Molecular Water Oxidation Catalysts with Dual-active Sites

Yaxuan Huang^{1,a,*}

¹Sino-French Engineer School, Nanjing University of Science and Technology, Jiangyin, China a. Cynthia2655@outlook.com *corresponding author

Abstract: With the continuous development of society, human demand for energy is constantly increasing, and the greenhouse gas emissions and global warming caused by the use of fossil fuels are becoming extremely serious. Therefore, developing low-carbon emission renewable energy is crucial. Hydrogen energy is considered one of the green energy sources, but currently the efficiency of water electrolysis for hydrogen production is not high, especially in the design and optimization of catalysts, which need further research. This review focuses on the current dual site catalytic strategies in water splitting catalysis. By comparing and analyzing the latest research progress, it explores the application of dual site catalysts with ruthenium, copper, iron, and cobalt as the core in water oxidation reactions. In particular, the article emphasizes methods to improve catalytic performance by changing ligands and doping heterogeneous elements, designing hetero nuclear and multi nuclear metals, and other strategies. Research has found that the multi-site synergistic effect of dual site catalysts reveals O-O bond formation mechanisms beyond the classical WNA and I2M pathways, which helps to understand the catalytic processes in natural photosynthesis. This article not only provides a new perspective for the design of homogeneous water oxidation catalysts, but also lays the foundation for the development of heterogeneous catalysts that can be applied in industry. The research conclusion indicates that this strategy can play a similar role in improving other energy related catalytic applications such as oxygen reduction and carbon dioxide reduction, and has broad practical application value.

Keywords: Dual-site catalysts, Water splitting catalysis, Transition metal catalysts, O-O bond formation mechanism.

1. Introduction

Continuous development of human society demands significant energy, and currently mainly from fossil fuels, leading to the significant greenhouse gas emissions, global warming and the energy-environment crisis [1]. Hence, to achieve the sustainable development of our society, a paradigm shift in the energy landscape is needed, necessitating the development and use of sustainable and renewable resources with less, zero and/or negative carbon emissions. Hydrogen has been recognized as one of the ultimate green energies, yet its current production is associated with considerable carbon footprints (e.g., via steam reforming of hydrocarbons, mainly methane, from fossil fuels) [2]. Conversely, hydrogen from water electrolysis, when green electricity from renewable sources (such as solar and wind) is employed, could be the solution for producing green hydrogen with significantly reduced carbon emissions [3]. The technology mimics photosynthesis in nature powered by electricity

to split water into hydrogen and oxygen, in which catalysts are needed to improve the process efficiency. However, the process efficiency of the current development is not satisfactory which demands further design and optimization of relevant catalysts to achieve better efficiency and economy.

The common state-of-the-art catalysts for water splitting processes are that based on noble metals, such as Ir and Ru, which are comparatively expensive and scarce. Comparatively, non-noble metals such as Fe, Co, Ni, and Cu could be more ideal, though their metal centers need to be engineered to improve the process efficiency of artificial water oxidation. It is recognized that the oxygen evolution process in photosynthesis is highly analogous to artificial water oxidation [4]. The oxygen evolution rate in natural photosynthesis ranges from 100 to 400 s⁻¹, hence, it is challenging to achieve such a good efficiency with non-noble metal catalysts. The high efficiency of oxygen evolution in photosynthesis is attributed to the participation of multiple catalytic cores. Therefore, introducing multi-core synergism for microscopic adjustments is an effective means to achieve this enhancement. Given that the metal center is key to catalytic activity, the development of catalysts with multi-active sites becomes particularly important.

This mini-review focuses on summarizing the most recent studies in the fields of dual-site catalysis, via comparative metanalysis of the state-of-the-arts, we provide critical comments on the current developments, as well as providing our perspective on the fields. The review is a timely snapshot of the field, establishing the current boundary of the technical development for progressing the research to the next stage.

2. Advances in Water Oxidation Catalysis

2.1. Ruthenium-based Catalysts

Ruthenium (Ru) is a noble metal commonly explored in water oxidation catalysis, holding a significant position in energy conversion and storage technologies due to its high efficiency, stability, and tunability. Ru-based catalysts typically exhibit high catalytic activity in water oxidation reactions, for example, Ru-bda based catalysts in Figure 1 (bda = 2,2'-bipyridine-6,6'-dicarboxylate) are the earliest catalysts that can match the rate of water oxidation in natural photosynthesis, achieved a turnover frequency (TOFs) over 300 s⁻¹, facilitating O–O bond formation via the interaction of two M–O units (I2M) pathway (Figure 1). Supramolecular interactions between the catalysts serve as the primary driving force for their dimerization, with the pyridine axial ligand in Catalyst 1 contributing through π - π interactions [5]. Based on Catalyst 1,further modifications to the axial ligand are anticipated to enhance catalytic performance.

