# UNDERSTANDING HETEROGENEOUS C1 CHEMISTRY BY NEW APPROACHES AND NEW CATALYSTS

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A dissertation

submitted to the Faculty of

the department of Chemistry

in partial fulfillment

of the requirements for the degree of

Doctor of Philosophy

Boston College Morrissey College of Arts and Sciences Graduate School

December, 2019

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# Understanding Heterogeneous C<sub>1</sub> Chemistry by New Approaches and New Catalysts

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C<sub>1</sub> chemistry, referring to CO<sub>2</sub> reduction and CH<sub>4</sub> conversion, is very important not only from environmental consideration, but also from chemical perspective. However, high activation barrier and poor product selectivity control hinder the development of both reactions. New approach like photo-assisted method is promising to solve these challenges. In addition, understanding the reaction mechanism and designing new catalysts could provide further insights and improve the performance. Specifically, I successfully demonstrated selective photoelectrochemical (PEC) CO<sub>2</sub> reduction to CO by Si photocathode and metal complex catalysts, resulting in low applied bias. Then I further studied how proton donor would affect the electrode-catalyst interaction by comparing two Re complex with almost identical structure, which further results in different product selectivity. Further, I studied PEC CH<sub>4</sub> oxidation by TiO<sub>2</sub>, where photoexcited species participate in the chemical reactions. Selective CH<sub>4</sub> oxidation to CO was demonstrated under room temperature and ambient pressure. Detailed mechanistic investigation by experimental and theoretical efforts revealed a synergistic effect by adjacent Ti<sup>3+</sup> for selective CO production. I also focused on direct CH<sub>4</sub> conversion to oxygenate by thermocatalysis. Single atom and dinuclear Ir center were created on silicon oxide (SBA-15), which showed great activity towards oxygenate production. Systematic experimental investigations implied a synergistic effect by adjacent Ir atom for acetic acid formation.

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# **TABLE OF ABBREVIATIONS**

- **PEC:** photoelectrochemical
- **TPA:** tris(2-pyridylmethyl)amine
- **HER:** hydrogen evolution reaction
- **OER:** oxygen evolution reaction
- **RHE:** reversible hydrogen electrode
- ALD: atomic layer deposition
- **SEM:** scanning electron microscopy
- STEM: scanning transmission electron microscopy
- **TEM:** transmission electron microscopy
- **XPS:** X-ray photoelectron spectroscopy
- **DFT:** density functional theory
- FTO: fluorine doped tin oxide
- **SRM:** steam reforming of methane
- **FTIR:** Fourier-transform infrared spectroscopy
- EPR: electron paramagnetic resonance spectroscopy

#### ACKNOWLEDGMENTS

I would like to thank my parents, Dr. Minglei He and Hong Ma, for all their love and support throughout my whole life and especially my PhD study. I would not have gotten this far without their love.

I would like to thank my academic advisor, Professor Dunwei Wang, for all the guidance and support for me during my graduate study. I will be grateful for the academic advices and life essences I received from him. I would also like to thank Professor Udayan Mohanty, and Professor Matthias M. Waegele for serving on my degree committee as well as generous guidance and support throughout the years.

I would like to thank all the collaborators: Professor Gary Brudvig, Gourab Banerjee in Yale University; Professor Matthias M. Waegele, Xiang Li, Jingyi Li in the Waegele group; Professor De-en Jiang, Dr. Guoxiang Hu and Qiang Wan in UC riverside; Professor Gonghu Li and Dr. Tong Jin in University of New Hampshire.

To all the past and present Wang group members I have been worked with: Dr. Wei Li, Dr. Xiahui Yao, Dr. Yumin He, Dr. James E. Thorne, Dr. Qi Dong, Yanyan Zhao, Chaochao Lang, Mary Gao, and Xizi Zhang: working with you guys has been my pleasure.

I would also like to thank my beloved girlfriend, Yuyang Zhang, for all her love and support. Life would not be the same without you by my side.

Lastly, I would like to thank the funding that has supported me during my graduate career:

National Science Foundation (DMR 1055762, CBET 1703663, 1703655 and 1924689), ACS Petroleum Research Fund (DND: Photocatalysis) and Boston College Ignite fund.

### **Chapter 1: Introduction**

This chapter is partly reprinted with permission from Wang, Y. †; He, D. †; Chen, H.; Wang, D., Catalysts in Electro-, Photo- and Photoelectrocatalytic CO<sub>2</sub> Reduction Reactions. *J. Photochem. Photobio. C: Photochem. Rev.*, **2019**, *40*, 117-149. Copyright 2019 Elsevier B.V.

#### 1.1 CO<sub>2</sub> reduction and its challenges

As the most stable product of fossil fuel utilizations, carbon dioxide (CO<sub>2</sub>) is considered a main contributor to the greenhouse effect that rapidly changes the environment in a negative fashion. One way to counteract the adverse effect is to reduce CO<sub>2</sub> in the atmosphere. Chemical reduction of CO<sub>2</sub> seems to be a promising way to solve this problem. In this way, a new route of carbon cycle may be built to offset CO<sub>2</sub> emitted in the atmosphere due to industrial consumption of fossil fuels. Economically, direct conversion from CO<sub>2</sub> to carbonaceous compounds offers additional benefits. The products may serve as alternative fuel sources and/or raw materials for industrial processes that traditionally rely on fossil fuels or photosynthesis products.

However, CO<sub>2</sub> reduction faces many intrinsic challenges. Chemically, CO<sub>2</sub> is the final oxidation product of carbon and a thermodynamically stable compound. It consists of two C=O bond, each of which has a bond dissociation energy (750 kJ mol<sup>-1</sup>) much higher than that of the C-C (336 kJ mol<sup>-1</sup>). C-O (327 kJ mol<sup>-1</sup>) or C-H (441 kJ mol<sup>-1</sup>) bond. This means that not only is the reduction of CO<sub>2</sub> non-spontaneous, it is also relatively more difficult in comparison with the reduction of many other organic molecules. Several commercial CO<sub>2</sub> reforming processes have already been developed, e.g., to convert CO<sub>2</sub> to methanol via syngas, with CH<sub>4</sub> as the reductant.<sup>1</sup> For instance, the dry reforming involves the reduction of CO<sub>2</sub> with CH<sub>4</sub> to produce CO and H<sub>2</sub> (the syngas), at high temperatures of 800–1000 °C and with the assistant of Ni/MgO<sup>2</sup> or Ni/MgAl<sub>2</sub>O<sub>4</sub> catalysts.<sup>3</sup> In addition, processes like the methanation reaction or reverse water gas shift are other strategies to reduce CO<sub>2</sub>, by which H<sub>2</sub> is applied as a reductant.<sup>4</sup> Alas, these industrial processes usually require considerable amount of thermal energy input, high-pressure environments and involves the oxidation of high energy-density species like H<sub>2</sub> or CH<sub>4</sub>. Another important consideration is that capturing and concentrating CO<sub>2</sub> consume significant energy itself.<sup>5</sup> Therefore, these processes can only be considered as green or carbon-efficient if the energy spent are generated by renewable energy sources.

Other than thermochemical  $CO_2$  reduction, electrochemical approach has been developed rapidly for the past several decades. However, the reactions still feature highly reactive intermediates, requiring high activation energies. In particular, the formation of the immediate by one electron reduction ( $CO_2^{-}$ ) is a well-known thermodynamically unfavorable process, and the redox potential of  $CO_2/CO_2^{-}$  is as negative as -1.9 V (vs

RHE at pH 7). Hence, the utility of catalysts in CO<sub>2</sub> reduction becomes critically important. Another important reason for the need of catalysts is the product selectivity, which is one of the key challenges for electrochemical reduction of CO<sub>2</sub> since direct reduction of CO<sub>2</sub> could result in one or more of a myriad of products. In other words, the reaction could proceed through multiple steps following different routes; which direction it actually takes is highly sensitive to factors such as the pH, the overpotential and the temperature.<sup>6-11</sup> In order to achieve desired selectivity and efficiency, various branches of the reactions need to be understood and, ultimately, controlled by the application of different catalysts.

#### **1.2** CH<sub>4</sub> conversion and its challenges

As the main component of natural gas, methane (CH<sub>4</sub>) is the most stable hydrocarbon. It represents an important energy source to replace oils and coals. However, methane poses significant threats to the environment as well. First, it is a far more effective greenhouse gas. It features a global warming potential (GWP) approximately 30 times of CO<sub>2</sub>.<sup>12</sup> Due to leaks and biogenic CH<sub>4</sub> production, it accounts for about 10% of total greenhouse emissions as of today.<sup>13</sup> Second, although CH<sub>4</sub> is an excellent energy resource, combustion of CH<sub>4</sub> leads to significant CO<sub>2</sub> emission. These motivate us to investigate CH<sub>4</sub> as a chemical building block.

In industry, CH<sub>4</sub> has already been converted into value-added products through two steps in large scales. Briefly, two types of transformations of CH<sub>4</sub>, steam/dry reforming<sup>14-</sup>

<sup>16</sup> and partial oxidation (POM),<sup>17,18</sup> have been widely implemented, producing syngas (CO and H<sub>2</sub>) for ready conversion to desired oxygenates or long-chain hydrocarbons by the Fischer-Tropsch process.<sup>19,20</sup> Moreover, by some estimates, steam reforming of CH<sub>4</sub> produces up to 48% of global H<sub>2</sub> supply.<sup>21</sup> Despite the large scales of these transformations, however, they face critical challenges. Consider steam reforming of methane (SRM) as an example. High temperature (> 700 °C) and pressure (3-25 bar) are necessary, leading to significant energy consumption because the process is endothermic. Approximately 30% of CH<sub>4</sub> feedstock in SRM is burned to supply the necessary heat.<sup>22</sup> And, more importantly, high temperature operation leads to severe coke formation (Figure 1.1) to deactivate the catalysts. Similarly, the (non-)oxidative coupling of methane (OCM or NOCM) also suffers from coke formation due to the high temperatures required.<sup>23</sup> These processes must be performed at high temperatures because the C-H bond in CH<sub>4</sub> is extremely difficult to activate; once activated, the oxidation of CH<sub>4</sub> often proceeds all the way to CO and/or CO<sub>2</sub>, making it exceedingly difficult to obtain value-added chemicals such as CH<sub>3</sub>OH, CH<sub>2</sub>=CH<sub>2</sub> by direct CH<sub>4</sub> transformation.<sup>24</sup> Indeed, it remains a critical challenge to selectively activate and transform CH<sub>4</sub> at low temperatures to produce high value chemicals.



**Figure 1.1** Coke formation of Ni nanoparticles during steam reforming of methane. Copyright 2011 John Wiley & Sons, Inc.

#### 1.3 Photo-assisted approaches and their challenges

High operating temperatures creates a great hurdle for C<sub>1</sub> chemistry, not only in terms of energetic perspective, but also stability of the catalysts. Other than thermochemical approach, the activation barriers of a chemical reaction can be overcome by (photo)electro-, and/or photo-chemical energy input (Figure 1.2). In comparison electrochemical activation, photoexcitation features a number of advantages, such as the ability to access high-energy states within a short time scale and the possibility to selectively activate chosen substrate(s) and/or reaction steps that are sensitive to optical stimulation.<sup>25</sup> Moreover, photoexcitation makes it possible to access intermediates that are difficult or impossible to access by other means.<sup>26,27</sup> Indeed, photocatalysis has been employed for a wide range of syntheses, especially those involving molecular complexes. For instance, a series of photocatalytic processes based on molecular complexes has been demonstrated using light-excited triplet species for unique C-C and/or C-O coupling via a reductive elimination mechanism.<sup>28,29</sup> More broadly, both homogeneous and heterogeneous photocatalyses have been intensely studied for over a century as a potential technology to directly harvest and convert solar energy to chemical energy. For large-scale implementations, heterogeneous photocatalysts hold particular promises owing to the prospect of utilizing them in fashions similar to how the modern chemical industry is enabled by heterogeneous thermocatalysts.



**Figure 1.2** Schematics illustrating electrochemical, photoelectrochemical and photocatalytic system for chemical reactions (reduction reaction as an example).

So, photo-assisted approaches are promising strategies to solve challenges in  $C_1$ chemistry, especially for the high activation barrier for both  $CH_4$  oxidation and  $CO_2$ reduction. A large amount of research efforts have been taken into this and rapid progress has been achieved.<sup>30-34</sup> These exciting prospects notwithstanding, heterogeneous photocatalysis, especially for C<sub>1</sub> chemistry, faces important challenges. For instance, as a potential large-scale solar energy harvesting technology, the promise of photocatalysis cannot be realized without catalysts that are efficient, inexpensive and stable for long durations. Such catalysts remain elusive, and a viable path forward has yet to be developed. When used for the synthesis of value-added products, heterogeneous photocatalysts generally feature poor product selectivity.<sup>32,35</sup> An important reason for this latter deficiency is the nature of photoexcitation, which often excites the system to a high-energy state that can access multiple reaction routes, making it exceedingly difficult to steer the reaction toward the desired products. While some examples have been recently demonstrated in selective biomass oxidation (e.g., HMF to FDCA conversion by CdS decorated with Ni particles),<sup>36</sup> a clear view on the underpinning principles, especially at the molecular level, has yet to be developed.

