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Optimizing Iridium Single Atom and Small Cluster Catalysts for CO Oxidation Coogan Bryce Thompson (ABSTRACT)

Single atom catalysis is a relatively new form of heterogeneous catalysis. While single atom catalysts probably are already used in a lot of catalysis, their identification and characterization has only recently become common place. As we now have the ability to synthesis relatively pure systems consisting of single atoms and then to characterize them, there are many interesting questions that we can answer about them. In this work we will use a combination of several different types of characterizations such as kinetic measurements, diffuse reflectance infrared Fourier transform spectroscopy, extended x-ray absorption fine structure, and many more to better understand how single atoms react and how we can attempt to make such systems more active. The work here is primarily based around Ir single atoms and/or small clusters on three different supports MgAl₂O₄, TiO₂, and CeO₂. In each of these cases we attempt to understand how the Ir and the support catalytically oxidize CO into CO₂ through a kinetic, and if possible, mechanistic study. Through these mechanistic studies we attempt to isolate the most important parameters of the catalyst so that we can create a more active catalyst. There are, of course, many different ways that we can use this information. The most obvious is by changing the catalyst support, but as the breadth of the research presented here will show, we can also optimize catalytic activity through using mixtures of single atoms with larger species as well as by changing the nuclearity of the said species, i.e., we can increase activity by controlling the size of the catalysts. However, in order to be able to control the activity in this way, we must 1) know how the size affects the activity and 2) know how the reaction conditions affect the size, i.e., we must establish the catalyst size is stable during reaction. Each of these topics are discussed to some extent here. Additionally, we also discuss how different sites of single atoms on the same support can be isolated and how this leads to single atom catalysts with different spectroscopic properties that might affect the catalytic activity. On the whole, we have studied single atom and small cluster catalysis in a variety of directions based on systems of Ir for CO oxidation. This work is also performed with the intent to compare these Ir systems to similar systems of Rh, Pt, Pd, etc. However here we will only

discuss the Ir pieces. Optimizing Iridium Single Atom and Small Cluster Catalysts for CO Oxidation Coogan Bryce Thompson (GENERAL AUDIENCE ABSTRACT) In this work we study various properties of Ir single atom and subnanometer cluster catalysts for CO oxidation in hopes that we might be able to design a better catalyst with this information. A catalyst is a substance that facilitates a chemical reaction but is not consumed. For this work we will be considering the reaction of carbon monoxide (CO), which is a common pollutant and highly toxic gas, with O₂ to create CO₂, a much less dangerous pollutant. Our catalyst thus makes this reaction happen much faster and thus allows us to remove CO from exhaust streams, such as car exhaust, better. A single atom catalyst is a catalyst that is primarily

a single atom on a metal oxide support. A

subnanometer cluster catalyst is thus a catalyst that is smaller than one nanometer (0.00000004 inches). These are typically 10-20 atoms grouped together. This size is interesting as it is bigger than a single atom, but it is still much smaller than a classical catalyst nanoparticle and is thus controlled or dominated by different properties. In this work we will look at how different characteristics of the single atom and cluster catalysts affect how good of a catalyst it is. The first is how the amount of single atoms and nanoparticles affect the overall activity of the catalyst. This study will tell us what the best mixture of single atoms is. The second study is how small clusters of Ir/MgAl₂O₄ react differently than single atoms and large nanoparticles. This tells us what the best size for Ir/MgAl₂O₄ catalysts are. The third study tells us how Ir/TiO₂ single atom catalysts react which is useful when compared to Ir/MgAl₂O₄ and Ir/CeO₂ (Chapter 7). The combination of single atom studies then allows us to make predictions on which supports (apart from Ir/MgAl₂O₄, Ir/TiO₂, and Ir/CeO₂) will be the best for CO oxidation. The fourth study compares different single atoms (all of Ir/TiO₂) and shows how they behave differently, this is another possibility to increase the effectiveness of the catalyst. The fifth study discusses how different conditions affect the size of the Ir/TiO₂ catalysts. Specifically, whether they exist as single atoms, subnanometer clusters, or larger clusters. All of these different studies represent another way that we can potentially increase catalytic activity and hopefully will allow our group, or another group to create even more active catalysts. Dedication To my parents, David and Michelle Thompson. vi

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Chapter 1 Background and Literature Review 1.1 History of the

Project This document is a summary of what I have achieved while conducting my research at Virginia Tech. The underlying theme of that research has always been to make a more active catalyst. We have focused that research on single atom catalysis for CO oxidation, as single atom systems are still largely not well understood and have huge untapped potential. While there are many ways that we can optimize a catalyst and we will discuss several in this work. The first approach discussed, in Chapter 2, is about how systems can be optimized by using the ratio of single atoms to nanoparticles. Single atom catalysts are not always better than traditional nanoparticle catalysts, so understanding when and how they are better is the first question that we attempt to answer. This is of course not the only way that we can try to increase catalyst activity. We can vary many different properties of the catalyst itself. So while in Chapter 2 we first asked when and where single atoms are better in regards to being mixed in with nanoparticles, in Chapter 3 we will investigate what size particle is best. Most of the techniques used to create single atoms also make very small clusters of atoms. Likewise the characterization techniques for these clusters are similar to single atoms so this is a logical side goal for the large focus of these studies. With the two extremes (single atoms and nanoparticles) understood, it follows that this intermediate piece would be useful in allowing us to fully understand how the size of the catalyst affected its properties. 1 2 CHAPTER 1. BACKGROUND AND LITERATURE REVIEW

These first two works were performed on Ir/MgAl₂O₄ as our group has previous experience with these systems and thus we were able to build off of the previous studies that had established the necessary kinetic pieces. We attempt to ask similar questions on the Ir/TiO₂ catalysts, but due to differences in the system, these studies went in a much different direction (see Chapter 6). With the Ir/MgAl₂O₄ catalysts understood at the mechanistic level, we began looking at the effect of the support (MgAl₂O₄). Previous mechanistic studies suggested that a more reducible support might be more active for the CO oxidation reaction so we chose Ir/TiO₂ and Ir/CeO₂ systems. These two systems are very commonly used for both industrial and scientific applications. These systems are also known primarily to be reducible supports and as such were logical targets to study next. These different supports were the motivation for the kinetic study of CO oxidation on Ir/TiO₂ (Chapter 4) and the kinetic study of CO oxidation of Ir/CeO₂ (Chapter 7) with the former having the higher priority and thus the larger amount of focus. This work culminated into the various studies of Ir/TiO₂ (Chapter 4, 5, and 6). The first priority was to study the mechanism of CO oxidation for the Ir/TiO₂ single atom catalysts. This involved many different attempts and strategies in terms of synthesis. Anatase TiO₂ showed some challenges in its use as we are limited by the transformation to rutile as well as TiO₂'s spillover effect. Thus we are limited in the temperatures we can expose the system to. However, we did successfully develop a synthesis method that we could make not only single atom catalysts, but also multiple different types of single atom Ir/TiO₂. This is what lead to the work comparing different sites for Ir/TiO₂ single atoms (Chapter 5). Once we were able to isolate one group of single atom sites, we were able to perform several different experiments as well as computational studies (from Liping Liu and the Xin group) to propose a mechanism for CO

oxidation. The culmination of that work is shown in Chapter 4. 1.2. OBJECTIVES FOR EACH PROJECT 3 With the single atom mechanism being established, we proceeded to the different synthesis conditions for Ir/TiO₂ single atoms. We had observed that some of the conditions would yield conflicting results. For example we detected what were apparently nanoparticles based on STEM results and kinetic measurements, but we could not detect these in the DRIFTS. This led us to look closer at the catalyst dispersion. This motivation, compared with the goals of creating small clusters similar to the MgAl₂O₄ systems, led us to discover that several systems of small clusters on TiO₂ can undergo a large amount of redispersion into single atoms. This was the origin of the 6th chapter. With the Ir/TiO₂ systems having few questions to answer, we now turn towards the Ir/CeO₂ (Chapter 7). While, the Ir/TiO₂ did not react as expected, it was significantly less active than the Ir/MgAl₂O₄. We wanted a third data point to help us identify where the expected correlation between support reducibility and catalysts activity had broken down. This question is still not fully answered, but we do have significant progress towards a kinetic understanding of Ir/CeO₂ which is the first step in answering said question. That work is discussed in Chapter 7. 1.2 Objectives for Each Project Here I present the objectives that I individually sought to satisfy for each project. They are given as bullet points for simplicity. The objectives are given in the order I attempted them. The order and content of these lists might be different than that in the published results as the conclusions are different than what I first expected and for the example of the Ir/MgAl₂O₄ subnanopaper, I was not the primary driver of the entire project. 1.2.

1 Kinetic Synergy between Supported Ir Single Atoms and Nanoparticles during CO Oxidation Light-Off

- Create kinetic model that can reproduce the activation energy, CO order, and O₂ order of Ir/MgAl₂O₄ single atoms and nanoparticles
- Investigate mixtures of single atoms and nanoparticles looking at the conditions where perhaps the measured results were incorrect: i.e. majority single atom systems that would show CO order of nanoparticles
- Once discovered, characterize the kinetic synergistic effect
- Generalize the conditions that give a synergistic effect

1.2.2 CO oxidation on MgAl₂O₄ supported Ir: activation of lattice oxygen in the subnanometer regime and emergence of nuclearity-activity volcano

- Optimize an appropriate Ir cluster to represent a subnanometer Ir/MgAl₂O₄ catalyst using things such as CO and O₂ calorimetry data to verify the catalyst properties were reasonable
- Propose a possible mechanism for CO oxidation on said cluster

1.2.3 CO as a Non-exchanging Ligand for CO Oxidation on Ir/TiO₂ Single Atom Catalysts • Synthesis Ir single atom catalysts of Ir/TiO₂ 1.2. OBJECTIVES FOR EACH PROJECT • Characterize said catalysts as single atoms through DRIFTS, HAADF-STEM, EXAFS, etc. • Characterize kinetics of said catalysts • Iteratively, propose mechanisms for CO oxidation on said catalyst, design an experiment/calculation in an attempt to disprove possible mechanism • Investigate kinetics at different conditions to isolate differences in properties

1.2.4 Comparison of Sites for Single Atom Catalysts of Ir/TiO₂ • Isolate various single atom sites through variations in oxidation and reduction temperature • Characterize said isolated site

1.2.5 Redispersion of Ir Catalysts on a Ir/TiO₂ Support: Catalysts with a Short Memory • Isolate clusters under 1 nm • Characterize changes in DRIFTS, STEM, EXAFS, etc. before and after reaction conditions

1.2.6 Kinetic Study of CO Oxidation on Ir/CeO₂ Single Atom Catalysts • Synthesis Ir single atom catalysts of Ir/CeO₂ • Characterize said catalysts as single atoms through DRIFTS, HAADF-STEM, EXAFS, etc. • Characterize kinetics of said catalyst • Iteratively, propose mechanisms for CO oxidation on said catalyst, design an experiment in an attempt to disprove possible mechanism

1.3 History of Small Cluster and Single Atom Catalysts Catalysis, as a field, is rather difficult to define and as such, its early history can potentially have many different starting points. However, the word first appeared in 1835 by Jöns Jakob Berzelius to describe how this new found "catalyst" which broke down (or katalūō) molecules, but the "catalyst" was not part of these broken down pieces [4, 62]. The concept of using a substance to help a reaction through was much older with researchers such as Elizabeth Fulhame (1794)[13] and Humphry Davy (1817)[8] having performed many experiments that we would now classify as catalysis. Many in the catalysis field quickly realized that at least for heterogeneous catalysis, the reactions were happening on the surfaces of the catalysts. This meant that smaller catalyst particles would have a higher surface area and thus would be better catalysts (see Figure 1.1). This led to a conventional wisdom that small catalysts were better, at least as far as people could observe as single atom and subnanometer clusters were beyond the scope of most characterization methods. This was of course not strictly true as some people theorized monodisperse systems and supported homogeneous catalysts existed but due to limited ability to characterize these systems, this field was not as well developed or studied

1.3. HISTORY OF SMALL CLUSTER AND SINGLE ATOM CATALYSTS [23, 53, 66]. Figure 1.1: Plot showing the surface atoms as a percentage of total atoms. Nanoparticles were made using the ASE nanoparticle generator tool [21]. The trend shows the inverse relationship between total atoms

and the fraction of surface atoms. The number represents the shell layers in each direction of the nanoparticles. This largely changed when Haruta [19, 20] and Hutchings [24] independently reported that small clusters of gold were far more active than anticipated. Not only was this a radical result for gold catalysts, which typically were viewed as inert at the time, it opened the eyes of catalysis researchers to other systems that might exhibit surprising properties. Particularly those of small clusters which were believed to be the reason for this surprisingly high activity on Au catalysts. This trend extended down into the single atom regime as single atoms have their own advantages, but particularly they were expected to have even different properties from the traditional nanoparticles and small clusters do the electronic differences in the systems [31, 61, 65]. However, it was not this discovery alone that renewed the interest in minimizing catalyst size. This discovery paired with incredible advances in characterization methods such as HAADF/AC-STEM and increases in popularity in methods such as EXAFS [28, 31, 65, 70] fueled this interest in investigating very small catalysts. Additionally, there were many other theories that pointed to single atom catalysts being potentially useful beyond their increased surface area/sites. For example single atom alloys (a single atom on a metallic support) were predicted to be able to combine properties of multiple systems to create more active catalysts [11, 18, 29] and small catalytic particles and/or single atoms could be used inside zeolites [33], a catalyst in its own right, where larger nanoparticles would not be able to fit. All of these factors mixed together to lead to a relative boom in single atom catalysis which sets the backdrop for this work.

1.4 Background of Single Atom Catalysts

Single atom catalysis as the modern field exists is a relatively new category for heterogeneous catalysis studies [26, 31, 70] and they provide many potential advantages over classic nanoparticle catalysts. The first is that single atoms are 100% atom efficient as there are no bulk atoms [59]. This is one of the primary factors in determining the size of even traditionally large nanoparticles and was demonstrated in Figure 1.1. The second is that single atoms provide an opportunity for a higher level of uniformity in the active site as the single atom does not allow for corners or edges to exist, while they might exist on the support and this can lead to differences in the single atom sites, this variation is significantly less than a typical nanoparticle would have. However, single atom catalysts are not just nanoparticles with the maximum amount of uniform surface area (or surface sites) possible, they typically have entirely different electronic structures compared to larger nanoparticles (Figure 1.2) which leads to a variety of different practical effects such as different selectivity and activity [26]. Examples of this include single atom systems of Ir, Pt, Rh, Ag, Au, etc. with differences in activity, reaction orders, activation energy, etc. for the single atoms and their nanoparticle analogs. We discuss several examples of this in the next section.

Figure 1.2: Geometric and electronic structures of single atom, clusters, and nanoparticles

Reproduced with permission from Reference [32] Perhaps the most interesting parameter related to single atom catalysts is the comparison to homogeneous catalysts. In fact there are many studies from the homogeneous catalysis community that focus more on making an existing homogeneous catalyst become bound to a support, thereby making it heterogeneous in nature and a type of single atom catalyst [12, 69]. However, there are similarities to homogeneous catalysts beyond that. The single atom catalysts that we discuss here are typically a transition metal atom attached to a metal oxide support. This support can in many ways be thought of as a ligand [7, 52]. This allows us some degree of control of the single atom [14, 45, 55, 63]. But perhaps even more importantly, due to the uniformity of the single atom sites, we can also consider the effects of having ligands on the single atom sites beyond just the support [52].

1.5 CO Oxidation on Single Atom Catalysts

In this work we will focus on the CO oxidation reaction, while single atoms have a broad application to many other reactions [10, 49], here we will focus on the catalyst itself and this necessitates keeping the work focused on one reaction. CO oxidation is a common probe reaction for its simple mechanism and abundant literature and is most notable for its use in exhaust treatment, specifically automobile exhaust. There has also been a renewed interest in catalysts for CO oxidation (as well as other catalytic exhaust treatments) linked to a desire to increase fuel performance for vehicles [3, 37, 48]. Before, we begin our discussion of the catalytic CO oxidation, it is useful to look at the non-catalytic, gas phase reaction. The non-catalytic CO oxidation reaction proceeds by a radical pathway [5, 17]. This reaction thus has an initiation phase consisting of creating an oxygen radical by breaking the 495 kJ/mol O-O double bond [54]. This would give an activation energy of approximately 495 kJ/mol. This represents the upper limit of activation energies for CO oxidation and explains the exceedingly high temperatures (> 600 °C [17]) required for CO oxidation in the gas phase and thus the necessity of a catalyst. CO oxidation has been studied on a wide number of single atom and nanoparticle systems. Most nanoparticle catalysts oxidize CO through a Langmuir-Hinshelwood type mechanism [2, 6, 50]. Single atoms, however, often do not show the apparent poisoning that dominates the nanoparticles in the Langmuir-Hinshelwood model [35, 44, 47]. This difference in mechanism as well as the general interest in single atoms being considerably different

than nanoparticles has led to several studies of CO oxidation on single atoms. In one of the first and possibly 1.6. BACKGROUND ON SUBNANOMETER CLUSTERS the most famous single atom catalysis work, Qiao et. al. showed that Pt/FeOx single atom catalysts were more 2-3 times more active for CO oxidation than previous, standard gold cluster catalysts under certain conditions [47]. This was followed by Moses-DeBusk and coworkers who showed that Pt/ Θ -Al₂O₃ who proposed an alternate Langmuir-Hinshelwood mechanism for the reaction where all the species reacted on the Pt [41]. Peterson et. al. showed that Pd/Al₂O₃ was more active than bulk Pd metal [46]. Nie et. al. showed that single atoms of Pt/CeO₂ were stable [44] while Lu et. al. proposed a reaction mechanism for said catalyst [39]. Lu et. al. also proposed a mechanism where Ir single atoms increased the reducibility of the MgAl₂O₄ support to oxidize CO [35]. This proposed a different route compared to the mechanism predicated by Moses-DeBusk and coworkers [41]. Hoang et. al. showed that Pt/TiO₂ catalysts were more active than Pt nanoparticles[22] and finally, Sarma and co-workers attempted the most ambitious of these studies, comparing the activities of single atom catalysts of Ru, Rh, Pd, Ir, Pt/MgO[51]. In our own group, we also have heavily studied the CO oxidation reaction on many single atom systems (outside of the work presented here). These include Ir/MgAl₂O₄[34, 35, 57, 60], Pt/CeO₂[36, 38]

1.6 Background on Subnanometer Clusters

Subnanometer clusters are rigorously defined as clusters that are under 1 nm. However, practically we seek clusters that show a significant departure from the single atoms and the nanoparticles. I.e., for our interests, a cluster that is 4 atoms but still behaves as a nanoparticle, i.e. appears to share the same mechanism, is a subnanometer cluster, but is not of significant interest in regards to this work. We can enforce this exclusivity due to the often varied nature of the small clusters and such inconsistency is what we are attempting to discover and describe. There are largely two different approaches used to create these clusters. The first is using a metal complex and attaching it to the surfaces. For example, Goellener et. al. attached an Ir₄(CO)₁₂ complex onto TiO₂ [15] and Guan et. al. attached a Rh₂ complex [16] as well as many others. Of course, the clusters can also be made by attaching single atoms and making them larger or by breaking apart nanoparticles. Examples of this include Kawi et. al. who created Ir₄ and Ir₆ clusters through what is believed to be a single atom intermediate [27] and Jeong et. al. who created highly active (for CO oxidation) Rh clusters on CeO₂ in this same manner [25]. Often times the change of the dominant mechanism is related to the change in relative sites. Typically this is due to the large increase in interfacial sites (interface of the catalyst and the support) relative to the extended surface sites as the particle sizes approach the subnanometer regime. Li et. al. showed this to be the case for CO oxidation on a Pt/TiO₂ catalyst [30] for example. This change in mechanism can also be caused by large rearrangements that the catalyst undertakes in reaction conditions such as that shown by Yin et. al. for CO oxidation on Pt₁₀/Al₂O₃ [68]. Due to the varied nature of the subnanometer clusters as well as the difficulties in creating these systems, the effect on clusters of each individual atoms are typically very difficult to isolate. It is beyond the capabilities of our lab (and most catalysis labs) to make clusters of exactly 5 or 6 atoms purely enough to perform catalysis measurements, however there are examples of this in the literature [58]. This is, however, prime territory for computational groups to investigate as model systems can easily be created with atomic precision. As such, several studies of atomically precise cluster counts have been performed. Examples of these include Pd/In₂O₃ [67], Ir_n [56], and Au_n [64]

1.7 DETAILED LOOK AT CO OXIDATION ON SINGLE ATOMS OF IR/MGAL₂O₄

1.7 Detailed look at CO oxidation on single atoms of Ir/MgAl₂O₄

Much of this work has its origin in the CO oxidation reaction on Ir/MgAl₂O₄ single atom catalysts [34, 35, 60]. As such, it is important that we take a moment to describe this reaction thoroughly. CO oxidation on Ir/MgAl₂O₄ single atoms shows an interesting positive order in CO and a 0 order in O₂ (Figure 1.3). This is immediately interesting as a positive order in CO for a transition metal catalyst is rather unusual. Typically, CO poisons the catalyst's surface and leads to a negative order in CO which is seen for the Ir/MgAl₂O₄ nanoparticles (Figure 1.3). However, for single atoms, there appears to be no poisoning of the system. Figure 1.3: (a) CO (b) O₂ order on Ir/MgAl₂O₄ single atom catalysts and nanoparticle catalysts. (c) CO order on a mixture of single atom and nanoparticle catalysts.

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2018 Even though CO does not act as a poison, it is predicated to still be on the Ir active site during the reaction (from DRIFTS, HERFD-XANES, and DFT studies). The role of this CO appears to be more like a ligand or part of the active site instead of the being a site blocker as is typically observed for nanoparticle catalysts. This is further emphasised in the DFT calculated mechanism for the single site as shown in Figure 1.4. In this mechanism, the CO is not only a spectator species, but it actually appears to help facilitate the reaction as the relevant kinetic barrier was calculated to be less favorable without the CO [60]. Figure 1.4: Proposed mechanism of CO oxidation on Ir/MgAl₂O₄ single atom catalysts

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2018 Furthermore the mechanism is described briefly as follows. State II (see Figure 1.4) is given as the MASI and consists of the Ir surrounded by 5 Os that are also part of the MgAl_2O_4 and an O_2 adsorbed onto a nearby, but not directly adjacent vacancy site of the MgAl_2O_4 ($\text{Ir}(\text{CO})(\text{Os})_5(\text{O}_2)$). The rate determining step (RDS) immediately follows and consists of a gas phase CO reacting with an adjacent surface O to form CO_2 . The intermediate of this reaction taking the form of $\text{Ir}(\text{CO})(\text{Os})_4(\text{Os}-\text{CO})(\text{O}_2)$ and the product taking the form of $\text{Ir}(\text{CO})(\text{Os})_4(\text{O}_2)$ where the O_2 forms a peroxide like species bridging the single atom Ir to the support. This structure however is not thermodynamically stable so the system relaxes to $\text{Ir}(\text{CO})(\text{Os})_5(\text{O})$. The last O that is completely on the support is then removed by a gas phase CO to return to the original state but with a vacancy, $\text{Ir}(\text{CO})(\text{Os})_5(*)$. This vacancy is then filled with an O_2 from the gas phase to complete the cycle.

1.7. DETAILED LOOK AT CO OXIDATION ON SINGLE ATOMS OF IR/MGAL2O4

There are 3 major takeaways from this work that heavily guide the work in this dissertation. The first is that the CO order is considerably different than nanoparticles. This inspired the investigation in Chapter 2 and the kinetic synergistic effect described therein. This also inspired us to investigate the intermediate sized (subnanometer) clusters on Ir/ MgAl_2O_4 (Chapter 3). The second major conclusion from the MgAl_2O_4 work is that the rate determining step was limited by the ability of CO to react with the gas phase CO as we see in the mechanism (Figure 1.4). This identification of the rate determining step was one of the greatest factors influencing our choice to study the more reducible supports of TiO_2 (Chapter 4) and CeO_2 (Chapter 7). The third observation from this mechanism is that the CO ligand was part of the active state, not actually a reactant itself. This was one of the main factors in motivating the ^{13}C O exchange experiments. While the exchange experiment was not shown for this MgAl_2O_4 experimentally, the theoretical results suggested that it should not exchange. These three works stem directly from the Ir/ MgAl_2O_4 work which then lead directly to the other chapters in this dissertation to which we now turn. Chapter 2 Kinetic Synergy between Supported

Ir Single Atoms and Nanoparticles during CO Oxidation Light-Off

This work was originally published in Industrial & Engineering Chemistry Research on October 29, 2021 [57]. In this work I performed all of the modeling, coding, and derivations and contributed to the originality of the idea. 16

Kinetic Synergy between Supported Ir Single Atoms and Nanoparticles during CO Oxidation Light-Off

Coogan B. Thompson, Yubing Lu, and Ayman M. Karim* Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24060, USA E-mail: *amkarim@vt.edu Abstract Supported metal single atom catalysts often exhibit different reactivities than their nanoparticle analogs. Such differences provide unique opportunities in terms of their practical applications. However, single atoms and nanoparticles often co-exist under reaction conditions. In this work, we modeled the CO oxidation on a MgAl_2O_4 supported Ir with different mixtures of single atoms and nanoparticles. We demonstrate the pitfalls in determining reaction parameters for isolated systems if a minority species is present. More importantly, we show a

kinetic synergy between single atoms and nanoparticles for CO oxidation light-off

and we present optimization strategies to increase the catalyst activity. Specifically, we optimize the ratio of the single atoms and nanoparticles and mass of catalyst to increase activity for established reaction conditions. The optimization results show that the temperature required for 99% conversion can be decreased or a lower metal usage can be used to achieve the same conversion. The results highlight how the different mechanisms and kinetics on single atoms and nanoparticles can be advantageous to optimize the catalyst performance for practical applications such as their use in catalytic converters. CHAPTER 2.

KINETIC SYNERGY BETWEEN SUPPORTED IR SINGLE ATOMS AND NANOPARTICLES DURING CO OXIDATION LIGHT-OFF

Introduction Supported single atom catalysts have provided a new and exciting opportunity to improve the performance of heterogeneous catalysts. Not only are the catalysts allowing for full usage of the expensive precious metals, they also can have different properties leading to improved activity and/or selectivity for some reactions. 1–4 CO oxidation is one such reaction that has seen much research into the ability of single atoms to improve the activity and metal utilization compared to small clusters and nanoparticles. This has been driven

in part by the 150 °C US department of energy (DOE

) challenge,⁵ which strives for a catalyst that is able to treat 90% of automobile exhaust pollutants at or below 150 °C with a focus on cold startup which is when most of the pollutants are released.⁶ This focus has led to many studies using CO (and other pollutants) light-off experiments to understand how to increase the catalyst activity and decrease the temperature required for 90% conversion. Light-off experiments are often used for

determining activity differences of single atoms and nanoparticles. For example, Nie et. al. studied Pt/CeO₂ light-off curves for a variety of pollutants, focusing on CO oxidation and found that steam treatment enhanced the activity of the single atoms and allowed for the catalyst to react through a different mechanism.⁷ Moses-DeBusk used the onset of CO oxidation light-offs to show that Pt/θ-Al₂O₃ single atoms were more catalytically active than nanoparticles.⁸ Peterson et. al. found that atomically dispersed Pd atoms have a different reaction order for CO oxidation than nanoparticles and demonstrated this through the changes in shape and onset of the light-off curves.⁹ These differences between single atoms and nanoparticles in light-off experiments reflect differences in electronic properties and/or nuclearity, and consequently different reaction mechanisms. Other studies have also shown differences in CO oxidation mechanisms on single atoms and nanoparticles including Ir/MgAl₂O₄,¹⁰ Pt/FeO_x,¹¹ Pt/TiO₂,¹² and Ru, Rh, Pd, Ir, Pt/MgO.¹³ The differing properties of single atoms and nanoparticles are often considered in terms of each isolated system to determine which is more active and/or selective. This leads most studies to focus on designing a catalyst that is either purely single atoms or purely nanoparticles and little attention has been paid to looking at mixtures

of single atoms and nanoparticles. Because of the difference in reaction mechanism

for the two systems, it could be possible that a mixture of single atoms and nanoparticles outperforms either system individually. Specifically, during practical applications at high conversions, the reaction conditions, such as temperature and partial pressures, change along the reactor bed which can be used to harness the advantageous properties of both single atoms and nanoparticles. In this work, we use the example of CO oxidation on Ir/MgAl₂O₄ catalysts which has single atom¹⁰ and nanoparticle^{10,14–16} activities thoroughly described as well as kinetic data for different mixtures of the two systems.¹⁷ We show that we can accurately capture kinetic data for the mixtures through the use of kinetic modeling of the pure systems of single atoms or nanoparticles. We then use that model to search for conditions with unique or unexpected results. We show situations where the minority species, i.e., 1% nanoparticles, 99% single atoms, completely dominate the observed kinetic data. More importantly, we show systems where a mixture of single atoms and nanoparticles can outperform either of the

pure systems. We refer to this as a kinetic synergistic effect. We define this synergistic effect as an increase in activity that comes from the mixture of two sites that are isolated from each other but act cooperatively due to differences in the reaction mechanism and orders on each site (i.e. kinetics).

This is in contrast to synergistic effects that arise when one system affects the properties of another system (i.e. alloying/doping effects^{18,19}). This is also in contrast to synergistic effects where the active site can be split into two separate sites containing half reactions (i.e. spillover mechanisms^{20–23} or tandem reactions^{24,25}). We then discuss the requirements in order for a kinetic synergistic effect to exist and optimize the catalyst using this synergism between the single atoms and nanoparticles to maximize the activity. DURING CO OXIDATION LIGHT-OFF Model Kinetic modeling is useful in reactor design to optimize catalyst usage and reactor conditions.^{26,27} Here, we use the design equation for a 1-D packed-bed reactor (PBR), Equation 1,²⁸ and a power rate law (Equation S1) in terms of activities, Equation 2, to model the conversion and concentration profiles along the reactor bed and at the exit of the bed. FA_{out} dFA W = ∫FA₀ -rA (1) Equation 1: Design Equation for a PBR. FA

is the molar flow rate of reactant A, the limiting reagent, rA is the rate of reaction of A, and

W is the mass of the catalyst in the reactor

. rA = N × A × e^{-ERAT} × anCCOO × anOO₂ (2) Equation 2: General rate equation used for both single atoms and nanoparticles. rA is the rate of reaction, N

is the number of sites per mass of catalyst

A is the pre-exponential factor (1/time), EA is the activation energy for the reaction, R is the ideal gas constant, T is the temperature

, ai is the activity of species i (either CO or O₂) with reference state 1 mol/m³, and ni is the reaction order of species i (either CO or O₂). In the PBR design equation (Equation 1), unless otherwise mentioned, the pressure and temperature are assumed to be constant across the reactor bed to simplify the model. We also assume plug flow so that we can use the 1-D PBR design equation. To create a light-off curve, we plot the steady state conversion at the exit of the reactor at different temperatures. This means we do not account for any transient effects that occur during the light-off. In other words, we assume that steady state reactivity dominates the light-off curve with no regard to effects that could occur such as temperature gradients

caused from the gradual heating of the catalyst bed and exothermicity of the reaction.²⁹ In order to investigate the existence of an ideal catalyst that can synergistically apply the advantages of single atoms and nanoparticles to CO oxidation, we first must build a model that captures the individualized cases. Specifically, for single atoms on Ir/MgAl₂O₄, the model needs to capture the positive first order in CO (0.9), the zero order in O₂ (0.1), and the apparent activation energy of 62 kJ/mol. For the nanoparticles we should match the negative first order in CO (-1), the first order in O₂ (0.9), and the apparent activation energy of 101 kJ/mol. These parameters were extracted from our previous work on Ir/MgAl₂O₄¹⁰ and are summarized in Table 1. The pre-exponential factors were calculated from fitting the reported data and minimizing the normalized error (Equation S5). As we are only trying to match the effect of the whole catalyst, the pre-exponential term and activation energy represent the average values measured experimentally on all the surface sites for single atoms (different binding sites on the oxide surface) and the surface sites on nanoparticles (terrace, edge, corner, etc.). This is reasonable as we only have information on the average kinetics for both single atoms and nanoparticles.¹⁰ Additionally, since the nanoparticles used experimentally were small (approximately 1 nm) and highly disperse (90%), there is little difference between the total and surface Ir sites when it comes to space velocity normalized to surface atoms. Similarly, there is little difference between mass and surface molar percentages when we consider

mixtures of single atoms and nanoparticles. The details of parameter fitting

are further discussed in the supporting information (SI)(section 2). The data compared well with the models over a large range of conditions as shown in Figure 1 and Figure S1. However, we

note that approximating the kinetics with a power law model is valid for nanoparticles and single atoms. This is due to the strong CO binding resulting in constant surface coverage, and consequently constant reaction orders and apparent activation energies on nanoparticles^{16,30} and on single atoms^{10,17} under the range of conditions we present here. Specifically, for Ir nanoparticles, due the strong nature of the CO binding, the coverage of CO remains close to saturation making CO the most abundant surface intermediate at all conversions and temperatures investigated (up to 99.5% and 350 °C, respectively). Therefore, even if we use a Langmuir-Hinshelwood model, it gets reduced to the power law model (Equation 2) under all conditions in our study (see SI section 3). DURING CO OXIDATION LIGHT-OFF Table 1: Catalyst parameters used in the model. The activation energies and reaction orders are taken from Lu et. al.¹⁰ The pre-exponential values are calculated from the existing data to minimize error with the experiments, see the SI (section 2) for more details. The units for the pre-exponential factor are CO₂/site/s or as is commonly given: 1/s.

Catalyst	Ir Single Atoms/MgAl ₂ O ₄	Ir Nanoparticles/MgAl ₂ O ₄
Activation Energy (kJ/mol)	62	101
CO Order	0.9	-1.0
O ₂ Order	0.1	0.9
Pre-exponential Factor (1/s)	2.76 × 10 ⁶	1.19 × 10 ⁹

Figure 1: Parity plot for the kinetic model vs. the experimental data. Separate model vs experimental data for each catalyst are further shown in Figure S1. The blue points represent the catalyst consisting of single atoms, while the red dots represent the catalyst consisting of nanoparticles. The definition of turnover frequency (TOF) is included in the SI (section 2.1). Single Atom and Nanoparticle Mixtures In addition to fitting the individual data, we also seek to capture the effects of mixtures of single atoms and nanoparticles. Previously, mixtures have been shown to exhibit combinations of the properties of the isolated species. For example, the positive order in CO from single atoms mixed with the negative order in CO from nanoparticles results in

a CO order that switches from negative to positive as the CO partial pressure increases. This is due to the single atoms dominating the reaction order at high CO partial pressures while nanoparticles dominate at low partial pressures.¹⁷ Our model manages to capture this effect (shown in Figure S6). The qualitative fit is very good with the shape matching that from experimental data. Additionally, our model indicates the system is 38% single atoms compared to the 32% predicted by simple linear fitting. The quantitative fitting is less accurate as can be seen by the lower activity of the model compared to the actual system, however, as we are interested in the effect of the difference in the reaction orders, the precise magnitude of the rate is much less important than the reaction order. Results Pitfalls in Kinetic Measurements and Their Use as a Characterization Tool A mixture of sites can significantly affect the measured reaction kinetics (orders and activation energy). As Lu et. al. showed for their mixture of single atoms and nanoparticles, the orders can switch from one mechanism to the other.¹⁷ This is expected for competing mechanisms on the two sites; however, a little bit of impurities can go a long way in affecting the measured kinetics, and especially in the interpretation of the results. Figure 2 shows two such cases. The first is the case where a minority (1%) of single atoms,

dominates the reaction system. The second is the case where a minority (1%) of nanoparticles dominates DURING CO OXIDATION LIGHT-OFF the system. Even at such low concentrations of single atoms (or nanoparticles), they still dominate the reaction order measurement above ≈ 2 kPa CO (below ≈ 0.01 kPa CO). These conditions are rather typical for a catalysis laboratory and speak to the possible dangers that can arise when dealing with impure samples. For a reference to what 1% impurities mean, it is below the threshold for detection in EXAFS and could easily go undetected by STEM due to the limited sampling volume. This effect is a combination of the increased reactivity of the single atoms, relative to the nanoparticles, at lower temperatures and higher CO concentrations. The two differences work in tandem to create a situation where the activity of the single atoms is over 100x higher than the nanoparticles. The inverse situation occurs at high temperatures and low CO concentrations to create a situation where the nanoparticles dominate. a 99% Nanoparticles at 135 °C b 99% Single Atoms at 190 °C

TOF (s⁻¹) 10³ 10² TOF (s⁻¹)

)

$n_{CO} = 0.9$ $n_{CO} = -0.7$ $n_{CO} = -0.9$ $n_{CO} = 0$

.5 10⁴ 10³ 10⁴ 10³ 10¹ 10² PCO (Pa) PCO (Pa) Figure 2: Model results for the effect of minority species (1% single atoms or nanoparticles) on the CO reaction order. Both mixtures are for 1 wt% Ir/MgAl₂O₄ at 100 sccm total flow, 1 atm, and 1 % O₂. Both systems are in the differential regime, i.e., conversion is less than 5% (a) 0.5 g of 99% nanoparticles, 1% single atom impurity at 135 °C at relatively high CO partial pressures: 0.5 to 15 kPa CO. (b) 0.1 mg of 99% single atoms, 1% nanoparticle impurity at 190 °C at relatively low CO partial pressures: 0.005 to 0.05 kPa CO. In addition to changing the apparent reaction order, the apparent activation energy can also be shifted significantly due to the presence of a small amount of minority species. Specifically, a 99% mixture of nanoparticles can give an apparent activation energy of 62 kJ/mol if the E_{App} measurements are performed at high CO partial pressure and at low temperatures (Figure S7a). Inversely, a 99% mixture of single atoms can give an apparent activation energy of 101 kJ/mol if the E_{App} measurements are performed at low CO partial pressure and high temperatures (Figure S7b). These conditions represent the most extreme cases of measuring the wrong activation energy, but there are of course more moderate cases which can shift the apparent values to a lesser extent. A small percentage of nanoparticles (or single atoms) can also affect the shape of the CO light-off curve as shown in the SI (section 5.2). The results show the challenges in measuring accurate kinetics (reaction orders and EA) on catalysts containing a mixture of sites having different mechanisms, even when one is present as a minority species. This demonstrates the importance to investigate reaction orders across multiple reaction conditions. Most notably, it is important to measure the reaction rate as a function of the partial pressure of interest across 1-2 orders of magnitude and it is important to vary the temperature and other partial pressures as well. For similar reasons, the same types of precautions are needed for the activation energy measurements. While the results show the possible pitfalls of kinetic measurements, they also demonstrate how detailed kinetic measurements provide a sensitive characterization tool for detecting a minority species displaying a different mechanism. This also brings self-reflection to the original claim of the orders of single atom and nanoparticle catalysts in Lu et. al.¹⁰ While it is impossible to prove there was no effect from minority species, the measurements were conducted under more than one condition to show that the contribution from possible minority species was minimal. Light-off Curves on Ir Single Atoms and Nanoparticles One of the most important measures of the activity of a catalyst for vehicle engine exhaust emission control is the temperature required to reach a certain conversion, e.g., 90% for the DOE 150 °C challenge.^{5,31} We use our model to capture the light-off curves of each of the

catalysts with different compositions ranging from pure single atoms to pure nanoparticles

DURING CO OXIDATION LIGHT-OFF using different amounts of catalyst in the reactor. The curves are modeled at 1% CO and 1% O₂ starting at 0 °C and ending at the temperature corresponding to over 99.5% conversion at which point the conversion is assumed to be 100%. For the light-off curves, a total flow rate of 100 sccm at 1 atm is used. Example light-off curves are given in Figure 3 and Figure 4. These conditions are practical for packed-bed reactors in catalysis laboratories such as ours. 1.0 Single Atoms Nanoparticles 0.8 50:50 Mixture Conversion 0.6 0.4 0.2 0.0 150 200 250 300 350 T (°C) Figure 3: Sample light-off curves showing the differences in the curve shape between single atoms, nanoparticles and their mixture. 10 mg of 1 wt% Ir/MgAl₂O₄ at 1% CO, 1% O₂, 1 atm, 100 sccm. From Figures 3 and 4 we see the expected characteristics of the individual systems. As expected for a system with a positive order limiting reagent, i.e., CO order for CO oxidation on single atoms, the activity approaches full conversion, but from a theoretical standpoint, never fully reaches it (Figure 3 and Figure 4, Single Atoms). Conversely, the nanoparticles with a

negative order in CO have a very steep light-off curve as the activity increases with an increase in conversion and in temperature due to the decreasing concentration of CO, as it reacts (Figure 3 and Figure 4, Nanoparticles).^{32,33} Additionally, the increase in conversion with temperature is further magnified by the higher activation energy on the nanoparticles leading to steeper light-off curves compared with single atoms. The difference in the activation energies means that the activity on nanoparticles (101 kJ/mol) will increase faster than on single atoms (62 kJ/mol) as the temperature increases in the light-off experiment. This has the net effect of making the single atoms (lower activation energy) dominate over nanoparticles (higher activation energy) at relatively low temperatures and the trend is reversed at higher temperatures.³² This can be seen in Figure 3 and Figure 4. We can somewhat deconvolute the effect of the differences in activation energy from the effect of the differences in order as shown in the SI (sections 7, and 8).

Light-off Curves on Mixtures We expect having a catalyst that is 50% single atoms and 50% nanoparticles might combine the properties of both in some manner. This is shown in Figure 3. Most notably, the mixture light-off curve appears to be a simple, almost linear, combination of the single atoms and nanoparticles curves. The conversion is closer to that of the nanoparticles at higher temperatures due to the significant increase in the nanoparticle light-off. However, as we increase the catalyst loading to 20 mg (i.e. the space velocity is half compared to that in Figure 3), a sweet spot occurs at intermediate temperatures where the conversion of the mixture is higher than that of the single atoms and nanoparticles. For the 20 mg of 1 wt% Ir catalyst (Figure 4), we see that the 50% mixture of single atoms and nanoparticles has a lower temperature for 67-80% conversion when compared to either exclusively single atoms (Figure 4 Single Atoms) or nanoparticles (Figure 4 Nanoparticles). The results in Figure 4 show evidence of some type of synergistic effect between the two competing mechanisms on single atoms and nanoparticles where the activity is greater than the sum of the individual activities. From the light-off curves, we can tell this effect happens when the two catalysts are relatively comparable in activity as we see the synergistic region appear near the crossing point (i.e. similar overall activity). We also notice from this simple example in Figure 4b that it appears that a lower space velocity leads to a greater effect. We will discuss this and other factors that cause the kinetic synergy further later.

