Hydrodeoxygenation of Acetic Acid Using Monometallic and Bimetallic Catalysts Supported on Carbon

José Luis Contreras Mora
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Hydrodeoxygenation of Acetic Acid Using Monometallic and Bimetallic Catalysts Supported on Carbon

by

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Bachelor of Science
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Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in
Chemical Engineering
College of Engineering and Computing
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2018

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DEDICATION

I dedicate this work to my mother Alma R. Mora Delgado, my brother Hector M. Contreras, my brother Carlos J. Mora and my girlfriend Niretzy M. Cortes Candelaria for the support, encouragement and love through my undergraduate and graduate studies.
ACKNOWLEDGMENTS

I will like to thank my mother, father and brothers for the support and encouragement to keep working hard for my graduate studies. To my girlfriend Niretzy, for been there as a friend for many years, and now as my girlfriend. To my crew in Puerto Rico: Steven Rodriguez, Christian Hernandez, Reinaldo Vazquez, José Herrera and Jonnathan Vega for the support, advice and love you guys always given me.

I would like to acknowledge people from SC that helped me a lot. First, to Abraham Rodriguez and Belmar Garcia since they helped me a lot in the first two years of my PhD. To Dr. Williams for his advice, guidance, patience and for letting me be creative and supporting my ideas. To my great friends Kate Mingle, Juan Santos, Nikolette Roque, Andrew Wong, Nick van der Munnik and Calvin Thomas for their friendship and for the love I received. This 5 years have been great thanks to all of you.

I am very grateful to Tengco, Chuli, Jayson and Xinbin for all their help through the years. Also, to Carol, Vernon, Marcia and Loretta for always helping me in many things through my studies. I would also like to thank my collaborators from different projects; Dr. Regalbuto, Ritu, Dr. Asakura, Dr. Ariga (and her group) and all the undergraduate students that I mentored.

Finally, I would like to thank the National Science Foundation (NSF IGERT Fellowship (DGE-1250052)) for financial support and my cultural trip to Japan.
Abstract

Heterogeneous catalytic hydrodeoxygenation (HDO) of biomass-derived feeds is a deoxygenation process that is of highly interest. Carboxylic acids are one of the main components of bio-oils and acetic acid is one of the most abundant of these carboxylic acids. This acid is rich in oxygen, therefore a lot of research to produce fuel and other valuable chemicals such as ethanol is of interest.

This dissertation explores the gas-phase catalytic HDO of AA over catalysts supported on activated carbon (Cp-97). Temperature-dependent conversion and selectivity were studied at 1 atm from 200-400 °C with an AA concentration of 1.1% and 20% H₂ balanced in He. The first part of this work focuses on commercial catalysts: 5%Pt, 5%Pd, 5%Ru and 5%Rh supported on Cp-97. For Pt, Pd and Rh the main pathway at low temperature was decarbonylation (200-300 °C) and at higher temperatures (350-400 °C) the main pathways were decarbonylation/decarboxylation and ketonization. However, for Ru at low temperatures (200-250 °C) the main pathway was decarboxylation, and at high temperature (300-400 °C), the main pathway was decarbonylation. The activity trend based on TOF at 200 °C was found to follow: Ru > Rh~Pt > Pd. The activities of all catalysts at 200 °C were found to decrease after reaction at 400 °C and returning to 200 °C. This is attributed to coking. The reaction orders in AA and H₂ measured at 200 °C for all catalysts are generally well below ~0.5, suggesting relatively strong adsorption of both reactants on all metal surfaces. The temperature-dependence of the reaction rates were examined over the range 200-240 °C having apparent activation energy values of around 20-23 kcal/mol.

The second project studies the HDO of AA at the same conditions, but adding
Sn as a second metal on Pt and Ru (SnPt, Sn₂Pt, SnRu and Sn₂Ru) using incipient wetness. The selectivity for SnPt and Sn₂Pt goes towards ethanol and for SnRu and Sn₂Ru goes mainly towards acetaldehyde from 200-300 °C, therefore at lower temperature the main pathway is hydrogenation. At higher temperatures (350-400 °C) the main pathways are hydrogenation and decarbonylation and ketonization. For the Pt-based catalysts, a bifunctional and geometrical effect were found and for Ru-based catalyst a strong electronic and bifunctional effect were deduced from XPS.

The activity at 200 °C based on TOF was as follow: Sn₂Ru>SnPt~Sn₂Pt~SnRu. The reaction order for AA were below ~0.5 for all catalyst and the reaction order for H₂ was low as well for the Pt-based catalysts. However, the reaction order for SnRu and Sn₂Ru was ~1. The apparent activation energy for the catalyst were in the range of 13-20 kcal/mol.

Finally, on a different project phosphorous nickel phosphide (Ni₂P) is investigated. This material is being used in the HDO reaction of different carboxylic acids. The focus of this work is to investigate (P) diffusion in bulk Ni₂P by density functional theory (DFT) to find the origin of the low temperature P diffusion into the surface. The Ni₂P bulk structure consists of two types of layers, Ni₃P₂ and Ni₃P stacked along the [0001] direction. Two types of P vacancies in Ni₂P were studied: V₁P (P deficient in Ni₃P₂), and V₂P (P deficient in Ni₃P). V₁P was a somewhat more stable point defect than V₂P by 0.20 eV. The P diffusions to vacancies (V₁P and V₂P) had large diffusion barriers of more than 1 eV, except the P diffusion path along [0001] direction through an interstitial site in Ni₃P (I₁→₂) and then to V₁P, which showed the lowest energy barrier of about 0.18 eV. The DFT calculations suggested that the two adjacent vacancies (both V₁P) allow the local rearrangement of the structure to form a tetrahedral structure at the intermediate state. We have proposed a new diffusion mechanism in the intermetallic compound named interstitial-vacancy diffusion mechanism.
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LIST OF ABBREVIATIONS

AA ........................................ Acetic Acid
BE ........................................ Binding Energy
BET ......................................... Brunauer-Emmett-Teller
cNEB .................................... Climbing Image Nudged Elastic Band
CNT ......................................... Carbon Nanotubes
DFT ......................................... Density Functional Theory
DOS ......................................... Density of State
Ea ............................................ Activation Energy
EXAFS .................................... X-ray Absorption Fine Structure
FID ........................................... Flame Ionization Detector
FWHM ..................................... Full Width at Half Maximum
GC ........................................... Gas Chromatography
HAADF .................................. High Angle Annular Dark-Field
HER ......................................... Hydrogen Evolution Reaction
HDN ......................................... Hydronitrogenation
HDO ......................................... Hydrodeoxygenation
HTR ......................................... High Temperature Reduction
HDS ......................................... Hydrodesulfurization
KHDO ...................................... Keto-Hydrodeoxygenation
LEED ...................................... Low Energy Electron Diffraction
LDOS ...................................... Local Density of State
MFC ......................................... Mass Flow Controller
MS ........................................... Mass Spectrometer
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<tr>
<td>PA</td>
<td>Propanoic Acid</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
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<tr>
<td>TCD</td>
<td>Thermal Conductivity Detector</td>
</tr>
<tr>
<td>TOF</td>
<td>Turn Over Frequency</td>
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<tr>
<td>TPO</td>
<td>Temperature Program Oxidation</td>
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<td>TPR</td>
<td>Temperature Program Reduction</td>
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<tr>
<td>UHV</td>
<td>Ultra-High Vacuum</td>
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<tr>
<td>VAM</td>
<td>Vinyl Acetate Monomer</td>
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Chapter 1

Overview

Fossil fuels have been used for years since they can be easily recovered and refined to produce transportation fuels and a variety of chemicals. Although it is economically favorable, the increasing use of fossil fuels in the past years has led to an incredible rise in greenhouse gases like CO$_2$, resulting in an increase in the overall atmosphere temperature (global warming) and climate change [1]. Also, particulate matter coming from combustion contains arsenic, mercury, heavy metals, etc., that are toxic to leaving beings [2–6]. Focus to use renewable sources such as biomass have started a while ago, but to truly exploit these resources, major changes in the social and political landscape must take place [7, 8]. In 2016, 5% of the principal energy in USA came from biomass fuels, which 48% were from ethanol (biofuels), 41% from wood and 11% from waste [9].

