

New progress of Keggin and Wells–Dawson type polyoxometalates catalyze acid and oxidative reactions

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Abstract

Polyoxometalates (abbreviated as POMs) are useful acids and oxidation catalysts in various reactions since its catalytic features can be controlled at a molecular level. This review summarizes some recent research progress in catalytic application of Keggin and Wells–Dawson type polyoxometalates. Particular attention is given to most developments of our recent studies on the use of POMs as heterogeneous and homogeneous catalysts for the selective oxidation and acid-catalyzed reactions.

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1. Introduction

Polyoxometalates (POMs) are metal-oxo anionic clusters whose chemical properties can be controlled by transition metal substitution and the counteraction used. The number of publications and patents pertaining to POMs continues to grow. Among numerous applications of POMs, catalysis is by far the most important. Presently, over 80% of the patents concerning with POMs application is related to catalysis [1].

POMs have been found wide applications in many fields such as catalysis, medicine, magnetic properties, materials, surface chemistry and photochromism and electrochromism owing to the so-called “value-adding properties”. Thus, on the one hand, combined with their ability to donate and accept electrons and their stability over a wide range of conditions, makes them attractive targets for catalysis; on the other hand, does them economically and environmentally attractive in both academic and industrial significance as useful acids and/or oxidation catalysts in various organic reactions since their catalytic features can be controlled at a molecular level [2–4]. In many cases,

molecular oxygen or H₂O₂ can be used as the oxidizing agent, which qualifies these as green reagents with POMs. Here we focus on catalytic application of POMs, particularly for some latest developments on the use of Keggin and Wells–Dawson type POMs as heterogeneous and homogeneous catalysts for the acid-catalyzed reactions and selective oxidation of hydrocarbons based on our group’s research.

2. Properties and catalysis of polyoxometalates

2.1. Structure and feature

POMs are coordination compounds containing more than two metal atoms, which are generally formed from simple inorganic salts via condensation, and are anionic d⁰ metal–oxygen clusters which consist of isopoly anions containing only one metal and heteropoly anions that are the larger, more studied and useful class of compounds. Two main types of structures of heteropoly-metalate are shown in Fig. 1. Each black ball represents a metal atom in the center of the octahedron, and each corner represents an oxygen atom in the structure [5]. Heteropoly anions have central heteroatom(s), typically tetrahedral, about which the metal-oxo framework is built [6]. The major structure is known as the Keggin structure which is roughly spherical and

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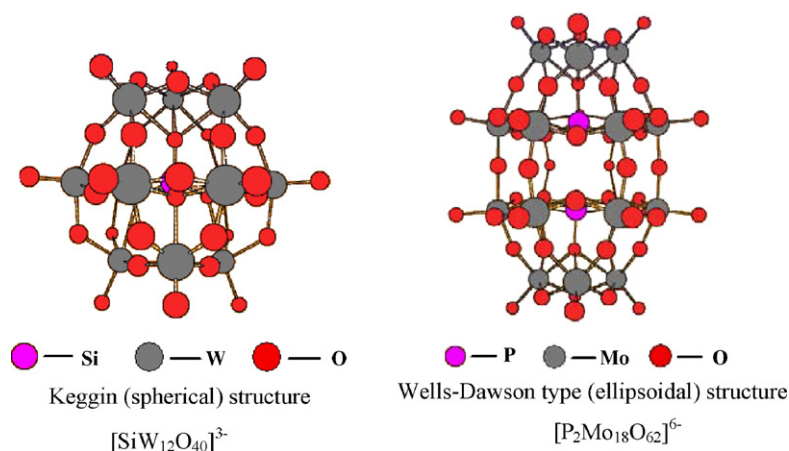


Fig. 1. The structure of Keggin and Wells–Dawson type anion [4].