Isoquinoline has a larger π -system than pyridine, and through stronger π - π interactions, it can enhance the rate and probability of O-O bond formation while lowering the energy barrier. Thus, replacing pyridine with isoquinoline results in Catalyst 2 (Figure 1). Kinetic measurements reveal that under pH=1 conditions, Catalyst 2 can achieve a TOF of 303 s⁻¹, which is approximately 40 times higher than that of Catalyst 1 for Ce(IV)-driven water oxidation at pH 1. This strategy of enhancing catalytic efficiency by modifying axial ligands is a common approach [6].

Building on this, Yi et al. have replaced the axial ligands with negatively charged sulfonate groups and positively charged bipyridine, resulting in Catalyst 3. The axial ligands interact through electrostatic forces due to the attraction between positive and negative charges, increasing the probability of O-O bond formation. Kinetic measurements have revealed that Catalyst 3 exhibits a TOF of 12.4 s⁻¹ under pH = 1 conditions, comparatively TOF was 7 s⁻¹ for Catalyst 1 [7]. Subsequently, Tong et al. replaced the bipyridine in the Ru-based catalyst with phenanthroline, resulting in Catalyst 4. However, due to the increased hydrophobicity of phenanthroline, the face-toface O-O bond formation pattern shifted to a back-to-back and face-to-back arrangement, significantly reducing the catalytic efficiency of the catalyst. Under the conditions of pH = 1, the TOF value is 0.04–0.1 s⁻¹. Ce(IV)-driven water oxidation results and Density functional theory (DFT) calculations indicated that the O-O bond formation mechanism had shifted to water nucleophilic attack (WNA).

To enhance the catalytic efficiency of catalysts containing phenanthroline ligands, researchers continued to employ axial ligand modification strategies. To increase π - π interactions and improve the rate of O-O bond formation, the axial ligand was changed from pyridine to isoquinoline, resulting in Catalyst 5. This ligand modification approach can alter the O-O bond formation pattern from back-to-back and face-to-back to face-to-face, enhancing the catalytic efficiency of the catalyst, with a TOF value of 2-7 s⁻¹ at pH = 1. Through DFT calculations, it was found that the O-O bond formation mechanism of Catalyst 5 is intermolecular interaction between two high-valent Ru-oxo species [8]. In addition to modifications of the axial ligands, Yang et al. have replaced the two carboxylic acid groups in the original Catalyst 1 with two sulfonic acid groups, resulting in Catalyst 6. Electrochemical measurements revealed that the sulfonic acid groups have a weaker electron-donating ability, which lowers the energy barrier for O-O bond formation. Under neutral conditions, the formation of a pentavalent ruthenium-oxo intermediate is not required; the O-O bond can be formed via an I2M mechanism among the tetravalent ruthenium-oxo intermediates. Catalyst 6 exhibits significantly higher electrocatalytic efficiency than Catalyst 1, with a TOF value of approximately 12900 s⁻¹ in neutral conditions, albeit the driving forces are different [5].

To explore the catalytic efficiency of replacing only one carboxylic acid group in the original Catalyst 1, Yang et al. further designed Catalyst 7, which replaces one carboxylic acid group with a sulfonic acid group. Kinetic isotope effect studies and DFT calculations revealed that the O-O bond formation mechanism of Catalyst 7 differs from that of Catalyst 6 and does not proceed via a bimolecular mechanism. Under neutral conditions, Catalyst 7 can rapidly form the O-O bond between tetravalent ruthenium-oxo intermediates via the WNA mechanism. The TOF value is 1013 s⁻¹ in neutral conditions, which is lower compared to the catalytic efficiency of Catalyst 6 but significantly higher than that of Catalyst 4, which shares the same O-O bond formation mechanism [9]. These catalysts represent the state-of-the-arts of the Ru-based bimolecular catalysts developed for water oxidation catalysis. The performance of the discussed catalysts, including their turnover frequencies (TOFs) and mechanisms, is summarized in Table 1.



