molybdophosphoric acid
$Na_5[PMo_{10}V_2O_{40}]$	sodium decamolybdodivanadophosphate

For simplicity, the countercations and the charge of polyanion and even the oxygen atoms may be omitted; for example, $Na_6[P_2Mo_{18}O_{62}]$ may be abbreviated to $\{P_2Mo_{18}O_{62}\}$ or P_2Mo_{18}.

1.3 HISTORICAL BACKGROUND

The history of polyoxometalates dates back to 1826 when Berzelius[4] discovered the first heteropoly salt, ammonium 12-molybdophosphate. Later on in 1848, Svanberg and Struve[5] introduced this compound in analytical chemistry as the basis for the determination of phosphorus that has been widely used since. By 1908, approximately 750 heteropoly compounds had been reported. However, the structure of polyoxometalates had remained a mystery for more than a century since their discovery. Werner,[6] Miolati,[7] Rosenheim,[8] and Pauling[9] proposed structures based on sharing metal–oxygen polyhedra. It was Keggin who in 1933 solved the structure of the most important 12:1 type of heteropoly anions by a powder X-ray diffraction study of $H_3[PW_{12}O_{40}]\cdot 5H_2O$.[10] This structure, now named after its discoverer, contained 12 WO_6 octahedra linked by edge and corner sharing, with the heteroatom occupying a tetrahedral hole in the centre. In 1948, Evans[11] determined the structure of another widespread type – the Anderson's heteropoly anion (6:1 series) – by single-crystal X-ray analysis of $[Te^{6+}Mo_6O_{24}]^{6-}$ salts; this structure is now often referred to as the Anderson–Evans structure. In 1953, Dawson[12] reported the next new structure (now frequently referred to as the Wells–Dawson's) of a 18:2 heteropoly anion $[P_2W_{18}O_{62}]^{6-}$. This structure was shown to be closely related to the Keggin structure. In 1968, Dexter and Silverton[13] reported the X-ray structure of $[Ce^{4+}Mo_{12}O_{42}]^{8-}$ and showed the large Ce heteroatom to be in a CeO_{12} central icosahedron. By the early 1970s, the chemistry of polyoxometalates had been greatly expanded. This period is associated with extensive work of many groups and especially those of Souchay (France), Ripan (Rumania), Spitsyn (USSR) and Baker (USA). In the 1980–90s, the number of groups involved in the field increased enormously in parallel with expanding applications of polyoxometalates. Recently Baker and Glick[14] reviewed the history of polyoxometalate chemistry and contributions of various groups to date. By 1995, the X-ray structures of approximately 180 polyoxometalates had been reported.[15] Among them, salts of giant heteropoly anions such as $[La_{16}As_{12}W_{148}O_{524}]^{76-}$ (ion mass ca. 40000, diameter 40 Å) and others were prepared and characterised by Müller *et al.*[16] The application of modern characterisation techniques had led to much better understanding of the structural principles of polyoxometalates and their properties. However, there is still plenty of scope for further work in this field, as many fundamental questions regarding the structural principles, mechanisms of synthesis and reactivity of polyoxometalates remain unanswered.

The chemistry of polyoxometalates has been reviewed extensively. This includes classical monographs by Souchay[1,17] and Pope[2] and also by Nikitina[18] and a large number of review articles, for example Ref.[15,19–26] Much useful information about the chemistry and various applications of polyoxometalates, including the nomenclature, synthesis of organic and organometallic derivatives of polyoxometalates, electron-transfer reactions, very large polyoxometalate clusters, solution equilibria, polyoxometalate-based molecular materials, scanning probe microscopy of polyoxometalate surfaces, photo- and electrochromism, and application of polyoxometalates in medicine, can be found in the recent collections.[27,28]

1.4 INTRODUCTION TO CATALYSIS BY POLYOXOMETALATES

Among numerous applications of heteropoly compounds, catalysis is by far the most important. Presently, over 80% of the patent applications concerning with polyoxometalates is related to catalysis.[29] First attempts to use polyoxometalates as catalysts can be traced back to the beginning of the twentieth century. Compilations of early works up to 1973 are available.[30]

Systematic investigation of catalysis by polyoxometalates began in the early 1970s when the great potential of these compounds for catalytic applications became apparent. Most of pioneering work at that time was carried out in Japan (Izumi, Misono, Ono, Otake, Yoneda and co-workers) and Russia (Matveev and co-workers). The string of successful industrial applications of polyoxometalate catalysts in the 1970–80s triggered an explosion of innovative research in this field; the rapid development has continued to date and is bound to move on in the future.

Heteropoly compounds have several advantages as catalysts, the most important being their *multifunctionality* and *structural mobility*. On the one hand, they (heteropoly acids) have a very strong Brønsted acidity; on the other, they are efficient oxidants, exhibiting fast reversible multielectron redox transformations under mild conditions. Their acid–base and redox properties can be varied over a wide range by changing the chemical composition. Solid heteropoly compounds possess a discrete ionic structure, comprising fairly mobile structural units – heteropoly anions and countercations – unlike the network structure of, e.g., zeolites and metal oxides. The structure is frequently preserved upon substitution or oxidation/reduction and manifests itself to exhibit extremely high proton mobility and a 'pseudoliquid phase' (Chapter 2). On top of that, many heteropoly compounds have a very high solubility in polar solvents and fairly high thermal stability in the solid state.

Because of their unique properties heteropoly compounds are promising acid, redox, and bifunctional (acid and redox) catalysts. The catalytic reactions can be performed in homogeneous as well as in heterogeneous (gas–solid, liquid–solid or biphasic liquid–liquid) systems. Heteropoly compounds are frequently used as model systems for fundamental research, providing unique opportunities for mechanistic studies on the molecular level. At the same time, they have become increasingly important for applied catalysis.

In the 1970–80s, several new industrial chemical processes utilising polyoxometalate catalysis were developed and commercialised in Japan.[31,32] The first commercial process was the liquid-phase hydration of propene to 2-propanol launched in 1972. It followed by the vapour-phase oxidation of methacrolein to methacrylic acid in 1982, the liquid-phase hydration of isobutene for its separation from the butane–butene fraction in 1984, the biphasic polymerisation of tetrahydrofuran to polymeric diol in 1985, the hydration of n-butenes to 2-butanol in 1989 and other processes. More recently, in 1997, the direct oxidation of ethylene to acetic acid was industrialised by Showa Denko and, in 2001, the production of ethyl acetate using a heteropoly acid catalyst was launched by BP Amoco (Chapter 7).

Many reviews on catalysis by polyoxometalates have been published. Otake and Onoda[33] (1976) reviewed early works on heterogeneous catalysis; Matveev[34] (1977), Matveev and Kozhevnikov[35–37] (1980, 1982, 1983), Kozhevnikov[38,39] (1987, 1998), and Jansen *et al.*[40] (1994) discussed the acid and oxidation catalysis in liquid phase; Izumi *et al.*[32] (1992) and Ono[41] (1992) gave comprehensive survey of polyoxometalate catalysis to that date; Kozhevnikov[42,43] (1993, 1995) described catalysis for fine chemicals synthesis; Misono[44,45] (1987, 1988, 1993), Moffat[46] (1987, 1989), Corma[47] (1995), Mizuno and Misono[48] (1998), and Misono (2001)[49] reviewed heterogeneous acid and oxidation catalysis by polyoxometalates; Misono and Nojiri[31] (1990) described industrial applications of polyoxometalate catalysts; Mizuno and Misono[50] (1998) described light alkane functionalisation by polyoxometalate catalysis; Okuhara, Mizuno, and Misono[51] (1996) published the most comprehensive review of the field to that date; Papaconstantinou[52] (1989, 2001) and Yamase[53] (1998) addressed photocatalysis; Ishii and Ogawa[54] (1990) described catalysis for hydroperoxide oxidations; Hill and Prosser-McCartha[55] (1995) and Neumann[56] (1998) discussed transition metal substituted polyoxometalates as catalysts for liquid-phase oxidation; Cavani[57] (1998) described catalysis for vapour-phase oxidation of hydrocarbons; Kuznetsova *et al.*[59] (1999) addressed the use of polyoxometalates for studies of catalyst active sites; and Misono[58] (2000) reviewed 'green' aspects of heteropoly acid catalysis. The recent monograph by Moffat[60] describes the surface properties of polyoxometalates and their use for heterogeneous catalysis. Centi, Cavani, and Trifirò[61] reviewed the heterogeneous catalysis by polyoxometalates for selective oxidation in their recent book.

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2 Properties of Polyoxometalates

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Properties of many polyoxometalates have been studied in detail and thoroughly reviewed[1–4] (see also Section 1.3). A variety of physicochemical and spectroscopic techniques have been applied for the characterisation of polyoxometalates both in solution and in solid state. For methods of characterisation in solution, the reader should consult the monograph by Pope,[1] for solid-state characterisation, the review by Okuhara *et al.*[2c] and the monograph by Moffat[2f] will be most useful.

In this chapter, we will discuss some physicochemical properties of polyoxometalates that are of great importance for their catalytic applications. These include the structure of polyoxometalates, their thermal stability, solubility, formation and state in solution, acid–base and redox properties.

2.1 STRUCTURES OF POLYOXOMETALATES

2.1.1 GENERAL PRINCIPLES

Dozens of structural types and stoichiometries of polyoxometalates are known to date. The minimum degree of condensation of addenda atoms is arbitrarily set to be in the range of 2 to 6.[1,2a] The maximum can go to as high as a few hundred. For example, the giant heteropoly tungstate $[La_{16}As_{12}W_{148}O_{524}]^{76-}$ (relative molecular mass ca. 40000, diameter 4 nm) includes 28 heteroatoms (La, As) and 148 addenda atoms (W).[3]

Two general principles apply to polyoxometalate structures:[1,4]

1. Addenda atoms occupy a metal–oxygen polyhedron MO_x that is most commonly an octahedron. In this polyhedron, the metal atom is displaced from the inversion centre towards the peripheral vertice because of metal–oxygen π bonding.
2. Structures with MO_6 octahedra that contain more than two free vertices are generally not found among the typical polyoxometalates. This is known as the Lipscomb restriction,[5] which may be explained as a result of the strong trans influence of the terminal M = O bonds that facilitates dissociation of MO_3 from the polyanion.

According to Pope and Müller,[4] it is convenient to discuss the variety of polyoxometalate structures starting from a few highly symmetrical 'parent' polyanions; then many other polyoxometalate structures may be considered as their 'derivatives'. There are three such parent structures, with a tetrahedron, an octahedron, and an icosahedron as their central polyhedron XO_n (n = 4, 6 or 12) that determines the symmetry of the whole polyanion. These structures, that have already been mentioned, are: the Keggin structure (T_d symmetry); the structure of a hypothetical anion $\{XM_{12}O_{38}\}$ (O_h), that has not yet been observed itself but its derivatives, for example the Anderson–Evans anion $\{XM_6O_{24}\}$, are well known; and the Dexter–Silverton structure (I_h). These structures will be briefly discussed below.

2.1.2 THE KEGGIN STRUCTURE

This is the first characterised[6] and the best-known structure that is adopted by many polyoxometalates. Among a wide variety of heteropoly compounds, the Keggins are the most stable and more easily available. These, together with some of their derivatives, are the most important for catalysis.

The Keggin heteropoly anions are typically represented by the formula $[XM_{12}O_{40}]^{x-8}$, where X is the heteroatom, x is its oxidation state, and M is the addenda atom (usually Mo^{6+} or W^{6+}). The M^{6+} ions can be substituted by many other metal ions, e.g., V^{5+}, Co^{2+}, Zn^{2+}, etc. The Keggin anion has a diameter of ca. 1.2 nm and is composed of a central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal–oxygen octahedra MO_6 (Figure 2.1).[1,6] The octahedra are arranged in four M_3O_{13} groups. Each group is formed by three octahedra sharing edges and having a common oxygen atom which is also shared with the central tetrahedron XO_4. The total assemblage contains 40 close-packed oxygen atoms. The oxygens are of four types: twelve terminal M = O, twelve edge-bridging angular M–O–M shared by the octahedra within a M_3O_{13} group, twelve corner-bridging quasi-linear M–O–M connecting two different M_3O_{13} groups, and four internal X–O–M. These oxygens can be discriminated by ^{17}O NMR.[1] The corresponding bonds exhibit characteristic infrared bands in the range of 600–1100 cm^{-1}.[1]

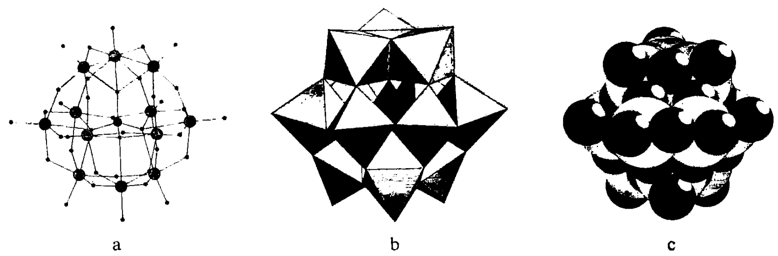


Figure 2.1 Bond (a), polyhedral (b) and space-filling (c) representations of the Keggin structure of the $[XM_{12}O_{40}]^{x-8}$ anion (α isomer).[1]

Each of the M_3O_{13} groups can be rotated 60° about its 3-fold axis which leads to geometrical isomers. The structure shown in Figure 2.1 is the most common α isomer of the Keggin structure. Rotation of one of its M_3O_{13} groups produces the β isomer; its structure is shown in Figure 2.2. In some cases, these isomers can be separated, e.g., by fractional crystallisation. Rotation of two, three or all four M_3O_{13} groups produces the γ, δ, and ε isomer, respectively.[1]

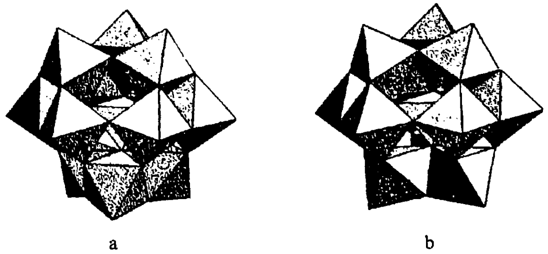


Figure 2.2 The Keggin structure of the $[XM_{12}O_{40}]^{x-8}$ anion: (a) α isomer and (b) β isomer.

Lacunary derivatives of the Keggin anion result from the removal of one or more M atoms. Examples of three lacunary derivatives (one monovacant and two trivacant) of the α-Keggin anion are shown in Figure 2.3. The two trivacant species correspond to loss of a corner-shared group of MO_6 octahedra (A-type $\{XM_9\}$) or an edge-shared group (B-type $\{XM_9\}$).[1] Such species can assemble into larger polyoxometalate structures, either directly or with incorporation of metal ion linkers.

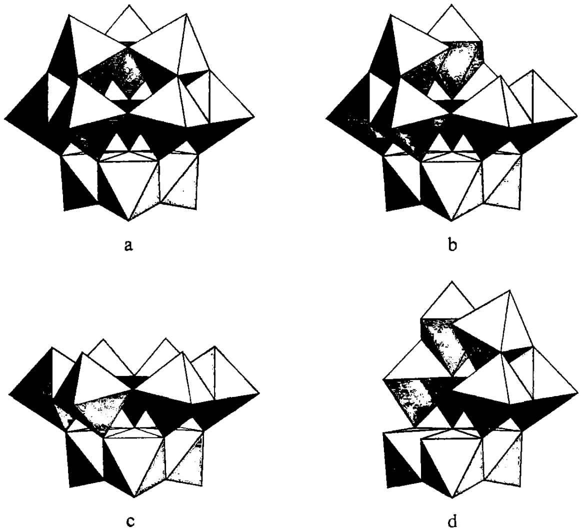


Figure 2.3 The structures of the α-Keggin anion $[XM_{12}O_{40}]^{x-8}$ (a) and its lacunary derivatives: (b) monovacant, (c) trivacant A-$\{XM_9\}$, and (d) trivacant B-$\{XM_9\}$.[1]

2.1.3 THE WELLS–DAWSON STRUCTURE

One of these derivatives is the Wells–Dawson dimeric (2:18) heteropoly anion $[X_2M_{18}O_{62}]^{2x-16}$($M = Mo^{6+}$ or $W^{6+}, X = P^{5+}$ or As^{5+}). Its structure (α isomer) is shown in Figure 2.4. The anion consists of two trivacant lacunary Keggin species $A-\{XM_9\}$ linked directly across the lacunae. The Wells–Dawson structure contains two M_3O_{13} groups. A 60° rotation of one of these groups about its 3-fold axis gives the β isomer. The molybdenum anion is chiral because of a displacement of the Mo atoms within their MoO_6 octahedra. The tungsten complex shows no such chirality probably because of the greater rigidity of the tungsten framework.[1,7]

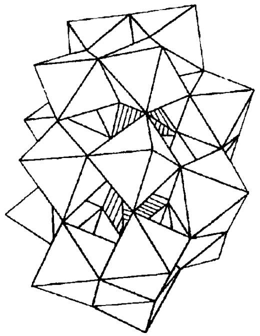


Figure 2.4 The Wells–Dawson structure of the $[X_2M_{18}O_{62}]^{2x-16}$ anion (α isomer).

2.1.4 THE ANDERSON–EVANS STRUCTURE

This example represents a different structural type with an octahedron as a central polyhedron. The Anderson–Evans structure is adopted by 6-heteropoly anions (e.g. $[Te^{6+}Mo_6O_{24}]^{6-}$).[1,8] It consists of six coplanar MO_6 octahedra arranged in a closed ring sharing edges. The heteroatom occupies the octahedral pocket in the centre of the ring (Figure 2.5).

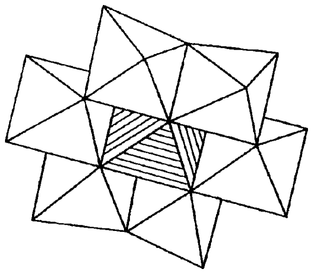


Figure 2.5 The Anderson–Evans structure of the $[Te^{6+}Mo_6O_{24}]^{6-}$ anion.[1]

2.1.5 THE DEXTER–SILVERTON STRUCTURE

A less common type of 12-heteropoly anions $[XM_{12}O_{42}]^{x-12}$, where M is molybdenum(VI) and X is cerium(IV), uranium(IV), or thorium(IV), adopt this structure (Figure 2.6). In this anion, the central atom is surrounded by twelve oxygen atoms that form an icosahedron as a central polyhedron. The MO_6 octahedra are arranged in face-sharing pairs.[1,9]

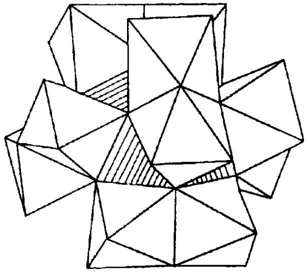


Figure 2.6 The Dexter–Silverton structure of the $[XM_{12}O_{42}]^{x-12}$ anion.[1]

2.2 CRYSTAL STRUCTURE OF HETEROPOLY COMPOUNDS

Generally, solid heteropoly compounds (heteropoly acids and salts) form ionic crystals.[10] Such solids frequently have large interstices between the big heteropoly anions which accommodate a large amount of water of crystallisation (up to 30 molecules per heteropoly unit and more) as well as the countercations. These water molecules are hydrogen-bonded together and are often zeolitic, i.e. easily and reversibly removable from the solid which can be usually done by heating to 100–150 °C. The crystal structure of heteropoly compounds varies with the extent of hydration, for example 12-tungstophosphoric acid exhibits different packing arrangements as the hydration water is lost (Table 2.1). The hydration–dehydration process is frequently accompanied by changing (expanding or shrinking) the volume of the crystal cell. Not only water but also many polar organic molecules, such as alcohols, ketones, ethers, amines, sulfoxides, etc., can enter and leave the structure – which can have important consequences on heterogeneous catalysis by solid heteropoly compounds (Section 4).[2c,11,12] The nature of organic solvates and their thermal decomposition have been investigated.[13]

Figure 2.7 shows a fragment of the structure of the Keggin heteropoly acid $H_3[PW_{12}O_{40}] \cdot 6H_2O$ determined by single-crystal X-ray analysis.[14a] The crystal lattice is formed by packing heteropoly anions into a body-centred cubic structure. Doubly hydrated protons $H_5O_2^+$ link four neighbouring anions by forming hydrogen bonds with the terminal W=O oxygens.

Table 2.1 Crystal structures of 12-tungstophosphoric acid hydrates.

Hydrate	Space group	Reference
$H_3[PW_{12}O_{40}]$ $29H_2O$	cubic *Fd3m*	14b
$H_3[PW_{12}O_{40}]$ $21H_2O$	orthorhombic *Pcca*	14c
$H_3[PW_{12}O_{40}]$ $14H_2O$	triclinic *P1*	14d
$H_3[PW_{12}O_{40}]$ $6H_2O$	cubic *Pn3m*	14a

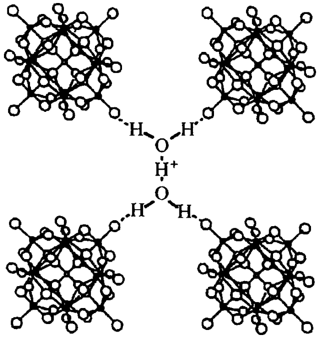


Figure 2.7 Crystal packing of $H_3[PW_{12}O_{40}]{\cdot}6H_2O$.[14a]

Crystals of heteropoly compounds usually have very low lattice energies. The anionic charge of the big heteropoly units is delocalised over a large number of atoms, thus greatly diminishing electrostatic attractions. The exterior of typical heteropoly anions consists of oxygens that are strongly polarised towards the addenda, and hence nonpolarisable in other directions. These nonbasic oxygens lack the ability to form hydrogen bonds of normal strength.[10] As a result, heteropoly anions are weakly solvated in solution, and the crystal structure of heteropoly compounds is frequently quite mobile unlike the rigid network structure of metal oxides or zeolites. Such structural flexibility is important when using these compounds as solid catalysts[2c,11,12] (Chapters 4 and 5).

Misono *et al.*[2c,11,12] advanced a special structural classification that recognises the importance of structural flexibility of solid heteropoly compounds. This classification, which is now widely adopted in heterogeneous catalysis by polyoxometalates, distinguishes the primary structure (polyoxoanion structure), the secondary structure (crystal structure and packing), and the tertiary structure (texture of solids, i.e. particle size, porosity, surface area, distribution of protons, etc.). This structural hierarchy is schematically illustrated in Figure 2.8.

2.3 THERMAL STABILITY

The thermal stability of heteropoly compounds is of great importance for their use in heterogeneous catalysis.[2c,2f] Some compounds are fairly stable and can be applied as catalysts at moderately high temperatures, up to 300–350 °C. The thermal stability, however, may not be sufficient for catalyst regeneration, for example, for burning coke that may form on the catalyst surface (Section 4.5).

Thermal decomposition of polyoxometalates (to eventually form a mixture of oxides) is a complex multistage process.[2f] The catalyst activity may be irreversibly lost at an early stage of decomposition. For example, solid acid

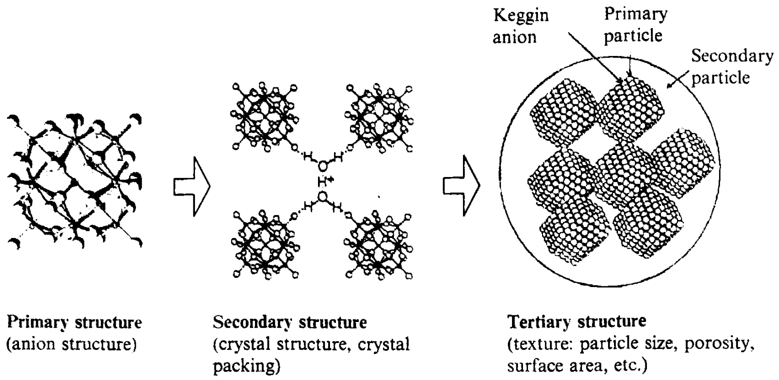


Figure 2.8 Structural hierarchy of heteropoly compounds.[2c]

catalysts based on tungsten heteropoly acids (e.g. $H_3[PW_{12}O_{40}]$) probably lose activity at the onset of thermal decomposition of the Keggin structure, when the acid protons are lost (see below), i.e. well before the formation of WO_3 and P_2O_5 is complete.

The thermal stability is usually determined by thermal analytical methods (thermal gravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC)) frequently in combination with other techniques, such as X-ray diffraction, infrared spectroscopy, solid state NMR, etc., Tsigdinos[15] introduced a simple method that allows estimating the thermal stability of heteropoly compounds. This method includes heat treatment followed by a solubility test. If, after heating, the compound is soluble in water its structure is deemed to remain intact; otherwise the structure has decomposed.

A great deal of caution should be taken when comparing the thermal stabilities from different sources. The decomposition temperatures are subject to many parameters such as the heating rate, the amount of sample, the shape of crucible, the purity of the sample, the atmosphere, etc. On top of that, the decomposition on the surface of the sample may occur at a lower temperature than in the bulk.

Figure 2.9 shows the TGA profile for $H_3[PW_{12}O_{40}]$ hydrate. Three main peaks can be observed: (1) a peak at a temperature below 100 °C corresponding to the loss of physisorbed (zeolitic) water (a variable amount depending on the number of hydration waters in the sample); (2) a peak in the temperature range of 100–280 °C centred at about 200 °C accounted for the loss of ca. $6H_2O$ molecules per Keggin unit, corresponding to the dehydration of a relatively stable hexahydrate $H_3[PW_{12}O_{40}] \cdot 6H_2O$ in which the waters are hydrogen-bonded to the acidic protons; and (3) a peak in the range of 370–600 °C centred at about 470 °C due to the loss of 1.5 H_2O molecules corresponding to the loss of all acidic protons and the beginning of decomposition of the Keggin structure.[2a,2c,2f,10]

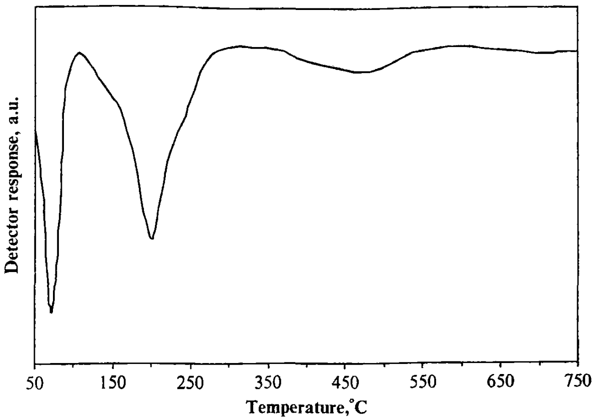


Figure 2.9 Derivative thermogravimetry for $H_3[PW_{12}O_{40}]$ hydrate.

Generally, Keggin-type heteropoly compounds are the most stable among various polyoxometalates. The decomposition temperature (°C) for the most typical Keggin heteropoly acids, as estimated from TGA, decreases in the following series:[16a]

$$\begin{array}{ccccccc} H_3[PW_{12}O_{40}] & < & H_4[SiW_{12}O_{40}] & < & H_3[PMo_{12}O_{40}] & < & H_4[SiMo_{12}O_{40}] \\ 465 & & 445 & & 375 & & 350 \end{array}$$

For practical purposes, the onset of decomposition should be taken into account. Such data have been compiled[2a] and some of them are presented in Table 2.2.

High-temperature exothermic peaks observed in DTA and DSC studies have been used to estimate the thermal stability of heteropoly acids.[2f] These peaks

Table 2.2 The onset of thermal decomposition of solid heteropoly acids[2a].

HPA	T (°C)	Reference
$H_3[PW_{12}O_{40}]$	400	15,17
$H_3[PMo_{12}O_{40}]$	300	15,17
$H_4[SiW_{12}O_{40}]$	370	15,17
$H_4[SiMo_{12}O_{40}]$	200	15
$H_3[BW_{12}O_{40}]$	240	15,17
$H_4[PW_{11}VO_{40}]$	300	15,18,19
$H_4[PMo_{11}VO_{40}]$	400	19

may be attributed to the complete decomposition of the Keggin structure to form a mixture of oxides. This method gives the decomposition temperatures that are too high to represent the stability of solid heteropoly acid catalysts. For example, for the above series of acids, Izumi *et al.*[16b] reported the decomposition temperatures of 610, 540, 495, and 375 °C, respectively. Similar results were also reported by Varga *et al.*[16c]

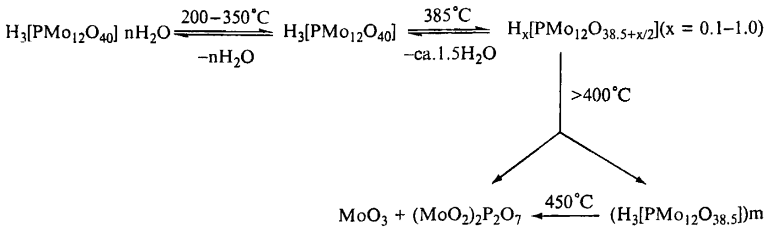
Heteropoly salts are frequently more stable than the parent acids. The relative stabilities, however, depend on the countercation. Thus, for $H_3[PMo_{12}O_{40}]$ and its salts the following decomposition temperatures (°C), estimated from DTA peaks, were reported:[20]

$$Ba^{2+}, Co^{2+}(400) < Cu^{2+}, Ni^{2+}(410) < H^+, Cd^{2+}(420) < Ca^{2+}, Mn^{2+}(427)$$
$$< Mg^{2+}(437) < La^{3+}, Ce^{3+}(457)$$

The acidic cesium salt $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ is more stable than $H_3[PW_{12}O_{40}]$; no decomposition of the salt was observed at 500 °C.[21] The Wells–Dawson heteropoly salts $K_6[P_2W_{18}O_{62}]$ and $K_7[P_2VW_{17}O_{62}]$ were found to be stable up to 400 °C.[22]

Partially reduced heteropoly acids may be more stable than the fully oxidised forms. For example, 12-molybdosilicic acid reduced by two or four electrons per Keggin unit was found to decompose at higher temperatures than the oxidised form.[2a,23]

Partially decomposed 12-molybdophosphoric acid may be reconstructed under wet atmosphere.[2f,24,25] As found by *in situ* XRD and ^{31}P NMR, the thermal decomposition of $H_3[PMo_{12}O_{40}]$ hydrate occurs in several steps, the first two steps being reversible, as shown in Scheme 2.1.[26] The compound $H_x[PMo_{12}O_{38.5+x/2}]$ rehydrates into $H_3[PMo_{12}O_{40}]$ hydrate upon exposure to wet air.



Scheme 2.1

Substitution of one vanadium(V) for molybdenum(VI) in $H_3[PMo_{12}O_{40}]$ increases the thermal stability; the stability decreases upon further substitution, however.[2a] Upon heat treatment of solid $H_4[PMo_{11}VO_{40}]$, vanadyl and molybdenyl species leave the Keggin unit.[27] Substitution of Cs^+ for proton in $H_4[PMo_{11}VO_{40}]$ stabilises the structure, while the presence of water vapour enhances its desintegration.[27b]

2.4 SOLUBILITY

As the lattice energies of heteropoly compounds are low, and so are the solvation energies of heteropoly anions, the solubility of heteropoly compounds largely depends on the solvation energy of the cation. Heteropoly acids are extremely soluble in water and oxygen-containing organic solvents such as lower alcohols, ethers, etc., but not in nonpolar solvents such as benzene or petroleum ether. For example, the solubility (wt%) of the acid $H_4[SiMo_{12}O_{40}] \cdot 8H_2O$ is 88 in water, 86 in ethyl acetate, and 85 in diethyl ether at 25 °C.[15] However, the solubility drops sharply when anhydrous heteropoly acids and thoroughly dried nonaqueous solvents are used. Salts with small cations, such as Li^+ or Na^+, are readily soluble as well. In contrast, salts of large cations, e.g., K^+, Cs^+, NH_4^+, etc., are insoluble in water. Salts of large organic cations such as tetrabutylammonium are insoluble in water but soluble in organic solvents,[1] which is frequently used for the isolation of polyoxometalates as well as for catalysis in organic media (Section 5.1).

2.5 FORMATION AND STATE IN SOLUTION

The majority of polyoxometalates have been obtained and studied in aqueous solution. Nonaqueous chemistry, although important for various applications, is less developed. Nearly spherical Keggin anions have a very low negative charge density on the peripheral oxygens, and the exterior oxygens form only very weak hydrogen bonds. As a result, the anions are weakly solvated in solution. Their hydrodynamic radii, as shown by viscosity and diffusion measurements, frequently coincide with their crystallographic radii.[10] Heteropoly anions are typically very weak ligands. The latter, however, does not apply to lacunary anions (see below). The Keggin heteropoly electrolytes (acids and salts) are usually fully dissociated in solution.[1,10]

2.5.1 STABILITY OF POLYOXOMETALATES IN SOLUTION

In solution of a polyoxometalate, several species frequently exist in equilibrium, depending on the pH,[28] as shown in Figure 2.10 for an aqueous solution containing HPO_4^{2-} and MoO_4^{2-} at a molar ratio of 1:12.[29] The compound that crystallises from solution may not necessarily be the most abundant one. Figure 2.11 shows the pH range of existence for various polyoxometalates in aqueous solution.[28] Polyoxometalate solutions frequently equilibrate quite quickly, in seconds; in some cases, however, it takes several months.[30]

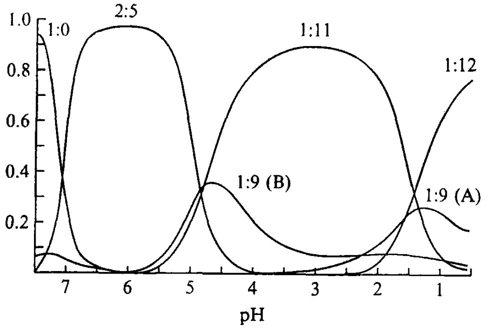


Figure 2.10 Distribution diagram for species present in fresh solutions containing $[MoO_4]^{2-}$ and $[HPO_4]^{2-}$ in a molar ratio of 12:1 at different pH values. The P:Mo ratio is shown for each complex.[29]

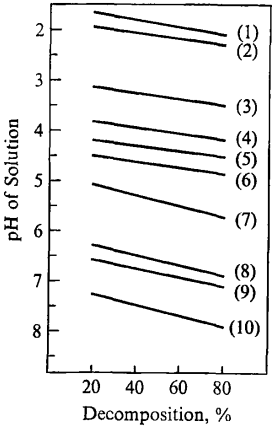


Figure 2.11 pH range of existence of polyoxometalates:[28] (1) $[PMo_{12}O_{40}]^{3-}$, (2) $[PW_{12}O_{40}]^{3-}$, (3) $[GeMo_{12}O_{40}]^{4-}$, (4) $[GeW_{12}O_{40}]^{4-}$, (5) $[P_2W_{18}O_{62}]^{6-}$, (6) $[SiW_{12}O_{40}]^{4-}$, (7) $[PMo_{11}O_{39}]^{7-}$, (8) $[P_2Mo_5O_{23}]^{6-}$, (9) $[H_2W_{12}O_{40}]^{6-}$, (10) $[PW_{11}O_{39}]^{7-}$.

Many studies show that the typical Keggin heteropoly acids retain the structure of polyanion in aqueous solution, at least at a relatively high concentration.[1] This has been demonstrated by XRD, IR and Raman spectroscopy as well as by ^{17}O NMR (Ref.[31] and references therein). However, in dilute ($<10^{-2}$ mol l^{-1}) solutions, degradation of polyanion may occur.

Generally the stability of 12-heteropoly anions towards hydrolysis in aqueous solution decreases in the order of addenda atoms:[15,28]

$$W(VI) > Mo(VI) > V(V).$$

The stability of the molybdenum(VI) heteropoly anions decreases in the series of heteroatoms:[15,28]

$$Si^{4+} > Ti^{4+}, Zr^{4+} > Ge^{4+} > P^{5+} > As^{5+}.$$

12-Molybdophosphate exists in aqueous solution at pH ≤ 1.5 (Figure 2.10). As the pH increases, it undergoes alkaline hydrolysis, which occurs via the following steps in dilute ($< 10^{-3}$ mol l^{-1}) solution:[15,28]

$$[PMo_{12}O_{40}]^{3-} \overset{OH^-}{\rightleftarrows} [PMo_{11}O_{39}]^{7-} + MoO_4{}^{2-} \overset{OH^-}{\rightleftarrows} H[P_2Mo_5O_{23}]^{5-} + MoO_4{}^{2-} \overset{OH^-}{\rightleftarrows} HPO_4{}^{2-} + MoO_4{}^{2-}$$

In concentrated solutions ($\sim 10^{-1}$ mol l^{-1}), the hydrolysis proceeds via the formation of the dimeric 9-molybdophosphate $[P_2Mo_{18}O_{62}]^{6-}$ as an intermediate. The polyanions with P:Mo ratios of 1:9, 2:18, and 2:5 predominate in the $H^+-MoO_4{}^{2-}-HPO_4{}^{2-}$ system at pH 1.5–6.0; their stability constants have been determined.[29] In stronger acidic media (pH < 1.5), the heteropoly anions undergo acid hydrolysis forming defect polyanions and oxomolybdenum(VI) cations.

The stability of polyoxometalates increases in organic media. It has been shown by the conductivity method that heteropoly acids such as $H_3[PW_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$, $H_4[SiMo_{12}O_{40}]$, $H_4[PW_{11}VO_{40}]$, and $H_4[PMo_{11}VO_{40}]$ are stable towards solvolysis in ethanol, acetone, and acetic acid at concentrations as low as $10^{-5}-10^{-6}$ mol l^{-1}.[32,33]

The solution chemistry of the mixed-addenda heteropoly anions $[PMo_{12-n}V_nO_{40}]^{(3+n)-}$ (HPA-n) that are used as catalysts for liquid-phase oxidation (Chapter 5) has been studied in detail. Substitution of vanadium(V) for molybdenum(VI) increases the stability of the heteropoly anion to a certain degree.[28] Stability of the corresponding acids in aqueous solution decreases with increasing n in the sequence HPA-1 > HPA-2 > HPA-3.[28] The acids with $n > 3$ have not been isolated,[34] but their salts are known. The most stable anion $[PMo_{11}VO_{40}]^{4-}$ begins to hydrolyse only in 0.8 mol l^{-1} HCl.[30] As the acidity increases, the anions with $n > 1$ lose vanadium to give the anions with smaller n, for example:[35]

$$10\{PMo_9V_3O_{40}\} + H^+ \rightleftarrows 9\{PMo_{10}V_2O_{40}\} + 12\,VO_2{}^+ + HPO_4{}^{2-}$$

In this equation, the acidic protons are omitted in polyanion formulas. The anions $\{PMo_9V_3O_{40}\}$ and $\{PMo_6V_6O_{40}\}$ are stable at the pH 2.5–5.5.[30] At the pH 1–3 the anions $\{PMo_{12-n}V_nO_{40}\}$ disproportionate:[35]

$$2\{PMo_{11}VO_{40}\} \rightleftarrows \{PMo_{12}O_{40}\} + \{PMo_{10}V_2O_{40}\}$$

Similar disproportionation of $\{PW_{11}VO_{40}\}$ was found to be second order with respect to the polyanion, the reaction rate increasing with the pH and ionic strength.[36]

The Keggin, Wells–Dawson and other types of heteropoly anions form lacunary (defect) species in solution at an appropriate pH.[1,28] The lacunary anions have one or more vacancies created by the loss of addenda atom(s) from the structure. For example, $[PW_{12}O_{40}]^{3-}$ forms the lacunary anion $[PW_{11}O_{39}]^{7-}$ at the pH 2 in aqueous solution:

$$[PW_{12}O_{40}]^{3-} \rightleftarrows [PW_9O_{39}]^{9-} + W(VI)$$

The lacunary anion is stable until pH ~ 8, then further degrades to give the trivacant lacunary species $[PW_9O_{34}]^{9-}$.[1] The vacancies thus formed have great coordination ability; numerous metal complexes with lacunary structures are known (Section 2.5.2).[1,37]

2.5.2 POLYOXOMETALATES AS LIGANDS

Two types of complex formation with polyoxometalate ligands can be distinguished: (1) whole structures binding metal cations via surface terminal and bridging oxygen atoms; and (2) lacunary structures enclosing metal cations in the vacancies.[1,4]

Complexes of the first type are relatively weak and infrequent. They are favoured in nonaqueous solutions, especially if the polyoxometalate has a high charge, and more than one oxygen atom of the anion is coordinated to the metal cation. An example of such complex is the species $[UMo_{12}O_{42}\{Ni(H_2O)_3\}_2]^{4-}$, with the Dexter–Silverton anion (Figure 2.6) acting as a tridentate ligand through three neighbouring terminal oxygen atoms.[38]

Complexes with lacunary polyoxometalate structures are numerous and of great variety. The vacancy, e.g., in a Keggin or Wells–Dawson anion, can act as a pentadentate coordination site, as in $[(SiW_{11}O_{39})Co(H_2O)]^{6-}$ with the octahedral Co^{2+}, or tetradentate site, as in $[(PW_{11}O_{39})Cu]^{5-}$ with square-planar Cu^{2+}.[4] Some examples of reactions of such complexes are shown in Figure 2.12.

Transition metal complexes of polyoxometalates such as $[(PW_{11}O_{39})M]^{n+}$ and $[(SiW_{11}O_{39})M]^{n+}$ have been considered as inorganic analogues of metalloporphyrins with the important advantage of being much more robust to oxidative and thermal degradation than porphyrins or other multidentate organic ligands.[4,39,40] Consequently, there has been a significant interest regarding their use as catalysts for liquid-phase oxidation (Chapter 5).

Lacunary polyoxometalates with more than one vacancy, e.g. PM_9 or SiM_9 anions, form numerous complexes with a range of structures.[1–4,37] Such lacunary anions may assemble into larger polyoxometalate structures, either directly, as in the case of the Wells–Dawson anion (Figure 2.4), or with the incorporation of metal ion linkers,[37] as shown in Figure 2.13. The latter clusters have attracted interest as oxidation catalysts (Chapter 5).

More about complexes of polyoxometalates with metal ions can be found in Refs.[1–4,37]

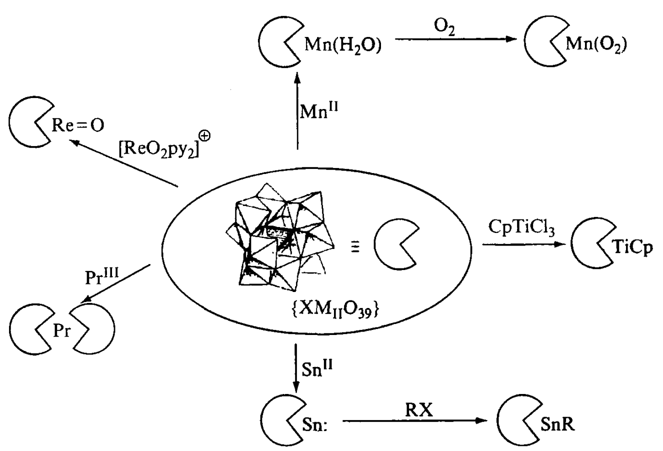


Figure 2.12 Examples of possible reactions of lacunary Keggin anions.[4]

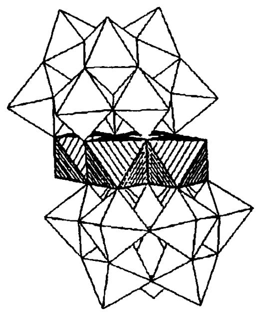


Figure 2.13 The structure of the $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ anions.[37] An M_4 cluster of four metal–oxygen octahedra ($M = Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}$, etc.) is sandwiched by two trivacant lacunary Keggin units B-$\{PW_9O_{34}\}$.

2.5.3 ISOTOPE EXCHANGE

Studies with the use of isotopes, such as ^{99}Mo, ^{185}W,[41,42] and ^{17}O,[43] show that heteropoly anions exchange their addenda and oxygens with solution, the exchange rate depending on the chemical composition of the anions. The ^{99}Mo exchange between $[PMo_{12}O_{40}]^{3-}$ (0.01 mol l^{-1}) and $Na_2{}^{99}MoO_4$ (0.1 mol l^{-1}) in aqueous solution at 20 °C and pH 1.2 is complete in 15 min.[41] The heteroatom does not exchange. According to ^{17}O NMR data, the terminal, bridging, and internal oxygen atoms in Keggin anions have different chemical shifts and different exchange rates with solvent.[43,44] The rate of ^{17}O exchange in $[PMo_{12-n}V_nO_{40}]^{(3+n)-}$ $(n = 0, 1, 2)$ anions decreases by an order of ten per each vanadium(V) added.[43] It is suggested that the exchange proceeds via dissociation of addenda from the polyanion followed by the exchange of the monomeric oxometal species with solvent.

Solid heteropoly compounds exchange oxygen with water vapour[2c,11] (Chapter 5).

2.5.4 KINETICS AND MECHANISM OF SUBSTITUTION IN POLYOXOMETALATES

Kinetics and mechanism of addenda substitution in heteropoly anions have been studied.[45–49] The reaction

$$[SiW_{12}O_{40}]^{4-} + VO^{2+} \rightarrow [SiW_{11}VO_{40}]^{5-} + W(VI)$$

in aqueous solution occurs in accordance with the kinetic equation $r = k[SiW_{12}][OH^-]$, where $k = 2.8 \times 10^6\ l\ mol^{-1}\ s^{-1}$ at 25 °C. The substitution is suggested to occur via a dissociative mechanism with the rate-limiting step of formation of the lacunary species:

$$[SiW_{12}O_{40}]^{4-} + OH^- \rightarrow [SiW_{11}O_{39}]^{8-} + W(VI)$$

followed by the fast migration of vanadium(IV) into the vacancy formed.[45,46] Similarly $[SiW_{11}O_{39}]^{8-}$ reacts with Co^{2+} to give $[SiW_{11}O_{39}Co]^{6-}$.[47] In the reaction of VO_2^+, VO^{2+}, MoO_2^{2+}, Fe^{2+}, or Fe^{3+} cations with $[PW_{12}O_{40}]^{3-}$ the dissociative pathway competes with the associative pathway, which includes the formation of an intermediate complex between $[PW_{12}O_{40}]^{3-}$ and the cations.[46,49]

The rate of reaction of $\{PMo_{12-n}V_nO_{40}\}$ $(n = 0-6)$ with VO^{2+}, i.e.

$$PMo_{12-n}V_n{}^{5+} + VO^{2+} \rightarrow PMo_{12-n}V_{n-1}{}^{5+}V^{4+} + V(V)\ (\text{or } Mo(VI))$$

at pH 2.2–3.0 obeys the kinetic equation $r = k[PMo_{12-n}V_n][VO^{2+}]/[H^+]^a$, where $1 < a < 2$.[48] The reactivity of polyanions decreases from $n = 0$ to $n = 6$. The mechanism of this reaction may depend on the composition of polyanions. With PMo_{12}, the reaction probably proceeds via fast migration of VO^{2+} into a vacancy of defect molybdophosphates; with $PMo_{11}V$, it is likely to be a V(IV) for Mo(VI) substitution; in the case of $n \geq 2$, an electron transfer between VO^{2+} and V(V) in polyanion is suggested to occur.[48] The reaction of $\{PW_{12-n}V_nO_{40}\}$ with VO^{2+} follows the same mechanism.[49a]

The kinetics and mechanism of the formation and decomposition of Keggin heteropoly anions have been investigated.[50–52] The formation of $[PMo_{12}O_{40}]^{3-}$ and $[PMo_{10}V_2O_{40}]^{5-}$ from phosphate, molybdate, and vanadate in acidic aqueous solution is very fast, on the timescale of the stopped-flow technique.[52] These reactions show a complex kinetics and their mechanism is not yet clear.

2.6 ACID PROPERTIES

Many heteropoly acids, for example the Keggins and Wells–Dawsons, are strong Brønsted acids.[1,2c,28,53] The acid properties of the most common Keggin acids both in solution and in solid state are well documented.[2c,53] The following discussion is mainly referred to acid properties of these acids. Supported acid catalysts are discussed in Chapter 4.

2.6.1 PROTON STRUCTURE

Structural characterisation of proton sites is an important step towards understanding the catalytic activity of heteropoly acids.[2c,12,53–55] In solid heteropoly acids, bulk and surface proton sites located respectively in the bulk and on the surface of the solid should be distinguished. The structure of these sites may be different. The bulk proton sites are suggested[2c,12] to play a key role in 'pseudoliquid' catalysis by solid heteropoly acids (Chapter 4). So far, most proton characterisations have been done for the bulk heteropoly acids, in particular for the strongest acid $H_3[PW_{12}O_{40}]$. The proton structure of supported heteropoly acids is scarcely characterised.

Two kinds of protons have been found in solid heteropoly acids: (i) hydrated protons $[H(H_2O)_n]^+$ and (ii) nonhydrated protons. The hydrated protons possess a high mobility; these are responsible for the extremely high proton conductivity of crystalline heteropoly acid hydrates. The nonhydrated protons are much less mobile; these are suggested to localise on the peripheral oxygens of the polyanion.[53]

The location of protons in heteropoly anions has been subject of many studies.[54,56–62] The Keggin anions have two types of outer oxygen atoms as potential protonation centres: terminal oxygens M=O and bridging oxygens M–O–M (edge-sharing and corner-sharing) (Figure 2.14). Bond length–bond strength correlations[56] as well as ^{17}O NMR data[57] indicate that in the free polyanions (e.g., $V_{10}O_{28}^{6-}$) in solution, the bridging oxygen atoms, having a higher electron density than the terminal oxygen atoms, are protonated. Extended Hückel molecular orbital calculations showed that the bridging oxygens are the most basic and thus the most likely to be protonated.[58] Recent density functional quantum chemical calculations of optimised isolated metal

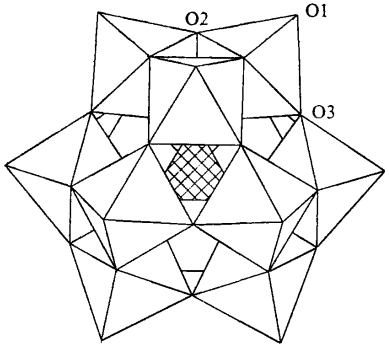


Figure 2.14 The Keggin structure of α-$[XM_{12}O_{40}]^{x-8}$: terminal (O1), edge-bridging (O2), and corner-bridging (O3) oxygen atoms.

oxygen clusters also show that the most energetically favourable protonation sites in such clusters are the bridging oxygens.[61] Hence, in the free Keggin anion in the gas phase, the bridging M–O–M oxygens may be assumed to be the predominant protonation sites.

In solid crystalline heteropoly acids, the protons, hydrated or nonhydrated, take part in the formation of the crystal structure, linking the neighbouring heteropoly anions. In this case, the proton locations are determined not only by the basicity of the outer oxygens in the descrete polyanion but also by the energy of the crystal lattice. It is conceivable, therefore, that in crystalline heteropoly acid the more accessible terminal oxygens may be protonated. There is one case – a relatively stable crystalline hexahydrate $H_3[PW_{12}O_{40}] \cdot 6H_2O$ – when the link of the hydrated protons to the terminal oxygens, not to the bridging ones, has been demonstrated by single-crystal X-ray and neutron diffraction.[14a] The crystal structure of $H_3[PW_{12}O_{40}]$ hexahydrate is formed by packing heteropoly anions into a body-centred cubic structure. The bulk proton sites in this solid are represented as diaquahydrogen ions, $H_5O_2{}^+$, which are almost planar, quasi-symmetrical hydrogen-bonded species $[H_2O \ldots H^+ \ldots OH_2]$. Each of these links four neighbouring heteropoly anions by forming hydrogen bonds with the terminal W=O oxygens (Figure 2.15a). Interestingly, the same structure was inferred[14a] for the structurally similar anhydrous heteropoly salt $Cs_3[PW_{12}O_{40}]$, in which the Cs^+ ions each have four equivalent terminal oxygens as the closest neighbours (Figure 2.15b).

It should be noted, however, that the protons cannot be found directly from X-ray data; their positions are localised on the basis of a sensible hydrogen-bonding scheme and the known geometry of the water molecule. Direct evidence of the predominant protonation of the terminal oxygens in solid $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ hydrates has been obtained by ^{17}O NMR, comparing the solution and solid-state spectra for these heteropoly acids.[59] The resonance for the terminal oxygen in solid $H_3[PW_{12}O_{40}]$ exhibits a large

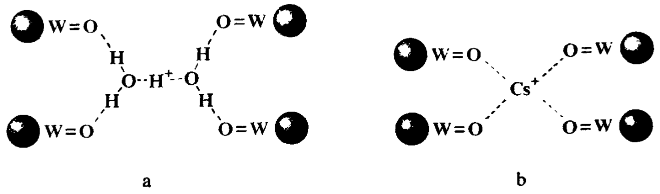


Figure 2.15 Schematic structure of (a) bulk proton sites in $H_3[PW_{12}O_{40}] \cdot 6H_2O$ and (b) Cs^+ location in $Cs_3[PW_{12}O_{40}]$.[59]

60 ppm upfield shift compared to the aqueous solution spectrum, whereas the bridging oxygen resonances have practically the same positions in both spectra (Figure 2.16).* Since in aqueous solution $H_3[PW_{12}O_{40}]$ is completely deprotonated (see below), this unambiguously identifies the terminal oxygens as the predominant protonation sites in the solid heteropoly acid.

The structure of bulk proton sites in dehydrated heteropoly acids is not yet clear. Investigation of dehydrated acids requires a strict control of traces of water in the solids. Lee *et al.*[54a] found from infrared spectroscopy that protons were most likely located on the bridging oxygens. On the basis of ^{17}O NMR results and by analogy with the structures of $H_3[PW_{12}O_{40}] \cdot 6H_2O$ and $Cs_3[PW_{12}O_{40}]$ (Figure 2.15), Kozhevnikov *et al.*[59] proposed a structure for the dehydrated $H_3[PW_{12}O_{40}]$ in which the proton migrates rapidly between four equivalent terminal oxygens (Figure 2.17). This structure was assumed to form directly from the proton structure of the $H_3[PW_{12}O_{40}]$ hydrate upon dehydration. However, Zecchina *et al.*[62] found no infrared bands characteristic of the $[O \ldots H^+ \ldots O]$ group in the dehydrated $H_3[PW_{12}O_{40}]$ which is thought to be incompatible with the structure shown in Figure 2.17. Uchida *et al.*,[54b] using ^1H, ^{17}O and ^{31}P MAS NMR, identified and quantitatively monitored three types of protons, namely H^+, H_3O^+, and $H_5O_2^+$, in solid $H_3[PW_{12}O_{40}]nH_2O$ $(0 < n < 6)$. Water molecules and acidic protons were found nearly uniformly distributed in the solid. The relative amounts of the three types of protons depend on the water content. The protonated dimer $CD_3CN \ldots H^+ \ldots NCCD_3$, similar to $H_5O_2^+$, was found to form upon the interaction of CD_3CN with the dehydrated $H_3[PW_{12}O_{40}]$.[62b]

The surface proton sites in solid heteropoly acids, apparently stronger than the bulk sites, are generally more important for heterogeneous acid catalysis. Their structure remains practically unknown, however. Crystalline heteropoly

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*Prior to measuring the ^{17}O NMR spectra, the solid $H_3[PW_{12}O_{40}]$ was dehydrated at 200 °C/ 0.4 mmHg and was believed to be anhydrous.[59] In fact, it contained some water because of the rapid rehydration even upon brief exposure to air. The spectrum for 'practically anhydrous' $H_3[PW_{12}O_{40}]$ reported by the author's group[60] and also by Uchida *et al.*[54b] is much broader with a poorly detectable resonance for the terminal W=O group; this spectrum transformed to the one shown in Figure 2.16 upon exposing the sample to air. Thus the ^{17}O NMR results[59] cannot support the proton structure of anhydrous $H_3[PW_{12}O_{40}]$ (Figure 2.17) but they do support the proton structure of the hydrated acid (Figure 2.15).