Bio-products can be branded into four biomass sources: 1) sugar and starch, 2) oil and lipids, 3) forest derivatives and 4) cellulose derivatives (plastics and fibers) [10]. From these sources, energy can be harness by physical, chemical, thermal and biological procedures. For instance, fermentation of corn (biological process) will produce ethanol [10], while aqueous phase processing of biomass carbohydrates produces liquid fuels [11]. Thermal chemical conversion techniques are for the most part gasification, combustion, carbonization and liquefaction. Gasification is one of the most popular techniques producing biosyngas (CO, CO$_2$, H$_2$, CH$_4$ and N$_2$), but transportation and storage is expensive [12]. These biosyngas can be used in turbines and boilers, but also can be converted in liquid alkanes by the Fischer-Tropsch synthesis (chemical
Biomass can be converted into biofuels, but since it contains contaminants such as ash, water and oxygen, it can be challenging [13]. Now, liquefaction has been getting great attention since it can be easily stored, it can be done at relatively low temperatures and it is easy to transport. This can be done using fast pyrolysis [10].

1.1 Fast Pyrolysis

The production of liquids via fast pyrolysis of biomass is the most promising thermal chemical technique because it yields liquids with high calorific value and the applications are similar to oil [14] and also contain low levels of aromatics and sulfur when compared to coal and petroleum oils [15]. This process consists of heating biomass (~450-650 °C) quickly (occurs within seconds) without any oxygen. The primary products are, char, bio-oil and fuel gas and can be viewed in Figure 1.1, therefore it is the only renewable energy source that yield solid, gaseous and liquid fuels [16].

![Figure 1.1 Fast pyrolysis processes for biomass [16].](image)

These bio-oils can be used as biofuels and chemicals [10].
1.2 Hydrothermal Processing for Biomass

Hydrothermal processing is a thermochemical conversion process that is used to convert biomass into biofuel [17, 18]. The conditions for such process are performed in water at a temperature ranging from 250-374 °C and pressures from 4 to 22 MPa [18]. Depending on the desired product, the temperature, pressure and time can be adjusted to produce either bio-oils, bio-gas or bio-carbon by degrading the biomass in water. A great advantage of using hydrothermal process is that most biomass feedstock already contains water (which is problematic for other biomass processes), therefore the hydrothermal process is effective.

1.3 Bio-oils

Bio-oils composition depends on many variables such as: biomass species used, if this biomass contains moisture, the heat transfer rate and final temperature during the reaction (i.e. pyrolysis reaction, hydrothermal process), the time and temperature of the vapors in the reactor, the efficiency of the condensation equipment to recover the volatiles from the condense gas stream, exposure to air, storage temperature among many more [19]. For instance, by fast pyrolysis, hundreds of organic compounds can be found in bio-oils, but the most investigated ones are: acids, esters, alcohols, ketones, aldehydes, phenols, guaiacols, syringols, sugars furans oxygenated products, alkanes, aromatics and nitrogen compounds [19].

Carboxylic acids are one of the main components of bio-oils. This acids will corrode the storage tanks, boilers and turbines, therefore separation of these acids is desired [20]. Zuo-gang et al. [21] used a molecular distillation technology at 50 °C to separate carboxylic acids from bio-oils, therefore this acids could be further utilized and would not damage the storage tanks. From this carboxylic acids, the most abundant compound is acetic acid [20]. Zhang et al. used a gas chromatograph
with an integrated mass spectrometer (GC/MS) and determined that the carboxylic acid content for crude bio-oil was 42.2% with acetic acid having a 35.93% of the total carboxylic acid content [22].

1.4 Acetic Acid

Acetic acid (CH$_3$COOH) is the second simplest carboxylic acid and it has different applications in research and industry. The global demand of acetic acid is around 6.5 million tons per year (Mt/a) [23, 24]. Acetic acid is rich in oxygen, therefore there is a lot of research for the catalytic hydrodeoxygenation (HDO) of acetic acid in order to produce fuel [25–29]. When diluted, acetic acid becomes vinegar and it is often use in foods.

1.4.1 Synthesis of Vinyl Acetate

One of the most important applications for acetic acid in industry is the synthesis of vinyl acetate monomer (VAM) [30–32]. VAM is a precursor to polyvinyl acetate, which is one of the most important polymers in industry. This synthesis consists of acetic acid, ethylene and oxygen to produce vinyl acetate, and equation 1.1 [33] shows the reaction:

\[ \text{CH}_3\text{COOH} + \text{C}_2\text{H}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_3\text{COOCHCH}_2 \]  

(1.1)

This process was developed in the 60’s by Hoechst and Bayer using homogeneous palladium catalyst, but in the late 60’s was replaced with heterogeneous palladium catalyst by Hoechst and Bayer [33–35]. When palladium is used in this reaction, there can be a selectivity towards VAM as high as 85% [36]. The selectivity towards VAM can be improved by analyzing the adsorption of acetic acid on the surface of the palladium metal. The reaction pathway on different palladium structures have been proposed in the literature [34, 37]. It is believed that there is an intermediate
that comes from acetic acid in acetate form, and this helps produce VAM [26, 34, 38, 39].

1.5 Hydrodeoxygenation of Carboxylic Acids

Heterogeneous catalytic hydrodeoxygenation (HDO) of biomass-derived feeds is a de-oxygenation process that is of highly interest. This method consists of a reactant (e.g. carboxylic acid) co-fed with hydrogen to facilitate hydrogenolysis and hydrogenation reactions for the removal of oxygen. For long chain fatty acids, this process results in the production of liquid with high energy density that are comparable to those of fossil fuels. When the HDO process is applied, the feed is heated in a presence of a heterogeneous catalyst to produce the deoxygenated stream. This depends on the hydrogen pressure, temperature, metal and its support. The HDO pathways consist of hydrogenation, decarbonylation and decarboxylation [40–44], and equations 1.2, 1.3 and 1.4 show those pathways.

\[
Hydrogenation: R - COOH + 3H_2 \rightleftharpoons R - CH_3 + 2H_2O \tag{1.2}
\]
\[
Decarbonylation: R - COOH + H_2 \rightleftharpoons R - H + CO + H_2O \tag{1.3}
\]
\[
Decarboxylation: R - COOH \rightleftharpoons R - H + CO_2 \tag{1.4}
\]

This dissertation explores the catalytic chemistry of HDO of carboxylic acids over supported metal catalysts. Acetic acid (CH₃COOH, AA) has been chosen as the molecule for this study since is the main product of carboxylic acids in bio-oils. AA is one of the simplest carboxylic acids, in addition to being cheap, abundant [25], and prevalent in bio-oils. Also, it differs from longer chain acids because its alpha carbon has a methyl (CH₃) instead of a methylene (CH₂), thus making the reaction rate different and interesting to study. Monometallic and bimetallic catalysts are proposed for this study. The current state of knowledge in the hydrogenation process of AA is reviewed. Here we will look at what kind of catalyst, conditions and systems
researchers are using for the hydrogenation/deoxygenation of AA. Then a description of the experimental procedures and methodologies is provided, followed by results and discussion of catalyst synthesis, characterization, temperature-dependence selectivity and evaluation and kinetics studies. Finally, a theoretical study of Ni$_2$P phosphorous diffusion will be discussed in detail.
Chapter 2

Literature Review

2.1 Hydrodeoxygenation of Acetic Acid: Gas Phase

2.1.1 Monometallic Catalysts

Gas phase hydrogenation of AA is the most common approach examined in the literature. For instance, Pt can show high selectivity and activity to ethanol and other fuel related products. Rachmady and Vannice [45] studied this reaction at atmospheric pressure and temperatures between 150-300 °C in a differential, fix-bed reactor. The catalysts studied were 0.49%Pt/SiO₂, 0.78%Pt/η-Al₂O₃, 0.69%Pt/TiO₂ (reduced at 200°C), 1.91%Pt/Fe₂O₃ and 0.69%Pt/TiO₂ (reduced at 498°C). Table 2.1 summarizes the selectivity and activity of each catalyst to ethanol, acetaldehyde, methane and ethane.