Figure 1: The molecular structure of the Ru catalysts discussed above.

Catalyst	pН	TOF ^a	[Ce ^{IV}] ^b	TOF ^c	Potential	Mechanism
1	1	33 s ⁻¹	0.48 M	7 s ⁻¹	1.8 V vs NHE	I2M
2	1	303 s ⁻¹	0.48 M	/	/	I2M
3	1	12.4 s ⁻¹	0.20 M	/	/	I2M
4	1	0.04-0.1 s ⁻¹	0.17 M	/	/	WNA
5	1	2-7 s ⁻¹	0.17 M	/	/	I2M
6	7	/	/	12900 s ⁻¹	1.63 V vs NHE	I2M
0	1	/	/	160 s ⁻¹	1.74 V vs NHE	I2M
7	7	/	/	1013 s ⁻¹	1.21 V vs NHE	WNA

Table 1: Comparison of the activity of the Ru catalysts (Figure 1) in water oxidation catalysis.

a. TOF for $[Ce^{N}]$ -driven water oxidation; b. Concentrations of Ce^{N} and catalysts for $[Ce^{N}]$ -driven water oxidation; c. TOF for voltage-driven water oxidation.

2.2. Copper-based Catalysts

Due to the scarcity and high costs of noble metals, non-noble metal catalysts with equivalent activity, such as copper, iron, cobalt, and manganese, can be more ideal for catalysis. For copper, a binuclear copper strategy was proposed, investigating the O-O bond formation mechanism, and attempting to enhance catalytic efficiency by altering the type of ligands. In the case of Catalyst 1 in Figure 2, Su et al. employed a naphthyridine ligand, which is a bidentate ligand capable of coordinating with two copper ions simultaneously [10]. The synergistic effect of the dual active sites facilitates the removal of electrons from both copper atoms, preventing charge build-up. The ligand features a π -conjugated system that can modulate the electronic properties of the catalyst, ultimately preventing the formation of high oxidation state Cu^{IV} = O. DFT calculations confirmed that the O-O bond forms through intramolecular direct coupling between Cu^{III}–O(H) and a μ -oxo without the need for intermediate Cu^{IV} = O formation. The formation pathway of the O-O bond is depicted in Figure 3. The TOF value of Catalyst 1 under neutral conditions is 0.6 s^{-1} .

Since peptide-like compounds can stabilize high oxidation state metal ions, Ruan et al. have designed a binuclear copper-peptide-like complex, which utilizes a peptide-like trimer as Catalyst 2 in Figure 2 [11]. In this complex, the bipyridine ligand, with its π -conjugated system, can modulate electronic properties and optimize redox properties, thereby enhancing catalytic activity. The two ethanol groups act as proton relays in Proton-coupled Electron Transfer (PCET) and stabilize intermediates through hydrogen bonding, reducing the reaction energy barrier. Unlike other studies, Catalyst 2 exhibits stable and rapid performance in borate buffer solution. This is attributed to the borate solution acting as an oxygen source, facilitating its participation in the O-O bond formation. DFT calculations also reveal that the O-O bond formation mechanism is intramolecular oxygen-oxygen coupling between Cu^{III}–O[•] and borate. The formation pathway of the O-O bond is depicted in Figure 3. Electrochemical measurements yield a TOF value of 129 s⁻¹ at pH = 9.35.

Apart from binuclear copper, Jiang et al. have also designed a tetranuclear copper catalyst, namely Catalyst 3 (Figure 2) [12]. This catalyst utilizes Schiff base ligands with multiple coordination sites, which can tightly connect metal centers to form polymetallic clusters, creating a complex with a synergistic effect of a tetranuclear copper center. On this basis, glycine and glutamic acid are chosen to coordinate with copper ions. Electrochemical measurements show that the complex with glycine coordination has a TOF value of 267 s^{-1} at pH = 12, whilst that achieved by the complex with glutamic acid coordination was about 105 s^{-1} under the same condition. The activity difference between the two catalysts lies in the dissociated state, the carboxylate anion can act as a ligand to form additional coordination bonds with the copper center and alter the geometric structure of the copper center, enhancing the binding capacity to the substrate and catalytic activity. In addition to the issue of ligand

types, researchers are also exploring the symmetry of ligands within the catalyst molecules. Hu et al. have designed catalyst 1 and Catalyst 4 (Figure 2) [13]. Both catalysts can avoid the formation of high-valent $Cu^{IV}=O$ and form O-O bonds through a binuclear cooperative pathway. Catalyst 1 is symmetrical, assisting in O-O bond formation with a semi-chelated pyridyl group. Catalyst 4 is asymmetrical, lacking one pyridyl group compared to Catalyst 1 and has an open coordination site, allowing water to participate in the catalysis more readily. It also exhibits a significant kinetic isotope effect, which can optimize the proton transfer step. The asymmetrical catalyst lacks an intramolecular proton acceptor, and the buffer solution can assist in proton transfer.