## 1.4 Development of new catalyst and understanding reaction mechanisms

Other than advanced approaches like photocatalysis, developing new catalysts is equally important. As mentioned in Chapter 1.3, photocatalytic approach faces the challenge of poor selectivity control, though it can reduce the energy input by other means by a large margin. A "good" catalyst, can not only lower the activation barrier of chemical reactions, but tune the product selectivity, as well. However, to design new catalysts and make improvement of  $C_1$  chemistry, detailed knowledge of the mechanisms is needed but is currently missing. For example, although efforts have been taken to identify the reaction intermediates,<sup>34</sup> little is known about the chemistry that takes place on the catalyst surfaces. The lack of knowledge presents a critical hurdle to further advance  $C_1$  in a rational fashion. Understanding the reaction mechanisms would allow us identify the most critical steps in chemical reactions and accelerate the catalyst screening with scientific guide rather than trial and error. In addition, the knowledge generated from mechanistic study could also be transferrable to photo-assisted approaches. The combination of both will significantly boost the development of  $C_1$  chemistry. Our eventual goal is to enable highly selective photo-assisted chemical reactions.

#### 1.5 Summary

In summary,  $C_1$  chemistry is important not only in environmental consideration but in chemical perspective, as well. However, two major challenges hinder the development: first is the high activation barrier, which results in high energy consumption and a series problems related to it; second is the poor control of product selectivity. Photo-assisted approach, together with new catalyst development, hold great promises to enable large scale selective  $C_1$  chemistry in the future. The existing examples show a very positive sign, but without systematic studies. So, in the following of this thesis, I will focus on the demonstration both photo-assisted approaches and new catalyst development, as well as detailed mechanistic investigation of each successful demonstration. In Chapter 2, I will show the demonstration of PEC CO<sub>2</sub> reduction by Si photocathode and a cobalt-based molecular catalyst, followed by the study of product selectivity correlation with photocathode-catalyst interaction in Chapter 3; In Chapter 4, I will focus on selective PEC CH<sub>4</sub> oxidation to CO production. Detailed mechanistic study was carried out by probing key reaction intermediates. The knowledge generated in this study also shed light on parallel CO<sub>2</sub> reduction; In Chapter 5, I will focus on the synergistic effect in direct CH<sub>4</sub> partial oxidation to oxygenate. Our findings will shed light on the selectivity control for the future catalyst development.

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## Chapter 2: PEC CO<sub>2</sub> reduction by Si photocathode and a Co-based catalyst

This chapter is reprinted with permission from He, D.†; Jin, T.†; Pantovich, S.; Wang, D.; Li, G., Photoelectrochemical CO<sub>2</sub> Reduction by a Molecular Cobalt(II) Catalyst on Planar and Nanostructured Silicon Surfaces. *Chem. Europe. J.* **2016**, *22*, 13064-13067. Copyright 2016 John Wiley & Sons, Inc.

# 2.1 Introduction of photocatalytic CO<sub>2</sub> reduction

Photochemical reduction is a promising approach towards sustainable CO<sub>2</sub> utilization since this process employs natural sunlight as a renewable energy input.<sup>1-5</sup> Both heterogeneous<sup>6-10</sup> and homogeneous systems<sup>11-16</sup> have been extensively investigated in attempts to achieve efficient CO<sub>2</sub>-to-fuel conversion under photochemical conditions. Homogeneous molecular catalysts could be highly efficient in mediating multi-electron CO<sub>2</sub> reduction. However, the most active homogenous CO<sub>2</sub> reduction catalysts<sup>17-21</sup> are often based on rare-earth metals, and great efforts have been made to seek for catalysts with high activities based on earth-abundant materials.<sup>22,23</sup>

Among these homogeneous catalysts are coordination complexes of cobalt.<sup>22,24-29</sup> For instance, Chan *et al.*<sup>22</sup> recently reported photochemical CO<sub>2</sub> reduction by a molecular

catalyst, [Co(TPA)Cl]Cl where TPA is tris(2-pyridylmethyl)amine. An Ir III photosensitizer was employed to harvest light and transfer electrons to [Co(TPA)Cl]Cl in the presence of triethylamine as a sacrificial electron donor. Yang *et al.*<sup>30</sup> synthesized a cyclometalated Ir III complex as a photosensitizer for photochemical CO<sub>2</sub> reduction. In both studies, high turnover numbers and reasonable selectivity towards CO formation were obtained. However, molecular complexes of rare-earth metals were needed as photosensitizers to harvest light for this and many other molecular catalysts,<sup>31,32</sup> which significantly increases the cost.

Light-absorbing solid-state materials, including inorganic semiconductors and metalorganic frameworks,<sup>33-39</sup> have been utilized as photosensitizers based on abundant materials for molecular catalysts.<sup>40</sup> For example, Jin *et al.*<sup>41</sup> deposited a macrocyclic cobalt catalyst onto different titanium dioxide surfaces for use in photochemical CO<sub>2</sub> reduction. The researchers demonstrated that titanium dioxide nanoparticles served to absorb UV light while the surface cobalt catalyst was responsible for reducing CO<sub>2</sub> to CO. Several molecular catalysts have been coupled with photoelectrodes for solar fuel production via CO<sub>2</sub> reduction.<sup>42-49</sup> This photoelectrochemical approach combines light-harvesting materials with homogeneous catalysts, and eliminates the need for amine-based sacrificial electron donors that are often required in photochemical CO<sub>2</sub> reduction.

Herein, we show photoelectrochemical  $CO_2$  reduction by a system based on earthabundant elements, in which Si photoelectrodes serve as robust photosensitizers for [Co(TPA)Cl]Cl. In addition, we investigate the effects of H<sub>2</sub>O addition and photoelectrode morphology on photoelectrochemical  $CO_2$  reduction using the Co<sup>II</sup> catalyst.

#### 2.2 Materials and methods

**Preparation of Si NWs:** Silicon nanowires (Si NWs) were prepared following a previously reported method. A p-Si (100) ( $10^{15}$  cm<sup>-3</sup> B doped;  $\rho$ : 10~20  $\Omega$ ·cm) wafer was cleaned sequentially in acetone, methanol, isopropanol, and deionized (DI) water. The cleaned wafer was oxidized in H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> (1:3) at 90 °C for 15 min to remove heavy metals and organic species. After rinsing with DI water, the substrate was cut into pieces and then immersed into an HF/AgNO<sub>3</sub> solution (4.6 M HF and 0.02 M AgNO<sub>3</sub>) for 30 min at 50 °C. Silver residue was removed from Si NWs' surface by soaking in 70% HNO<sub>3</sub> for 30 min. The Si NWs were then rinsed by DI water and dried by N<sub>2</sub> flow.

**Photoelectrode fabrication:** In order to fabricate photoelectrodes, a film of Al (300 nm) was sputtered onto the backside of the substrates (as-prepared Si NWs and clean p-Si wafer) by radio frequency magnetron sputtering (AJA International, Orion 8, USA). The samples were annealed in Ar at 450 °C for 5 min. Afterwards, a Cu wire was stuck to Al film by Ag paste (MG Chemicals, 8331 Silver Conductive Epoxy Adhesive) and then protected with non-conductive epoxy (Loctite® 615 Hysol Epoxy Adhesive) to cover all the Al film

Synthesis and characteristics of [Co(TPA)CI]CI: he molecular catalyst, [Co(TPA)CI]CI, was synthesized by mixing  $CoCl_2 \cdot 6H_2O$  with TPA according to a reported procedure. Briefly, Cobalt (II) chloride hexahydrate was dissolved in methanol. A solution of TPA in methanol was added forming a greenish solution. Diethyl ether was added to force the coordination complex out of solution to form a viscous oil. Excess supernatant was decanted and the oil dried under vacuum to form a green solid. Recrystallization was effected by redissolving in  $CH_2Cl_2$  and carefully layering in diethyl ether to form a cloudy solution. The solution was allowed to stand overnight at room temperature, producing green crystals. 1H NMR of [Co(TPA)Cl]Cl (400 MHz, Acetonitrile-d3):  $\delta$  132.9 (s, 1H), 108.2 (s, 2H), 58.0 (s, 1H), 47.4 (s, 1H), -2.3 (s, 1H). FTIR of [Co(TPA)Cl]Cl (KBr grind): v/cm<sup>-1</sup>= 3069 (w), 2918 (w), 1608 (s), 1570 (m), 1483 (s), 1438 (s), 1370 (m), 1311 (s), 1294 (m), 1265 (s), 1159 (m), 1103 (m), 1054 (m), and 1025 (s)

**Photoelectrochemical characterizations**: PEC characterizations were carried out using a PAR model VersaSTAT 4 potentiostat by using a single compartment cell in a three-electrode configuration. Si-based photoelectrode served as the working electrode, with an Pt wire in Luggin capillary as a pseudo reference calibrated by  $Fc^+/Fc$ , and a Pt wire as the counter electrode. The electrolyte was a 0.1M TBAPF<sub>6</sub> in acetonitrile. The light source for data presented in this work was a 300 W Xe lamp with a water filter. Light intensity was kept at 113 mW/cm<sup>2</sup>. In a typical CV experiment, the voltage was swept linearly at a rate of 100 mV/s<sup>1</sup>. The electrochemical cell was purged with Ar or CO<sub>2</sub> (99.999%, Airgas) for 20 min before every scan. Bulk electrolysis was carried out in an H-shape electrochemical cell, in which the working electrode was separated from the counter electrode by a sintered glass frit. Prior to bulk electrolysis with the Si NWs and planar Si photoelectrodes, the solution was bubbled with CO<sub>2</sub> for 20 min. The solution was then irradiated with the light source.

**Material Characterizations:** The UV–visible spectrum of [Co(TPA)Cl]Cl in acetonitrile was obtained on a Cary 50 Bio spectrophotometer. Infrared spectra were recorded on a Thermo Nicolet 6700 spectrometer. The morphology of Si NWs was analyzed with a JOEL JSM 6340F scanning electron microscope. Transmission electron microscopy (TEM) was taken on a JOEL 2010F microscope operating at an acceleration voltage of 200 kV. X-ray photoelectron spectra (XPS) were collected on a K-Alpha X-ray photoelectron spectrometer (Thermo Scientific).

**Product detection by GC-TCD:** The headspace above the reaction solution was sampled with a gas-tight syringe at different time intervals for product analysis using an Agilent 7820 GC equipped with a TCD detector and a 60/80 Carboxen-1000 packed column (Supelco).

# 2.3 Cobalt-based molecular catalyst as a electrochemical CO<sub>2</sub> reduction catalyst

The molecular  $Co^{II}$  complex was synthesized following an established procedure.<sup>50</sup> Characterization with UV–visible, 1H NMR and infrared spectroscopies and comparison with results in the literature<sup>22</sup> indicate the synthesized  $Co^{II}$  complex has a trigonal bipyramidal geometry. Under an atmosphere of Ar, two irreversible redox waves were observed with reduction peaks at -1.93 and -2.15 V (all the potentials mentioned in this report are versus Fc<sup>+</sup>/Fc) in the cyclic voltammogram (CV) of [Co(TPA)CI]Cl obtained on an Au electrode (Figure 2.1). Corresponding oxidation peaks are also clearly observed. These two waves are assigned to the  $Co^{II}/Co^{I}$  and  $Co^{I}/Co^{0}$  redox couples, respectively.<sup>22</sup> Significant current enhancement was observed when the same solution was saturated with CO<sub>2</sub>, indicating that the Co<sup>II</sup> complex is a potential catalyst for electrochemical CO<sub>2</sub> reduction. Under CO<sub>2</sub>, the oxidation peaks disappeared since the electrochemically generated species, such as Co<sup>I</sup>, were oxidized upon reducing CO<sub>2</sub> molecules.



**Figure 2.1** Cyclic voltammograms of [Co(TPA)CI]CI under: a) Ar, and b)  $CO_2$  on an Au electrode. Supporting electrolyte 0.1m TBAPF<sub>6</sub> in acetonitrile, scan rate 100 mVs<sup>-1</sup>.

Adding a small amount of  $H_2O$  to the acetonitrile solution of [Co(TPA)CI]Cl altered its redox properties. In our study, proton reduction by reduced cobalt species was observed in the CVs collected in the presence of 1%  $H_2O$  (by volume), although the reduction potentials did not change significantly. We note that while  $CO_2$  reduction occurs readily at the first reduction potential of [Co(TPA)CI]Cl (Figure 2.1), proton reduction is likely mediated by  $Co^0$  species.