Table 2.1 Gas phase hydrogenation of AA activity and selectivity on the different catalysts at 0.101MPa [45].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature (°C)</th>
<th>TOF (h⁻¹)</th>
<th>Ethanol (%)</th>
<th>Acetaldehyde (%)</th>
<th>Methane (%)</th>
<th>Ethane (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.49%Pt/SiO₂</td>
<td>238</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>0.78%Pt/η-Al₂O₃</td>
<td>250</td>
<td>5</td>
<td>8</td>
<td>0</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>0.69%Pt/TiO₂ (LTR)</td>
<td>170</td>
<td>122</td>
<td>50</td>
<td>0</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>1.91%Pt/Fe₂O₃</td>
<td>250</td>
<td>54</td>
<td>20</td>
<td>80</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.69%Pt/TiO₂ (HTR)</td>
<td>174</td>
<td>881</td>
<td>59</td>
<td>0</td>
<td>0</td>
<td>14</td>
</tr>
</tbody>
</table>
The 0.69%Pt/TiO$_2$ catalyst that employed a high temperature reduction (HTR) treatment was found to be seven times more active than the one that used low temperature reduction, with similar selectivity to fuel products. The platinum supported on iron (III) oxide has high selectivity to acetaldehyde and ethanol; however, the activity was much lower compared to platinum over titania with high temperature reduction treatment.

Witsuthammakul et al. project was to convert acetic acid to higher hydrocarbons [46]. In this work, they converted acetic acid into propylene via keto-hydrodeoxygenation (KHDO) which selectively ketonized acetic acid over metal oxides such as CeO$_2$ due to high activity at low temperature [47]. Two acid zeolites were used: CeO$_2$-Cu/HZSM-5I25 and CeO$_2$-Cu/HYI25 at atmospheric pressures and at 300 °C. First, the ketonization of acetic acid take place to produce acetone, followed by hydrogenation-dehydration of acetone to produce propylene. This group also observed direct HDO of acetic acid producing ethylene and other C$_2$-oxygenates. The more selective and sable catalyst was CeO$_2$-Cu/HYI25 due to higher Cu dispersion (65%).

2.1.2 Bimetallic Catalysts

Rachmady and Vannice also examined the bimetallic catalyst Pt-Fe/SiO$_2$ at different loadings [27]. They demonstrated that both platinum [45] and iron[48, 49] have high selectivity and activity to ethanol or acetaldehyde. The bimetallic catalyst experiments used a micro reactor at atmospheric pressure, weight hourly space velocity (WHSV) = 19.7 L (STP) g$^{-1}$ h$^{-1}$, and H$_2$/AA=47.6. The Pt-Fe/SiO$_2$ at very low atomic ratio ~0.08 (Pt/Fe) was found to have 100% selectivity to acetaldehyde (Figure 2.1).
In Figure 2.1 it is perceived that when the ratio of Pt/Fe increases, the selectivity to ethanol increases until the ratio is ~0.5, above which it decreases. The turn over frequency (TOF) of the Pt-Fe/SiO$_2$ at ~6% atomic Pt is around 720 h$^{-1}$. Comparing this catalyst with the 0.69%Pt/TiO$_2$ [45], both have comparable TOF values at 720 and 881 h$^{-1}$, respectively. However, the Pt-Fe/SiO$_2$ at low Pt/Fe ratio has a higher selectivity to acetaldehyde. When the ratio is about 0.3, the selectivity to acetaldehyde is 56% and for ethanol is 43%, compared with 59% and 0% for 0.69%Pt/TiO$_2$ at high temperature reduction. Zhang et al. [29] also worked with platinum, but added tin as a second metal to produce a bimetallic catalyst. They prepared 1%Pt-5%Sn catalysts over ZrO$_2$, TiO$_2$, SiO$_2$, SiC and carbon nanotubes (CNT) and they concluded that the catalyst with the carbon nanotube support was the best one because of higher activity and selectivity to ethanol. It was proposed that this high activity and selectivity to ethanol resulted due to the ability of the CNTs to concentrate the AA and hydrogen in an area near the active metal. Also, CNTs have high me-
chanical strength, and are stable and unreactive. In addition, Zhang and co-workers suggest that the thermal conductivity of CNTs might help the exothermic catalytic reduction of AA. Different loadings of Sn at a constant 1% Pt loading on CNT support were also examined: 1%Pt/CNT, 1%Pt-0.5%Sn/CNT, 1%Pt-1.2%Sn/CNT and 1%Pt-2%Sn/CNT. The reaction was carried out in a stainless-steel tubular fixed bed reactor at 350 °C, 2.0MPa and 0.2g of catalyst. The results are shown in Table 2.2.

Table 2.2  Gas phase hydrogenation of AA activity and selectivity towards ethanol with catalysts supported on CNT [29].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF (h⁻¹)</th>
<th>Ethanol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%Pt/CNT</td>
<td>417</td>
<td>29</td>
</tr>
<tr>
<td>1%Pt-0.5%Sn/CNT</td>
<td>980</td>
<td>80</td>
</tr>
<tr>
<td>1%Pt-1.2%Sn/CNT</td>
<td>3242</td>
<td>90</td>
</tr>
<tr>
<td>1%Pt-2%Sn/CNT</td>
<td>2265</td>
<td>87</td>
</tr>
</tbody>
</table>

It can be observed that when the percentage of tin increased, the turnover frequency and the selectivity to ethanol also increased, up to an apparent maximum between 1.2 and 2% Sn. In this case, adding another metal increases the activity and selectivity of the desired product. If we compare Table 2.1 and Table 2.2, the best platinum monometallic catalyst of Rachmady et al. (0.69%Pt/TiO₂ (HTR), Table 2.1) gives lower selectivity and activity than the 1%Pt-2%Sn/CNT catalyst (Table 2.2) made by Zhang and his group. One of the reasons given for the bimetallic catalyst to be so active and selective is because the Sn was well spread on the support and that the Sn nanoparticles were smaller [29]. Comparison of the Rachmady Pt-Fe/SiO₂ bimetallic catalyst with 1%Pt-1.2%Sn/CNT also shows that the activity and selectivity to ethanol is higher for the 1%Pt-1.2%Sn/CNT than for any atomic ratio.
from Pt-Fe/SiO$_2$ shown in Figure 2.1. K. Zhang added Sn to Pt as well, but this time in alumina (Al$_2$O$_3$) [50]. They conducted their experiment in a fixed bed reactor at temperatures from 195-275 °C and pressures from 0.1-4 MPa. The bimetallic catalysts had different Pt/Sn ratio (1/3, 2/2 and 3/1) with a loading of 2 wt%. The conversion of acetic acid increased from 16 to 68 % over the temperature range (P=0.1MPa) studied due to the promotion of reaction rate caused by the rise of temperature. The selectivity of ethanol decreased as the temperature increased and methane and ethane were only found at 275 °C. Now, when changing the pressure with constant temperature (255 °C) the conversion of acetic acid rose as the pressure increased, therefore enhancing the density of active acetate surface species and increasing collision probability of reactants and the active sites on catalyst surface [50]. The selectivity of ethanol increased while that of ethyl acetate decreased since the hydrogenation of acetic acid to ethanol and theesterification (acetic acid and ethanol) to ethyl acetate are two consecutive reactions, the author suggests. The production of ethanol is a molecule reduced reaction while the molecule number of the esterification is constant, therefore when increasing the pressure, the production of ethanol is enhanced. As previously stated before, many researchers are working with platinum on various supports to make catalysts with high selectivity and activity to products such as ethanol. There are several different kinds of bimetal Pt catalysts that have been explored [27–29, 49]. An interesting recent possibility for a second metal is indium. Onestyák and coworkers [51] used a bimetallic catalyst made of different weight loadings of platinum and indium over an alumina support. They used a fixed bed flow-through reactor with hydrogen at 21 bar and temperature range from 222 to 380 °C. Platinum catalysts generally have low selectivity to ethanol [29, 51]; it does not favor the addition of hydrogen to carbon-oxygen bonds because of its high hydrogenolysis activity that produces H$_2$O, CO and CH$_4$. The indium metal enhances the AA activity and ethanol selectivity by eliminating the decarbonylation pathway. The
Onestyák group believes that the indium's promotion is related to the formation of an alloy phase or intermetallic platinum-indium compound, just as the platinum-tin alloy discussed earlier in [29, 50].

2.2 Hydrogenation of Acetic Acid: Aqueous Phase

Wan et al. [28] explored the hydrogenation of AA in a 100 mL batch reactor with 0.2g of catalyst, 0.05 mol of AA and 40mL of water at 300 °C and 4.8MPa of H₂ for 1 hour. The catalysts studied were Ru/C, Ru/Al₂O₃, Pt/C, Pt/Al₂O₃, Pd/C, and Pd/Al₂O₃. At the conditions stated before, the catalyst with the highest activity was Ru/C with a turn over frequency (TOF) of 479 h⁻¹ and 3% selectivity for ethane. Table 2.3 summarizes the TOF and selectivity for ethane and methane for all the catalysts.

