

Invited Review

Molecular complexes in water oxidation: Pre-catalysts or real catalysts



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ARTICLE INFO

Article history:

Received 8 May 2015

Received in revised form 2 July 2015

Accepted 10 July 2015

Available online 21 July 2015

Keywords:

Water oxidation
Molecular catalysts
Metal oxides

ABSTRACT

Artificial photosynthesis is considered a promising method to produce clean and renewable energy by sunlight. To accomplish this aim, development of efficient and robust catalysts for water oxidation and hydrogen production is extremely important. Owing to the advantages of easily modified structures and traceable catalytic processes, molecular water oxidation catalysts (WOCs) attract much attention during the past decade. However, the transformation of molecular WOCs to metal oxides/hydroxides or metal ions may occur under the harsh catalytic conditions, making the identification of true active species difficult. In this article, recent progress on molecular complexes acting as real catalysts or precursors toward water oxidation was briefly reviewed. We summarized the commonly used physical techniques and chemical methods that enable to distinguish homogeneous catalysts from heterogeneous catalysts. The factors that affect the nature of WOCs, such as reaction conditions, transition metal centers, and supporting ligands were discussed as well.

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Contents

1. Introduction.....	72
2. Homogeneous or heterogeneous: how to identify the real WOCs.....	73
2.1. Physical techniques for detection of heterogeneous species.....	73
2.1.1. Transmission electron microscopy (TEM).....	73
2.1.2. Dynamic light scattering (DLS).....	73
2.1.3. Energy-dispersive X-ray spectroscopy (EDX).....	73
2.1.4. X-ray photoelectron spectroscopy (XPS).....	73
2.1.5. Electrochemical quartz crystal nanobalance (EQCN).....	73
2.2. Spectroscopic methods for detection of homogeneous species.....	73
2.2.1. Ultraviolet–visible (UV–vis) spectroscopy and infrared radiation (IR) spectroscopy.....	73
2.2.2. Mass spectrometry (MS) and nuclear magnetic resonance (NMR).....	73
2.3. Other detection methods.....	73
2.3.1. Electrochemical method.....	73
2.3.2. Metal ions scavenger.....	73
3. Molecular WOCs based on precious metals.....	74
3.1. Ruthenium-based WOCs.....	74
3.1.1. WNA pathway.....	74
3.1.2. I2M pathway.....	74

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3.2.	Iridium-based WOCs	76
3.2.1.	First example of molecular iridium-based catalyst	76
3.2.2.	Iridium-based catalysts containing cyclopentadiene type ligands	76
3.2.3.	Molecular iridium complexes as pre-catalysts	77
4.	Molecular WOCs based on earth-abundant metals	77
4.1.	Manganese-based WOCs	77
4.1.1.	Dual-core molecular manganese-based catalysts	77
4.1.2.	Single-core molecular manganese-based catalysts	79
4.1.3.	Molecular manganese complexes as precursors	79
4.2.	Iron-based WOCs	80
4.2.1.	Molecular iron-based catalysts	80
4.2.2.	Molecular iron complexes as precursors	81
4.3.	Cobalt-based WOCs	82
4.3.1.	Cobalt-based polyoxometalates (Co-POM)	82
4.3.2.	Cobalt-based cubanes containing Co ₄ O ₄ core	82
4.3.3.	Molecular cobalt-based catalysts containing organic ligands	83
4.3.4.	Molecular cobalt complexes as precursors	83
4.4.	Nickel-based WOCs	85
4.5.	Copper-based WOCs	86
5.	Conclusions	86
	Acknowledgements	86
	References	86



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1. Introduction

Photosynthesis converts solar energy into chemical energy by plants and other organisms, which plays a crucial role in nature. This chemical energy exists in various forms, such as carbohydrates (food), oxygen (O₂), and fuels, supporting all life forms on the earth. Photosystem II (PS II) is one of the essential enzymes of photosynthesis, which produces O₂ and four protons (4H⁺) via successive proton coupled electron transfer (PCET) processes by a Mn₄CaO₅ cluster of oxygen-evolving complex (OEC, Fig. 1) in water oxidation [1–4].

To produce clean and renewable energy by sunlight, artificial photosynthesis serves as one of the most promising methods. In an artificial photosynthetic cell, solar energy is collected and used to split water into O₂ and H₂ (Eqs. (1)–(3)). As one of the half reactions in water splitting, water oxidation releases O₂ with the production of four protons and four electrons, which is considered as the bottleneck of overall water splitting [5–7].

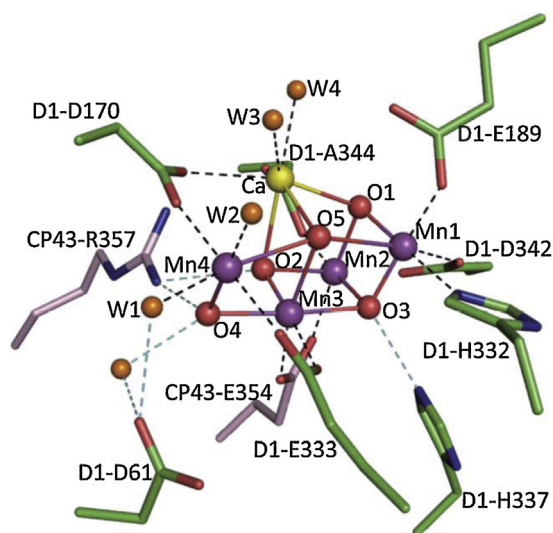


Fig. 1. Stereo view of the Mn₄CaO₅ cluster and its ligand environment. Reprinted with permission from Ref. [2]. Copyright 2011 Macmillan Publishers Ltd.

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