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SYNTHESIS, CHARACTERIZATION AND EVALUATION OF DILUTE LIMIT ALLOY BIMETALLIC CATALYSTS FOR BIO-OIL UPGRADING

by

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Dedication

This work is dedicated to Anzel, Cielo, Dein and Hazel.
Acknowledgments

So far, in this part of my journey to what we call life, I would like to make this opportunity to say thank you. First of all, to my adviser Dr. John Regalbuto for the expertise and guidance in the course of this study, your unending support and motivation allowed me to continue and finish this work; to my co-adviser Dr. Christopher Williams, who lend his precious time during the entire duration of this program; to my panel members Dr Chen, Dr Heyden and Dr Monnier, for imparting the knowledge and constructive criticism to this work; to all my colleagues in Regalbuto research group (Meynard, Bahareh, Andrew, Ritu, Tien, Ben, Amp, Alaba, Mozhdeh, Anhua, Fahim, Saqib, Jeremiah, Sean), William’s and Monnier’s group (Weijan, WEN, Greg, Masud, Haiying, Kevin, Yanjiao, Nick, Nabi, Xinbin), and Vannucci’s group (Dr. Aaron, James, Pooja, Jake, Joseph, Mevan, Victoria), all of whom help me in one way or another during my stay here at USC; to my classmates during the years of coursework (Shiv, Dia, Horie, Masud, Saqib, Yiwei); to my colleagues at the department of chemical engineering, UPLB, thank you for the unending support and encouragements; to the heads and staff of DOST-ERDT whom for the last four years have worked hard to provide us the needed support; to the Filipino people whose taxes constitute this financial support; to all my new friends at USC who made my stay here tolerable; to my family way back home for the regular communication; and lastly, I thank God Almighty for giving me this opportunity of fulfilling my dream.
Abstract

Well-defined single-atom catalytic sites with unique geometric and electronic properties are at the forefront of catalyst research. One type of SAC is a so-called dilute limit alloy (DLA), where single metal atom sites are supported on (or in) the surface of a second metal. This category of well-dispersed atoms alloyed on a metal surface has shown to be effective in reactions like selective hydrogenation of alkynes and dienes to alkenes, ethanol dehydrogenation, and the Ullmann reaction of aryl chlorides. In biomass conversion, this type of catalyst may find its way to address and improve conversion and yield that are crucial for it to be economically feasible, given that the cost of production is greatly dependent on catalyst cost and catalyst life cycle. In this work, the generalizable, scalable, and facile synthesis method of strong electrostatic adsorption (SEA) is pushed to the limit of metal dilution to prepare single atom alloy catalysts. It is evaluated for the upgrading of a bio-oil model compound.

First, silica-supported dilute limit alloy (DLA) bimetallic catalysts (Y₁X/SiO₂, Y=Pt, Pd and Ru; X=Cu, Co and Ni) were prepared using modified simultaneous strong electrostatic adsorption (co-SEA) with controllable metal ratio deposition to obtain ultrasmall nanoparticles of the abundant metal X alloyed with an isolated atom Y on the surface. Monometallic catalysts (Pd, Pt, Ru, Cu, Co, and Ni) were also prepared by SEA. H₂-TPR of dried DLA catalysts suggest close interaction between the two metals involve even at high dilution and the diffraction patterns of as-synthesized reduced catalysts
implies ultrasmall nanoparticle. Confirming the existence of this isolated atom was the next step with the application of CO probe Fourier transform infrared (CO-FTIR) spectroscopy on a two-metal surface where a convoluted spectra complicates the analysis. A summary of CO vibration frequencies adsorbed on these isolated atoms were made. Finally, these DLA catalysts were evaluated in aqueous phase furfural hydrogenation reaction in a batch reactor. Monometallic nickel was activated with the addition of single atom sites on the surface. Also, changes in product selectivity were observed for cobalt- and copper-based catalyst with the addition of single atom sites. It was observed that Pd-X DLA and Y-Co based DLA are resistant to sintering after 10 hours of aqueous-phase reaction (150 °C, 430 psig H₂). Minimal dissolution of the abundant metal was observed for Cu-based DLA.
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Chapter 1. Introduction

Driven by strong economic growth, increased access to marketed energy and rapid population growth, the overall world energy consumption is projected to rise by nearly 50% (635 to 905 quadrillion Btu) from 2018 to 2050. Almost half of this increase is expected to be contributed by Asian countries, mainly China and India. Based on a reference case with a 3% increase per year of global renewable energy consumption, by 2050 it will surpass petroleum and liquid fuels as the leading source of primary energy. However, the forecast still shows that the total nonrenewable energy source will still be the leading contributor (Figure 1.1). In 2018, U.S. energy consumption derived from biomass accounted for 46% of the total renewable energy with the remaining part coming from non-organic sources such as hydro, geothermal, photovoltaic and wind. The intensive use of renewable energy is one way to stabilize CO₂ atmospheric concentration and the use of biomass derived energy will have a significant effect by displacing fossil fuels. High dependence on finite fuel sources and adherence to climate change mitigation have led to a significant number of studies on renewable sources, green chemistry, and sustainable technology. Biomass is a low cost and abundant resource, making its conversion to transportation fuels and chemicals a promising clean alternative to nonrenewable-based processes.
Biomass conversion to biofuels and chemicals has evolved from the use of oil, starch and sugar-based crops (the so-called first generation feedstocks) to low value, high-yielding lignocellulosic biomass (termed the second generation feedstocks). In addition, specially engineered energy crops or improved biomass such as algae, are being considered as third generation feedstocks. The significant drawback of the first generation was the required competition for land and water use with the food supply, leading to the increased interest in lignocellulosic biomass. Lignocellulose refers to the biopolymer of cellulose, hemicellulose and lignin that gives plants its structure. The concept of a biorefinery, analogous to crude oil refinery, involves replacing the carbon source with biomass, separation and breakdown of lignocellulosic components, and conversion of intermediates for further reaction and separation. From this concept, the key strategy in lignocellulosic conversion is in determining the upgradable platform components which could be derived from the decomposition of lignocellulose. Figure 1.2 shows the chemical structure of lignocellulosic components and the simple repeating units available from the biopolymer. Catalytic decomposition of crystalline cellulose and amorphous hemicellulose produces ketones, aldehydes, acids, sugars and furan derivatives.
Lignin, which is a complex three dimensional polymer of phenolpropane, decomposes to form phenolic compound derivatives.⁵

Figure 1.2. Intermediate functional compounds derived from the breakdown of lignocellulosic material (adapted from Nguyen, 2013)
Several pathways or strategies have been developed in the conversion of lignocellulosic biomass to liquid fuels and chemicals. Figure 1.3 shows the general pathways in the transformation. The general objective in biomass conversion is the removal of oxygen on the carbon units, the decomposition of the lignocellulosic part into upgradable intermediates and the final conversion to drop-in fuel and value-added chemicals. The oxygen removal is generally categorized as either hydrolysis or thermochemical conversion. In the hydrolysis of lignocellulose, the breakdown of linkages allows for the separation of sugars and lignin, which could undergo biochemical or catalytic conversion. The biochemical route follows the first-generation technologies using microbial fermentation of sugars to produce bioethanol. Having key platform intermediates such as sorbitol and furfural-based chemicals resulting from hydrolysis, catalytic upgrading to specific desired final product can be made. The accessibility of these platform chemicals makes the flexibility of this route advantageous as compared to that of thermochemical conversion method. In the thermochemical conversion, the two competing routes in the conversion of low moisture biomass to liquid fuel are biooil production via direct thermochemical treatment and further hydroprocessing, and gasification of biomass forming syngas followed by Fischer-Tropsch (FT) synthesis and further hydrotreatment. In biooil production, either liquefaction or fast pyrolysis technology is used with the latter being commercially favored due to its lower capital cost.

Results of techno-economic feasibility comparing the gasification with direct thermochemical treatment varies depending on the feedstocks and location being considered. Utilizing sugarcane bagasse as feedstock, Michailos et. al.(2017), found gasification–FT as more energetically and financially efficient as compared with the fast
pyrolysis route. Their sensitivity analysis shows that catalyst cost and catalyst life cycle are vital on biofuel cost with conversion and yield as the most crucial. In a recent study by Bora et.al. (2020) on the conversion of regional poultry waste with spatial analysis, they found that for New York State location, centralize fast pyrolysis outperforms distributed FP biorefineries with carbon credits, products’ market price, and plant capacity significantly affecting the results. Anex et. al. (2010) found that in a capacity of 2000 tonnes per day of biomass, the pyrolysis scenario would give the lowest product value and low capital cost but on a larger scale would require more research and development cost.

In either route, the use of catalytic conversion in downstream processing is crucial, which makes development of improved catalysts an integral part in improving the overall performance.

Conversion of biomass to a suitable form is needed for ease of usage and to be competitive with existing source of energy like fossil fuels. Transformation to higher density in liquid form provides ease in transportation and storage until usage.

The upgrading process of primary oils has long been recognized as important to address technical and economic issues associated with the conversion of biomass to liquid form. Implementation of a commercial scale biooil upgrading plant has not been achieved to date due to difficulty in finding techno-economically feasible catalytic hydroprocessing steps. Finding simpler and easier hydroprocessing steps that would trigger large-scale production of biomass derived fuel products is therefore of critical importance.
Figure 1.3. Conversion Strategies for lignocellulosic biomass to liquid fuels and Chemicals (adapted from Alonso, 2010)

Inherent to lignocellulosic biomass, biooils arising from thermochemical treatment contains high water and oxygen content and have problems related to storage stability, which limits its use and application. As shown in Table 1.1, a typical pyrolysis oil has 15-30% water content, which lowers its heating value. The presence of many reactive and complex oxygenated compounds in biooils contributes to its undesirable properties like low energy density and immiscibility with hydrocarbon fuels. The change in viscosity overtime during storage is also a concern in the use of biooil.\cite{11} Further treatment of biooils to address these issues are being developed in catalytic hydrotreatment with the aim of achieving higher thermal stability, reduced oxygen and water content, and higher energy density among others.
Table 1.1. Typical pyrolysis oil composition

<table>
<thead>
<tr>
<th>Composition</th>
<th>Percentage, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>15-30</td>
</tr>
<tr>
<td>light oxygenates</td>
<td>8-26</td>
</tr>
<tr>
<td>monophenols</td>
<td>2-7</td>
</tr>
<tr>
<td>water insoluble oligomers derived from lignin</td>
<td>15-25</td>
</tr>
<tr>
<td>water-soluble molecules</td>
<td>10-30</td>
</tr>
</tbody>
</table>

Biooil upgrading also aims to produce high value fuel oil substitutes like transportation fuels. Recent studies find the combination of renewable second generation feedstocks (biooil) and conventional feedstocks (crude oil) as a promising route to utilize existing petroleum refineries.\(^{12}\) Co-processing of pyrolysis oil in refineries provides the easiest and ready-to-use approach in biofuels production and the low sulphur content and reduced carbon footprint reduces the environmental impact of fossil fuel use.\(^{13}\)

One major drawback of biooil upgrading is the reactive chemical innate to biooil. These compounds readily react forming polymerization products via thermal reactions. Hence, by lowering the concentration of these highly reactive compounds, the stability of the biooil will be enhanced thereby making the upgrading steps more manageable.\(^{14}\)

Upgrading of pyrolysis vapor has attracted researchers in recent years as a way of improving condensed biooil stability prior to final upgrading step. In a study by Asadieragh et al. (2014), a vapor-phase cascade catalytic upgrading of pyrolysis vapor was incorporated in a typical fast pyrolysis process flow.\(^{15}\) The proposed cascading process utilized a suitable catalyst for each step performing specific reactions like aldol condensation, deoxygenation, alkylation and aromatization. Catalyst selection was based on the survey of existing catalysts evaluated using model compounds. In their study the selection of catalyst focused on stabilization of biooil, which will further undergo a final upgrading step to the desired product. They reviewed representative model compounds
based on functional groups for small oxygenates such as alcohols, aldehydes, ketones and carbonyl for lignin derivatives and for sugar derivatives to determine the required reactions and mechanisms for the cascaded steps.

From Figure 1.2, the sources of various compounds obtained in biomass conversion are complex and for a huge number of intermediates having functionalities that makes it difficult to manage. Knowing this group of intermediates, representative model compounds can be utilized to investigate reaction pathways and catalysts suitable to achieve a desired outcome. Also, variation of bio-oil properties from different biomass used, process types and operating conditions makes the use of model compounds in evaluating potential catalyst a simpler approach to give fundamental insights and understanding of the multiple parameters involved. However, it is important to understand that in real system, catalyst deactivation can complicate and, in some cases, negate the results obtained from using model compounds.

Previous studies subdivided model mixtures based on reaction temperatures: low temperature and high temperature. The low temperature (<300 °C) addresses the most reactive species such as aromatic ketones, carboxylic esters and aromatic ethers. After achieving a stable biooil suitable for further treatment, the high temperature mimics the total hydrodeoxygenation process that occurs above 340 °C. Examples of compounds for low and high temperature treatment include 4-methylacetophenone, diethyl-decanedioate and guiacol for the former; and 4-methylphenol, 2-ethylphenole and dibenzofuran for the latter.14

In the final step, the two main routes for upgrading oxygenated hydrocarbon in biooils includes catalytic hydrotreatment by hydrodeoxygenation (HDO) and catalytic
cracking. In hydrodeoxygenation, oxygen is extracted from compound by catalytic reaction with hydrogen. This reaction produces a much higher H/C ratio than the catalytic cracking. In catalytic cracking, high pressure reactors are used to depolymerize biooil, forming much lower molecular weight molecules. Figure 1.4 shows the two step process of bio-oil upgrading prior to separation into the desired final product.\(^{16}\) This process was patented by PNNL with the first stage (stabilization) operated at below 300 °C and the second stage (deep HDO and Hydrocracking) operated from 300 °C to 500 °C at 10-14 MPa.

![Figure 1.4. Hydrotreating and Hydrocracking of biooil (adapted from Pinheiro Pires, 2019)](image)

For the last 15 years, several reviews were made in relation to biooil treatment. Recently Han et. al.(2019) reviewed hydrotreatment of pyrolysis biooil.\(^{17}\) They also divided the treatment of biooil as stabilization or low temperature reaction and final upgrading or high temperature reaction. In the stabilization steps between 373K and 573K, platinum, ruthenium and palladium on carbon and metal oxides support were commonly used while ruthenium, nickel and sulfided CoMo catalysts were used for cracking and hydrodeoxygenation at temperature between 623K and 675K. In a review by Gollakota et. al. (2016) on the upgrading techniques for biooil, a conclusion was made that the search
for suitable catalyst is still an ongoing task and hydrodeoxygenation is still a promising steps for industrial scale application.\textsuperscript{18}

Table 1.1 shows recent papers on catalysts used in biooil upgrading and shows the common sets of metals used. It is quite common that monometallic supported catalyst with bifunctional characteristics are being employed. Based on the recent review by Han et. al. (2019), only a limited number of supported bimetallic catalysts are evaluated in the literature.\textsuperscript{17} The use of sulfided CoMo bimetallic catalyst supported by either alumina or carbon is the common catalyst used based on an earlier study by Centeno et.al (1994) on the hydrodeoxygenation of carbonyl, carboxyl and guaiacol-type molecules.\textsuperscript{19} They suggested the use of neutral support to avoid coke formation as manifested in the use of alumina. The low activity of silica supported CoMo was attributed to low dispersion and is not due to low acidity silica as compared with alumina supported catalyst. Although no characterization was performed to determine the nanoparticle sizes, the synthesis method used (i.e., wet impregnation method using four times pore volume of solution) would suggest that a relatively low dispersion was achieved.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant/Reaction</th>
<th>Rationale</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Al\textsubscript{2}O\textsubscript{3}</td>
<td>selective 5-hydroxymethylfurfural hydrogenation towards 2,5-dimethylfuran</td>
<td>5-hydroxymethylfurfural most abundant component in lignocellulosic biomass. DMF as gasoline substitute</td>
<td>20</td>
</tr>
<tr>
<td>Pt/Solid Acid (bifunctional)</td>
<td>Hydroisomerization of model oil of 1-tetradecene and oleic acid</td>
<td>Triglyceride thermal cracking long-chain hydrocarbons and fatty acid degrade fuel properties.</td>
<td>21</td>
</tr>
<tr>
<td>Ru/TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} (bifunctional)</td>
<td>Hydrodeoxygenation of phenolic compounds and raw bio-oil</td>
<td>Phenolic compounds are hard to covert</td>
<td>22</td>
</tr>
<tr>
<td>Ni-based catalysts modified by Al, La and Ga</td>
<td>Hydrodeoxygenation (HDO) of phenols, acids, and ketones as bio-oil</td>
<td>Phenols causes instability in biooil and difficult to convert</td>
<td>23</td>
</tr>
</tbody>
</table>
Furfural is one of the abundant components in fast-pyrolysis oils. At elevated temperature, the aldehyde functional group easily polymerize with other compounds present which precipitate and deactivate the catalyst. In a thermal treatment of biooil, Xiong et.al. (2020) found that furfural and biooil components interacts while in liquid phase (low temperature) by forming intermediates and polymerize to form larger compounds. At temperature greater than 300 °C, these compounds eventually form coke. As the conversion of furfural increase, the amount of coke formation also increased. Furfural derived radicals and its recombination with other radical components is the reaction involve which makes its presence significant. Aside from biooil stabilization, furfural is also a key chemical platform for the synthesis of higher value chemicals and liquid fuels in the biorefinery concept. Table 1.3 shows recent catalyst used for selective hydrogenation of furfural. Derivative products are used as fuel additives and as intermediates in making value-added chemicals. However, reduction of furfural in large scale uses chromium-based copper catalyst which produces harmful environmental waste. Hence, recent studies aim to find an alternative catalyst in furfural reduction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Model compounds for hydrocarbon fuel</th>
<th>Carboxylic strong acidity causing corrosion.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/SiO₂</td>
<td>Guaiacol HDO reaction</td>
<td>Aromatic Hydrocarbon selectivity and stability, for the hydrotreatment of pyrolysis oil</td>
</tr>
<tr>
<td>Pt/Al₂O₃ and Pd/C</td>
<td>Lignin fraction of pyrolysis oil. Pt shows ring saturation, demethylation and hydrodeoxygenation, Pd shows ring saturation followed by methanol abstraction</td>
<td>Lowering of oxygen content forming hydrocarbon fuel for blending in petroleum-based gasoline</td>
</tr>
</tbody>
</table>
Single metal catalyst such as Pt, Ru and Pd evaluated for catalytic conversion of bio-oil model compounds shows high activity and could lead to over reaction of alcohols forming gaseous components.\textsuperscript{17} It also leads to poor selectivity to specific reduction product. Adding a dopant or a second metal to form alloys reduces catalytic activity and inhibits further reduction. Mixing of noble metals with non-precious metals to form a bimetallic catalyst is desirable to lower the cost but also harness the advantages associated with it. The promotion effect of adding a second metal in bimetallic catalyst offers wide possibilities such as maximizing yield to a specific product especially for biomass derived materials where multiple functional groups exist in the reacting compounds; increasing the selectivity to lessen the burden in product separation and purification; improving stability by inhibiting sintering or formation of carbonaceous deposits on catalyst; and creation of new reaction pathway due to synergistic and bi-functionally effects.\textsuperscript{30}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant/Reaction</th>
<th>Rationale</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-Au/SiO\textsubscript{2}</td>
<td>Reduction of Furfural in Water</td>
<td>Environment friendly replacement for chromium-based, copper chromite catalysts in furfural reduction</td>
<td>\textsuperscript{20}</td>
</tr>
<tr>
<td>AuRu on Doped Zirconia Support</td>
<td>Furfural hydrogenation using isopropanol as the hydrogen donor.</td>
<td>Furfural hydrogenation to furfuryl alcohol have different activity with different support.</td>
<td>\textsuperscript{31}</td>
</tr>
<tr>
<td>Ru-M (M=Ga, In, Ge, Sn, Ni) on mesoporous sulfur-doped carbon</td>
<td>Selective hydrogenation of quinolone and furfural</td>
<td>strongly chemical interaction between metals and the sulfur atoms that are doped in the carbon supports,</td>
<td>\textsuperscript{32}</td>
</tr>
<tr>
<td>Ni-M(3.0)/TiO\textsubscript{2}; M = Co and Fe; 3.0 is Ni/M molar ratio</td>
<td>Selective conversion of biomass-derived furfural (FFald) into cyclopentanone (CPO) or cyclopentanol (CPL)</td>
<td>Ni-based exhibited a unique catalytic performance for the hydrogenation and rearrangement of furfural to cyclopentanone/ cyclopentanol</td>
<td>\textsuperscript{33}</td>
</tr>
<tr>
<td>Pd/Ni/Ni(OH)\textsubscript{2}/C</td>
<td>Furfural hydrogenation at low temperatures</td>
<td>Synergistic effect between different metals, outperforms corresponding monometallic catalysts in stability, selectivity and activity</td>
<td>\textsuperscript{34}</td>
</tr>
<tr>
<td>Magnetic Cu–Co/C</td>
<td>Highly Selective Hydrogenation of Furfural to Furan-2-ylmethanol (FM) (Furfuryl alcohol)</td>
<td>active and recyclable non-noble metal catalysts for highly selective hydrogenating furfural to FM</td>
<td>\textsuperscript{35}</td>
</tr>
<tr>
<td>Pd–Co@UiO-66</td>
<td>Selective Conversion of Furfural to Cyclopentanone</td>
<td>UiO-66 material exhibits excellent thermal and chemical stability</td>
<td>\textsuperscript{36}</td>
</tr>
</tbody>
</table>
In this dissertation, silica-supported bimetallic catalysts were synthesized, characterized, and evaluated using a model compound for bio-oil upgrading. Specifically, chapter 2 presents the characterization method using CO-FTIR developed to characterize dilute limit alloy bimetallic catalyst prepared using simultaneous strong electrostatic adsorption. Also, to exploit the potential beneficial effects of single-atom alloys, chapter 3 presents supported bimetallic catalysts synthesis and characterization using the method of strong electrostatic adsorption extended to the dilution limit of one metal. Chapter 4 evaluates Cu-based dilute limit alloy bimetallic catalysts X-Cu/SiO$_2$ (where X=Pd, Pt, and Ru) for aqueous phase hydrogenation reaction using furfural as a model compound. Finally, chapter 5 presents insights on Co-based and Ni-based DLA for aqueous-phase hydrogenation of furfural.
Chapter 2. CO-FTIR Characterization of Dilute Limit Alloy Pd-Cu Catalysts

Introduction

Maximum utilization (atom-efficient) of precious metals and the unique catalytic activity of catalysts that are used in pharmaceutical industry, liquid fuel and energy generation, greener chemical production, emission control, and greenhouse gas reduction are the key factors that drives for the continuous development of synthesis methods, characterization techniques and activity tests associated with single-sites heterogeneous catalyst (SSHC).\textsuperscript{37,38} Aside from potentially having a high activity and selectivity towards certain type of reaction, attention into the activity of single-atom sites where nanoparticles does not participate in the reaction highlighted the unique properties of this type of catalysts.\textsuperscript{39–41} Using this simple model, the determination of reaction kinetics and mechanisms involve in a reaction in both experimental and computational setup becomes straightforward.\textsuperscript{42,43} Isolating a known active metal (e.g., Pd, Pt, etc.) in a “sea” of another metal is another strategy to produce a type of single site catalyst. Such a “dilute limit alloy” might have unique properties if the electronic structure of the isolated palladium is altered or the resulting isolated site geometry causes an ensemble effect. Small utilization of the active precious metal with similar or enhanced catalytic performance should increase atom efficiency. Several reports have appeared in the literature that show the effectiveness of single metal alloy catalysts for a range of reactions. For example, pioneering work by Flytzani-Stephanopoulos and co-workers explored small surface concentrations of
palladium atoms dispersed on a Cu(111) surface and on alumina-supported Cu particles (Pd$_{0.18}$Cu$_{15}$/Al$_2$O$_3$). Significant improvement was observed for the selective hydrogenation of phenylacetylene to styrene as compared with a monometallic palladium catalyst.\textsuperscript{44} The higher selectivity was attributed to spillover of Pd site-dissociated hydrogen atoms to the Cu surface, thus allowing for the inactive copper catalyst to serve as an effective bifunctional hydrogenation catalyst. Silica-supported PdCu single atom alloy prepared in the same manner were also found to be active in selective oxidation of methanol towards methylformate at low temperature. The active site giving the high selectivity in this case is the formation of atomically dispersed Pd oxide on the copper matrix.\textsuperscript{45} Selective oxidation of methacrolein with methanol to methyl methacrylate where also found to be enhanced by doping isolated Ni atoms on Au surface. The single atom of nickel acted as binding site for methanol, acted as base to stabilize the reaction intermediate, and increased the number of Au-Ox active sites.\textsuperscript{46} Improvements in dehydrogenation (NiCu), selective partial hydrogenation (PtCu), selective hydrogenation (PdAg, PdAu), hydrogenolysis (PtCu) were also made with the use SSHC catalysts.\textsuperscript{47–51}

These promising results using single atom alloys have motivated researchers in both computational and experimental catalysis.\textsuperscript{52,53} Computational studies readily allow for exploring metal combinations to target a specific reaction and can also aid in the interpretation of experimental results.\textsuperscript{54,55} However, while the structures of single metal alloy active sites are relatively simple (as compared to standard bimetallic catalysts), synthesis of such structures is a major challenge. A variety of methods have been used with varying success and complexity. For example, galvanic displacement (GD) has been successfully applied to make a variety of single metal alloy catalysts.\textsuperscript{48,56,57}
Flytzani-Stephanopulos et. al. dispersed Pd atoms alloyed on a Cu metal nanoparticle surface on an alumina support via galvanic displacement of Cu by Pd. The method was extended to prepare NiCu and PtCu single atom alloy nanoparticles supported on silica and alumina, respectively. One limitation of this method is the reduction potential compatibility of the two metals involved. Second, the metal to be displaced must be present in reduced state, requiring inert gas protection during the GD process.

