DINUCLEAR HETEROGENEOUS CATALYSTS ON METAL OXIDE SUPPORTS

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Atomically dispersed catalysts refer to substrate-supported heterogeneous catalysts featuring one or a few active metal atoms that are separated from one another. They represent an important class of materials ranging from single atom catalysts (SACs) and nanoparticles (NPs). The study of SACs has brought an attention of understanding the reaction mechanism at the molecular level. SACs is a promising field, however, there are still many challenges and opportunities in developing the next generation of catalysts. Catalysts featuring two atoms with well-defined structures as active sites are poorly studied. It is expected that this class of catalysts will show uniqueness in activity, selectivity, and stability. However, the difficulty in synthesizing such structures has been a critical challenge. I tackled this challenge by using a facile photochemical method to generate active metal centers consisting of two iridium metal atoms bridged by O ligands and bound to a support by stripping the ligands of the organometallic complex. My research also unveiled the structure of this dinuclear heterogeneous catalysts (DHCs) by integrating various characterization resources. Direct evidence unambiguously supporting the dinuclear nature of catalysts anchored on metal oxides is obtained by aberration-corrected scanning transmission electron microscopy. In addition, different binding modes have been achieved on two categories of metal oxides with distinguishable surface oxygen densities and interatomic distances of binding sites. Side-on bound DHCs was demonstrated on iron oxide and ceria where both Ir atoms are affixed to the surface with similar coordination environment. The binding sites on the OH-terminated surface of Fe₂O₃ and CeO₂ anchor

the catalysts to provide outstanding stability against detachment, diffusion and aggregation. The competing end-on binding mode, where only one Ir atom is attached to the substrate and the other one is dangling was observed on WO₃. Evidence supporting the binding modes was obtained by *in situ* diffuse reflectance infrared Fourier transform spectroscopy. In addition, the synergistic effect between two adjacent Ir atoms and the uniqueness of different coordinative oxygen atoms around Ir atoms were investigated by a series of operando spectroscopy such as X-ray absorption spectroscopy and microscopy at atomic level under the reaction condition. The resulting catalysts exhibit high activities and stabilities toward H₂O photo-oxidation and preferential CO oxidation. Density functional theory calculations provide additional support for atomic structure, binding sites modes on metal oxides, as well as insights into how DHCs may be beneficial for these catalytic reactions. This research has important implications for future studies of highly effective heterogeneous catalysts for complex chemical reactions.

TABLE OF CONTENTS

TABLE OF CONTENTS	iii
TABLE OF ABBREVIATIONS	vi
ACKNOWLEDGMENTS	. viii
Chapter 1: Introduction	1
1.1 Heterogeneous catalyst and its challenges	1
1.2 Introduction of single atom catalysts and its challenges	3
1.2.1 Single atom catalysts are developed to solve some of the issues faced by heterogeneous catalysts.	3
1.2.2 Exciting progress has been made on SACs.	3
1.2.3 Challenges of SACs	5
1.3 Introduction of dinuclear heterogeneous catalysts (DHCs)	6
1.3.1 Why dinuclear heterogeneous catalysts?	6
1.3.2 Preliminary progress on DHCs	7
1.3.3 Challenges of DHCs	9
1.4. Applications of DHCs for electrochemical and thermal catalytic reactions	9
1.4.1 DHCs for OER	10
1.4.2 DHCs for PROX	11
1.5 Summary	12
1.6 References	12
Chapter 2: Stable Iridium Dinuclear Heterogeneous Catalysts Supported on Metal-Ox Substrate for Solar Water Oxidation	ide 18
2.1 Dinuclear heterogenous catalysts for water oxidation	18
2.2 Materials and methods	20
2.2.1 Materials synthesis	20
2.2.2 Structural characterizations	21
2.2.3 Photoelectrochemical (PEC) characterization	23
2.2.4 Computational details	24
2.3 Results and discussions	24

2.3.1 Synthesis strategy for Ir DHCs	24
2.3.2 Direct structure characterization of Ir DHCs	27
2.3.3 Determination of binding sites by DFT and HAADF simulation	34
2.3.4 Catalytic characterization of Ir DHCs	35
2.3.5 Proposed catalytic mechanism by DFT calculations	
2.3.6 Stability characterization of Ir DHCs	40
2.4 Conclusion	44
2.5 References	45
Chapter 3: End-on Bound Ir Dinuclear Heterogeneous Catalysts on WO ₃ for Solar Oxidation	Water 48
3.1 Introduction of end-on binding mode dinuclear heterogeneous catalysts	48
3.2 Materials and methods	50
3.2.1 Catalyst preparation	50
3.2.2 Catalyst characterizations	51
3.2.3 Catalysts performance test	54
3.2.4 Computational details	55
3.3 Results and discussions	57
3.3.1 Synthesis strategy for end-on bound Ir DHCs	57
3.3.2 Evidence of the binding mode by <i>in-situ</i> DRIFTS	58
3.3.3 Structural evolution from Ir DHCs to Ir SACs	60
3.3.4 Further confirmation of the end-on binding mode by HAADF-STEM	62
3.3.5 Catalytic characterization of end-on bound Ir DHCs.	66
3.3.6 Computional understanding of catalytic cycle	67
3.4 Conclusions	70
3.5 References	72
Chapter 4: Highly Stable Preferential CO Oxidation by Dinuclear Heterogeneous Catalysts	76
4.1 Preferential CO oxidation and its challenges	76
4.2 Materials and methods	77
4.2.1 Catalysts preparation	77
4.2.2 Preferential CO oxidation activity tests	78

4.2.3 Catalyst characterization	78
4.2.4 Computational details	81
4.2.5 EXAFS fitting:	83
4.3 Results and discussions	84
4.4 Conclusion	
4.5 References	101
PUBLICATION LIST	104

TABLE OF ABBREVIATIONS

DHCs: dinuclear heterogeneous catalysts

SACs: single atom catalysts

NP: nanoparticle

OER: oxygen evolution reaction

ORR: oxygen reduction reaction

RHE: reversible hydrogen electrode

SEM: scanning electron microscopy

STEM: scanning transmission electron microscopy

TEM: transmission electron microscopy

HAADF-STEM: high angle annular dark field scanning transmission electron

microscopy

EELS: electron energy-loss spectroscopy

EDS: Energy dispersive X-ray spectroscopy

XAS: X-ray absorption spectroscopy

EXAFS: extended X-ray absorption fine structure spectroscopy

XANES: X-ray absorption near edge spectroscopy

XPS: X-ray photoelectron spectroscopy

XRD: X-ray powder diffraction

DRIFTS: Diffuse reflectance infrared Fourier transform spectroscopy

DFT: density functional theory

FTO: fluorine doped tin oxide

FTIR: Fourier-transform infrared spectroscopy

PROX: Preferential oxidation of CO in the excess of H₂

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Chapter 1: Introduction

1.1 Heterogeneous catalyst and its challenges

Research on catalysis has been divided into subfields of homogenous and heterogeneous catalysis.¹⁻⁷ A shared goal in these efforts is the quest for ever-better performance with respect to the activity, selectivity and cost. As far as catalyst optimization is concerned, studies on homogenous catalysis benefit tremendously from the well-defined catalyst structures.⁸ Indeed, the rich knowledge on structure-reactivity relationships of homogenous catalysts makes it possible to tailor-design and fine-tune their activities for better performance as measured by turn-over frequencies (TOFs).^{9, 10} By comparison, heterogeneous catalysts excel in terms of stability as measured by the turn-over numbers (TONs).¹¹ They are also easier to separate for repeated usage and have, therefore, dominated large-scale industrial implementations. The poor understanding of the active centers of heterogeneous catalysts, especially the structures at the atomic level, nonetheless, makes it difficult to optimize them in a fashion that has enabled the rapid development of homogeneous catalysis.¹² Research on catalysis has advanced to the point where researchers see a need for convergence.^{1,13} One way to bridge the gap between heterogeneous and homogeneous catalysis is to heterogenize homogeneous catalysts.¹⁴⁻¹⁶ The idea is to create catalysts featuring well-defined active motifs originated from the molecular precursor but in a heterogeneous form, so as to take advantage of benefits offered by heterogeneous catalysts. Significant efforts have been undertaken toward this end. For instance, within the context of water oxidation, Meyer et al. have done pioneering work by immobilizing Ru molecular water oxidation catalysts onto the metal oxide electrode.^{1,17} Brudvig *et al.* have shown that Ir-based heterogenized catalysts are more active than the amorphous Ir oxide.^{14,18} Tilley and Bell *et al.* have anchored Co- and Mn-based molecular catalysts onto SiO₂.^{19,20} In terms of other chemical transformations,

Chang *et al.* explored immobilized supramolecular structures for C-C coupling by CO and CO₂ reduction.^{21,22} Gates *et al.* anchored Ru, Rh and Ir homogenous complexes onto MgO and Al₂O₃ for olefin hydrogenation.^{23–29}

The lack of a clear picture of the resulting heterogeneous catalyst has been a key challenge. Although exciting progress in terms of performance has been reported, the aforementioned efforts faced a critical caveat — the catalytic centers are often poorly defined.^{11, 30, 31} A number of reasons contribute to this issue. For example, the resulting catalysts often exhibit inadequate stability for high-resolution characterization. When studied by high-intensity experimental tools such as high angle annular dark field scanning transmission electron microcopy (HAADF-STEM), these catalysts undergo rapid structure evolution, rendering structural information on the active centers elusive.^{24, 28, 32} The challenge reminds us of the difficulties in studying crystalline and amorphous heterogeneous catalysts. The lack of detailed structural information of active sites makes it exceedingly difficult to capitalize on the molecular identities of the catalyst to systematically study their mechanisms, which would be critical to further performance optimizations.³³ While the challenge could be partially addressed by spectroscopic studies such as X-ray absorption spectroscopy (XAS), a more direct evidence of the structures is critical but was missing.^{34, 35}

My doctoral work is designed to fill in this knowledge gap. I hope this work could have potential to advance research on heterogeneous catalysis by providing key missing information at the molecular level. This thesis is inspired by recent success in single atom catalysts but take an important step forward.

1.2 Introduction of single atom catalysts and its challenges

1.2.1 Single atom catalysts are developed to solve some of the issues faced by heterogeneous catalysts.

In recognition of the limitations of heterogeneous catalysts, researchers have recently turned their attention to a new class of catalyst design, the single atom catalyst (SAC).^{2–13} The idea is to reduce the active site of a heterogeneous catalyst down to a single atom level. On the one hand, this remarkable size reduction improves the catalyst atomic utilization efficiency to near unity.^{14–20} As such, the cost associated with "dormant" catalyst atoms is removed. On the other hand, we are presented with a well-defined catalytic center, where the catalytic mechanisms can be studied without confounding factors due to adjacent catalytic atoms or the dynamic changes of the structures.²¹ Most importantly, research on SAC represents a critical step toward rational design of heterogeneous catalysts guided by the understanding of the reaction mechanisms at the molecular level. Indeed, exciting results have already been generated by researches on SACs.

1.2.2 Exciting progress has been made on SACs.

SACs were first proposed by Zhang *et al.* in 2011. They prepared isolated single Pt atoms on the Fe₂O₃ support (Pt SAC/Fe₂O₃). When used for CO oxidation, Pt SACs have been shown far less susceptible to poisoning by CO than Pt nanoparticles.^{22, 23} This is because for a Pt SAC, the binding affinity between O₂ and Pt may be stronger than that between CO and Pt.²⁴ By comparison, CO binds more strongly with an active Pt site on a Pt nanoparticle catalyst due to the synergistic effect with adjacent Pt atoms, thereby poisoning the catalyst. Reactions like this highlight the uniqueness of SACs. As a new class of catalysts, SACs not only maximize the utilization of catalytically active atoms, they also enable new reaction routes to solve issues that are detrimental to bulk or nanocluster catalysts.^{16, 25-27} The development of SAC is promoted by the rapid advancement of characterization techniques. Researchers develop a series of characterization techniques to identify the existence of SACs and further explore their special distribution. For example, scanning tunneling microscopy (STM) and aberration-corrected scanning transmission electron microscopy (AC-STEM) can directly help capture the image of single metal atoms dispersed. X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy can provide information about the chemical valence state, the special configuration and the coordination environment of the SAC. One of the infrared (IR) spectroscopy—diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) can also be used to distinguish the existence of single metal atoms and nanoparticle.

In most cases, metal oxides have been used as supports to anchor SACs. Inspired by the work of Pt₁/Fe₂O₃, Chen *et al.* performed systematic DFT study on various SACs systems to develop more efficient catalysts with low cost for CO oxidation reactions. They found that non-Pt metal supported on FeOx, such as Co₁/FeO_x, Ti₁/FeO_x and Pd₁/FeO_x all showed improved catalytic performance compared with Pt₁/FeO_x. CeO₂ is also often used as the support to synthesize SACs due to its capability to form surface metal complex, which inhibits sintering effectively.²⁸ Datye *et al.* explored the effectiveness of different shapes of CeO₂ (polyhedral, nanorods, and cubes) with distinguished density of defects for anchoring Pt atoms under 800 °C in air.²⁹ However, this Pt₁/CeO₂ has failed to meet the criteria (set by the US Department of Energy) of converting 90% pollutants at 150 °C for diesel oxidation. Datye *et al.* further constructed Pt²⁺ site with several kinds of oxygen in CeO₂ by high temperature steam treatment.³⁰ The temperature of 100% CO conversion decreased from 320 °C to 148 °C, and there was no obvious deactivation for Pt₁/CeO₂ in cycle CO oxidation reactions.

1.2.3 Challenges of SACs

These recent developments prompt us to ask the question: <u>Can SACs catalyze chemical</u> <u>reactions that require concerted activities between multiple active sites at the same time?</u> The question is important because there are a large number of reactions that require more than one active site. The intuitive answer to this question is no. However, there have been rare research activities designed to answer this important question. I am therefore motivated to correct the deficiency by studying multi-atom catalysts during my graduate study. It is a critical research need to develop multi-atom catalysts. A large number of chemical reactions require concerted catalytic

activities by more than one catalytic center. For example, it has been recently proposed that oxygen reduction reactions (ORRs), which are critical to fuel cell-based energy conversion applications, require two adjacent active Pt sites to break the O-O bond (Figure 1.1). When only one site is available, the reaction will proceed through a



Figure 1.1 Proposed mechanisms for one and two-catalytic centers for ORR (top) and OER (bottom). A critical difference in the ORR is the product, whereas a single Pt site favors the formation of H_2O_2 while a dual Pt site favors H_2O . For OER, it is unknown whether a single site is more (or less) active at the present time, although some recent studies suggest that a dual site may be more active.

route in which the O-O bond is maintained. Experimental results support this conjecture.^{31, 32} Another example is the water oxidation-based oxygen evolution reaction (OER) (Figure 1.1). There has been rare reports on SACs for OER, whereas a great number of heterogeneous catalysts have been reported active toward this intensely studied reaction.³³ The disparity raises an important question regarding the OER mechanism at the molecular level: <u>*What is the smallest unit that is*</u> <u>active toward OER?</u> If a single atom site is active, would it be more (or less) effective than a catalyst with multiple active sties? Questions like these remind us of the development of studies on homogeneous OER catalysts, where mononuclear catalysts were a minority for more than two decades, and most active homogeneous OER catalysts feature di- or multi-nuclear structures.³⁴⁻³⁸ It was not until recently that more and more mononuclear catalysts have been found to be active toward OER.³⁹ Learning from the parallel field of homogeneous catalysis, we see the need to design, synthesize and study catalysts with well-defined active centers featuring muti-metal atoms per site for heterogeneous catalysis (Figure 1.2). Presently, such efforts are rare, and the field mainly began to see research focused on SACs. My thesis will bridge this gap. We would like to design the catalyst, which can provide critical insight into the reaction mechanisms at the molecular level and contribute significantly to the rational design of heterogeneous catalysts.

1.3 Introduction of dinuclear heterogeneous catalysts (DHCs)

1.3.1 Why dinuclear heterogeneous catalysts?

As a first step toward this research direction, we proposed to design, synthesize and study dinuclear heterogeneous catalysts (DHCs). Compared with more complex catalyst structures such as nanoclusters that typically contain >10 atoms, DHCs are much better





Figure 1.2 Summary of the state of knowledge and utility of heterogeneous catalysts. Although bulk catalysts are relatively easy to prepare, they are typically poorly understood. An important gap between fundamental understanding and the rational design of heterogeneous catalysts is the lack of catalysts with well-defined muti-atomic structures. My thesis will generate knowledge to bridge the gap.

defined in their structures. It is defined as two atoms are connected by bridge oxygen atoms and attached to the metal oxide surface by OH group from substrate (Figure 1.3). The simplicity of the

structure permits mechanistic studies at the molecular level. Compared with SACs, DHCs allow for reactions that require more than one catalytic center. It is a critical step toward understanding more complex heterogeneous catalyst.



