

# Synthesis of Homogenous Metal-Complex-based Catalysts for Oxidising Water

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## DESCRIPTION

Water's four-electron oxidation ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ ) is regarded as the primary artificial photosynthesis bottleneck. A  $\text{Mn}_4\text{CaO}_5$  cluster found inside of photosystem II's oxygen-evolving complex naturally catalyses this process. Artificial molecular catalysts based on ruthenium have been effective in simulating this process. However, due to their high natural abundance, minimal risk of depletion, and inexpensive cost, first-row transition metal ions in molecular catalysts are favoured for practical and large-scale application. One of the biggest issues facing humanity is the lack of energy and another is global warming. Systems that mimic natural photosynthesis have garnered a lot of interest as potential answers to these issues.

The energy from sunlight is transformed into chemical energy in the form of carbohydrates during natural photosynthesis. The synthetic photosynthesis reaction imitates natural photosynthesis and can generate valuable chemical fuels from environmentally favourable sources like  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . In artificial photosynthesis, the reduction and oxidation reactions make up the majority of the reactions. The oxidation reaction involves the oxidation of water by four electrons ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ ), which produces energy-rich electrons that are then used to create chemical fuels. As a result, water oxidation is required to achieve artificial photosynthesis. However, because the water oxidation reaction requires the transfer of four electrons and the formation of a double bond between two oxygen atoms, the reaction has been identified as the primary bottleneck in the artificial photosynthesis reaction sequence.

A  $\mu$ -oxo-bridged dinuclear ruthenium complex, also known as the "blue dimer," was first described by Meyer et al. in 1982 as a synthetic homogeneous catalyst for the oxidation of water. Ruthenium-based complexes have mostly been researched as potential homogeneous water oxidation catalysts, building on

the groundbreaking discovery of the blue dimer, and various instances of ruthenium-based complexes with excellent catalytic activity have been reported. However, due to the scarcity and high price of elemental ruthenium, these complexes may not be suited for prospective large-scale practical applications. It has been thoroughly researched how to catalyse water oxidation effectively. The presented catalysts can primarily be divided into heterogeneous and homogeneous catalysts. The latter typically contains metal complexes, whereas the former primarily comprises of metal oxides. Among these, homogeneous catalysts are ideal for using well-established spectroscopic techniques to examine reaction processes at the molecular level. Homogeneous catalysis systems also have the advantages of high tunability of the catalysts and reaction mechanism-based design. In this condition, earth-abundant first-row transition metal ions including manganese, iron, cobalt, nickel, and copper are preferable options because to their low cost and lower risk of natural depletion. In contrast to ruthenium-based complexes, complexes with these earth-abundant metal ions have received far less research as water oxidation catalysts, and the creation of earth-abundant metal-based molecular catalysts is still a relatively new subject.

The  $\text{Mn}_4\text{CaO}_5$  cluster serves as the catalytic centre of the natural enzyme for oxidising water, hence complexes with earth-abundant first-row transition metal ions are expected to provide great candidates for synthetic catalysts. Additionally, a wide range of examples of synthetic catalysts based on ruthenium complexes provide an overview of the essential elements necessary for efficient artificial water oxidation: (1) O-O bond formation, which is usually the rate-determining step in the catalysis (2) accumulation of four oxidation equivalents, (3) production of a high-valent crucial intermediate in which an oxygen atom is bonded to the metal centre, and accumulation of four oxidation equivalents.

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