Furthermore, the addition of 1% H<sub>2</sub>O resulted in significantly greater current enhancement (2.0-fold in Figure 2.1) when the solution of [Co(TPA)CI]CI was saturated with CO<sub>2</sub>. This comparison suggests that the addition of 1% H<sub>2</sub>O promotes CO<sub>2</sub> reduction by the Co<sup>II</sup> catalyst. Detailed study of the reaction mechanisms in the presence of H<sub>2</sub>O is still under investigation.

### 2.4 Coupling Si NWs photocathode with cobalt catalyst

However, this Co<sup>II</sup> catalyst is only active at highly negative potentials in electrochemical CO<sub>2</sub> reduction (Figure 2.1). The potential for two-electron reduction of CO<sub>2</sub> to CO is -0.53 V versus NHE at pH 7 (corresponding to -1.17 V vs. Fc<sup>+</sup>/Fc),<sup>51</sup> suggesting an overpotential of approximately 800 mV using the Co<sup>II</sup> catalyst. Photovoltaic effects of some semiconductors have been utilized to achieve CO<sub>2</sub> reduction at modest potentials.<sup>48,49,52</sup> For example, Kumar *et al.*<sup>52</sup> investigated CO<sub>2</sub> reduction by a molecular Re<sup>I</sup> catalyst on a p-type Si photoelectrode. Selective reduction of CO<sub>2</sub> to CO was observed at a potential

approximately 600 mV less negative than that required on a Pt electrode. Recent work by Liu *et al.*<sup>53,54</sup> demonstrated successful applications of Si nanowires (Si NWs) in high-efficiency solar energy conversion. In this present study, we couple the Co<sup>II</sup> catalyst with an Si NWs photoelectrode consisting of vertically aligned arrays of Si NWs (Figure 2.2) for use in photoelectrochemical CO<sub>2</sub> reduction. In the absence of the Co<sup>II</sup> catalyst, a much lower photocurrent was observed on the Si NWs photoelectrode.



**Figure 2.2** SEM images of an Si NWs photoelectrode: a) side view (scale bar: 1 mm), and b) top view (scale bar: 10 mm).

# 2.5 Low-bias CO<sub>2</sub> reduction and product analysis

A Xe lamp was used to provide simulated solar irradiation for Si NWs in our photoelectrochemical studies. In dry acetonitrile, multiple broadened redox peaks are present in the CV collected on Si NWs under Ar (Figure 2.3) in comparison to two distinct redox waves on the Au electrode (Figure 2.1). This broadening in the reduction peaks is likely due to the heterogeneity of the SiNWs, which are multifaceted nanowires with a variety of crystal planes exposed.<sup>54</sup> The various crystal plans might differ in light harvesting and electron-transfer kinetics. Under an atmosphere of CO<sub>2</sub>, significant enhancement in photocurrent is observed on Si NWs in a wide range of potentials (Figure 2.3). This enhancement in photocurrent is likely associated with CO<sub>2</sub> reduction by Co<sup>1</sup> species.



Figure 2.3 Cyclic voltammograms of [Co(TPA)Cl]Cl in dry acetonitrile on an SiNWs photoelectrode under: a) Ar, and b) CO<sub>2</sub>. Supporting electrolyte 0.1m TBAPF<sub>6</sub>, scan rate 100 mVs<sup>-1</sup>.

The advantages of using Si NWs over the Au electrode were clearly demonstrated in the presence of H<sub>2</sub>O. In the CV collected under Ar, the first reduction corresponding to the Co<sup>II</sup>/Co<sup>I</sup> redox couple occurs at -1.35 V (determined at maximum photocurrent), representing a photovoltage of 580 mV as a result of light irradiation compared to that on the Au electrode. The second reduction occurs around -1.65 V as a shoulder to a proton reduction peak at -1.94 V. A significant photovoltage was also observed using a planar Si photoelectrode which contains the Si (100) crystal plane. On planar Si, the two reduction waves of [Co(TPA)Cl]Cl overlap significantly, but occur in a much narrower potential range than on Si NWs. This is attributed to the fact that only the (100) crystal plane is present on the planar Si surface while the Si NWs are multifaceted. The presence of 1% H<sub>2</sub>O resulted in anodic potential shifts in the reduction potentials of [Co(TPA)Cl]Cl on the planar Si photoelectrode. In addition, the Co<sup>II</sup>/Co<sup>I</sup> reduction wave was observed at around -1.61 V indicating a photovoltage of 320 mV compared to that on the Au electrode. In the presence of 1% H<sub>2</sub>O, CO<sub>2</sub> reduction was observed at -1.57 V on Si NWs (Figure 2.4c), compared to -1.80 V on planar Si (Figure 2.4b), and -1.96 V on Au (Figure 2.4a). Therefore, the use of Si NWs is advantageous since it allows CO<sub>2</sub> reduction at a less negative potential than using the planar Si photoelectrode and the Au electrode. The comparison shown in Figure 2.4 is similar to the previous study of a Ni<sup>II</sup> catalyst on Si photoelectrodes by Liu et al.<sup>54</sup> We attribute this effect of photoelectrode geometry to the unique multifaceted feature and excellent light harvesting of Si NWs. Other contributing factors include the greater surface area of Si NWs in comparison with the planar Si photoelectrode, orthogonal light absorption and charge transfer directions in Si NWs.



Figure 2.4 Cyclic voltammograms of [Co(TPA)Cl]Cl in an acetonitrile solution containing 1% H<sub>2</sub>O on: a) Au, b) planar Si, and c) Si NWs under CO<sub>2</sub>. Supporting electrolyte 0.1m TBAPF<sub>6</sub>, scan rate 100 mVs<sup>-1</sup>.

Bulk electrolysis was carried out in an acetonitrile solution containing 1% H<sub>2</sub>O and 1 mM [Co(TPA)Cl]Cl on the photoelectrodes under an atmosphere of CO<sub>2</sub>. Faradaic efficiencies for CO formation were measured to be 69 and 57% on Si NWs and planar Si, respectively. Formation of H<sub>2</sub> (Faradaic efficiencies 26 and 22%, respectively) was also observed. In our study, the production of CO from CO<sub>2</sub> using [Co(TPA)Cl]Cl on Si NWs was confirmed by infrared spectroscopy combined with isotope labeling (Figure 2.5). On the Si NWs photoelectrode, a turnover number of approximately 4.2 was obtained for CO production after bulk electrolysis of a solution containing 10 mmol [Co(TPA)Cl]Cl on Si NWs for 4.6 h.

During bulk electrolysis in the presence of 1% H<sub>2</sub>O, the photocurrent generated on Si NWs showed negligible decay over a period of 5 h. In addition, heterogeneous deposition of the Co<sup>II</sup> catalyst was not observed under the experimental conditions, as shown by microscopic images of Si NWs collected before and after bulk electrolysis for 3 h. The stability of [Co(TPA)CI]Cl was further confirmed by surface analysis of Si NWs with X-ray photoelectron spectroscopy (XPS). In particular, a fresh Si NWs photoelectrode was soaked in the electrolysis solution in the dark. The XPS spectrum of this soaked photoelectrode was then collected and compared with that of a photoelectrode used in bulk electrolysis. Spectra of these two photoelectrodes were found to be almost identical, indicating that the Co<sup>II</sup> catalyst remained intact during bulk electrolysis. Our results suggest that a robust system based on abundant materials for CO<sub>2</sub>-to-fuel conversion could be developed using the combination of the Co<sup>II</sup> catalyst and the Si NWs photoelectrode.



**Figure 2.5** FTIR spectrum of <sup>13</sup>CO produced in bulk electrolysis using [Co(TPA)Cl]Cl on Si NWs under <sup>13</sup>CO<sub>2</sub>. The rotational-vibrational band of <sup>13</sup>CO is centered at 2096 cm<sup>-1</sup>.
#### 2.6 Summary

In summary, we have demonstrated that Si photoelectrodes are viable solid-state photosensitizers for a molecular  $Co^{II}$  catalyst in  $CO_2$  reduction. The use of Si NWs is advantageous since it allows  $CO_2$  reduction at less negative potentials than using planar Si due to the unique multifaceted feature of Si NWs. The addition of a small amount of H<sub>2</sub>O enabled  $CO_2$  reduction with less applied bias. Further studies with electrochemistry and spectroscopy are underway to elucidate how H<sub>2</sub>O alters  $CO_2$  reduction catalysis by [Co(TPA)CI]Cl on Si NWs.

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# Chapter 3: Determining the correlation between catalyst adsorption and product selectivity

This chapter is reprinted with permission from Jin, T.<sup>†</sup>; He, D.<sup>†</sup>; Stanton, C. III; Pantovich, S., Majetich, G., Schaefer, H. III, Agarwal, J., Wang, D.; Li, G., CO<sub>2</sub> Reduction with Re(I)-NHC Compounds: Driving Selective Catalysis with a Silicon Nanowire Photoelectrode. *Chem. Commun.* **2016**, *52*, 14258-14261. Copyright The Royal Society of Chemistry 2016.

# 3.1 Two Re-based catalysts with similar chemical structures

Many transition metal complexes have exhibited catalytic activity for multi-electron  $CO_2$  reduction.<sup>1-7</sup> Among these, diiminetricarbonyl rhenium(I) complexes, including fac-ReCl(bpy)(CO)<sub>3</sub> where bpy = 2,20 -bipyridine, have been extensively investigated in both photocatalytic and electrocatalytic applications.<sup>8-20</sup> Several recent examples of Re(I) complexes have used N-heterocyclic carbene (NHC)–aryl frameworks as redox-active ligands,<sup>21-25</sup> but few have been examined for catalysis.<sup>26-30</sup> In this work, we show that coupling with silicon nanowire (Si NWs) photoelectrodes significantly improves the selectivity of Re(I)–NHC complexes in CO<sub>2</sub> reduction. Recent reports by Delcamp and co-workers<sup>28,29</sup> and Agarwal and co-workers<sup>30</sup> are among the few examples for CO<sub>2</sub> reduction

using Re(I)-NHC compounds. In one of the studies by Delcamp and co-workers,<sup>28</sup> the efficacy of Re(I) complexes containing a NHC-pyridyl motif was recorded under irradiation with and without a molecular Ir(III) photosensitizer. The authors noted that the addition of an electron-deficient substituent on the NHC moiety improved photocatalytic performance.<sup>28</sup> Conversely, electron-deficient substituents on bpy often reduce the activity of ReCl(bpy)(CO)<sub>3</sub>-type catalysts.<sup>31,32</sup> In the study by Agarwal and co-workers,<sup>30</sup> NHCpyridyl and NHC–pyrimidyl ligands were employed, using a benzimidazole-based NHC. CO was observed as the primary electrolysis product (Faradaic efficiency  $\geq 60\%$ ), along with production of H<sub>2</sub> and HCOOH. In this present report, we compare the performance of the latter two Re(I)–NHC compounds (1 and 2 in Figure 3.1) under photoelectrochemical conditions. We demonstrate that utilizing Si NWs significantly improves selectivity towards CO over H<sub>2</sub> formation during solar-assisted CO<sub>2</sub> reduction, providing evidence that metal-NHC molecular catalysts may be successfully combined with this nanostructured material. The photoelectrode surface after catalysis are examined with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in order to explore interactions between the catalysts and Si NWs.



**Figure 3.1** Molecular structures of the Re(I)-NHC compounds under study:  $ReCl(N-methyl-N'-2-pyridylbenzimidazol-2-ylidine)(CO)_3$  (1) and  $ReCl(N-methyl-N'-2-pyrimidylbenzimidazol-2-ylidine)(CO)_3$  (2).

The synthesis, characterization, and electrocatalytic efficiency of compounds **1** and **2** have been previously reported.<sup>30</sup> As further confirmation, cyclic voltammograms were recorded for each Re(I)–NHC compound in acetonitrile with tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte. Aligned with prior work, two irreversible reduction waves were observed under Ar saturation for each compound at 100 mVs<sup>-1</sup>, with peak currents at -2.06 V and -2.45 V for **1** (Figure 2.2, potentials are versus Fc<sup>+</sup>/Fc), and at -1.91 and -2.30 V for **2**. Under an atmosphere of CO<sub>2</sub>, current enhancement was observed at both the first and second reduction waves. The current enhancement for **2** is less significant than for **1** (Figure 3.2).



**Figure 3.2** Cyclic voltammograms of **1** under (a) Ar and (b) CO<sub>2</sub> atmospheres on a glassy carbon electrode in acetonitrile.