Another method has been proposed by Zhang and co-workers (2015), which involves the formation of hydroxide species M(OH)$_z$ on a reducible oxide support A$_x$O$_y$, followed by calcination to form M-O-A bonds between the singly dispersed M(OH)$_z$ and A$_x$O$_y$, and finally a controlled reduction to remove some oxygen atoms to form isolated M$_1$A$_n$ sites. This method finds the reduction of precursors crucial in preparing the catalyst. There is also a limitation on the support availability, which should be reducible to form the isolated bimetallic sites. In vapor phase, one method involves the use of atomic layer deposition of a second metal onto a metal nanoparticle. For example, Wang et al. used a combination of deposition-precipitation of Ni followed by selective atomic layer deposition of Pd to produce single metal alloy PdNi on silica. The ALD method was able to selectively target the Pd onto the Ni surface rather than on silica support surface. However, this selective ALD procedure appears to only work for silica support.

Recently, Filie, A. et al. (2021), prepared a dilute palladium-in-gold nanoparticles supported on raspberry-colloid-templetated (RCT) silica. It is a three-step synthesis method identical with the typical galvanic displacement strategy. First they made monometallic gold nanoparticles (NPs) using trisodium citrate and sodium borohydride added on a vigorously stirred HAuCl$_4$ and H$_2$O to form a narrowly sized nanoparticles of
gold (~5nm). To this gold nanoparticles, bimetallic Pd\textsubscript{x}Au\textsubscript{1-x} was prepared with low atomic fraction of palladium was prepared by adding palladium (II) nitrate hydrate (Pd(NO\textsubscript{3})\textsubscript{2}) to a solution containing as-synthesized Au NPs and ascorbic acid aqueous solution and stirred for 12 hours at room temperature. Lastly, these bimetallic nanoparticles were then added to silica support using the raspberry colloid templated (RCT) approach.\textsuperscript{66}

More traditional co- and sequential- incipient wetness (IW) impregnation methods have also been used to make single metal alloy catalysts.\textsuperscript{67–72} For example, Pd-Ag/SiO\textsubscript{2} with dilute levels of Pd were synthesized using nitrates as precursors.\textsuperscript{73} The resulting improvement in activity and selectivity for hydrogenation of acrolein was attributed to the addition of atomically dispersed Pd. However, as is typical with IW methods, the particle sizes were on the order of 5-9 nm, which is not a high degree of dispersion.

One key consideration in designing a single atom alloy catalyst is the possible environment condition effect on the segregation of the active isolated surface atom into the bulk phase of the abundant host metal. Zhang et. al. (2015) reported surface atom migration during the conduct of galvanic replacement of Pd on Ag metal surface due to the large difference in surface free energy. Pd tends to diffuse to the bulk of the base Ag particle, and vice-versa, providing fresh Ag atoms for galvanic displacement.\textsuperscript{49} Thermodynamic limitations depending on the surface free energies dictate how a given metal would preferentially segregate to a nanoparticle surface, thus possibly avoiding bulk migration. In addition, for a given reaction, strong interaction of a single metal site with a specific adsorbate (e.g., CO) might serve to stabilize the atom on the surface. In the context of ultrasmall bimetallic catalyst as prepared by Wong et.al. (2017), the significantly low number of bulk atoms provides a low probability for an isolated surface atom to bulk
segregate. This strategy would allow for a one-pot facile synthesis of any dilute limit alloy bimetallic catalyst (DLA) using the method of simultaneous strong electrostatic adsorption (co-SEA).\textsuperscript{74}

One challenging aspect of isolated metal atoms is characterization, due to their inherent small concentration in catalysts. X-ray photoelectron spectroscopy typically does not provide high enough signal for the isolated atoms and would require a synchrotron beam line for brighter X-ray source.\textsuperscript{75} A better spatial resolution by Z-contrast imaging using aberration corrected scanning transmission electron microscopy (AC-STEM) results between single atom and its neighboring atoms given a high atomic number difference but becomes difficult when the difference becomes smaller.\textsuperscript{76} Other techniques such as temperature programmed reduction, may provide information about the interaction between the dilute metal and its host, but not the direct surface environment.\textsuperscript{77,78}

One approach that shows some promise for characterizing single atom alloy catalysts is Fourier transform infrared spectroscopy (FTIR) of CO adsorption. The highly sensitive signal can allow the vibrational properties of various single atom sites to be explored. FTIR is a well-established method used to characterized monometallic and bimetallic catalyst surfaces. A significant number of publications can be obtained for most of the metals used in catalysis. In a book chapter writer by Sheppard and Nguyen (1978), they consolidated IR results from various studies (single crystals and oxide supported metals) and suggested schemes on interpreting spectral results. In the recent review made by Sheppard and De la Cruz on the reliability of vibrational spectroscopy for structure identification of chemisorbed species such as CO on (111) surfaces, they concluded a 2130-2000 cm\textsuperscript{-1} range for linear (on-top) sites and an extended range 1950-1800 cm\textsuperscript{-1} for 3-fold
FTIR characterization of CO adsorption is relatively straightforward for monometallic catalysts, since the CO surface species are associated with only one metal (albeit with various coordination and geometric structure. For a bimetallic catalyst that has only one metal adsorbing CO, the analysis of spectra will be similar to that of the monometallic counterpart. However, in systems where both metals adsorb CO, the resulting spectra involve a convolution of vibrational features that can make even a qualitative analysis challenging.

In this study, silica-supported Pd-Cu bimetallic catalysts were synthesized using a dilute limit approach involving a simultaneous strong electrostatic adsorption (co-SEA). The molar ratio of Pd to Cu was varied in an attempt to achieve single atom alloy sites of Pd on Cu. These catalysts have been characterized by a range of structural approaches, and especially with FTIR during CO adsorption to probe the evolution of the Pd$_1$Cu single metal alloy sites. Extensive spectral curve fitting over a range of conditions was used to identify unique vibrational features, which were then confirmed using density functional theory (DFT) modeling of various adsorbed species. This powerful combination of experimental and computational approaches revealed the presence of two types of single atom Pd$_1$Cu species that appear in the dilute limit.

Experimental and Computational Details

Catalyst Preparation

Dilute limit alloy of palladium-copper bimetallic catalyst on a silica support was prepared by simultaneous strong electrostatic adsorption (co-SEA) as described in the previous work. Silica supported monometallic palladium and copper catalyst were also
prepared using the same method but using only the associated single metal precursors. Evonik Aerosil 300® (BET=304 m2/gm) was used as silica support for an adsorption with a surface loading of 1000 m2/L. Weighed amount of silica was poured into a pH 12-, ammonium hydroxide-adjusted solution containing cationic palladium and copper ammine complex precursors. In making the dilute limit alloy, palladium to copper metal ratio range from 1:15 to 1:60 with an initial metal concentration based on one monolayer theoretical surface adsorption density (~1.2 µmole/m2) for metal ammine complexes were prepared. Silica having a PZC=3.6 deprotonates at pH > PZC and develops the negatively charged surface thereby allowing for the strong adsorption of one monolayer of hydrated cationic ammine complex on the surface. The mixture was placed in an orbital shaker for 15 minutes and the support was recovered using vacuum filtration. The recovered silica containing the adsorbed precursors was dried at room temperature for at least 12 hours followed by muffle furnace oven drying at 120°C for 4 hours. Finally, the catalysts were reduced in a horizontal tubular furnace under a gas mixture of 20% H2 balanced N2 with a total flowrate of 500 sccm. A ramp of 5 °C/min to 400 °C and a soak time of 1 hour were employed.

Catalysts Characterization

Aliquots of solution were taken before and after contacting with the support to determine metal adsorption. Metal concentrations were measured accurately using an inductively-coupled plasma optical emission spectrometer (ICP-OES) using multiwavelength calibration, multiple replicate data and multiple view mode (PerkinElmer Avio 200). To minimize the effect of highly volatile compound on plasma stability, the samples were diluted to reduce the volatility of the solution before ICP analysis.
X-ray diffraction (XRD) patterns were obtained using a Rigaku MiniFlex II equipped with a high sensitivity D/tex Ultra Si slit detector. Patterns were recorded from 10-80° \( \theta \) using a step size of 0.02° and a Cu-K\( \alpha \) radiation source (\( \lambda=1.5406 \) Å) operated at 30 mA and 15 kV.

X-ray photoelectron spectroscopy measurements were performed with a Kratos AXIS Ultra DLD XPS system, using a monochromatic Al K\( \alpha \) source that was operated at 15 keV and 150W and a hemispherical energy analyzer. The X-rays were incident at an angle of 45° with respect to the surface normal. Analysis was performed at the pressure of 1x10-9 mbar. High resolution core level spectra were measured with a pass energy of 40 eV and analysis of the data was carried out using XPSPEAK 41 software.

Scanning transmission electron microscopy (STEM) images were obtained with a JEOL 2100F 200kV FEG-STEM/TEM equipped with a CEOS Cs corrector on the illumination system. The equipment was controlled to have an aperture of 17.5 mrad which at 200 kV provides a nominal probe size of <0.1 nm. High angle annular dark-field (HAADF) STEM images were acquired on a Fischione Model 3000 HAADF detector with a camera length such that the detector spanned 50–191 mrad. The dwell time per pixel was 15.8 \( \mu \)s. The samples were prepared for STEM by dropping the powder onto 300 mesh Cu grids coated with a holey amorphous carbon film.

Temperature programed reduction was performed on the oven dried catalysts by using a Micromeritics 2920 equipped with a TCD. The temperature was set at a ramp rate of 5°C/min, and the reducing gas of 10% H2 balanced Ar was set at a flowrate of 50 SCCM.

A Nicolet Nexus 470 spectrometer equipped with liquid nitrogen-cooled MCT-B detector was used in transmission to obtain a series of transient CO adsorption spectra with
a resolution of 2 cm\(^{-1}\) averaging 32 scans using a single beam mode. Catalyst samples were compressed to obtain a self-supporting 12 mm thin disks with density for a given thickness of approximately 25 mg/cm\(^2\). The sample is contained inside a transmission cell made of 10 cm long stainless steel capped with IR-transparent NaCl windows on both ends that is cooled with flowing water. The cell body is wrapped with heating tape and is heated using a temperature controller. A thermocouple is located near the sample to monitor temperature during sample pretreatment and measurement. Prior to each measurement, in situ drying and reduction pretreatment were made. Samples were dried for 1 hour at 100°C with flowing nitrogen gas. Upon cooling to room temperature, the samples were then reduced at 400°C for 1 hour in a 20% H\(_2\) balanced N\(_2\) gas mixture with a total flow rate of 250 sccm. A ramp rate of 5°C/minute were used in both the drying and reduction steps and the cooling steps only uses nitrogen gas. A series of spectral measurement, with background spectra measured with nitrogen gas flowing were recorded in 3 minutes interval starting with the introduction of 1% CO/He\(_2\). The first stage (CO adsorption) involves measurements starting with the introduction of CO gas into the system until saturation condition within 90-120 minutes. The second stage (N\(_2\) purging) starts upon replacing the CO gas mixture with nitrogen gas until a final purge spectrum at approximately 90-120 minutes. All measurements were made under atmospheric pressure and room temperature.

Spectral fitting using Gaussian functions was made according to Figure 2.1. Prior to fitting the dilute limit alloy spectra, the corresponding monometallic spectra were deconvoluted and fitted first. A review of the adsorbed CO vibration wavenumber found in the literature was made for each metal to determine the spectral similarities and peaks observed. Curve fitting for the series of spectra was made using a general purpose curve
fitting program Fityk. The optimized gaussian function widths (FWHM) of the relevant peaks are kept the same across a given series of spectra. The peak center wavenumber and height/area were allowed to change from spectrum to spectrum. Thus, for the purpose of analysis, it was assumed that the FWHM of contributing adsorbed CO peaks do not change as a function of their intensity. In the case of spectra from the Pd-Cu system, the obtained gaussian functions from the monometallic copper fitting were used as part of the starting set of fitting functions for the bimetallic catalyst spectra. The same FWHM and peak ratios from monometallic copper were used to obtain the contribution from adsorbed CO on copper. Additional Gaussian functions associated with isolated palladium were then included in fitting using the series of spectra obtained during the N$_2$ purging stage. The set of gaussian functions for monometallic palladium were also included in the fitting function to determine any presence of isolated monometallic palladium nanoparticles. All deconvoluted spectra presented on this paper converge with an R-square above 0.99 and residual standard deviation of less than 0.002.

Figure 2.1. General fitting scheme for dilute limit alloy bimetallic catalyst

Computational Methods

First principle calculations were performed using non-spin polarized plane-wave Density Functional Theory (DFT) as implemented in the Vienna Ab-initio Simulation
A frozen-core, all-electron projector augmented wave (PAW) approach was used to describe the electron-ion interactions. The Revised Perdew-Burke-Ernzerhof (RPBE) functional proposed by Hammer et al. was used to treat the exchange-correlation effects. Compared to other functionals within the Generalized Gradient Approximation (GGA), RPBE functional is reported in the literature to predict accurate adsorption geometries for adsorbed CO over transition metals. In particular, RPBE predicted experimentally observed CO adsorption sites over several facets of Cu.

Basis sets included wavefunctions with kinetic energy up to 600 eV. A $1.0 \times 10^{-7}$ eV convergence criterion was set for the electronic Self-Consistent Field (SCF) loops. Structures were considered relaxed when the maximum force on any atom was less than 0.01 eV/Å. Harris corrections based on the Harris-Foulkes formalism have been applied to the forces and stress tensors, and the total energy was corrected for dipole effects using a modified version of the Makov-Payne scheme. The Brillouin zone was sampled using a Monkhorst-Pack $4 \times 4 \times 1$ k-point grid. First-order Methfessel-Paxton smearing ($\sigma = 0.10$ eV) was used to speed up the convergence of reciprocal space integrals with respect to the number of k-points. Bulk lattice constants for FCC-Cu and FCC-Pd were calculated to be ($a_{\text{Cu}} = 3.672$ Å) and ($a_{\text{Pd}} = 3.972$ Å), values that are in good agreement with reported experimental values of ($a_{\text{Cu}} = 3.597$ Å) and ($a_{\text{Pd}} = 3.859$ Å). Different CO-metal surface complexes were modeled using slab models consisting of 4 surface layers. For the (111) and (100) surface models we used supercell of size $(3 \times 4)$. A $(2 \times 3)$ supercell was used for the (211) and (110) surface models. For the embedded site models, a single Cu surface atom was replaced with a single Pd atom. For ad-atom site models a single Pd atom was located over the surface in the energetically most favorable position. For all surface models,
the Pd surface concentration is 1/12 ML (1/13 ML for the ad-atom models), except for (211) where we have a surface concentration of 1/18 ML. The top two layers were relaxed in all calculations while the bottom two layers were fixed to their bulk positions. A vacuum space of 15 Å was added along the perpendicular to the surface normal to ensure that the charge density trails off to zero along the surface normal. Such a vacuum gap is also sufficient to ensure that slabs do not interact with their periodic images in the vertical direction.

Harmonic vibrational frequencies were calculated using a numerical computation of the Hessian matrix using the tools implemented in the VTST package for VASP developed by the Henkelman group. Numerical calculations needed to compute second derivatives of the energy were performed using the central-difference approximation, wherein the adsorbate atoms were displaced by 0.005 Å from their equilibrium positions. To account for the systematic deviation between DFT-calculated vibrational frequencies and experimental frequencies, a scaling factor of 1.0314 was applied to the RPBE frequencies. The scaling factor was selected such that the scaled calculated C—O stretching frequency in the gas phase is equal to the experimental value of 2170 cm$^{-1}$.

Results and Discussion

Characterization of Catalysts

Calculated nominal weight loadings and surface densities of as-synthesized monometallic palladium and copper catalysts and dilute limit alloy Pd-Cu bimetallic catalysts are shown in Table 2.1. The weight loading of monometallic palladium is comparable with that of the bimetallic catalysts. Applying the synthesis method of Wong et.al. (2017), the adsorption of copper complex on amorphous silica surface falls within the
theoretical monolayer predicted for strong electrostatic adsorption of ammine complex precursor (~1.2 μmole/m²). This suggests the absence of copper dimer formation as observed in previous works wherein the amount of adsorbed copper is beyond one monolayer of hydration sheath. The observed total surface density also conforms with the maximum density observed in the uptake survey for the Pd-Cu co-SEA system.

Table 2.1. As synthesized silica-supported Pd, Cu and dilute limit Pd-Cu catalyst weight loading

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Measured Molar Cu/Pd Ratio</th>
<th>Weight Loading, wt%</th>
<th>Surface Density, μmole/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>0.09</td>
<td>0.028</td>
<td>0.028</td>
</tr>
<tr>
<td>Cu</td>
<td>2.38</td>
<td>1.217</td>
<td>1.217</td>
</tr>
<tr>
<td>1Pd-15Cu</td>
<td>19/1</td>
<td>0.19</td>
<td>2.21 0.06</td>
</tr>
<tr>
<td>1Pd-30Cu</td>
<td>36/1</td>
<td>0.11</td>
<td>2.35 0.034</td>
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<tr>
<td>1Pd-60Cu</td>
<td>74/1</td>
<td>0.05</td>
<td>2.34 0.016</td>
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</table>

Within the limit of high-resolution XRD, the powder diffraction pattern (Figure 2.2) for both the SEA-prepared monometallic and bimetallic catalysts show the absence of sharp peaks for the palladium and copper grain. Silica supported copper prepared by dry-impregnation method having similar weight loading shows the peak intensity of relatively larger particle of copper. This suggests a small particle size (<2 nm) that is typical for catalyst prepared by SEA, with the strong metal precursor-support interaction limiting atomic migration during nanoparticle formation.
Figure 2.2. Powder X-Ray Diffraction Pattern for Cu, Pd and Dilute Limit Alloy Pd-Cu Catalyst.

The H$_2$-TPR profiles provide insight into how the strongly adsorbed precursors become reduced to form metal particles. In Figure 2.3, the peak reduction temperature of a series of increasing dilution of palladium in copper shows a reduction peak shift towards the monometallic copper peak. The overall reduction profile resembles that of the monometallic copper. At a dilute amount of palladium, the reduction peak of the copper metal precursor is decreased significantly. This suggests a close interaction between the two metals and confirms the formation of an alloyed particle. Since the palladium precursor reduces first (peak at 156 °C), these reduced Pd atoms dissociate dihydrogen, which spillover and lowers the reduction temperature of the copper precursors. This explains the downshift in reduction temperature peak as the amount of palladium increases.
Figure 2.3. H₂-TPR of Pd, Cu and dilute limit alloy Pd-Cu dried catalyst prepared by strong electrostatic adsorption.

XPS measurements show identical behavior in Cu 2p binding energy for both the monometallic copper and bimetallic dilute limit alloy catalyst. Formation of Cu(OH)₂ species and Cu²⁺ state were present on pre-reduced samples exposed to atmospheric conditions. After in-situ reduction, only one peak corresponding to a fully reduced copper (Cu⁰) (BE=932.5 eV) was observed. XPS measurement of this reduced copper after CO exposure shows two peaks (Cu⁺ and Cu³⁺) with higher binding energy (B.E.=933.1 eV and B.E.=934.6 eV, respectively), suggesting a copper in a much lower electronic state. CO adsorbed on the copper surface has its anti-bonding π bond orbitals filled by electron π-backdonation, thereby losing electrons from the copper metal surface. The same increase
is shown on the Pd 3d binding energy after CO exposure. An increase in B.E. of Pd 3d from 335.2 eV for the reduced isolated Pd on copper to B.E. 335.9 eV with the Pd-CO system. In a NAP (near ambient pressure)-XPS study by Bukhtiyarov, A.V. et al. (2018) on Pd-Au bimetallic catalysts, they found the same blue shift in B.E. from Pd state (B.E. = 334.7 eV) to Pd-CO state with linear and bridge CO contribution (B.E.=335.6 eV and B.E.= 336.2 eV, respectively).\textsuperscript{105,106} The Pd-Cu DLA also shows the same trend as that of monometallic Cu, which suggests the absence of electron transfer between Pd and Cu atoms. This could be attributed to strong metal-support interaction that overshadows the electron transfer between Pd and Cu atoms. Spectra for C 1s suggest an adsorbed CO giving a binding energy at ~289.8 eV. The increased C-C peak after CO exposure for both monometallic copper and Pd-Cu DLA suggests a decomposition of adsorbed CO on the surface (Figure A. 7). In a study by Ichikawa, S. et al. (1985), they found disproportionation of CO to CO\textsubscript{2} and carbon on a small palladium particles on a silica support.\textsuperscript{107} They found a decrease in CO chemisorption sites after seven cycles of CO adsorption and desorption. Although the XPS experiment of CO exposure were made in high vacuum system, the disproportionation of CO during the FTIR CO exposure stage is not known. The loss of site for CO adsorption could lower the signal and detection of Pd-CO isolated sites due to surface poisoning.

FTIR of Adsorbed CO

To probe the surface of the dilute limit alloy catalysts prepared by co-SEA, FTIR spectra were obtained during and after exposure to CO. In addition, spectra of monometallic Cu and Pd catalysts (at similar loadings found in the dilute limit alloy samples) were also acquired for comparison. The in-situ reduction performed prior to CO-
FTIR measurements presumes that the CO species is adsorbed on a reduced metal surface. Selected spectra are reported to show the relevant trends, with the full sets of raw spectra provided in the supporting information.