Figure 1.3 Proposed structure of DHCs on metal oxide supports. The electric lime and camouflage green colors indicate M_1 from DHCs and M_2 from support; the polo blue, russet, and brandy rose balls represent interfacial O atom, bridge O atom, and O atom in bulk metal oxide support, respectively.

1.3.2 Preliminary progress on DHCs

DHCs supported on 2D materials 2D materials are promising supports for active metal atoms due to their large specific areas. A 0.2 wt. % loading of single Pt atoms can be achieved by using 2D MoS₂, and the loading can be increased to up to 7.5wt.% with atomic dispersion (creating neighboring Pt monomers, so called Pt DHCs).⁴⁰ Interestingly, neighboring Pt monomers showed higher activity and lower activation energy barrier for CO₂ hydrogenation to methanol reaction. It approach paves a way to manipulate the active center of the catalysts.

Graphene has been widely used as the support for SACs due to the sufficient defect sites⁴¹⁻⁴³. However, it remains a challenge that to construct metal DHCs on high surface area graphene. Lu *et al.* applied bottom up strategy to form Pt DHCs by atomic layer deposition (ALD) on graphene support.^{44, 45} This catalytic performance of graphene-supported Pt DHCs catalyst is about 45 and 17-fold higher than graphene-supported nanoparticles and SACs for hydrolysis reaction.

In addition, a dinuclear motif Co DHCs/N_xC_y structure was obtained by pyrolysis of di-metal organic frameworks.⁴⁶ The synthesized DHC catalyst exhibits 12 times higher activity than the Co SACs for ORR reaction, which is comparable to the commercial Pt/C catalyst.

DHCs on porous structures The zeolite-based catal, with the advantage of confinement effect, may be a promising platform to tackle this challenge. Cu-ZSM-5, prepared via copper exchanged ZSM-5 zeolite, exhibits the excellent ability to decompose NO.⁴⁷ The formation of Cu DHCs where the Cu DHCs are separated by one or two SiO₄ tetrahedra was proposed to contribute to this enhanced performance.

MOFs has proven to be ideal supports to synthesize SACs due to their abundant anchoring sites, especially in the pores.^{48, 49} A multi-gram scale production of Pt DHCs supported by MOFs could be obtained.⁵⁰ Various techniques including microscopy and spectroscopy have been used collaboratively to demonstrate the nature of Pt DHCs sites. This catalyst shows outstanding catalytic performance for many reactions, such as alkene hydrogenation and NH₄CN synthesis reactions.

The uniform huge holes existed on C₂N might provide the anchoring sites for DHCs.^{51, 52} Therefore, a computational work was carried out for non-precious DHCs (Co, Cr, Fe, Mn, and Ni) anchored on this layered C₂N.⁵³ The calculated results showed that all DHCs systems exhibit better catalytic performance than SACs for nitrogen reduction reaction (NRR). This system was further extended by Zhou *et al.* to other metals (Ag, Au, Cu, Ir, Mo, Pt, Pd, Rh, Ru, and Ti), and they discovered that Mo₂-C₂N owned the best catalytic performance.⁵⁴ Except for NRR, compared to SACs, the TM₂-C₂N (TM- Co, Cu, and Ni) also showed lower O₂ dissociation barriers and higher O_2 adsorption energies, which indicates that DHCs might be an promising candidate for oxidative reaction such as CO oxidation or methane oxidation.⁵⁵

The uniformly distributed pores in C_3N_4 make them suitable platform to anchor metal atoms. Whereas, preparing pure DHCs with C_3N_4 is a great challenge. To tackle this challenge, Li *et al.* reported to apply the strategy of "precursor-preselection" to synthesize Fe₂/C₃N₄.⁵⁶ Interestingly, the synthesized Fe₂/C₃N₄ exhibits excellent catalytic performance for the reaction of trans-stilbene to trans-stilbene oxide.

1.3.3 Challenges of DHCs

Synthesis of DHCs on metal oxides substrates is still challenging because dual adjacent binding sites are needed. Furthermore, DHCs tend to aggregate on the surface of supports during catalytic reactions, especially under reductive gas condition. Therefore, how to construct a clean and well-defined dinuclear motif with structural stability under the reaction condition is an issue, which needs a significant attention. In addition, further distinguishing dinuclear motifs and adjacent monuclear motifs which randomly distribute will also facilitate the development of atomically dispersed catalysts. Moreover, the understanding of structure-property relationship is limited up to now. Specifically, roles of metal centers and coordinative soft atoms need to be further delineated.

1.4. Applications of DHCs for electrochemical and thermal catalytic reactions

We plan to study two model reactions oxygen evolution reaction (OER) and preferential CO oxidation in the excess of H_2 (PROX) catalyzed by DHCs and try to understand the structureproperty relationship by these two catalytic systems. First, we would like to know the key questions that need to be answered in these two reactions.

1.4.1 DHCs for OER

OER is the first step of natural photosynthesis. OER has been recognized as a critical reaction for a future powered by renewable energy.⁵⁷⁻⁶⁰ Great research efforts have been devoted to developing efficient OER catalysts that are based on earth-abundant elements.⁶¹ Among those studied, the NiFeO_x (or NiFe(OH)_x) and CoO_x systems have received significant attention.⁶²⁻⁶⁵ For the Ni-Fe system, it has been generally agreed upon that the presence of Fe is critical. However, which sites are the true active sites remains a hotly debated subject.^{66–68} For instance, Boettcher and co-workers proposed that Fe is the active site and demonstrated that the incorporation of Fe into a NiOOH lattice enhances the oxide conductivity, even though they showed that this effect may not be sufficient to explain the dramatic enhancement of the catalytic activity.⁶⁶ Computational studies by Nørskov and co-workers also support that Fe species are the active sites.⁶⁷ However, Strasser and co-workers suggested that Ni in the Ni-Fe films is the active site.⁶⁸ They reported under OER conditions, 75% of the Ni centers are oxidized from Ni²⁺ to Ni³⁺, while up to 25% are oxidized to Ni⁴⁺ within the NiOOH catalyst. By contrast, the Fe centers remain in the Fe^{3+} state under these conditions. It is important to note that at the present stage, all existing studies of the Ni-Fe are based on bulk catalysts with poorly defined structures of the catalytic centers. As such, the understanding of the reaction mechanism remains coarse-grained in nature. Little is known about the mechanism at the molecular level. This is an important reason why existing reports apparently contradict each other. Another example of similar debates may be found in research on Co-based OERs. For instance, it has been reported by Frei et al. that the "edge sites" which consist of two Co atoms are the fast sites for water oxidation, although their research also shows that a single Co atom site may also catalyze water oxidation, albeit at a much slower rate.⁶⁹ Nocera et al.'s recent research supports that the dual-atom Co "edge sites" are the active sites for water oxidation.⁷⁰ This line of research on both the Ni-Fe and CoO_x OER catalysts

raises an important question: *Is a dinulear catalytic center inherently more active than a single atom site for OER*? Answers to this question will play important roles in accelerating catalyst discovery for OER. To answer this question, catalytic moieties with comparable DHCs and SACs structures are needed. Presently, such catalyst analogues are missing. My thesis will meet this critical need. The structures we seek to synthesize and study feature two active atoms.

1.4.2 DHCs for PROX



Figure 1.4 Proposed mechanism of CO

As a major impurity in H₂ produced by steam methane reforming, CO in the feeding gas of Protonexchange membrane fuel cell poisons Pt catalysts through bridge binding, hampering the prospect of large-scale implementations of this promising technology. PROX offers a solution to this issue, for which a variety of noble metal catalysts have been

oxidation by Pt SACs. shown effective,⁶⁴⁻⁶⁷ including Pt SACs.⁵² In understanding the mechanisms, researchers raised an important new question: *How is O₂ activated on SACs?* This is an important question because SACs only feature a single apparent active metal center. One hypothesis is that the reaction would involve synergistic effects between Pt and the oxide support, where CO binds to the Pt center, and O₂ binds to the supporting substrate (Figure 1.4). It is, however, difficult to obtain direct evidence to prove such a hypothesis, and most reported evidence tends to be indirect, leaving room for alternative interpretations. Let us consider CO oxidation as an example. As shown in Figure 1.4, while Pt SACs have been shown active toward CO oxidation, it remains a debate whether the synergistic effect between Pt and the oxide support is critical.^{52, 53} That is, once a CO is adsorbed onto SACs, *how does an O₂ molecule get dissociated to oxidize CO in the absence of another apparent active metal center*? It was proposed that such a function was provided by the supporting oxide substrate. Definitive proof of this hypothesis has been missing. Questions like this are important because answers to them hold the key to further development of practical catalysts for applications such as proton-exchange membrane fuel cells. Finding answers to them will require heterogeneous catalysts with more than one active site but of well-defined structures. DHCs meet this critical need and present an opportunity to correct this deficiency.^{68, 69} Not only can we study the mechanisms at a new level, but we are presented with a more effective catalyst for PROX.

1.5 Summary

As has been demonstrated by research on homogeneous catalysis, the well-defined structure of the catalytic site is crucial to the study of the reaction mechanisms at the molecular level.^{37, 38, 71, 72} Such an understanding is the key inspiration for this thesis. Our long-term goal is to build heterogeneous catalysts with well-defined structures for optimized activities. In this thesis, we chose to study catalysts with two active metal atoms per site as the first step. In the chapter two, we mainly focused on the preparation of DHCs. We further explored how to control spatial configurations of DHCs in the chapter three. Last, the structure-property relationship was delineated in the chapter four. Our findings will shed light on the design of well-defined atomically dispersed catalysts with multiple metal atoms.

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Chapter 2: Stable Iridium Dinuclear Heterogeneous Catalysts Supported on Metal-Oxide Substrate for Solar Water Oxidation

2.1 Dinuclear heterogenous catalysts for water oxidation

Atomically dispersed catalysts have recently gained significant attention for their advantages of high atomic efficiency, activity, and selectivity.^{1, 2} Different from bulk heterogeneous catalysts, the atomically dispersed ones feature well-defined structural moieties at the atomic level.³ This feature opens a window to understand mechanisms that underpin heterogeneous catalysts in a similar fashion to how homogeneous catalysts are studied.⁴ It also presents opportunities to tailor the functionalities of heterogeneous catalysts with unprecedented controls.⁵ New and unique reaction pathways have been discovered on these new catalysts. For instance, when used for CO oxidation, Pt SAC has been shown far less susceptible to poisoning by CO than Pt nanoparticles.² Within this context, research on SACs has thrived, where significant progress in synthesis, characterization and mechanistic understanding has been made. Notwithstanding, these prior efforts primarily mainly focused on reactions that may require only a single metal active site, such as CO oxidation⁶ and water-gas shift.⁴ Atomically dispersed catalysts featuring more than one metal active site are rare in the literature. Consequently, reactions dependent on multiple metal active sites without organic ligands remain poorly studied. Pioneering works by Iwasawa et al. and Gates et al. have demonstrated several systems featuring multiple metal atoms per active site for hydroformylation and hydrogenation reactions.^{7–9} Another class of catalysts featuring such structures is found in dinuclear Cu or Ni catalyst for methane oxidation reactions.^{10, 11} However, two key challenges remain in this field: (i) to prepare the dinuclear catalyst with the high yield by a facile and general approach and (ii) to achieve a direct observation to unambiguously support the dinuclear nature. To fill in this important knowledge gap, here we report the synthesis of DHCs consisting of two Ir atoms per catalytic site stably bound to a support.

The structure was enabled by a heterogenization method followed by a room-temperature photochemical ligand removal treatment. The resulting DHCs exhibit outstanding stability against detachment and aggregation yet is highly active toward water oxidation.

Water oxidation was chosen for this present work because as an essential step in natural and artificial photosynthesis it has been a topic of intense research.¹² A large number of catalysts have been extensively studied, and their performance has been benchmarked.¹³ Despite these successes, gaps in the understanding of catalytic water oxidation exist.¹⁴ For instance, the mechanisms of heterogeneous catalysts for water oxidation, especially at the molecular level, are poorly understood.¹⁵ An important reason has been the high-performance heterogeneous catalysts are often poorly defined in their structures, especially at the molecular and atomic levels. Despite recent successes in this area,¹⁶ the complex interactions between water-oxidation catalysts and light absorbers for integrated solar-to-fuel conversion are still poorly understood.¹⁷ Controlled synthesis of high-performance heterogeneous catalysts with well-defined structures and integration with light absorbers are therefore of great importance. Taking an important step aimed at addressing these issues, here we report a facile method for direct synthesis of heterogeneous catalysts consisting of two Ir atoms per catalytic site on the α -Fe₂O₃ substrate. The resulting catalysts preserve the atomic arrangements of the active two metal centers (Ir–O–Ir) but present two key new features. First, the Ir DHCs are tightly bound to the supporting substrate (α -Fe₂O₃) and show outstanding stability against aggregation or detachment. Second, the catalysts are highly active toward water oxidation even without the organic ligands, which are critical to the functionality of the homogeneous analog.¹⁸ Significantly, better performance than Ir SACs or Ir NPs was measured on Ir DHCs.

2.2 Materials and methods

2.2.1 Materials synthesis

Preparation of Ir dinuclear catalysts on α-Fe₂O₃ (Ir DHC) and loading estimate

Step 1: An α -Fe₂O₃ substrate was soaked in the Ir homo-dimer solution for 10 h and then thoroughly rinsed with DI water to form the Ir intermediate. The loading amount was estimated by comparing the change of the UV-Vis absorbance of the Ir homo-dimer solution. We used the average absorbance decrease for a 32-time loading procedure, the overall geometry area being ca. 94.4 cm². The Ir loading was calculated to be ca. 30-36 nmol/cm², which was confirmed by ICP-OES measurements.

Step 2: The photochemical treatments were conducted using a UVO cleaner system (Jelight Company Inc.) equipped with a UV light. In a typical procedure, the Ir intermediate sample was placed in the middle of the UVO chamber. The process lasted 28 min to get Ir DHCs.

Preparation of Ir single atom catalysts on α-Fe₂O₃ (Ir SAC)

Similar to the preparation of Ir DHC, Ir SAC was obtained by carrying out step 2, the photochemical treatments for 40 min. The loading of Ir SAC is the same as the loading of Ir DHC sample, because no Ir evaporates during the photochemical treatment.

Preparation of Ir-based nanoparticles on α-Fe₂O₃ (Ir NP)

Method 1: As-prepared Ir intermediate/ α -Fe₂O₃ was annealed at 550 °C under Ar atmosphere for 30 min to form Ir NPs/ α -Fe₂O₃.

Method 2: Ir intermediate/ α -Fe₂O₃ was placed in the middle of the UVO generator chamber for 60 min under UV-ozone conditions.

2.2.2 Structural characterizations

Scanning transmission electron microscopy (STEM)

All samples were scraped from the FTO electrode and collected on Lacey carbon grids. HAADF-STEM images were collected using a double aberration corrected FEI Titan3 G² 60-300 instrument operating at 300 kV. The semi-angle of the probe-forming aperture was ca. 22 mrad. The inner and outer semi-angles of the HAADF detector were ca. 80 and 200 mrad, respectively. A probe current of 76 pA and dwelling time of 16 µs per pixel were chosen for desirable signalto-noise ratios. Energy dispersive X-ray spectroscopy (EDS) was performed on a Super-X EDS system consisting of four Bruker Silicon Drift Detectors (SDD). During EDS mapping, sample drifting was corrected by a simultaneous image collector. The Fe K-edge, O K-edge and Ir M-edge were used for elemental mapping. Electron energy-loss spectra (EELS) were collected with a GIF quantum EELS spectrometer; a standard power-law background subtraction was utilized to remove the background. Some STEM images were collected on an FEI Titan G2 80-200 Crewley "ChemiSTEM" microscope, which was equipped with a high-brightness field emission gun (X-FEG), a probe spherical aberration (Cs) corrector and a super-X EDS system.¹⁹ The semiconvergence angle for imaging was ca. 24.7 mrad, while the collection semi-angle was ca. 70-200 mrad. A higher beam current of 280 pA was used with a longer dwell time of 0.1 msec per pixel and repeated 200 times for atomic-resolution EDXS mapping. Spatial drifting was corrected using a simultaneous image collector. All high-resolution HAADF images shown in this work are raw data without any post-filtering.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

In situ DRIFTS measurements were performed using a Nicolet iS50 FTIR spectrometer equipped with a DTGS KBr detector and a Harrick praying mantis HVC-DRP4 cell equipped with

KBr windows.²⁰ After each sample was placed in the cell, it was heated to 105 °C under pure He for at least 15 min to remove physically adsorbed H₂O and was then gradually cooled to room temperature. Ir NPs/ α -Fe₂O₃ prepared by method 1 was further treated under 20% H₂ at 150 °C for 2 h to remove potential thin oxide surface coatings. Background spectra were then recorded at room temperature. Subsequently, the gas flow was changed to CO for 15 min and was changed back to He to avoid possible interference of gaseous CO to the spectra. DRIFT spectra were recorded in the CO absorption region, 2200-1800 cm⁻¹ after varying the He purging time (5, 10, 40 and 70 min). The resolution was selected at 4 cm⁻¹. 64 scans were recorded for each spectrum shown in the work.