## 3.2 Materials and methods

**General:** All reagents were obtained from commercial suppliers and used as received unless otherwise noted. DRIFTS spectra were recorded on a ThermoNicolet 6700 spectrophotometer. Cyclic voltammograms were collected on a PAR model VersaSTAT 4 potentiostat using a single compartment cell. Conditions for electrochemical studies: supporting electrolyte 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile, scan rate 100 mV/s, a glassy carbon working electrode (geometric surface area 0.0314 cm<sup>2</sup>), a Pt counter electrode, a non-aqueous Ag/AgNO<sub>3</sub> reference electrode (AgNO<sub>3</sub> concentration 0.01 M), and ferrocene as an internal standard. The electrochemical cell was purged with Ar or CO<sub>2</sub> for 20 min before every scan. The morphology of Si NWs was analyzed with a JOEL JSM 6340F scanning electron microscope

**Photoelectrode Fabrication:** Si NWs were prepared following a previously reported method. A p-Si (100) ( $10^{15}$  cm<sup>-3</sup> B doped; ρ:  $10\sim20 \Omega \cdot$ cm) wafer was cleaned sequentially in acetone, methanol, isopropanol, and deionized (DI) water. The cleaned wafer was oxidized in H2O2/H2SO4 (1:3) at 90 °C for 15 min to remove heavy metals and organic species. After rinsing with DI water, the substrate was cut into pieces and then immersed into an HF/AgNO<sub>3</sub> solution (4.6 M HF and 0.02 M AgNO<sub>3</sub>) for 30 min at 50 °C. Silver residue was removed from Si NWs' surface by soaking in 70% HNO<sub>3</sub> for 30 min. The Si NWs were then rinsed by DI water and dried by N<sub>2</sub> flow. A film of Al (300 nm) was sputtered onto the backside of the substrates (as-prepared Si NWs and clean p-Si (100) wafer) by radio frequency magnetron sputtering (AJA International, Orion 8, USA). Then the samples were annealed in Ar (flow rate: 5000 standard cubic centimeter per minute,

SCCM) at 450 °C for 5 min. Afterwards, a Cu wire was stuck to Al film by Ag paste (MG Chemicals, 8331 Silver Conductive Epoxy Adhesive) and then protected with nonconductive epoxy (Loctite® 615 Hysol Epoxy Adhesive) to cover all the Al film.

**Photocatalytic CO<sub>2</sub> reduction:** In photocatalysis, 1.0  $\mu$ mol of a Re(I)-NHC complex and 4.0  $\mu$ mol of Ru(dmb)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> were dissolved in 4.0 mL of a dimethylformamidetriethanolamine (3:1 v/v) solution in a Pyrex test tube. Prior to photocatalytic testing, the reaction solution was bubbled with CO<sub>2</sub> (99.999%, Airgas) for 20 min. The reaction solution was then irradiated with a 300 W xenon lamp equipped with a water filter (light intensity 113 mW/cm<sup>2</sup>). The head space above the reaction solution was sampled with a gas-tight syringe at different time intervals for product analysis using an Agilent 7820 GC equipped with a TCD detector and a 60/80 Carboxen-1000 packed column (Supelco)

**Photoelectrochemical CO<sub>2</sub> reduction:** In controlled potential experiments, cyclic voltammograms were collected prior to bulk electrolysis studies, which were carried out in a three-necked flask containing 10.0 ml of 1 mM catalyst in acetonitrile. Prior to photoelectrochemical measurements, the flask (total cell volume 22.7 ml) was bubbled with CO2 (99.999%, Airgas) for 20 min. A Si NWs photoelectrode (geometric surface area measured individually, varies around 0.05 cm2) were used as the working electrode in photoelectrochemical CO2 reduction. The reaction solution was then irradiated with a 300 W xenon lamp equipped with a water filter (light intensity 113 mW/cm<sup>2</sup>). The head space (volume 12.7 ml) above the reaction solution was sampled with a gas-tight syringe for product analysis using the Agilent 7820 GC

## **3.3** PEC CO<sub>2</sub> reduction w/o proton donor

Given the promising electrocatalytic activity exhibited by **1** and **2**, we sought to examine both compounds for photoelectrochemical CO<sub>2</sub> reduction, since harnessing sunlight to drive CO<sub>2</sub> conversion is a compelling solution to utilize CO<sub>2</sub>. In particular, the photoelectrochemical approach eliminates the need for sacrificial donors by combining well-defined molecular catalysts with a photoactive electrode surface.<sup>33,34</sup> Several molecular catalysts have been coupled with photoelectrodes for solar fuel production via CO<sub>2</sub> reduction.<sup>35-45</sup> We employ Si NWs photoelectrodes, which consist of vertically aligned arrays of Si NWs,<sup>45</sup> as the electron source for Re(I)-catalyzed CO<sub>2</sub> reduction in this research. The nanostructured morphology of Si NWs has been reported to be well-suited for high-efficiency solar energy applications.<sup>46,47</sup>

Figure 3.3 shows cyclic voltammograms of 1 recorded on a Si NWs photoelectrode in acetonitrile under light irradiation provided by a Xe lamp. Under an atmosphere of Ar, the first reduction wave of **1** displays a peak current at -1.58 V (Figure 3.3a), representing a photovoltage of 480 mV. A catalytic photocurrent is observed under CO<sub>2</sub> saturation (Figure 3.3b), indicating that CO<sub>2</sub> reduction persists under photoelectrochemical conditions. The first reduction wave for **2** appears at -1.47 V, yielding a slightly lower photovoltage of 440 mV. A photocurrent enhancement was also observed under CO<sub>2</sub>, although less pronounced than for **1**, which matches the results under electrocatalytic conditions.<sup>30</sup>



**Figure 3.3** Cyclic voltammograms of **1** under (a) Ar and (b) CO<sub>2</sub> atmospheres on a Si NWs photoelectrode in acetonitrile under light irradiation. The cyclic voltammogram under Ar on a glassy carbon electrode is also plotted for comparison (dotted trace, same as Figure 3.2).

On the preparative scale at the potential of the first reduction, 1 and 2 displayed modest Faradaic efficiencies for CO production ( $FE_{CO} = 57\%$  and 53%, respectively) in photoelectrolysis on Si NWs. Likely, residual water in the acetonitrile used in our study served as the proton source for CO<sub>2</sub> reduction. Complex **2** demonstrated excellent stability over four hours, while the photocurrent decayed gradually over time when **1** was used as the CO<sub>2</sub> reduction catalyst. This is likely due to the relatively low photostability of **1**. In recent studies by Vaughan and co-workers, photochemical dissociation of CO was observed for a Re(I) NHC–pyridyl complex (similar to **1**) but not for a Re(I) NHC–pyrimidyl complex (similar to **2**).<sup>22,23</sup> Nevertheless, more CO was produced by **1** in photoelectrolysis than by **2**, which is consistent with the more significant photocurrent enhancement observed for **1** at the first reduction potential (Figure 3.3).

The differing photochemical stability of **1** and **2** was further probed with surface analysis after photoelectrolysis. Specifically, the Si NWs were thoroughly washed with acetonitrile and dried at room temperature after being used for catalysis. Then, infrared spectra of the used Si NWs were collected on a DRIFTS spectrometer (Figure 3.4). Prominent absorptions corresponding to surface-adsorbed Re(I) complexes are seen in the C–O stretching region of the collected spectra. For **2**, these transitions appear at 2021 and 1918 cm<sup>-1</sup> (Figure 3.4b), and resemble the features of fac-ReCl(bpy)(CO)<sub>3</sub> grafted on silica surfaces found in our previous work.<sup>48,49</sup> Moreover, the similarity of these bands to peaks of **2** collected from infrared spectrochemistry (IR-SEC) at resting potential (2022, 1926, and 1899 cm<sup>-1</sup>)<sup>30</sup> would suggest that the tricarbonyl moiety is retained after photoelectrolysis, assuming coalescence of the 1926 and 1899 cm<sup>-1</sup> peaks in the DRIFTS

spectrum. In the infrared spectrum of Si NWs used with **1**, two carbonyl bands are present at 2011 and 1879 cm<sup>-1</sup> (Figure 3.4a). Compared to previous IR-SEC data, these transitions are redshifted with respect to the starting complex (2020, 1923, and 1894 cm<sup>-1</sup>),<sup>30</sup> which is consistent with structural changes during photoelectrolysis. This presumed degradation aligns with the aforementioned literature<sup>22</sup> regarding the photostability of Re(I)–NHC complexes. From these data, we can conclude that **1** and **2** are strongly adsorbed to the Si NWs surface, and that **1** undergoes significant structural changes under photoelectrochemical conditions.



Figure 3.7 DRIFTS spectra of Si NWs used in photoelectrochemical  $CO_2$  reduction using (a) 1 and (b) 2 in acetonitrile for 4 h.

## **3.4** Importance of catalyst adsorption

The introduction of Brønsted acids into the electrolyte is a popular technique to improve catalyst turnover.<sup>50</sup> In our study, the presence of 5% H<sub>2</sub>O (by volume) significantly improved CO<sub>2</sub>-to-CO conversion using 1 and 2 on Si NWs, and yielded a new photocurrent for proton reduction. Consequently, the formation of  $H_2$  was confirmed with product analysis during photoelectrolysis. For 1, the presence of 5%  $H_2O$  resulted in a lower Faradaic efficiency for CO production ( $FE_{CO} = 20\%$ ) along with significant H<sub>2</sub> formation (FE<sub>H<sup>2</sup></sub> = 54%). Surface analysis of Si NWs after photoelectrolysis showed a negligible amount of surface-adsorbed 1 (Figure 3.5a). Control experiments confirmed that the addition of 5%  $H_2O$  had negligible effect on the photostability of 1 or 2. These observations imply that the presence of 5% H<sub>2</sub>O inhibited the adsorption of **1** on Si NWs and subsequent electron transfer from Si NWs to 1 for CO<sub>2</sub>-to-CO conversion. In addition, the photocurrent obtained for 1 displayed a time course profile similar to that of H<sub>2</sub> production, suggesting that proton reduction dominated in the presence of H<sub>2</sub>O. Conversely, 2 displayed a Faradaic efficiency of 68% for CO production after the addition of H<sub>2</sub>O, with only minor quantities of H<sub>2</sub> (FE<sub>H<sup>2</sup></sub> = 9%). After photoelectrolysis with **2**, surface analysis with DRIFTS showed infrared absorptions at 2021 and 1918 cm<sup>-1</sup> (Figure 3.5b), indicating the presence of strongly adsorbed 2 on SiNWs even with 5% H<sub>2</sub>O added to the acetonitrile solution. In the absence of the Re(I) catalysts, the values of  $FE_{H_2}$  on the Si NWs photoelectrode were measured to be 0% in acetonitrile and 49% in an acetonitrile solution containing H<sub>2</sub>O. These results suggest that in our system CO<sub>2</sub> reduction is mediated by the Re(I) catalysts while proton reduction mainly occurs on the Si NWs surface. Complexes 1

and **2** were also tested in photocatalytic CO<sub>2</sub> reduction using a molecular photosensitizer, Ru(dmb)<sub>3</sub><sup>2+</sup> where dmb is 4,40-dimethyl-2,20-bipyridine, and triethanolamine as a sacrificial electron donor in acetonitrile. Under light irradiation, the two Re(I)–NHC complexes demonstrated similar reactivity. Using **2** as a catalyst led to a slightly higher turnover number for CO production than using **1**, but significant H<sub>2</sub> formation (H<sub>2</sub>/CO  $\sim$ 0.5) was observed for both catalysts. Therefore, the Si NWs photoelectrode appears to be a better energy source for the Re(I)–NHC catalysts than the Ru(dmb)<sub>3</sub><sup>2+</sup> photosensitizer to selectively drive CO<sub>2</sub> reduction over proton reduction. We expect that CO<sub>2</sub> reduction using the Re(I) catalysts on Si NWs could be further improved by employing a two-compartment cell which separates the Si NWs photoelectrode from the counter electrode, constantly stirring the reaction solution, and carrying out photoelectrolysis for a longer period of time.



**Figure 3.5** DRIFTS spectra of Si NWs used in photoelectrochemical  $CO_2$  reduction using (a) 1 and (b) 2 in an acetonitrile solution containing 5% H<sub>2</sub>O (by volume).

## 3.5 Summary

In summary, the presence of strongly adsorbed Re(I)-NHC complexes on the Si NWs photoelectrode surface is clearly associated with selective CO<sub>2</sub>-reduction catalysis. We expect that both the efficiency and selectivity in solar fuel generation could be enhanced by tuning the interactions between molecular catalysts and photoelectrode surfaces. Further studies are underway to test this hypothesis.

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## Chapter 4: Selective CO production by PEC CH<sub>4</sub> oxidation on TiO<sub>2</sub>

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D., Selective CO Production by Photoelectrochemical Methane Oxidation on TiO<sub>2</sub>. *ACS Cent. Sci.*, **2018**, *4*, 631-637. Copyright 2018 American Chemical Society.

# 5.3 Existing approaches for CH<sub>4</sub> oxidation and our motivation

Steam reforming of methane (SRM) is an important process that produces H<sub>2</sub> and syngas, which are key feedstocks for downstream chemical processes such as Fischer– Tropsch synthesis.<sup>1,2</sup> Despite the scale, as mentioned in Chapter 1, SRM faces critical challenges, including catalyst deactivation and high energy consumption, most of which are associated with the high temperatures needed to activate the C-H bond. To solve these issues, one may meet the energy needs for CH<sub>4</sub> activation by photochemical instead of thermochemical activation.<sup>3-11</sup> Indeed, promising results have already been obtained. The pioneering work by Yoshida *et al.* succeeded in oxidizing CH<sub>4</sub> by photocatalysts, but mostly produced CO<sub>2</sub> instead of CO or other valuable products.<sup>12-17</sup> An important reason is the lack of understanding of the reaction mechanisms by these photocatalytic processes.

