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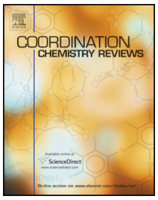

Review

Environmentally benign polyoxometalate materials

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ABSTRACT

Polyoxometalates (POMs) are a class of versatile and discrete anionic metal oxides in groups 5 and 6. POMs have unique physical and chemical properties, e.g., strong Brønsted acidity, strong oxidizing agents, an unmatched range of molecular structures, efficient adsorbents, green catalysts, and redox activity. These properties have been utilized in the design of multifunctional POM materials with the ability to address different environmental issues, such as toxic gas sequestration, wastewater decontamination, fine chemical production, corrosion, and radioactive waste processing. In this study, we discuss the chemical mechanisms that involve POMs, and which have been used to solve important environmental problems. Understanding of these mechanisms will facilitate the design and synthesis of more environmentally benign POM-containing materials to solve various environmental problems.

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1. Introduction

Polyoxometalates (POMs) are a class of discrete anionic metal oxides in groups 5 and 6. They are constructed *via* the condensation of metal oxide polyhedra (MO_x, M = W^{VI}, Mo^{VI}, V^V, Nb^V, Ta^V, etc., and $x = 4–7$) with each other in a corner-, edge-, or rarely in a face-sharing manner [1–7]. The metal atoms are referred to as addenda atoms. The atoms that can function as addenda include those that can change their coordination with oxygen from 4 to 6 because the MO_x polyhedra condense in solution upon acidification [6,7]. Although oxygen is the main ligand that coordinates with the addenda atoms, other atoms/groups such as sulfur, bromine, nitrosyl, and alkoxy have been substituted in some previously reported POM clusters [8,9].

When the POM frameworks exclusively contain the addenda metals (from groups 5 and/or 6) and oxygen, the clusters are called isopolymetalates, such as the Lindqvist type anion $[M_6O_{19}]^{2-}$ (Fig. 1). When the POMs include additional elements as well as the addenda metals and oxygen, they are known as heteropoly complexes, which can be formed *via* the condensation of MO_x polyhedra around a central heteroatom when the solution is acidified [6,7,10]. Many different elements can act as heteroatoms in heteropoly complexes with various coordination numbers: 4-coordinate (tetrahedral) in Keggin and Wells-Dawson structures (e.g., PO_4^{3-}, SiO_4^{4-}, and AsO_4^{3-}); 6-coordinate (octahedral) in Anderson-Evans structures (e.g., $Al(OH)_6^{3-}$ and TeO_6^{6-}); and 12-coordinate (Silverton) in $[(UO_{12})Mo_{12}O_{30}]^{8-}$. Fig. 1 shows some classical POM structures in polyhedra representations. Further details of the chemistry of POMs have been summarized in various books, reviews, and thematic issues [10–20], including books by Pope and Müller [10–13], a review by Pope and Müller [14], thematic POM issues in *Chemical Reviews*, *Chemical Society Reviews, and Dalton Transaction* [2,15,16], and several contributions in *Coordination Chemistry Reviews* [17–20].

POMs have been used in the design of various multifunctional materials with different techniques [3,15]. These POM-based multifunctional materials have been used to solve different emerging issues [15,16]. Their contributions to handling environmental problems such as toxic gas sequestration, wastewater decontamination, fine chemical production, corrosion, and radioactive waste processing are particularly important. Since the 1998 thematic review of POMs [15], there have been tremendous developments, including the synthesis of new multifunctional materials, solutions to diverse environmental problems, and a better understanding of the working mechanisms due to improved instrumentation. This review article highlights the recent progress in solving environmentally related problems using POM-based functional materials. Importantly, a better understanding of the working mechanisms of the chemical processes in these reactions may facilitate the rational design of new multifunctional POM materials and solutions to other important environmental problems.