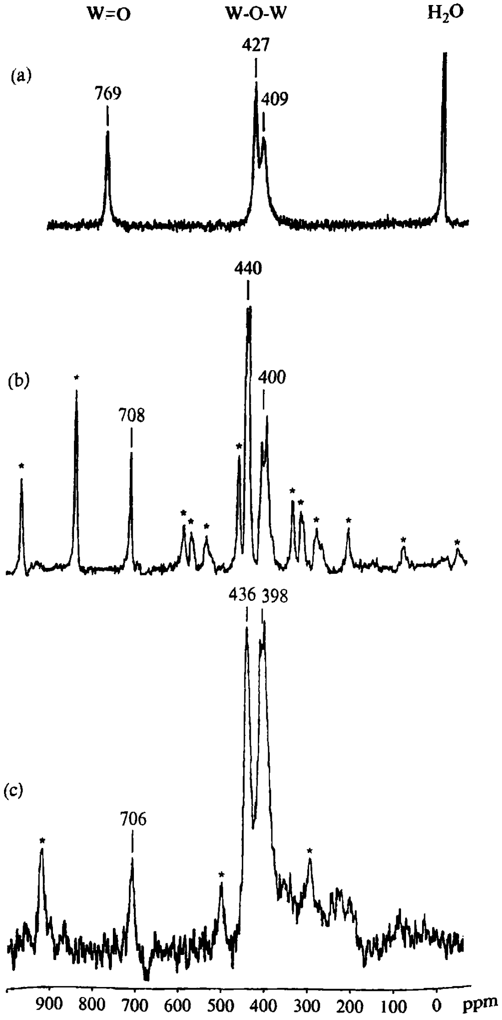

Figure 2.16 ^{17}O NMR spectra for ^{17}O-enriched $H_3[PW_{12}O_{40}]$: (a) 0.12 mol l^{-1} H_3 $[PW_{12}O_{40}]$ aqueous solution; (b) and (c) magic-angle spinning spectra for solid $H_3[PW_{12}O_{40}]$ at a spinning rate of 6.8 and 11 kHz, respectively; positions of centre bands are indicated; spinning side bands are asterisked.[55] Reprinted with permission from *Chem. Rev.* 1998, **98**, 171. Copyright 1998 American Chemical Society.

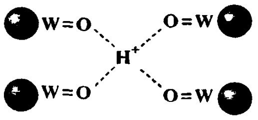

Figure 2.17 Schematic structure of bulk proton sites in anhydrous $H_3[PW_{12}O_{40}]$.[59]

acids possess a very low surface area ($1–5\,m^2\,g^{-1}$) and low porosity ($< 0.1\,cm^3\,g^{-1}$).[2c,2f,55] To increase the surface area, they are frequently supported on an inert porous support, e.g. silica (Chapter 4). It was suggested that the surface proton sites in bulk and supported catalysts might be represented by protons localised on the bridging oxygen atoms in the surface heteropoly anions.[53]

2.6.2 HETEROPOLY ACIDS IN SOLUTION

In solutions, the acid properties of heteropoly acids have been characterised in terms of dissociation constants and Hammett acidity function.[53] As heteropoly acids have very high solubilities in polar solvents, such as water, lower alcohols, ketones, ethers, esters, etc., these solvents have been primarily used in these studies. The dissociation constants of heteropoly acids were measured in H_2O,[63] Me_2CO, EtOH, and AcOH[32,33]. The Hammett acidity function was determined in H_2O and $H_2O–AcOH$, H_2O–dioxane, $H_2O–EtOH$ and $H_2O–Me_2CO$ mixtures.[64]

In aqueous solution, heteropoly acids such as $H_3[PW_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$, and $H_3[PMo_{12}O_{40}]$ are strong, fully dissociated acids.[53] The $[SiW_{12}O_{40}]^{4-}$ and $[PW_{12}O_{40}]^{3-}$ anions remain deprotonated even after accepting two and three extra electrons, respectively, upon polarographic reduction in aqueous solution at pH 1.[65] Stepwise dissociation is not observable because of the levelling effect of the solvent. The dissociation constants, starting with K_4, have been measured for some Keggin and Dexter–Silverton acids in water[53] (Table 2.3).

Nonaqueous solvents exert a differentiating influence upon the acid dissociation, hence they are more suitable for studying the dissociation steps of

Table 2.3 Dissociation constants of heteropoly acids in water at 20 °C[53].

Acid	pK_4	pK_5	pK_6	pK_7	pK_8
$H_5[PMo_{10}V_2O_{40}]^a$	1.2	2.1			
$H_6[PMo_9V_3O_{40}]^a$	1.3	1.6	2.0		
$H_8[NpMo_{12}O_{42}]$	3.2	3.4	3.6	4.3	5.7
$H_8[CeMo_{12}O_{42}]$		2.1	2.0	3.0	4.2
$H_8[UMo_{12}O_{42}]$			2.1	3.0	4.3

a) At 25 °C

poly-protonic acids. It is also noteworthy that polyoxometalates are more stable in nonaqueous media than in water.[53] As shown by conductivity method,[32,33] the first two protons in $H_3[PW_{12}O_{40}]$ are fully dissociated and the third only partly in ethanol and acetone, while the weaker acids $H_4[SiW_{12}O_{40}]$ and $H_3[PMo_{12}O_{40}]$ are fully dissociated in the first step and partly in the second. In the less polar acetic acid, Keggin acids behave as 1–1 electrolytes.[53] Table 2.4 presents the stepwise dissociation constants, pK_a, for heteropoly acids as well as for typical mineral acids in acetone and acetic acid. The pK_a values in ethanol are very similar to those in acetone. It can be seen that heteropoly acids are much stronger than mineral acids; for example, they are stronger than H_2SO_4 by 2–5 pK units.

The effect of chemical composition on the acid strength of heteropoly acids is surprisingly weak. The heteroatom (P or Si) has a very little effect despite the fact that the acid strengths of H_3PO_4 and H_4SiO_4 differ significantly ($pK_1 = 2.1$ and 9.7, respectively). Heteropoly acids are much stronger that the corresponding acids of their heteroatoms (cf., e.g. $H_3[PW_{12}O_{40}]$ and H_3PO_4). This can be explained on the basis of the electrostatic theory taking into account the large size of heteropoly anions and the large number of external oxygen atoms available for the delocalisation of anion charge.[53]

In polar solvents such as acetone the acid strength of Keggin heteropoly acids follows the order:

$$H_3[PW_{12}O_{40}] > H_4[PW_{11}VO_{40}] > H_5[PW_{10}V_2O_{40}] \approx H_4[SiW_{12}O_{40}] >$$
$$H_3[PMo_{12}O_{40}] > H_4[PMo_{11}Mo^{5+}O_{40}] \approx H_4[PMo_{12}VO_{40}] > H_4[SiMo_{12}O_{40}]$$

Table 2.4 Dissociation constants of heteropoly acids in acetone and acetic acid at 25 °C and zero ionic strength[53].

	Acetone			Acetic acid
Acid	pK_1	pK_2	pK_3	pK_1
$H_3[PW_{12}O_{40}]$	1.6	3.0	4.0	4.8
$H_4[PW_{11}VO_{40}]$	1.8	3.2	4.4	4.7
$H_5[PW_{10}V_2O_{40}]$				4.8
$H_4[SiW_{12}O_{40}]$	2.0	3.6	5.3	5.0
$H_3[PMo_{12}O_{40}]$	2.0	3.6	5.3	4.7
$H_4[PMo_{11}Mo^{5+}O_{40}]$	2.1	3.7	5.5	
$H_4[PMo_{12}VO_{40}]$	2.1	3.7	5.6	4.7
$H_4[SiMo_{12}O_{40}]$	2.1	3.9	5.9	4.8
$H_4[GeW_{12}O_{40}]$				4.3
$H_5[GeW_{11}VO_{40}]$				4.7
$H_6[GeW_{10}V_2O_{40}]$				4.6
$HClO_4$				4.9
HBr				5.6
H_2SO_4	6.6			7.0
HCl	4.3			8.4
HNO_3	9.4			10.1

Tungsten acids are stronger than molybdenum ones. The strongest acid in the Keggin series is $H_3[PW_{12}O_{40}]$.[53] However, the difference between the strongest and the weakest acid is quite small.

It is important to note that the acid strength decreases upon reduction of the heteropoly anion (cf. $H_3[PMo_{12}O_{40}]$ and $H_4[PMo_{11}Mo^{5+}O_{40}]$).[53] This frequently accounts for the inefficiency of molybdenum acids as acid catalysts in reducing organic media (Chapter 4). Being much weaker oxidants, tungsten heteropoly acids are not affected by the reduction and thus generally preferred as acid catalysts.[55]

Deprotonation of a heteropoly acid (HPA) in solution can be viewed as an ionisation–dissociation process with the formation of a solvent-separated ion pair between the heteropoly anion (HPAN) and H^+ as an intermediate.[53]

$$\mathrm{HPA} \overset{K_i}{\rightleftarrows} \mathrm{HPAN^-}\|\mathrm{H^+} \overset{K_d}{\rightleftarrows} \mathrm{HPAN^-} + \mathrm{H^+}$$

From the conductivity study,[33] it was inferred that in polar nonaqueous solvents such as acetone heteropoly acids are fully ionised ($K_i \gg 1$). From ^{17}O NMR data,[59c] $H_3[PW_{12}O_{40}]$ is fully ionised even in 94:6v/v $AcOH–H_2O$ solution; the solvated protons are loosely bound to the anion as a whole rather than to a certain oxygen atom in the anion, in contrast to the crystalline acid.

Concentrated solutions of heteropoly acids are of great interest for homogeneous acid catalysis. The acidity of concentrated solutions of heteropoly acids, in terms of the Hammett acidity function (H_o), depends weakly on their composition (Table 2.5) and is stronger than that of equimolar solutions of H_2SO_4 by 1–1.5 H_o units.[53,64]

Izumi *et al.*,[66] by measuring the chemical shift of the hydroxyl protons in chloral hydrate $Cl_3CCH(OH)_2$, found the following order of acid strength for Keggin acids in $C_6D_5NO_2$ solution:

$$H_3[PW_{12}O_{40}] > H_3[PMo_{12}O_{40}] > H_4[SiW_{12}O_{40}] \approx H_4[GeW_{12}O_{40}] >$$
$$H_4[SiMo_{12}O_{40}] > H_4[GeMo_{12}O_{40}]$$

This order is similar to that in aqueous solution.

Drago *et al.*[67] studied the acidity of $[H_3[PW_{12}O_{40}]$ by the calorimetric titration with a series of bases in CH_3CN solution and determined equilibrium constants and enthalpies for the three deprotonation steps. The results indicate that the three protons are not of equal strength. The enthalpies of reactions with pyridine with a series of Brønsted acids in dilute acetonitrile solution lead to the following acidity order:

$$H_3[PW_{12}O_{40}] > CF_3SO_3H > p\text{-}CH_3C_6H_4SO_3H \approx H_2SO_4(97\,\%) >$$
$$CF_3COOH > ClC_6H_4COOH$$

i.e. the heteropoly acid is stronger than triflic acid in CH_3CN solution.

Table 2.5 Hammett acidity function H_o for aqueous solutions of $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$[64a].

[HPA]	Temperature, °C				
mol l^{-1}	20	25	40	60	80
			$H_3[PW_{12}O_{40}]$		
0.05	+0.27				
0.07	+0.11	+0.12	+0.13	+0.17	+0.24
0.10	−0.05	−0.03	+0.01	+0.03	+0.04
0.15	−0.24	−0.22	−0.21	−0.17	−0.15
0.20	−0.35	−0.33	−0.32	−0.26	−0.23
0.25	−0.47	−0.46	−0.45	−0.41	−0.40
0.30	−0.56	−0.55	−0.54	−0.53	−0.52
0.35	−0.68	−0.66	−0.61	−0.59	−0.55
0.40	−0.83	−0.82	−0.80	−0.78	−0.74
0.45	−1.00	−0.96	−0.93	−0.92	−0.84
0.50	−1.21	−1.16	−1.14	−1.11	−0.96
			$H_4[SiW_{12}O_{40}]$		
0.05	+0.23	+0.24	+0.25	+0.27	+0.34
0.10	−0.03	−0.01	0	+0.02	+0.11
0.15	−0.25	−0.24	−0.22	−0.13	−0.09
0.20	−0.38	−0.36	−0.34	−0.28	−0.26
0.25	−0.53	−0.49	−0.46	−0.45	−0.41
0.30	−0.70	−0.67	−0.64	−0.57	−0.54
0.35	−0.79	−0.77	−0.74	−0.64	−0.62
0.40	−0.98	−0.93	−0.90	−0.89	−0.83
0.45	−1.10	−1.05	−1.01	−0.95	−0.90
0.50	−1.21	−1.15	−1.08	−1.00	−0.99

2.6.3 ACIDITY OF SOLID HETEROPOLY ACIDS

Generally, solid heteropoly acids form ionic crystals composed of heteropoly anions, variably hydrated protons ($H^+, H_3O^+, H_5O_2^+$, etc.) and crystallisation water (Section 2.6.1). The crystal structure of heteropoly acids depends on the amount of crystallisation water (Table 2.1). This water can be easily removed on heating, whereby the acid strength is increased due to the dehydration of protons.

Solid heteropoly acid hydrates possess high proton conductivities.[68–71] The conductivity of solid $H_3[PW_{12}O_{40}]$ is comparable to the proton conductivity in water. The conductance of heteropoly acids hydrates has low activation energies (3.3 kcal mol^{-1}). The high conductivity is attributed to the location of waters of crystallisation and hydrated protons in the interstices between the large heteropoly anions.

Solid heteropoly acids possess purely Brønsted acidity, as established by IR spectroscopy of adsorbed pyridine. They are stronger than conventional solid acids such as SiO_2–Al_2O_3, H_3PO_4/SiO_2, and HX and HY zeolites.[2c,11] For example, pyridine adsorbed on SiO_2–Al_2O_3 fully desorbs at 300 °C, whereas on $H_3[PW_{12}O_{40}]$ it retains as pyridinium ion at much higher temperature.[72] Like other strong solid acids, heteropoly acids are capable of generating carbocations from adsorbed olefins and arenes.[73]

As found by temperature-programmed desorption (TPD) of ammonia, the acid strength of crystalline heteropoly acids decrease in the order (desorption temperatures in °C):[74]

$$\underset{592}{H_3[PW_{12}O_{40}]} > \underset{532}{H_4[SiW_{12}O_{40}]} \geq \underset{463}{H_3[PMo_{12}O_{40}]} > \underset{423}{H_4[SiMo_{12}O_{40}]}$$

This order is identical to that in polar solvents (Table 2.4). The TPD data should be treated with caution, however. The NH_3–TPD measures the temperature of decomposition of the ammonium salts of heteropoly acids to form NH_3, nitrogen oxides, and H_2O together with a mixture of oxides of the heteroatom and addenda. Hence, the measured desorption temperature may not reflect correctly the acid strength of heteropoly acids.

Microcalorimetry of ammonia sorption appears to be the best technique for measuring the acid strength of heteropoly acids.[75–77] According to the microcalorimetric data,[75] the bulk proton sites in dehydrated $H_3[PW_{12}O_{40}]$ are essentially uniform and characterised by the differential heat of ammonia adsorption of 180 kJ mol^{-1} (Figure 2.18). Other microcalorimetric studies[76,77] have examined the acid strengths of a number of heteropoly acids by the sorption of NH_3 after pretreatment of the solids under various conditions. Typically, the heat of ammonia adsorption on bulk Keggin heteropoly acids is found in the range of 180–200 kJ mol^{-1}, which is considerably higher than that for SiO_2–Al_2O_3 and zeolites. The Wells–Dawson acid $H_6[P_2W_{18}O_{62}]$ (ca. 150 kJ mol^{-1}) was found to be significantly weaker than $H_3[PW_{12}O_{40}]$.[77b] An effect of activation conditions was observed in that a lower activation temperature resulted in a higher differential heat of sorption.[61,76] This may be explained by an inductive effect of water on the acid strength of the proton[76] or by solvation of ammonia in the waters of crystallisation.[61] The order of acid strengths of solid heteropoly acids, as determined by microcalorimetry is:[61,76]

$$H_3[PW_{12}O_{40}] \geq H_4[SiW_{12}O_{40}] \gg H_3[PMo_{12}O_{40}] \geq H_4[SiMo_{12}O_{40}]$$

which is in agreement with that found by temperature-programmed desorption. Usually, relative catalytic activities of heteropoly acids are consistent with this order both in homogeneous and in heterogeneous systems.[2c,53,55] Density functional quantum chemical calculations of optimised metal oxygen clusters reveal that the proton affinity of tungsten clusters is lower than that of analogous molybdenum clusters by 20–40 kJ mol^{-1}.[61]

The acidity of solid 12-tungstophosphoric acid has been measured using slurry calorimetry in cyclohexane with pyridine as a probe.[78] Two types of

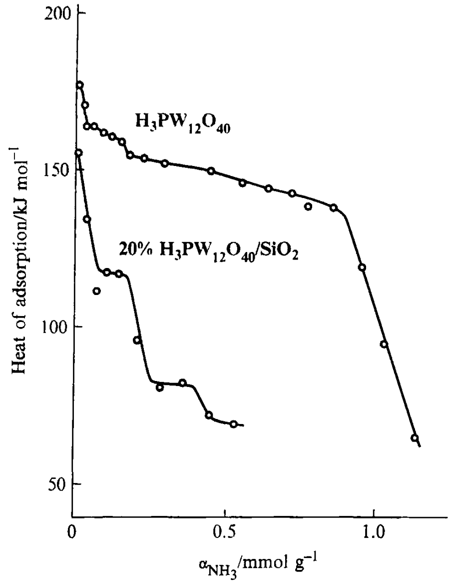

Figure 2.18 Differential heat of ammonia adsorption onto $H_3[PW_{12}O_{40}]$ and 20% $H_3[PW_{12}O_{40}]/SiO_2$ measured at 150 °C after pretreatment at 300 °C/10^{-3} mmHg.[75] Reprinted with permission from *Catal. Rev. Sci. Eng.* 1995, **37**, 311. Copyright 1995 Marcel Dekker.

Brønsted sites with different strengths (137 and 82 kJ mol^{-1}) have been found, which disagrees with the microcalorimetry of gaseous ammonia adsorption that shows that all protons in solid $H_3[PW_{12}O_{40}]$ are almost equivalent. The differences have been attributed to the small size and stronger basicity of ammonia. The smaller NH_3 molecule is able to occupy the interstices in the lattice without appreciable change in lattice dimensions or energy, whereas penetration of the solid by pyridine causes expansion of the lattice.

Osegovic and Drago[79] demonstrated that the bonding of triethylphosphine oxide (TEPO) to the acid site of a surface produces a systematic change in the ^{31}P isotropic chemical shift that is proportional to the acid strength of the acid site. They measured the acidity of crystalline $H_3[PW_{12}O_{40}]$ as well as several amorphous solid acids and zeolites. A single parameter scale was developed based on the ^{31}P chemical shift, $\Delta\delta$, of TEPO adsorbed on solid acids, which allows a good linear correlation between $\Delta\delta$ and the enthalpies of pyridine adsorption, ΔH, measured by calorimetry (Figure 2.19). It can be seen, however, that for $H_3[PW_{12}O_{40}]$ a larger acidity is measured by TEPO than by calorimetry.

Solid $H_3[PW_{12}O_{40}]$ and its acidic salt $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ after pretreatment at 300–400 °C have been claimed to acquire superacid sites.[80–82] By the definition,[83] superacids are acids stronger than 100% H_2SO_4, i.e. they have the Hammett acidity function H_o less than -12.2. Using titration with Hammett indicators, Okuhara *et al.*[81] found that the calcined $H_3[PW_{12}O_{40}]$ and $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ possessed the acid sites with the Hammett acidity function of $-13.8 < H_o < -13.2$ (Table 2.6). However, the application of Hammett indicators to characterise the surface acidity of solid acids can be misleading because the surface acidity function H_o, in contrast to the solution H_o, has no explicit physicochemical meaning.[84,85] Although it was demonstrated that $H_3[PW_{12}O_{40}]$ is stronger than H_2SO_4^{53} and even than CF_3SO_3H^{67} in dilute solution, it does not necessarily mean that this will stand for the neat acids. Another useful yet insufficient criterion to identify superacids is based on their catalytic activity: superacids will catalyse the low-temperature (below 100 °C) skeletal isomerisation of light alkanes.[83] This test is insufficient because, when the result is positive, the isomerisation must be proved to occur via the genuine acid-catalysed path and not a redox mechanism, e.g. one-electron transfer. According to this criterion, neither solid (($H_3[PW_{12}O_{40}]$ or $Cs_{2.5}H_{0.5}$ $[PW_{12}O_{40}]$) can be regarded as superacids because they catalyse n-butane isomerisation only at about 300 °C.[82] Nowinska *et al.*[80] reported that bulk

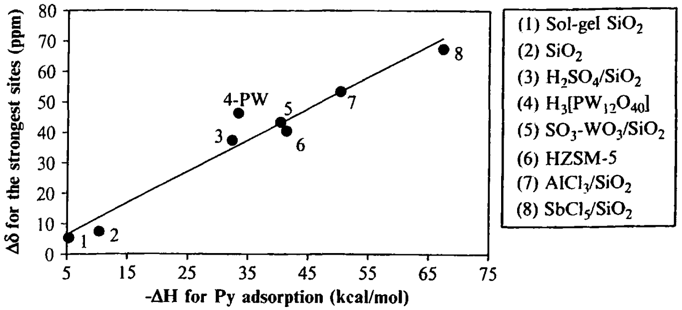

Figure 2.19 Correlation between $\Delta\delta$ (^{31}P NMR) and ΔH (calorimetry of pyridine adsorption) for solid acids.[79]

Table 2.6 Hammett acidity function H_o for solid acid catalysts^{2c,81}.

Catalyst (pretreatment)	pK$_a$ of indicator (H_o)^a					
	-8.2	-11.4	-12.7	-13.2	-13.8	-14.5
$Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ (300 °C)	+	+	+	+	−	−
$H_3[PW_{12}O_{40}]$ (300 °C)	+	+	+	+	−	−
HZSM-5 (535 °C)	+	+	+	−	−	−
SO_4^{2-}/ZrO_2 (370 °C)	+	+	+	+	+	+
SiO_2-Al_2O_3 (450 °C)	+	+	+	−	−	−

a) The indicator has changed its colour (+) or remained unchanged (−)

and silica-supported $H_3[PW_{12}O_{40}]$ showed a very low catalytic activity in the skeletal isomerisation of n-hexane at 75 °C. Therefore, for heteropoly acids, the isomerisation test seems quite conclusive. The study by Essayem *et al.*[85] of the H/D exchange between the deuterated solid catalysts $D_3[PW_{12}O_{40}]$ and $Cs_{1.9}D_{1.1}[PW_{12}O_{40}]$ and isobutane revealed that these solid acids are strong acids but not superacids. Apparently, to answer the question whether or not solid heteropoly acids are superacids we need much better understanding of what the solid superacids are and how to measure their acidity in the first place.

In this connection, recent data on sulfated zirconia are of interest.[86,87] The ability to perform the low-temperature alkane isomerisations has led to claims that sulfated zirconia is a superacid. Recently Drago *et al.*,[87] by calorimetry of pyridine adsorption, have found that sulfated zirconia has two types of acid sites with strengths of 130 and 108 kJ mol^{-1}, which places its acidity lower than that of HZSM-5 (170 kJ mol^{-1}) and about the same as that of HY (140 kJ mol^{-1}). On the other hand, it has been shown that alkane conversions on sulfated zirconia may be initiated by one-electron oxidation of the alkane by sulfated zirconia leading to an ion–radical intermediate, with no requirement of superacidity. As demonstrated by ESR spectroscopy,[73] cation radicals are formed upon adsorption of arenes, such as styrene, naphthalene, and anthracene, on $H_3[PW_{12}O_{40}]$ and $H_3[PW_{12}O_{40}]/SiO_2$ at 25–150 °C (Figure 2.20). Hence, one-electron oxidation might play a role in acid-catalysed reactions with heteropoly acids as well.

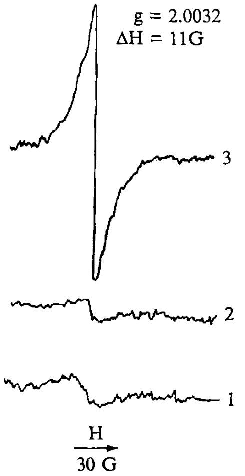

Figure 2.20 ESR spectra: (1) 25% $H_3[PW_{12}O_{40}]/SiO_2$ pre-evacuated at 200 °C; (2) styrene adsorbed on this catalyst at 25 °C; (3) sample 2 after heating at 150 °C for 0.5 h.[73] Reprinted with permission from *J. Mol. Catal.* 1993, **79**, 21. Copyright 1993 Elsevier Science.

2.7 REDOX PROPERTIES

Redox chemistry of polyoxometalates is extremely diverse.[1,28] It has been subject of many studies and found many applications in chemical analysis (Chapter 8) as well as in selective catalytic oxidation[31] (Chapter 5).

According to Pope,[1,4] polyoxometalates, regarding their redox abilities, can be divided into two groups – 'mono-oxo' (type I) and 'cis-dioxo' (type II). This classification is based on the number of terminal oxygen atoms attached to each addenda atom, e.g. molybdenum or tungsten, in the polyanion. Examples of type I polyanions are the Keggins, the Wells–Dawsons and their derivatives that have one terminal oxygen atom $M=O$ per each addenda atom (Figures 2.1 and 2.2). Type II polyanions can be represented by the Dexter–Silverton anion which has two terminal oxygens in cis positions on each addenda atom (Figure 2.6).

In type I octahedra MO_6, the lowest unoccupied molecular orbital (LUMO) is a nonbonding metal-centred orbital, whereas the LUMO for type II octahedra is antibonding with respect to the terminal $M=O$ bonds. Consequently, type I polyoxometalates are reduced easily and frequently reversibly to form mixed-valence species, heteropoly blues, which retain the structure of the parent oxidised anions. In contrast, type II polyoxometalates are reduced with more difficulty and irreversibly to complexes with yet unknown structures.[1,4] For this reason, only type I heteropoly compounds, by and large the Keggins, are of interest for oxidation catalysis.

The total number of accepted electrons on reduction of type I polyoxometalates can be quite high. As the anion structure retains upon this process, the additional negative charge is compensated for by protonation of the anion from solvent. Thus, the reduction is frequently pH-dependent, which can be represented by equation 2.1:

$$[XM_{12}{}^{6+}O_{40}]^{x-8} + p\,e^- + q\,H^+ \rightleftarrows H_q[XM_{12-p}{}^{6+}M_p{}^{5+}O_{40}]^{x+q-p-8} \quad (2.1)$$

where $q \leq p$.[1,28] On reduction in acidic aqueous solution at $pH \leq 1$, the Keggin tungsten anions, e.g. $[SiW_{12}O_{40}]^{4-}$, can add two electrons without protonation, i.e. the anion charge becoming −6. In a more neutral solution, the pH-independent reduction can proceed up to the anion charge of −9. The reduced Wells–Dawson anions $\{X_2W_{18}O_{62}\}$ can bear the charge up to −12 without protonation.[1]

Cyclic voltammograms of type I polyoxometalates, e.g. Keggin molybdates and tungstates, show a sequence of reversible one- or two-electron reductions[1,4,28] (Figure 2.21) which yield deeply coloured heteropoly blues, the colour intensifying with the number of electrons gained. The blues exhibit strong d–d bands in the visible area in their electronic spectra.

ESR spectroscopy demonstrates that the unpaired electron in one-electron blues is weakly trapped at low temperatures, but undergoes fast hopping at

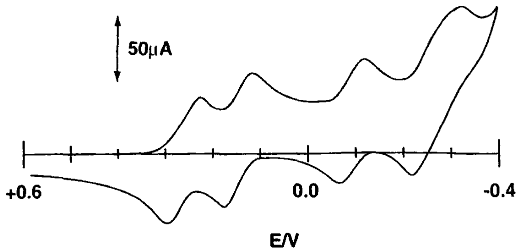

Figure 2.21 Cyclic voltammogram of α-$[PMo_{12}O_{40}]^{3-}$ in 0.1 mol l^{-1} HCl (50% H_2O/EtOH).[4]

room temperature. Two- and four-electron blues are ESR-silent, the additional electrons being fully delocalised at room temperature.[1,4]

The oxidation potentials, E, of polyoxometalates depend strongly on their addenda and to a lesser degree on their heteroatom. Generally, the E values parallel the corresponding oxidation potentials of the addenda[1,4,53] (Table 2.7):

$$\mathrm{V(V)} > \mathrm{Mo(VI)} \gg \mathrm{W(VI)}$$

Typical heteroatoms that are not redox active affect the oxidation potential via the overall anion charge. Very good linear correlations between E and the anion charge have been demonstrated[1] (Figure 2.22). Heteroatoms that are themselves strong oxidants can increase the oxidation potential significantly. For example, for the $\{Co^{3+}W_{12}O_{40}\}/\{Co^{2+}W_{12}O_{40}\}$ redox couple $E = 1.0$ V (vs. standard hydrogen electrode).[88]

Table 2.7 Oxidation potentials of Keggin anions in aqueous solution (vs. SHE[a])[53].

Redox system	Electrons transferred	E (V)
	V(V) → V(IV)	
$PV^{V}W_{11}/PV^{IV}W_{11}$	1	0.78
$PV^{V}Mo_{11}/PV^{IV}Mo_{11}$	1	0.68
$PV_2{}^{V}Mo_{10}/PV_2{}^{IV}Mo_{10}$	2	0.71
$PV_3{}^{V}Mo_9/PV_3{}^{IV}Mo_9$	3	0.71
$PV_4{}^{V}Mo_8/PV_4{}^{IV}Mo_8$	4	0.71
	Mo(VI) → Mo(V)	
$PMo_{12}{}^{VI}/PMo_9{}^{VI}Mo_3{}^{V}$	3	0.65
$SiMo_{12}{}^{VI}/SiMo_9{}^{VI}Mo_3{}^{V}$	3	0.63
	W(VI) → W(V)	
$BW_{12}{}^{VI}/BW_{11}{}^{VI}W^{V}$	1	−0.36
$GeW_{12}{}^{VI}/GeW_{11}{}^{VI}W^{V}$	1	−0.02
$SiW_{12}{}^{VI}/SiW_{11}{}^{VI}W^{V}$	1	−0.05
$PW_{12}{}^{VI}/PW_{11}{}^{VI}W^{V}$	1	0.15
	Co(III) → Co(II)	
$Co^{III}W_{12}/Co^{II}W_{12}$	1	1.0

a) SHE is the standard hydrogen electrode

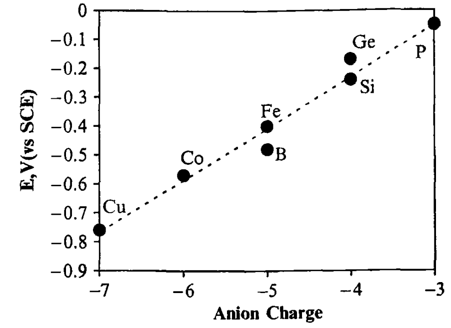

Figure 2.22 Plot of one-electron reduction potential E vs. anion charge for α-$[XW_{12}O_{40}]^{x-8}$; SCE denotes saturated calomel electrode.[1]

Redox properties of the mixed-addenda anions $\{PMo_{12-n}V_nO_{40}\}$ have been studied in considerable detail,[1,28] especially in connection with their application for catalytic oxidation.[31,89,90] These anions are remarkable because they possess not only a fairly high oxidation potential (ca. 0.7 V) but also their reduced forms are very easily reoxidised by oxygen (air) in solution. These redox reactions can be represented by the equations:

$$\{PMo_{12-n}V_nO_{40}\} + \mathrm{Red} + mH^+ \rightarrow H_m\{PMo_{12-n}V_nO_{40}\} + \mathrm{Ox} \quad (2.2)$$

$$H_m\{PMo_{12-n}V_nO_{40}\} + (m/4)O_2 \rightarrow \{PMo_{12-n}V_nO_{40}\} + (m/2)H_2O \quad (2.3)$$

where Red is the reductant, Ox its oxidised form; typically $n = 2-6$. The mechanism of these reactions will be discussed later in Chapter 5. The anions $\{PMo_{12-n}W_nO_{40}\}$ show similar behaviour,[16b] although less readily. The reduced form of $[PMo_{12}O_{40}]^{3-}$ practically does not oxidise with O_2 in solution,[31] but the solid acid $H_3[PMo_{12}O_{40}]$ can be reduced and then reoxidised with O_2 at temperatures above 200 °C[2c,11] (Chapter 5). Tungsten blues $\{XW_{12}O_{40}\}$ are very easily oxidised with O_2 in aqueous solution.[91]

Electron-transfer reactions of Keggin polyoxometalates in solution can be viewed as the outer-sphere electron transfers,[91–94] which is in line with their very low solvation energies as well as their weakness as ligands. Kozhevnikov and Kholdeeva[92] studied the kinetics of a series of one-electron redox reactions of Keggin polyoxometalates (Table 2.8) using both conventional and stopped-flow techniques. These reactions were found to obey the rate equation

$$r = k[\mathrm{Ox}][\mathrm{Red}]$$

where k is the rate constant (dependent on the pH and the ionic strength μ), Ox and Red are the oxidant and reductant, respectively. The mechanism was analysed[92] using the Marcus theory,[95] which relates the free energy of activation for an outer-sphere electron-transfer reaction, $\Delta G^{\neq}$, to the free energy of the reaction, $\Delta G^{o'}$, adjusted to account for the Coulombic interaction. Applying the Eyring equation (eq. 2.4)

$$k = Z\exp(-\Delta G^{\neq}/RT) \tag{2.4}$$

for the bimolecular rate constant and the Marcus equation (eq. 2.5) for $\Delta G^{\neq}$

$$\Delta G^{\neq} = W + \frac{\lambda}{4}\left(1 + \frac{\Delta G^{o'}}{\lambda}\right)^2 - RT\ln Z \tag{2.5}$$

one can obtain the equation

$$RT\ln k_o + W = -(\lambda/4)(1 + \Delta G^{o'}/\lambda)^2 - RT\ln Z \tag{2.6}$$

which can be applied to experimental data. In this equation k_o is the k extrapolated to $\mu = 0$, $W = z_1z_2e^2/Dr$ is the Coulombic work term that is calculated from the ion charges and radii, λ is the reorganisation energy associated with electron transfer within the precursor complex, and $Z = 10^{11}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ is the preexponential factor. At $|\Delta G^{o'}| \leq \lambda$ this equation transforms to equation 2.7:

$$RT\ln k_o + W = -\lambda/4 - \Delta G^{o'}/2 - RT\ln Z \tag{2.7}$$

which, for such conditions, predicts a linear dependence of $RT\ln k_o + W$ on $\Delta G^{o'}$ with a slope of −0.5. Values of $RT\ln k_o + W$ are plotted as function of $\Delta G^{o'}$ in Figure 2.23, assuming λ to be a constant throughout the reaction series. This plot fits well a quadratic equation of the type of equation 2.6, the linear term having a slop of −0.50, which is in excellent agreement with the Marcus theory. Thus these results support the outer-sphere electron-transfer mechanism for one-electron redox reactions of polyoxometalates.[92] Recently, Weinstock[94] discussed thoroughly the electron-transfer reactions of polyoxometalates in solution and the use of the Marcus theory for these.

Table 2.8 Kinetics of redox reactions of Keggin anions in water at 25 °C[92].

Entry	Reaction	$k(\mathrm{l\,mol^{-1}s^{-1}})^a$	$\ln k_o{}^b$
1	$[SiW_{12}]^{5-} + [Co^{III}W_{12}]^{5-} \rightarrow [SiW_{12}]^{4-} + [Co^{II}W_{12}]^{6-}$	7×10^6	3.8
2	$[PW_{12}]^{4-} + [Co^{III}W_{12}]^{5-} \rightarrow [PW_{12}]^{3-} + [Co^{II}W_{12}]^{6-}$	2.9×10^6	5.3
3	$[PW_{12}]^{4-} + Fe^{3+} \rightarrow [PW_{12}]^{3-} + Fe^{2+}$	6×10^6	24.9
4	$[SiW_{12}]^{5-} + [Co^{III}W_{12}]^{5-} \rightarrow [SiW_{12}]^{4-} + [Co^{II}W_{12}]^{6-}$	6×10^6	23.4
5	$[SiW_{12}]^{5-} + [Fe(CN)_6]^{3-} \rightarrow [SiW_{12}]^{4-} + [Fe(CN)_6]^{4-}$	3.3×10^5	5.5
6	$[PW_{12}]^{4-} + [Fe(CN)_6]^{3-} \rightarrow [PW_{12}]^{3-} + [Fe(CN)_6]^{4-}$	2.2×10^5	6.6
7	$[SiW_{12}]^{5-} + Cu^{2+} \rightarrow [SiW_{12}]^{4-} + Cu^{+}$	9.1×10^4	19.2
8	$[PW_{12}]^{4-} + Cu^{2+} \rightarrow [PW_{12}]^{3-} + Cu^{+}$	3.5×10^2	12
9	$[PV_2W_{10}]^{6-} + [PV_2Mo_{10}]^{5-} \rightarrow [PV_2W_{10}]^{5-} + [PV_2Mo_{10}]^{6-}$	5.7	−11.9
10	$[PV_2W_{10}]^{5-} + [PV_2Mo_{10}]^{6-} \rightarrow [PV_2W_{10}]^{6-} + [PV_2Mo_{10}]^{5-}$	80	−9.2
11[c]	$[Co^{II}W_{12}]^{6-} + [Co^{III}W_{12}]^{5-} \rightarrow [Co^{II}W_{12}]^{5-} + [Co^{III}W_{12}]^{6-}$	0.24	−12.2
12[d]	$HA^- + [Co^{III}W_{12}]^{5-} \rightarrow HA^\bullet + [Co^{II}W_{12}]^{6-}$	2.4×10^5	8.6
13[d]	$H_2A + [Co^{III}W_{12}]^{5-} \rightarrow HA^\bullet + H^+ + [Co^{II}W_{12}]^{6-}$	1.4×10^4	9.6
14[d]	$H_2Cat + [Co^{III}W_{12}]^{5-} \rightarrow HCat^\bullet + H^+ + [Co^{II}W_{12}]^{6-}$	9.5×10^2	6.9
15[d]	$H_2Q + [Co^{III}W_{12}]^{5-} \rightarrow HQ^\bullet + H^+ + [Co^{II}W_{12}]^{6-}$	77	4.3
16	$[SiW_{12}]^{5-} + O_2 + H^+ \rightarrow [SiW_{12}]^{4-} + HO_2{}^\bullet$	127	4.8
17	$[PW_{12}]^{4-} + O_2 + H^+ \rightarrow [PW_{12}]^{3-} + HO_2{}^\bullet$	2.9	1.1

a) Most of the data obtained at $\mu = 1.0\,\mathrm{mol\,l^{-1}}(0.5\,\mathrm{mol\,l^{-1}}\ HClO_4 + 0.5\,\mathrm{moll^{-1}}\ NaClO_4)$
b) Rate constants extrapolated to $\mu = 0$
c) From Ref.[96]
d) From Ref.[97] HA^- is ascorbate anion, H_2A is ascorbic acid, H_2Cat is catechol, H_2Q is hydroquinone

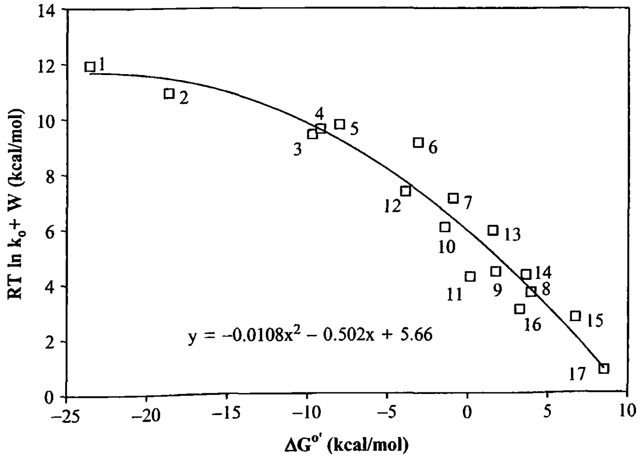

Figure 2.23 Marcus plot for redox reaction of polyoxometalates.[92] Data points are labelled as in Table 2.8.

As demonstrated by temperature-programmed reduction,[98] the activity of solid Keggin heteropoly acids towards their reduction by hydrogen decreases in the order: $H_5[PMo_{10}V_2O_{40}] \approx H_4[SiMo_{12}O_{40}] \geq H_3[PMo_{12}O_{40}] \approx H_3[PMo_6$

$W_6O_{40}] > H_3[PMo_2W_{10}O_{40}] > H_3[PW_{12}O_{40}] \approx H_4[SiW_{12}O_{40}]$. Salts of 12-molybdophosphoric acid are reduced in the order of cations: $Ag^+ > Cu^{2+} > Ni^{2+}$. The reduction is facilitated in the presence of Pd/C catalysts in the solid mixture. Thus, the reduction activity of solid heteropoly acids is fairly well in line with their oxidation potentials in solution.

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3 Synthesis of Polyoxometalates

CONTENTS

General methods of synthesis of heteropoly- and isopolyoxometalates are well documented.[1–5] Much current research is directed towards the development of new synthetic strategies in polyoxometalate chemistry. These involve, among others, synthesis in both aqueous and nonaqueous solvents,[6] the incorporation of organic and organometallic functionalities[7] as well as sulfur[8] in polyoxometalates, and the synthesis of extremely large polyoxometalates using pre-organised metal–oxide building blocks (synthons).[9]

This chapter gives an overview of some general preparation methods. Subsequent sections present a collection of syntheses of most typical heteropoly compounds that are used as acid and oxidation catalysts, including some supported solid acid catalysts. In some cases, mixtures of polyoxometalates, that are much easier to prepare, rather than pure individual compounds are used as catalysts. Examples of these are given in the last sections of this chapter.

3.1 GENERAL METHODS OF SYNTHESIS

Generally, polyoxometalates form in solutions from simple oxoanions and the necessary heteroatoms by a self-assembly process upon acidification.[1–5] For example:

$$12\,WO_4^{2-} + HPO_4^{2-} + 23\,H^+ \rightarrow [PW_{12}O_{40}]^{3-} + 12\,H_2O \qquad (3.1)$$

$$11\,MoO_4^{2-} + VO_3^- + HPO_4^{2-} + 21\,H^+ \rightarrow [PMo_{11}VO_{40}]^{4-} + 11\,H_2O \qquad (3.2)$$

Most polyoxometalates have been prepared in aqueous solutions. However, nonaqueous[6] and solid-state syntheses[10] have also been developed. A few commonest heteropoly acids such as $H_3[PW_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$, and $H_3[PMo_{12}O_{40}]$, that are of great importance for catalysis, are commercially available as crystalline hydrates. The vast majority of polyoxometalates have to be synthesised in-house; the preparation techniques vary considerably depending on the type of polyoxometalate. In many cases, when the equilibrium is favourable, polyoxometalates can be prepared in good yields at room temperature from nearly stoichiometric amounts of their components.[1–5] Otherwise, excess heteroelement and a precise reaction control are required.

Acidification is generally achieved by addition of mineral acids such as HCl, H_2SO_4, $HClO_4$, or HNO_3. It can also be done by using an acidic ion-exchange resin (e.g. Amberlyst-15) or electrolytically.[4,5] The heteropoly anions are usually isolated from aqueous solution by addition of an appropriate countercation, for example, an alkali metal, ammonium, or tetraalkylammonium. Lithium and sodium salts are generally more water-soluble than those of potassium, rubidium or cesium. Tetrabutylammonium salts are usually insoluble in water; they can be recrystallised from solvents such as acetonitrile or acetone.[4]

The free Keggin and Wells–Dawson heteropoly acids are sufficiently stable to allow crystallisation from aqueous solution. These acids can be prepared by the classical 'etherate' method developed by Drechsel.[11] This method includes the extraction of the heteropoly acid with diethyl ether from a strongly acidified (e.g. with HCl) aqueous solution of the heteropoly anion to form a heavy oily etherate of the heteropoly acid as a bottom layer. The etherate layer is drawn off and decomposed by adding water under air stream. Then the product heteropoly acid is crystallised from the aqueous solution. Heteropoly acids can also be prepared from solutions of their salts by ion exchange.[4,5] The etherate method and ion exchange can also be used for regeneration of heteropoly acid catalysts.

Electrodialysis has attracted interest as an effective method for clean production of heteropoly acids with high yields.[12–15] The synthesis is carried out in an electrolytic cell separated into anodic and cathodic sides by a cation-exchange membrane. An electric potential (ca. 12 V) is applied across the membrane. Initially, the anodic side is in contact with an aqueous solution of sodium tungstate or molybdate and a salt of the heteroatom taken in an almost stoichiometric ratio; the cathodic side is filled with distilled water. The anodic side is acidified by electrolysis of water, and Na^+ ions are transferred from the anode to cathode side by the applied potential through the cation-exchange membrane to yield the pure heteropoly acid in the anodic chamber. For example, an efficient electromembrane synthesis of $H_3[PW_{12}O_{40}]$ from Na_2WO_4 with H_3PO_4 has been developed.[13,14] This method is illustrated schematically in Figure 3.1. The $[PW_{12}O_{40}]^{3-}$ anion is formed in the anionic side of electrodialyser in two stages. In the first stage, which is carried out in the absence of phosphate ions, the WO_4^{2-} ions are converted electrochemically into the isopolytungstate $[W_7O_{24}]^{6-}$. Then H_3PO_4 is introduced and the electrodialysis process is continued until completion to yield $H_3[PW_{12}O_{40}]$ and NaOH aqueous solutions in the anodic and cathodic sides, respectively. The heteropoly acid is isolated from aqueous solution by crystallisation with an almost 100% yield based on Na_2WO_3. The NaOH so obtained can be used for the preparation of Na_2WO_3 from WO_3. No waste is therefore formed in the process. The sodium content does not exceed 0.01 wt% in the final product. Similarly, other heteropoly acids such as $H_4[SiW_{12}O_{40}]$, $H_5[PW_{11}TiO_{40}]$, $H_5[PW_{11}ZrO_{40}]$, $H_6[PW_{11}BiO_{40}]$, and $H_6[P_2W_{21}O_{71}]$ have been obtained.[12,15]

Lacunary heteropoly anions are frequently used for the preparation of transition metal-substituted polyoxometalates. The most common Keggin and Wells–Dawson lacunary polyanions are formed by adding controlled amounts of alkali to the parent polyanions in aqueous solution.[1–5]

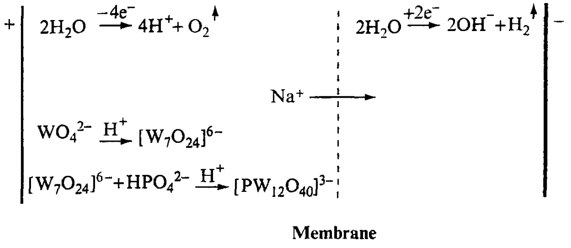

Figure 3.1 The scheme of electromembrane synthesis of $H_3[PW_{12}O_{40}]$.[13,14]

$$[PW_{12}O_{40}]^{3-} \xrightarrow{OH} [PW_{11}O_{39}]^{7-} + W(VI) \qquad (3.3)$$

$$[P_2W_{18}O_{62}]^{6-} \xrightarrow{OH^-} [P_2W_{17}O_{61}]^{10-} + W(VI) \qquad (3.4)$$

Further incorporation of a transition metal cation into the lacuna leads to the transition metal-substituted polyoxometalate, for example:

$$[PW_{11}O_{39}]^{7-} + Co^{2+} \rightarrow [PW_{11}CoO_{39}]^{5-} \qquad (3.5)$$

The following sections give examples of syntheses of some typical polyoxometalates that are used as acid or oxidation catalysts. The corresponding characterisation data can be found in the references provided.

3.2 KEGGIN POLYOXOMETALATES

3.2.1 12-MOLYBDOSILICIC ACID, α-$H_4[SiMo_{12}O_{40}]$

The following modification of the procedures[16–18] was used. Sodium molybdate, $Na_2MoO_4 \cdot 2H_2O$ (50 g, 0.21 mol) was dissolved in water (200 ml), and the solution heated to 80 °C. To this solution was added concentrated hydrochloric acid (20 ml). The mixture was stirred vigorously with a magnetic stirrer while sodium metasilicate (0.045 mol) dissolved in water (50 ml) was added dropwise over 30 min. The resulting solution turned yellow. While the stirring was continued, concentrated hydrochloric acid (60 ml) was added dropwise from a dropping funnel. The slight precipitate of silicic acid was filtered off through a porous glass filter. The filtrate was cooled and extracted with diethyl ether. The ether complex was diluted with one-half of its volume of water, and the diethyl ether rapidly displaced by a stream of air. Should the solution become green due to reduction, the yellow colour could be restored by adding a small amount of concentrated nitric acid. The product crystallised readily.

For purification, the product was dissolved in a mixture of water (50 ml) and concentrated hydrochloric acid (15 ml) and extracted with diethyl ether. The ether was removed as previously described, and the yellow liquid was concentrated at 40 °C and crystallised at room temperature to yield 12-molybdosilicic acid hydrate, α-$H_4[SiMo_{12}O_{40}]xH_2O$. Care must be taken to guard against reduction. A small amount of concentrated nitric acid could reoxidise the acid and restore the yellow colour. The crystals formed contained about 29 molecules of water of hydration. Most of this water could be removed by heating the acid at 60 °C under vacuum or drying in a desiccator over P_2O_5. The product then contained five to six molecules of water. IR (KBr, cm^{-1}): 957 Mo=O), 904 (Si–O) 855 (Mo–O–Mo), 770 (Mo–O–Mo).[18]

3.2.2 12-TUNGSTOSILICIC ACID, α-$H_4[SiW_{12}O_{40}]$

Sodium tungstate hydrate, $Na_2WO_4 \cdot 2H_2O$ (20.0 g, 0.061 mol) was dissolved in water (40 ml), and to this solution was added sodium metasilicate (0.0071 mol). The mixture was stirred with a magnetic stirrer and heated to boiling while concentrated hydrochloric acid (12 ml) was added over 90 minutes using a dropping funnel. The slight precipitate of silicic acid was filtered off, and the mixture cooled. Concentrated hydrochloric acid was added (8 ml) and the solution cooled again. This solution was shaken with a slight excess of diethyl ether, and the bottom oily layer of the ether complex was drawn off. This complex was dissolved in 3 M hydrochloric acid (20 ml) and extracted again with diethyl ether. The ether complex was separated, and the diethyl ether removed by passing air over the mixture while it was heated on a water bath. This was continued until crystals appeared at the edge of the liquid. The solution was then set aside for slow crystallisation or evaporated to dryness. This procedure was repeated until the product no longer smelled of HCl. When the acid was sufficiently dry, it was ground in a mortar and dried to constant weight at 70 °C to give α-$H_4[SiW_{12}O_{40}]$ 6–9H_2O.[16] In our hands, the yield was 80–85 % based on sodium tungstate. IR (KBr, cm^{-1}): 981 (W=O), 928 (Si–O), 880 (W–O–W), 785 (W–O–W).[18]

3.2.3 12-TUNGSTOPHOSPHORIC ACID, α-$H_3[PW_{12}O_{40}]$

Sodium tungstate, $Na_2WO_4 \cdot 2H_2O$, (100 g, 0.303 mol) and disodium phosphate, Na_2HPO_4, (13 g, 0.090 mol) were dissolved in boiling water (150 ml) while magnetically stirred. Concentrated hydrochloric acid (80 ml) was added dropwise with constant stirring. Tungstophosphoric acid began to precipitate when most of the acid was added. After the solution was cooled, diethyl ether (about 60 ml) was added until, after shaking, three layers formed. More water could be used to dissolve the sodium chloride, if necessary. The heteropoly etherate, which constituted the lower layer, was washed several times with water to which enough diethyl ether was added to form a third layer. It was then separated and evaporated to dryness while mildly heated under air current. The solid material was dried to constant weight at 70 °C to give α-$H_3[PW_{12}O_{40}]$ 6–7H_2O with about 80% yield based on the sodium tungstate.[16] IR (KBr, cm^{-1}): 1080 (P–O), 990 (W=O), 890 (W–O–W), 810 (W–O–W).[18] ^{31}P NMR (H_2O, ppm): −14.9.[19]

3.2.4 12-MOLYBDOPHOSPHORIC ACID, α-$H_3[PMo_{12}O_{40}]$

This acid was prepared from its disodium salt, α-$Na_2H[PMo_{12}O_{40}]$, by extraction with diethyl ether from acidified aqueous solution.[16] The preparation of α-$Na_2H[PMo_{12}O_{40}]$ was as follows. To an aqueous solution of Na_2MoO_4

(420 ml, 2.85 M) were added successively H_3PO_4 (85%, 14.7 M, 6.8 ml) and $HClO_4$ (70%, 12 M, 284 ml). The disodium salt α-$Na_2H[PMo_{12}O_{40}]$ precipitated from the yellow warm solution. After the mixture was cooled to room temperature, the microcrystalline powder was filtered and air-dried to yield 250 g of product. Recrystallisation in a mixture of ether/water (40 ml/200 ml) gave 180 g of greenish microcrystals of the α-$Na_2H[PMo_{12}O_{40}]$ hydrate. IR (KBr, cm^{-1}): 1068 (P–O), 962 (Mo=O), 869 (Mo–O–Mo), 785 (Mo–O–Mo).[18]

α-$H_3[PMo_{12}O_{40}]$ was obtained from an aqueous solution of α-$Na_2H[PMo_{12}O_{40}] \cdot 14H_2O$ (250 g/200 ml), acidified by 50 ml of 12 M HCl, and extracted by ether (400 ml). The heavy layer (300 ml), added with half its volume of water, gave yellow crystals after desiccation (190 g). IR (KBr, cm^{-1}): 1067 (P–O), 975 (Mo=O), 963 (vs), 870 (Mo–O–Mo), 810 (Mo–O–Mo).[18] ^{31}P NMR (H_2O, ppm): −3.9.[19]

12-Molybdophosphoric acid can be prepared by a clean procedure from MoO_3 and 85% H_3PO_4 without ether extraction.[20] In our laboratory a modification of this method was used. A mixture of MoO_3 (100 g, 0.695 mol) and H_3PO_4 (85%, 0.14 mol) in 500 ml of deionised water was refluxed with intense stirring for 20 h until most of the MoO_3 dissolved to form a greenish solution. The undissolved MoO_3 was filtered off. The solution was evaporated until crust appeared. A small amount of concentrated nitric acid was added to oxidise Mo(V) to Mo(IV); the green solution turned yellow. The solution was set aside for slow crystallisation that afforded α-$H_3[PMo_{12}O_{40}]$ hydrate as yellow crystals (55–60% based on MoO_3). The product was recrystallised from water. The filtrate after crystallisation, containing Mo(VI) and H_3PO_4, could be used in further preparations.