More broadly, poor understanding of reaction mechanisms, especially at the molecular level, is a critical weakness of researches on heterogeneous catalysis.<sup>18,19</sup> In recognition of this deficiency, great research efforts have been made to unravel the mechanisms that govern the selectivity of heterogeneous catalytic reactions.<sup>20,21</sup> Within the context of CH<sub>4</sub> oxidation, the demonstrations of colloidal PdAu nanoparticles catalysts with >98% selectivity toward CH<sub>3</sub>OH formation highlight the importance of initial activation of CH<sub>4</sub> by  $\cdot$ OH.<sup>22</sup> *In situ* XANES (X-ray absorption near edge spectroscopy) and Fourier-transform infrared (FTIR) spectroscopic studies of copper-exchanged mordenite zeolite (CuMOR) have revealed that the bridging O in Cu-O-Cu is key to CH<sub>3</sub>OH production.<sup>23</sup> Notably, these examples were all thermochemical transformations. Recent advances in a parallel field of CO<sub>2</sub> reduction studies also exemplify the importance of mechanistic understanding to heterogeneous catalysis.<sup>24-30</sup>

Inspired by these previous efforts and the importance of CH<sub>4</sub> oxidation, we studied this reaction under photoelectrochemical (PEC) conditions, wherein the chemical reaction proceeds at the semiconductor photoelectrode/electrolyte interface under light with an applied bias. The externally applied potential creates an extra electric field to facilitate charge separation between photogenerated electrons and holes. Our goal was to enable the reaction at room temperature so as to address the critical challenges faced by conventional SRM. It was found that the product selectivity is highly sensitive to the applied potentials, and photoexcitation is critical to the selective formation of CO. Detailed mechanistic studies by spectroscopic and computational methods revealed that surface O· radical formation is key to the observed results, and that the synergistic effect between adjacent Ti sites plays a critical role. Our results shed new light on the interactions of C species with metal centers of heterogeneous catalyst substrates.<sup>31-33</sup> They highlight the importance of synergistic effects in defining the reaction routes.<sup>34-36</sup> The insights may find applications in CO<sub>2</sub> reduction, as well.<sup>24,26,27,37</sup>

# 5.3 Materials and methods

ALD TiO<sub>2</sub>: TiO<sub>2</sub> was deposited on a 2.2 mm thick glass slide coated with fluorinedoped tin oxide conductive film (7  $\Omega$ /sq surface resistivity, Sigma-Aldrich) in a Cambridge nanotech (Savannah 100) system. FTO coated glass substrate was cleaned in acetone, methanol, and deionized (DI) water. The reaction was performed at 275°C with a constant flow of N<sub>2</sub> (UHP, 99.999%, Airgas) at 20 sccm (background pressure ~1000 mTorr). Ti(i-PrO)<sub>4</sub> (99.999% trace metals basis, Sigma-Aldrich) served as the Ti precursor, and was heated to 75°C. DI H<sub>2</sub>O at room temperature was used as the oxygen precursor. The pulse and purge time for Ti(i-PrO)<sub>4</sub> and H<sub>2</sub>O was 0.1s & 5s, and 0.01s & 10s, respectively. The dependence of photocurrent density on TiO<sub>2</sub> thickness was discussed in the application of solar water splitting, the optimum TiO<sub>2</sub> thickness was  $\sim$ 50 nm for planar devices corresponding with 3000 cycles growth. The ALD TiO<sub>2</sub> featured anatase (101) surface. Raman spectra confirmed the anatase phase of ALD TiO<sub>2</sub>, using an XploRA micro-Raman system (Horiba) with an excitation laser of 638 nm. **Commercial anatase TiO<sub>2</sub> and P25 TiO<sub>2</sub>:** Commercial anatase TiO<sub>2</sub> powder (Sigma Aldrich, 99.8% trace metal basis) or P25 TiO<sub>2</sub> powder (Evonik Industries, Aeroxide TiO<sub>2</sub> P25) was dispersed in ethanol to make a TiO<sub>2</sub> suspension solution with a concentration of 0.1 g/mL. The resulted solution was drop-casted on FTO substrate and followed a spin coating procedure at a rate of 2500 rpm. Then, the TiO<sub>2</sub> coated FTO substrate was annealed at 475°C in air for 3 h to remove the solvents and improve the adhesion between FTO substrate and TiO<sub>2</sub>.

**CO detection:** Similar to a typical PEC measurement, a three-electrode configuration was employed, except that CH<sub>4</sub> (UHP, 99.99%, Airgas) or N<sub>2</sub> (UHP, 99.999%, Airgas) gas was encapsulated during bulk electrolysis with coulometry. The evolved CO in the headspace was sampled with a gastight syringe (100  $\mu$ L) for product analysis using GC-MS (Shimadzu QP2010 Ultra, with Carboxen 1010 PLOT column). CO (UHP, 99.9%, Airgas) was used to calibrate the GC-MS.

**Carbonate detection:** Measuring the weight increase of carbonate precipitation after bulk electrolysis was used to quantify the carbonate formed in electrolyte. Prior to experiments, DI water was boiled to remove dissolved CO<sub>2</sub>. After bulk electrolysis of ALD TiO<sub>2</sub> photoelectrode in the presence of CH<sub>4</sub> was finished, 10.0 mL of 1.0 M Ba(NO<sub>3</sub>)<sub>2</sub> (ACS, > 99%, Alfa Aesar) was added to the electrolyte (also to fresh electrolyte as controlled experiment). No significant difference was obtained, suggesting the amount of carbonate product in the electrolyte was beyond the detection limit by this method.

Carbonate adsorbed on the TiO<sub>2</sub> surface was characterized by XPS and attenuated total reflection-Fourier transformed infrared spectroscopy (ATR-FTIR). XPS spectra in

were obtained using K-alpha<sup>+</sup> XPS (Thermo Scientific, Al K $\alpha$  = 1486.7 eV), showing the carbonate formation on ALD TiO<sub>2</sub> surface only after PEC bulk electrolysis in the presence of CH<sub>4</sub>. ATR spectra were obtained using a Brüker ATR model Alpha spectrometer with diamond as the ATR crystal. ALD TiO<sub>2</sub> with different electrolysis history was placed on ATR plate with elastic pressing to improve the contact between the sample and the crystal. Acetone was used to clean the ATR substrates between each measurement. Air spectrum was measured as background. Data were collected using the Omnic software package. Each spectrum was collected with 32 scans at a 2 cm<sup>-1</sup> spectral resolution.

H<sub>2</sub>O<sub>2</sub> detection: After PEC electrolysis, 1 M HCl was used to adjust the pH of electrolyte to 2~2.5. Then 50  $\mu$ L of the Mo catalyst was added into the solution and incubated for 3 min. Finally, 0.5 mL starch solution with concentration of 2 wt% was added to the solution. If there was H<sub>2</sub>O<sub>2</sub>, the solution would turn blue.

**EPR spectroscopy:** A Bruker ELEXSYS E500 spectrometer equipped with a SHQ resonator was used for the EPR experiments. An Oxford ESR-900 continuous flow cryostat was used to measure spectra at 7.5 K. The EPR parameters used for recording the spectra are as follows: microwave frequency, 9.38 GHz; modulation frequency, 100 kHz; modulation amplitude, 19.95 G; microwave power, 5 mW; sweep time, 84 s; conversion time, 41 ms; time constant, 82 ms. Each spectrum was the average of two scans. Since the signal intensity is proportional to radical concentration, the quantity of Ti<sup>3+</sup> was calculated and the results of three samples are listed in Table S3. The standard used was carefully weighed out 2,2-Diphenyl-1-picrylhydrazy (DPPH) standard (Analytical grade, Sigma Aldrich). The EPR spectrum of the standard was taken under identical conditions.

**Raman spectroscopy:** Raman spectra were obtained using a Horiba XploRA micro Raman system with excitation laser of 638 nm. Commercial anatase TiO<sub>2</sub> (Sigma Aldrich, 99.8% trace metal basis) was employed instead of ALD anatase TiO<sub>2</sub> film for more sufficient interaction with CH<sub>4</sub>; 3% H<sub>2</sub>O-saturated CH<sub>4</sub> was circulated and enclosed in a homemade quartz cell (Schematic S2). Spectra were collected under air, CH<sub>4</sub>/H<sub>2</sub>O and CD<sub>4</sub> (99 atom% D, Assay 99%, Sigma Aldrich)/H<sub>2</sub>O with/without illumination by UV light respectively (the same light source in PEC characterizations).

**ATR-FTIR spectroscopy:** ATR-FTIR spectra were recorded using a Bruker Vertex 70 FTIR spectrometer (Billerica, MA) equipped with an MCT detector (FTIR-16; Infrared Associates; Stuart, FL). The TiO<sub>2</sub> coated FTO glass slide was pressed on the ATR Si prism crystal. Electrochemical experiments were carried out in a two-electrode configuration with a Pt foil (99.95%; BASi Inc.; West Lafayette, IN) as the reference/counter electrode. 0.10 M KNO<sub>3</sub> (99.999% trace metals basis, Sigma Aldrich) was used as the electrolyte at room temperature and it was purged for at least one hour by either N<sub>2</sub> (control experiment) or CH<sub>4</sub> before being added into the electrochemical cell. The linear sweep voltammogram (at a rate of 20 mV•s<sup>-1</sup>) of ALD TiO<sub>2</sub> was scanned under light illumination in CH<sub>4</sub>-saturated 1.0 M KNO<sub>3</sub> electrolyte in the FTIR set-up. To ensure steady-state conditions, the target potential was held at 0.3 V vs. internal Pt. The applied potential 0.3 V vs. internal Pt in Figure 4.4b would correspond to 0.9 V vs. RHE in a 3-electrode configuration. The appearance of specific adsorbed intermediates on the electrode is highly sensitive to surface heterogeneity, applied potential, and the amount of dissolved CH<sub>4</sub>. Pressing of the working electrode against the IR transparent prism results in an electrochemical cell configuration that brings about uncertainties in the applied potential and unfavorable mass-transport conditions. As a result, while the three bands reported in Figure 4.4 were observed in multiple experiments, they did not always appear concurrently and/or with the same magnitude.

Each reported spectrum was collected at a 2 cm<sup>-1</sup> spectral resolution and a 40 kHz scanner velocity with 64 scans. The spectrum collected in the beginning of PEC bulk electrolysis was used as the reference, followed by the single beam spectrum collected at each corresponding time point. The change of optical density was calculated as follows,  $\Delta mOD = -1000 \cdot \log(S_{sample}/S_{reference}).$ 

# 5.3 Unique product selectivity by PEC approach

A typical representation of our experimental setup is schematically shown in Figure 4.1a, where a 3-electrode configuration was employed. A  $TiO_2$  photoelectrode (ca. 50 nm in thickness) was used as the working electrode.<sup>38</sup> A Pt wire served as the counter electrode, and the reference electrode was a saturated calomel electrode. In comparison with previous studies on photochemical oxidation of CH<sub>4</sub>,<sup>7,8,12-17</sup> we introduced two key innovations. First, ALD grown TiO<sub>2</sub> was studied, which shows critical differences in product selectivity when compared with TiO<sub>2</sub> prepared by other methods. Second, the separation of the oxidation (TiO<sub>2</sub> working electrode) and reduction (Pt counter electrode) reactions permitted us to focus on CH<sub>4</sub> oxidation without confounding effects by the reduction reactions of H<sub>2</sub> generation. The light source used for this body of research was a UV lamp  $(\lambda = 254 \text{ nm}; \text{ intensity } 0.1 \text{ mW/cm}^2)$ . The electrolyte was 1.0 M NaOH (pH 13.6). CH<sub>4</sub> was bubbled into the electrolyte under standard conditions. The solubility is expected to be ca. 0.0010 mol/kg.<sup>39,40</sup> The turn-on potential was 0.2 V vs. RHE in current voltage curve. A stability test was carried out at 0.6 V vs. RHE, and no obvious decay was observed during the first 15 h. Under our experimental conditions, the measured anodic photocurrents could be due to CH<sub>4</sub> oxidation or H<sub>2</sub>O oxidation or both. Care was taken to ensure that no other parasitic reactions (such as oxidation of organic impurities) contributed to the measured currents. The products of CH<sub>4</sub> oxidation were detected using a GC-MS (Shimadzu QP2010 Ultra, with a Carboxen 1010 PLOT column). The products of H<sub>2</sub>O oxidation were quantified by a Clark-type BOD oxygen electrode (Thermo Scientific 9708 DOP).<sup>41</sup> No production of H<sub>2</sub>O<sub>2</sub>, which was examined by iodine clock reactions, was detected. The  $V_{app}$ 's were limited within 0.4 to 1.2 V vs. RHE for this body of study, so that CO oxidation was ruled out. The possibility that H<sub>2</sub> oxidation contributes to the measured photocurrent was ruled out by the measurement of ca. 100% Faradaic efficiency of H<sub>2</sub> detection. For a typical data set as shown in Figure 4.1b, at least 3 different samples were tested for each CO or O<sub>2</sub> detection, and the statistical variation (the standard deviation at each  $V_{app}$  was less than 5.1%) was insignificant. Taken together, the selectivity trend as shown in Figures 4.1 and 4.3 is statistically significant.