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Conversion	0.6	0.75	0.4	0.70	0.2	0.65	0.0	150	200	250	300	0.60	265	270	275	280	285	290
Single Atoms	0.85																	
Nanoparticles																		
50:50 Mixture	0.80																	

Figure 4: (a) Sample light-off curves showing the kinetic synergy between single atoms and nanoparticles. 20 mg of 1 wt% Ir/MgAl₂O₄ at 1% CO, 1% O₂, 1 atm, 100 sccm. Note the lower temperatures required to reach 67%-80% conversion on the 50:50 mixture (b) Identical data as (a), however it is focused on the synergistic region which is highlighted in yellow. Identifying the Origin of the Kinetic Synergistic Effect Since the mechanisms on single atoms and nanoparticles vary in two regards, their activation energy and their reaction orders, one of these parameters, or both, could lead to the observed kinetic synergy. Using simplified case studies, we deconvoluted the effects of the reaction orders and activation energies and the results show that, for isothermal operation, the origin of the kinetic synergistic effect is the difference in the reaction order (SI sections 7 and 8). Here we look into the consequences of the difference in reaction orders on the reaction rate that lead to the kinetic synergy. If we look at a system that operates inside the boundaries of the synergistic region (e.g. 1.3 g of 1 wt% Ir/MgAl₂O₄ at 150 °C in 1% CO and 10% O₂, the optimized conditions we will see later), we see how the rate changes across the catalyst bed as shown in Figure 5a. Specifically, the dominant activity/mechanism switches along the catalyst bed from the positive order (blue) to the negative order (red). This is due to the fact that at high exit conversion the concentration of the reactant changes significantly along the reactor bed. Initially, the purely positive order sites are more active (analogous to the single atoms being more active in Figure 4 and Figure S11 at low conversion/high CO partial pressure), however, this changes to the negative order sites being more active (analogous to the nanoparticles being more active in Figure 4 and Figure S11 at higher conversions/lower CO partial pressure). Additionally, once we get close to full conversion, the negative order begins to “light-off”. Most importantly to achieving higher conversion on the mixture is the point at which the negative order mechanism “lights-off”. As we see at the higher conversions in Figure 5, when we are in the synergistic region, the negative order sites in the mixture can light-off (red line in Figure 5a), but the purely negative order system cannot as it has not reached a high enough conversion (red line in Figure 5c). Essentially, the negative order sites can “light-off” only because the positive order sites (Figure 5 blue lines) got it to the point it could from a conversion/CO partial pressure perspective. Thus, being below the synergistic region represents the point before the mixture can “light-off” and being above the synergistic region represents the region where both the mixture and pure negative order sites “light-off”. We do not see a synergistic effect above the synergistic region because the pure negative order sites have a stronger “light-off”

due to the larger number of sites compared to the mixture. For more examples see SI section 9. It is important to note that strictly speaking, the effect is not limited to this case of the positive order sites being active enough to cause the negative order sites to light-off. It is instead whenever the total integral of the activities of the mixture is larger than the isolated species. More precisely, it is whenever the net effect of having the negative order sites at the end of the reactor is worth the cost of losing positive order sites at the beginning of the reactor. This understanding for the case of isothermal operation also introduces the possibility that if the reactor is non-isothermal, a similar kinetic synergistic effect might originate in the case of the different activation energy in each mechanism. This would be in the form of having the higher activation energy mechanism being dominant in the hotter part of the reactor while the lower activation energy mechanism is dominant in the cooler part of the reactor. This also means that if we can be more selective about the placement of type sites

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0.200	0.175	0.150	0.8	0.8	0.70%	0.125	0.6	0.6	0.100
0.075	0.4	0.4	0.050	0.2	0.2	0.025	0.000	0.0	0.0
0.0	0.0	0.0	0.2	0.4	0.6	0.8	1.0	1.2	0.0
0.2	0.4	0.6	0.8	1.0	1.2	0.0	0.2	0.4	0.6
0.8	1.0	1.2	0.0	0.2	0.4	0.6	0.8	1.0	1.2

Catalyst Mass (g) 0.200 c
 Purely Single Atom Sites 0.175 Purely Nanoparticle Sites Reaction Rate (s⁻¹) 0.150 70% Single Atom Mixture 0.125 0.100 0.075 0.050 0.025 0.000
 0.2 0.4 0.6 0.8 1.0 1.2 0.0 Catalyst Mass (g) Figure 5: Conversion and reaction rates along the catalyst bed showing the origin of the kinetic synergy for 1.3 g of 1 wt% Ir/MgAl₂O₄ that is 70% single atoms at 150 °C in 1% CO and 10% O₂. These conditions were chosen because they are inside the synergistic region and represent a large extent of kinetic synergism. (a) The combined reaction rate (purple) is the sum of the single atom (blue) and nanoparticle (red) reaction rates for the mixture system. (b) Conversion across the catalyst bed for purely single atom sites (blue), purely nanoparticle sites (red) and the 70% single atom mixture (purple). (c) Reaction rate across the catalyst bed for purely single atom sites (blue), purely nanoparticle sites (red) and the mixture (purple).

in the reactor, we can further increase the overall activity. For example, in the previous case shown in Figure 5, the nanoparticle (negative order) sites are more efficient at the end of the reactor as opposed to the front. The opposite is true for the single atom (positive order) sites. These cases will be discussed in the catalyst and reactor optimization section below.

Effect of Reaction Conditions on the Extent of Kinetic Synergy between Single Atoms and Nanoparticles

The simplified case studies allowed us to mathematically identify the origin of the synergy, the range of conditions where the synergy occurs, and the optimum catalyst mixture to maximize the catalyst activity for specific reaction conditions. The details of the simplified case studies and derivations can be found in the SI (Section 8). Specifically, the results show that there is intrinsically only one parameter that determines whether a kinetic synergistic effect will occur, C , as defined in Equation S59 (derivation in the SI section 8.4), and adapted below as Equation 3. This lumped reaction rate ratio, C , has to be within a certain range for a given mixture and reaction temperature to be more active than the pure systems as shown below (see Equations S63 in SI). In order to demonstrate the increase in activity and its dependence on C , we plot the decrease in required catalyst mass from the simplified case studies as a function of the desired conversion and the non-dimensional constant C . As we can see in Figure 6, the increase in activity occurs for certain ranges of C and the range increases at high conversion and extends to infinity at 100% conversion. This is because the purely first order system cannot reach 100% conversion due to the exponential nature of the positive order (+1) kinetics. More importantly, the results in Figure 6 show the the potential to decrease the amount of catalyst required by up to approximately 60% assuming we want a high conversion near 100% and have a C (reaction rate ratio of SA to NP) value of approximately 10. $C = r_{SA,0} / r_{NP,0} = A_{SA} a_{SA,0} e^{-E_{SA}/RT} / A_{NP} a_{NP,0} e^{-E_{NP}/RT}$ Equation 3: Reaction ratio constant as defined for the full model. r_i is the rate of reaction for the i site, the 0 denotes that this is the initial reaction rate, A_i is the pre-exponential factor for site i , R is the ideal gas constant, T is the temperature, $a_{0,i}$ is the initial activity of species i (either CO or O₂) with reference state 1 mol/m³.

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103	0.6	0.5	102	0.4
0.3	101	0.2	0.1	1000.0
0.2	0.4	0.6	0.8	1.0
0.0	0.0	0.0	0.0	0.0

Conversion Desired (x) Figure 6: Decrease in required catalyst mass to achieve conversion (x) as a function of the non-dimensional constant (C). The decrease in required catalyst is given by 1 minus the ratio of the mass of the mixture to the mass of

either the pure positive order or the pure negative order sites, whichever is less, that corresponds to the same conversion at the same conditions ($1 - W_{\text{Mixture}}/\min(W+1, W-1)$). A value of zero corresponds to no reduction in catalyst mass for the mixture of sites (W_{Mixture}) while increasing values correspond to % reduction compared to the lower mass of the pure positive order or pure negative order sites ($\min(W+1, W-1)$). The white areas represent the conditions where either positive order or negative order sites are more active on their own. The plot is used to approximate the full model case with the positive order sites being analogous to the single atom sites and the negative order sites analogous to the nanoparticles. Knowing that the only way to increase this synergistic effect is to vary the non-dimensional constant C or change the desired conversion, it is important to understand what affects this C constant. From equation 3 there are two ways that we can affect C : changing concentrations and changing temperature. Changing concentration has a direct effect on C as can be seen from the equation. However, changing the temperature has a less direct effect as the ratio of the activation energies now determines the direction of the effect. To model the changes in concentration, we change the total flow rate of the feed and keep the molar flow rates of the reactants (CO and O_2) constant. This has the effect of changing the initial concentration of the reactants and thus C , but keeps the temperatures approximately the same as to minimize that effect. With our full model for the $\text{Ir}/\text{MgAl}_2\text{O}_4$ catalyst (Figure 7), we see that increasing the initial concentrations (lowest concentration in panel a and highest in panel c), increases the range for a synergistic effect (the range in C values shown in Figure 6) and the effect itself (Color in Figure 6). We see this as an increase in conversion in Figure 7 a \rightarrow b. However, it appears that as we increase the initial concentration further, we get closer to having a C value that is too large as the effect starts to be seen only at very high conversions, (Figure 7 b \rightarrow c) as expected. DURING CO OXIDATION LIGHT-OFF a 1.0 Nanoparticles b 1.0

Nanoparticles 80% Nanoparticles 80% Nanoparticles 0.8 50:50 Mixture 50:50 Mixture 80% Single Atoms 0.8 80% Single Atoms Conversion 0.6 Single Atoms Single Atoms 0.4 Conversion 0.6 0.4 0.2 0.2 0.0 0.0 160 180 200 220 240 260 280 300 160 180 200 220 240 260 280 300 T ($^{\circ}\text{C}$) T ($^{\circ}\text{C}$) 1.0 c Nanoparticles 80% Nanoparticles 0.8 50:50 Mixture 80% Single Atoms Conversion 0.6 Single Atoms 0.4 0.2 0.0 160 180 200 220 240 260 280 300 T ($^{\circ}\text{C}$) Figure 7: Comparison of light-off curves showing the effect of the initial concentrations on the extent of kinetic synergy. 20 mg of 1 wt% $\text{Ir}/\text{MgAl}_2\text{O}_4$. 1 sccm of CO , 1 sccm of O_2 , 1 atm at 100 (a), 70 (b), and 50 (c) sccm of total flowrate. The synergistic regions are highlighted in yellow. To model the changes in temperature, we change the W/FA_0 ratio while keeping the initial CO and O_2 concentrations constant. Increasing the W/FA_0 ratio has the effect of lowering the needed reaction rate constant to reach a certain conversion and thus moves the light-off curve to lower temperatures. Figure 8 shows this change by increasing the mass of the catalyst (5, 50, and 500 mg) which corresponds to increasing the value of C (Equation S170). Note that we see a very similar trend as in Figure 7, the range and extent of synergy increases and then decreases. This is because the different temperatures similarly make a line through Figure 6. Specifically, C increases with decreasing temperature as the activation energy of the nanoparticles (-1 order) is higher than the single atoms

(+1 order). If the single atoms had the larger activation energy, the kinetic synergistic effect would still increase then decrease, however it would be because the C value started high and then moved lower in Figure 6. a 1.0 Nanoparticles b 1.0 Nanoparticles 80% Nanoparticles 80% Nanoparticles 0.8 0.8 50:50 Mixture 50:50 Mixture 80% Single Atoms 80% Single Atoms Conversion 0.6 Single Atoms Conversion 0.6 Single Atoms 0.4 0.4 0.2 0.2 0.0 0.0 50 100 150 200 250 300 50 100 150 200 250 300 T ($^{\circ}\text{C}$) T ($^{\circ}\text{C}$) 1.0 c Nanoparticles 80% Nanoparticles 0.8 50:50 Mixture 80% Single Atoms Conversion 0.6 Single Atoms 0.4 0.2 0.0 50 100 150 200 250 300 T ($^{\circ}\text{C}$) Figure 8: Comparison of light-off curves showing the effect of the space velocity on the extent of kinetic synergy. Light-off curves for 1 sccm CO , 1 sccm O_2 , 100 sccm, 1 atm for 5 (a), 50 (b), and 500 (c) mg of 1 wt% $\text{Ir}/\text{MgAl}_2\text{O}_4$ catalyst, respectively. The synergistic regions are highlighted in yellow. Catalyst and Reactor Optimization With the understanding of which parameters affect the kinetic synergy between Ir single atoms and nanoparticles, we can now optimize a catalyst for a given set of reaction conditions. For this, we will consider an inlet blend that is more commonly expected for engine exhaust and in line with the 150 $^{\circ}\text{C}$ DOE challenge.^{5,6} We chose conditions of 1% CO and 10% O_2 with 99% conversion being the target conversion at 150 $^{\circ}\text{C}$. From the general definition of C (Equation 3), $C = 13.5$ at 150 $^{\circ}\text{C}$ for the

Ir single atoms and nanoparticles on MgAl_2O_4 . DURING CO OXIDATION LIGHT-OFF

This is within the range needed for 99% conversion derived for the simplified case studies (Equation S63: $2.00 < C < 1086$) so a mixture system that outperforms the pure catalysts should exist under these conditions. Additionally, as an initial guess, we calculated the fraction of single atoms (f) needed to minimize the catalyst mass using the solution from the simplified case studies (Equation S63) and the resulting f is 0.73, meaning that the

optimum catalyst should be around 73% single atoms. With this as our initial guess we began to minimize the amount of catalyst required to reach 99% conversion using the full model. To meet these criteria, the solution from the numerical minimization requires 1.3 g of 1 wt% Ir/MgAl₂O₄ that is 70% single atoms. As we can see in the light-off plots of Figure 9, this mixture outperforms the pure single atom and nanoparticles systems under these same conditions using the same mass of the catalyst (1.3 g of 1 wt% Ir/MgAl₂O₄). At 150 °C, the catalyst consisting of 100% single atoms is only able to achieve 89% conversion while the catalyst consisting of 100% nanoparticles can only achieve 42% conversion. Clearly the mixture is better for this example where the conversion at 150 °C is 99%. Likewise, if we look at the temperature required for 99% conversion, the pure single atom and nanoparticle catalysts require a temperature of 166 and 158 °C, respectively. Again, we see a clear advantage for the mixed system. Finally, if we compare the amount of catalyst required to reach this conversion at 150 °C, while we only needed 1.3 g 1% Ir/MgAl₂O₄ of the mixture, we would have needed 2.2 g of pure nanoparticles and 2.6 g of pure single atoms. Therefore, the the optimum mixture provides a reduction in catalyst mass of 50% and 41% compared to the pure single atoms and pure nanoparticles, respectively. It is worth noting that the optimum of 70% single atoms for the ideal catalyst is very similar to the 73% predicted from the simplified case studies. This implies that the simplified case study is fairly representative of the full model for the real catalyst. With an understanding of the origins of the kinetic synergistic effect and how to optimize the catalyst in an isothermal operation, we can look at more ambitious optimizations. The first is ideal site loadings. While this work is motivated by the inability to fully isolate either a 1.0 Single Atoms 1.00 b Single Atoms Nanoparticles Nanoparticles 0.8 Optimum Mixture 0.95 Optimum Mixture Conversion 0.6 Conversion 0.90 0.85 0.4 0.80 0.2 0.75 0.0 0 25 50 75 100 125 150 0.70 135 140 145 150 155 160 T (° C) T (° C) Figure 9:

Optimized mixture catalyst at 1% CO, 10% O₂, 100 sccm, and 1 atm. The optimum mixture here is 1.3 g of 1 wt% Ir/MgAl₂O₄ consisting of 70% single atoms and 30% nanoparticles. The light-off of 1.3 g of 1 wt% Ir/MgAl₂O₄ of pure single atoms and pure nanoparticles are also shown for comparison. The synergistic region for the optimum mixture catalyst is highlighted in yellow. single atom or nanoparticle species, it is useful to consider what would happen if we could place them in their ideal locations within the catalyst bed to increase the overall activity. For the Ir/MgAl₂O₄ catalyst given here, this would require placing all of the positive order single atom sites in the first part of the bed and then changing the bed to all nanoparticles when the nanoparticles become more active (Figure 10a). Strictly speaking to show this, we repeat the previous procedure, however, the model places a single atom site or a nanoparticle site in the differential equation depending on which is more active. This leads to the catalyst bed automatically being optimized for the fraction of single atom/nanoparticle sites at each temperature. This is shown in Figure 10b, note that the proportion of each site is different along the light-off curve. As expected, the idealized site ordering mixture follows the pure single atom case until it approaches the synergistic region since at these lower temperatures and lower conversions, the single atom sites are always more active. At this point, we reach a high enough conversion for the nanoparticles to “light-off” and as such the model starts to include nanoparticle sites. This site ordering has a significant increase in activity, corresponding to a required temperature of only 144 °C to reach 99% conversion as compared to the previously required 150 °C. Alternatively, we could reach 99% conversion at 150 °C DURING CO OXIDATION LIGHT-OFF with only 1.0 g of catalyst instead of 1.3 g. a FA0 Optimum Mixture FA out Site Ordering FA0 FA out Single Atom Sites Nanoparticle Sites 1.0 b 0.8 Conversion 0.6 0.4 0.2 0.0 Single Atoms Nanoparticles Optimum Mixture Site Ordering 0 25 50 75 100 125 150 T (° C) Figure 10: Ideal site ordering compared to previously optimized mixture catalyst (see Figure 9). (a) Schematic showing the mixed sites compared to the ideal site ordering catalyst bed. (b) Light-off plot comparing the ideal site ordering case to the previously optimized mixed site system. Note the ideal site ordering in (b) is not 70% single atoms (as in the optimized case), it is variable as the ideal ratio of single atoms to nanoparticles is not consistent but changes with different temperatures. The section below 125 °C corresponds to all single atom sites. At 140 °C (81% conversion) the catalyst is 79% single atoms. At 144 °C (99% conversion) the catalyst is 66% single atoms. Conditions are set to match the optimized case: 1.3 g of 1 wt% Ir/MgAl₂O₄ at 1% CO, 10% O₂, 100 sccm and 1 atm. The synergistic region is highlighted in yellow. Additionally, we can also take advantage of the fact that the nanoparticles have a higher activation energy than the single atoms. As the single atoms are relatively more active at low temperatures and the nanoparticles are more active at high temperatures, we can further maximize this effect if there is a positive temperature gradient (Figure 11a) along the reactor, a common occurrence for exothermic reactions such as CO oxidation. From Figure 11b, we see that the synergistic effect is increased by this temperature gradient. Using the same optimized catalyst conditions as before, we introduce a 30 °C temperature gradient across the reactor. Now, the 1.3 g of 70% single atom mixture reaches 99% conversion at an initial reaction temperature of 126 °C. This is compared to 152 °C and 139 °C for single atoms and

nanoparticles respectively. While it is difficult to compare the two reactors (isothermal vs non-isothermal), the synergistic effect seems to increase for the non-isothermal case. Expanding on this principle, it appears that there are useful applications where the mixture of two different systems can outperform pure systems. While it is doubtful that a 1.0 b 0.8 Temperature Increase 0.6 FA0 FA out Tin Tout = Tin + 30 °C Conversion 0.4 0.2 0.0 Single Atoms Nanoparticles Optimum Mixture 0 25 50 75 100 125 150 Initial T (° C) Figure 11: Effect of including a temperature profile on the kinetic synergy. (a) Schematic showing the temperature change across the bed. (b) The light-off curves generated with the temperature profile in (a). The conversion is plotted with the x-value as the inlet temperature. The apparent jumps in the single atom light-off curve are due to numerical precision limitations and numerical noise in the solver used. See note in the SI (section 11.1). The synergistic region is highlighted in yellow. we could see orders of magnitude improvements with just a simple effect such as this in a commercial system that has been optimized for ideally pure catalysts, the potential for a 40-60% reduction in catalyst mass is significant. This method also represents another parameter (fraction of single atoms) that can be optimized in the ever-increasing search for better catalysts in a similar way to temperature and pressure. Additionally, most catalysts, especially those that are single atoms, are never purely isolated. It is very common that what we refer to as single atom catalysts, even those verified through microscopy and spectroscopy and even reactivity measurements, might have a small number of nanoparticles that can become kinetically relevant under some reaction conditions. These nanoparticles can make identification and optimization difficult. The existence of this mixture is often seen as being a negative, however this can be thought of as an opportunity to maximize the activity as opposed to something that must be removed entirely. If we can instead harness the advantages of both, ideally through site specific loading, then significant increases in activity can be achieved. Here we show through simple kinetic modeling the desire for greater control not directed at isolating single atoms from nanoparticles, but instead maximizing overall catalyst activity. As our work shows, we do not have to be able to create pure catalyst DURING CO OXIDATION LIGHT-OFF systems, but instead only need to create conditions that favor activity through optimizing the reaction conditions and composition and placement of the mixture along the catalyst bed. Conclusions We have shown that mixtures of single atoms and nanoparticles can produce a kinetic synergistic effect due to their differing reaction kinetics: positive order in CO for single atoms and negative order in CO for nanoparticles. This is beneficial as separating these systems into isolated species is often difficult. We demonstrate this synergistic effect with modeled light-off curves comparing the conversion of the pure single atoms, pure nanoparticles, and mixtures of the two. We found the origins of the increase in activity to be related to the different dependence of the reaction rates on partial pressures on both sites across the catalyst bed. We developed a method to relate the reaction kinetics of the two isolated systems to a non-dimensional constant that can be used to predict the occurrence of this synergism as well as the ideal ratio of single atom sites to nanoparticle sites to maximize the overall activity. We give an example of this optimization method which resulted in the overall activity increasing by 40% for the conditions desired. We also showed other ways of maximizing the kinetic synergistic effect by changing the temperature and/or the location of the specific sites within the catalyst bed. Acknowledgement This research was primarily sponsored by the Army Research Office and was accomplished under Grant Numbers W911NF -19- 1 -0308 and W911NF -20-2-0058. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Army Research Office or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation herein

. Supporting Information Available Variable definitions and explanations; calculation of pre-exponential factors; derivation of the CO isotherms; further details on the usage of the Langmuir-Hinshelwood model; derivations of the relationship between activation energy and apparent activation energy; additional kinetic data where the minority species dominate (pitfalls); additional light-off curves; derivations and demonstrations for the various simplified models; and coding considerations are included in the supporting information. References (1) Lin, J.; Wang, A.; Qiao, B.; Liu, X.; Yang, X.; Wang, X.; Liang, J.; Li, J.; Liu, J.; Zhang, T. Remarkable Performance of Ir/FeOx Single-Atom Catalyst in Water Gas Shift Reaction. *Journal of the American Chemical Society* 2013, 135, 15314–15317, PMID: 24090210. (2) Jeong, H.; Lee, G.; Kim, B.-S.; Bae, J.; Han, J. W.; Lee, H. Fully Dispersed Rh Ensemble Catalyst To Enhance Low-Temperature Activity. *Journal of the American Chemical Society* 2018, 140, 9558–9565, PMID: 29975515. (3) Yang, X.-F.; Wang, A.; Qiao, B.; Li, J.; Liu, J.; Zhang, T. Single-Atom Catalysts: A New Frontier in Heterogeneous Catalysis. *Accounts of Chemical Research* 2013, 46, 1740–1748, PMID: 23815772. (4) Kuo, C.-T.; Lu, Y.; Kovarik, L.; Engelhard, M.; Karim, A. M. Structure Sensitivity of Acetylene Semi-Hydrogenation on Pt Single Atoms and Subnanometer Clusters. *ACS Catalysis* 2019, 9, 11030–11041. DURING CO

OXIDATION LIGHT-OFF Supporting Information for: Kinetic Synergy between Supported Ir Single Atoms and Nanoparticles during CO Oxidation
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 for Simplified Model of Sites with Different Reaction Order . . 8.5.1 Full Conversion: The Minimum Equation and the Existence Criteria . 8.5.2 Full
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 94 94 References 95 1 Variables 1.1 List of Variables The following table defines all variables used in the work. The dimensions are given as the SI
 dimension symbols: T for time, L for length, M for mass, Θ for Temperature, N for amount Variable Dimension(s) Description ai none Activity of
 species i ai,0 none Initial activity of species i A T-1 Pre-exponential factor for an Arrhenius temperature depen- dence A' various Pre-exponential
 factor for an Arrhenius temperature depen- dence with units A+1 T-1 Pre-exponential factor for the positive order sites in the sim- plified model A-1
 T-1 Pre-exponential factor for the negative order sites in the simplified model A50 T-1 Pre-exponential factor for the 50 kJ/mol sites in the simpli- fied
 model A100 T-1 Pre-exponential factor for the 100 kJ/mol sites in the sim- plified model ALH T-1 Pre-exponential factor for the nanoparticle
 Langmuir- Hinshelwood model ANP T-1 Pre-exponential factor for the nanoparticle power law model ASA T-1 Pre-exponential factor for the single
 atom power law model C none Reaction ratio normalized by the initial activities C0 N L-3 Reference state that relates the concentrations to activities
 Ci N L-3 Concentration of species i DURING CO OXIDATION LIGHT-OFF EA EApp EApp,i error f FA FA0 FAout K Ki k kLH kLH,f ull ni
 nabsorbed ntot N N+1 N-1 N50 M L2 T-2 N-1
 M L2 T-2 N-1 M L2 T-2 N-1 none none N T-1 N T- 1 N T- 1 none M- 1 L T2 T-1 T- 1 T
 -1 none N N N
 M-1 N M-1 N M-1 N M
 -1
 Activation energy Apparent activation energy Apparent activation energy for model i Sum of
 the differences between model and experiment Fraction of single atom (or analog) sites Molar flow rate of species A Molar flow rate of species A into
 reactor Molar flow rate of species A out of reactor A lumped constant equal to C 1-ff Equilibrium constant for species i for the gas phase to the
 surface phase Reaction rate constant Reaction rate constant for the Langmuir-Hinshelwood mech- anism Reaction rate constant for the full Langmuir-
 Hinshelwood mechanism Reaction order for species i Number of sites with CO adsorbed Number of sites capable of CO adsorption Number of sites
 per mass Number of sites per mass for the positive order sites in the simplified model Number of sites per mass for the negative order sites in the
 simplified model Number of sites per mass for the 50 kJ/mol sites in the simplified model N100 Pi R rA
 r+1 r+1,0 r- 1 r-1,0

r50 r100 rLH rLH,full rNP rNP,0 rSA rSA,0 T T OFexp T OFmod W x X N M-1

M L-1 T-2 M L2 T -2 N- 1 Θ - 1

N M-1 T- 1 N M-1 T-1 N M-1 T -1 N M-1 T-1 N M-1 T- 1 N M-1

T-1

N M-1 T- 1 N M-1 T-1 N M-1 T -1 N M-1 T-1 N M-1 T- 1 N M-1 T-1 N M -1 T- 1 Θ T

-1 T-1 M none none Number of sites per mass for the 100 kJ/mol sites in the simplified model Partial pressure of species i Ideal gas constant Reaction rate of species A Reaction rate for the positive order site in the simplified model Initial reaction rate for the positive order site in the simplified model Reaction rate for the negative order site in the simplified model Initial reaction rate for the negative order site in the simplified model Reaction rate for the 50 kJ/mol site in the simplified model Reaction rate for the 100 kJ/mol site in the simplified model Reaction rate for the Langmuir-Hinshelwood mechanism Reaction rate for the full Langmuir-Hinshelwood mechanism Reaction rate for the nanoparticle site Initial reaction rate for the nanoparticle site Reaction rate for the single atom site Initial reaction rate for the single atom site Temperature Turnover frequency from the experimental data Turnover frequency from the model used here Mass of catalyst Total conversion at the end of the reactor Conversion at any point in a reactor DURING CO OXIDATION LIGHT-OFF 1.2 Note on Variables Used For generalization, activities are used in place of concentration. This is a simplification that is common but often overlooked. For example the original power rate law is given by: $r_A = N \times A' \times e^{-ERAT} \times CCnCOO \times COnO22$ (S1) Equation S1: General power law rate equation. r_A is the rate of reaction, N is the number of sites per mass of catalyst

A' is the pre-exponential factor with units, EA is the activation energy for the reaction, R is the ideal gas constant, T is the temperature, C_i is the concentration of species i (either CO or O₂), and n_i is the reaction order of species i (either CO or O₂). However, the units of A' are dependent upon the order of the reaction. This is simplified when using activities as shown: $r_A = N \times A' \times e^{-ERAT} \times CCnCOO \times COnO22$ (S2) $r_A = N \times A' \times C0nCO+nO2 \times e^{-ERAT} \times anCCOO \times anOO22$ (S3) $r_A = N \times A \times e^{-ERAT} \times anCCOO \times anOO22$ (S4) This is Equation 2. This change has the net effect of lumping the concentration units all into the one constant, A . This is how the power rate law can have fractional powers of concentration without causing a problem with the units. 2 Parameter Optimization In order to capture the values of the pre-exponential factors, the sum of the normalized squared error between the experimental turnover frequency and the model turnover frequency was minimized. This is shown in Equation S5. This yielded the results shown in Figure 1 and Figure S1. The results show qualitative agreement with all parameters given. However, quantitatively we see some slight differences across the different groupings. The orders and $T OFexp - T OFmod$ 2 error2 = $T OFexp$ (S5) data $\sum_{points} ()$ Equation S5: Design Equation for a PBR. FA is the flow rate of reactant A, the limiting reagent, r_A is the rate of reaction, and W is the mass of the catalyst in the reactor. the

activation energy measurements all match very well, which is a confirmation of the low conversion assumptions. However, the magnitudes do not appear to match as well as the trends. This is due to convolution of different variables in the experiment and slight deactivation during the experiments. As was noted by Lu et. al., there are slight changes in the orders and activation energies.1 This implies that the equations cannot be broken up perfectly into the form shown in Equation 2. DURING CO OXIDATION LIGHT-OFF a 10 1 Single Atoms Nanoparticles b Single Atoms Nanoparticles TOF (s⁻¹) TOF (s⁻¹) 10 2 10 2 10 3 102 103 103 104 PCO (Pa) PO2 (Pa) c172 164 15T6 (°C)149 142 135 10 1 Single Atoms Nanoparticles TOF (s⁻¹) 10 2 10 3 0.275 1/RT (kJ/mol) 1 0.280 0.285 0.290 Figure S1: (a,b,c) CO order, O₂ order, and Arrhenius plot comparison of model fit with experimental data. The experimental data is represented by points while the model data is represented by lines. The systematic error in each of the individual plots is due to the experimental variability in absolute activity from the three experiments being represented. The parity plots (Figure 1) show a clearer picture as they show all data points being fitted. 2.1 Definition of Turnover Frequency $T OF = FA_{out} W \times N$ (S6) Equation S6: Definition of turnover frequency. FA_{out}

is the molar flow rate of products out of the reactor. W is mass of the catalyst and N is the moles of sites per mass of catalyst

3 Langmuir-Hinshelwood Mechanism on Ir Nanoparticles Power law models are typically used to approximate the reaction kinetics over a small range of conditions, especially conditions that do not change surface coverages. However, Langmuir-Hinshelwood (LH) mechanisms describe the reaction kinetics over the entire range of coverages of the reactants and products. Many reaction mechanisms such as that of CO oxidation often can be better described with an LH model, especially when the model needs to describe a wide range of partial pressures and the resulting changes in the surface coverages and apparent orders. CO oxidation on metal nanoparticles fits this category, with CO orders flipping from negative for relatively high partial pressures of CO to positive for relatively low partial pressures of CO (e.g., close to 100% conversion). This trend has been observed for CO oxidation on extended iridium surfaces,^{2,3} however previous studies on nanoparticle catalysts have shown that the order remains negative for lower partial pressures than the extended surfaces have shown.^{1,4,5} In order to account for this, we apply a LH dependency to the CO order. This gives us the expected rate law given in Equation S7 at the regime where CO is the most abundant surface intermediate (MASI).⁵ We can similarly use this model; however, we must first determine the equilibrium constant for CO adsorption, K_{CO} , which can be measured through CO chemisorption. Room temperature chemisorption data for Ir/MgAl₂O₄ nanoparticles is DURING CO OXIDATION LIGHT-OFF given in Figure S2 with the fitting process and temperature adjustments given in sections 3.1. We do not perform this rigorous analysis on the oxygen as it is typically in excess for these types of reaction and its effects would be much smaller than those from CO. As such, the oxygen orders are treated the same as they were for the power law model. The parity plots and fits are given in Figure S5 for the LH mechanism. We then fit the pre-exponential factor as before and the results are shown in Table S2. $r_{LH} = k_{LH} a_{O_2}^{0.29} (1 + K_{CO} P_{CO})^{-2}$ (S7) Equation S7: Rate equation for a LH CO oxidation mechanism on Ir nanoparticles where CO is the MASI. k_{LH} is the rate constant (its Arrhenius dependence of T is omitted for simplification), P_{CO} is the partial pressure of CO, K_{CO} is the equilibrium constant for CO adsorption, a_{O_2} is the activity of O₂. The general form of the LH mechanism for competitive CO and O₂ adsorption is shown in Equation S22. Table S2: Catalyst Parameters taken/calculated for the LH model. The apparent activation energy was taken to be the 101 kJ/mol from before. Details on how this becomes the activation energy given are in section 3.5. The CO equilibrium constant was taken from chemisorption data on nanoparticles of Ir/MgAl₂O₄. The pre-exponential was taken from fitting the experimental data from literature¹ The oxygen parameter is unchanged. T(K) is temperature in Kelvin. Activation Energy (kJ/mol) 86 Equilibrium Constant (K_{CO}) (1/Pa) $3.8 \times 10^{11} \times T(K)^{-4.3}$ Pre-exponential Factor (ALH) (1/s) 1.11×10^{11} While the LH mechanism does show the expected switch from negative order kinetics to positive order kinetics in CO, it happens at a very high conversion. Equation S21 gives the exact partial pressure at which the model switches order in CO, at which point CO is no longer the MASI and the full LH mechanism that includes competitive adsorption between CO and O₂ has to be used (Equation S22). Because the shift is at such low partial pressures, typically well beyond 99% conversion at the inlet CO partial pressures and temperatures used in our work (1 kPa CO and up to 350 °C), the simpler, power law model suffices for the scope of this paper and the effects that we wish to present here. Because of the differences between the LH model and the power law model, we include some of the results for the LH model in this document (Figure S9) for comparison and completion.

3.1 Fitting Isotherm Data In order to accurately apply an LH mechanism, we must first fit the L (Langmuir) part of the mechanism. In order to do that, we perform linear regression on the linear form of the Langmuir Isotherm⁶ given in Equation S8. $\frac{P_{CO}}{n_{CO,adsorbed}} = \frac{1}{n_{tot}} \left(\frac{1}{K_{CO}} + \frac{P_{CO}}{n_{tot} K_{CO}} \right)$ (S8) Equation S8: Linearized Form of the Langmuir Isotherm. P_{CO} is the partial pressure of CO, $n_{CO,adsorbed}$ is the number of sites with CO adsorbed, n_{tot} is the total number of sites, K_{CO} is the equilibrium constant. This was then slightly modified to better capture the lower pressure regime as this is more important to this modeling exercise. From this exercise, we gather that the equilibrium constant should be 7.5/Pa at 30 °C. We also need to account for how K_{CO} changes with temperature since the temperature changes during CO oxidation light-off and this isotherm is at 30 °C. If we look at other isotherms in the literature,⁷ we see that CO isotherms change little with respect to temperature as shown in Figure S3. DURING CO OXIDATION LIGHT-OFF 105 Fit Data $\frac{P_{CO}}{n_{CO}} (Pa \cdot kg/mol)$ 104 103 102 101 100 10 1 101 P_{CO} (Pa) 103 Figure S2: Fit used to model the CO isotherm. Parameters are 0.06 mmol CO/g cat total sites (n_{tot}) and 7.5/Pa equilibrium constant (K_{CO}). 1.2 25 °C, $K=0.38/Pa$ 1.0 200 °C, $K=0.053/Pa$ Fractional Coverage 300 °C, $K=0.023/Pa$ 0.8 400 °C, $K=0.011/Pa$ 0.6 0.4 0.2 0.00 200 400 600 800 P_{CO} (Pa) Figure S3: Isotherms for several different temperatures on 2 - 5 nm Pt nanoparticles supported on SiO₂. Data was taken from Podkolzin et al.⁷

Adapted with permission from .7 Copyright 2001 American Chemical Society.). We

fit these Langmuir isotherms and plot their corresponding values on a log-log plot with their temperatures. This gave a reasonably good fit to allow us to estimate the changes in temperature. DURING CO OXIDATION LIGHT-OFF

In order to fully describe the effect of temperature, we note that the

data is linear in a log-log plot (Figure S4). We assume that Ir nanoparticles on MgAl₂O₄ will have the same or similar temperature dependence and thus fit the equilibrium constant to a power law model using the point slope method. The point being the experimentally determined $K_{CO}=7.5/\text{Pa}$ at 30 °C and the slope being the power -4.3. The result is given in (Equation S9). $K=1.7 \times 10^{11} \times T^{-4.3}$ Data 100 K (Pa) 10 1 10 2 102 103 T (°C) Figure S4: Temperature dependence of the CO equilibrium constant for Pt/SiO₂ $K_{CO}(\text{Pa}) = 3.8 \times 10^{11} \times T(\text{K})^{-4.3}$ (S9) Equation S9: Temperature dependence of the CO equilibrium constant equation for Ir/MgAl₂O₄. $K_{CO}(\text{Pa})$ is the equilibrium constant in units of 1/Pa and $T(\text{K})^{-4.3}$ is the Temperature in Kelvin The data clearly show that even up to a temperature of 400 °C, there is little more than an order of magnitude change in the equilibrium constant. Thus, a conservative estimate would mean that the equilibrium constant at reaction temperatures of 150-300 °C would be up to, but not less than one order of magnitude lower. We use a value of 1.8/Pa (K_{CO} at 155 °C) to reflect this change in the demonstrations below. At the reaction conditions used in our previous work, the initial partial pressure of CO is approximately 1.8 kPa. Plugging this in: $r_{LH} = k_{LH} a_{CO}^{0.29} (1 + K_{CO} P_{CO})^{-2}$ (S10) $K_{CO} P_{CO} = P_{CO} \times 1000 P_{CO} = 1800 \gg 1$ 1.8 (S11) If fact, even at 99% conversion (10 Pa), this approximation is only 5% off. $K_{CO} P_{CO} = P_{CO} \times 10 P_{CO} = 18 \gg 1$ 1.8 (S12) Repeating this analysis at 250 °C ($K_{CO}=0.77/\text{Pa}$) and 99% conversion reveals similar results. $K_{CO} P_{CO} = P_{CO} \times 10 P_{CO} = 7.7 \gg 1$ 0.77 (S13) As such, it is unlikely that this isotherm would result in a mechanism shift drastic enough to overcome the kinetic synergistic effect shown here, however we cannot rule out that this might be possible for other metals that adsorb CO less strongly.

Furthermore, we include a comparison of the effect using this LH mechanism and see no significant changes to the overall effect (Figure S9). 3.2 Predicted Order Shift of LH Mechanism The point of the order switching is defined as: $\frac{\partial \ln(r_{LH})}{\partial \ln(P_{CO})} = 0$ (S14) DURING CO OXIDATION LIGHT-OFF $\frac{\partial \ln(r_{LH})}{\partial \ln(P_{CO})} = 0$ $\frac{\partial \ln(k_{LH} a_{CO}^{0.29} (1 + K_{CO} P_{CO})^{-2})}{\partial \ln(P_{CO})} = 0$ $\frac{\partial \ln(k_{LH} a_{CO}^{0.29} (1 + K_{CO} P_{CO})^{-2})}{\partial \ln(P_{CO})} = 0$ (S15) (S16) (S17) $1 - K_{CO} P_{CO} = 0$ (S18) $P_{CO} = 1$ (S19) K_{CO} This gives the location of the order change. If we wish to put this back in the temperature dependence from: $P_{CO} = 1$ $3.8 \times 10^{11} \times T(\text{K})^{-4.3}$ (S20) $P_{CO}(\text{Pa}) = 2.7 \times 10^{-12} \times T(\text{K})^{4.3}$ (S21) Equation S21: Equation giving the partial pressure where the reaction order for the LH mechanism switches from negative (high CO) to positive order (low CO). For reference, this means that we will see the order change at a partial pressure of 0.30 Pa at 100 °C, 0.55 Pa at 155 °C, 0.84 Pa at 200 °C, and 1.93 Pa at 300 °C. For 1% CO at atmospheric conditions (≈ 1 kPa), this corresponds to a conversion of over 99.8% for all temperatures up to 300 °C. 3.3 Full Langmuir-Hinshelwood Model for CO oxidation The full Langmuir-Hinshelwood model as given in equation S22 covers the entire span of partial pressure ranges. This full model is needed when there is significant coverage changes of both CO and O₂ (i.e. when CO is no longer close to full coverage and thus no longer the MASI). $r_{LH,full} = k_{LH,full} K_{CO} P_{CO} K_{O_2} P_{O_2}^2 (1 + K_{CO} P_{CO} + K_{O_2} P_{O_2})^{-2}$ Equation S22: Full model for the LH mechanism for CO oxidation. $r_{LH,full}$ is the rate of CO oxidation, $k_{LH,full}$ is the kinetic rate constant. K_i is the equilibrium constant for species i , P_i is the partial pressure of species i . DURING CO OXIDATION LIGHT-OFF

3.4 Parameter Optimization with LH Mechanism on the Nanoparticles 10 1 a Model TOF (s) 10 2 $y=x$ Single Atoms Nanoparticles 10 b1 Single Atoms Nanoparticles TOF (s) 10 2 10 3 10 3 10 2 10 1 c Experiment TOF (s) 1) Single Atoms Nanoparticles 102 d172 10 1 P_{CO} (Pa) T (°C) 164 156 149 Single Atoms Nanoparticles 103 142 135

TOF (s) 10 2 TOF (s) 10 2 10

3 103 104 P_{O_2} (Pa) 10 3 0.275 1/RT (kJ/mol) 1 0.280 0.285 0.290 Figure S5: (a) Parity plot for the LH mechanism and comparison of model fit with experimental data for the LH mechanism. (b,c,d) CO order, O₂ order, and Arrhenius plots and the LH mechanism fits. The experimental data is represented by points while the model data is represented by lines. 3.5 From Activation Energy to Apparent Activation Energy Experimentally, activation energy of an elementary surface reaction is rather difficult to measure. As such, what is measured is the apparent activation energy of the overall complex reaction that involves a set of elementary reactions including the rate limiting step. The difference being in their definitions. EA is defined in terms of the model, as in Equation 2 and implied in Equation S7 through the Arrhenius equation. Apparent activation is defined in a more experimentally favorable way using the overall rate: $E_{App} = \frac{\partial \ln(r_A)}{\partial (1/T)} = RT^2 \frac{\partial \ln(r_A)}{\partial T}$ For situations like the power law, the (se are) the same: (S23) $E_{App,P L} = RT^2 \frac{\partial \ln(r_A)}{\partial T}$ (S24) $E_{App,P L} = RT^2 \frac{\partial \ln(N A e^{-E/RT})}{\partial T}$ (S25) $E_{App,P L} = RT^2 \frac{\partial \ln(N A e^{-E/RT})}{\partial T}$

$E_{app,P} L = RT \ln \frac{A}{A_0} e^{-E_a/RT}$ (S26) $E_{app,P} L = EA$ (S28) However, for the LH mechanism, this is not the case: (note the variable A is used for 3.8×10^{11} and -n is used for -4.3. $E_{app,LH} = RT \ln \frac{A}{A_0} e^{-E_a/RT}$ (S29) $E_{app,LH} = RT \ln \frac{A}{A_0} e^{-E_a/RT}$ (S30) DURING CO OXIDATION LIGHT-OFF $E_{app,LH} = RT \ln \frac{A}{A_0} e^{-E_a/RT}$ (S31) $E_{app,LH} = EA + RnT$ (S32) $E_{app,LH} = EA + RnT$ (S33) We know that the reaction order is taken at approximately 150 °C and 10000 Pa of CO and this gives the apparent activation energy of 101 kJ/mol. kJ kJ kJ EA = 101 mol - 15 mol = 86 mol (S34) 4 Comparison for Mixed Systems Model 10 1 Experiment TOF (s⁻¹) 10 2 102 103 PCO (Pa) Figure S6: Comparison of the model and experimental data for a catalyst consisting of a mixture of single atoms and nanoparticles. Data taken from Lu. et. al.4 The lower activity is due to the variability in the experimental data. DURING CO OXIDATION LIGHT-OFF 5 Additional Pitfalls 5.1 Activation Energy Pitfall 10 3 a 156 142 T1(2°C8) 115 103 99% Nanoparticles 1b0 2150 228 208T (°C)189 172 156 99% Single Atoms TOF (s⁻¹) E_{app} = 61 kJ/mol TOF (s⁻¹) E_{app} = 101 kJ/mol 10 4 0.28 0.29 1/RT (kJ/mol) 1 0.30 0.31 0.32 10 2 0.24 1/RT (kJ/mol) 1 0.25 0.26 0.27 Figure S7: Arrhenius plots for mixtures of single atoms and nanoparticles exhibiting minority properties. Both are for 1 wt% Ir/MgAl₂O₄ at 100 sccm total flow, 1 atm, and 1 kPa O₂. Both systems are in the differential regime, i.e., conversion is less than 5% (a) 0.5 g of 99% nanoparticles, 1% single atom impurity at 115-135 °C at 5 kPa CO. (b) 0.1 mg of 99% single atoms, 1% nanoparticle impurity at 190-210 °C at 0.005 kPa CO. 5.2 Light-off Plot Pitfall Another misleading observation is that of the case of a small number of nanoparticles in the single atom system. Because the single atoms are positive order, at high conversions the activity trails towards 0. However, this activates the negative order nanoparticles. Because of this, the shape of the light-off curve is misleading. The curve looks like it is positive order until the conversion is close to 100%. As the conversion approaches 100% the curve abruptly changes to a very negative order looking light-off curve. This can happen for very small amounts of impurities as shown in Figure S8. While this still will fit better to a positive order mechanism in a rigorous analysis, depending on the relative activities of the single atoms and nanoparticles, the nanoparticles can dominate a significant portion of the curve, especially the higher conversions which we tend to focus on, and thus can easily disguise the true reaction order. a 1.0 b Single Atoms Single Atoms 99.9% Single Atoms 1.00 99.9% Single Atoms 0.8 99% Single Atoms 99% Single Atoms 90% Single Atoms 0.95 90% Single Atoms Conversion 0.6 Nanoparticles Nanoparticles 0.90 0.4 Conversion 0.85 0.2 0.80 0.0 100 150 200 250 300 230 240 250 260 270 280 290 T (°C) T (°C) Figure S8: Light-off curves for mostly single atom catalysts. This model is for 0.05 g of 1% Ir at 1 kPa CO, 1 kPa O₂, and 1 atm. The mixtures follow as expected from single atoms to nanoparticles. Note the sudden jump in conversion in the mostly single atom systems that would not happen for pure single atom systems. Panel b zooms on the effect. DURING CO OXIDATION LIGHT-OFF 6 Additional Light-off Curves 1.0 a b Single Atoms 1.0 Single Atoms Nanoparticles Nanoparticles 0.8 50:50 Mixture 0.8 50:50 Mixture Conversion 0.6 Conversion 0.6 0.4 0.4 0.2 0.2 0.0 0.0 150 200 250 300 350 150 200 250 300 T (°C) T (°C) 0.85 c Single Atoms Nanoparticles 0.80 50:50 Mixture Conversion 0.75 0.70 0.65 0.60 265 270 275 280 285 290 T (°C) Figure S9: Light-off curves for 1% CO, 1% O₂, 100 sccm, 1 atm for 10 (a) and 20 (b,c) mg of 1 wt% Ir/MgAl₂O₄ catalyst, respectively for the LH mechanism on nanoparticles. The effect is still seen, however, the kinetics on the nanoparticles continue to deviate the further we are from the 150 °C temperature range. 7 Simplified Model of Sites with Different Activation Energy There are two variables that could be causing the existence of the kinetic synergistic effect of mixing single atoms and nanoparticles. The first is the difference in the activation energies and the second is the difference in the reaction orders. Both affect the light-off curve in different ways as discussed previously. The effects of the reaction orders and activation energies are thus convoluted, and we will attempt to detangle this convolution here using more idealized systems. 7.1 Effect of Different Activation Energies The first simplified system we consider assumes that the only difference between the single atom and the nanoparticle systems is the activation energy while there is no change in reaction orders.