Monometallic Copper and Palladium Catalysts

Selected blank-subtracted spectra obtained during transient CO adsorption and nitrogen gas purging are shown in Figure 2.4. for monometallic copper. At the onset of CO adsorption, the band intensity in the region 2070-2140 cm\(^{-1}\) immediately reached its highest intensity. However, upon continuous exposure to CO, the band envelope from 1900-2050 cm\(^{-1}\) gradually gains in intensity while the 2070-2140 cm\(^{-1}\) region decreased slightly. This transition also produced an isosbestic point at 2070 cm\(^{-1}\). The entire band envelope became stable after 90 minutes of exposure, with two peaks becoming prominent at 2050 cm\(^{-1}\) and 2010 cm\(^{-1}\) near the end. When the CO gas was purged with N\(_2\), both the 2070-2140 cm\(^{-1}\) region and the 2050 cm\(^{-1}\) peak intensities rapidly decreased while the 2010 cm\(^{-1}\) peak increased beyond its CO-saturated intensity. Another isosbestic point at 2030 cm\(^{-1}\) was also visible during this transition but not so clear due to the transient nature of the experiment. It is also evident that the 1900-2000 cm\(^{-1}\) region slightly increased in intensity.
Figure 2.4. Selected blank-subtracted transient spectra for CO adsorption and desorption on monometallic copper catalyst.

Figure 2.5 shows the fitted functions from the saturated CO spectra to the final N$_2$-purged spectra of copper monometallic catalyst. From these fits, the integrated area of each associated peak was obtained, and are plotted in Figure A. 3a. The total integrated intensity during the CO exposure stage shows a gradual increasing trend suggesting transformation of adsorbed species upon prolonged CO exposure. Figure A. 3 reveals that the 2104 cm$^{-1}$ peak decreased while the peaks in the region 1970 cm$^{-1}$ to 2050 cm$^{-1}$ increased, suggesting a probable switch in adsorption mode. In the FTIR study by Hadjivanov et.al. (2001) on Cu/SiO$_2$, adsorbed CO species were observed at 2045 and 2018 cm$^{-1}$, with the former dominating at high CO partial pressure and the latter at low CO partial pressure. The 2045 cm$^{-1}$ peak was assigned to dicarbonyl species that transitioned to monocarbonyl species at
The second expected peak associated with a dicarbonyl CO species was not evident in their spectra due to possible masking of Cu\(^0\)-CO band at 2129 cm\(^{-1}\). In the present case, during the N\(_2\) purge the 2104 and 2050 cm\(^{-1}\) peaks decreased markedly and remained in roughly the same ratio. From this trend, we assign the 2104 cm\(^{-1}\) absorption as the second peak of the dicarbonyl species together with the 2050 cm\(^{-1}\) peak analogous to the dicarbonyl as proposed by Hajivanov et. al.. Also, the increase in integrated area for the 2009 cm\(^{-1}\) peak during the nitrogen purging stage could be associated with the linear CO formed from the geminal CO species.

Metal-CO sites assignments were made using the interpretation of IR bands of CO adsorbed on metals as described by G. Blyholder (1964) using the Huckel molecular orbitals for metal-carbon-oxygen bonds.\(^{109}\) This interpretation highlights the effect of metal ligands atoms with partially filled d-orbitals a surrounding a particular surface atom which competes for electrons with the adsorbed CO thereby affecting degree of π-back donation. The in-situ reduction at 400 °C assures that most of the copper are in reduced state given that the reduction temperature peak obtained for pure copper catalyst is at 210 °C. With this, the 2125 cm\(^{-1}\) is assigned to linear CO adsorbed on top of a reduced copper atom (Cu\(^0\) – CO) situated in low index terrace sites which in the literature assigned this to either Cu\(^0\)-CO, Cu\(^{\delta+}\)- or Cu\(^+\)-CO vibration.\(^{110-114}\) The low intensity high wavenumber at 2156 cm\(^{-1}\) can be attributed to unreduced copper in defect sites or corners. Bridge CO was assigned to the two low wavenumbers in the region of 1981 cm\(^{-1}\) and 1879 cm\(^{-1}\) and are given to terrace and edge/step sites of copper respectively. Wavenumber assignments for monometallic copper are presented in Table 2.2.
Figure 2.5. Fitted Gaussian functions for 2.38%Cu/SiO$_2$ spectra at the N$_2$-purging stage with the corresponding Cu-CO site peak assignment.

Table 2.2. FTIR CO frequency surface sites assignment for monometallic copper.

<table>
<thead>
<tr>
<th>Metal-CO Species</th>
<th>Surface Sites</th>
<th>Corners/Defects</th>
<th>Terraces</th>
<th>Steps/Edges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-(CO)$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-CO</td>
<td></td>
<td>2167</td>
<td>2151</td>
<td></td>
</tr>
<tr>
<td>Cu$_2$-CO</td>
<td></td>
<td>1980</td>
<td>1981</td>
<td></td>
</tr>
</tbody>
</table>
Figure 2.6. Band separation between linearly (>2000 cm\(^{-1}\)) and non-linearly (<2000 cm\(^{-1}\)).

Spectra obtained for 0.09\%\textsubscript{Pd}/SiO\(_2\) during CO adsorption and N\(_2\) purging are shown in adsorbed CO is evident and agrees well with the literature\textsuperscript{107,117–120}. The asymmetric band envelope in the linear region involves a main peak at \(\sim 2086\ \text{cm}^{-1}\) with a shoulder at \(\sim 2047\ \text{cm}^{-1}\) becoming somewhat more prominent upon longer CO exposure. Upon purging with N\(_2\), the absorbance in this region decreased but eventually reached a steady state. The non-linear region is characterized by a broad and unresolved band from 1700-2000 cm\(^{-1}\), suggesting convolution of several peaks arising from various highly coordinated CO surface species. At saturation, this band has a high intensity peak at 1940 cm\(^{-1}\), which decreases in intensity upon N\(_2\) purging. Also, the shoulder at \(\sim 1800\ \text{cm}^{-1}\) in
the final purge spectra shows a relatively higher intensity with respect to that obtained at saturation.

![Figure 2.7. Selected blank-subtracted transient spectra for CO adsorption and desorption on monometallic palladium catalyst.](image)

The fitted functions from the saturated CO spectra to the final N\textsubscript{2}-purged spectrum for Pd/SiO\textsubscript{2} are shown in Figure 2.8. Six gaussian functions with unique constant FWHM were obtained to fit across the series of spectra. In the fitting process, two gaussian functions were utilized for the linear region and the respective wavenumbers were allowed to shift. From initial CO introduction to saturation, the high wavenumber linear CO peak (2086 cm\textsuperscript{-1}) reached the saturation intensity instantly (not shown) and during the desorption stage, the peak downshifted to 2069 cm\textsuperscript{-1}. After almost two hours of continuous nitrogen gas purging a non-changing and lower absorption intensity was obtained in both the linear...
and nonlinear CO vibration regions. This observation suggests that a palladium cluster was formed with the synthesis method at low weight loading and conforms with the results obtained in previous studies.\textsuperscript{81,121}

![Figure 2.8. Fitted gaussian functions for 0.09\%Pd/SiO\textsubscript{2} spectra at N\textsubscript{2}-purging stage with the corresponding Pd-CO site peak assignment.](image)

Table 2.3. FTIR CO frequency surface sites assignments for monometallic palladium.

<table>
<thead>
<tr>
<th>Metal-CO Species</th>
<th>Surface Sites</th>
<th>Metal-CO Species</th>
<th>Surface Sites</th>
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<tr>
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<td>Terraces</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low Cov.</td>
<td>High Cov.</td>
<td>Ref.</td>
</tr>
<tr>
<td>Pd-CO</td>
<td>2069</td>
<td>2086</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2095\textsuperscript{121}, 2092\textsuperscript{122}, 2077\textsuperscript{123}</td>
<td>2038</td>
<td>2047</td>
</tr>
<tr>
<td></td>
<td>2073\textsuperscript{124}</td>
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<td></td>
</tr>
<tr>
<td>Pd\textsubscript{2}-CO</td>
<td>1949</td>
<td>1951</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1949\textsuperscript{122}, 1951\textsuperscript{124}, 1937\textsuperscript{45}, 1956\textsuperscript{121}</td>
<td>1904</td>
<td>1904</td>
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<td></td>
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</table>

\textsuperscript{81,121}
**Pd-Cu Dilute Limit Alloy**

Transient spectra for the 1/19, 1/30 and 1/74 (Figure 2.9a-b) dilute limit alloy catalysts were acquired during CO adsorption and nitrogen gas purging. Overall, the progression of the spectra are similar to that obtained for monometallic copper. Two prominent features at ~2050 and ~2010 cm\(^{-1}\) are observed, together with a gradual decrease in ~2100 cm\(^{-1}\) intensity as CO reaches saturation. There is a rapid decrease in intensity in the ~2100 cm\(^{-1}\) region and 2050 cm\(^{-1}\) region together with an increase in 2010 cm\(^{-1}\) region during the N\(_2\) purging step. Overall, the results suggest that the nanoparticle surfaces are largely made up of Cu sites, as expected for a dilute limit alloy.

The clearest comparison between monometallic Cu and the dilute limit alloys can be made by considering the most strongly adsorbed species on each sample. Figure 2.10 shows the normalized (to the ~2010 feature) final N\(_2\) purged raw spectra for each DLA sample and for monometallic copper. Once again, the overall similarity in the absorbance shape of these spectra is noted. However, two regions (2000-2100 cm\(^{-1}\), 1830-1940 cm\(^{-1}\), highlighted in red) clearly show an added CO absorbance that is absent from monometallic copper. These contributions to the spectra can be attributed to the presence of Pd as either DLA sites or monometallic Pd.

Figure 2.11a shows the fitted spectra for monometallic 0.09 wt\% Pd/SiO\(_2\) (top) and 2.38 wt\% Cu/SiO\(_2\) (bottom), and the most dilute Pd-Cu catalyst (middle). Deconvolution of DLA Pd-Cu catalyst made use of the fitted gaussian function parameters obtained from monometallic Cu (green peaks). During fitting, the FWHM and peak positions of the Cu peaks were kept constant while some peak ratios (minimal) and the overall intensity height were allowed to change. As can be seen, there are no obvious features in the DLA that can
be associated with monometallic Pd (blue peaks). In order to fit the remaining spectral features, three new gaussian peaks were required. As seen more clearly in Figure 2.11b, a pair of linear CO peaks at 2046 and 2021 cm\(^{-1}\) were found, with a single lower-frequency feature at 1908 cm\(^{-1}\) in the bridging region. Table S2 gives the summary of Gaussian function parameters obtained during the fitting. It should be noted that these three new peaks are present to varying extents in the other dilute limit alloy samples as shown in Figure A. 8.

![Figure 2.9](image)

**Figure 2.9.** Selected blank-subtracted spectra for (a) 1/19, (b) 1/36 and (c) 1/74 Pd dilution on Cu
Figure 2.10. Normalized CO-FTIR spectra at final nitrogen purged for monometallic copper and dilute limit alloy series Pd-Cu.
Figure 2.11. a) Fitted spectra (final N$_2$ purged) for monometallic Pd and Cu, and bimetallic Pd-Cu system and b) three additional peak assignment for isolated palladium atom sites on Pd-Cu dilute limit alloy.
DFT Calculation Results

DFT simulations were employed to assist in the band assignments of the three new peaks observed in the DLA samples as well as for the monometallic palladium and copper catalysts. Low coverage calculations were performed for four surface models (111, 100, 211 and 110) of monometallic palladium and copper surfaces and single atom alloy surfaces of bimetallic palladium-copper systems. Figure 2.12 and Figure A. 4 illustrate the surface models and CO adsorption sites.

Table 2.4 shows the calculated wavenumber for adsorbed CO species on the various sites for the monometallic copper and palladium systems with the corresponding observed experimental CO-FTIR peaks. In all configurations, linearly adsorbed CO shows a wavenumber greater than 2000 cm\(^{-1}\). The calculated wavenumbers for linearly adsorbed CO does not go beyond 2102 cm\(^{-1}\) (which we compute for a Cu adatom on Cu(111)). This conforms with the experimental results for monometallic palladium. For copper, the measured peak at 2124 cm\(^{-1}\) was assigned to a CO adsorbed linearly atop a Cu-adatom on the Cu(111) surface facet (Table 4). The DFT calculated wavenumber (2102 cm\(^{-1}\)) close to this value suggests a linear CO adsorbed on an undercoordinated copper adatom situated over a low index terrace site (although all Cu-adatom models display somewhat similar frequencies –Table 2.4).

DFT calculations also confirmed the presence of gem-carbonyl species where a Cu(CO)\(_2\) complex was predicted to form over Cu(111) surface facets. The \textit{gem}-dicarbonyl was oriented such that the (C-Cu-C) angle is 118.83° (Figure S8a,b). For the asymmetric stretching, we computed a frequency of 2064 cm\(^{-1}\) versus 2095 cm\(^{-1}\) for the symmetric stretching (Table 2.4)\(^{125}\). The difference of the calculated dicarbonyl wavenumbers (31 cm\(^{-1}\)
1) is somewhat lower than that of the experimental observation (52 cm\(^{-1}\)); however, it is difficult to determine if this difference originates from computational uncertainties or the presence of another Cu site not investigated in this study.

For terrace surface facets, the calculated wavenumber for linear CO adsorbed on Cu(100) is greater than that of Cu (111) site, which implies a lesser degree of \(\pi\)-electron back donation on Cu(100). For copper, the degree of \(\pi\) back donation is in direct correlation with the coordination number of the adsorption site with the fcc(111) surface atoms having CN=9 as compared with fcc(100) with CN=8. However, for monometallic palladium, the degree of \(\pi\) back donation is lesser with increasing coordination number. This suggests that sharing of available electrons is dominating in palladium surface atoms. The higher coordination number of Pd (111) terrace sites as compared with Pd (100) shows a higher wavenumber, which implies less available electrons for \(\pi\) back donation. With respect to the number of metal atoms coordinated with the adsorbed CO, the calculated frequency obeys the trend as atop > bridge > 3-fold-hollow > 4-fold-hollow.

Table 2.5 shows the calculated frequencies for CO adsorbed on isolated palladium on four types of copper surface facets with an embedded and ad-atom configuration (Figure 10 & 12). From the experimental CO vibration results for the isolated Pd, the association with the calculated wavenumbers was made accordingly. For a linearly adsorbed CO on an isolated palladium atom, a wavenumber of 2052 cm\(^{-1}\) was calculated for atop CO on Pd embedded on a Cu(100) facet (Figure 2.12e). Within the range of computation certainty, vibration frequencies for CO adsorbed on Pd adatoms on Cu(100) (2052 cm\(^{-1}\)), Cu(111) (2058 cm\(^{-1}\)) and Cu(211) (2048 cm\(^{-1}\)) were also calculated (Table 2.5). A significantly lower wavenumber at 2026 cm\(^{-1}\) was obtained for Pd single-atoms embedded in a Cu(111)
facet (Figure 2.12c). The trend in CO frequency can be explained by the Dewar–Chatt–
Duncanson (DCD) model. With copper acting as a ligand that donates electrons to the
isolated palladium atom, as the coordination number of Pd with Cu increases, the number
of electrons available for backdonation also increases giving a much lower CO
wavenumber. DFT calculated a 1911 cm$^{-1}$ frequency on CO forming a bridge between Pd
and Cu on a Pd embedded on a Cu(211) terrace site. This frequency is within the region of
the additional bridge peak that was required to fit the spectra for the Pd-Cu DLA (1908 cm$^{-1}$).

As the particle gets smaller, the percentage of undercoordinated atoms such as, e.g.
edges and steps, increases relative to terrace surface atoms. The Benfield (1992) model on
cuboctahedral cluster particles suggests that as the particle size falls below 2 nm the
fraction of edge atoms can go beyond 50%. Given this surface atom distribution, there
is a high probability of this isolated Pd atom situated on step-edge sites of the abundant
metal. For clusters, geometrical factors could change, such as a shorter span of the terrace
facet making no significant difference in (111) and (100) facets CO adsorption.
Table 2.4. DFT calculation on CO vibration frequency for monometallic copper and palladium systems. If the adsorption site is not located at a potential energy minimum it is considered unstable hence no frequency was calculated.

<table>
<thead>
<tr>
<th>System</th>
<th>Adsorption Site</th>
<th>C-O stretching frequency (cm(^{-1}))</th>
<th>Copper</th>
<th>Palladium</th>
</tr>
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<tbody>
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<td></td>
<td></td>
<td></td>
<td>Calculated</td>
<td>Observed (range)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calculated</td>
<td>Observed (range)</td>
</tr>
<tr>
<td>(100)</td>
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<td>2052</td>
<td>2050 to 2058</td>
<td>2057</td>
</tr>
<tr>
<td></td>
<td>bridge (b)</td>
<td>1913</td>
<td></td>
<td>1890</td>
</tr>
<tr>
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<td>4-fold-hollow (4f)</td>
<td>1727</td>
<td></td>
<td>1756</td>
</tr>
<tr>
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<td>2050 to 2058</td>
<td>2050</td>
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<td>terrace bridge (tb)</td>
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<td>1822</td>
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<td></td>
<td>step bridge (sb)</td>
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<td></td>
<td>1881</td>
</tr>
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<td>2017</td>
<td>2009</td>
<td>2072</td>
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<td>1879</td>
<td>1882</td>
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<td>1879</td>
<td>1801</td>
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<td>2050 to 2058</td>
<td>2054</td>
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<td></td>
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<td></td>
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<td>1893</td>
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<td>step-terrace bridge</td>
<td>unstable</td>
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<td></td>
<td>3-fold-hollow (h)</td>
<td>1828</td>
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<td>1873</td>
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<td>Cu-adatom/Cu(100)</td>
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<td>2084</td>
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</table>
Figure 2.12. Stable adsorption sites for Pd-Cu bimetallic catalyst. a) Cu(110) facet alloyed with a Pd atom replacing a step Cu atom, b) Cu(110) facet alloyed with a Pd atom replacing a terrace Cu atom, c) Cu(111) facet alloyed with a Pd atom (Pd/Cu111), d) Cu(211) facet alloyed with a Pd atom (Pd/Cu211) where the Pd atom has a coordination number (CN) of 10, and e) Cu(100) facet alloyed with a Pd atom (Pd/Cu100).
Table 2.5. DFT calculation on CO vibration frequency for dilute limit alloy bimetallic palladium-copper system

<table>
<thead>
<tr>
<th>System</th>
<th>Adsorption Site</th>
<th>C-O stretching frequency (cm(^{-1}))</th>
<th>DFT Calculated</th>
<th>Observed (Pd)</th>
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<td>atop-Cu (a2)</td>
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<td></td>
<td>Pd-Cu bridge (b1)</td>
<td>1930</td>
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<td>Cu-Cu bridge (b2)</td>
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<td>hollow (4-fold)</td>
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<td>2021</td>
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<td>Pd-Cu step-terrace bridge (sb2)</td>
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<td></td>
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<tr>
<td></td>
<td>atop-Cu step (ts)</td>
<td>2066</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Atop-Cu terrace (tt)</td>
<td>2044</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd/Cu(110) (Pd in step)</td>
<td>atop-Pd (a1)</td>
<td>2046</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>atop-Cu (a2)</td>
<td>2061</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-step bridge Pd-Cu (b2)</td>
<td>1882</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1-step bridge Pd-Cu (b1)</td>
<td>1934</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd/Cu(110) (Pd in terrace)</td>
<td>atop-Cu (a)</td>
<td>2063</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>bridge-Cu-Cu (b)</td>
<td>1932</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3-fold-hollow (h)</td>
<td>1822</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd-adatom/Cu(100)</td>
<td>atop-Pd</td>
<td>2052</td>
<td>2046</td>
<td></td>
</tr>
<tr>
<td>Pd-adatom/Cu(111)</td>
<td>atop-Pd</td>
<td>2059</td>
<td>2046</td>
<td></td>
</tr>
<tr>
<td>Pd-adatom/Cu(211)</td>
<td>atop-Pd</td>
<td>2048</td>
<td>2046</td>
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</table>
Figure 2.13. Top and side views of surface models corresponding to experimentally observed CO vibration; a) 2052 cm\(^{-1}\) atop CO on Pd/Cu(100), b) 2026 cm\(^{-1}\) atop CO on Pd/Cu(111), and c) 1911 cm\(^{-1}\) bridge CO (SB2) on Pd/Cu(211).

Figure 2.14. Top and side views of surface models of Pd-adatom with CO vibrations; (a,b) 2059 cm\(^{-1}\) on Cu(111), (c,d) 2052 cm\(^{-1}\) on Cu(100), and (e,f) 2048 cm\(^{-1}\) on Cu(211).
Conclusions

A facile synthesis method in preparing a dilute limit alloy of precious metal with a non-precious metal using simultaneous electrostatic adsorption was proven possible to synthesis single atom alloy catalyst. The strong metal support interaction associated surface charging and adsorption of precursor complex with a controlled removal of ligands and reduction of metal allowed the formation of small metallic clusters on the surface. The presence of a dilute amount of precious metal thermodynamically placed an isolated atom on the surface of another abundant metal. It was shown that in a typical 1:1 ratio of bimetallic catalyst, co-SEA could produce ultrasmall bimetallic nanoparticles. This concept has now been extended to dilute limit alloy to form single atom alloy nanoparticles. The robustness of the method makes it suitable to synthesize various two metal combination having the unique active site characteristics of a single atom. A much higher metal ratio of 1:30 was achieved in this synthesis method as compared with the published galvanic displacement method. One limitation of this method is that it is geared towards small particle size and only those reactions favoring such scale could benefit. Also, limitation on reaction condition to prevent metal sintering is also one key performance worth investigating given the unique geometric and electronic properties that this single atom alloy poses. Finally, the method of CO probe-FTIR can also be used to characterize single atom sites to metal systems where both metals contribute to the resulting overall spectra.

Introduction

Experimental study on single atom alloy falls short with that of the computational due to the few methods to synthesize this kind of catalyst. The commonly used method of galvanic displacement comes with the reduction potential compatibility between the two metals for the method to work. Hence results on single atom alloy computational studies often lack experimental confirmation that includes single-atom sites characterization and evaluation for various metal combinations. The method based on strong electrostatic adsorption (SEA) has been recently applied to synthesize ultrasmall bimetallic (Pd, Pt, Cu, Co, Ni) catalysts with a 1:1 atomic ratio supported on an amorphous and mesoporous silica support. The simplicity of this preparation is comparable with the impregnation method traditionally applied in making supported metal catalysts but with the advantage of forming very dispersed, well-alloyed, and ultrasmall nanoparticles particles. As the synthesis goes towards smaller particle size, the more efficient the use of metals is, which is significant for precious metals. The method is also easily scalable to industrial-scale applications.

In a typical wet or dry impregnation method, a known amount of metal salt precursor based on the desired metal loading for a given mass of support is dissolved in a solution (usually aqueous) at a volume matching or slightly beyond the pore volume of the support. The metal precursor solution is then added to the support and allowed to fill the
pore. Further treatment to remove ligands that include drying and reduction or calcination follow to make the final catalyst. In this method, the mobility of the metal precursors on the surface of the support during the removal of ligands causes larger nanoparticles to form (at least partially). The columbic effect in strong electrostatic adsorption comes into play in producing a highly dispersed nanoparticle.

In strong electrostatic adsorption, the support surface develops a surface charge depending on the pH of the solution and the point-of-zero charge (PZC) of the support. For oxide supports, protonation occurs when the pH of the solution is below the PZC, making the surface positive charged; and deprotonation happens when the pH is above, which makes the surface negatively charged. Oppositely charged metal complex precursors can then be used in a solution with the appropriate pH, adsorb on the surface of the charged support. The strong attraction between the support and the metal complex precursors would limit the movement of the metal during the ligand removal steps. This limited movement is the reason for forming smaller and more uniform particle sizes compared with dry impregnation.

A significant number of publications on the use of SEA to synthesize monometallic and bimetallic catalysts exist. Monometallic metal catalysts supported on amorphous and mesoporous types were previously fully evaluated for silica support. Cho, H-R, and Regalbuto, J. (2014) prepared Pt-Pd bimetallic catalysts in various support such as silica, carbon, alumina, and oxidized carbon and applied simultaneous and sequential steps of SEA to prepare the bimetallic.

