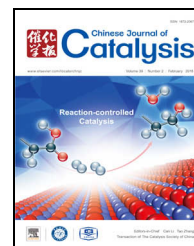


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Review

Mononuclear first-row transition-metal complexes as molecular catalysts for water oxidation

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ABSTRACT

Water oxidation is significant in both natural and artificial photosynthesis. In nature, water oxidation occurs at the oxygen-evolving center of photosystem II, and leads to the generation of oxygen, protons, and electrons. The last two are used for fixation of carbon dioxide to give carbohydrates. In artificial processes, the coupling of water oxidation to evolve O₂ and water reduction to evolve H₂ is known as water splitting, which is an attractive method for solar energy conversion and storage. Because water oxidation is a thermodynamically uphill reaction and is kinetically slow, this reaction causes a bottleneck in large-scale water splitting. As a consequence, the development of new and efficient water oxidation catalysts (WOCs) has attracted extensive attention. Recent efforts have identified a variety of mononuclear earth-abundant transition-metal complexes as active and stable molecular WOCs. This review article summarizes recent progress in research on mononuclear catalysts that are based on first-row transition-metal elements, namely manganese, iron, cobalt, nickel, and copper. Particular attention is paid to catalytic mechanisms and the key O–O bond formation steps. This information is critical for designing new catalysts that are highly efficient and stable.

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1. Introduction

The use and burning of fossil fuels have resulted in a series of energy and environmental problems. This has made it necessary to find and use new energy resources that are sustainable, clean, and environmentally benign [1–4]. Solar energy is the most promising energy source for future consumption. Artificial photosynthesis, achieved via water splitting, enables the harvesting and use of solar energy by converting it to chemical energy [5–8]. This process mimics natural photosynthesis, in which solar energy is used to oxidize water, with evolution of O₂ and generation of protons and electrons. The released O₂ is essential for living beings, and the protons and

electrons extracted from water participate in the reduction of carbon dioxide to produce carbohydrates, a process by which solar energy is stored in chemical forms. If the protons and electrons combine directly to produce H₂, this process enables light-driven water splitting to O₂ and H₂ gases. The production of H₂ gas by this method is clean and carbon-free [9–11], and reaction of the produced H₂ with O₂ (i.e., in fuel cells) generates electrical energy with water as the only product. Water splitting is therefore important in new energy technologies.

Water oxidation, which is one of the half reactions in water splitting, is challenging both thermodynamically (2H₂O → O₂ + 4H⁺ + 4e⁻, ΔE = 1.23 V vs normal hydrogen electrode (NHE)) and kinetically (extensive rearrangement of atoms) [1,3]. Wa-

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ter oxidation therefore limits the overall efficiency of water splitting. Catalysts are required for water oxidation. Much effort has been made recently to design and develop efficient and stable catalysts for this process [12–49]. In general, catalysts can be divided into material catalysts and molecular catalysts. Molecular complexes have the following advantages over material catalysts. (1) Their structures are much clearer and are much easier to modify. (2) They are more amenable to mechanistic studies in solution by various spectroscopic methods. (3) The structure–function relationships of molecular catalysts can be systematically studied. (4) They can be easily integrated into molecular assemblies for the construction of practical water oxidation devices. (5) The key O–O bond formation step can be better understood both experimentally and theoretically in molecular systems.

Recently, mononuclear metal complexes have been found to be active and stable catalysts for water oxidation [3,50,51]. Although ruthenium and iridium complexes show high activities [52–70], the low natural abundances and high costs of these noble-metal elements limit their widespread applications. The use of cheap and efficient catalysts based on earth-abundant metal elements is therefore desirable. This review article summarizes recent rapid progress in mononuclear WOCs based on first-row transition-metal elements, namely manganese, iron, cobalt, nickel, and copper. Particular attention is paid to catalytic mechanisms and the key O–O bond formation steps. Progress in this area has enabled advances in catalyst design. We believe that such information is critical for designing new catalysts that are more efficient and stable than currently available catalysts.