3.2.5 12-TUNGSTOGERMANIC ACID, α-$H_4[GeW_{12}O_{40}]$

An aqueous solution of $Na_2WO_4 \cdot 2H_2O$ (1.25 M, 250 ml) was mixed with the germanate solution (70 ml) containing powdered Ge metal (99.999%, 10.5 g, 0.144 mol) suspended in NaOH (6.25 M, 60 ml). The mixture was heated to 80 °C. Concentrated HNO_3 (13 M, 45 ml) was added dropwise with stirring until pH 0.5. (Cloudiness that appeared at the beginning of the addition progressively dissolved, and the solution became clear at the pH 0.5.) After keeping for six hours at 80 °C to complete $\beta \rightarrow \alpha$ isomerisation, the solution was cooled to room temperature. A further addition of HNO_3 (13 M, 10 ml) allowed the extraction with diethyl ether. After separation, the organic layer was added with half its volume of water and put in a vacuum desiccator over concentrated sulfuric acid. The crystallisation was performed in a refrigerator to yield 66 g of α-$H_4[GeW_{12}O_{40}] \cdot 14H_2O$. IR (KBr, cm^{-1}): 980 (W=O), 903 (W–O–W), 818 (Ge–O), 760 (W–O–W).[18]

3.2.6 11-MOLYBDO-1-VANADOPHOSPHORIC ACID, $H_4[PMo_{11}VO_{40}]$

Na_2HPO_4 (7.1 g, 0.050 mol) was dissolved in water (100 ml) and mixed with sodium metavanadate (6.1 g, 0.050 mol) that had been dissolved by boiling in water (100 ml). The mixture was cooled and acidified to a red colour with concentrated sulfuric acid (5 ml). To this mixture was added a solution of $Na_2MoO_4 \cdot 2H_2O$ (133 g, 0.55 mol) dissolved in water (200 ml). Finally, concentrated sulfuric acid (85 ml) was added slowly with vigorous stirring of the solution. With this addition the dark red colour changed to a lighter red. The heteropoly acid was then extracted with diethyl ether (400 ml) after the water solution was cooled. In this extraction the heteropoly etherate was present in the middle layer; the aqueous layer (bottom) was yellow and probably contained vanadyl species. After separation, a stream of air was passed through the heteropoly etherate layer to free it of diethyl ether. The orange solid that remained was dissolved in water (50 ml), concentrated to the first appearance of crystals in a vacuum desiccator over concentrated sulfuric acid, and then allowed to crystallise further. The orange crystals that formed were filtered, washed with water, and air-dried (28 g, 23%). The amount of water of crystallisation varied slightly from sample to sample.[21]

3.2.7 10-MOLYBDO-2-VANADOPHOSPHORIC ACID, $H_5[PMo_{10}V_2O_{40}]$

Sodium metavanadate (24.4 g, 0.20 mol) was dissolved by boiling water (100 ml) and then mixed with Na_2HPO_4 (7.1 g, 0.050 mol) in water (100 ml). After the solution was cooled, concentrated sulfuric acid (5 ml) was added, and the solution developed a red colour. An addition of $Na_2MoO_4 \cdot 2H_2O$ (121 g, 0.50 mol) dissolved in water (200 ml) was then made. While the solution was vigorously stirred, concentrated sulfuric acid (85 ml) was added slowly, and the hot solution was allowed to cool to room temperature. The 10-molybdo-2-vanadophosphoric acid was then extracted with diethyl ether (500 ml). Air was passed through the heteropoly etherate to free of diethyl ether. The solid remaining was dissolved in water, concentrated to first crystal formation, as already described for $H_4[PMo_{11}VO_{40}]$, and then allowed to crystallise further. The large red crystals that formed were filtered, washed with water and air-dried (35 g, 30% based on molybdate).[21]

3.2.8 9-MOLYBDO-3-VANADOPHOSPHORIC ACID, $H_6[PMo_9V_3O_{40}]$

Na_2HPO_4 (7.1 g, 0.050 mol) was dissolved in water (50 ml) and mixed with sodium metavanadate (36.6 g, 0.30 mol) that had been dissolved by heating in water (200 ml). Concentrated sulfuric acid (5 ml) was added to the cooled mixture, and it attained a cherry red colour. This solution was mixed with $Na_2MoO_4 \cdot 2H_2O$ (54.4 g, 0.225 mol) dissolved in water (150 ml), and then, while it was being vigorously stirred, concentrated sulfuric acid (85 ml) was slowly added. The hot solution was allowed to cool to room temperature. The free acid was extracted with diethyl ether (400 ml), the heteropoly etherate being the middle layer. The etherate was freed of diethyl ether by passing a stream of air through the solution. The red solid remaining was dissolved in water (40 ml) and concentrated to crystal formation in a vacuum desiccator over concentrated sulfuric acid. The red crystals were filtered and washed with water (the yield, 7.2 g).[21]

3.2.9 TRANSITION-METAL-SUBSTITUTED TUNGSTOPHOSPHATES, $\{PW_{11}MO_{39}\}$

The salts $(TBA)_4H_x[PW_{11}M(H_2O)O_{39}]nH_2O(M = Co^{2+}, Ni^{2+}, Mn^{2+}, Fe^{3+}$, etc.; TBA = tetra-n-butylammonium) were synthesised by the following procedure[22] that is a modification of the general protocol elaborated by Tourné *et al.*[23] An aqueous solution of the anion $[PW_{11}M(H_2O)O_{39}]^{5-}$ was prepared by mixing Na_2HPO_4 (9.1 mmol), $Na_2WO_4 \cdot 2H_2O$ (100 mmol) and a nitrate or sulfate salt of M (12 mmol) in 200 ml of water and adjusting the pH to 4.8 by adding acetic acid or dilute nitric acid solution dropwise. An aqueous solution of TBA bromide (45 mmol) in water (20 ml) was added dropwise, with stirring, at 80–85°C. The solid formed was filtered off and recrystallised from acetonitrile. Upon recrystallisation some insoluble material was separated and the salt $(TBA)_4H_x[PW_{11}M(H_2O)O_{39}]nH_2O$ precipitated by addition of water (1:1). In the case of iron(III)-substituted compound, a few drops of nitric acid were added to the acetonitrile solution so as to turn the solution from green to yellow (conversion of the dimeric anion). All salts were dried in vacuum at 100 °C.

The following compounds were prepared as hydrates: $[(C_4H_9)_4N]_4H[PW_{11}Mn(H_2O)O_{39}]$, $[(C_4H_9)_4N]_4H[PW_{11}Co(H_2O)O_{39}]$, $[(C_4H_9)_4N]_4H[PW_{11}Ni(H_2O)O_{39}]$, $[(C_4H_9)_4N]_4H[PW_{11}Cu(H_2O)O_{39}]$, and $[(C_4H_9)_4N]_4[PW_{11}Fe(H_2O)O_{39}]$.

$(TBA)_4H_3[PW_{11}O_{39}]$ was prepared using a similar procedure except for the addition of the salt of M.

3.3 WELLS–DAWSON POLYOXOMETALATES

3.3.1 18-TUNGSTODIPHOSPHORIC ACID, $H_6[P_2W_{18}O_{62}]$

$Na_2WO_4 \cdot 2H_2O$ (150 g) was dissolved in hot water (150 ml), and then were added an aqueous solution of H_3PO_4 (85%, 125 ml) and water (30 ml) with vigorous stirring. The solution was boiled for 5 hours, the volume of the solution being kept at 250 ml by adding water. To prevent reduction, a small amount of HNO_3 was added to the light yellow solution. The solution was evaporated until crust appeared, cooled to 0 °C and the precipitate was separated by filtration. The precipitate was dissolved in water (30 ml) and recrystallised at room temperature. The product was extracted with diethyl ether. By recrystallisation from water, yellow crystals of $H_6[P_2W_{18}O_{62}] \cdot 32H_2O$ were obtained.[24,25] IR (KBr, cm^{-1}): 1091 (P–O), 962 (W = O), 914 (W–O–W), 780 (W–O–W).[25]

3.4 SANDWICH-TYPE POLYOXOMETALATES

3.4.1 $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$

A solution of $Na_2WO_4 \cdot 2H_2O$ (127 g, 0.38 mol) in water (350 ml) was treated with nitric acid (14 N, 2 ml, 0.35 mol) at 80–85 °C with vigorous stirring until the precipitate that formed initially dissolved entirely. A solution of zinc nitrate hexahydrate (29.8 g, 0.10 mol) in water (100 ml) was then added with continuous stirring and heating at 90–95 °C (not boiling). The addition was carried out first in small aliquots (ca. 3–4 ml), giving a white precipitate which redissolved rapidly (until 2/3 of the zinc nitrate solution was added), then dropwise, more and more slowly, in such a way that the mixture remained clear till the end. The process required 2–3 hours. The final pH was about 7.5. If necessary, the solution was filtered (a possible slight turbidity might not be filterable). A first crystallisation occurred on moderate cooling (to about 40 °C), affording a first crop as fine needles. The liquid was evaporated to half volume and left unstirred, covered, at 50 °C. Overnight, needle-like crystals appeared and were left to grow for 3–4 days. Thus the product (90–95 g, 65–68%) was initially separated. The resulting cold filtrate was shaken with equal volume of acetone to extract the major part of the sodium nitrate produced (two layers). The dense lower layer was diluted with an equal volume of water, heated to 50 °C, and left at this temperature to yield an additional amount of product. The process was repeated until the filtrate no longer crystallised at room temperature. A total yield of 85–90% was obtained. The collected crops were recrystallised together from water to give a homogeneously hydrated product $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2] \cdot 46{-}48H_2O$. A similar procedure can be carried out using different reagents (HCl or acetic acid and chloride or acetate). The nitric acid medium allowed, however, the best separation of the sodium salt formed.[26]

3.4.2 $Na_{12}[WCo_3^{II}(H_2O)_2(Co^{II}W_9O_{34})_2]$

The preparation of the cobalt(II) homologue was identical.[26] The solution was initially emerald-green, but turned olive-green on prolonged heating, indicating the formation of the expected polyanion. A pink precipitate eventually appeared and readily separated to give $Na_{12}[WCo^{II}_3(H_2O)_2(Co^{II}W_9O_{34})_2] \cdot 46-48H_2O$. The yield varied between 50 and 80%.

3.4.3 $K_{11}[WZnRu^{III}{}_2(OH)(H_2O)(ZnW_9O_{34})_2]$

To a solution of $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2] \cdot 46H_2O$ (23 g, 3.9 mmol) in water (10 ml) at 90 °C under argon was added $Ru(DMSO)_4Cl_2$ (4 g, 12.2 mmol). The solution was stirred at this temperature for 18 h and then cooled and opened to air. A brown solution was obtained which, upon addition of potassium chloride (2 g), yielded a crude precipitate of the ruthenium-substituted polyoxometalate (10.9 g, 46%). The product was crystallised twice from hot water to give $K_{11}[WZnRu^{III}{}_2(OH)(H_2O)(ZnW_9O_{34})_2] \cdot 13H_2O$ (24%).[27]

The sodium salt $Na_{11}[WZnRu^{III}{}_2(OH)(H_2O)(ZnW_9O_{34})_2] \cdot 42H_2O$ was obtained by dissolution of potassium salt in 0.5 M solution of NaCl.[27]

3.4.4 $K_{10}[WZnRh^{III}{}_2(H_2O)(ZnW_9O_{34})_2]$

A similar procedure using $RhCl_3 \cdot 3H_2O$ instead than $Ru(DMSO)_4Cl_2$ gave rhodium analogue $K_{10}[WZnRh^{III}{}_2(H_2O)(ZnW_9O_{34})_2] \cdot 40H_2O$.[28] A hot aqueous solution containing $RhCl_3 \cdot 3H_2O$ (2.5 eq) and $Na_{12}[(WZn_3)(ZnW_9O_{34})_2]$ (1 eq) was stirred for four hours. A colour change from deep brown to light brown was observed. After addition of KCl and cooling, a light brown solid was precipitated. The crude polyoxometalate was then purified by recrystallisation from water (27%).

3.5 PEROXO POLYOXOMETALATES

3.5.1 VENTURELLO COMPLEX, $\{PO_4[WO(O_2)_2]_4\}^{3-}$

A suspension of tungstic acid (2.5 g, 10 mmol) in aqueous H_2O_2 (30%, 7 ml) was stirred and heated to 60 °C until a colourless solution was obtained. To this solution, filtered and cooled to room temperature, was added 40% H_3PO_4 (0.62 ml, 2.5 mmol), and the solution was diluted with water (30 ml). Then methyltrioctylammonium chloride (2.03 g, 5 mmol) in dichloromethane (40 ml) was added dropwise with stirring over about two minutes. Stirring was continued for an additional 15 minutes. The organic phase was then separated, dried over sodium sulfate, filtered, and gently evaporated under reduced pressure at 40–50 °C to give an almost colourless syrup of the salt $[(C_8H_{17})_3NCH_3]_3\{PO_4[WO(O_2)_2]_4\}$ (3.7 g, 98%, based on the quaternary ammonium salt charged). *Anal.* Calcd for $C_{75}H_{162}N_3PW_4O_{24}$: C, 39.91; H, 7.24; N, 1.86; W, 32.6; P, 1.37; O (active), 5.68. Found: C, 40.30; H, 7.39; N, 1.84; W, 31.0; P, 1.31; O (active), 5.66. Molecular weight ($CHCl_3$): M_r calculated 2256.7, M_r observed 2190. IR (neat, KBr plates, cm^{-1}): 1088, 1058 and 1035 (sh) (P–O), 975 (W = O), 856 and 846 (O–O), 591 and 523 (W–O–O); other bands at 725, 651, 576 and 549.[29]

3.6 POLYOXOMETALATE CATALYSTS

3.6.1 SOLID ACID CATALYSTS

3.6.1.1 $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$

This insoluble salt was prepared simply by adding a stoichiometric amount of caesium carbonate to $H_3[PW_{12}O_{40}]$ in concentrated aqueous solution.[30] The caesium salt precipitated quantitatively, with CO_2 evolving, and isolated by evaporation.

$$H_3[PW_{12}O_{40}] + 1.25\,Cs_2CO_3 \rightarrow Cs_{2.5}H_{0.5}[PW_{12}O_{40}] + 1.25\,CO_2 + 1.25\,H_2O$$

A stoichiometric amount of aqueous caesium carbonate (0.47 M) was added dropwise with stirring to an aqueous solution of $H_3[PW_{12}O_{40}]$ (0.75 M) at room temperature. The white precipitate obtained was aged in water for 20 hours at room temperature, then evaporated to dryness at 45 °C under vacuum (25 Torr). The solid obtained was ground in a mortar and finally calcined at 300 °C for 3 hours under vacuum (25 Torr). Caesium tungstophosphates with various Cs/P ratios were prepared similarly.

Acidic caesium tungstophosphates $Cs_xH_{3-x}[PW_{12}O_{40}]$ were also prepared by grinding a mixture of $H_3[PW_{12}O_{40}]$ and $Cs_3[PW_{12}O_{40}]$.[31] This procedure was claimed to lead to high surface area catalysts that showed better activities for n-butane isomerisation compared to the catalysts prepared by precipitation.

3.6.1.2 Silica-Supported $H_3[PW_{12}O_{40}]$

Catalysts containing 10 to 50 wt% $H_3[PW_{12}O_{40}]$ on silica were prepared by shaking a suspension of Aerosil 380 (Degussa) in an aqueous solution (3–5 ml), containing a certain amount of heteropoly acid, in a glass vessel overnight at room temperature.[32] The pH of the impregnating aqueous solution varied from 1 to 2 depending on the heteropoly acid loading. For the loadings ≤ 20 wt%, methanol was preferably used instead of water to prevent decomposition of heteropoly acid. The solvent was evaporated in a rotary evaporator at the temperature below 60 °C. The catalysts were ground in a mortar, calcined at 150 °C/0.3 Torr for 1.5 hour and stored in a desiccator over P_2O_5. Similarly, other heteropoly acids, e.g., $H_4[SiW_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, etc., can be supported on silica or another support. Prior to use, the silica-supported catalysts may require treatment at higher temperatures (200–300 °C) to remove traces of water.

3.6.1.3 Sol–Gel Catalysts

Silica-included $H_3[PW_{12}O_{40}]$ and $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ were prepared by a sol–gel technique through the hydrolysis of ethyl orthosilicate conducted at 40 °C for one hour and then at 80 °C for three hours in the presence of $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ or $H_3[PW_{12}O_{40}]$ dispersed or dissolved in ethanol.[30] The hydrogel obtained was dehydrated slowly at 45 °C under vacuum (25 Torr), followed by grinding to fine particles. In the case of salt inclusion, the dried gel was extracted with water at 80 °C for 10 hours to remove the nontrapped salt and organics, and finally calcined at 300 °C for three hours under vacuum (25 Torr). As for the acid inclusion, the dried gel was once calcined at 150 °C for three hours under vacuum (25 Torr) to fasten the silica network, then extracted with water at 80 °C for three hours, and finally calcined at 150 °C for three hours under vacuum (25 Torr).

3.6.2 HOMOGENEOUS CATALYSTS

3.6.2.1 Molybdovanadophosphates, $[PMo_{12-n}V_nO_{40}]^{(3+n)-}$

Aqueous solutions of sodium salts of the $H_{3+n}[PMo_{12-n}V_nO_{40}]$ heteropoly acids ($n = 2 - 6$) of the formula $Na_nH_3[PMo_{12-n}V_nO_{40}]$ or $Na_{n+1}H_2[PMo_{12-n}V_nO_{40}]$, consisting of a complex mixture of P–Mo–V polyanions, to be used as catalysts for liquid-phase oxidation were prepared by a modification of the method of Matveev *et al.*[33] Stoichiometric amounts of vanadium pentoxide, molybdenum trioxide, sodium phosphate, and sodium carbonate were refluxed in distilled water, cooled and the pH adjusted by addition of concentrated sulfuric acid. A 0.20 M solution of $Na_4H_3[PMo_8V_4O_{40}]$ was prepared as follows. $NaH_2PO_4 \cdot H_2O$ (4.80 g, 0.0348 mol), MoO_3 (40.0 g, 0.278 mol), V_2O_5 (12.6 g, 0.0695 mol), and anhydrous Na_2CO_3 (7.38 g, 0.0695 mol) were refluxed in distilled water (150 ml) for 2 h with stirring. Normally, the solids were dissolved completely to form a dark brown solution. The solution was cooled to room temperature and diluted with distilled water to a volume of 175 ml corresponding to the concentration of 0.20 M $Na_4H_3[PMo_8V_4O_{40}]$ (pH ca. 2.5). Traces of undissolved solids were filtered off. The stock solution, containing known amounts of P, Mo, and V, was stable in a stoppered glass bottle for at least a couple of years. Prior to using for liquid-phase oxidation, the pH was adjusted, typically to 0.5–2.0, by addition of concentrated sulfuric acid. Other compounds, e.g. H_3PO_4, $NaVO_3$, or Na_2MoO_4, could be used as a source of P, V, or Mo in this synthesis.

Several methods allowing the preparation of $[PMo_{12-n}V_nO_{40}]^{(3+n)-}$ solutions with lower concentrations of sodium ions have been reported.[34,35] The production of aqueous molybdovanadophosphates for use as oxidation catalysts on a large scale as well as in the laboratory has been described.[34]

3.6.2.2 Molybdophosphoric Acid, $H_3PO_4 \cdot 6MoO_3$

An aqueous solution of heteropoly acid catalyst of the composition $H_3PO_4 \cdot 6MoO_3$ with excellent stability and a long shelf-life was prepared in our laboratory by the following procedure.[36] Molybdenum trioxide (21.6 g, 0.15 mol) and H_3PO_4 (85 %, 0.025 mol) were refluxed in distilled water (100 ml) for 20 h until MoO_3 almost completely dissolved to form a green solution. Undissolved MoO_3 was filtered off, and the solution was evaporated to a volume of 30 ml to afford a dark green solution of molybdophosphates with a formal composition of $H_3PO_4 \cdot 6MoO_3$ (98.6 % yield). The catalyst solution had a concentration of ca. 50 wt%, 1.54 g cm^{-3} density, and pH ≈ 0. The catalyst was stable in a stoppered glass bottle for years. From ^{31}P NMR, the fresh catalyst solution mainly contained a mixture of H_3PO_4 and $H_3[PMo_{12}O_{40}]$. After two years on the shelf, it turned to be H_3PO_4 and $H_6[P_2Mo_{18}O_{62}]$.[37] This catalyst was tested in many homogeneous acid-catalysed reactions. It was particularly effective for hydration of olefins (e.g. isobutene) and decomposition of cumene hydroperoxide into phenol and acetone.[36]

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4 Acid Catalysis by Heteropoly Compounds

CONTENTS

Heteropoly acids have found numerous applications as acid catalysts, including several industrial applications, for example, for hydration of olefins, polymerisation of tetrahydrofuran, and esterification (Chapter 7). In this chapter, we will discuss homogeneous and heterogeneous acid catalysis by heteropoly acids for organic reactions in liquid phase and gas phase. Various aspects of this topic have been reviewed.[1–12]

4.1 GENERAL OVERVIEW

4.1.1 THE SCOPE OF APPLICATIONS

Table 4.1 shows some typical examples of acid-catalysed reactions with the use of heteropoly acids as catalysts. The reactions are placed in the order of decreasing catalyst acid strength required for the reaction to occur, ranging from the highly demanding reactions such as alkane isomerisation to very mild additions and the Diels–Alder reaction. These reactions are carried out in homogeneous or heterogeneous (gas–solid, liquid–solid or biphasic liquid–liquid) systems.

Table 4.1 Reactions catalysed by heteropoly acids[1,2].

Isomerisation of alkanes
Conversion of MeOH to olefins
Alkylation of paraffins
Oligomerisation of alkenes
Friedel–Crafts and related reactions
Beckmann rearrangement: cyclohexanone oxime → ε-caprolactam
Esterification and transesterification
Hydration of alkenes
Hydrolysis
Prins reaction: alkene + HCHO → 1,3-dioxane
Polymerisation of tetrahydrofuran
Trimerisation of aldehydes: RCHO → 1,3,5-trioxane
Decomposition: $Ph(Me)_2COOH \rightarrow PhOH + Me_2CO$
Addition: isobutene + MeOH → MTBE
    alkene + AcOH → alkyl acetate
Diels–Alder reaction

4.1.2 MECHANISTIC PRINCIPLES

Generally, reactions catalysed by heteropoly acids may be represented by the conventional mechanisms of Brønsted acid catalysis. In a simple case of single proton transfer, the mechanism may include the protonation of the substrate followed by the conversion of the ionic intermediate to yield the reaction product:[2,3]

$$S_1 + H^+ \rightleftharpoons S_1H^+ \xrightarrow{(S_2)} P + H^+ \tag{4.1}$$

In this equation, S_1 and S_2 are the substrates and P is the product. In accordance with this mechanism, the catalytic activity of heteropoly acids, both in homogeneous and heterogeneous systems, usually parallels their acid strength, i.e. $H_3[PW_{12}O_{40}] > H_4[SiW_{12}O_{40}] > H_3[PMo_{12}O_{40}] > H_4[SiMo_{12}O_{40}]$.[2] Being stronger acids and therefore more efficient proton donors, heteropoly acids usually exhibit higher catalytic activities than conventional mineral acids. Relatively strong oxidants, molybdenum heteropoly acids are frequently deactivated due to their reduction by the organic reaction medium; it is not uncommon for them to show lower activities than those expected from their acid strengths.[2]

4.1.2.1 Homogeneous Systems

Kinetics of several HPA-catalysed homogeneous reactions, such as hydration of isobutene,[4,13] decomposition of cumene hydroperoxide,[14] esterification,[15] hydrolysis of t-butyl fluoride,[16] and others,[1,4] has been studied in aqueous or nonaqueous solutions. Fairly good correlations between the reaction rates and the dissociation constants or Hammett acidity function, H_o, of heteropoly acids have been demonstrated.

Linear relationships between the logarithm of the observed rate constants and H_o with the slope of ca. 1 for the hydration of isobutene[13] and hydrolysis of t-butyl fluoride[16] in concentrated aqueous solutions of heteropoly acids have been obtained (Figure 4.1) – which is in agreement with the mechanism of these reactions. Importantly, the conventional mineral acids such as H_2SO_4, HNO_3, and $HClO_4$ also fit well these plots. This indicates that the principal mechanisms of these reactions are largely the same in the case of heteropoly acids and mineral acids.

In aqueous solution, typical Keggin heteropoly acids are fully dissociated 3–1 or 4–1 polyelectrolytes (e.g. $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$, respectively). Hence they can exert strong salt effects on catalysed reactions that may be significantly stronger than those in the case of mineral acids. Such salt effects may account for higher reaction orders with respect to HPA.[13] Thus for the hydration of isobutene,[4,13] the reaction order with respect to $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ was found to be 1.2–1.5 in dilute solutions (0.02–0.1 M HPA) and 2.0–2.2 in concentrated solutions (up to 0.5 M), whereas with nitric acid it is 1.0 regardless of the HNO_3 concentration.

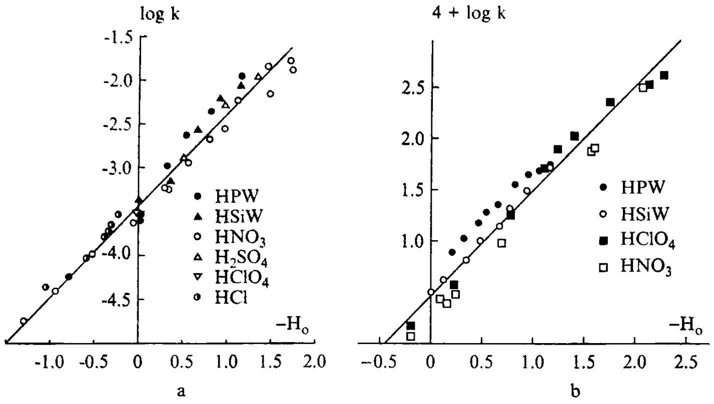


Figure 4.1 The Hammett plots for acid-catalysed reactions: (a) hydration of isobutene in water at 25 °C; the plot obeys an equation $\log k = -1.04\ H_o - 3.46$;[13] (b) hydration of tertbutyl fluoride in water at 25 °C; the plot obeys an equation $\log k = -1.03\ H_o - 3.52$.[16]

Electrolyte salt effects on activity coefficients of nonelectrolytes (e.g. organic substrates), f, generally follow the empirical Setschenow equation:[17,18]

$$\log f = B\ C_s \tag{4.2}$$

where C_s is the molar electrolyte concentration and B is the Setschenow salt effect parameter. Equation 4.2 is frequently used to account for salt effects on the reaction rate.[18] For a monomolecular reaction, the conventional rate constant k is given as

$$\log k = \log k_o + (B - B^{\neq})\ C_s \tag{4.3}$$

where k_o is the rate constant in pure solvent, B and $B^{\neq}$ are the Setschenow salt effect parameters for the ground state and transition state, respectively.

This approach was used for the hydration of isobutene catalysed by heteropoly acids and mineral acids (Table 4.2).[13] It was shown that $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ cause ten times stronger overall salt effect on the reaction rate ($B - B^{\neq} = 2.1$) than the 1–1 electrolyte HNO_3($B - B^{\neq} = 0.2$). This is in agreement with the relative ionic strengths of these acids. All the acids salt-in both the ground state and the transition state of the reaction, i.e. increase the solubility of isobutene and decrease the energy of the transition state. For heteropoly acids, the rate constants k_o extrapolated to zero molar concentration of acid catalysts ($C_s \rightarrow 0$) are greater than for HNO_3, as expected. Based on unit proton concentration, however, these rate constants (k_o') are quite similar, as may be expected assuming the same reaction mechanism for all these acids.

Table 4.2 Salt effects of acids on the hydration of isobutene in aqueous solution at 25 °C and 1 atm pressure[13].

	$10^4 k_o$ a $l\ mol^{-1}\ s^{-1}$	$10^4 k'_o$ b $l\ mol^{-1}\ s^{-1}$	B $l\ mol^{-1}$	$B^{\neq}$ $l\ mol^{-1}$	$B-B^{\neq}$ $l\ mol^{-1}$
$H_3[PW_{12}O_{40}]$	20.0 ± 3	6.7	−0.87	−3.0	2.1
$H_4[SiW_{12}O_{40}]$	17.0 ± 4	4.3	−0.87	−3.0	2.1
HNO_3	3.8 ± 0.4	3.8	−0.02	−0.2	0.2

a) Second-order rate constants of hydration of dissolved isobutene at unit concentration, per 1 mole l^{-1} of acid catalyst
b) The same rate constants, per 1 mole l^{-1} of H^+

It is suggested that heteropoly anions can stabilise cationic reaction intermediates (e.g. carbocations), thus promoting acid catalysed reactions in solution and in pseudoliquid phase.[1,4] Izumi *et al.* proposed such mechanism for the liquid-phase hydration of isobutene (Section 4.2.2.1).[4]

4.1.2.2 Heterogeneous Systems

Misono *et al.*[1,5,6] advanced a mechanistic classification for heterogeneous acid and oxidation catalysis by solid heteropoly compounds which distinguishes three types of catalysis, namely (i) surface type, (ii) bulk type I (or "pseudoliquid"), and (iii) bulk type II (Table 4.3). The surface type is a conventional acid or oxidation catalysis on the gas–solid or liquid–solid interface, e.g. a Langmuir–Hinshelwood type process. This type applies to processes occurring on the surface of both bulk and supported heteropoly compounds. The bulk types of mechanism are largely relevant to reactions on bulk heteropoly compounds. The bulk type I represents the acid catalysis by a bulk solid heteropoly acid for the conversion of a polar substrate (e.g. alcohol, ether, ketone, amine, etc.) that is capable of absorbing into the catalyst bulk. In this

Table 4.3 Three types of heterogeneous acid and oxidation catalysis by solid heteropoly compounds[1,5].

Type	Comment	Example
Surface type	Common type of surface reaction, e.g. Langmuir–Hinshelwood type *Rate ∝ catalyst surface area*	Alkane isomerisation Oxidation of aldehydes, CO
Bulk type I	'Pseudoliquid phase'; reactants absorb in the solid bulk and react pseudohomogeneously *Rate ∝ catalyst volume (weight)*	Dehydration of *i*-PrOH
Bulk type II	Reaction occurs on the surface, with the bulk diffusion of e^- and H^+ playing a key role *Rate ∝ catalyst volume (weight)*	Oxidative dehydrogenation Oxidation of H_2

case, the solid behaves like a concentrated solution (pseudoliquid phase), both the surface and the bulk acid sites participating in the reaction. The bulk type II is suggested to apply to certain catalytic oxidations that largely occur on the catalyst surface, with the bulk diffusion of electrons and protons assisting the redox process (Chapter 5).

Acid-catalysed reactions over bulk solid heteropoly acids occur by one of the two mechanisms: surface-type catalysis (nonpolar substrates) or bulk-type I (pseudoliquid) catalysis (polar substrates).[1] In the case of surface catalysis, that is common for heterogeneous acid catalysis, the catalytic activity usually depends on the surface acidity of heteropoly acid, i.e. the reaction rate is parallel to the number and the strength of the accessible surface acid sites. Polar molecules, such as alcohols, ethers, amines, etc., may react differently with crystalline heteropoly acids. Such molecules can absorb in large quantities into the catalyst bulk, forming HPA solvates[1] (Table 4.4). As the surface area of bulk heteropoly acids is very low, only 1–5 m^2 g^{-1}, the absorption may be equivalent to dozens of monolayers.[1] Thus, towards polar substances, solid heteropoly acids behave like highly concentrated solutions, i.e. all protons, both in the bulk and on the surface of heteropoly acid, participate in the catalytic reaction. This phenomenon is frequently referred to as 'pseudoliquid phase'.[1] Unlike polar molecules, nonpolar reactants (e.g., hydrocarbons) are incapable of absorbing in the bulk of heteropoly acids (Table 4.4). They interact only with the surface of the catalyst. The pseudoliquid behaviour appears to be important for reactions of polar molecules at relatively low temperatures, i.e., when the sorption of substrate in the catalyst bulk is significant. Surface and bulk catalysis may operate with strongly differing selectivities.[1] On top of that, the uniformity of pseudoliquid phase allows using spectroscopic techniques for studying the mechanism of catalytic processes. For example, probable reaction intermediates in the ethanol dehydration such as the protonated ethanol dimer $(EtOH)_2^+$, monomeric $EtOH_2^+$, protonated ether, and ethoxide were observed in the pseudoliquid $H_3[PW_{12}O_{40}]$ phase by solid-state NMR and IR spectroscopy.[1]

Table 4.4 Sorption of polar and nonpolar substances onto bulk $H_3[PW_{12}O_{40}]$ at 25 °C[1].

Substance	Sorption (molecules per Keggin unit)	
	Irreversible[a]	Total
Pyridine	6.0	9
Ammonia	3.2	4.3
Methanol	2.2	> 10
Isopropanol	6.3	> 10
Ethylene	0.03	0.04
1-Butene	0.2	0.25
Benzene	0.1	0.5

a) The amount irreversibly retained after evacuation at 25 °C

4.2 HOMOGENEOUS ACID CATALYSIS

4.2.1 INTRODUCTION

Heteropoly acids catalyse a wide variety of reactions in homogeneous liquid phase offering strong options for more efficient and cleaner processing compared to conventional mineral acids.[1–4,7–11] Being stronger acids, heteropoly acids will have significantly higher catalytic activity than mineral acids. In particular in organic media, the molar catalytic activity of heteropoly acid is often 100–1000 times higher than that of H_2SO_4[1,3] (Table 4.5). This makes it possible to carry out the catalytic process at a lower catalyst concentration and/or at a lower temperature. Further, heteropoly acid catalysis lacks side reactions such as sulfonation, chlorination, nitration, etc., which occur with mineral acids.[2,3] As stable, relatively nontoxic crystalline substances, heteropoly acids are also preferable regarding safety and ease of handling.

The relative activity of Keggin heteropoly acids primarily depends on their acid strength. Other properties, such as the oxidation potential as well as the thermal and hydrolytic stability are also important. These properties for the most common heteropoly acids are summarised below:[2]

Acid strength	PW $>$ SiW $\geq$ PMo $>$ SiMo
Oxidation potential	PMo $>$ SiMo $\gg$ PW $>$ SiW
Thermal stability	PW $>$ SiW $>$ PMo $>$ SiMo
Hydrolytic stability	SiW $>$ PW $>$ SiMo $>$ PMo

Usually, tungsten heteropoly acids are the catalysts of choice because of their stronger acidity, higher thermal stability and lower oxidation potential compared to molybdenum acids.[2,3] Generally, if the reaction rate is controlled by the catalyst acid strength, $H_3[PW_{12}O_{40}]$ shows the highest catalytic activity in the Keggin series. However, in the case of less demanding reactions as well as in reactions at higher temperatures in the presence of water, $H_4[SiW_{12}O_{40}]$, having lower oxidation potential and higher hydrolytic stability, could be superior to $H_3[PW_{12}O_{40}]$.

Table 4.5 Homogeneous reactions catalysed by heteropoly acids[2].

Reaction[a]	Rate ratio[b]	T °C	Ref.
Hydration of isobutene[c]	2–4	40	11
Hydration of phenylacetylene	100	60	11
$PhC(CH_3)_2OOH \rightarrow PhOH + CH_3COCH_3$	1000	25	3
Olefin + HOAc → ester	90	110	3
Ester → olefin + carboxylic acid	100	128	112
$n THF + Ac_2O \rightarrow AcO(CH_2CH_2CH_2CH_2O)_nAc$	> 1000	50	11
Styrene + HCHO → 1,3-dioxane	50	50	11

a) Unless otherwise stated, reactions were performed in organic media

b) HPA/H_2SO_4 (per proton)

c) In aqueous solution

The major problem, limiting the utility of homogeneously catalysed processes, is the well-known difficulty in catalyst recovery and recycling. As the cost of heteropoly acids is higher than that of mineral acids, the recycling of HPA catalysts is the key issue to their application. Only a few homogeneous reactions allow for easy recycling, for example, hydration of olefins (see below). In some cases, heteropoly acid can be recovered from polar organic solution without neutralisation by precipitating with a hydrocarbon solvent. Heteropoly acid can also be extracted from an acidified aqueous solution of its salt with a polar organic solvent. Even though the neutralisation of heteropoly acid is necessary, the amount of alkali needed and hence the amount of waste formed thereupon is much less than with mineral acids. A more effective way to overcome the separation problem is the use of biphasic systems or solid acid catalysts, which will be discussed in Sections 4.3 and 4.4. In the subsequent sections are given selected examples of HPA-catalysed homogeneous reactions. More can be found elsewhere.[1–4,7,8,10,11]

4.2.2 ACID-CATALYSED REACTIONS

4.2.2.1 Hydration of Olefins

The HPA-catalysed hydration of C_3-C_4 olefins (eq. 4.4) is an industrially important reaction, the hydration of propene being the first commercial process based on heteropoly acid catalysis.[12]

$$RCH{=}CH_2 + H_2O \rightarrow RCH(OH)CH_3 \qquad (4.4)$$

The hydration of isobutene is used for the separation of isobutene from the C_4 hydrocarbon stream produced by cracking. As the catalyst, a concentrated aqueous solution of heteropoly acid is used. Compared to mineral acids, such as H_2SO_4, HNO_3, and $HClO_4$, heteropoly acid is 2–4 times more active per equal H_3O^+ concentration and shows a higher selectivity, minimising side reactions such as isobutene oligomerisation.[19,20] Izumi *et al.*[4,19] showed that the reaction order with respect to heteropoly acid depends on the HPA concentration: first-order in dilute solution and nearly second-order in concentrated solution. In contrast, the reaction with mineral acids is first-order in the catalyst. The solubility of isobutene also significantly increases with increasing the concentration of heteropoly acid. On these bases, a two-path reaction mechanism is suggested (Figure 4.2).[4,19] Path I is a common mechanism with the formation of the intermediate carbenium ion. This mechanism operates with mineral acids. Path II includes the formation of a complex of heteropoly anion with the carbenium ion. It is path II that is assumed to be responsible for promoting the reaction by stabilising the intermediate carbenium ion in the above complex. From this mechanism, the rate of isobutene hydration can be expressed as:

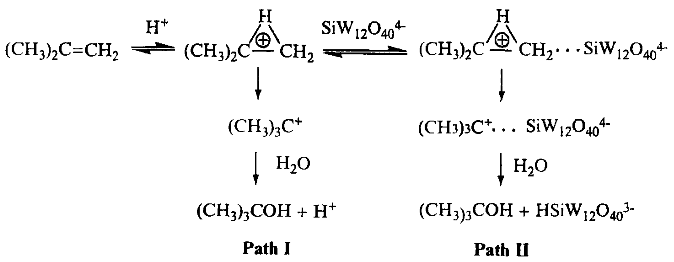


Figure 4.2 The mechanism of hydration of isobutene.[4,19]

$$r = k_1[\mathrm{Ol}][H_3O^+] + k_2[\mathrm{Ol}][H_3O^+][\mathrm{HPA}^{n-}] \qquad (4.5)$$

where k_1 and k_2 are the rate constants of paths I and II, and [Ol] and $[\mathrm{HPA}^{n-}]$ are the concentrations of olefin and heteropoly anion, respectively. This equation is in agreement with the experiment.[19]

On the other hand, as found by Kozhevnikov *et al.*,[13] the rate of isobutene hydration catalysed by heteropoly acids obeys the Hammett plot (Figure 4.1):

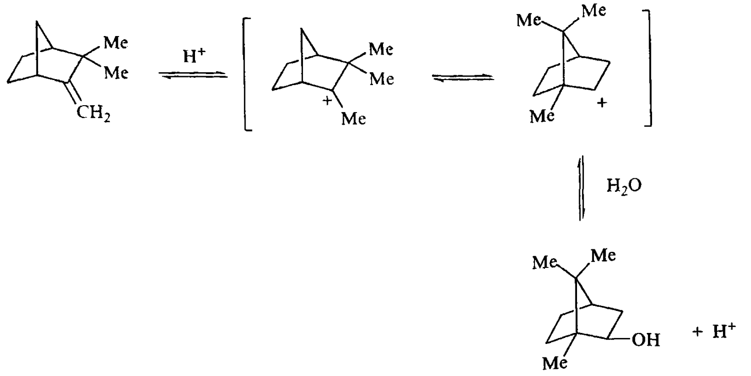
$$\log k = -1.04\ H_o - 3.46 \qquad (4.6)$$

This plot is also valid for mineral acids such as H_2SO_4, HCl, HNO_3, and $HClO_4$, which indicates that with both heteropoly acids and mineral acids the reaction proceeds via the same principal mechanism which may be represented by path I. The high order with respect to heteropoly acid is explained as a result of the strong specific salt effect of highly charged heteropoly anions[13] (Section 4.1.2.1).

Heteropoly acids were reported to be more efficient catalysts than H_2SO_4 and $HClO_4$ for the hydration of phenylacetylene[4] (eq. 4.7).

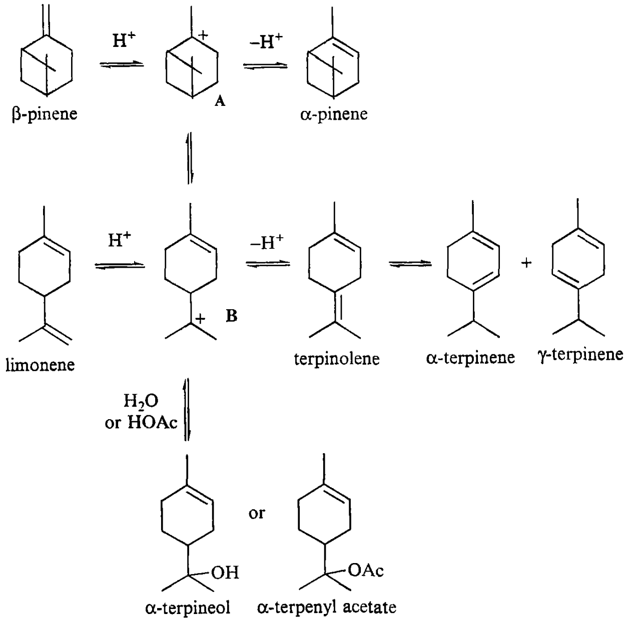
$$PhC{\equiv}CH + H_2O \rightarrow PhCOCH_3 \qquad (4.7)$$

Cycloalkenes are hydrated to cycloalkanols with 99 % selectivity in the presence of a catalyst consisting of a concentrated aqueous solution of an arylsulfonic acid and tungsten heteropoly acid.[21] $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ are efficient catalysts for the homogeneous hydration of camphene to isoborneol (eq. 4.8), which is an intermediate in the synthesis of camphor.[22]



(4.8)

The liquid-phase hydration and acetoxylation of limonene, β-pinene and α-pinene (Scheme 4.1) catalysed by dissolved and silica-supported heteropoly acid $H_3[PW_{12}O_{40}]$ in acetic acid and acetic acid/water solutions have been studied.[23] All three substrates give α-terpineol as the main product along with α-terpenyl acetate. The reaction rate increases in the order: limonene < α-pinene < β-pinene. At room temperature under optimised conditions, β-pinene and α-pinene form a mixture of α-terpineol and α-terpenyl acetate with 85 % selectivity at 90 % substrate conversion. Limonene gives α-terpineol and α-terpenyl acetate with 85 % selectivity at 50 % conversion, with the main product being α-terpenyl acetate in acetic acid and α-terpineol in $HOAc/H_2O$ (90/10 v/v) solutions. Virtually no oligomerisation of monoterpenes occurs under the optimised conditions. The catalyst can be separated without neutralisation and may be reused. $H_3[PW_{12}O_{40}]$ shows a much higher catalytic activity than H_2SO_4 and Amberlyst-15.



Scheme 4.1

4.2.2.2 Esterification and Related Reactions

These reactions have been extensively studied in the presence of Keggin and Wells–Dawson heteropoly acids as homogeneous catalysts.[2,4,24] Generally, such reactions are performed in organic media, and water greatly affects the reaction rate.[24] The catalytic activities of heteropoly acids usually follow the order of their acid strengths, as expected for Brønsted acid catalysis. However, molybdenum acids may exhibit a lower activity than that expected from their acid strengths due to reduction by the reaction medium.[2,4]

Misono *et al.*[24] have studied a series of homogeneous reactions such as decomposition of isobutyl propionate, transesterification of isobutyl propionate with acetic acid and n-propanol, and esterification of propionic acid with isobutanol (eq. 4.9–4.12).

$$C_2H_5COOCH_2CH(CH_3)_2 \rightarrow (CH_3)_2C{=}CH_2 + C_2H_5COOH \quad (4.9)$$

$$\begin{aligned} &C_2H_5COOCH_2CH(CH_3)_2 + CH_3COOH) \\ &\quad \rightarrow CH_3COOCH_2CH(CH_3)_2 + C_2H_5COOH \end{aligned} \quad (4.10)$$

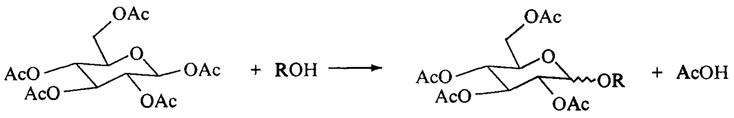
$$\begin{aligned} &C_2H_5COOCH_2CH(CH_3)_2 + n\text{-}C_3H_7OH \rightarrow C_2H_5COOC_3H_7 \\ &\quad + (CH_3)_2CHCH_2OH \end{aligned} \quad (4.11)$$

$$(CH_3)_2CHCH_2OH + C_2H_5COOH \rightarrow C_2H_5COOCH_2CH(CH_3)_2 + H_2O \quad (4.12)$$

In reaction 4.9, heteropoly acids are 60–100 times more active than H_2SO_4 or p-toluenesulfonic acid (TsOH). The activity is in the order: $H_3[PW_{12}O_{40}] > H_4[SiW_{12}O_{40}] \geq H_4[GeW_{12}O_{40}] > H_5[BW_{12}O_{40}] > H_6[P_2W_{18}O_{62}] > H_6[CoW_{12}O_{40}]$. The same activity pattern is observed for reaction 4.10 in the absence of water. The addition of water greatly accelerates reaction 4.10 and probably changes its course to proceed via the hydrolysis of isobutyl propionate to propionic acid and isobutanol, followed by the esterification of isobutanol with acetic acid. On the other hand, for reactions 4.11 and 4.12 no significant difference in activity between heteropoly acids and H_2SO_4 is observed probably due to the levelling effect of the reactant alcohols on the acid strength of the catalysts.

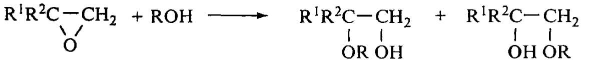
Dialkyl phthalates, utilised as plasticisers, have been obtained by esterifying phthalic anhydride with C_8-C_{10} alcohols at 100–120 °C in the presence of $H_3[PW_{12}O_{40}]$ (1–2 %) as a homogeneous catalyst.[25] The catalytic activity of heteropoly acid is significantly higher than that of H_2SO_4 and TsOH. Heteropoly acid supported on activated carbon can also be used as a heterogeneous catalyst. Although the carbon-supported heteropoly acid is less active than the homogeneous catalyst, it can be easily separated from the reaction mixture and reused.

Synthesis of glycosides catalysed by heteropoly acid is of industrial importance.[11,12] Glycosides are used as effective and biodegradable surfactants. Heteropoly acid is several times more active than the conventional catalysts such as TsOH and $ZnCl_2$. Thus acetylated monosaccharides readily interact with alcohols in a homogeneous phase in the presence of 2 % of heteropoly acid with respect to sugar derivative at 70–130 °C, yielding 70–90 % of glycosides[26] (eq. 4.13).



(4.13)

Heteropoly acid is more active and more selective catalyst than H_2SO_4 and TsOH for the homogeneous alcoholysis of epoxides (epichlorohydrin, 1,2-epoxybutane, isobutene oxide, styrene oxide, etc.) under mild conditions (45 °C, excess alcohol)[4] (eq. 4.14). In contrast to heteropoly acid, H_2SO_4 is rapidly deactivated probably due to the formation of alkyl sulfate, resulting in loss of acidity. Likewise, in the acetolysis of epoxides, tetrahydrofuran, and linear esters, performed in excess of acetic acid, heteropoly acid is far more effective than other acid catalysts such as TsOH and $BF_3 \cdot H_2O$. The activity of TsOH decreases in the early stage of the reaction due to the formation of a tosyl ester.[4]



$$\underset{\diagdown O \diagup}{R^1R^2C{-}CH_2} + ROH \longrightarrow \underset{OR\ \ OH}{R^1R^2C{-}CH_2} + \underset{OH\ \ OR}{R^1R^2C{-}CH_2} \tag{4.14}$$

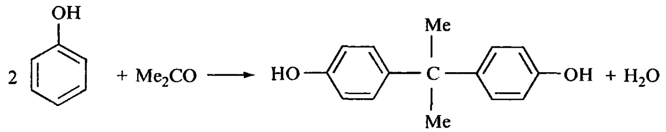
Methyl t-butyl ether (MTBE) – a gasoline octane booster – is produced industrially on a large scale by reacting isobutene with methanol in the presence of an acid catalyst, usually acidic ion-exchange resin (eq. 4.15).

$$(CH_3)_2C{=}CH_2 + CH_3OH \rightarrow CH_3OC(CH_3)_3 \tag{4.15}$$

Heteropoly acids and their salts also catalyse this reaction in homogeneous and heterogeneous systems.[7] Maksimov and Kozhevnikov[27] showed that in the homogeneous reaction at 42 °C, Keggin acids such as $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ are 2–4 times more active than the conventional catalysts per unit proton site. Interestingly, the Wells–Dawson acid, $H_6[P_2W_{18}O_{62}]$, shows two times higher activity than $H_3[PW_{12}O_{40}]$. However, regarding the activity per unit catalyst weight, H_2SO_4 is the most active catalyst. Liquid-phase synthesis of MTBE[28] and ethyl t-butyl ether[29] by HPA-catalysed etherification of t-butanol with methanol and ethanol, respectively, has been studied.

4.2.2.3 Condensation

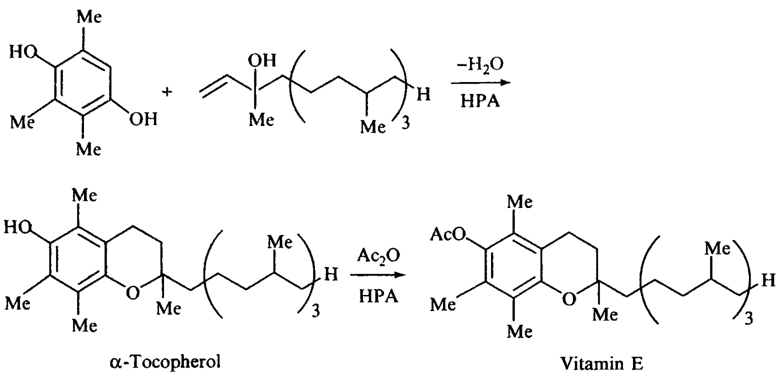
Heteropoly acids have long been known as catalysts for condensation reactions, e.g., the condensation of acetone to mesityl oxide and alkylbenzenes.[2,30] Bisphenols are obtained by the condensation of ketones and phenols in the presence of heteropoly acids (eq. 4.16).[31,32]



(4.16)

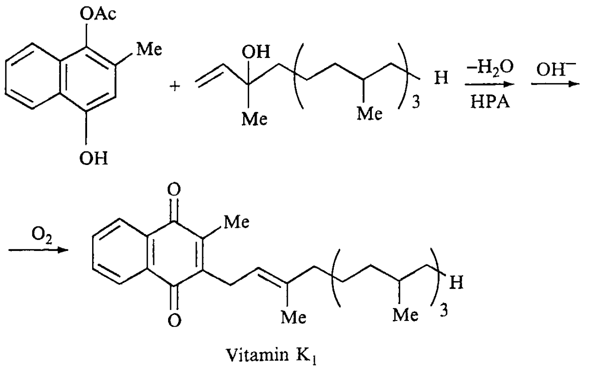
$H_3[PW_{12}O_{40}]$ and its Cs^+ and NH_4^+ salts encapsulated into MCM-41 molecular sieve also catalyse reaction 4.16, the Cs^+ salt being the most selective towards para, para′ isomer formation.[33]

Kozhevnikov *et al.*[34,35] have shown that heteropoly acid is an efficient catalyst for condensations in the syntheses of vitamins E, K_1 and C. Thus, $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ catalyse the condensation of isophytol with 2,3,5-trimethylhydroquinone (TMHQ) to α-tocopherol (eq. 4.17), which is the active form of vitamin E.[34] The reaction is carried out in homogeneous phase (in butyl acetate or acetic acid) or in heterogeneous system (in toluene) with ca. 1 wt% HPA based on TMHQ. With heteropoly acid, the yield and quality of vitamin E are practically the same as those with $ZnCl_2$ which is a commercial catalyst. The drawback to $ZnCl_2$ is that it is used in stoichiometric quantities, generating large amount of waste. Heteropoly acid can be recovered after reaction and reused.



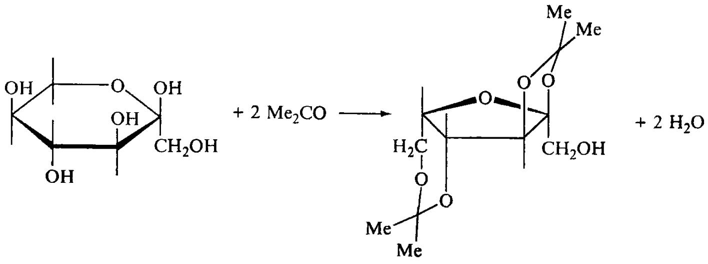
(4.17)

A solid-acid catalyst 30% WO_3/SnO_2, which may contain a surface-bound heteropoly acid, has been found to be active in the synthesis of α-tocopherol, albeit less efficient than $H_3[PW_{12}O_{40}]$.[36] The catalyst can be reused without loss of its activity. Heteropoly acids are also efficient in the related condensation of isophytol and 1-acetoxy-4-hydroxy-2-methylnaphthalene (eq. 4.18) which is a key step in the synthesis of vitamin K_1.[34] Heteropoly acids are almost 50 times more active than $ZnCl_2$ or aluminosilicates in this reaction.



(4.18)

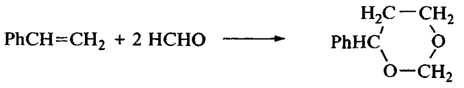
The acetonation of L-sorbose – a step in the synthesis of L-ascorbic acid (vitamin C) – occurs in acetone solution in the presence of 0.1–0.35% of $H_3[PW_{12}O_{40}]$ or $H_4[SiW_{12}O_{40}]$ to yield 85% of diacetone-L-sorbose (DAS) (eq. 4.19).



(4.19)

Water formed in the reaction is removed by distillation or absorption with NaA zeolite. In industry, this reaction is carried out with excess oleum to yield ca. 80% DAS, the oleum serving as both the catalysts and the desiccant. The major drawback to this process is the formation of large amount of sodium sulfate by oleum neutralisation. The use of heteropoly acid allows increasing the DAS yield, the amount of waste being greatly reduced.[35]

Heteropoly acids catalyse the Prins reaction of alkenes with formaldehyde to yield 1,3-dioxanes. For example, in the reaction of styrene (eq. 4.20), Keggin-type acids were shown to be superior to H_2SO_4 and TsOH, the activity differing only slightly in the series of heteropoly acids.[4]

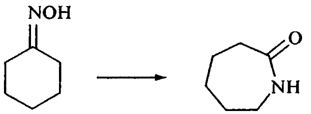


(4.20)

Condensation of formaldehyde and methyl formate to methyl glucolate and methylmethoxy acetate using heteropoly acids and salts has been reported.[37]

4.2.2.4 Miscellaneous Reactions

Izumi and Fujita[38] reported that an iminium salt, prepared by interacting N,N-dimethylformamide with epichlorohydrin in the presence of $H_3[PW_{12}O_{40}]$ or $H_4[SiW_{12}O_{40}]$, effectively catalyses the liquid-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam (eq. 4.21) under mild conditions (50–60 °C). The product lactam was found to poison the catalyst, though reversibly. The turnover of the catalyst attained 200.

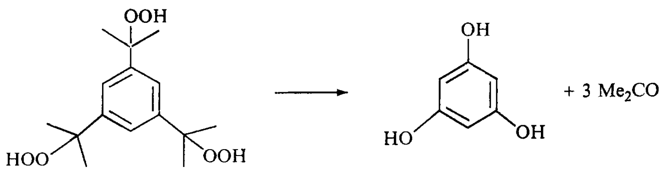


(4.21)

Heteropoly acids have long been known as very efficient catalysts for the decomposition of cumene hydroperoxide to phenol and acetone[14,39,40] (eq. 4.22).