In order to isolate the effect of the activation energy, we will simplify the

two rate equations from those given in Equation 2 (and parameters in Table 1) to those given in Equation S35 and Equation S36 for a more generic reaction. To simplify the model and isolate the effect, we make both rate laws 0 order in both reactants and ignore the change in moles of gas for the reaction. $r_{SA} \approx r_{50} = N_{50} \times A_{50} \times e^{-5R_0mTkJol}$ (S35) Equation S35: Simplified single atom/low activation energy mechanism. r_{50} is the corresponding rate of reaction (r_{SA}) for the low activation energy mechanism (50 kJ/mol). N_{50} is the corresponding number of sites (N_{SA}) for the low activation energy mechanism. A_{50} is the corresponding pre-exponential factor for the low activation energy mechanism. $r_{N} P \approx r_{100} = N_{100} \times A_{100}$

$\times e^{-10R0TmkJol}$ (S36) Equation S36: Simplified nanoparticle/high activation energy mechanism. r_{100} is the corresponding rate of reaction (rNP) for the high activation energy mechanism (100 kJ/mol). N_{100} is the corresponding number of sites (NNP) for the high activation energy mechanism. A_{100}

is the corresponding pre-exponential factor for the high activation energy mechanism. Solving the design equation (Equation 1), using the rate laws in Equation S35 and Equation S36, yields Equation S37 (section 7.2). From here, in order to investigate whether a mixture can outperform either individual species, we will need to find a minimum mass of catalyst such that $W(\text{mixture}) < W(\text{single atoms})$ and $W(\text{mixture}) < W(\text{nanoparticles})$ for a given set of conditions. We find mathematically that this can never be the case. The full derivation and proof are given in section 7.3. DURING CO OXIDATION LIGHT-OFF $W = FA_0 \times N_{50} A_{50} e^{-5R0mTkJol} + N_{100} A_{100} e^{-10R0TmkJol}$ (S37) Equation S37: Design equation for two different mechanisms with different activation energies. FA_0 is the initial flow rate of reactant, x is the conversion. The other terms are defined in Equation S35 or S36. We can graphically verify that no solution exists where the mixture outperforms the pure systems by plotting the light-off curves for the three systems as shown in Figure S10. Similar to the full models shown in Figure 3 and Figure 4, the higher activation energy system dominates in the higher temperature regime, while the lower activation energy system dominates in the lower temperature regime. However, no matter how much we zoom in on the intermediate temperatures, where the lines cross, the mixture will never outperform the pure species, regardless of the space velocity used in the calculations. This is contrary to the full kinetic model where the reaction orders are different on the single atoms and nanoparticles and the mixture can outperform the pure species (Figure 4). 1.0 a 50 kJ/mol 0.4100 b 50 kJ/mol 100 kJ/mol 0.8 50:50 Mixture 0.4075 100 kJ/mol 0.4050 50:50 Mixture Conversion 0.6 Conversion 0.4025 0.4000 0.4 0.3975 0.2 0.3950 0.3925 0.0 0.3900 150 175 200 225 250 275 300 325 350 280.5 281.0 281.5 282.0 282.5 283.0 283.5 284.0 T (° C) T (° C) Figure S10: Light-off curve for a 0-order mechanism with an activation

energy of 50 kJ/mol compared to that of 100 kJ/mol and a 50% mixture of each (Equation S37). The mass and pre-exponential factor for each catalyst is arbitrary as the characteristic curves exhibit this same trend regardless. $W/FA_0 = 10 \text{ kg}^*s/mol$, $N_{50} * A_{50} = 1 \times 10^3 \text{ mol/kg/s}$, $N_{100} * A_{100} = 5 \times 10^7 \text{ mol/kg/s}$ were chosen due to their proximity (same order of magnitude) to experimental conditions used elsewhere. 7.2 Derivation of the Design Equation for Simplified Model (Sites with Different Activation Energy) With two mechanisms (Equation S35 and Equation S36): $r_{50} = N_{50} \times A_{50} \times e^{-5R0mTkoJl - 100 \text{ kJ}}$ $r_{100} = N_{100} \times A_{100} \times e^{-RTmol}$ The design equation can be solved with (Equation 1): $W = FA_{out} dFA \int FA_0 - r_A x dX$ $W = FA_0 \int_0^x -r_A x W = FA_0 dX \int_0^x r_{50} + r_{100} x W = FA_0 dX \int_0^x N_{50} A_{50} e^{-RmTol} + N_{100} A_{100} e^{-RTmol} - 50 \text{ kJ} - 100 \text{ kJ}$ $W = FA_0 \times N_{50} A_{50} e^{-5R0mTkJol} + N_{100} A_{100} e^{-100 \text{ kJ}} RTmol$ Or for light-off plots: (S38) (S39) (S40) (S41) (S42) (S43) (S44) $-50 \text{ kJ} - 100 \text{ kJ}$ $x = FA_0 N_{50} A_{50} e^{-RTmol} + N_{100} A_{100} e^{-RTmol}$ W (S45) () Note that whatever order the reaction is, as long as it is separated from the sites, as it is here, then it will remain a constant when we get to the minimum. DURING CO OXIDATION LIGHT-OFF 7.3 Derivation of Existence Criteria for Mixture to Outperform Pure Cases for Simplified Model (Sites with Different Activation Energy) First, let's introduce the fraction of sites: $N_{50} f = N$ (S46) $N_{50} = N f$ (S47) $N_{100} = N - N_{50} = N(1 - f)$ (S48) Combining: $W = FA_0 \times N f A_{50} e^{-5R0mTkJol} + N(1 - f) A_{100} e^{-RTmol} - 100 \text{ kJ}$ $W = N f A_{50} e^{-5R0mTkJol} + (1 - f) A_{100} e^{-100 \text{ kJ}} RT$ (S49) (S50) We use calculus to find the minimum mass for a given conversion and fraction of single sites, we apply the conditions: $\partial W / \partial f = 0$ and $0 < f = N_{50} / N < 1$ (S51) $\partial W / \partial FA_0 x - 100 \text{ mkJol} - 1 \partial f / \partial N = f A_{50} e^{-RT} + (1 - f) A_{100} e^{-RT} - 50 \text{ mkJol} = 0$ (S52) () $FA_0 x f A_{50} e^{-RT} + (1 - f) A_{100} e^{-RT} - 50 \text{ mkJol} - 100 \text{ mkJol} - 2 - 50 \text{ mkJol} - 100 \text{ mkJol} N A_{50} e^{-RT} - A_{100} e^{-RT} = 0$ (S53) () () We can throw out the null case of no conversion ($x = 0$). $f A_{50} e^{-5R0TmkJol} + (1 - f) A_{100} e^{-10R0TmkJol} - 2 A_{50} e^{-5R0mTkJol} - A_{100} e^{-10R0TmkJol} = 0$ (S54) () () Additionally, since f is bounded between 0 and 1, exclusive, the left term is always positive and greater than 0, thus can be divided out. This gives: $A_{50} e^{-5R0TmkJol} = A_{100} e^{-10R0TmkJol}$ (S55) This is now the condition of a maximum (or minimum) existing. However, this quickly runs into a problem. This is the condition that the two sites have exactly the same activity. Thus, mathematically, the only time a mixture can require less catalyst than either pure system is when the two systems (high activation energy and low activation energy) have the same reaction rate. This is a null solution as under this condition all three (high activation energy, low activation energy, and the mixture) systems have exactly the same reaction rate. 8 Simplified Model of Sites with Different Reaction Order 8.1 Effect of Different Reaction Orders We focus here on the changes in the reaction orders. We will simplify the rate equations to get a generalized case for the effect of reaction orders. This time, however, we set the activation energies to be equal, and thus the

ratio of the rate constants for the two sites remains constant at all temperatures. Thus Equation 2 (and Table 1) become Equation S56 and Equation S57. We also set the O₂ orders to 0 on the single atom and nanoparticle analogs. This simplification allows us to verify whether it is the change in one reaction order, specifically that of the limiting reagent, or if multiple reaction orders are required to observe the synergy between single atoms and nanoparticles. We similarly ignore the change in moles of gas during the reaction. We can once again use this information to solve the PBR reactor model, Equation 1, yielding Equation S58. The derivation is included in section 8.2. DURING CO OXIDATION LIGHT-OFF $r_{SA} \approx r_{+1} = N_{+1} \times A_{+1} \times e^{-R_{ETA}} \times a_{+1}$ (S56) Equation S56: Simplified single atom/positive order mechanism. r_{+1} is the corresponding rate of reaction (r_{SA}) for the positive order mechanism. N_{+1} is the corresponding number of sites (NSA) for the positive order mechanism. A_{+1} is the corresponding pre-exponential factor for the positive order mechanism. E_A

is the activation energy and is equal to the activation energy

in Equation S57, a_A is the activity of species A (CO). $r_{NP} \approx r_{-1} = N_{-1} \times A_{-1} \times e^{-R_{ETA}} \times a_{-1}$ (S57) Equation S57: Simplified nanoparticle/negative order mechanism. r_{-1} is the corresponding rate of reaction (r_{NP}) for the negative order mechanism. N_{-1} is the corresponding number of sites (NNP) for the negative order mechanism. A_{-1} is the corresponding pre-exponential factor for the negative order mechanism. E_A

is the activation energy and is equal to the activation energy

in Equation S56, a_A is the activity of species A (CO) $W = 2N_{+1}A_{+1}FA_0e^{-R_{ETA}} a_{A,0} \ln \left(\frac{N_{+1}N_{-1} + 1 + 1A_{-1}A_{+1}a_{A,0}^2}{(a_{A,0}^2 - 1)N_{-1} + 1 + 1A_{-1}A_{+1}} \right)$ (S58) Equation S58: Design equation for competing first order and inverse first order reaction mechanisms in a general PBR. W

is the mass of the catalyst, FA_0 is the initial molar flow rate of the

reactant, $a_{A,0}$ is the initial activity of the reactant and x is the conversion. In order to simplify this equation, we can introduce a nondimensional parameter into the equation and focus on the fraction of each type of site and the ratio of their initial reactivities at the inlet of the reactor. These are shown in Equation S59. $C = r_{+1,0} = A_{+1}a_{A,0} f = N_{-1} r_{-1,0} A_{-1} N_{+1} = 1 - \frac{N_{-1}}{N_{+1}}$ (S59) Equation S59: C is a nondimensional parameter combining reactivity parameters. f is the fraction of sites (N) that are first order sites (N_{+1}). With these parameters, the design equation simplifies to Equation S60. $FA_0 - E f W = \ln \frac{1-fC+1}{2fN_{+1}} e^{R_{ETA}} a_{A,0} \left(\frac{1-fC}{1-x} + 1 \right)$ (S60) Equation S60: Simplified PBR design equation for competing first order and inverse first order reaction mechanisms. As we have shown in the full two-mechanism model given for CO oxidation, the synergy is generally most likely to be observed at higher conversions. Setting the conversion to 1, simplifies the equation. We can make this simplification as we are looking to see if a synergistic effect can occur at one location, thus a proof by example will suffice (the general derivation is included in section 8.4). We can now find the fraction of each site that the minimum mass required for full conversion. This solution is shown in Equation S61.

Additionally, we can find when such a system will occur. This is given in Equation S62. $f f \ln C + 1 = 1 - f \left(\frac{1-f}{f-1} \right) \left(\frac{1-f}{1-f} \right)$ (S61) Equation S61: Solution for minimum mass of catalyst required for full conversion. $C = \frac{A_{+1}a_{A,0}}{A_{-1}a_{A,0}} > 2$ (S62) Equation S62: Criteria for a mixture of sites to

be more effective than purely first order or inverse first order kinetics. With Equation S61, we can begin to pick systems that will show kinetic synergism more easily. To find a practical example of where a mixture would be better, we pick the case where $f=0.5$. This corresponds to a mixture of half positive order sites and half negative order sites. If we plug $f=0.5$ into Equation S61, we get that $C=3.92$. This means that for a value of $C=3.92$, the ideal catalyst for reaching 100% conversion is a 50:50 mixture of positive DURING CO OXIDATION LIGHT-OFF order and negative order sites. This is shown graphically in Figure S11. At 100% conversion, the mixture of 50% positive and 50% negative order sites requires less catalyst than either of the pure systems. Additionally, we can see that 100% conversion is not required to have the synergistic effect as we can see the mixture outperforming either pure system for conversions as low as 80% (Figure S11). With this effect being observed for a system where only one order is changed, we can conclude that both orders being different is not necessary. 1.0 Positive Order 0.8 Negative Order 50:50 Mixture Conversion

0.6 0.4 0.2 0.1050 175 200 225 250 275 300 325 350 T (° C) Figure S11: Light-off curves for a 75 kJ/mol activation energy mechanism with a positive order compared to that of a negative order and a 50% mixture of each. $C=3.92$ was chosen to highlight the difference (see text). The other parameters are arbitrary. $W \times N/FA_0 = 1$ s, $A_{-1} = 106.3$ 1/s, $a_{A,0} = 1$, were chosen due to their proximity to experimental conditions used elsewhere. The synergistic region is highlighted in yellow. See note on variables in section 1.2. The general requirement for a kinetic synergistic effect at any conversion is given in Equation S63. As can be seen, the bounds of the existence of the kinetic synergistic effect broaden for higher conversions but are not limited to a minimum conversion strictly speaking. However, practically the effect is limited to relatively high conversions. Furthermore,

Equation S64 gives the relationship between the ideal (highest activity) mixture of positive order and negative order sites (f) and the catalyst parameters (C) at a given conversion (x). Typically, the desired conversion and catalyst parameters are fixed, thus the equation is solved for f which specifies what the ideal mixture should be. We discuss with further in Figure 6. $2 A + 1 a_2 A, 0 < 2x - x^2$

$$1 + (1 - x)^2 < C = A - 1 (1 - x)^2 (-2) \ln(1 - x)$$

(S63) Equation S63: Existence criteria for a kinetic synergistic effect to occur with a pure positive order site and a pure negative order site. x is the desired conversion and C is the nondimensional lumped constant defined in Equation S59. $1 -$

$$f + 1 f C f \ln = f 1 - f 1 2x - x^2 (1$$

$-ff C (1 - x)^2 + 1) (1-f) 1- f) (1-ff x)^2 + 1)$ (S64) (Equation S64: Equation for the fraction of positive order sites (f) at a given conversion (x) and for a given system defined by C which requires the least amount of catalyst. Note that C must be on the range defined in Equation S63. 8.2

Derivation of the Design Equation for Simplified Model (Sites with Different Reaction Order) With two mechanisms (Equation S56 and Equation S57): $r+1 = N+1 \times A+1 \times e^{-RETA} \times a_1 A$ $r-1 = N-1 \times A-1 \times e^{-RETA} \times a-1$ Given that (remember we are ignoring the change in moles): $a = a_{A,0}(1 - X)$ The design equation can be solved with (Equation 1): (S65) (S66) (S67) DURING CO OXIDATION LIGHT-OFF $FA_{out} dFA W = \int FA_0 -r_A x dX W = FA_0 \int_0^x -r_A x W = FA_0 dX \int_0^x r+1 + r-1 x dX W = FA_0 \int_0^x N+1 A+1 e^{-RETA} a_1 A + N-1 A-1 e^{-RETA} a-1 x W = FA_0 dX \int_0^x N+1 A+1 e^{-RETA} a-1 E A, 0(1 - X) + N-1 A-1 e^{-RETA} a-1, 0(1 - X) -1 W = FA_0 -EA x (1 - X) dX N+1 A+1 e^{-RT} a_{A,0} \int_0^x (1 - X)^2 + N+N-1 A+1 A-1 a_1 A_2, 0$

Let's group together the constants into one nondimensional parameter: $C = A-1 A+1 a_2 A, 0$ (S68) (S69) (S70) (S71) (S72) (S73) (S74) $x W = (1 - X) dX N+1 A+1 e^{-RT} a_{A,0} FA_0 -E \int_0^x (1 - X)^2 + NN+-11 C W = 2N+1 A+1 e^{-RT} a_{A,0} (C NN+-11 (1 - x)^2 + 1) FA_0 -EA \ln C NN+-11 + 1$ Or if we want this without the non-dimensional number: $W = N+1 A+1 a_2 A, 0 + N-1 A-1 2N+1 A+1 e^{-RT} a_{A,0} (N+1 A+1 a_2 A, 0(1 - x)^2 + N-1 A-1) FA_0 -EA \ln$ Or if we want to know the conversion across a reactor, we can rewrite this as: $C NN+-11 + 1 e^{-2WN+1 A+1 e^{-RT} a_{A,0} -EA FA_0 x = 1 - 1 () C NN+-11 \sqrt{(S75) (S76) (S77) (S78)}$

8.3 Verification of Design Equation for the Simplified Model (Sites with Different Reaction Order) Checking that this equation works, we now consider the extreme cases. If we only have the first order mechanism: $r+1 = N+1 A+1 e^{-RETA} a_A$ (S79) $a_A = a_{A,0}(1 - X)$ (S80) $W = FA_0 x dX \int_0^x r+1$ (S81) $W = dX$ (S82) $N+1 A+1 e^{-RT} a_{A,0} FA_0 -EA x \int_0^x (1 - X) FA_0 -EA x W = \ln 1 N+1 A+1 e^{-RT} a_{A,0} \int_0^x (1 - x)$ (S83) Equation S83: Design equation for purely positive order sites. W

is the mass of the catalyst, FA_0 is the initial flow rate of the

limiting reagent, $N+1$ is the number of positive order sites, $A+1$ is the pre-exponential term for the positive order rate, EA is the activation energy of the positive order rate, $a_{A,0}$ is the inlet activity of the limiting reagent. For conversion: $-WN+1 A+1 e^{-RT} a_{A,0} -EA x = 1 - e FA_0$ This is equivalent to having no sites of the inverse order mechanism, i.e.: $N-1 = 0 W = CNN+-11 + 1 2N+1 A+1 e^{-RT} a_{A,0} (CNN+-11(1-x)^2+1) FA_0 -EA \ln$ (S84)

(S85) (S86) DURING CO OXIDATION LIGHT-OFF Let's do some slight rearrangement: $W = FA_0 C N+1 + N-1 2N+1 A+1 e^{-RT} a_{A,0} -E \ln (C N+1(1 - x)^2 + N-1) W = FA_0 \ln 1 2N+1 A+1 e^{-RETA} a_{A,0} ((1 - x)^2) W = FA_0 N+1 A+1 e^{-RT} a_{A,0} -E \ln 1 (1 - x)$ This is the same as before.

Now for the case of where we have only the negative order mechanism: (S87) (S88) (S89) $r-1 = N-1 A-1 e^{-RETA} a-1$ $a_A = a_{A,0}(1 - X)$ $W = FA_0 x dX \int_0^x r-1 x W = FA_0 a_{A,0} dX \int_0^x N-1 A-1 e^{-RETA} W = FA_0 a_{A,0} -EA x (1 - X) dX N-1 A-1 e^{-RT} \int_0^x W = 2N-1 A-1 e^{-RT} FA_0 a_{A,0} -EA 2x - x^2 ()$ (S90) (S91) (S92) (S93) (S94) (S95) For conversion: $x = 1 - 1 - 2W N-1 A-1 e^{-RETA} \sqrt{FA_0 a_{A,0}}$ This is equivalent to having no sites of the positive order mechanism, i.e.: $N+1 = 0$ (S97) $W = CNN+-11 + 1 2N+1 A+1 e^{-RT} a_{A,0} (CNN+-11(1-x)^2+1) FA_0 -E \ln$ (S98) However, this gives a problem as the positive order site term is in the denominator. But, we can fix this with a series expansion about 0:

$$f(x) = f(0) + f'(0)x + f''(0)x^2 + f'''(0)x^3 + \dots$$
 (S99)

$$(N+1) = \ln (C NN+-11 (1 - x)^2 + 1) C NN+-11 + 1 \rightarrow f(0) = 0$$
 (S100) $f'(N+1) = N-1 - NC-1 (1 - x)^2 C \rightarrow f'(0) = C - (1 - x)^2 C C NN+-11 (1 - x)^2 + 1 + C^2 NN+-2211 (1 - x)^2 + C NN+-11 N-$

$$1 N-1$$
 (S101) $f(N+1) = 0 + C - (1 - x)^2 C N+1 + (N-1 N-1) f''(0) N + 21 + f'''(0) N$

$$+ 31 + \dots 2 6$$
 (S102) $\ln C NN+-11 + 1 (C NN+-11 (1 -$

$$x)^2 + 1) (N-1 = C - (1 - x)^2 C N+1 + N$$

$$-1 f''(0) N + 21 + f'''(0) N + 31 + \dots$$
 (S103)) 2 6 Plugging this into the original : $W = FA_0 -EA C 2N+1 A+1 e^{-RT} a_{A,0} (($

$$N-1 - (1 - x)^2 C N+1 + N-1) f''(0) N + 21 + f'''(0) N$$

$+31 + \dots 26 (S104)) W = C C f''(0) 2A+1e RTA aA,0 (($
 $N-1 F -AE0 - (1-x)^2 + N-1) 2 N+1 + f'''(0) N$
 $+21 + \dots 6 (S105))$ Applying $N+1 = 0$: $W = F-AE0 C - (1-x)^2 C 2A+1e RTA aA,0 ((N-1 + 0 + 0 + \dots N-1)) W = FA0 C 2A+1e RTA aA,0 N-1$
 $-E 2x - x^2 ()$ Applying C : (S106) (S107) DURING CO OXIDATION LIGHT-OFF $W = 2N-1A-1e RTA FA0aA,0-E 2x - x^2 (S108) ()$ Again, we
 have the same end result. 8.4 Derivation of Existence Criteria for Mixture to Outperform Pure Cases for Simplified Model (Sites with Different Reaction Order) First, we will need the equation in terms of fraction of sites: $W = CNN+-11 +1 2N+1A+1e RTAaA,0 (CNN+-11(1-x)^2+1) FA0-E \ln$
 (S109) $f W = 2f N A+1e RT aA,0 (1-ff C(1-x)^2 + 1) FA0-EA \ln 1-f C + 1 (S110) C = A+1e -RET-AEa2A,0 A-1e RTA (S111)$ Now, a mixture
 will outperform pure systems if there is a minimum in mass required to reach a given conversion that occurs between the pure positive order and pure
 negative order conditions. In calculus this means: $\partial W (1) \partial f = 0 (2) \partial^2 f W^2 > 0$ and $(3) 0 < f = N+1 < 1 N (S112)$ The second condition we have
 already analyzed rigorously in Figure 6 through numerical methods. The fact that the improvement is greater than 1 means that we have in fact
 reached a minimum mass (as opposed to a maximum) for the thousands of points considered. For the first condition: $\partial W \partial f = 0 (S113) \partial FA0 1-ff C +$
 $1 \partial f 2f N A+1 e -RETA aA,0 (1-ff C (1-x)^2 + 1) \ln = 0 (S114) \partial 1 \partial f (f \ln 1-ff C + 1 (1-f C (1-x)^2 + 1)) f = 0 (S115) 1-f + 1 f C -1 1 C 1 2 \ln$
 $2x - x^2 (1-ff C (1-x)^2 + 1) f^2 + = 0 () (1-ff C + 1) 1 - f (1-ff C (1-x)^2 + 1) f () (S116)$ Because f cannot be 0, as this is outside the
 domain of the equations, we can multiply through by $f - \ln 1-f C + 1 f + f C 1 2x - x^2 (1-ff C (1-x)^2 + 1) (1-f f - C f + 1) (1 - f (1-ff C (1-x)^2$
 $+ 1) = 0 (S117) (1-ff C 1-(1f C- +x)12 + 1) (1-f f - f (1-f) (1-ff f f \ln = 1 2x - x^2) x)^2 + 1) (S118)$ This is Equation S64. This is a
 transcendental equation and as such, we cannot use common methods to find the range of possible values that solve the above equation, the existence
 criteria. In order to determine where this equation is solvable, we will use the intermediate value theorem to show that given certain conditions, there
 will exist at least one solution in the range of $0 < f < 1$, criteria (3). Strictly speaking, if: $f(f) > 0$ and $f(f + \delta f) < 0$ or $f(f) < 0$ and $f(f + \delta f) > 0$
 $f(0) > 0$ and $f(1) < 0$ or $f(0) < 0$ and $f(1) > 0$
 (S119) (S120) Then there must be at least one solution on the range $f < x < f + \delta$. However, our situation is a bit more complicated than this as the $f =$
 0 boundary conditions is also a null solution. i.e.: DURING CO OXIDATION LIGHT-OFF $f(0) = 0 (S121) 0 0 - \ln 1-0 x)^2 + 1) (1-010-0 + 1 2x -$
 $x^2) x)^2 + 1) = 0 (S122) (1-0 0 (1-0) (1-0 0 - \ln (1) + 0) 1 (1) 2x - x^2 = 0 (S123) () 0+0 = 0 (S124)$ However, we can solve this by instead
 looking at the first derivative. If the first derivative is positive then there exists a value just greater than $f = 0$, where $f(f)$ will be positive. The
 condition now becomes:
 $f'(0) > 0$ and $f(1) < 0$ or $f'(0) < 0$ and $f(1) > 0$
 (S125) However, we run into the same problem and we again solve it in the same way: $f'(f) = f C (x-2)x (2f(C-1)(C(x-1)^2-1) - 2 + C ($
 $2 + (x-2)x) (1 + f(C-1))^2 (1 + f(C(x-1)^2-1))^2$
 $f'(0) = 0$ Now, for the same reason as before, we will use:
 $f''(0) > 0$ and $f(1) < 0$ or $f''(0) < 0$ and $f(1) > 0$
 Investigating the first case: (S126) (S127) (S128) $\partial 2 1-ff C + 1 - 1-ff C 1 2x - x^2 \partial f 2 (- \ln (1-ff$
 $C (1-x)^2 + 1) (1-ff C + 1) (1-f) (1-ff C$
 $(1-x)^2 + 1)) > 0 (S129) C(2-x)x(2f(C-1)(C(x-1)^2-1) - 2 + C($
 $2 + (x-2)x) (1 + f(C-1))^2 (1 + f(C(x-1)^2-1))^2 - (2C(2-x$
 $)x(2 - 3f(C-1)(C($
 $x-1)^2 - 1) + f^3(C-1)^2 (C(x-1)^2-1)^2 - C(2 + (x$
 $- 2)x)) (1 + f(C-1))^3 (1 + f(C(x-1)^2-1))^3 > 0 (S130)$ At $f = 0 C ($
 $x-2)x (C (2 + (x-2)x) - 2) > 0 (S131) C < 1 + (1-x)^2$
 $2 (S132)$ Now for the function at $f = 1$, $-\ln 1-f + 1 f C (1-ff C (1-x)^2 + 1) + 1 f f C 1 2x - x^2 (1-ff-C + 1) (1-f) (1-ff C (1-x)^2 + 1) < 0$
 (S133) After some rearrangement, and plugging in $f = 1$: $-\ln f C + 1 - f f C 2x - x^2 (f C (1 -$
 $x)^2 + 1 - f) (f C + f - 1) (f C (1-x)^2$
 $+ f - 1) + < 0 (S134) - \ln 1C + 1 - 1 1C 2x - x^2 (1C ($

$(1-x)^2 + 1 - 1) (1C + 1 - 1) (1C (1-x)^2 + 1 - 1) + <0$ (S135) $2 \ln(1-x)$
 $) + (C(1-x)^2) 2x - x^2 < 0$ (S136) $C > x^2 - 2x(1-x)^2 \ln(1-x)$ (S137) This however is a problem as:
 $2 < x^2 - 2x + (1-x)^2 (1-x)$
 $)^2 \ln(1-x)$ (S138) DURING CO OXIDATION LIGHT-OFF For all $x > 0$, thus there is not solutions of interest here. Trying the second case is just like the first, however the signs are flipped: $f'(0) < 0$ (S139) $C > 2 + (1-x)^2$ (S140) $f(1) > 0$ (S141) $C < x^2 - 2x(1-x)^2 \ln(1-x)$ (S142) This has a solution space of interest: $2 < C < x^2 - 2x$
 $1 + (1-x)^2 (1-x)^2 \ln(1-x)$
 $)$ (S143) Strictly speaking, the above proof is only for the existence of at least one solution. We must also prove that this is the only solution. For that, we will first look at the number of solutions. As the existence criteria is continuance on the range $0 < f < 1$, there can be at most 1 plus the number of critical points. Getting the critical points: $\partial \ln fC + 1 - f \partial f / ((fC(1-x)^2 + 1 - f) ((fC + 1 - f)(1 - f(1 - ffC(1-x)^2 + 1))) - fC$
 $1 - f) ((fC + 1 - f)(1 - f(1 - ffC(1-x)^2 + 1))) - fC$
 $2x - x^2 = 0$) (S144) $C(2 - x)x C(f^2(C - 1)(C(x - 1)^2 - 1) - 1)(x - 2)x(1 + f(C - 1))(1 + f(C(x - 1)^2 - 1))(1 + f(C - 1))^2(1 + f(C(x - 1)^2 - 1))^2 = 0$ - (S145) $(1 + f(C - 1))1 + f(C(x - 1)^2 - 1) + f^2(C - 1)(C(x - 1)^2 - 1) - 1$
 $= 0$ (S146) $C(2(-x)x)(1 + f(C - 1))(1 + f(C(x - 1)^2 - 1))(1 + f(C - 1))^2(1 + f(C(x - 1)^2 - 1))^2 = 0 - C((f^2(C - 1)(C(x - 1)^2 - 1) - 1))(x - 2)x$ (S147) $a = 2 - C(x - 1)^2 - C2(1 - C - C(x - 1)^2 + C2(x - 1)^2)$ (S148) While this is not well reduced, it is obvious from the form of the equation that for any C and x , there can be at most one critical point in the range $0 < f < 1$. This means that there can be at most 2 solutions as the function is continuous. We know that one of these solutions is at $f = 0$. This leaves only one possible solution that is left. The solution when the previous condition is met. There are two points in this discussion that are worth further mentioning. The first point is that while Equation S64 might not appear to be the simplest solution, it is quite elegant, by remembering that: $C = A + 1e^{-RET - AEa} / 2A, 0 A - 1e^{RTA}$ (S149) $K = a^{N+1} A + 1e^{-RETA} / a^2, 0 1 - a C = N - 1A - 1e^{-RETA}$ (S150) We can group together more of the catalyst parameters. $\ln K + 1 K 1 2x - x^2 (K(1-x)^2 + 1) (K + 1) (1 - a) (K(1 - x)^2 + 1) =$ (S151) The second point is clarifying what does this all mean in terms of numbers. Equation S63: $2 2x - x^2 1 + (1-x)^2 < C < (1-x)^2 (-2) \ln(1-x)$
 $)$ (S152) shows the existence criteria. To help better understand this, let's look at the examples of nearly full conversion ($x = 0.99$). Thus, the existence criteria are reduced to: $2 2(0.99) - (0.99)^2 1 + (1 - 0.99)^2 < C < (1 - 0.99)^2 (-2) \ln(1 - 0.99)$ (S153) $1.9998 < C < 1085.6$ (S154) Thus if we want nearly full conversion we have a large range of possible C values that DURING CO OXIDATION LIGHT-OFF might lead to a kinetic synergistic effect. This makes sense because a higher conversion is where positive order sites cannot reach full (or require much more catalyst for near full) conversion. Some other meaningful results: $x = 0.95 \rightarrow 1.995 < C < 66.6$ $x = 0.9 \rightarrow 1.98 < C < 21.5$ $x = 0.5 \rightarrow 1.6 < C < 2.2$ (S155) (S156) (S157) Additionally, it is important to remember that this represents the cases where an ideal mixture is any degree more active than either the pure positive order or negative order systems. This says nothing to how much better that system is. 8.5 Special Cases for Simplified Model of Sites with Different Re- action Order 8.5.1 Full Conversion: The Minimum Equation and the Existence Criteria At full conversion, the minimum equation simplifies to: $f \ln(1 - ffC - (1fC - +x)^2 + 1) ((1 - ffC - Cf + 1) (1 - f) (1 - ffC - C 1 2x - x^2 x)^2 + 1)) \ln f f (1 - f C + 1 = 1 - f 1) (f 1 - f) (1 - f)$ Likewise, the existence criteria becomes: $2 12 x^2 - x 1 + (1-x)^2 < C < (1-x)^2 \ln(1-x)$
 $)$ (S158) (S159) (S160) $2 < C < \infty C > 2$ (S161) (S162) 8.5.2 Full Conversion with Minima at 50:50 $f \ln f C + 1 =$

$$\frac{1-fC}{(1-f)} \frac{1}{1-\ln 2} \frac{1}{2} \frac{1}{C+1} = \frac{1-2f}{1-(1-2f)} \frac{1}{1-12} \frac{1}{12} \frac{1}{C+1} \left(\frac{1-12}{1-12} \right) \ln(C+1) = C^2 (C+1) C = 3.92 \quad (S163) \quad (S164) \quad (S165) \quad (S166) \quad 9$$

Origin of Synergistic Effect for the Simplified Model (Sites with Different Reaction Order)

In order to further establish the origins of the kinetic synergistic effect beyond the change in orders of the two mechanisms, we use the simplified model to highlight the difference between two systems. One that shows the synergistic effect (figure S12) and one that does not (figure S13). For the first case, we see the same case as the full model, however for the second case we see that neither the mixed or the negative order sites can light-off. DURING CO OXIDATION LIGHT-OFF a 2.5 Positive Order Sites in Mix Conversion 1.0 b 1.0 Purely Positive Order Sites Negative Order Sites in Mix Purely Negative Order Sites Combined Reaction Rate (s⁻¹) 2.0 0.8 0.8 50:50 Mixture 1.5 0.6 0.6 1.0 0.4 Conversion Conversion 0.4 0.5 0.2 0.2 0.0 0.0 0.0 0.0 0.2 0.4 0.6 0.8 1.0 0.0 0.2 0.4 0.6 0.8 1.0 Cataylst Mass *FA0/Nsites (s) Cataylst Mass *FA0/Nsites (s) 2.5 c Purely Positive Order Sites Purely Negative Order Sites 50:50 Mixture Reaction Rate (s⁻¹) 2.0 1.5 1.0 0.5 0.0 0.0 0.2 0.4 0.6 0.8 1.0 Cataylst Mass *FA0/Nsites (s) Figure S12: Conversion and reaction rates along the catalyst bed at 312 °C for the 50:50 mixture as shown in Figure S11. This temperature was chosen because it is inside the synergistic region. (a) The Combined reaction rate (purple) is the sum of the Positive Order (blue) and Negative Order (red) reaction rates for this 50:50 system. (b) Conversion across the catalyst bed for purely positive order sites (blue), purely negative order sites (red) and the 50:50 mixture (purple). (c) Reaction rate across the catalyst bed for purely positive order sites (blue), purely negative order sites (red) and the 50:50 mixture (purple). a 2.5 Positive Order Sites in Mix Conversion 1.0 b 1.0 Purely Positive Order Sites Negative Order Sites in Mix Purely Negative Order Sites Reaction Rate (s⁻¹) 2.0 Combined 0.8 0.8 50:50 Mixture 1.5 0.6 1.0 0.4 Conversion Conversion 0.6 0.4 0.5 0.2 0.2 0.0 0.0 0.0 0.0 0.2 0.4 0.6 0.8 1.0 0.0 0.2 0.4 0.6 0.8 1.0 Cataylst Mass *FA0/Nsites (s) Cataylst Mass *FA0/Nsites (s) 2.5 c Purely Positive Order Sites Purely Negative Order Sites 50:50 Mixture Reaction Rate (s⁻¹) 2.0 1.5 1.0 0.5 0.0 0.0 0.2 0.4 0.6 0.8 1.0 Cataylst Mass *FA0/Nsites (s) Figure S13: Conversion and reaction rates along the catalyst bed at 295 °C. All other parameters are the same as Figure S11. This temperature was chosen because it is below the synergistic region (Figure S11). (a) The Combined reaction rate (purple) is the sum of the Positive Order (blue) and Negative Order (red) reaction rates for this 50:50 system. (b) Conversion across the catalyst bed for all positive order sites (blue), all negative order sites (red) and the 50:50 mixture (purple). (c) Reaction rate across the catalyst bed for all positive order sites (blue), all negative order sites (red) and the 50:50 mixture (purple).

10 Effect of Temperature on C From Equation S59 $C = r+1, 0 = A+1e^{-R-TE} a_2A, 0 -EA, +1$ (S167) $r-1, 0 A-1e^{-RAT, -1}$ Let's define: $\Delta E = EA, +1 - EA, -1$ (S168) DURING CO OXIDATION LIGHT-OFF $C = A+1e^{-\Delta E-RETA, -1} a_2A, 0$

$A-1e^{-ERAT, -1}$ (S169) $A+1e^{-A-R-\Delta TIE} a_2A, 0 AA+-11 e(= EA, -1 -EA, +1 C = RT) a_2A, 0$ (S170) Equation S170: Temperature dependence on the reaction ratio, C.

11 Coding Considerations The models were developed in Python 3.8. Data was imported through the pandas toolbox.⁸ Many calculations were done using NumPy.⁹ Reactor optimizations and numerical integrations were performed using the SciPy modules.¹⁰ Optimizations for the design equation were done using the Nelder-Mead¹¹ method as implemented in the SciPy toolbox.¹⁰ Optimizations for the ideal catalysts were performed using the Brentq method¹² also as implemented in the SciPy toolbox.¹⁰ Plotting was performed with Matplotlib.¹³ 11.1 Note on Numerical Noise Several figures show kinks at the high conversion. This is generally from numeric noise due to either the nature of the first order kinetics being unable to reach 100% conversion or the general stiffness of the equations, especially the temperature gradient calculations. In order to verify that the results are not from this noise, data has been selected that minimizes this noise and the discussed conclusions have been externally verified through different ODE solvers such as Radau (which is shown), BDF, and LSODA as implemented in the `scipy.integrate.solve_ivp` package.¹⁰ Chapter 3 CO oxidation on MgAl₂O₄ supported Irn:

activation of lattice oxygen in the subnanometer regime and emergence of nuclearity-activity volcano

This work was originally published in Journal of Materials Chemistry A on January 20, 2022 [40]. In this work I performed all of the (DFT) computational, the derivations of the rate equations, and the XRD of the catalysts. 97 CHAPTER 3. CO OXIDATION ON MGAL₂O₄ SUPPORTED IRN:

ACTIVATION OF LATTICE OXYGEN IN THE 98 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO

CO oxidation on MgAl₂O₄ supported Irn:

activation of lattice oxygen in the subnanometer regime and emergence of nuclearity-activity volcano Yubin Lu,[†] Coogan B. Thompson,[†] Chun -T Kuo,[†] Xiwen Zhang,[†] Adam S. Hoffman,[‡] Alexey Boubnov,[‡] Simon R. Bare,[‡] Libor Kovarik,[¶] Hongliang Xin,[†] and Ayman M. Karim ^{*},[†] [†]Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24060, USA [‡]Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA [¶]Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, Washington, USA E-mail: *amkarim@vt.edu

Abstract CO oxidation on Pt group metals is affected by the metal size and reducibility of the oxide support. Here, we report that Ir supported on MgAl₂O₄, traditionally considered non-reducible, exhibits properties similar to reducible oxides when the Ir size is in the subnanometer regime. To show this effect, we synthesized subnanometer Ir clusters and compared their properties to single atoms and nanoparticles (1-1.5 nm). The CO oxidation activity is highest on Ir_{0.6–0.8nm} while showing distinctly different reaction orders in CO and O₂ (0, +0.4), than single atoms (1, 0) and nanoparticles (-1, +1). Microcalorimetry, in situ X-ray absorption, and infrared spectroscopies show that the CO-saturated Ir_{0.6–0.8nm} clusters could adsorb and activate O₂ despite binding CO more strongly than nanoparticles. Density functional theory calculations on CO saturated Ir₄ clusters suggest that the increased activity is due to the ability to activate O₂ on oxygen vacancies at the Ir-MgAl₂O₄ interface. The findings show the important effect of the metal nuclearity on the support and catalyst properties and can guide future design of CO oxidation catalysts.