Combining two cationic metal ammine complexes in the adsorption process within the pH of maximum uptake has been found feasible. It shows the advantage of strong
adsorption to achieve a highly dispersed and well alloyed bimetallic catalyst.\textsuperscript{77} In a typical monometallic SEA synthesis, an excess amount of metal precursor beyond a monolayer of complex adsorption on a given surface loading is present in the starting solution. The initial concentration is the same as the one used in the uptake survey that shows the volcano plot where the peak gives the optimum pH of strong and maximum adsorption (one monolayer). For a monometallic synthesis, only the initial pH obtained from the pH shift experiment and surface loading is determined prior to actual synthesis. The adsorption is usually given ample time to assume equilibrium has taken place. However, for a bimetallic synthesis, the resulting metal ratio of the final catalyst now becomes dependent on the initial concentrations of the two metals, adsorption pH, and adsorption time and is commonly made at room temperature. It was observed that an initial equivalent metal complex concentration in the adsorption mixture does not translate to the same metal ratio of the final bimetallic catalyst. In the paper by Wong et al. (2017), it was evident from the starting solution concentration that a 1:1 ratio requires an optimized initial concentration. Hence, it becomes more problematic when the desired ratio is not 1:1, which is the basis of this study.

The previous work by Wong et al. (2017) demonstrated the straightforward synthesis of silica supported, ultrasmall, homogeneously alloyed bimetallic catalyst at 1:1 atomic ratios by co-SEA. In the same manner, we extend the method to the dilution limit of one or two atoms in a crystallite of 30 or 40 atoms. The synthesis of various combinations of representative metals (Ru, Pd, Pt, Ni, Co, and Cu) on high surface area amorphous silica will be presented.
For a given support surface area in the adsorption process with one monolayer of metal complex adsorbed on the surface, if one cluster of particle will be made of 36 atoms, the area needed to form a particle for this number of atoms described by hexagonally divided area as shown in Figure 3.1. Here, an ideally distributed dilute metal is presented and becomes the center to determine the area coverage from where the atoms will be coming during the reduction process. On this assumption, assuming the configuration contribution to entropy will prevail where isolation will be favored over aggregation, as long as a small cluster will be formed, an isolated metal will form together with the diluent metal.

![Figure 3.1. Schematic of metal complex partitioning for metal particle formation.](image)

Particle surface type distributions were mathematically presented by the work of Van Hardeveld and Hartog (1999). They were able to provide, for a given particle model, mathematical equations giving the total number of surface atoms and the proportions of the various types of surface atoms that is a function of particle size and crystal structures. Many catalytic reactions that are particle size sensitive dependent could be explained based on this model by providing information of the specific site types where a reaction would prefer to occur. However, their model is usually valid for particle sizes that are big enough to fit the model. Calculating the equivalent sphere diameter of palladium particle from the calculated total number of atoms and lattice parameter for fcc structure given by
Equation 3.1, the distribution could be plotted as a function of particle diameter as shown in Figure 10.

\[ d = a \cdot \left( \frac{3 \cdot N_{\text{Total}}}{2 \cdot \pi} \right)^{\frac{1}{3}} \]

Equation 3.1

Figure 3.2. Cubooctahedron based on van Hardeveld & Hartog for palladium

In another model presented by Benfeld (1992), a small cluster particle was used and provided mathematical formulas for the number of surface atoms and surface type distribution.\(^\text{127}\) The model would require a much lower total number of atoms for particle sizes below the 2nm size. shows the distribution of the surface types as presented in the model. The edge sites dominate the distribution up to the 2.3 nm particle diameter for palladium. From Table 3.1, van hardeveld and Hartog model would require more atoms as compared with the Benfield model.
Figure 3.3. Surface sites distribution for cubo-octahedron (cluster) for Palladium.

Table 3.1. Total number of atoms and surface atoms comparison between van Hardeveld & Hartog and Benfield cubo-octahedron models.

<table>
<thead>
<tr>
<th>Parameter, m</th>
<th>van Hardeveld &amp; Hartog</th>
<th>Benfield</th>
</tr>
</thead>
<tbody>
<tr>
<td>d, nm</td>
<td>Total Atoms</td>
<td>Surface Atoms</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>38</td>
</tr>
<tr>
<td>3</td>
<td>1.7</td>
<td>201</td>
</tr>
<tr>
<td>4</td>
<td>2.4</td>
<td>586</td>
</tr>
<tr>
<td>5</td>
<td>3.1</td>
<td>1289</td>
</tr>
<tr>
<td>6</td>
<td>3.8</td>
<td>2406</td>
</tr>
<tr>
<td>7</td>
<td>4.5</td>
<td>4033</td>
</tr>
<tr>
<td>8</td>
<td>5.2</td>
<td>6266</td>
</tr>
<tr>
<td>9</td>
<td>5.9</td>
<td>9201</td>
</tr>
</tbody>
</table>

It should be noted that this atom count refers to the entire particle with spherical basis which is likely to be somewhat less when a supported metal particle is considered. Assuming the particle formed by the method of co-SEA follows the Benfield model, the assumption that a dilute atom would be occupying the surface sites instead of the bulk would be possible.
Doing the adsorption with a total metal complexes concentration within the one monolayer of surface coverage with adequate adsorption time will control the deposited metal ratio. Adsorption at the optimum pH is ideal for a strong electrostatic effect, but adsorption can still occur at a pH within the peak of the volcano plot. Electrostatic adsorption can still occur if the adsorption pH is far from the point-of-zero charge of the support. When surface charging is strong like in amorphous silica, it is postulated that the same concentration on the initial metal complex solution will be adsorbed on the support surface as long as the total solution concentration is within the one monolayer of adsorbed complex precursor for a given surface loading. This approach assumes that the concentration gradient from the surface to the boundary of the diffusion layer is minimal. This mechanism falls within the multiple component adsorption equilibrium isotherms, which could provide a much more detailed understanding and prediction of the final adsorbed species during co-SEA. Hence, the proposed synthesis method for a given surface loading calculates the total amount of metal complex needed to saturate one monolayer of the support surface. For amorphous silica as a support, this assumes the use of maximum surface density obtained in the literature for cationic ammine complex precursor, typically around 0.8 to 1.2 µmole/m². An excess amount, typically 10%, is added to assume that this will be the remaining metal precursors in the solution after total saturation (one monolayer surface density) of the adsorbing surface.

In preparation of copper monometallic catalyst using SEA, an ammine complex is prepared by adding ammonium hydroxide solution in a solution of copper nitrate. Here, complex formation depends on the ammonia concentration present and the pH of the solution. It is important in any adsorption process that the precursor does not change in
coordination number with the ligand and form another complex species. In the copper ammine complex, this takes the form of an equilibrium between the complex and the ammonia present in the solution. Hence, excess ammonia prevents complex transformation and maintains a well-substituted ammine complex form. Extending this to a bimetallic system, the presence of ammonia in the solution would push the equilibrium of the metal complexes to the ammine form, maintaining the same hydration sheath size and keeping the adsorption rate amount consistent. Also, within the adsorption layer domain near the surface, the presence of ammonia would prevent the ligand substitution, especially for copper that forms copper hydroxide.  

The ammonium hydroxide solution forms a buffer solution maintaining the pH at the desired value simultaneously, providing the excess ammonia in the solution. Deprotonation of the silica support during adsorption consumes hydroxyl ions. These hydroxide ions can then be replenished by the conversion of ammonia to form the \( \cdot \text{OH} \) in the solution. Unlike in sodium hydroxide solution, where the hydroxide consumption shifts the solution pH to a much higher degree, ammonium hydroxide reduces the pH shifts. The degree of pH shift is dependent on the surface loading employed, which gives the number of surface hydroxyl sites present in the solution. In the case of the copper ammine complex, a drop in pH below 11.6 would start the formation of the Cu(OH) complex in the solution. The absence of buffering effect would create a strong pH gradient in the adsorption layer. That explains the high uptake of copper (more than theoretical) observed in the literature when NaOH is used due to the change in hydration sheath and formation of dimers. In this proposed method, ammonium hydroxide instead of NaOH is applied to serve two purposes: to have ammonia in the solution for ammine complex stability and to minimize
the change in hydroxide ions concentration for pH stability. The study by Toupance et al. (2001) shows that the presence of ammonium ions prevents the formation of copper phyllosilicates. The approach also prevents the introduction of trace amounts of sodium on the surface, which could remain in the solution upon filtration and drying.

Materials and Methods

Metal precursors used are hexaamminenickel (II) chloride (American Elements 99.999%), hexaamminecobalt (III) chloride (Sigma-Aldrich 99%), copper (II) nitrate hydrate (Sigma-Aldrich 99.999%), tetraamminepalladium (II) chloride monohydrate (Sigma-Aldrich 99.99%), tetraammineplatinum (II) chloride hydrate (Sigma-Aldrich), and hexaammineruthenium (III) chloride (Sigma-Aldrich). In making the initial adsorption solution, one method weighs the calculated amount of metal precursors and dissolves the precursors in pH-adjusted ammonium hydroxide. The other method is to prepare a stock solution of each precursor with a pH-adjusted solution of ammonium hydroxide. The needed amount of each stock solution is then calculated based on the required initial concentration. Dissolving copper (II) nitrate with ammonium hydroxide at pH 12 makes the copper ammine complex. Below solution pH of 11.6, Cu(OH) complex will form, making the actual total adsorbed species higher than the theoretical. Also, ammonium hydroxide prevents the precipitation of Ni(NH$_3$)$_6$Cl$_2$ in the solution. This condition forms the basis of the adsorption at pH 12 for all syntheses and limits the adsorption to 15 minutes to minimize dissolution. Adjusting the pH of all ammonium hydroxide solutions used in preparing the mixture to the initial pH of adsorption ensures that the starting concentration of the metal precursors is within the calculated amount. This final pH adjustment that
changes the initial concentration is not critical for monometallic synthesis but becomes significant in bimetallic, especially for a targeted metal ratio.

Table 3.2. Simultaneous SEA synthesis condition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Surface Area Support</td>
<td>Amorphous Silica (Aerosil® 300)</td>
</tr>
<tr>
<td>Support Surface Area</td>
<td>~315 m²/g</td>
</tr>
<tr>
<td>Surface Loading for SEA</td>
<td>1000 m²/L</td>
</tr>
<tr>
<td>Initial pH</td>
<td>12 (adjusted using Ammonium Hydroxide)</td>
</tr>
<tr>
<td>Adsorption time</td>
<td>15 mins</td>
</tr>
<tr>
<td>Shaking speed</td>
<td>120 rpm</td>
</tr>
<tr>
<td>Metal Precursors</td>
<td>Metal Ammine Complexes</td>
</tr>
<tr>
<td>Metal Complex Total Concentration</td>
<td>~1 µmole/m²</td>
</tr>
<tr>
<td>Desired Metal Molar Ratios</td>
<td>1:15, 1:30, 1:60 for DLA</td>
</tr>
<tr>
<td>Drying Conditions</td>
<td>Overnight RT drying + 4 hrs @120°C in muffle furnace</td>
</tr>
<tr>
<td>Reduction condition</td>
<td>1 hr at 400°C, 5°C/min ramp rate under 20%H₂/80%N₂ Gas</td>
</tr>
</tbody>
</table>

Synthesis could start from either a given support mass or adsorption volume. Both of which depend on the surface loading for the adsorption process and surface area of the support. This study uses typical surface loading of 1000 m²/L. Hence the amount of support or volume of solution for a given preparation is calculated as,

\[
Mass_{Support}(gm) = \frac{Surface\ Loading(m²/Liter)}{Surface\ Area(m²/grams)} \times Volume(Liter) \quad \text{Equation 3.2}
\]

Given the theoretical metal surface density of one monolayer of metal complexes (0.8 to 1 µmole/m²) with hydration sheath on the support surface and the desired metal ratio, the theoretical adsorbed metal surface densities can be calculated. Hence, the corresponding metal mass can be determined using the equation

\[
Metall\ Mass = Metall\ Surface\ Density \left( \frac{\mu\text{mole}}{m²} \right) \times \frac{\text{mole}}{10^6\mu\text{mole}} \times MW_{metall} \left( \frac{gm}{\text{mole}} \right) \times Surface\ Area \left( \frac{m²}{gm} \right) \times [Mass\ Support\ (gm)] \quad \text{Equation 3.3}
\]

where \( MW = \) molecular weight of the metal
Surface Area = surface area of support

The mass loading for each metal is also calculated by

\[
\text{Metal1 Loading (\%)} = \frac{\text{Mass_{Metal1}} \cdot (gm)}{\text{Mass_{Metal1}} \cdot (gm) + \text{Mass_{Metal2}} \cdot (gm) + \text{Mass_{Support}} \cdot (gm)} \times 100
\]

Equation 3.4

The needed metal mass uses the corresponding volume of metal precursors stock solution for calculation. The initial adsorption solution utilizes a 10% excess of theoretical metal precursors concentration. The hypothesis for this study is that one monolayer of metal complexes will be adsorbed based on the available surface area, and 10% will remain in the bulk solution. MS Excel worksheet serves as a tool to calculate the amount of precursors needed (see Appendix B).

In a typical preparation, a given mass of support was added to a pH 12 of metal complex solution mixture with the desired metal ratio in a wide mouth HDPE plastic bottle. After 15 minutes of shaking, the solid was filtered and dried overnight. The initial and final pH of the solution was also measured. Prior to the final reduction steps, removal of excess water from the filtered catalyst is important to avoid the capillary effect during the reduction steps that cause unwanted migration of metal precursors on the support surface. Although columbic forces help stabilize the precursor on the surface, the capillary effect could still cause migration of the precursors. The drying steps at room temperature (RT) followed by muffle furnace drying were employed in the synthesis. At least an overnight RT drying under the hood was made for the filtered samples. After room temperature drying, the samples were removed from the filter, transferred to a crucible, and dried at 120 °C in a muffle furnace for 4 hours. Dried samples were then reduced in a horizontal cylindrical furnace under a 20% \( \text{H}_2/\text{N}_2 \) gas flow rate of 250 SCCM at ambient pressure for 1 hr at 400 °C (stated otherwise) with a ramp rate of 5°C/min.
In the preparation of catalyst by the impregnation method, the known mass of metal precursors is added to DI water with a volume equivalent to the total pore volume of a given mass of support. This pore volume was determined by gradually adding a known volume of DI water on the support with mixing in between addition. The pore volume is then determined when a well-formed ball of wet support is formed with the total volume of added solution as occupied pore volume.

Characterization of the as-prepared catalysts included ICP-OES, X-ray diffraction, hydrogen temperature program reduction, and CO-probe Fourier transform infrared spectroscopy. Chapter 2 describes the details of the methods. In fitting CO-FTIR spectra, multiple software was used. An MS-excel workbook was developed to process spectral data and generate script for fitting in fityk®. Origin-Pro ® was used in multiple spectra batch processing and data plotting (Figure B. 7).

Results and Discussions

The as-prepared catalysts weight loadings of palladium, platinum, and ruthenium dilute limit alloy on copper-, cobalt-, and nickel-based catalysts, each having three dilution levels, and the monometallic catalysts prepared by simultaneous strong electrostatic adsorption (co-SEA) and SEA respectively, are shown inTable 3.3. Similar to previous studies, the adsorbed ammine complex precursors fall within the theoretical monolayer of the metal complex calculated for having a single hydration sheath. The strong electrostatic charge developed on silica surface at pH greater than its PZC enables almost complete adsorption of precursors from the bulk solution within 15 minutes of adsorption time. As hypothesized in the moderate metal ratio synthesis, working within one theoretical monolayer of metal ammine precursor concentration enables the controlled deposition of
the same bulk solution initial metal ratio. The cationic metal complex precursors should maintain their structure to retain the same ratio. The ammonia-containing solution stabilizes the ammine complex with the use of excess. This excess amount of ammonia prevents the formation of ammine/aqua and hydroxide(hydroxo) complex, especially near the support surface where the local environment condition such as pH is lower for the case of silica. Another advantage of using NH$_4^+$ is the lowering of silica dissolution and the suppression of phyllosilicate formation, which occurs when a strong base (NaOH) in typical SEA synthesis is used in pH adjustment to charge the support surface.\textsuperscript{132,134} Hence the presence of ammonia with the equilibrium \( \text{NH}_3 \Leftrightarrow \text{NH}_4^+ + \text{OH}^- \) has three functions, to supply NH$_3$ that stabilizes the ammine complex, to supply the OH$^-$ that charges the silica surface, and to protect the silica surface from dissolution and phyllosilicate formation.

Within the limit of XRD detection, all catalysts synthesized show no visible/sharp XRD peaks that would be present when grain dimensions are greater than 1.5 nm. The consistent small particle size obtained by the method of SEA is achieved with proper drying of sample to remove excess amount of water followed by the controlled metal reduction and ligand (NH$_3$) decomposition during the reduction step in the stream of hydrogen. This procedure prevents forming a relatively large nanoparticle, evident in the typical dry impregnation method. The immobilization of metal precursors due to strong precursor-support interactions limits the migration of atoms in forming the supported metal clusters, thereby having a smaller and tighter particle size distribution.\textsuperscript{130}
Table 3.3. Typical weight loadings and surface densities of dilute limit alloy bimetallic and monometallic catalyst.

<table>
<thead>
<tr>
<th>Metal 1</th>
<th>Metal 2</th>
<th>As Synthesized Catalysts, Weight Loading, wt%</th>
<th>Molar Ratio (M2/M1)</th>
<th>Total Surface Density (µmole/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palladium</td>
<td>Copper</td>
<td>0.19%Pd2.21%Cu/SiO₂ 19</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.11%Pd2.35%Cu/SiO₂ 36</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05%Pd2.34%Cu/SiO₂ 74</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cobalt</td>
<td>0.25%Pd1.76%Co/SiO₂ 13</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.11%Pd1.81%Co/SiO₂ 29</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.06%Pd1.80%Co/SiO₂ 51</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>Copper</td>
<td>0.27%Pd1.61%Ni/SiO₂ 11</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.11%Pd1.65%Ni/SiO₂ 27</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.07%Pd1.64%Ni/SiO₂ 41</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Platinum</td>
<td>Copper</td>
<td>0.39%Pt1.80%Cu/SiO₂ 14</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.16%Pt1.73%Cu/SiO₂ 34</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.08%Pt1.76%Cu/SiO₂ 69</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cobalt</td>
<td>0.29%Pt1.91%Co/SiO₂ 22</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.17%Pt1.93%Co/SiO₂ 37</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.08%Pt1.91%Co/SiO₂ 76</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>Copper</td>
<td>0.40%Pt1.64%Ni/SiO₂ 14</td>
<td>1.0</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>0.20%Pt1.68%Ni/SiO₂ 28</td>
<td>1.0</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>0.11%Pt1.70%Ni/SiO₂ 51</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Ruthenium</td>
<td>Copper</td>
<td>0.15%Ru1.88%Cu/SiO₂ 21</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.07%Ru1.86%Cu/SiO₂ 40</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.04%Ru1.86%Cu/SiO₂ 75</td>
<td>1.0</td>
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</tr>
<tr>
<td></td>
<td>Cobalt</td>
<td>0.12%Ru1.98%Co/SiO₂ 29</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.06%Ru1.99%Co/SiO₂ 53</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.03%Ru1.95%Co/SiO₂ 105</td>
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</tr>
<tr>
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<td>Copper</td>
<td>0.16%Ru1.73%Ni/SiO₂ 18</td>
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<td></td>
</tr>
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<td>0.9</td>
<td></td>
</tr>
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<td></td>
<td></td>
<td>0.04%Ru1.72%Ni/SiO₂ 73</td>
<td>1.0</td>
<td></td>
</tr>
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<td>Palladium</td>
<td></td>
<td>0.09%Pd/SiO₂</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Platinum</td>
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<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Ruthenium</td>
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<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
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<td>2.38%Cu/SiO₂</td>
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</tr>
<tr>
<td>Cobalt</td>
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<td>1.64%Co/SiO₂</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td></td>
<td>1.43%Ni/SiO₂</td>
<td>0.8</td>
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</tr>
</tbody>
</table>
Figure 3.4 XRD pattern of a) monometallic and b) bimetallic dilute limit alloy catalysts.

An indirect proof of bimetallic particle formation is when the reduction temperature of one metal precursor is affected by the presence of another metal. As shown in Figure 3.5, Figure 3.6, and Figure 3.7, the dried catalyst reduction profile of the monometallic catalyst differs from that of the bimetallic. The strong metal precursor-support interaction
is evident with the wide peak width in all cases. Unlike the copper-based TPR profile that shows a clean reduction peak, the cobalt and nickel-based catalysts show a positive peak in the 175 °C and 300 °C regions, respectively. These peaks hide the actual reduction peak of the abundant metal and can be due to decomposition products of the ammine complex. However, removing the effect of this positive peak would show a much lower reduction peak temperature for the dilute limit bimetallic catalysts as given by the early onset of the peak shoulder. The pattern for monometallic cobalt shows a second reduction peak (701 °C). From Figure 3.8, adding the dilute amount of Pd, Pt, or Ru greatly reduced this second reduction peak. All these reductions in temperature are due to the hydrogen spillover effect that affects the profile of the other metal precursors.

Figure 3.5. H2-TPR profile for Pd-X dilute limit alloy catalysts.
Figure 3.6. H2-TPR profile for Pt-X dilute limit alloy catalysts.

Figure 3.7. H2-TPR profile for Ru-X dilute limit alloy catalysts.
FTIR of Adsorbed CO

Monometallic Catalysts

Chapter 2 presented the spectra for monometallic palladium and copper catalysts. Figure 3.9a-d shows the blank subtracted CO-FTIR spectra for monometallic platinum, ruthenium, nickel, and cobalt. The transition spectra for platinum (Figure 3.9a) show a stable absorbance from the start of CO introduction to the final nitrogen purged spectra. The almost unchanged intensity suggests a strong CO binding on platinum even for linear Pt-CO species. There is no evidence of strong peak shifting due to the coupling effect or changing electron surface density during the CO exposure stage and N$_2$ purging step. The observed absorbance in the region with the highest peak at 2070 cm$^{-1}$ and the broad spectrum from 1780 cm$^{-1}$ to 1900 cm$^{-1}$ is associated with linearly and bridged adsorbed CO, respectively. Linear CO adsorbed on the platinum surface gives the same wavenumber as the literature.$^{135,136}$
Spectra for ruthenium monometallic catalysts (Figure 3.9b) with weight loading comparable with the DLA catalysts also shows an almost stable response during the unsteady state exposure. However, it also shows a slight decrease in the 2120 cm\(^{-1}\) and 2060 cm\(^{-1}\) bands and a slight increase in the 2060 cm\(^{-1}\) and 1950 cm\(^{-1}\) bands. Chen, H. et al. (1984) observed three bands around 2030 cm\(^{-1}\), 2080 cm\(^{-1}\), and 2140 cm\(^{-1}\) on silica-supported ruthenium. These three bands exist in the current spectra, with the 2080 cm\(^{-1}\) being a shoulder of a much higher intensity peak at 2061 cm\(^{-1}\).\(^{137}\) The current spectra show a much closer resemblance to that obtained by Chin, S. et al. (2006). The visible bands (2140 cm\(^{-1}\), 2060 cm\(^{-1}\), and 2030 cm\(^{-1}\)) are present in the fitted peaks in their study. However, their 2060 cm\(^{-1}\) band relative intensity spectra are lower than the present one. This variation in spectra is because of the different synthesis methods affecting the final surface structure of the as-prepared supported catalysts.