HAADF-STEM image simulation

Multislice HAADF-STEM image simulations were performed using Dr. Probe software ²¹ on the basis of atomic models relaxed by first-principle DFT calculations as shown in Figure 3 and using experimental imaging parameters. The Fe₂O₃ structural model for simulation consists of 6 Fe layers, corresponding to ca. 2 nm in thickness. The sample misalignment angle and the aberrations of the microscope were set to zero for the simulations. Structural models were visualized using the VESTA software.²²

X-ray Absorption Spectroscopy (XAS)

Ir L3-edge XAS data were recorded at the microprobe beamline 10.3.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory (ALS, LBL). The storage ring was operated in top-off mode (1.9 GeV, 296 buckets, 500 mA). Using a Si (111) monochromator, the data collection was carried out in fluorescence mode for all samples under ambient conditions. An Ir foil (1st derivative taken at 11215.5 eV) and IrO₂ standard were measured for energy calibration purposes. The beam spot size was $15 \times 3 \ \mu m^2$ for XANES and EXAFS measurements.

The raw XAS data were deadtime corrected and calibrated using a suite of LabVIEW custom software available at the beamline. Data were subsequently analyzed using Athena Demeter version 0.9.24. The experimental data were fitted by EXAFS scattering path simulations using Artemis Demeter version 0.9.24.²³ The coordination number of Ir-O for IrO₂ standard was fixed at 6 to determine the amplitude reduction factor (S₀²). The work-up of XAS data to k-space and Fourier transformed R-space was done using a consistent methodology of background subtraction, post-edge normalization, conversion to k-space, and FT conversion in R-space. All sample data were refined using k³-weighting, a Kaiser-bessel window k-range of 3-14 Å⁻¹ and R-range of 1.0-2.2 Å for the first shell fitting, R-range of 1.0-4.0 Å for the second shell fitting.

The S_0^2 value was determined to be 0.90 (fixed in all proceeding fits) by fitting the first Ir-O shell of the IrO₂ reference and fixing the CN parameter at 6. The Nyquist criterion was used to calculate the number of independent data points for each EXAFS spectrum that was fit. The number of dependent parameters was maintained to be less than or 1/2 the value of the maximum number of independent data points. Uncertainties in EXAFS fitting parameters were weighted by the square root of the reduced chi-squared value obtained for the simulated fit.

2.2.3 Photoelectrochemical (PEC) characterization

PEC measurements were carried out using a potentiostat (Modulab XM equipped with Modulab XM ECS software). The light source was a solar simulator (100 mW/cm², Solarlight Model 16S-300-M Air Mass Solar Simulator, AM 1.5). Ir DHC/ α -Fe₂O₃, Ir SAC/ α -Fe₂O₃, Ir NPs/ α -Fe₂O₃, and α -Fe₂O₃ were used as the working electrodes, with an SCE electrode as the reference electrode, and a Pt wire used as the counter electrode. The electrolyte was a 0.1M KNO₃ solution with the pH adjusted to 6.0. The potential was corrected to the reversible hydrogen

electrode (RHE) scale by Nernst equation ($E_{RHE} = E_{SCE} + 0.059 pH + 0.241$). For linear sweep voltammetry data, the scan rate was 20 mV/s.

2.2.4 Computational details

We used the Vienna ab initio simulation package (VASP) for all periodic boundary calculations.²⁴ Projector augmented plane wave (PAW) method²⁵ together with the Perdew-Burke-Ernzerh (PBE) exchange-correlation functional²⁶ were employed to describe the electron-ion interactions. A cutoff of 450 eV was chosen for the plane wave basis set in all calculations. A $5\times5\times5$ Monckhorst-Pack type k-point grid was chosen for the optimization of bulk Fe₂O₃. The Gaussian smear method was used for Fe₂O₃. The σ value was chosen to be 0.1 eV. The energy convergence criterion was set to be 10^{-4} eV per unit cell and the geometry convergence criterion was set to be 10^{-3} eV per unit cell for energy difference between two consective ionic steps.

2.3 Results and discussions

2.3.1 Synthesis strategy for Ir DHCs



Figure 2.1 Synthesis procedure of Ir DHC. It starts with the immobilization of molecular Ir catalysts, followed by photochemical removal of organic ligands. The binding details of H₂O and OH groups are proposed.

Building upon our previous successes in immobilizing homogeneous water oxidation catalysts (Ir homo-dimer), ²⁷ we designed the synthesis of Ir DHCs as shown in Figure 2.1. The key new step added to this work is the photochemical treatment, which was implemented to remove

the organic ligands. The STEM characterization of the α -Fe₂O₃ substrate and the resulting catalysts at each stage is presented in the Figure 2.2.



Figure 2.2 STEM characterization of Ir intermediate on α -Fe₂O₃. (A) HAADF-STEM image and (B-F) EDS elemental mapping of O, Sn, Ir, Fe and C in the same region. The location of FTO and α -Fe₂O₃ are indicated in (A) with arrows. (G-I) HAADF-STEM images of Ir intermediate on α -Fe₂O₃. The yellow dashed lines in each images show the surface amorphous layer, which is formed as a result of the burning of organic ligands under electron beam irradiation. The Ir atoms are not observed on the surface due to the presence of this amorphous layer.

In addition to structure results to be presented below, X-ray photoelectron spectroscopy (XPS) (Figure 2.3) and electron energy loss spectroscopy (EELS) (Figure 2.4) clearly support that there is no N signal after the photochemical treatment. This provides strong evidence that the pyridyl ligands in the precursor have been removed.


Figure 2.3. XPS spectra of Ir intermediate (left) and Ir DHC (right) on α -Fe₂O₃. A, A' Survey scans revealing that the only elements present are Fe, O, C, Ir, C, Sn and I. B, B' The peaks at 65 eV and 62 eV correspond to Ir 4f_{5/2} and Ir 4f_{7/2}, respectively. Compared with Ir intermediate (C, D), high resolution spectra of C and N confirm the absence of the organic ligands in Ir DHC (C', D').



Figure 2.4. A, EELS spectra of the Fe $L_{2,3}$ -edge of Ir DHC on α -Fe₂O₃ and the reference samples. From the EELS data, it is clear that the valence state and the coordination environment of Fe do not change, demonstrating that the

heterogenization process and the photochemical treatment do not fundamentally alter the α -Fe₂O₃ substrate. B, XRD patterns indicating that there are no Ir-containing crystalline NPs present after the heterogenization process and the photochemical treatment. The # symbol represents the peaks of SnO₂, which were due to the conductive substrate. C, EDS spectrum between 0.2 and 1.0 keV of Ir DHC. The EDS peak value of N K-edge should be 0.392 keV, which is absent in this spectrum. D, EELS spectrum from surface region of Ir DHC. The EELS peak of N K-edge should be at 401 eV, which is absent in the EELS spectrum. These data strongly support that the N-containing ligands have been successfully removed by the simple photochemical treatment.

2.3.2 Direct structure characterization of Ir DHCs

The most direct evidence that proves we have obtained a new dinuclear structure of Ir atoms that are not in direct contact but connected by an oxygen bridge is from the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) data (Figure 2.5 and Figure 2.6). The bright two-point features in Figure 2.5A were identified as Ir DHCs, and the lighter grey points in the background were ascribed to Fe atoms.



Figure 2.5 Direct structural characterization of Ir DHC on α -Fe₂O₃. (A and B) Representative HAADF-STEM micrographs along [241] zone axis, in which the bright pairs are ascribed to Ir DHCs. The dotted line between the two stars in B represents the linescan for HAADF intensity analysis as shown in C. (D) Darkfield image of the region (outlined by white window) mapped in E–G for the distribution of Fe, O, and Ir, respectively. [Scale bars: (A) 2 nm; (B) 1 nm; (D–G): 4 nm.]



Figure 2.6 STEM characterization of Ir DHC on α -Fe₂O₃. (A & E) HAADF-STEM images and (B-H) EDS elemental mapping of Fe, O and Ir in the same region at different magnifications. EDS spectra for Figure 2.5 D (I), Figure 2.6 A (J) and Figure 2.6 E (K). We highlight the uniformity of the Ir distribution.

Tilting experiments confirmed that the Ir atoms are on top of the Fe columns (Figure 2.7). Nevertheless, we caution that we could not fully rule out the existence of other species not aligned with the Fe columns by TEM characterization alone. Spectroscopic evidence lent additional support on this front (*vide infra*). The ultra-high signal-to-noise ratio was enabled by the high Z-contrast of Ir and Fe. Importantly, few other components, such as Ir SACs or Ir NPs were observed within the viewing field (more discussions on the distribution in Figure 2.8), which is critical to this work because the SACs and NPs would otherwise complicate the mechanistic understanding of water oxidation by Ir DHCs. To further study the atomic arrangement of the Ir DHCs, a line-

scan for HAADF intensity was taken across the bright spots (Figure 2.5B), and the intensity data are plotted in Figure 2.5C. The average distance between the two Ir atoms within a DHC was measured at ca. 3 Å. Elemental mapping using STEM-EDS (Figure 2.5D-G, Figure 2.6) further supported that there were no large aggregates of Ir clusters. The lack of Ir SACs or clusters was proven by spectroscopic characterization to be discussed below. Taken as a whole, the unique two-atom arrangement and the lack of aggregated byproducts set the stage for detailed studies of DHCs as a new class of water-oxidation catalyst.



Figure 2.7. Top view model and STEM image along [001] zone axis before (left) and after ca. 40° rotation (right). Scale bar: 1 nm



Figure 2.8 Species distribution in samples by photochemical treatment for different durations.

Our previous work has proven that the Ir–O–Ir arrangement within the Ir homo-dimer (Figure 2.1) is key to its high activity toward water oxidation.^{18, 27} We, therefore, expect that Ir–O–Ir rather than Ir–Ir arrangement is preserved in the Ir DHC. Evidence from at least two complementary experimental techniques strongly support our expectation. First, we performed *in situ* CO Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopic characterization, and the purpose was to use CO as a probe to study the Ir atomic arrangement within the DHC. While the dinuclear nature of the structure is unambiguously confirmed by the HAADF data, an alternative arrangement to the proposed one could feature Ir–Ir bonding. In the *in situ* CO DRIFT experiment, the two arrangements are expected to be readily distinguished by the characteristic absorption features at ca. 1850 cm⁻¹, which is indicative of the bridge adsorption of CO at the Ir-Ir site.²⁸ Indeed, the broad peak at ca. 1850 cm⁻¹ was observed for Ir NPs control samples with known Ir-Ir bonding (Figure 2.9B) but absent from Ir DHCs (Figure 2.9A). Additionally, a strong dipole-dipole coupling effect between adjacent CO probe molecules was evident in the control

sample with Ir aggregates but was absent in Ir DHCs, further confirming the atomic dispersity of the latter.



Figure 2.9 *In situ* DRIFT spectra of Ir DHCs (A) and NPs (B) in He flow 5 (black), 40 (red), and 70 (blue) min after CO adsorption at room temperature. The schematic atomic arrangement of the structures corresponding to the spectra are shown as insets. Green ball is Ir, red ball is O, and brown ball is C.

Second, XAS data were acquired to reveal the coordination environment of the Ir center. We see from Figure 2.10–2.12 and Table 2.1 that the first shell coordination of Ir in DHCs is dominated by Ir–O,²⁹ in excellent agreement with the proposed bonding of Ir–O–Ir but not Ir–Ir. To avoid interference from the post-edge of the Fe signal from the α -Fe₂O₃ substrate, as well as the potential Ir–Fe scattering pathways, EXAFS data were collected on a mesoporous silica SBA-15 substrate instead of on α -Fe₂O₃. The XANES spectra showed almost identical spectral features for Ir DHC on SBA-15 and on α -Fe₂O₃ substrate, proving that it is an appropriate substitute to collect the EXAFS signals from the substrate transferred from α -Fe₂O₃ to SBA-15. We do caution, however, that further research is needed to fully understand whether Ir DHCs form the same way they do on α -Fe₂O₃. The Fourier transformed EXAFS spectra indicate that there is one notable peak in the region 1 to 2 Å from the Ir–O contribution, with no peak in the region 2 to 3 Å from the Ir–Ir contribution. These would be characteristic peaks from Ir NPs. Compared with the spectrum of IrO₂, negligible signals have been observed in the position of 2.92 and 3.54 Å from the second shell scattering contribution of Ir DHC, indicating that the loss or weakening of the scattering from the second shell. This is consistent with the structure of the Ir DHC, where only one Ir–O–Ir exists, much fewer than the 10 scattering pathways for Ir–O–Ir of IrO₂.

The XANES probes the transition from the core level to the conduction band, i.e., $2p_{3/2}$ to $5d_{5/2}$ for Ir L₃-edge.²³ The diversities of the intensity and the position of the white line (WL) peak provide a basis to examine the electronic structure of the samples. The stronger WL peak intensity and higher photon energy peak represent a higher valence state. The XANES spectra suggest that the valence state of Ir DHC is IV. Importantly, there is no observable difference between the Ir DHC XANES signals on SiO₂ and α -Fe₂O₃.



Figure 2.10 Fourier transforms of Ir L3-edge EXAFS experimental data for Ir foil, IrO_2 and Ir DHC on SiO₂ (A) and the corresponding k³-weighted EXAFS data (B).



Figure 2.11 Ir L3-edge XANES of Ir DHC, reference samples Ir foil, IrO₂, Cp*Ir^(III)(pyalc)OH and Ir intermediate (A). Corresponding first order derivative of the data (B). The comparison of Ir DHC on different substrates (C).

The XANES probes the transition from the core level to the conduction band, i.e., $2p_{3/2}$ to $5d_{5/2}$ for Ir L₃-edge ²³. The diversities of the intensity and the position of the white line (WL) peak provide a basis to examine the electronic structure of the samples. The stronger WL peak intensity and higher photon energy peak represent a higher valence state. The XANES spectra suggest that the valence state of Ir DHC is IV. Importantly, there is no observable difference between the Ir DHC XANES signals on SiO₂ and α -Fe₂O₃.



Figure 2.12 Fourier transforms of Ir L3-edge EXAFS experimental data for Ir DHC and fitting for Ir DHC in R space (A) and k space (B). Fourier transforms of Ir L3-edge EXAFS experimental data for IrO_2 and fitting data for IrO_2 in R space (C) and k space (D).

Scattering Path	CN	R(Å)	$\sigma^2(Å^2)$	$\Delta E_0(eV)$
Ir–O (Ir DHC)	5.85	2.01625	0.00458977	11.23889765
Ir–O (IrO ₂)	6	1.98960	0.00959470	14.09129971

Table 1. Structural parameters obtained from the fits of the EXAFS spectra.

CN, coordination number; R, bonding distance; σ^2 , Debye-Waller factor; ΔE_0 shift in absorption edge energy. Fitting parameters: $\Delta k=3-14$ Å⁻¹, dk=0 Å⁻¹, $\Delta R=1-2.2$ Å⁻¹, $S_0^2=0.90$

Taken as a whole, the microscopic and spectroscopic characterization unambiguously confirmed that we have obtained a dinuclear Ir catalyst that features discrete Ir–O–Ir rather than Ir-Ir structures without organic ligands. Here we further highlight the uniqueness of the synthesis method. Our previous experiments show that other treatments such as thermal annealing²⁷ or electrochemical decomposition³⁰ lead to obvious Ir aggregation. Only by photochemical treatments could we achieve the DHC structure in the high yield (>80%).

2.3.3 Determination of binding sites by DFT and HAADF simulation

The strong metal-support interaction (SMSI) is crucial to maintaining the catalytic structure under catalytic operation conditions for many systems.⁴ How SACs can be anchored onto supporting substrates by defect sites has been demonstrated on reducible metal oxides.³¹ Nevertheless, it would be a significant challenge to rely on the randomly distributed defect sites as the binding sites for DHCs that feature well-defined and uniform M–O–M arrangements. To understand how our Ir DHCs bind to the α -Fe₂O₃ support, we carried out density functional theory (DFT) calculations. Our strategy was to construct hydroxyl-terminated α -Fe₂O₃ (001) surfaces, as shown in Figure 2.13C. Previous studies have shown that hydroxyl termination is the most stable in the presence of gas-phase H₂O.³² The optimized surface structures suggested that the Ir– O–Ir structure is stabilized by substrate O, H₂O and –OH ligands. Taken together, the two Ir atoms in the resulting DHC are bound by five surface O atoms, each Ir atom occupying a three-fold hollow site on the OH-terminated α -Fe₂O₃ surface. Importantly, the model built here allowed us to simulate the expected HAADF image under the experimental condition (Figure 2.13E), which is in excellent agreement with the experimental data in terms of the Ir atomic location (Figure 2.13A). Similarly, the simulated intensity line scan data reproduced the experimental ones as well, illustrating the accuracy of the interatomic distance in Ir–O–Ir site (Figure 2.13B & F). We note that the data presented here represents a typical example of one facet of α -Fe₂O₃ (001), which provides a basis for more comprehensive future studies of other facets.