**Figure 4.1** (a) Schematic illustration of selective CH<sub>4</sub> oxidation to CO on a TiO<sub>2</sub> photoelectrode, starting with charge separation between  $O^{2-}$  and Ti<sup>4+</sup> to produce  $-O-Ti^{3+}$  upon illumination. The separation of the redox half reactions permitted us to focus on CH<sub>4</sub> oxidation. (b) Dependence of the CO efficiency and selectivity on the applied potentials (left axis: efficiency, %; right axis: selectivity of CO over all carbonaceous products, %). PEC bulk electrolysis was conducted on ALD TiO<sub>2</sub> in CH<sub>4</sub>-saturated 1.0 M NaOH electrolyte at the corresponding applied potentials.

For the comparison of reaction selectivity under different conditions, we present the Faradaic efficiencies in Figure 4.1b. As can be seen, the detected CO and O<sub>2</sub> collectively account for 80% to 90% of the overall charges as measured by PEC bulk electrolysis. The unaccounted charges were attributed to the production of carbonates, the existence of which was confirmed by spectroscopic measurements. Although the amount of carbonates was too insignificant to quantify by weighing precipitates with Ba(II), the yield is estimated based on the balance of charge transferred (Figure 4.1b). It is noted that for this body of research, the most important quantitative information is the yield of CO. We see from Figure 4.1b and Figure 4.3a the following trends. *First*, the yield of CO is highly sensitive to the applied potentials. At 0.4 V vs. RHE, CO accounts for 81.9% of all charges other than O<sub>2</sub> formation. Given the low concentration of CH<sub>4</sub> (0.0010 mol/kg) under STP,<sup>39,40</sup> H<sub>2</sub>O oxidation is expected to compete favorably in receiving photogenerated holes, which explains the relatively high yield of O<sub>2</sub>. The yield of CH<sub>4</sub> oxidation (such as CO) is expected to be readily improved by increasing the partial pressure of CH<sub>4</sub>.<sup>10</sup> By comparison, at 1.2 V vs. RHE, CO only accounts for 24.7% of all charges other than O<sub>2</sub> formation. **Second**, the yield is sensitive to the type of  $TiO_2$  substrate used. For ALD grown  $TiO_2$ , at 0.6 V vs. RHE, CO accounts for 62.7% of the total charges other than O<sub>2</sub> formation; the yield was <4% for commercially obtained anatase TiO<sub>2</sub> or P25 TiO<sub>2</sub> nanoparticles. *Third*, we observed no CH<sub>4</sub> oxidation products in the absence of illumination or applied potentials or both. The observation is consistent with the understanding that the activation of the first C-H bond requires significant energy input. It further highlights the importance of photoexcitation for CH<sub>4</sub> oxidation.

## 5.3 **Proposed reaction mechanisms**

Significant research efforts have been attracted to understanding the activation of CH<sub>4</sub>. For heterogeneous catalysis, homolytic C-H dissociation has been reported as one of the activation mechanisms by hydrogen (H) abstraction on an active oxygen (O<sup>-</sup>) center, forming methyl radicals (•CH<sub>3</sub>).<sup>33</sup> How to effectively regenerate the surface-active oxygen species for continuous CH<sub>4</sub> activation was a major challenge. A solution was found in TiO<sub>2</sub> under photocatalytic conditions. It has been established by previous research that photooxidation on TiO<sub>2</sub> starts with charge separation between O<sup>2-</sup> and Ti<sup>4+</sup>, producing  ${}^{-\bullet}O$ -Ti<sup>3+,42</sup>, <sup>43</sup> The oxygen radical then attacks the C-H bond in CH<sub>4</sub> to yield Ti-O-CH<sub>3</sub>. Subsequent reactions turn this species back to  $Ti^{4+}$ -OH (or  $Ti^{4+}$ -O<sup>2-</sup> in the deprotonated form), ready for regeneration of the reactive site by photo-excitation. The oxygen radical then attacks the C-H bond in CH<sub>4</sub> to yield surface-adsorbed methoxy (OCH<sub>3</sub>) species.<sup>22</sup> The understanding is summarized in Figure 4.2. The evolution of this methoxy species and surface adsorbed CH<sub>4</sub> upon light illumination was detected by *in situ* Raman spectroscopy. The applied potential facilitates electron transport away from the Ti site through the conduction band of TiO2.42,43 Subsequent photoexcited electron transfers between O and Ti drive the reaction to reach a quasi-stable intermediate state of Ti-O=CH<sub>2</sub>, which was observed by in operando attenuated total reflection-Fourier transformed infrared spectroscopy (ATR-FTIR). To explain the dependence of CO product selectivity on the type of TiO<sub>2</sub> substrates and the applied potentials, we hypothesize that the mechanism of Ti-O=CH<sub>2</sub> oxidation depends on the nature of the adjacent Ti sites. In the presence of  $Ti^{3+}$ ,

it favors the formation of a  $Ti^{3+}$ -C bond, leading to selective production of CO. An increase in CO selectivity was observed at higher light intensity, since more  $Ti^{3+}$  sites would be induced and stabilized. Otherwise, the lack of  $Ti^{3+}$  sites would favor the formation of a  $Ti^{4+}$ -O-C bond, resulting in the formation of carbonates and, hence, complete oxidation of CH<sub>4</sub>. The proposed mechanism shown in Figure 4.2 is inspired by recent advances on CO<sub>2</sub> reduction and supported by the detection of key intermediates.<sup>26</sup> The mechanism is also supported by computational calculations. Below, we present detailed evidence to support the proposed reaction mechanisms.


**Figure 4.2** Proposed mechanisms of photooxidation of  $CH_4$  on  $TiO_2$ . The species highlighted by dotted circles have been confirmed by various spectroscopic techniques. The key distinguishing step is identified at the bottom of the catalytic cycle, where the synergistic effect between two adjacent Ti sites promote the switching of C=O-Ti to O=C-Ti, leading to selective formation of CO. Alternatively, in the absence of such a switching,  $CO_2$  is the preferred oxidation product.

# 5.3 The importance of Ti<sup>3+</sup> species

Our first task was to examine the difference between different  $TiO_2$  substrates. Three prototypical TiO<sub>2</sub> substrates, namely TiO<sub>2</sub> by ALD (Sample 1), anatase TiO<sub>2</sub> (Sigma Aldrich, 99.8% trace metal basis; Sample 2), and P25 (Evonik Industries, Aeroxide TiO<sub>2</sub> P25; Sample 3), were compared. Electron paramagnetic resonance (EPR) spectroscopy was employed for this purpose. While the true nature of the  $Ti^{3+}$  sites may not be fully understood until later, a theoretical study by Selloni et al. has shed important light on the problem. Their results showed that photo-generated charges become self-trapped on Ti, reducing the site to become Ti<sup>3+</sup>. EPR detects unpaired electrons, which reports on the localized Ti<sup>3+</sup> sites in TiO<sub>2</sub>.<sup>45</sup> As shown in Figure 4.3b, a significantly higher intensity of the EPR signal associated with Ti<sup>3+</sup> was observed for Sample 1 than the other samples,  $^{8,44,45}$  which is indicative of electrons trapped at the Ti<sup>3+</sup> sites. It is important to note that the EPR data as shown in Figure 4.3b were obtained in an atmosphere with CH<sub>4</sub> (97%) and H<sub>2</sub>O (3%), immediately after illumination (<120 s delay). Our results indicate a clear correlation of the Ti<sup>3+</sup> concentration as detected by EPR with the CO selectivity as detected by GC-MS. That is, reaction routes involving Ti<sup>3+</sup> would be favored when Sample 1 is used as the substrate, which is the CO pathway as shown in Figure 4.2. Further research would be needed to fully explain the high concentration of unpaired electrons in the trapped sites in Sample 1. Possible reasons include high concentration of O vacancies or incomplete removal of the ligands (isopropoxide).<sup>46</sup> It is, nevertheless, emphasized that Sample 1 has been shown highly active and stable toward PEC water splitting, suggesting that the high concentration of Ti<sup>3+</sup> does not undermine its optoelectronic properties.<sup>38</sup>



**Figure 4.3** Product selectivity dependence on substrates. (a) Comparison of CO selectivity on three different types of TiO<sub>2</sub> samples. PEC bulk electrolysis was conducted in CH<sub>4</sub> saturated 1.0 M NaOH electrolyte at 0.6 V vs. RHE. (b) EPR spectra showing the EPR signals consistent with the presence of Ti<sup>3+</sup> in the three samples (the color coding of the spectra is the same as the left panel). Of them, ALD TiO<sub>2</sub> (**Sample 1**) features the highest intensity ( $g_{\perp} = 1.99$  and  $g_{\parallel} = 1.96$ ).

## 5.3 Probing key reaction intermediates by spectroscopies

Next, we carried out a multimodal study to detect several key intermediates as shown in Figure 4.2. The techniques we employed include *in situ* Raman and *in operando* ATR-FTIR measurements. Among them, in situ Raman allowed us to detect Ti-O-CH<sub>3</sub> (Figure 4.4a), which is a product of the initial oxidation of  $CH_4$  after photoexcitation of electrons from O 2p orbitals to Ti 3d orbitals. The Raman spectra as shown in Figure 4.4a were collected in a homemade quartz cell filled with CH<sub>4</sub> (97%) and H<sub>2</sub>O (3%) at 1 atm. Without photoexcitation, we only observed a characteristic peak at 2917 cm<sup>-1</sup> that is due to free CH<sub>4</sub> molecules.<sup>47</sup> With photoexcitation, a shoulder peak at 2905 cm<sup>-1</sup> appeared, which is ascribed to adsorbed CH<sub>4</sub>.<sup>47</sup> The red shift in comparison with free CH<sub>4</sub> is due to a weakened bond as a result of adsorption to the TiO<sub>2</sub> substrate. Most prominently, two satellite peaks at 2850 cm<sup>-1</sup> and 2965 cm<sup>-1</sup> gradually evolved during the *in situ* photoexcitation experiments. Similar peaks have been assigned to the C-H symmetric stretching and asymmetric stretching modes of O-CH<sub>3</sub> on TiO<sub>2</sub>, respectively, in the literature.<sup>48</sup> These results provide strong support for the conclusion that we have obtained CH<sub>3</sub>-O-Ti bonds upon photoexcitation under our experimental conditions. To rule out the possibility that these two satellite peaks are due to impurities, we performed Raman characterization using isotope-labelled methane (CD<sub>4</sub>). The characteristic Raman shifts of the C-D stretching modes (1800~2500 cm<sup>-1</sup>) are distinctly different from the C-H stretching modes (2800~3000 cm<sup>-1</sup>).<sup>49</sup> Similar satellite peaks were observed, providing additional strong support for our interpretation. The proposed reaction mechanism that governs the formation of CH<sub>3</sub>-O-Ti is illustrated in the top panel of Figure 4.4. Alternatively, Ti-O-

 $CH_3$  may be generated by an indirect oxidation of  $CH_4$  by water oxidation intermediates, such as  $H_2O_2$ . A series of control experiments have been performed by adding  $H_2O_2$  to the electrolyte under different conditions. The results indicate that the last suggested alternative route is unlikely.

Next, we conducted in operando ATR-FTIR measurements to probe the reaction intermediates in the subsequent oxidation steps. Similar to the implementations by Hamann et al.,<sup>50</sup> we carried out the experiments by pressing the working electrode against the IRtransparent Si ATR crystal. The electrolyte sandwiched between  $TiO_2$  and Si was either saturated with CH<sub>4</sub> or N<sub>2</sub> (as a control). The IR data were collected at a constant applied potential of 0.3 V (vs. Pt counter electrode) under illumination. They are presented in Figure 4.4b after correction for background absorption. We focused our attention on the region between 1700 cm<sup>-1</sup> and 2300 cm<sup>-1</sup> because the IR absorption beyond 2700 cm<sup>-1</sup> is cut off by a long-pass IR filter in front of the detector and other regions (below 1600 cm<sup>-1</sup>, 2300 cm<sup>-1</sup> to 2700 cm<sup>-1</sup>) are interfered by broad H<sub>2</sub>O and CO<sub>2</sub> absorptions. Within the observation window, three distinct peaks at 1735, 1763, and 2065 cm<sup>-1</sup> were observed, but only in the presence of CH<sub>4</sub>. All three peaks exhibited an obvious dependence on the illumination duration, strongly suggesting that they are due to photooxidation reactions on the surface of TiO<sub>2</sub>. Of them, the most prominent peak at 1763 cm<sup>-1</sup> is assigned to the C=O stretch due to surface adsorbed formic acid species.<sup>51-54</sup> The peak at 1735 cm<sup>-1</sup> is assigned to the C=O stretch due to surface adsorbed formaldehyde species, where the oxygen adatoms are coordinated to Ti atoms.<sup>51,54,55</sup> The peak at 2065 cm<sup>-1</sup> is assigned to the C=O stretch due to surface adsorbed CO species.<sup>56,57</sup> The assignments of these peaks are supported by literature reports. The importance of these reaction intermediates to the overall reactions is illustrated in the proposed catalytic cycle (Figure 4.2).