Previous studies on nickel catalyst surfaces use probe molecules and interpretes resulting spectra to give insights into the distribution of surface sites. Variation in precursors, support, synthesis methods gives a unique metal particle characteristic. Hardeveld and Hartog (1972) studied and modeled the surface atom, and site statistics on metal particles using infrared measurement on CO adsorbs on the surface to determine surface structure information.\(^{138}\)

At the onset of CO gas exposure on nickel catalyst, a high-intensity band at 2049 cm\(^{-1}\) is visible together with a high-frequency shoulder at 2086 cm\(^{-1}\). Broadband in the 1820 cm\(^{-1}\) region is also visible, with a much more intense peak at 1930 cm\(^{-1}\). A band separation suggests linear and bridge CO vibration like that of palladium. It also shows that the high-intensity region decreases in CO exposure and N\(_2\) purging steps. Unlike the
transition spectra of monometallic copper, where an isosbestic point suggests transformation from one adsorbed CO species to another, in the nickel catalysts, it shows that the surface is changing, and possibly the surface atom is being removed.

Mihaylov, M. et al. (2001) observed an identical spectrum behavior on silica-supported nickel. They attributed the 2049 cm\(^{-1}\) peak to the formation of adsorbed Ni(CO)\(_4\) that eventually leave the surface to form vapor phase Ni(CO)\(_4\).\(^{139}\) By exposing nickel catalyst to pressure above 5 mm Hg, Yates, J. and Garland, C. (1961) was able to reduce the nickel concentration on alumina supported catalysts. The stripped nickel catalysts eventually show an identical spectrum as the lower loading catalyst in their study. Medvedev, V. K. et al. (1998) suggested the complete mechanism associated with Ni(CO)\(_4\) formation on a stepped Ni in a sputter-defect Ni surface.\(^{140}\) The formation of Ni(CO)\(_2\)\(_{\text{ad}}\) on kink sites induces Ni-Ni bond breaking, creating new kink sites, thus repeating the cycle. This phenomenon is likely to happen in small particle sizes (~1nm) where the edge/step sites dominate.

Another possible explanation for the decreasing intensity is the disproportionation of CO on Ni(111) to carbon and carbon dioxide (Boudouard reaction). In their LEED study, Edmonds, T. and Pitkethly, R. (1969) claimed that CO disproportionation dominates over CO dissociation in Ni(111). The co-existence of CO\(_2\) and CO in their respective domains supported this claim. The formation of Ni(CO)\(_4\) was also not observed in their run, which can be explained by the lack of kink sites that initiates Ni(CO)\(_2\)\(_{\text{ad}}\) formation, as previously discussed. Also, in Galuzska, J. et al. (1981) study on Ni/Al\(_2\)O\(_3\), a high dispersion catalyst of nickel shows poor activity in disproportionation reaction. They concluded that an
ensemble of surface atoms of nickel is required for the disproportionation reaction to proceed based on the linear plot of the amount of CO₂ formed vs. (1-θ)⁰ where n=4.¹⁴¹

The spectra for monometallic cobalt reduced at 400 °C show one peak at 2180 cm⁻¹ and a weak absorption in the 2050 cm⁻¹ region. This high intensity beyond the gas CO wavenumber suggests a linear CO on unreduced cobalt (Co⁰⁺). From the H₂-TPR profile, the reduction peak temperature reached 750 °C. Hence at 400 °C reduction temperature used for this sample, the cobalt precursors are still in ammine complex form. Souza, L. et al.(2007) study show that the cobalt hexaammine is transformed into cobalt tetraammine during the drying step and would require 100% H₂ at 650 °C to form an hcp structure.¹⁴²

![Figure 3.9](image_url)

Figure 3.9. Selected blank-subtracted CO-FTIR spectra for a) 0.12%Pt/SiO₂, b) 0.10%Ru/SiO₂, c) 1.43%Ni/SiO₂ and d) 1.64%Co/SiO₂ monometallic catalysts.
Figure 3.10 shows the six Gaussian functions that fit the transition spectra for monometallic platinum. A low-intensity shoulder peak having a center wavenumber of 2090 cm\(^{-1}\) could be a Pt-CO species on unreduced platinum or isolated platinum on the support given the small FWHM (11 cm\(^{-1}\)). The highly coordinated CO region requires two Gaussian functions, while the linear CO region needs three. Table 3.3 shows the adsorbed CO species wavenumber assignment for platinum (0.12\%Pt/SiO\(_2\)) following the DCD model. The high intensity, high-frequency peak (2070 cm\(^{-1}\)) is assigned to terrace sites, and the two shoulder, low frequencies are assigned to edge/step sites. Two bridge sites were assigned to 1833 cm\(^{-1}\) and 1807 cm\(^{-1}\) peaks, respectively. Nitrogen purging exhibits a small redshift (6-11 cm\(^{-1}\)) in the center wavenumber of the linear CO peaks. This shift results from the increase in available electrons for back donation during nitrogen purging. However, the total integrated area does not show a significant decrease compared with palladium and copper (Figure A. 3). It is also evident how the integrated area of the edge/step linear CO peak (2045 cm\(^{-1}\)) increases while the bridge CO peak (1807 cm\(^{-1}\)) decreases upon nitrogen purging, suggesting possible transformation from a bridge to linear. Greenler, R. and Brandt, R. (1995) have shown that coupling of linearly adsorbed CO forms the normal modes observed in experimental spectra and could cause a shift in vibration frequency from its isolated frequency. Hence the decoupling of CO vibration modes on removing some adsorbed CO leads to this shift. The preference of forming linear CO contradicts the usual trend of forming bridge CO at low coverage, which should be more stable than a linear CO. In a study by Gruene, P. et al. (2008) on group 10 metal clusters, they explained the behavior of platinum favoring linear CO because of the relativistic contraction (shorter) of the Pt-CO bond stabilizes the atop CO configuration.\(^{143}\)
The other bridge CO peak (1833 cm\(^{-1}\)), which disappeared upon purging, suggests being on terrace sites and less stable than that of linear CO peak (2070 cm\(^{-1}\)) on the terrace. Bartók, M. et al. (1981) associated the 2070 cm\(^{-1}\) linear CO peak with adsorptive CO, nonordered structure with large dipole-dipole interaction, and the 2047 cm\(^{-1}\) desorptive CO, ordered structure on low surface coordination. In the current method, the desorption started from high coverage. Based on Bartók conclusion, the desorption begins from low miller index planes (terrace sites, high coordination) followed by the low-coordination sites. In the current study with nitrogen purging instead of evacuation, the intensity of the 2070 cm\(^{-1}\) did not change from the start of nitrogen purging. However, the 2060 cm\(^{-1}\) decreased while the 2047 cm\(^{-1}\) increased in area. It is important to note that previous spectral analysis does not deconvolute their spectra and relies much on the observed high-intensity peak, and they associated this with one peak. A study by Su, X et al. (1996) suggested the increase in the 2045 cm\(^{-1}\) peak due to surface reconstruction or relocation of metal atoms, especially in low coordinated atoms. Tao, F. et al. (2010) proposed that the relaxation of the repulsive CO-CO interaction forces the break-up of stepped sites atom of platinum (with adsorbed CO).\(^{144}\) This movement of metal atoms could explain the loss in bridge CO (1807 cm\(^{-1}\)) and the formation of terminal sites with a wavenumber of 2045 cm\(^{-1}\) while the total integrated area does not change.\(^{145}\)

Using the peaks obtained by Chin, S. et al. (2006) as the starting parameter for fitting the monometallic ruthenium spectra establishes a good fit for the selected transition spectra. The peak center wavenumber of the fitted Gaussian functions, as shown in Figure 3.11, closely matches that of Chin’s study (Table C.1). A modification of band assignment
was made from their fitted peaks, as presented later. Table 3.5 shows the summary of the site assigned.

![Figure 3.10 Fitted gaussian functions for monometallic 0.12%Pt/SiO2.]

**Table 3.4. Surface sites assignment for Pt-CO species on Pt/SiO2**

<table>
<thead>
<tr>
<th>Metal-CO Species</th>
<th>Surface Sites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Corners/Defects</td>
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<tr>
<td>Pt-CO</td>
<td>2085</td>
</tr>
<tr>
<td>Pt2-CO</td>
<td>1833</td>
</tr>
</tbody>
</table>
Figure 3.11. Fitted Gaussian functions for monometallic Ruthenium

Table 3.5. Surface sites assignment for Ru-CO species on Ru/SiO$_2$

<table>
<thead>
<tr>
<th>Metal-CO Species</th>
<th>Corners/Defects</th>
<th>Surface Sites</th>
<th>Steps/Edges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru$^{n+}$-(CO)$_3$</td>
<td>2140, 2123, 2079</td>
<td>2140, 2122, 2078</td>
<td>80</td>
</tr>
<tr>
<td>Ru-(CO)$_2$</td>
<td>2039, 2038, 2099, 2096</td>
<td>2038, 2096</td>
<td>80</td>
</tr>
<tr>
<td>Ru-CO</td>
<td>2079, 2078</td>
<td>2063, 2063</td>
<td>2009, 2012</td>
</tr>
<tr>
<td>Ru$^{n+}$-CO</td>
<td>2079, 2078</td>
<td>2063, 2063</td>
<td>2009, 2012</td>
</tr>
<tr>
<td>Ru$_2$-CO</td>
<td>1976, 1984</td>
<td>1829, 1826</td>
<td>80</td>
</tr>
</tbody>
</table>

For a monometallic nickel, the deterioration of the surface atom makes the fitting challenging. However, during the nitrogen purging steps, the overall shape of the spectra is the same, with only the intensity changing. Even during the nitrogen purging step, the decreasing intensity suggests the continuous removal of the surface atom. From Figure C. 3c, a constant rate (excluding CO at 3 mins.) of decrease in the total integrated area was
obtained before and after nitrogen purging, thus supporting the continuous deterioration of nickel surface atom even in the absence of CO gas. Fitting the nickel spectra utilizes nine Gaussian functions (Table 3.6), with one isolated peak appearing at a low center wavenumber of 1621 cm\(^{-1}\). The band in this region is commonly associated with adsorbed water on a silica surface (1633 cm\(^{-1}\)).\(^{152}\) However, the 12 cm\(^{-1}\) difference may suggest a different species. Garland, C. et al. (1965) observed a 1620 cm\(^{-1}\) peak in their CO-FTIR study on evaporated nickel films. The outgassing procedure made and that other transition metal evaluated lacks this band shows that this is not water contamination. They suggested the 1621 cm\(^{-1}\) coming from adsorbed bridge CO with a weaker vibration energy due to the association of oxygen with another Ni atom. \(^{153}\) In the current study, there was no significant increase in the integrated area of this peak, unlike in the results by Garland. This behavior may also suggest that flowing nitrogen gas is insufficient to desorb CO.

The high-intensity peak at 2082 cm\(^{-1}\) results from a single linear CO adsorbed on a Ni atom.\(^{154}\) For this peak, Yates, J. and Garland, C. (1961) observed an increase in intensity after stepwise addition of Ni(CO)\(_4\) gas which decomposes completely and produces 3 moles of CO gas for every mole of Ni(CO)\(_4\) decomposed. These findings further support the results of current measurements showing nickel surface corrosion.
Figure 3.12. Fitted gaussian functions for monometallic 1.43\% Ni/SiO$_2$.

Table 3.6. Surface sites assignment for Ni-CO species on Ni/SiO$_2$

<table>
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<tr>
<th>Metal-CO Species</th>
<th>Corners/Defects</th>
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<th>Steps/Edges</th>
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<td>Ni-(CO)$_2$</td>
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<tr>
<td>Ni-CO</td>
<td>2074</td>
<td>2082 $^{154, 155}$</td>
<td>2056</td>
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<tr>
<td>Ni$_2$-CO</td>
<td>1925</td>
<td>1930 $^{154, 155}$</td>
<td>1874</td>
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<tr>
<td>Ni$_3$-CO</td>
<td>1678</td>
<td>1678</td>
<td>1802</td>
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Bimetallic Dilute Limit Alloy (Cu-Based)

Characterization of single-atom sites having a low concentration of the isolated atom is one of the challenges in studying this type of catalyst, which shows in the limited number of publications. With a dilute amount of single-atom metal present, CO probe infrared study is the viable technique to show the presence of the isolated surface atom. The analysis is complicated when both metals give absorbance. As presented in the Pd-Cu
DLA system, the same method was applied to Pt-Cu DLA. Error! Reference source not found. Figure 3.13, shows transient CO-FTIR spectra for platinum at three dilutions with copper. The dynamic behavior of the spectra resembles that of the monometallic copper. The same isosbestic points (2070 cm\(^{-1}\) and 2030 cm\(^{-1}\)) are also present. However, from the normalized plot shown in Figure 3.14, two additional peaks appear at the 2030 cm\(^{-1}\) and 2130 cm\(^{-1}\) regions. For monometallic copper, it is evident that the intensity ratio of the high-frequency band to the low-frequency band approaches that of the monometallic copper intensity ratio. At the 3 minutes spectra, the low dilution (higher platinum loading) shows a stronger intensity in the 1990 cm\(^{-1}\) region, decreasing as the dilution increases (Figure 3.13). This additional band is not visible in the normalized spectra, but this region shows a positive deviation (Figure 3.14b).

Figure 3.13. Selected blank-subtracted spectra for Pt-Cu DLA at varying dilution; a) 1/14, b) 1/34, and c) 1/69.
Figure 3.14. Normalize spectra of Pt-Cu DLA a) at high frequency and b) at low frequency.

As shown in Figure 3.15, three additional Gaussian functions are needed to fit the bimetallic Pt-Cu DLA catalysts transition spectra as suggested in the normalized spectra. These Gaussian functions also fit the other two Pt-Cu dilutions prepared (Figure C. 4). These peaks with a wavenumber greater than 2000 cm\(^{-1}\) can be associated with linear CO species. Considering the high-frequency peak (2123 cm\(^{-1}\)) coming from linear CO on a single platinum atom, it would be strongly blue-shifted considering the high-intensity peak for monometallic platinum (2070-2064 cm\(^{-1}\)). This peak greatly overlapped the linear CO band for monometallic copper (2125 cm\(^{-1}\)). In the study by Yang, C. (2018) on Pt-Cu/SiO\(_2\) SAA, they associated a 2111 cm\(^{-1}\) as a frequency for the isolated linear Pt-CO, which blue-shifted from the linear CO obtained in monometallic Pt (2063 cm\(^{-1}\), 2046 cm\(^{-1}\)). In the current Pt-Cu DLA spectra, no Gaussian function showed an intensity peak in this region. There is also no shift in the linear Cu-CO peak due to the dilute amount of platinum. In another study, a much lower frequency (2088 cm\(^{-1}\)) was associated with linear CO on isolated platinum on Pt-Cu supported on mixed metal oxide (MMO) that also blue-shifted from the corresponding monometallic Pt (2020 cm\(^{-1}\)). In both studies, the linear CO obtained from monometallic platinum shows a blue shift in CO vibration. Contrary to this
trend, Sun, G. et al. (2018) obtained a unique band centered at 2018 cm$^{-1}$ for isolated Pt-CO on Pt-Cu/Al$_2$O$_3$ SAA.\textsuperscript{67} The current spectra have one frequency at a much higher wavenumber (2123 cm$^{-1}$) and two lower frequencies (2032 cm$^{-1}$ and 1985 cm$^{-1}$).

![Graph showing comparison of fitted Gaussian functions for monometallic and bimetallic Pt-Cu DLA catalysts.](image)

**Figure 3.15.** Comparison of fitted Gaussian functions for monometallic and bimetallic Pt-Cu DLA catalysts.
The high frequency can also be associated with a single atom of platinum on silica support instead of platinum on a copper surface. The platinum supported on H-mordenite in the study by Zholobenko, V.L. et al.(1994) shows a 2123 cm\(^{-1}\) wavenumber. Moreover, they associated this with CO on isolated platinum sites. The observed blue-shift from 2095 cm\(^{-1}\) frequency obtained from linear CO on Pt cluster is due to electron-deficient platinum atom interacting with zeolite protons.\(^{157}\) The same wavenumber was also observed by Aguilar, J. J. (2021) on atomically dispersed platinum on SAPO-37 (via oxidation synthesis) rapidly transforms into Pt cluster after hydrogen exposure. A much close peak at 2120 cm\(^{-1}\) was observed by Bo, Z. et al. (2019) on isolated Pt on a SiO\(_2\) modified Al\(_2\)O\(_3\) support with the Pt on the alumina surface. The same catalyst shows the nanoparticle size of platinum having deconvoluted linear CO peaks (2090, 2070, 2050, and 2020 cm\(^{-1}\)) that match some of the frequencies obtained in this study for monometallic platinum (2090, 2070, and 2045 cm\(^{-1}\)).

The other two peaks (2032 cm\(^{-1}\) and 1985 cm\(^{-1}\)) are red-shifted with respect to the linear CO bands for monometallic platinum, which unlike in previous studies of Pt-Cu SAA, the peaks blue shifted.\(^{72}\)

As shown in Figure 3.16 for the selected blank-subtracted spectra of Ru-Cu DLA, the start of CO introduction shows a rapid high-intensity peak in the region greater than 2000 cm\(^{-1}\), which is similar in behavior to that of the monometallic copper. Similar to the Pt-Cu DLA, the band in the 1960 cm-1 region during the first 3 minutes of CO introduction shows an active absorbance (peak) that decreases in intensity as the dilution increases (Figure 3.16). Unlike the palladium- and platinum-copper dilute limit alloy, the final purged spectra deviate much from the monometallic copper characteristic spectra. This
deviation makes the Gaussian function fitting vary from the peak ratio control imposed on the monometallic copper fitted parameters. Even at the highest dilution (Ru/Cu=1/75), the normalized spectra (Figure 3.17) shows several regions deviating from monometallic copper spectra. From the normalized spectra, an increasing dilution shows an increasing trend (Figure 3.17a) in the max peak ratio of the high (2020 cm\(^{-1}\)) to low frequency (1980 cm\(^{-1}\)) region. This behavior is evident in Figure 3.16, as described previously, where the low-frequency band decreases in intensity as the dilution is increased (low Ru concentration) with almost the same high-frequency peak intensity. A peak in the 2050 cm\(^{-1}\) region appears in the nitrogen purging stage and has a maximum intensity at the final purge.

**Figure 3.16.** Selected blank-subtracted spectra for Ru-Cu DLA at varying dilution; a) 1/21, b) 1/40, and c) 1/75.
Several overlapping frequencies exist between the fitted monometallic ruthenium and copper (2124, 2104, 2009 and 1981 to 2122, 2096, 2012, and 1984 respectively). These suggest that $\pi$-back donation is almost the same in those sites. With this resemblance, band reassignment from Chin, S. et al.(2006) follows the current copper assignments. The 2096 cm$^{-1}$ and 2038 cm$^{-1}$ are due to geminal CO on edge/step sites. A linear CO on terrace sites makes the 2063 cm$^{-1}$ and the 2012 cm$^{-1}$ makes linear Ru-CO on the edge/step sites. The tricarbonyls are assigned to 2140 cm$^{-1}$, 2122 cm$^{-1}$, and 2078 cm$^{-1}$. The two low wavenumbers (1984 cm$^{-1}$ and 1826 cm$^{-1}$) are assigned to bridge CO on the terrace and edge/step sites. This similarity in vibration energy may suggest a similar ligand effect when an atom of ruthenium is coordinated with a ruthenium or copper atom. This similarity may explain the deviation in spectra of Ru-Cu DLA with that of monometallic copper.

![Figure 3.17](image)

Figure 3.17. Normalized spectra of Ru-Cu DLA a) at high frequency and b) at low frequency.

Some considerations were made in fitting the Ru-Cu DLA due to its deviation from monometallic copper spectra. From the fitted final N$_2$-purged spectra in Figure 3.18, the 2009 cm$^{-1}$ band associated with a linear CO on copper assigned to edge/step decreased in intensity with respect to other peaks of Cu-CO. Also, the bridge region for copper (1880 cm$^{-1}$) shows a relatively high intensity. Hence, in fitting the Ru-Cu DLA spectra, the peak
ratio in these regions for Cu-CO species was relaxed with the 2125 cm$^{-1}$ peak in the high-frequency region. This relaxation assumes that the copper surface characteristic is affected by the addition of ruthenium.

An additional six Gaussian functions were needed to fit the Ru-Cu DLA for the isolated ruthenium sites (Figure 3.18). Figure 3.19 shows the integrated area of these Gaussian functions during the transition stage. The 2064 cm$^{-1}$ peak matches the 2063 cm$^{-1}$ peak associated with the linear Ru-CO of monometallic ruthenium. The integrated area of this peak is stable during the nitrogen purging step suggesting strong adsorption even at a high frequency. The 1983 cm$^{-1}$ peak for Ru-Cu DLA closely matches the monometallic catalyst’s wavenumbers for the bridge Ru$_2$-CO (1984 cm$^{-1}$) and Cu$_2$-CO (1981 cm$^{-1}$) assigned on terrace sites. However, this new frequency is assigned to bridge CO between Ru and Cu on terrace sites since the bridge CO on monometallic copper is already accounted for. As shown in the integrated area during the nitrogen purging step, the 1951 cm$^{-1}$ peak decreased significantly while other peaks remained in intensity or increased (2044 cm$^{-1}$). The disappearance of this peak during N$_2$ purging and the appearance of 2044 cm$^{-1}$ suggests that these species reside on the same site. Hence, the 1951 cm$^{-1}$ peak is assigned to a bridge CO on Ru-Cu edge/step sites that transforms into linear CO (2044 cm$^{-1}$) on isolated Ru at low CO coverage. The other low frequency (1914 cm$^{-1}$) is assigned to stable bridge CO between Ru and Cu on the edge/step sites following the Pd-Cu DLA bridge CO on Pd and Cu. The last peak, 2032 cm$^{-1}$ with low intensity could be assigned to an asymmetric vibration of CO formed on edge/step sites. However, this is not justified based on the current spectra, and the symmetric vibration is not identified in the current assignment.
It should be noted that the presence of frequency identical with that of bridge CO (Ru2-CO) for monometallic ruthenium could also suggest two ruthenium atoms on a copper surface. However, this arrangement is assumed to be absent given the series of dilutions showing the same trend. Also, considering the overall spectra of the Ru-Cu DLA, the red-shift in the bridge region with respect to the monometallic copper spectra may suggest a surface where more electrons are available for π-back donation for the surface Cu-CO species. Ruthenium may be coordinated on a surface copper atom but is not accessible for CO adsorption (sublayer). Based on the XPS analysis on a set of Ru-Cu DLA and moderate ratio Ru-Cu, a redshift in the binding energy of Cu 2p coupled with blueshift in Ru 2p is evident only in the moderate ratio Ru-Cu system, suggesting interaction with the two metals at this ratio. However, no significant shift was observed for Cu 2p in the high dilution of the Ru-Cu DLA series, mainly due to the small amount of Ru. For Ru 2p, a gradual blueshift could be detected as the amount of Ru is increased, suggesting an interaction between the two metals even at dilution amount (Figure C.6).
Figure 3.18. a) Comparison of fitted Gaussian functions for monometallic and bimetallic Ru-Cu DLA catalysts, b) Assigned peak for isolated Ru.
As presented in chapter 3, monometallic nickel gives high and low CO vibration associated with the linear and bridge CO on a nickel surface. The corrosion of CO is also present, which complicates the analysis of bimetallic spectra. The assumption that the surface of the nickel cluster is not significantly affected when a dilute amount of palladium, platinum, and ruthenium is added may not hold strong if the final surface characteristic of the abundant metal varies significantly. The ruthenium on the copper cluster already gave a different spectral characteristic with monometallic copper. In the case of nickel, the overall characteristic of the bimetallic DLA prepared gave an identical behavior as that of monometallic nickel.

As shown in Figure 3.20, the high and low bands are still visible for Pd₁Ni DLA. Also, the high-intensity peak at the onset of CO introduction is the same characteristic behavior as monometallic nickel. The normalization at high and low frequency was made to identify possible new peaks not associated with the abundant metal. From Figure 3.21,
the lower dilution (1/11) deviates from the monometallic nickel when normalized at high frequency, while the higher dilutions (1/27 and 1/41) are almost identical. From the deviation, two band locations that change the monometallic nickel’s normalized spectra were explored.