Introduction Supported precious metal catalysts are used to perform many important chemical transformations. Dispersing the metals as single atoms and small clusters has become a common strategy to increase the percentage of atoms available for binding and transformation of the reactants.^{1,2} However, supported metal single atoms and subnanometer clusters typically have different reactivity compared with their nanoparticle counterparts.^{3–6} As the metal nuclearity decreases into the subnanometer regime, the metal electronic properties can change substantially due to the lower number of neighboring metal atoms and enhanced interaction with the support.^{7–9} The different properties of isolated atoms, dimers and subnanometer clusters can lead to different reaction mechanisms and/or improved reactivity (e.g. superior activity and/or selectivity),^{10–15} but this is highly dependent on the reaction, the type of metal, and support. For low-temperature (<200 °C) CO oxidation on platinum group metals, there are reports of both higher (e.g. Pt/FeOx,¹⁵ Pt/mesoporous-Al₂O₃ (ref. 16) Rh/CeO₂ (ref. 17)) and Ir/MgAl₂O₄ (ref. 18 and 19) and lower (e.g. Pt/Al₂O₃ (ref. 20) Pt/H-ZSM5 (ref. 21), Pt/CeO₂ (ref. 22 and 23) and Rh/TiO₂ (ref. 24)) activity on supported metal single atoms compared to nanoparticles. Additionally, the activity can be strongly dependent on metal nuclearity as shown for size selected Pd_n clusters (n = 1-25) deposited on 100 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO rutile TiO₂(110) where the activity was highest on Pd₂₀.²⁵ In this regard, understanding the effect of metal nuclearity on reactivity is important on a fundamental level and offers an opportunity to tune the metal properties and design highly active catalysts. For low temperature CO oxidation on supported precious metals, the metal nuclearity and support strongly affect the adsorption of CO and O₂, the reaction mechanism, and the catalyst activity. O₂ activation is highly dependent on the type of the support. On non-reducible oxides (Al₂O₃, MgAl₂O₄, etc.), O₂ activation proceeds via the Langmuir–Hinshelwood (L- H) mechanism on the nanoparticles, and due to the strong CO adsorption on the metal and lack of adjacent sites for O₂ adsorption and activation, the activation proceeds on one empty metal site assisted by an adsorbed CO on an adjacent metal site.²⁶ On reducible metal oxides (e.g. CeO₂ and TiO₂), CO oxidation proceeds at the interface where CO on the metal nanoparticle reacts with O* at the metal/support interface.^{23,27–31} The metal support interaction also plays an important role in O₂ activation. For example, Oh et al. showed that the O₂ shows promoted activation on a defect site at the Pt-TiO₂ interface.³² On the other hand, for single atoms on both reducible and non-reducible supports, most studies show that the support plays a crucial part in O₂ activation.^{33–36} In the subnanometer regime, less is known about O₂ activation but it is likely size- and support-dependent. For example, Kaden et al. showed that Pd₂₀/TiO₂ can activate O₂ more efficiently than Pd₇/TiO₂ and Pd₄/TiO₂.³⁷ However, there are limited studies on the effect of metal nuclearity on CO oxidation in the subnanometer regime, especially on supports traditionally considered to be non-reducible.

Results and discussion By combining advanced experimental and theoretical approaches including aberration-corrected transmission electron microscopy, microcalorimetry, in situ and operando X-ray absorption spectroscopy (XAS), infrared spectroscopy, and density functional theory (DFT) calculations, we investigated the effect of

Ir metal nuclearity on interaction with CO/O₂ and on the CO oxidation kinetics on Ir/MgAl₂O₄. We show that supported Ir subnanometer clusters are more active than single atoms and nanoparticles (>1 nm) and we attribute their superior activity to enhanced cooperation between the metal and support in the subnanometer regime. To achieve this, we synthesized a sample consisting of mostly Ir subnanometer clusters supported on MgAl₂O₄ (denoted as IrSubnano/MgAl₂O₄, Fig. 1b) and compared it with MgAl₂O₄ supported nanoparticles (denoted as IrNP/MgAl₂O₄, Fig. 1a) and single atoms (denoted as IrSA/MgAl₂O₄, Fig. 1c). Size analysis of multiple high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images show that IrSubnano/MgAl₂O₄ contains mostly subnanometer clusters having an average cluster size of ~0.7 nm and ~28% of Ir is present as single atoms. HAADF-STEM characterization on the spent IrSubnano/MgAl₂O₄ confirmed the stability of the subnanometer Ir clusters under CO oxidation reaction conditions at 155 °C (ESI, Fig. S1, Tables S1 and S2†). Powder X-ray diffraction spectroscopy (XRD) results (ESI Fig. S2†) show that there were no significant changes to the support (MgAl₂O₄) structure due to the synthesis and that all species on the support were small as indicated by the lack of non-support peaks. This is consistent with the STEM, EXAFS, and chemisorption results indicating single atoms, subnanometer clusters, and small (1-1.5 nm) nanoparticles. To provide more insights on the electronic properties and local coordination of Ir, we conducted XAS on the IrSubnano/MgAl₂O₄ (Fig. 1e and f).

The magnitude of the Fourier transformed extended X-ray absorption fine structure (EXAFS)

) spectra (Fig. 1f) show peaks consistent with Ir–Ir and Ir–O scattering paths. Indeed, the EXAFS modeling results (ESI Table S3†) for IrSubnano/MgAl₂O₄ after reduction in H₂ show Ir–Ir and Ir–O coordination numbers of 3.5 ± 1.3 and 3.2 ± 0.5 , respectively. The EXAFS results are consistent with the small subnanometer Ir clusters measured by HAADF-STEM (ESI Fig. S3–S6†). The Ir–O coordination number for IrSubnano/MgAl₂O₄ is significantly higher than IrNP/MgAl₂O₄ (also in ESI, Table S3†), which can be attributed to the contribution from the presence of Ir single atoms (~28%, Fig. 1a) and Ir atoms in the subnanometer clusters at the MgAl₂O₄ 102 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO Figure 1: Structural characterization and CO oxidation performance of MgAl₂O₄ supported Ir catalysts. HAADF-STEM images and histograms of (a) IrNP/MgAl₂O₄, (b) IrSubnano/MgAl₂O₄, and (c) IrSA/MgAl₂O₄. (d) Low-temperature CO oxidation performance of IrSA/MgAl₂O₄, IrSubnano/MgAl₂O₄ and IrNP/MgAl₂O₄ measured at 155 °C, at various PCO (0.3 kPa, 0.6 kPa, 1 kPa) and PO₂ at 10 kPa. (e) XANES and (f) EXAFS results of the Fourier transformed k²-weighted $\chi(k)$ data measured on pretreated IrSubnano/MgAl₂O₄, pre-treated IrNP/MgAl₂O₄ (1 wt%) and Ir foil. $\Delta k = 2.6$ – 12.5 Å⁻¹ interface. Additionally, the high Ir–O coordination is consistent with the higher

white line intensity observed in X-ray absorption near edge structure (XANES

) region compared with that on Ir foil and Ir nanoparticles on MgAl₂O₄ (Fig. 1e). The results indicate that Ir in the subnanometer clusters in IrSubnano/MgAl₂O₄ is more electron deficient compared to 1–1.5 nm nanoparticles on the MgAl₂O₄ (IrNP/MgAl₂O₄). The activity of the supported metal catalysts is dependent on the metal oxidation state.³⁸ The oxidation state of the pretreated IrSubnano/MgAl₂O₄ was analyzed by the white-line intensity of the XANES spectra at Ir L₃-edge by comparing to Ir references. ESI Fig. S7† shows that the white-line intensity of IrSubnano/MgAl₂O₄ is between the Ir foil (Ir⁰) and IrO₂ (Ir⁴⁺). This shows that the average Ir oxidation of the IrSubnano/MgAl₂O₄ is between 0 and +4 and around +2. In comparison, the white-line intensity of IrNP/MgAl₂O₄ is only slightly higher than the Ir foil which suggests the Ir oxidation state is close to 0. The higher oxidation state of the IrSubnano/MgAl₂O₄ is attributed to the higher contribution of the metal-support interaction (formation of Ir–O bond at the interface) on smaller-sized clusters (0.6–0.8 nm), which can be seen by the Ir–O coordination from the EXAFS modeling results (ESI Table S3†). The oxidation state of the IrSA/MgAl₂O₄, was found to be higher than IrSubnano/MgAl₂O₄ and close to IrO₂ (i.e. oxidation state ~+4, consistent with our previous DFT calculations)³⁹ due to the lack of Ir–Ir coordination and the higher coordination with oxygen from the support. During low-temperature CO oxidation at 155 °C, the turnover frequency (TOF) on IrSubnano/MgAl₂O₄ at various CO partial pressures is up to 10 and 5 times higher than IrNP/MgAl₂O₄ and IrSA/MgAl₂O₄, respectively (Fig. 1d) where the TOF is the reaction rate normalized with the surface Ir atoms measured by chemisorption for all three catalysts. The reaction orders in CO and O₂ and the apparent activation energy (Table 1 and ESI Fig. S8–S10†) provide insights on the CO oxidation mechanism and how it changes with Ir nuclearity in the three catalysts. For IrNP/MgAl₂O₄, the negative order (-1) in CO and positive order (+1) in O₂ indicate that the surface is poisoned by CO and O₂ activation is the rate limiting step as typically

observed on supported platinum group metal nanoparticles.⁴⁰ On 104 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO Ir single atoms, a facile O₂ activation, and an Eley–Rideal rate limiting step were reported in our previous work resulting in a zero order in O₂ and positive order (+1) in CO.¹⁹ In contrast, the Ir subnanometer clusters (~0.7 nm, IrSubnano/MgAl₂O₄) show 0 order in CO and +0.4 order in O₂ (ESI Fig S8 and S9†). The results indicate a different reaction mechanism on Ir subnanometer clusters than that on single atoms or nanoparticles (1–1.5 nm). The CO oxidation activity is almost independent of CO partial pressure over a large CO partial pressure range (0 ± 0.2 order over a 50× increase in CO partial pressure, ESI Fig. S8a†) suggesting that CO adsorption requires a different site than O₂ adsorption. In fact, the reaction orders are similar to those measured for Pt clusters supported on CeO₂ (ref. 31 and 41) and on TiO₂ (ref. 42) where the reaction follows a two-site mechanism at the metal-support interfacial sites. Therefore, we hypothesize that the abundant metal-support interfacial sites on the Ir subnanometer clusters are likely involved in facilitating the O₂ adsorption and activation steps. Table 1: Reaction orders and heats of adsorption (ΔH_{ads}) of CO and O₂ on MgAl₂O₄ supported Ir nanoparticles, subnanometer clusters and single atoms Catalyst IrNP/MgAl₂O₄

Catalyst	CO reaction order ^a	O ₂ reaction order ^b	ΔH _{ads} of CO (kJ mol ⁻¹)	ΔH _{ads} of O ₂ (kJ mol ⁻¹)
IrSubnano/MgAl ₂ O ₄	0 ± 0.02	+0.4 ± 0.03	-207 (-254) ^c	-150 (-330)
IrSA/MgAl ₂ O ₄	0 ± 0.02	+0.4 ± 0.03	-207 (-254) ^c	-150 (-330)

IrSubnano/MgAl₂O₄ IrSA/MgAl₂O₄ CO reaction order^a O₂ reaction order^b ΔH_{ads} of CO (kJ mol⁻¹) ΔH_{ads} of O₂ (kJ mol⁻¹) -1 0.1 ± +0.9 0.1 ± -150 -330 0 ± 0.02 +0.4 ± 0.03 -207 (-254)^c -515 (-529)^c +0.9 ± 0.1 +0.1 ± 0.05 -230 (ref. 19) -1

The binding energies of CO and O₂ provide important insights on the reaction mechanism. CO microcalorimetry results (Table 1 and ESI Fig. S13–S15†) show that subnanometer clusters adsorb CO strongly with an adsorption energy of -207 kJ mol⁻¹ (average at low coverage, based on two measurements), which is much stronger than the binding of CO to Ir nanoparticles (-150 kJ mol⁻¹ at low CO coverage), and similar to the CO binding to Ir single atoms (-230 kJ mol⁻¹ from DFT calculations¹⁹). Similarly, the O₂ adsorption energy on the Ir subnanometer clusters is also much stronger than that on nanoparticles -515 vs. -330 kJ mol⁻¹ 1a The CO reaction order was measured at P_{O₂} = 10 kPa and P_{CO} between 0.3–10 kPa (see ESI Fig. S8). b The O₂ reaction order was measured at P_{CO} = 1 kPa and P_{O₂} between 2–14 kPa (see ESI Fig. S8). c Heat of adsorption from DFT calculations on Ir₄ cluster supported on MgAl₂O₄ as shown in ESI Fig. S11d (CO) and ESI Fig. S12 (O₂). at low coverage. The strong O₂ adsorption on the Ir subnanometer clusters suggests that O₂ adsorption and activation could be more competitive than on Ir nanoparticles. However, competitive adsorption on the same Ir site should result in a CO order that changes with the CO partial pressure. Since the CO order was close to zero over 50× change in CO partial pressure (ESI Fig. S8a†), the reaction orders are more consistent with O₂ adsorption and activation at the Ir–MgAl₂O₄ interfacial sites while the remaining sites are covered by strongly adsorbed CO (i.e. a two-site mechanism, which will be discussed further below). To test the hypothesis of a two-site mechanism and provide more details on the reaction mechanism, we conducted in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and EXAFS coupled with in situ and operando high energy resolution fluorescence detected (HERFD)-XANES experiments. In situ CO/O₂ cycling spectroscopic experiments were first performed at room temperature to probe the surface structure via CO/O₂ adsorptions and to depict an incomplete reaction cycle. In situ HERFD-XANES and DRIFTS spectra on the CO saturated IrSubnano/MgAl₂O₄ (after reduction in IrSubnano/MgAl₂O₄) are shown in Fig. 2a and b (red spectra).

When flowing O₂ on the CO covered IrSubnano/MgAl₂O₄ at room temperature, a significant increase in the white line intensity in HERFD-XANES was observed (Fig. 2a, blue) and the corresponding DRIFTS spectrum (Fig. 2b, blue) showed a blue shift where the ν_{CO} band shifted from 2033 to 2040 cm⁻¹ indicating

an increase in the oxidation state of Ir. In addition to the changes observed in HERFD-XANES and DRIFTS when flowing O₂, CO₂ was also detected in the on-line mass spectrometer (ESI Fig. S16†), which indicates that O₂ could react with some of the adsorbed CO followed by co-adsorption with CO on the subnanometer Ir clusters at room temperature. In addition, surface carbonates at 1691 cm⁻¹ in DRIFTS, were also detected during the room-temperature O₂ flow, which is another indication of CO₂ formation (ESI Fig. S17†). Consistent with HERFD-XANES and DRIFTS, when the gas was switched from CO to O₂, the Ir–O coordination number from EXAFS increased from 3.2 to 4.1 indicating oxidation of the Ir subnanometer clusters (Fig. 2c, d and ESI,† Table S3 and Fig. S18). When flowing CO again after the 106 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO oxygen step, a decrease in the white line intensity was observed in HERFD-XANES (Fig. 2a, orange), but it was still higher than the

white line of the initial spectrum in CO indicating that Ir does not return to the initial reduced state and that some adsorbed O* was still present. This can also be seen in DRIFTS after CO re-adsorption (yellow spectrum in Fig. 2b) where an extra shoulder at 2075 cm⁻¹ was observed which is consistent with adsorbed CO on more oxidized Ir sites (i.e. CO* co-adsorbed with O* on Ir). It is important to note that CO was detected on Ir in DRIFTS under all conditions indicating that CO is strongly adsorbed on the reduced Ir subnanometer clusters which is consistent with the CO microcalorimetry results. More importantly, similar results were observed on another subnanometer Ir/MgAl₂O₄ catalyst prepared using Ir₄(CO)₁₂ (average size 0.5–0.6 nm, denoted as IrSubnano Ir₄/MgAl₂O₄, see ESI† Fig. S19 and S20) indicating that the observed Ir behavior is due to the size being in the subnanometer regime and not necessarily specific to the synthesis or pretreatment conditions. The in situ HERFD-XANES and DRIFTS results at room temperature are qualitatively similar to those we previously reported on single atom Ir supported on MgAl₂O₄ (ref. 19) and strongly suggest that oxygen vacancies at the Ir–MgAl₂O₄ are involved in the CO oxidation reaction mechanism. To provide more insight, we performed DFT calculations on Ir₄ clusters supported on the (111) O₂(Al) terminated MgAl₂O₄ surface as a representative model of the Ir subnanometer clusters in the IrSubnano/MgAl₂O₄ catalyst (see model and DFT calculation details in the ESI†). To be consistent with the experimental conditions, the DFT model structure simulated the Ir₄/MgAl₂O₄ catalyst after IrSubnano/MgAl₂O₄ reduction, and the optimized structure is shown in ESI Fig. S21.† Specifically, the initial state has an oxygen vacancy at the Ir–MgAl₂O₄ interface to model the vacancies generated during the IrSubnano/MgAl₂O₄ catalyst reduction at high temperature (700 °C). This can be explained by the presence of the Ir₄ cluster which lowers the average oxygen vacancy formation energy from 220 kJ mol⁻¹ to 174 kJ mol⁻¹ for nearby surface oxygens. Using this structure of Ir₄/MgAl₂O₄ after reduction, the DFT calculation results show an average adsorption energy of -254 kJ mol⁻¹ for CO (ESI Fig. S11†) and average initial adsorption energy of -529 kJ mol⁻¹ for O₂ (ESI Fig. S12†), which are very similar to the experimentally measured initial heats of adsorption of -207 and -515 kJ mol⁻¹ for CO and O₂, respectively. The agreement of heats of adsorption between experiments and DFT calculations indicate that the Ir₄ clusters provide a reasonable model for the IrSubnano/MgAl₂O₄ catalyst and will be used to provide insights on the CO oxidation mechanism. Fig. 2e shows a CO saturated Ir₄ cluster that represents the starting state after reduction followed by CO adsorption in the in situ experiments, including an oxygen vacancy at the Ir–MgAl₂O₄ interface as discussed above. Adsorption of O₂ is exothermic and O₂ gets activated between the vacancy and CO adsorbed on the closest Ir atom before they react to form CO₂ and fill the vacancy with a total reaction energy of -489 kJ mol⁻¹ for adsorption and reaction (Fig. 3e). Similar behavior was reported theoretically using DFT calculations where the interfacial Pt–O sites of Pt₁₀/Al₂O₃ were predicted to adsorb O₂ strongly and activate O₂ more readily than the non-interfacial Pt atoms.⁴³ The estimated barrier for CO₂ formation on the Ir₄ cluster is negligible, consistent with the CO₂ formation detected experimentally when the CO saturated catalyst was exposed to O₂ at room temperature (ESI Fig. S16 and S17†). This is expected due to the large exothermic reaction energy (-489 kJ mol⁻¹) for CO reacting with an O₂ that is readily activated upon adsorption. Lastly, re-adsorption of CO leaves the Ir₄ cluster saturated with CO similar to the initial structure, but with a filled oxygen vacancy at the interface. This oxygen reacts with CO adsorbed to a nearby Ir site, forming a CO₂ like structure that is bound strongly to the surface, similar to those reported by Thang et al.⁴⁴ on Pt₄/TiO₂ and Nie et al.¹¹ on Pt₁/CeO₂. This ends the room temperature reaction pathway as this structure requires ΔH of +137 kJ mol⁻¹ to desorb also in line with results from Thang et al. on Pt₄/TiO₂,⁴⁴ and consistent with our experiments where no further reaction was observed at room temperature. In agreement with the white line intensities from HERFD-XANES, the average DFT calculated Bader charges of the Ir₄ cluster at the same states

measured experimentally show that Ir gets partially oxidized upon exposure to O₂ (from +1.46e to +1.69e) then it does not get fully reduced (compared to the initial CO saturated cluster) when CO is re-adsorbed (+1.59e)

due to the filling of the oxygen vacancy. Figure 3: Probing the surface structure of

IrSubnano/MgAl₂O₄ under reaction condition. HERFD-XANES spectra of IrSubnano/MgAl₂O₄ (a) flowing CO (1 kPa) at room temperature after flowing O₂ (orange), then flowing CO (1 kPa) and O₂ (1 kPa) at room temperature, and then flowed CO (1 kPa) and O₂ (1 kPa) at 160 °C; (b) flow CO (1 kPa) only at 160 °C and in comparison with the CO + O₂ at 160 °C and the initial spectrum at room temperature in CO (after IrSubnano/MgAl₂O₄ reduction). (c) Proposed reaction cycle involving the lattice oxygen activation observed with IrSubnano/MgAl₂O₄ at 160 °C. In order to complete the reaction cycle, the oxygen vacancy at the Ir–MgAl₂O₄ interface needs to be regenerated by reaction with CO which did not occur at room temperature as the in situ DRIFTS and HERFD-XANES indicate. In situ/operando HERFD-XANES experiments were performed at 160 °C (same temperature used for kinetics measurements in Fig. 1) to determine the state of Ir under reaction conditions. The Ir L₃ HERFD-XANES spectra were almost unchanged during CO and O₂ co-flow at both room temperature and reaction temperature of 160 °C (Fig. 3a), which indicates that the state of Ir under reaction conditions is similar to the state where Ir is saturated with CO and the oxygen vacancies at the Ir–MgAl₂O₄ interface are filled (last structure in Fig. 2e). Furthermore, when the O₂ flow was stopped, a significant decrease in the white line intensity was observed and the HERFD-XANES spectrum was almost identical to the initial CO adsorption after IrSubnano/MgAl₂O₄ reduction (Fig. 3b). The results indicate that exposure to CO at the reaction temperature can regenerate the vacancies at the Ir–MgAl₂O₄ interface which was not possible at room temperature.

110 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO temperature (Fig. 2). Therefore, the results suggest that the rate limiting step involves a reaction between CO adsorbed on Ir and O* at the Ir–MgAl₂O₄ interface

which was also proposed to be rate limiting for CO oxidation on Au/TiSBA-15.45 Fig. 2e shows the final step containing a CO₂-like structure that is bound to the Ir₄ through the CO* and to the MgAl₂O₄ through the O*. This complex requires a high ΔH of +137 kJ mol⁻¹ to desorb thus making it kinetically similar to a reaction between an adsorbed CO*/Ir and O*/MgAl₂O₄ being rate limiting. Fig. 3c shows a proposed reaction cycle and the accompanied structural changes observed on IrSubnano/MgAl₂O₄ involving lattice O activation at the Ir–MgAl₂O₄ interface. The interfacial lattice O vacancy (i) is filled by O₂ adsorption and reaction with adsorbed CO on Ir to form CO₂ (ii). CO then adsorbs on (ii) and the resulting structure with a filled O vacancy (iii) is the most stable intermediate in CO + O₂ at both room temperature and 160 °C. The rate determining step involves

[the reaction between adsorbed CO and the interfacial lattice O in \(iii\) to regenerate the O](#)

vacancy (iv), which was observed when flowing CO in the absence of O₂ at 160 °C. The cycle is then complete by adsorption of CO on (iv). The steps for this two-site mechanism are written as elementary steps in Scheme 1. In this scheme, the rate determining step (RDS), step (4), is the reaction of a CO adsorbed on the Ir cluster with an O filled vacancy. We can eliminate the other steps as being rate determining as the reaction orders would be +1 in CO for step (1) being rate determining and +1 in O₂ for step (2) or (3) being rate determining. The DRIFTS and HERFD-XANES spectroscopy results in Fig. 2 and 3

[indicate that the iridium clusters are covered in CO under reaction conditions](#)

due to the strong Ir–CO binding (see Table 1). The high CO coverage observed experimentally on Ir justifies the approximation of setting the coverage equal to 1 in the model. Additionally, since the reaction of CO on Ir with O₂ adsorbed on a vacancy at the Ir-support interface is facile (Fig. 2), the O*₂ coverage can be neglected, making the O* the most abundant surface intermediate (MASI) for the support sites. These all combine to give the rate equation presented in Scheme 1 (derivation in the ESI†) which is consistent with the 0 order in CO and the partial positive order in O₂ measured experimentally and also consistent with the in situ/operando spectroscopy results in Fig. 2 and 3. Scheme 1: Elementary steps, site balances, and kinetic equations for the proposed reaction mechanism. Note: step (1) is exercised twice per mechanism cycle. The site balances have already included the assumptions that Ir is fully covered by CO and that O*₂ coverage is negligible as discussed in the text. Fig. 4 shows a scheme summarizing the proposed CO oxidation reaction mechanism on MgAl₂O₄ supported subnanometer clusters in comparison to previously reported mechanisms on Ir single atoms and nanoparticles. On IrSA/MgAl₂O₄, a previous study by our group showed that CO binds very strongly to Ir₁ (-230 kJ mol⁻¹) and forms an Ir(CO) active complex that promotes the O₂ activation at the Ir–MgAl₂O₄ interfacial site. A second gas phase CO

molecule then reacts with an interfacial surface O^* via an Eley–Rideal mechanism. In this work, our results strongly suggest that a similar interfacial O_2 activation is involved on $MgAl_2O_4$ supported subnanometer Ir clusters. Different from the Eley–Rideal mechanism observed on IrSA/ $MgAl_2O_4$, the reaction proceeds via a dual-site mechanism at the Ir– $MgAl_2O_4$ interface where CO from the Ir cluster reacts with O^* from the support. For the rate determining step on SA and subnanometer clusters, the preference for an adsorbed CO to react with the interfacial O^* as opposed to have a gas phase CO molecule on IrSA can be due to the availability of multiple CO molecules near the interface on the clusters (unlike one CO molecule for Ir1). In contrast, the number of interfacial sites is limited on larger nanoparticles and CO oxidation is dominated by the reaction on the Ir metal sites via a Langmuir–Hinshelwood reaction mechanism where O_2 activation proceeds on a vacant site assisted by CO adsorbed on a neighboring site. Therefore, despite the stronger CO adsorption on Ir subnanometer clusters, the support provides CO-free sites at the Ir– $MgAl_2O_4$ interface where O_2 activation can proceed while on nanoparticles all neighboring Ir sites are poisoned by CO. We note that our results demonstrate that the activity of Ir subnanometer clusters is mostly contributed by the metal-support interfacial sites and the non-interfacial sites are almost inactive. Therefore, a correction could be made for the TOF results shown Fig. 1d to normalize the TOF of Ir subnanometer clusters with the interfacial Ir sites instead of all the surface Ir sites. At 0.3 kPa CO and 10 kPa O_2 , the estimated TOF normalized to the interfacial sites of 0.77 nm subnanometer clusters is 6.2 and 8.6 times of the TOF of Ir NP and Ir SA, respectively (see ESI Table S5† for more details). Figure 4: Proposed reaction mechanisms

of CO oxidation on $MgAl_2O_4$ supported single atoms, subnanometer clusters and nanoparticles

. CO molecules that saturate the Ir subnanometer cluster and nanoparticle are not shown for simplicity. To put our results in perspective, we will first discuss CO oxidation on metal clusters and nanoparticles supported on reducible oxides. On reducible oxides, the interfacial

sites between the metal and the support play an important role in CO oxidation

by providing sites for O_2 adsorption and activation. For Pt/ CeO_2 (ref. 31, 41 and 46) and Pt/ TiO_2 ,⁴⁷ the lattice oxygen activation is facile and the reaction is dominated by the metal-support interfacial sites. For example, by varying the Pt size between 1.6–3 nm for Pt/ CeO_2 , Cargnello et al.

showed that the low-temperature CO oxidation reactivity scales with the number of interfacial sites.⁴⁸ Similarly for Pt/ TiO_2 , the TOF based on interfacial Pt atoms is independent of Pt particle size between 1–10 nm.⁴⁷ On the other hand, in the subnanometer regime (<1 nm), significant promotion of O_2 activation at the Rh– TiO_2 interface was reported, where 0.4–0.8 nm Rh clusters showed better CO oxidation performance than the single atoms and nanoparticles.²⁴ The reports on reducible metal oxide supports further show the significance of our work on $MgAl_2O_4$.

Traditionally, $MgAl_2O_4$ is considered a non-reducible support and CO oxidation proceeds only on the metal sites of the supported nanoparticles.

Our results are consistent with this definition when $MgAl_2O_4$ is used to support Ir metal nanoparticles (>1 nm). However, we show that by decreasing the Ir size in the subnanometer regime, the strong interaction between $MgAl_2O_4$ and Ir single atoms and subnanometer clusters activates the interfacial lattice oxygens similar to a reducible oxide. More importantly, the activation of interfacial lattice oxygens provides new, more efficient CO oxidation pathway compared to nanoparticles where the rate is limited by O_2 activation on a CO poisoned surface. Additionally, despite the similarity in lattice oxygen being involved in CO oxidation on Ir single atoms and subnanometer clusters, we show that the metal nuclearity has a strong effect on the mechanism and activity. Specifically, increasing the metal nuclearity from single atoms to subnanometer clusters resulted in the mechanism changing from Eley–Rideal/Mars–van Krevelen to a dual-site Langmuir–Hinshelwood/Mars–van Krevelen mechanism. Notably, the change in mechanism

from single atoms, to subnanometer clusters, to nanoparticles, leads to

a volcano-type dependence with the Ir subnanometer clusters being the most active. Furthermore, due to the different mechanism in the subnanometer regime, the initial CO binding energy fails to predict the activity of the catalysts. Therefore, our work shows that the change in mechanism in the subnanometer regime on metal supported catalysts provides

opportunities to escape traditional reactivity descriptors and design more active metal catalysts. Conclusions Our work

demonstrates that on a traditionally non-reducible oxide, decreasing the size of the metal into the subnanometer regime results in the emergence of properties similar to reducible oxides. Using advanced in situ/operando characterization complemented by DFT calculations we show that the Ir–O interfacial sites of $MgAl_2O_4$ supported Ir subnanometer clusters (0.6–0.8 nm) participate in efficient CO oxidation and O_2 activation leading to en-

hanced activity compared with Ir nanoparticles (1–1.5 nm). Furthermore, detailed kinetic measurements reveal that the reaction mechanism for CO oxidation in the subnanometer regime is intrinsically different from that on nanoparticles and is strongly dependent on the metal nuclearity. While Ir single atoms are more active than nanoparticles due to their ability to activate interfacial O*, increasing the metal nuclearity in the subnanometer regime resulted in a change in the mechanism from Eley–Rideal to a dual-site Langmuir–Hinshelwood mechanism and enhanced activity. We show that the change in the reaction mechanism as a function of Ir nuclearity leads to a volcano-type dependence of the CO oxidation reactivity on MgAl₂O₄, a traditionally non-reducible oxide. Experimental section Synthesis and pretreatment Two subnanometer clusters catalysts were prepared using different precursors. The first Ir/MgAl₂O₄ subnanometer clusters catalyst (0.05 wt%, denoted as IrSubnano/MgAl₂O₄) was prepared by wet impregnation using Ir nitrate. The MgAl₂O₄ support (Puralox MG 30, Sasol) was calcined at 500 °C for 4 h before impregnation. 200 mL DI water was added to a Pyrex bottle and the pH was adjusted with nitric acid to 2.8. Proper amount of the Ir nitrate precursor (8.7 wt% Ir, Furuya Metal Co. Ltd) was added into the pH adjusted solution. 5 g of the MgAl₂O₄ support was then added into the solution while stirring for 2 h. The final pH of the solution was 9.5. The solution was filtered out, and the solid sample was dried in air for 24 h at room temperature. The sample was then dried at 80 °C (0.5 °C min⁻¹) for 4 h and 100 °C (0.5 °C min⁻¹) for 4 h before calcination at 500 °C for 4 h with a ramp rate of 5 °C min⁻¹. The Ir in the solution after filtration was measured by inductively coupled plasma atomic emission spectroscopy and no Ir was detected. The sample was pretreated in 20 kPa IrSubnano/MgAl₂O₄ in situ (80 sccm total) at 700 °C for 2 h and cooled down to room temperature in the same gas. The second Ir/MgAl₂O₄ subnanometer clusters catalyst (0.1 wt%, denoted as IrSubnano Ir₄/MgAl₂O₄) was prepared by wet impregnation using Ir₄(CO)₁₂. Proper amount Ir₄(CO)₁₂ (Sigma Aldrich) precursor was dissolved in 16 mL of toluene (Sigma Aldrich) in a 20 mL vial while flowing N₂ at room temperature. Then the dissolved Ir₄(CO)₁₂ toluene solution was injected into another vial containing 5 g MgAl₂O₄ (Puralox MG 28, Sasol) under N₂ flow. The sample was then dried under N₂ flow at room temperature overnight to evaporate the toluene. No calcination was performed on this catalyst. The CO and acac ligands were removed in situ by treatment in He at 400 °C (10 °C min⁻¹) and then IrSubnano/MgAl₂O₄ at 200 °C which led to the formation of subnanometer clusters. The 2% Ir/γ-Al₂O₃ (Ir nanoparticle sample, NP, average size 5–12 nm, denoted as IrNP/γ-Al₂O₃) was synthesized by incipient wetness impregnation. Ir nitrate (8.7 wt% Ir, Furuya Metal CO. Ltd) in aqueous solution was used as precursor and was diluted to achieve a final Ir weight loading of 2%. The Al₂O₃ support (Puralox TH 100/150, Sasol) was calcined at 550 °C for 4 h before impregnation. After impregnation at room temperature for 24 h, the 2% Ir/γ-Al₂O₃ sample was dried at 80 °C for 12 h with a slow ramp rate of 0.5 °C min⁻¹ followed by heating to 100 °C (at 0.5 °C min⁻¹) and dwelling for 4 h. The dried sample was then calcined at 500 °C in air for 4 h (5 °C min⁻¹). The preparation of the IrSA/MgAl₂O₄ and IrNP/MgAl₂O₄ were reported in our previous work.¹⁹ 116 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO

High energy resolution fluorescence detected-X-ray absorption near energy spectroscopy

(HERFD-XANES) HERFD-XANES measurements were collected at beam line 6-2 at the Stanford Synchrotron Radiation Light Source (SSRL). A liquid-nitrogen-cooled double-crystal Si(311) monochromator was equipped to select the energy of the incident beam with a flux of 3×10^{12} photons s⁻¹. A Rowland circle spectrometer (radius 1 m) equipped with three spherically bent Si(800) analyzers and a silicon drift detector was used to select the Ir L_α (9175 eV) emission line with a measured resolution of 1.3 eV. An iridium foil was scanned in the transmission mode for initial energy calibration. Each sample (120 mg in mass, 25–90 microns) was loaded into a packed bed flow reactor. The catalysts were characterized by in situ XAS at the Ir L₃-edge (11215 eV) using an in-house built cell⁴⁹ with a 4 mm ID glassy carbon tube connected to the gas line using graphite ferrules and heated by a stainless-steel heating block equipped with four 100 W heating cartridges (Watlow). The in situ reactor assembly was protected from oxidation by an air-free box with polyimide film X-rays windows and continuous He or N₂ flow. Two type-K thermocouples were used to monitor and control the heating block and the catalytic bed temperature. A portable gas delivery system equipped with 5 MFCs (Brooks – SLA5800) was used to control the gas flow. The composition of effluent gases was measured by an online quadrupole mass spectrometer (Hiden HPR20). Samples were pretreated the

same as the previous section.

All HERFD-XANES spectra were measured within 2 min and three to six scans were averaged to improve signal-to-noise ratio. The analysis of the HERFD-XANES data was carried out with the software Athena of the Demeter package .50,51 The edge, determined by the first inflection point of the absorption edge of the Ir foil, was calibrated to the reported Ir L3 energy , 11215 eV. This calibration was used to calibrate a known glitch in the monochromator observed in the I0 signal of each scan. A least-squares Gaussian fit of the glitch, determined the error in the energy calibration of the samples to be 0.022 eV. Energy calibration was achieved by aligning the glitch in each scan to the glitch in the Ir foil reference scans. Three to six scans per sample were averaged with the averaged spectra being used for deglitching and normalization. The averaged spectrum was processed by fitting a second- order polynomial to the pre-edge region and subtracting this from the entire spectrum. Edge energy was determined by the first derivative of the normalized absorbance. The data were normalized by dividing the absorption intensity by the height of the absorption edge

Extended X-ray absorption fine structure (EXAFS) In situ XAS measurements at Ir

L3 (11215 eV) edge was

performed at the Stanford Syn- chrotron Radiation Light Source (SSRL) beam line 9-3 in fluorescence mode

at the Ir L3-edge (11215 eV) using an in-house built cell with a 4 mm ID glassy carbon

tube16,17 Beam line

9-3 is a 16-pole, 2 Tesla wiggler side station with vertically collimating mirror for harmonic rejection and a cylindrically bent mirror for focusing. The photon energy was selected using a liquid-nitrogen-cooled, double-crystal Si (220) $\phi = 90^\circ$ monochromator. Samples were scanned simultaneously in transmission and fluorescence detection modes using ion chambers (I0 filled with N2 and

I1 and Iref filled with Ar) and

a 100-element solid-state Ge monolith detector (Canberra), respectively. An Ir standard (Ir black powder) was scanned simultaneously with each sample for energy calibration. Step-scanning X-ray absorption spectra were measured from up to

photoelectron wavenumber k of 14

\AA^{-1} . The catalysts were pre- treated similar to before the catalytic measurements, then cooled to room temperature in pure IrSubnano/MgAl2O4 flow (50 sccm) and the extended X-ray absorption fine structure (EXAFS) spectra were collected at room temperature under pure IrSubnano/MgAl2O4 flow

XANES and EXAFS data processing and analysis were performed using Athena and Artemis programs of the Demeter data analysis package

.18,19 Nine

scans were collected and merged after alignment. $\chi(k)$ was obtained by subtracting smooth atomic background from the normalized absorption coefficient using the AUTOBK code. The theoretical EXAFS signal was constructed using the FEFF6 code20 and fitted to the data in R-space using the Artemis

118 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO program. For modeling the Ir-Ir scattering, an fcc crystal structure with a lattice constant of 3.92 \AA was used. The Ir-Al/Mg, Ir-O, Ir-C, Ir-O(CO) scattering paths were simulated from density functional theory calculated structure of CO adsorbed on Ir on the (211) step site.9 The theoretical EXAFS scattering paths were fit to the data in R-space using the Artemis program of the Demeter package. The spectra were fit by varying the coordination number of the single scattering Ir-O, Ir-C, Ir-O(CO), Ir-Ir and Ir-Al/Mg paths, the bond length disorder (σ^2), and the effective scattering lengths for each path and the correction to the threshold energy, ΔE_0 (except for Ir-Ir, ΔE_0 was the same for all scattering paths since they are calculated from one FEFF calculation on the same structure). The double (O-C-Ir, degeneracy = 2) and triple (C-O-C-Ir, degeneracy = 1) scattering paths of Ir-C-O were included in the model using the same scattering length and σ^2 as Ir-O(CO) and therefore did not add any extra parameters to the model. S02 (the passive electron reduction factor) was obtained by first analyzing the spectrum for an Ir black, and the best fit value (0.83) was fixed during the fitting. The k-range used for Fourier-transform of the $\chi(k)$ was 2.6–12.5 \AA^{-1} and the R-range for fitting was 1.1–2.9 \AA . The best parameters fit using k-weight of 1,2,3 are reported.

We note that the spectra under the different conditions were fit simultaneously with shared common parameters (i.e. ΔE_0 for the same paths) to minimize the fit uncertainty. Diffuse-reflectance infrared Fourier-transform spectroscopy DRIFTS was used to characterize the interaction of the supported Ir catalysts with CO. The in situ DRIFTS experiments were performed using a Thermo Scientific IS-50R Fourier-transform infrared spectrometer (FTIR) equipped with an MCT/A detector. A spectral resolution of 4 cm^{-1} was used to collect spectra, which are reported in the Kubelka–Munk (KM) units. Approximately 50 mg sample (25–90 μm diameter particles) was loaded in the Harrick Praying Mantis high-temperature DRIFTS reaction chamber. The chamber was sealed and connected to a flow system with temperature control, and gases were flown through the sample at atmospheric pressure. Each reported spectrum is an average of 32 scans. The supported Ir samples were pretreated in situ in the DRIFTS cell before collecting the spectra. The gas pretreatment procedure was the same as mentioned above. A spectrum under N_2 after the pretreatment was collected as the background for each catalyst. Microcalorimetry was performed on a Setaram SENSYS Evo DSC calorimeter with a self-built fork-shape sample tube. The forked sample tube was connected to a Micromeritics 3Flex for the adsorption quantity measurement and temperature control. 70 mg catalyst was put in on side of the forked reactor each time, while the other side was used as the reference in the calorimeter. The gas pretreatment procedure was the same as mentioned above. After pretreatment, the samples were exposed to ultra-high vacuum (UHV) with pressure below 10⁻⁵ mm Hg. For the first set of doses, adsorption heat of both chemisorption and physisorption CO/O_2 was measured. The CO/O_2 adsorption experiments were measured at 30 °C with pressure between 0–300 mm Hg for O_2 calorimetry and 0–20 mm Hg for CO calorimetry. Scanning transmission electron microscopy Aberration-corrected electron microscopy images for Ir/MgAl₂O₄ samples were taken on FEI TITAN 80-300 in STEM mode using a high angle annular dark field (HAADF) detector. The resolution is 0.1 nm, with the CEOS GmbH double-hexapole aberration corrector. To calculate the atomic percentage from multiple STEM images, the number of atoms per particle (N) was estimated with a hemispherical model: $18,52 \pi D^3 \rho N_A N = 6M_w$ (1)

where D is the nanoparticle diameter, ρ is the bulk metal density, N_A is Avogadro's number, and M_w is the metal molecular weight. X-ray diffraction (XRD) was performed on fine powdered samples of the indicated pre-treatment. XRD was performed on a Bruker D2 PHASER operating at 30 kV and 10 mA. The radiation source was a Cu filament at the $K\alpha$ edge ($\lambda = 1.54184 \text{ \AA}$). The samples were measured from 20° to 80° (2 θ) with a step size of 0.1° and a dwell time of 1 s at each step. CO oxidation kinetic measurements were performed under differential conditions (<3% conversion) in a conventional laboratory tubular plug flow reactor (7 mm ID quartz tube). Dilution experiments were performed according to Koros–Nowak test to determine the necessary dilution ratio for measurements under strict kinetic control without mass and heat transfer effects.^{53–55} The catalysts (after intraparticle dilution) were pressed and sieved into a 106–250 μm diameter fraction. The dilution ratio test to eliminate transport limitations was performed on IrNP/MgAl₂O₄ (1 wt%) using SiO₂ (silica gel, for chromatography, 0.075–0.250 mm particle size and 150 Å pore size) calcined at 850 °C as the diluent. Intraparticle dilutions ratio of 1:40, 1:200 and 1:1000 showed no difference in activity under different CO and O₂ conditions between 145 °C and 170 °C, which indicates the measured catalytic activity were evaluated under kinetic control without transport artifacts. Based on the dilution test, the IrNP/MgAl₂O₄ (0.2 wt%) was diluted with silica at a 1:20 ratio, and the IrSA+NP/MgAl₂O₄ (1 wt%) and IrNP/MgAl₂O₄ (1 wt%) were diluted with silica at a 1:40 ratio, and the IrSA/MgAl₂O₄ and the IrSubnano/MgAl₂O₄ required no dilution because of the low Ir loading. 0.2–0.6 g of each catalyst (including dilution) was loaded in the reactor to keep the conversion below 3% under all conditions measured. The total flow rate during the measurements was between 75–100 sccm. Negligible activity ($\sim 1/10$ activity of the lowest loading catalyst, 0.0025 wt%, sample 4) was measured on the ceMgAl₂O₄ support compared to all the catalysts. Each catalyst pretreatment was the same as mentioned above, and the total flow rate during pretreatment was kept at 80 sccm. The catalyst temperature was measured by a K-type thermocouple (OMEGA) attached at the center of the catalyst bed on the outside of the tube. After pretreatment, CO (5%, balance N₂, certified grade Airgas) was mixed with pure O₂ (99.999% Airgas) and He (99.999% Airgas, equipped with moisture/O₂ trap, Agilent OT3-2) at 35 °C to control the partial pressures of CO and O₂ (by varying their flowrates using Brooks mass flow controllers SLA5800 series). The CO gas line was equipped with a metal carbonyl purifier (Matheson, NanoChem Metal-X) to remove the trace amount of metal carbonyl and a molecular sieve 3A (8–12 mesh) trap to remove trace (ppm) levels of CO₂. No CO₂ (above baseline level in He) was detected in the mass spectrometer with the CO or O₂ flowing during a blank test. The reactor was heated from room temperature to the reaction

temperature at 3 °C min⁻¹ in 0.5 kPa CO and 10 kPa O₂ balanced with He. During the steady state kinetic measurements, the conversion of CO was always below 3% by varying the total flow rate between 75–100 sccm. To investigate the effect of CO partial pressure on reaction rate, the partial pressure of O₂ was held constant at 10 (or 2) kPa and the partial pressure of CO was varied between 0.2–1.0 kPa. To investigate the effect of O₂ partial pressure, the CO partial pressure was held constant at 0.2 kPa and the partial pressure of O₂ was varied between 2–14 kPa. To investigate the effect of temperature and measure the apparent activation energy, the CO and O₂ partial pressures were kept at 1 kPa and 10 kPa, respectively. The temperature was varied between 145–160 °C. The kinetic experiments were reproduced using two different aliquots from the same batch and also reproduced using two different batches of catalyst. We note that we rigorously monitored the catalyst stability by re-measuring the catalyst activity periodically throughout the experiment under the first condition measured. The activity was stable (<10% deactivation) for each catalyst tested during the entire kinetic measurement. The composition of the effluent gases was measured by a gas chromatograph, Inficon Micro GC Fusion with two modules each with a separate carrier gas, injector, column and thermal conductivity detector (TCD). Column A: Rt-Molsieve 5A, 0.25 mm ID (10 m) using Ar as carrier gas. Column B: Rt-Q-Bond 0.25 mm ID (12 m) using He as carrier gas. Calculation of Ir dispersion and turnover frequency (TOF) Ir dispersion is defined as the ratio of surface Ir sites to total Ir atoms in the catalyst. Ir dispersion could be calculated by the following equation: Surface Ir sites (mol) Ir dispersion = Total Ir sites (mol) (2). Dispersion of Ir in the IrSA/MgAl₂O₄, IrSubnano/MgAl₂O₄ and IrNP/MgAl₂O₄ catalysts was calculated based on the volumetric CO chemisorption measurements and the Ir loading. To convert the measured CO uptake from chemisorption to Ir sites, we used CO:Ir ratio. The CO:Ir for IrSA/MgAl₂O₄ is 2:1 based on the dicarbonyl (Ir(CO)₂) configuration. The CO:Ir for IrSubnano/MgAl₂O₄ or IrNP/MgAl₂O₄ is both assumed as 1:1 based on the adsorption configuration. Based on the volumetric CO adsorption results (ESI Table S4†) and the above CO to Ir ratios, the dispersion of the IrSA/MgAl₂O₄, IrSubnano/MgAl₂O₄ and IrNP/MgAl₂O₄ catalysts is 100%, 90% and 90%. TOF is defined as the number of molecules reacted at each available surface site per unit time. TOF(s⁻¹) = Reaction rate per g catalyst(mol s⁻¹ g⁻¹) (3) Molar concentration of surface Ir per g catalyst(mol g⁻¹). Molar concentration of surface Ir per g catalyst (mol g⁻¹) is obtained from the volumetric CO adsorption measurement by measuring the molar of CO per g catalyst and using the CO:surface Ir ratio mentioned above. Molar concentration of surface Ir per g catalyst(mol g⁻¹) = CO adsorbed per g of catalyst(mol g⁻¹) CO:surface Ir (4)

Computational details DFT calculations were performed using the CP2K computational code

.56–61 The generalized gradient approximation parameterized by the spin-polarized Perdew–Burke–Ernzerhof (PBE) functional was used to treat the exchange–correlation potential.62–66 All elements used the double ζ valence polarized Gaussian basis sets with an auxiliary plane-wave basis set with a cutoff energy of 480 Ry with Goedecker–Teter–Hutter potentials used for the core electrons.67,68 The calculations consist of only gamma point sampling. The DFT-D3 van der Waals correction was applied.69 In

geometry optimizations, 70 the forces were converged to 4.5×10^{-4} Hartree Bohr⁻¹.