Table 2.3  Aqueous phase hydrogenation of AA activity and selectivity for methane and ethane [28].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF (h⁻¹)</th>
<th>Methane (%)</th>
<th>Ethane (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/C</td>
<td>479</td>
<td>55</td>
<td>3</td>
</tr>
<tr>
<td>Ru/Al₂O₃</td>
<td>379</td>
<td>42</td>
<td>0</td>
</tr>
<tr>
<td>Pt/C</td>
<td>453</td>
<td>47</td>
<td>1</td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>155</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>Pd/C</td>
<td>21</td>
<td>54</td>
<td>0</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>111</td>
<td>40</td>
<td>0</td>
</tr>
</tbody>
</table>

While there was a low selectivity towards ethane for all catalysts, a high selectivity for methane was found. However, AA has two carbons, and therefore a product with at least the same amount of carbon is desired to retain higher energy density. Wan
et al. also tested the hydrogenation of p-cresol (CH₃C₆H₄OH), which is a bio-oil phenolic compound, in the presence of aqueous phase AA. They fed 0.05 mol of AA and the same amount of p-cresol at the same conditions stated before. They only tested this reaction on Ru/C because it was the catalyst with the highest activity. The selectivity for methane and ethane increased in comparison to the case of pure AA as the feed (Figure 2.2). In Figure 2.2 an increase in the ethane and methane production can be seen when p-cresol is added.

![Figure 2.2](image_url)  

**Figure 2.2** AA selectivity towards methane (gray) and ethane (horizontal lines) at 300 °C and 4.8MPa [28].

However, this increment is not high enough to conclude that adding a phenolic compound with seven carbons is profitable. Adding p-cresol means higher cost with a negligible increment in production. This effect probably results from strong adsorption of p-cresol on the catalyst surface, which in turns suppresses the hydrogenation of acetic acid. The effect of AA on the selectivity of p-cresol was also noted, as shown in Figure 2.3.
Figure 2.3  P-cresol selectivity towards methylcyclohexane (black) and C$_1$-C$_6$ hydrocarbons (horizontal lines) at 300 °C and 4.8MPa [28].

It was seen that there are different products such as C$_1$-C$_6$ hydrocarbons and methylcyclohexane (C$_7$H$_{14}$), which is a component of jet fuel. The selectivity towards methylcyclohexane was 60% and 7% for the other hydrocarbons. This is a significant increase in fuel products with high carbons compounds. It was suggested that AA in this case promotes the dehydration reaction. An experiment was performed in water with 0.05 mole of AA and 0.05 mole of 4-methylcyclohexanol with the same conditions as before but without the Ru/C catalyst. Wan’s group observed that 89% of 4-methylcyclohexanol was converted with total selectivity to 4-methylcyclohexene, confirming that AA promotes the dehydration reaction. Wang et al. [52] carried out the aqueous hydrogenation of AA using a stainless steel tubular flow reactor. This reaction was conducted at 100 °C and 6 MPa, with 10 wt% of AA and 2.0g catalyst. The catalysts used were 4% Ir/SiO$_2$, 4% Ir-MoO$_x$/SiO$_2$, MoO$_x$/SiO$_2$ and a physical mixture of 4% Ir/SiO$_2$ + MoO$_x$/SiO$_2$. The main product of interest for this work was ethanol, and Figure 2.4 summarizes the activity and selectivity towards ethanol using the different catalysts. The most active and selective catalyst was the
4% Ir-MoOx/SiO2 due to the synergy effect between the closely contacted Ir and Mo.

Figure 2.4 AA selectivity (black) and TOF (gray) to ethanol at 100 °C and 6MPa [52].

2.3 Nickel Phosphide as a Catalyst

For around a decade nickel phosphide (Ni2P) has been used as a catalyst for different reactions such as: hydrodesulfurization (HDS) [53, 54] hydronitrogenation (HDN) [54], hydrodeoxygenation (HDO) [55–57] with different supports [58] (and support effects). Another use for this catalyst is for the electrocatalytic reaction of hydrogen evolution reaction (HER) in acidic media. It has been observed that Ni2P is one of the most active and stable catalyst for this reaction, even so that it is almost comparable to the activity of noble metals such as Pt [59, 60]. Many characterization techniques have been used under ultra-high vacuum (UHV) for (0001) and (1010) such as scanning transmission electron microscope (STEM), low energy electron diffraction (LEED), extended x-ray absorption fine structure (EXAFS), to understand this material [58, 61–63]. For instance, for the (0001) surface structure, it was addressed that having the P atoms on the surface, in part by diffusion from thermal annealing,
stabilizes the structure [61, 64].

2.3.1 Defects in Materials

Point defects in materials is a topic that has been of interest for quite some time, for metals, even as early as in the 1950’s [65]. One of the most studied crystalline structures for these defects are metal oxides. Defects can help increase stability and activity of a catalyst, and they can be responsible for atomic diffusion [65, 66]. Generally, point defects has been investigated for TiO$_2$ (for rutile and anatase), such as oxygen vacancy and Ti interstitial [66–68], and recently Ti vacancies as well [69]. By synthesizing undoped anatase with Ti vacancies, the lattice constant changed, the conductivity changed from n-type to p-type and the activity in photocatalytic reactions increased, among other things [69].
Chapter 3

Experimental Procedures

3.1 Materials

Acetic acid 99%, Acetaldehyde 99% and Tin (II) chloride dehydrate (SnCl$_2$-2H$_2$O) were purchased from VWR. The Cp-97 support and the 5%Pt/Cp-97, 5%Pd/Cp-97, 5%Ru/Cp-97 and 5%Rh/Cp-97 catalyst was obtained from B.A.S.F chemical company.

3.2 Catalyst Preparation

3.2.1 Incipient Wetness

Bimetallic catalysts using Pt/Cp-97 and Ru/Cp-97 as based catalyst (both 5wt% from B.A.S.F) with different molar ratios (Sn:M, 1:1 and 2:1 where M=Pt or Ru) and a 6%Sn/Cp-97 were synthetized by using the incipient wetness method [70]. The precursor used for the synthesis was Tin (II) chloride dehydrate (SnCl$_2$-2H$_2$O). The pore volume was measured for the carbon, adding drops of DI water to to fill the pores without an excess of water. For the Cp-97, the pore volume was 2.5 cc/g. After knowing the pore volume of the support, the salt solution was added (SnCl$_2$-2H$_2$O) drop by drop until a paste-like material was observed. Next, the material was dried in the oven overnight at 120 °C and then the catalysts were reduced (see Table 3.1) with H$_2$ flow for two hours in a horizontal furnace. After the reduction was done, experiments such as XRD, TPO, TPR, XPS and O$_2$-H$_2$ titration experiments were performed.
Table 3.1  Reduction and H₂-Pulse chemisorption temperatures for the catalyst samples.

<table>
<thead>
<tr>
<th>Catalyst supported on Cp-97</th>
<th>Reduction Temperature (°C)</th>
<th>H₂-Pulse Chemisorption Conditions (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Pt</td>
<td>250</td>
<td>40</td>
</tr>
<tr>
<td>5% Pd</td>
<td>250</td>
<td>40</td>
</tr>
<tr>
<td>5% Ru</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>5% Rh</td>
<td>250</td>
<td>40</td>
</tr>
<tr>
<td>6% Sn</td>
<td>350</td>
<td>--</td>
</tr>
<tr>
<td>SnRu</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Sn₂Ru</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>SnPt</td>
<td>400</td>
<td>300</td>
</tr>
<tr>
<td>Sn₂Pt</td>
<td>400</td>
<td>400</td>
</tr>
</tbody>
</table>

– Does not chemisorb.