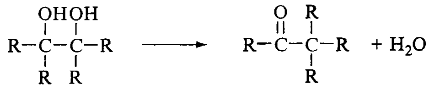
$$PhC(CH_3)_2OOH \rightarrow PhOH + CH_3COCH_3 \qquad (4.22)$$

Similarly, 1,3,5-trihydroxybenzene is formed via the decomposition of 1,3,5-triisopropylbenzene hydroperoxide at 50–100 °C with 97% selectivity at 89% hydroperoxide conversion (eq. 4.23).[41]



(4.23)

1,2-Diols (1,2-propanediol, 2,3-butanediol and 2,3-dimethyl-2,3-butanediol) readily undergo the pinacol rearrangement to yield the corresponding carbonyl compounds (propanal, 2-butanone and 3,3-dimethyl-2-butanone, respectively) in the presence of $H_3[PW_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, or $H_4[SiMo_{12}O_{40}]$ (eq. 4.24). Under such conditions, 1,4- and 1,5-diols selectively form cyclic ethers.[42]



$$R-\underset{R}{\overset{OH}{C}}-\underset{R}{\overset{OH}{C}}-R \longrightarrow R-\overset{O}{\overset{\|}{C}}-\underset{R}{\overset{R}{C}}-R + H_2O \qquad (4.24)$$

The hydrolysis of sucrose in the presence of $H_4[SiW_{12}O_{40}]$ has been reported.[43]

Kortz and Pope[44] have synthesized and fully characterised two new polyoxomolybdate–diphosphate complexes with the formula $[(O_3PXPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ $(X = O$ or $CH_2)$. The polyanion with $X = O$ is a possible intermediate in the molybdate-catalysed hydrolysis of pyrophosphate.

4.3 ACID-CATALYSED REACTIONS IN BIPHASIC LIQUID–LIQUID SYSTEMS

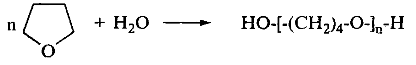
4.3.1 INTRODUCTION

Separation of products and recovery and recycling of catalysts often becomes much easier when homogeneously catalysed reactions are performed in biphasic systems consisting of two immiscible liquid phases – a catalyst phase and a product/reactant phase – with intense mass transfer between them. Heteropoly acids due to their special solubility properties, i.e., high solubility in a variety of polar solvents and insolubility in nonpolar solvents, are promising catalysts for operating under phase-transfer conditions.[2] There are two types of such biphasic systems: 1) initially homogeneous a reaction system separates in two liquid phases in the course of the reaction; 2) a reaction system is biphasic from the very beginning. The catalyst phase, usually the lower one, is a solution of heteropoly acid in a polar reactant. The reaction predominantly proceeds in the catalyst phase, and the product formed is transferred to the less polar product phase. The amount of heteropoly acid in the product phase must be negligible to allow easy catalyst separation.

4.3.2 BIPHASIC REACTIONS

4.3.2.1 Polymerisation of Tetrahydrofuran

Polymerisation of tetrahydrofuran (THF) is used for the preparation of polyoxytetramethyleneglycol (PTMG), which is used for manufacturing Spandex fibres and polyurethanes. PTMG is commercially produced by a two-step process, including ring-opening polymerisation of THF with acetic anhydride catalysed by $HClO_4$, followed by hydrolysis of the terminal acetate groups in the prepolymer. Izumi *et al.*[45] found that heteropoly acid is more active than $HClO_4$ in the polymerisation of THF. Aoshima *et al.*[46a] developed a one-step process for the THF polymerisation to directly yield PTMG (eq 4.25). This process is used commercially in Japan.[4,12]



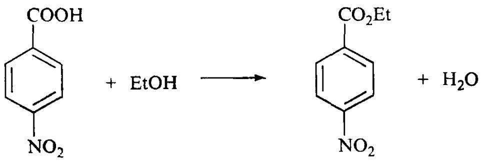
(4.25)

PTMG is obtained by ring-opening THF with water in the presence of $H_3[PW_{12}O_{40}]$ at 60 °C. The $H_2O/H_3[PW_{12}O_{40}]$ molar ratio is critical for the process, controlling the reaction rate and molecular weight of polymer. When the $H_2O/H_3[PW_{12}O_{40}]$ molar ratio is above 15, a homogeneous phase forms, and no reaction takes place. When the ratio is below 15, the solution separates in two liquid phases – a THF (upper) phase and a $H_3[PW_{12}O_{40}]$ – THF–H_2O (lower) phase. The polymerisation starts when $H_2O/H_3[PW_{12}O_{40}]$ ratio is decreased below 10. The polymer is formed in the HPA phase and transferred to the THF phase. The reaction rate increases with decreasing $H_2O/H_3[PW_{12}O_{40}]$ ratio, and so does the molecular weight of polymer. The process is performed continuously. The PTMG with a molecular weight of 500–2000 and a narrow molecular weight distribution is obtained from the THF phase. Various improvements to this process have been claimed.[46b–46e]

Similarly, $H_3[PW_{12}O_{40}]$ and $H_3[PMo_{12}O_{40}]$ catalyse the polymerisation of cyclic formaldehyde acetal and trimer, 1,3-dioxolane and 1,3,5-trioxane, respectively. For example, in the polymerisation of 1,3,5-trioxane, the comparable reaction rates can be obtained with 25 times less heteropoly acid weight than for conventional catalyst like $BF_3 \cdot OR_2$.[47]

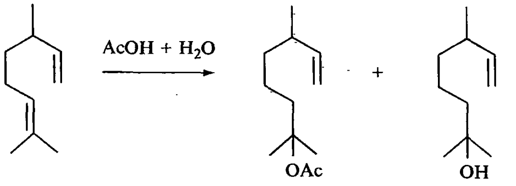
4.3.2.2 Esterification

Esterification of p-nitrobenzoic acid is a step of the anaesthetic synthesis. Ethyl p-nitrobenzoate is obtained in 99% yield by esterification of p-nitrobenzoic acid with ethanol (eq. 4.26) in the presence of $H_3[PW_{12}O_{40}]$ (3–7 wt%) at 75 °C.[11] Water formed in the reaction course is separated by azeotropic distillation with toluene. Initially homogeneous, the reaction mixture becomes a two-phase system in the end of reaction. The upper phase contains the product, the lower phase is a concentrated solution of heteropoly acid in ethanol. The catalyst phase is easily separated and can be reused.



(4.26)

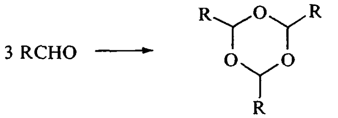
Acetoxylation and hydration of dihydromyrcene (DHM) give dihydromyrcenol (DHM–OH) and dihydromyrcenyl acetate (DHM–OAc) (eq. 4.27), respectively, which are useful as perfume ingredients. These reactions occur simultaneously in a two-phase system in the presence of $H_3[PW_{12}O_{40}]$ at 14–30 °C.[48] The upper phase mainly consists of DHM and the lower phase is a concentrated solution of heteropoly acid in aqueous acetic acid. Acetic acid is approximately equally distributed between the two phases. The reaction proceeds in the catalyst phase to form DHM–OH and DHM–OAc, which are transferred to the DHM phase. The process reaches equilibrium at ca. 30% DHM conversion and is strongly complicated by acid-catalysed isomerisation and cyclisation of DHM. The selectivity to DHM–OH and DHM–OAc totals 90% at 21% DHM conversion. The catalyst phase can be reused without loss of activity.



(4.27)

4.3.2.3 Other Reactions

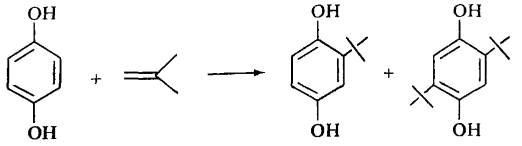
Keggin-type heteropoly acids such as $H_3[PMo_{12}O_{40}]$, $H_3[PW_{12}O_{40}]$, and $H_4[SiW_{12}O_{40}]$ catalyse the cyclotrimerisation of aldehydes, such as ethanal, propanal, butanal, 2-methylpropanal, etc., to produce 2,4,6,-trialkyl-1,3,5-trioxanes in high yields (eq. 4.28), as reported by Sato *et al.*[49,50] Catalyst turnover number is more than 10000 for the propanal cyclotrimerisation. At high conversions of aldehyde, the reaction mixture spontaneously separates into two phases, a product phase and a catalyst phase, which, depending on aldehyde, can be solid or liquid. For the propanal cyclotrimerisation, the reaction mixture separates into two liquid phases, and the recovered catalyst phase can be easily reused. The vapour-phase trimerisation of formaldehyde to trioxane catalysed by $H_4[PMo_{11}VO_{40}]$ supported on silicon carbide at 110 °C has been studied.[51]



(4.28)

Sato *et al.*[52] examined various acetal formation reactions between monoalcohols or diols and a range of aldehydes or ketones catalysed by Keggin-type heteropoly acids in comparison with other acid catalysts. The reaction is strongly inhibited by water produced in the reaction course. The catalyst activity was found to decrease in the order: $H_4[SiW_{12}O_{40}] > H_3[PMo_{12}O_{40}] > H_3[PW_{12}O_{40}] > TsOH > H_2SO_4$. For several reactions between a carbonyl compound and a diol, the reaction mixture is spontaneously separated into two liquid phases, enabling easy catalyst recycling.

Timofeeva and Kozhevnikov[53] reported the alkylation of hydroquinone with isobutene to yield 2-t-butylhydroquinone and 2,5-di-t-butylhydroquinone (eq. 4.29) catalysed by $H_3[PW_{12}O_{40}]$, $H_6[P_2W_{18}O_{62}]$ and $H_6[P_2W_{21}O_{71}]$ under phase-transfer conditions in a biphasic system, including toluene (upper phase) and a dioxane heteropoly etherate (lower phase). In this case, the two phases are immiscible from the very beginning, and the products are obtained from the toluene phase. The yield of 2-t-butylhydroquinone increases in the series: $H_6[P_2W_{18}O_{62}] < H_6[P_2W_{21}O_{71}] < H_3[PW_{12}O_{40}]$. With $H_3[PW_{12}O_{40}]$, a 70% yield is obtained (85 °C). $H_3[PW_{12}O_{40}]$ shows a higher efficiency than H_2SO_4 or H_3PO_4.



(4.29)

4.4 HETEROGENEOUS ACID CATALYSIS

Heterogeneous acid catalysis by heteropoly acids has attracted much interest.[1-7,9] Generally, solid heteropoly acids have greater catalytic activities than conventional solid-acid catalysts such as mixed oxides, zeolites, etc. The downside of heteropoly acids is their relatively low thermal stability, which may cause problems with regeneration of these catalysts. This section describes the heterogeneously catalysed reactions in liquid–solid and gas–solid systems with the use of solid heteropoly acid catalysts.

4.4.1 HETEROPOLY ACID CATALYSTS

4.4.1.1 Acid Sites

Bulk and supported heteropoly acids and salts are used as catalysts in heterogeneous acid-catalysed reactions. Several types of acid sites are present in these catalysts:[1]

1. Proton sites in heteropoly acids (e.g. $H_3[PW_{12}O_{40}]$).
2. Proton sites in acidic salts (e.g. $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$).
3. Lewis acid sites in salts (metal countercations, e.g. in $La^{III}[PMo_{12}O_{40}]$).
4. Proton sites generated by dissociation of coordinated water:
   $Ln(H_2O)_n^{3+} \rightarrow Ln(H_2O)_n(OH)^{2+} + H^+$
5. Proton sites generated by reduction of salts:
   $Pd_2[SiW_{12}O_{40}] + 4\{H\} \rightarrow 2\,Pd^{\circ} + H_4[SiW_{12}O_{40}]$
6. Protons generated by partial hydrolysis of polyanions:
   $[PW_{12}O_{40}]^{3-} + 2\,H_2O \rightarrow [PW_{11}O_{39}]^{7-} + \{WO_3\} + 4\,H^+$

4.4.1.2 Bulk Heteropoly Acids

Solid heteropoly acids possess purely Brønsted acidity and are stronger than such conventional solid acids as $SiO_2-Al_2O_3$, H_3PO_4/SiO_2, and HX and HY zeolites.[54,55] The acids $H_3[PW_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, and $H_4[SiMo_{12}O_{40}]$ are readily available and most frequently used as catalysts, usually the first two being preferred. These acids have fairly high thermal stabilities, decomposing at 465, 445, 375, and 350 °C, respectively[2] (Chapter 2). Decomposed molybdenum acids may be reconstructed under exposure to water vapour.[1] For much less labile tungsten acids such reconstruction is unlikely.

The acid strength of crystalline heteropoly acids decreases in the series:

$$H_3[PW_{12}O_{40}] > H_4[SiW_{12}O_{40}] > H_3[PMo_{12}O_{40}] > H_4[SiMo_{12}O_{40}]$$

which is identical to that in solutions (Chapter 2).[1,3] Usually relative catalytic activities of heteropoly acids are consistent with this order both in homogeneous and in heterogeneous systems.[2,3] Like other strong solid acids, heteropoly acids are capable of generating carbocations from adsorbed olefins and arenes.[56] The drawback to the bulk acids is their low surface area (1–5 m^2 g^{-1}) and low porosity (< 0.1 cm^3 g^{-1}).

4.4.1.3 Supported Heteropoly Acids

Supported heteropoly acid catalysts have much greater surface areas; hence they are more important for applications.[1-12] The acidity and catalytic activity of supported heteropoly acids depends on the type of carrier, the HPA loading, conditions of pretreatment, etc. Acidic or neutral substances such as SiO_2,[57] active carbon,[25,58] acidic ion-exchange resin,[59] etc., are suitable as supports, the most often used being SiO_2. Basic solids like MgO tend to decompose heteropoly acids.[3,60] Adsorption of heteropoly acids onto silica, alumina and active carbon from aqueous and organic solutions has been studied.[61-63]

Heteropoly acids on silica SiO_2 is relatively inert towards heteropoly acids, at least above a certain loading level, although some chemical interaction takes place between heteropoly acids and SiO_2 (see below). The thermal stability of heteropoly acids on SiO_2 seems to be comparable to or slightly lower than that of the parent HPA.[5,64] On the other hand, thermally decomposed Keggin structure of molybdenum acids on the silica surface may be reconstructed on exposure to water vapour.[65,66]

At low loadings, $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ form finely dispersed species on the SiO_2 surface; HPA crystal phase on silica (200–300 m^2 g^{-1}) is developed at HPA loading above 20 wt%.[57,61] Various HPA forms were observed on the silica surface by transmission electron microscopy (TEM): discrete molecules, clusters 50 Å in size and large crystallites of 500 Å. Their relative amounts depend on the HPA loading.[61]

^1H and ^{31}P magic-angle spinning (MAS) NMR studies indicate a chemical interaction of $H_3[PW_{12}O_{40}]$ with SiO_2.[67-70] Impregnating SiO_2 with an aqueous solution of $H_3[PW_{12}O_{40}]$ gives catalysts with, in general, two HPA species which are characterised by ^{31}P MAS NMR: one at −15 ppm with intact Keggin structure (A) and the other at −14 ppm with a different structure (B) (Figure 4.3).[69,70] The relative amount of species A and B depends on HPA loading, with A dominating. At higher loadings, 30–50 %, A is practically the only one present on the SiO_2 surface; at lower loadings, both species exist, the amount of B increasing as the HPA loading decreases. In contrast, catalysts prepared by impregnation with a methanol solution of $H_3[PW_{12}O_{40}]$ contain exclusively Keggin-type A over the whole range of HPA loading.[70] Forms A and B were assumed to be bulk crystalline $H_3[PW_{12}O_{40}]$ and the 'interacting' species $(\equiv SiOH_2^+)(H_2[PW_{12}O_{40}]^-)$, respectively.[69] More recently evidence has been obtained that B may be $H_6[P_2W_{18}O_{62}]$ or $H_6[P_2W_{21}O_{71}]$, formed from $H_3[PW_{12}O_{40}]$ in the course of catalyst preparation.[70] Species B was found more active than A in liquid-phase dealkylation of alkylphenols.[70] The

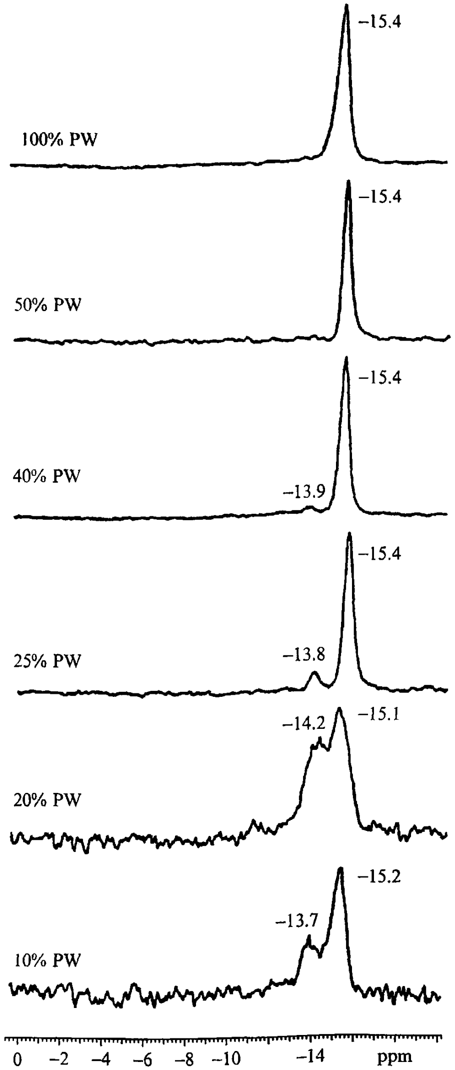


Figure 4.3 ^{31}P MAS NMR spectra for $H_3[PW_{12}O_{40}]$ and $H_3[PW_{12}O_{40}]/SiO_2$ at various HPA loadings.[2] Reprinted with permission from *Chem. Rev.* 1998, **98**, 171. Copyright 1998 American Chemical Society.

^{1}H MAS NMR study[67] also shows the interaction of $H_3[PW_{12}O_{40}]$ with silica and the formation of a new type of proton sites on the silica surface.

As shown by microcalorimetry,[71] when loading $H_3[PW_{12}O_{40}]$ (20 wt%) on SiO_2, the proton sites become weaker and less uniform. Only 20% of the total amount of proton sites remain as strong as in bulk $H_3[PW_{12}O_{40}]$. The rest have the differential heat of ammonia adsorption about 120 kJ/mol, approaching that for acid sites of HX and HY zeolites (Figure 2.18, Section 2.6.3). The recent study[72] showed that the initial heat of ammonia adsorption on $H_3[PW_{12}O_{40}]/SiO_2$ increases with HPA loading in the range of 5–25 wt%. Like for bulk heteropoly acid, the differential heat of NH_3 adsorption on SiO_2-supported HPA strongly depends on the pretreatment temperature.[73] According to the ammonia thermal desorption data,[71] the acid strength of supported $H_3[PW_{12}O_{40}]$ decreases in the series of carriers: $SiO_2 > \alpha\text{-}Al_2O_3 >$ activated carbon (Figure 4.4). The catalysts comprising $H_3[PW_{12}O_{40}]$ supported on various porous silicas have been characterised.[74,75]

SiO_2-supported molybdenum heteropoly acids, such as $H_4[SiMo_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, and $H_5[PMo_{10}V_2O_{40}]$, retain the Keggin structure at high loadings but decompose at very low loadings due to their strong interactions with surface silanol groups.[64,65,76–79] A correlation was established between the catalytic behaviour in the methanol oxidation/dehydration reaction and the state of $H_4[SiMo_{12}O_{40}]$ and $H_3[PMo_{12}O_{40}]$ on the silica surface.[64,76,78,79] At

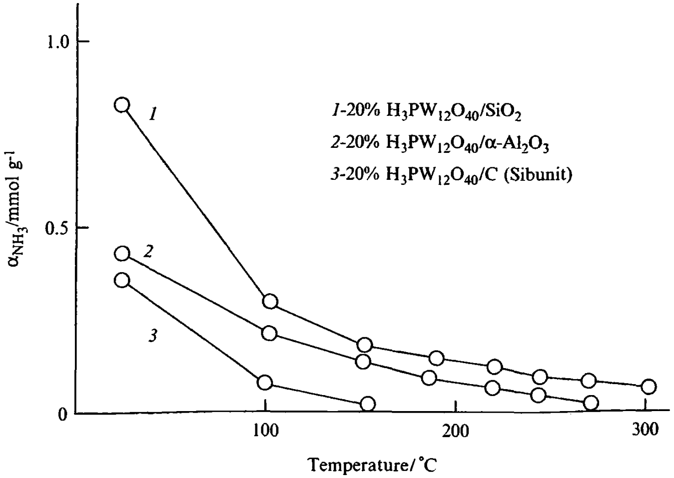


Figure 4.4 Ammonia thermal desorption from supported $H_3[PW_{12}O_{40}]$ catalysts.[71] Reprinted with permission from *Catal. Rev. Sci. Eng.* 1995, **37**, 311. Copyright 1995 Marcel Dekker.

high loadings, supported heteropoly acids behave similarly to bulk acids. In this case, acid catalysis predominates to yield dimethyl ether. In contrast, at low loadings, when heteropoly acid decomposes to MoO_3, loosing the acidity, only redox catalysis is observed to give formaldehyde.

Heteropoly acids on carbon While weaker acids, heteropoly acids supported on certain activated carbons are considered to be promising fixed-bed acid catalysts for liquid-phase reactions, e.g., esterification, because of their high stability towards HPA leaching from the carrier.[25,58] However, as shown by microcalorimetry,[80] the acid strength of $H_3[PW_{12}O_{40}]$ is greatly reduced when loading on activated carbon. As evidenced by IR and ^{31}P MAS NMR, $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ supported on a chemically (H_3PO_4) activated carbon retain the Keggin structure at the HPA loading > 5 wt% but decompose at lower loadings. Heteropoly acids form finely dispersed species on the carbon surface; no HPA crystal phase is developed even at the HPA loading as high as 45 wt%.[81] In ^{31}P MAS NMR spectra of carbon-supported $H_3[PW_{12}O_{40}]$, a great line broadening is observed due to a strong interaction of the HPA with carbon.[81] The acidity of a series of bulk and carbon-supported tungsten heteropoly acids has been studied by ammonia adsorption microcalorimetry.[82] The bulk acids exhibit strong acidity, decreasing in the order $H_3[PW_{12}O_{40}] > H_4[SiW_{12}O_{40}] > H_5[BW_{12}O_{40}]$. For carbon-supported acids at high HPA loadings (55–63%), the order of acid strength remained the same, the strength slightly reduced, however. Carbon-supported acids $H_{3+n}[PMo_{12-n}V_nO_{40}]$ have been studied as catalysts for liquid-phase oxidation.[83,84] Scanning tunnelling microscopy and tunnelling spectroscopy studies of heteropoly acids supported on graphite have been reported.[85–87] Recently, $H_3[PW_{12}O_{40}]/C$ and $H_4[SiW_{12}O_{40}]/C$ have been characterised by various spectroscopic techniques.[88]

Other supported heteropoly acid catalysts Catalysts comprising 12-tungstophosphoric acid supported on titania[89] and zirconia[90,91] have been characterised.

Pillaring hydrotalcite-type anionic clays (layered double hydroxides) by polyanions to form expanded layered catalysts for redox reactions has attracted considerable interest. These materials are often used as precursors for molecularly mixed oxide catalysts, which possess basic and/or redox properties.[92] Pillared layered double hydroxides have been prepared by ion-exchange reaction of $[Zn_2Al(OH)_6]NO_3 \cdot nH_2O$ with Keggin-type heteropoly anions.[93] Complete replacement of NO_3^- is achieved for the Keggin anions, such as $[PW_9V_3O_{40}]^{6-}$, $H_2[W_{12}O_{40}]^{6-}$, $[SiW_9V_3O_{40}]^{7-}$, etc., with the charge of −6 or higher. No exchange was observed for anions such as $[PW_{12}O_{40}]^{3-}$ and $[SiW_{12}O_{40}]^{3-}$. The intercalated anions are accessible for catalytic chemical conversions below 200 °C, e.g., for photocatalytic oxidation of isopropanol to acetone. The intercalation of $H_3[PW_{12}O_{40}]$ into ZnAl–CO_3 hydrotalcite has been studied.[94] Upon interacting with the clay, $H_3[PW_{12}O_{40}]$ is probably partially decomposed to form a highly dispersed PW_9 species, which, nevertheless, shows a higher catalytic activity and selectivity in dehydration of n-butanol than the bulk heteropoly acid at 230–250 °C.

The intercalation of a variety of transition-metal-substituted polyoxometalates into ZnAl–NO_3 and MgAl–Cl host clays has been reported.[95,96] The pillaring of MgAl layered double hydroxides by $[H_2W_{12}O_{40}]^{6-}$, $[P_2W_{18}O_{62}]^{6-}$ and $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ anions has been accomplished by ion-exchange reaction.[97] Polyoxometalate-intercalated hydrotalcites show catalytic activities for the liquid-phase oxidation of cyclohexene with O_2[98] and shape-selective epoxidation of alkenes with H_2O_2.[99]

Heteropoly acid immobilised into an organic polymer, e.g., PMo–polysulfone, PMo–polyethersulfone,[100] PMo–polyacetylene[101], PMo– and PW– polypyrrole[102], SiW–polyaniline,[103,104] and PMo– and PW–poly(1,4-phenylenemethylidynenitrilo-1,4-phenylenenitrilomethylidyne),[105] have been prepared and characterised. These are claimed to have an improved catalytic activity compared to bulk heteropoly acid in gas-phase ethanol conversion. $H_3[PMo_{12}O_{40}]$–polymer composite film catalysts have been tested for the liquid-phase hydration of isobutene.[106]

4.4.1.4 Intrazeolite Heteropoly Acids

Incorporation of heteropoly acids into zeolite pores to obtain shape-selective catalysts has long been a challenge.[2] However, conventional zeolites are not suitable for this because their pores are too small to adsorb large (12 Å) HPA molecules. $H_3[PW_{12}O_{40}]$ encapsulated into a mesoporous pure-silica molecular sieve MCM-41 (BET surface area 1200 $m^2\ g^{-1}$, uniform pores 32 Å in size) has been prepared[107,108] and characterised by nitrogen physisorption, XRD, Fourier-transform infrared spectroscopy (FT-IR), TEM, and ^{31}P MAS NMR.[70,107] The $H_3[PW_{12}O_{40}]$ / MCM-41 compositions with HPA loadings from 10 to 50 wt% have ~30 Å uniformly sized mesopores (Figure 4.5). Heteropoly acid retains the Keggin structure on the MCM-41 surface at an HPA loading above 20 wt%. At lower loadings a partial decomposition of $H_3[PW_{12}O_{40}]$ is observed, as in the case of amorphous SiO_2,[70] Heteropoly acid forms finely dispersed species on the MCM-41 surface. No HPA crystal phase is observed at HPA loadings as high as 50 wt%. As shown by TEM,[70] the $H_3[PW_{12}O_{40}]$ species are mainly located inside the MCM-41 pores rather than on the outer surface (Figure 4.6). $H_3[PW_{12}O_{40}]$/MCM-41 has a higher catalytic activity than H_2SO_4 or bulk $H_3[PW_{12}O_{40}]$ and exhibits shape selectivity in liquid-phase phenol alkylation.[107] $H_3[PW_{12}O_{40}]$/MCM-41 has been characterised by ^1H and ^{31}P MAS NMR and tested in the gas-phase conversion of 1,3,5-triisopropyl benzene.[109] This catalyst is very active in n-hexane cracking, albeit deactivate rapidly due to coke deposition on the acid sites.[110] $H_4[SiW_{12}O_{40}]$/MCM-41 has been characterised and tested in the esterification of acetic acid with n-butanol.[111] This catalyst is very similar to $H_3[PW_{12}O_{40}]$/MCM-41. Caesium salt of $H_3[PW_{12}O_{40}]$ supported on MCM-41 mesoporous silica has been studied.[112]

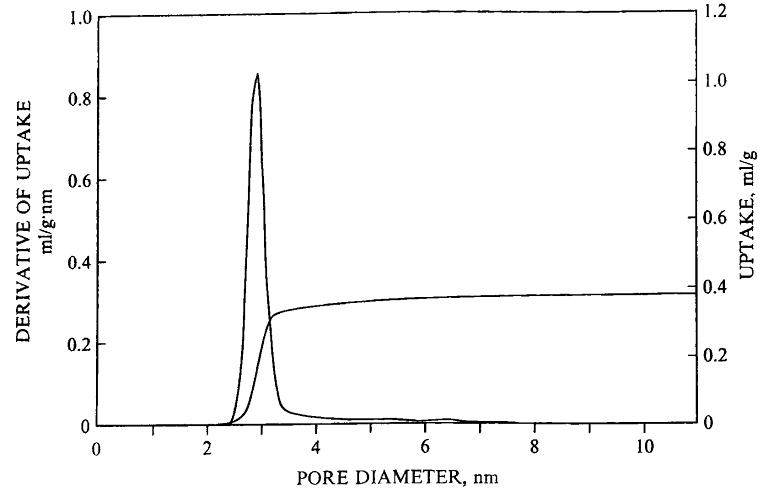


Figure 4.5 Pore size distribution for 40% $H_3[PW_{12}O_{40}]$/MCM-41 from N_2 physisorption.[2] Reprinted with permission from *Chem. Rev.* 1998, **98**, 171. Copyright 1998 American Chemical Society.

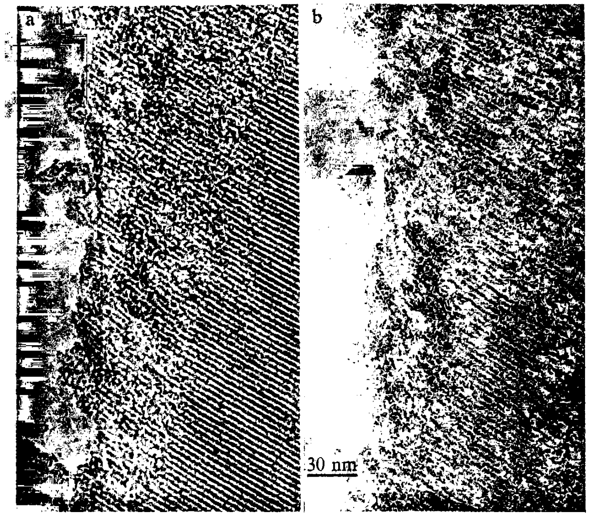


Figure 4.6 TEM images of the same area of 40% $H_3[PW_{12}O_{40}]$/MCM-41: (a) before and (b) after amorphisation.[70] The same structure observed before and after amorphisation is a clear indication that heteropoly acid is mainly located inside the MCM-41 pores. Reprinted with permission from *Chem. Rev.* 1998, **98**, 171. Copyright 1998 American Chemical Society.

The encapsulation of $H_3[PW_{12}O_{40}]$ in the cage of synthetic faujasite has been claimed,[113] however, more characterisation is needed to prove it; no preparation details has been disclosed. $H_3[PW_{12}O_{40}]$ supported on dealuminated zeolite Y has been characterised and tested in isomerisation, disproportionation and dealkylation of m-xylene.[114]

The synthesis of 12-molybdophosphoric acid in the supercages of Y-type zeolite has been reported.[115] This 'ship-in-the-bottle' catalyst has been used for liquid phase reactions.[116] The effect of the Si/Al ratio and the countercation in zeolite Y on the encapsulation of Keggin heteropoly acids has been studied.[117]

4.4.1.5 Heteropoly Salts

The nature of countercation in heteropoly salts is critical to their acidity, solubility, porosity, and thermal stability. Salts with rather small cations resemble the parent heteropoly acids; they are readily soluble in water, nonporous, and possess surface areas under 10 m^2 g^{-1} (Table 4.6). In contrast, salts with large monovalent cations, such as NH_4^+, K^+, Cs^+, etc., are water-insoluble, have a rigid microporous/mesoporous structure and can be prepared with surface areas over 100 m^2 g^{-1}.[118] Even if these solids are maid (by precipitation from aqueous solutions) to be stoichiometric, residual quantities of protons still remain, which are apparently responsible for the catalytic activity of these salts.[119] Parent and Moffat[120–122] investigated the effect of substitution of protons in Keggin heteropoly acids by 1A, 1B, and 3B group monovalent cations on their catalytic properties in alcohol dehydration and double bond migration. As demonstrated by Misono, Okuhara *et al.*,[123,124] the acidic Cs salt, $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$, has strong acid sites and high surface area (100–200 m^2 g^{-1}) and is a very efficient solid acid catalyst for a variety of

Table 4.6 Physicochemical properties of heteropoly salts.

Cation	Ionic radius, Å	Solubility[a]	Surface area, m^2 g^{-1}
Li^+	0.68	S	< 10
Na^+	0.97	S	< 10
Ag^+	1.26	S	< 10
Mg^{2+}	0.66	S	< 10
Ca^{2+}	0.99	S	< 10
Cu^{2+}	0.72	S	< 10
Zn^{2+}	0.74	S	< 10
Al^{3+}	0.51	S	< 10
Fe^{3+}	0.64	S	< 10
La^{3+}	1.02	S	< 10
Ce^{3+}	1.03	S	< 10
K^+	1.33	N	> 100
Rb^+	1.47	N	> 100
Cs^+	1.67	N	> 100
NH_4^+	1.43	N	> 100

a) Solubility in water: S, soluble; N, insoluble organic reactions, especially promising for liquid-phase reactions. The pore size of salts $Cs_xH_{3-x}[PW_{12}O_{40}]$ can be controlled by the Cs content. $Cs_{2.2}H_{0.8}[PW_{12}O_{40}]$ possesses micropores of 6.2 to 7.5 Å diameter and exhibits shape selective catalysis in liquid-phase reactions.[125] Izumi *et al.*[126,127] reported that SiO_2-bound $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$, prepared through the hydrolysis of ethyl orthosilicate in the presence of colloidal $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ in ethanol, is catalytically more active than Amberlyst-15 and H-ZSM-5 per unit acid site. Catalysts obtained by loading heteropoly acids on their insoluble salts, e.g., $H_3[PMo_{12}O_{40}]$ /$K_3[PMo_{12}O_{40}]$, have been studied.[128,129] Various methods of the preparation of bulk and supported heteropoly salts have been described.[130,131] The preparation of silica-supported Cs^+ salts of $H_3[PW_{12}O_{40}]$ with the egg-white morphology has been reported.[132] The surface acidity of $Cs_xH_{3-x}[PW_{12}O_{40}]$ has been characterised by FT-IR measurement of the low-temperature adsorption of CO. The intensity of the 2165 cm^{-1} band for CO adsorption on H^+ changes in parallel with the catalytic activity for surface-type reactions.[133] The proton sites in $H_3[PW_{12}O_{40}]$ and its caesium salts have been characterised by ^1H, ^2H, ^{31}P MAS NMR and inelastic neutron scattering[134] and *in situ* FT-IR.[135] The ^{129}Xe NMR technique has been applied to characterise the pore structure of NH_4^+, K^+, and Cs^+ salts of $H_3[PW_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, and $H_4[SiW_{12}O_{40}]$ and confirmed the presence of microporosity in these salts.[136]

Certain 'neutral' heteropoly salts can also gain proton sites upon interaction with reaction medium. Two mechanisms of the proton generation in heteropoly salts are distinguished: the dissociation of coordinated water (for salts with the cations like Al^{3+}, Zn^{2+}, etc.) and the reduction of the metal cation (e.g. Ag^+, Cu^{2+}, and Pd^{2+}).[5,7]

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+$$

$$Ag^+ + \tfrac{1}{2}H_2 \rightarrow Ag^o + H^+$$

Ono *et al.*[7,137] have studied the Pt(II) and Pd(II) salts of $H_3[PW_{12}O_{40}]$; these are capable of acting as bifunctional catalysts in alkane isomerisation. ^1H NMR studies of protons in the catalysts consisting of Pd^0 metal and $H_3[PW_{12}O_{40}]$ show that the presence of H_2 and Pd^0 greatly modifies the dynamic nature of protons in $H_3[PW_{12}O_{40}]$.[137] Under H_2 at 60 °C, the interconversion occurs between the hydrogen atoms on Pd^0 and protons in $H_3[PW_{12}O_{40}]$ and that hydrogen atoms formed on Pd^0 spill-over to the surrounding heteropoly anions. Two types of protons are observed by ^1H MAS NMR at 6.4 and 9.3 ppm in $Ag_3[PW_{12}O_{40}]$ when the salt is reduced by hydrogen.[138] The protons at 6.4 ppm exist only when hydrogen is present in the gas phase. They are mobile even at room temperature and catalytically more active than the protons at 9.3 ppm. The exchange between the two kinds of protons proceeds upon raising temperature. Combining the salt $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ with noble metals such as Pt enhances the catalytic activity for the n-butane isomerisation to isobutane in the presence of H_2 at 300 °C.[139,140]

4.4.1.6 Sol–gel Catalysts

Izumi *et al.*[127,141] reported that $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ and even water-soluble $H_3[PW_{12}O_{40}]$ itself can be included in the silica matrix by means of a sol–gel technique to become water-insoluble and easily separable microporous solid-acid catalysts. The catalysts thus obtained have large surface areas (400–800 m^2 g^{-1}), fairly strong acidity and are thermally more stable than Amberlyst-15. They catalyse the hydrolysis of ethyl acetate in aqueous phase, showing higher turnover frequencies than Amberlyst-15 and HZSM-5. Remarkably, the incorporation of $H_3[PW_{12}O_{40}]$ into the silica matrix effectively suppresses HPA leaching during the hydrolysis, whereas in the case of the usual silica-supported $H_3[PW_{12}O_{40}]$, the heteropoly acid completely dissolves in the reaction medium. It is expected that silica-included heteropoly compounds may find applications for acid-catalysed liquid-phase reactions in aqueous media as alternatives to H_2SO_4 and ion-exchange resins.[141] The Keggin-type heteropoly acids $H_n[XM_{12}O_{40}]$ (where n = 3, 4; X = Si, P; M = Mo, W) immobilised into a silica matrix by sol–gel technique and have been tested in Friedel–Crafts alkylations[142]. However, the sol-gel HPA catalysts, because of stronger interactions between their protons and the silica matrix, probably have a weakened strength compared to silica-supported HPA.

4.4.2 HETEROGENEOUS CATALYSIS IN LIQUID–SOLID SYSTEMS

In this section, reactions in liquid–solid systems catalysed by bulk and supported heteropoly acids and their insoluble salts are discussed. In heterogeneous as well as in homogeneous systems, heteropoly acids are generally more efficient than conventional catalysts, such as $SiO_2-Al_2O_3$, zeolites, etc., which is in line with their relative acid strengths.[1–4] Obvious advantage of heterogeneous systems over homogeneous is the easy separation of catalyst from reaction products. Furthermore, since heteropoly acids are soluble only in wet nucleophilic solvents levelling the acid strength (dehydrated heteropoly acids are scarcely soluble in dry polar media), their intrinsic strong acidity cannot be fully utilised in homogeneous systems. Hence, for catalysing highly demanding reactions, e.g., the Friedel–Crafts reaction, heteropoly acid must be used as a solid–acid catalyst in a dry nonnucleophilic medium. To enhance the acid strength, solid heteropoly acid catalysts are usually dehydrated at 150–300 °C.[2,3]

4.4.2.1 Paraffin Alkylation

The paraffin/olefin alkylation is used in industry for obtaining higher-octane paraffins which are blended into gasoline. H_2SO_4 or HF are used as homogeneous catalysts in this process. Heteropoly acids and salts have attracted interest as catalysts for this reaction.[108,143–147] $H_3[PW_{12}O_{40}]$ supported (75 %) on a series of carriers, such as mesoporous molecular sieve MCM-41, amorphous silica, and alumina, has been studied as the catalyst for the isobutane/2-butene alkylation in comparison with a MCM-22 zeolite.[108] The reaction was performed in a stirred autoclave at 120 °C and 30 atm with a 50:1 isobutane/2-butene feed. The greatest olefin conversion (87%) is observed with $H_3[PW_{12}O_{40}]$/MCM-41. The alkylate quality (trimethylpentane to dimethylhexane ratio) observed with $H_3[PW_{12}O_{40}]$/MCM-41, albeit worse compared with MCM-22, is better than with $H_3[PW_{12}O_{40}]/SiO_2$ or $H_3[PW_{12}O_{40}]/Al_2O_3$. Isobutane/2-butene alkylation catalysed by potassium salt of $H_3[PW_{12}O_{40}]$ under supercritical conditions has been studied.[147]

4.4.2.2 Friedel–Crafts and related reactions

The Friedel–Crafts reactions (aromatic alkylation and acylation) are the major route to alkylaromatics and aromatic ketones. The conventional homogeneous catalysts for these reactions, such as $AlCl_3$, BF_3, and H_2SO_4, bring about serious environmental and operational problems – high toxicity, corrosion, spent acid disposal, difficulty of separation and recovery, etc.[4] Heteropoly acids and their salts are promising solid-acid catalysts that could replace the conventional catalysts in some Friedel–Crafts reactions.

Izumi *et al.*[4] found that silica-supported $H_3[PW_{12}O_{40}]$ is a very active catalyst, superior to other heteropoly acids, for the alkylation of benzene with 1-octene. At a low reaction temperature of 35 °C and an excess of benzene, the major product is 2-phenyloctane (50–80 mol%), 3- and 4-phenyloctanes also being formed. The catalytic activity depends on the pretreatment temperature and the HPA loading. In contrast, in the alkylation of arenes with benzyl chloride, the most efficient catalyst is $H_3[PMo_{12}O_{40}]/SiO_2$.

As found by Soeda *et al.*,[148] bulk $H_3[PW_{12}O_{40}]$ shows a better performance than the conventional liquid (H_2SO_4, CF_3COOH) or solid (Amberlyst-15, $SiO_2{-}Al_2O_3$) catalysts for the selective alkylation of p-xylene with isobutene at 30 °C to afford t-butyl-p-xylene – a precursor for liquid crystalline polymers – with 75% selectivity.

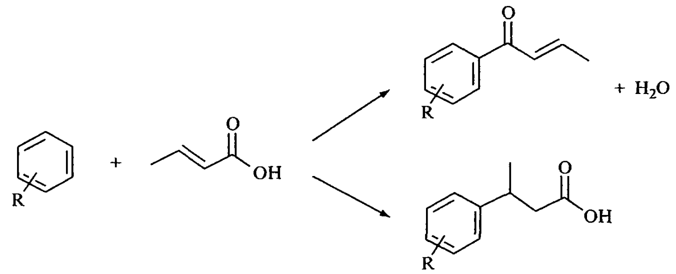
Misono, Okuhara *et al.*[149,150] reported that the salt $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ is more active catalyst than the parent acid $H_3[PW_{12}O_{40}]$ for the alkylation of 1,3,5-trimethylbenzene by cyclohexene. It is suggested that the higher hydrophobicity of the Cs salt compared to HPA is beneficial for the adsorption of the nonpolar reacting molecules. In addition, it is claimed that the Cs^+ cation could favourably change the softness of heteropoly anion, thus enhancing the stabilisation of the intermediate cyclohexyl cation by the polyanion.

$H_3[PW_{12}O_{40}]$ supported on zirconia doped with iron(III) and treated with sulfuric acid was reported to be a very active catalyst for the alkylation of benzene with propene to isopropylbenzene (100–150 °C, 4 MPa). This catalyst gives a low yield of n-propylbenzene and can be regenerated under an air flow at 350 °C for 2 h.[151]

In the acylation of p-xylene with benzoyl chloride $H_3[PMo_{12}O_{40}]$ in the PMo/SiO_2 catalyst was found to decompose during the reaction.[4] Probably, the real active species is not the supported $H_3[PMo_{12}O_{40}]$, but some soluble species which might be formed by the interaction between $H_3[PMo_{12}O_{40}]$ and benzoyl chloride. In contrast to $H_3[PMo_{12}O_{40}]$, the acids $H_4[SiW_{12}O_{40}]$ and $H_3[PW_{12}O_{40}]$ both effectively catalyse the acylation and remain unchanged on the SiO_2 surface after the reaction. But in a more polar reaction medium such as chlorobenzene even $H_4[SiW_{12}O_{40}]$ leaches from the silica support and decomposes in the course of reaction like $H_3[PMo_{12}O_{40}]$. Benzoic anhydride can be used as an acylating agent with the $H_4[SiW_{12}O_{40}]/SiO_2$ catalyst, but benzoic acid cannot. A weaker solid acid, $H_4[SiW_{12}O_{40}]$/carbon, can also catalyse the acylation, but less efficiently than $H_4[SiW_{12}O_{40}]/SiO_2$.[4]

$Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ shows high efficiency in acylation of activated arenes, such as p-xylene, anisole, mesitylene, etc., by acetic and benzoic anhydrides and acyl chlorides (Table 4.7). This catalyst provides higher yields of acylated arenes than the parent acid $H_3[PW_{12}O_{40}]$, the latter being partly soluble in the reaction mixture.[152]

Silica-supported 12-tungstophosphoric acid and its Cs^+ salts catalyse the acylation of toluene, p-xylene and m-xylene with crotonic acid (eq. 4.30).[153a,b] Some alkylation of aromatic compounds with crotonic acid is also observed. Heteropoly acid is more active than zeolites HY and Beta.



(4.30)

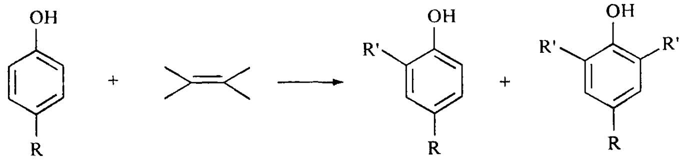
Heteropoly acid $H_3[PW_{12}O_{40}]$ has been shown to be a very efficient and environmentally benign catalyst for the Fries rearrangement of phenyl acetate in homogeneous or heterogeneous liquid-phase systems at 100 – 150°C.[153c]

Bulk and silica-supported tungsten heteropoly acids are very efficient and versatile catalysts for alkylation, dealkylation, and transalkylation of phenols[154–161] (eqs 4.31–4.33). Such reactions are widely used for the preparation

Table 4.7 Friedel–Crafts acylation[152].

Substrates		Product yield[a]	
Acylating agent	Arene	$Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$	$H_3[PW_{12}O_{40}]$
$(PhCO)_2O$	*p*-xylene	57	3
$(PhCO)_2O$	anisole	85	69
Ac_2O	anisole	89	50
n-$C_7H_{15}COCl$	mesitylene	80	44

a) Acylating agent/arene/catalyst = 5/100/0.01 mmol, reflux, 2 h of antioxidants, bioactive substances as well as for positional protection in organic synthesis. As found by Kulikov *et al.*,[154–157] $H_3[PW_{12}O_{40}]$ is much more active and generally provides higher yields of products in these reactions than conventional acid catalysts, such as H_2SO_4, ion-exchange resin, aluminosilicates, etc. Even Nafion-H®, a perfluorinated ion-exchange resin comparable in its acid strength to 100% H_2SO_4, is less active than $H_3[PW_{12}O_{40}]$.[157]



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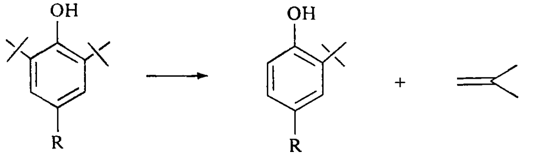
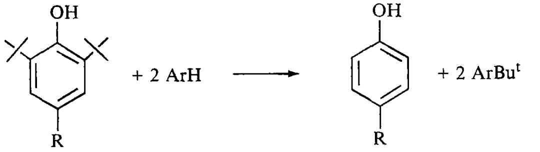


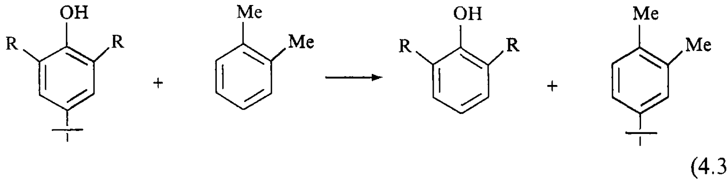
(4.32)



(4.33)

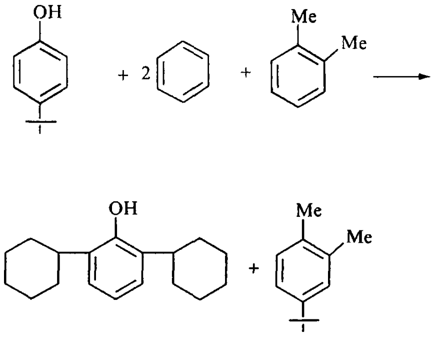
The alkylation of p-*tert*-butylphenol (TBP) with cyclohexene, 1-hexene, styrene, and benzyl chloride in the presence of bulk or silica-supported acids $H_3[PW_{12}O_{40}]$ or $H_4[SiW_{12}O_{40}]$ (1 % relative to TBP) at 100–150 °C affords 2,6-dialkyl-4-*tert*-butylphenols in 63–90% yield (eq. 4.31). In the reaction with styrene the yield reaches 90% at 100% TBP conversion (100–110 °C, 1 h). In the case of α-methylstyrene, monoalkylation occurs preferentially to yield 70% 4-*tert*-butyl-2-cumenylphenol.

The alkylation of TBP with olefins in the presence of heteropoly acids in o-xylene, which is a good acceptor of the *tert*-butyl group, makes it possible to obtain 2,6-dialkylphenols directly without isolating 2,6-dialkyl-4-*tert*-butylphenol. The *tert*-butyl group is eliminated quantitatively by reaction 4.34.



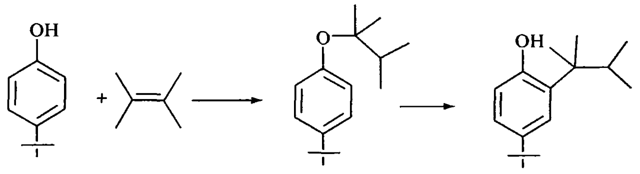
(4.34)

This procedure allowed obtaining 2,6-dicyclohexylphenol in 77% yield (eq. 4.35). Heteropoly acids are insoluble in the reaction mixture, readily separated and can be reused.



(4.35)

The alkylation of TBP apparently proceeds via a mechanism involving the formation of phenyl ethers as the primary products followed by their rearrangement to the more stable C-alkylation products (eq. 4.36). This was confirmed by the observation of the ethers in the initial stage of reaction.



(4.36)

The alkylation of p-cresol with isobutene (eq. 4.31 where R = CH_3 and R′ = $C(CH_3)_3$) with the use of $H_3[PW_{12}O_{40}]$[162] has been commercialised in Russia.[10b] It is a step in the synthesis of antioxidants. The use of heteropoly acid instead of H_2SO_4 in this process provides a higher selectivity (by 7–10%) and almost completely eliminates toxic water pollution.

Phenols can be alkylated with a terminally unsaturated olefin polymer in the presence of heteropoly acid. Thus ethylene/1-butene copolymer (M_n 3300) can be used to alkylate phenol in o-dichlorobenzene with $H_3[PW_{12}O_{40}]$ precalcined at 300 °C as the catalyst. The alkylphenols so formed are useful as precursors for the preparation of fuel and lubricant additives.[160]

$H_3[PW_{12}O_{40}]$ supported (20–50 wt%) on a mesoporous pure-silica molecular sieve MCM-41, having 30 Å uniformly sized pores, exhibits a higher catalytic activity than H_2SO_4 or bulk $H_3[PW_{12}O_{40}]$ and shows shape selectivity in alkylation of 4-*tert*-butylphenol with olefins[107] (eq. 4.31 where R = $C(CH_3)_3$). In the alkylation with styrene, $H_3[PW_{12}O_{40}]$/MCM-41 provides a higher yield of the monosubstituted product 2-(1-phenylethyl)-4-*tert*-butylphenol (I) than bulk

$H_3[PW_{12}O_{40}]$ or heteropoly acid supported on amorphous silica, at the expense of the more bulky disubstituted product 2,6-*bis*-(1-phenylethyl)-4-*tert*-butylphenol (II) (Table 4.8). HPA/MCM-41 may be a promising solid-acid catalyst for conversion and formation of organic compounds of large molecular size.

The dealkylation of *tert*-butylphenol derivatives is widely used in organic synthesis, e.g. for the synthesis of antioxidants. $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ are very efficient catalysts for reaction 4.32 in homogeneous and heterogeneous systems, where R = H, Me, Et, CH_2CH_2COOMe, etc.[155,156] The heterogeneous reaction occurs at 130–150 °C with less than 1 % catalyst in the substrate melt. Under such conditions, molybdenum heteropoly acids are rapidly deactivated because of their reduction by the reaction medium. Heteropoly acids are tens of times more active than other solid acid catalysts such as ion-exchange resin, $Al_2O_3-SiO_2$, etc. The homogeneous reaction is even more effective. Thus in acetic acid solution, the dealkylation proceeds at 80 °C. The catalytic activity of heteropoly acids is in line with their acid strength and is a factor of 100 higher than that of sulfuric acid.

Heteropoly acid-catalysed transdealkylation of 2,6-di-*tert*-butylphenols (eq. 4.33) has been studied in detail.[157,158] This reaction is useful for regioselective introduction of functional groups in phenols. Aromatic compounds (ArH) such as benzene, toluene, o-xylene, naphthalene, etc. are frequently used as acceptors of the *tert*-butyl group and H_2SO_4, $4\text{-}MeC_6H_4SO_3H$, $MeSO_3H$, CF_3SO_3H, zeolites, and Nafion-H® as catalysts. Bulk and supported tungsten heteropoly acids are versatile solid catalysts for the trans-de-*tert*-butylation of phenols (eq. 4.33), where R = H, Me, Et, CH_2CH_2COMe, CH_2CH_2COOMe, $CH_2CH_2CH_2OCOMe$, $CH_2CH_2CH_2Cl$, and $CH_2CH_2CH_2OCOC_{17}H_{35}$. These reactions occur at 100–140 °C and the ArH/phenol molar ratio of 2:1 in 0.2–4 h with 92–98 % yield, the best *tert*-butyl acceptors being toluene and o-xylene. Heteropoly acids are more active than many conventional acid catalysts including Nafion-H®. The HPA catalyst can be separated from the reaction mixture and reused.

The trans-de-*tert*-butylation of phenols (eq. 4.33; R = Me, ArH = PhMe) is first-order with respect to both phenol and heteropoly acid.[158] With $H_3[PW_{12}O_{40}]/SiO_2$ catalysts, the rate depends dramatically on HPA loading. The catalysts with the HPA loading less than 10 wt% show a negligible activity.

Table 4.8 Alkylation of p-*tert*-butylphenol (TBP) by styrene catalysed by $H_3[PW_{12}O_{40}]/MCM\text{-}41$[107]a.

Catalyst	Selectivity, mol%		
	I	II	Other products
$H_3[PW_{12}O_{40}]$	23	68	9
40% $H_3[PW_{12}O_{40}]/MCM\text{-}41$	66	21	13
40% $H_3[PW_{12}O_{40}]/SiO_2$	24	64	12

a) 4.0 wt% catalyst, in n-octane, 105 °C, 90% TBP conversion

This may be explained by the interaction of heteropoly acid with support reducing the acid strength. The rate based on the total number of protons in HPA increases with increasing HPA loading, passing a maximum at ca. 30 wt% HPA loading. This dependence is explained as a result of the competitive influence of enhancing the acid strength and reducing the number of the surface proton sites as the HPA loading increases. Similar dependencies have been reported for gas-phase reactions such as dehydration of isopropanol, esterification of acetic acid with ethanol,[4] and cumene cracking.[163] The effect of ArH on the rate of reaction 4.33 is typical of electrophilic aromatic substitution as illustrated by the rates of different ArH relative to benzene (2 wt% $H_3[PW_{12}O_{40}]$, 20 °C):[158]

ArH	PhH	PhMe	$PhBu^t$	$o\text{-}Me_2C_6H_4$	$m\text{-}Me_2C_6H_4$
k_{ArH}/k_{PhH}	1.0	6.9	1.5	12	0.95

4.4.2.3 Esterification, Hydrolysis and Related Reactions

There is a strong demand for new solid-acid catalysts, having advanced characteristics, to replace conventional liquid and solid catalysts, such as sulfuric acid and ion-exchange resins, in the title reactions.[4] Sulfuric acid, as already mentioned, poses serious environmental and operational problems. Acidic ion-exchange resins such as Amberlyst-15 are widely employed, but only at temperatures below 100 °C because of their low thermal stability. It should be noted that in these reactions in which water participates as a reactant or a product, there are only a few solid acid catalysts that may meet the criteria of activity and stability. As demonstrated by Izumi *et al.*,[4,127] certain supported heteropoly acid catalysts as well as insoluble heteropoly salts have advantages as catalysts for liquid-phase reactions in aqueous media because they are practically insoluble, thermally more stable than acidic resins and have strong acidity.