Figure 2.13 Binding sites of Ir DHC on α -Fe₂O₃. Atomic resolution experimental (A) and simulated (E) HAADF-STEM micrographs of Ir DHC. The basis for the HAADF-STEM simulation is the atomic structure as shown in C and D. (Scale bars: A, 1 nm, E, 0.5 nm.) Proposed atomic structure of Ir DHC (support: α -Fe₂O₃). Top view along [001] zone axis (C) and side view (D). In the atomic model, green ball is Ir, gold ball is Fe, red ball is O, and white ball is H. The corresponding experimental (B) and simulated (F) HAADF line-intensity profiles show excellent match.

2.3.4 Catalytic characterization of Ir DHCs

Photoelectrochemical (PEC) characterization was next carried out to study the catalytic activity of the Ir DHC following previously developed protocols. The Ir-based catalysts are known

to be most active under acidic conditions.²⁷ As such, it is desirable to study them at low pHs. The support (α -Fe₂O₃), however, would be dissolved by acids, leading to possible detachment of Ir that would undermine efforts to study its inherent catalytic activity and stability. For these reasons, we optimized the test conditions at a pH of 6.0. As shown in Figure 2.14, compared with control samples with only α -Fe₂O₃ support (bare in Figure 2.14), the addition of Ir catalysts improved the overall performance by shifting the polarization curves toward the cathodic direction. Previous thermodynamic and kinetic studies have revealed that such a shift may be due to either improved charge separation within the support or better charge-transfer kinetics or a combination of both.³³, ³⁴.



Figure 2.14 Catalytic performance of Ir DHC in water photooxidation. (A) The polarization curve of the Ir DHC (pink) in comparison with three control samples, the Ir SAC (green), Ir NP (gray), and bare α -Fe₂O₃ support (black). The electrolyte was 0.1 M KNO₃ (pH 6.0), and the illumination intensity was 100 mW cm⁻² with AM 1.5 filters.

Given that the surface coverage of Ir DHCs on α -Fe₂O₃ is sparse, we strongly believe faster kinetics is the true reason for such a shift. The understanding is consistent with our previous kinetic

studies.³³ The per-atom turn over frequency (TOF) of Ir DHCs at 1.23 V (vs. RHE) is 2.6 and 5 times higher than the corresponding Ir SACs (Figure 2.15) and Ir NPs (Figure 2.16), respectively, at the same potential. In addition, when compared with similar systems that feature Ir-based water photooxidation reactions ^{30, 33, 35–37}, the Ir DHC on α -Fe₂O₃ features the higher normalized TOFs (Table 2.2). That the sample with Ir DHCs exhibited the high activity attests to its functionality as an effective water-oxidation catalyst despite the fact that the organic ligands of the molecular precursor have been removed.



Figure 2.15 STEM characterization of Ir SAC on α -Fe₂O₃. Bright points represent a single Ir atom. Yellow circle represents the dominated species single atom. Peachblow and white circle represents the very limited amount of dinuclear species and nanoparticles. HAADF intensity line profiles were taken along the atoms. Based on the HAADF intensity profile, the sharp bumps are attributed to the existence of a single Ir atom with a diameter of ca. 0.1 nm.



Figure 2.16 STEM characterization of Ir-based NPs on α **-Fe₂O₃.** Bright points represent aggregated Ir-based NPs. HAADF intensity line profiles were taken along the nanoparticles. Based on the HAADF intensity profile, the sharp bumps are attributed to the existence of Ir-based NPs with diameters of ca. 2 nm.

Materials	Preparation Method	V _{on} (V vs. RHE)	Photocurrent density @ 1.23 V vs. RHE (mA/cm ²)	Per Ir atom turnover frequency (h ⁻¹)	Ref.
α-Fe 2 O 3/IrO2	Electrodeposition	1.1	0.15	N/A	(37)
α-Fe2O3/IrO 2	Photoelectro- deposition	0.6	0.8	1.7	(30)
α-Fe 2 O 3/IrO2	Electrophoresis	0.8	3.2	N/A	(36)
α-Fe2O3/anchored Ir complex (1)	Heterogenization	0.6	1.1	83	(33)
α-Fe2O3/anchored Ir complex (2)	Heterogenization	1.2	N/A	N/A	(35)
α-Fe ₂ O ₃ /Ir DHC	Photochemical deposition	0.55	1.51	212	This work
α-Fe2O3/Ir SAC	Photochemical deposition	0.63	1.01	80	This work
α-Fe ₂ O ₃ /Ir NPs	Post-annealing	0.63	0.89	42	This work

 Table 2.2 Comparison of representative Ir-based catalysts for solar water oxidation.

2.3.5 Proposed catalytic mechanism by DFT calculations

Inspired by previous studies on the Ir homogeneous catalysts,¹⁸ we propose a mechanism that involves multiple proton-coupled electron transfer (PCET) steps by DFT calculations using the model built. Ir DHCs and Ir homogenous Ir homo-dimer molecules¹⁸ share similar Ir^{IV}(OH₂)-

O-Ir^{IV}(OH_x) structural motifs (x = 2 for Ir homo-dimer and x = 1 for Ir DHCs). Thus, it is reasonable to assume that the water oxidation mechanism of Ir DHCs is similar to their homogeneous molecular analogs, albeit in the absence of the organic supporting ligands. As shown in Figure 2.17, Ir DHCs are proposed to undergo three PCET processes to build enough oxidation potential to oxidize H₂O and produce Ir-OOH (Step E to F). The free energy changes of the three PCET steps are 1.06, 1.37, and 1.21 eV, respectively, at U = 0 V (U is the applied potential; Figure 2.17A). A substrate H₂O molecule binds to the Ir DHC with a free energy increase of 0.44 eV, which then undergoes nucleophilic attack to form hydrogen peroxide with a free energy increase of 0.36 eV. The oxidation of Ir-OOH intermediate F is easy to proceed through a PCET, requiring only 0.75 eV. The subsequent O_2 release is driven by the following substrate H_2O binding. By comparing the free energy changes under different applied potentials, an overpotential as low as 0.14 V is enough for the overall four-electron oxidation to be thermodynamically downhill. The calculated overpotential indicates that the Ir DHC is an efficient catalyst for water oxidation, consistent with the experimentally observed low onset potential of the Ir DHC/ α -Fe₂O₃ (Von=0.55 V, corresponding to an applied potential of ca. 1.35 V by assuming a photovoltage of $0.8 \text{ V by } \alpha \text{-Fe}_2 O_3$).³⁴



Figure 2.17. Reaction mechanisms. Proposed reaction pathway and DFT calculated reactions free energies at zero bias potential (U = 0 V) of Ir DHC (A) and Ir SAC (B). Reaction free energies in green correspond to proton-coupled electron transfer steps which could be driven by applying bias potentials.

As an important control experiment, we carried out DFT calculations to compare the catalytic steps between the Ir DHC and SAC. The atomic structure of Ir SAC was built by placing one Ir atom in one three-fold O site. The resting state of Ir SAC was identified as an Ir (IV) bound with a OH⁻ and two H₂O ligands (Figure 2.17B). For water oxidation, Ir SAC first undergoes PCET processes twice, which is similar to the first two steps of water oxidation by Ir DHC. The key difference between the two catalysts lies in the next step. Whereas Ir DHC undergoes another PCET (Steps C to D in Figure 2.17a) before forming the O-O bond, Ir SAC has to bind to a H₂O substrate and form the O-O bond first (Steps C to E in Figure 2.17B) before the third PCET. This is because direct oxidation of Ir SAC after the second PCET step would require too high an energy (more than 1.8 eV). By comparison, the availability of another Ir atom nearby in Ir DHC reduces the energy need to 1.2 eV. We note that more accurate calculations of the energy need for catalytic steps would require the inclusion of the supporting substrate (α -Fe₂O₃) and solvation effects, which is beyond the scope of the present work. Our results nonetheless highlight the benefits of the synergistic effects between a dinuclear catalytic site (Ir DHC) over a mononuclear site (Ir SAC). The understanding aligns with recent experiment observations that a dinuclear site may be more active toward water oxidation.^{38,39} We emphasize that the well-defined structure of Ir DHC is key to our understanding reported here, which permits the construction of mechanistic models for detailed studies of the processes.

2.3.6 Stability characterization of Ir DHCs

We characterized the stability of Ir DHCs in two different settings. First, the chronoamperometry data of Ir DHCs on α -Fe₂O₃ for the first 10 h were compared with other Ir

catalysts. No measurable degradation was observed (Figure 2.18), suggesting that under PEC conditions the Ir DHC on α -Fe₂O₃ is stable. The stability is better than Ir SACs and Ir NPs (Figure 2.19).



Figure 2.18 Chronoamperometry showing the stability of Ir DHC over 10 h with negligible decay.



Figure 2.19 Chronoamperometry showing the stability of reference samples over 10 h at 1.23 V vs. RHE in 0.1M KNO₃ (pH 6.0).

ICP-OES characterization indicated that no Ir was detected in the electrolytes of the Ir DHCs. In addition, the key features in the data of STEM-EDS, *in-situ* DRIFTS and XPS by Ir DHCs after PEC test are similar to those by fresh samples, indicating that there was no aggregation (Figure 2.20–2.23).



Figure 2.20 Characterization of Ir DHC after 10h chronoamperometry stability test. (B-D) Elemental mapping of Ir, Fe and O, respectively. The corresponding HAADF-STEM image for the mapped area is shown in a. Aggregation of Ir atoms was not observed. (E) The peak at 2 keV is ascribed to the Ir M-edge. (F) The XPS peaks at 65 eV and 62 eV correspond to Ir $4f_{5/2}$ and Ir $4f_{7/2}$, respectively. The features are similar to fresh Ir DHC on α -Fe₂O₃.



Figure 2.21 *In situ* DRIFT spectra of Ir DHC on α -Fe₂O₃ after 10 h stability test in He after CO treatment at room temperature. The features are similar to fresh Ir DHC on α -Fe₂O₃.



Figure 2.22 EELS spectra of Fe L_{2, 3} edge (A) and O K edge (B) of Ir DHC on α -Fe₂O₃ before and after 10 h electrolysis.

Second, the Ir DHCs were subjected to focused electron beam irradiation under HAADF-STEM conditions; the purpose was to observe the inherent thermal stability of Ir DHCs. As seen in Figure 2.23, no aggregation or detachment was observed for up to ca. 1 min of irradiation, which is longer than the reported systems under the similar condition.⁴⁰ The O₃-binding site offered by the α -Fe₂O₃ substrate has proven critical to the formation and stability of Ir DHCs. We envision, however, that the binding is not unique to the chemical nature of the α -Fe₂O₃ substrate. As long as similar binding sites are available, Ir DHC structures with comparable stabilities and catalytic activities are expected on other supporting substrates.



Figure 2.23 Evolution of Ir DHC on α -Fe₂O₃ during electron beam exposure for the following times: (A) 0 s, (B) 35 s, (C) 75 s. The electron dose received by the sample was ~100 eV/Å²/s. (Scale bar: 2 nm.)

2.4 Conclusion

Heterogeneous catalysts with active moieties that are well defined in their atomic and/or molecular structures are expected to play important roles in the development of catalysis. The main challenge of this research direction lies in the synthesis and characterization of such catalysts. Within this context, the Ir DHCs reported here represent a significant advance. Not only are Ir DHCs a new heterogeneous catalyst featuring two active metal atoms, their structures are also well characterized at the atomic level. The atomic arrangement of the catalytic center (Ir–O–Ir), which is key to the water-oxidation activities, is preserved by the strong binding provided by the supporting substrate. The resulting Ir DHC exhibits outstanding stability against aggregation or detachment. It shows high activity toward water oxidation. The finding is built upon recent advances aimed at synthesizing and studying SACs but takes a crucial step forward. It presents opportunities to study the detailed mechanisms of heterogeneous catalysis involving multiple but individually separated active atoms, which was carried out using DFT in this report. The insights

are expected to contribute to the design and optimization of heterogeneous catalysts and electro-

catalyst.

2.5 References

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Chapter 3: End-on Bound Ir Dinuclear Heterogeneous Catalysts on WO₃ for Solar Water Oxidation

3.1 Introduction of end-on binding mode dinuclear heterogeneous catalysts

Research on catalysis has been traditionally divided into subfields of molecular catalysis and heterogeneous catalysis, depending on the nature of the catalysts that are being studied. Such a division has played a positive role in the development of the respective subfields because there are indeed significant differences in the methodologies best suited for the studies of these different systems. The understanding of catalysis, however, has advanced to a point where we see a clear need for convergence, as manifested by a rapidly growing body of literature aimed at advancing both molecular and heterogeneous catalysts. On the one hand, the rich knowledge on molecular catalysis makes it possible to tailor-design and fine tune catalyst activities for ever-better performance as measured by metrics such as turn-over frequencies (TOFs).¹ On the other hand, the outstanding stability of heterogeneous catalysts render them a desired form for practical applications as measured by metrics such as high overall turn-over numbers (TONs).² Together, a heterogeneous catalyst that features active moieties with molecular level understanding and control is the most coveted for both activity and longevity.³ More importantly, such a catalyst would be far more versatile for a wide range of chemical transformations. Indeed, within the context of solar fuel synthesis, significant efforts have been recently undertaken toward the direction of heterogenizing molecular catalysts. For instance, Meyer et al. have pioneered in this area by anchoring Ru mononuclear and dinuclear water oxidation catalysts (WOCs) onto metal oxides.⁴⁻⁶ Similar approaches have been demonstrated by Sun et al. on Ru- and Co-based molecular WOCs.^{7, 8} To this end, some of us (Brudvig and Batista) have shown that Ir-based heterogenized molecular catalysts are more active than the amorphous oxide derivatives, highlighting the importance of maintaining the molecular structure for the reactivity.^{9,10} Similarly, Tilley and Bell et al. have immobilized Co- and Mn-based molecular catalysts onto SiO₂.^{11, 12} Li et al. have also demonstrated both photoelectrochemical (PEC) and photocatalytic water oxidation on anchored Co molecular catalysts.^{13, 14} For the reduction reactions, Reisner et al. have coupled TiO₂ with Ni- and Co-molecular catalysts for CO₂ and H₂O reduction.^{15, 16} Chang *et al.* explored anchored supermolecular complexes for C-C coupling reactions by CO and CO₂ reduction.^{17, 18} These progresses notwithstanding, the community saw a critical deficiency in this line of research

in that there was a lack of direct experimental evidence to unambiguously support the proposed structures of the heterogenized catalysts. The deficiency has been partially addressed by Iwasawa *et al.*¹⁹ and Gates *et al.*, separately.^{20–23} A breakthrough in studying the detailed structures of immobilized molecular catalysts was made recently by us on Ir DHCs as discussed in the Chapter 2, where unambiguous experimental data were obtained using HAADF-STEM, extended X-ray EXAFS and DRIFTS.²⁴

While our result in Chapter 2 highlights the importance of the supporting substrate in facilitating the transformation of the molecular precursor Ir homogenous precursor to Ir DHC, it raises an important question concerning the binding mode of the newly formed heterogeneous catalysts. That is, is the side-on binding mode as shown in Figure 3.1A the only way to stabilize the catalyst on a substrate? In other words, in the event where the supporting substrate lacks the binding pockets that would match the atomic distance between the two Ir centers, would we expect an end-on binding mode as shown in Figure 3.1B. Answers to this question are important not only because they hold the key to broad implementations of the synthesis strategy, but also because it has implications for the study of reaction mechanisms that would benefit from a second, dangling active metal center, similar to the Mn center of the WOCs in natural photosystem II.²⁵ In this chapter, we report the first direct experimental observation of the end-on binding mode that provides a definitive answer to this question. The end-on bound Ir DHCs exhibit a higher activity toward water oxidation than the side-on bound Ir DHC or Ir SACs, possibly due to the flexibility of the top Ir center.



Figure 3.1 Schematics of our synthesis strategy for side-on and end-on bound DHCs. Starting from molecular dinuclear catalyst precursors, the catalyst is first adsorbed onto a substrate, and then the organic ligands are removed by photochemical treatments. The binding mode is defined by the structure of the substrate. When dual sites with the suitable density and distance are available (such as on Fe₂O₃, panel A), a side-on mode is preferred. Otherwise, the end-on mode is preferred (such as on WO₃, panel B).