3.3 Catalyst Characterization

3.3.1 Brunauer-Emmett-Teller Measurements

The total Brunauer-Emmett-Teller (BET) surface area (m²/g) of the Cp-97 supports was determined by a Micromeritics Asap 2020 instrument. The BET technique determines the physical adsorption of an inert gas on the surface of the solid sample. The amount of gas absorbed at a given pressure gives the surface area. The experiments were carried out by placing ~0.16 g of the support in a cell. The sample was pre-treated by flowing He at 250 °C for about 2 hours to remove the remaining water and impurities. Afterward, the support was exposed to mixtures of nitrogen (10, 20 and 30%) balance He. The sample was cooled over liquid nitrogen and a thermal conductivity detector measured the adsorption and desorption peaks. The surface area of Cp-97 was found to be and 615 m²/g.
3.3.2 Pulse Chemisorption (Hydrogen Titration of Oxygen Pre-Covered Catalyst)

Around 0.100 g of catalyst was added to the Micromeritics 2920 AutoChem II Analyzer equipment. The \( \text{H}_2 \) chemisorption experiment started with a reduction of the catalyst with hydrogen (10%) with a flow of 50 sccm at reduction temperature (see Table 3.1) for one hour. Then, the gas was changed to argon to flush the hydrogen out for 1 hour, followed by cooling to 40 °C. For all the catalysts a flow of 50 sccm of 10% \( \text{O}_2/\text{Ar} \) was added and then 30 minutes of Ar to remove any \( \text{O}_2 \) (at 40 °C). After that, \( \text{H}_2 \) balance with Ar was added at the corresponding conditions (see Table 3.1). This was repeated three times for reproducibility.

3.3.3 X-ray Diffraction (XRD)

The X-ray diffraction (XRD) patterns were recorded using a Rigaku MiniFlex II diffractometer system with a D/tex Ultra detector with Cu Kα radiation (\( \lambda = 1.54 \) Å). Data were collected from 10-80° 2θ with a step size of 0.04° and a scan rate of 2°/min. Particle size was estimated using the Scherrer equation with PDXL2 as a reference for instrumental broadening. The Scherrer equation which is defined as:

\[
d = \frac{\lambda K}{\beta \cos(\theta)}
\]

where: d is the particle diameter, \( \lambda \) is the wavelength of the incident radiation, \( \theta \) is the Bragg angle, \( \beta \) is the full width at half maximum (FWHM) of the diffracted peak, and K is the shape factor of the particle which is designated to be 0.92 assuming spherical particles.

3.3.4 Electron Microscopy

Imaging of catalysts for determining particle size distributions was performed using a JEOL 2100F 200 kV scanning transmission electron microscope (STEM) equipped with a CEOS Cs corrector on the illumination system. The geometrical aberrations were measured and controlled to provide less than a \( \pi/4 \) phase shift of the incoming
electron wave over the probe-defining 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 captured on a Fischione Model 3000 HAADF detector with a camera length such that the detector spanned 50-163 mrad. The scanning acquisition was synchronized to 60 Hz AC electrical power to minimize 60Hz noise in the images and a pixel dwell time of 15.8\(\mu s\) was chosen. Around 20 images per catalyst were taken, and > 600 particles were counted per each catalyst in different images.

3.3.5 X-ray Photoemission Spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos AXIS Ultra DLD XPS system with a monochromatic Al K\(\alpha\) source operated at 15 keV and 150 W, using a hemispherical energy analyzer. The X-rays were incident at an angle of 45° with respect to the surface normal. Analysis was performed at a pressure below 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 XPSPEAK41 software. The XPS experiments were performed while using an electron gun directed on the sample, for charge neutralization. The XPS system was equipped with a catalyst treatment cell directly attached to the analysis chamber. The catalysts were transferred in the catalysis cell from ultrahigh vacuum and back, without exposure to the atmosphere. The in-situ treatments in the cell were performed under flow conditions for all catalyst samples.

3.3.6 Temperature Program Oxidation and Reduction (TPO, TPR)

The catalyst samples and support were loaded in a custom TPX System fitted with an Inficon Transpector 2 Mass Spectrometer. Temperature Program Oxidation (TPO) was performed with a ramp of 5 °C/min, flowing 10% oxygen in helium at 20 sccm for 5%Pt, 5%Pd, 5%Ru and 5%Rh supported on Cp-97. The oxygen and carbon dioxide
signals were monitored during the experiment. The spectrum from 1 to 50 amu was recorded. For the Temperature programmed reduction (TPR) of oxygen-pretreated on 6%Sn, SnPt, Sn₂Pt, SnRu and Sn₂Ru surfaces was conducted to know the temperature to be used for pulse chemisorption experiments. Samples were reduced at 400 °C at a ramp rate of 10 °C/min for two hours in a stream of 10% H₂/balance in Ar (20 sccm) followed by a purge for one hour in flowing Ar (20 sccm) at the reduction temperatures. After that, samples were cooled to ambient temperature (~40 °C) in flowing Ar and then exposed to a gas stream of 10% O₂/balance He for 30 minutes to cover each catalyst surface with a layer of chemisorbed oxygen atoms. Next, remaining gas O₂ was removed flowing Ar for 30 minutes (until no O₂ signal was seen). Finally, for the TPR experiment, 20 sccm of 10% H₂/balance in Ar over from 25-450 °C at a ramp rate of 5 °C/min. Spectrum from 1 to 50 amu were recorded with a focus on H₂O signal.

3.3.7 Plug Flow Reactor System

The catalysts were evaluated in a single pass, packed bed, plug flow reactor system. The reactor consisted of a stainless steel (SS) reactor (5.68 mm I.D, 9.52 mm O.D) attached to a vertical split-tube furnace (Applied Test Systems Inc, 15” Series 3210, 1210 W, 115 V) with a maximum temperature capacity of 700 °C (controlled by Thermo Electric Instruments). The reactor was loaded with 200 mg of catalyst supported on quartz wool and a 4.76 mm O.D, 127 mm length stainless steel tube. A thermocouple was inserted in the middle of the reactor that touches the powder catalyst, to offer an accurate reaction temperature. The catalysts were reduced in-situ at temperatures ranging from 250-400 °C in 20% H₂/balance He (50 sccm total flow) for 1 hour. The flow of hydrogen and helium were controlled utilizing Tylon mass flow controllers (MFC). The feed stream for the reaction consisted of 1.1% AA, 20% H₂/balance He. The pressure remained constant at 1 atm. The liquid reactant
(AA) was stored in a jacketed vapor-liquid equilibrium (VLE) saturator attached to a recirculating ethylene glycol refrigeration system to control the temperature. The VLE temperature was 30 °C. Acetic Acid was loaded into the VLE through the liquid fill port. Controlled flow of helium (sweep gas), was supplied to the VLE beneath the liquid level to create bubbles in the liquid. Overhead of the liquid level, AA and He vapor reached a thermodynamic equilibrium state. The Helium saturated with AA exited at the top of the VLE and mixed with the diluent gas stream. The VLE temperature was monitored and controlled so that the desired AA concentration was reached. Undesired condensation of the feed lines was prevented by wrapping them with heating tape and keeping them at 125 °C. Heating tapes were regulated by a Variac (Staco energy products Co. Input: 120 V, 50/60 Hz). Figure 3.1 illustrates a schematic of the reactor system including the MFC, the VLE, the valve box and the GC inlet [40].

Figure 3.1  Schematic of the plug-flow reactor system [40].
The sweep gas coming from the VLE and the diluent gases coming from the primary manifold are mixed prior to entering the reactor. The valve box (Vici Valco Instruments Inc.) consists of a series of valves connected that direct the feed and product gas stream, where a sample is collected for the GC. The valve box and the lines connected to the GC are maintained at 100 °C by a Furotherm 91e temperature controller. The reaction feed and product were analyzed utilizing an on-line Hewlett-Packard 5890 gas chromatograph with one 30 m HP-PlotQ capillary column for the product detected by the flame ionization detector (FID) and a Poraplot Q plot FS 25X column for the products detected by the thermal conductivity detector (TCD).

3.3.8 Gas Chromatography (GC) Analysis

The products were analyzed by gas chromatography. The temperature ramp was set at 70 °C for 2 minutes, then a 15 °C/min ramp until it reaches 220 °C, and it remains at this temperature for 10 mins. Prior to running any experiments, the chart speed, attenuation, peak width was configured. Acetic Acid was calibrated by varying the temperature of the VLE for the different concentration (0-450 nmoles). The estimated nmoles was calculated by the Antoine equation and revised with the

\[ \text{loopcapacity} = \text{nmoles gases-injected} \times y_{AA} \] (estimated based on the flow rate of the sweep and diluent gas). The Antoine’s estimation for the concentration of acetic acid is illustrated in Figure 3.2. Ethanol, acetone, ethyl acetate and acetaldehyde were calibrated by liquid phase injection using a 10 µL syringe. Methane and ethane were calibrated using a Matheson Tri-gas (1000 ppm) disposable liters. The products response factor were determined by flowing the gases (or the injected liquids) at the temperature ramp for a period of time until the integration area was obtained.
Figure 3.2  Antoine’s estimation for the concentration of acetic acid.