Active carbon strongly adsorbs a certain amount of heteropoly acid, and carbon-supported acid catalysts thus obtained catalyse liquid-phase esterification and related reactions in polar media.[4] The maximum HPA loading tightly retained on carbon in water or methanol is ca. 10 wt%, slightly depending on the type of carbon and its pretreatment. The carbon-supported $H_3[PW_{12}O_{40}]$ catalyse the formation of butyl t-butyl ether from n-butanol and t-butanol at 106 °C and the esterification of acetic acid with n-butanol at 60 °C.[4] Schwegler et al.[25] applied this catalyst for the esterification of phthalic anhydride with C_8-C_{10} alcohols at 100–120 °C to yield dialkyl phthalates. In all these reactions, the catalyst can be reused, no HPA leaching from carbon being observed. However, the carbon-supported HPA catalysts have a rather low catalytic activity because of their weak acidity. In addition, active carbon strongly adsorbs polar organic substances which makes the work-up more difficult.

Dupont and Lefebvre[164] have studied the esterification of propanoic acid by butanol or 2-ethylhexanol catalysed by $H_4[SiW_{12}O_{40}]$ and $H_3[PW_{12}O_{40}]$, pure or supported on carbon supports. In the homogeneous reaction, the reaction rate is proportional to the concentration of protons. Accordingly, $H_4[SiW_{12}O_{40}]$ shows slightly higher activity than $H_3[PW_{12}O_{40}]$. Carbon-supported heteropoly acids in all cases exhibit lower activity than the pure heteropoly acids, the activity depending on the carbon support and the HPA loading. In addition, a deactivation occurs during the recycling of these catalysts because of the leaching of heteropoly acid from support.

Izumi *et al.*[126] showed that the insoluble salt $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ is an active solid-acid catalyst for esterification and hydrolysis. For example, it is much more active than zeolite H-ZSM-5 for the hydrolysis of ethyl acetate and esterification of acetic acid with ethanol.[126] However, this salt consists of very fine particles (ca. 10 nm) and readily forms a colloidal solution in water or alcohol, which makes it inseparable by filtration. The salt $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ was found to be much more active than H-ZSM-5, Nb_2O_5, or SO_4^{2-}/ZrO_2 in hydrolysis 2-methylphenyl acetate in excess water.[165]

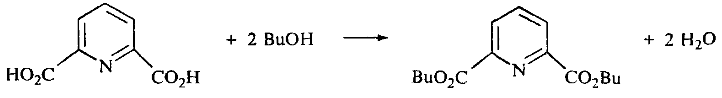
Izumi *et al.*[127,141] reported that the sol–gel silica-included $H_3[PW_{12}O_{40}]$ and $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ (Section 4.4.1.6) effectively catalyse the hydrolysis of ethyl acetate in aqueous phase, showing higher turnover rates than Amberlyst-15 and H-ZSM-5. Remarkably, the immobilisation of $H_3[PW_{12}O_{40}]$ into the silica matrix effectively suppresses the HPA leaching to as low as 0.3% during the hydrolysis reaction (60 °C, 3 h). It should be noted that in the case of the usual silica-supported $H_3[PW_{12}O_{40}]$ catalyst, the acid completely dissolves in the reaction medium. Interestingly, the catalytic activity of the silica-included heteropoly acid is higher than that of the homogeneous acid. It is suggested that $H_3[PW_{12}O_{40}]$ is entrapped in the silica network as a highly concentrated aqueous solution, and the silica network is probably narrow enough to prevent the Keggin anion from leaching outside.

Okuhara *et al.* used $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ for the liquid-phase hydration of olefins such as 2,3-dimethyl-2-butene and cyclohexene.[166,167]

In the acetoxylation of dihydromyrcene (DHM) (eq. 4.27), the 40% $H_3[PW_{12}O_{40}]/SiO_2$ catalyst shows a comparable activity with the homogeneous $H_3[PW_{12}O_{40}]$ catalyst, while the selectivity of the solid catalyst is higher.[48] The latter is probably because it is more difficult for the carbenium-ion intermediate to isomerise on the catalyst surface than in solution. With a stoichiometric 1:1 DHM-AcOH mixture, no HPA leaching from the catalyst is observed. The $H_3[PW_{12}O_{40}]/SiO_2$ catalyst can be reused, a gradual deactivation being observed, however. Bulk $H_3[PW_{12}O_{40}]$ has a very low activity probably because of the small surface area and the blocking of proton sites by DHM oligomers.

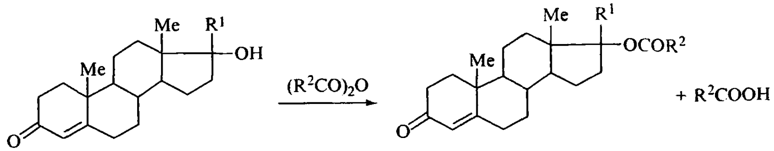
Okuhara *et al.*[150] reported that $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ is more active for liquid-phase decomposition of cyclohexyl acetate than other solid-acid catalysts such as Nafion-H, HY, and H-ZSM-5 zeolites, and SO_4^{2-}/ZrO_2.

Timofeeva *et al.*[168] found that the esterification of dipicolinic acid (DA) with butanol (eq. 4.37), which is a step of the synthesis of pharmaceutics, is catalysed by $H_3[PW_{12}O_{40}]$ as well as by its insoluble salts. $H_3[PW_{12}O_{40}]$ (1 wt%) as a homogeneous catalyst is almost as efficient as sulfuric acid, yielding 100% of the DA diester (118 °C, 3 h). The acidic Ce^{3+} salt, $Ce_{0.87}H_{0.4}[PW_{12}O_{40}]$, practically insoluble in butanol, has been found to be fairly active as a heterogeneous catalyst to give a 100% yield of the DA diester (5.4 wt%, 118 °C, 4 h). Although less active than the parent heteropoly acid, $Ce_{0.87}H_{0.4}[PW_{12}O_{40}]$ can be easily separated and reused. Insoluble NH_4^+, K^+, and Cs^+ salts of $H_3[PW_{12}O_{40}]$ showed only moderate activities in this reaction.



(4.37)

The esterification and acetalisation of steroids (eq. 4.38 and 4.39) occur with quantitative yields in the presence of bulk or silica-supported $H_3[PW_{12}O_{40}]$ (1.5–9%) in MeCN, CH_2Cl_2, or benzene (40–82 °C, 0.5–4 h):[169]



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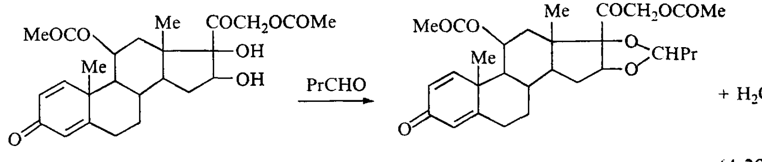


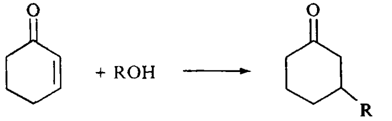
(4.39)

where R^1 = H or COMe and R^2 = Et or Am. These reactions represent steps in the synthesis of modified hormones. In benzene, where heteropoly acid is insoluble, the reactions proceed heterogeneously; the catalyst can be separated from the reaction mixture without neutralisation and reused. The catalytic activity of heteropoly acid is much greater than that of 5-sulfosalicylic acid and similar to that of $HClO_4$.

12-Tungstophosphoric acid supported on montmorillonite has been found to be a very efficient catalyst, in comparison with several conventional acid catalysts, for the etherification of phenylethyl alcohol with a variety of alkanols (eq. 4.40).[170] The reactions are 100% selective towards the ethers that are useful in the perfumery industry.

$$PhCH_2CH_2OH + ROH \rightarrow PhCH_2CH_2OR + H_2O \qquad (4.40)$$

Keggin and Wells–Dawson heteropoly acids catalyse the addition of alcohols to cyclohexenone (eq. 4.41, R = Me, Et, iso-Pr, t-Bu).[171] $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ show much higher activities than $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$, H-ZSM-5, and SO_4^{2-}/ZrO_2 and almost 100% selectivities. Evidence is provided that the reactions occur in pseudoliquid phase.



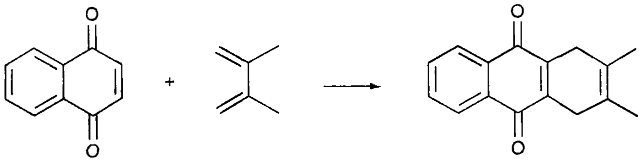
(4.41)

12-Tungstophosphoric acid on titania can be used as a catalyst for separating isobutene from mixed C_4 hydrocarbon streams. The procedure involves the etherification of the C_4 mixture with a diol, such as ethylene glycol or 1,2-propylene glycol, over the HPA catalyst to give the glycol mono-t-butyl ether (eq. 4.42), followed by deetherification of the monoethers at higher temperatures to yield pure isobutene and regenerated glycol.[172]

$$(CH_3)_2C = CH_2 + HOCH_2CH_2OH \rightarrow (CH_3)_3COCH_2CH_2OH + H_2O \qquad (4.42)$$

4.4.2.4 Miscellaneous Reactions

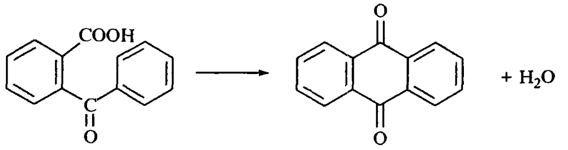
Silica-supported $H_3[PW_{12}O_{40}]$ has been found to be an active and recyclable catalyst for the Diels–Alder reaction (eq. 4.43) in toluene medium, providing a 70–80% yield.[173,174] The Ce^{3+} salt, $Ce_{0.87}H_{0.4}[PW_{12}O_{40}]$, shows a fairly high activity too, while $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ is practically inactive. Bulk $H_3[PW_{12}O_{40}]$ exhibits a very low activity probably because of the small surface area and site blocking by diene polymers.



(4.43)

Sol-gel derived $H_3[PW_{12}O_{40}]$ on silica has been applied for Diels–Alder reactions.[175]

Silica-supported Keggin heteropoly acids have been found to be efficient and recyclable catalysts for the dehydration of alcohols, such as 1,2-diphenylethanol, 1-(3,4-dimethoxyphenyl)-2-phenylethanol and cholesterol, in liquid phase.[176a] $H_3[PW_{12}O_{40}]$ can be used instead of sulfuric acid as the catalyst for the dehydration of o-benzoylbenzoic acid to anthraquinone.[176b]



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4.4.3 HETEROGENEOUS CATALYSIS IN GAS–SOLID SYSTEMS

Gas-phase reactions over heteropoly acids have attracted much interest.[1,3,9] Acid catalysed reactions in gas–solid systems are carried out using bulk or supported heteropoly acids and salts. The reaction temperatures are limited by catalyst thermal stabilities and normally do not exceed 350–400 °C. Supported heteropoly acids (usually on silica) are generally preferred because of their high surface area. HPA loadings vary from about 20 to 50 wt% or even higher, which corresponds to a coverage of more than one monolayer. At lower loadings, the acidity of heteropoly acid decreases because of interaction with support; such catalysts are also quite sensitive to poisoning by impurities that may be present in the support or feed. For these reasons, the catalysts containing less than 10 wt% HPA usually show poor activities and are rarely used.[1,2] Chemical modification of the surface of support could reduce the negative effect of support on the HPA acidity and lead to lower HPA loadings in practical catalysts.

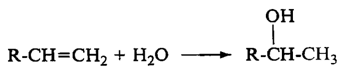
Control of water content in heteropoly acid catalysts is essential for their efficient performance. This can be achieved by thermal pre-treatment of the catalysts, typically at 130–200 °C. The effect of water may be attributed to the HPA acid strength and the number of proton sites as well as to catalyst deactivation. Excess water causes a decrease in the HPA acid strength – and thus in its activity. Dehydration of the catalyst increases the acid strength but decreases the number of acid sites, which may reduce the overall catalytic activity unless the reaction is highly demanding for catalysts acid strength. In addition, too strong acid sites thus created tend to deactivate (coke) faster.[2]

Two types of mechanism of catalysis have been proposed for heterogeneously catalysed reactions over solid heteropoly acids – surface type and bulk type I (Section 4.1.2).[1,6] In most cases, the acid-catalysed conversions of organic molecules probably occur via the conventional surface catalysis. With bulk heteropoly acids at relatively low temperatures, small polar molecules possessing a high affinity to heteropoly acid (e.g. lower alcohols) may react pseudohomogeneously in the catalyst bulk.[1] With supported heteropoly acids, reactions of polar substrates are more likely to occur via the surface type catalysis. This is backed by the observation that both polar and nonpolar substrates show similar dependencies between the catalytic activity and the surface area of supported heteropoly acid catalysts. Typically, for gas-phase reactions of both polar and nonpolar molecules, the catalytic activity increases with HPA loading, reaching a plateau or passing a maximum at 25–40 wt% loading. This is observed for the alkylation of benzene with ethylene, the esterification of acetic acid with ethanol, and the dehydration of isopropanol over $H_3[PW_{12}O_{40}]$ or $H_4[SiW_{12}O_{40}]$ on silica,[4] as well as for the cracking of cumene and the disproportionation of toluene over $H_3[PW_{12}O_{40}]$ on silica or alumina.[163] Such a behaviour is explained as a result of decreasing the HPA surface area as the loading increases. Water-insoluble heteropoly salts (e.g. $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$) are incapable of absorbing polar molecules into the bulk; they exhibit surface-type catalysis towards both polar and nonpolar molecules.[1]

Like other solid-acid catalysts, the solid heteropoly acids tend to deactivate during organic reactions because of the formation of carbonaceous deposit (coke) on the catalyst surface. Subsequent regeneration of heteropoly acid catalyst is difficult. The conventional regeneration by burning coke at 500–550 °C, which is routinely used in the case of aluminosilicates and zeolites, is not applicable to heteropoly acids because their thermal stability is low. This problem remains to be solved to put heterogeneous heteropoly acid catalysis in practice. Supporting heteropoly acid on a carrier may inhibit the formation of coke,[4] while bulk heteropoly acids, having very strong acid sites and low surface area, coke more rapidly.

4.4.3.1 Hydration of Olefins

Supported heteropoly acids are known for long time as the efficient catalysts for gas phase hydration of olefins such as ethylene and propylene to the corresponding alcohols.[177,178]



$$\text{R-CH=CH}_2 + \text{H}_2\text{O} \longrightarrow \text{R-}\overset{\text{OH}}{\overset{|}{\text{C}}}\text{H-CH}_3 \qquad (4.45)$$

More recently, several heteropoly acid catalysts for this reaction have been patented, including heteropoly acids supported on niobia,[179] acid-treated clay,[180] and siliceous supports.[181,182] These may challenge the industrial catalyst H_3PO_4/SiO_2 which has a drawback of polluting phosphoric acid.

The gas-phase hydration of isobutene over bulk $H_4[SiW_{12}O_{40}]$[183] and supported $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$[184] has been studied. Baba and Ono[184] found that the activity of supported $H_4[SiW_{12}O_{40}]$ decreases in the following order of supports: Amberlyst-15 > activated carbon > SiO_2 > TiO_2. The maximum activity was found for 30% $H_4[SiW_{12}O_{40}]$/Amberlyst-15.

4.4.3.2 Dehydration of Alcohols

Solid heteropoly acids and salts also efficiently catalyse the dehydration of alcohols – the reverse reaction of olefin hydration. The dehydration of isopropanol – a standard test reaction in heterogeneous acid catalysis – was studied in detail by Misono *et al.*[1] with the aim of proving the bulk type I (pseudoliquid phase) mechanism. $H_3[PW_{12}O_{40}]$ was found to be much more active for the dehydration of isopropanol than $SiO_2-Al_2O_3$ (a factor of 30 by weight) at 25 °C. The activity of heteropoly acids decreases in the series: $H_3[PW_{12}O_{40}] > H_4[SiW_{12}O_{40}] > H_5[PW_{10}V_2O_{40}] > H_3[PMo_{12}O_{40}] > H_5[PMo_{10}V_2O_{40}] \approx H_4[SiMo_{12}O_{40}]$ which is in line with their acid strengths. Using a transient response method and the deuterated isopropanol, it was demonstrated that a large amount of alcohol, corresponding to about 100 surface monolayers, is present in the bulk of crystalline $H_3[PW_{12}O_{40}]$ during the course of dehydration at 80 °C. It was also estimated that the rate of isopropanol absorption and desorption is about 50 times greater than the reaction rate. These results were considered to support the dehydration proceeding pseudohomogeneously in the catalyst bulk. These observations do not prove, however, that the bulk protons are the true catalytically active sites. It is conceivable that the reaction might predominantly occur on the more accessible and stronger surface protons rather than on the bulk protons, with the catalyst bulk serving as a reservoir supplying the alcohol molecules to the surface acid sites.

Izumi *et al.*[4] found no straight correlation between the HPA loading and the catalytic activity for the dehydration of isopropanol catalysed by silica-supported $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ at 150 °C; the activity levelled at the HPA loading of 25–30 wt%, as usual. This shows that the bulk catalysis is not efficient in the case of supported heteropoly acids.

4.4.3.3 Esterification

Bulk and supported heteropoly acids are active catalysts for the esterification of acetic acid with ethanol.[4] Typically, supported acids are more active than bulk ones. Various supports such as silica, active carbon, alumina, and titania have been studied. Among them, silica and active carbon give better activities and selectivities. Tungsten acids are more active than molybdenum ones; the latter tend to reduce during the reaction (Table 4.9). No catalyst deactivation is observed after 7 h on stream. The catalyst activity of silica-supported $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ for the esterification of acetic acid with ethanol at 150 °C increases with the HPA loading until 25–30 wt% and remains unchanged at higher loadings. This indicates that the esterification mainly occurs via the surface type catalysis.[4]

The synthesis of ethyl acetate by the direct addition of acetic acid to ethylene catalysed by silica-supported $H_4[SiW_{12}O_{40}]$ in vapour phase has been developed by BP Amoco (Chapter 6).[185]

4.4.3.4 Friedel–Crafts and related reactions

The alkylation of benzene with ethylene in vapour phase with heteropoly acid catalysts occurs at temperatures below 200 °C.[4] At higher temperatures an increased coke formation is observed. This is a clear example of surface

Table 4.9 Esterification of acetic acid with ethanol over heteropoly acid catalysts (flow reactor, 150 °C, 1 atm, EtOH/AcOH = 2.5)[4].

Catalyst	AcOH	Selectivity[a], %		
	conversion, %	EtOAc	Et_2O	Alkenes
5% $H_3[PW_{12}O_{40}]/SiO_2$	90.1	91	9	0
5% $H_4[SiW_{12}O_{40}]/SiO_2$	96.2	88	12	0
5% $H_3[PMo_{12}O_{40}]/SiO_2$	55.4	91	9	0
5% $H_4[SiMo_{12}O_{40}]/SiO_2$	60.7	91	9	0
$H_3[PW_{12}O_{40}]$	57.0	72	27	1
$H_4[SiW_{12}O_{40}]$	60.7	69	30	1
$H_3[PMo_{12}O_{40}]$	26.9	86	14	0
$H_4[SiMo_{12}O_{40}]$	44.6	85	15	0

a) Selectivity based on EtOH

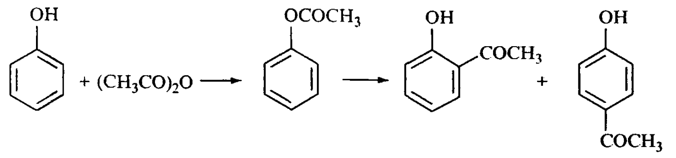
reaction as both the substrates have weak affinity towards heteropoly acid, and the HPA is insoluble in hydrocarbons. A comparative study[4] has shown that tungsten acids such as $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$ supported on silica catalyse the gas-phase alkylation of benzene more effectively than other typical solid acids such as silicoalumina and supported phosphoric acid (Table 4.10). The activity is comparable to that for zeolites CaY and LaY, which are highly active catalysts for the alkylation of benzene. With the tungsten heteropoly acids, the selectivity for monoalkylation is higher as compared with the zeolite catalysts. In the case of zeolites, the product ethylbenzene probably undergoes further ethylation more easily as it resides for longer time inside zeolite micropores than on the surface of supported HPA catalyst. Among the supports studied, silica is the best for this reaction. Molybdic acids such as $H_3[PMo_{12}O_{40}]$ and $H_4[SiMo_{12}O_{40}]$ were totally inactive for this reaction probably due to their reduction during the reaction. The effect of HPA loading on the alkylation activity has also been studied. The activity reaches a maximum at HPA loadings of 15–20 wt% and remains unchanged at higher loadings.

Table 4.10 Alkylation of benzene with ethylene over solid acids[4]a.

Catalyst	Temperature, °C	C_6H_6 conversion, %	EtPh selectivity, %
23% $H_3[PW_{12}O_{40}]/SiO_2$	200	3.8	85
23% $H_3[SiW_{12}O_{40}]/SiO_2$	200	3.9	80
CaY	200	4.5	66
LaY	200	3.6	45
$SiO_2-Al_2O_3$	250	0.6	100
23% H_3PO_4/SiO_2	300	0.3	100

a) Reaction conditions: $C_6H_6/C_2H_4 = 0.5$, 1 atm

12-Tungstophosphoric acid supported on silica or γ-alumina catalyses cumene cracking at 150 °C with 90% conversion and toluene disproportionation at 250 °C. The catalytic activity increases with increasing HPA loading, reaching its maximum in the loading range of 38–50 wt%. $H_3[PW_{12}O_{40}]/MgO$ shows no activity in these reactions.[163] A continuous gas-phase catalytic acetylation of phenol with acetic anhydride to phenyl acetate followed by simultaneous Fries rearrangement to yield ortho- and para-hydroxyacetophenones (eq. 4.46) over a silica-supported heteropoly acid has been described.[186]



(4.46)

A complete conversion of phenol to phenyl acetate is achieved at 140 °C. Upon increasing the temperature to 200 °C, the phenyl acetate formed isomerises into hydroxyacetophenones with 10% yield and 90% selectivity to the para isomer.

4.4.3.5 Oligomerisation of Olefins

12-Tungstosilicic acid catalyses the oligomerisation of propene to distillate fuels.[187] The catalytic activity depends upon the calcination temperature, the optimum activity being achieved for the catalyst calcined at 240 °C. $H_4[SiW_{12}O_{40}]$ supported on bauxite has been found to coke less rapidly than the bulk acid. At 170–180 °C and a pressure of 12 MPa a 95% conversion of propene over $H_4[SiW_{12}O_{40}]$ is achieved. The selectivity to the C_{12}^+ fraction is higher than in the case of the classical oligomerisation catalyst H_3PO_4/SiO_2.

The activity of bulk 12-tungstophosphoric acid and its salts for propene oligomerisation at 220–230 °C and a propene pressure of 5 MPa in a flow reactor decreases in the order of countercations (Table 4.11): $Al^{3+} \gg Co^{2+} > Ni^{2+} > NH_4^+ > H^+$, $Cu^{2+} > Fe^{3+}$, $Ce^{3+} > K^+$.[188] Fast catalyst deactivation is observed due to strong coking. Diluting the catalyst with acid-washed sand greatly increases the liquid product yield and the catalyst lifetime, the activity order remaining the same as for the undiluted powders. The aluminium salt is the most active, achieving 90% conversion at 230–240 °C and 5 MPa, the main product being the trimer. The sand-diluted aluminium salt achieves 100% conversion under these conditions with no deactivation after 150 h on stream.

4.4.3.6 Isomerisation of Alkanes

The skeletal isomerisation of linear alkanes is important for increasing the octane number of gasoline. The isomerisation of n-butane is a direct route to isobutane, a feedstock for the olefin/paraffin alkylation and MTBE synthesis. The alkane isomerisation requires very strong acid sites in the catalyst. Hence, heteropoly acids, because of their strong acidity, have attracted much interest as the catalysts for this reaction.[72,108,163,189–196] Bulk and supported tungsten acids, $H_3[PW_{12}O_{40}]$ and $H_4[SiW_{12}O_{40}]$, as well as heteropoly salts, e.g. $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$, neat or doped by platinum group metals, have been used.

Table 4.11 Propene oligomeristion catalysed by heteropoly acids and salts (flow reactor, 220–230 °C, 5 MPa, WHSV = $12\,h^{-1}$)[188].

Catalyst	Initial conversion^a, %	Steady state conversion, %	C_{12}^+ wt%
$H_3[PW_{12}O_{40}]$	17	–	68
$(NH_4)_3[PW_{12}O_{40}]$	22	21	44
$K_3[PW_{12}O_{40}]$	11	–	55
$Cu_{3/2}[PW_{12}O_{40}]$	15	–	41
$Co_{3/2}[PW_{12}O_{40}]$	28	22	41
$Ni_{3/2}[PW_{12}O_{40}]$	35	20	41
$NiH[PW_{12}O_{40}]$	24	20	44
$Fe[PW_{12}O_{40}]$	11	10	56
$Ce[PW_{12}O_{40}]$	9	7	51
$Al[PW_{12}O_{40}]$	42	87	36
$H_3[PW_{12}O_{40}]/Al_2O_3$	26	20	47
$H_4[SiW_{12}O_{40}]$	40	25	47

a) Conversion of propene to liquid product after 1 h

Nowinska *et al.*[163] reported the isomerisation of n-hexane over $H_3[PW_{12}O_{40}]$ supported on silica or alumina at 75 °C, however, with a very low activity. $H_3[PW_{12}O_{40}]$ supported (75 wt%) on MCM-41 molecular sieve ($800\,m^2\,g^{-1}$ surface area) has been reported to efficiently catalyse the isomerisation of n-butane, with much higher selectivity to isobutane compared to H-ZSM-5 (Table 4.12).[108] In the case of H-ZSM-5, the main process is the cracking of n-butane.

Bardin and Davis[72] found that the catalytic activity of bulk and silica-supported $H_3[PW_{12}O_{40}]$ for n-butane and n-pentane isomerisation at 200 °C decreases with increasing pre-treatment temperature, which suggests that the level of hydration is important. After pre-treatment at 300 °C, a well dispersed catalyst 5% HPA/SiO_2 was inactive, apparently lacking sufficient acidity required for this reaction, while higher loaded samples (10 and 25 wt%) were active. Ammonia sorption microcalorimetry results are well in line with reactivity, showing a significant increase in the acid strength as the loading increases from 5 to 25%. Catalyst deactivation was observed during the reaction, supposedly due to dehydration of the surface of heteropoly acid. Addition of water to the feed recovered the catalytic activity.

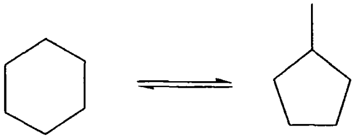
Table 4.12 Isomerisation of n-butane over $H_3[PW_{12}O_{40}]$/MCM-41 (flow reactor, 54 atm, WHSV = 1)[108].

Catalyst	Temperature	Conversion	Selectivity, wt%		
	°C	wt%	C_1-C_3	i-C_4	C_5^+
75% $H_3[PW_{12}O_{40}]$/MCM-41	178	23.9	2.1	94.1	3.8
75% $H_3[PW_{12}O_{40}]$/MCM-41	263	35.5	2.4	92.5	5.1
H-ZSM-5	260	34	40	24	36

Bulk $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ catalyses the isomerisation of n-butane at 300 °C.[189] This salt, because of its high surface area, has a higher activity than the bulk parent acid $H_3[PW_{12}O_{40}]$. Acidic salts $Cs_xH_{3-x}[PW_{12}O_{40}]$ prepared by grinding mixtures of $H_3[PW_{12}O_{40}]$ and $Cs_3[PW_{12}O_{40}]$ showed a higher catalytic activity in n-butane isomerisation at 200 °C than the salts prepared by precipitation.[194]

Bifunctional catalysts, comprising a Pd(II) salt of heteropoly acid or Pt-doped $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$, in the presence of hydrogen exhibit high activities in n-alkane isomerisation as well as better stabilities to deactivation.[190–193] In this case, the process occurs through the dehydrogenation of alkane on Pt or Pd, followed by the acid catalysed skeletal isomerisation of the alkene formed and finally by hydrogenation.

Methylcyclopentane is ring-expanded and cyclohexane is ring-contracted to methylcyclopentane (eq. 4.47) on 12-tungstophosphoric acid supported on silica and on microporous acidic silver salt $Ag_{3-x}H_x[PW_{12}O_{40}]$. The conversions of the two substrates increase with the loading of heteropoly acid on silica while achieving significantly higher values on the silver salt. The conversions pass through a maximum as the Ag^+/H^+ ratio increases; at 250 °C, a maximum conversion of cyclohexane of 18% with 92% selectivity to methylcyclopentane is obtained for $Ag_{1.7}H_{1.3}[PW_{12}O_{40}]$.[197]



(4.47)

4.4.3.7 Conversion of Methanol to Hydrocarbons

Similar to zeolites, heteropoly acids and salts catalyse the conversion of methanol to hydrocarbons.[198–201] Ono *et al.*[198] found that $H_3[PW_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$, and their silver(I) and copper(II) salts catalyse this reaction at 300 °C, the main products being the C_2-C_5 aliphatic hydrocarbons (Table 4.13). The silver(I) salts show the highest activity, the copper(II) salts perform similarly to the parent heteropoly acids. As compared to H-ZSM-5 zeolite, the activities of heteropoly compounds are lower and so is the yield of aromatics (<2.5%). It is suggested[199] that the active proton sites in the heteropoly salts are generated by reduction with hydrogen that forms by dehydrogenation of methanol:

$$Ag^+ + \tfrac{1}{2}H_2 \rightarrow Ag + H^+$$

$$Cu^{2+} + \tfrac{1}{2}H_2 \rightarrow Cu^+ + H^+$$

Table 4.13 Product distribution for the conversion of methanol to hydrocarbons (flow reactor, 300 °C)[198].

	Catalyst		
	$H_3[PW_{12}O_{40}]$	$Cu_{3/2}[PW_{12}O_{40}]$	$Ag_3[PW_{12}O_{40}]$
Product distribution, %			
MeOH	1.3	1.2	0
MeOMe	38.6	37.3	2.0
Hydrocarbons	60.1	61.5	98.0
Hydrocarbon distribution, %			
CH_4	3.7	5.2	9.0
C_2H_4	11.3	9.5	9.0
C_2H_6	0.9	0.8	5.2
C_3H_6	8.3	8.5	3.8
C_3H_8	16.1	13.4	34.0
C_4	39.3	39.2	26.1
C_5	12.5	13.7	7.2
C_6	7.9	9.7	5.7

Cesium salts of heteropoly acids exhibit better selectivities to C_2-C_4 olefins, up to 64% for $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$.[201]

4.4.3.8 Synthesis of MTBE

The synthesis of MTBE in the gas phase using solid heteropoly acid catalysts has been of considerable interest in the last couple of decades.[1,202–206] A range of bulk and silica-supported (20 wt%) Keggin and Wells–Dawson acids have been examined in a flow reactor at atmospheric pressure and 50–110 °C (Table 4.14).[202,203] The supported heteropoly acids show similar activities to Amberlyst-15, $SiO_2-Al_2O_3$, and H-ZSM-5 per unit catalyst weight and are twice as active as the bulk heteropoly acids. The selectivities based on both methanol and isobutene are significantly higher for heteropoly acids than for Amberlyst-15, $SiO_2-Al_2O_3$, and H-ZSM-5. Interestingly, the Wells–Dawson acid $H_6[P_2W_{18}O_{62}]$ is more active than the Keggin acid $H_3[PW_{12}O_{40}]$ despite the fact that the latter is stronger. The same was found for MTBE synthesis in homogeneous liquid phase.[27]

Heteropoly acids have also been used as catalysts for the synthesis of MTBE from tert-butanol and methanol (Ref.[1] and references therein).

The performance of shell- and tube-type membrane reactors equipped with heteropoly acid–polymer composite catalytic membranes for the vapour-phase decomposition of MTBE has been described.[207]

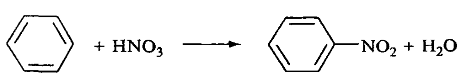
4.4.3.9 Nitration of Benzene

The vapour-phase nitration of benzene over solid acid catalysts has been investigated extensively for some decades as a cleaner alternative to the conventional liquid-phase nitration by mixed acid comprising concentrated nitric and sulfuric acids.[208]

Table 4.14 Synthesis of MTBE over solid acid catalysts in gas phase at 110 °C[202,203].

Catalyst[a]	Yield, %	Selectivity[b], %	Selectivity[c], %
$H_6[P_2W_{18}O_{62}]/SiO_2$	14.2	99	82
$H_3[PW_{12}O_{40}]/SiO_2$	7.7	96	52
$H_4[SiW_{12}O_{40}]/SiO_2$	7.0	98	70
$H_4[GeW_{12}O_{40}]/SiO_2$	13.4	99	69
$H_5[BW_{12}O_{40}]/SiO_2$	10.0	99	76
$H_6[CoW_{12}O_{40}]/SiO_2$	13.7	100	94
$H_6[P_2W_{18}O_{62}]$	7.2	80	98
$H_3[PW_{12}O_{40}]$	6.6	100	96
$H_4[SiW_{12}O_{40}]$	4.6	100	97
$H_4[GeW_{12}O_{40}]$	11.2	100	99
$H_5[BW_{12}O_{40}]$	7.2	100	100
$H_6[CoW_{12}O_{40}]$	5.7	100	98
Amberlyst-15	8.1	69	50
$SiO_2-Al_2O_3$	11.5	55	80
H-ZSM-5	8.9	21	100

a) Catalyst weight: 0.5 g; HPA loading on SiO_2: 20 wt%
b) Selectivity based on methanol at 2 h
c) Selectivity based on isobutene at 2 h



(4.48)

Partially substituted thallium and cesium salts of $H_3[PW_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$, and $H_3[PMo_{12}O_{40}]$ catalyse the vapour-phase nitration of benzene with dilute (70%) nitric acid.[209] With the salt $Cs_{1.5}H_{1.5}[PMo_{12}O_{40}]$ in a fixed bed flow reactor at atmospheric pressure and 160 °C, an initial yield of nitrobenzene of 90% (based on nitric acid) was obtained which, however, declined to 70% after 200 h on stream. The mixed oxide TiO_2-MoO_3 catalyst treated with sulfuric acid showed a stable catalytic activity for more than 500 h on stream providing 87% yield of nitrobenzene.

4.5 DEACTIVATION AND REGENERATION OF SOLID HETEROPOLY ACID CATALYSTS

A serious problem with the solid heteropoly acid catalysts is their deactivation during organic reactions because of the formation of carbonaceous deposit (coke) on the catalyst surface. Conventional regeneration by burning coke at 500–550 °C, which is routinely used in the case of aluminosilicates and zeolites, is not applicable to heteropoly acids because their thermal stability is not high enough.[2] Therefore, for heteropoly acids to be more widely used for heterogeneous acid catalysis an efficient and reliable methodology of their regeneration would be beneficial. In particular, the development of a technique leading to a reduction in the temperature of coke removal is of importance for the regeneration of deactivated solid heteropoly acid catalysts.

The coking and regeneration of silica-supported $H_3[PW_{12}O_{40}]$ during propene oligomerisation has been studied.[210,211] Coke formation causes rapid deactivation of the catalyst. The coked versus fresh catalysts have been characterised by ^{31}P and ^{13}C MAS NMR, XRD, XPS and TGA/TPO to reveal that the Keggin structure of the catalysts remains unaffected by coke deposition. The Pd doping has been shown to affect the nature of coke formed, inhibiting the formation of polynuclear aromatics. Co-feeding water to the propene flow greatly inhibits coke formation. The removal of coke from HPA catalysts has been attempted using solvent extraction, ozone treatment and aerobic oxidation. The aerobic burning of coke on the undoped $H_3[PW_{12}O_{40}]/SiO_2$ proceeds to completion at the temperature of 500–560 °C, which is higher than the temperature of $H_3[PW_{12}O_{40}]$ decomposition. Doping the catalyst with Pd significantly decreases this temperature (Figure 4.7) to allow catalyst regeneration at temperatures as low as 350 °C without loss of catalytic activity (Figure 4.8).

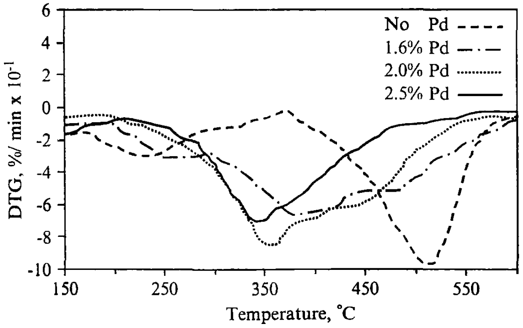


Figure 4.7 TGA/TPO for 20% PW/SiO_2 coked with propene at 200 °C for 1 h.[210,211]

The catalyst comprising $H_3[PW_{12}O_{40}]$ supported on sulfated zirconia doped with iron(III) for the alkylation of benzene with propene (100–150 °C, 4 MPa) was reported to have been regenerated under an air flow at 350 °C for 2 h.[151]

It was claimed that a heteropoly acid catalyst, e.g. a molybdophosphoric acid catalyst, whose activity had been lowered could be regenerated by dissolving and/or suspending it in an aqueous medium and then treating with an inorganic ion-exchange material, e.g. crystalline antimonic acid.[212]

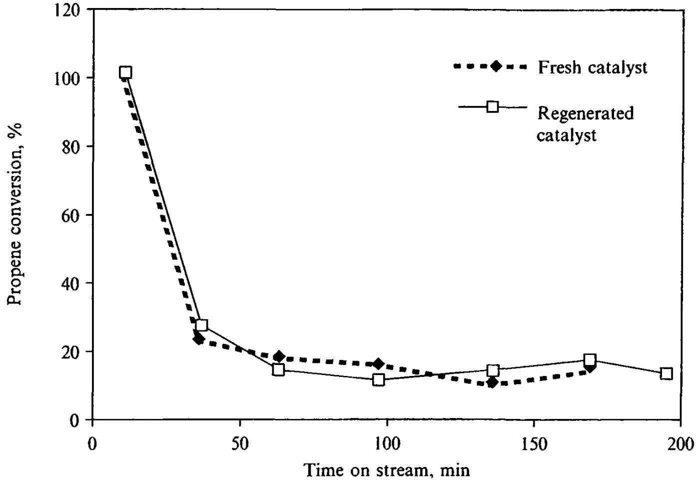


Figure 4.8 Catalyst performance of fresh and regenerated 2.5% Pd-doped 20% PW/SiO_2 for propene oligomerisation.[210,211]

Generally, prevention of catalyst deactivation is preferable to catalyst regeneration because the latter is usually difficult and expensive. In the case of gas-phase oligomerisation of propene catalysed by $H_4[SiW_{12}O_{40}]$, the catalyst cokes less rapidly when supported on silica than in the pure form.[187] Diluting bulk heteropoly acid catalyst with acid-washed sand (1 part catalyst to 10 parts sand) dramatically increases the product yield and catalyst lifetime in the gas-phase oligomerisation of propene (230 °C, 5 MPa).[188] Treatment of the deactivated heteropoly acid catalyst for the 1-butene and n-pentane isomerisation with water recovers activity, whereas treatment in air or N_2O is ineffective. It is suggested that water treatment regenerates acid sites by rehydrating partially decomposed Keggin units.[72] Co-feeding water is crucial to the stable activity of the silica-supported $H_4[SiW_{12}O_{40}]$ catalyst for the industrial synthesis of ethyl acetate from ethylene and acetic acid (Chapter 7).[185]

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5 Polyoxometalates as Catalysts for Selective Oxidation

CONTENTS

Selective (partial) oxidation of organic compounds catalysed by heteropoly compounds, both homogeneous and heterogeneous, has attracted much attention in the last three decades. Two types of processes are feasible: (i) oxygenation, i.e. oxygen atom transfer to a substrate, and (ii) oxidative dehydrogenation. In liquid-phase oxidation a broad range of oxidants, such as dioxygen, hydrogen peroxide, alkylperoxides, etc., can be used, whereas in gas-phase reactions mostly O_2 and infrequently N_2O have been applied. In contrast to acid catalysis, where easily available classical Keggin-type heteropoly acids dominate (Chapter 4), in catalytic oxidation, a wide variety of transition metal-substituted polyoxometalates (POM) are used. In this chapter, we will mainly discuss liquid-phase and gas-phase oxidations with the use of the most important and environmentally benign oxidants – dioxygen and hydrogen peroxide. Several reviews on catalysis by polyoxometalates for selective oxidation are available.[1-17]

5.1 LIQUID-PHASE OXIDATION

The liquid-phase oxidation of organic substances catalysed by polyoxometalates is usually carried out in homogeneous or biphasic systems. Heterogeneous liquid-solid systems are also used but less frequently. Amongst various oxidants that can be used in these reactions, dioxygen and hydrogen peroxide are by far the most important. In regard to catalytic oxidation, polyoxometalates are frequently viewed as robust, oxidation-resistant inorganic analogues of metalloporphyrins because the polyoxometalate ligand in transition-metal-substituted polyoxometalates is not susceptible to oxidative degradation and generally is thermally more stable than porphyrins or other macrocyclic ligands.[8,9,12,17,18,19] However, the solvolytic stability of polyoxometalates may be a problem in liquid-phase reactions. For example, in oxidations with hydrogen peroxide, the decomposition of polyoxometalates by interaction with H_2O_2 is frequently observed. The state of polyoxometalates in solution is generally complicated by a series of pH-dependent equilibria, involving a variety of polyanions and mononuclear metallospecies. These equilibria are largely unknown; consequently, relatively little exact knowledge of mechanisms of POM-catalysed oxidation is available.

5.1.1 OXIDATION WITH DIOXYGEN

This section mainly reviews the application of Keggin-type mixed-addenda heteropoly anions $[PMo_{12-n}V_nO_{40}]^{(3+n)-}$ (HPA-n) as catalysts for liquid-phase oxidation with O_2. Here HPA-n can mean either anion or acid as well as a partially protonated anion. The HPA-n system was first used for liquid-phase oxidation by Matveev *et al.*[1,20] This is the most efficient and versatile system in the polyoxometalate series for oxidation by O_2.[1,2,7,10,12,21,22] Discussed in this section are the HPA-n-catalysed oxidations in homogeneous, biphasic, and heterogeneous systems as well as mechanistic aspects of the HPA-n catalysis.

Numerous attempts have been made to perform aerobic oxidations by other kinds of polyoxometalates; for a review, see.[8,12,15] Finke *et al.*[19] have developed a new type of polyoxoanion-supported organometallic catalysts in which a metal complex is bound to the surface of a polyoxometalate. This type can be exemplified by $[(1,5\text{-COD})Ir \cdot P_2W_{15}Nb_3O_{62}]^{8-}$ ($M = Ir^I$ or Rh^I, COD = cyclooctadiene) where the M ion is probably bound to the $\{Nb_3O_{13}\}$ cap in the Wells–Dawson anion. These systems show a high activity in cyclohexene oxidation with oxygen. Although little catalytic chemistry has been reported so far for such systems, they may be promising for future studies.

5.1.1.1 General Principles

In liquid-phase oxidation, HPA-n with n = 2–6 are used. These polyanions are capable of acting extremely efficiently as a reversible redox system in conjunction with dioxygen (or air) under mild conditions.[1,10] Generally reactions catalysed by HPA-n proceed via a stepwise redox mechanism represented by equations 5.1 and 5.2:

$$\text{HPA-n} + \text{Red} + m\,H^+ \rightarrow H_m(\text{HPA-n}) + \text{Ox} \qquad (5.1)$$

$$H_m(\text{HPA-n}) + m/4\ O_2 \rightarrow \text{HPA-n} + m/2\ H_2O \qquad (5.2)$$

This mechanism includes stoichiometric *m*-electron oxidation of the substrate, Red, by HPA-n to form the product, Ox, followed by reoxidation of the reduced form of the oxidant, H_m(HPA-n), with dioxygen, where $H_m(\text{HPA-n}) = H_m[PMo_{12-n}{}^{6+}V_{n-m}{}^{5+}V_m{}^{4+}O_{40}]^{(3+n)-}$. The presence of a certain number of V^{5+} ions in the heteropoly anions is essential. Thus, the parent molybdenum anion $[PMo_{12}O_{40}]^{3-}$ (HPA-0) fails to possess such redox properties under mild conditions in solution, and so does HPA-1 for reasons that will be discussed later. Reactions 5.1 and 5.2 involve the reversible $V^{5+} \rightleftarrows V^{4+}$ transformations that are responsible for the redox properties of HPA-n. The reduction of HPA-n in solution is accompanied by protonation to maintain the charge of the polyanion. In aqueous solution, HPA-n are generally used in the pH range from 0.5 to 3.5, where they are relatively stable.

Operationally, reactions 5.1 and 5.2 can be carried out in the same reactor (one-stage process) or separately as a combination of two stoichiometric reactions (two-stage process).[1,10,21] In the two-stage process, the direct contact between the organic substrate and O_2 is excluded, hence this process is usually preferred for safety reasons.

As the catalysts, either one-component or two- and multicomponent systems are used. The most important two-component system includes HPA-n and Pd(II).[1,2,7,10,21] This is analogous to the redox system $CuCl_2$ + Pd(II) that is used for the industrial oxidation of ethylene to acetaldehyde (the Wacker process). The important advantage of the HPA-n + Pd(II) system is that it can work in the absence of Cl^- ions, hence it is more selective and less corrosive. Other two-component systems are also known, for example, those including HPA-n and Tl(III)/Tl(I), Pt(IV)/Pt(II), Ru(IV)/Ru(III), Ir(IV)/Ir(III), Br_2/Br^-, or I_2/I^-.[2,7] In two-component systems, the substrate is usually oxidised by the co-catalyst, and the polyoxometalate enhances the reoxidation of the co-catalyst by reactions 5.1 and 5.2. The two-component systems POM + Pd(II) and POM + Rh(I) have been used for carbonylation, hydroformylation and hydrogenation reactions.[23–28]

The thermodynamic condition for the occurrence of reactions 5.1 and 5.2 can be represented using redox potentials of the substrate, HPA-n, and dioxygen:[2,7,10]

$$E(\mathrm{Red}) \leq E(\text{HPA-n}) \leq E(\mathrm{O_2})$$

The reduction potential E(HPA-n) is ca. 0.7 V versus standard hydrogen electrode (SHE) for HPA-n with n = 1–4 at pH 1,[29,30] and the standard reduction potential of oxygen $E(O_2/2H_2O)$ is 1.23 V at 25 °C and 1 atm. Hence the above condition fulfils for a wide variety of organic substrates as well as for many inorganic redox systems to be used as co-catalysts with HPA-n. Some other polyoxometalates having similar properties, for example $[PMo_6W_6O_{40}]^{3-}$, can also be used for this purpose.[31]

5.1.1.2 Homogeneous Oxidation

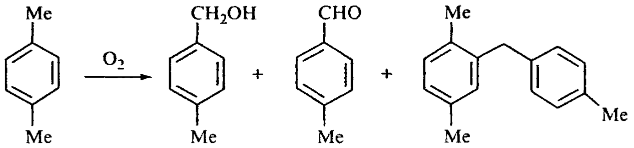
One-component HPA-n system A range of hydrocarbons can be homogeneously oxidised with HPA-n as catalyst under mild conditions. HPA-n catalyse the oxidation of alkanes to oxygenates by O_2. Arzamaskova *et al.*[32] and Geletii and Shilov[33] reported the oxidation of alkanes by HPA-6 under mild conditions in the presence Ru(III), Ir(III)[32] and Pt(II).[33] Lyons *et al.*[34] oxidised alkanes by O_2 with HPA-n as one-component catalyst. For example, propane is oxidised in AcOH – H_2O solution in the presence of HPA-n at 150 °C to give a mixture of isopropanol and acetone in 42 % and 52 % selectivity, respectively (eq. 5.3).

$$C_3H_8 + O_2 \rightarrow CH_3CH(OH)CH_3 + CH_3COCH_3 \qquad (5.3)$$

The mixed-addenda HPA-n are more efficient catalysts than the all-molybdenum heteropoly anions.

Other types of polyoxometalates are also active in alkane oxidation, for example, a trisubstituted Keggin anion $[PW_9Fe_2NiO_{37}]^{7-}$.[35] As shown by Mizuno *et al.*,[36] this polyanion also catalyses the oxidation of cyclohexane, adamantane, cyclohexene, and ethylbenzene. The dimanganese(III) anion $[SiW_{10}O_{38}Mn_2]^{6-}$ is efficient in the oxidation of cyclohexane with O_2.[37] Neumann *et al.*[38,39] reported that the Ru(III)-substituted sandwich type polyanion, $[(WZnRu_2)(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$, catalyses the hydroxylation of alkanes by O_2.

The HPA-n anions stoichiometrically oxidise methylbenzenes in acetic acid solution to form mixtures of aromatic alcohols, aldehydes, and di-and polyarylmethanes (eq. 5.4).[40] In the presence of O_2, the reaction occurs catalytically. The active oxidants are probably the VO_2^+ ions which form by dissociation of HPA-n. The rate of oxidation decreases in the order of arenes: durene > mesitylene > p-xylene > toluene, i.e. in parallel with their ionisation potentials. The reaction is suggested to proceed via the formation of aromatic radical cation intermediates.



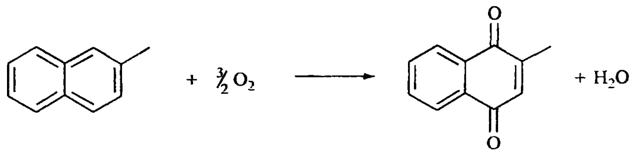
(5.4)

Many synthetically attractive oxidations of hydrocarbons catalysed by HPA-n have been developed to date. Neumann *et al.*[41] reported highly efficient dehydrogenations with HPA-2 as a catalyst in CH_2ClCH_2Cl/tetraglyme solution. For example, reaction 5.5 yields 98 % anthracene (70 °C, 16 h).

(5.5)

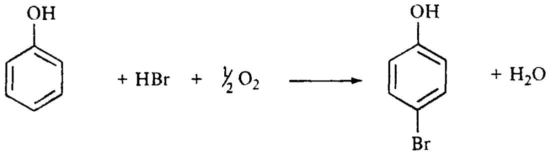
The HPA-2-catalysed dehydrogenation of α-terpinene to p-cymene in acetonitrile solution was found to be zero-order in α-terpinene, first-order in dioxygen, and second-order in HPA-2.[42] On the basis of these kinetic results and spectroscopic data, a reaction mechanism was formulated. This involves the formation of a stable substrate–catalyst complex in the catalyst reduction stage 5.1 and a μ-peroxo catalyst intermediate in the catalyst reoxidation stage 5.2 where dioxygen is reduced in a four-electron redox reaction. However, the above kinetic evidence may not be sufficient to support the μ-peroxo catalyst intermediate.

Oxidation of 2-methylnaphthalene to quinone (eq. 5.6) is a step of the vitamin K_3 synthesis. In industry it is carried out with highly toxic CrO_3 as a stoichiometric oxidant with a low yield (ca. 50 %). With HPA-n, it occurs catalytically in AcOH – H_2O solution at 120–140 °C with 82 % selectivity at 78 % conversion.[43]



(5.6)

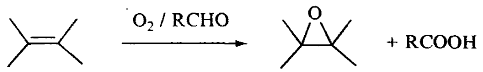
Gorodetskaya *et al.*[44] reported the oxidative bromination of a range of aromatic compounds catalysed by HPA-n with HBr as a brominating agent and O_2 as a terminal oxidant. Neumann *et al.*[45] reported the oxidative bromination of phenols in the para-position (eq. 5.7) in a homogeneous HPA-2/CH_2ClCH_2Cl/tetraglyme system with a remarkably high 99% yield (20 °C, 5 h).



(5.7)

The antimony-substituted Keggin polyoxomolybdate $[PMo_{11}O_{39}Sb^{III}]^{4-}$ has been synthesised and used as a catalyst for aerobic oxidation of benzylic alcohols to aldehydes.[46]

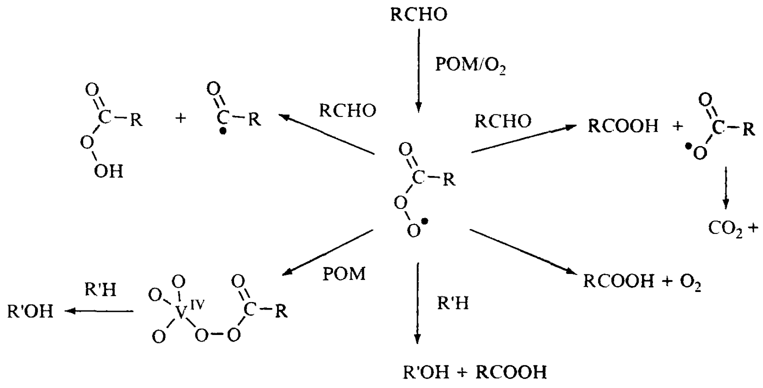
Ishii *et al.*[47] have studied a number of oxidations with O_2 in the presence of an aldehyde, e.g., 2-methylpropanal, as a sacrificial reductant and $(NH_4)_5H_4[PMo_6V_6O_{40}]$ as a catalyst in dichloroethane solution. The addition of aldehydes is a well-known method to promote the liquid-phase free radical oxidation of organic compounds by O_2. Many metal complexes, such as Co(III), Mn(III), Cu(II), Fe(III), etc., can initiate such reactions.[48] The aldehyde-initiated epoxidation of olefins proceeds at 25 °C with a very high selectivity of 81–100% (eq. 5.8). A carboxylic acid as a co-oxidation product from the aldehyde is also formed. In addition, the Baeyer–Villiger oxidation of cyclic ketones to lactones was accomplished with 78–87% selectivity using benzaldehyde as the sacrificial aldehyde (25 °C, 20 h, 1 atm O_2). These reactions may be synthetically useful if the carboxylic acid is a useful product, provided a less harmful solvent instead of CH_2ClCH_2Cl is employed.



(5.8)

Mizuno *et al.*[49] reported that the selective epoxidation of olefins by O_2 in the presence of an aldehyde is also catalysed at 25 °C by transition metal-substituted 12-tungstophosphates $[PW_{11}O_{39}M]^{x-}$, where M = Co(II), Mn(II), Fe(III), Cu(II) or Ni(II), whose activity decreases in that order. The order of the effectiveness of the aldehydes is: pivalaldehyde > isobutyraldehyde ≫ butyraldehyde ≥ acetaldehyde > valeraldehyde > benzaldehyde. The catalytic activity of polyoxometalates is solvent dependent. Thus the activity of $[PW_{11}O_{39}Co]^{5-}$ decreases in the series: $CHCl_3 > CH_2Cl_2 > 1,2\text{-}C_2H_4Cl_2 \geq CH_3CN > C_6H_6 >$ DMF > DMSO. There is evidence that the POM-catalysed co-oxidative epoxidation of olefins with O_2 in the presence of aldehyde proceeds by a radical chain mechanism.[47,50,51]

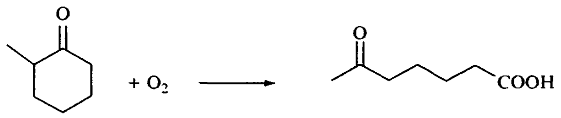
The co-oxidation of alkanes and isobutyraldehyde with oxygen in the presence of $H_5[PMo_{10}V_2O_{40}]$ has been shown to occur with a significant nonproductive oxidation of aldehyde.[52] Thus in the oxidation of cyclooctane only 16% of isobutyraldehyde is used to form cyclooctanol and cyclooctanone, 72% is oxidised to isobutyric acid without oxidation of cyclooctane, and 12% is decomposed to acetone and CO_2. A free radical mechanism is suggested with acyl peroxo radicals as active oxidising intermediates (Scheme 5.1).