3.2 Materials and methods

3.2.1 Catalyst preparation

Fabrication of WO₃ photoanodes

Ammonium metatungstate hydrate (Sigma-Aldrich, 99.99% trace metals basis) was dissolved in a 1:1 (volume ratio) mixture of diethylene glycol butyl ether (Sigma-Aldrich, purity \geq 99%) and ethanol (Sigma-Aldrich, anhydrous, purity \geq 99.5%) with a concentration of 0.2 mol L⁻¹. This solution was used as precursor for flame spray pyrolysis. This solution was fed at 5 ml min⁻¹ rate through a custom build nozzle, and atomized with an oxygen flow (O₂ = 5 L min⁻¹) at a set pressure drop ($\Delta P = 2$ bar). The resulting spray was ignited with a surrounding annular set of premixed methane/oxygen flame (CH₄ = 0.5 L min⁻¹, O₂ = 0.8 L min⁻¹). To prepare the photoelectrodes, the FTO coated glass substrates (TEC7, Dyesol) were cleaned by sonication for 10 min in acetone before deposition. The clean substates were mounted at a height above burner of 6 cm on a copper substrate holder. The deposition time is 60 seconds.

Preparation of Ir DHC on WO₃ and loading estimate

Step 1: A WO₃ substrate was soaked in the Ir dimer solution²⁴ for 16 h and then thoroughly rinsed with DI water to form the Ir heterogenized catalyst. The loading amount was estimated by comparing the change of the UV-Vis absorbance of the Ir molecular catalyst solution. We used the average absorbance decrease for a 26-time loading procedure. The Ir loading was calculated to be ca. 16 nmol/cm².

Step 2: The photochemical treatments were conducted using a UVO cleaner system (Jelight Company Inc.) equipped with a UV light. The process lasted 40 min to yield Ir DHCs.

Preparation of Ir SAC on WO₃

Similar to the preparation of Ir DHC, Ir SAC was obtained by placing the Ir heterogenized catalyst in the DRIFTS cell, which was heated to 105 °C under pure He for at least 15 min to

remove physically adsorbed H_2O and was then gradually cooled to room temperature. Afterwards, the cell was subjected to UV light irradiation under O_2 gas flow (5 ml/min) for up to 60 min.

3.2.2 Catalyst characterizations

STEM characterizations

All samples were scraped from the FTO electrode and collected by Lacey carbon grids. All as-prepared TEM grids were loaded into electron microscope without any further treatments.

High-resolution STEM-HAADF imaging was performed using a double aberration corrected JEOL Grand-ARM instrument operated at 300kV. The semi-angle of the probe-forming aperture was ca. 30 mrad. A 63 pm spatial resolution can be routinely achieved with a probe spherical-aberration corrector. The inner and outer semi-angles of the HAADF detector were ca. 70 and 200 mrad, respectively. A probe current of 10 pA and dwelling time of 16 µs per pixel were chosen for desirable signal-to-noise ratios. Energy dispersive X-ray spectroscopy (EDS) was performed by two JEOL Dry SD100GV silicon drift detectors. W M-edge, O K-edge and Ir M-edge were used for mapping the corresponding element distributions. Electron energy-loss spectrum (EELS) was collected by a Gatan 965 GIF Quantum ER spectrometer. A standard power-law background subtraction was utilized to remove the spectrum background, and the thickness was calculated from the low-loss EELS data in the commercial software package Digital Micrograph.

Discussions of in-situ STEM observation

Generally, the beam effects on an observed sample include one or a combination of two principal mechanisms: direct displacement of atoms (knock-on damage) by breaking the chemical bonds and heating effect caused by the phonons.²⁶ The heating effect may arise due to numerous factors, including the electron energy, thermal conductivity of the sample and/or sample thicknesses. Quantitatively, the maximal temperature enhancement (ΔT_{max}) on Ir DHC/WO₃ can be estimated by the following equation.²⁷

$$\Delta T_{\max} = \frac{I}{4\pi\kappa e} \left(\frac{\Delta E}{d}\right) \left(1 + 2\ln\frac{b}{r_0}\right) ,$$

where *I* is the total electron dose current (10 pA), κ is the thermal conductivity of WO₃ (1.63 Wm⁻¹K⁻¹),²⁸ ΔE is the total energy loss per electron in the sample of thickness *d*, and $\Delta E /d$ is linearly

dependent on the atomic number and sample density, and close to 2.568 eV/nm for WO₃ at 300 kV, *b* is the radius of the heat sink, equal to the sample radius and approximately 50 nm~100 nm in our case, and r_0 can be treated as the size of the electron probe (0.05 nm). The *in-situ* observation was conducted at room temperature (25 °C). Based on all parameters as outlined above, ΔT_{max} was obtained as ca. 0.0186 K. Due to the lower probe current in STEM in comparison to traditional TEM observations, the heating effect is concluded to be negligible under our STEM conditions. The knock-on damage may be quantitatively described by the maximum energy E_{m} transferred from incident electron with energy *E* to atomic nucleus as follows,²⁹

$$E_{\rm m} = 2.1477 \times 10^{-9} \times E(E + 1.022 \times 10^6) / A$$

where *A* is the relative atomic mass, and the energies are in eV. Under our experimental conditions, the maximum transfer-energies are 4.43, 4.63 and 53.2 eV for Ir, W and O atoms, respectively. The transfer energies are rather large and are expected to break the Ir–O bonds, to yield displacement of Ir atoms on the surface of WO_3 .³⁰

TEM specimen thickness measurement

For accurate interpretation of the STEM data, we need information on the specimen thickness. This was obtained by three independent methods: STEM images, low-loss EEL spectra and convergent beam electron diffraction (CBED) patterns.

(a) *Low-loss EEL spectra*. The thickness of the sample can be calculated by the ratio between the intensity of zero-loss peak (ZLP) and low-loss spectra. By measuring and analyzing the ZLP spectra, we obtained the local thickness (t) by the following equation:

$$t = \lambda \ln(\frac{I_t}{I_0}),$$

where λ is the inelastic mean free path (IMFP) for the material, I_0 is the area under ZLP and I_t is the total area under the whole spectrum (0-180 eV in our experiments). An absolute thickness measurement requires knowledge of the IMFP, which depends on the material, electron energy and collection semi-angle. $\lambda = 73.64$ nm was used for WO₃ under our experimental conditions.³¹ Figure 3.8A and 3.8C show two mapping images of the measured thickness from the low-loss EELS at low and high magnifications, respectively. From Figure 3.8B and 3.8D, we calculated the thickness of the region where Ir DHC STEM observations were made as 0.69-1.55 nm. (b) *STEM images*. Because the HAADF-STEM intensity should be proportional to the thickness of the sample for uniform materials, it is possible to use the STEM intensity to estimate the sample thickness. As shown in Figure 3.8F and 3.8H, we compared the STEM intensities at the center of the particle and the edge (where SETM observations were made) and obtained a thickness estimate of ca. 1 nm.

(c) Position averaged convergent beam electron diffraction (PACBED). The PACBED technique may be the most accurate to estimate the thickness. It has been demonstrated that visual comparison on the intensity distribution within the PACBED disks and the overlapping area can provide an estimate of the sample thickness at a precision of <1 nm.^{32, 33} For this body of research, we compared experimental PACBED patterns to a series of simulated ones. Figure 3.9A represents a PACBED pattern acquired at the region 1 nm away from the edge along the [002] direction. There are (200) and (002) discs in the PACBED pattern. The simulated PACBED pattern of a sample with a 0.77 nm thickness is shown in Figure 3.9C. We see a close match of these two sets of data. To further confirm the thickness, line profiles of PACBED patterns along the [002] direction are plotted in band compared to the simulated data of samples with thicknesses of 0.77, 1.55, 2.326 and 3.10 nm, respectively (Figure 3.10). The closest match was obtained for a sample thickness 0.77 nm, consistent with our estimates made by analyzing EELS and STEM images as discussed above. Based on these set of experiments, we chose the WO₃ substrate with the thickness of 0.77 as the simulation model.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

In situ DRIFTS measurements were performed on a Nicolet iS50 FTIR spectrometer equipped with a DTGS KBr detector and a Harrick praying mantis HVC-DRP4 cell ewith KBr windows.²¹ Once the sample was placed in the cell, it was heated to 105 °C under pure He flow for at 15 min to remove physically adsorbed H₂O and was then cooled to room temperature. Background spectra were then recorded. Afterwards, the gas flow was changed to CO for 15 min before switching back to He to avoid possible interference of gaseous CO to the spectra. DRIFT spectra were recorded in the CO absorption region, 2200–1800 cm⁻¹ with varying He purging times. The spectral resolution was set at 4 cm⁻¹. 64 scans were recorded and averaged for each spectrum shown in this work to improve the signal-to-noise ratios.

3.2.3 Catalysts performance test Photoelectrochemical (PEC) characterization

PEC measurements were carried out using a potentiostat (Modulab XM equipped with Modulab XM ECS software). The light source was a solar simulator (100 mW/cm², Solarlight Model 16S-300-M Air Mass Solar Simulator, AM 1.5). Ir DHC/WO₃, Ir SAC/WO₃, and WO₃ were used as the working electrodes, with an SCE electrode as the reference electrode, and a Pt wire was used as the counter electrode. The electrolyte was a 0.1 M K₂SO₄ solution with the pH adjusted to 3.0 by H₂SO₄. The potential was corrected to the reversible hydrogen electrode (RHE) scale following the Nernst equation ($E_{RHE} = E_{SCE} + 0.059$ pH + 0.241). For the linear sweep voltammetry data, the scan rate was 20 mV/s.

Oxygen and peroxide species detection

Oxygen was quantified using a Clark-type BOD oxygen electrode (Thermo Scientific 9708 DOP). O_2 evolution experiments were carried out in a two-chamber cell, where the O_2 probe, the working electrode, and the reference electrode were in one chamber, and the Pt auxiliary electrode was in the other chamber. N_2 gas was used to purge out dissolved O_2 and gaseous O_2 in the headspace for at least 1 h prior to the experiment. During the experiment, the oxygen sensor was allowed to stabilize to 0 ppm for at least 30 min. The O_2 yield during photoelectrolysis was read directly using a pH meter connected to the oxygen sensor.

Non-oxygen byproducts from photoelectrolysis were measured by quantifying the amount of O_2^{2-} that was reduced by I⁻ reductant in solution (mainly H_2O_2 and $S_2O_8^{2-}$) according to the following reactions.

$$O_2^{2^-} + 2I^- \rightarrow I_2 + 2O^{2^-}$$
 (1)
 $I_2 + 2S_2O_3^{2^-} \rightarrow S_4O_6^{2^-} + 2I^-$ (2)

Iodometry titration was carried out using ca. 6 mL electrolyte that was subjected to varying extent of photoelectrolysis. 1 M HCl was added to the electrolyte to adjust the pH to ca. 2.5. Then, 2 mL of 2 wt. % KI aqueous solution and 50 μ L of a molybdate-based catalyst solution were added. The solution turned yellow, indicating the formation of I₂. The solution was then titrated by Na₂S₂O₃ to light yellow. 1 mL of 2 wt. % starch indicator was then added, and the solution was

titrated continuously until the blue indicator color disappeared. The quantity of $O_2^{2^2}$ was back calculated by the amount of $Na_2S_2O_3$ used.

3.2.4 Computational details

We used the Vienna ab initio simulation package (VASP) for all periodic boundary calculations. ³⁴⁻³⁸ Projector augmented plane wave (PAW) method^{39, 40} together with the Perdew-Burke-Ernzerh (PBE) exchange-correlation functional⁴¹ were employed to describe the electronion interactions. A cutoff of 500 eV was chosen for the plane wave basis set in all calculations. The Gaussian smear method was used to accelerate self-consistent field (SCF) convergence and the smearing parameter σ was chosen to be 0.1 eV. A 3 × 3 × 3 Monckhorst-Pack type k-point grid was chosen for the optimization of bulk WO₃. The energy convergence criterion was set to be 10⁻³ eV per unit cell for energy difference between two consecutive ionic steps.

Based on XRD and HAADF-STEM results, we focused on WO₃ (020) surfaces which have O termination as in the case of WO₃ (002) surfaces.⁴² We considered the adsorption of water molecules on O-terminated WO₃ (020) surface. Our results suggest water molecule are adsorbed molecularly on O terminated WO₃ (020), yielding O+OH₂ terminated WO₃ (020) surface as the most stable WO₃ (020) in aqueous condition. Therefore, we used O+OH₂ terminated WO₃ (020) surfaces for the rest of our study. Ir DHC and SAC models were prepared by adsorbing Ir(OH)₄(OH₂)₂ units on O+OH₂ terminated WO₃ (020) surfaces. Slab models were chosen to have 4 unit cells in the (020) plane and full geometry relaxation was performed for the adsorbed Ir unit, the top and bottom layers, while atoms in the middle layer were frozen at their bulk positions. A vacuum layer of more than 20 Å was used to avoid the interactions between periodic images. The resulting supercell of our slab models of WO₃ (020) surfaces has the dimension of 14.95 Å \times 40.75 $Å \times 15.69$ Å. We used a $1 \times 1 \times 1$ Monckhorst-Pack type k-point grid for slab calculations. Because of the strong d-electron correlation effects of Ir, the calculations were carried out with the DFT+Umethod, using the formalism suggested by Dudarev et al.⁴³ The U_{eff} parameter for Ir was set to 3 eV according to our recent study of Ir DHC on hematite. The energy convergence criterion was set to be 10⁻⁴ eV per super cell and a force convergence criterion of 0.03 eV Å⁻¹ was used in the structure optimization of all slab models.

The catalytic mechanisms of Ir SAC and DHC were studied with our Ir SAC and DHC models. All intermediates were optimized with the same setting of Ir SAC and DHC models with the exception that the atoms in the bottom layers were frozen at their positions in Ir SAC and DHC models to save computation time. A supercell of $15 \text{ Å} \times 15 \text{ Å} \times 15 \text{ Å}$ and $1 \times 1 \times 1$ Monckhorst-Pack type k-point grid were used for the calculations of isolated molecules. The Gaussian smear method was used for molecule calculations and the σ value was chosen to be 0.1 eV.

The change of reaction free energy was calculated according to $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, where ΔE is the change of electronic energy, ΔZPE is the change of zero point energy, ΔS is the change of entropy, and *T* is the reaction temperate (298.15 K in our calculations). Partial frequency analysis was performed all intermediates in the catalytic cycle of Ir DHC and used to obtain the zero-point energy contribution for the absorbed species (*OH₂, *OH, *O*OOH, *OO) and hydrogen bonded water molecule (---H₂O). The entropies of H₂O(1), O₂(g), and H₂(g) were used to consider the entropic energy contribution.⁴⁴ The entropic contributions from absorbed species on the surfaces are small, so we omitted them, which is a common practice in the literature.⁴⁵⁻⁴⁶

For reaction steps involving the H⁺ and e⁻, the computational hydrogen electrode (CHE) technique developed by Nørskov *et al.* was used to take into account the dependence of relative energies on pH and applied bias potential.⁴⁷ The potential for oxidation of H₂O(1) \rightarrow O₂(g) + 4H⁺(aq) + 4e⁻ is calculated to 1.11 V, while the experimental value is 1.23 V. We used this potential as an internal reference to obtain more reliable potentials for each oxidation process.

The simulation of *in situ* DRIFTS were performed by replacing the H₂O molecules coordinated to Ir centers to CO molecules and performing frequency analysis for the probe CO molecules. In *in situ* DRIFTS experiments, samples were heated to 105 °C under pure He flow for at 15 min to remove adsorbed H₂O, therefore, we removed all molecularly adsorbed H₂O on WO₃ (020) surfaces and re-optimized the CO adsorbed Ir SAC and DHC model before frequency analysis. The calculated frequencies were scaled with a scaling factor of 0.988.

All calculations mentioned above were done in vacuum. We also investigated solvation effects on the relative stability of side-on and end-on binding modes of Ir DHC and the evolution of Ir DHC to Ir SAC. Solvation effects were considered with an implicit solvation model implemented in VASPsol⁴⁸ and a value of 80.0 was used to account the dielectric constant of water.

3.3 Results and discussions

3.3.1 Synthesis strategy for end-on bound Ir DHCs

Our first task for this present work was to identify a supporting substrate that would favor the end-on binding mode. It was hypothesized that the side-on binding mode would be obtained when there are dual surface binding sites separated at or close to ca. 3.5 Å, which is the separation between two Iridium atoms in the Ir molecular precursor. To test this hypothesis, we examined the following oxides, Fe_2O_3 , TiO_2 , CeO_2 , and WO_3 , which have been widely studied as supports for WOCs. It was found that other than WO_3 , all other oxides feature thermodynamically stable surfaces with a sufficiently high O density to construct two binding sites with suitable distances to stabilize a side-on bound Ir DHC (Figure 3.2 and Table 3.1). We, therefore, have chosen WO_3 as a study platform for this work.



Figure. 3.2 Surface oxygen distribution on metal oxide surfaces.

Facet	WO ₃ (020)	CeO ₂ (110)	TiO ₂ (101)	Fe ₂ O ₃ (001)
Surface O densities (nm ⁻²)	3.6	9.7	10.4	13.5

Binding sites distance (Å)	4.12	3.8	3.8	3.0

Building upon our recent successes in synthesizing Ir DHCs on Fe₂O₃, we carried out the synthesis by a soaking method, followed by UV treatments. Subsequent XPS and EELS studies confirmed that the N-containing pyalc ligands were completely removed (Figure 3.3).