gives a general formula of XM_{12} , where X is the heteroatom and M is the d^0 metal. Each corner of the heteroatom tetrahedron is associated with an M_3O_{13} unit. An anion $\text{SiW}_{12}\text{O}_{40}^{3-}$ (Fig. 1) can be obtained by acidifying the mixed solution of metasilicate and tungstate with a molar ratio of 1:12. The Si atom is called the heteroatom, while the W atoms are called the addenda atoms which are coordinated octahedrally by oxygen atoms and can be substituted by other metal atoms. Three WO_6 of octahedron unit form a triplet M_3O_{13} by sharing octahedral edges, and four such triplets share the octahedral vertexes and arrange tetrahedrally around the heteroatom Si, that is, the three-fold shared oxygen atoms in the triplet M_3O_{13} are coordinated to a Si atom, resulting in a Td symmetric polyoxometalate. In fact, more than 70 elements in the periodic table may act as the constituents of POMs.

Another structure is the Wells–Dawson type structure that is ellipsoidal, of formula X_2M_{18} [6,7]. This structure consists of two heteroatoms stacked one atop the other, and each end is composed of an M_3O_{13} cap, with two six-metal belts circling the molecule. Under basic conditions, the POM structure can lose an $\text{M}=\text{O}$ unit and become what is known as a lacunary species. This species acts as a pentadentate ligand for transition metals that can be substituted into the POM structure. These metals (not d^0) are known as addenda atoms. POMs can be made to be mono-, di- and tri-lacunary. This allows the synthesis of a wide array of compounds. Lacunary species can share addenda atoms forming sandwich compounds, with a POM structure on the top and bottom joined by addenda transition metals.

It is attractive that solid POMs have hierarchical structure (the example shown as Fig. 2) [8], which are important for the understanding of the heterogeneous POM catalysis process. The primary structure is the structure of heteropoly anion itself, i.e. the metal oxide cluster. The secondary structure is the three-dimensional arrangement consisting of polyanions, counter cations and additional molecules. The tertiary structure represents the manner in which the secondary structure assembles into solid particles and relates to properties such as particle size, surface area and pore structure.

2.2. Properties and catalysis

Based on POMs' hierarchical structure, it can be demonstrated that there are three completely different modes of catalysis for solid POMs: surface-type catalysis, pseudo-liquid bulk-type catalysis and bulk-type catalysis in the presence of electrons or protons (Fig. 3) [9]. Surface-type catalysis (a) is ordinary heterogeneous catalysis that takes place on the solid surface (two-dimensional reaction field on outer surface), (b and c) represent bulk-type catalysis where the reaction fields are three-dimensional in contrast to the surface-type catalysis. When the diffusion of reactant molecules in the solid (diffusion in the lattice rather than pores) is faster than the reaction, the solid bulk forms a pseudo-liquid phase in which catalytic reaction can proceed (Fig. 3 (b)). In the pseudo-liquid phase the catalysts appear as solids but behave like liquids (solvent). As the active sites in the solid bulk, e.g. protons, take part in catalysis, the very high catalytic activities are often observed in the bulk phase [9,10]. Due to the flexible nature of the solid structure of some POMs (variable secondary structure), reactant molecules having polarity or basicity are readily absorbed into the solid lattice (between the polyanions in the lattice, sometimes expanding the lattice) and react therein. In other words, the reaction field becomes three-dimensional like reactions in solution. Owing to this behaviour, POMs catalysts often exhibit high catalytic activities and unique selectivity [4].

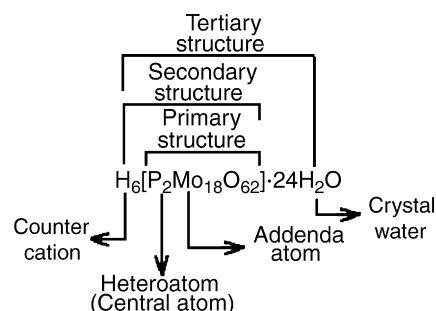


Fig. 2. Primary, secondary and tertiary structure of Wells–Dawson POM.

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