Figure 3.20. Selected blank-subtracted spectra for Pd-Ni DLA at varying dilution; a) 1/11, b) 1/27, and c) 1/41.

Figure 3.21. Normalize spectra of Pd-Ni DLA a) at high frequency and b) at low frequency.
Three additional Gaussian functions are needed to fit Pd-Ni DLA, as shown in Figure 3.22. Additional peaks in the 2000 region where the high and low-frequency
overlaps and a signal in the low frequency are needed to fit the spectra series. The bridge CO at 1860 cm\(^{-1}\) can be assigned to adsorbed CO coordinated to Pd and Ni atoms.

The blank-subtracted spectra for the series of Pt-Ni DLA at varying dilutions are shown in Figure 3.23. The dynamic behavior of the spectra is identical to that of monometallic nickel. As seen in the normalized spectra, the ratio of the high band max peak intensity to low band intensity peak is negatively correlated with the dilution. When the dilution is high, the ratio is low and approaches that of monometallic nickel. This behavior is the effect of platinum which shows a strong, stable intensity in the linear region. These deviations in normalized intensity are used to explore the overlapping peaks associated with the platinum surface atoms.

Figure 3.23. Selected blank-subtracted spectra for Pt-Ni DLA at varying dilution; a) 1/14, b) 1/28, and c) 1/51
Figure 3.24. Normalize spectra of Pt-Ni DLA a) at high frequency and b) at low frequency.
Figure 3.25. a) Comparison of fitted Gaussian functions for monometallic and bimetallic Pt-Ni DLA catalysts, b) Assigned peak for isolated Pt.

From Figure 3.25, three gaussian functions with center wavenumber 1957, 2022, and 2053 cm$^{-1}$ fit the series of spectra across transition spectra for each dilution. The peaks above 2000 cm$^{-1}$ are assigned to linear CO on isolated platinum atom and the 1957 cm$^{-1}$ to bridge CO between Pt and Ni. The 2053 cm$^{-1}$ vibration matches in center wavenumber and FWHM to that of monometallic platinum assigned to linear CO adsorbed on the step/edges. This similarity may suggest that isolated platinum located on the step/edges of a nickel cluster may have the same level of electron density and CO binding energy. However, the assumption that platinum is randomly distributed and isolated for the given high dilution (1/51) should allow isolated platinum atoms to exist. Since bridge CO is negligible in monometallic platinum, its lack does not guarantee an isolated platinum atom since a dimer or trimer of platinum may form and still adsorbed CO linearly.

The blank-subtracted spectra for the series of Ru-Ni DLA show the same behavior as that of other Ni-based DLA. However, it is observed that ruthenium-containing catalysts always give a high absorbance even in low loading samples. From the normalized spectra
of Ru-Ni DLA, an isolated peak at 2140 cm\(^{-1}\) that matches that of monometallic Ru exists. It also shows that the high-frequency region's shape when normalized is almost unchanged. The only factor seen in the normalized spectra is the peak ratio of the high to the low frequency, which also correlated with the dilution.

In fitting the Ru-Ni DLA, the peaks for the additional gaussian function were allowed to shift across the different dilutions, but the FWHM is maintained. For the low dilution with a higher amount of ruthenium, the fitting allowed for incorporating monometallic ruthenium since the new peaks identified for the high dilution could not fit the higher ruthenium loading. This difficulty can be due to the multi carbonyl that could be adsorbed on ruthenium and the possible formation of dimers. Hence what is presented here is the highest dilution fit.
Figure 3.26. Selected blank-subtracted spectra for Ru-Ni DLA at varying dilution; a) 1/18, b) 1/47, and c) 1/73.

Figure 3.27. Normalize spectra of Ru-Ni DLA a) at high frequency and b) at low frequency.
Figure 3.28. a) Comparison of fitted Gaussian functions for monometallic and bimetallic Ru-Ni DLA catalysts, b) Assigned peak for isolated Ru.

Seven new peaks were obtained to fit the spectra of Ru-Ni DLA across the transient spectra used during the nitrogen purged stage. The tricarbonyls were almost identical in frequencies as that of monometallic ruthenium. The existence of dicarbonyl is also
assigned with the 2106 cm\(^{-1}\) and 2046 cm\(^{-1}\). One linear CO with 2001 cm\(^{-1}\) wavenumber and a bridge between Ru and Ni was assigned with the 1950 cm\(^{-1}\) peak.

**Bimetallic Dilute Limit Alloy (Co-Based)**

The CO infrared analysis of cobalt-based DLA used a series of catalysts reduced at 400 °C like the rest of DLA catalysts. Since the isolation of the dilute metal is being evaluated, the measured CO vibration does not give the actual vibration when the isolated atom is coordinated with a totally reduced metal. A separate analysis should be made using a fully reduced catalyst. Monometallic cobalt prepared by SEA can be reduced with 20% H\(_2\)/N\(_2\) gas flow at 650 °C, in which the FTIR cell used in this study is not capable of in-situ reduction.

As seen in the monometallic spectra (Figure C. 1d), CO has weak adsorption with a peak at 2182 cm\(^{-1}\) associated with unreduced cobalt and minimal adsorption in the 2050 cm\(^{-1}\) region. Fitting using the highest dilution was made instead of all the catalysts at various dilutions prepared in this study. The final nitrogen purged spectra for all Co-based DLA show no CO vibration on the cobalt surface. The vibration in 2181 cm\(^{-1}\) is present at initial CO introduction and gradually decreases after prolonged CO exposure. This is due to the reduction induced by CO on unreduced cobalt metal. Although it is assumed that the cobalt is not fully reduced, some cobalt sites could adsorb CO and reduce the metal. The loss in intensity has no corresponding vibration appearing in the linear and bridge region except in the 1621 cm\(^{-1}\) region, where the intensity increase as the 2181 cm\(^{-1}\) decrease. In fitting the Co-based DLA, all the peaks at the final purged are assumed to come from the isolated metal and adjacent abundant metal.
Figure 3.29. Selected blank-subtracted spectra for Co-based DLA at highest dilution. a) Pd$_1$Co, b) Pt$_1$Co, and c) Ru$_1$Co.

Four gaussian functions are needed to fit the Pd-Co DLA, as shown in Figure 3.30. The 1867 cm$^{-1}$ and 1966 cm$^{-1}$ are assigned to bridge CO coordinated to isolated Pd and Co. The 2012 cm$^{-1}$ and 2046 cm$^{-1}$ are associated with linear CO on isolated palladium. Following the linear and bridge CO assignment, the higher wavenumber is assigned to the isolated atom on the terrace site. The lower is assigned to edge/step site location for isolated atom.

For Pt$_1$Co DLA, four Gaussian functions (1961, 2011, 2036, 2060 cm$^{-1}$) remain absorbed at the final N2-purged spectra, while one lower wavenumber (1838 cm$^{-1}$) exists
at higher CO coverage. Adsorbed CO with wavenumber greater than 2000 cm\(^{-1}\) are assigned to linear CO while the rest are assigned to bridge CO between Pt and Co.

In fitting the Ru-Co DLA, eight additional Gaussian functions are needed for the isolated ruthenium. The CO vibration peaks from monometallic ruthenium fall within the same region for the Ru-Co DLA but with different peak ratios and slightly shifted for some peaks. One observable peak is the 2063 cm\(^{-1}\) which is resent in all dilute limit alloy of ruthenium. The tricarbonyl peaks from monometallic ruthenium are also present. A much higher wavenumber (2019 cm\(^{-1}\)) than the monometallic Ru linear CO (2012 cm\(^{-1}\)) is also fitted. The 1984 cm\(^{-1}\) and 1943 cm\(^{-1}\) are assigned to bridge CO coordinated with Ru and Co.
Figure 3.30. a) Comparison of fitted Gaussian functions for monometallic and bimetallic Pd-Co DLA catalysts, b) Assigned peak for isolated Pd.
Figure 3.31. a) Comparison of fitted Gaussian functions for monometallic and bimetallic Pt-Co DLA catalysts, b) Assigned peak for isolated Pt.
Figure 3.32. a) Comparison of fitted Gaussian functions for monometallic and bimetallic Ru-Co DLA catalysts, b) Assigned peak for isolated Ru.
Conclusions

The simultaneous strong electrostatic adsorption method was applied to dilute limit of palladium, platinum, ruthenium on copper, cobalt, and nickel on silica support to prepare a single atom alloy. Characterization by X-ray diffraction shows ultrasmall nanoparticles, and an interaction between the two metals is evident by the change in the $\text{H}_2$-TPR reduction peak temperature of dried bimetallic catalysts. Detailed CO-FTIR analysis of the reduced bimetallic catalysts shows isolated sites of palladium, platinum, and ruthenium on a copper, cobalt, and nickel surface. The adsorption within the theoretical monolayer of metal precursors needed to populate the available support surface makes it possible to control the desired metal ratio on the catalyst's surface even at a higher dilution. The stability of the precursor from the bulk phase to the adsorption surface with ammonium hydroxide is important in controlling the metal ratio. The high ammonia concentration stabilizes the cationic ammine complex, which helps maintain the initial bulk metal ratio and the final adsorbed metal precursor ratio.

The ability to synthesize a single-atom alloy of palladium, platinum, and ruthenium on copper, cobalt, and nickel enabled the characterization of these isolated atoms using CO probe infrared spectroscopy. The correlation between Metal-CO vibration energy and the strength of adsorption can be used as a descriptor on how a metal surface or isolated atom would behave in a reaction. Aside from the adsorption properties of the isolated atom, the tendency for CO to coordinate with both metals is also a good indicator of whether a given compound with the same functional group would orient itself on the surface. For the first case of Pd-Cu DLA, a bridge CO coordinated with Pd and Cu was assigned to a low wavenumber and was confirmed by a computational method. With this, vibrations in the
bridge CO region obtained from the rest of the dilute limit alloy catalysts characterized here were assigned to this type of bridged CO.
Chapter 4. Evaluation of Copper-based Dilute Limit Alloy Catalyst

Introduction

The diminishing supply of fossil fuels has continuously driven the effort to develop a practical solution to reduce its consumption. As a low-cost and abundant carbon source, biomass has always been considered a renewable and sustainable alternative. Its conversion to transportation fuels and chemicals is a promising path in reducing the dependence on nonrenewable supplies. Biomass conversion has evolved from oil, starch, and sugar-based crops (first-generation feedstocks) to low-value, high-yielding lignocellulosic biomass (second-generation feedstocks). Lignocellulose refers to the biopolymer of cellulose, hemicellulose, and lignin that gives plants their structure. A biorefinery concept, analogous to the crude oil refinery, involves replacing the carbon source with biomass, separating and breaking down lignocellulosic components, and converting intermediates for further reaction and separation. Realizing a bio-based industry like the biorefinery model is feasible only through the integration of processes from biomass conversion to fuel and power generation and value-added chemicals production. From this concept, the key strategy in lignocellulosic conversion is to determine the upgraded platform components derived from lignocellulose decomposition.

Furfural is considered a key chemical platform in the biorefinery concept. Catalytic hydrolysis of lignocellulosic materials allows for greater flexibility in producing a wider base of fuels and targeted functionalized chemicals. Catalytic decomposition of crystalline
cellulose and amorphous hemicellulose produces ketones, aldehydes, acids, sugars, and furan derivatives such as 2-furaldehyde or furfural. In a higher fraction, it is a natural product of xylose dehydration, a hemicellulose polymer component. Furfural is also an abundant component in fast-pyrolysis oils. The presence of furfural and its role in the subsequent bio-oil upgrading steps makes it a compound of interest in bio-oil stabilization efforts.

At present, China dominates the global furfural production (>75%) from agricultural wastes (corncobs, oat hulls, cottonseed hulls, rice hulls, and bagasse) thru the hydrolysis of pentosans. Quaker Oats Company patented the popular technology for industrial production in 1922 that utilizes mineral acids as a catalyst to break and recover furfural from lignocellulose materials. Majority of the furfural is converted to furfuryl alcohol for use in furan-based resins, and others are used as solvents and as intermediate to chemicals used in pharmaceuticals and food industries.

The aldehyde (C=O) and two olefins (C=C) functional groups in furfural make it a versatile platform chemical that transforms to a wide range of value-added chemicals. In the bio-oil upgrading process, the main objective is to reduce the reactivity of furfural by hydrogenation of these two functional groups. Complete hydrogenation without ring opening forms tetrahydrofurfuryl alcohol (THFAL) thru the furfuryl alcohol or tetrahydrofurfural pathway, as shown in Figure 4.1. Selectivity in furfural hydrogenation is greatly affected by the reaction environment. High selectivity towards high-demand compounds like furfuryl alcohol for compound-specific reactions is the common objective.
One major drawback of bio-oil upgrading is the reactive chemical functions inherent to bio-oil. These compounds readily react, forming polymerization products via thermal reactions.\textsuperscript{6} Hence, by lowering the concentration of these highly reactive compounds, the bio-oil stability will be enhanced, making the next upgrading steps more manageable.\textsuperscript{161} In addressing this, gas-phase hydrogenation became a focus in recent research to mimic the post pyrolysis/gas product hydrogenation prior to condensation. Another way is thru a liquid phase hydrogenation reaction. The medium used in the liquid phase reaction affects the selectivity of furfural hydrogenation. In the aqueous phase, water can participate in transforming furfuryl alcohol thru Piancatelli rearrangement, forming 4-hydroxy-2-cyclopentenone that leads to cyclopentanone (Figure 4.2) or thru furan ring-opening forming 4-oxopnetanal and 5-hydroxy-2-pentanone.\textsuperscript{162} Hydrogenation of the aromatic ring is a competitive pathway towards cyclopentanone. In using organic solvents under hydrogen gas, ring-opening does not usually occur, and the typical hydrogenation reaction takes place and possible oligomerization (Figure 4.3). Other upgrading processes
are also employed, such as using hydrogen-donor like isopropyl alcohol, where metal sites promote hydrogen transfer, and acid sites promote ring-opening, ether formation, and complete hydrogenation of furfural.\textsuperscript{36}

Figure 4.2 Proposed reaction network for the aqueous-phase hydrogenation of FAL over supported Pd catalysts (adapted from \textsuperscript{162–164}).

![Reaction network diagram]

Figure 4.3. Typical reaction routes for furfural hydrogenation in organic solvents (adapted from Chen \textsuperscript{165})
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Phase</th>
<th>Reaction Condition</th>
<th>Reactions</th>
<th>Selectivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Fe/SiO₂</td>
<td>Gas phase</td>
<td>1 atm, 210-250°C</td>
<td>Hydrogenation, decarboxylation</td>
<td>Methyl Furan</td>
<td>166</td>
</tr>
<tr>
<td>Pd-Cu/SiO₂</td>
<td>Gas phase</td>
<td>1 atm, 210-250°C</td>
<td>Hydrogenation, decarboxylation</td>
<td>Furfuryl Alcohol</td>
<td>167</td>
</tr>
<tr>
<td>Cu-Co/Al₂O₃</td>
<td>liquid phase (2-propanol)</td>
<td>H₂ 40 bar, 150-230°C</td>
<td>Hydrogenation</td>
<td>Methyl Furan</td>
<td>168</td>
</tr>
<tr>
<td>Ni-Co on (SiC, γ-Al₂O₃, and SBA-15)</td>
<td>Liquid phase (isopropyl alcohol)</td>
<td>H₂ 7 MPa, 220°C</td>
<td>Hydrogenation</td>
<td>Tetrahydrofurfuryl Alcohol</td>
<td>160</td>
</tr>
<tr>
<td>Ni-M (M-Co, Fe)/TiO₂</td>
<td>Liquid phase (ethanol/water)</td>
<td>H₂ 3 MPa, 110°C-170°C</td>
<td>Hydrogenation</td>
<td>Cyclopentanol/Cyclopentanol</td>
<td>33</td>
</tr>
<tr>
<td>NiCu/SBA-15</td>
<td>Liquid phase (water)</td>
<td>H₂ 4 MPa, 160°C</td>
<td>Hydrogenation</td>
<td>Cyclopentanolne</td>
<td>169</td>
</tr>
<tr>
<td>Pt-Pd/C (porous)</td>
<td>Liquid phase (octane)</td>
<td>H₂ 60 bar, 140 °C</td>
<td>hydrogenation</td>
<td>furfuryl alcohol, tetrahydrofurfuryl alcohol.</td>
<td>170</td>
</tr>
<tr>
<td>Pd-Cu/C</td>
<td>Liquid phase (Aqueous)</td>
<td>H₂ 3 MPa, 160°C</td>
<td>Hydrogenation</td>
<td>Cyclopentanolne</td>
<td>171</td>
</tr>
<tr>
<td>Pd-Cu/MgO, Mg(OH)₂</td>
<td>Liquid phase (Aqueous)</td>
<td>0.6MPa, 110°C</td>
<td>Hydrogenation</td>
<td>Furfuryl alcohol</td>
<td>172</td>
</tr>
<tr>
<td>Ru-Sn/meso_SC</td>
<td>Liquid phase (isopropanol)</td>
<td>H₂ 2 MPa, 100°C</td>
<td>Hydrogenation</td>
<td>Furfuryl alcohol</td>
<td>32</td>
</tr>
<tr>
<td>Pd-Ru/TiO₂</td>
<td>Liquid phase (organic solvents)</td>
<td>3 bar H₂, Ambient temperature</td>
<td>Hydrogenation</td>
<td>Methylfuran, furfuryl alcohol</td>
<td>173</td>
</tr>
<tr>
<td>Zr-Al/SBA-15 (30:10)</td>
<td>Liquid phase (ethanol)</td>
<td>453 K in N₂ gas 150°C in 5 Bar N₂ gas 180°C</td>
<td>Transfer Hydrogenation Transfer Hydrogenation Transfer hydrogenation and hydrolysis</td>
<td>174</td>
<td></td>
</tr>
<tr>
<td>AuRu/ZrO₂, Y-ZrO₂, La-ZrO₂, Sn-Al-Beta zeolite</td>
<td>Liquid phase (2-propanoll)</td>
<td>H₂ 220°C</td>
<td>Transfer Hydrogenation</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>10Cu-3Pd/ZrO₂</td>
<td>Liquid phase (2-propanoll)</td>
<td>453 K in N₂ gas 150°C in 5 Bar N₂ gas 180°C</td>
<td>Transfer Hydrogenation Transfer Hydrogenation Transfer hydrogenation and hydrolysis</td>
<td>175</td>
<td></td>
</tr>
<tr>
<td>Pd-Ag/C</td>
<td>Liquid phase (ethanol/water)</td>
<td>H₂ 0.1 MPa, 25 ºC</td>
<td>Hydrogenation</td>
<td>Ethyl levulinate g-valerolactone</td>
<td>176</td>
</tr>
<tr>
<td>Pt₃-Fe/CeO₂</td>
<td>Liquid phase (solvent)</td>
<td>H₂ 20 bar of H₂, 100 ºC</td>
<td>Hydrogenation</td>
<td>g-valerolactone from 2-Methylfuran, 2-Methylytetrahydrofuran furfuryl alcohol furfuryl alcohol</td>
<td>177</td>
</tr>
</tbody>
</table>

Table 4.1. The current bimetallic catalysts for furfural hydrogenation reactions, as shown in Table 4.1. Although single atom alloy class of
catalysts have already been evaluated in various hydrogenation reactions, limited studies can be found in the literature for furfural hydrogenation. Recently Pd-Cu and Pt-Cu single atom alloy were used for selective hydrogenation of furfural to furfuryl alcohol under mild conditions (50 °C, 1.5 Bar) using methanol as solvent. However, no literature on single atom alloy catalysts for aqueous phase hydrogenation of furfural has been found. This chapter will present the evaluation of copper-based dilute limit alloy for the aqueous phase hydrogenation of furfural to a much lower oxygen, higher-value hydrogenation compound.

Materials and Methods

Copper-based DLA bimetallic (Pd-Cu, Pt-Cu, and Ru-Cu) and monometallic (Pd, Pt, Ru, Cu) catalysts were prepared using the strong electrostatic adsorption method as described in chapter 3. The weight loadings for the monometallic catalysts were made close to the corresponding weight loading in the bimetallic. Characterization using XRD and ICP-OES method, as described in chapter 2, were also made to determine the particle size and metal content.

The aqueous phase hydrogenation of furfural was carried out using a 100 mL stainless-steel autoclave batch-type reactor (Autoclave Engineers) equipped with a mechanical stirrer, tach meter, temperature-controlled ceramic band heater, gas inlet, thermocouple, and sampling port, as shown in Figure 4.4. Hydrogenation was conducted at 1000 rpm propeller speed to overcome mass transfer limitation, 430 psi H₂, and 150 °C in DI water for 3-10 hours. For every reaction run, pretreatment steps were conducted. A certain amount of reduced catalyst, 200 µL of 1,4 dioxane (Sigma-Aldrich, 99%) as internal standard, and 57 grams of degassed DI water were loaded into the reactor. Nitrogen
gas purging for 15 minutes followed by hydrogen gas purging for 15 minutes was made before pretreatment in H₂ gas for 1 hr at a temperature of 150 ºC. After pretreatment, 3.0 grams of furfural (Sigma-Aldrich, 99%) was pumped into the reactor using a high-pressure HPLC pump, which signals the reaction's start. A 250μL aliquot was sampled before and after injecting furfural at a certain interval until the final reaction time. Samples were diluted with acetone to minimize the water content and were analyzed by gas chromatography by internal standard method. Conversion and selectivity were calculated according to equations 1 to 2, respectively. Blank runs without catalysts and control runs with monometallic catalysts were made. Quantitative analysis of reaction solutions was performed using an HP 5890 Series II gas chromatogram with a guard column (5m, 0.25mm ID), Stabilwax-DA column (30m, 0.25mm, 0.25μm), and an FID detector. Figure D. 3 shows a typical chromatogram for a 10 hours run. Compounds identification was made using GC-MS spectroscopy using available chemical standards.

\[
Conversion = \frac{n_{FFA_{Initial}} - n_{FFA}}{n_{FFA_{Initial}}} \quad \text{Equation 4.1}
\]

\[
Selectivity_i = \frac{n_i}{\sum n_i} \quad \text{Equation 4.2}
\]

Figure 4.4. 100 mL batch type reactor (Autoclave Engineer). a) schematic diagram, and b) reactor setup.
XRD analyses of spent catalysts were made. Final reaction medium metal content was measured using ICP-OES of the digested sample. Digestion was carried out by weighing a known amount sample and evaporating water to dryness in a 50 ml round bottom flask on an oil bath at 100°C. Concentrated HCl (1.5 mL) and concentrated HNO$_3$ (0.5 mL) were added to the dried sample and digested at 180°C for 4 hours with the same amount of acids once the sample was dry. The final digested samples were then diluted in 3% HNO$_3$ and were analyzed using ICP-OES for the metal content.

Results and Discussion

Catalysts metal weight loadings for the Pd-Cu, Pt-Cu, and Ru-Cu DLA bimetallic and monometallic catalysts are shown in Table 4.2. Similar to the catalysts used in the characterization study (Chapter 3), the metal deposited on the silica support with an average surface area of 300 m$^2$/gram is within the one monolayer of metal precursors adsorption. The diffraction pattern of all these catalysts implies less than 1.5 nm particle sizes (no shown).