Bader charge analysis was calculated using the Bader Charge Analysis code from the Henkelman group.71–74 Enthalpies were approximated as the DFT energetics reported in CP2K. In order to compensate for the known O₂ over-binding from PBE functional, the gas phase energy of O₂ was increased by 0.75 eV.19 Optimized spinel bulk calculations and surface calculations were taken from previous work19,75 and were used to determine lattice constants and surface terminations respectively. Those previous results showed that the (111) O₂(Al) terminated spinel surface was the most stable under a wide variety of conditions and was thus chosen. The slabs (ESI Fig. S1a†) were composed of 2 unit cells in the two surface lattice directions and 3 unit cells in the dimension perpendicular to the surface. The bottom two layers of the slab were then fixed to reduce computational time and simulate bulk behavior. 15 Å of vacuum separated the slabs, as this is a periodic calculation. Different geometries of four iridium atom clusters were placed on the (111) spinel surface, including the square planar geometry.76 The most energetically favorable was the near 124 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY

VOLCANO tetrahedral configuration with three iridium atoms bound to the surface.^{77,78} ESI Fig. S21a† was chosen to be our representative Ir₄ cluster. With a representative Ir₄ cluster established, we began investigating the effects this would have on the surface termination, specifically number of surface oxygens. The addition of the Ir₄ cluster lead to a decrease in the average oxygen vacancy formation energy from 220 to 174 kJ mol⁻¹ for the O* around the cluster. We define “the O* around the Ir₄ cluster” as all surface O in the model. Since the cluster is in a periodic unit cell, this equates to approximately all O within ~4.7 angstroms from an Ir atom. In order to investigate the proper surface termination to use, we calculated the surface vacancy formation energy of each O and removed a single O at a time until all surface O had a vacancy formation energy of 1 eV or more. This was done to simulate the reducing environment the catalyst was exposed to. The O’s removed are those highlighted in ESI Fig. S21b.† To calculate the initial binding energies of O₂ on Ir₄, different combinations of 2 O species were added individually to the iridium cluster (ESI Fig. S12†). We calculated the dissociative binding energy to be -529 kJ mol⁻¹ O₂. This compares favorably to the -480 to -550 kJ mol⁻¹ observed from experiments for the initial binding energy of oxygen. Similarly, CO was added to the cluster in various amounts (1–4 molecules at a time) until saturated to represent a CO covered cluster (ESI Fig. S4†). The average binding energy for CO was -254 kJ mol⁻¹. The resulting CO covered structure is similar in structure to a distorted Ir₄(CO)₁₂ organometallic species⁷⁹ but with three CO molecules replaced with surface bonds (ESI Fig. S11†). With the CO covered Ir₄ cluster established as our model after reduction and CO dosing, we probed the surface oxygen vacancies again to see if any oxygens would be removed after the addition of the CO. All Os were found to have a vacancy formation energy of at least 1 eV, the cut-off we considered. The average surface vacancy formation energy for the oxygen species increased from 339 kJ mol⁻¹ to 419 kJ mol⁻¹ from the addition of the COs.

Conflicts of interest There are no conflicts to declare. Acknowledgements

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computational resource used in this work is provided by the advanced research computing at Virginia Polytechnic Institute and State University . 134 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO 76. M. Tayyem, B. Hamad and B. Paulus, Chem. Phys., 2017, 495, 10-15. 77. V. Stevanović, Ž. Šljivančanin and A. Baldereschi, J. Phys. Chem. C, 2010, 114, 15653-15660. 78. F. S. Lai and B. C. Gates, Nano Lett., 2001, 1, 583-587. 79. M. R. Churchill and J. P. Hutchinson, Inorg. Chem., 1978, 17, 3528-3535. Footnotes † Electronic supplementary information (ESI) available: Size distribution of Ir samples, details of EXAFS modeling, details of reaction kinetic measurements, CO microcalorimetry results, DFT optimized structures. See DOI: 10.1039/d1ta09740g ‡

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2022 Supplementary Information CO oxidation on MgAl₂O₄ supported Irn:

Activation of lattice oxygen in the subnanometer regime and emergence of nuclearity-activity volcano Yubing Lu ,[‡]a Coogan Thompson ,[‡]a Chun-Te Kuo ,^a Xiwen Zhang ,^a Adam S. Hoffman ,^b Alexey Boubnov ,^b Simon R. Bare ,^b Libor Kovarik ,^c Hongliang Xin ,^a Ayman M. Karim
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USA [‡] These authors contributed equally *E-mail: amkarim@vt.edu 136 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO Table S1. Atomic percentage size distribution of two catalysts containing Ir subnanometer clusters, IrSubnano/MgAl₂O₄ and IrSubnano_Ir₄/MgAl₂O₄. Sample 0.1-0.3 nm 0.

3-0.5 nm 0.5-0.7 nm 0.7-0.9 nm

0.9-1 nm IrSubnano/MgAl₂O₄ before reaction IrSubnano/MgAl₂O₄ after reaction IrSubnano_Ir₄/MgAl₂O₄ before reaction 28% 6% 30% 29% 7%

25% 2% 31% 32% 10% 13% 24% 44% 21% 0% Table S2. Size distribution of MgAl₂O₄ supported Ir samples measured from STEM. Sample Ir weight Percentage of 0.3-0.7 nm 0.7-1 nm > 1nm Major species Loading single atoms (SA) IrSubnano/MgAl₂O₄ 0.05% 28% 36% 36% 0%

IrSubnano_Ir₄/MgAl₂O₄ 0.1% 13% 68% 21% 0% IrNP /MgAl₂O₄ 0.2% 2% 0% 22% 76% IrSA/MgAl₂O₄ 0.0025% ~100% 0% 0% 0%

IrSA+NP/MgAl₂O₄ 1% 35% 1% 18% 46% IrNP/MgAl₂O₄ (1wt.%) 1% 16% 0% 7% 77% Subnano Subnano NP SA SA+NP Mostly NP 138

SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO Table S3. Summary of

EXAFS modeling of IrSubnano/MgAl₂O₄ catalysts under different conditions. Sample Ir subnano Ir subnano H₂ 30 °C CO 30 °C Ir subnano CO 160

°C Ir subnano O₂ 30 °C Ir NP He 30 °C 1 NIr-Ir NIr-C 3.5±1.3 3.3±1.8 0.6±0.5 3.3±1.8 0.6±0.5 2.7±1.9 – a 6.6±0.4 NIr-O 3.2±0.5 3.3±0.6 3.3±0.6

4.1±0.6 0.2±0.1 NIr-Al/Mg 3.9±0.9 3.8±0.8 3.8±0.8 3.4±1.0 0.2±0.1 RIr-Ir (Å) 2.65±0.01 2.66±0.05 2.64±0.06 2.62±0.03 2.689±0.002 RIr-C (Å)

1.88±0.1 1.95±0.1 RIr-O(CO) (Å) 3.04±0.1 3.08±0.1 RIr-O (Å) 2.04±0.01 2.06±0.02 2.07±0.02 2.02±0.01 2.06±0.04 RIr-Al/Mg (Å) 2.95±0.01

2.95±0.04 2.94±0.05 2.94±0.02 2.93±0.04 σ₂Ir-Ir × 10³ (Å²) 5±3 6±5 8±7 9±9 5.8±0.3 σ₂Ir-C × 10³ (Å²) 0±9 0±9 σ₂Ir-O(CO) × 10³ (Å²) 2±10

3±10 σ₂Ir-O × 10³ (Å²) 4±2 3±3 1±1 3±2 1±7 σ₂Ir-Al/Mg × 10³ (Å²) 3±6 2±4 1±4 2±4 0±5 ΔE₀ Ir-Ir (eV) 1±7 1±7 1±7 1±7 7.0±0.7 ΔE₀ Ir-C (eV)

8±4 8±4 ΔE₀ Ir-O (eV) 8±4 8±4 8±4 8±4 10±5 ΔE₀ Ir-Al/Mg (eV) 8±4 8±4 8±4 8±4 10±5 Reduced χ² 103 103 103 103 16 R-factor 0.0039 0.0039

0.0039 0.0039 0.0003 a The fit was not reliable with scattering paths for Ir-CO. However, CO was observed in DRIFTS (Figure 2 in the manuscript)

Notation: N, coordination number of absorber-backscatterer pair; R, radial absorber-backscatterer distance ; σ₂, the mean square displacement of the half-path length and represents the stiffness of the bond for a single scattering path, ΔE₀, correction to the threshold energy

. Table S4. CO volumetric chemisorption on different samples. Sample Ir weight loading Gas Qty. adsorbed μmol/g Gas:Ir IrSubnano/MgAl₂O₄

0.05% IrNP /MgAl₂O₄ 0.2% IrSA+NP/MgAl₂O₄ 1% Ir/MgAl₂O₄ IrNP/MgAl₂O₄ (1wt.%) 1% Ir/MgAl₂O₄ CO 2.38 CO 9.4 CO 72.3 CO 53 CO:Ir

= 0.9:1 CO:Ir = 0.9:1 CO:Ir = 1.4:1 CO:Ir = 1:1 140

SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO Table S5. TOF of

Ir catalysts with different ways of active site normalization. Sample Active site Active Ir/surface Ir TOF (normalized with surface Ir)a TOF

(normalized with the active Ir)a Ir NP Surface Ir site 1:1 ~ 0.53:1b 1.75 1.75 Ir subnano Interfacial site 5.74 9.33 Ir SA Ir atom 1:1 1.26 1.26 a.

measurement condition: 0.3 kPa CO, 10 kPa O₂, at 155 °C. b. The active site is estimated based on a hemispherical Ir cluster model with a 0.77 nm

radius. The cluster has 14 atoms in total, 13 surface Ir atoms, and 8 perimeter Ir atom at the Ir-MgAl₂O₄ interface. The ratio of active Ir (i.e.

interfacial/perimeter Ir) to surface Ir sites is estimated as 0.62:1. a b nm Figure S1. HAADF-STEM images of the IrSubnano_Ir₄/MgAl₂O₄.

Histogram obtained from multiple images is shown in (a). 142 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY

VOLCANO Fig. S2. XRD for the samples in this work. The support (MgAl₂O₄) was calcined at 500 °C as described in the synthesis section. The

preparation of the IrSA/MgAl₂O₄ and IrNP/MgAl₂O₄ were reported in our previous work.¹⁹ The preparation of the Irsubnano/MgAl₂O₄ is

described in the synthesis section. The calcined sample was taken after the ex-situ calcination while the reduced sample was taken after ex-situ

reduction (700 °C in H₂ followed by exposure to air). The peak at $2\theta = 50^\circ$ is a background peak from the sample compartment/holder. Figure S3. Ir L₃-edge X-ray absorption spectroscopy k-space data measured on IrSubnano/MgAl₂O₄ after H₂ pretreatment, IrNP/MgAl₂O₄ after H₂ pretreatment and Ir foil. 144 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO a b Figure S4. Ir L₃-edge Fourier transformed EXAFS spectra and fit of IrSubnano/MgAl₂O₄ after H₂ pretreatment. (

a) magnitude and (b) imaginary part of the Fourier transformed k^2 - weighted $\chi(k)$ data ($Dk = 2.5-12 \text{ \AA}^{-1}$

) ($Dk = 2.7-16 \text{ \AA}^{-1}$). The r-range for the fit was 1.3-3.0 Å a b Figure S5. EXAFS fit to IrSubnano/MgAl₂O₄ after H₂ pretreatment. Contribution of different scattering paths. (Ir path = Ir-Ir; O path = Ir-O; Al path = Ir-Al) (a) R space magnitude and (b) R space imaginary. 146 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO Figure S6. Ir L₃-edge X-ray absorption near edge spectroscopy characterizing IrSubnano/MgAl₂O₄, IrNP+SA/MgAl₂O₄ and IrNP/MgAl₂O₄ (1wt.%). Figure S7. Ir L₃-edge X-ray absorption near edge spectroscopy characterizing IrSA/MgAl₂O₄, Irsubnano/MgAl₂O₄, IrNP/MgAl₂O₄, and Ir references include Ir foil, IrO₂ and Ir₄CO₁₂. All three Ir/MgAl₂O₄ catalysts were measured after H₂ pretreatment. 148 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO a b Figure S8. Effect of (a) CO partial pressure and (b) O₂ partial pressure on turnover frequency (TOF) on IrSubnano/MgAl₂O₄ (blue), IrSA/MgAl₂O₄ (black)² and IrNP/MgAl₂O₄ (red)² (a) O₂ partial pressure = 10 kPa, CO partial pressure = 0.3-10 kPa. Measured at 155 °C. (b) O₂ partial pressure = 2-14 kPa, CO partial pressure = 1 kPa.

Measured at 155 °C . Figure S9. Effect of O₂ pressure on turnover frequency (TOF) on

IrSubnano/MgAl₂O₄ measured at two CO partial pressures: 1 and

0.2 kPa . O₂ partial pressure was varied between 2 -14 kPa

. Measured at 155 °C. 150 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO E_{app} : 72 kJ/mol Figure S10. Effect of temperature on turnover frequency (TOF) on IrSubnano/MgAl₂O₄. O₂ partial pressure was kept at 10 kPa, CO partial pressure was measured at 1 kPa. Measured between 143 - 160 °C. Figure S11. DFT optimized structures representing various levels of CO coverage: 0, 4, 8, and 9 COs. 9 CO is treated as full coverage. ΔE_{ads} is the average binding energy of the COs on the structure and q is the average Bader charge for the structures. 152

SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO Figure S12. Examples of

structures used to calculate the initial dissociative binding energy of O₂ on the Ir₄ cluster. a CO calorimetry b O₂ calorimetry Figure S13. CO (a) and O₂ (b) calorimetry of IrSubnano/MgAl₂O₄ and the IrNP/MgAl₂O₄ (1 wt.%). Measured at 30 °C for both CO and O₂ calorimetry. Differential heat (kJ mol⁻¹) in (a) and (b) is normalized by mol of CO and O₂ adsorbed, respectively. The coverage of 1 is defined as the point when the heat reached ~40 kJ/mol. 154 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO a CO calorimetry b O₂

calorimetry Figure S14. CO and O₂ calorimetry of three Ir catalysts with different particle sizes. IrNP/ γ -Al₂O₃ serves as a Ir standard with larger particle size. Representative TEM images of Ir nanoparticle in IrNP/ γ -Al₂O₃ with average size 5-12 nm is shown in Fig. S20. Differential heat (kJ mol⁻¹) is normalized with per mol of CO and O₂ adsorbed, respectively. The coverage of 1 is defined as the point when the heat reached ~40 kJ/mol. a CO calorimetry b O₂ calorimetry Figure S15. CO (a) and O₂ calorimetry of IrSubnano/MgAl₂O₄ repeated on two different batches. Measured at 30 °C for both CO and O₂ calorimetry. Mol of CO in (a) and mol of O in (b) are normalized with mol of surface Ir of the catalyst obtained with CO chemisorption. Differential heat (kJ mol⁻¹) is normalized with per mol of CO and O₂ adsorbed, respectively. The coverage of 1 is defined as the point when the heat reached ~40 kJ/mol. 156 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO a b Figure

S16. Mass spectrometry results of the gas concentration from the reactor effluent at 30 °C during EXAFS experiment on (a) IrSubnano/MgAl₂O₄ (b) IrSubnano_Ir₄/MgAl₂O₄. (a) Flowed 1 kPa and then 4 kPa CO, 4 kPa O₂, and 1kPa CO in sequence on IrSubnano/MgAl₂O₄. (b) Flowed 1 kPa CO, 4 kPa O₂, and 1 kPa CO in sequence on IrSubnano_Ir₄/MgAl₂O₄. 1691 Figure S17. In-situ DRIFTS spectra characterizing IrSubnano/MgAl₂O₄ during O₂ (1 kPa) flow at room temperature after pretreatment and CO chemisorption at room temperature. Spectra was collected every 1 min. 158

SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO a c IrSubnano/MgAl₂O₄ IrSubnano/MgAl₂O₄ b IrSubnano/MgAl₂O₄ Figure S18. Ir L₃-edge X-ray absorption spectroscopy of IrSubnano/MgAl₂O₄ under H₂/CO/O₂ flow at room temperature. (a)

XANES of IrSubnano/MgAl₂O₄ after H₂ pretreatment (20 kPa) and measured at room temperature, and then flow CO (1 kPa) at room temperature followed by O₂ (1kPa) at room temperature. (b) EXAFS magnitude of the Fourier transformed k₂-weighted $\chi(k)$ data measured on IrSubnano/MgAl₂O₄ after H₂ pretreatment (20 kPa) and measured at room temperature, and then flow CO (1 kPa) at room temperature followed by O₂ (1kPa) at room temperature. $Dk = 2.6-12.5 \text{ \AA}^{-1}$. (c) k-space data measured on IrSubnano/MgAl₂O₄ after H₂ pretreatment (20 kPa) and measured at room temperature, and then flow CO (1 kPa) at room temperature followed by O₂ (1kPa) at room temperature. a Before reaction 2 nm b After reaction 2 nm nm nm Figure S19. HAADF-STEM images of the IrSubnano_Ir₄/MgAl₂O₄ before and after the reaction. Histograms were obtained by measuring Ir clusters from multiple images. 160 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO a b IrSubnano/MgAl₂O₄ IrSubnano_Ir₄/MgAl₂O₄ c d CO RT Figure S20. HERFD-XANES at Ir L₃-edge characterizing IrSubnano/MgAl₂O₄, IrSubnano_Ir₄/MgAl₂O₄ and the Ir₄(CO)₁₂ standard. IrSubnano/MgAl₂O₄ and IrSubnano_Ir₄/MgAl₂O₄ represent MgAl₂O₄ supported Ir subnanometer clusters with different size distributions. See Table S1 for size distribution. (a) HERFD- XANES spectra of IrSubnano/MgAl₂O₄ after H₂ pretreatment and measured at room temperature (black), flowed CO (1 kPa) at room temperature (red), flowed O₂ (1 kPa) at room temperature (blue), and then flowed CO (1 kPa) at room temperature (orange). (b) HERFD-XANES spectra of IrSubnano/MgAl₂O₄ after H₂ pretreatment and measured at room temperature (black), flowed CO (1 kPa) at room temperature (red), flowed O₂ (1 kPa) at room temperature (blue), and then flowed CO (1 kPa) at room temperature (orange). (c) HERFD-XANES spectra of IrSubnano/MgAl₂O₄ after the first CO flow at room temperature as shown in a, IrSubnano_Ir₄/MgAl₂O₄ after the first CO flow at room temperature as shown in b, and the IrNP/ γ -Al₂O₃ sample with the average particle size between 5-8 nm. (d) HERFD-XANES spectra of IrSubnano_Ir₄/MgAl₂O₄ after the first CO flow at room temperature as shown in b, and Ir₄(CO)₁₂ standard. 162 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO Figure S21. (a) Most stable Ir₄ surface species on MgAl₂O₄ (111) before changes to surface termination were considered. Dark blue represents Ir. (b) Optimized surface structure for MgAl₂O₄ (111)_{2, 3} before the addition of Ir₄. The light blue Os in (b) were removed after the addition of the Ir₄ cluster (cluster not shown in (b) for clarity) as the Ir₄ cluster decreased the oxygen vacancy formation energy considerably (220 to 174 kJ/mol). The Os were chosen as their oxygen vacancy formation energy was below 1 eV. The surface energy was recalculated to arrive at the state used for the CO addition (Figure S9a). a b Figure S22. Representative TEM images of the IrNP/ γ -Al₂O₃ sample before and after the reaction. Histogram was obtained by measuring nanoparticles from multiple images. 164

SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO Derivation of

the rate equation Here we assume that the Ir(CO)* dominates the Ir clusters and O* dominates the interfacial support sites Steps: $k. CO(*) + Ir* \leftrightarrow Ir CO * k_0. k_1 O_1' + \# \leftrightarrow O_1\# k_01 Ir CO * + O_1\# 34 CO_1(*) + Ir* + O\# Ir CO * + O\# 35 CO_1(*) + Ir* + \#$ The equations: $Ir CO * + [Ir*] = 1 O_1\# + O\# + \# = 1 \partial Ir CO * \partial t = k.P \Rightarrow Ir* - k_0. Ir CO * - k@ Ir CO * O_1\# - kA Ir CO * O\# = 0 \partial \partial O_1\# = k_1P > C \# - k_01[O_1\#] - k@ Ir CO * O_1\# = 0 \partial O\# \partial t = k@ Ir CO * O_1\# - kA Ir CO * O\# = 0 rate = kA Ir CO * O\#$ We assume that the surface is fully covered by CO thus $[Ir CO *] = 1$.

Note that this assumption means $F GH \Rightarrow *$ we have no need for the FI term. Plugging in the Ir site balance: $Ir CO * + [Ir*] = 1 Ir CO * = 1 O_1\# + O\# + \# = 1 k_1P > C \# - k_01[O_1\#] - k@ O_1\# = 0 k@ O_1\# - kA O\# = 0 rate = kA O\#$ We also assume that the surface vacancy site is dominated by O*.

$O_1\# + O\# + \# = 1 O\# + \# = 1$ Solving for $O_1\#$ and plugging it in: $k@ O_1\# - kA O\# = 0 O_1\# k kA@ = O\# O\# + \# = 1 k_1P > C \# - k_01kA O\# - kA O\# = 0 k@ rate = kA O\#$ Solving for $O\#$ and plugging it in: $k_1P > C \# - k_01kA O\# - kA O\# = 0 k@ O\# = k_1P > C k_0k_1@kA + kA \# k_1P > C k_0k_1@kA + kA \# \# = 1 k_1P > C rate = k_01 + 1 k@ \#$ 166 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO Solving the surface site balance and plugging in: $k_1P > C \# + \# = 1 k_0k_1@kA + kA \# = 1 + k_0k_1k@k_1AP > + C kA rate = k_1P > C k_01 + 1 k@ 1 + k_1P > C k_0k_1@kA + kA k_1 P > C k_01 + 1 rate = k@ 1 + k_0k_1k@k_1AP > + C kA$ Simplifying the fractions: $rate = k_1k@kAP > C kA k_01 + k@ + k_1k@P > C$ This gives two regimes a positive order one (* dominant) and zero order (O* dominant).

zero order (O* dominant, LM3CCLJ5KC $\gg 1$) L 4 N35 positive order (* dominant, LM3CCLJ5KNC35 $\ll 1$) L 4 $k_1 P > C k_1 P > C rate = k k_0@1 + 1 1 + k_0k_1k@k_1AP > + C kA rate = k k_0@1 + 1 1 + k_0k_1k@k_1AP > + C kA k_1 P > C k_01 + 1 rate = k @ k_1P > C k_0k_1@kA + kA k_1 P > C rate = k k_0@1 + 1 1 rate = kA k_1k@ rate = k_01 + k@ P > C$ If the system is half covered: $O* = * k_1P > C k_0k_1@kA + kA = 1 \partial \ln(rate) P > C \partial (rate) O_1 order = \partial \ln P > C rate$

$\partial P > C = P > C \partial k_1 k @ k A P > C k_1 k @ k A P > C \partial P > C k A k_0 1 + k @ + k_1 k @ P > C k A k_0 1 + k @ + k_1 k @ P > C = k A k_0 1 + k @ + k_1 k @ P > C k A k_0 1 + k @ k A k_0 1 + k @ + k_1 k @ P > C 1 + k_1 k @ P > C - k_1 k @ P > C = k A k_0 1 + k @ k A k_0 1 + k @ + k_1 k @ P > C$ 168 SUBNANOMETER REGIME AND EMERGENCE OF NUCLEARITY-ACTIVITY VOLCANO Applying the half-covered condition: $k_1 P > C = 1 k_0 k_1 @ k A + k A k_1 k @ P > C = k A k_0 1 + k @ k A k_0 1 + k @ 0 1$ order = $k A k_0 1 + k @ + k A k_0 1 + k @ = 1$ 2 References 1. Y. Lu, C. Kuo, L. Kovarik, A. S. Hoffman, A. Boubnov, D. M. Driscoll, J. R. Morris, S. R. Bare and A. M. Karim, *J. Catal.*, 2019, 378, 121-130. 2. Y. Lu, J. Wang, L. Yu, L. Kovarik, X. Zhang, A. S. Hoffman, A. Gallo, S. R. Bare, D. Sokaras, T. Kroll, V. Dagle, H. Xin and A. M. Karim, *Nat. Catal.*, 2019, 2, 149-156. 3. Q. X. Cai, J. G. Wang, Y. Wang and D. H. Mei, *J. Phys. Chem. C*, 2016, 120, 19087-19096. Chapter 4 CO as a Non-exchanging Ligand for CO Oxidation on Ir/TiO₂ Single Atom Catalysts This work is not yet published. We currently are incorporating these results with computational (DFT) results. In this work I performed all of the synthesis, DRIFTS, kinetic measurements, and derivations (that are not related to the DFT that will be added before publication). I was also the lead for the XAS experiments and performed many of them myself. 169 CHAPTER 4. CO AS A NON-EXCHANGING LIGAND FOR CO OXIDATION ON IR/TIO₂ SINGLE ATOM 170 CATALYSTS CO as a Non-exchanging Ligand for CO Oxidation on Ir/TiO₂ Single Atom Catalysts Coogan B. Thompson,† Denis S. Leshchev,‡ Adam S. Hoffman,¶ Jiyun Hong,¶ Simon R. Bare,¶ Raymond R. Unocic,§ Eli Stavitski,‡ and Ayman M. Karim*,† †Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24060

, USA ‡National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973, USA ¶Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA §Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA E-mail: *amkarim@vt.edu Abstract One major advantage of homogeneous catalysts compared to heterogeneous catalysts is the use and availability of ligands as part of the active catalytic site. Ligands were shown to have many uses in heterogeneous catalysis, however their use has been limited largely to the synthesis. Here we present the unusual case of a heterogeneous, single atom catalyst that uses one of the reactants as a fixed ligand as part of its active state. Specifically, we show that for the Ir/TiO₂ single atom catalyst the CO oxidation reaction mechanism has an Ir(CO) (2086 cm⁻¹) resting state that remains part of the active complex throughout the reaction. This is despite the mechanism being positive order in CO (0.37-0.70) and a dicarbonyl state (2077 & 1995 cm⁻¹) being observed under reducing conditions. We also show that the mechanism has two rate determining steps: one Eley-Rideal step and one surface oxygen migration step. The two steps have similar energetic barriers and thus share a significant degree of rate control. To show this, we use a combination of reactivity and isotope exchange measurements coupled with in-situ/operando infrared and X-ray absorption spectroscopies, and aberration-corrected microscopy to show the CO oxidation mechanism on Ir/TiO₂ proceeds with a CO acting as a permanent part of the active site. This work shows how the nature of the single atom site can bring together the advantages of heterogeneous and homogeneous catalysis. It also further develops the control of the reaction site that can be created in heterogeneous catalysis, which while not as developed as that in homogeneous catalysis, does have significant potential.

Introduction Supported single atom catalysts have shown great potential

to bridge the gap between homogeneous catalysts and heterogeneous catalysts and have the potential to maintain the advantages of each.^{1,2} Specifically, they can bring together the easy separation of heterogeneous catalysis with the uniformity and atomic usage³ of homogeneous catalysis. Supported single atom catalysts have also been shown to exhibit radically differing properties than nanoparticles.¹ For CO oxidation alone, there have been many cases of the single atoms exhibiting different kinetics than nanoparticles: Pd/CeO₂,⁴ Pt/FeOx,⁵ Pt/TiO₂,⁶ Pd/Al₂O₃,⁷ Pt/CeO₂,^{8,9} Pt/Θ-Al₂O₃,¹⁰ and Ir/MgAl₂O₄¹¹ for example. The difference in kinetics is typically due to the change in the reaction mechanism from a Langmuir-Hinshelwood type mechanism¹²⁻¹⁵ to some other type, such as an Eley-Rideal or Mars van Krevelen mechanism.^{5,9,11} Perhaps the largest advantage that single atom catalysts have is that they have the potential to use ligands to increase activity, selectivity, or stability in the same manner¹⁷² CATALYSTS as homogeneous catalysts. Traditional nanoparticle catalysts typically limit their use of ligands to synthesis¹⁶ and indirect changes to adsorbate energetics.¹⁷ However, single atom catalysts consist of isolated metal atoms bound to the support and to reaction intermediates and thus the local environment of the catalytic atom shares much of the same properties of a traditional homogeneous catalyst. This includes the ability to use ligands to control the catalytic properties of the catalyst. For example,

Lu et. al. compared the activity of ethene hydrogenation and HD exchange reactions for different combinations of CO and C₂H₄ ligands for an Ir/DAY zeolite and found that the CO ligands typically decrease the activity of the catalyst.¹⁸ Similar studies were performed on other zeolites¹⁹ and Ir/MgO¹⁸ single atom catalysts. Zhou et. al. claimed that the reactivity of ethylene dehydrogenation was affected by the addition of an organic ligand for single atom Pt/TiO₂,²¹ and later Chen et. al. expanded on this idea and showed similar effects for Ir/CeO₂ and Ir/MgO single atom catalysts.²² CO oxidation is one of the primary functions of the commercial three way catalysts used to treat the exhaust gases in automobiles. CO oxidation also serves as an important probe reaction that provides insights on the strength of CO binding and O₂ activation on heterogeneous catalysts. Strong binding of CO to Ir (and other Pt group metals) nanoparticles (150 kJ/mol)²³ results in poisoning of the surface and low activity due to inefficient O₂ activation. On the other hand, stronger binding of CO (230 kJ/mol)¹¹ to Ir single atoms supported on MgAl₂O₄ leads to Ir(CO) being the active complex. The active Ir(CO) complex opens a new pathway for CO oxidation through an Eley-Rideal type mechanism and facile O₂ activation at the Ir-MgAl₂O₄ interface. As a CO molecule appears to be bound to Ir throughout the reaction cycle, it is imperative that we understand if this is general for Ir single atoms on other supports and what role does it play in the reaction mechanism. Specifically, it is not clear if CO is a spectator species or part of a reactive intermediate that reacts with O* in one of the steps in the reaction cycle. Therefore, to understand how Ir single atoms catalyze CO oxidation, it is important to identify the resting state (most stable reaction intermediate), follow the changes to the Ir coordination during reaction, and identify which ligands are permanent and act as part of the active state. In this work, we will show that we can create single atom Ir sites on an anatase support. We will show that they are catalytically active for CO oxidation and proceed through a mechanism with two rate determining steps. We propose that one of these steps is an Eley-Rideal (ER) type mechanism with a gas phase CO acting to remove a surface oxygen while the other step is a surface oxygen reconfiguration similar to a Langmuir-Hinshelwood (LH) type mechanism that is 0 order in both CO and O₂. We will then show through isotopic labeling that the mechanism proceeds with a permanent CO ligand on the active site indicating that CO ligand present is not directly involved in the reaction mechanism despite being present on the single atom center throughout the entire mechanism.

Results and discussion

Characterization of the atomic dispersion and local coordination of Ir¹/TiO₂

To identify the effect of reduction and CO oxidation on the dispersion and local coordination of Ir, we conducted a suite of complementary in-situ and ex-situ characterization experiments. Figure 1a,b show representative STEM images of the catalyst after reduction and after CO oxidation. The STEM images showed single atoms only across multiple images on different areas of the sample after reduction (17 images) and after CO oxidation (10 images) with no clusters detected. These results indicate that clusters, if they exist, are a minute minority of the sample. In-situ DRIFTS, EXAFS and HERFD-XANES were used to identify the coordination of Ir single atoms. DRIFTS spectra of the Ir/TiO₂ catalyst in Figure 1c show two CO bands at 2077 and 1995 cm⁻¹ after reduction. It is known that single atom species of Rh and Ir form gem-dicarbonyl species when exposed to CO.^{1,24,25} Therefore, we assign the bands to Ir(CO)₂ species.

3.0 CATALYSTS After Reduction

3.1 Active State After Reaction

2.5 Reduced State

Kubelka-Munk (a.u.)

2086	1995	2.0	1.5	2077	Normalized Intensity	1.0	0.5	2100	2050	2000	1950	0.0
Wavenumber (cm ⁻¹)												
11200	11220	11240	11260	Energy (eV)								
8	After Reaction											
7	6	After Reduction										
8	After Reaction											
6	4	After Reduction										

(R) | (A) 3) 5
2 4 3 Im[(R)] (A) 3) 0 2 2 4 1 6 0 8 0 1 2 R (Å) 3 4 5 6 0 1 2 R (Å) 3 4 5 6

Figure 1: Atomic-level characterization of Ir/TiO₂. (a) STEM of 0.1 wt% Ir/TiO₂ catalyst after reaction kinetic measurements. (b) STEM of 0.1 wt% Ir/TiO₂ after reaction and reduction of the catalyst. (c) DRIFTS spectra of the after reaction (red) and after reduction (blue) states. (d) XANES region of the EXAFS data for samples representative of the active state (red) and the reduced state (blue). (e) Fourier transformed k²-weighted χ(k) (R-space) spectra of the EXAFS data for 0.1 wt% Ir/TiO₂ for samples representative of the active state (red) and the reduced state (blue). (f) Imaginary component of the R-space data shown in (g) schematic of the two states identified at 2077 and 1995 cm⁻¹ to the symmetric and asymmetric vibrations of Ir gem dicarbonyl (Ir(CO)₂). The assignment was also confirmed through ¹²CO - ¹³CO exchange experiments (see Figure S1b and associated text). The Ir(CO)₂ bands in our work are consistent with previous reports in the literature. For example, CO bands at 2069 and 1997 cm⁻¹ were reported for Ir(CO)₂/TiO₂ (rutile)²⁶ and bands at 2070 and 1988/1990 were reported for Ir(CO)₂(acac)/TiO₂ (P25 Degussa).²⁷ This also compares well with the 2085/2002 cm⁻¹ bands for the Ir(CO)₂(pydic) complex²⁸ and the 2082/2002 cm⁻¹ bands for Ir(CO)₂(acac) complex.²⁹ A comparison of the band positions for Ir(CO)₂ on different supports is provided in the SI (Table S1). Consistent with DRIFTS, our EXAFS modeling results show that Ir is coordinated to two CO

molecules and two oxygens from the support (see Table S3 and fit details in the experimental section). During reaction, the Ir(CO)₂ is transformed to Ir(CO) (see Figure S1a for time resolved spectra) as seen from only the CO band at 2086 cm⁻¹ being detected after reaction in Figure 1c and from the EXAFS modeling results (Figure 1e,f) showing Ir being coordinated to one CO and three oxygens from the support. The Ir oxidation state also increases as seen from the white line intensity in the XANES spectra (Figure 1d). CO Oxidation Mechanism on Ir1/TiO₂ In order to understand the mechanism of CO oxidation on Ir1/TiO₂, and especially the role of the adsorbed CO on Ir, several kinetic and spectroscopic measurements were performed. The CO order was found to be positive across all regimes (Figure 2a). Additionally, the O₂ order was found to be approximately 0 in all regimes. This is indicative of a CO (and not an O₂) being involved in the rate determining step. Given that the most abundant surface intermediate is an Ir(CO) species, it is apparent that a second CO in the gas phase is involved in the rate determining step which must be an Eley-Rideal type mechanism. Furthermore if the first CO was the active state and it proceeded by a Langmuir-Hinshelwood mechanism, then we would not expect to see a stable Ir(CO). However, if this were the only factor 176 CATALYSTS determining the rate, then we would expect the overall reaction rate to be +1, thus this model is not enough to completely describe the kinetics seen. In order to fully describe the kinetics, we investigated the effect of temperature on the kinetics. Interestingly, the CO order was found to vary strongly with temperature. Figure 2b shows that the order varies from +0.37 at 150 °C to +0.70 °C at 200 °C. This indicates that the rate determining step varies in these two regimes. Specifically, the simplest explanation is that two rate determining steps, the first with a +1 order and a second with a 0 order in CO, split the degree of rate control. For reasons we discussed in the last paragraph, it appears that the positive (in CO) order step is most likely a dominated by an Eley-Rideal type mechanism while the zero order (in CO) step is most likely a type of O₂ surface activation given its apparent 0 order in CO and O₂. We contrast this hypothesis with the difference in order being from a competing different species, i.e. a minute concentration of clusters or large nanoparticles. If the change in CO order was caused by two competing species, we would see a change in the CO order at a given partial pressure of CO as the dominant species shifts. This critical point would be a function of temperature, but the orders away from that point, would not be affected. Here however, we see no such effect of CO partial pressure on the CO order and no such critical point where the order changes. This allows us to rule out competing parallel mechanisms. In order to further demonstrate this shared rate control effect, the activation energy can also be shown to be a function of CO partial pressure. This is because an increase in the partial pressure of CO will push the rate control to the 0 order step while a decrease in CO partial pressure will push the rate control to the +1 ordered step. This is shown in Figure 2c where the activation energy is shifted from 100 kJ/mol at 1% CO to 139 kJ/mol at 10% CO. This clearly indicates that the 0 order step has the higher activation energy compared to the +1 order step. A mathematical version of this is shown in the supporting information (section 7). To rule out the effect being caused by a competitive adsorption between the CO and O₂, we can perform the same test but by varying the O₂ partial pressure. As shown in Figure S5b, the O₂ partial pressure has no effect on the activation energy implying the change is not due to a competitive adsorption.