Figure 3.3 XPS and EEL spectra of Ir DHC on WO₃. (A) The binding energies at ~65 eV and ~62 eV correspond to Ir $4f_{5/2}$ and Ir $4f_{7/2}$, respectively. (B) High resolution spectra of N confirm the absence of the organic ligands in Ir DHC. (C) EEL spectra from the surface region of Ir DHCs. The obvious N signal before photochemical treatments and its absence afterwards support that N-containing ligands have been successfully removed.

3.3.2 Evidence of the binding mode by in-situ DRIFTS

We next employed *in-situ* DRIFTS to probe the Ir DHC structures. As has been shown by others and us, DRIFTS is a powerful technique to report on the relative positions of Ir atoms on a substrate.^{24, 49} Here our main goal was to distinguish the structure of the targeted end-on bound Ir DHCs from the following alternatives, (*i*) side-on bound Ir DHC, (*ii*) Ir SAC and (*iii*) aggregated Ir clusters. From the data shown in Figure 3.4A, we immediately ruled out the possibility that Ir clusters were present, which would correspond to a broad peak at ca. 1850 cm⁻¹ due to the stretching mode of bridging C=O adsorption between adjacent Ir atoms.²⁴ The second structure we ruled out was Ir SACs, which would yield two characteristic singlet peaks at 2096 cm⁻¹ and 2050 cm⁻¹ (Figure 3.5 as well as simulation details). Similarly, we excluded the possibility of side-on bound Ir DHCs on WO₃ by the lack of the dual singlet peaks in the DRIFTS spectra. With all these alternative possibilities considered, the only natural conclusion supported by this set of data was that the unique dual doublet DRIFTS peaks centering at ca. 2100 cm⁻¹ and 2050 cm⁻¹ are due to the end-on bound Ir DHCs. Of these two groups of peaks, the doublet at the high wavenumber (ca. 2100 cm⁻¹) is ascribed to the asymmetric stretching of the C=O probe, and that at the low

wavenumber (ca. 2050 cm⁻¹) is due to the symmetric stretching. Within each doublet, the higher wavenumber peak (2110 cm⁻¹ and 2062 cm⁻¹) reports on the bottom Ir atom, and the lower wavenumber peak (2090 cm⁻¹ and 2044 cm⁻¹) reports on the top Ir atom.



Figure 3.4: Determination of the binding mode of Ir DHCs on WO₃. (A) *In situ* CO DRIFTS spectra and the simulated peaks by DFT. (B) The structure model used for the simulation. Green ball: Ir, brown ball: C, red ball: O, white ball: H, and grey ball: W.

Our understanding of the DRIFTS data is supported by density-functional theory (DFT) calculations. For this purpose, we relaxed the Ir DHCs on WO₃ (020) surfaces terminated with O and H₂O (Figure 3.4B). The DFT-optimized surface structure suggested that the Ir–O–Ir structure is bound to WO₃ by a single O atom. Importantly, the structure model stabilized by DFT permitted us to simulate the expected stretching frequencies of adsorbed CO on the end-on bound Ir DHCs. The calculated peak positions (2119, 2058 cm⁻¹ and 2087, 2043 cm⁻¹) are in excellent agreement with the experimental data, providing us strong confidence of the proposed structure as shown in Figure 3.4B.



Figure 3.5 Identification of the binding nature of Ir SAC on WO₃ by *in-situ* CO DRIFTS and DRIFTS simulations. (A) The atomic model used for the simulation. Green ball: Ir, brown ball: C, red ball: O, white ball: H, and grey ball: W. (B) Experimental and simulated DRIFTS spectra.

3.3.3 Structural evolution from Ir DHCs to Ir SACs

Examinations of the structure as shown in Figure 3.4B prompted us to study how the structure of end-on bound Ir DHCs change under synthesis conditions. A critical concern we had to address was whether the end-on bound Ir DHCs would be readily transformed to Ir SACs by the breaking of the μ -oxo bridge. It was found that under the preparation conditions (UVO cleaner system), we observed only Ir DHCs for durations at or shorter than 40 min. Interestingly, longer photochemical treatments (>40 min) only yielded aggregated Ir clusters, but not Ir SACs. As a control experiment, we observed Ir SACs on WO₃ by *in situ* photochemical treatments in the DRIFTS apparatus or under e-beam irradiation in the STEM chamber (Figure 3.6).



Figure 3.6 The formation of Ir SACon WO3 in the *in-situ* **STEM chamber.** (A) A series of STEM-HAADF images showing the change of Ir DHCs to SAC as a function of e-beam irradiation times (0 s to 99 s). Scale bars: 1 nm. (B) Comparison of line scan profiles of the same atomic chains from 0 s to 31 s and 99 s. The orange arrows mark the location of Ir. (C) Atomic model to show how Ir atoms move on the surface.

It is noted that the DRIFTS spectral features of Ir SAC on WO₃ are distinctly different from those of Ir DHCs, whereas the former exhibits two single peaks at 2096 cm⁻¹ and 2050 cm⁻¹ (Figure 3.4) in good agreement with the simulated data based on the DFT model of Ir SAC on WO₃. We were, therefore, encouraged to propose that H₂O in the atmosphere during the photochemical treatments in the UVO cleaner chamber facilitates Ir diffusion on the surface of WO₃, which would favor aggregation of Ir atoms once an Ir DHC is decomposed. Preliminary DFT calculations support this conjecture (Figure 3.7). To study how the end-on bound Ir DHCs change on the surface of WO₃, we considered the hydrolysis of Ir–O–Ir and Ir–O–W bonds in both pure gas phase and aqueous solution including the solvation effects. In gas phase computational condition which corresponds to the DRIFTS experimental condition with a limited amount of H₂O molecules, the hydrolysis of Ir–O–Ir bond requires 0.78 eV while the hydrolysis of Ir–O–W bond requires a higher energy, 0.98 eV. Therefore, the 0.2 eV energy difference makes it possible for the hydrolysis to stop at the Ir SAC stage, which is consistent with our experimental observation that under the DRIFTS experimental condition, we obtained Ir SACs evolved from Ir DHC. On the other hand, when the same process proceeds in quasi-aqueous condition including the solvation effects to mimic the UVO chamber with the relatively high humidity, the hydrolysis of Ir–O–Ir
bond requires 0.71 eV of energy, comparable to the energy to hydrolyze the Ir–O–W bond (0.73 eV). It is thus expected that the hydrolysis of Ir DHC in this case may not stop at the Ir SAC stage, but could further aggregate to form Ir clusters. In other words, H_2O promotes Ir atom diffusion on WO₃ surfaces to form Ir clusters.



A. Gas phase condition

Figure 3.7 The energetic profiles of hydrolysis of Ir DHC on WO₃ (020) surfaces in the gas phase condition (A) and the quasi-aqueous condition (B).

3.3.4 Further confirmation of the end-on binding mode by HAADF-STEM

HAADF-STEM was subsequently carried out to directly visualize the end-on bound Ir DHCs on WO₃. While Ir DHCs may be readily distinguished from aggregated Ir clusters by STEM, it is difficult to differentiate an end-on bound Ir DHC from an Ir SAC as both would appear in an STEM image as a single bright spot, due to the projective nature of STEM observations. The challenge is exacerbated by the fact that Ir and W feature comparable Z contrasts as a result of their close atomic weights. To combat this challenge, we simulated the HAADF-STEM data based on the structure model. For quantitative comparisons, the thickness of the simulated structure model (ca. 0.77 nm) was chosen to represent that of the observed sample, which was confirmed by the following complementary techniques for accuracy, including low-loss EELS, STEM analysis and position averaged convergent beam electron diffraction (PACBED) as well as the associated simulations (Figures 3.8-3.10).



Figure 3.8 (A) Absolute thickness mapping of the whole particle on which the high resolution STEM observations were made at a low magnification. The thickness was calculated using the low loss EELS data. (B) Line profile of the thickness mapping along the cyan arrow in (A). The maxim thickness was estimated as 91.2 nm. (C) Absolute thickness mapping of the same sample surface near the edge at a high magnification. (D) Corresponding line profile along the cyan arrow in (C). The thickness of the sample near the edge where the Ir DHCs were observed was estimated as 0.92 nm. (E) Low magnification STEM image of the same particle as shown in (A). (F) Line profile of the STEM intensity along the blue arrow as shown in (E). The maxim intensity was measured as ca. 1.18x10⁶ counts in the thickest region. (G) High magnification STEM image of the same region as shown in (C). (H) Line profile of the STEM intensity along the blue arrow in (G). The red dashing line marks the region where the high resolution STEM Ir DHC data were obtained.



Figure 3.9 Thickness measurement by the PACBED method. (A) Experimental PACBED pattern. The (200) and (002) disks are marked by yellow dashed circles. (B) Line profile along the [002] direction, as shown the red arrow in (A). The regions of (200), (400) and (600) disks are shown by blue dashed lines and arrows. (C) Simulated CBED patterns with a thickness of 7.5 Å. (D) Line profiles of CBED patterns of four samples with different thickness along the [002] direction, as shown the red dashed arrow in (C). The two black dashed arrows mark the overlapping region

between (200) and (400), and that between (400) and (600), respectively. We see by comparing (B) and (D) that the sample thickness should be between 0.75 nm and 1.51 nm.



Figure 3.10 Comparison of line profiles from simulated HAADF images with different thickness through the [020] zone axis. The data used are from the same region as shown in Figure 3A and 3D in the main text. From top to bottom, the thicknesses are (1) 13.5 Å, (2) 7.7 Å as labeled on the right side. The Ir DHC positions are marked with two orange dashed lines. From this set of data, we concluded that Ir DHC on WO₃ (020) surface would be indistinguishable by HAADF-STEM if the thickness of WO₃ along the [020] direction is > 1.35 nm.

We see from Figure 3.11A and 3.11D that the presence of Ir DHC would yield an increase of the line scan intensity by 55%, whereas Ir SAC would increase the intensity by 45%. Experimentally, we observed a ca. 55% increase in the Ir DHC (Figure 3.11C) and a ca. 40% increase in the Ir SAC (Figure 3.11F). Combining this set of data with the HAADF-STEM images, as well as the DRIFTS data, we concluded that we have successfully synthesized Ir DHCs in an end-on binding mode.



Figure 3.11 HAADF-STEM studies of end-on bound Ir DHCs on WO₃. (A) Atomic structure of Ir DHC on top of WO₃ (020). Top left: top view; bottom left: side view. Simulated STEM image from the top view (top right), as well as a representative line scan profile of one Ir DHC against the WO₃ supporting substrate (bottom right). The positions of the Ir DHCs are marked by orange circles in the simulated STEM image, and the orange-shaded peaks indicate the position of Ir DHCs. (B) Experimental STEM image, in which the regions for the line scan profile is marked by the light blue box. The white circles highlight Ir DHCs. (C) Line scan profile of the region highlighted in (B). (D) Simulated atomic structure of Ir SACs on top of WO₃ (020). The arrangement of the panels is identical to (A). (E) Experimental STEM image, in which Ir SACs are highlighted by the white circles. The green box marks the region where the line scan profile in (F) was obtained. (F) Line scan profile of the region shown in (E). Scale bars: 5 Å.

3.3.5 Catalytic characterization of end-on bound Ir DHCs.



Figure 3.12. The catalytic activity of Ir DHC and SAC on WO₃, as well as bare WO₃. (A) Photocurrent density voltage data. (B) Product selectivity toward O₂ evolution vs. peroxide species formation.

With the structure and the binding mode of Ir DHCs on WO₃ confirmed, we next carried out H₂O oxidation reactions to characterize the catalytic properties (Figure 3.12). For these experiments, we employed an electrolyte with a pH of 3.0 (0.1 M K₂SO₄, pH adjusted by H₂SO₄). Previous research has shown that WO₃ is active toward H₂O oxidation, and the associated photocurrent-voltage (*J-V*) curves feature high fill factors (FF), indicative of fast charge transfer.⁵⁰ Such a characteristic was indeed observed by us. If we used the photocurrent density at 1.23 V vs. RHE as the short-circuit current density, and the voltage where 0.1 mA/cm² photocurrent was measured as the open-circuit potential⁵¹ and treated the data as a diode-based solar cell, a FF of 0.37 would be obtained. By comparison, bare Fe₂O₃ would yield a FF of 0.19 without co-catalysts. The presence of Ir DHCs and SACs improved the FF marginally to 0.42, and 0.47, respectively. No measureable difference was observed between their turn-on characteristics. The difference of the saturation photocurrent density is within the typical variations among different samples and, therefore, is statistically insignificant.

The most critical difference between samples with and without Ir DHCs or SACs was found in the product selectivity. Due to slow kinetics towards a 4-electon pathway to produce O_2 , WO₃ is known to facilitate a 2-electron pathway of H₂O oxidation, yielding peroxide as a product.⁵² By comparison, Ir-based catalysts are expected to favor the 4-electron pathway of complete H₂O oxidation to O_2 .^{53–56} We, therefore, performed product detections. As shown in Figure 3.12, the total detected O_2 and peroxide account for ca. 100% of all charges measured. Among the samples studied, 39% of peroxide was measured on bare WO₃ under our experimental conditions; the numbers for Ir DHCs on WO₃ was only 9%, and that for Ir SACs on WO₃ was 24%. Given that the estimated disperse density of Ir atoms on WO₃ was low (ca. 16 nmol/cm²) for Ir DHCs, the results are significant. They strongly suggest that despite the catalytic activity of WO₃ toward H₂O oxidation, charges prefer to find Ir catalytic sites for 4-electron H₂O oxidations. The competing process would be 2-electron H₂O oxidation on exposed WO₃ surfaces. The comparison between Ir DHCs and SACs further highlight the benefit of the second, dangling Ir atom in facilitating H₂O oxidation reactions, the details of which were studied next by DFT.

3.3.6 Computional understanding of catalytic cycle

The DFT calculations were conducted based on the proposed mechanism as shown in Figure 3.13, where multiple proton-coupled electron transfer (PCET) steps are involved. Due to the electron affinity difference of the two Ir atoms in an Ir DHC, Ir_{top} was assumed to be slightly more electron rich. It would undergo PCET to build an oxidizing potential first (steps $\mathbf{A} \rightarrow \mathbf{B}$ in Figure 3.13), followed by two consecutive PCET processes to yield Ir-OOH (F in Figure 3.13). The free energy changes of the three PCET steps are 1.30, 1.33, and 1.11 eV, respectively, at U = 0 V (U is the applied potential). When similar calculations were performed on Ir SACs on WO₃, it was found that a different pathway would be preferred (Figure 3.14 and Figure 3.15) because a third PCET to oxidize Ir SAC after the first two PCET steps would require too high an energy (1.85 eV). The results further highlight the benefit of having a second Ir site for 4-electron H₂O oxidation reactions. They set the stage for more accurate calculations to include potential influences by the supporting substrate (WO₃) and solvents.



Figure 3.13 Proposed mechanism of Ir DHC as studied by DFT calculations.

The DFT results of end-on bound Ir DHCs can also be compared with side-on bound Ir DHCs. As detailed in Figure 3.14, compared with side-on bound Ir DHC, the end-on bound one consumed lower energy to stabilize water during the nucleophilic attack ($\mathbf{D} \rightarrow \mathbf{E}$) and oxygen release ($\mathbf{G} \rightarrow \mathbf{H}$) due to the flexibility of the Ir–O–Ir unit. Ideally, the comparison would be more meaningful if one could construct end-on and side-on bound Ir DHCs on the same substrate. Unfortunately, such a possibility is not yet observed experimentally. Our results show that when side-on binding is possible (owing to the relative closeness of Ir binding sites on the surface, such as on Fe₂O₃), no end-on bound Ir DHCs is observed. We, therefore, caution the qualitative nature of such a comparison. Notwithstanding, the excellent performance of end-on bound Ir DHCs reminds us of the Mn_{dangling} moiety in the Mn₃CaO₅ catalytic center in PSII, where it has been proposed that the dangling atom will lose an electron, and that H₂O nucleophillic attack for the O-O bond formation may occur on the dangling Mn.⁵⁷ Within this context, we see that the results

presented here may have significant implications for constructing catalysts with similar structure flexibility for complex chemical reactions.



Figure 14 Comparison of catalytic cycles between the end-on bound Ir DHC (A) and side-on bound Ir DHC (B).²⁴ Key difference is found in the chemical steps (highlighted by light yellow shadows), which are usually regarded as the rate limiting steps.



Figure 3.15 Proposed catalytic cycle I for Ir SAC with calculated reactions free energies at zero bias potential (U = 0 V) (inset). DFT optimized structures of intermediates.



Figure 3.16 Proposed catalytic cycle II for Ir SAC with calculated reactions free energies at zero bias potential (U = 0 V) (inset). DFT optimized structures of intermediates.