Scheme 5.1

When $H_5[PMo_{10}V_2O_{40}]$ supported on MCM-41 is used, the co-oxidation occurs similarly, although with a lower catalytic activity.[53]

A variety of oxygenates, e.g., aldehydes, ketones, phenols, etc., can be oxidised with HPA-n under mild conditions with very good yields. Brégeault *et al.*[54] reported the oxidative cleavage of cyclic ketones. For example, the cleavage of 2-methylcyclohexanone is catalysed by HPA-4 in aqueous solution to yield 97% of ketoacid (60 °C, 8 h) (eq. 5.9).



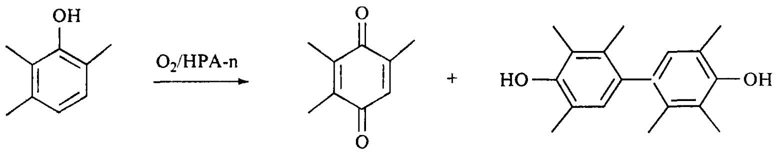
(5.9)

HPA-n-catalysed oxidation of cyclohexanone to adipic acid was studied as an alternative to the industrial nitric acid oxidation.[54] The reaction was found to be solvent-dependent, aqueous acetic acid being the best solvent, yielding 50% adipic acid together with 19% glutaric and 3% succinic acids at 99% cyclohexanone conversion (HPA-4, 1 atm O_2, 70 °C, 7 h). Adipic acid was found to be stable to degradation by the HPA-n/O_2 system. This system has the advantage over the nitric acid oxidation of being less corrosive and no nitric oxides evolve. However, the selectivity to adipic acid is still not high enough for practical application.

Ishii *et al.*[47] studied the oxidation of aldehydes to carboxylic acids with the use of the NH_4^+ salt of HPA-6 as a catalyst (eq. 5.10). The reaction proceeds under very mild conditions (25 °C, 1 h) in dichloroethane with 96–100 % selectivity at 60–78 % aldehyde conversion.

$$RCHO + \tfrac{1}{2}O_2 \rightarrow RCOOH \qquad (5.10)$$

Kholdeeva *et al.*[56] and Neumann *et al.*[57] reported the oxidation of alkylphenols by HPA-n. The oxidation of 2,3,5-trimethylphenol (TMP) to trimethylbenzoquinone (TMBQ) (eq. 5.11) is of practical interest as a step to synthesise vitamin E. This reaction yields TMBQ with 86 % selectivity at 100 % TMP conversion (HPA-4, AcOH–H_2O, 50 °C).[56]



(5.11)

2,2′,3,3′,6,6′-Hexamethyl-4,4′-bisphenol (HMBP), the product of the oxidative coupling of TMP, is also formed under these conditions. The product selectivity depends on the water concentration in the reaction mixture. With [H_2O] increasing, the yield of HMBP increases at the expense of TMBQ. The HMBP itself undergoes oxidative conversion into TMBQ via the intermediate formation of hexamethyldiphenoquinone (HMDQ). Evidence has been obtained that the oxidation occurs by the VO_2^+ ions which form as a result of dissociation of HPA-n. A mechanism has been proposed involving the one-electron oxidation of TMP by VO_2^+ followed by the oxidation of vanadium(IV) to vanadium(V) by oxygen inside of HPA-n[56] (eq. 5.12–5.17, where ArOH stands for TMP).

$$\text{HPA-n} \rightleftarrows VO_2^+ + \text{HPA-(n} - 1) \qquad (5.12)$$

$$VO_2^+ + ArOH + H^+ \xrightarrow[\text{slow}]{} ArO^\bullet + VO^{2+} + H_2O \qquad (5.13)$$

$$2\,ArO^\bullet \rightarrow HMBP \rightarrow HMDQ \rightarrow TMBQ \qquad (5.14)$$

$$VO^{2+} + \text{HPA-n} + H_2O \rightleftarrows VO_2^+ + \text{H(HPA-n)} + H^+ \qquad (5.15)$$

or

$$VO^{2+} + \text{HPA-(n} - 1) + H^+ \rightleftarrows \text{H(HPA-n)} \qquad (5.16)$$

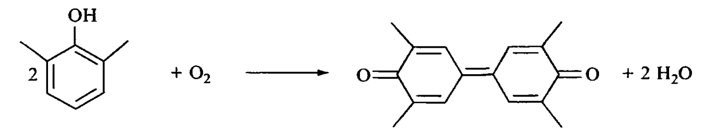
$$4\,\text{H(HPA-n)} + O_2 \rightarrow 4\,\text{HPA-n} + 2\,H_2O \qquad (5.17)$$

Step 5.13 involving the formation of the phenoxyl radical is probably rate-limiting. Subsequent transformations of the phenoxyl radical give TMBQ via HMBP and HMDQ. VO^{2+} either interacts with HPA-n by electron transfer (eq. 5.15) or enters the lacunary species HPA-(n−1) (eq. 5.16) to form the reduced heteropoly anion H(HPA-n). Eventually, H(HPA-n) is oxidised by O_2 (eq. 5.17) by a multielectron-transfer mechanism which will be discussed later. It should be noted that the free VO^{2+} ion is not oxidised by O_2 in acidic solution.

Interestingly, the tungsten analogues of HPA-n, $[PW_{12-n}V_nO]_{40}^{(3+n)-}$, which are much less labile than $[PMo_{12-n}V_nO]_{40}^{(3+n)-}$ in aqueous solution,[58] show a very low activity in the oxidation of TMP[56] as well as in some other reactions, for example, oxidation of H_2S.[59] A possible reason for this is that in the case of $\{PW_{12-n}V_n\}$, reactions 5.12 and 5.16 are too slow.

The oxidation of sterically hindered phenols to benzoquinones with oxygen catalysed by manganese(II) complexes of heteropolytungstates has been investigated.[60]

The oxidative coupling of 2,6-dialkylphenols to diphenoquinones (eq. 5.18) catalysed by copper amine complexes is used for the synthesis of antioxidants. In this reaction, HPA-n shows a higher activity than copper complexes. The oxidative coupling proceeds in H_2O, AcOH – H_2O, or MeOH – H_2O as solvents at 25–50 °C and under O_2 pressure of 1–5 atm. Diphenoquinones, insoluble under these conditions, can be readily isolated from the reaction mixture by crystallisation. Thus, 2,2′,6,6′-tetramethyl- and 2,2′,6,6′-tetra-*t*-butyl-diphenoquinones are obtained in a nearly 100 % yield. The catalyst can be recycled without loss of its activity.[61]



(5.18)

Oxidation of sulfur compounds with oxygen can be efficiently carried out with HPA-n. For example, the oxidation of H_2S to sulfur[62] and thioethers to sulfoxides and sulfones[63] proceed with nearly 100 % yield.

$$H_2S + \tfrac{1}{2}O_2 \rightarrow S + H_2O \qquad (5.19)$$

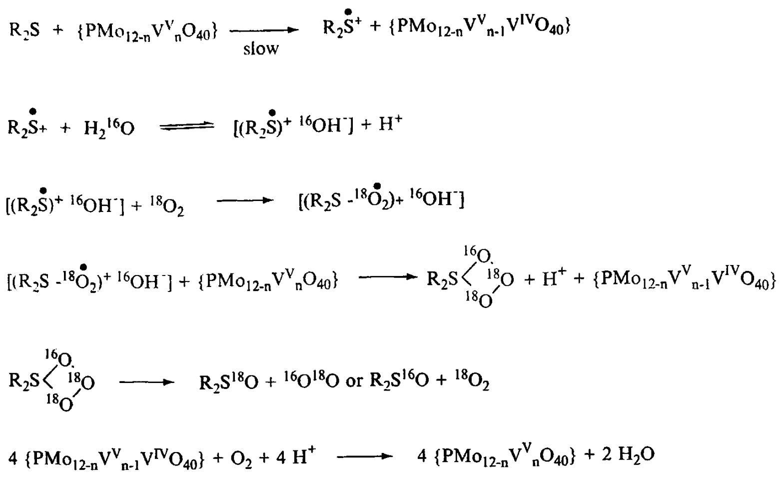
$$2\,RSH + \tfrac{1}{2}O_2 \rightarrow RSSR + H_2O \qquad (5.20)$$

$$R_2S + \tfrac{1}{2}O_2 \rightarrow R_2SO \qquad (5.21)$$

$$R_2SO + \tfrac{1}{2}O_2 \rightarrow R_2SO_2 \qquad (5.22)$$

The HPA-n-catalysed oxidation of diethyl sulfide with $^{18}O_2$ in $CH_3C^{16}O_2H$ – $H_2{}^{16}O$ solution at 96 °C leads to the incorporation of 44–54 %

^{18}O in the product sulfoxide. The process is accompanied by isotope exchange of dioxygen. On these bases, a radical mechanism (Scheme 5.2) is suggested.[64]



Scheme 5.2

Harrup and Hill[65] have reported POM-based catalyst systems – $[PW_{11}O_{39}Zn]^{5-}$, $[SiW_{11}O_{39}]^{8-}$, $[SiW_{11}O_{39}Zn]^{6-}$, $[NaP_5W_{30}O_{110}]^{14-}$, etc. – for the selective aerobic oxidation of H_2S in aqueous solution to yield a high purity (>99.5 %) sulfur. Selective oxidation of tetrahydrothiophene to the corresponding sulfoxide by O_2 is achieved in high selectivity (>99 %) at 95 °C in the presence of HPA-2 as a catalyst.[66]

Another interesting field is the application of HPA-n redox catalysis for environmentally benign delignifying wood pulp.[67] Lignin – a complex polymer derived from aromatic alcohols – is, besides cellulose, one of the main constituents of wood. Delignification is a step in manufacturing paper. Currently, it is typically done by treatment of the pulp by chlorine, which poses a great environmental concern. Weinstock, Hill *et al.*[67] have developed a new method of removing residual lignin from wood pulp by a two-step process involving the oxidative degradation of lignin by polyoxometalates, e.g., HPA-2, followed by separation of bleached pulp and reoxidation of the reduced polyoxometalate by a nonpolluting oxidant, such as air, O_2, H_2O_2, etc. The process can be represented by equations 5.1 and 5.2 where Red is now the pulp and Ox is the bleached pulp. The net reaction is the selective oxidative removal of lignin from wood yielding only high quality cellulose, CO_2 and H_2O:

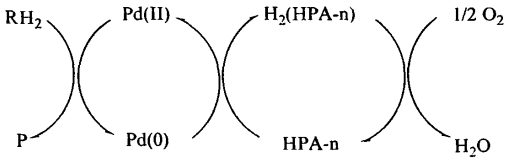
$$\text{Wood (cellulose + lignin)} + O_2 \rightarrow \text{cellulose} + CO_2 + H_2O \qquad (5.23)$$

As such, this method allows producing a paper quality bleached pulp and is claimed to be an effective alternative to the chlorine bleaching. Evtuguin *et al.*[68] have studied in detail the one-step delignification by O_2/HPA-n system.

Two-component system HPA-n + Pd(II) The two-component redox system HPA-n + Pd(II)[1] has attracted considerable attention. A wide variety of stoichiometric oxidations of organic compounds (RH_2), e.g., olefins, alcohols, arenes, etc., by Pd(II) can be carried out catalytically with the use of HPA-n as a cocatalyst and O_2 as an oxidant[2,7,10,21,69] (eq. 5.24).

$$RH_2 + \tfrac{1}{2}O_2 \rightarrow P + H_2O \qquad (5.24)$$

Generally, such reactions proceed via a stepwise redox mechanism (Scheme 5.3).[2,10,21] It is analogous to the Wacker-type oxidation with $CuCl_2 - PdCl_2$ as the catalyst. But the HPA-n + Pd(II) catalyst can work in the absence of or at a very low concentration of Cl^- ions. Consequently, this redox system has the advantage of being higher selective and less corrosive.[1,21]



Scheme 5.3

Most interesting is the application of the HPA-n + Pd(II) system for the Wacker-type oxidation of olefins (eq. 5.25):

$$RCH = CH_2 + \tfrac{1}{2}O_2 \rightarrow RCOCH_3 \qquad (5.25)$$

The Wacker process is industrially employed for manufacturing acetaldehyde from ethylene, the $CuCl_2 + PdCl_2$ redox system being used as a catalyst.[70] However, this process has several drawbacks such as formation of chlorinated byproducts and strong corrosion of the reaction vessel. So the development of chloride-free oxidants to replace $CuCl_2$ has long been a challenge. Matveev[1,20,71] first used HPA-n as a chloride-free oxidant in the Wacker reaction. The oxidation of ethylene can be represented by equations 5.26–5.28.

$$C_2H_4 + Pd(II) + H_2O \rightarrow CH_3CHO + Pd(0) + 2\,H^+ \qquad (5.26)$$

$$Pd(0) + \text{HPA-n} + 2\,H^+ \rightarrow Pd(II) + H_2(\text{HPA-n}) \qquad (5.27)$$

$$H_2(\text{HPA-n}) + \tfrac{1}{2}O_2 \rightarrow \text{HPA-n} + H_2O \qquad (5.28)$$

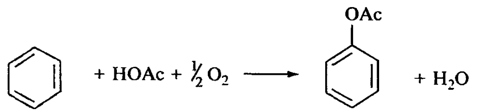
Later on, Catalytica[21] has developed a new technology for the Wacker oxidation of ethylene with the use of the HPA-n + Pd(II) system. In order to enhance the reaction rate and stabilise Pd(II) in solution, the reaction is yet carried out in the presence of Cl^- ions, but at a very low concentration, much lower than in the conventional Wacker process (Table 5.1). In the Catalytica's process, over 99% of the production of chlorinated by products is eliminated, decreasing to less than 0.01% yield on ethylene. The practical production of aqueous HPA-n for use at large scale as well as in the laboratory and the reoxidation of aqueous reduced HPA-n by O_2 has been described.[72] There is no evidence of commercial use of this process, however.

Other homogeneous oxidations catalysed by the HPA-n + Pd(II) system have been reported. These include the acetoxylation of ethylene to vinyl acetate and of propylene to allyl and propenyl acetates,[73] the oxidation of primary and secondary alcohols,[74] the acetoxylation,[75a] hydroxylation[75b,c] and oxidative coupling[76] of aromatic compounds, and the arylation of olefins[77] (eq. 5.29–5.34).

$$CH_2 = CH_2 + HOAc + \tfrac{1}{2}O_2 \longrightarrow CH_2 = CHOAc + H_2O \qquad (5.29)$$

$$CH_2 = CH\text{-}CH_3 + HOAc + \tfrac{1}{2}O_2 \longrightarrow CH_2 = CH\text{-}CH_2OAc + H_2O \qquad (5.30)$$

$$RR'CHOH + \tfrac{1}{2}O_2 \longrightarrow RR'CHO + H_2O \qquad (5.31)$$



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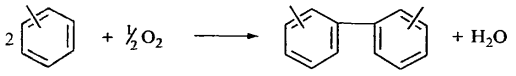

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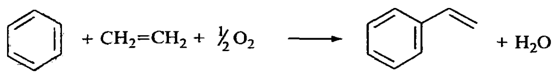
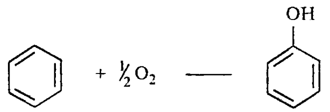


(5.34)

Table 5.1 Catalyst solutions for Wacker oxidation of ethylene to acetaldehyde[21].

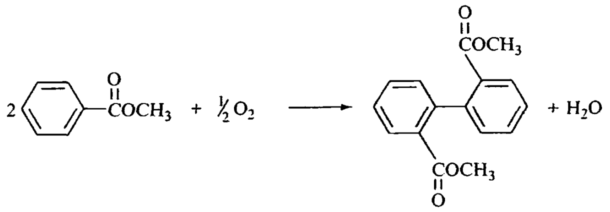
Catalytica's system		$CuCl_2 + PdCl_2$ system	
Pd(II)	0.1 mM	Pd(II)	10 mM
Cl^-	5–25 mM	Cl^-	2 M
$[PMo_{10}V_2O_{40}]^{5-}$	0.3 M	$CuCl_2$	1 M

Passoni *et al.*[75b] reported the oxidation of benzene to phenol by O_2 catalysed by the Pd(II) + HPA-n redox system with 70% selectivity at 15% benzene conversion and 800 Pd(II) turnovers (130 °C, 60 atm O_2, in AcOH – H_2O).



When $H_3[PMo_9V_3O_{40}]$ supported on MCM-41 is used as a catalyst for this reaction, the heteropoly acid leaches from the support, and the reaction occurs homogeneously.[75c]

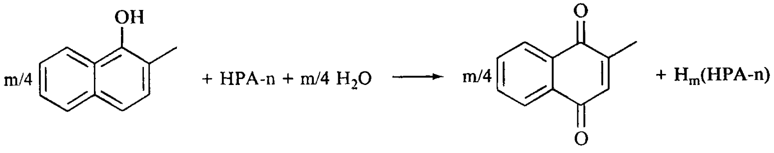
Multicomponent systems Three-component redox system, including HPA-n, hydroquinone (HQ) and Pd(II), was found to be an efficient homogeneous catalyst for Wacker-type oxidation of alkenes.[78,79] In this system, HPA-n smoothly oxidises HQ to benzoquinone; the latter rapidly oxidises Pd(0) to Pd(II), thus greatly enhancing the overall reaction rate. Addition of Cu(II) to the HPA-n + Pd(II) redox system can also benefit Wacker-type oxidation.[80,81] Pd(II) + HPA-n is an efficient homogeneous catalyst for the oxidative coupling of arenes (eq. 5.33) which is a useful route to the synthesis of biphenyl derivatives (for a review, see[82]). Hg(II) is often employed as a promoter in the coupling of alkylbenzenes to improve the activity and selectivity to 4,4'-isomers. The oxidative coupling of methyl benzoate catalysed by $Pd(OAc)_2$+ HPA-n, yielding 2,2'-biphenic acid dimethyl ester with unusually high selectivity (80%), has been reported.[83] An ortho cyclopalladated intermediate is suggested to be responsible for this. Addition of $Hg(OAc)_2$ increased greatly the conversion of methyl benzoate without impairing the selectivity to the 2,2'-isomer.



5.1.1.3 Biphasic Oxidation

The advantage of biphasic systems is that they combine a catalytic reaction and product separation in one unit, which allows avoiding difficult separation problem. Like in acid catalysis discussed in Chapter 4, polyoxometalates can be profitably used as catalysts for selective oxidation in biphasic systems.

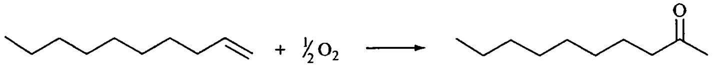
Matveev *et al.*[84] reported two-stage oxidation of 2-methyl-1-naphthol to menadione in a high yield (eqs 5.35 and 5.36). Step 5.35 is carried out in a water-hydrocarbon biphasic system at 50 °C with 89 % yield of menadione at a 100 % naphthol conversion. This is a promising alternative to the conventional synthesis of vitamin K_3 by oxidising 2-methylnaphthalene with CrO_3. 2-Methyl-1-naphthol can be produced in a high yield by a heterogeneously catalysed gas-phase alkylation of naphthalene by methanol.



(5.35)

$$H_m(HPA\text{-}n) + m/4\,O_2 \rightarrow HPA\text{-}n + m/2\,H_2O \qquad (5.36)$$

Kozhevnikov *et al.*[85] have developed the efficient one-stage oxidation of TMP to TMBQ with 84 % yield at a 100 % TMP conversion in a two-phase system at 50 °C and 1 atm O_2 pressure (eq. 5.11). The catalyst (lower) phase is an HPA-4 solution in AcOH – H_2O. The upper phase is a TMP + TMBQ solution in a hydrocarbon solvent, e.g., heptane, benzene, etc. The oxidation of 2, 6-dialkylphenols to 2,6-dialkyl-1,4-benzoquinones by oxygen catalysed by HPA-n in biphasic water-organic systems has been reported.[86,87] Monflier *et al.*[80] reported the biphasic Wacker oxidation of 1-decene to 2-decanone at 80 °C with excellent yield (98 %) and practically no double bond migration (eq. 5.37).



(5.37)

In this case, the catalyst (lower) phase is a three-component system, containing Pd(II), HPA-6 and Cu(II) in an aqueous solution, where Cu(II) is suggested to promote the Pd(O) reoxidation. β-Cyclodextrin as a phase-transfer catalyst is used to transfer 1-decene to the aqueous phase by a host-guest interaction. However, no evidence of the integrity of β-cyclodextrin during the reaction course is provided.

5.1.1.4 Heterogeneously Catalysed Oxidation

Neumann *et al.*[88] reported the liquid-phase oxidative dehydrogenation of benzylic alcohols and amines catalysed by carbon-supported HPA-n in toluene at 100 °C with excellent yields (94–100 %). The oxidation of benzylic alcohols to benzaldehydes (eq. 5.38) proceeds without overoxidation to carboxylic acids. Reaction 5.39 proceeds via the oxidative dehydrogenation of benzyl amine to imine, ArCH = NH, followed by the hydrolysis of the imine to form benzaldehyde, and, finally, the interaction between the benzyl amine and benzaldehyde yields a Schiff-base.

$$ArCH_2OH + ½O_2 \rightarrow ArCHO + H_2O \qquad (5.38)$$

$$ArCH_2NH_2 + O_2 \rightarrow ArCH{=}NCH_2Ar \qquad (5.39)$$

Jansen[89] applied HPA-n (n = 2, 3) supported on a variety of chemically modified carbon supports as catalysts for the oxidation of TMP to TMBQ (eq. 5.11) in polar media.

Ishii *et al.*[90] studied the aerobic oxidation of various organic compounds catalysed by a carbon-supported (10 %) NH_4^+ salt of HPA-n with an average composition of $(NH_4)_5H_6[PMo_4V_8O_{40}]$. This catalyst shows high catalytic activity for the oxidative dehydrogenation of benzylic and allylic alcohols to the corresponding aldehydes and ketones (46–92 % yield) in toluene. The catalyst can be recycled without loss of its activity. In contrast, the unsupported catalyst is inactive for these oxidations. The enhancement of catalytic activity by supporting the heteropoly salt on the active carbon is believed to be the result of an increase in concentration of substrate and oxygen due to their adsorption in the vicinity of the active site. In addition, the active carbon could be a good mediator of the electron transfer in redox steps involved in the catalytic process. It should be noted, that the supported catalyst has a large surface area compared to the bulk heteropoly salt, which may be a reason for the greater activity of the supported system. Other aerobic oxidations, such as the oxidation of phenols and amines, were also examined.[90] In the case of reactions in polar media a significant leaching of polyoxometalate from the active carbon was observed. Thus in the oxidation of TMP to TMBQ (eq. 5.11) in AcOH-H_2O, 7 % of POM supported on active carbon dissolved from the support, which could give rise to homogeneously catalysed reaction. Although the recycled catalyst showed almost the same performance as the original one, the homogeneous reaction could not be ruled out. The best way to examine the role of homogeneous catalysis would be to filter off the catalyst at the reaction temperature and test out the filtrate.

The heteropoly acid $H_5[PMo_{10}V_2O_{40}]$ deposited on cotton cloth, polyacrylic fibre, nylon fibre, or carbon powder has been used as a catalyst for aerobic liquid-phase oxidation of acetaldehyde, 1-propanethiol, and tetrahydrothiophene.[91]

5.1.1.5 Mechanism

Despite the importance and versatility of oxidations catalysed by HPA-n, there is only limited knowledge about their mechanism. The state of HPA-n in solution is extremely complex, and the higher the *n* value, the more complex the system. These solutions contain a great number of polyanions, their positional isomers as well as monomeric metallospecies.[2,10,21] Figure 5.1 shows the ^{31}P NMR spectrum for HPA-4 aqueous solution, which was used as the catalyst for the oxidation of TMP to TMBQ.[85] As can be seen, this system contains heteropoly anions with one, two, three, and four vanadium ions. Moreover, each type is represented by an array of positional isomers. Such a complexity makes mechanistic studies very difficult. Much work on the characterisation of HPA-n solutions was done in the 1960–80s by Souchay,[92,93] Pope,[94] Matveev[1,2] and co-workers. More recently Pettersson *et al.*[95] have fully characterised HPA-2 in aqueous solution by combined potentiometry and ^{31}P and ^{31}V NMR techniques. This system, which is relevant to the Catalytica's technology for the Wacker oxidation of olefins,[21] consists of five positional α-isomers and some β-isomers of $[PMo_{10}V_2O_{40}]^{5-}$.

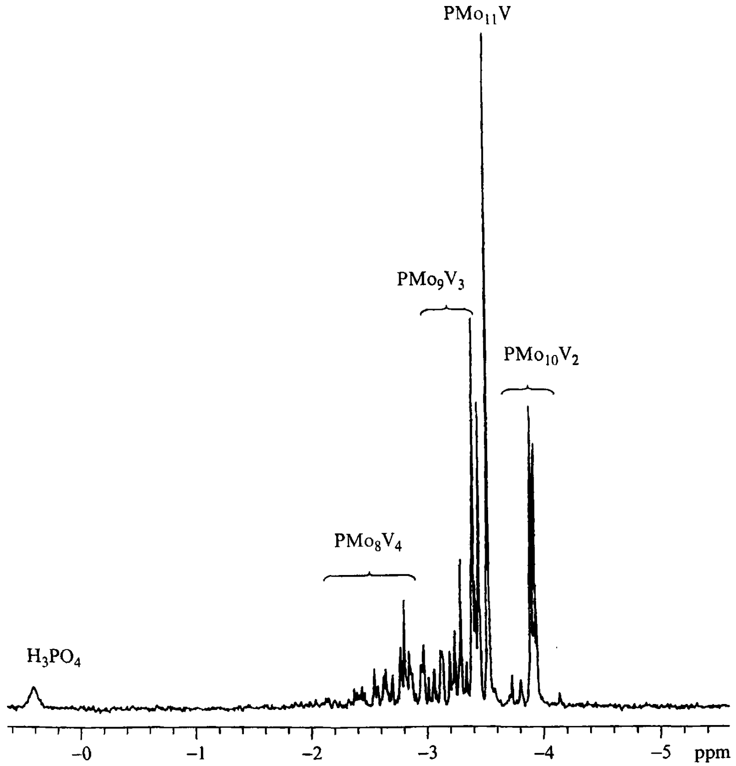
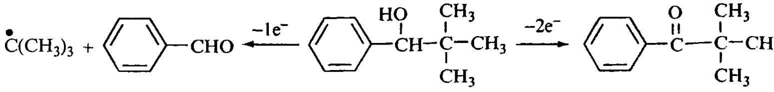


Figure 5.1 162 MHz ^{31}P NMR spectrum for 0.2 mol l^{-1} $Na_5H_2[PMo_8V_4O_{40}]$ aqueous solution (pH 2.5, 1% H_3PO_4 as external reference).[10] Reprinted with permission from *Chem. Rev.* 1998, **98**, 171. Copyright 1998 American Chemical Society.

As stated earlier, the overall catalytic process can be represented schematically by steps 5.1 and 5.2. The question is what is the mechanism of these steps? What kind of active species is involved? In step 5.1, two types of active species can be considered – the monomeric VO_2^+ cation (and/or complexes thereof) and heteropoly anions.[2] The VO_2^+ cation can be formed by dissociation of parent HPA-n (eq. 5.12). This is likely to occur for HPA-n with higher *n* and in strongly acidic media. There is evidence that VO_2^+ is the active species in the oxidation of TMP to TMBQ (eqs 5.12–5.17).[56] Recent calorimetric study[96] shows that in HPA-n solutions, VO_2^+ in the outer sphere reduces first, followed by reduction of V^{5+} inside polyanion.

The parent heteropoly anions may also be the active species in step 5.1.[2] This is likely in the case of more stable polyanions with fewer V^{5+} ions such as HPA-2. Since the heteropoly anions are multielectron oxidants, they could, in principle, react via a multielectron-transfer mechanism. In this sense, the oxidation of a test alcohol 2,2-dimethyl-1-phenyl-1-propanol is of interest[97] (eq. 5.40).



(5.40)

With two-electron oxidants, such as Pd(II), this alcohol gives ketone with the same carbon backbone. With one-electron oxidants, e.g., Ce^{4+} or persulfate, the C–C bond cleaves to yield benzaldehyde and t-butyl radical as the primary products (Table 5.2). It can be seen that VO_2^+ mainly reacts as a one-electron oxidant, as expected, yielding 63% benzaldehyde. In contrast, HPA-6 predominantly reacts as a two-electron oxidant, giving the ketone in 67% yield. Simultaneously some one-electron oxidation, probably by VO_2^+ ions, also takes place to give benzaldehyde (33%). These results indicate a direct involvement of heteropoly anions in reaction 5.40.

Efforts have been made to clarify the mechanism of oxidation of the reduced form of HPA-n (heteropoly blue) by O_2 in solution (eq. 5.2).[2,22] However, the complexity of the system makes conclusions rather speculative. The redox reactions involved in the reduction of dioxygen in an acidic aqueous solution

Table 5.2 One-vs. two-electron oxidation of 2,2-dimethyl-1-phenyl-1-propanol[97],[a].

Oxidant	$PdCl_2$	Ce^{4+}	$S_2O_8^{2-}$	VO_2^+	HPA-6
Ketone, %	100	6	6	11	67
PhCHO, %	None	94	89	63	33

a) Yields (mol%) on converted alcohol; a little PhCOOH is also formed

Table 5.3 Reactions involved in the reduction of O_2 in acidic aqueous solution and the corresponding standard reduction potentials (versus SHE, pH 0)[98].

$O_2 + e^- + H^+ \rightarrow HO_2^\bullet$	$E = -0.05$ V
$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$	$E = 0.68$ V
$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$	$E = 1.23$ V
$HO_2^\bullet + e^- + H^+ \rightarrow H_2O_2$	$E = 1.44$ V
$H_2O_2 + e^- + H^+ \rightarrow HO^\bullet + H_2O$	$E = 0.71$ V
$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O$	$E = 1.76$ V
$HO^\bullet + e^- + H^+ \rightarrow H_2O$	$E = 2.81$ V

together with the corresponding standard redox potentials[98] are given in Table 5.3. These data allow to make thermodynamic assessment as to how the oxidation of blues may proceed. The O_2 itself is a poor one-electron oxidant. One-electron oxidation of the reduced HPA-n ($E = 0.7$ V) with O_2 to form $HO_2^\bullet$ radical is highly unfavourable thermodynamically. However two-, three-or four-electron oxidations are feasible. Consequently, the HPA-1 blue, $[PMo_{11}V^{4+}O_{40}]^{4-}$, is practically not oxidised by O_2 under mild conditions in solution. The all-molybdenum HPA-0 blue is not oxidised either for reasons that are not clear yet. Because of this, only the HPA-n with n > 1 are used as catalysts for liquid-phase aerobic oxidations. It should be noted, however, that the reoxidation of HPA-0 and HPA-1 blues by O_2 proceeds readily at higher temperatures (> 200 °C) which allows applying them for gas-phase oxidations, e.g., for the oxidation of methacrolein and oxidative dehydrogenation of isobutyric acid, which will be discussed later in this chapter.

The mechanism of step 5.2 was shown to depend on the degree of reduction of the blue. The oxidation of a deeply reduced blue ($n \geq 4$, all the V present reduced to V^{4+}) follows a simple kinetics, being first-order in both the blue and O_2.[99] In the presence of a radical scavenger, i-PrOH, no acetone is found. This indicates that no free radicals are formed during the reaction. (However, the formation of short-lived free radicals is not excluded.) Hence a four-electron-transfer mechanism was proposed, including the formation of a complex between the blue and O_2 followed by a stepwise four-electron transfer therein (eq. 5.41).[99] Each electron-transfer step is probably accompanied by the protonation of the oxidant.

$$H_m(\text{HPA-n}) + O_2 \rightleftarrows \{H_m(\text{HPA-n})\ldots O_2\} \xrightarrow[\text{slow}]{(4e^-)} H_{m-4}(\text{HPA-n}) + 2\,H_2O \tag{5.41}$$

In contrast, the oxidation of a weakly reduced blue (by less than one electron per Keggin unit) shows a more complex kinetics.[100] This system is adequate to a real one-stage catalytic process. For simplicity, it can be considered as a system consisting of two species: one-electron blue H(HPA-n) and the fully oxidised form HPA-n; $[H(\text{HPA-n})]/\{[H(\text{HPA-n})] + [\text{HPA-n}]\} \ll 1$. Under such conditions, the rate of oxidation of blues was found to be in the order: HPA-2 < HPA-3 > HPA-4 > HPA-6. In the case of the HPA-3 blue, at a constant pH and ionic strength, the reaction is third-order in H(HPA-n), minus second-order in HPA-n, and first-order in O_2.

$$Rate = \frac{k[H(\text{HPA-n})]^3[O_2]}{[\text{HPA-n}]^2} \tag{5.42}$$

The test with i-PrOH clearly shows the formation of free radicals. On these bases, a mechanism was proposed, which is represented for the HPA-3 blue by eqs 5.43–5.46.

$$2\{PMo_9V_2{}^{5+}V^{4+}\} \rightleftarrows \{PMo_9V^{5+}V_2{}^{4+}\} + \{PMo_9V_3{}^{5+}\} \tag{5.43}$$

$$\{PMo_9V^{5+}V_2{}^{4+}\} + \{PMo_9V_2{}^{5+}V^{4+}\} \rightleftarrows \{PMo_9V_3{}^{4+}\} + \{PMo_9V_3{}^{5+}\} \tag{5.44}$$

$$\{PMo_9V_3{}^{4+}\} + O_2 + 3\,H^+ \xrightarrow[\text{slow}]{(3e^-)} \{PMo_9V_3{}^{5+}\} + H_2O + HO^\bullet \tag{5.45}$$

$$\{PMo_9V_2{}^{5+}V^{4+}\} + HO^\bullet + H^+ \rightarrow \{PMo_9V_3{}^{5+}\} + H_2O \tag{5.46}$$

In steps 5.43 and 5.44, a three-electron blue is formed by the fast electron exchange between one-electron blues. Then the three-electron blue is slowly oxidised by O_2 via a stepwise transfer of three electrons from the blue to O_2, accompanied by the protonation of the oxidant, to form $HO^\bullet$ radical which is finally trapped by any V^{4+} species.[100]

The slower rate of oxidation of the HPA-2 blue may be explained assuming that the process occurs via the slow disproportionation 2 HPA-2 $\rightleftharpoons$ HPA-3 + HPA-1, leading to the more active HPA-3 blue.[100] The lower reactivity of the HPA-4 and HPA-6 blues may be due to their low stability in solution.

Further, it was found that the free radicals generated in step 5.2 can, to some extent, affect the selectivity of the one-stage catalytic process.[101] But, obviously, they will not affect the two-stage process.

Several types of intermediate complexes between heteropoly blues and O_2 have been suggested.[42,100,102] As HPA-n is labile, easily exchanging oxygen atoms in the polyanion with aqueous solution,[58] Kozhevnikov *et al.*[100] proposed the formation of an adduct with the direct bonding of O_2 to the V^{4+} ion in the HPA-n blue by incorporating O_2 into a coordination vacancy at the V^{4+} ion. Neumann and Levin[42] suggested a μ-peroxo intermediate involving two polyanions and O_2 in the reoxidation of HPA-2 blue. For tungsten blues, e.g. $[SiW_{12}O_{40}]^{5-}$, which are inert towards oxygen exchange, an association of O_2 with polyanion through the terminal or bridging oxygen atom in the Keggin structure, forming an ozonide-type adduct or a seven-coordinate peroxo moiety was suggested.[102]

A mechanism involving a covalently-bonded metal–oxygen intermediate would lead to O_2 incorporation into the polyanion. Duncan and Hill[103] quantified by ^{17}O NMR the incorporation of ^{17}O from $^{17}O_2$ in the oxidation of reduced $[W_{10}O_{32}]^{4}$, $[P_2W_{18}O_{62}]^{6-}$, and HPA-2 in CH_3CN solution. In the case of tungsten polyoxometalates, no ^{17}O incorporation into polyanion was found; nor did ^{17}O exchange occur between the polyoxometalates and solvent. All the ^{17}O is found in H_2O and H_2O_2 that form in the reaction. These data rule out the formation of covalently-bonded metal–oxygen intermediates in the case of tungsten heteropoly blues and are consistent with an outer sphere electron transfer between O_2 and the blues.[103] Such a mechanism is, indeed, likely from the thermodynamic point of view for the anions such as $[H_2W_{12}O_{40}]^{6-}$, $[W_{10}O_{32}]^{4-}$, $[SiW_{12}O_{40}]^{4-}$, etc., having the redox potential $E \sim 0$ V.[102] In contrast, the mechanism for HPA-2 is not as clear as that for tungsten polyanions. For HPA-2, the ^{17}O incorporation was measured in the HPA-2-catalysed oxidation of 1,3-cyclohexadiene with $^{17}O_2$. In this system, some ^{17}O did incorporate into the POM as well as the ^{17}O exchange between the polyanion and solvent took place. The total enrichment of polyanion represented 6% of all ^{17}O products. Kinetic measurements indicated that the ^{17}O enrichment mainly occurred by the ^{17}O exchange between the product $H_2^{17}O$ and polyanion. These data, too, may be considered as inconsistent with a covalent-bonded metal–oxygen intermediate.[103] However, if the oxidation in question were a radical chain process, reactions 5.1 and 5.2 could play only a minor role in the overall O_2 consumption. In this case, indeed, the ^{17}O exchange between the polyanion and the product $H_2{}^{17}O$ would contribute the most to the ^{17}O enrichment of POM regardless of the mechanism of reaction 5.2.

Kozhevnikov and Kholdeeva[104] have studied the kinetics of a number of one-electron reactions between tungsten heteropoly anions and various reductants or oxidants, including the oxidation of $[SiW_{12}O_{40}]^{5-}$ and $[PW_{12}O_{40}]^{4-}$ blues with O_2, by a stopped-flow technique. The reaction rates were found to be in good agreement with the Marcus theory for outer sphere electron transfer (Chapter 2), which supports this mechanism for the oxidation of $\{SiW_{12}O_{40}\}$ and $\{PW_{12}O_{40}\}$ blues by O_2. Hiskia and Papaconstantinou[102] studied the kinetics and mechanism of the oxidation of reduced tungsten polyoxometalates, such as $[SiW_{12}O_{40}]^{4-}$, $[H_2W_{12}O_{40}]^{6-}$, and $[P_2W_{18}O_{62}]^{6-}$, with dioxygen.

In conclusion, HPA-n is the efficient and versatile catalyst system for oxidising by O_2. Several promising liquid-phase oxidation processes based on the HPA-n catalysis have been developed, for example, the Wacker oxidation of olefins. However, many mechanistic details are yet to be disclosed.

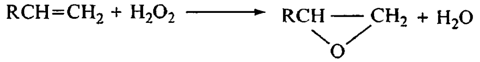
5.1.2 OXIDATION WITH HYDROGEN PEROXIDE

It has long been known that tungsten and molybdenum compounds are efficient catalysts for oxidations by hydrogen peroxide.[105,106] Tungsten and molybdenum polyoxometalates also catalyse various oxidations of organic substances by hydrogen peroxide, such as epoxidation of olefins, oxidation of alcohols, glycols, phenols, etc., in homogeneous or two-phase systems.[3,8,10,12,107–112] There is sufficient evidence that the Keggin type and related polyanions are decomposed by excess hydrogen peroxide in solution to form peroxo (poly)oxometalate species. These may be the active intermediates in oxidations with H_2O_2.

5.1.2.1 Venturello–Ishii System

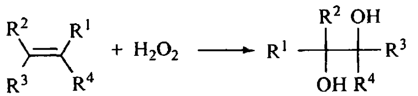
Venturello and Ishii independently developed two highly effective catalyst systems based on polyoxometalates for hydroperoxide oxidation, especially for the epoxidation of alkenes. Later on, it was found that these systems were closely related mechanistically and included the same peroxo polyoxometalate as active intermediate.

Epoxidation of alkenes Venturello *et al.*,[109,113,114] performed the epoxidation of alkenes (eq. 5.47) in a biphasic system, e.g., $CHCl_3 - H_2O$, at 60–70 °C with the use of dilute H_2O_2 (2–15%) and tungstate and phosphate ions as catalyst precursors in the presence of a phase-transfer catalyst – quaternary ammonium cation (Q^+) with $C_6 - C_{18}$ alkyl groups.



(5.47)

In this system, a peroxo polyoxometalate, $\{PO_4[WO(O_2)_2]_4\}^{3-}$, analogous to the molybdenum peroxo polyanion first reported by Beiles *et al.*,[115] was isolated and characterised.[109] This peroxo complex was found to be remarkably effective in stoichiometric as well as in catalytic biphasic oxidation of alkenes by H_2O_2 and was postulated to be the active oxygen transfer agent in reaction 5.47. For example, the epoxidation of 1-octene with 15% H_2O_2 in the presence of $\{PO_4[WO(O_2)_2]_4\}^{3-}$ in a CH_2ClCH_2Cl-H_2O system affords epoxyoctane in 89% yield (based on the initial H_2O_2) at 100% H_2O_2 conversion (70 °C, 1.5 h). The reaction is stereoselective: *cis*-2-hexene is converted solely into the *cis*-epoxide, while *trans*-2-hexene gives the *trans*-epoxide.[109] Likewise, but in a stronger acidic medium, the biphasic oxidation of alkenes produces water-soluble vicinal *trans*-glycols in 71–88% yield (60–70 °C, 1–4 h, 2–4% H_2O_2, pH 1.2–1.5) (eq. 5.48). The glycols formed are present almost entirely in the aqueous phase and can be readily isolated from the reaction mixture.[114]



(5.48)

The anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$ was characterised crystallographically (Figure 5.2).[109] It has the C_2 symmetry and consists of the central PO_4

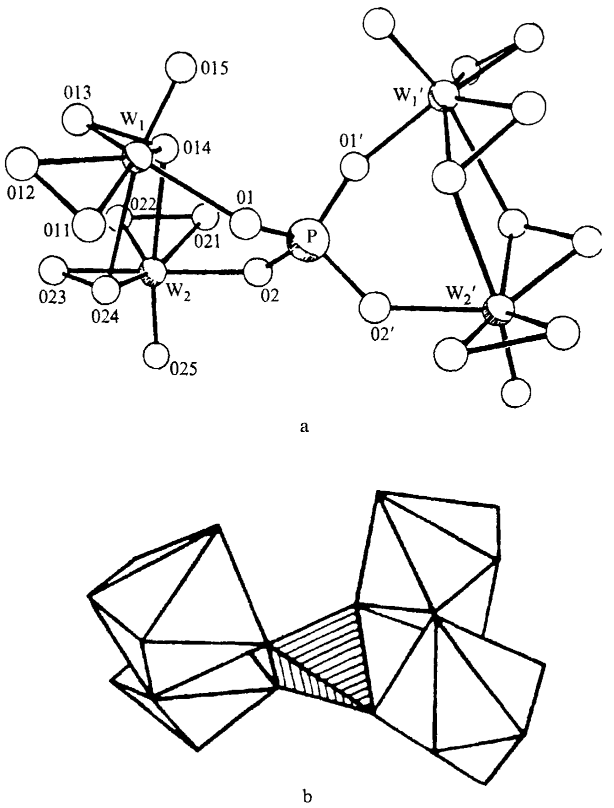


Figure 5.2 The structure of peroxo polyanion $\{PO_4[WO(O_2)_2]_4\}^{3-}$:[109] (a) ball-and-stick and (b) polyhedral representation. Reprinted with permission from *Chem. Rev.* 1998, **98**, 171. Copyright 1998 American Chemical Society.

tetrahedron linked through its oxygen atoms to two pairs of edge-sharing distorted pentagonal bipyramids $W(O_2)_2O_3$. Each tungsten atom is linked to two peroxo groups – one non-bridging (η^2) and the other bridging (η^2, η^1) – located in the equatorial plane of the pentagonal bipyramid.

Ishii *et al.*[111,116–125] demonstrated that oxidations of a wide variety of organic substrates with commercially available 35 % H_2O_2 can be effectively performed in homogeneous phase or even better in a biphasic system with the use of a catalyst comprising heteropoly acids $H_3[PW_{12}O_{40}]$ or $H_3[PMo_{12}O_{40}]$ and cetylpyridinium chloride, the latter providing phase-transfer function. The $H_3[PW_{12}O_{40}]$ catalyst is usually superior to $H_3[PMo_{12}O_{40}]$. Tris-cetylpyridinium salt of $H_3[PW_{12}O_{40}]$, $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3[PW_{12}O_{40}]^{3-}$ (CPW), is prepared by interacting $H_3[PW_{12}O_{40}]$ with three equivalents of cetylpyridinium chloride.

This salt catalyses the epoxidation of alkenes[116] and allylic alcohols[120] with H_2O_2 in a biphasic system using $CHCl_3$ as a solvent, while α, β-unsaturated carboxylic acids are readily epoxidised in water at pH 6 to 7.[121]

According to a schematic mechanism proposed by Ishii *et al.*,[111] the two-phase epoxidation of alkenes by hydrogen peroxide in the presence of $[PW_{12}O_{40}]^{3-}$ as the catalyst precursor proceeds as follows (Figure 5.3). An active peroxo polyoxometalate is formed in the aqueous phase by interacting the Keggin heteropoly anion with hydrogen peroxide. With the phase-transfer agent, Q^+, the peroxo polyoxometalate is almost fully transferred into the organic phase because its Q^+ salt is readily soluble in organic solvents. The reaction takes place preferentially in the organic phase via the oxygen atom transfer from the peroxo polyoxometalate to the substrate. The peroxo polyoxometalate is then regenerated at the interface by the interaction with H_2O_2. However, the nature of peroxo polyoxometalate intermediates was not established in these studies.

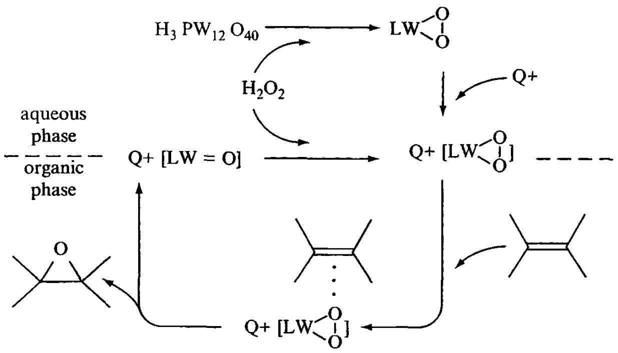


Figure 5.3 Schematic mechanism of the phase-transfer epoxidation of olefins catalysed by peroxo polyoxometalate.[111]

In recent years, the Venturello–Ishii chemistry has been investigated in detail by several groups.[126–136] These studies showed that the epoxidation of alkenes in the Venturello system and in the Ishii system despite the use of different catalysts precursors includes nearly identical peroxo polyoxometalate intermediates. Csanyi and Jaky[126] demonstrated that $H_3[PW_{12}O_{40}]$ and $H_3[PMo_{12}O_{40}]$ by interacting with excess H_2O_2 in a two-phase system in the presence of a phase-transfer agent, decompose to form a variety of peroxo complexes including $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and $\{PO_4[MoO(O_2)_2]_4\}^{3-}$, respectively, which are transferred into the organic phase. These authors suggested that the peroxo anions derived from $H_3[PW_{12}O_{40}]$ or $H_3[PMo_{12}O_{40}]$ are the catalytically active species in the biphasic epoxidation of olefins. Brégeault *et al.*[127] studied the epoxidation of 1-octene by hydrogen peroxide in the

$CHCl_3 - H_2O$ system in the presence of the heteropoly anions $[XM_{12}O_{40}]^{n-}$ and $[X_2M_{18}O_{62}]^{m}$ and isopolyanions $[M_xO_y]^{z-}$ ($M = Mo^{6+}$ or W^{6+}; $X = P^{5+}$, Si^{4+}, or B^{3+}) as precursors of catalytically active peroxo polyoxometalates. The anions $[BW_{12}O_{40}]^{5-}$, $[SiW_{12}O_{40}]^{4-}$, and $[P_2W_{18}O_{62}]^{6-}$ are inactive and, as shown by a number of spectroscopic methods, do not change their structure during the reaction. $[PMo_{12}O_{40}]^{3-}$ exhibits a low activity. On the other hand, $[PW_{12}O_{40}]^{3-}$ exhibits a high activity (79% yield of epoxide based on 1-octene) when the catalytic system is prepared beforehand by interacting the heteropoly anion with H_2O_2 in aqueous solution in the absence of Q^+ and 1-octene. When all the reagents are mixed simultaneously, no activity is observed. Tungstic acid, 'H_2WO_4', and $[H_2W_{12}O_{42}]^{10-}$ show high activities regardless of the preparation method used, the yields being 76 and 67%, respectively. The Keggin heteropoly anions $[PW_{12}O_{40}]^{3-}$ are decomposed by excess H_2O_2 $\{[H_2O_2]/[M] = 30 - 355\,\text{mol/mol}\}$ to form the peroxo polyoxometalates $\{PO_4[MO(O_2)_2]_4\}^{3-}$ and $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$. It is suggested that $\{PO_4[MO(O_2)_2]_4\}^{3-}$ is the active species responsible for the olefin epoxidation with the Keggin anions $[PM_{12}O_{40}]^{3-}$ in two-phase systems.[127]

Later on, ^{31}P and ^{183}W NMR study[128] showed that several peroxo polyoxometalates of the composition $[PW_xO_y]^{z-}(x = 1 - 4)$ form in the aqueous $H_3[PW_{12}O_{40}]/H_2O_2$ system, and these may well be the active species or their precursors in the olefin epoxidation by phase-transfer catalysis. The novel $\{HPO_4[WO(O_2)_2]_2\}^{2-}$ anion was studied in the crystalline state and in solution. The crystal structure of $[(n\text{-}Bu)_4N]_2\{HPO_4[WO(O_2)_2]_2\}$ (Figure 5.4) is closely related to that of the Venturello complex $[(n\text{-}Bu)_4N]_3\{PO_4[WO(O_2)_2]_4\}$ (Figure 5.2). The two anions, $\{HPO_4[WO(O_2)_2]_2\}^{2-}$ and $\{PO_4[WO(O_2)_2]_4\}^{3-}$, include the $[W_2O_2(\mu\text{-}O_2)_2(O_2)_2]$ moiety as a principal building block. In the two-phase epoxidation of limonene by H_2O_2, tungsten species $Q_3\{PO_4[WO(O_2)_2]_4\}$ and $Q_2\{HPO_4[WO(O_2)_2]_4\}$ proved to be 30 times more active than the molybdenum analogue, $Q_3\{PO_4[MoO(O_2)_2]_4\}$.[128] Another mechanistically important result is that the $MO(O_2)_2$ moieties in $\{PO_4[MO(O_2)_2]_4\}^{3-}$ are remarkably mobile in solution. Thus mixing solutions of $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ at room temperature results in the fast formation of mixed-addenda species $\{PO_4[Mo_{4-x}W_xO_{20}]\}^{3-}$.[129] Thus, the whole array of peroxo species $[PW_xO_y]^{z-}(x = 1 - 4)$ is likely to exist in a fast and very complex equilibrium. This makes it difficult to identify the active species kinetically.

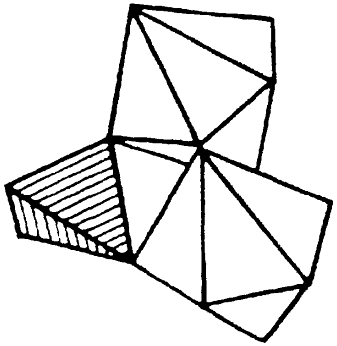


Figure 5.4 The structure of peroxo polyanion $\{HPO_4[WO(O_2)_2]_2\}^{2-}$.[128] Reprinted with permission from *Chem. Rev.* 1998, **98**, 171. Copyright 1998 American Chemical Society.

Brégeault, Gelbard *et al.*[129,130] and Griffith *et al.*[131-134] have isolated a wide variety of new mono-, di-, tri-, and tetranuclear tungsten and molybdemum peroxo polyoxometalates with η^2, η^1-peroxo moieties and various central groups such as PO_4, $PhPO_3$, Ph_2PO_2, SO_4, AsO_4, $HAsO_4$, CH_3AsO_3, etc. These have been characterised by X-ray and tested in oxidations with H_2O_2. Schwendt *et al.* reported the synthesis and characterisation of vanadium(V) peroxo complexes $(NH_4)_5[V_2O_2(O_2)_4PO_4]$[137] and $K_7[V_4O_4(O_2)_8PO_4]$.[138]

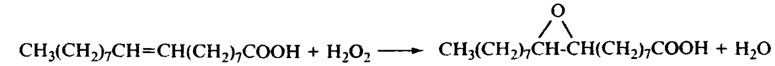
Ballistreri *et al.*[135] and Hill *et al.*[136] have shown that the Venturello–Ishii epoxidation is first-order in both $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and alkene. Hill *et al.*[136] obtained kinetic and spectroscopic evidence that two processes dominate during the reaction: (i) the slow epoxidation by oxygen atom transfer from the peroxo polyoxometalate to alkene (eq. 5.49)

$$\{PO_4[WO(O_2)_2]_4\}^{3-} + \text{alkene} \rightarrow PW_4, PW_3, \text{and } PW_2 + \text{epoxide} \quad (5.49)$$

followed by (ii) the rapid regeneration of $\{PO_4[WO(O_2)_2]_4\}^{3-}$ with H_2O_2. Catalyst deactivation as well as the use of chlorinated hydrocarbons as solvents is noted as the major drawback to the Venturello–Ishii process.[136]

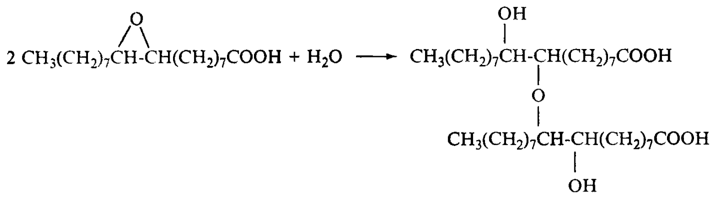
In alkene epoxidation catalysed by transition metal complexes, the mechanism of the oxygen atom transfer from a peroxo complex to alkene is still a matter of debate. According to Mimoun,[139] the mechanism of the oxygen-to-alkene transfer from a side-bonded η^2-peroxo group involves a precoordination of the alkene to the metal centre. Alternatively, Sharpless[140] proposed a coordination of the alkene to one oxygen atom from the peroxo group, forming a three-centre transition state. Although it is not easy to make a choice between the two, experimental results on mononuclear peroxo complexes are in a better agreement with the Sharpless mechanism.[141,142] This may well be the case with peroxo polyoxometalates, but no direct information is available.

The peroxo tungstophosphate $Q_3\{PO_4[WO(O_2)_2]_4\}$ is a highly efficient catalyst for the phase-transfer epoxidation of oleic acid (OA) by aqueous 35–60% hydrogen peroxide.[143]



$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH + H_2O_2 \longrightarrow CH_3(CH_2)_7\overset{\overset{O}{\diagup\;\diagdown}}{CH\text{-}CH}(CH_2)_7COOH + H_2O \quad (5.50)$$

The reaction is carried out in oleic acid medium without solvent at 50–80 °C and OA/H_2O_2 molar ratio of 1:1.2, yielding 84% epoxide (based on oleic acid) at 95% oleic acid conversion and 800–1200 catalyst turnovers (Table 5.4). High molecular weight byproducts (HMW) are also formed probably by acid-catalysed reactions 5.51–5.52.