TOF (s⁻¹) 10⁻² TOF (s⁻¹) 10⁻²

$E_{app} = 139 \text{ kJ/mol}$ 10⁻³ $n_{CO} = 0.37$ 10⁻³ $E_{app} = 100 \text{ kJ/mol}$ 10⁻³ 10⁻⁴ 10⁻⁵ $PCO \text{ (Pa)}$ 0.27 $1/RT \text{ (kJ/mol)}$ 1 0.28 0.29 Figure 2: (a) Reaction orders of single atoms for Ir/TiO₂. The single atom orders are +0.5 in CO at 10% O₂ and -0.1 in O₂ at 1% CO both at 155 °C. (b) Arrhenius comparisons for changing CO partial pressures. Both samples are in 10 % O₂. There is a clear increase in activation energy with CO partial pressure (c) Effect of temperature on the CO order. The 150 °C sample was measured at 10 % O₂ with a total flow rate of 80 sccm while the 200 °C sample was measured at 20 % O₂ with a total flow rate of 40 sccm. The increase in temperature corresponds to an increase in the reaction order. The pretreatment and other details for each sample are given in the supporting information. To further probe the mechanism, half reaction experiments were performed in HERFD- XANES (Figure 3). The results show three distinct states. We assume the state under reaction conditions to be the monocarbonyl mentioned previously and the reduced state to potentially be a dicarbonyl state or a further reduced monocarbonyl. This is not necessarily the same dicarbonyl state as shown in the DRIFTS, but is a more reduced intermediate. The existence of three distinct states points to a rate determining step that does not involve a gas phase species. Our proposed mechanism (Figure 4) accounts for this with the surface O₂ activation step. Furthermore, we can estimate the charges of the three states using the height of the normalized peak which was found to correlate with the Ir charge (Figure S4). The active state was found to have a formal charge of 3.0 while the reduced state and oxidized state have charges of 2.3 and 3.3 respectively (see the experimental

section and Table S2 for more information). This oxidized state is believed to also be a monocarbonyl that is convoluted with/part of the active state and thus not able to be detected on its own through 178 CATALYSTS other methods, namely DRIFTS. 7 CO + O₂ 6 Charges 3.3 O₂ Normalized Intensity 5 3.0 CO 2.3 CO + O₂ 4 3 2 1 0 11210 11220 11230 Energy (eV) Figure 3: HERFD spectra of the sample under reaction conditions. The spectra were taken at reaction/half reaction conditions in the order of CO+O₂ (blue), O₂ (red), CO (green), and CO+O₂ (magenta). The charges were assigned using the heights of the reference states shown in S3 and the process described in the experimental section. We can not fully determine what the state of this reduced system is. However we cannot rule out that it is a weak dicarbonyl state from the data shown. Previously, this was not seen in the DRIFTS when exposed to CO gas as the CO gas obscures much of the spectra due to its weak binding with TiO₂. These weakly adsorbed bands dominate the spectra from approximately 2200 to 2050 cm⁻¹ and obscure many potential CO peaks. If this intermediate Ir(CO)₂ existed, then we would be unable to see it in the DRIFTS unless the decomposition of the species was significantly slower than the CO-TiO₂ desorption. Interestingly though, if we flow ¹³CO on the system at reaction temperatures, we get a complete exchange without any Ir(1213) This gives credit to the unstable intermediate as a stable Ir(CO)₂ intermediate should give only the Ir(1213) under such reduction conditions. This experiment is shown in Figure S9d. Combining all of this information, we propose the reaction mechanism in Figure 4. The resting state is believed to be a monocarbonyl state based on the DRIFTS and the EXAFS fits. Furthermore, from the EXAFS fits, we expect there to be approximately 3 O molecules surrounding the Ir single atom. This is given as the Ir(CO)(Os)₃ (I) state. As established earlier, the first rate determining step is believed to be an ER step involving a gas phase CO. This is shown proceeding state I. This ER step is required to remove a surface oxygen giving us the proposed state (II). This intermediate is expected to be short lived and we are not able to detect a state that fits its description. A second CO is then expected to add to the Ir site to create a dicarbonyl state (III). The bottom half of the mechanism is thus needed to complete the cycle. The addition of O₂ is the apparent next step as the dicarbonyl state is stable on its own under the reducing environment, i.e. CO with no O₂. This addition leads us to state IV. The most likely place for O₂ to react is at the vacancy reacted by the ER step that was the first rate determining step. In our proposed mechanism this is then followed by a fast surface reaction to create the second CO₂ and state V. State IV and V are not believed to be detected in either the DRIFTS or the EXAFS. Thus we have little information about the structure of the two states and the structures shown are largely conjecture. This then leaves the final step as a form of O₂ surface migration or activation. This final step is needed to be somewhat rate determining for two reasons. The first is that this is the only option were a suitable rate determining step can be zero order in both CO and O₂. This is needed to explaining the change in kinetics described earlier. The second reason that this step is needed is to explain the third state that is observed from the HERFD-XANES. Under reaction conditions, a combination of states I and V are observed. This is the active state as seen in HERFD-XANES. However, under O₂ only conditions (or inert conditions such as the purge step used in DRIFTS and EXAFS measurements), the state measured is all state I. And in a similar manner, in CO only conditions the measured state is the dicarbonyl reduced state. 180 CATALYSTS Figure 4: Proposed mechanism for CO oxidation on Ir1/TiO₂. Starting from the most stable state: Ir(CO)(Os)₃, the mechanism proceeds through an Eley-Rideal step (I-II) involving a gas phase CO reacting with a surface O to create CO₂ and leaving an unstable monocarbonyl Ir(CO)(Os)₂. This is followed by the adsorption of a gas phase CO (II-III) this is likely not the dicarbonyl (Ir(CO)₂(Os)₂) seen in Figure 1 (c). The next step is a gas phase O₂ absorbing onto the surface at an adjacent site (III-IV) to give Ir(CO)₂(Os)₂O₂. This reacts with the CO adsorbed in step (II-III) through a Langmuir-Hinshelwood type mechanism leaving a O₂ species adjacent to the Ir and a return to the monocarbonyl state: Ir(CO)(Os)₂O₂ (step IV-V). The final step is the reconfiguration of the O₂ to a return to the original, most stable monocarbonyl (step V-I). A more detailed discussion on how this mechanism explains the changes in order and the changes in activation energy is in order. The full details of the kinetic mechanism are derived in the supporting information (Section 7). Two regimes become apparent. The first is when the conditions favor the the first RDS. This happens at high CO and low temperatures. In this regime, the reaction is dominated by the 0 order high activation energy mechanism. The second regime is at low CO and high temperatures. In this regime the reaction is dominated by the ER step which is the lower activation energy step. This is shown in Figure 5 Figure 5: Schema of which RDS has the larger control This mechanism is comparable to other single atoms for CO oxidation. For example, Ir1/MgAl₂O₄ was shown to have a positive order in CO and have a RDS that matches similarly the ER step that we propose here to be one of the rate determining steps.¹¹ This is also comparable to Pt1/CeO₂, which also has a positive order in CO and appears to have an ER like RDS that causes said CO order.⁹ ¹³CO Exchange Experiment From this mechanism, we predict that at least one CO will remain on the Ir complex at all times and there is a brief intermediate that contains two COs (Ir(CO)₂). In order to probe

these two ligands, we performed ^{13}CO exchange reactions on the catalyst. The results show that the $\text{Ir}(\text{CO})$ state was not affected. The lack of exchange of the $\text{Ir}(\text{12CO})$ to $\text{Ir}(\text{13CO})$ as shown in Figure 6 shows that this ligand that remains on the surface throughout the reaction mechanism. Furthermore this shows that the dicarbonyl intermediate does not contain two 182 CATALYSTS identical COs. There must be some difference in the two that causes one to react much more readily than the other. This also further implies that the dicarbonyl is too short lived to be able to rotate or perform other exchanges such as the pseudo-associative exchange mechanism that is shown in Figure 6 when in the presence of O_2 . Without the presence of O_2 , this does seem to be possible. Furthermore, we do see exchange for the case without O_2 being present (Figure S9). Repeating the same analysis but without the addition of O_2 , i.e. just a reduction in ^{13}CO , we do see exchange. Interestingly it results in the direct appearance of the $\text{Ir}(\text{13CO})_2$ state with no intermediate $\text{Ir}(\text{12CO})(\text{13CO})$ being detected. This result shows that the O_2 can dictate the CO exchange mechanism. Specifically, the presence of O_2 , likely on the surface, suppresses the exchange of the $\text{Ir}(\text{CO})_2$ gem-dicarbonyl. The lack of exchange observed on the catalyst has a large implication for catalysis of single atoms on reducible oxides. The $\text{Ir}(\text{CO})$ state that is observed as the resting state, including the CO ligand, appears to be the active complex for the reaction mechanism. Because the CO ligand is acting entirely as part of the active site and is unwilling to play the role of a reactant, it would appear that this opens the gateway to be able to replace this ligand with any other ligand of similar properties to allow the catalytic system to be finely tuned to increase activity or selectivity. Most notably, this lack of exchange is typically reserved for highly engineered homogeneous catalysts as opposed to heterogeneous catalysts which are normally not able to control which ligands react and which ligands are left on the surface. Additionally, as the existence of this ligand is believed to affect the kinetics of the single atom catalyst, the properties of this CO ligand could possibly explain the disconnect between the strong adsorption of CO causing CO poisoning (negative order in CO) in CO oxidation for nanoparticles, but facilitating (positive order in CO) that same reaction on single atoms. The difference being that the first CO adsorbs strongly, but unlike nanoparticles, this does not block the active site. It instead might actually facilitate the active site.¹¹ After ^{12}CO Reaction After ^{13}CO Reaction Kubelka-Munk (a.u.) $\text{Ir}(\text{12CO})$ Expected $\text{Ir}(\text{13CO})$

2100 2050 2000 Wavenumber (cm⁻¹) 1950 Figure 6: Top: results of the

^{13}CO exchange experiment. The catalyst was reacted for 12 hours followed by cooling and purging to produce the $\text{Ir}(\text{12CO})$ active state. This was then followed by 100 TON of reaction under 10% CO and 10% O_2 at 165 °C. Bottom: Schematic for the associative exchange mechanism. One of the possible ways the CO ligands could have exchanged. ¹⁸⁴ CATALYSTS Conclusions In this work we have demonstrated the ability to synthesize single atom Ir/TiO_2 catalysts. We show that the mechanism has two competitive rate determining steps. The first is an Eley-Rideal step consisting of a gas phase CO reacting with a surface O. The second is a Langmuir-Hinshelwood step. The mechanism predicts that despite the presence of a dicarbonyl in the reaction mechanism, the two CO ligands are not equivalent. This leads to the COs not exchanging under reaction conditions and this is verified through ^{13}CO exchange tests. One CO appears to act as part of the active state, only being involved in the reaction as a spectator ligand. This represents the interesting case of a CO ligand that is not reactive. This also helps bridge the gap in understanding how single atoms can adsorb CO without being poisoned. This also opens the door to potentially use other ligands on the active site to adjust the activity of the Ir/TiO_2 .

Experimental Synthesis The catalysts were synthesized in one of two ways. The first method was strong electrostatic adsorption.^{30,31} In this method, 1 g of dried support was added to 1 L of DI water. The resulting solution was then adjusted to a pH of 3 with HCl. A second 10 mL solution of pH 3 HCl in DI water was used to dissolve the appropriate amount of IrCl_3 precursor. The appropriate amount being defined by the weight loading. i.e. for a 0.1 wt% catalyst, 1 mg Ir of IrCl_3 was added. The precursor solution was then added drop-wise to the support solution at a rate of 10 mL/hr. The resulting mixture was then vacuum filtered through a Q5 sized filter. The resulting catalyst was then dried at 80 °C for 12 hours. The precursor solution and resulting filtrate was collected for ICP analysis to help give an accurate representation of the amount of Ir on the sample. Typically, 15% of the added Ir was passed on into the filtrate meaning the actual weight loadings are typically 85% of the nominal weight loading. These weight loading changes are considered in the normalization of data, however they are not included in the nominal names for clarity. If a calcination was performed, it was performed immediately following the drying process. The second method which was used only for the 5 wt% catalyst used as a nanoparticle reference was incipient wetness impregnation.^{30,31} For this sample, 2 mL of pH 2, HCl in DI water was found to fully saturate 1 g of dried TiO_2 . As such, 0.05 g (Ir) of IrCl_3 was then added to 2 mL of pH 2, HCl in DI water and added to 1 g of dried TiO_2 . The solution was then

mixed into the solid drop-wise with rigorous stirring in between each drop. The solid was then set on a hotplate at 50 °C to remove excess moisture. The $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ (CAS: 14996-61-3) was purchased from Sigma-Aldrich (lot: MKCM7998). The anatase TiO_2 was purchased from U.S. Research Nanomaterials (stock US3838) and re-reported to have average particle size of approximately 5 nm. The support was found to maintain its size and phase through similar pretreatments with Pt/ TiO_2 catalysts.³² STEM The first (1a) is after measurements of the activation energy and reaction orders for the sample. This gives the monocarbonyl, active state. This procedure is further elaborated on in the experimental section. The second state of which we collected STEM images (1b) were taken of the reduced, dicarbonyl state. To obtain the reduced state, the sample was first treated under reaction conditions (10% O_2 , 10% CO , 170 °C) for 10 hours and

then reduced in 10 % CO at 150 °C for 1 hour. The reaction

conditions are necessary to fully reduce the catalyst, however reduction at higher temperatures results in agglomeration of the single atoms. This is further elaborated on in the supporting information. This set of images shows 49 single atoms across 8 images and no clusters once again showing that the clusters, if they do exist, are a minority species. 186 CATALYSTS STEM samples were performed at ORNL DRIFTS DRIFTS experiments were performed in a Thermo Scientific Nicolet™ iSTM50R FT-IR spectrometer with a MCT-A detector. In order to perform DRIFTS experiments, the Harrick Scientific Praying Mantis™ attachment was used.

A spectral resolution of 4 cm^{-1} was used

for each spectrum and reported spectrum are 64 scan averages. An approximately 50 mg sample was first sized between 75-106 μm . The sample was then pretreated in-situ. The background was taken on the fresh sample at 35 °C in inert (N_2) atmosphere. This is contrary to the typical backgrounds taken after all pretreatment but before the addition of CO . This discrepancy is due to the necessity to reduce the catalyst in CO which is also the probe molecule. For samples that were oxidized in-situ, the background spectra were taken after the oxidation. Additionally, all spectra not taken at temperature were taken at 35 °C (room temperature). Spectral analysis, namely peak identification, peak resolvment, and background correction was performed in the OMNIC software. For peak resolvment, the peaks were first identified with OMNIC's Find Peaks function and then iteratively fit with peaks going to 0 area removed. An initial noise target of 0 was found to converge the spectra the most reliably. In order to remove background shifts due to the removal of OH groups on the support during the treatments, the spectrum was first changed to absorbance or $\log(1/R)$ units which were found to be more linear for this system³³ and then OMNIC's Baseline Correct function was applied to the spectrum. Results were then converted back to K-M units to be more comparable to other literature results. Analysis of the effluent gas from the DRIFTS cell was analyzed using a Pfeifer Vacuum GSD320 OmniStar Mass Spectrometer. The system was used to track $^{12}\text{CO} + \text{N}_2$ ($m/z = 28$), ^{13}CO ($m/z = 29$), $^{12}\text{CO}_2$ ($m/z = 44$), $^{13}\text{CO}_2$ ($m/z = 45$)

to ensure that the CO from the gas phase was reacting. The spectral features discussed in this work are entirely due to adsorbed CO species. The CO bands shown are either redshifted (lower wavenumber) or blueshifted (higher wavenumber) from the gas phase value of 2143 cm^{-1} due to changes induced by the CO adsorbing onto the catalyst. We can categorize these shifts into three contributing factors: electrostatic interaction, sigma donation, and pi back bonding. We attribute the red shifts seen here to be due to the pi-back bonding, which populates the antibonding orbital of CO , thereby reducing the bond order and lowering the energy spacing between the ground and first vibrational energy level. The effect is similar to the classical mechanical description of a mass oscillating on a spring: the vibrational frequency

is directly proportional to the square root of the

spring constant (i.e., bond rigidity) and

inversely proportional to the square root of the mass (atomic mass of species

involved). Thus, a ^{13}CO isotope would be expected to have a similar strength bond, however its larger mass would then lead to a redshift in the peak location

inversely proportional to the square root of the ratio of the

masses. On a further note, many of the species shown in this work exist as dicarbonyl species. Due to the interaction of the two CO , the IR bands deconvolute into their symmetric and antisymmetric stretching frequencies providing yet another shift in the band locations. Additionally, CO was

found not to adsorb to anatase TiO₂ at room temperature in previous experiments from our lab³² and in the literature.^{34–37} HERFD-XANES HERFD measurements were performed at SSRL beam line 6-2.³⁸ Processing was done with the Athena program that is part of the Demeter package.³⁹ The reactor setup is fully described in reference.⁴⁰ To calibrate the energy, an Ir reference foil was used to calibrate a glitch in the mono. This glitch was used as a reference to align the sample data. This was used instead of collecting the Ir foil with each sample directly due to the high adsorption of the Ir/TiO₂ sample. The reference foil was collected in transmission mode ($\ln(I_0/I_1)$) while the glitch 188 CATALYSTS reference was the directly measured beam intensity before the sample (I_0). In order to verify the fully oxidized case is fully oxidized, the 150°C oxidized sample is compared to a 0.1 wt% sample that was calcined ex-situ at 350 °C and oxidized in-situ at 310 °C. This sample appeared to be mostly Ir in the TiO₂ bulk and thus was assumed to be the +4 state. Because the two states are similar, we can conclude that the low temperature oxidation is sufficient to fully cover the Ir. This higher calcined, bulk sample was used as the +4 reference. To get additional points for calibration of the oxidation state, we used an Ir(CO)₂(acac) standard that was assumed to be a +1 reference state and a previously well characterized Ir/Al₂O₃ nanoparticle standard to be a +0 reference. These references are shown in Figure S3. The samples were ran in HERFD mode (FF1/I0) with 5 scans in each section that were merged together. The 5 scans were all taken once the conditions had reached steady state (i.e. the spectra were not changing). The experimental data was collected as follows. The sample was oxidized in-situ at 150 °C in 10% O₂ for 1 hour and then reduced in-situ at 150 °C in 10% CO. XANES scans were taken throughout the entire pre-treatment and we report merged averages at room temperature after the oxidation and reduction. In order to verify that the reducing conditions did not cause significant differences to the catalysts, multiple locations on the sample bed were compared and found to have no significant difference. After the pretreatment, the sample was heated in 1% CO and 10% O₂ to 150 °C. Spectra were collected on the state at reaction temperatures and the reported spectra are all at temperatures. Each part of the half reaction was allowed to reach steady state before merging the last 5 scans. The conditions were at 150 °C and as follows: 1% CO and 10% O₂, 10% O₂, 1% CO, 1% CO and 10% O₂. There was no discernible difference between the first and last 1% CO and 10% O₂ conditions implying that the results are probing the active state and that there were no additional changes. The samples are shown in Figure 1d. The spectra were normalized with a pre-edge range of -50 to -30 eV relative to the step edge while the post edge range was 100 to 250 eV. A second order normalization was found to be optimal. The height of each peak was taken to be the normalized maximum of the white line peak and to get the total area under the peak, the peaks were integrated from -20 to 30 eV and -10 to 10 eV in reference to the step energy. The values are then given in Table S2. The heights of the peaks were found to correlate well with the formal charge of the species in the reference spectra. That trend is assumed to carry over into the single atom species. This linearized trend was then used to calculate the charge of each state as shown in the half reaction experiment (Figure S4). Interestingly, the area and peak location were not found to correlate with the expected trends and thus were not used in the charge prediction. The peak location shifts in the wrong direction for the samples of interest which has been reported for CO species in other places in the literature.^{41–43} The overall area of the peaks is thought to be a more reliable way to predict the charge of a system, but those trends are often empirical and require knowledge of the full band space, most importantly the L2 step edge. Without knowing the shifts of the L2 edge, it is difficult to extract a complete picture of the charge from the area of the L3 edge alone.⁴³ EXAFS EXAFS data was obtained from NSLS-II BL 08-ID. The experiments were performed in-situ using the in house reactor setup that is described in detail in reference ?(I assume Eli has published a more detailed description of the reactor than is appropriate here). The reactor was a polyamide tube with a inner/outer diameter of 0.0710/0.0750 inches and length of approximately 8 cm. The reactor was heated by one heating element adjacent to the reactor and out of the path of the beam. A thermocouple in the reactor bed was used to measure the temperature. The pretreatment and reaction conditions were the same as those previously measured but with the flow rates scaled to 40 sccm. The data was collected in fluorescence mode at the Ir L3 step edge. The fluorescence mode was preferred as the adsorption of the TiO₂ support severely diminished the quality of 190 CATALYSTS the transmission data. Additionally, the solid state 4-element Vortex Silicon Drift Detector was used to measure the low amount of Ir signal. EXAFS fits were performed on the two designated samples (reduced at temperature and after reduction with oxygen exposure). First the fitted data were normalized in Athena with a pre-edge normalization range of -150 to -30 (in reference to E₀) and a post-edge normalization range of 150 to 650 and a 3rd order normalization. The k-range was chosen to be from 3 to 12 Å consistent with the data quality (Figure S6) Fitting was performed in the Artemis software. In order to obtain the amplitude reduction factor (SO₂),

iridium foil was fit. The iridium foil was found to give an amplitude reduction factor of 0.83. This value was used throughout the other fits. For fitting, the Ir-O (first and second shell), Ir-CO, Ir-Ti, and Ir-Ir scatterings were considered. For fitting, fits were considered for the first and second shell corresponding to a radial distance between 1.25 and 3.11 Å for the monocarbonyl state and between 1.35 and 2.9 Å for the dicarbonyl state. Due to data quality considerations and given the number of species that needed to be fit, the mean square displacement (σ^2) was initially set to the reported values. This value was found to have minimal effect on the resulting fits and thus was not optimized. Similarly, the e_0 was manually optimized to limit the fitting parameters required in each iteration of the Artemis fits. The best fits for each system are given in table S3 with the fits themselves given in figure 1e and 1f. In order to verify that the models that were purposed are the best fits, we also tested other possible models. Figure S8 shows the various fits that described the data less accurately with a critical piece missing. Additionally, no Ir-Ir was found to fit into the data when it was fitted alone. Kinetic measurements were performed in our in lab reactor. Before loading, the catalyst was ground and sieved to be between 106-300 μm . For samples that were diluted to verify we were in the kinetic regime, the catalyst was ground with inert silica (put the silica specs here) until no distinction in the two systems could be determined and then pressed into a pellet, then ground and sieved to be in the same size regime. The catalyst was then loaded into a 7 mm i.d. .. 9.6 mm o.d. fused quartz tube with quartz wool being used to secure the catalyst bed from. The tube containing the catalyst bed was then mounted in a Mellen tube furnace using a Watlow temperature controller. To maintain a constant reaction temperature a K-type thermocouple was mounted to the wall of the tube containing the sample and was used to measure the temperature of the catalyst bed. The gases, 5% CO (balance N₂), CO, O₂ and He (carrier gas), were controlled through Brooks mass flow controllers. The controllers were used to change the fraction of reactant gas entering the catalyst bed. The inlet pressure was measured relative to atmospheric pressure to ensure pressure drops across the catalyst bed never exceeded 0.1 bar. Exit gas

from the reactor was measured using an Inficon Micro GC Fusion

® that was calibrated to 0.5% CO, 10% O₂, and 0.5% CO₂. Kinetic measurements were kept in the differential regime (i.e. never exceeding 5% conversion) in order to ensure the gas profile across the bed stayed consistent. To ensure that the reported values are caused by kinetics instead of transfer limitations, the Koros-Nowak test^{44,45} was used and is shown in Figure S5a.

Acknowledgement Please use “The authors thank . . . ” rather than “The authors would like to thank . . . ”. The author thanks Mats Dahlgren for version one of achemso, and Donald Arseneau for the code taken from cite to move citations after punctuation. Many users have provided feedback on the class, which is reflected in all of the different demonstrations shown in this document . 198 CATALYSTS Supporting Information : Supporting Information for: CO as a Non-exchanging Ligand for CO Oxidation on Ir/TiO₂ Single Atom Catalysts Coogan B. Thompson,[†] Denis S. Leshchev,[‡] Adam S. Hoffman,[¶] Jiyun Hong,[¶] Simon R. Bare,[¶] Raymond R. Unocic,[§]

Eli Stavitski,[‡] and Ayman M. Karim*,[†] [†]Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg , VA 24060

, USA [‡]National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973, USA [¶]Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA [§]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA E-mail: *amkarim@vt.edu 1 Pretreatment Conditions for Figures 1.1 Figure 1 (a) STEM of 0.1 wt % Ir/TiO₂ catalyst after reaction kinetic measurements. The fresh sam- ple was treated for 1 hour under reaction conditions (1% CO, 10% O₂ at 170 °C) to remove precursor ligands. After the removal of the precursor ligands, the sample was measured for the activation energy (10% CO, 10% O₂, 160-180 °C), the CO order (160 °C, 10% O₂, 1-15% CO), and the O₂ order (160 °C, 10% CO, 3-14% O₂). Finally, the catalyst was exposed to 1% CO and 10% O₂ at 160 °C for 1 hour before being cooled of the reaction gases and purged. (b) STEM of 0.1 wt% Ir/TiO₂ after reaction and reduction of the catalyst. The fresh sample was treated for 10 hours in 10% O₂ and 10% CO at 170 °

C for 10 hours. The sample was then cooled to 150 ° C and was

exposed to 10% CO (no O₂) for 1 hour to recover the dicarbonyl state. The sample was then cooled and purged. This method of reducing after reaction was used instead of just reduction as the reduction only (or reduction after oxidation) created a layer on the catalyst that could not be removed through vacuum to an acceptable extent that the STEM could be performed. We presume this is part of the catalyst precursor that is not

removed at 150 °C. Additionally, higher temperatures (200 °C) in CO result in structural changes and/or agglomeration of the single atoms in nanoparticles and thus are not useful to the current goals. (c) DRIFTS spectra of the after reaction (red) and after reduction (blue) states. The fresh sample was used as the background for the spectra collected throughout the experiment. This is notable as the fresh spectra incurs noticeable background changes. These background changes are then corrected in post processing. The fresh sample is treated in 1% CO, 10% O₂ at 170 °C for 1 hour. The sample is then purged and cooled to 35 °C. This process is then repeated to ensure the sample is fully reduced, i.e. the monocarbonyl has reached its max height. The second spectrum is shown in the figure. The process is then repeated a third time but at 160 °C to ensure there is not a temperature effect. The sample is then reduced in 1% CO for 1 hour at 160 °C to arrive at the dicarbonyl state shown. (d-f) R-space of the EXAFS spectra for samples representative of the active state (red) and the reduced state (blue). This experiment was performed at NSLS-II. I will need to add more details once we settle on the result.

200 CATALYSTS 1.2 Figure 2 (a) The pretreatment for the sample was a 150 °C oxidation followed by a 150 °C reduction in CO. The experiments were done in the order of the Arrhenius experiment (part b) followed by the CO order and then the O₂ order. The sample was 0.1 wt% Ir/TiO₂ (b) The pretreatment for the 1% CO Arrhenius measurement was a 150 °C oxidation followed by a 150 °C reduction in CO. The sample was 0.1 wt% Ir/TiO₂. There was no pretreatment for the 10% CO Arrhenius measurement. The pretreatment was found to have no effect on the reaction kinetics (see Figure S5). The sample was 0.1 wt% Ir/TiO₂. (c) There was no pretreatment for the CO order measurement. The sample was 0.1 wt% Ir/TiO₂. The 150 °C at 40 sccm CO order was measured first followed by the 200 °C at 80 sccm CO order.

1.3 Figure 3 HERFD-XANES spectra of the active state under reaction conditions (blue), oxygen only half reaction (red), and CO only half reaction (green) for the 0.1 wt% Ir/TiO₂ catalyst. The 150 °C calcined sample was loaded into the in-situ HERFD-XANES cell. While being exposed to the beam, the sample was reoxidized (10% for 1 hour at 150 °C) and reduced (10% CO for 1 hour at 150 °C). While still under the beam, the sample was then exposed to 1% CO, inert (He), 10% O₂, 1% CO and 10% O₂ all at 35 °C in that respective order. The catalyst was then heated to 150 °C and exposed to 1% CO and 10% O₂, inert, 1% CO and 10% O₂, 10% O₂, 1% CO, 1% CO and 10% O₂ respectively. The spectra shown correspond to the second reaction conditions (1% CO, 10% O₂) and the proceeding O₂ and CO steps. There was minimal change between the spectra for the three half reactions.

2 Further DRIFTS comparisons After Reduction After Reaction Kubelka-Munk (a.u.) Kubelka-Munk (a.u.) Composite Spectra Original Spectra 12CO peaks 13CO peaks Mixed CO peaks 2100 2050 2000 Wavenumber (cm⁻¹) 1950 2100 2050 2000 1950 Wavenumber (cm⁻¹) Figure S1: (a) Transient conditions of the monocarbonyl state to the dicarbonyl state (b) Ir/TiO₂ single atoms that have been reduced in a mixture of 12CO and 13CO. The result is a dicarbonyl that has a mixture of Ir₁₂(CO)₂, Ir₁₃(CO)₂, and Ir₁₂(CO)₁₂(CO)₂. Furthermore, we can rule out this being absorbed onto the TiO₂ support as CO on anatase shows bands at approximately 2181 cm⁻¹ and is only seen under cryogenic temperatures. At room temperature, the CO bands are unstable. S10 These bands are also contrasted with the bands shown on iridium nanoparticles and small clusters on TiO₂ which show one broad peak and are at approximately 2060 cm⁻¹ for larger clusters S7 and 2080 cm⁻¹ for smaller clusters. Comparisons of these spectra are shown in Figure S1. There is also no indication of a peak in the 1850 cm⁻¹ range which is typically attributed to the bridging CO peak on nanoparticles. S11 Additionally, the dicarbonyls showed a splitting into 6 bands when the catalyst was reduced in a 50:50 mixture of 12CO and 13CO indicating that the species did in fact form Ir(CO)₂ instead of forming two different Ir(CO) species which would have created 4 bands. This is shown in Figure S1.

202 CATALYSTS After Reaction After Reduction Kubelka-Munk (a.u.) Kubelka-Munk (a.u.) After Reduction After Reaction 2100 2050 2000 Wavenumber (cm⁻¹) 1950 2100 2050 2000 Wavenumber (cm⁻¹) 1950 Ir/TiO₂ Nanoparticles Ir/TiO₂ Single Atoms Kubelka-Munk (a.u.) 2053 1996 2083 2080 2100 2050 2000 Wavenumber (cm⁻¹) 1950 Figure S2: (a) Comparison of the active state then reduced state vs the calcined then reduced state followed by the active state. (b) Figure 1c on the same scale (c) Ir/TiO₂ single atoms compared to nanoparticles. The single atoms are those presented in Figure 1c. The Ir/TiO₂ nanoparticles were made through in-situ reduction at 450 °C in 20% H₂

Table S1: List of similar dicarbonyls in the literature Species Support Peak Locations (cm⁻¹) References Ir(CO)₂ TiO₂(anatase) Ir(CO)₂ TiO₂ (rutile) Ir(CO)₂(acac) TiO₂ (P25 Degussa) Ir(CO)₂ (pydic) Ir(CO)₂ (acac) Ir(CO)₂ NaX Ir(CO)₂ MgAl₂O₄ Ir(CO)₂ Al₂O₃ Ir(CO)₂ MgO Ir(CO)₂ DAY zeolite 1995, 2077 1997, 2069 1988/1990, 2070 2002, 2085 2002, 2082 1984, 2082 1989, 2070 2010-2037, 2090-2107 1967, 2051 2038, 2109

This work S1 S2 S3 S4 S5 S6 S7 S8 S9

This dicarbonyl state is further confirmed by the reduction that is shown in the white line intensity of the HERFD when exposed to the same conditions and the EXAFS fitting which shows the existence of 2 CO species and 2 surface oxygen species being bound to the Ir (and no Ir-Ir species being present) and I will elaborate on this when we agree on the final EXAFS fits. 204 CATALYSTS 3 HERFD-XANES Reference Standards for Charge 8 Fully Oxidized Ir/TiO₂ Ir(CO)₂(acac) Normalized Intensity Ir/Al₂O₃ NP 6 4 2 0 11210 11220 11230 Energy (eV) Figure S3: HERFD spectra of the +4 (high temperature calcined Ir/TiO₂), +1 (Ir(CO)₂(acac)), and +0 (Ir/Al₂O₃ nanoparticles) reference states. Table S2: Areas and heights of the HERFD-XANES data shown in 1d and S3. The two different areas differ in the bounds of the area. Sample References Ir/TiO₂ cal 350 °C Ir(CO)₂(acac) Ir/Al₂O₃ NP Samples Ir/TiO₂ cal 150 °C Ir/TiO₂ red 150 °C CO+O₂ O₂ CO CO+O₂ Measured Values Charge From References -20 to 30 eV -10 to 10 eV Height -20 to 30 eV -10 to 10 eV Height 42.2 27.4 41.7 22.2 42.2 20.9 41.7 26.7 42.3 26.7 42.1 27.3 41.6 26.8 41.8 26.8 42.1 27.1 6.55 2.1 4.52 0.8 3.95 2.0 6.57 0.9 4.89 2.2 5.93 1.9 6.05 0.6 5.39 1.1 5.81 1.7 4.0 0.9 0.1 3.6 3.6 4.0 3.7 3.7 3.9 4.0 0.9 0.1 4.0 1.5 3.1 3.3 2.3 2.9 10 Peak Height 55 8 4.5 45 4.0 50 Area -30 to 20 eV Area -10 to 10 eV 3.5 Height Peak Height 6 40 35 Peak Area Charge From Method 3.0 2.5 2.0 4 30 1.5 1.0 2 25 0.5 Area -10 to 10 eV 20 0.0 Area -20 to 30 eV Ox °C O₂ O₂ O₂ CO °C ac) NP 0 0 1 Charge 2 3 4 15 Ir/TiO₂Fully all150 in inCO+ inCO+ in Red150Ir(CO)₂(ac Ir/Al₂O₃ C Figure S4: (a) Plot of height or area of each of the calibration standards. (b) Plot of the resulting charges assuming the standards in (a) are linearly related. The x-axis is based loosely on the expected charges of the systems in descending order with a more reduced catalyst expected to have a lower charge than a oxidized catalyst. The two sets of using the area to get the charge (blue and orange) show a weak correlation with the reference standards and the expected trends for the catalyst states. The height (gray) on the other hand, shows a reasonable trend with all the species being in their expected relative locations. 206 CATALYSTS 4 Further Reactivity Comparison 208 T (°C) 189 172 156 189 T (°C) 172 156 142 128 0.1 wt% 0.1 wt%% Diluted 10x 10 1 0.02 wt% 10 2

TOF (s 1) 10 3 TOF (s 1) 10 2 10 3 10

% O₂ 1% O₂ 0.25 1/RT (kJ/mol) 1 0.26 0.27 0.27 1/RT (kJ/mol) 1 0.28 0.29 Figure S5: (a) Dilution studies for the Ir/TiO₂. Arrhenius plots are for 1% CO, 10% O₂. The spectra are for 0.02 wt% and 0.1 wt% (nominal). The lower weight loading and the diluted sample were calcined at 150 °C in air for 1 hour and reduced in 1% CO at 150 °C for 1 hour prior to reaction. The other sample underwent no pretreatment after synthesis. The insensitivity to weight loading indicates that we are making all (or near all) single atoms. The insensitivity to pretreatment conditions speaks to the robustness of the synthesis. (b) Arrhenius comparison for changing O₂ concentrations. 0.1 wt% no pretreatment. Reaction conditions are 1% CO and 1 or 10% O₂. The change in activity validates the slight negative order reported for oxygen while the lack of change in activation energy means the reaction mechanism is not changed in any meaningful way. 5 EXAFS Fittings Scattering Path Ir-O (1) Ir-CO (C) Ir-CO (O) Ir-Ti Table S3: caption Active State s₀₂=0.83, delE=3.0 eV N Distance 3.00 +/- 0.98 2.02 +/- 0.02 1.36 +/- 0.37 1.96 +/- 0.07 2.99 +/- 0.02 0.92 +/- 0.30 2.62 +/- 0.02 Reduced State s₀₂=0.83, delE=5.0 eV N Distance 1.65 +/- 0.80 2.07 +/- 0.07 1.90 +/- 0.92 1.95 +/- 0.06 2.96 +/- 0.08 0.66 +/- 1.89 2.87 +/- 0.07 208 CATALYSTS 1.5 1.0 k² (k) (A 2) 0.5 0.0 0.5 1.0 0 Monocarbonyl Dicarbonyl 2 4 Wavenumber (Å⁻¹) 6 8 10 12 1 4 Figure S6: k-space used for fitting the EXAFS data. 8 Fit Ir-O contribution 7 Ir-Ti contribution Ir-C contribution 6 Ir-(C)O contribution | (R)| (A 3) 5 4 3 2 1 0 0 1 2 R (Å) 3 4 5 6 8 Fit 6 Ir-O contribution Ir-Ti contribution 4 Ir-C contribution Ir-(C)O contribution Im[(R)] (A 3) 2 0 2 4 6 8 0 1 2 R (Å) 3 4 5 6 Fit Ir-O contribution 8 Ir-Ti contribution Ir-C contribution Ir-(C)O contribution | (R)] (A 3) 6 4 2 0 0 1 2 3 R (Å) 4 5 6 7 8 6 Fit 4 Ir-O contribution Ir-Ti contribution Ir-C contribution Ir-(C)O contribution Im[(R)] (A 3) 2 0 2 4 6 0 1 2 R (Å) 3 4 5 6 Figure S7: (a-b) EXAFS fits for the active (monocarbonyl) state showing the contributions of different scattering paths in (a) R space magnitude and (b) R space imaginary. EXAFS fits for the reduced (dicarbonyl) state showing the contributions of different scattering paths in (c) R space magnitude and (d) R space imaginary. 210 CATALYSTS Active State 8 data model 7 | (R)] (A 3) 6 5 4 3 2 1 0 0 1 2 R (Å) 3 4 5 6 Reduced State data 5 model 4 | (R)] (A 3) 3 2 1 0 0 1 2 R (Å) 3 4 5 6 8 data model 7 | (R)] (A 3) 6 5 4 3 2 1 0 0 1 2 R (Å) 3 4 5 6 data 5 model | (R)] (A 3) 4 3 2 1 0 0 1 2 R (Å) 3 4 5 6 8 data model 7 | (R)] (A 3) 6 5 4 3 2 1 0 0 1 2 R (Å) 3 4 5 6 data 5 model 4 | (R)] (A 3) 3 2 1 0 0 1 2 R (Å) 3 4 5 6 Figure S8: (a-b) fit without CO (c-d) without Ti (e-f) trying to fit Ir-Ir (in place of Ir-Ti). 6 Other Evidence for ¹³CO Non-Exchange 212 CATALYSTS During ¹²CO Reaction During ¹³CO Reaction During ¹²CO Reaction During ¹³CO Reaction Kubelka-Munk (a.u.) Kubelka-Munk (a.u.) ¹²CO₂ ¹³CO₂ 24 00 2300 2200 2100 2000 Wavenumber (cm⁻¹) 24 00 2350 2300 2250 Wavenumber (cm⁻¹) 22 00 Intensity (a.u.)

m/z = 44 m/z = 45 m/z = 12 m/z

= 13 Kubelka-Munk (a.u.) Ir(12CO) After 12CO Reaction After 13CO Reduction Expected Ir(13CO) Time 2100 2050 2000 Wavenumber (cm⁻¹) 1950 Figure S9: (a) DRIFTS spectra during the reaction with 12CO and 13CO. Note the appearance of 44CO₂ and 45CO₂ in their respective locations in the zoomed in figure (b). (c) Mass spectrometry of the 13, 44, and 45 m/z peaks over the course of the experiment. The length of the 13CO section corresponds to 100 TONs. Additionally, in order to better observe these effects, this data is for 10% CO and 10% O₂ (d) Comparison of the 13CO exchange reaction without O₂. There is clear exchange with the Ir(CO) site. Rate Law Analysis Reaction steps as shown in Figure 4: Ir(CO)(Os)₃ + CO(g) \rightleftharpoons Ir(CO)(Os)₂ + CO₂(g) (1) Ir(CO)(Os)₂ + CO(g) \rightleftharpoons Ir(CO)₂(Os)₂ (2) Ir(CO)₂(Os)₂ + O₂(g) \rightleftharpoons Ir(CO)₂(Os)₂(O₂) (3) Ir(CO)₂(Os)₂(O₂) \rightleftharpoons Ir(CO)(Os)₂O₂ + CO₂(g) (4) Ir(CO)(Os)₂O₂ \rightleftharpoons Ir(CO)(Os)₃ (5) Steady state equations d[Ir(CO)(Os)₃]/dt = 0 = -k₁PCO[Ir(CO)(Os)₃] + k₅[Ir(CO)(Os)₂O₂] (6) d[Ir(CO)(Os)₂]/dt = 0 = k₁PCO[Ir(CO)(Os)₃] - k₂PCO[Ir(CO)(Os)₂] + k₋₂[Ir(CO)₂(Os)₂] (7) d[Ir(CO)₂(Os)₂]/dt = 0 = k₂PCO[Ir(CO)(Os)₂] - k₋₂[Ir(CO)₂(Os)₂] - k₃PO₂[Ir(CO)₂(Os)₂] + k₋₃[Ir(CO)₂(Os)₂(O₂)] (8) d[Ir(CO)₂(Os)₂(O₂)]/dt = 0 = k₃PO₂[Ir(CO)₂(Os)₂] - k₋₃[Ir(CO)₂(Os)₂(O₂)] - k₄[Ir(CO)₂(Os)₂(O₂)] + k₋₄PCO₂[Ir(CO)(Os)₂O₂] (9) 214 CATALYSTS d[Ir(CO)(Os)₂O₂]/dt = 0 = k₄[Ir(CO)₂(Os)₂(O₂)] - k₋₄PCO₂[Ir(CO)(Os)₂O₂] - k₅[Ir(CO)(Os)₂O₂] (10) Site balance: [Ir(CO)(Os)₃] + [Ir(CO)₂(Os)₂] + [Ir(CO)₂(Os)₂(O₂)] + [Ir(CO)(Os)₂O₂] = 1 (11) We can assume that the only states that are present under reaction conditions are those before the two rate determining steps. This reduces the site balance considerably [Ir(CO)(Os)₃] + [Ir(CO)(Os)₂O₂] = 1. Additionally, the rate is given by: r_{CO₂} = 2r₁ = 2k₁PCO[Ir(CO)(Os)₃] Solving the site balance and the first steady state balance: 0 = -k₁PCO[Ir(CO)(Os)₃] + k₅[Ir(CO)(Os)₂O₂] [Ir(CO)(Os)₃] = k₅[Ir(CO)(Os)₂O₂] / (k₁PCO + k₅) [Ir(CO)(Os)₂O₂] = k₅ / (k₁PCO + k₅) (12) (13) (14) (15) (16) (17) (18) r_{CO₂} = 2k₁PCO[Ir(CO)(Os)₃] (19) r_{CO₂} = 2k₁PCO k₅[Ir(CO)(Os)₂O₂] / (k₁PCO + k₅) (20) r_{CO₂} = 2k₁PCO k₅ / (k₁PCO + k₅) (21) k₁PCO r_{CO₂} = 2k₅ k₅ / (k₁PCO + k₅) (22) This result indicates that the order varies from 0 to +1 order in CO. Additionally, at low CO partial pressure the activation energy associated with the first reaction dominates while at high CO partial pressure the activation energy associated with step 5 dominates. r_{CO₂} = 2k₅ k₅ / (k₁PCO + k₅) (23) r_{CO₂} = 2k₅ (24) r_{CO₂} = 2k₅ k₅ / (k₁PCO + k₅) (25) k₅ r_{CO₂} = 2k₁PCO (26) Chapter 5 Comparison of Sites for Single Atom Catalysts of Ir/TiO₂ This work is not yet published. We currently are trying to change the sites from one to another. We have some evidence that suggests this is possible. In this work I performed all of the synthesis, DRIFTS, and kinetics for these samples. I was also the lead for the XAS experiments and performed many of them myself. 218 Comparison of Sites for Single Atom Catalysts of Ir/TiO₂ Coogan B. Thompson,[†] Raymond R. Unocic,[‡] and

Ayman M. Karim*,[†] [†]Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24060, USA

[‡]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA E-mail: *amkarim@vt.edu Abstract One of the primary advantages that single atom catalysts offer over nanoparticles is the homogeneity of the single atom site. This however is not always possible as the metal oxide supports provide differing anchoring sites for the single atoms. Understanding the effect of the different sites on the same catalyst is of utmost importance in creating truly homogeneous single atom catalysts. In this work, we will compare two different single atom sites of Ir₁/TiO₂. We will discuss synthesis methods to produce each site individually as well as a mixture of the two sites. We will also explore the differing kinetic properties of the two sites with a focus on CO oxidation. Introduction Heterogeneous catalysis is called so because the catalyst particles are a different phase than the reactants and products, but it is often heterogeneous in the nature of the catalyst itself. 220 CHAPTER 5. COMPARISON OF SITES FOR SINGLE ATOM CATALYSTS OF IR/TIO₂ A typical catalytic nanoparticle is made up of 10s to 1000s of individual atoms grouped together into a semi-spherical shape. These particles take many forms and are often somewhat irregular. This leads to many different site geometries. In the simplest cases, the particles form neat facets which we can safely assume dominate the surface and the active sites, however often times, it is the irregular sites that are of interest. Single atoms are thought to solve this problem; however, the oxide supports that contain the single atoms are subject to the same drawbacks. Typically, the oxide support is a multi-faceted spherical object. This gives different possible anchoring sites in which

single atoms can bind. It has yet to be established what, if any, effect this will have on single atom catalysis.² Additionally, while some groups have claimed to have purely homogeneous sites where the sites are all identical, other groups have claimed that they have multifaceted single atom sites that are irresolvable with characterization techniques. As such, the question on the differences in such sites remains open. As single atoms are monodispersed, it is expected that the neighboring oxygen atoms will have some effect on the reactivity of the catalyst or other properties.³ Kinetically, this has already been seen in a number of catalysts in which the surface oxygen has been shown to be reactive through an Eley-Rideal mechanism or a two-site mechanism.^{4–7} In each case, the neighboring oxygens

play a critical role in the activity of the catalyst

^{2,8,9} It also might affect the central, single atom indirectly whether this is through a change in the co-ordination or a change in the surface or transition metal charge.^{10–12} With all of these possibilities, we are interested in the ability to compare sites of the same catalyst across the different possible anchoring locations. In addition to establishing the kinetic differences in the two sites, it is imperative that we also learn to compare single atom catalysts across different systems. While these trends have been well established for metal and metal oxide nanoparticles,¹³ there has yet to be many trends established on single atom catalysts. Given that the differences in single atom anchoring sites exists in at least some instances, it is imperative that we understand the affect this has on the overall trends that single atoms are believed to show. It is expected that the relationships between the transition metal nanoparticles are related to the trends that are expected on single atoms and thus the facet the single atom exists on is expected to play a role in the larger trends on single atom catalysts, however these trends are not yet established and studies approaching this question are still early in their development. However, there have been several studies on this heterogeneity in single atom sites. Chang et. al. identified 5 possible sites that a Pt atom could adsorb onto a TiO₂ (110) surface.¹⁴ Hoffman et. al. showed that the width of CO bands from IR spectroscopy could be used to determine if the sites were uniform¹⁵ while Khivantsev et. al. showed that the number of bonding oxygens (as well as bonding H₂) could cause a shift in the peaks.¹⁶ Results Synthesis of Different Sites In this work we will refer to two different sites. In lieu of greater structural information, we will refer to the sites in regards to the reduction temperature that each site is observed in. Therefore we will speak of the low temperature site, which is isolated through a low temperature calcination/oxidation (150-170 °C) followed by a low temperature reduction (also 150-170 °C) in CO. This is contrasted with the high temperature site which is isolated through a high temperature calcination (350 °C) followed by a high temperature CO reduction (270 °C). Otherwise, both samples have the same synthesis procedure as is described here. Both systems were synthesised using the strong electrostatic adsorption method as defined in previous works (Chapter 4). 1 mg Ir of IrCl₃ was first dissolved in 10 mL water also at pH 3 with HCl and allowed to set overnight to ensure complete dissolution of the IrCl₃. In a separate vessel, 1 gram of anatase TiO₂ was added to 1 L deionized water and adjusted to a pH of 3 using HCl. The solution was stirred at 600 rpm. The 10 mL precursor solution was then slowly added to the 1 L support solution at a rate of 10 mL/hr over the course of an hour. The resulting mixture was then vacuum filtered using Q5 sized filter paper. The resulting solid was then dried in a muffle furnace (80 °C for 12

hours) and then calcined immediately after, if required. ICP results on the resulting liquid solution show that approximately 90 % of the Ir introduced into the system was impregnated onto the TiO₂ while the resulting 10 % was left in the filtrate and thus not added to the catalyst. STEM Characterization of Single Atoms To ensure the creation of single atoms, we perform a variety of characterization techniques on the two proposed single atom systems. Figure 1 shows representative STEM images for each site. For the high temperature site, we were able to verify that the systems were mostly single atoms after pretreatment and after reaction conditions. For the sample that was exposed to the high temperature pretreatment (350 °C calcination, 270 °C reduction in CO), we identified 67 single atoms across 11 images with 1 cluster of approximately 4 atoms. For the sample following the same pretreatment followed by overnight reaction conditions the sample remained mostly single atoms (Figure 1). The reacted sample showed 210 single atoms across 13 STEM images with one cluster approximately 0.63 nm in diameter. Similar to the high temperature site, the low temperature site also showed single atoms. While we were unable to capture high resolution images on the freshly reduced state, we did manage to capture images of the state after reaction and the re-reduced state (reaction followed by reduction in CO at 170 °C). Figure 1 shows a representative image of the low temperature state after reaction. The STEM results showed 110 single atoms across the 17 images without the discovery of any clusters. Similarly, the re-reduced sample (Figure 1) showed 49 single atoms across 11 images also without any clusters. Figure 1: Representative

STEM images for the high temperature site (top row) and the low temperature site (bottom row). The left column is made up of images of the catalyst after reduction, while the right column is made up of images after reaction. Full treatment conditions are given in Appendix A.