**Figure 4.4** In situ Raman and FTIR detection of key reaction intermediates. (a) In situ Raman spectra of samples in dark (left) and in light (right) confirm the H<sub>3</sub>C-O-Ti species as a result of the initial oxidation of CH<sub>4</sub>. No electrical potential was applied. (b) Evolution of H<sub>2</sub>C=O-Ti, Ti-CO and HCOO(H)-Ti surface species as a function of time as detected by FTIR. The IR data were collected at  $V_{app} = 0.3$  V (vs. Pt counter electrode) under illumination.

#### 5.3 Mechanistic insight in parallel CO<sub>2</sub> reduction

Our investigations of the catalytic cycle highlight the importance of the Ti<sup>3+</sup> site adjacent to Ti-O=CH<sub>2</sub> in promoting CO formation. This understanding is consistent with the potential dependence we observed. At relatively high applied potentials (e.g., 1.2 V vs. RHE), photoexcited electrons are readily removed from the Ti<sup>3+</sup> site, which would favor the pathway leading to CO<sub>2</sub> (or carbonate) formation. At less positive potentials (e.g., 0.4 V vs. RHE), the higher concentration of Ti<sup>3+</sup> sites facilitates the formation of Ti-C(H)=O bonds, leading to CO formation. In essence, the switching between Ti-O-C and Ti-C-O bonding appears to be critical to the selectivity for CO production. The conclusion reminds us of parallel studies on CO<sub>2</sub> reduction by metal catalysts. It is well accepted that the reaction starts with a M-C bond (where M represents the metal catalytic center). Computational results suggest that formation of more reduced products such as CH<sub>4</sub> or CH<sub>3</sub>OH often requires switching from M-C-O to M-O-C bonding (Figure 4.5.);<sup>24</sup> otherwise, the reaction favors the formation of CO. While experimental evidence to explicitly verify this understanding is still missing, multiple computational studies provide strong supports for this hypothesis.<sup>24,58,59</sup> The switching likely proceeds through a concerted mechanism with adjacent metal sites, in a similar fashion to our proposed mechanism as shown in Figure 4.5. We suggest that insights into CO<sub>2</sub> reduction could be drawn from studies of CH<sub>4</sub> oxidation, given the similarities of the key steps.



**Figure 4.5** The switching between Ti-O-C and Ti-C-O bonding is critical to the selective production of CO from CH<sub>4</sub> (top). In parallel studies of CO<sub>2</sub> reduction, the selective production of CH<sub>4</sub> or CH<sub>3</sub>OH may proceed by switching between M-C-O and M-O-C bonding in a similar fashion (bottom). The key steps are highlighted in the dotted boxes.

### 5.3 Summary

In conclusion, we have observed highly selective CO production by CH<sub>4</sub> photoelectrochemical oxidation. Only with a moderately positive applied potentials (between 0.4 and 1.2 V vs. RHE) and on ALD-grown TiO<sub>2</sub> did we obtain a high yield of CO production. EPR studies revealed that the key difference between ALD-grown TiO<sub>2</sub> and commercially obtained samples is the concentration of Ti<sup>3+</sup> sites. We propose that the adjacent Ti<sup>3+</sup> sites to the Ti-C=O bond are key to the high selectivity for CO formation. Spectroscopic evidence from *in situ* Raman and FTIR spectroscopy provides strong support to the proposed mechanism. The feasibility of the proposed mechanism is also supported by computational studies as well. The proposed mechanism draws similarities to heterogeneous CO<sub>2</sub> reduction reactions. Together, the results highlight the importance of synergistic effects in promoting complex chemical reactions such as CH<sub>4</sub> oxidation and CO<sub>2</sub> reduction. The photooxidation reaction as presented here opens up new doors toward highly selective reforming of CH<sub>4</sub> for high-value industrial chemicals such as CO.

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### Chapter 5: New catalyst design for direct CH4 to acetic acid production

### 5.1 Direct CH<sub>4</sub> partial oxidation to acetic acid

In the previous chapters, I have shown that operation temperature of CH<sub>4</sub> oxidation can be significantly reduced to room temperature by photo-assisted approaches. However, the products we can get from photo-assisted approaches are usually CO or CO<sub>2</sub>, which needs to be further converted by H<sub>2</sub> to generate oxygenate or hydrocarbons. So, other than photo-assisted approaches, new catalyst development is essential to control product selectivity of CH<sub>4</sub> partial oxidation. A suitable catalyst can not only lower the activation barrier to avoid high energy processes, but mildly oxidize CH<sub>4</sub> into oxygenate. Recently, researchers have developed single atom catalysts (SACs) to direct convert methane into oxygenates in one step.<sup>1-3</sup> Consider CH<sub>4</sub> oxidation to acetic acid as an example, which is a very important chemical and typically produced by reforming of CH<sub>4</sub>, methanol synthesis and methanol carbonylation processes. Shan *et al.* demonstrated Rh SACs on ZSM-5 for direct CH<sub>4</sub> carbonylation to acetic acid.<sup>4</sup> Tang *et al.* showed similar results on the same system and carried out isotope labelling measurements to further investigate the reaction mechanisms.<sup>5</sup> Although great results have been achieved in this direction, it is still not clear how to rationalize the high selectivity towards acetic acid production. Specifically, the metal center-support interaction has not been explicitly discussed and could be very critical to acetic acid formation. Several studies have indicated that metal-support synergistic effect might facilitate C-C coupling. For example, Narsimhan *et al.* have revealed that methyl group may migrate from copper site to bronsted acid site on the substrate in the acidic acid formation pathway;<sup>6</sup> similarly, a theoretical study about Au SACs on ZSM-5 also found that with the help of adjacent Bronsted acid site, reaction barrier is significantly reduced.<sup>7</sup>

To better understand the acidic acid formation pathway and how the synergistic effect could help, herein, we developed well-defined Ir di-nuclear heterogeneous catalysts (DHCs)<sup>8</sup> on SBA-15, which is an inert oxide support. By comparing Ir DHCs with Ir SACs and Ir nanoparticles (NPs), an extraordinary selectivity towards acetic acid was observed on Ir DHCs without any methanol formation, while Ir SACs majorly produce methanol and Ir NPs only generate over-oxidation product, formic acid. Structure characterizations have distinctly shown the atomically dispersion and di-nuclear nature of Ir DHCs. Temperature-dependent measurement revealed that Ir DHCs show a much lower reaction barrier than Ir SACs in terms of forming acidic acid. Finally, DFT calculation results agreed well with our experimental results that the adjacent Ir in Ir DHCs could significantly lower the activation barrier in acidic acid formation pathways. The knowledge generated in this work

is not only prominent for future development of CH<sub>4</sub> transformation, but also sheds light on the general heterogeneous catalysis.

# 5.2 Materials and methods

Ir homogeneous dimer complex: Synthesis of Ir homo-dimer was based on previously established methods. The Cp\*Ir[pyalc(OH)] (Cp\*: precursor, pentamethylcyclopentadienyl, C<sub>5</sub>Me<sub>5</sub>, pyalc:2-(2'-pyridyl)-2-propanoate), was synthesized by a well-established procedure. A typical procedure for the formation of Ir homo-dimer is as follows: 0.024 g (0.049 mmol) of Cp\*Ir[pyalc(OH)] was added to a 100 mL flask, and dissolved in 50.0 mL of water to form a 1 mM solution of Cp\*Ir[pyalc(OH)]. The solution was stirred for approximately one minute at room temperature in air, forming a clear, red solution. Then, 1.07 g (5.00 mmol) of NaIO<sub>4</sub> was added to the solution (100 mM concentration with respect to NaIO<sub>4</sub>), which immediately began bubbling. The solution was stirred at room temperature in air for two hours upon which the color of the solution changed from red to green to blue. UV-Vis absorption spectroscopy of the solution after two hours showed the expected absorption features for Ir homo-dimer, having a broad absorption around 600 nm.

Ir dinuclear heterogeneous catalyst on SBA-15: *Step 1*. SBA-15 (Alfa Aesar) substrate was soaked in the Ir homodimer solution for 10 h and then thoroughly rinsed with deionized water to form the Ir intermediate. The loading amount was estimated by ICP-OES calibrated by standard H<sub>2</sub>IrCl<sub>6</sub> solution. The Ir loading was calculated to be 0.1%wt. *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 16-18 min to get Ir DHCs.

**Ir nanoparticles on SBA-15:** As prepared Ir DHCs on SBA-15 was annealed at 200 °C under 5% H<sub>2</sub>/95% N<sub>2</sub> (v/v) atmosphere at 600 torr for 1 h.

**HADDF-STEM:** HAADF-STEM images were collected using a double-aberrationcorrected FEI Titan3 G2 60-300 instrument operating at 300 kV. The semiangle of the probe-forming aperture was  $\sim$ 22 mrad. The inner and outer semiangles of the HAADF detector were  $\sim$ 80 and 200 mrad, respectively. A probe current of 76 pA and dwelling time of 16 µs per pixel were chosen for desirable signal-to-noise ratios. EDS was performed on a Super-X EDS system consisting of four Bruker silicon drift detectors. The semiconvergence angle for imaging was  $\sim$ 24.7 mrad, while the collection semiangle was  $\sim$ 70–200 mrad. A higher beam current of 280 pA was used with a longer dwell time of 0.1 ms per pixel and repeated 200× 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 postfiltering.

**In situ 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. 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 H<sub>2</sub>O and was then gradually cooled to room temperature. 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, 2,200–1,800 cm<sup>-1</sup> after varying the He purging time (5, 10, 40, and 70 min). The resolution was selected at 4 cm<sup>-1</sup>. Sixty-four scans were recorded for each spectrum shown in the work.

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 IrO<sub>2</sub> 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. The coordination number of Ir-O for IrO<sub>2</sub> standard was fixed at 6 to determine the amplitude reduction factor  $(S_0^2)$ . 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<sup>-1</sup> 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 IrO<sub>2</sub> 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.

**Catalytic performance test:** Methane oxidation was conducted in aqueous phase in a 50 mL pressurized Parr reactor (series 4790). The reactor was fitted with a Teflon liner and a K type thermocouple inserted into the aqueous phase. 15 mg catalysts were dispersed in 10 mL deionized water in the Teflon liner under vigorous stirring. Then, the liner was placed in the catalytic reactor. The reactor vessel was pressurized with O<sub>2</sub>, CO and CH<sub>4</sub> with certain partial pressure. The reactor was then placed in an oil bath that was pre-heated to the desired temperature. The solution temperature was kept heating up to the desired temperature for 2 h. After the reaction, the reactor was removed from the oil bath and cooled with ice bath. Once the temperature of the reaction solution was below 10 °C, the liquid was collected in a vial after centrifuging out the solid particles.

The concentration of oxygenates in the liquid was quantified by NMR. <sup>1</sup>H-NMR were carried out based on a water suppression method. Typically, 0.6 mL reaction solution was mixed with 0.1 mL  $D_2O$  and 0.1 mL 0.3 mM DMSO internal standard in an NMR sample tube for the measurement.

