

# Catalysis by Polyoxometalates

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Catalysts for Fine  
Chemical Synthesis

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Volume 2

# Catalysis by Polyoxometalates

Ivan Kozhevnikov

*University of Liverpool, UK*



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# Catalysts for Fine Chemical Synthesis

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Volume 2

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# Catalysts for Fine Chemical Synthesis

## Series Preface

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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  
I. KOZHEVNIKOV  
E. DEROUANE  
LIVERPOOL, 2002**

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# Preface for Volume 2: Catalysis by Polyoxometalates

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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

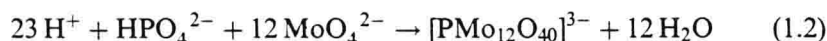
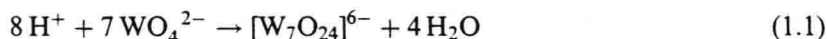
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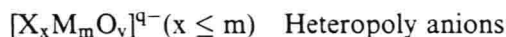
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### 1.1 SCOPE AND DEFINITIONS

Polyoxometalates belong to a large class of nanosized metal–oxygen cluster anions.<sup>[1,2]</sup> 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.



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:<sup>[1,2]</sup>



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.<sup>[2]</sup> 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  $\pi$  bonding.<sup>[2]</sup>

## 1.2 NOMENCLATURE

A systematic nomenclature of polyoxometalates has been developed.<sup>[2,3]</sup> 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.<sup>[2]</sup> 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 counteranions before the heteroatoms; the heteropoly anion is placed in square brackets and thus separated from the counteranions, 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 counteranions 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<sup>[4]</sup> discovered the first heteropoly salt, ammonium 12-molybdophosphate. Later on in 1848, Svanberg and Struve<sup>[5]</sup> 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,<sup>[6]</sup> Miolati,<sup>[7]</sup> Rosenheim,<sup>[8]</sup> and Pauling<sup>[9]</sup> 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  $\text{H}_3[\text{PW}_{12}\text{O}_{40}] \cdot 5\text{H}_2\text{O}$ .<sup>[10]</sup> This structure, now named after its discoverer, contained 12  $\text{WO}_6$  octahedra linked by edge and corner sharing, with the heteroatom occupying a tetrahedral hole in the centre. In 1948, Evans<sup>[11]</sup> determined the structure of another widespread type – the Anderson's heteropoly anion (6:1 series) – by single-crystal X-ray analysis of  $[\text{Te}^{6+}\text{Mo}_6\text{O}_{24}]^{6-}$  salts; this structure is now often referred to as the Anderson-Evans structure. In 1953, Dawson<sup>[12]</sup> reported the next new structure (now frequently referred to as the Wells-Dawson's) of a 18:2 heteropoly anion  $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ . This structure was shown to be closely related to the Keggin structure. In 1968, Dexter and Silverton<sup>[13]</sup> reported the X-ray structure of  $[\text{Ce}^{4+}\text{Mo}_{12}\text{O}_{42}]^{8-}$  and showed the large Ce heteroatom to be in a  $\text{CeO}_{12}$  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<sup>[14]</sup> 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.<sup>[15]</sup> Among them, salts of giant heteropoly anions such as  $[\text{La}_{16}\text{As}_{12}\text{W}_{148}\text{O}_{524}]^{76-}$  (ion mass ca. 40000, diameter 40 Å) and others were prepared and characterised by Müller *et al.*<sup>[16]</sup> 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<sup>[1,17]</sup> and Pope<sup>[2]</sup> and also by Nikitina<sup>[18]</sup> and a large number of review articles, for example Ref.<sup>[15,19–26]</sup> 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.<sup>[27,28]</sup>



## 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.<sup>[29]</sup> 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.<sup>[30]</sup>

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.<sup>[31,32]</sup> 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,