We proposed two catalytic cycles for Ir SAC (Figure 3.15 and Figure 3.16). In both cycles, Ir SAC would undergo PCET processes twice in the beginning. The key difference between the two cycles lies in the third step. The proposed cycle II undergoes a third PCET (Steps **C'** to **D'** in Figure 3.13) before forming the O-O bond, similar to Ir DHC. However, the third PCET would require too high an energy (1.85 eV). Alternatively, the Ir SAC could bind to a H₂O substrate and form the O-O bond first (Steps **C** to **E** in Figure 3.15) before the third PCET in the proposed cycle I, which is more favorable.

3.4 Conclusions

The development of catalysis sees a clear trend of convergence, where the benefits of both homogeneous and heterogeneous catalysis may be combined for better overall performance in terms of TOFs and TONs. Within this context, we obtained an Ir DHC that maintains the atomic arrangement of the molecular precursor but is bound to the supporting substrate of WO₃ in an endon mode. Spectroscopic (DRIFTS) and HAADF-STEM results strongly support the dinuclear nature of the catalyst, as well as the end-on binding mode. The binding mode is further supported by DFT calculations. Together with the previously reported side-on bound Ir DHCs, the results prove that rich configurations of atomically dispersed heterogeneous catalysts are possible. Importantly, the resulting catalysts show superior performance for H_2O oxidation in comparison to bare WO_3 . As such, the results represent an important step toward tailor-designed, atomically defined heterogeneous catalysts for important chemical transformations such as solar fuel synthesis.

3.5 References

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Chapter 4: Highly Stable Preferential CO Oxidation by Dinuclear Heterogeneous Catalysts

4.1 Preferential CO oxidation and its challenges

Preferential CO oxidation in the presence of excess H₂ (PROX) promises a route to removing CO as a key contaminant in H₂ for a wide range of applications.¹ Significant research has been attracted to carry out PROX at low temperatures (e.g., < 200 °C) so as to maximize the selectivity toward CO removal rather than H₂ oxidation.² Driven by the understanding that strong CO binding between adjacent metal atoms in metallic nanoparticles (NPs) would block the active site, which leads to inferior activity, much of recent attention has been directed toward studying atomically dispersed catalysts. Indeed, exciting progress has been made.³ Outstanding per atom catalytic activity, for example, has been reported on Pt single atom catalysts (SACs) dispersed on a variety of supports.⁴ Moving forward, how to maintain the high activity for prolonged operations becomes a critical issue that has received relatively little attention. The handful of studies that address the stability issue of atomically dispersed catalysts describe a strong dependence of such stability on the substrate support.^{5, 6} That is, the interactions between the metal active center and the supporting substrate (often metal oxides) are critical to the performance of the atomically dispersed catalysts.^{7, 8} While intuitive, this hypothesis raises critical questions concerning the mechanisms by which PROX proceeds on a single atom site.⁹ A growing body of evidence suggests that the synergistic effect between the active center and the substrate, mediated by the interfacial atoms (often O-based species) is of vital importance.¹⁰⁻¹⁴ However, while the pivotal role played by interfacial O atoms toward activity has been inferred in the literature,¹⁵ the implications of these species to the stability of the catalyst under operating conditions are poorly understood. More importantly, it remains unclear how to capitalize on the existing knowledge to

achieve atomically dispersed catalysts that are both active *and* stable. Here, we report a study aimed at correcting this important deficiency. In this chapter, using a combination of super high resolution *in situ* imaging and DFT calculations, we identified two types of O atoms, bridge and interfacial, in the atomically dispersed dinuclear Ir catalysts (Figure 4.1A). It was found that outstanding stability can be afforded by the *bridge* O atom between two active metal centers, whereas the activity was mainly connected to the *interfacial* O atom between the active center and the supporting substrate. This chapter shed important new light on the principles governing the stability and activity of atomically dispersed catalysts.

4.2 Materials and methods

4.2.1 Catalysts preparation

Preparation of Ir catalyst on CeO2 and loading estimation

Nanoparticle CeO₂ was purchased from US Research Nanomaterials, Inc with the surface area of 35-70 m²/g and was used as the support for various Ir/CeO₂ catalysts. Prior to each catalyst preparation, the support was calcined in air at 400 °C for 5 h, then stored under vacuum in the dark. The preparation of the Ir homogenous dimer solution was based on previously established methods 16 The monomer for the dimer solution preparation, Cp*Ir[pyalc(OH)] (Cp*: pentamethylcyclopentadienyl, C5Me5, pyalc: 2-(2-pyridyl)-2-propanolate), was synthesized following an established procedure.^{16, 17} The CeO₂ substrate as treated above was soaked and stirred in 5 M Ir homogenous dimer solution for 30 h. The samples were obtained by filtering the slurry, continuously washing with DI water at 50 °C, then drying in vacuum at room temperature overnight. The procedure was repeated 3 times. Afterwards, it was further treated by photochemical methods using a UVO cleaner system (Jelight Company Inc.) for 50 min to remove organic ligands. The obtained catalysts were calcined in 5% H₂ (bal. He) at 150 °C for 2 h to yield Ir DHC/CeO₂. Ir SAC was prepared by a similar procedure but with 70 min UV treatment. Inductively coupled plasma (ICP) spectroscopy confirmed the Ir loading as ca. 1 wt.%. The asprepared catalysts were stored under vacuum in the dark for all characterizations.

4.2.2 Preferential CO oxidation activity tests

Preferential CO oxidation (CO PROX) reactions were performed in a continuous flow reactor at ambient pressure. The reactant gases (1% CO, 1% O₂, 40% H₂, bal. He, purchased from Airgas) were introduced into the reaction system by a mass flow controller connected to the cylinder. The catalyst bed was composed of solid powder of supported catalysts and inert quartz. The ramping rate of temperature was set at 5 °C/min. The mixed gases passing through the catalysts bed were analyzed by an online mass spectrometer. The conversion of CO was calculated by equation I, and the selectivity of O₂ was calculated by equation II. CO conversion was controlled between 8–20% to permit steady-state kinetic study. Each sample was pelleted into particles (50–125 μ m) and placed on the glass wool in the cell and then pretreated by 5% H₂ at 150 °C for 1 h.

$$CO \ conversion = \frac{co_{in} - co_{out}}{co_{in}} \qquad (I)$$

$$O_2 selectivity = \frac{CO_{in} - CO_{out}}{2*(O_{2 in} - O_{2 out})} \quad (II)$$

4.2.3 Catalyst characterization

CO diffuse reflectance infrared Fourier transform spectroscopy

CO diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFTS) was done by using a Nicolet iS50 FTIR spectrometer equipped with a mercury cadmium telluride detector and a Harrick praying mantis HVC-DRP4 cell with KBr windows. Each sample was pelleted into particles (50–125 μ m) and placed on the glass wool in the cell and then pretreated by He at 105 °C for 1 h. The background spectra were collected at RT. The spectra were collected with a resolution of 4 cm⁻¹ and 128 scans. The catalyst powder was purged with diluted CO for 30 min and then pure He to desorb physically adsorbed CO, at which time the data were collected.

X-ray absorption spectroscopy

The *in-situ* X-ray absorption spectroscopy (XAS) data were collected in fluorescence mode with a 13-channel germanium detector. The facility is located at 12-BM beamline at the Advanced Photon Source (APS) at Argonne National Lab. The Ir L₃ absorption edge energy was calibrated by measurement on an Ir foil with an energy of 11215 eV. Sixteen consecutive scans were collected for each data point. For the *in-situ* EXAFS experiments, the samples were pretreated under the reaction condition (20 mL/min flow rate, 1% CO, 1% O₂, 40% H₂, bal. He, 473 K, 2 h, ~10 mg catalyst loading) for 2 h and then the data were collected after the temperature was decreased to room temperature (with reactant gases flowing).

The *ex-situ* Ir L3-edge XAS data were collected at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, bending magnet microprobe beamline 10.3.2 (2.1–17 keV) with the storage ring operating at 500 mA and 1.9 GeV, using a Si (111) double-crystal monochromator. All data were collected under ambient conditions in fluorescence mode at the Ir L3-edge (11215 eV). The monochromator energy was calibrated using an Ir foil, with the 1st derivative maximum set to 11215 eV. Fluorescence emission counts were recorded with a seven-element Gesolid-state detector (Canberra) and XIA electronics. Ir L3-edge X-ray absorption spectra were recorded in fluorescence mode from 11060 to 12200 eV, by continuously scanning the Si (111) monochromator (Quick XASmode). All data were processed using the LabVIEW custom beamline 10.3.2 software to perform deadtime correction, energy calibration, glitch

removal, pre-edge subtraction, and post-edge normalization. EXAFS spectra were recorded up to 985 eV above the edge (i.e., up to $k \approx 12.5 \text{ Å}^{-1}$), and 20 scans were averaged.

Scanning transmission electron microscopy

Aberration-corrected scanning transmission electron microscopy (AC-STEM) was performed on a JEOL Grand ARM300CF microscope equipped with two spherical aberration correctors, operated at 200 kV. High angle annular dark field (HAADF)-STEM images were recorded using a convergence semi-angle of 22 mrad, and inner- and outer- collection angles of 83 and 165 mrad, respectively. The *in situ* STEM experiment was performed using a Denssolution Climate system, which allows for dynamic observation of nanomaterials heated under atmospheric pressure inside a transmission electron microscope.

Discussion on electron beam effect for in-situ STEM experiment under gas phase condition

In order to minimize effects of the electron beam during the *in-situ* STEM experiment under gas-phase conditions, a very small probe current (<10 pA) was used for *in-situ* STEM imaging. Typical probe currents for normal STEM imaging are between 50–100 pA. Meanwhile, the magnification was always kept below 8.0 M, and the acquisition time was controlled to be less than 12 seconds to reduce the electron dose. Considering the imaging condition (a pixel dwell time of 12 µs/pixel and a pixel size of 0.08 Å²) of our STEM observation, the electron dose we used was less than 1.0×10^4 e/Å², which is about 2 orders of magnitude lower than typical values for atomic-resolution STEM imaging. Particularly, the electron beam was turned off except during image collection for the *in-situ* STEM experiment. According to the experimental evidence, the Ir DHC and the CeO₂ support were stable, and no obvious irradiation damage was found during image collection.

Moreover, additional experiments were carried out to compare images of the same area before and after an exposure to the electron beam during image acquisition. Here, Figure 4.16 is an image taken under an inert atmosphere (760 Torr of N₂) at 473 K, showing an Ir single atom on the CeO₂ support, as indicated by the yellow circle. Then, one more image was taken afterwards, using the same imaging condition. Apparently, no obvious motion of this Ir atom was observed according to the comparison confirming that the beam condition we used did not introduce a movement of Ir atoms on the CeO₂ surface under the gas phase condition. Therefore, these results rule out the possible artifact from the electron beam effect, and the observed Ir atom motion in our *in-situ* experiment was indeed caused by the pseudo-PROX reaction condition.

4.2.4 Computational details

All periodic boundary calculations were performed with the Vienna Ab initio Simulation Package (VASP).^{18–21} We use the Perdew-Burke-Ernzerhof (PBE)²² exchange-correlation functional in conjugation with the projected-augmented wave (PAW) method.^{23, 24} A cutoff energy of 500 eV was chosen for the plane wave basis set in all calculations. We used the Gaussian smearing method to accelerate SCF convergence and the σ value was chosen to be 0.1 eV. Dispersion interactions were considered using Grimme's D3 empirical correction with Becke-Johnson damping.²⁵ The standard GGAs fail for strongly correlated systems such as the d electrons of Ir and f electron of Ce. All calculations involving Ir and Ce atoms were performed with the spin-polarized DFT+U method, using the rotational-invariant formalism developed by Dudarev *et al.*²⁶ The empirical U_{eff} parameters were chosen to be 5.0 eV for Ce 4f orbitals ^{27, 28} and 3.0 eV for Ir 5d electrons.²⁹

A $9 \times 9 \times 9$ Monckhorst-Pack type k-point grid³⁰ was chosen for the optimization of bulk ceria. The energy convergence criterion was set to be 10^{-6} eV per unit cell and the geometry convergence criterion was set to be 10^{-5} eV per unit cell for energy difference between two consecutive ionic steps. The optimized lattice constant is 5.46 Å, in good agreement with experimental lattice constant of 5.41 Å.³¹

We prepared slab models for the CeO_2 (110) surface to study Ir SAC and DHC since the CeO_2 (110) facet provides surface O atom pairs to bind Ir SAC and DHC. In addition, it is also the facet observed in our HAADF-STEM experiments. The lattice constants from the bulk optimization were fixed for all our slab calculations. We calculated surface energy of the CeO₂ (110) facet with 4, 5, and 6 layers of Ce and O atoms and found that the calculated surface energy already converges with 4 layers of Ce and O atoms. Therefore, we constructed slab models of the CeO₂ (110) facet with 4 layers of Ce and O atoms to study the stability and reactivity of Ir SAC and DHC. A vacuum layer of ~ 20 Å is used to minimize the artificial interactions between periodic images. A supercell of 15.44 Å \times 30.44 Å \times 10.92 Å was used to model the CeO₂ (110) surface, which contains 4 layers of Ce and O atoms. The atoms in the bottom two layers were fixed at their bulk position, while the atoms in the top two layers, as well as the adsorbates, were allowed to relax during geometry optimization. A $1 \times 1 \times 1$ Monckhorst-Pack type k-point grid was used for all surface structure relaxations unless otherwise noted. The energy convergence criterion was set to be 10⁻⁵ eV per super cell and the force convergence criterion of 0.03 eV Å⁻¹. The nudged elastic band (NEB) method³² was used to get the initial guess for transition states, which were fully optimized with the improved dimer method³³ implemented in VASP.

The calculations of isolated small molecules were performed with a supercell of 15.0 Å × 15.0 Å. A × 15.0 Å. The Gaussian smearing method and a σ value of 0.1 eV were used in the calculations. A 1 × 1 × 1 Monckhorst-Pack type k-point grid was used to sample the Brillouin zone and the SCF convergence criterion was set to be 10⁻⁵ eV per unit cell.

4.2.5 EXAFS fitting:

The classical EXAFS equation is shown below

$$\chi(k) = \sum_{j}^{\text{paths}} N_{j} S_{0}^{2} \frac{|f(k)|}{kR_{j}^{2}} \sin(2kR_{j} + 2\delta_{c} + \phi) e^{-2R_{j}/\lambda(k)} e^{-2\sigma^{2}k^{2}}, \quad (S1)$$

where *j* goes over all scattering paths, *k* is the momentum vector, $2\delta_c + \phi$ is phase shift. The structural parameters are the interatomic distances R_j , the coordination number (or number of equivalent scatterers) N_j , and the temperature-dependent root-mean-square (rms) fluctuation in bond length σ , which also includes effects due to structural disorder. In addition, $f(k) = \left| f^{\text{eff}}(k) \right| e^{i\phi(k)}$ is the backscattering amplitude, δ_c is central-atom partial-wave phase shift

of the final state, and $\lambda(k)$ is the energy-dependent XAFS mean free path. S_0^2 is the overall amplitude factor.

Isotropic Ir L₃-edge EXAF spectra of considered structures were calculated using the *ab initio* real space Green function approach as implemented in the FEFF program (version 6) ³⁴. The experimental EXAFS data $\chi(E)$, that is the fractional change in absorption coefficient of Ir atoms induced by neighboring atoms, are converted into momentum (*k*) space using the transformation

$$k = \left[\frac{2m_e}{(h/2\pi)^2}(E-E_0)\right]^{1/2}$$
, where m_e is the mass of the electron and h is the Planck's constant.

The calculated EXAFS data are obtained by fitting the energy of the absorption edge (E_0) and the reduced factor (S_0^2) against the experimental results, using the IFEFFIT code.³⁵

All calculations using Feff6 were performed using the following parameters: "NLEG 8", and "CRITERIA 10.0 9.0", "RMAX 5.5", and "HOLE 4 1.0". A fractional cosine-square (Hanning) window with $\Delta k = 1$ was applied to the experimental and calculated EXAFS data. A grid of k points equally spaced at 0.05 Å⁻¹ was used for the Fourier transformation (FT) of in the k range of 3.0-12.0 Å⁻¹ for Ir DHC. The DFT optimized Ir DHC structures were used to calculate the scattering amplitude, phase shift, XAFS mean free path in Eq. (S1), while the edge shift ΔE_0 and the Debye-Waller factors (DWF) σ^2 were determined using IFEFFIT. The simulated EXAFS results are given in Figure 4.6 and the fitting and structural parameters in the EXAFS simulation are given in Table 4.1.

4.3 Results and discussions

This study was enabled by a unique study platform, the Ir dinuclear heterogeneous catalysts (DHCs) on CeO₂. It features an active center consisting of two Ir atoms, linked and separated by *bridge O species*. The unit is anchored onto the CeO₂ support by *interfacial O species* (Figure 4.1 and Figure 4.2).



Figure 4.1 Proposed atomic structure of Ir DHC on CeO_2 (side view). The electric lime and camouflage green colors indicate Ir and Ce; the polo blue, russet, and brandy rose balls represent interfacial O atom, bridge O atom, and O atom in bulk CeO₂, respectively.