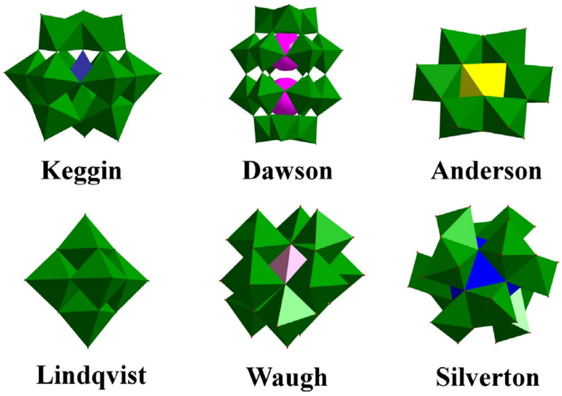

Fig. 1. Classical POM structures in polyhedral representations.

2. Chemical properties of POMs

Most POMs, such as $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMO_{12}O_{40}$, $H_4SiMo_{12}O_{40}$, $H_6P_2W_{18}O_{62}$, $[X^{IV}Mo_{12}O_{42}]$: X = Ce, Th, U, have stronger acidity than conventional inorganic acids in the Brønsted sense [12]. The corresponding POM anions have weak Brønsted basicity, which is softer than that of nitrate and sulfate anions [21]. This softness makes POM materials easy to handle without the danger of hazardous corrosive effects, unlike mineral acids [21,22]. Furthermore, the addenda metal atoms of POMs are mostly in their highest oxidation states (d^0) and thus the POM complexes exhibit fast reversible redox transformations under mild conditions. These redox properties can be adjusted over a wide range. In particular, the 12-molybdo Keggin-type anions are readily reduced to blue species ("molybdenum blues" and "heteropoly blues"), which are now used widely for colorimetric determination [12]. POMs anions can also function as efficient Lewis acids, especially the lanthanide-containing POMs [23].

POM anions have also been demonstrated to undergo photochemical reduction with water as an electron donor [24]. This property has proved very useful in the application of POMs as photo-catalysts in pollutant photo-degradation, as discussed later. In addition, some POMs, especially the spherical $\{Mo_{132}\}$ [12] Keplerate type, the cyclic $\{P_8W_{48}\}$ type, the dimeric $\{X^{III}{}_2W_{18}\}$ (X = As, Sb) type, and dimeric-fused $\{Si_2W_{18}\}$ type, contain *3d* paramagnetic centers where the number of magnetic ions incorporated in the structure ranges from 3 to 30 [25,26]. These POMs anions have strong magnetic properties.

Moreover, most POMs are highly soluble in a variety of polar and polar-organic solvents. This is due to the ability of POMs to interact with most solutions *via* electrostatic forces, hydrogen bonding, and covalent and non-covalent interactions [3]. These special bonding abilities of POMs have also facilitated the design of POM-containing multifunctional materials using techniques such as layer-by-layer, Langmuir–Blodgett, or self-assembled monolayer films [3]. The resulting multifunctional POM materials are more thermally and oxidatively stable compared with other organometallic complexes.

3. Environmentally benign multifunctional POM materials

Multifunctional POM-based materials have been used to solve various environmental problems due to their diverse chemical properties (Table 1). For example, the most frequently used function of POMs is catalysis due to their redox and photochemical reduction properties. However, we can exploit the other properties of POMs such as their magnetism, Brønsted acidity, and large pore sizes to solve environmental problems, as highlighted in the following sections.

4. Environmental problems with POM solutions

4.1. *Toxic gas sequestration*

Global warming, i.e., the continuing rise in the average temperature of the earth's climate system, is due to the heat-retaining effects of greenhouse gases such as CO_2, CH_4, H_2O, O_3, and N_2O. The average temperature of the earth would be −19 °C without greenhouse gases (currently, it is 14 °C) [64]. Initially, the gases were generated naturally and maintained by processes such as the water and carbon cycles. However, anthropogenic activities such as land-fills, burning fossil fuels, deforestation, industrial processes, and power stations, are currently increasing their levels at