### 5.3 Synergistic effect of adjacent Ir for acetic acid formation

A general schematic of our study is shown in Figure 5.1a. In this study, the most important thing is the comparison of three platforms, Ir SACs, Ir DHCs, and Ir NPs on SBA-15. We hypothesize that Ir SACs and Ir DHCs would help facilitate selective C-H bond activation to form stable Ir-CH<sub>3</sub> intermediate and produce low-valent carbon oxygenates, while Ir NPs, due to its metallic nature, would completely activate CH<sub>4</sub>, leading to over-oxidation products. In addition, by adding an adjacent Ir center, we propose that Ir DHCs could lower the barrier of acetic acid formation, and thus improve its selectivity. So, to confirm our hypothesis, catalytic performance was evaluated on all three catalysts. A typical high pressure vessel was employed as a batch reactor. 15 mg catalyst was dispersed into 10 mL of deionized water and vigorously stirred at a speed of 1000 rpm. CH<sub>4</sub>, CO and O<sub>2</sub> were then pressurized into the vessel as reactants at room temperature and the gas composition were adjusted as needed. Then the reactor was heated to a certain temperature and kept for 2 hours. After reaction, the liquid products were analyzed by H-NMR. More experimental details are shown in Materials and Methods. The catalytic performances of Ir NPs, Ir SACs, and Ir DHCs are shown in Figure 5.1b and the results agree well with our expectation. Ir NPs doesn't show CH<sub>3</sub>OH or CH<sub>3</sub>COOH production but only produce formic acid as over-oxidation product, indicating the strong activity towards C-H bond activation. Also, Ir NPs with a larger size show increase production of formic acid, which further illustrates that metallic Ir-Ir is too active for C-H bond activation. Ir SACs, which are in cationic nature, are able to prevent over-activation of CH<sub>4</sub> and produce CH<sub>3</sub>OH. Ir DHCs, with one additional adjacent Ir center, show similar behavior as Ir SACs in terms of preventing over-oxidation, but exhibit extraordinary selectivity towards acetic acid formation with no CH<sub>3</sub>OH production. The direct comparison of all three catalysts further strengthen our hypothesis: atomically dispersed catalysts are able to stabilize M-CH<sub>3</sub> (M represents the active metal center) intermediate and produce low valent carbon oxygenates such as CH<sub>3</sub>OH and CH<sub>3</sub>COOH; more importantly, the synergistic effect of two adjacent Ir significantly change the product selectivity and the

results imply that C-C coupling is more favorable when there are two active center close to each other. To further investigate the effect of adjacent Ir atom, catalytic performances under different reactant pressure were measured on both Ir SACs and Ir DHCs. When the oxygen partial pressure is changed from 2 bar to 4 bar, Ir SACs and Ir DHCs behave very differently in CH<sub>4</sub> oxidation activity. Catalytic performance of Ir SACs increases as oxygen partial pressure increases, indicating oxygen activation or oxygen mediated steps are involved in the rate-limiting step. On the contrary, Ir DHCs show a negative relationship towards oxygen partial pressure increase. These different results on Ir DHCs imply that oxygen does not participate in the rate limiting step and the increase of oxygen may further over-oxidize CH<sub>4</sub>, which leads to the decrease of liquid products production. What's more, CO partial pressure also plays an important role in the reaction selectivity and activity. CO pressure was changed from 1 bar to 5 bar and the activity of both Ir DHCs and Ir SACs show similar trends. When the CO pressure was increased from 1 bar to 3 bar, the amount of acetic acid and formic acid also increased, indicating CO may participate in the formation of acetic acid and improve the formic acid formation by changing the Ir electronic structure through its coordination. However, further increasing CO pressure would lead to a decrease in the formation of oxygenates. This could be explained that high CO pressure would poison the Ir center, which blocks activation of oxygen and CH<sub>4</sub> and leads to the deactivation of the catalysts.



**Figure 5.1** (a) Schematic illustration of selective  $CH_4$  oxidation to acetic acid on Ir DHCs. Ir SACs majorly produce methanol (b) Product distribution of three catalysts. Reaction conditions: 20 bar  $CH_4$ , 5 bar CO, 3 bar  $O_2$ , 150 °C for 2 h.

To rationalize the comparison, detailed structural characterizations were carried out on all three catalysts. Ir DHCs was synthesized by immobilizing homogeneous Ir dimer complex and followed by photochemical treatment, which was reported in our previous work. Ir SACs was prepared through a well-established wet impregnation method using IrCl<sub>3</sub> as precursor. Ir NPs with different sizes was obtained by annealing Ir DHCs at 200 or 400 °C for 1 to 3 hours under 5% H<sub>2</sub>/95% N<sub>2</sub> atmosphere, respectively. More details are shown in Materials and Methods. The most direct evidence that distinguish the mononuclear and dinuclear structures from the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) data (Figure 5.2a). Mostly in Ir DHCs, dual Ir clusters were observed on SBA-15 substrate, while isolated single Ir atom was obtained in Ir SACs.



**Figure 5.2** (a) ac-HADDF-STEM images of Ir DHCs on SBA-15. Isolated iridium dual atoms are makrked with yellow circles. (b) TEM image of Ir DHCs on SBA-15. (c), (e), (f) Elemental mapping of O, Si and Ir, respectively. (d) Atomic model of Ir DHCs on SBA-15 surface. Distance between two Ir is 3.693 Å.

Based on HADDF-STEM images, we can clearly distinguish Ir SACs and Ir DHCs. However, the coordination environment of Ir center is of critical importance for catalytic activity but is not known. Therefore, two spectroscopic techniques were adopted to determine electronic and chemical structure of both catalysts. First, we performed in situ CO diffuse reflectance infrared Fourier transform spectroscopic (DRIFTS) characterization (Figure 5.3), and the purpose was to use CO as a probe to study the Ir atomic arrangement of Ir DHCs and Ir SACs. For both Ir DHCs and Ir SACs, we expect there should be no Ir-Ir motif according to our previous work of Ir DHCs on other metal oxides and Ir-Ir feature could only be observed on Ir NPs. Indeed, the broad peak at  $\sim 1.850$  cm<sup>-1</sup> was observed for Ir NPs control samples with known Ir–Ir bonding but absent from Ir DHCs. 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. The Ir SACs show a similar dicarbonyl species absorption but a redshift around 6 cm<sup>-1</sup>, indicating a slightly lower Ir oxidation state. Some CO bridge absorption can be observed in Ir SACs and a linear absorption mode related to interfacial Ir. But overall, the most dominant species are Ir isolated atoms and the small portion of Ir NPs would not complicate our comparison based on the catalytic performance of Ir NPs.



Figure 5.3 CO-DRIFTS spectra of Ir DHCs on SBA-15. No bridge CO adsorption.

Second, X-ray absorption spectroscopy data were acquired to reveal the coordination environment of the Ir center. We see from Figure 5.4a that the first shell coordination of Ir in DHCs is dominated by Ir-O, in great agreement with the proposed bonding of Ir-O-Ir rather than Ir-Ir. Ir SACs also show dominantly Ir-O coordination in the first shell, indicating the dominant species are the isolated Ir atoms. From the detailed fitting results, Ir in both DHCs and SACs show a positive oxidation state but less positive than IrO<sub>2</sub>. Also Ir centers in both catalysts are a little under coordinated. These observations showed that the Ir center in DHCs and SACs is partially electron-rich, which is suitable for C-H bond activation and Ir-CH<sub>3</sub> formation.



Figure 5.4 EXAFS characterization of Ir foil, IrO<sub>2</sub> and Ir DHCs.

### 5.4 Arrhenius relationship

Next, we have carried out activation barrier measurement for both Ir SACs and Ir DHCs, together with the reaction pathway simulation by DFT. Experimental activation barrier of acetic acid formation was obtained by measuring the activity at different temperatures. Both Ir SACs and Ir DHCs showed good Arrhenius relationship at the temperature range from 140 to 170  $\mathbb{C}$  (Figure 5.5). The calculated activation barriers of Ir SACs and Ir DHCs are 77.14 kJ/mol and 29.62 kJ/mol, respectively. These results strengthen our hypothesis that the synergistic effect of adjacent Ir could facilitate the acetic acid formation pathway. To further investigate the reaction mechanisms, we have simulated reaction pathways by DFT calculations. From DFT calculations, both Ir SACs and Ir DHCs show a very stable structure on SBA-15 substrate. More importantly, spectroscopic features were simulated based on both simulated catalyst structures, which are almost identical to the experimental results.



**Figure 5.5** Arrhenius plots of Ir SACs and Ir DHCs under optimized reaction conditions for acetic acid formation.

### 5.5 Summary and future work

In conclusion, we have synthesized two Ir catalysts: DHCs and SACs, with welldefined active moieties. HADDF-STEM images distinctly shows the difference of DHCs and SACs. CO DRIFTS and EXAFS experiments further confirm the atomic dispersion of both catalysts. In terms of catalytic performance, Ir DHCs show a much higher acetic acid formation than Ir SACs and Ir NPs under same reaction conditions. Arrhenius plots reveals that Ir DHCs undergo a much lower activation barrier than Ir SACs. Those results point out the importance of synergistic effect of adjacent active sites, which sheds light on the future catalyst design for selective acetic acid formation. Future study, such as DFT calculations, is needed to theoretically simulate the reaction pathways.

#### 5.6 Reference

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### **Chapter 6: Conclusions**

C<sub>1</sub> chemistry, representing CH<sub>4</sub> conversion and CO<sub>2</sub> reduction, is very important, in both environmental and chemical considerations. Both CH<sub>4</sub> and CO<sub>2</sub> are promising as candidates for chemical feedstocks. Indeed, chemical industry has widely applied C<sub>1</sub> chemistry for various chemical syntheses. However, it faces critical challenges. High activation energy for both CH<sub>4</sub> and CO<sub>2</sub> requires high thermal or electric energy input, which also affects the stability of catalysts in a negative way. In addition, product selectivity is difficult to control for both processes. To solve these challenges, we adopt two strategies: developing new approaches and new catalysts. Advanced approach like photocatalysis (including PEC) helps significantly reduce energy input by other means. New catalyst development by understanding reaction mechanisms helps control product selectivity.

We first focused on low bias  $CO_2$  reduction by PEC approach. Si NWs has been chosen as photocathode material for light harvesting, because Si has suitable band position, small band gap and nanostructure helps charge collection and light absorption. In this study, we incorporated a Co-based molecular catalyst for selective  $CO_2$  to CO conversion. Compared with planar Si and Au electrode, Si NWs showed a much higher photocurrent and photovoltage. Product analysis showed that most charges are attributed to CO and  $H_2$ production. FE of CO was around 70%. So, we have demonstrated selective CO<sub>2</sub> reduction with low applied bias by coupling Si NWs and a molecular catalyst.

We then focused on understanding this system. We introduced two Re-NHC-based molecular catalysts and tried to investigate the effects of proton donor by comparing them. When no proton donor presented, both catalysts showed similar performances and no H<sub>2</sub> were detected. DRIFTS study on Si NWs surface after bulk electrolysis in both catalysts showed that both catalysts strongly adsorbed on the electrode surface. After introducing 5% H<sub>2</sub>O as proton donor, both catalysts showed a much higher CO production, indicating the acceleration of CO<sub>2</sub> reduction by proton coupled electron transfer. However, catalyst **1** shows a much higher H<sub>2</sub> production while catalyst **2** shows minimum H<sub>2</sub> generation. Similar DRIFTS study were also carried out. Adsorption of catalyst **1** is much worse after bulk electrolysis, while catalyst **2** showed similar adsorption behavior as no proton donor presented. This indicates that strong adsorption of catalyst on electrode surface might be the key to enable high selectivity of CO<sub>2</sub> reduction.

Furthermore, we demonstrated selective  $CH_4$  conversion to CO on  $TiO_2$  by PEC approach. In addition, the PEC approach permits us to effectively separate excited charges at catalytic surface, and applied potential makes it possible that surface active species are controlled. More importantly, detailed mechanistic investigations at molecular level were

carried out by the combination of experimental (Raman, Infrared spectroscopy, EPR spectroscopy) efforts. It is revealing the formation of methoxy species proceeded through radical mechanism, and tuning selectivity offered by active Ti species and anodic applied potentials under PEC working conditions. In addition, a bond switch from metal-oxygen (M-O) to metal-carbon (M-C) was observed in the process of CH<sub>4</sub> to CO, which might shed light on controlling the selectivity of the reverse CO<sub>2</sub>/CO reduction towards CH<sub>4</sub> or CH<sub>3</sub>OH. We believe the knowledges generated in this work will provide insights on developments of CH<sub>4</sub> conversion catalyst under mild reaction conditions to achieve high yield and selectivity towards certain product. Our study also emphasize the synergistic effect of adjacent metal active centers and this will contribute to catalytic reactions, not only limited to CH<sub>4</sub> oxidation.

Lastly, we focused on developing new catalysts for direct CH<sub>4</sub> partial oxidation to oxygenates. Single atom catalysts (SACs) has been utilized to enable direct CH<sub>4</sub> to acetic acid formation, recently. Despite the promising results, however, the reaction mechanism of acetic acid formation still remains unclear, which hinders the development of this process. According to previous literatures, we hypothesized that two close active centers could boost acetic acid formation by synergistic effects. So, we have synthesized Ir SACs (single active center) and Ir DHCs (dual active centers) on SBA-15. A series of characterizations, such as HADDF-STEM, DRIFTS and EXAFS, helped distinguish SACs and DHCs and prove the excellent atomic dispersion on the substrate. Catalytic
performances were tested for both catalysts. To our expectation, Ir DHCs showed a much higher acetic acid formation than Ir SACs, which mainly produced methanol. Arrhenius plots also showed that Ir DHCs undergo a lower activation barrier than Ir SACs. Further studies, such as DFT calculation and intermediate detection, are needed in the future. Based on our preliminary results, we have already revealed the importance of two adjacent active sites for C<sub>2</sub> products. This finding might also shed light on other coupling reactions.

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