In addition to ligand modifications, researchers are also dedicated to studying the impact of linker arms on catalyst activity. Emphasizing the investigation of the geometric structure of catalysts on O-O bond formation, Chen et al. have designed three binuclear complexes with different linker arms to delve into the relationship between O-O bond formation and optimal bonding geometry [14]. The linkers in Catalysts 7, 1, and 8 (Figure 2) are Biologically Inspired Processing and Analysis of Neural Modules (BPMAN) Cu₂, 6-hydroxypicolinic acid (6-HPA) Cu₂, and bpy-6,6'-dimethylamide (BPMAD) Cu₂, respectively, with rigidity order as Catalyst 7 > Catalyst 1 > Catalyst 8. At pH = 7, the TOF values correspond to the rigidity order, being 2.01 s⁻¹, 0.6 s⁻¹, and 0.17 s⁻¹, respectively. Thus, it is concluded that catalytic activity correlates positively with linker arm rigidity, with O-O bond formation occurring via intramolecular oxygen-oxygen coupling. Apart from rigid linkers, Zhang et al. designed a binuclear copper complex with a flexible linker arm, namely Catalyst 5 (Figure 2) [15]. The introduction of a flexible linker arm allows free rotation and positional changes of the two active centers, promoting cooperative action. DFT calculations reveal that flexible linker arms can lower the catalytic reaction energy barrier from 21.7 kcal/mol to 9.1 kcal/mol. Additionally, the linker arm contains pyridine, providing a π -conjugated system that is beneficial for electron transfer. The O-O bond formation follows a single-molecule dual-site mechanism (Figure 3), with a TOF value of 144 s⁻¹ at pH = 12 conditions. For a direct comparison, the authors also designed a monomeric counterpart, Catalyst 6 (Figure 2). DFT calculations indicate that the catalytic process of this monomeric counterpart requires the formation of high-valent copper-oxygen intermediates with a higher energy barrier, and the O-O bond formation mechanism is the WNA mechanism, with a TOF value of 4.86 s⁻¹ under pH = 12 conditions. To provide a clear comparative overview of the catalytic efficiencies and mechanisms discussed for each catalyst, the key performance metrics, including turnover frequency (TOF), pH conditions, and mechanistic pathways, are summarized in Table 2.



Figure 2: The molecular structure of the Cu catalysts discussed above.

Table 2: Comparison of the activity of the Cu catalysts (Figure 2) in water oxidation catalysis.

Catalyst	pН	Potential	TOF	Mechanism
1	7	1.87 V vs NHE	0.6 s ⁻¹	1

2	9.35	1.8 V vs NHE	129 s ⁻¹ (CV) 5503 s ⁻¹ (FOWA)	2
3 (Gly)	12	1.7 V vs NHE	267 s ⁻¹	3
3 (Glu)	12	1.56 V vs NHE	105 s ⁻¹	3
4	7	1.87 V vs NHE	0.78 s ⁻¹	1
5	12	1.5 V vs NHE	144 s ⁻¹	4
6	12	1.5 V vs NHE	4.86 s ⁻¹	5
7	7	1.87 V vs NHE	0.17 s ⁻¹	1
8	7	1.87 V vs NHE	2.01 s ⁻¹	1

Table 2: (continued).

In the table, the mechanism for O-O bond formation, Mechanism 1, 2, 4 are depicted in Figure 3; Mechanism 3 corresponds to I2M; Mechanism 5 is referred to as WNA.







The oxidation pathway of Catalyst 1 Mechanism 1



The oxidation pathway of Catalyst 5 Mechanism 4

Figure 3: The oxidation pathway of Catalyst 1, 2, 5.



Figure 4: Divergent O-O bond formation modes in Cu-Core and Fe-Core catalysts.