DRIFTS Characterization of Sites

In addition to the STEM showing single atoms, the DRIFTS spectra show dicarbonyls for each site (Figure 2) after reduction. Dicarbonyls are common for single atoms on oxide supports and have been shown to exist for a variety of single atom systems^{17–21} with many examples of Ir and Rh such as Ir/TiO₂ (rutile),²² Ir/TiO₂ (P25 Degussa),²³ Ir/MgAl₂O₄,⁴ and Rh/Al₂O₃.^{24,25} Thus the presence of dicarbonyls here implies the existence of single atoms. To further confirm that the dicarbonyls belong to single atoms, the reduction step was repeated in a mixture of ¹³CO and ¹²CO and created six peaked systems. The peaks correspond to the original dicarbonyl, the dicarbonyl with ¹³CO only and the mixture containing one ¹³CO and one ¹²CO. The isotopic mixture for the high temperature site is shown in Figure 2, while the isotopic mixture for the low temperature site was shown previously in Chapter 4. In addition to the ¹³CO mixtures, the peaks are also different from those expected for nanoparticles and extended Ir surfaces^{17,26} and those expected on TiO₂. The latter of which are not stable at room temperature where the spectra were measured.²⁷ Interestingly, the dicarbonyl peaks are different for the two systems. This indicates that the two systems are inherently different in some regard. The higher wavenumber for the high temperature site implies that the CO is bound more weakly to the higher temperature site. While we expect this trend to hold due to the similarities of the two sites, this correlation is not guaranteed due to the back bonding nature of the CO. In order to further investigate the temperature of the changes shown, we also performed a series of intermediate conditions to look at the shift in the peak. Figure 2 shows that we begin seeing the shift in the peak location somewhere between 150 °C and 250 °C calcination or between 150 °C and 200 °C reduction. There also does appear to be a slight shift due to the differences in reduction between 233 °C and 270 °C, but this result is indistinguishable from noise. To further compare the two sites, it is possible to create both sites on the sample. This is shown in Figure 2.

The low temperature site is first created through a low temperature Ir/TiO₂. High T Site Ir/TiO₂ Low T Site Kubelka-Munk (a.u.) 2093 2015 1995 2077 Kubelka-Munk (a.u.) Composite Spectra Original Spectra ¹²CO peaks ¹³CO peaks Mixed CO peaks 2100 2050 2000 Wavenumber (cm⁻¹) 1950 2100 2050 2000 1950 Wavenumber (cm⁻¹) Cal 350 °C Red 270 °C Cal 300 °C Red 233 °C Kubelka-Munk (a.u.) Cal 250 °C Red 197 °C Cal 170 °C Red 170 °C Kubelka-Munk (a.u.) Red 170 °C Only Red 150 °C and 270 °C 2006 1995 1989 2090 2077 2100 2050 2000 Wavenumber (cm⁻¹) 1950 2100 2050 2000 Wavenumber (cm⁻¹) 1950

Figure 2 : Collection of normalized DRIFTS comparison showing the two different sites. (a) Comparison of the two sites directly. (b) Decomposition of the high temperature site after reduction in a 50 % mixture of ¹²CO and ¹³CO. The spectra has been decomposed into Ir(¹²CO)₂ peaks, Ir(¹³CO)₂ peaks, and Ir(¹²CO¹³CO) peaks. (c) Comparison of various intermediate temperatures for calcination/reduction. (d) Comparison of the low T site before and after the high temperature reduction. This reduction adds additional high temperature sites, but does not destroy the existing low temperature sites. oxidation followed by a low temperature reduction in CO (both at 150 °C). This creates the low temperature site. This is followed by a high temperature reduction (270 °C), which creates the high temperature sites, but does not remove the already created low temperature sites. Interestingly, this result combined with the previous suggests that if we increase the calcination temperature, we no longer produce the low temperature sites regardless of the reduction temperature. The method just described also creates a number of clusters as can be seen in the STEM images (Figure 7). This clusters are most likely covered in carbonates instead of CO as their presence is not detected in the DRIFTS.

Reactivity of the Sites

Unfortunately, we were unable to create an isolated sample of only the high temperature site appropriate for kinetic studies. When the sample was heated under oxidative conditions, i.e. during the calcination, a large amount of the Ir went into the bulk. This makes it impossible to quantify the number of surface atoms and thus we are unable to measure the activity of the surface sites. Additionally, reduction at high temperatures without this high calcination, resulted in the creation of clusters. However, we can still make several claims about the catalyst activity with just the DRIFTS spectra. Under reaction conditions, both sites appear to go to a monocarbonyl site (Figure 3). In addition to both sites going to a monocarbonyl under extended reaction conditions, there is some indication that they go to the same monocarbonyl. This is evidenced by the lower wavenumber shift in the high temperature site and the higher wavenumber shift in the low temperature site. Additionally, while the dicarbonyl that returns on the low temperature site matches well with the dicarbonyl before reaction conditions, the high temperature site does something different. For the high temperature site after reaction, a following reduction creates a dicarbonyl that is more shifted to the lower wavenumbers. This site is closer to the low temperature sites dicarbonyl.

This is an indication that the active site for the high temperature site is more in line with the low temperature site as shown in Figure 3. After Reduction After Reaction Kubelka-Munk (a.u.) 2083 1995 2077 1995 2100 2050 2000 Wavenumber (cm⁻¹) 1950 After Reduction After Reaction Kubelka-Munk (a.u.) After Second Reduction 2100 2050 2000 Wavenumber (cm⁻¹) 1950 Figure 3

: Comparison of the two sites before and after reaction. (a) low temperature site first oxidized in 10 % O₂ at 170 °C for 1 hour followed by reduction in 1 % CO for 12 hours at 170 °C to get the reduced state. The extended reduction time is added to ensure complete reduction. The reaction state is thus achieved by reacting 1% CO and 10% O₂ at 170 °C for 12 hours (b) DRIFTS spectra of the high temperature site following the high temperature reduction (1% CO at 270 °C for 1 hour) followed by reaction conditions (1% CO and 10% O₂ at 170 °C for 12 hours) to obtain a monocarbonyl state. Further reduction in 1% CO (at 170 °C for 0.5 hours) resulted in the dicarbonyl peak returning, but shifted towards the low temperature site. We also see the relationship between the two sites played out in the TPDs and TPOs of each system (Figure 4). Performing a TPD on the high temperature site shows that the two dicarbonyls are very stable in inert atmospheres and are not completely removed until temperatures over 350 °C. This is compared to heating up in oxygen (TPO) which shows that the dicarbonyl peak turns to the monocarbonyl peak, which is also seen under reaction conditions, at approximately 200 °C. This is close to the reaction temperature as well and thus is believed to proceed through a similar mechanism as the reaction mechanism. However, the low temperature site is dominated by the existence of the high temperature site. Performing a TPD on the reduced state for the low temperature site, we see a shift in the site. In Figure 4 we see the low temperature sites shifting in the DRIFTS to be more in line to the high temperature sites. This is an indication that the sites are migrating to the more stable high temperature site when the temperature reaches approximately 250 °C. This is in line with what temperature we saw the formation of the second site (Figure 2). Finally, the TPO (Figure 4) on the low temperature site is dominated by the change to the monocarbonyl site. There is also a significant shift in the location of the peak implying that there might be some creation of the high temperature site, however this is difficult to discern as the direction to the high temperature site is the same as the direction to the active, monocarbonyl site and the locations are somewhat similar. Possibly the most interesting comparison is in the ¹³CO exchange experiments. As we have shown previously in our mechanistic study of Ir₁/TiO₂, the mechanism for CO oxidation has an attached CO ligand that acts as part of the active site of the catalysts. Specifically, we can verify that the gas phase COs are much more likely to react than the adsorbed CO. This indicates that the adsorbed CO is more part of the reactive site as opposed to a reactant. This same experiment is repeated here with the high temperature site and yields the same result (Figure 5). Similar to the low temperature site (Chapter 4), the high temperature site shows no exchange of the ²³CO ligand for the ¹³CO ligand. This is a further indication that the two species proceed by the same, or at least very similar mechanisms. Base 85 °C 185 °C 285 °C Kubelka-Munk (a.u.) 385 °C 485 °C After TPD 2100 2050 2000 Wavenumber (cm⁻¹) 1950 Kubelka-Munk (a.u.) Base 89 °C 161 °C 233 °C 306 °C 2100 2050 2000 1950 Wavenumber (cm⁻¹) Base 100 °C 150 °C 200 °C Kubelka-Munk (a.u.) 250 °C 300 °C 350 °C Base 110 °C 160 °C 285 °C Kubelka-Munk (a.u.) 210 °C 235 °C 260 °C 285 °C 310 °C 2100 2050 2000 Wavenumber (cm⁻¹) 1950

2100 2050 2000 Wavenumber (cm⁻¹) 1950 Figure 4

: TPD/TPO for the two different sites. The top (bottom) row contains the high (low) temperature cases. The left (right) column contains the temperature programmed desorptions (oxidations). The high temperature sites show a clear preference for reacting with O₂ and appear to bond rather strongly to the surface in inert. In the case of the low temperature site, the TPO show much the same trends, however there is a clear change in the nature of the peak as the low temperature site is heated. This is believed to be a migration to the high temperature site. The increase in peak height suggests a significantly higher extinction coefficient for the high temperature site. Before ¹³CO Reaction During ¹³CO Reaction Kubelka-Munk (a.u.) After ¹³CO Reaction 2300 2200

Wavenumber (cm⁻¹) 2100 2000 Figure 5: DRIFTS spectra of the

¹³CO exchange experiment. The pretreated (350 °C calcination, 270 °C reduction in CO) sample was exposed to reaction conditions (1 % CO, 10% O₂ at 170 °C for 12 hours) to achieve the active state. Once the state was reached, reaction conditions (1 % CO, 10% O₂ at 170 °C) with ¹³CO instead of ¹²CO were exposed to the catalyst. The lack of ¹³CO in the spectra shows that the gas phase ¹³CO did not exchange with the surface ¹²CO Discussion The existence of multiple sites is well established to exist on several different catalyst systems. Typically, the different sites are not

resolvable but instead are determined by the peak width associated with the type of peak. This is similar to the intermediate temperature (200 °C) reduction case (Figure 2) where the peak is considerably broader.² However, typically the sites cannot be resolved to such isolated differences. This level of isolation can be expanded on to study the differences in kinetics of the two systems. While this is beyond what our lab can currently do, we hope the example demonstrated here might encourage others with the means to further explore what differences in site, such as this, might mean for the reactivity of such a system. Additionally, the difference in peak location suggests a difference in the binding (energy) of CO on the two different sites. Binding energy of CO has been shown to be an indicator of the activity for transition metal nanoparticle catalysts for CO oxidation. This is because the mechanism typically proceeds through an open site on the otherwise CO covered (or poisoned) surface. Thus, a weaker CO binding suggests the potential for a more active catalyst. This exact trend has been shown to not extend to single atoms as the strength of CO binding for iridium nanoparticles, subnanometer clusters, and single atoms has been found to not accurately represent the activities of these species when compared to each other.^{4,7} This is due to a change in the mechanism over the 3 different regimes. However, due to a lack of data, there has not been a comprehensive study looking at the effect of CO binding across the different single atom systems. Additionally, since the adsorption of CO is still likely to occur in the CO oxidation mechanism for single atom systems, it is expected that the strength of CO binding will play some role in the activity of the system. This then suggests that there would be slightly different kinetics for the two different sites we present here. That is assuming however, that the sites do not go to the same site under reaction conditions. An additional highlight that this paper suggests is the ability to protect certain sites use CO as a stabilizing force. As we saw in the twice reduced sample, we can create both sites on the same system, if we first reduce the low temperature site. Presumably, these are the easier to reduce single atoms. This implies that the reduced low temperature dicarbonyl is somehow stabilized by the CO. As the site does appear to move when heated to the same conditions in O₂. An alternative theory to this is that it is not the Ir that is moving, but instead the TiO₂ support that is moving, or rather restructuring around the Ir. TiO₂ is well known for its reducible properties and thus is cannot be ruled out that the vacancies created by the higher temperature reduction of the TiO₂ could have allowed for the migration of the Ir to occur or could cause a permanent change in the structure near the unprotected single atoms. This would likely happen through some kind of surface oxygen vacancy. Additionally, the bare Ir (assumed to be fully oxidized before it is used), could in fact be the catalyst that allows for a more extensive reduction to occur. In this theory, the surface Ir would be reduced at low temperatures and would explain the low T site. Then to explain the high temperature site we look to the Ir that went into the bulk during the oxidation which is known to happen. When this system sees reduction conditions, we quickly see the surface sites reduced, however the bulk Ir could catalyse a higher degree of reduction and actually allow the removal of the TiO₂ overlayer. This would result in an Ir potentially surrounded by step edges instead of a clean facet and would result in a much more stable Ir single atom. In this method, the Ir atoms put into the bulk would be extracted back onto the surface. Conclusions In this work we have synthesized two different single atom sites for the Ir₁/TiO₂ catalyst. We verified each were single atoms through STEM and DRIFTS spectroscopy. We have shown that while both sites have their own differing properties, they are linked by ability to transform from one into another and critically both use the same active site for CO oxidation. We further show that we are able to control the sites individually through various treatment methods. Future Direction As a final proof of concept and to demonstrate the control we have over these two sites, it should be possible to create a cycle with the various states. This is shown in Figure 6. If we start with the active state, we can reduce in CO at low temperatures to return to the dicarbonyl state. Further higher temperature reduction should be able to convert this state to the high temperature site. This high temperature state can then be reconverted back to the active state through reaction conditions for an extended period of time (12 hours at 170 °C in 1% CO, 10% O₂). This is demonstrated by the cycle in Figure 6. Currently, we are unable to complete this cycle, possibly due to the agglomeration of the single atom sites or possibly due to the stubbornness of the low temperature site to convert to the high temperature site. Future work is focused on showing that we can complete this cycle. This cycle also would open the door to a potential pathway to create the high temperature site without the problem of Ir going into the bulk. This would allow for a much more thorough investigation in the differences between these two sites. In possible this would allow direct comparisons of the kinetics and EXAFS/HERFD analysis of the single atoms at this high temperature site. With that information, it is likely we would identify what the cause of this difference is. References (1) Kurtoğlu-Öztulum, S. F.; Uzun, A. Reference Module in Chemistry, Molecular Sciences and Chemical Engineering ; 2021. Figure 6: Site cycle for the Ir/TiO₂ single atom catalyst. Starting with any state, the other two states should be reachable. Starting

from the upper left, the low T site. It is expected that a long dwell at slightly elevated temperatures (200 °C or higher) should allow the Ir to move to the high temperature site. As is shown in Figure 3, The high temperature site can be converted to the monocarbonyl active site. Furthermore, we can go from the active state to the low temperature dicarbonyl state by a low temperature CO reduction as is see in Chapter 4 and Figure 3. Appendix A. Full Treatment History for STEM Samples Top left, high temperature after reduction: The catalyst was calcined at 350 °C in a muffle furnace immediately after synthesis.

The catalyst was then treated in a tube furnace at 350 °C in

10% O₂ following by a reduction in the same furnace at 270 °C in 1% CO. Top right, high temperature after reaction: The catalyst was exposed to the exact same conditions as before, however, this was followed at 12 hours in 1% CO and 10% O₂ at 170 °C. Bottom left, low temperature after

reduction: The catalyst was not calcined immediately after synthesis. The catalyst was treated for 12 hours in 10% CO and 10% O₂ at 170 °C. The catalyst was then re-reduced through exposure to 10% CO only at 170 °C. This was verified to go to the same state in the DRIFTS and was used as a replacement as the fresh sample that was only reduced was unable to be ran in the HAADF-STEM. Bottom right, low temperature after reaction: The catalyst was not calcined immediately after synthesis. The catalyst was treated for 12 hours in 10% CO and 10% O₂ at 170 °C. Additional STEM

images Figure 7: Additional STEM images referenced in this work. (a) STEM of the catalyst with both sites. The pretreatment for this sample is 150 °C calcination/oxidation followed by reduction at 150 °C and then another at 270 °C. Chapter 6 Redispersion of Ir Catalysts on a Ir/TiO₂ Support: Catalysts with a Short Memory This work is not yet published. The last round of experiments revealed that this redispersion is much more intense than we first expected. This required us to change some of our baseline experiments. Essentially our baseline non-redispersion sample actually was dispersing. This requires a significant redo of some experiments and we are currently in the midst of that process. We also have one species from the spectroscopy that we need to fully characterize, we believe it to be CO on IrO₂ that exists as particles (as opposed to single atoms). In this work I performed all of the synthesis, DRIFTS, and kinetics for these samples. I was also the lead for the XAS experiments and performed many of them myself.

241 CHAPTER 6. REDISPERSION OF IR CATALYSTS ON A IR/TIO₂ SUPPORT: CATALYSTS WITH A SHORT 242 MEMORY Redispersion of Ir Catalysts on a TiO₂ Support: Catalysts with a Short Memory Coogan B. Thompson,[†] Adam S. Hoffman,[‡] Jiyun Hong,[‡] Jorge Perez-Aguilar,[‡] Simon R. Bare,[‡] Abhijit Shrotri,[¶] and

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[¶]Hokkaido University, Sapporo, Japan, 001-0021 E-mail: *amkarim@vt.edu Abstract For catalysts in the 1 nm size regime and lower, dispersion, or the general size of a catalyst begins to become the most dominant characteristic of the catalyst. This has far reaching affects for catalysis as this often leads to single atom catalysts and small cluster catalysts having very different properties and reaction mechanisms than their nanoparticle analogs.

Furthermore, these systems sometimes have much different levels of stability based on their size. For the case of Ir/TiO₂, we show here that small clusters (those under 1 nm) are not stable under CO oxidation conditions. Instead they prefer to disperse into single atoms. We show this for systems reduced in CO at 270 °C and H₂ at 150 °C. Specifically we use HAADF-STEM, EXAFS, DRIFTS, and kinetic measurements to show that systems synthesised as small clusters are not stable under reaction conditions and prefer to disperse into single atoms. Introduction One of the most important considerations for a heterogeneous catalyst is the physical size and shape of the active metal. Many studies have looked extensively at how catalyst activity and selectivity is affected by the catalyst's configuration and dispersion. In general, we can classify the effects into three classes: surface site to total site ratio, ratio of active to inactive sites, and the change in electronic properties going from lattice dominated (large) species to local dominated (small) species. The first is by changing the number of active sites through controlling the size of the particle. This is well understood and is the driving force behind why catalysts are typically nanosized particles instead of bulk metals. Bulk metals typically have a lot of metal atoms that are completely surrounded by other metal atoms instead of being on the metal's surface. This means that the gas (or liquid) phase reactants cannot get to these atoms and thus the bulk metal atoms are not kinetically relevant. The second kind of affect to describe is that is that of shape. Specifically, by shape we mean the relative ratios of different types of active sites. Heterogeneous catalysts typically have multiple different types of sites due to the

lack of homogeneity on the catalyst surface. Examples of this include edge and corner sites, where two non parallel surfaces of a catalysts meet, literally the edges of the particles; Step edges, which are boundaries of where the catalysts surface changes from one surface to another parallel surface; defect sites, which are imperfection in the surface lattice, and surface sites, which can refer to all sites or can exclude the previously mentioned sites. Each of these sites has its own exact kinetic properties. For example, ammonia decomposition is believed to happen on the B5 site of Ru/Al₂O₃.¹ Because of this, it is much more important to maximize the number of B5 sites instead of just surface sites as these are mostly, relatively inert. A less specific example happens in several supported metal catalyst systems where the kinetically dominant step happens at the interface of the “catalyst” and the support. This has been shown to be the case for subnanometer clusters of Ir/MgAl₂O₄² where CO from the Ir reacts with O from the MgAl₂O₄ support. Additionally, many single atoms would arguably fall into this category, ²⁴⁴ MEMORY however for those systems it only seems fair to include the nearby pieces of the support as part of the active site instead of arbitrarily defining a species as being part of the catalyst and part of the support. The third category of how the catalysts size and shape affects its activity is the inert differences between a particle of thousands of atoms vs that of a couple atoms or even a single atom supported or free. Due to the metallic bonding of large metal nanoparticles, the catalysts form well defined bands. Because of this, nanoparticle catalysts are better defined by properties such as d-band center and dispersion. However, as the particles get smaller, these concepts begin to lose their descriptive power. The d-band literally is broken apart into discrete states and while some of the trends from d-band theory seem to still work without the d-band,³ the original idea of the d-band does not. Likewise, as nanoparticles get smaller, the assumptions of uniform sites that are inherent in measurements such as dispersion begin to break. For example. Many single atoms form dicarbonyls thus they would be double counted in any CO chemisorption measurement compared to nanoparticles.^{4–6} In the same manner, it becomes harder and harder to assign uniform properties to small clusters due to the large degree of heterogeneity that they can exhibit in conformation and facet location.^{7–11} There are still further effects that can play an out-sized role in catalysis, and this is especially true for systems that are small clusters and single atoms. As the catalyst gets smaller, it is much easier for the support and the gas phase properties to bully the transition metal. For example, Rh/TiO₂ has been shown to undergo restructuring of single atoms¹² and small nanoparticles¹³ due to changes in the gases flowing across them, i.e. going from pretreatment to treatment conditions with the single atoms having the additional influence of the surface vacancy of the TiO₂ (rutile) support^{12,14} which has its own effects on the catalyst and its properties. Furthermore, Rh/TiO₂ (anatase) single atoms have also been shown to have slightly different properties depending on whether they were reduced in CO or H₂.¹⁵ In addition, Rh/TiO₂ (anatase) single atoms were found to have been affected by the strong support metal interaction, giving yet another parameter that affects these species.¹⁴ Pt/TiO₂, similarly, showed a strong SMSI for single atom catalysts. The SMSI led to a deactivation of the single atoms for the 3-nitrostyrene hydrogenation reaction.¹⁶ Due to the large effect that the catalyst nuclearity has on the system, it is important to be aware of the fact that for many catalysts, the particle size varies considerably under different conditions. Iridium in particular has been shown to be able to be redispersed on a variety of different supports and conditions. Berkó et. al. showed that CO causes agglomeration at high temperature (600 K) and redispersion at low temperatures (300 K) for Ir nanoparticles on TiO₂ (110) crystal surface.^{17,18} Fogar et. al. showed that nanoparticles in 1-100 nm can be redispersed on Al₂O₃ and SiO₂ using Cl₂ gas, however they had limited ability to detect to what extent the particles dispersed.¹⁹ This was followed by Solymosi et. al. who showed the agglomeration of Ir/Al₂O₃ single atoms could be tracked using IR measurements and paved the way studies such as this.²⁰ Redispersion is certainly not limited to Ir either. It is found in a variety of different conditions for several different systems such as MXene,²¹ Rh/CeO₂,²² Au/C,²³ Pt/TiO₂²⁴ and many others. In this work we will look at the interesting case of Ir/TiO₂ (anatase) catalysts that redisperse under CO oxidation conditions. We will show that catalytic nanoparticles of up to 1 nm redisperse into single atoms when exposed to CO oxidation (1% CO, 10% O₂) at 170 °C. These results are verified through STEM microscopy, DRIFTS spectroscopy, EXAFS, and kinetic measurements. Results Synthesis and Pretreatment Three samples are compared here to show the effect of synthesis method and reduction conditions. The first sample was created using the strong electrostatic adsorption method. 1 mg Ir of IrCl₃ was dissolved in 10 mL pH = 3 (HCl) water overnight to ensure full dissolution. ²⁴⁶ MEMORY 1 g of TiO₂ was dissolved in 1 L DI water and stirred at 600 rpm. Once fully dissolved, the catalyst solution was adjusted to a pH of 3 with HCl. The precursor solution containing the IrCl₃ precursor was then added to the support solution slowly (10 mL/hr). The mixed solution was then vacuum filtered overnight. The 5 wt% SEA sample was prepared in the same manner but with 50 mg Ir of IrCl₃ instead of 1 mg Ir. In order to better measure the amount of Ir put onto the support. ICP measurements were performed on the precursor solution and the resulting liquid filtrate. For the 0.1 wt%

catalyst, 80% of the Ir was found to go onto the support, meaning the true weight loading was 0.08 wt%. Similarly for the 5 wt% catalyst 60% of the Ir went onto the surface giving a true weight loading of 3.0 wt%. The names 0.1 wt% and 5 wt% are kept as the nominal names of the sample for simplicity while the true weight loadings are used for normalizations. A third sample was prepared via wet impregnation.

50 mg Ir of IrCl₃ was dissolved in 2 mL of DI water

, which was found to be the appropriate amount of liquid for the TiO₂ of interest. This solution was then added dropwise into the dried TiO₂ with rigorous mixing in between each drop. The resulting solid

was then dried on a hot plate overnight at 50 °C. In addition to

the synthesis, each of the different systems was given a unique pretreatment. The low (0.1 wt%) weight loading catalyst prepared by SEA was treated first with an oxidation at 150 °C followed by a reduction in CO at 270 °C. The higher weight loading (5 wt%) catalyst prepared by SEA was reduced

in H₂ at 150 °C. The IW sample was reduced in CO at

270 °C with no oxidation step. These are the conditions used to create the nanoparticles in the samples. In addition to the pretreatment of the samples, the samples were also exposed to reaction conditions in order to redisperse the samples. For the SEA samples this was 12 hours at 10 % CO and 10 % O₂ with the balance inert at atmospheric pressure at 180 °C. While the IW sample this was 12 hours at 1% CO and 10% O₂ with the balance inert at atmospheric pressure at 180 °C. HAADF-STEM In order to characterize the different samples, HAADF-STEM images were taken of each of the samples. The STEM images were taken by our collaborators from Japan. All samples showed the creation of nanoparticles with a significant number of single atoms also being measured. Representative images of both of the two SEA samples (0.1 wt% and 5 wt%) are shown in Figure 1. The low weight loading sample showed the fewest number of nanoparticles (with regard to the number of single atoms) as well as the smallest diameter (0.68 nm) of nanoparticles for the species considered. This sample showed 57 nanoparticles and 366 single atoms across the 134 images analyzed for this sample. After reaction, significantly fewer nanoparticles were detected indicating that a significant redispersion had occurred. After the reaction conditions, only 3 nanoparticles were detected

with an average diameter of 0.41 nm. The majority of the

nanoparticles were believed to have been redispersed as among the 107 images analyzed there were 576 single atoms counted after reaction conditions. This is approximately twice the density of single atoms as the images taken before reaction. In a similar manner, the 5 wt% SEA sample reduced in H₂ at 150 °C also showed a large amount of redispersion. The images after reduction and before the reaction were found to contain 1216 single atoms and 562 nanoparticles across the 79 images analyzed but then increased/decreased to 1724 single atoms and 310 nanoparticles in the 52 images analyzed after reaction. This is a more than a doubling of the single atom per nanoparticle ratio which is a strong indication that the nanoparticles were to a certain extent redispersed. Furthermore, the nanoparticles that remained in the STEM images are significantly smaller with the average size of the nanoparticles going from 0.98 +/- 0.31 Å to 0.81 +/- 0.28 Å. The CO reduced at 270 °C, is currently awaiting analysis, however from the preponderance of data from other sources, we are confident that the results will show that this system is large nanoparticles under both reduced conditions and reaction conditions. 248 MEMORY Figure 1: HAADF-STEM characterization of Ir/TiO₂ samples. (a) 0.1 wt% Ir/TiO₂ catalyst after CO reduction at 270 °C (before reaction). (b) 0.1 wt% Ir/TiO₂ catalyst (CO reduction at 270 °C) after reaction. (c) 5 wt% Ir/TiO₂ catalyst after H₂ reduction at 150 °C (before reaction). (d) 5 wt% Ir/TiO₂ catalyst (H₂ reduction at 150 °C) after reaction. A summary of the atom counts is given in Table 1 EXAFS To further probe this redispersion effect for the Ir/TiO₂ catalyst considered, we performed the same experiments in-situ at BL 9-3 at SSRL. Further details are provided in the SI. All samples were reduced in-situ with the conditions specified previously and then reacted for 1 hour of the reaction conditions (1% CO, 10% O₂ at 180 °C). The results are shown in Figure 2. The 0.1 wt% sample reduced at 270 °C was the least descriptive sample due to the lack of catalyst signal from the low weight loading of Ir and the strong adsorption of the Ti. However, the results (Figure 2 a, b) still show a distinct change in the bonding environment of the Ir. Specifically, the dominant feature shows a distinct shift in location going from 1.9 Å to 1.7 Å. This is likely due to a shift in either the Ir-Ir or the Ir-Ti. While the fitting is unable to distinguish this difference, we can see a distinct qualitative differences in this sample compared to the reduced single atoms. This qualitative difference largely goes away once the catalyst is exposed to reaction conditions. The second data set, the 5 wt% reduced in H₂ at 150 °C shows a clear and drastic change in the reduced

and reacted states (Figure 2 c, d). The R-space data shows a clear change in the dominate features as well as several secondary characteristics. There is a clear indication that the Ir-O peak (1.8 Å) grows significantly under reaction conditions and a clear removal of the 2.3 Å which is believed to be a combination of the Ir-Ti and Ir-Ir. This reduced state is in line with small clusters as they retain some Ir-O features as well as Ir-Ir features as the nanoparticles are too small to be dominated by the Ir-Ir as shown in the following sample. This is removed however under reaction conditions where there is little features outside of the strong Ir-O peak. The final data set, 5 wt% CO reduced at 270 °C (Figure 2 e, f), we see the before and after reaction spectra are both dominated by the Ir-Ir scattering peaks centered at 2.5 Å. There is a slight increase in the feature at 1.7 Å which is likely due to an increase in the Ir-O scatter due to either IrO₂ formation, single atom formation, or simply O adsorbed on 250 MEMORY Figure 2: EXAFS data for the samples considered in this work after reduction to nanopar- ticles (blue) and after reaction/redispersion (red). All samples shown here are in He and at 35 °C. (a) XANES region of the spectra and (b) R-space data for the 0.1 wt% sample after pretreatment (oxidation at 150 °C, CO reduction at 270 °C) and after reaction (1% CO, 10% O₂ at 180 °C). (c) XANES region of the spectra and (d) R-space data for the 5 wt% sample after pretreatment (H₂ reduction at 150 °C) and after reaction (1% CO, 10% O₂ at 180 °C). (e) XANES region of the spectra and (f) R-space data for the 5 wt% sample after pretreatment (CO reduction at 270 °C) and after reaction (1% CO, 10% O₂ at 180 °C). the nanoparticle surface. However, the dominate feature remains the strong Ir-Ir scattering which indicates that the system remains as large nanoparticles. Fitting for these data sets remains ongoing, however the conclusions discussed herein are well warranted from the data alone as well as partial fits. Fitting of the CO reduced at 270 °C sample show an Ir-Ir coordination of approximately 10.5. This corresponds with a nanoparticle size of approximately 4 nm.²⁵ DRIFTS The DRIFTS results show the least change of all the experiments considered. From previous studies of ours and others,^{20,26} it is well established that the single atoms of Ir/TiO₂ form a dicarbonyl after reduction and a monocarbonyl after reaction. Additionally, this mono- carbonyl is approximately at the same location as the symmetric peak of the dicarbonyl. Furthermore from studies on extended surfaces and nanoparticles, it is expected that Ir nanoparticles will have a peak at approximately 2050 cm⁻¹.^{20,26,27} With these in mind, we can interpret the results shown in Figure 3. Starting again with the low weight loading reduced in CO at 270 °C. We see what appears to be mostly single atoms. Specifically, we see two groups of dicarbonyls that are representative of the two different types of single atoms. This was discussed extensively in the previous chapter. From the STEM and EXAFS, we expect to see some nanoparticles, however there is no indication of them existing in the spectra. This is likely due to coking of the nanoparticles, a common problem when reducing with carbon species.^{28–30} After reaction conditions, the spectra still show single atoms, however now in the monocarbonyl state that is expected for the single atoms. There appears to be a residual amount of dicarbonyl remaining however most of the dicarbonyl has transferred to the monocarbonyl state as well as a significant amount of what is believed to be Ir(CO)(O) based on the previous chapters and other related studies of Rh.³¹ Moving onto the high weight loading sample reduced in H₂ at 150 °C, we see something 252 MEMORY Reduced (270 °C in CO 0.1 wt%) Reactive State Kubelka-Munk (a.u.) 2074 2088 2151 1987 1986 2150 2100 2050 2000 Wavenumber (cm⁻¹) 1950 Reduced (150 °C in H₂) Reactive State 2093 Kubelka-Munk (a.u.) 2082 2156 1974 2150 2100 2050 2000 Wavenumber (cm⁻¹) 1950 Reduced (270 °C in CO 5wt%) Reactive State Kubelka-Munk (a.u.) 2087 2102 2022 1973 2158 2150 2100 2050 2000 1950 Wavenumber (cm⁻¹) Kubelka-Munk (a.u.) After Reduction After Reaction 2086 1995 2077 2100 2050 2000 Wavenumber (cm⁻¹) 1950 Figure 3

: Comparison of the DRIFTS of the different cluster samples considered. The treatment details are provided in the synthesis and pretreatment section. A summary of peak assignments is as follows: for the reduced states, 2075+ 1995 single atom dicarbonyls, 2080 alone small clusters, 2050 linear bound CO on nanoparticles; for active states, 2150 single atoms in the Ir(CO)(O) state, 2100 CO on IrO₂ nanoparticles, 2090 small clusters retaining CO, 2085 single atoms in the Ir(CO) state. (a) Reduced and reacted states for the 0.1 wt% sample reduced in CO at 270 °C (b) Reduced and reacted states for the 5 wt% sample reduced in H₂ at 150 °C (c) Reduced and reacted states for the 5 wt% sample reduced in CO at 270 °C (d) Reduced and reacted state for single atom systems from previous sections given as a reference. rather peculiar. After the initial reduction, we see a single broad peak at 2082 cm⁻¹ and likely shoulders on each side with an additional small shoulder at approximately 2050 cm⁻¹ but no peak in the asymmetric range (i.e. no dicarbonyls). This is consistent with small clusters of Ir. Small clusters of platinum group metals are known to shift to the right as they get bigger and the 2082-1 number is a reasonable guess for the approximately 1 nm particle size that is seen from STEM. After the reaction of this sample, we see a significant growth in the peak as well as a shift to 2093-1 and the creation of a 2156 cm⁻¹ peak. This new location is still consistent

with the monocarbonyl from the single atom catalysts from the previous works and is shown in Figure 3d. The increase in intensity of 2082-1 (now 2093-1) peak is likely a result of the increased extinction coefficient of the single atoms compared to the small clusters while the width increase is likely due to the larger variation of single atom sites when compared to the preparation of the dispersed samples that were used previously. However, we cannot fully rule out that this increase is caused from a potential increase in the clusters that are reduced under reaction conditions as compared to the H₂ reduction conditions. Previous results on single atoms discussed in the earlier chapters show that a mixture (CO + O₂) of gases at a slightly higher temperature can reduce more iridium species than a slightly lower temperature in just CO. Additionally, CO is well known to be a more reductive agent than H₂ so there is a possibility that H₂ at 150 °C cannot reduce the entire system. For the final sample, 5 wt% reduced in CO at 270 °C, there appears to be even larger nanoparticles being created from the STEM and EXAFS, however the spectra shows peaks at 2087, 2022, and 1973 cm⁻¹. The 2087 and 2022 cm⁻¹ combination is most similar to the single atoms and it is likely that some are shown here, however, there are likely a large number of nanoparticles that are not seen in the DRIFTS (but were seen in STEM and EXAFS). Similar to the low weight loading catalyst, the most likely explanation for this missing CO peak is likely due to coke build up on the nanoparticles. Additionally the 1973 cm⁻¹ peak is believed to be a possible bridging species of (Ir)₂(CO), however, this is largely unknown. After the reaction, two peaks remain, the first being at 2158 cm⁻¹ consist with at least some single atoms still being present while the larger peak at 2102 cm⁻¹ is associated with monocarbonyl bands of IrO₂.³²

Kinetic Comparisons One of the most important reasons to understand the ability of a catalysts to redisperse is how this affects the kinetics of the catalyst. Looking at the kinetics for these catalysts, it is apparent that some of them go through substantial changes. We first consider the case of the 5 wt% sample reduced at 270 °C. This sample produced the largest nanoparticles from STEM and EXAFS and was the catalyst that remained as nanoparticles under reaction conditions according to the EXAFS. This catalyst shows a distinct negative order in CO (Figure 4b) and presumably a positive order in O₂ (this experiment needs to be reproduced). This is somewhat unusual as a typical nanoparticle catalyst is expected to display an approximate 0 order in CO due to the reaction happening on the catalyst, surface interface. However it is not unprecedented. Ir extended surfaces show a reaction order of -1 in CO and +1 in O₂, however this is dependent upon the ratio of CO and O₂ as the LH mechanism is dominated by the CO vs O₂ competitive adsorption.^{26,33–35} The two SEA samples, 270 °C reduced in CO and the 150 °C reduced in H₂, show clear single atom activity. Despite the nanoparticles being significantly more active at the low CO partial pressures, there is still a significant amount of positive order CO being measured. The 0.3 CO order for the 5 wt% reduced at 150 °C in H₂ and the 0.1 wt% reduced at 270 °C sample is what is expected for single atoms measured at 148/163 °C respectively. This order is not quite positive 1 as the competitive mechanism discussed in the work sections lower the magnitude of the reaction order. The approximate 0 order in O₂ also agrees with these being single atoms. However, we cannot fully rule out that some clusters or nanoparticles are not still present in this system. That is further discussed in the discussion section. Comparing the data sets together, the 5 wt% CO reduced at 270 °C has the highest Single Atoms

TOF (s⁻¹) 10 2 TOF (s⁻¹) 10 3 10

3 nO₂ = 0.15 10 1402 nO₂ = -0.16 103 104 105 PCO (Pa) 103 104 105 PO₂ (Pa) 208 189 T (°C) 172 156 142 128 115 Reduced in H₂ 150 °C 5 wt% Reduced in CO 270 °C 10 1 Single Atoms TOF (s⁻¹) E_{app} = 118 kJ/mol 10 2 10 3 E_{app} = 91 kJ/mol E_{app} = 100 kJ/mol 0.25 0.26 0.27 0.28 0.29 0.30 1/RT (kJ/mol) 1 Figure 4: (a) The Arrhenius plots were performed at 1% CO, 10% O₂, 80 sccm. The CO/O₂ (b/c) order plots were performed at 10% O₂/1% CO and at similar, but different temperatures based around catalyst activity limits. Single atoms, 154 °C; 0.1 wt% Reduced in CO at 270 °C, 163 °C; H₂ reduced at 150 °C, 148 °C; From previous sections, the CO order of single atoms is higher at higher temperatures. From the activation energy comparison, higher E_a leads to relatively more activity at higher temperatures. 256 MEMORY activation energy at 119 kJ/mol (compared to 105 for Ir/SiO₂) followed by the single atom catalysts from the previous chapter and then closely followed by the redispersed clusters from the 150 °C reduction in H₂ sample implying the two systems are closely related. When looking at the reaction orders as a whole, there is an obvious trend. The order goes up with decreasing size. This analysis shows the CO order goes in the order of 5 wt% Reduced in CO at 270 °C, H₂ reduced at 150 °C, and 0.1 wt% reduced in CO at 270 °C. This is in line with the sizes from largest to smallest of the catalysts in question from the STEM measurements and the EXAFS results. Given that the CO order of the single atoms is known to be positive from the mechanistic study shown earlier and the nanoparticles is known to be negative,^{33–35} the trend is as we expected. The same trend, albeit much noisier can be made with the O₂ order as

well. The larger catalysts are expected to be more positive in O₂ than the single atoms. Thus, the trend is as expected: reduced 150 °C in H₂ is greater than the single atoms. Summary of Results Discussion

From the data summarized in Table 1, it is apparent that the nanoparticles in this small size regime do redisperse to varying extents. It also appears that the redispersion happens more to smaller clusters which are more likely to redisperse all the way to single atoms which can be seen to the large increase in the number and fraction of single atoms. However, even large clusters are not immune to the effects of the redispersion as can be seen from the decrease in average size of the before and after reaction samples for the larger samples.