Table 4.2. Weight loading of as-prepared Copper-based DLA bimetallic and Monometallic catalysts

<table>
<thead>
<tr>
<th>Metal 1</th>
<th>Metal 2</th>
<th>As Synthesized Catalysts, Weight Loading, wt%</th>
<th>Molar Ratio (M2/M1)</th>
<th>Total Surface Density (µmole/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>Cu</td>
<td>0.12%Pd2.05%Cu/SiO$_2$</td>
<td>28</td>
<td>1.1</td>
</tr>
<tr>
<td>Pt</td>
<td>Cu</td>
<td>0.18%Pt2.16%Cu/SiO$_2$</td>
<td>37</td>
<td>1.2</td>
</tr>
<tr>
<td>Ru</td>
<td>Cu</td>
<td>0.07%Ru2.17%Cu/SiO$_2$</td>
<td>48</td>
<td>1.2</td>
</tr>
<tr>
<td>Pd</td>
<td></td>
<td>0.06%Pd/SiO$_2$</td>
<td></td>
<td>0.018</td>
</tr>
<tr>
<td>Pt</td>
<td></td>
<td>0.04%Pt/SiO$_2$</td>
<td></td>
<td>0.008</td>
</tr>
<tr>
<td>Ru</td>
<td></td>
<td>0.05%Ru/SiO$_2$</td>
<td></td>
<td>0.017</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td>2.22%Cu/SiO$_2$</td>
<td></td>
<td>1.189</td>
</tr>
</tbody>
</table>
Catalyst Activity and Selectivity

The silica-supported DLA bimetallic catalysts (Pd\textsubscript{1}Cu, Pt\textsubscript{1}Cu, and Ru\textsubscript{1}Cu) and the monometallic catalysts (Pd, Pt, Ru, and Cu) were evaluated under semi-batch aqueous phase hydrogenation of furfural at 430 Psig H\textsubscript{2}, 150 °C and mixing speed of 1000 rpm using degassed DI water as a liquid medium. The calculated concentration is corrected with the assumption that there is no carbon loss and has a total carbon balance equivalent to the initial carbon loading of 3.0 grams of furfural. Figure 4.5 shows the conversion of furfural as a function of time for the copper-based DLA and monometallic copper. The reaction's typical catalyst loading is 2% (w/v) of reaction volume. The dilute metal's almost identical weight loading was used for the monometallic and bimetallic DLA. Monometallic copper catalyst shows activity for the given reaction condition (Figure 4.5). Copper with a dilute amount of palladium has the highest activity, followed by copper with a dilute amount of ruthenium. However, the activity was lower than monometallic copper in the catalyst containing a dilute amount of platinum. The deactivation of copper with platinum suggests either active site poisoning before or during the reaction. The monometallic platinum also shows a much lower activity suggesting the same cause of deactivation on the copper surface.
As shown in Figure 4.6, palladium catalyst has high selectivity to 4-oxopentanal (4OPAL), which is the ring-opening hydrogenation product of furfuryl alcohol (FOL) (Figure 4.2). There was no accumulation of furfuryl alcohol, but the formation of tetrahydrofurfuryl alcohol was observed. This formation shows the palladium catalyst's preference to hydrogenate the unsaturated C=C bond of the furan ring. Cyclopentanone (CPONE) and 5-hydroxy-2-pentanone (5HPONE) were produced but much lesser than 4OPAL. At higher conversion, monometallic copper on the other hand, has high selectivity towards cyclopentanone (CPONE), which is the product of ring-rearrangement of FOL. 4OPAL was also produced with a further reduction to 5HPONE at a much lower rate than palladium. By adding palladium to the copper surface as single-atom sites, 4OPAL, the dominating compound at low conversion, was further reduced to 5HPONE. This trend
shows that palladium alone has difficulty hydrogenating the terminal aldehyde group of 4OPAL. The low FOL concentration in both Pd and Pd\textsubscript{1}Cu reaction suggest fast hydrogenation of FOL towards either ring-opening or rearrangement path. This fast reaction can be attributed to an abundant supply of reactive hydrogen on the metal surface and a spillover effect caused by the presence of isolated palladium. On the copper surface, the splitting of hydrogen is not as good as that of palladium, but copper is good in activating the aldehyde C=O functional group. Here FOL accumulates and eventually reacts toward the cyclopentanone pathway. An unidentified intermediate compound (Peak J, MW 98) was produced and accumulated, which could be an intermediate product prior to cyclopentanone generation. With GC MS spectra, this unknown compound is later found to be 4-hydroxy-2-cyclopentenone (4HCPONE). In a detailed study by Hronec, M. et al. (2016) on aqueous phase furfural hydrogenation using Pd-Cu bimetallic catalyst, they found high selectivity towards CPONE, high yield of primary formed FOL, and its subsequent conversion to CPONE without the 4-hydroxy-2-cyclopentenone intermediate (4HCP). In the current study, 2-cyclopentenone (CP2ONE) and 3-hydroxycyclopentanone (3HCPONE) are produced as intermediate for the monometallic copper, and Peak J with molecular weight of 98 gram/mole is assigned to 4HCP.
Monometallic platinum shows higher selectivity towards 4OPAL and less selectivity towards cyclopentanone. The start of the reaction shows Low FOL. Platinum addition to copper shows an improvement in 4OPAL formation. Intermediates products for cyclopentanone routes are also present, but unlike monometallic copper, there is no FOL accumulation due to its consumption towards the 4OPAL pathway. The Pt1Cu DLA also shows a much lesser activity towards hydrogenation of the aldehyde functional group of 4OPAL to 5HPONE. At higher furfural conversion, the formation of 5HPONE starts to increase, the same as that of the Pd1Cu DLA.
Figure 4.7. Furfural hydrogenation product reaction profile for Pt, Pt\textsubscript{1}Cu, and Cu catalysts.

Figure 4.8. Furfural hydrogenation product reaction profile for Ru, Ru\textsubscript{1}Cu, and Cu catalysts.

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Monometallic ruthenium shows activity towards 4OPAL, just like platinum and palladium, but the rate is low. However, unlike platinum, ruthenium accumulates 4HCPONE, which slowly proceeds to cyclopentanone. When ruthenium was added to copper, a significant improvement in activity was observed with a behavior similar to that of Pd$_1$Cu DLA. A summary of product selectivity is shown in Figure 4.9, showing the changes in product selectivity with respect to copper monometallic. It also shows how an isolated atom of palladium, platinum, and ruthenium performs much better than when with the same atom.

![Figure 4.9. Selectivity vs. furfural conversion for monometallic and bimetallic Cu-Based DLA catalysts.](image)

In all catalysts used except copper, the selectivity towards 4OPAL is evident for the monometallic Pd, Pt, and Ru. With these atoms acting as isolated atoms, further hydrogenation of 4OPAL to 5HPONE was enhanced. Fujita, S. et al. (2020) have shown
the selective transformation of biofuranic aldehydes to 2,5-diketones using nickel phosphide nanoparticles. The plausible reaction pathways involve hydrogenation of the aldehyde group in Ni-Ni metal sites to alcohol followed by a ring-opening reaction promoted by surface acid sites of PO-H. The bifunctionality of the catalysts' ability to activate hydrogen and the presence of acid sites enables the formation of diketones. Aside from acid sites on the catalyst's surface, the oxygen functionality of the support could act as Bronsted acid sites and interact with the metal cluster on the metal-support interface. Under a metal-water environment, adsorbed atomic hydrogen can react with water to form hydronium ions. The ultrasmall particle size nature of the catalysts prepared by SEA implies high metal-support interface interaction. The water/hydroxyls on silica on this interface could function as surface acid sites that favor the ring-opening without rearrangement route. However, the hydrogenation of 4OPAL to 5HPONE was enhanced with single-atom sites on copper that actives the C=O aldehyde with the isolated atom of Pd, Pt, and Ru as active sites for hydrogen dissociation and activation.

Due to variation in the copper loading in each reaction, the rates at 10% and 50% conversion normalized to the moles of copper are calculated. In Figure 4.10, Ru$_1$Cu DLA shows an identical normalized rate with that of monometallic copper. The Pd$_1$Cu DLA gave more than twice the rate for monometallic copper, while Pt$_1$Cu DLA gave the lowest rate.
Post-Reaction Characterization

Spent catalysts were separated from the reaction medium by centrifugation and were repeatedly washed with acetone with subsequent centrifugation until a clear supernatant liquid was observed. The spent catalysts were then dried at room temperature prior to X-ray diffraction measurement. As shown in Figure 4.11, no sharp peak is visible from the monometallic catalyst of Ru, Pd, and Pt. These catalysts have low weight loading comparable with the DLA counterpart. Using bimodal size fitting, the calculated particle size for monometallic copper was the highest at 6.3/21.4 nm. Particle size-dependent reactions rely on the site distribution, which changes with size. Here, copper catalyst gave high selectivity towards cyclopentanone at the higher conversion of furfural. Since the particle size of copper increased, this may suggest that the bigger particle size of copper prefers cyclopentanone production. However, in the case of Pt$_1$Cu and Ru$_1$Cu, the
platinum-containing copper has a much bigger particle size than Ru₁Cu, but the reactivity of the Pt₁Cu DLA is much lower.

Figure 4.11. a) XRD pattern of spent catalyst of monometallic and bimetallic Cu-based DLA catalysts; and b) fitted Gaussian functions for Cu, Pt₁Cu, and Ru₁Cu background subtracted pattern.
To determine if metal leaching occurred during the reaction, a known amount of the end-of-reaction liquid solution was digested to remove the organic components prior to ICP measurement. Table 4.3 shows the solution metal concentration of the final reaction mixture for the Cu-based DLA and monometallic catalyst runs. In all Cu containing catalysts, the amount of abundant metal (Cu) leaching is below 1% of the initial loading. The Ru single atom has the highest metal loss compared with the Pd and Pt. Catalyst recovery after centrifugation and subsequent washing has an average of 86% with the monometallic palladium having the highest recovery at 93%. Catalyst is lost due to adhesion to the reactor vessel inner wall and propeller surface. Also, possible dissolution of the silica support in aqueous phase environment at elevated temperature and pressure leads to catalyst lost and metal leaching.

Table 4.3. Metal leaching in reaction medium and percent catalysts recovery.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial Metal Loading in Reactor, mg</th>
<th>Aqueous solution metal concentration, ppm</th>
<th>Percent Metal Leaching</th>
<th>Percent Catalyst Mass Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M1</td>
<td>M2</td>
<td>M1</td>
<td>M2</td>
</tr>
<tr>
<td>Pd</td>
<td>1.17</td>
<td>-</td>
<td>0.0017</td>
<td>0.009%</td>
</tr>
<tr>
<td>Pt</td>
<td>0.57</td>
<td>0.0002</td>
<td>0.002%</td>
<td>79%</td>
</tr>
<tr>
<td>Ru</td>
<td>1.06</td>
<td>0.0081</td>
<td>0.046%</td>
<td>89%</td>
</tr>
<tr>
<td>Cu</td>
<td>28.48</td>
<td>4.0600</td>
<td>0.855%</td>
<td>87%</td>
</tr>
<tr>
<td>Pd₁Cu</td>
<td>1.23</td>
<td>20.47</td>
<td>0.0016</td>
<td>0.008%</td>
</tr>
<tr>
<td>Pt₁Cu</td>
<td>2.18</td>
<td>21.78</td>
<td>0.0005</td>
<td>0.001%</td>
</tr>
<tr>
<td>Ru₁Cu</td>
<td>1.09</td>
<td>21.85</td>
<td>0.0363</td>
<td>0.196%</td>
</tr>
</tbody>
</table>

Conclusions

The limited synthesis method in preparing single atom alloy catalysts for experimental evaluation widens the gap between experimental and computational studies. In this chapter, the use of a single-atom alloy of palladium, platinum, and ruthenium on copper in aqueous phase hydrogenation of furfural has been successfully presented.
Palladium and ruthenium improved the catalytic activity of copper catalysts and even changed the selectivity towards 4OPAL and 5HPONE. Platinum lowers the activity of copper but still changes the selectivity towards 4OPAL.

At present, the use of single-atom alloy in biomass conversion is very limited, and nothing has been published for the aqueous-phase hydrogenation of model compounds. With the simple synthesis method presented here, the study on the performance of these isolated atom active sites can be extended to various metal combinations and various chemical reactions requiring efficient use of precious metal.
Chapter 5. Insights into Nickel- and Cobalt-based Dilute Limit Alloy Bimetallic Catalysts

Evaluation of Nickel-Based Catalyst

The weight loading of as-synthesized Ni-based DLA catalysts and monometallic Nickel are shown in Table 5.1 with the resulting metal surface density within the adsorbed one-monolayer of hydration-sheath covered cationic ammine complex precursors.

Table 5.1. As synthesized Ni-Based DLA weight loading.

<table>
<thead>
<tr>
<th>Metal 1</th>
<th>Metal 2</th>
<th>As Synthesized Catalysts, Weight Loading, wt%</th>
<th>Molar Ratio (M2/M1)</th>
<th>Total Surface Density (µmole/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>Ni</td>
<td>0.12%Pd1.47%Ni/SiO₂</td>
<td>22</td>
<td>0.90</td>
</tr>
<tr>
<td>Pt</td>
<td>Ni</td>
<td>0.18%Pt1.52%Ni/SiO₂</td>
<td>29</td>
<td>0.91</td>
</tr>
<tr>
<td>Ru</td>
<td>Ni</td>
<td>0.09%Ru1.62%Ni/SiO₂</td>
<td>30</td>
<td>0.96</td>
</tr>
<tr>
<td>Ni</td>
<td>N/A</td>
<td>1.51%Ni/SiO₂</td>
<td>N/A</td>
<td>0.96</td>
</tr>
</tbody>
</table>

A low concentration FOL, THFOL, and 4HCPONE are produced. The HCPONE gradually increase in amount without further conversion. Hydrogenation of the unsaturated furan ring to form THFOL suggests an orientation-dependent activation of furfural on the nickel surface. In a solvent-based furfural hydrogenation study by Seemala et al. (2017), they found that alumina-supported Ni-Cu bimetallic catalysts promoted the hydrogenation of furan-ring over that of the aldehyde. This selectivity was attributed to the surface segregation of Ni on a Ni-Cu bimetallic particle induced by the use of Al₂O₃ as support. In the current study using an aqueous phase, the furan ring hydrogenation is also manifested.
Monometallic nickel showed negligible activity. One reason for this lack of activity is the poisoning of the nickel surface. Carbonaceous species can act as poison to nickel surface affected by factors such as the strength of adsorption and their reactivity to neighboring compounds such as water and hydrogen. In the study by Hronec, M. et al. (2014) on the conversion of furfuryl alcohol to cyclopentanone using nickel catalysts, two parallel reactions involving hydrogen ions from water dissociation and metal catalysts were proposed. In their study, a low metal weight loading (Cat/Furfuryl alcohol=0.01) and low hydrogen pressure (116 psig) at 160 °C gave the highest selectivity towards cyclopentanone. The nickel catalysts they evaluated have particle size >10 nm and suggest that with the given reaction condition, the hydrogenation of furfuryl alcohol to cyclopentanone is not dependent on size. However, a small nickel particle may suffer from nickel leaching and covering of nickel surface by polymers of furfuryl alcohol. Hence, in the case of the present catalyst with particle size <1.5 nm, poisoning due to the adsorption of these polymers could be the cause of low activity. Since Ni surface can activate furan ring, it also suggests a preference towards flat adsorption orientation on a nickel facet. However, when polymerization of FOL occurs to form a high molecular weight compound with furan rings, this would preferentially adsorb on the surface and deactivate it. Looking at the trace compounds detected by gas chromatography, the accumulation of 4HCPONE suggests the lack of an active site for successive hydrogenation to CPONE.
The addition of a single atom site of palladium on the nickel surface prevented the deactivation of the nickel surface. As shown in Figure 5.1, Pd\textsubscript{1}Ni gave a much faster rate with the same palladium loading as that of monometallic palladium (0.011 mmoles). There is also an improvement in selectivity towards CPONE, although 4OPAL is still a dominant product. Similar to a single atom of palladium on copper, at the higher conversion of furfural, the 5HPONE starts to increase at the expense of 4OPAL. This transition suggests that the active site for furfural hydrogenation is also the same site for the hydrogenation of 4OPAL to 5HPONE, and this site is missing in the monometallic palladium.

In the case of a single atom of platinum on nickel, the activity also improved with respect to monometallic platinum and nickel. Also, even at low conversion, the selectivity is shifted towards CPONE. Previous works believe that furfuryl alcohol undergoes Piancatelli rearrangement in the presence of Bronsted acid/Lewis acids.\textsuperscript{183} Primarily, this ring-opening step could proceed to form 4-HCPONE, which is hydrogenated towards
CPONE. Moronenko, R. M. et al. (2019) proposed that an intermediate in the Piancatelli rearrangement could undergo hydrogenation to form 4-OPAL instead.

An almost identical reaction profile as that of Pt\textsubscript{1}Ni DLA can be observed using Ru\textsubscript{1}Ni DLA. The presence of this unique site changes the environment and the adsorption characteristics that cause surface poisoning. For monometallic ruthenium, an accumulation of 4HCPONE can also be observed without the formation of the next intermediate towards CPONE. Changing the neighboring atom of Ru from Ru to Ni removes the poisoning effect for both monometallic ruthenium and nickel.

Figure 5.2. Furfural hydrogenation product reaction profile for Pt, Pt\textsubscript{1}Ni and Ni Catalysts.
Figure 5.3. Furfural hydrogenation product reaction profile for Ru, Ru\textsubscript{1}Ni and Ni catalysts.

Figure 5.4 shows the calculated rate of reaction at 10% and 50% furfural conversion. Unlike monometallic copper, which shows activity, nickel shows a 90 times increase in activity using palladium as single-atom sites. This high activity corresponds to high selectivity in the 4OPAL to 5HPONE pathway. Relative to nickel activity, platinum and ruthenium single atom alloy still shows 10 and 5 times activity, respectively. At the given activity for Pt- and Ru-Ni DLA, the selectivity to cyclopentanone at higher conversion is evident (Figure 5.5). Also, for Ru\textsubscript{1}Ni DLA, a linear conversion can be observed as shown by almost the same rate at 5% and 10% conversion.
Figure 5.4. Normalized rate comparison for Ni-based DLA catalysts.

Figure 5.5. Comparison of selectivity vs. conversion for Ni-based DLA and monometallic catalysts.
Evaluation of Cobalt-Based Catalysts

Cobalt-based catalysts are commonly used with another metal to form bimetallic catalysts. It is commonly used in solvent liquid-phase hydrogenation reactions but has limited literature in an aqueous phase environment. Recently, MA, Y. F. et al. (2017) used cobalt for selective aqueous-phase hydrogenation of furfural to cyclopentanol. They found ZrO$_2$-La$_2$O$_3$ supported cobalt to give 82 mol% yield at 160 °C and 2 MPa H$_2$. However, they reported the deactivation of the catalysts due to polymer formation.

As shown in Table 5.2, the same metal surface density can be achieved with good control on the desired metal ratio using the adsorption within the theoretical monolayer. It should be noted that the characteristic of silica that strongly generates static charges makes this synthesis condition feasible.

Table 5.2. As synthesized Co-Based DLA weight loading.

<table>
<thead>
<tr>
<th>Metal 1</th>
<th>Metal 2</th>
<th>As Synthesized Catalysts, Weight Loading, wt%</th>
<th>Molar Ratio (M2/M1)</th>
<th>Total Surface Density (µmole/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>Co</td>
<td>0.09%Pd1.63%Co/SiO$_2$</td>
<td>33</td>
<td>0.94</td>
</tr>
<tr>
<td>Pt</td>
<td>Co</td>
<td>0.16%Pt1.80%Co/SiO$_2$</td>
<td>38</td>
<td>1.06</td>
</tr>
<tr>
<td>Ru</td>
<td>Co</td>
<td>0.10%Ru1.79%Co/SiO$_2$</td>
<td>30</td>
<td>1.07</td>
</tr>
<tr>
<td>Co</td>
<td>N/A</td>
<td>2.18%Co/SiO$_2$</td>
<td></td>
<td>1.26</td>
</tr>
</tbody>
</table>

At the current catalyst loading, monometallic cobalt activity to furfural conversion is much faster than monometallic copper on a per mole basis. Monometallic cobalt did not show any 4OPAL production but with furfuryl alcohol accumulation at the start of the reaction. This furfuryl alcohol is converted to CPONE, which is eventually converted to CPOL. In monometallic copper (Figure 4.6), FOL is easily converted to 4HCPONE and CP2ONE giving a lower amount of FOL, while for cobalt, FOL is accumulated at low conversion. Once the 4HCPONE is produced, the next hydrogenation steps towards
CPONE occur relatively much faster. There is also a formation of higher molecular weight compound (PEAK L) which follows the same profile as that of FOL. It is believed that these are polymerization compound included by the presence of FOL Interestingly this unknown compound is further converted as shown by the decreasing amount leading to byproducts with more than five-carbon compounds as detected (Figure D. 17, D.17 and D.18).

An interesting reaction occurs when a single atom of palladium is added to cobalt. Some of the intermediates in the 4HCPONE to CPONE pathway were not detected in the reaction medium, and only a trace amount of 3HCPONE was present. This absence may suggest either a direct conversion of furfuryl alcohol to CPONE or the intermediates' relatively faster surface reaction with the single palladium atom on cobalt as the active site. At the level of cyclopentanone concentration achieved, the formation of cyclopentanol is just about to start. This catalyst is the only dilute limit alloy evaluated in this study to give this high selectivity towards cyclopentanone. In a recent study by Wang et al. (2020), they found a bimetallic Pd-Co nanoparticles encapsulated within UiO-66 forming a core-shell PD-Co@UiO-66 catalysts to be highly selective to CPO (96%) at 99% FAL conversion. The aqueous-phase batch hydrogenation reaction was made in a 20 mL H₂O, 30 mg catalyst, 1.8 mmole of FAL operated at 120 °C and 3 Mpa of H₂. For a 12 hours reaction using the 2.4% Pd-Co catalysts the rate of furfural conversion is about 1316 mole FAL/(mole-Pd hr). In the current study for 10 hours of reaction at 82% conversion, the rate is at 14136 mole FAL/(mole-Pd hr) which is 10 times faster. However, the selectivity towards CPONE only reached to 71% (Figure 5.10). It should be noted that in the current study, furfural is injected in the operating condition at time zero.
As shown in Figure 5.7, the addition of platinum in dilute amount shows an identical profile as that of monometallic cobalt but with much lower activity. There was
no accumulation of 4OPAL at early conversion, but eventually, 5HPONE is formed at the higher conversion of furfural. This suggests that platinum sites promotes the 4OPAL pathway which is absent in cobalt surface.

By adding ruthenium to cobalt, deactivation of the catalysts, just like with the monometallic ruthenium, occurred. There is an accumulation of 4HCPONE and CP2ONE making the formation of CPONE slow. Also, there was no accumulation of furfuryl alcohol dominating monometallic cobalt at the start of the reaction. The low activity could be attributed to the same deactivation observed in monometallic ruthenium.

Figure 5.8. Furfural hydrogenation product reaction profile for Ru, RuCo and Co catalysts.

At 10% conversion, monometallic cobalt gave the highest rate (69 mole FAL/(moles Co·hr)). The addition of palladium and ruthenium decreased the activity significantly but with improvements in CPONE selectivity at lower conversion. It was observed in the study by Hronec at al. (2014) using Pd catalysts, that low catalysts loading and hydrogen
ions created by self-dissociation of water plays an important role in the selectivity of FOL to CPONE. A lower catalyst concentration reduces the amount of FOL being converted to THFOL without affecting the CPONE pathway and the hydrogen ions catalyzes the irreversible ring rearrangement. It should be noted that in their study, 4OPAL was not detected making THFOL formation as the competing pathway. The addition of Pd and Ru increased the amount of hydrogen on the surface due to spillover effect and produces more hydrogen ions. This hastens the hydrogenation of FOL as compared with the monometallic Co. The resulting compound from FOL conversion poisons the cobalt active sites that leads to the decrease in activity. The rate for Pd$_1$Co and Ru$_1$Co at 10% and 50% conversion are almost the same for both catalysts. This suggests an almost linear conversion of furfural. The monometallic cobalt catalyst has a combined CPONE and CPOL selectivity reaching 95% selectivity after 10 hours of reaction. Comparing this to Pd$_1$Co DLA, the selectivity to CPONE – CPOL pathway reached only to 72% but with significant improvement in selectivity to CPONE at lower conversion.
Figure 5.9. Normalized rate comparison for Co-based DLA catalysts.