2.3. Ferrum-based Catalysts

Due to the abundant presence of Fe in nature, iron-core catalysts also hold significant research value. It can be observed that the O-O bond formation in Cu catalysts 7 and 8 (Figure 2) involves the oxygen on the metal and the oxygen in the oxo-bridge. In contrast, Figure 4 illustrates that in iron-core catalysts, the bond is formed between the oxygens on the two metals, indicating a distinct mechanistic difference. Below, the paper analyzes the mechanism of the iron core catalyst.

Wickramasinghe et al. synthesized a binuclear iron complex Fe^{III}(ppq) containing a novel tetradentate ligand ppq (2-(pyrid-2"-yl)-8(1",10"-phenanthrolin-2"-yl)-quinoline), which is referred

to as Catalyst 4 in Figure 5 [16]. The ligand features a tetrapyridine framework with an additional sp²-hybridized center at the quinoline C8 position, providing a square planar coordination environment for the iron center. Over a period of more than 6 hours of observation, there were no changes in the UV-vis spectra of Catalyst 4, indicating that the dimeric catalyst remains intact in aqueous solution. The oxygen evolution rate of Catalyst 4 follows first-order kinetics with respect to the catalyst concentration in presence of Ce^{IV}, with a TOF of 7920 h⁻¹. Subsequently, the reaction solution after the cessation of oxygen generation was examined using dynamic light scattering, and no formation of iron oxide nanoparticles was detected, suggesting that the catalyst remains stable during the turnover. Electrochemical results suggest that the Fe^{III}(ppq) complex undergoes a two-electron oxidation followed by a disproportionation process, wherein the Fe^{III}Fe^V = O intermediate acts as the active species in water oxidation process, enabling the further oxidation of water molecules to generate oxygen.

Further research into iron-core catalysts has focused on ligand modifications for enhanced efficiency. Zhang et al. developed three dinuclear iron complexes by adjusting ligand rigidity, namely $[Fe_2(\mu-O)(OH_2)_2(TPA)_2]^{4+}$ (1), $[Fe_2(\mu-O)(OH_2)_2(6-HPA)]^{4+}$ (2), and $[Fe_2(\mu-O)(OH_2)_2(BPMAN)]^{4+}$ (3), as electrocatalysts in alkaline conditions (0.1 M NaHCO₃, pH 8.4) [17]. Complexes 1 and 2 effectively catalyzed water oxidation via oxo-oxo coupling, while the rigidity in complex 3's BPMAN ligand hindered isomerization necessary for O-O bond formation, diminishing its catalytic activity. DFT calculations highlighted ligand flexibility as crucial for this process. These results elucidate that the O-O bond is formed through intramolecular oxo/oxo or oxo/oxyl coupling, with bimetallic synergism and ligand rigidity profoundly affecting catalytic performance, offering insights for designing iron-based catalysts.

Li et al. proposed an alternative reaction mechanism based on DFT results. The Catalyst 4 undergoes two PCET processes to generate intermediate $[Cl-Fe^{IV}-O-Fe^{IV}=O]^{3+}$ [18]. The first PCET process occurs at 1.66 V to form $[Cl-Fe^{III}-O-Fe^{IV}-OH]^{3+}$, and the second PCET process requires 1.44 V to produce complex $[Cl-Fe^{IV}-O-Fe^{IV}=O]^{3+}$. Subsequent calculation revealed that further oxidation to $[Cl-Fe^{IV}-O-Fe^{V}=O]^{4+}$ necessitates a potential of 2.15 V, which cannot be achieved under experimental conditions, thus avoiding reliance on further high-potential oxidation steps. The article also proposes a mechanism for O-O bond formation, where complex $[Cl-Fe^{IV}-O-Fe^{IV}=O]^{3+}$ is nucleophilically attacked by chloride ions, breaking down into two subunits to initiate O-O bond formation, which is coupling of two $[Fe^{IV}=O]^+$ radicals.