Figure 4.2 Side view (A) and top view (B) of the optimized CeO_2 (110) facet with surface O pairs as possible binding sites for Ir SAC and DHC. Once Ir DHC and SAC are anchored on the surface, the binding surface O is regarded as the interfacial O.

As can be seen in Figure 4.3 and Figure 4.4, the dinuclear nature is most directly revealed by *ex situ* aberration-corrected scanning transmission electron microscopy (AC-STEM). The high angle annular dark field STEM (HAADF-STEM) image as shown in Figure 4.3 was taken along the $[10\overline{1}]$ zone axis of CeO₂. Notably, under this specific condition with UV treatment for 20 min after immersing the CeO₂ in an Ir dimer precursor solution,²⁹ we observed Ir heterogeneous atoms in pairs. In Figure 4.3, a single pair was examined (top panel), where a line scan of the Z-contrast (bottom panel) permitted the measurement of the atomic spacing between the two Ir atoms at ca. 3.7 Å. This value is in agreement with the DFT-optimized structure models as shown in Figure 4.1, where Ir atoms are coordinated by O atoms with an average Ir–O distance of 2.03 Å, and they are connected by bridge O atoms with an Ir–Ir distance of 3.7 Å (Ir–O–Ir).



Figure 4.3 Direct characterization of Ir DHC/CeO₂ catalyst A false-colored HAADF-STEM image of Ir DHC/CeO₂ along the $[10\overline{1}]$ zone axis of CeO₂, where the Ir atoms are highlighted (within yellow dashed rectangles). A magnified view of a single Ir DHC on CeO₂ (right top). Normalized intensity profile taken along the line indicated by the yellow arrows (right bottom).



Figure 4.4 STEM characterization of Ir DHC on CeO₂. (A) HAADF-STEM images and EDS elemental mapping of Ce, O and Ir in the same region. (B) A false-colored magnified HAADF-STEM image of a single Ir DHC on CeO₂ and corresponding 3D intensity profile taken along the single Ir DHC.

The structure of the Ir DHCs was further studied EXAFS and DRIFTS. The EXAFS data shown in Figure 4.5 provided strong support to the DFT structure model, which is evidenced by the good match between the simulated and experimental spectra. The presence of Ir–O bonds in the first coordination shell as well as an Ir–O–Ir interaction in the second coordination shell from the EXAFS simulation (Figure 4.6 and Table 4.1) also confirmed that there were no significant byproducts such as Ir mononuclear (often referred to as SACs in the literature) or nanoscale clusters (often referred to as nanoparticles, NPs). The homogeneity of the Ir DHCs on CeO₂ was also further supported by the DRIFTS spectra (Figure 4.7). Together, this set of data demonstrates that we have successfully obtained monodispersed Ir DHCs on CeO₂, whose structure is resolved as shown in Figure 4.1.



Figure 4.5 EXAFS experimental and fitted spectra based on the DFT atomic model of Ir DHC on CeO₂ and bulk Ir foil at the Ir L-edge.



Figure 4.6 Experimental (Red) and calculated (black) EXAFS spectra of Ir DHC in both *k* (A and B) and **reduced distance** *R* **space (C and D).** The DFT optimized Ir DHC structure with surface reconstruction was used to calculate the EXAFS spectra. In A and C, only the first coordinate shell (Ir–O) was included in the EXAFS simulation, while in B and D, both the first coordination shell (Ir–O) and second coordination shell (Ir–O–Ir and Ir–O–Ce) were included. The comparison between the experimental and calculated EXAFS spectra demonstrates the reliability of our surface reconstructed Ir DHC model from DFT calculations.

Table 4.1	Fitting and	structural	parameters	in the	EXAFS	simulation	of Ir DHC.
			p				

Fitting Parameters						
ΔE_0	3.35 eV					
S_0^2	1.00					
<i>k</i> range	3.0–12.0 Å ⁻¹					
R range	1.0–4.0 Å					
Structural Parameters						
Scattering path	CN^a	R (Å) ^b	σ^2 (Å ²)			

Ir–O	6	1.94, 1.99, 2.04,	0.001
		2.04, 2.08, 2.11	
		(2.02)	
Ir–Ir	1	3.18	0.002
Ir–Ce	5	3.42, 3.62, 3.76,	0.012
		3.83, 4.13	
		(3.75)	

^a CN denotes Coordination Number. Coordination numbers in our simulation are determined from our DFT optimized structure rather than fitting parameters.

^b Rather than adjustable average bond distances in a typical shell model fitting, the distances from our optimized structure are using in the ab initio real Green function calculations in the FEFF program. The DFT optimized bond lengths are given in the unit of Å. The numbers in the parentheses are average bond lengths.



Figure 4.7 In situ DRIFTS spectra of Ir DHCs.

With the structural information confirmed, we next performed PROX using Ir DHCs on CeO₂ at 453 K (Figure 4.8). As an important control, Ir SACs with well-defined structures (Figure 4.9) were also prepared and subjected to similar catalytic conditions. It was observed that while Ir DHCs and SACs exhibited comparable initial activity, the main benefit of Ir DHCs was the outstanding durability, with 7% decay for 120 h. In contrast, only 75% of the initial activity was measured on Ir SACs at 40 h, which further decreased to 63% after 120 h.



Figure 4.8 Catalytic stability characterization: CO PROX stability test over Ir DHC and SAC on CeO₂. Reaction conditions: 40 mL/min flow rate, 1% CO, 1% O₂, 40% H₂, bal. He, 50 mg catalyst loading, T = 453 K.



Figure 4.9 HAADF-STEM characterization of Ir SAC on CeO₂. (B) DFT-optimized model of Ir SAC on CeO₂ (110) facet. (C) EXAFS spectra of Ir SAC.

Most strikingly, the Ir DHCs were much more stable than Ir SACs despite similar synthesis conditions, almost identical loading amount of active elements, and the same supporting substrate. The characterization of DHC and SAC after reaction was carried out. Negligible change was observed in Ir DHC (Figure 4.10), whereas the features characteristic of Ir NPs can be found in Ir SAC samples after the reaction (Figure 4.11). The result suggests that significant Ir aggregation

took place for Ir SAC but not for Ir DHC. Intrigued by the observation, we were prompted to ask the following question: *What is the key difference between DHCs and SACs that lead to such a stark contrast in their stability*?



Figure 4.10 (A) HAADF-STEM and (B) EXAFS characterization of Ir DHC after 40 h. Scale bar: 1 nm. Dual atomic pair was indicated by yellow rectangles and single atom was indicated by green triangles.



Figure 4.11 (A) HAADF-STEM and (B) *In-situ* DRIFTS spectra of Ir SAC after 40 h. Nanoclusters and nanoparticles were indicated by yellow circles and single atoms were indicated by pink circles.

Answers to this research question have significant implications. While a range of SACs has been shown active toward PROX, a critical question remains unanswered. It concerns the mechanism by which O_2 is activated by the single atom site where CO is also strongly bonded. The most compelling working hypothesis invokes the participation of various O species such as the interfacial O, which serve to anchor the single atom site to the supporting oxide or the lattice O that is part of the supporting substrate or both.^{36, 37} The Ir DHCs are different from Ir SACs and, by extension of structural similarities, many reported SACs of other compositions, in that they feature additional O species like the bridge O (Figure 4.1). Moreover, the close vicinity of a second Ir atom that is not directly bonded with Ir (*i.e.*, no metal-metal interactions) might enable synergistic effects for simultaneous O_2 and CO activation. We are, therefore, encouraged to explore two new possibilities: 1. bridge O may enhance the stability of atomically dispersed active sites; 2. synergistic effects between adjacent Ir atoms may promote PROX. As will be discussed next, our results confirmed the former but ruled out the latter.



Figure 4.12 *In-situ* EXAFS spectra of Ir DHC and SAC. Reaction conditions: 20 mL/min flow rate, 1% CO, 1% O₂, 40% H₂, bal. He, 473 K, 2 h, ~10 mg catalyst loading.

To test the first possibility, we have examined the structural changes of Ir SACs and DHCs during the PROX reaction. While no significant difference was observed between the EXAFS spectra for Ir DHCs before and after PROX (Figure 4.12), a rise of the peak at ca. 2.6 Å (not phase corrected) that is indicative of Ir–Ir bonding became apparent for Ir SACs under *in operando* XAS at 473 K (ambient pressure, 1% CO, 1% O₂, 40% H₂ balanced by He). The data imply that agglomeration of Ir SACs to form clusters or NPs took place during PROX. But under similar conditions, such changes were not observed for Ir DHCs.



Figure 4.13 *In situ* HAADF-STEM images showing the mobility of DHC (A) at pure CO gas phase (760 Torr of 5% CO, 473 K) to mimic the CO-related reaction condition, such as CO oxidation. (B) Normalized intensity profile. (C) DFT-optimized DHC model under CO condition.



Figure 4.14 (A) *In situ* HAADF-STEM images showing the mobility of SAC at the pure CO gas phase (760 Torr of 5% CO, 473 K). The number is used to mark the crystal facets from the top. (B) DFT-optimized SAC before and after the diffusion.

To obtain direct evidence to support this understanding, we carried out *in situ* AC-STEM observations by placing Ir DHCs and SACs inside a TEM nanoreactor and exposed them to pure gas (760 Torr of 5% CO, Figures 4.13 and Figure 4.14) and a gas mixture (400 Torr of 5% H₂ and 10 Torr of 5% CO, Figures 4.15A and 4.15B), respectively, at 473 K. In these experiments, internal features of CeO₂ (such as grain boundaries in Figure 4.15B) were used as alignment marks for locating the relative positions of the individual Ir DHCs and SACs and a comparable experiment under pure N₂ clearly showed negligible electron beam effect of image acquisition on the Ir species (Figure 4.16). Under conditions similar to PROX (400 Torr of 5% H₂ and 10 Torr of 5% CO), a diffusion of 15.4 Å was observed for Ir SACs within the first 5 min; then, the additional diffusion distance was 16.2 Å from 5 min to 10 min (Figure 4.15B). By contrast, no measurable movement was observed for Ir DHCs under the same conditions for 60 min (Figure

4.15A). It is noted that strong binding of CO has been previously reported to weaken the anchoring of SACs on metal oxide supports.³⁸



Figure 4.15 Direct stability observation. In situ AC-STEM characterization of Ir DHC/CeO₂ under gas phase condition. In situ HAADF-STEM images showing the mobility of Ir DHC (A) and SAC (B) at gas phase (400 Torr of 5% H₂ + 10 Torr of 5% CO, 473 K) to mimic the PROX condition (Scale bar: 2 nm). The colored circles highlight the same Ir SAC and Ir DHC, respectively. Calculated reaction energy changes (ΔE) and associated barrier height (ΔE^{\ddagger}) for (C) diffusion of Ir SAC, (D) detachment of Ir DHC and (E) dissociation of Ir DHC on CeO₂ surface. All energies are in the unit of eV.



Figure 4.16 *In situ* STEM result showing negligible electron beam effect of image acquisition on the Ir species. Two *in-situ* HAADF-STEM images of Ir SAC/CeO₂ under 760 Torr of N_2 at 473 K at different time periods. Yellow circles highlight the Ir single atoms.

Our DFT calculations support the observation, too. It is seen in Figure 4.15C that the diffusion of Ir SACs on the CeO₂ (110) facet is an isothermal process with an estimated activation energy of 1.7 eV, indicating that diffusion is highly possible. The detachment of Ir DHCs on CeO₂, however, incurs a significant thermodynamic penalty of ca. 8.9 eV, making detachment an unlikely pathway (Figure 4.15D). A more likely route by which Ir DHCs can be removed from the surface would be initial dissociation of the two Ir ions on the surface, which corresponds to a 0.7 eV increase of the thermodynamic energy with an estimated activation energy of 2.2 eV (Figure 4.15E). Indeed, by exposing the Ir DHC under intentional strong electron beam irradiation in the vacuum chamber during the AC-STEM observation, we only observed dissociation of Ir DHCs, which led to the formation of Ir SACs that exhibited diffusion behaviors subsequently (Figure 4.17). It is conceivable that the diffusion of Ir SACs would lead to eventual aggregations that form Ir NPs (Figure 4.18). The understanding is also confirmed by STEM and DRIFTS data for postreaction samples. Taken as a whole, this set of data confirms that the dinuclear nature of the Ir DHCs greatly enhances their stability as compared with SACs. With bridge O being the key differentiating feature between Ir DHCs and SACs, it is concluded that the stability directly benefits from the presence of this species. Next, we will demonstrate that bridge O indeed does not participate in the catalytic cycles.



Figure 4.17 Evolution of Ir DHC during intentional strong electron beam irradiation in the vacuum chamber for the following times: 60 s (A), 120 s (B).



Figure 4.18 (A) Evolution of Ir SAC during electron beam exposure in the vacuum chamber for the following times: 0 s, 5 s, 10 s, and 30 s. The circles are drawn around SAC (blue) and cluster (orange). The size distribution (B) is based on species counted in (A).

A growing body of literature on SACs-based PROX or CO oxidation supports that interfacial O plays a critical role in the catalytic cycle. The working hypotheses often involves the combination of interfacial O with adsorbed CO, resulting in CO_2 as a leaving product and an O vacancy to be replenished by adsorbed O_2 , which completes the catalytic cycle. When examining the structural details of Ir DHCs and SACs, we propose that the same function could be played by bridge O, as well, in which case a fundamental difference would be expected in the apparent activation energies of the overall reactions. To test this possibility, we next performed CO oxidation at varying temperatures (Figure 4.19). CO was already converted to CO_2 by Ir DHC at
temperatures as low as 373 K and was almost depleted at 453 K. A kinetic study was carried out at the kinetic region (< 20% conversion) to construct the Arrhenius plots as shown in Figure 4.18B. It is obvious that the apparent activation energies for Ir DHCs and SACs were nearly identical. As such, it is concluded that CO oxidation proceeds on the two types of catalysts following similar mechanisms, which would invoke the participation by interfacial O but not bridge O.



Figure 4.19 Low-temperature activity initiated by interfacial oxygen. (A) CO conversion and O₂ selectivity of Ir DHC for CO PROX reaction at different temperatures. Test conditions: 30 mL/min flow rate, 1% CO, 1% O₂, 40% H₂, bal. He, 250 mg catalyst loading. (B) Arrhenius-type plot of CO PROX reaction over Ir SAC and DHC. Test conditions: 100 mL/min flow rate, 1% CO, 1% O₂, 40% H₂, bal. He, 100 mg catalyst loading, conversion of CO is

controlled below 20% to be in the kinetic region. (C) The reaction pathway of CO oxidation on Ir DHC on CeO_2 suggested by DFT calculations. The vertical axis shows the relative energies of intermediates and transition states in the unit of eV. The DFT optimized structures of intermediates are shown with labels associated with them.

The understanding is strongly supported by computational studies of the catalytic cycle, the results of which are detailed in Figures 4.19C. Our proposed catalytic mechanism starts with an *in situ* generated intermediate I that features 2 square-planar Ir(I) centers connected by a bridge O atom. Intermediate I can bind to an O₂ molecule at the Ir(I) center with an energy change of -1.21 eV to form intermediate II, which reacts with a physiosorbed CO molecule (intermediate III) to form CO_2 (intermediate IV). Afterwards, CO_2 is readily released to generate a coordinatively unsaturated Ir(III) complex (intermediate V), the open site of which will then be occupied by another CO, forming intermediate VI. The oxidation of the second CO molecule is the rate determining step (rds) with a calculated activation energy of 0.84 eV, consistent with experimentally measured apparent activation energy. The release of the second CO₂ in intermediate VII regenerates intermediate I with two Ir(I) centers and an O vacancy. In the proposed catalytic cycle, O₂ is activated at the O vacancy to replenish the interfacial oxygen between the Ir(I) center and CeO₂ surface, and two CO molecules are sequentially oxidized to two CO₂ molecules. It is emphasized that only the Ir center and interfacial O are involved in the catalytic cycle, whereas the bridging O atom serves to hold the two Ir centers together to afford the supreme stability of Ir DHC.

4.4 Conclusion

In conclusion, two types of O species are identified for atomically-dispersed Ir catalysts. The first is interfacial O that connects the active metal center to the substrate. It participates in the PROX reaction by adsorbing O_2 and oxidizing CO and may be considered a critical component for the reactivity. Similar O species are abundant in single atom catalysts, which may help to explain the high activity that has been reported on these catalysts. The second type of O species bridges two metal active centers and is independent of the metal-substrate interactions. There is no evidence that the bridge O participates in the catalytic cycles of PROX. Rather, the bridge O mainly helps to minimize diffusion of the metal active centers to afford outstanding stability. Building on the recent successes in achieving high activity on atomically dispersed catalysts, our results imply that introducing structural components may contribute significantly to the eventual goal of achieving catalysts that are both active and stable.

4.5 References

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