The integration area counts or response factor was calculated as $RF = \frac{nmoles_x}{IntAreaCount}$. The retention time and response factor are shown in Table 3.2 and they are based on the FID and TCD column (HP-PlotQ [L=30 m, ID=0.320 mm]).

Table 3.2  Calibration parameters based on the FID and TCD columns.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention Time (RT) (min)</th>
<th>Response Factor (RF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1.857</td>
<td>2.049E-03</td>
</tr>
<tr>
<td>Methane</td>
<td>1.860</td>
<td>8.370E-04</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.189</td>
<td>1.804E-03</td>
</tr>
<tr>
<td>Ethane</td>
<td>2.873</td>
<td>5.140E-04</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>7.434</td>
<td>3.700E-03</td>
</tr>
<tr>
<td>Ethanol</td>
<td>9.514</td>
<td>2.774E-03</td>
</tr>
<tr>
<td>Acetone</td>
<td>10.542</td>
<td>1.579E-03</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>13.191</td>
<td>7.338E-04</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>14.053</td>
<td>6.887E-04</td>
</tr>
</tbody>
</table>
3.4 Density Functional Theory (DFT) Calculations

The DFT calculations were performed using the Vienna ab initio Simulation Package code (VASP 5.4.1) [71, 72] for the Ni$_2$P project (see Chapter 6). The Perdew-Burke-Ernzerhof exchange-correlation functional with a generalized gradient approximation was used [73, 74]. Projector-augmented wave approach [75, 76] has been used together with plane wave basis sets with a 4x4x4 k-points mesh Brillouin-zone integration to obtain the optimized structures and a 8x8x12 k-points mesh for the density of state (DOS) calculation. Spin-polarized calculations were performed for all the systems with an energy convergence tolerance of $1 \times 10^{-8}$ eV/atom. The density of states for $\alpha$ and $\beta$ spins did not show any differences, and thus the spin effect on diffusion was not discussed in this paper. The transition and intermediate steps were analyzed with the climbing image nudged elastic band (cNEB) method [77]. The unit cell was increased to a 2x2x3 supercell with a=b=1.178 nm, c=1.011 nm for this study.
Chapter 4
Characterization and Evaluation of Carbon-Supported Noble Metals for the Hydrodeoxygenation of Acetic Acid

4.1 Introduction

Acetic acid (AA, CH₃COOH) is the second simplest carboxylic acid, with many different industrial applications. For example, it is used for the production of cellulose acetate [78], and when diluted, it becomes vinegar and is used in a variety of food products. Another important industrial application for this carboxylic acid is the synthesis of the vinyl acetate monomer [30–32]. Based on these and other chemical processes, the global demand of acetic acid is around ~6.5 million tons per year (Mt/a) [23, 24]. Substantial research has been focused on replacing fossil fuels and chemicals with those derived from biomass, which is an alternative and renewable resource [10]. With fast pyrolysis of biomass [28], bio-oils can be obtained that contain many components. These include lignin, sugars, furans and carboxylic acids, many of which contain high oxygen content [25, 28]. From carboxylic acid feeds, which can contain a lot of acetic acid [79], desirable products such as alcohols and hydrocarbons can be obtained with hydrogenation. For example 1,4-butanediol can be produced via the hydrogenation of maleic acid [26], while hydrogenation of aqueous-phase levulinic acid over a variety of supported catalysts (e.g., Ru/C [80–82], Ru/Al₂O₃ [81, 82], AuPd/TiO₂ [25], Ru/TiO₂ [81]) can produce γ-valerolactone. One method to convert
acetic acid into fuels and chemicals is through hydrodeoxygenation (HDO) [25, 26, 28, 29, 49]. The HDO process consists of the reactant (e.g. carboxylic acids) being co-fed with hydrogen to facilitate hydrogenolysis and hydrogenation reactions required for the removal of oxygen. This results in the production of some liquids with high energy density that are similar to those of conventional fossil fuels, but also some gaseous products such as ethane and methane. The HDO pathways (Equations 4.1, 4.2 and 4.3) consist of hydrogenation, de carbonylation and decarboxylation, and have been discussed in detail elsewhere [40–44].

\[
\text{Hydrogenation} : R - \text{COOH} + 3H_2 \rightleftharpoons R - \text{CH}_3 + 2H_2O \quad (4.1)
\]

\[
\text{Decarbonylation} : R - \text{COOH} + H_2 \rightleftharpoons R - H + CO + H_2O \quad (4.2)
\]

\[
\text{Decarboxylation} : R - \text{COOH} \rightleftharpoons R - H + CO_2 \quad (4.3)
\]

Rachmady and Vannice were among the first to investigate hydrogenation of AA over catalysts consisting of Pt supported on different types of materials [45]. Recently other researchers have been using noble metals such as Pt [25] ,Ru, Pd, Ir and non-noble metals such MoO\(_x\) [52] to obtain high activity for AA hydrogenation. In this work, several different commercial group VIII noble metal catalysts have been studied to explore their catalytic chemistry towards AA HDO. These catalysts include Pt, Pd, Ru and Rh supported on an activated carbon. The various features of the reaction kinetics, including activities, selectivities, reactant reaction orders, and apparent activation energies, are compared with a view towards elucidating the mechanism that governs these reactions.

4.2 Experimental

4.2.1 Catalysts

Four different commercial (BASF) carbon-supported metal catalysts were used for the HDO of AA: 5%Pt/Cp-97, 5%Pd/Cp-97, 5%Ru/Cp-97 and 5%Rh/Cp-97. The
carbon support was an activated carbon from BASF (Cp-97 SBET=615m$^2$/g).

4.2.2 Catalyst Characterization

Pulse H$_2$ Chemisorption

The metal dispersions of the catalysts were determined by pulsed hydrogen titration of oxygen pre-covered sites using a Micromeritics 2920 AutoChem II Analyzer equipment. The catalysts were reduced at 200 °C for Pt, Ru and Rh and 250 °C for Pd in 10% H$_2$ for two hours. Then, the gas was changed to argon to flush the hydrogen out for 1 hour, followed by cooling to 40 °C. For all the catalysts a flow of 50 sccm of 10% O$_2$/Ar was added and then 30 minutes of Ar to remove any O$_2$ (at 40 °C). Then, 10% H$_2$/Ar at 40 °C for Pt, Pd, Rh and at 250 °C for Ru (since there is no H$_2$ adsorption at 40 °C [83]) was added until there were no more uptake of H$_2$. This was repeated at least three times for reproducibility for each catalyst.

Electron Microscopy

Imaging of catalysts for determining particle size distributions was performed using a JEOL 2100F 200 kV scanning transmission electron microscope (STEM) equipped with a CEOS Cs corrector on the illumination system. The geometrical aberrations were measured and controlled to provide less than a π/4 phase shift of the incoming electron wave over the probe-defining aperture of 17.5 mrad, which at 200kV provides a nominal probe size of <0.1nm. High angle annular dark-field (HAADF) STEM images were captured on a Fischione Model 3000 HAADF detector with a camera length such that the detector spanned 50-163 mrad. The scanning acquisition was synchronized to 60 Hz AC electrical power to minimize 60Hz noise in the images and a pixel dwell time of 15.8µs was chosen. Around 20 images per catalyst were taken, and 650-950 particles were counted per each catalyst in different images (not all presented here).
X-ray Photoemission Spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos AXIS Ultra DLD XPS system with a monochromatic Al Kα source operated at 15 keV and 150W, using a hemispherical energy analyzer. The X-rays were incident at an angle of 45° with respect to the surface normal. Analysis was performed at a pressure below 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 XPSPEAK41 software. The XPS experiments were performed while using an electron gun directed on the sample, for charge neutralization. The XPS system was equipped with a catalyst treatment cell directly attached to the analysis chamber. The catalysts were transferred in the catalysis cell from ultrahigh vacuum and back, without exposure to the atmosphere. The in-situ treatments in the cell were performed under flow conditions, of a 5% H₂/Ar for 2 hours at the 200 °C for Pt, Ru and Rh and 250 °C for Pd.