Masaoka et al. described a pentanuclear iron-based water oxidation catalyst with neighboring coordinatively unsaturated active sites to facilitate water binding, activation, and O-O bond formation, referring to Catalyst 6, which is depicted in Figure 6 [19]. In the absence of water, the CV exhibited five reversible redox waves at -0.55, 0.13, 0.30, 0.68, and 1.08 V versus Fc/Fc⁺ (ferrocene/ferrocenium couple), corresponding to sequential one-electron oxidations of the iron centers from Fe^{II}₅ to Fe^{III}₅. Adding about 10% water led to a significant catalytic current after the fourth redox peak, with TOF values from 140 to 1400 s⁻¹. Electrochemical, UV-vis, and X-ray Photoelectron Spectroscopy analyses confirmed the catalyst's homogeneous nature. The catalytic mechanism was proposed based on crystal structures of reaction intermediates, electrochemical and spectroelectrochemical measurements, ⁵⁷Fe Mössbauer spectroscopy, and DFT calculations. The catalyst first oxidized to Fe^{III}₅ species (S4) and then reacted with water to form Fe^{III}₅(OH2) state (A) with an estimated reaction barrier of 15 kcal/mol. Coordination with another water molecule, coupled with four proton transfers, produced a key reaction intermediate (B) containing two Fe^{IV}–oxo sites. DFT calculations suggested that electron rearrangement among the five iron centers generated two co-facial $Fe^{IV} = O$ sites, where the O–O bond formed intramolecularly with an estimated reaction barrier of less than 10 kcal/mol. The catalyst mimics the mechanism of the Oxygen Evolving Center

(OEC) by accumulating multiple charges on multinuclear sites, demonstrating that multi-site assisted charge transfer and dual-site O–O bond formation represent a promising strategy for catalyst design.

Incorporating other metals into iron-core catalysts to form heterometallic catalysts is a novel exploratory approach. Inspired by the heterometallic metal catalyst $CaMn_4O_5$ in OEC, the authors designed a heterometallic catalyst with Ni and Fe, referred to as Catalyst 5 (Figure 5) [20]. Through the analysis of structure-activity relationships with Zn^{II} ion-substituted heterometallic binuclear complexes, it was determined that Ni and Fe are both indispensable in the catalysis jointly participated by the NiFe center. The O-O bond formation mechanism of this complex involves a series of oxidations to form a high-valent Ni^{III}(μ -O)Fe^{IV} core, in which the bridging O atom and the terminal Fe^{IV} = O group form the O-O bond through oxyl-oxo coupling. In addition, the authors confirmed that FeFe and NiNi analogs are not suitable as water oxidation catalysts. The FeFe complex remains stable but exhibits no activity, whereas the NiNi catalyst is readily converted into active Ni_xO_y nanoparticles during the electrocatalysis process. In contrast, the NiFe catalyst remains stable in long-term electrolysis, as confirmed by UV-Vis spectral tests. The catalyst exhibits a TOF value of 11.5 s⁻¹ at pH = 10 and applied potential of 1.4 V vs NHE, as summarized in Table 3, which compares the activity of the Fe catalysts.



Figure 5: The molecular structure of the Fe catalysts discussed above.

Catalyst	pН	TOF	Potential	Ce
1	8.4	0.55 s ⁻¹	/	/
2	8.4	0.04 s ⁻¹	/	/
3	8.4	/	/	/
4	1	7920 h ⁻¹	/	0.1 M
5	10	11.5 s ⁻¹	1.26 V vs NHE	/
6	7	1900 s ⁻¹	1.8 V vs Fc/Fc^+	/

Table 3: Comparison of the activity of the Fe catalysts.

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Figure 6: The molecular structure and proposed mechanism for pentanuclear iron-based electrocatalyst (Catalyst 6).



Figure 7: The O-O bond formation of Catalyst 1, Catalyst 2, and Catalyst 3.

2.4. Cobalt-based Catalysts

Apart from Cu and Fe, Co has also been utilized in water oxidation catalysts. Here, only one is cited as a representative example. Xie et al. designed a binuclear hydrazide-bridged ligand (LH₄) with penta- and hexa-coordinate sites, and synthesized the binuclear cobalt-based catalyst $[(L_4^-)Co^{III}_2(OH)]$ by reacting the LH₄ with Co(ClO₄)₂·6H₂O in methanol in Figure 8 [21]. This novel catalyst achieves electrocatalytic water oxidation under pH 7 with a TOF of 2.2 s⁻¹ at an applied potential 1.8 V vs NHE. Regarding the formation pathway of the O-O bond, the catalyst $[(L_4^-)Co^{III}_2(OH)]^+$ is first oxidized through a PCET process to generate a mixed-valence intermediate $[Co^{III}Co^{IV}=O]^+$. The generated intermediate is further oxidized to form the $[Co^{IV}Co^{IV}=O]^{2+}$ intermediate. The $[Co^{IV}Co^{II}=O]^{2+}$ intermediate reacts with water to form the O-O bond via a WNA mechanism, producing the $[Co^{III}Co^{III}-OOH]^+$ intermediate, with the electrons from the attacking water molecule being distributed across both Co centers.