Figure 5.10. Comparison of selectivity vs. conversion of Co-based DLA and monometallic catalysts.
Post-Reaction Characterization

X-ray diffraction patterns of spent catalysts for Co- and Ni-based catalysts are shown in Figure 5.11. All DLA of palladium did not show any sintering of the abundant metal, whereas the monometallic patterns of the abundant metal show an increase in particle grain size. Also, cobalt-based DLA maintains a small grain size. It should be noted that the Co-based DLAs were reduced at 550 °C. This is based on the reduction peak temperature of the dried SEA catalysts. In another experiment involving a moderate ratio (1:1) of palladium with copper, cobalt, and nickel, the particle size increased after 3 hours of reaction in the same reaction conditions (Figure D. 1). However, no sintering was observed when a single atom was present on the surface. The presence of palladium in the bulk of a bimetallic 1:1 palladium catalyst could enhance the sintering of the metal alloy particle (Figure D. 1). The low Pd loading (0.06% Pd/SiO₂) used for the DLA series of catalysts also shows no sintering as compared with the high loading of Pd (3.17% Pd/SiO₂) used in the moderate ratio.
Figure 5.11. XRD pattern of spent catalyst for Cobalt and Nickel DLA catalysts.

Table 5.3. Metal concentration in final reaction medium using Ni- and Co-based DLA.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial Metal Loading in Reactor, mg</th>
<th>Aqueous solution metal concentration, ppm</th>
<th>Percent Metal Leaching</th>
<th>Percent Catalyst Mass Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M1</td>
<td>M2</td>
<td>M1</td>
<td>M2</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd_Ni</td>
<td>1.21</td>
<td>14.90</td>
<td>0.0001</td>
<td>57.9</td>
</tr>
<tr>
<td>Pt_Ni</td>
<td>2.15</td>
<td>18.64</td>
<td>0.0007</td>
<td>80.0</td>
</tr>
<tr>
<td>Ru_Ni</td>
<td>1.11</td>
<td>19.47</td>
<td>0.0216</td>
<td>79.8</td>
</tr>
<tr>
<td>Pd_Co</td>
<td>1.20</td>
<td>16.49</td>
<td>-</td>
<td>153.8</td>
</tr>
<tr>
<td>Pt_Co</td>
<td>2.17</td>
<td>18.17</td>
<td>0.0011</td>
<td>122.5</td>
</tr>
<tr>
<td>Ru_Co</td>
<td>1.11</td>
<td>18.16</td>
<td>.00558</td>
<td>175.0</td>
</tr>
</tbody>
</table>

Cobalt-based DLA shows high metal leaching with an average of 42%. These bimetallic Co DLA catalysts were reduced at 550 °C while the monometallic which gave a much lower metal loss was reduced at 650 °C. All the Ni-based catalysts shows identical
metal loss averaging at 24%. Unlike copper, Ni and Co based catalysts has high metal dissolution in the aqueous-phase hydrogenation. The small particle size with high surface area is prone to water attack that may lead to metal hydroxide formation.

Cobalt catalysts have high recovery but could be due to carbon compounds deposited on the surface which cannot be removed by the washing and centrifugation method employed.

Conclusions

After evaluating all the dilute limit alloy catalysts prepared in this study, results shows that the addition of single-atom sites of one metal on the surface of another metal can change the activity and selectivity of certain reaction types. This study shows that a single atom site of palladium, platinum, and ruthenium on copper, cobalt, and nickel could change the selectivity and activity of a monometallic catalyst. The adsorption characteristics of reactants, intermediates, and products are affected, causing changes in reaction pathway preference. The geometrically unique characteristic of these isolated atoms could provide the active site for direct conversion of a reactant to the desired product without leaving the metal surface or giving a faster reaction rate leading to the final product. This faster rate provides a very high selectivity in a wide range of conversions. The performance of Pd$_1$Co DLA may have shown this unique site for the conversion of furfural to cyclopentanone. In small nanoparticles (~1 nm), surface poisoning with carbonaceous compounds on the metal surface could easily deactivate the active sites. Highly active surfaces may eventually form intermediates or polymerization products that could deactivate the surface. However, the presence of another site where hydrogenation can still proceed could make the catalyst active and resistant to poisoning. Although it was not part
of this study, the effect of support on the adsorption of compounds, especially in the aqueous phase, should be taken into consideration.

From the aqueous phase furfural hydrogenation where the Pd$_1$Co DLA gave a unique reaction mechanism, it can be noted that this catalyst has low CO wavenumber (1867 cm$^{-1}$) assigned to a bridge CO on Pd and Co. The second DLA with a low wavenumber is Pd$_1$Ni with a bridge CO vibration of 1860 cm$^{-1}$ also gave the highest rate. The palladium DLA gave a low bridge CO vibration in all three abundant metal groups of the three single atoms characterized. Further studies to determine if there is a correlation in catalysts performance to the CO vibration on catalysts surface.

Correlations with CO vibrations obtained here can still be studied with other types of reactions. Other factors such as which site is responsible for the reaction are another area that can be explored. The assignments made in this study on the probable location of the isolated atom need to be supported by computational results.

The evaluation of high PZC support for DLA synthesis is recommended for future study. Support with higher resistance to hydrothermal conditions can be evaluated for the DLA nanoparticle synthesis. The same concept can be applied with the bulk solution metal ratio being deposited on the support surface within the theoretical monolayer of adsorption.

The experimental study on single atom alloys with the use of strong electrostatic adsorption can fill the gap between computational and experimental results, especially in the characterization and evaluation of catalysts prepared with this strategy. Exploration and optimization of reaction conditions is also needed to determine other unique potential of SAA and to verify computational results.
References


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https://doi.org/10.1016/j.apcata.2015.05.006.


https://doi.org/10.1016/j.jiec.2016.06.007.


Appendix A Supplemental for Chapter 2

Figure A.1. Raw spectra for CO adsorption and desorption on monometallic a) copper and b) palladium catalysts.
Figure A. 2. Raw CO-FTIR spectra for a) 1:19, b) 1:36 and c) 1:74 Pd:Cu dilute limit alloy.

Figure A. 3. Fitted gaussian function integrated area for a) Cu/SiO$_2$ catalyst and b) Pd/SiO$_2$ catalyst.
Table A. 1. Gaussian function fitting parameters for monometallic Pd and Cu spectra and isolated Pd on bimetallic Pd-Cu spectra.

<table>
<thead>
<tr>
<th>System</th>
<th>Metal-CO</th>
<th>Parameter</th>
<th>Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/SiO₂</td>
<td>Copper</td>
<td>CW</td>
<td>1879 1981 2009 2050 2104 2124 2151</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>124 34 48 42 23 35</td>
</tr>
<tr>
<td>Pd/SiO₂</td>
<td>Palladium</td>
<td>CW</td>
<td>1755 1847 1904 1951 2047 2086</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>160 81 60 62 40</td>
</tr>
<tr>
<td>Pd-Cu/SiO₂</td>
<td>Palladium</td>
<td>CW</td>
<td>1908 2021 2046</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>63 21 32</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>CW</td>
<td>1879 1981 2009 2050 2104 2124 2151</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>124 34 48 42 23 35</td>
</tr>
</tbody>
</table>

Figure A. 4 Stable adsorption sites over monometallic surface facets, a) over (111) facet, b) over (100) facet, c) over (110) facet and d) over (211) facet.
Silica as a non-conducting material accumulates charges when bombarded with electrons. This makes it hard if not impossible to obtain clear images in scanning transmission electron microscopy (STEM). Aside from atomic number difference, an isolated atom of palladium is difficult to resolved due to signal dilution by the abundant metal (Cu). Figure 3 shows a STEM image of a Pd-Cu dilute limit alloy with cluster particles of copper. A closer look on one copper cluster at higher magnification does not give a sharp resolution of an isolated atom as shown in figure 4b which could also imply the absence of palladium atom on one copper particle.

Figure A. 5. STEM images of as synthesized Pd-Cu dilute limit alloy bimetallic catalyst.
Figure A. 6. XPS spectra for Cu-2P and Pd-3d of reduced Cu (a), Pd (b) and DLA Pd-Cu (c,d) catalyst measured in three conditions (before in-situ reduction, after in-situ reduction and after CO exposure).
Figure A. 7. XPS spectra for C 1s for Pd, Cu and Pd-Cu DLA catalysts after in-situ reduction and after CO exposure.

Figure A. 8. Fitted Gaussian Functions for a) 1/19, b) 1/36 and c) 1/74 Pd-Cu DLA catalysts.
Appendix B Calculations templates

In using the bimetallic synthesis template, the metal names, support surface area, and the adsorption surface loading should be specified. Sample calculation can be made either for a given amount of support or for a given adsorption volume of precursor solution. This can be selected from the dropdown list as shown in Figure B. 2. The desired metal ratio is then entered with the corresponding part in the desired ratio field. If surface density will be the basis of calculation, the surface density should be selected on the dropdown list as shown in Figure B. 2b. Otherwise, if total metal loading (in wt%) will be the basis, “Metal Loading” should be selected. The mass loading or surface density can then be calculated by pressing the “Calc.” button and specifying the total surface density (typically ~1-1.2 μmole/m²) or total weight percent loading for the given metal precursor-support combination. The used total surface density or total weight percent will be displayed and other parameters will be calculated and presented. The resulting metal ratio will also be presented.
The metal precursor for the synthesis should be selected for each metal as shown in Figure B. 3 to calculate the amount needed in the synthesis portion of the template. The list of precursors are tabulated in “Precursors” worksheet. Once the right precursors are selected, the amount needed for the synthesis will be calculated and will be presented in the synthesis portion of the template as shown in Figure B. 4. Synthesis conditions can be noted on this section such as initial pH, shaking duration and speed. Data blanks are available for 3 trials of synthesis. Once the actual amount used are entered in the appropriate boxes, the estimated metal concentrations will be shown by selecting the reference column to calculate. The % excess for each compound is also included on the table with a default value of 10%. If a stock solution will be used in preparing the adsorption mixture, the actual stock metal concentration should be entered. A combination of solid or solution based preparation can be employed depending on the given metal source. The actual initial and final pH can be written together with the mass of the support used and the actual volume of the prepared solution used noting the 10 mL solution.
removed prior to adsorption which is already incorporated in the solution initial volume preparation.

Figure B. 2. Synthesis Basis dropdown list

![Sample Calculations]

Figure B. 3. Metal precursors selection table
Figure B. 4. Synthesis section with metal precursors quantity

The final section of the synthesis template if the measurement section where the initial and final metal concentration measured by ICP are entered averaging three measurements. The calculated surface density and weight loading will be calculated together with the measured metal ratio (Figure B. 6).

Figure B. 5. Data blank for synthesis
Figure B. 6. Measurement section

Figure B. 7. Detail fitting steps using MS Excel, Fityk and OriginPro.

Figure B. 8. CO-FTIR spectra fitting workbook interface.

Figure B. 9. Raw data transfer interface for selected spectra capture.
Figure B. 10. Fityk script generation window and data processing.

Figure B. 11. Fityk Gaussian function fitting interface.
Appendix C Supplementary on FTIR

Figure C. 1 Raw spectra for CO adsorption and desorption on monometallic a) platinum, b) ruthenium, c) nickel, and d) cobalt catalysts.

Table C. 1. Fitted Gaussian Functions Center wavenumber comparison

<table>
<thead>
<tr>
<th>Source</th>
<th>Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chin et al. (2006)</td>
<td>1866 1988 2020 2043 2063 2086 2111 2131 2146 2165</td>
</tr>
<tr>
<td>Current Study</td>
<td>1826 1984 2012 2038 2063 2078 2096 2122 2140</td>
</tr>
</tbody>
</table>
Table C. 2. Fitted Gaussian Function Parameters for Monometallic Catalysts.

<table>
<thead>
<tr>
<th>System</th>
<th>Metal-CO</th>
<th>Parameter</th>
<th>Fitted Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/SiO₂</td>
<td>Pt</td>
<td>CW</td>
<td>1807 1833 2045 2060 2070 2091</td>
</tr>
<tr>
<td>Ru/SiO₂</td>
<td>Ru</td>
<td>CW</td>
<td>1826 1984 2012 2038 2063 2078 2096 2122 2140</td>
</tr>
<tr>
<td>Ni/SiO₂</td>
<td>Ni</td>
<td>CW</td>
<td>1621 1678 1802 1874 1925 1990 2031 2056 2074 2106</td>
</tr>
<tr>
<td>Co/SiO₂</td>
<td>Co</td>
<td>CW</td>
<td>2043 2181</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>118 22 87 38 19 10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>230 90 40 33 16 20 37 20 18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>44a 196 97 76 59 54 44 29 22 28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>50 19</td>
</tr>
</tbody>
</table>

* Water Peak

Figure C. 2. Raw CO-FTIR spectra for a) 1:19, b) 1:36 and c) 1:74 Pt-Cu dilute limit alloy

Table C. 3. Gaussian Function Fitting Parameters for Monometallic Pt and Cu Spectra and isolated Pt on Bimetallic Pt-Cu Spectra

<table>
<thead>
<tr>
<th>System</th>
<th>Metal-CO</th>
<th>Parameter</th>
<th>Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/SiO₂</td>
<td>Copper</td>
<td>CW</td>
<td>1879 1981 2009 2050 2104 2124 2151</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>124 80 34 48 42 23 35</td>
</tr>
<tr>
<td>Pt/SiO₂</td>
<td>Platinum</td>
<td>CW</td>
<td>1805 1833 2034 2053 2064 2085</td>
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<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>118 22 87 38 19 10</td>
</tr>
<tr>
<td>Pt-Cu/SiO₂</td>
<td>Platinum</td>
<td>CW</td>
<td>1985 2032 2123</td>
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<td></td>
<td></td>
<td>FWHM</td>
<td>28 30 22</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>CW</td>
<td>1879 1981 2009 2050 2104 2124 2151</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>124 80 34 48 42 23 35</td>
</tr>
</tbody>
</table>
Figure C. 3. Peak Integrated Area for a) platinum, b) ruthenium, and c) nickel
Figure C. 4. Fitted Gaussian functions for Pt-Cu DLA at final N\textsubscript{2}-purged spectra.

Figure C. 5. Fitted Gaussian functions for Ru-Cu DLA at final N\textsubscript{2}-purged spectra.
Table C. 4. Gaussian function fitting parameters for monometallic Ru and Cu spectra and isolated Ru on bimetallic Ru-Cu DLA spectra

<table>
<thead>
<tr>
<th>System</th>
<th>Metal</th>
<th>CO</th>
<th>Parameter</th>
<th>Fitted Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/SiO₂</td>
<td>Cu</td>
<td></td>
<td>CW</td>
<td>1879 1981 2009 2050 2104 2124 2151</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>FWHM</td>
<td>124 80 34 48 42 23 35</td>
</tr>
<tr>
<td>Ru/SiO₂</td>
<td>Ru</td>
<td></td>
<td>CW</td>
<td>1826 1984 2012 2038 2063 2078 2096 2122 2140</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>FWHM</td>
<td>230 90 40 33 16 20 37 20 18</td>
</tr>
<tr>
<td>Ru-Cu/SiO₂</td>
<td>Ru</td>
<td></td>
<td>CW</td>
<td>1914 1951 1983 2032 2044 2064</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>FWHM</td>
<td>56 53 39 27 22 31</td>
</tr>
<tr>
<td>Ru-Cu/SiO₂</td>
<td>Cu</td>
<td></td>
<td>CW</td>
<td>1879 1981 2009 2050 2104 2124 2151</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>FWHM</td>
<td>124 80 34 48 42 23 35</td>
</tr>
</tbody>
</table>

Figure C. 6. XPS spectra of Ru-Cu DLA with varying dilutions a) Cu 2p and b) Ru 2p.
Figure C. 7. Fitted Gaussian functions for Pd-Ni DLA at final N$_2$-purged spectra.

Table C. 5. Gaussian function fitting parameters for monometallic Pd and Ni spectra and isolated Pd on bimetallic Pd-Ni DLA spectra

<table>
<thead>
<tr>
<th>System</th>
<th>Metal</th>
<th>CO</th>
<th>Param.</th>
<th>Fitted Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/SiO$_2$</td>
<td>Ni</td>
<td>CW</td>
<td>1621</td>
<td>1925</td>
</tr>
<tr>
<td>Pd/SiO$_2$</td>
<td>Pd</td>
<td>CW</td>
<td>1860</td>
<td>1886</td>
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<tr>
<td>Pd-Ni/SiO$_2$</td>
<td>Ni</td>
<td>CW</td>
<td>1621</td>
<td>1925</td>
</tr>
<tr>
<td>Ni/SiO$_2$</td>
<td>Ni</td>
<td>FWHM</td>
<td>196</td>
<td>59</td>
</tr>
<tr>
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<td></td>
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<td>1976</td>
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<td>Pd/SiO$_2$</td>
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<td>FWHM</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>196</td>
<td>54</td>
</tr>
<tr>
<td>Pd-Ni/SiO$_2$</td>
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<td>FWHM</td>
<td>196</td>
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</table>

$^a$ Used at lower dilution
Figure C. 8. Fitted Gaussian functions for Pt-Ni DLA at final N$_2$-purged spectra.

Table C. 6. Gaussian function fitting parameters for monometallic Pt and Ni spectra and isolated Pd on bimetallic Pt-Ni DLA spectra

<table>
<thead>
<tr>
<th>System</th>
<th>Metal-CO</th>
<th>Param.</th>
<th>Fitted Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/SiO$_2$</td>
<td>Ni</td>
<td>CW</td>
<td>1621 1678 1802 1874 1925 1990 2031 2056 2074 2106</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>44 196 97 76 59 54 44 29 22 28</td>
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<td>Pt/SiO$_2$</td>
<td>Pt</td>
<td>CW</td>
<td>1807 1833 2045 2060 2070 2091</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>118 22 87 38 19 10</td>
</tr>
<tr>
<td>Pt-Ni/SiO$_2$</td>
<td>Pt</td>
<td>CW</td>
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<td>FWHM</td>
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<td>Ni</td>
<td>CW</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>FWHM</td>
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</tr>
</tbody>
</table>

$^a$ Used at lower dilution
Figure C. 9. Fitted Gaussian functions for Ru-Ni DLA at final N2-purged spectra.

Table C. 7. Gaussian function fitting parameters for monometallic Ru and Ni spectra and isolated Pd on bimetallic Ru-Ni DLA spectra.

<table>
<thead>
<tr>
<th>System</th>
<th>Metal-CO</th>
<th>Param.</th>
<th>Fitted Peaks</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1621 1678 1802 1874 1925 1990 2031 2056 2074 2106</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>44 196 97 76 59 54 44 29 22 28</td>
</tr>
<tr>
<td>Ru/SiO2</td>
<td>Ru</td>
<td>CW</td>
<td>1826 1984 2012 2038 2063 2078 2096 2122 2140</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>230 90 40 33 16 20 37 20 18</td>
</tr>
<tr>
<td>Ru-Ni/SiO2</td>
<td>Ni</td>
<td>CW</td>
<td>1950 2001 2046 2072 2106 2135 2142</td>
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<tr>
<td></td>
<td></td>
<td>FWHM</td>
<td>33 65 41 31 22 25a 11a</td>
</tr>
</tbody>
</table>

a tricarbonyls on isolated Ru
b dicarbonyl on isolated Ru
Table C. 8. Gaussian function fitting parameters for Co-based DLA catalysts spectra.

<table>
<thead>
<tr>
<th>System</th>
<th>Metal-CO</th>
<th>Parameter</th>
<th>Peaks</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
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<tr>
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<td>1966</td>
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<td>2043</td>
<td>2181</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>19</td>
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<tr>
<td></td>
<td>Co</td>
<td>2043</td>
<td>2181</td>
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<tr>
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<td>50</td>
<td>19</td>
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<tr>
<td>Pt-Co/SiO₂</td>
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<td>1961</td>
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<td>2043</td>
<td>2181</td>
</tr>
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<td></td>
<td></td>
<td>50</td>
<td>19</td>
</tr>
<tr>
<td>Ru-Co/SiO₂</td>
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<td>51</td>
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<td>2043</td>
<td>2181</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>2043</td>
<td>2181</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>19</td>
</tr>
</tbody>
</table>
Appendix D. Supplementary for Hydrogenation Reaction

GC-MS Method

Samples were run on a HP 5890 gas chromatograph interfaced to a Waters VG70S magnetic sector mass spectrometer. The column used was a 30 meter Stabilwax-DA (Restek). The injection port was maintained at 250 C and the column oven was programmed from 50C (hold 3 minutes) at 5C/min to 120C then 10C/min to 250C (hold 4 minutes). Electron ionization was at 70 ev and the mass spectrometer was scanned from 41 to 400 m/z.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>M1</th>
<th>M2</th>
<th>Mass Catalysts, mg</th>
<th>M1, mmole</th>
<th>M2, mmole</th>
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</thead>
<tbody>
<tr>
<td>Pd</td>
<td>Pd</td>
<td>-</td>
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<tr>
<td>Pt</td>
<td>Pt</td>
<td>-</td>
<td>1271</td>
<td>0.003</td>
<td>-</td>
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<tr>
<td>Ru</td>
<td>Ru</td>
<td>-</td>
<td>2006</td>
<td>0.010</td>
<td>-</td>
</tr>
<tr>
<td>Pd_{1}Cu</td>
<td>Pd</td>
<td>Cu</td>
<td>1022</td>
<td>0.012</td>
<td>0.329</td>
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<tr>
<td>Pt_{1}Cu</td>
<td>Pt</td>
<td>Cu</td>
<td>1214</td>
<td>0.011</td>
<td>0.413</td>
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<td>Ru</td>
<td>Cu</td>
<td>1557</td>
<td>0.011</td>
<td>0.532</td>
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<td>Cu</td>
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<td>Cu</td>
<td>1285</td>
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<td>Ni</td>
<td>1153</td>
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<tr>
<td>Pt_{1}Co</td>
<td>Pt</td>
<td>Co</td>
<td>1356</td>
<td>0.011</td>
<td>0.413</td>
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<td>Ru_{1}Co</td>
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<td>Co</td>
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<td>0.011</td>
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<tr>
<td>Co</td>
<td>-</td>
<td>Co</td>
<td>1270</td>
<td>-</td>
<td>0.470</td>
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</tbody>
</table>
Figure D.1. XRD pattern for Spent Moderate Ratio Pd-Based Bimetallic Catalysts. (Reaction time = 3 hrs, Reaction temp. = 150 °C, Reaction pressure=430 psig)
GC-MS Hydrogenation Product Chromatogram

Figure D. 2. Calibration Standard Solution GC spectrogram.

Figure D. 3. Sample GC-FID chromatogram for a typical 10 hours reaction.
Figure D. 4. Mass Spectra for 1,4 dioxane
Figure D. 5. Mass Spectra for cyclopentanone (CPONE)

Figure D. 6. Mass spectra for cyclopentanol (CPOL)
Figure D. 7. Mass spectra for 2-cyclopenten-1-one (2CPONE)

Figure D. 8. Mass Spectra for Furfural (FAL)
Figure D. 9. Mass Spectra for 4-oxopentanal (4OPAL)

Figure D. 10. Mass Spectra for tetrahydrofurfuryl alcohol (THFOL)
Figure D. 11. Mass Spectra for furfuryl alcohol (FOL)

Figure D. 12. Mass Spectra for 5-hydroxy-2-pentanone (5HPONE)
Figure D. 13. Mass Spectra for 3-hydroxycyclopentanone (3HCPONE).

Figure D. 14. Mass Spectra for 4-hydroxy-2-cyclopentenone (4HCPONE).
Figure D. 15. Mass Spectra for PEAK K (MW=100)

Figure D. 16. Mass Spectra for PEAK L (MW=164)
Figure D. 17. Mass Spectra for 5-methylfurfural (5MFAL, MW=110)

Figure D. 18. Mass Spectra for PeakN1 (MW=114)
Figure D. 19. Mass Spectra for Peak N2 (MW=110)