4.2.3 Catalyst Evaluation

The reactor system has been explained in detail in previous articles [40, 84], but a brief description is presented here. The HDO of AA was carried out in a single pass, packed bed, plug flow reactor system. The catalysts were reduced in situ for 1 h at 250 °C for Pt, Ru, Rh and Pd. The feed stream for the reaction consisted of 1.1% AA (VWR, 99%), 20% H₂ and the balance He, with a total flow of 50 sccm. The pressure remained constant at 1 atm. The activity and selectivity of the reactions on the different commercial catalyst was investigated over the temperature range from 200-400 °C. For kinetic experiments, AA and H₂ mole fractions ranged from X_{AA}~0.0016-0.051 and X_{H₂}~0.20-0.99 at 200 °C, while the total flows ranged from 50-200 sccm depending on the catalyst in order to ensure no external mass transfer limitations (Figure A.1) and differential conversion. Reaction products were analyzed
by an in-line Hewlett-Packard 5890 gas chromatograph (GC) equipped with a flame ionization detector (FID) for analysis of organic products and unreacted AA, and a thermal conductivity detector (TCD) for analysis of small gas molecules such as CO and CO$_2$.

4.3 Results and Discussion

4.3.1 Catalyst Characterization

Representative STEM images with the particle size distribution for Pt/Cp-97, Pd/Cp-97, Ru/Cp-97 and Rh/Cp-97 are shown in Figure 4.1. Table 4.1 summarizes the dispersions and estimated average particle sizes obtained from chemisorption, assuming that the metals have spherical shape. The dispersion was found to be in the following order from most disperse to least: Pt>Pd>Ru~Rh. In addition, Table 4.1 shows surface mean diameters calculated from STEM ($D_s = \frac{\sum n_i D_i^3}{\sum n_i D_i^2}$) where $D_i$ is the diameter and $n_i$ is the number of particles [85, 86]. The dispersion and particle size ($D_s$) taken from the H$_2$-pulse chemisorption are the only measurements performed in a reduced environment, thus ensuring the reduction of the catalyst (or at least most of the sample) to its metal form. Figure A.2 shows the XPS data for the fresh catalyst sample (already reduced ex-situ) and in-situ reduced (in the XPS catalyst cell) sample for: a) Pt (Pt$^0$-71.3 eV [87], PtO$_2$-74.5 eV [88]), b) Pd (Pd$^0$-335.3 eV [89], PdO-337.0 eV [90]), c) Ru (Ru$^0$-280.3 eV [91], RuO$_2$-281.3 [92]) and e) Rh (Rh$^0$-307.3 eV [93], Rh$_2$O$_3$-308.9 eV [94]). While every fresh catalyst sample showed metal oxides, the in-situ reduced samples are completely reduced except for Pt, which is 91% reduced (our reactor system reduces the catalyst with 20% H$_2$ which might reduce Pt entirely). Usually, particle sizes derived from STEM and chemisorption should be consistent. However, in Table 4.1 it is observed that when the chemisorption particle size is compared with the STEM surface mean diameter ($D_s$), both measurements
are comparable for Pt/Cp-97 and Pd/Cp-97 but not for Ru/Cp-97 and Rh/Cp-97.

Figure 4.1 Representative STEM images for a) 5%Pt/Cp-97, b) 5%Pd/Cp-97, c) 5%Ru/Cp-97 and d) 5%Rh/Cp-97. Size distributions of particles are shown in the insets.

Carbon decoration phenomena may explain these discrepancies between characterization techniques. When catalysts are supported on activated carbon such as Cp-97, a carbon decoration from the support to the metal surface can occur [86]. This results in the blocking of some of the active sites of the metals, effectively reducing the metal dispersion (and thus increasing the estimated particle size from chemisorption). For the purposes of calculating the intrinsic rates of reaction using turnover frequencies
(i.e., molecules site$^{-1}$ min$^{-1}$), the metal dispersions based on chemisorption were used to estimate the active sites in the reactor.

Table 4.1  Particle sizes for catalysts obtained using chemisorption and STEM.

<table>
<thead>
<tr>
<th>Catalyst supported on Cp-97</th>
<th>$H_2$-Titration</th>
<th>STEM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dispersion (%)</td>
<td>$D_a$ (nm)</td>
</tr>
<tr>
<td>5%Pt</td>
<td>24</td>
<td>4.7</td>
</tr>
<tr>
<td>5%Pd</td>
<td>20</td>
<td>5.6</td>
</tr>
<tr>
<td>5%Ru</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>5%Rh</td>
<td>12</td>
<td>9</td>
</tr>
</tbody>
</table>

a- Fresh sample
b- After reaction sample

This was chosen since the chemisorption measurement if made on a reduced catalyst surface such as that found within the reactor at the start of the HDO reaction. In addition, XRD measurements were performed for all the fresh and after reaction catalysts. In all cases, oxides were observed, which is likely a result of their exposure to air during the measurement [95]. The analysis of these complex data will be the subject of a separate forthcoming publication.

4.3.2 Catalytic Evaluation of Carbon-supported Noble Metals

Temperature-dependent conversion and selectivity plots for each catalyst are shown in Figure 4.2. For all the plots, selectivity is on the left Y-axis and is represented by bars, CO ratio is on the right Y-axis and is represented by open circles, and conversion on the top X-axis. To ensure that the water-gas shift (WGS) reaction was not taking place at any temperature and catalyst, the maximum amounts of CO$_2$ that could be produced by the WGS reaction at different temperatures were calculated using the equilibrium constants $K_{eq}$ [96].

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These results show that the WGS reaction does not account for any of the CO$_2$ observed in the present studies and can be seen in Table A.1. Overall, the highest conversion for all temperatures was obtained over Ru, followed by Pt, Rh and Pd. For Pt/Cp-97 (Fig. 4.2a) methane is the most selective product since it is relatively easy for the C-C bond of AA to cleave over Pt [29]. For instance, at 200 °C the reaction of AA results in the production of methane (96% selectivity), and ethane. As the temperature increases from 250-400 °C, acetone is produced as well, including trace amounts of ethanol (< 2% selectivity) at around 300 °C. Decarbonylation is the main pathway (with the production of CO) from the whole temperature range followed by ketonization (CO$_2$ and water), decarboxylation (CO$_2$ production) and then hydrogenation. For Pd/Cp-97 (Fig.4.2b), the selectivity is mostly towards methane.
over the selected temperature range. At 200 °C there is methane (93% selectivity) and acetone, with no ethane, in contrast to Pt. As the temperature increases, the selectivity remains high towards methane, with the remainder acetone and some traces of ethane. When the temperature reaches 300 °C and higher, a trace amount (1-3% selectivity) of acetaldehyde begins to be produced. The main pathway for this reaction on Pd/Cp-97 is decarbonylation (from 200 °C to 300 °C), with a shift to ketonization, some decarboxylation and hydrogenation (traces amount of acetaldehyde) from 350-400 °C. For Ru (Fig. 4.2c) at 200 °C the main product was methane (94% selective), followed by ethane (5% selective) and acetone (1% selective). As the temperature increases, the selectivity goes completely to methane, and this can be due to Ru promoting C-C bond cleavage [28, 97]. The main pathway is decarbonylation, decarboxylation (production of CO₂), ketonization (trace amount of acetone) and hydrogenation to form ethane from 200-250 °C, and then completely towards decarbonylation at higher temperature. For Rh (Fig. 4.2d) at 200 °C the only product is methane and as the temperature increases there is some acetone and ethane formed. The main pathway at lower temperatures is decarbonylation, with some ketonization and decarboxylation occurring at elevated temperatures. The activity of the catalysts at 200 °C measured before, and after the reaction was carried out at 400 °C, are shown in Table 4.2 as turn over frequencies (TOF, 1/min) based on the chemisorption site estimate. The comparison is made at 200 °C since at this temperature the measured conversions are differential (i.e., < 10%). The activity trend goes as follows: Ru>Rh~Pt>Pd and this trend is in agreement with aqueous-phase hydrogenation of acetic acid for a continuous-flow packed-bed reactor from 110-290 °C and 5.17 MPa total pressure [98]. After reaction at elevated temperature (200-400 °C), the activities for all the catalysts were reduced significantly when measured again at 200 °C (Table 4.2). The decrease in activity goes as follows: Rh>Pd>Ru~Pt. Therefore, the Pt and Ru supported on carbon are the most stable catalyst under HDO of acetic acid at the
corresponding conditions. Particle sizes estimated from STEM images after reaction at elevated temperature are shown in Table 4.1. The particle sizes after reaction are larger compared to the ones at 200 °C, suggesting sintering. Figure A.3 shows typical STEM images of Pt, Pd, Ru and Rh, respectively, after reaction at high temperature, clearly showing sintering. Given the differences in activity after elevated temperature reaction, TPO was used to look for evidence of coking. Figure 4.3 shows the fresh catalyst, the support and the after reaction catalyst curves. CO$_2$ peaks are seen at 160 °C and 180 °C for Pt, 220 °C for Pd, 244 °C for Ru, and 260 °C for Rh for the after reaction samples. Essentially, the activity for all the catalysts are reduced due to coking.