Figure 8: The structure of $[(L^{4-})Co_2(OH)](ClO_4)$.

2.5. Manganese-based Catalysts

Aside from Cobalt, Manganese has also been employed in water oxidation catalysis. Given that the OEC is a manganese-oxo cluster, researchers have mimicked this structure in the design of the catalyst $[Mn_{12}O_{12}(O_2CC_6H_2(OH)_3)_{16}(H_2O)_4]$ ($Mn_{12}TH$) [22]. Previous Mn-based nuclear catalysts were not highly efficient, prompting the researchers in this study to modify the ligand from 2,3-dihydroxybenzoic acid (dhbH) to 3,4,5-trihydroxybenzoic acid (thbH). Electrocatalytic activity measurements revealed that this minor alteration led to an almost three orders of magnitude faster (kobs = 22 s⁻¹) and more efficient (93% FE) catalytic water oxidation activity, with an overpotential of only 74 mV at pH 6, which is the lowest overpotential reported to date for homogeneous water oxidation electrocatalysts. The authors propose that the hydroxyl groups on the ligand may facilitate catalysis by promoting the formation of high-valent species required for water oxidation through ligand-assisted PCET as shown in Figure 9. Electron transfer occurs not only on the Mn center, but also involves the non-innocent phenolate ligand, which gets oxidized to a quinone during the catalytic process, accompanied by the change in the para-carboxylate anion (from -C(OH)=O to =C(OH)_2). The latter is more favorable for stabilizing the high-valent Mn state.



Figure 9: The possible oxidation pathway of Mn center in 0.1 M acetate buffer solution at pH 6.

3. Conclusion

This paper presents a comprehensive review on the design strategies for dual-site catalysts based on different metals, especially transition ones, which include the modification of lateral and axial ligands, doping with heterogenous elements, and the design of hetero-nuclear and multi-nuclear metals. The roles of dual-site encompass: the formation of O-O bonds via the I2M pathway, which circumvents the formation of high-energy intermediates such as M-OOH through the WNA pathway; electron transfer occurs at the dual-sites, preventing the accumulation of charge at single sites; through multi-site synergy, it reveals other O-O bond formation methods beyond WNA and I2M, thereby enhancing the understanding of natural photosynthesis, where catalytic centers comprise multi-nuclear structures whose mechanisms remain debated.

Based on summary of the relevant state-of-the-arts, the dual-site homogeneous water oxidation catalysts (molecular catalysts), and the dual-site strategy could be extended to heterogeneous water oxidation catalysts. Introducing Mn atoms into the RuO₂ catalyst to create $Mn^{4-\delta}$ -O-Ru^{4+\delta} dual-active sites with local structural symmetry but oxidation state asymmetry can transform the traditional adsorbate evolution mechanism into the oxide path mechanism, significantly enhancing efficiency

[23]. Similarly, the A-Fe₂S₁N₅/SNC catalyst enhances catalytic performance by configuring asymmetric iron diatomic sites (Fe-Fe) on highly defective nitrogen-sulfur co-doped carbon nanosheets (SNC) [24]. In another example, Ni-Fe dual-site catalysts, utilizing graphitic carbon nitride as a support, demonstrate substantial performance improvements in heterogeneous catalysis for the oxygen evolution reaction [25]. Heterogeneous catalysts possess a higher practical value in industry. Broadly speaking, the dual-site strategy can also be extended to other energy-related catalytic applications, such as oxygen reduction (the reverse reaction of water oxidation): by precisely regulating the electronic structure and spin state of metal sites, dual-metal atomically dispersed Fe,Mn/N-C catalysts have been designed to achieve high activity and stability of Oxygen Reduction Reaction catalysts in both alkaline and acidic media [26]. Moreover, dual-site catalysts incorporating platinum-group metal atoms have been designed to enhance the performance of copper-based catalysts in CO₂ reduction, particularly in converting CO₂ into energy-dense hydrocarbon molecules, such as CH₄ and C₂H₄ [27].

Overall, these advancements underscore the versatility and broad applicability of dual-site catalysts in enhancing the efficiency of various catalytic processes essential for energy conversion and environmental sustainability.

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