2. First-row transition-metal mononuclear catalysts

2.1. Manganese catalysts

Nature uses a Mn_4CaO_x cluster to catalyze the oxidation of water to O_2 [71–73]. On the basis of this natural process, many Mn complexes have been synthesized and investigated for use as WOCs. The first well-studied mononuclear Mn catalyst for water oxidation was reported by Sun and co-workers in 2007 [74]. The Mn–corrole complex **1** (Fig. 1) was designed as a bio-inspired model of the oxygen-evolving center of photosystem II. Cyclic voltammetry (CV) of **1** in dichloromethane showed two reversible redox events at $E_{1/2} = -0.32$ and 0.61 V (vs Ag/Ag^+), assigned to $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$ and $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$, respectively. This low oxidation potential of $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ indicates that it can be easily oxidized to its high-valent state for water oxidation. On addition of $n\text{-Bu}_4\text{NOH}$, the cyclic voltammogram of **1** displayed an additional peak at $E_{\text{pa}} = 0.79$ V (vs Ag/Ag^+). This new peak arises from water oxidation and the evolved O_2 was detected by electrochemical reduction at -1.29 V (vs Ag/Ag^+). Privalov and Sun [75] subsequently reported a detailed computational study of O–O bond formation with the monomeric Mn–corrole **1**. The formally $\text{Mn}^{\text{V}}=\text{O}$ species was suggested to be responsible for O–O bond formation. This d^2 Mn–oxo species has a closed-shell singlet ground state, but is converted to a quintet $\text{Mn}^{\text{IV}}\text{-oxyl}$ species in a polar solvent. Two O–O bond

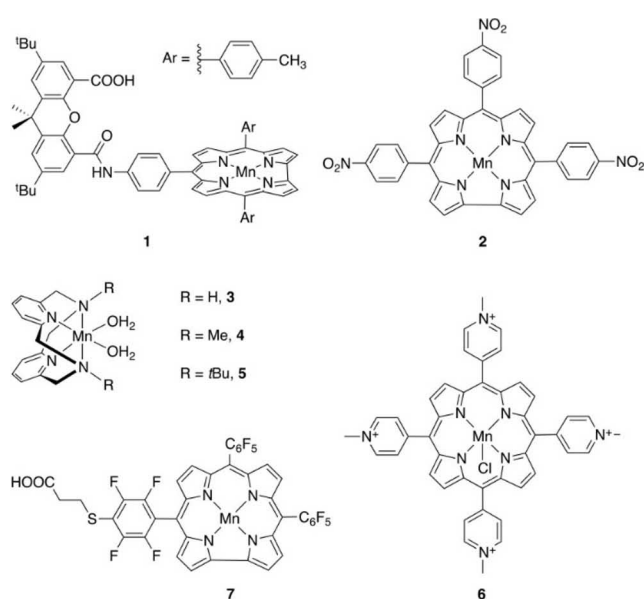


Fig. 1. Mn-based molecular catalysts for water oxidation.

formation processes were compared: a concerted pathway and a two-step pathway via coordination of a hydroxide anion on the Mn ion to produce MnOOH . A density functional theory (DFT) study showed that the concerted pathway was more favorable, with an activation energy barrier of 8–10 kcal/mol. However, it should be noted that the energy difference between these two processes is moderate. It is therefore possible that the reaction proceeds via both reaction pathways simultaneously.

This O–O bond formation step was further probed by Sun and co-workers [76], who used a Mn complex with 5,10,15-tris(4-nitrophenyl)corrole (**2**, Fig. 1) to investigate nucleophilic attack by a hydroxide anion on a $\text{Mn}^{\text{V}}=\text{O}$ unit. The oxidation of **2** with $t\text{-BuOOH}$ afforded the $\text{Mn}^{\text{V}}=\text{O}$ species, which was characterized using various spectroscopic methods. In a subsequent reaction with $n\text{-Bu}_4\text{NOH}$, O_2 was rapidly evolved. The $\text{Mn}^{\text{IV}}\text{-OO}^-$ intermediate, which is probably formed by nucleophilic attack of a hydroxide anion on the $\text{Mn}^{\text{V}}=\text{O}$ unit, followed by one-electron oxidation, was examined using electronic absorption spectroscopy, high-resolution mass spectrometry (HRMS), and isotopic ^{18}O -labeling experiments. The results show that one atom of O_2 came from $n\text{-Bu}_4\text{NOH}$ and the other came from water. On the basis of these experiments, Sun and co-workers proposed the reaction mechanism shown in Fig. 2. This work is significant because it shows that nucleophilic attack of a hydroxide anion on a $\text{Mn}^{\text{V}}=\text{O}$ unit can form an O–O bond, and this sheds light on water oxidation at the oxygen-evolving center of photosystem II.

In 2010, Anxolabéhère-Mallart and co-workers [77] reported activation of a water molecule by electrochemical oxidation of a $\text{Mn}^{\text{II}}\text{-OH}_2$ complex to a $\text{Mn}^{\text{IV}}=\text{O}$ species. The intermediates $\text{Mn}^{\text{II}}\text{-OH}_2$, $\text{Mn}^{\text{III}}\text{-OH}$, and $\text{Mn}^{\text{IV}}=\text{O}$ were all investigated. Extended X-ray absorption fine structure analysis showed a gradual shortening of the Mn–O bond from $\text{Mn}^{\text{II}}\text{-OH}_2$ to $\text{Mn}^{\text{III}}\text{-OH}$ and $\text{Mn}^{\text{IV}}=\text{O}$. Experimental results and DFT calculations suggested that the $\text{Mn}^{\text{IV}}=\text{O}$ unit is best described as

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