This change in dispersion creates a distinct change in the properties of the catalyst

. This is most apparent here in the change in the CO order but will likely affect the catalytic properties for these systems in a variety of ways for different reactions of interest. Due to this redispersion, it appears that we are unable to measure the CO oxidation Table 1: Summary of characterization of catalysts Catalyst A B C Synthesis Conditions 0.1 wt% SEA Pretreatment 150 °C in O₂ 270 °C in CO 5 wt% SEA 5wt% IW 150 °C in H₂ 270 °C in CO DRIFTS Before (cm⁻¹) DRIFTS After (cm⁻¹) 1987, 2074 1986, 2088, 2151 1974, 2082 2093, 2156 2102, 2158 1973, 2022, 2087 CO/O₂ Order 0.3/? 0.3/0.2 -0.9/? STEM Before Single Atoms Dimers Nanoparticles Size 366 23 57 0.68 +/- 0.21 Å 1216 106 562 0.98 +/- 0.31 Å Not Yet Measured STEM After Single Atoms Dimers Nanoparticles Size 576 29 3 0.41 +/- 0.08 Å 1724 222 310 0.81 +/- 0.28 Å Not Yet Measured Fraction SA (STEM) Before 49% 12% After 99% 37% Not Yet Measured EXAFS Qualitative Before Mostly SA, Some NP NP NP EXAFS Qualitative After SA SA/IrO₂ NP 258 MEMORY kinetics of small clusters of Ir/TiO₂ and it might not be possible. However, to fully rule out that possibility, we must analyze the data looking for that possibility. Because this size regime is not well defined, we will define it in terms of utility. We are looking for a size regime that displays significantly different kinetics than either the single atoms or the large nanoparticles. Typically small clusters display different properties, including kinetics in the subnanometer regime. For example, Lu et. al. showed that for Ir/MgAl₂O₄ catalysts, the single atoms, the subnanometer clusters, and the nanoparticles all proceeded by different mechanisms (see Chapter 3). There are several other examples, including Au/TiO₂, Au/α-Al₂O₃ 36 and Pt/CeO₂ 37 where the subnanometer clusters display different kinetics in this regime, often through a metal-support interface mechanism that is 0 order in CO. If this mechanism shows a 0 order in CO and a near 0 order in O₂. There is the potential that we are just missing it. A 0 order in CO mechanism that is slightly less active than the single atoms and/or the nanoparticles here would be dwarfed in the kinetic measurements (see Chapter 2). The most likely candidates for this effect would be the 150 °C reduced in H₂ sample and the 450 °C reduced in H₂ sample. These two samples show a somewhat more shallow (closer to 0) order than is expected based on the single atom and nanoparticle mechanisms. While this is believed to be an effect of the mixture of the two different mechanisms, we cannot fully rule out the possibility of a 3rd, 0 order mechanism being the explanation. To do this comparison we would need some way to filter out the small cluster sized particles or be more selective in the synthesis conditions through a method such as mass loading or using a custom-tailored precursor as was done in Chapter 3. Setting aside the idea of a third potential mechanism, from the STEM and DRIFTS images, it is apparent that many of the systems are likely mixtures of single atoms, small clusters, and larger nanoparticles. As previously mentioned, the small clusters show the possibility of existing in the kinetic measurements, but the analysis fits well without considering them. There is however also the consideration of how the mixtures of single atoms and nanoparticles reacts without this additional consideration. As has been shown in Chapter 2, the two can interact in interesting ways and we need to consider this when looking at kinetic details. Specifically of interest is the effect that the minority nanoparticles might have on the single atom systems at low partial pressures of CO as the nanoparticles become more active at lower partial pressures of CO. From the kinetic data it appears that there is no contribution from the nanoparticles after the two samples have redispersed and the EXAFS agrees with this assessment. However, the STEM analyzes and the DRIFTS show potential disagreement. The DRIFTS was explained by the coking of the catalysts and that likely we cannot discern peaks after the redispersion and oxidation of the nanoparticle. However, the STEM of the H₂ reduced at 150 °C still shows a relatively large number of nanoparticles compared to the EXAFS and the kinetics. In fact, if we use the STEM results to predict the activity (using the single atom catalyst and the 5 wt% CO reduced at 270 °C as baselines), we can predict the expected reaction order. Doing so (Figure ?) suggests that the dispersion is likely much higher than measured in STEM. There are two possible reasons for this. The first is that the HAADF-STEM images have a large degree of sampling bias, likely due to the ease of which you can capture images of clusters compared to single atoms. The second of which is

the potential of the beam itself to either cause agglomeration, as electron beams are known to be very reductive, or destroy single atom sites. Either way, the preponderance of evidence suggests that the STEM is more likely to be the experiment with the largest error as opposed to the EXAFS and kinetics. With the largest discrepancy resolved, it is apparent that we should revisit the IrO₂ theory. As can be seen from the model of the system at 97% single atoms compared to the actual data, there is potential for a different mechanism to be present, specifically one that is 0 order in CO. This has the potential to be the missing cluster piece. Additionally, this also fits the EXAFS data by allowing the system to be IrO₂ instead of clusters of Ir. In addition there has been a thorough characterization of IrO₂ being formed on rutile TiO₂ and it has also been found to be active towards CO oxidation.^{38–41} The IrO₂ has the potential to be the missing link in the data, assuming that the IrO₂ can also form on anatase TiO₂. 260 MEMORY Reduced in H₂ 150 °C STEM results modeled Assuming 97 % SA 10 2 10 2 TOF (s 1) TOF (s 1) 10 3 10 3 Reduced in H₂ 150 °C STEM results assuming 97% SA STEM results with IrO₂ 10 1402 103 104 105 10 1402 103 104 105 PCO (Pa) PCO (Pa) Figure 5: (a) Comparison of the redispersed sample with the results expected from the STEM results. The reduced in H₂ at 150 °C is the data measured for that sample. The STEM results modeled is the expected reaction order given the single atom to nanoparticle ratio measured from the STEM images. The third data set is the best fit of the data allowing the ratio of

single atoms to nanoparticles vary (97% single atoms. These results, coupled with the EXAFS, show that the STEM measurement is unrepresentative of the single atom to nanoparticle ratio. (b) The same comparison but with an added 0 order in CO mechanism meant to simulate the possibility or an IrO₂ species being present Throughout these samples, there is a consistent lack of nanoparticles being shown in the DRIFTS experiments. This is unusual as the samples show nanoparticles in all the different reductions. There are largely two reasons proposed for this lack of the nanoparticle peak. The first is that the peak appears to be dependent upon size. The largest nanoparticles appear to have peaks at approximately 2050 cm⁻¹, however smaller nanoparticles have peaks at approximately 2080 cm⁻¹. At this point it is hard to distinguish what is part of a small cluster and what is part of a single atom as the two are impossible to synthesis purely which would be the first step to quantitatively assign the peaks. The second problem is that for those catalysts exposed to CO at high temperature, the Ir catalyst is at risk of coking over which is common for platinum group metals. After reaction conditions there are little to no nanoparticles due to two competing factors. The first is the redispersion that is seen in both the EXAFS, STEM, and the kinetics. The second is the moving of the Ir metal peak to that of potentially the IrO₂ peak. IrO₂ peaks were proposed to have CO bands at approximately 2100 cm⁻¹ and thus the larger nanoparticles that do not redisperse begin to look very similar to the single atom mononuclear which also has a peak here. However, the shape of the peaks is distinctly different implying that there is some difference in the states that can be used to distinguish them. Due to these competing factors, there are little in the way of nanoparticle peaks to see for these small catalysts. This leaves only one question unanswered. Why is the peak at approximately 2150 cm⁻¹ so much more prominent for the redispersed species as compared to the single atom species. This is largely unknown, but it is believed to be related to the single atom site. As we have established in a different Chapter, there are multiple Ir/TiO₂ sites. Second, it appears that the redispersion leads to a broad collection of single atom sites than does the single atom synthesis. Combining these two data sets, it seems that the most likely case is that the Ir(CO)(O) state is much more favorable on a single atom site that is not the single atom site that we performed the mechanistic study on. For simplicity sake, we leave that analysis here, but point out that it has the potential to replace many of the inferred arguments here. For example that single atom site could be the 0 order in CO site.

Conclusions In this work we use HAADF-STEM, EXAFS fitting, DRIFTS, and kinetic measurements to show that small clusters of Ir/TiO₂ redisperse into single atoms and smaller clusters for a variety of different systems. The range of pretreatment conditions show that there is little dependence on the catalyst synthesis or the pretreatment of the sample instead the dominating effect appears to be the shear size of the catalysts with only catalysts of a certain size being able to avoid redispersion in CO oxidation environments. This work further shows that because of this lack of stability in the small size regime, it is unlikely Ir subnanometer sized clusters will be stable for reactions involving CO and/or O₂ at these temperatures. 268 MEMORY Supporting Information: Redispersion of Ir Catalysts on a TiO₂ Support: Catalysts with a Short Memory Coogan B. Thompson,[†] Adam S. Hoffman,[‡] Jiyun Hong,[‡] Jorge Perez-Aguilar,[‡] Simon R. Bare,[‡] Abhijit Shrotri,[¶] and

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¶Hokkaido University, Sapporo, Japan, 001-0021 E-mail: *amkarim@vt.edu TOF calculation In order to calculate the activity of each catalyst, turnover frequency (TOF) was used. For all samples, TOF was give as the reaction rate in mols CO₂ produced per time per gram of catalyst divided by the amount of iridium per gram of catalyst. This assumes that all catalysts in the system are potential active sites. This assumption is good for single atoms and small clusters where there are few atoms in the bulk, but it is less accurate for larger nanoparticles such as those reduced in CO at 270 °C. Those will be corrected when we finalize the EXAFS fits so that we can get an accurate representation of the catalyst particles size. CO order measurements from SSRL Chapter 7 Kinetic Study of CO Oxidation on Ir/CeO₂ Single Atom Catalysts This work is not yet published. In a similar manner to the Ir/TiO₂ I have struggled to get consistent kinetics. This problem was due to the competitive RDS for Ir/TiO₂. I recently found evidence for a second MASI on Ir/CeO₂. Current work is focused on isolating the differences between these two MASIs and use that to isolate the differences in kinetics. In this work I performed all of the synthesis, DRIFTS, and kinetics for these samples. I was also the lead for the XAS experiments and performed many of them myself. 270 Kinetic Study of CO oxidation on Ir/CeO₂ Single Atoms: Optimizing a Mechanism by Selecting the Catalyst Coogan B. Thompson,† Denis S. Leshchev,‡ Adam S. Hoffman,¶ Jiyun Hong,¶ Simon R. Bare,¶ Eli Stavitski,‡ Raymond R. Unocic,§ and Ayman M. Karim*,† †Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24060, USA ‡National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973, USA ¶Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA §Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA E-mail: *amkarim@vt.edu Abstract Introduction Supported

single atom catalysts have shown great promise in the field of catalysis

. Single atom catalysts have several advantages over traditional nanoparticle heterogeneous catalysts 272 CHAPTER 7. KINETIC STUDY OF CO OXIDATION ON IR/CEO₂ SINGLE ATOM CATALYSTS and homogeneous catalysts. Single atom catalysts provide 100% atom efficiency meaning that every single atom is able to perform catalysis. There is no wasted bulk metal that is required for the structure of the nanoparticle, but it is not on the surface, it cannot contribute to the catalyst activity. Single atom catalysts avoid this problem as their definition implies that there are no bulk atoms. In addition to the atom efficiency, since the atom is by nature isolated and typically on an oxide support, this means that the catalyst is not characterized by the metallic bonding as it would be if it were part of a metal nanoparticle. This large shift in the bonding leads to large changes in the electronic nature of the single atom compared to the atoms in the nanoparticle catalyst. This can have a variety of effects of the catalytic properties of the catalyst and as a result it means that reactions that are not possible on metal nanoparticles might be possible for the same metal as a single atom on the same support. The third potential advantage of single atom catalysts is that typical nanoparticles have a variety of types of sites. A single atom only has the sites immediately

on the single atom and often times, the support sites adjacent to that atom

are involved. A cluster of 2 atoms has all of these sites and the site between the two atoms. When we get to large nanoparticles, there are still the sites adjacent to the surface, there are now crystal facets of the nanoparticle each with there own sets of site types and then edges and corners of the nanoparticle. This variety of sites all have their own potential catalytic properties which can lead to unproductive side reactions. Single atom catalysts avoid this problem by having significantly less types of sites. While the possibility of different types of sites is still possible, it is severely reduced leading to a much more homogeneous like system without the drawbacks of a homogeneous catalyst. One potential support for the development of these single atom catalysts is CeO₂. CeO₂ has many potential benefits. CeO₂ is primarily used when oxygen storage is beneficial to the desired catalysis as CeO₂ being a highly reducible support has the ability to adsorb excess oxygen and then release the oxygen in oxygen deprived conditions.¹ The most well known example of this is in automotive catalysts where CeO₂ is commonly used² to help keep the catalyst within the ideal range of oxygen partial pressures to optimize the conversion of pollutants. While this effect is focused more on macroscopic few of the catalyst as opposed to the atomic scale where catalysts mechanism happen, a similar effect is certainly possible. Thus CeO₂ is especially interesting as a catalyst for reactions involving a Mars van Krevelen (MvK) mechanism as these mechanisms involve a kinetically slow step where a surface oxygen is used.³ The theory thus being that if the reaction is limited by the ability of a surface O (that is part of the support lattice) to react, then a more reducible support, such as Ceo₂ might be a more active catalyst. Figure 1: Schematic showing various types of kinetic mechanisms possible for CO oxida- tion steps on single atoms. (a) Langmuir-Hinshelwood (LH) mechanism characterized for adsorption of CO and O₂ followed by a surface

reaction. (b) Eley-Rideal (ER) mechanism characterized by a gas phase species (CO in this example) reacting with an adsorbed species (O in this example), (c) Mars-van-Krevelen (MvK) mechanism characterized by the reaction of gas phase system (CO in this sample) reacting with a species in the lattice (O in this example). A further discussion on the difference between the three systems is given in the Support Information section 1 CO oxidation on single atom catalyst has been shown to fall into this category of MvK type of reactions. For example Pt/CeO₂ has been shown to proceed through a MvK type mechanism⁴ and Han et. al. showed that CO oxidation on Rh₁/CeO₂ proceeded by a MVK step.⁵ Additionally, there are several computational studies showing this same idea. In fact, Kropp et. al. even was able to use the predominance of this mechanism to develop BEP relations for the different oxides including some single atom and cluster systems. Their result showed a linear trend between the O vacancy formation energy of the oxide to the activation barrier.⁶ However, the most relevant, for this study, comparison is to Ir/MgAl₂O₄ and Ir/TiO₂. These systems each proceed via a MvK type of mechanism⁷ (see Chapter 4 for Ir/TiO₂). More specifically, the MvK step is the removal of a lattice from the oxygen being reacted with a gas phase CO. A comparison of this mechanism with other common surface reaction mechanisms is given in Figure 1. Because the rate determining step for these systems is the ability of a gas phase CO to react with a surface oxygen, it stands to reason that performing this same reaction mechanism on a support that had an oxygen that was easier to remove would increase the reaction rate. In this work we attempt to make such a catalyst. Specifically, in this work we will show that we can make Ir/CeO₂ single atom catalysts that are active for CO oxidation. We will show that this catalyst is more active than Ir/TiO₂ and approximately as active as Ir/MgAl₂O₄. Furthermore, we will show some of the interesting kinetic features relevant to CO oxidation on Ir/CeO₂ and use these to explain why and where the trend among the catalysts acts as expected and where it does not.

Synthesis The catalysts were synthesized through the use of strong electrostatic adsorption.^{8,9} First 1 g of dried support was added to 1 L of DI water. This solution was adjusted to a pH of 4 with HCl. In 20 mL vial, 1 mg Ir of IrCl₃ was added to a 10 mL solution of pH 3 (HCl) DI water. This solution was allowed to set overnight to dissolve the IrCl₃. This solution was then added drop-wise to the 1 L solution at a rate of 10 mL/hr. The combined mixture was then vacuum filtered through a Q5 sized filter. The precursor solution and resulting filtrate were collected for ICP analysis to help give an accurate representation of the amount of Ir on the sample. The ICP results showed that the resulting filtrate Ir concentration was below the detectable limit (0.015 mg/L) and thus assumed to be negligible. Assuming the filtrate was at the limit, this would result in a 0.098 wt% catalysts instead of a 0.1 wt% catalyst, so this approximation is justified.

HAADF-STEM In order to better characterize the dispersion of the Ir/CeO₂ samples, HAADF-STEM was performed on the samples. Unfortunately do to the relatively small z contrast between the Ir (77) and the Ce (58) atoms, the single atoms are much more difficult to see compared to the comparable systems of interest (Ir/MgAl₂O₄ and Ir/TiO₂ with z values of 12 (Mg), 13 (Al), and 22 (Ti). However, there are still a handful of likely single atoms that can be seen such as in Figure 2. Knowing that the single atoms can be seen, it is likely that we have little to no clusters of Ir. Clusters are much easier to see as clusters are typically reduced by the electron beam and as such, the Ir clusters would show up as fuzzy spots on the lattice as can be seen in similar studies in the literature.¹⁰ However, as can be seen from the image, there is an intact lattice for almost all of the sample which implies that the hidden species are likely single atoms of Ir as opposed to clusters. More information on how this system relates to rest of the document is included in the SI (Section 2)

EXAFS In order to investigate the local structure of the Ir/CeO₂ catalysts, we performed in-situ XAS experiments for the calcined, reduced and reactive state for the catalyst. These results are shown in Figure S1. The reduced state was obtained by first reacting the catalyst with 10% CO and 10% O₂ at 225 °C for 1 hour. This was followed by a reduction at 250 °C in 10% CO for 1 hour (Figure 3). The catalyst was again reacted in 10% CO and 10% O₂ at 225 °C for 1 hour to return to the active state (Figure 4). Similar to the HAADF-STEM, low weight Figure 2: STEM images of Ir/CeO₂. The results are for a system that was pretreated in O₂ at 310 °C followed by reduction in CO at 270 °C. This pretreatment is different than the typical pretreatment used (being exposed to reaction conditions directly). However, it is useful to show the difficulties in performing a STEM analysis for Ir/CeO₂. Additionally, there are no nanoparticles detected in the STEM images. loading Ir/CeO₂ catalysts are not ideal systems for EXAFS studies, however we can parse out some details (See SI section 3.1). Figures 3 and 4 show the wavelet transform of the Ir/CeO₂ data.¹¹ Due to the disorder of the CeO₂ lattice, which is related to its reducibility, and the supports ability to adsorb x-rays, which lowers the signal to noise ratio, a full EXAFS fitting approach is not useful beyond the first shell. The wavelet transforms show a clear change in the dominant bonding features of the two systems. The reduced state shows a binding species at 1.5 Å (Note that this is not an atom at 1.5 Å, it is a scattering path at 1.5 Å) with an additional feature starting

to appear at approximately 2.1 Å. The reactive state retains the same 1.5 Å feature, but the 2.1 Å feature appears to be either lost or moves as a second feature appears at approximately 2.5 Å. Past this region, we are unable to discern any features as the spectra are too noisy. We hold off on assigning these features as without the full fitting profile we cannot distinguish between O, CO, Ir, or Ce scattering paths. However, Ir-Ir scatters are unlikely as they would be expected to appear first in the reduced state at approximately 2.7 Å. It is rather unlikely that the Ir-Ir scattering would appear from the addition of O₂. So while we cannot identify the species fully, we can conclude that there is minimal Ir-Ir present in the same and that the sample is the vast majority isolate species. DRIFTS In order to better characterize the reduced state and the active, in-situ DRIFTS was performed on those states. Figure 5 shows the CO region of the spectra. From these results we see the active state is likely a monocarbonyl species at 2054 cm⁻¹. This is interesting as this is approximately where nanoparticle species are expected to appear, however as we do not see any evidence of Ir clusters, much less the large nanoparticles that are associated with the 2050 cm⁻¹ linear CO peak, in the STEM or Ir-Ir scattering paths in the EXAFS, we can conclude that this is a monocarbonyl species on the single atoms. This then can be transformed into a more narrow, apparent dicarbonyl species with peaks at 1994 and 2067 Figure 3: Wavelet transform of the EXAFS data of the reduced state. The left image is the Fourier transform of the k-space data, R-space, and shows the pseudo-radial distribution for the Ir single atoms. The bottom image is the k-space data for the EXAFS region. The heat map is the wavelet transform for the k-space data. The heat map shows the location of the scattering pathway as well as the k-values associated with it. The graphs are laid out in a way that the heat map and R-space data share the same R-space coordinate while the heat map and k-space data share the same k value. Figure 4: EXAFS data of the active state. The description of the graphs is provided in Figure 3 cm⁻¹. These two peaks are in line with the list of dicarbonyl species shown in Chapter 4. Reactive State Reduced State Kubelka-Munk (a.u.) 1994 2067 2054 2100 Wavenumber (cm⁻¹) 2050 2000 1950 Active Reaction 150 °C Active Reaction 190 °C Kubelka-Munk (a.u.) 2052 1993 2061 2050 2100 Wavenumber (cm⁻¹) 2050 2000 1950 Figure 5: (a) DRIFTS spectra of the sample after reaction (1% CO, 10% O₂ at 175 °C for 1 hr) followed by reduction (1% CO at 270 °C for 1 hr). (b) DRIFTS spectra of the active states after reactions at 150 °C and 190 °C both in 1% CO and 10% O₂. Interestingly a closer look at the spectra after reaction (Figure 5b) reveals apparent wiggles in the monocarbonyl peak after reaction. This is unlikely noise as this is not in the asymmetric vibration peak (1993 cm⁻¹) that appears at higher temperature reactions. This suggests that there are multiple closely related single atom sites. Coupling this with the lack of order seen in the EXAFS experiments and the knowledge that CeO₂ is a highly reducible support, we believe these individual site differences are caused by differences in the local structure of the single Ir site due to the easily created oxygen vacancies on the CeO₂. Additionally, this line of reasoning suggests that the reduced state, the Ir(CO)₂ state, is then a uniform species as once the system is reduced, we likely have reduced the neighboring CeO₂ support to the fullest extent possible and thus there is only one structure possible. Figure 5b shows that the after reaction state is different for reactions at the two different temperatures. This shows a likely difference in the MASI at these two different temperatures. Specifically, it appears that the MASI for low temperatures is an Ir(CO) species, while at higher reaction temperatures, there appears to be a significant contribution from Ir(CO)₂ species. This implies that the reactions happen either by different mechanisms at these two conditions or that they are the same mechanism, but in different regimes. This idea shapes the basis of the future work on the project. Kinetic Comparisons One of the most important considerations of this work is the comparison of the activity and mechanism to other catalysts such as Ir/MgAl₂O₄ 7 and Ir/TiO₂ (Chapter 4). Recall that the Ir/MgAl₂O₄ single atom catalyst was +0.9 order in CO and 0.1 order in O₂ 7 and that the Ir/TiO₂ single atom catalyst was +0.4-0.7 order in CO and -0.1 order in O₂. This trend would suggest that the Ir/CeO₂ catalyst would have orders of approximately 0 in both CO and O₂ if the support reducibility is the key parameter of the catalyst. In fact this is precisely what we see in Figure 6a where the CO order is 0.1 and the O₂ order is 0.2. This trend is evidence (albeit weak) that the mechanisms are related in some manner and is an indication that the support reducibility might be related to the catalyst activity. TOF (s⁻¹) 10 1 10 2 10 2 172 T (°C) CO order 189 156 142 128 O₂ order 10 1 Ir/MgAl₂O₄ Ir/TiO₂ Ir/CeO₂ nCO = 0.1 nO₂ = 0.2 TOF (s⁻¹) 10 2 10 3 E_a = 103 kJ/mol 103 PO₂ (Pa) 104 10 0.26 0.27 0.28 1/RT (kJ/mol) 1 0.29 0.30 Figure 6: (a) Comparison of the orders for the Ir/CeO₂ catalyst. The orders are measured at 170 °C. The CO order is measured at 10% O₂ and 1% CO. (b) Comparison of single atom catalyst of Ir/MgAl₂O₄, Ir/TiO₂ (Chapter 5), and Ir/CeO₂. Each sample is measured at 1% CO and 10% O₂. The Ir/CeO₂ samples underwent no pretreatment apart from the reaction conditions specified. Comparing the activities of the catalysts it is apparent that the

Ir/CeO₂ is much more active than the Ir/TiO₂ and has comparable activity to the Ir/MgAl₂O₄. Thus the expected trend holds for the TiO₂ and CeO₂, but it appears to not hold when the Ir/MgAl₂O₄ species is introduced. This suggests that the mechanisms of the two reducible supports are more similar than the non-reducible Ir/MgAl₂O₄ despite, the mechanisms proposed for both the Ir/TiO₂ and Ir/MgAl₂O₄ both relying on the reducibility of the neighboring oxygens. Furthermore, there is a discrepancy between this trend and the activation energy for each catalyst. If the rate determining step is the neighboring oxygen being removed we would have expected that the lower activation energy barrier would also be the most active. However, in order for this to be strictly true, all other steps would also have to be similar as the measured activation energy barrier (often called the apparent activation barrier) is a function of many different surface properties. Because of these differences, this comparison is not as meaningful as the activity and CO orders. Discussion and Future Work The motivation for this work is that assuming the Ir/CeO₂ follows the same mechanism as the Ir/TiO₂, then we would expect Ir/CeO₂ to be more active as the barriers related to the surface activation of O in the CeO₂ lattice would be significantly lowered. If we adapt the Ir/TiO₂ mechanism to be Ir/CeO₂ instead, to first approximation, we expect the mechanism to be as that shown in Figure 7. This mechanism fits with the bulk of the data we see. The EXAFS and STEM both show the system remains as single atoms while the DRIFTS show the active state is a mono- carbonyl which is predicated for the mechanism in a similar way to the Ir/TiO₂. However, there is an important difference here that must be addressed. While the Ir/TiO₂ split rate determination between the MvK step and the surface activation step, the Ir/CeO₂ catalyst appears to have all the rate control in the surface activation step. This explains why the Figure 7: Proposed mechanism of Ir/CeO₂. Due to the limited data that we can collect on this system, we propose that the Ir/CeO₂ catalyst will behave in a similar manner to the Ir/TiO₂ catalyst shown in Chapter 5. We do not mean to imply the states have exactly the same structures, but schematically there is a similarity that forms the basis of how we think about the Ir/CeO₂. We will continue to use this framework until we have evidence to suggest that there is a significant departure between what this mechanism suggests and what we see experimentally. orders are significantly lower than the Ir/TiO₂ and the Ir/MgAl₂O₄. For the Ir/MgAl₂O₄, the RDS was controlled by the MvK step entirely (referred to as ER step, see note in SI, section 1). This gave a large order in CO. If we compare this to the Ir/TiO₂, we still see that the MvK step involving the gas phase CO has a large degree of rate control, however, it must share rate control with the surface migration step. This suppresses the CO order. As we move to an even more reducible support, the Ir/CeO₂, it is largely unaffected by this ER step. This has the affect of dropping the CO order to 0. This explains the difference in order clearly, however this explanation is not complete. With just this analysis, we would expect that the activity would be the greatest for Ir/CeO₂ followed by TiO₂ and with MgAl₂O₄ being the lest active. However, from

Figure 6, it is apparent that the activities of Ir

/CeO₂ and Ir/MgAl₂O₄ are comparable while the activity of Ir/TiO₂ is much lower. This cannot be explained by only the surface reducibility alone. This is believed to be related to the changes in the structure which can be seen in both the EXAFS and in the DFT results for Ir/MgAl₂O₄ and Ir/TiO₂. The most obvious difference between the two structures is that the Ir on the MgAl₂O₄ has 5 Ir-O bonds while the TiO₂, and likely the CeO₂, has 3 Ir-O. This difference we propose is enough to explain why the trend in surface reducibility is broken. There is also a second difference between the two systems. Because the Ir/TiO₂ is positive order, we assign the MASI to be that of Ir(CO)(Os)₃. However, the Ir/CeO₂ is 0 order and the surface reaction step appears to be the RDS. This means that the MASI for Ir/CeO₂ is not the same. As it is written in the mechanism in Figure 7, the MASI for Ir/CeO₂ would be the Ir(CO)(Os)₂(O₂) state. This suggests that there might be possible differences in certain properties of the Ir/CeO₂ despite it having a similar mechanism. For example this might allow different states to appear under certain conditions such as the dicarbonyl state that appears at higher temperatures. Additionally, this might open up the possibility for a ¹³C exchange, which was not seen for the Ir/TiO₂. While there are interesting comparisons that can be done for the Ir/CeO₂ to continue to compare it to the Ir/TiO₂ work, the most pressing matter for the Ir/CeO₂ is determining the differences in what appears to be two different regimes of the Ir/CeO₂, the low temperature Ir(CO) MASI and the high temperature Ir(CO)₂ MASI. To do this, we plan to optimize the conditions for both regimes. Temperature and CO partial pressure are expected to be the two most important parameters, but O₂ partial pressure will also be considered. With the two regimes optimized, we expect to see different kinetics for these two regimes. The synthesis of these two regimes could possibly be the key in explaining the mechanism that we see for Ir/CeO₂ similar to how it was for Ir/TiO₂. Conclusions In conclusion, based on the rate determining step of single atoms of Ir/TiO₂, we expected an Ir/CeO₂ catalyst to be more active for CO oxidation. We were able to synthesis and characterize said single atom catalysts. We then found the Ir/CeO₂ catalyst

to be more active than Ir/TiO₂ and we attribute this increase in activity to the greater reducibility of the Ir/CeO₂ catalyst. We also use this paradigm to explain the change in reaction order. Additionally, we have found two possible regimes for the CO oxidation mechanism. The low temperature being characterized by the MASI of Ir(CO) and the high temperature being characterized by Ir(CO)₂. Future studies of this system will be based around discovering these two parts of the mechanism as well as bridging the holes between the Ir/CeO₂/Ir/TiO₂ with the surprisingly active Ir/MgAl₂O₄

Supporting Information: Kinetic Study of CO oxidation on Ir/CeO₂ Single Atoms: Optimizing a Mechanism by Selecting the Catalyst Coogan B. Thompson,[†] Denis S. Leshchev,[‡] Adam S. Hoffman,[¶] Jiyun Hong,[¶] Simon R. Bare,[¶] Eli Stavitski,[‡] Raymond R. Unocic,[§] and Ayman M. Karim*,[†]

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1 Note on Different Mechanisms The distinction between these three mechanisms is one of practice to describe subtle differences in the mechanisms considered. To better understand this, let's consider the LH mechanism that we show in Figure 1. This mechanism has a CO adsorbed onto the Ir, followed by a reaction with an adsorbed O. Let's suppose that this LH mechanism adsorbs CO very weakly, too weakly for the adsorbed state to be detected. In this situation by all of our measurements, this will appear to be a ER mechanism. Thus while we say that the difference is whether the CO adsorbs onto the surface, the practical answer is more related to the ability to detect this adsorbed state. In a similar manner, the difference between an ER step and a MvK step is related more to how we define the surface and how we define an adsorbate. Historically, this difference was determined based on diffusion limitations^{S1} and the color change associated with the oxidation of Vanadium in VO_x catalysts. Here we define a support O as being one that binds to a support Ti or Ce as well as the single atom Ir. This of course could also be considered an ER step as well because the O does bind to the Ir. However, for this work we refer to this as an MvK reaction to further emphasize that it is a surface species from the support that effects the rate, however referring to this as an ER mechanism is correct as well.^{S2} In a similar manner, this can also be referred to as an interface reaction, similar to what we see for the Ir clusters discussed in Chapter 3. However, this framework is not preferred as single atom catalysts only have an interface and as such this approach offers little of value.

2 Note on HAADF-STEM imaging Due to limitations on the throughput of samples that our collaborators can perform and the low z-contrast between the Ir (77) and Ce (58) it seems unfruitful to perform more STEM analyses on this catalyst type. As such, while we would ideally hope to include STEM images of this sample that are more similar to the systems we are working with, it seems unlikely that it will be a priority for our collaborators. As such, this is the extent of microscopy, however there is sufficient to argue that clusters will not be present on the untreated samples. The samples we show in STEM versus those that we show in the rest of the chapter differ in their pretreatments, which we argue have minimal affect on the catalysts dispersion, i.e. both are likely single atoms. The first is that from the results of Ir/TiO₂, we expect that the higher CO reduction temperature is more likely to create nanoparticles as opposed to disperse them. I.e., if we were going to see nanoparticles, it is more likely that we would see them after the 270 °C reduction (the STEM images we show) as opposed to the reaction conditions we use in the rest of the paper.

3 EXAFS data

3.1 Note on EXAFS collection For the 0.1 wt% Ir/CeO₂, the dilution of the Ir makes observation of the Ir L₃ step edge difficult. This is due to CeO₂ being a highly absorbent support in the range of the Ir L₃ step edge. This high absorbance leads to lower signal and thus a lower signal to noise ratio which means the data quality is significantly lower. Additionally, because the Ir/CeO₂ is a much more reducible support, the coordination of the Ir, specifically the Ir-O bonds of the Ir single atom to the O from the CeO₂ support are less consistent. As a highly reducible support, the CeO₂ is very likely to have vacancies in the surface lattice and especially near defects such as the Ir. This is exactly why we used CeO₂ as a support, but this increase in reducibility also decreases the uniformity of the bonding O on the Ir single atoms. Because the Ir-O bonds are highly disordered, the constructive/destructive interference pattern that creates the EXAFS signal, the signal that contains the structural information, simply has less information to use to fit a structure. Because of this, we forgo the full EXAFS fitting procedure and prefer to speak only broadly of the wavelet transform results.

3.0 Calcined 3.0 Calcined 2.5 Reduced Active 2.5 Reduced Active Normalized Intensity 2.0 1.5 Normalized Intensity 2.0 1.5 1.0 1.0 0.5 0.5 0.0 11200 11400 11600 11800 120 00 Energy (eV) 0.0 11200 11210 11220 11230 11240 11250 11260 Energy (eV) k₂ (k) (Å⁻²) 1.5 0 2 4 Wavenumber (Å⁻¹) 6 8 10 2.0 1.5 1.0 0.5 0.0 0.5 1.0 Calcined Reduced Active 12 1 4 2.0 1.5 | (R)| (Å⁻³) 1.0 0.5 0.0 0 1 2 R (Å) 3 4 Calcined Reduced Active 5 6 Re[(R)] (Å⁻³) 2.0 1.5 1.0 0.5 0.0 0.5 1.0 1.5 2.0 0 1 2 R (Å) 3 4 Calcined Reduced Active 5 6 2.0 1.5 1.0 Im[(R)] (Å⁻³) 0.5 0.0 0.5 1.0 1.5 2.0 0 1 2 R (Å) 3 4 Calcined Reduced Active 5 6

Figure S1:

(a) normalized XAS spectra for the 3 samples (b) Highlight of the XANES regions for the same data (c) k-space data (d,e,f) R-space data for the three samples showing the magnitude, the real portion, and the imaginary portions respectively.

Chapter 8 Conclusions and Future Work There are many conclusions we can draw from each of these works, however it is beneficial to describe them here as well as describe the current directions each of these projects will take from here. We will start with Chapter 2 which primarily discussed the kinetic synergistic effect. In this work we showed that nanoparticles of Ir/MgAl₂O₄ mixed with single atoms of Ir/MgAl₂O₄ can be more active than either system can be alone. The reason for this is the positive CO order for the single atoms and the negative CO order of the nanoparticles work together to make a more active catalyst. We also derived an expression to characterize this effect. The usefulness of this project was to first be able to demonstrate and characterize this effect that we believed was possible and second to emphasise that we are ultimately trying to optimize catalysts at an industrial scale. Practically this means being able to make a material that can perform a given chemistry as reliably and as cheaply as possible. We often do this by trying to isolate individual species so that we can study them and understand them better in hopes that we can then improve them. But at some point, we likely will never fully isolate single atoms on an industrial scale, but perhaps we do not need to. That is what this work shows. It shows that sometimes, the systems are better off being mixtures. This not only makes the creation of these systems easier, it also allows for another degree of optimization of the catalysts. For these systems, optimization is no longer trying to reach some level of purity as it is in the lab scale, it is instead about getting as close 293 CHAPTER 8. CONCLUSIONS AND FUTURE WORK as possible to the correct mixture. This often is an easier goal to achieve and effectively minimizes one of the hardest problems in single atom catalysis which is how to get a high purity of single atom sites. The most logical next experiment is to see if this result can be replicated in the lab for an experimental system. This is something that our lab has the ability to do, but has not yet done. Given the results from our models, we should be able to perform a light-off curve for mixtures of the appropriate amounts of single atoms and nanoparticles and compare these to light off curves to the isolated species. These results should show the characteristic curves of the single atoms, the nanoparticles, and the mixture. If successful, this experiment would demonstrate that this mixture effect is real beyond just what our models predict. For the third chapter, we focused on the CO oxidation performed on the subnanometer supported Ir clusters, we showed that the mechanism occurred at the interface of the Ir subnanometer particles and the MgAl₂O₄ support. This explained the kinetics shown and contrasted interestingly with the single atoms and nanoparticles of Ir/MgAl₂O₄. There are barely any more questions that we can answer given the current capabilities of the lab as they relate to Ir/MgAl₂O₄, however there are always new directions. One of the most interesting is comparison of the Ir/MgAl₂O₄ systems to those of Ir/ZnAl₂O₄. Having a similar spinel structure, Ir/ZnAl₂O₄ allows us to look at the effect of the Mg vs Zn in near isolation. As we have shown the subnanometer clusters are reactive at the interface, it is thus expected that changing the support would change the kinetics of the catalyst. In a similar manner, the projects following up on Chapter 4 and 7, the mechanistic studies of CO oxidation on Ir/TiO₂ and Ir/CeO₂ respectively, are also related to the effect of the support. The original idea to study Ir/TiO₂ (and later Ir/CeO₂) was to improve the catalytic capabilities of single atoms of Ir. From the mechanism of Ir/MgAl₂O₄ it was expected that a more reducible support would facilitate a faster reaction by decreasing the kinetic barrier of the RDS step, which was an ER (or MvK) step involving a gas phase CO molecule with a O bonded to the Ir and support. This model is useful to explain the differences in the Ir/TiO₂ and the Ir/CeO₂, however it fails to explain why the Ir/MgAl₂O₄ is more active than the trend suggests. That is the Ir/MgAl₂O₄ being as active as Ir/CeO₂ and considerably more active than Ir/TiO₂ despite Ir/TiO₂ being the more reducible support. We believe that the explanation of the difference lies in the structural differences between the three systems. The precise difference is probably impossible to determine beyond a theoretical level as the difference in kinetics is by its very nature related to unstable intermediates (otherwise we would call it thermodynamics). However we can still test the effective surface oxygen lability which should act as a reasonable analog as it should be directly related to this unstable intermediate. Specifically, we are trying to test how easy it is to remove a surface oxygen under the reaction conditions. The reducibility of a system is often defined in reference to its stoichiometric value. However, under steady state reaction conditions the surface of the support will not be stoichiometric apart from the very most non-reducible oxides. This means that the support reducibility is not the exact reducibility that we are interested in. Instead we are interesting in the reducibility of the neighboring oxygens under reaction conditions. We expect this difference to be larger in more reducible supports as under reaction conditions we expect there to be some surface O that are so labile that they are not relevant to the catalysis in that regime. In order to measure this local reducibility, we purpose performing a CO TPR type experiment that involves performing the TPR on the active state. This allows us to see how reducible the oxygens that are kinetically

relevant are. As opposed to a general TPR experiment that would show potentially many non-kinetically relevant surface Os that likely exist on reducible systems. This TPR should isolate the important kinetically relevant Os. In practice this type of study would require comparisons of TPRs on the active state to those on the CHAPTER 8. CONCLUSIONS AND FUTURE WORK oxidized and reduced states for the three types of catalysts we wish to compare (Ir/MgAl₂O₄, Ir/TiO₂, Ir/CeO₂). The different systems should of course show different kinetically relevant CO₂ bands based on the activity of the catalyst. Based on the activity we would expect Ir/MgAl₂O₄ and Ir/CeO₂ to have a similar CO₂ band (i.e. see the greatest amount of CO₂ at similar temperatures), while we expect the Ir/TiO₂ to have a band shifted to a higher temperature. Additionally, we would want to perform the same experiment on the oxidized and reduced states of the catalysts in an attempt to measure any overall shift in the number of Os reduced during the reaction. Specifically, we would hope to capture some O species that are able to be reduced on the Ir/TiO₂ and Ir/CeO₂ systems that are too labile to be kinetically relevant in the reaction conditions of interest. These species would help to explain why Ir/TiO₂ and Ir/CeO₂ are less active compared to Ir/MgAl₂O₄ than the support reducibility would suggest. These species would be the difference between the general, local reducibility of the support and the reducibility of only the active site. In a similar manner it would also be possible to measure the reducibility of the support with and without the added Ir. This would show how much (if any) difference the single atom causes in the reducibility of the support. This is primarily focused on the Ir/MgAl₂O₄ where the current mechanism suggests that the Ir single atom causes a large change in the reducibility of the local surface O species. However it easily generalizes to any support (and could possibly generalize to many different single atoms) and could be used on its own as an indicator for CO oxidation activity, before ever needing to synthesize the single atom system itself. Moving onto the study of the different single atom sites for the Ir/TiO₂ catalysts (Chapter 5). One of the greatest advantages of single atom catalysis is that theoretically they have the potential to be homogeneous in site types. this however is practically difficult as even though the single atoms do not have corners or edges, the supports that the single atoms are anchored to do. This leads to the situation where the single atom sites are not always identical. In this work we show that we can isolate two different sites and can describe some of the differences between them. However, we were unable to compare the activities of the two different sites, which is the main objective for catalysis studies. While we were unable to measure the kinetics of the two different isolate sites as it appears the two different sites are somewhat interchangeable, however, there are perhaps ways to prevent that. First we would have to understand what this difference actually is. If for example, the difference is between Ir sites being on different facets of the Ir/TiO₂, then extended surface studies could isolate the two systems. This is beyond our current labs capability however. Additionally, now that we know that multiple sites can exist, we have a reason to explore larger ranges of pretreatments that might lead to the discovery of new sites and hopefully for some of these sites, we will be able to study them in more detail. In addition to looking at different single atom sites on Ir/TiO₂, it seems logical that we would also look at small clusters, similar to the Ir/MgAl₂O₄. This effort however did not yield small clusters and instead we saw that these small clusters were largely unstable and preferred to redisperse. This formed the basis for the study on the Ir/TiO₂ redispersion (Chapter 6). In that project we show that the small clusters of Ir break up into single atoms under reaction conditions, while larger nanoparticles tend not to. Interestingly, we also appear to be seeing that many small clusters probably are forming IrO₂ species (or more accurately named IrO_x species). This was not readily expected and is something that we hope to be able to isolate and study. Specifically, we hope to get the kinetic parameters of these system and compare them to single atoms and nanoparticles in a way similar to what we did in Chapter 3 for the Ir/MgAl₂O₄ subnanometer particles. App endices 298 App endix A Other Works In addition to the work here described, I have had the pleasure to work on other projects that do not fit into this work. They are included here with a short description of the work. A.1 First Author Publications

Reduction and Agglomeration of Supported Metal Clusters Induced by High- Flux X-ray Absorption Spectroscopy Measurements

[1] In this work we showed that the relatively new beamline at Brookhaven National Lab is powerful enough to cause changes to the samples under certain conditions. This is significant as the EXAFS characterizations that were performed at this beamline reported significantly larger size distributions than other methods due to these changes.

A.2 Non-first Author Publications from Graduate Studies

Rh promoted In₂O₃ as a highly active catalyst for CO₂ hydrogenation to methanol

[9] 299 APPENDIX A. OTHER WORKS In this work we were looking at the effect of monodisperse Rh on catalytically active In₂O₃ for methanol synthesis. I performed the EXAFS experiments on the Rh that was used to verify the location of the Rh on the In₂O₃ surface.

Effect of Pd Coordination and Isolation on the Catalytic Reduction of O₂ to H₂O₂ over PdAu Bimetallic Nanoparticles

[49] In this work we were looking at the formation of hydrogen peroxide on AuPd alloys. I provided the chemisorption experiments that were used to help normalize the surface Pd in the alloys.

Origin of the High CO Oxidation Activity on CeO₂ Supported Pt Nanoparticles: Weaker Binding of CO or Facile Oxygen Transfer from the Support ?

[36] In this work we explore the activity of Pt/CeO₂ for CO oxidation. Specifically, we are looking for possible reasons why the catalysts is active despite having strongly bonded CO. I contributed pieces to the activity measurements and the calorimetry of the samples.

Unraveling the Intermediate Reaction Complexes and Critical Role of Support-Derived Oxygen Atoms in CO Oxidation on Single-Atom Pt/CeO₂

[38] In this work we propose a mechanism of CO oxidation on Pt/CeO₂ single atom catalysts. I provided some of the DRIFTS experiments that verified the mechanism through the relative intensity of the CO containing state. A.3. NON-FIRST AUTHOR PUBLICATIONS FROM BEFORE MY GRADUATE STUDIES 301 A.3 Non-first Author Publications from Before my Graduate Studies

Colloidal Nanoparticle Size Control: Experimental and Kinetic Modeling Investigation of the Ligand-metal Binding Role in Controlling the Nucleation and Growth Kinetics

[42] In this work, we modeled the growth of Pd nanoparticles in varying ligand solution. This is the final result of the work I performed over the summer between my undergrad and graduate studies. I contributed much of modeling aspect of the paper, largely the codes that were used to turn the mechanism proposed into data comparable to experiments.

Ligand-Mediated Nucleation and Growth of Palladium Metal Nanoparticles

[43] This paper focuses more on the methods that were used in the proceeding

paper "Colloidal nanoparticle size control: experimental and kinetic modeling investigation of the ligand-metal binding role in controlling the nucleation and growth kinetics

". Similarly, in this work I contributed much of the modeling aspect that was used to relate the proposed mechanism with the experimental data. 6 8

10 12 14 18 20 22 24 26 28 30 32 34 36 38 40 46 48 50 52 54 56 58 60 62 64 66 68 70 72 74 76 78 80 82 84 86 88 90 92 94 222 224 226 228 230 232 234 240 274 276 278 280 282 284 288 290 294 296 300 4

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CHAPTER 2.

KINETIC SYNERGY BETWEEN SUPPORTED IR SINGLE ATOMS AND NANOPARTICLES

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