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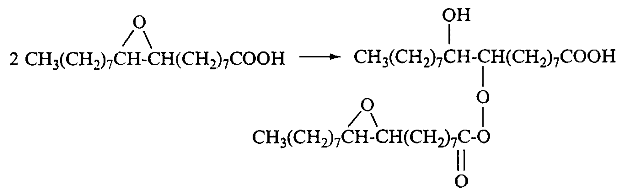

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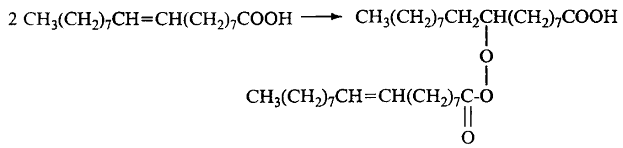


$$2\,CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH \longrightarrow CH_3(CH_2)_7CH_2\underset{\underset{CH_3(CH_2)_7CH=CH(CH_2)_7\overset{\overset{}{}}{C}(=O)-O}{|}}{C}H(CH_2)_7COOH$$

(5.53)

Table 5.4 Epoxidation of oleic acid (OA) by H_2O_2 catalysed by $Q_3\{PO_4[WO(O_2)_2]_4\}$[a] [143].

Catalyst	H_2O_2	T	Time	Conversion[b]	Selectivity, %[c]		HMW
mmol%	mol%	°C	min	%	epoxide	diol	wt%
0.038	0.050	80	50	99	57	5.7	25.8
0.038	0.050	60	30	98	80	3.1	9.3
0.038	0.050	60	105	99	75	1.7	15.7
0.038	0.050	60	70	99	54	4.9	15.8
0.038	0.041	60	35	98	77	6.4	9.5
0.038	0.041	60	50	95	89	1.3	5.0
0.038	0.035	50	45	94	88	1.3	6.4

a) 10 g (0.03 mol) of the OA feed, containing 76% OA, 7% linoleic acid, 5% palmitic acid, 6% stearic acid, 1% erucic acid, and 5% HMW, was charged

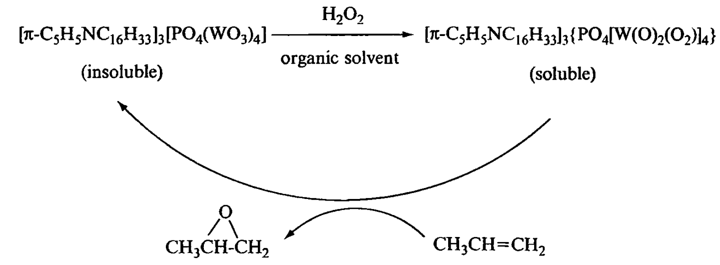
b) Total conversion of oleic and linoleic acids

c) Total selectivity to epoxides and diols derived from oleic and linoleic acids

These byproducts may be of interest as monomers for polycondensation. As can be seen from Table 5.4, the yield of HMW depends mainly on the temperature and the reaction length. At 80 °C the HMW content is quite high, ca. 26 wt%, but under optimum conditions at 50–60 °C, it drops down to 5–6 wt%. Given the HMW amount of 5 wt% present in the OA feed, practically no HMW is formed under such conditions.

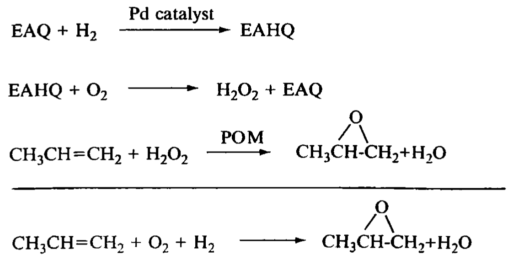
The epoxidation of styrene–butadiene and isobutene–isoprene copolymers by hydrogen peroxide in the presence of $Q_3\{PO_4[MO(O_2)_2]_4\}$ has been reported.[144]

An interesting modification of the Venturello–Ishii system for the epoxidation of propene has been developed by Xi *et al.*[145] The epoxidation is carried out homogeneously by H_2O_2 in the presence of a peroxo polyoxometalate $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3\{PO_4[W(O)_2(O_2)]_4\}$ (which has slightly different polyanion than the Venturello complex) in a mixture of toluene and tributylphosphate at 35 °C. When the H_2O_2 is used up, the catalyst precipitates and can be recycled (Scheme 5.4).



Scheme 5.4

The epoxidation is further coupled with the 2-ethylanthraquinone/2-ethylanthrahydroquinone (EAQ/EAHQ) process for H_2O_2 production, so that O_2 and

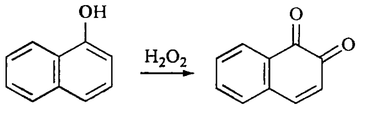


Scheme 5.5

H_2 can be used instead of H_2O_2 for the epoxidation. This method is claimed to give 85% yield of propene oxide based on 2-ethylanthrahydroquinone without any byproducts. The overall process is represented by Scheme 5.5.

Miscellaneous oxidations Ishii *et al.* reported many other hydroperoxide oxidations with the tris-cetylpyridinium salt of $H_3[PW_{12}O_{40}]$ (CPW). *sec*-Alcohols and diols are dehydrogenated by the CPW – H_2O_2 system in t-butyl alcohol to give the corresponding ketones in good yields.[120] Primary alcohols are much less reactive under such conditions. However, α, ω-diols give lactones in fair yields.[111] The CPW – H_2O_2 system is also efficient for the oxidative cleavage of carbon–carbon bonds of *vic*-glycols and alkenes to yield carboxylic acids.[120] Other reactions that can be readily carried out with this system include the conversion of internal alkynes to the corresponding α, β-epoxy ketones,[123] allenes to α-alkoxy or α-hydroxy ketones,[124] amines to oximes and nitrones,[122] anilines to azoxy-nitroso- and nitrobenzenes[119] and sulfides to sulfoxides and sulfones.[125]

α- and β-Naphthols ($\sim 10^{-3}$ mol l^{-1}) are oxidised by H_2O_2 (2–15%) to 1, 2-naphthoquinone in 80–98% yield at 20 °C in the 1,2-dichloroethane–water biphasic system in the presence of peroxo heteropolytungstates and trioctylbenzylammonium chloride (TOBAC) (eqs 5.54–5.55). When the naphthol concentration is increased, C–C coupling products are formed. The catalytic system is prepared by mixing PO_4^{3-}, WO_4^{2-}, and TOBAC in a molar ratio of 8:4:3. It is suggested that the active form of the catalyst is $\{PO_4[WO(O_2)_2]_4\}^{3-}$. The reaction proceeds via the semiquinone radical intermediates, which were detected by ESR.[146]



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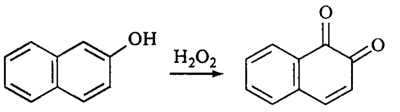


(5.55)

Mechanistic aspects of the oxidation of N,N-benzylalkylamines to nitrones by $Q_3\{PO_4[MO(O_2)_2]_4\}$ (where M = Mo or W) have been studied.[147]

5.1.2.2 Other Polyoxometalate Systems

Epoxidation of alkenes Heteropolytungstophosphates $[PW_{12}O_{40}]^{3-}$, $[PW_{11}O_{39}]^{7-}$, and $\{PW_{11}O_{39}M\}$, where M = Ni(II), Co(II), Cu(II), Fe(II), Cr(III), Ru(IV), Ti(IV), and V(V) have been studied as catalysts for the oxidation of cyclohexene by hydrogen peroxide in acetonitrile at 35 °C. The lacunary anion $[PW_{11}O_{39}]^{7-}$ shows the highest activity and selectivity for epoxidation. $[PW_{12}O_{40}]^{3-}$ is much less active. The complexes of Co(II), Cu(II), and Ru(IV) are inactive in the oxidation of cyclohexene but rapidly decompose H_2O_2. The Ni(II), Ti(IV), and V(V) complexes are inert in both the oxidation of the substrate and the decomposition of H_2O_2. The Fe(II) and Cr(III) complexes are moderately active in the oxidation, but the reaction is nonselective.[108]

Polyoxometalates $[WM_3(H_2O)_2(XW_9O_{34})_2]^{12-}$ ($X = M = Zn^{2+}$ or Co^{2+}, which can be substituted by a variety of transition metal ions)[148] proved to be promising oxidation catalysts. These anions contain two α-Keggin-type trivacant lacunary units B-$\{XW_9O_{34}\}$ which are linked by four coplanar octahedrally coordinated and close-packed metal ions (Figure 2.13). In contrast to Keggin anions, which are stable only in acidic solutions, these polyoxometalates are stable in the pH region from about 6 to about 10.[148] The ions in M positions can be substituted by $Mn^{2+}, Mn^{3+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}, Pt^{2+}, V^{4+}$, etc., which provides interesting opportunities for catalyst design. Unlike the Keggin anions, these polyoxometalates are fairly stable not only to hydrolysis but also to degradation by H_2O_2. Thus Khenkin and Hill[149] reported that the $[Fe_4(PW_9O_{34})_2]^{10-}$ anion is quite stable with respect to solvolysis by H_2O_2; it catalyses the selective homogeneous epoxidation of alkenes by H_2O_2 in aqueous acetonitrile at 20 °C.

Neumann *et al.*,[150,151] found that the solvolytically stable disubstituted manganese(II) polyanion, $[WZnMn_2(H_2O)_2(ZnW_9O_{34})_2]^{12-}$, is a highly active catalyst for the epoxidation of alkenes and oxidation of alcohols by 30% H_2O_2 in a biphasic system at ambient temperature with very high selectivities (>99%) and hundreds to thousands of catalyst turnovers. Interestingly, the trisubstituted polyanion, $[WMn_3(H_2O)_2(ZnW_9O_{34})_2]^{12-}$, is significantly less efficient, followed by Zn^{2+} and Co^{2+} derivatives. The Rh^{3+} anion, $[WZnRh_2(H_2O)_2(ZnW_9O_{34})_2]^{10-}$, is about as active as the disubstituted Mn^{2+} analogue.[152] Other substrates, e.g. alkenols, diols, amines, etc., can be oxidised in such systems.[153]

Polyoxometalate-based solid catalysts for the epoxidation of alkenes have been reported.[154] These contain polyanions $\{PO_4[WO(O_2)_2]_4\}^{3-}$ or $[WZnMn_2(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ immobilised on a silicate xerogel covalently modified with phenyl groups and quaternary ammonium groups. The catalysts epoxidise alkenes by 30% H_2O_2 at room temperature in the absence of an organic solvent. Another technique for immobilisation of polyoxometalates using polyethers has been reported.[155] The Ti-substituted Keggin-type anions, $[PW_{11}TiO_{40}]^{5-}$, $[PW_{10}Ti_2O_{40}]^{7-}$, etc., have been studied as catalysts for the epoxidation of alkenes with H_2O_2. The kinetic data obtained imply the involvement of $HO^{\bullet}$ radicals generated by the decomposition of H_2O_2.[156] The kinetics of epoxidation of cyclooctene with H_2O_2 catalysed by the peroxo polyoxometalate $[PW_{10}Ti_2O_{38}(O_2)_2]^{7-}$ has been studied.[157]

Triniobium (V) heteropolytungtophosphates have been structurally characterised and tested as catalysts for alkene epoxidation by hydrogen peroxide.[158]

Cyclopentene is oxidised by hydrogen peroxide to glutaraldehyde in the presence of mixed-addenda heteropoly acids $H_3[PMo_{12-n}W_nO_{40}](n = 1-9)$ in tributyl phosphate (TBP) solution in 60% yield based on H_2O_2 (35 °C, 3 h). Water is removed from the H_2O_2 – TBP system by vacuum distillation. Other heteropoly acids are also active; the yield of glutaraldehyde (%) decreases in the order: $H_3[PMo_{10}W_2O_{40}]$ (61) > $H_3[PMo_{12}O_{40}]$(47) > $H_4[GeMo_{12}O_{40}]$ (21) > $H_5[PMo_{10}V_2O_{40}]$(6) > $H_3[PW_{12}O_{40}]$(5) > $H_4[SiMo_{12}O_{40}]$(1).[159]

Reaction of alkenes with aqueous hydrogen peroxide and a catalytic quantity of Keggin heteropoly acid supported on MgO, Al_2O_3, or ZnO leads to complete cleavage of the alkenes to give carbonyl compounds.[160]

Oxidation of alkanes Oxidation of alkanes, including methane, with hydrogen peroxide in the presence of various polyoxometalates has been attempted.[161–164] Mizuno *et al.*[162–164] reported the selective oxidation of various alkanes from methane to n-hexane, cyclohexane, and adamantane with H_2O_2 catalysed by the Keggin type diiron(III)-subsituted tungstosilicate $[SiW_{10}O_{38}Fe_2]^{6-}$ (Table 5.5). The tetrabutylammonium salt is effective in acetonitrile solution and the water-soluble potassium salt is active in water. The efficiency of hydrogen peroxide utilisation to oxygenated products is ca. 100 % for the oxidation of cyclohexane and adamantane. It is suggested that the Keggin polyanions with two Fe(III) ions occupying the neighbouring octahedra are the catalytically active species and their performance may be related to the catalysis by methane monooxygenase.

Table 5.5 Oxidation of alkanes with hydrogen peroxide catalysed by $[SiW_{10}O_{38}Fe_2]^{6-}$ in acetonitrile at 32 °C, 96 h[163].

Substrate	Conversion, %	Product	Selectivity, %
Methane	0.4	Methanol	73
		CO_2	27
Ethane	1.2	Acetaldehyde	57
		Acetic acid	40
		CO_2	3
Propane	4.0	Acetone	86
		Acetaldehyde	12
		CO_2	2
n-Butane	11	Methylethylketone	82
		Acetaldehyde	17
		CO_2	1
n-Pentane	9.0	Pentanols	33
		Pentanones	67
n-Hexane	15	Hexanols	25
		Hexanones	75
Cyclohexane	25	Cyclohexanol	32
		Cyclohexanone	68
Adamantane	42	1-Adamantanol	20
		2-Adamantanol	71
		2-Adamantanone	9

Oxidation of aromatic compounds The HPA-n anions catalyse the oxidation of alkylaromatic compounds by 30% H_2O_2 in AcOH at 80 °C to form the respective acetates or alcohols and aldehydes or ketones, HPA-2 being the most effective catalyst.[165] There is spectroscopic evidence that HPA-2 is not degraded during the reaction. However, there is a significant decomposition of H_2O_2 accompanying the oxidation of the alkylaromatic substrates. The mechanism proposed includes the homolytic cleavage of peroxo species at the vanadium atom of HPA-2 to form $HO^\bullet$ and $HO_2^\bullet$ radicals, which react with the alkyl aromatic substrate to give the observed products, as represented by equations 5.56–5.60.[165]

$$\text{HPA-2} + H_2O_2 \rightarrow \text{H(HPA-2)} + HO_2^\bullet \tag{5.56}$$

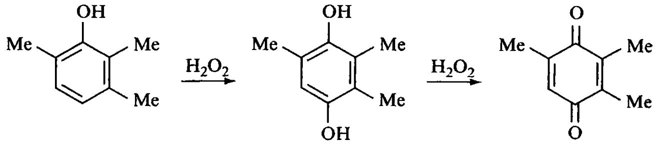
$$\text{H(HPA-2)} + H_2O_2 \rightarrow \text{HPA-2} + HO^\bullet + H_2O \tag{5.57}$$

$$\text{ArH} + HO^\bullet(\text{or } HO_2^\bullet) \rightarrow \text{Ar}^\bullet + H_2O(\text{or } H_2O_2) \tag{5.58}$$

$$\text{Ar}^\bullet + \text{HPA-2} + H^+ \rightarrow \text{Ar}^+ + \text{H(HPA-2)} \tag{5.59}$$

$$\text{Ar}^+ + \text{AcOH (or } H_2O) \rightarrow \text{ArOAc} + H^+ \text{ (or ArOH)} \tag{5.60}$$

As shown by Shimizu *et al.*,[166] the Keggin heteropoly acids catalyse the oxidation of 2,3,5- and 2,3,6-trimethylphenol (TMP) to 2,3,5-trimethyl-1, 4-benzoquinone (TMBQ) by hydrogen peroxide in acetic acid solution in 65–78 % selectivity at 94–100 % TMP conversion. The mechanism proposed involves the HPA-catalysed hydroxylation of the aromatic ring to form 2,3,5-trimethylhydroquinone, followed by its fast oxidation to TMBQ (eq. 5.61). In this reaction, heteropoly acids apparently behave as Brønsted acid catalysts, enhancing the formation of peracetic acid; the latter is probably the true hydroxylating species.[166] *vic*-Diols are oxidised with 30 % aqueous H_2O_2 in the presence of heteropoly acids to yield carboxylic acid.[167]



(5.61)

Tungsten and molybdenum polyoxometalates have been studied as catalysts for the oxidation of benzene to phenol with 30 % aqueous H_2O_2 at 25 °C by Nomiya *et al.*[168–171] The Keggin anions, $\{PW_{10}V_2\}$ and $\{PW_9V_3\}$, show 92–98 % selectivity to phenol (based on benzene) at <8 % benzene conversion. The activity of $\{PW_9V_3\}$ is initially high, but decreases after 48 h due to decomposition of the Keggin structure. The $\{PW_{10}V_2\}$ anion remains intact and maintains its activity even after 576 h.[168] In the case of molybdovanadophosphates, the oxidation of benzene is catalysed by the vanadium(V) species within the Keggin anions or by the peroxo vanadium species $VO(O_2)^+$ derived from polyanions.[169] Kuznetsova *et al.*[172,173] reported that the Fe^{3+}-substituted polyoxometalate, $[PW_{11}O_{39}Fe]^{4-}$, catalyses the oxidation of benzene to phenol by H_2O_2 in CH_3CN solution at 70 C, with the decomposition of H_2O_2 being the main reaction. A mechanism, including the oxidation of C_6H_6 by $HO^\bullet$ radicals formed via the H_2O_2 decomposition, is suggested. Pd(II) and Pt(II) complexes of $[PW_{11}O_{39}]^{7-}$ as well as sandwich type polyoxometalates catalyse the co-oxidative hydroxylation of benzene to phenol by a gas mixture of O_2 and H_2 in a two-phase system at 10–40 °C.[174,175] Liquid-phase oxidation of benzene to phenol by O_2 (10 atm, 25 °C) in the presence of Fe^{2+} + $\{PW_{12}O_{40}\}$ has been reported.[176] This reaction is likely to be a free radical co-oxidation of an Fe^{2+}-POM and benzene by O_2.

Oxidation of sulfur compounds Polyoxometalate-catalysed oxidation of sulfur compounds with H_2O_2 may be promising for desulfurisation of oils. For example, the oxidation of dibenzothiophene with H_2O_2 using $\{PW_{12}O_{40}\}$ as a catalyst and $(C_8H_{17})_4NBr$ as phase transfer agent in a two-phase water–toluene system yields nearly 100 % of dibenzothiophene sulfone. Treatment of gas oils with this method shows that all the sulfur compounds present are oxidised by this catalyst system. Oxidised products can be separated from oil by adsorption on silica gel.[177] Kinetics and mechanism of thioether oxidation with H_2O_2 in the presence of Ti(IV) containing heteropoly tungstates has been studied by Kholdeeva *et al.*[178,179]

5.1.3 OXIDATION BY ORGANIC PEROXIDES

The epoxidation of 1-hexene by cumene hydroperoxide (ROOH) in isopropanol solution is catalysed by Keggin heteropoly salts at 110 °C to give the epoxide with 100 % selectivity at 80 % ROOH conversion. The reaction obeys the kinetic equation $r = k[POM]^p[ROOH][C_6H_{12}]$, where $p =$ 0.5–0.9 at $[POM] = (0.2 - 0.9)\ 10^{-5}\,mol\,l^{-1}$. The catalytic activity of heteropoly salts decreases in the order $Na_3[PMo_{12}O_{40}] > Al[PMo_{12}O_{40}] > Na_4[PMo_{11}VO_{40}] > Na_4[SiMo_{12}O_{40}] \gg Na_3[PW_{12}O_{40}]$. The heteropoly acids themselves are ineffective as they catalyse the decomposition of cumene hydroperoxide to phenol and acetone. There is evidence that the heteropolymolybdates decompose in the reaction course. Monomeric molybdenum(VI) complexes are suggested as the catalytically active species.[180]

Transition metal-substituted polyoxometalates $(n\text{-}Bu_4N)_4H[PW_{11}O_{39}M]$, where M = Mn(II), Co(II), Cu(II), Fe(II), etc., catalyse the oxidation of cyclohexanol and adamantane by t-butyl hydroperoxide (TBHP) in benzene. The selectivity to the oxidation products (cyclohexanone or 1-adamantanol, 2-adamantanol, and 2-adamantanone) reaches 90 % based on TBHP. These polyoxometalates also catalyse the oxidation of olefins such as cyclohexene, 1-hexene, norbornene, and cyclooctene by iodosobenzene and pentafluoroiodosobenzene in acetonitrile. The Mn(II) and Co(II) complexes exhibit the highest activity.[181] A radical chain mechanism for the oxidation of cyclohexane and adamantane by TBHP catalysed by $\{PW_{11}O_{39}M\}$ has been suggested.[181] $[R_4N]_5[SiW_{11}O_{39}Ru(H_2O)]$ catalyses the liquid-phase oxidation of alkanes and alkenes by TBHP, potassium persulfite, sodium periodate, and iodosobenzene.[183,184]

A number of polyoxometalates catalyse the selective oxidation of thioethers to the corresponding sulfoxides by t-butyl hydroperoxide at 25 °C, HPA-2 being particularly selective (>99.9 %). A mechanism, including outer sphere electron transfer from thioether to polyanion, is suggested.[185]

The molybdovanadium isopoly acids $\{V_{12-x}Mo_xO_{31}\}$ $(x = 0 - 4)$ catalyse the oxidation of 1,2,4-trimethylbenzene to trimethylbenzoquinone by peracetic acid in acetic acid solution (20 °C, 4 h) with a 12–31 % selectivity at 15–22 % trimethylbenzene conversion.[186]

5.1.4 MISCELLANEOUS OXIDATIONS

Methane is converted to methyl trifluoroacetate in 95 % yield using vanadium containing Keggin heteropoly acids as catalysts and $K_2S_2O_8$ as an oxidant in $CF_3COOH/(CF_3CO)_2O$ solution (80 °C, 24 h, 20 atm).[187]

p-Toluenesulfonic acid is electrocatalytically hydroxylated to the alcohol, $p\text{-}HO_3SC_6H_4CH_2OH$, by a system consisting of aqueous $PtCl_4{}^{2-}$ as C-H activation catalyst, 12-molybdophosphoric acid as redox mediator, in an electrochemical cell containing a carbon cloth anode.[188]

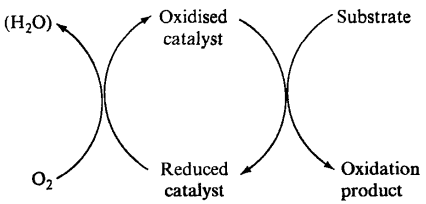
The manganese-substituted heteropolytungstates $[SiW_{11}O_{39}Mn]^{6-}$, $[SiW_{10}O_{38}Mn_2]^{8-}$, $[SiW_9O_{37}Mn_3]^{10-}$, and $[PW_9O_{37}Mn_3]^{9-}$ have been applied as catalysts for low-temperature bleaching of stained cotton cloth with sodium percarbonate. These polyoxometalates are interesting alternatives to conventional complexes with organic ligands as catalysts in bleach processes. However, their instability under bleaching conditions and the fibre-damage induced to cotton cloths prevent their practical application.[189]

5.2 GAS-PHASE OXIDATION

5.2.1 GENERAL OVERVIEW

Polyoxometalate-catalysed selective oxidation of organic compounds (oxygenation or oxidative dehydrogenation) in gas phase is carried out with use of O_2 (air) or sometimes N_2O as oxidants. These reactions are generally highly exothermic, and the heat transfer from the reaction zone may be a serious issue. Usually, total oxidation (combustion) of an organic substrate is thermodynamically more favourable than the partial oxidation; hence for partial oxidation, the selectivity is a key issue, and care must be taken to avoid overoxidation of the desired products. For gas-phase oxidation by polyoxometalates, the major concern is the relatively low thermal stability of heteropoly compounds. Consequently, these reactions are usually carried out at moderately high temperatures, below 350–400 °C. The Keggin heteropoly acids and salts, both bulk and supported, are the most frequently used as the catalysts. In addition, polyoxometalates can be used as precursors to catalytically active mixed oxide materials; in this case the reaction temperature is no longer restricted by the thermal stability of parent heteropoly compounds. Certain acidity/basicity in the catalyst as well as the presence of steam in the feed are essential for gas-phase oxidation. These may be required to enhance the formation or conversion of reaction intermediates as well as to facilitate desorption of products from catalyst surface. There is sufficient evidence that such reactions often involve bifunctional acid and redox catalysis.[9,13,16,17]

Selective oxidation with mixed oxides and oxide-like catalysts such as polyoxometalates involves the activation of C–H or C–C bonds as well as of the oxidant on the catalyst surface and frequently occurs by a Mars–van Krevelen redox mechanism,[9,17] which may be represented by Scheme 5.6.



Scheme 5.6

The catalyst oxidises the substrate and then, in a separate step, is reoxidised by O_2. Either step can be rate-determining to control the overall reaction rate.

In this section, some basic features of the gas-phase selective oxidation with oxygen over polyoxometalate catalysts are reviewed. For more comprehensive discussion, the reader should consult the recent books by Moffat[16] and by Centi, Cavani, and Trifiro.[17]

5.2.2 OXIDATION CATALYSTS

Selection of oxidation catalysts is largely based on the redox properties of polyoxometalates, which have been discussed in Chapter 2. A sufficiently high oxidation potential and fast, reversible redox transformations of polyoxometalates are key factors determining their efficiency as oxidation catalysts. Also important is the ability of polyoxometalates to activate the substrate and/or the oxidant, i.e. O_2. On these bases, among various polyoxometalates, the Keggin compounds containing molybdenum and vanadium make the most efficient oxidation catalysts. The type of countercation is essential as well, providing the catalyst with an optimal acidity, thermal stability and texture (surface area, porosity, framework mobility, etc.).[9,16]

The Keggin heteropoly acids and salts with the $[PMo_{12-n}V_nO_{40}]^{(3+n)-}$ anions (HPA-n, n = 0–2) are the most frequently used as solid catalysts for selective oxidation with oxygen in the gas phase.[9,16] The same polyoxometalates, but with n = 2 – 6, are widely used as homogeneous catalysts for aerobic oxidation in solution (Section 5.1.1). In solution, the HPA-n-catalysed oxidation follows the stepwise redox mechanism (eqs 5.1 and 5.2) that has already been thoroughly discussed. A similar mechanism (Mars–van Krevelen type) is suggested to operate in the case of gas-phase oxidation.

5.2.3 REACTIONS

Table 5.6 shows some typical examples of gas-phase selective oxidations of organic compounds over polyoxometalate catalysts. These reactions are usually carried out at temperatures of 150–400 °C. A number of bulk and supported heteropoly compounds are used as the catalysts, frequently various promoters (e.g. As, Pb, Bi, Fe, Cu, etc.) added.

Ai[190] compared the catalytic properties of HPA-n with those of vanadyl pyrophosphate, $(VO)_2P_2O_7$ (VPO), and iron phosphate, $FePO_4$, for selective gas-phase oxidations (Table 5.7). Generally, the catalytic activity of HPA-n is about the same order of magnitude as that of VPO. HPA-n show higher selectivities than VPO for reactions such as the oxidative dehydrogenation of carboxylic acids and the oxidation of butadiene or crotonaldehyde to furan. For the oxidation of methacrolein and allylic oxidation of isobutene or butadiene the selectivities are similar.

Misono *et al.*[9,11] proposed two types of oxidation catalysis by solid heteropoly compounds, namely (i) surface type and (ii) bulk type II. (The bulk type I

Table 5.6 Heterogeneous gas-phase oxidation over heteropoly compounds[9].

Reaction	Catalyst	T (°C)
Methacrolein $+O_2 \rightarrow$ methacrylic acid	$CsH_3[PMo_{11}VO_{40}]$	260
Isobutyric acid $+O_2 \rightarrow$ methacrylic acid	$H_5[PMo_{10}V_2O_{40}]$	300
$CH_3OH + O_2 \rightarrow HCHO, (CH_3)_2O$	$H_3[PMo_{12}O_{40}]$	200–290
$C_2H_5OH + O_2 \rightarrow CH_3CHO, (C_2H_5)_2O$	$H_3[PMo_{12}O_{40}]$ (+ polysulfone)	170
$C_2H_4 + O_2 \rightarrow CH_3COOH$	$Pd + H_4[SiW_{12}O_{40}]/SiO_2$	150
Isobutene $+O_2 \rightarrow$ methacrolein	$PbFeBi[PMo_{12}O_x]$	400
1-Butene $+O_2 \rightarrow$ maleic anhydride	$Cs_{2.5}H_{0.5}[PMo_{12}O_{40}] + VO^{2+}$	290
$CH_4 + N_2O \rightarrow HCHO, CH_3OH$	$H_3[PMo_{12}O_{40}]/SiO_2$	570
$C_2H_6 + N_2O\ (O_2) \rightarrow C_2H_4, CH_3CHO$	$H_3[PMo_{12}O_{40}]/SiO_2$	267
$C_3H_8 + O_2 \rightarrow$ acrylic acid	$H_3[PMo_{12}O_{40}]$(+ As)	340
n-Butane $+O_2 \rightarrow$ maleic anhydride	$Bi[PMo_{12}O_x] + VO^{2+}$	360
Isobutane $+O_2 \rightarrow$ methacrylic acid	$H_3[PMo_{12}O_{40}]$	350

Table 5.7 Comparison of selectivities of different oxidations[190].

Reaction	HPA-n	VPO	$FePO_4$
Propane → acrylic acid	M	G	B
n-Butane → maleic anhydride	M	G	B
Propene → acrylic acid	M	G	B
n-Butene → maleic anhydride	M	G	B
Isobutene → methacrylic acid + methacrolein	M	M	B
Butadiene → furan	G	M	B
Methanol → formaldehyde	M	G	B
Crotonaldehyde → furan	G	M	B
Acrolein → acrylic acid	M	G	B
Methacrolein → methacrylic acid	G	G	B
Propionic acid → acrylic acid	M	M	B
Isobutyric acid → methacrylic acid	M	M	G

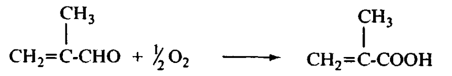
G = good, M = medium, B = bad

(pseudoliquid), discussed in Chapter 4, is relevant to the acid catalysis by bulk heteropoly acids.) The surface type is the conventional oxidation catalysis at a gas–solid or liquid–solid interface; such processes can occur on the surface of both bulk and supported heteropoly compounds. The bulk type II is relevant to reactions on bulk heteropoly compounds. This mechanism is suggested to operate in the case of certain catalytic oxidations that largely occur on the catalyst surface, with the bulk diffusion of electrons and protons assisting the redox process. It is thought that this type does not normally involve the oxygenation of organic compounds, which is more likely to proceed via the surface type catalysis. The surface type and the bulk type II catalysis over solid heteropoly compounds may be exemplified by the oxidation of CO and H_2, respectively.[9,11]

Two practically important oxidations – one oxygenation and the other oxidative dehydrogenation – that have been studied in detail in the past two decades may represent the surface type and bulk type II mechanisms. These are the oxidation of methacrolein to methacrylic acid and the oxidative dehydrogenation of isobutyric acid to methacrylic acid, respectively.

5.2.3.1 Oxidation of Methacrolein to Methacrylic Acid[9,11,191]

Methacrylic acid is used for the production of methyl methacrylate which in turn is used for manufacturing a crystal-clear plastic Plexiglas®. The oxidation of methacrolein to methacrylic acid over a heteropoly compound catalyst has been developed and commercialised in Japan (Chapter 7).



$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CHO + \tfrac{1}{2}O_2 \longrightarrow CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}COOH \qquad (5.62)$$

The reaction is carried out at 270–350 °C with a gas feed consisting of 2–5 % methacrolein, 10–20 % steam and a methacrolein/oxygen molar ratio of 2–4. At

a methacrolein conversion of 70–90 %, the selectivity to methacrylic acid is between 80–85 %.

The catalyst is an acidic caesium salt of HPA-n, $H_{3+n-x}Cs_x$ $[PMo_{12-n}V_nO_{40}]$ ($2 < x < 3$; $0 < n < 2$). These salts have advantage of the increased surface area and higher thermal stability compared to the parent heteropoly acids. It has been shown that both acidity and oxidation ability of catalysts are necessary for the selective oxidation of methacrolein to occur. The preferred acidic salts are nearly stoichiometric. But the stoichiometric caesium salts $Cs_{3+n}[PMo_{12-n}V_nO_{40}]$ are not catalytically active, probably due to the absence of acidity. The vanadium substitution for part of the molybdenum increases the oxidising ability. The effect of caesium-for-proton substitution in $H_4[PMo_{11}VO_{40}]$ on the catalytic activity and selectivity for the oxidation of methacrolein is shown in Figure 5.5.

Substitution of one vanadium(V) for molybdenum(VI) in $H_3[PMo_{12}O_{40}]$ increases the thermal stability; the stability decreases, however, upon further substitution. There is evidence that the Keggin structure is not intact during the reaction. Upon heat treatment of solid $H_4[PMo_{11}VO_{40}]$, vanadyl and molybdenyl species leave the Keggin unit. Substitution of Cs^+ for proton in $H_4[PMo_{11}VO_{40}]$ stabilises the structure, while the presence of water vapour enhances its desintegration.[192] The role of the vanadyl and molybdenyl species is not yet clear. It is conceivable that, like in homogeneous catalysis

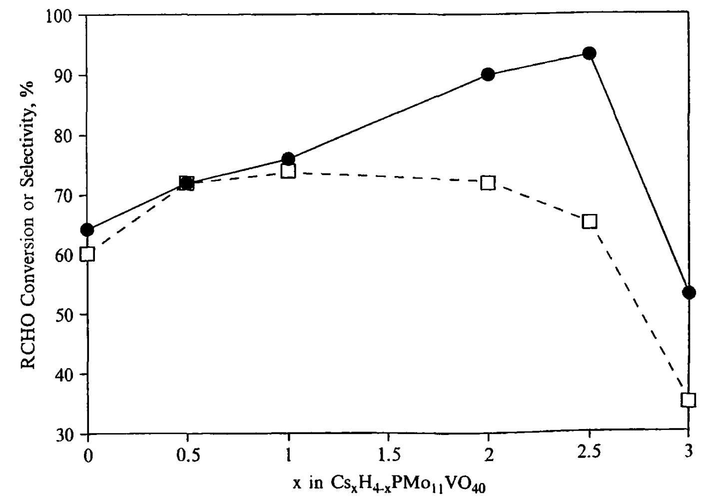


Figure 5.5 Effect of caesium substitution in $Cs_xH_{4-x}[PMo_{11}VO_{40}]$ on catalytic activity (solid circles) and selectivity (open squares) for the oxidation of methacrolein to methacrylic acid.[191]

(Section 5.1.1), these may be active species in oxidising the substrate, then re-entering the polyanion to become reoxidised by dioxygen.

Mechanistic studies show that the oxidation of methacrolein is a surface type oxidation and involves a bifunctional, i.e. both acid–base and redox catalysis.[9,11,191] Presence of water is essential for the reaction to occur; water may be required for the formation of reaction intermediates, maintaining the stability of catalyst active sites, as well as to enhance product desorption from the catalyst surface. Apparently, one of the important acid-catalysed steps is the conversion of methacrolein to methacrolein hydrate:

$$RCHO + H_2O \rightarrow RCH(OH)_2 \qquad (5.63)$$

Further oxidative dehydrogenation of $RCH(OH)_2$, which is probably rate-determining, is suggested to proceed via a Mars–van Krevelen mechanism. This mechanism includes the oxidation of the intermediate by the catalyst, followed by the reoxidation of the reduced catalyst with dioxygen.

$$RCH(OH)_2 + \text{HPA-n} \rightarrow RCOOH + H_2[\text{HPA-n}] \qquad (5.64)$$

$$H_2[\text{HPA-n}] + \tfrac{1}{2}O_2 \rightarrow \text{HPA-n} + H_2O \qquad (5.65)$$

This mechanism is supported by the following experimental results. There is a fairly good correlation between the oxidising ability of polyoxometalate and the reaction rate. The selectivity remains the same for a prolonged period when the supply of oxygen is stopped at the stationary state of catalytic reaction, which supports the involvement of the polyoxometalate framework oxygen in step 5.64. There is also rapid isotopic exchange of oxygen between the catalyst and either RCHO or water.

The following rate equation has been reported for the reaction catalysed by $H_3[PMo_{12}O_{40}]$ at 300 °C, where in square brackets are the pressures of reactants:[191]

$$\text{rate} = k\,[RCHO]^{0.6-1}[O_2]^{0-0.2}[H_2O]^0$$

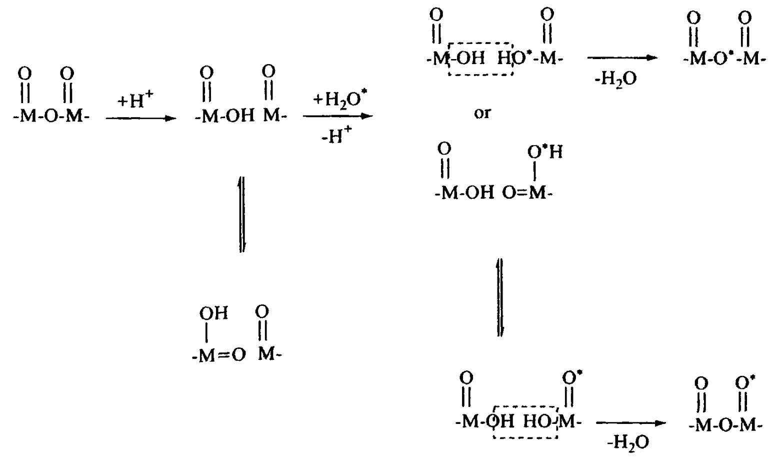
This equation indicates that step 5.64 is rate-limiting in the above mechanism.

The role of acidity is deemed manifold; it may enhance:

- The formation of methacrolein hydrate (eq. 5.63) and its interaction with the polyoxometalate catalyst to form an ester intermediate.
- Oxygen transfer (water → POM; POM → substrate; O_2 → POM, or water → organic intermediate).
- Product desorption from catalyst surface.

Another question is which oxygen is transferred to the substrate? If from the polyoxometalate, is it the terminal or bridging oxygen? Alternatively, it could be an oxygen atom from the breakaway vanadyl or molybdyl species. Besides, as the oxidation occurs in the presence of steam, oxygen transfer from water vapour is not excluded; if so, the mechanism would largely be the same as that for the homogeneous oxidation by HPA-n (eqs 5.1 and 5.2). This is still an open question, though.

Attempts have been made to discriminate the reactivity of terminal and bridging oxygens in Keggin heteropolymolybdates by measuring the oxygen exchange between solid heteropoly compounds and water vapour using IR spectroscopy[193–195] and more recently ^{17}O NMR.[196] These studies show that the oxygen exchange with $H_3[PMo_{12}O_{40}]$ occurs at temperatures above 200 °C (Table 5.8) and is accompanied by fast mixing of terminal and bridging oxygens in the Keggin unit, which makes it difficult to discriminate between the two types of oxygen atoms. On the basis of ^{17}O NMR results, a mechanism of oxygen exchange has been suggested (Scheme 5.7).[196] It includes the breaking



Scheme 5.7

Table 5.8 Oxygen exchange between ^{17}O-enriched heteropoly acid and H_2 ^{16}O vapour from ^{17}O MAS NMR[a],[196].

Heteropoly acid	T,°C	Time, h	Exchange, %[b]
$H_3[PMo_{12}{}^{17}O_{40}]$	200	1	≤ 5
$H_3[PMo_{12}{}^{17}O_{40}]$	250	1	20
$H_3[PMo_{12}{}^{17}O_{40}]$	250	5	60
$H_3[PW_{12}{}^{17}O_{40}]$	300	2	0

a) $H_2{}^{16}O$ 20 torr, atmospheric pressure

b) Percentage of outer oxygens in the Keggin anion exchanged. Fast mixing of the terminal and bridging oxygens takes place of an oxygen bridge initiated by protonation to form a pentacoordinate Mo(VI). The latter is attacked by an H_2O molecule to give an octahedral Mo(VI), containing the entering OH group in the equatorial or axial position with almost equal probabilities. Finally, the release of an H_2O molecule restores the Keggin structure, with either the terminal or the bridging oxygen atom exchanged.

5.2.3.2 Oxidative Dehydrogenation of Isobutyric Acid

The oxidative dehydrogenation of isobutyric acid has attracted interest as another route to methacrylic acid.[9,11,16,191]

$$CH_2\text{-}\underset{}{\overset{CH_3}{\overset{|}{C}}}H\text{-}COOH + \tfrac{1}{2}O_2 \longrightarrow CH_2{=}\overset{CH_3}{\overset{|}{C}}\text{-}COOH + H_2O \qquad (5.66)$$

Heteropoly compounds $H_{3+n-x}Cs_x[PMo_{12-n}V_nO_{40}]$ $(2 < x < 3;\ 0 < n < 2)$ (HPA-n) have been found to be very efficient catalysts for this reaction. With HPA-n, 78% selectivity to methacrylic acid at 97% conversion at 350 °C has been reported.[9,11]

Spectroscopic characterisations show that vanadium is removed from the Keggin heteropoly anion under reaction conditions.[197] The reaction follows the Mars–van Krevelen mechanism. There is evidence that the oxidative dehydrogenation of isobutyric acid over bulk HPA-n is a bulk type II reaction, i.e. bulk diffusion of electrons and protons assist the oxidation process.[9,11]

5.2.3.3 Heterogeneous Wacker Reaction

Attempts have been made to apply the solid two-component Pd(II) + HPA-n system for the gas-phase Wacker oxidation and related reactions.[17,198–204] These reactions are usually carried out at relatively low temperatures, 70–100 °C, in the presence of steam. Mechanistically, they may be considered as pseudohomogeneous, i.e., occurring in the liquid catalyst phase entrapped in a support. As a support, silica is often used, which is relatively inert towards polyoxometalates. The real mechanism, however, may be more complex, but little data is available so far. There are two main problems in applying this system to the gas-phase oxidation: (i) the reoxidation of the catalyst by O_2 proceeds much slower than in solution and (ii) the catalyst is rapidly deactivated probably due to aggregation of palladium.

The heterogeneous oxidation of n-butene to methylethylketone is a challenging goal.[17]

$$CH_3CH_2CH = CH_2 + \tfrac{1}{2}O_2 \rightarrow CH_3CH_2COCH_3 \qquad (5.67)$$

Stobbe-Kreemers *et al.*[198,199] and Nowinska *et al.*[204] studied this reaction with the solid Pd(II) + HPA-n catalyst system at 70 °C. Not only HPA-n but also their $Cu^{2+}, Ni^{2+}, Pd^{2+}$ and Cs^{+} salts were used. A strong catalyst deactivation is observed:[198,199] the conversion of butene drops ten-fold from 60% to 6% after 1 h on stream, while the selectivity decreases less dramatically, only from 98% to 90%.

Nowinska *et al.*[200–203] reported a very stable activity in the oxidation of ethylene to acetaldehyde with a Mn^{2+}-promoted catalyst, $(PdCl_2 + Mn^{2+} + \text{HPA-2})/SiO_2$. After 50 h on stream at 70 °C, a constant 98% selectivity at 80% ethylene conversion is observed.

5.2.3.4 Oxidation of Ethylene to Acetic Acid

Another combination of palladium and polyoxometalate – Pd(0) and a non-oxidising heteropoly acid $H_4[SiW_{12}O_{40}]$ – is effective for the gas-phase oxidation of ethylene to acetic acid with oxygen.[205] This process has been developed and commercialised by Showa Denko in Japan (Chapter 7).

$$CH_2 = CH_2 + O_2 \rightarrow CH_3COOH \qquad (5.68)$$

Remarkably, even a simple combination of Pd metal and heteropoly acid gives a relatively high yield of acetic acid (Table 5.9). In the absence of HPA, when Pd metal is supported on silica, no partial oxidation is observed, only complete oxidation to carbon dioxide. Without Pd, when only heteropoly acid such as tungstosilicic acid on silica is used, no oxidation of ethylene occurs either; only a small amount of ethanol is obtained. With the palladium(II) salt of HPA as a catalyst, almost equal amount of acetaldehyde and acetic acid are obtained. In this case, the reaction may proceed through the equations:

$$C_2H_4 + \tfrac{1}{2}O_2 \rightarrow CH_3CHO \qquad (5.69)$$

$$CH_3CHO + \tfrac{1}{2}O_2 \rightarrow CH_3COOH \qquad (5.70)$$

Table 5.9 Oxidation of ethylene over Pd and HPA catalyst systems[a],[205].

Catalyst	STY[b]	Selectivity, %		
	g/l h	HOAc[c]	HAc[d]	CO_2
Pd-$H_4[SiW_{12}O_{40}]$	93.1	78.5	5.5	14.2
Pd-$H_3[PW_{12}O_{40}]$	83.3	78.0	5.0	16.0
Pd-$H_3[PMo_{12}O_{40}]$	68.5	77.5	4.6	17.8
Pd-$Ga_{0.05}H_{3.85}[SiW_{12}O_{40}]$	90.4	80.1	4.1	15.6
Pd-$Mg_{0.05}H_{3.85}[SiW_{12}O_{40}]$	90.8	79.7	5.5	14.6
Pd-$H_5[PMo_{10}V_2O_{40}]$	94.0	61.4	19.4	17.6
Pd	0	0	0	100
$H_3[PW_{12}O_{40}]$	0	0	0	0

a) Reaction conditions: 150 °C; 5 atm pressure; GHSV = 3000 h^{-1}; gas mixture $C_2H_4/O_2/H_2O$ inert gas = 50/7/30/13
b) Space time yield (g/l-catalyst h)
c) HOAc = acetic acid
d) HAc = acetaldehyde

The same mechanism may be operating in the case of Pd – $H_5[PMo_{10}V_2O_{40}]$, as this heteropoly acid is capable of oxidising Pd^0 to Pd^{2+}.

In the case of the most efficient systems including Pd metal and strong, nonoxidising tungsten heteropoly acids, such as $H_4[SiW_{12}O_{40}]$ or $H_3[PW_{12}O_{40}]$, the reaction is likely to proceed through the acid-catalysed hydration of ethylene to ethanol, followed by the oxidation of ethanol to acetaldehyde catalysed by palladium:

$$C_2H_4 + H_2O \rightarrow CH_3CH_2OH \qquad (5.71)$$

$$CH_3CH_2OH + O_2 \rightarrow CH_3COOH + H_2O \qquad (5.72)$$

It has been found that the higher the acid strength of heteropoly acid, the higher the catalytic efficiency. Heteropoly acids and salts with a weaker acidic strength showed a lower catalytic activity, but these catalysts displayed extended lifetime.

5.2.3.5 Oxidation of Alkanes

Heteropoly compounds have attracted interest as catalysts for the partial oxidation of alkanes in the gas phase.[9,11,16,17] Generally, heteropoly molybdates, both bulk and supported, are used for such reactions. Other transition metals are frequently added as promoters to improve the catalytic activity and selectivity. The mechanisms are yet unknown, but there is evidence that the proton acidity is important for these reactions. The reader can find a detailed account on alkane oxidation in the monograph by Moffat.[16]

Mizuno *et al.*[11,206] have studied Keggin-type molybdovanadophosphates HPA-n as catalysts for the selective oxidation of light alkanes from methane to isobutane (Table 5.10). Most of these catalysts are bulk Cs acidic salts of HPA-1 promoted by transition metal cations. No selective oxidation of methane is observed in the absence of H_2. With an H_2 co-feed, formic acid is obtained, but the yield is very low. Ethane is oxidatively dehydrogenated to ethene in a 4% yield over the Mn-promoted catalyst. Fe-promoted catalyst oxidises propane to acrylic acid in 13% yield. On the other hand, Cu-catalyst dehydrogenates propane to propene in a 10% yield. Ni-catalyst shows the best performance in the direct oxidation of isobutane to methacrylic acid (9% yield). The catalysts reportedly retain the Keggin structure during the oxidation.

Table 5.10 Alkane oxidation by oxygen over HPA-n heteropoly compounds[a],[206].

Alkane	Product	Catalyst	T°C	Conversion %	Yield %
Methane[b]	Formic acid	$Cs_{2.5}Pd_{0.08}H_{1.34}[PVMo_{11}O_{40}]$	300	0.05	0.05
Ethane	Ethene	$Cs_{2.5}Mn_{0.08}H_{1.34}[PVMo_{11}O_{40}]$	425	10	4.3
Propane	Acrylic acid	$Cs_{2.5}Fe_{0.08}H_{1.26}[PVMo_{11}O_{40}]$	380	47	13
Propane	Propene	$Cs_{2.5}Cu_{0.08}H_{3.34}[PV_3Mo_9O_{40}]$	380	40	10
Isobutane	Methacrylic acid	$Cs_{2.5}Ni_{0.08}H_{1.26}[PVMo_{11}O_{40}]$	340		9.0

a) Fixed-bed reactor; feed: alkane/O_2/N_2

b) In the presence of H_2

Albonetti *et al.*[207] reported the efficient oxidative dehydrogenation of ethane on a modified potassium salt of $H_3[PMo_{12}O_{40}]$. The addition of antimony leads to a remarkable increase in the thermal stability of the catalyst. Fe, Ce and Cr additives were found to greatly improve the activity and selectivity towards ethene formation. Under the optimal conditions (fixed-bed reactor, 510 °C, 1 atm), this catalyst gives 74% selectivity for ethene at 26% conversion. No acetic acid is formed, only CO_x as by-products. The catalyst shows a stable performance for at least 100 h and reportedly retains its structure after the reaction.

Li *et al.*[208] reported that a Py salt of $H_3[PMo_{12}O_{40}]$, pre-activated at 420 °C under N_2, catalyses the direct oxidation of propane to acrylic acid and isobutane to methacrylic acid in the presence of steam. Methacrylic acid is obtained in 11% yield, which is probably the highest yield reported so far. The catalyst contains oxygen-deficient heteropoly anions with reduced Mo. Proton sites are also present, which is considered essential for the reaction. The catalyst shows a stable performance for at least 10 h.

Volkova *et al.*[209] reported that $(PdCl_2 + HPA\text{-}6)/SiO_2$ catalyses the oxidation of methane and other alkanes by O_2 at 300 °C. Methane is converted to CH_3Cl and CO_2 with selectivities of 20 and 25%, respectively. No reaction occurs without $PdCl_2$. HPA-6 is suggested to mediate the reoxidation of reduced palladium by O_2. The relative oxidation rate increases in the series of alkanes: $CH_4(0.14) < C_2H_6(1.0) < C_3H_8(2.0) < \text{i-}C_4H_{10}(2.2) < \text{n-}C_4H_{10}(3.4) < \text{cyclopentane}(6.8) = \text{cyclohexane}(6.8) < \text{n-}C_5H_{12}(7.2)$.[210]

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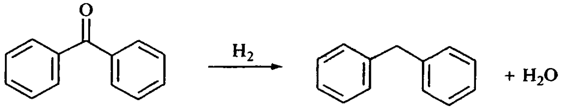
6 Miscellaneous Catalytic Applications of Polyoxometalates

CONTENTS

This chapter presents an overview of the application of polyoxometalates in other fields of catalysis such as hydrogenation, carbonylation and related reactions. Also discussed are polyanion-stabilised metal clusters, the anchoring of homogeneous catalysts by polyoxometalates, and the use of polyoxometalates as catalyst precursors. For more information on these topics, the reader should consult the references provided.

6.1 HYDROGENATION, CARBONYLATION AND RELATED REACTIONS

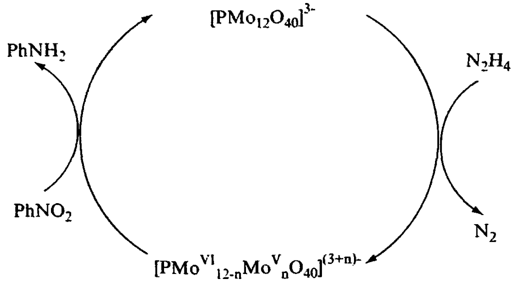
Polyoxometalates have attracted interest for catalysing the above reactions recently. The reduction of aromatic and aliphatic aldehydes and ketones with dihydrogen is catalysed by potassium heteropoly salts supported on γ-alumina at 300 °C and H_2 pressure of 23–54 atm without solvent.[1] The order of catalytic activity correlates with the oxidation potentials of polyoxometalates: $[SiW_{12}O_{40}]^{4-} < [PW_{12}O_{40}]^{3-} < [PMo_{12}O_{40}]^{3-} < [PMo_{10}V_2O_{40}]^{5-}$. For $[PMo_{10}V_2O_{40}]^{5-}$, the conversion of benzophenone into diphenylmethane (eq. 6.1) is quantitative (300 °C, 23 atm, 3.5 h).



(6.1)

The IR spectra and XRD pattern for the catalyst before and after the reaction are identical, indicating that the structure of polyoxometalate is unchanged.

12-Molybdophosphoric acid catalyses transfer hydrogenation of nitrobenzene to aniline by hydrazine in a homogeneous phase.[2] Protic solvents such as water or methanol enhance the reduction. In methanol, the reaction occurs with 100% yield at room temperature. A redox mechanism (Scheme 6.1) involving the reduction of Mo(VI) to Mo(V) in polyanion by hydrazine followed by oxidation of Mo(V) with nitrobenzene is suggested.



Scheme 6.1

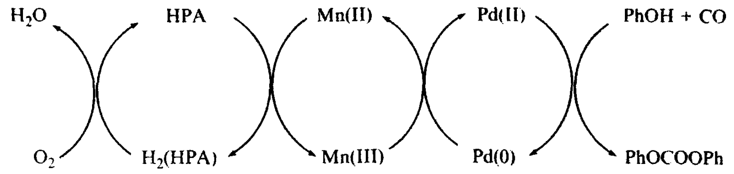
The two-component systems POM + Pd(II) and POM + Rh(I) have been used for carbonylation, hydroformylation and hydrogenation reactions.[3–8] The catalytic system

$PdCl_2$–POM is efficient for carbonylation of nitrobenzene to methyl phenylcarbamate.[8]

$$ArNO_2 + MeOH + 3\,CO \rightarrow ArNHCOOMe + 2\,CO_2 \qquad (6.2)$$

The catalytic activity is in line with the reducibility of polyanions. The $[PMo_{10}VO_{40}]^{4-}$ anion shows the highest activity, whereas 12-molybdosilicate and heteropolytungstates are much less active. Medium polarity solvents such as acetone and other ketones give the best results. There is evidence that polyoxometalates are reduced during the reaction but maintain their structure intact.

A multicomponent redox system consisting of $Pd(OAc)_2$, a Keggin heteropoly acid $\{XMo_{12-n}W_nO_{40}\}$ (X = P or Si), and $Mn(OAc)_2$ catalyses the oxidative carbonylation of phenol to diphenyl carbonate at 80 °C and 8 atm pressure without solvent.[9] The efficiency of the catalysts depends on the composition of heteropoly anion. The best yield, 22%, is obtained for $H_3[PMo_6W_6O_{40}]$. The heteroatom has little effect on catalyst performance. A stepwise redox mechanism (Scheme 6.2), with Mn(II)/Mn(III) enhancing the reoxidation of palladium, is suggested.



Scheme 6.2

6.2 POLYANION-STABILISED CLUSTERS

Transition metal nanoclusters and their catalytic properties are currently an important area of nanoscale chemistry. Finke *et al.*[10–13] reported the preparation of near monodisperse nanoclusters of Ir(0) and Rh(0) stabilised by heteropoly anions. For example, the 20±3 Å Ir(0) clusters of an average composition $Ir(0)_{\sim 300}$ were synthesised by reduction of polyanion-supported Ir(I) complex $[(1,5\text{-COD})Ir \cdot P_2W_{15}Nb_3O_{62}]^{8-}$ with H_2. The process may be represented as

$$\begin{aligned}&300\,[(1,5\text{-COD})Ir \cdot P_2W_{15}Nb_3O_{62}]^{8-} + 750\,H_2 \rightarrow 300\,C_8H_{16} +\\ &Ir(0)_{\sim 300} + 300\,[P_2W_{15}Nb_3O_{62}]^{9-} + 300\,H^+\end{aligned} \qquad (6.3)$$

The Ir(0) clusters show very high catalytic activity and stability in cyclohexene hydrogenation. Although the mechanism of self-assembly reaction 6.3 is not clear, it is conceivable that the presence of polyanions is the key to the stabilisation of this system.

Augustine *et al.*[14] have used polyoxometalates for immobilisation of homogeneous metal-complex catalysts for enantioselective hydrogenation, which may be viewed as an extension of the Finke's approach. In this work, heteropoly acids (e.g. $H_3[PW_{12}O_{40}]$) preadsorbed on a support material serve as anchoring agents for a homogeneous catalytic complex. A Rh(DiPamp) complex supported on montmorillonite treated with $H_3[PW_{12}O_{40}]$ runs fifteen successive hydrogenations of methyl 2-acetamidoacrylate with no loss of activity or selectivity.

Maksimov *et al.*[15,16] prepared highly stable colloidal systems containing nanoclusters of precious metals by treating aqueous solutions of precursor metal complexes and polyoxometalates with reductants. The size of clusters so prepared, measured by transmission electron microscopy, depends on the type of polyoxometalate and the POM/metal ratio (Table 6.1). Supported metal catalysts were prepared by adsorption of these colloids on Al_2O_3, MgO, or carbon support. The metal dispersion in these catalysts was the same as that in the colloid systems.

Table 6.1 Nanoclusters of precious metals stabilised by polyoxometalates[15].

Metal (M)	[M] 10^{-2}mol l^{-1}	[M]/[POM] mol/mol	POM	Cluster size nm
Pt	0.2	1.3	$[V_{10}O_{28}]^{6-}$	2–3
Rh	0.3	1.8	$[Mo_7O_{24}]^{6-}$	2–3
Ru	0.3	1.8	$[Mo_7O_{24}]^{6-}$	≤ 1.5
Ir	0.4	2	$[SiW_{11}O_{39}]^{8-}$	≤ 2
Au	0.2	3	$[Nb_6O_{19}]^{8-}$	7.5–40
Ag	1.0	5.5	$[SiW_{11}O_{39}]^{8-}$	1–150
Pd	1.0	5	$[V_{10}O_{28}]^{6-}$	1–7
Pd	1.0	14	$[Mo_7O_{24}]^{6-}$	3–9
Pd	1.0	24	$[H_2W_{12}O_{40}]^{6-}$	3–10
Pd/Rh 10:1	0.3	3.9	$[Mo_7O_{24}]^{6-}$	3–4
Pd/Pt 1:1	0.3	7	$[Mo_7O_{24}]^{6-}$	2–2.5
Pd/Pt 5:1	0.3	8.4	$[Mo_7O_{24}]^{6-}$	2–6
Pd/Au 1:1	0.3	7	$[Mo_7O_{24}]^{6-}$	3–100
Pd/Ag 1:1	0.3	22	$[SiW_{11}O_{39}]^{8-}$	3–150

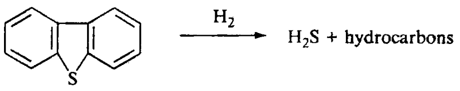
6.3 POLYOXOMETALATES AS CATALYST PRECURSORS

Use of polyoxometalates as catalyst precursors for heterogeneous catalysis is attracting interest. Preparation of mixed oxide precatalysts by incorporating metal components into the polyoxometalate framework followed by a thermal treatment may be more effective than traditional coprecipitation or successive impregnation. In particular, this methodology has been explored for the preparation of catalysts for hydrodesulfurisation (HDS).[17–26]

Griboval *et al.*[23] have used two salts of 12-molybdophosphoric acid, nonreduced $Co_{3/2}[PMo_{12}O_{40}]$ and reduced $Co_{7/2}[PMo_{12}O_{40}]$, as precatalysts for the HDS of thiophene. The salts were supported on γ-alumina by impregnating from aqueous solution. The nonreduced salt was decomposed on impregnation and produced a well-dispersed surface polymolybdate phase. In contrast, the reduced salt was stable on the alumina surface after impregnation and drying. The use of the reduced salt is beneficial because it enhances the interaction of the Co(II) with polyoxomolybdate in the impregnating solution and allows avoiding the formation of the surface polymolybdate phase obtained with the nonreduced salt.

Demirel *et al.*[24] have studied conversion of 12-phosphomolybdates, the heteropoly acid and its Ni(II), Co(II), and K(I) salts, under typical HDS conditions. In the presence of H_2 without H_2S, these compounds are stable to temperatures of ca. 350 °C, loosing only hydration water. When H_2S is present, decomposition is observed at much lower temperatures. The initial reaction with H_2S occurs as water of hydration is being lost and is complete up to 200 °C. The oxidation state of Mo in the materials sulfided at 300 °C was found to be 3.8+ for $H_3[PMo_{12}O_{40}]$, 4.8+ for $Ni_{3/2}[PMo_{12}O_{40}]$, 4.6+for $Co_{3/2}[PMo_{12}O_{40}]$, and 5.4+ for $K_3[PMo_{12}O_{40}]$. The results suggest that the active catalyst in the HDS processes will not retain the Keggin structure and may consist of mixed thio/oxomolybdates and bulk metal sulfides, e.g. MoS_2.

Silica-supported tungstophosphoric heteropoly acid, $H_3PW_{12}O_{40}$, has been found to be an efficient catalyst for the HDS of dibenzothiophene (DBT).[26]



(6.4)

Over 30 wt% HPA/SiO_2 catalyst in a trickle bed flow reactor at industrially relevant gas and liquid space velocities (GHSV 600 h^{-1} and LHSV 6 h^{-1} and an H_2 pressure of 30 bar the HDS proceeds with a DBT conversion of 58% at 290 °C and 80% at 350 °C. These values are comparable to the performance of the industrial Co–Mo/Al_2O_3 catalyst (Figure 6.1). No loss of catalytic activity was observed at 290 °C for a period of 56 h. ^{31}P MAS NMR (Figure 6.2) and TGA data show that the heteropoly acid was decomposed upon the interaction with H_2S/H_2 to yield an active HDS catalyst, whose composition is yet unknown.

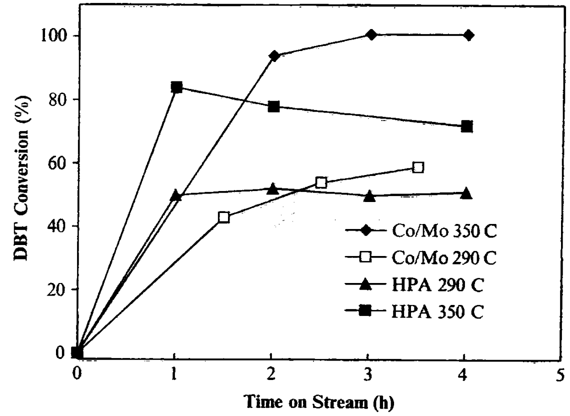


Figure 6.1 Dibenzothiophene conversion for heteropoly acid and Co–Mo catalysts.[26]

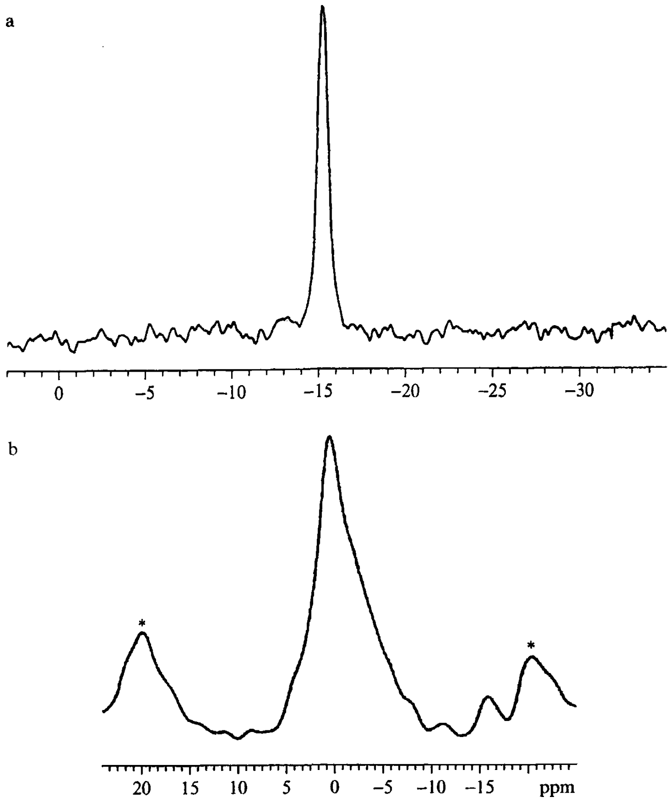


Figure 6.2 ^{31}P MAS NMR spectra: (a) fresh 30% $H_3[PW_{12}O_{40}]/SiO_2$ catalyst; (b) the catalyst after use for HDS, spinning sidebands asterisked.[26] Reprinted with permission from *Appl. Catal. A* 2000, **204**, 251. Copyright 2000 Elsevier Science.

Pillaring hydrotalcite-type anionic clays (layered double hydroxides) by polyanions to form expanded layered materials has attracted considerable interest. These materials may be used as precursors to mixed oxide catalysts, which possess basic and/or redox properties (see[27,28] and references therein).

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7 Catalysis by Polyoxometalates in Industry

CONTENTS

In the last three decades, heteropoly compounds have found use as catalysts in many industrial processes, Japan being the world leader in their commercialisation.[1–3] After first successful industrial application of heteropoly acid as a homogeneous catalyst for the hydration of propene (Tokuyama process) in 1972,[1,3] several new large-scale processes have been commercialised. In these processes, heteropoly acids or their salts are used as acid or oxidation catalysts in homogeneous or heterogeneous systems (Table 7.1). Among them are the liquid-phase hydration of butenes, the vapour-phase oxidation of methacrolein to methacrylic acid and of ethylene to acetic acid, and the gas-phase synthesis

Table 7.1 Industrial processes catalysed by heteropoly acids.

Reaction	Catalyst	Type[a]	Start (Ref.)
$CH_2{=}CHCH_3 + H_2O \rightarrow CH_3CH(OH)CH_3$	$H_4[SiW_{12}O_{40}]$	hom	1972 (4)
$CH_2{=}C(CH_3)CHO + O_2 \rightarrow CH_2{=}C(CH_3)COOH$	Mo–V–P–HPA	het	1982 (1)
$CH_2{=}C(CH_3)_2 + H_2O \rightarrow (CH_3)_3COH$	$H_3[PMo_{12}O_{40}]$	hom	1984 (1)
$nTHF + H_2O \rightarrow HO{-}[{-}(CH_2)_4{-}O{-}]_n{-}H$	$H_3[PW_{12}O_{40}]$	bip	1985 (2,5a)
$CH_3CH{=}CHCH_3 + H_2O \rightarrow CH_3CH(OH)CH_2CH_3$	$H_3[PMo_{12}O_{40}]$	hom	1989 (3)
Ketone amination to imine	Supported HPA	het	1996 (5b)
$CH_2{=}CH_2 + O_2 \rightarrow CH_3COOH$	$Pd\text{-}H_4[SiW_{12}O_{40}]/SiO_2$	het	1997 (6)
$CH_2{=}CH_2 + CH_3COOH \rightarrow CH_3CH_2O_2CCH_3$	$H_4[SiW_{12}O_{40}]/SiO_2$	het	2001 (7)

a) hom = homogeneous, het = heterogeneous, and bip = biphasic of ethyl acetate from ethanol and acetic acid. On a smaller scale, heteropoly acids are used as acid catalysts for the polymerisation of tetrahydrofuran in a liquid/liquid biphasic system and synthesis of glycosides in a homogeneous system.[1] Armor[5h] discussed, amongst others, recent industrial applications of heteropoly acid catalysts in USA, which include the continuous animation of a ketone to imine over a supported HPA in the synthesis of isophorone nitrileimine by DuPont (1996 start) as well as pilot scale testing in several other processes.

This section briefly describes several industrial processes that use heteropoly compounds as acid or oxidation catalysts, including the hydration of olefins, the synthesis of ethyl acetate, the oxidation of methacrolein to methacrylic acid, and the oxidation of ethylene to acetic acid.

7.1 ACID CATALYSIS

7.1.1 HYDRATION OF OLEFINS

Hydration of alkenes is catalysed by acid to yield a secondary or tertiary alcohol through the addition of water to alkene that obeys the Markovnikov's rule.

$$\mathrm{RCH{=}CHR' + H_2O \rightarrow RCH(OH)CH_2R'}$$

Light C_2–C_4 alkene hydrations are all large-scale industrial processes carried out with either homogeneous or heterogeneous acid catalysis.[4] Alcohols thus obtained are mainly used as solvents. Heteropoly acids are the most active catalysts for the hydration of alkenes, and they play an increasing role in commercial production of alcohols by this route.[1–3]

7.1.1.1 Hydration of Propene

There are several conventional industrial processes that are currently used for manufacturing isopropanol by liquid- or vapour-phase hydration of propene, H_2SO_4, H_3PO_4/SiO_2 or sulfonic acid ion-exchange resin being used as catalysts. The selectivity to isopropanol is from 93 to 97%.[4]

Tokuyama in Japan developed a new highly selective process for the production of isopropanol that uses water-soluble 12-tungstosilicic acid or its acid salts to convert propene to isopropanol in the liquid phase at 270–280 °C and 200 bar.[3,4] The aqueous catalyst is recycled after distilling off the alcohol/water azeotrope. Propene conversion reaches 60–70% with selectivity to isopropanol of about 99%. The first commercial plant with a production capacity of 30000 tonnes per year began operation in 1972. Figure 7.1 shows a flow chart for the Tokuyama process of hydration of propene.

7.1.1.2 Hydration of Isobutene

The C_4 raffinate obtained from steam cracking of naphtha typically contains 44–49% isobutene, 24–28% 1-butene, 19–21% 2-butene, the rest being

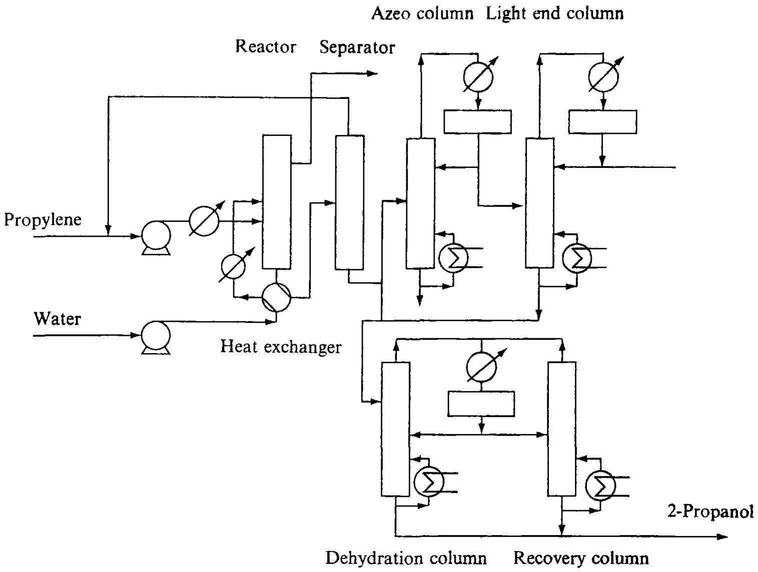

Figure 7.1 Flow chart for the Tokuyama process of propene hydration.[3] Reprinted with permission from *Catal. Today* 1997, **33**, 371. Copyright 1997 Elsevier Science.

n-butane and isobutane. Isobutene is the most reactive component in this mixture, and this property can be utilised for a chemical separation. The selective hydration of isobutene to t-butanol by reacting the C_4 mixture with water in the presence of dilute mineral acid (e.g. H_2SO_4) or an acid ion-exchange resin is a common method of isobutene separation in industry. t-Butanol is then catalytically dehydrated to yield pure isobutene.[4]

Asahi Chemical Industry in Japan developed a new process for highly selective hydration of isobutene using heteropoly acid as a homogeneous catalyst.[1–3,8] This process was commercialised in 1984 on a scale of 50000 t/year.[1] The catalyst is $H_3[PMo_{12}O_{40}]$ as a concentrated aqueous solution, 0.15–0.8 mol/l, which corresponds to 10–50 wt%. The reaction is carried out in a counter-current multistage reactor at a relatively low temperature of 60–80 °C under pressure in a binary liquid system of water and butenes. t-Butanol is mainly dissolved in the aqueous phase and is easily separated from unreacted butene layer. The conversion of isobutene can be increased to almost 100%, while the conversion of n-butene is less than 0.1%. After separation of t-butanol, the water phase containing the catalyst is recycled to the reactor. The catalyst lifetime is long enough; phosphoric acid is added to the catalyst solution to stabilise $H_3[PMo_{12}O_{40}]$.

The process has the following advantages compared to the hydration of isobutene using conventional mineral acids:[1,8]

1. High catalytic activity. The stronger acidity of heteropoly acid solution compared to mineral acid at the same concentration and the differing reaction mechanism, leading to the higher reaction order with respect to heteropoly acid in concentrated solutions (Section 4.2.2), are the reasons for higher reaction rate.
2. High selectivity. Yields of byproducts, *sec*-butanol and diisobutene, are significantly lower.
3. Low corrosion activity. It is claimed that heteropoly acid forms a passivated layer on the surface of stainless steel, protecting the reactor from corrosion.

7.1.2 SYNTHESIS OF ETHYL ACETATE FROM ETHYLENE AND ACETIC ACID

Ethyl acetate is an industrially significant derivative of acetic acid, with the present world manufacturing capacity about 1 million tonnes per year. It is used as solvent in paints, inks and the pharmaceutical industry. Presently, two processes are used for manufacturing ethyl acetate: the esterification of ethanol and the Tischenko reaction of acetaldehyde. Both processes have their limitations, and there is a need for a cost effective and environmentally benign process using ethylene feed.[4,7] A number of patents have been published on the production of ethyl acetate by direct reaction of ethylene with acetic acid in vapour phase using solid acid catalysts. Among them, heteropoly acids have shown a great promise.[9]

BP Amoco has developed a new process for manufacturing ethyl acetate by the direct reaction of ethylene with acetic acid in the gas phase using 12-tungstosilicic acid on silica as the catalyst.[7,10]

$$CH_2{=}CH_2 + HOAc \rightarrow CH_3CH_2OAc \qquad (7.1)$$

Table 7.2 shows the excellent performance of the $H_4[SiW_{12}O_{40}]/SiO_2$ catalyst in reaction 7.1 in comparison with other solid acid catalysts.[7] Such a comparison, however, should be treated with caution because of differing experimental parameters in literature reports.

Table 7.2 Solid acid catalysts for the reaction of ethylene with acetic acid to ethyl acetate[7].

Catalyst	C_2H_4/AcOH mol/mol	Temp. °C	Pressure bar	Contact time s	H_2O in feed % mol	STY g/l h
H-montmorillonite	5/1	200	50	4	0	144
XE386 resin	5/1	155	50	4	0	120
Nafion-H	5/1	170	50	4	0	102
H-Zeolite Y	5/1	200	50	4	0	2
$H_4[SiW_{12}O_{40}]/SiO_2$	12/1	180	10	2	6	380

Pilot scale work showed that the following factors are important for efficient operating this process with the highly active $H_4[SiW_{12}O_{40}]/SiO_2$ catalyst at an optimal temperature of 170 to 200 °C and elevated pressure:[7]

1. Operation with high ethylene/acetic acid feed molar ratio of 10/1 to 14/1.
2. Addition of 3–8 mol% steam to the reactor feed to minimise coke formation on the catalyst surface. This also leads to a reversible formation of ethanol and diethyl ether by-products.
3. Recycle of ethanol and diethyl ether by-products to the reactor.
4. To limit the level of acetaldehyde by-product recycled to the reactor.
5. Protection of the catalyst from ingression of basic impurities (corrosion metal ions, other metal salts, nitrogen containing compounds, etc.).

The reaction is only mildly exothermic and can be carried out in a series of adiabatic fixed beds of catalyst.

In 2001, BP Amoco started commercial production of ethyl acetate in their new plant at Hull, England.

7.2 SELECTIVE OXIDATION

7.2.1 OXIDATION OF METHACROLEIN TO METHACRYLIC ACID

Methacrylic acid has a limited use, but the methyl ester is the most frequently used derivative. In 1995, the world capacity for methyl methacrylate was 2.2 million tonnes per annum. Most methyl methacrylate is used for the manufacture of a crystal-clear plastic Plexiglas®. Acetone cyanohydrin method is still the main commercial route to methacrylic acid derivatives, although it suffers from the overproduction of ammonium bisulfate, the coproduct of this route.[4]

In the 1980s alternative routes to methyl methacrylate were developed to avoid the overproduction of NH_4HSO_4. One of these is the direct oxidation of isobutene to methacrylic acid, with heteropoly acid as a catalyst. This process has been jointly developed by Nippon Shokubai-Sumitomo Chemical and Mitsubishi Rayon and industrialised in 1982 on a scale of over 150000 ton/year of methacrylic acid.[1]

The process consists of two stages, both vapour-phase oxidations: (i) oxidation of isobutene to methacrolein over a Bi-Mo mixed oxide catalyst and (ii) methacrolein to methacrylic acid over heteropoly compounds based on molybdenum, vanadium and phosphorus.

The oxidation of methacrolein to methacrylic acid is carried out in a fixed-bed flow reactor at 270–350 °C, contact time of 2–6 s, with a gas feed consisting of 2–5 % methacrolein, 10–20 % steam and a methacrolein/oxygen molar ratio of 2–4. At a methacrolein conversion of 70–90 %, the selectivity to methacrylic acid is between 80–85 %.

Catalysts used in the commercial processes are reportedly the acidic caesium salts $H_{3+n-x}Cs_x[PMo_{12-n}V_nO_{40}]$ ($2 < x < 3$; $0 < n < 2$). The acidic salts that are nearly stoichiometric are preferred.[1] Caesium and potassium acidic salts of heteropoly acids may be considered as solids consisting of an epitaxial thin film of the heteropoly acid formed on the surface of the stoichiometric caesium or potassium salt.[11–13]

Extensive mechanistic studies show that the oxidation of methacrolein requires a bifunctional catalysis, i.e. both acid-base and redox catalysis (Section 5.2.3).

7.2.2 OXIDATION OF ETHYLENE TO ACETIC ACID

Acetic acid is most commonly manufactured from methanol and carbon monoxide by the Monsanto process.[4] At present, this process accounts for 60 % of the world's production capacity. In the Monsanto process, the selectivities based on methanol and carbon monoxide for the acetic acid production are 99 and 90 %, respectively. Conventionally, rhodium as the catalyst and an iodide as an activator are used for this process. A new version of this process called "CATIVA" which is based on a promoted iridium/methyl iodide catalyst has been developed and commercialised by BP.[7]

Acetic acid is also manufactured by the oxidation of ethylene to acetaldehyde with the Wacker catalyst system $PdCl_2-CuCl_2$ (Section 5.1.1), which is subsequently oxidised to acetic acid with a manganese acetate catalyst.[4] At present this accounts for 22 % of the world production of acetic acid.

$$C_2H_4 + \tfrac{1}{2}O_2 \rightarrow CH_3CHO \qquad (7.2)$$

$$CH_3CHO + \tfrac{1}{2}O_2 \rightarrow CH_3COOH \qquad (7.3)$$

Acetic acid is also produced industrially by the direct liquid-phase oxidation of hydrocarbons like butane and naphtha.[4] This accounts for 9 % of the world's production capacity. Cobalt and manganese acetates are used as catalysts in this process. This process is usually employed when simultaneous manufacturing various acids is desired or when the raw material makes it economically feasible.

Several catalysts have been reported[6] for the direct gas-phase oxidation of ethylene to acetic acid (Table 7.3). All these catalysts are based on palladium, and the selectivity to acetic acid is quite high. None of these catalysts are, however, suitable for the industrial production of acetic acid.

There are two main reaction mechanisms that have been proposed for the direct oxidation of ethylene to acetic acid.[6] The first one involves the hydration of ethylene to ethanol, which is then oxidised to acetic acid.

$$C_2H_4 + H_2O \rightarrow CH_3CH_2OH \qquad (7.4)$$

$$CH_3CH_2OH + O_2 \rightarrow CH_3COOH + H_2O \qquad (7.5)$$

Table 7.3 Catalysts for the direct oxidation of ethylene to acetic acid[6].

Catalyst	Temp. °C	Pressure atm	Selectivity %	STY^a g/l h
$Pd-Cr/Al_2O_3$	180	1	60	–
$Pd-V_2O_5$	248	1	74	2
$Pd-V_2O_5-Sb_2O_5/Al_2O_3$	250	1	84	27
$Pd-H_3PO_4/SiO_2$	150	1	90	56
$Pd-Au-H_2SO_4$/active carbon	150	3.4	85	107

a) Space time yield (g/l-catalyst h)

The catalysts $Pd-H_3PO_4/SiO_2$ and $Pd-Au-H_2SO_4$/active carbon are suggested to follow this mechanism.

In the other route, ethylene is first converted into acetaldehyde by the Wacker type reaction, and the acetaldehyde is then oxidised to acetic acid[6] (eqs 7.2 and 7.3). This mechanism requires the reoxidation of palladium: $Pd^0 \rightarrow Pd^{2+}$. The catalyst systems, such as $Pd-V_2O_5$ and $Pd-V_2O_5-Sb_2O_5/Al_2O_3$, are believed to follow this mechanism, as in these systems the reduced palladium can be oxidised by vanadium(V). Oxygen or air then reoxidises the reduced vanadium. In spite of extensive efforts on the second route, no industrially promising results have been obtained. The first route, through ethanol intermediate, has proved to be more efficient.

Showa Denko developed a one-stage process for the production of acetic acid by direct oxidation of ethylene with O_2 over a catalyst based on a combination of palladium and nonoxidising heteropoly acid $H_4[SiW_{12}O_{40}]$.[6] Illustrative examples of the performance of this system are shown in Table 5.9, Section 5.2.3.4. In this process, acetic acid is manufactured with high selectivity from a mixture of ethylene and oxygen in the vapour phase at 160–210 °C. The reaction is likely to proceed through the acid-catalysed hydration of ethylene to ethanol, followed by the oxidation of ethanol to acetaldehyde catalysed by palladium (eqs 7.4 and 7.5).

The flow chart of this process is shown in Figure 7.2. The product gas from the reactor is cooled to ambient temperature to separate acetic acid and other organic by-products and water from the uncondensed gas. The condensate is separated from the reaction section and led to the crude acetic acid tank, which is connected to the purification system. The uncondensed gas is recycled to the reactor. The crude acetic acid, which is stored in a tank, is sent to the light-ends column. This column separates the light-end by-products, such as acetaldehyde, ethyl acetate, ethanol and others, from acetic acid. Then water is separated by extraction. The acetic acid is further purified to obtain a highly pure acid as the product.

Showa Denko constructed a commercial plant based on the new process with a capacity of 100000 tons/year of acetic acid in Japan. The plant is in operation from 1997.[6]

Compared to methanol carbonylation, the direct oxidation of ethylene has several advantages. The methanol carbonylation requires expensive materials

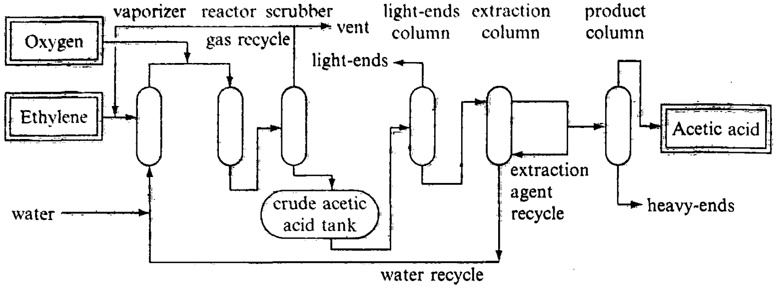

Figure 7.2 Flow chart for the Showa Denko process of oxidation of ethylene to acetic acid.[6] Reprinted with permission from *Catal. Surv. Japan* 1999, **3**, 55. Copyright 1999 Kluwer Academic/Plenum Publisher.

like Hastelloy, due to the highly corrosive catalyst system. The process also requires pure carbon monoxide production. All this necessitates a heavy investment; hence the carbonylation process only becomes feasible on a large scale, more than 200000 tons/year. In contrast, the direct oxidation of ethylene is feasible even for a plant with a half the capacity, i.e. 100000 tons/year.[6]

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8 Other Applications of Polyoxometalates

CONTENTS

Various applications of polyoxometalates are based on their unique physicochemical properties (Table 8.1). These include large anion size and mass,

Table 8.1 Physicochemical properties of polyoxometalates utilised in various applications[1].

Mixed oxide like
Discrete ionic structure
Nanosized anions (diameter, 0.6–4 nm)
Large anion charge (from −3 to greater than −14)
High molecular weight (10^3 – 10^4)
Incorporate over 70 elements inside heteropoly anions
High conductivity of solids
Strong Brønsted acidity
Multielectron redox agents
Photoreducible/oxidisible
Colour of oxidised forms different from colour of reduced forms
High solubility of heteropoly acids in H_2O and polar organic solvents
Transferability of heteropoly anions into nonpolar solvents

Table 8.2 Main applications of polyoxometalates[1,2].

Catalysis
Analytical chemistry
Corrosion resistant coatings
Separations, processing radioactive waste, and sorbents of gases
Membranes
Sensors
Cation exchangers
Dyes and pigments
Electrooptics
Electrochemistry, electrodes, fuel cells, and capacitors
Dopants in sol–gel and polymer matrices
Flammability control
Medicine

electron- and proton-transfer abilities, high Brønsted acidity of the corresponding acids, solubility and extractability, etc. Among the applications of polyoxometalates, catalysis is by far the most important (Chapter 7). About 80–85% of the patent and applied literature on polyoxometalates is relevant to their catalytic properties.[1] Other uses include many fields such as chemical and biochemical analysis, new materials with advanced characteristics, electrochemistry and electrochemical devices, protection from corrosion, medicine, etc. (Table 8.2). The easier available and better-studied Keggin type polyoxometalates dominate in the applications. Other structural types attract an increasing interest as well. The various uses of polyoxometalates have been reviewed by Katsoulis[1] and by Pope and Müller.[2,3] Some of the applications, other than catalysis, are briefly discussed in this chapter.

8.1 ANALYTICAL CHEMISTRY

Polyoxometalates have long been used for elemental analysis and determination of biomaterials. This is mainly based on properties of polyoxometalates such as their high molecular weight, reducibility to form coloured species (heteropoly blues), and the variety of elements that can be incorporated in polyanions. Only through heteropoly molybdate formation can some 26 elements be determined.[4]

8.1.1 ELEMENTAL ANALYSIS

Table 8.3 shows some illustrative examples of elemental analyses using polyoxometalates. The most widely used is the analysis of P and Si.[4] This is based on the incorporation of the element in a heteropoly anion followed by its determination either gravimetrically or by spectroscopic or electrochemical

Table 8.3 Elemental analysis based on polyoxometalate chemistry[1].

Element	Method
Si	Voltammetry, $SiMo_{12}$; polarography, $SiMo_{12}$; photometry, $SiMo_{12}$ blue
P	Spectrophotometry, PMo_{12} reduced by ascorbic acid
As	Spectrophotometry, reduced Mo–Sb–As complex
Ge	Spectrophotometry, $GeMo_{12}$
Sn	Spectrometry, after reduction of $SiMo_{12}$ by Sn(II)
Al	Spectrophotometry, an ion-association complex of molybdoaluminium heteropoly acid with crystal violet
Ti	Spectrophotometry, as ion-association complex of molybdotitanophosphoric acid with Nile Blue
V	Spectrophotometry, $[PW_{11}V^{IV}O_{40}]^{5-}$; photometry, vanadomolybdophosphate
Cu	Spectrophotometry, based on Cu(II) catalytic effect on PMo_{12}/I redox reaction
Mo	Spectrophotometry, tungstomolybdophosphate blue
W	Spectrophotometry, tungstomolybdovanadophosphate
Nb	Spectrophotometry, ion-associated complex of molybdoniobate with crystal violet in PVA and arabic gum
Hf	Spectrophotometry, ion-associated complex of molybdolanthanohafnic acid with Nile Blue in PVA
Zr	Spectrophotometry, an ion-associated complex of zirconomolybdic acid with Nile Blue in PVA
Sc	Spectrophotometry, an ion-associated complex of molybdoscandic acid with Nile Blue in PVA
Th	Spectrophotometry, an ion-associated complex of molybdothoric acid with Nile Blue in PVA
Y	Spectrophotometry, using Nile Blue, MoO_4^{2-}, and PVA
Te	Spectrophotometry, an ion-associated complex of molybdotelluric acid with butylrhodamine B in PVA
Ta	Spectrophotometry, an ion-associated complex of molybdotantalic acid with Nile Blue in PVA
Hg	Colorimetry, with dithizone in the presence of PW_{12}
Bi	Spectrophotometry, molybdobismuthophosphoric acid, reduction with ascorbic acid
Au	Kinetic spectrometric method using the reduction of PMo_{12} by formic acid
Tl	Precipitation with PW_{12} and n-Bu_4NBr, redissolution of precipitate in alkaline solution and determination of Tl by spectrophotometry
Sb	Spectrophotometry, ternary HPA Sb–As–Mo–ascorbic acid
S	Spectrophotometry, after conversion to sulfide form; an HPA is used as reagent

techniques after reduction to heteropoly blues. Some of these techniques allow determination of nanomolar concentrations of P or Si in solutions.[1,2]

Polytungstates have long been employed as imaging agents for electron microscopy.[5]

8.1.2 ANALYSIS OF BIOMATERIALS

Clinical chemists routinely use polyoxometalates to analyse various biomaterials such as proteins, alkaloids, drugs, etc.[2,6] These analyses are based on the well-known ability of polyoxometalates to coagulate proteins and precipitate many bioactive organic molecules. Some examples are shown in Table 8.4. The methods involve gravimetry, spectrophotometry after reduction to blues, thin layer chromatography, etc. (for a review, see[6]).

8.2 SEPARATION

8.2.1 PROCESSING OF RADIOACTIVE WASTE

There is considerable analytical and patent literature on the use of polyoxometalates for the processing of radioactive nuclei.[1] Macrocyclic crown ethers and heteropoly acids were claimed to extract caesium ions[7] from aqueous solutions. ^{134}Cs and ^{137}Cs are usually present in small quantities in radioactive aqueous waste. Their presence makes solidification of this waste difficult because they evaporate to a noticeable degree and leach out of the solid products which are intended for permanent storage such as, e.g., cement or bitumen blocks. Solid adducts of $H_n[XM_{12}O_{40}]$ (X = Si, P; M = Mo, W) with crown ethers were prepared by mixing the two components in a crown ether/POM molar ratio of 0.5:1–2:1 in a solvent like acetone. The preferred crown ethers were benzo-15-crown-5, dibenzo-21-crown-7, and dibenzo-30-crown-10. Ion exchangers were prepared when the solid adduct was formed in the presence of alumina or silica gel. These ion exchangers were claimed to remove Cs^+ from waste solutions. Crown ether/POM adducts were used to extract Cs^+ from aqueous solution into nitrobenzene or nitromethane.[8] It was demonstrated that more than 99% of caesium can be extracted in nitrobenzene. Another method claimed to separate Cs^+ from radioactive waste by precipitation with $H_3[PM_{12}O_{40}]$ (M = Mo or W), followed by ammonium hydroxide treatment to dissolve the precipitate and subjecting it to an electric field. The cathode solution contained all the Cs as CsCl with less than 1% of P or Mo.[9]

Table 8.4 Analysis of biomaterials using polyoxometalates[6].

Sample	Substance	Method
Whole blood	Si	spectrophotometry, $SiMo_{12}$ blue
Blood serum	Si	spectrophotometry, $SiMo_{12}$ blue
Blood urine	As	spectrophotometry or nephelometry, $AsMo_{12}$ blue
Biosolutions	uric acid uric acid	spectrophotometry, $SiMo_{12}$ blue gravimetry, PMo_{12}
Cell nuclei	histones	spectrophotometry, PMo_{12} blue
Animal tissues	cocaine amidopyrine	thin layer chromatography, PMo_{12} in ethanol gravimetry, $SiMo_{12}$

Other separations of radioactive nuclei with the use of polyoxometalates include Sr,[10,11] U,[12] Np and Pu.[13]

8.2.2 SORPTION OF GASES

Solid polyoxometalates have been claimed as sorbents of gases for environmental protection. Most applications of polyoxometalates have dealt with the removal of flue gases, treatment of toxic organic compounds, removal of amines and mercaptans, etc.[1] Keggin heteropoly acids and salts were used to adsorb flue gases, such as NO_x, SO_2, and CO_2.[14] A complex catalyst system including $H_3[PM_{12}O_{40}]$ (M = Mo or W) was used for the decomposition of toxic organic compounds in gases from incineration of municipal refuse.[15] Keggin heteropoly acids were also used as absorbents for H_2S, the final products being sulfur, heteropoly blue and water. The heteropoly blue was reoxidised with the use of oxidants such as NO_2, Fe^{3+}, Cl_2, etc.[16] $H_3[PMo_6W_6O_{40}]$ on a porous support was used for the purification of vent air from odorous components, such as amines and mercaptans.[17] A catalytic converter for the reduction NO_2 to NO in polluted air or flue gases with the use of $H_3[PMo_{12}O_{40}]$ was described.[18] Insoluble heteropoly salts and polyalkylene glycols were claimed as sorbents for Ra gas.[19]

8.3 CORROSION-RESISTANT COATINGS

Metal surfaces are commonly protected from corrosion using corrosion inhibitors such as chromates, phosphates, or silicates. These compounds form a corrosion-resistant coating on the metal surface by adsorption and/or formation of an oxide layer. Although toxic, the chromates are efficient corrosion inhibitors, known as anodic passivating inhibitors.[1]

Many reports on the use of polyoxometalates as corrosion inhibitors have been published (for a review, see[1]). Polyoxometalates are generally less toxic than the chromates. Their easy redox transformations without major structural changes and the formation of insoluble salts with large cations make them promising oxidising and film-forming corrosion inhibitors.

Polyoxometalates have been studied for corrosion inhibition of aluminium and its alloys in aqueous media at high temperatures.[20] Such alloys are used in atomic industry, and therefore a corrosion inhibitor should have high radiation stability. In the presence of isopoly or heteropoly tungstates, such as $(NH_4)_{10}[H_2W_{12}O_{42}]$ or $(NH_4)_6[P_2W_{18}O_{62}]$ (100 g/l), the rate of corrosion decreased significantly, factor of ten compared to that in pure water at 250 °C. However, the $[PMo_{12}O_{40}]^{3-}$ anion increased the rate of corrosion which was attributed to the instability of this polyanion in dilute solutions. XPS studies showed the presence of W^{6+} and W^{5+} in the film. Apparently, the reduction of W^{6+} to W^{5+} was caused by Al^0. Similarly, when molybdophosphates were used, molybdate was incorporated in the film, with Mo^{6+} reduced to Mo^{5+}. The nature of the polytungstate film remains unknown. Aluminium-containing heteropolytungstates might have formed in the film.

Polyoxometalates were reported as corrosion inhibitors for other metals such as zinc and galvanised steel. The common Keggin type heteropoly acids, $H_n[XM_{12}O_{40}]$ (X = P, Si; M = Mo, W), were tested as passivators for zinc plating, the most efficient acid being $H_3[PMo_{12}O_{40}]$.[21]

Asahi Chemical Industry claimed[22] that stainless steel showed high corrosion resistance after treatment with a 10% sulfuric acid solution containing 100 ppm $H_3[PMo_{12}O_{40}]$ for a short time at 100 °C. As discussed in Chapter 7, $H_3[PMo_{12}O_{40}]$ is used as the catalyst for the Asahi Chemical Industry process of liquid-phase hydration of isobutene. The lower corrosion activity of the heteropoly acid as compared to conventional mineral acids is the important advantage of this process.[23]

Interestingly, molybdovanadophosphates were reported to inhibit corrosion of steel St3 (mild steel) in a solution containing 150 mg/l Cl^- and 540 mg/l SO_4^{2-} at 40 °C during 100 h.[24,25] Since these polyoxometalates are widely used as catalysts for selective oxidation in liquid phase (Chapter 5), their passivating ability would be an important value-adding contribution to their catalytic properties.

Salts of polyoxometalates with organic cations, e.g. quaternary ammonium cations, which themselves are known as a class of corrosion inhibitors, were claimed to exhibit good anticorrosive properties.[26]

Little is known so far about the mechanisms of corrosion inhibition by polyoxometalates. Significant ongoing research should increase the understanding of these effects and help to develop and improve the inhibitors based on polyoxometalates.

8.4 POLYOXOMETALATES AS ADDITIVES TO INORGANIC AND ORGANIC MATRICES

8.4.1 ADDITIVES IN SOL–GEL MATRICES

Polyoxometalate additives can be introduced in inorganic matrices by sol–gel methods that are now widely used for the preparation of inorganic designer materials.[27,28] The primary application of these composite systems is in coatings where characteristics such as optical properties, adhesion, hardness and abrasion resistance are of great importance. Common inorganic matrices are usually derivatives of Al, Si, Ge, Ti, or Zr alkoxides and, to a lesser extent, of Sn, Pb, or Nb alkoxides.[27,28]

Using sol–gel techniques, polyanions such as $[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$, or $[W_{10}O_{32}]^{4-}$ were included into gel matrices.[29] This led to ionic conductors, also possessing electrochromic and photochromic properties.

Siloxane coatings on steel were made by the hydrolysis/condensation of alkoxysilanes and/or silanols in the presence of a heteropoly acid, e.g. $H_4[SiMo_{12}O_{40}]$.[30] These siloxane coatings showed good adhesion and water-repellent properties as well as self-cleaning characteristics. Siloxane-POM coatings were reported to exhibit antistatic properties.[31]

Stable insoluble $H_3[PW_{12}O_{40}]$/titania gels were claimed to have electrochromic properties and ionic conductivity.[32] Their electrochromic properties were attributed to the titania gels and their conductivity to the presence of polyoxometalates. Proton conductive solid materials were obtained by doping heteropoly acids into the amorphous oxide matrixes of elements such as B, Al, Si, Ge, Sn, P, Ti, or Zr.[33] Some doped oxides were claimed as solid electrolytes for fuel cells.[34]

The POM-doped gels may find applications in solid-state electrochromic displays and windows for reliable light control for buildings and automobiles.[1]

8.4.2 ADDITIVES IN POLYMER MATRICES

The incorporation of polyoxometalates into organic matrices of conductive polymers has attracted considerable interest. The materials thus obtained are useful as solid catalysts for chemical and electrochemical redox processes in liquid phase, as well as electrodes, sensors, etc. The organic matrices include conductive polymers such as polypyrrole, polythiophene, polyaniline, poly(1-naphthol), or poly(*p*-phenylene). The incorporation of polyoxometalates typically involves the chemical or electrochemical oxidation of polymerisable monomer in the presence of a polyoxometalate solution. The POM-doped polymer can be deposited on electrodes (e.g. carbon or graphite) and used in electrochemical catalysis.[1] Table 8.5 lists some examples of POM-doped conductive polymers and their applications.

Polyoxometalates are also incorporated in organic nonconductive polymer matrices to form composite materials. Such composites are claimed to have advanced optoelectronic properties due to the presence of polyoxometalates. The polymers include polyvinyl alcohol, butadiene–styrene rubber, epoxide resins, etc.[1] For example, a photochromic recording material consisting of (γ-glycidoxypropyl)trimethoxysilane/$H_4[SiW_{12}O_{40}]$ on a polyacrylate plate was patented. Information was recorded by irradiation with light and erased by exposing the coated surface to air or oxygen.[42]

Table 8.5 Polyoxometalate-doped conductive polymers.

POM	Polymer	Application	Ref.
$[H_2W_{12}O_{40}]^{6-}$	Polypyrrole	Proton permeability	[35]
$[PMo_{12}O_{40}]^{3-}$	Polypyrrole	Electrocatalytic reduction of O_2 and ClO_3^-	[36]
$[PMo_{12}O_{40}]^{3-}$	Poly (5-amino-1-naphthol)	Detection of catecholamines, chemical polymerisation, electrocatalysis	[37--39]
$[SiW_{12}O_{40}]^{4-}$	Polyaniline	Electrocatalytic reduction of ClO_3^-, BrO_3^-	[40]
$[P_2W_{18}O_{62}]^{6-}$	Polypyrrole	Catalysis of O_2 reduction	[41]
$[Dy(SiMo_{11}O_{39})_2]^{13-}$	Polypyrrole	Electrocatalytic reduction of ClO_3^-, BrO_3^-	[35]

8.5 MEMBRANES

Much ongoing research concentrates on the development of new membranes that include polyoxometalates as conductive components. These studies exploit the high ionic conductivity of polyoxometalates, especially their acid forms, in the solid state. These membranes are commonly used in various electrochemical devices such as electrolytic (fuel) cells, selective electrodes, gas sensors, etc.

8.5.1 FUEL CELLS

Solid hydrated heteropoly acids and their salts exhibit extremely high protonic conductivity.[43] Their conductivity is comparable to that of conventional liquid electrolytes (Table 8.6), with much easier handling compared to the liquid systems. This property has been used for designing electrochemical cells.[44,45]

The heteropoly acid plates were demonstrated to function effectively as solid separators between the anode and cathode chambers of H_2/O_2 fuel cells, with Pt or Pd as a catalyst (Figure 8.1).[44,45] They allowed the selective permeation of protons from the anode to the cathode chamber, probably through hydrogen bonded networks facilitated by solvent molecules. The electrons generated by the oxidation were supplied into the anode by an external circuit. The O^{2-} produced by reduction of O_2 combined with the arriving protons to form H_2O. This device could be used for measuring partial pressure of H_2 or O_2. The electrolytic generation of H_2 from steam using a sheet of polycrystalline $H_3[PMo_{12}O_{40}]\cdot 30H_2O$ as a solid separator was patented.[46] Limitations of these cells are the strong influence of humidity on their protonic conductivity, diffusional problems, and the high ionic resistance associated with excessive electrolyte thickness.

Other types of liquid and solid fuel cells based on heteropoly acids have been described in the literature.[1]

Table 8.6 Specific resistance of polyoxometalate plates at room temperature[a,45].

Compound	Specific resistance, Ω · cm
$H_3[PMo_{12}O_{40}]\cdot 30H_2O$ single crystal	5
$H_3[PMo_{12}O_{40}]\cdot 30H_2O$	11
$H_3[PW_{12}O_{40}]\cdot 30H_2O$ single crystal	7
$H_3[PW_{12}O_{40}]\cdot 30H_2O$	12
$(NH_4)_3[PMo_{12}O_{40}]\cdot 3H_2O$	21
$K_3[PMo_{12}O_{40}]\cdot 6H_2O$	22
$Na_3[PMo_{12}O_{40}]\cdot 21H_2O$	17
$(NH_4)_3[PW_{12}O_{40}]\cdot 3H_2O$	20
$K_3[PMo_{12}O_{40}]\cdot 6H_2O$	20
$Na_3[PW_{12}O_{40}]\cdot 21H_2O$	19
$H_4[SiMo_{12}O_{40}]\cdot 26H_2O$	12
$H_4[SiMo_{12}O_{40}]\cdot 22H_2O$	24
$Na_4[SiW_{12}O_{40}]\cdot 30H_2O$	13
$Na_4[SiW_{12}O_{40}]\cdot 22H_2O$	22
$H_5[BW_{12}O_{40}]\cdot 30H_2O$	13
$K_6[P_2W_{18}O_{62}]\cdot 14H_2O$	123
$Na_5[W_6O_{24}]\cdot 8H_2O$	235
$ZrO_2 - CaO$ (solid solution)	10000 (600 °C); 40 (1000 °C)
β-Al_2O_3	700 (RT); 14 (300 °C)

a) The plates, 15 mm × 15 mm × 2 mm, prepared under pressure of 1000 atm; specific resistance measured at an AC frequency of 1 kHz

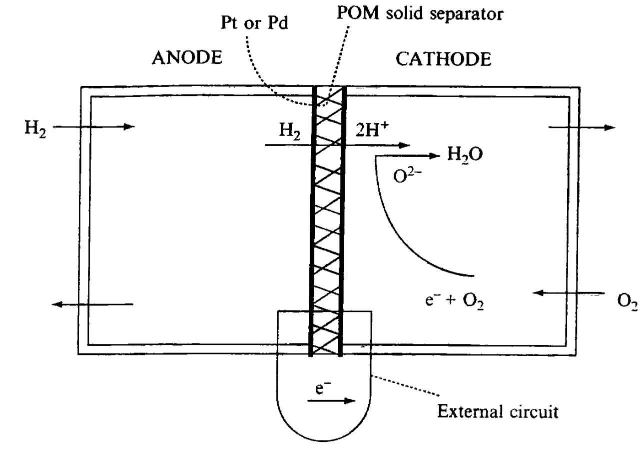

Figure 8.1 Schematic representation of an electrochemical cell utilising a polycrystalline heteropoly acid as a solid separator.[1] Reprinted with permission from *Chem. Rev.* 1998, **98**, 359. Copyright 1998 American Chemical Society.

8.5.2 SELECTIVE ELECTRODES

Many ion-selective electrodes based on polyoxometalates and polyvinyl chloride (PVC) have been developed.[1] The electrodes based on $H_3[PW_{12}O_{40}]$ and crown ethers (e.g. 18-crown-6) precipitated on a PVC membrane showed good selectivity for organic ammonium ions such as $BuNH_3^+$, $C_6H_5CH_2NH_3^+$, $Et_2NH_2^+$, and Et_3NH^+ within the concentration range of $10^{-1} - 10^{-5}$ M.[47] POM-based ion-selective membrane electrodes for determination of Al^{3+}, Ga^{3+}, and Pb^{2+} were reported.[48,49]

8.5.3 GAS SENSORS

Membranes made of water-soluble organic polymers, such as polyvinyl alcohol, polyethylene oxide, polyethylene glycol, cellulose acetate, etc., and heteropoly acids or salts were used in gas sensors. Specifically, they were used for the detection of hydrogen and gaseous compounds capable of dissociating into or combining with hydrogen ions.[50]

The reversibility of heteropoly acid redox transformation was exploited to develop a solid-state optical sensor for CO.[51] The sensor included a Pd(II), Ru(VIII) or Os(VIII) compound as a catalyst for the oxidation of CO to CO_2, a polyoxometalate (e.g. heteropoly molybdate) that reoxidised the catalyst and an Fe(III), Cr(VI) or Ce(IV) complex that reoxidised the polyoxometalates. The redox chemistry involved is quite similar to that discussed in Chapter 5 for the catalytic selective oxidation.

8.6 POLYOXOMETALATES IN MEDICINE: ANTIVIRAL AND ANTITUMORAL ACTIVITY

Many polyoxometalates have been shown to be biologically active. Two types of activity, antiviral and, to a lesser extent, antitumoral, have dominated the medicinal chemistry of polyoxometalates to date (for a recent review, see[52]).

The antiviral activity of polyoxometalates was reported as early as 1971 when Raynaud *et al.*[53] found that heteropoly tungstosilicates inhibited murine leukemia sarcoma virus *in vitro*. Further studies of various groups showed the effectiveness of these polyoxometalates against several viruses such as vesicular stomatitis, polio, rubella, Rauscher leukemia, rabies, etc.[52] One particular heteropolytungstate, HPA-23 of formula $(NH_4)_{17}Na[NaSb_9W_{21}O_{86}]$, that exhibited promising results *in vitro*,[54] was used for treatment of AIDS patients in France and the USA. Later on, the drug was found unacceptable because of its marked toxicity and insufficient antiviral activity.[55,56] These results encouraged several groups to develop less toxic and more efficient second-generation POM antiviral agents that could be effective against HIV.

The mechanism of antiviral activity of polyoxometalates remains unknown. There is strong evidence that polyoxometalates can penetrate cell membranes and localise intracellularly.[52] Reasons for biological activity of polyoxometalates may include ionic size and charge, electron-transfer properties, behaviour of polyanions in extremely dilute solutions at physiological pH, etc.

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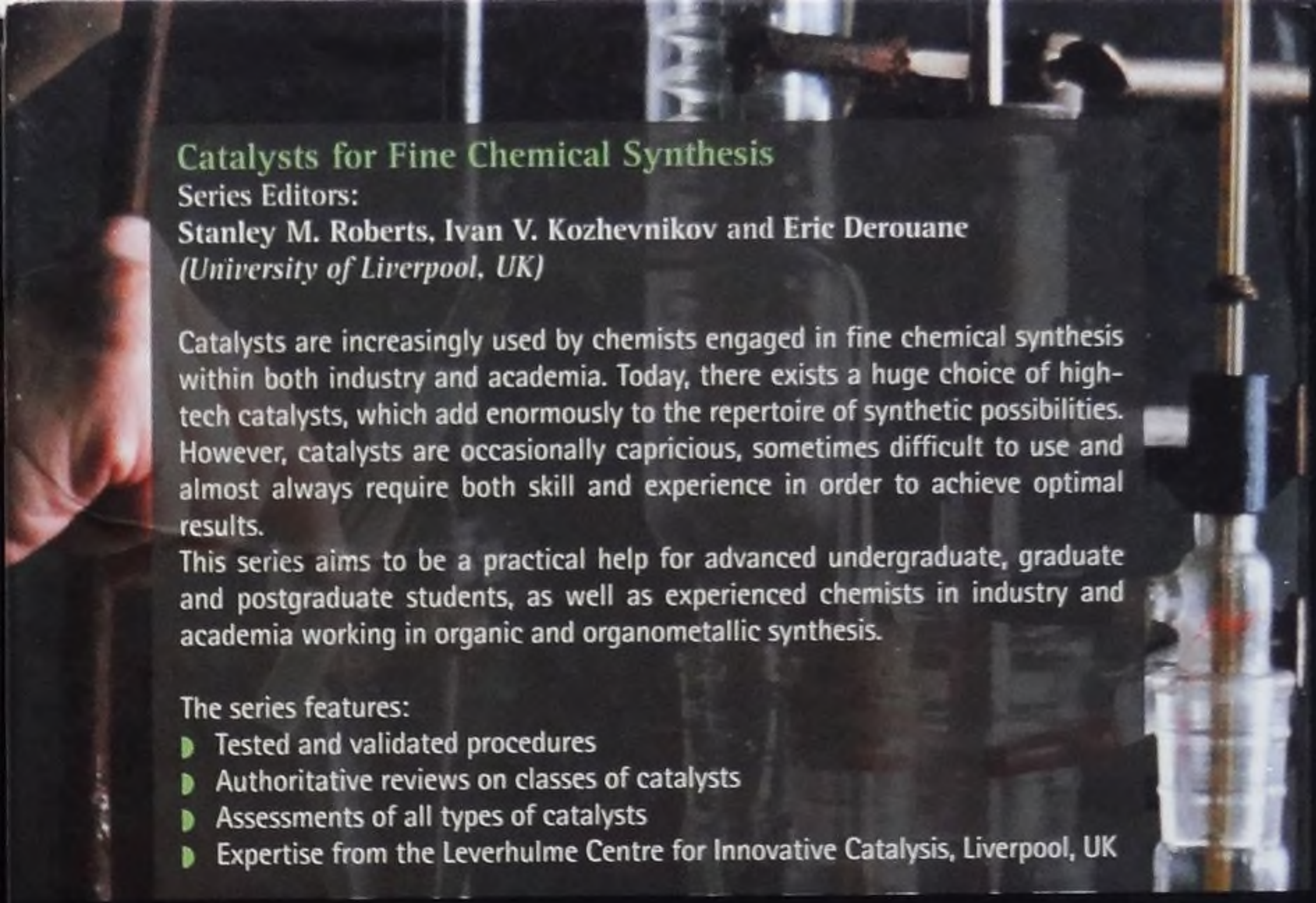

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