Table 4.2 Activity of catalyst at 200 °C before and after reaction at 400 °C.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>5%Pt (TOF (1/min))</th>
<th>5%Pd (TOF (1/min))</th>
<th>5%Ru (TOF (1/min))</th>
<th>5%Rh (TOF (1/min))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh (200 °C)</td>
<td>0.018±0.005</td>
<td>0.011±0.003</td>
<td>0.091±0.011</td>
<td>0.028±0.005</td>
</tr>
<tr>
<td>After Reaction (200 °C)</td>
<td>0.010±0.007</td>
<td>0.003±0.008</td>
<td>0.049±0.006</td>
<td>0.006±0.040</td>
</tr>
</tbody>
</table>

Reactant reaction order studies were conducted at 200 °C by varying the concentration of AA or hydrogen, while holding all other parameters constant. The lower temperature was chosen for two reasons. First, it allowed the reaction to be carried out at very low differential conversion, ensuring that true kinetics could be measured. Second, this temperature essentially eliminates the above issue of deactivation that occurs at higher temperatures. External mass transfer limitations were eliminated for each catalyst by choosing an appropriate flow rate (Fig. A.1).
Figure 4.3  Temperature program oxidation for fresh catalyst (gray), after reaction (black) showing coking and support (dashed curve) on: a) Pt/Cp-97, b) Pd/Cp-97, c) Ru/Cp-7 and d) Rh/Cp-97.

Also, the possible presence of internal mass transfer limitations was investigated using the Weisz-Prater criterion (Eq. A.1 [99, 100]), with calculations indicating that there were no pore diffusion limitations (details provided in Appendix A). The kinetics were modeled by a power rate law \( r_A = k[P_{AA}]^\alpha[P_{H2}]^\beta \), with Figures 4.4 and 4.5 showing ln(rA) plotted versus the mole fraction of AA and H\(_2\), respectively, for each of the catalysts. The slopes of the lines therefore indicate the reaction orders. The AA reaction order (\( \alpha \)) was found to be 0.21 ± 0.08, 0.09 ± 0.08, 0.36 ± 0.04 and 0.20 ± 0.04 for Pt, Ru, Rh and Pd, respectively. In the case of H\(_2\), the reaction order (\( \beta \)) was found to be 0.61 ± 0.12, 0.40 ± 0.08, 0.05 ± 0.04 and 0.23 ±0.07 for Pt, Ru, Rh
and Pd, respectively. There has not been much discussion about reaction orders for AA HDO in the literature. Rachmady and coworkers [45] determined reaction orders for AA (from 0.2-0.4) and H$_2$ (0.4-0.6) for Pt/TiO$_2$ at different conditions, which is similar to the reaction orders found here for Pt/Cp-97.

![Figure 4.4](image)

Figure 4.4 Power rate law for the kinetic dependencies of AA for activity at 200 °C and 1 atm pressure for 20% H$_2$. Total flow rates were 150 sccm for 5%Pt/Cp-97 (circles), 50 sccm for 5%Ru/Cp-97 (squares), 200 sccm for 5%Pd/Cp-97 (triangles) and 100 sccm for 5%Rh/Cp-97 (diamonds).

Also, for a single crystal Pt (111) hydrogenation at 97 °C, the reaction order for H$_2$ was found to be 0.5 [101]. A study on HDO of a microalgae-derived palmitic acid compound over 1% Pt/γ-Al$_2$O$_3$ in a microreactor reported reaction orders of ~1 for both α and β [102]. The low reaction orders for both reactants in the present case suggest relatively strong adsorption of acetic acid and H$_2$ on the metal surfaces based on a Langmuir-Hinshelwood adsorption assumption [103].
Figure 4.5  Power rate law for the kinetic dependencies of H2 for activity at 200 °C and 1 atm pressure and 1.1% AA. Total flow rates were 150 sccm for 5% Pt/Cp-97 (circles), 50 sccm for 5%Ru/Cp-97 (squares), 200 sccm for 5%Pd/Cp-97 (triangles) and 100 sccm for 5%Rh/Cp-97 (diamonds).

The temperature-dependence of the reaction rates was examined over the range 200-240 °C. Apparent activation energy values were extracted through an Arrhenius analysis, as shown in Figure 4.6. The apparent activation energy values were found to be 23.6 ± 2.8, 21.8 ± 2.0, 20.4 ± 1.5 and 20.3 ± 0.8 kcal/mol for Pt, Ru, Rh and Pd respectively. Rachmady et al. found an apparent activation energy for Pt/TiO2 of 11 kcal/mol, which not only depended on the product distribution but also on the AA and H₂ partial pressure [45]. The apparent activation energies for all catalyst in this study are similar, likely due to the fact that the main pathways at the temperature range are decarbonylation/decarboxylation reactions. Similar activation energies were observed for such pathways for the HDO of propanoic acid (PA) using Pd/C, with an activation energy of 16.7 ± 0.6, for a decarbonylation/decarboxylation
The HDO of acetic acid at 300 psig using NiMo/Al₂O₃ [104] exhibited an activation energy of 20.9 kcal/mol for a combination of hydrogenation, ketonization and decarboxylation/decarbonylation pathways. Activation energies based on the rates of product formation were also calculated, and are shown in Table 4.3.

![Graph showing Arrhenius apparent activation energies for various catalysts.](image)

**Figure 4.6** Arrhenius apparent activation energies for (circle) 5% Pt/Cp-97 (circles), 5%Ru/Cp-97 (squares), 5%Pd/Cp-97 (triangles), and 5%Rh/Cp-97 (diamonds).

**Table 4.3** Activation energy for individual products on Pt, Pd, Ru and Rh supported on Cp-97.

<table>
<thead>
<tr>
<th>Catalysts supported on Cp-97</th>
<th>$E_a$ methane (kcal/mol)</th>
<th>$E_a$ ethane (kcal/mol)</th>
<th>$E_a$ acetone (kcal/mol)</th>
<th>$E_a$ total (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%Pt</td>
<td>23.3</td>
<td>19</td>
<td>23.2</td>
<td>23.6</td>
</tr>
<tr>
<td>5%Pd</td>
<td>18.7</td>
<td>--</td>
<td>27.9</td>
<td>20.3</td>
</tr>
<tr>
<td>5%Ru</td>
<td>19.8</td>
<td>20.5</td>
<td>24.5</td>
<td>21.8</td>
</tr>
<tr>
<td>5%Rh</td>
<td>19.8</td>
<td>--</td>
<td>--</td>
<td>20.4</td>
</tr>
</tbody>
</table>
For Pt, the highest activation energy was from acetone and methane production (~23 kcal/mol), while for Pd and Ru, acetone was produced with the highest activation energy, and methane for Rh. Other studies have suggested that ketonization of AA have a greater activation energy (~38 kcal/mol, Ru/TiO$_2$) [105] than that of C-C cleavage (~16 kcal/mol, Ru (0001)) [106], which provides an explanation for the present observation.

4.4 Conclusion

In conclusion, it has been found that the main pathway for the gas-phase HDO of AA on carbon supported noble metals is decarbonylation, with decarboxylation only becoming significant at elevated temperatures (350-400 °C) for Pt, Rh and Pd. Over the entire temperature range, the main product was methane, although small quantities of ethane (from C-O bond cleavage and hydrogenation) and acetone (from ketonization) were detected. Kinetic measurements revealed AA reaction orders < 0.4 and H$_2$ reaction orders < 0.6, suggesting relatively strong adsorption of both reactants on these metals. This may suggest that there are different sites for adsorption, since two species cannot both be strongly adsorbed on the same site. In addition, the activation energies were very similar on all catalysts, ranging from 20-24 kcal/mol. Overall, the results suggest that these monometallic catalysts are too active for C-C bond cleavage, which results in the formation of undesired C$_1$ products rather than C$_2$ oxygenates. A strategy that we are pursuing is to add Sn as a second metal to these catalysts, with a view towards increasing selectivity towards oxygenate products through geometric and bifunctional bimetallic effects.
Chapter 5

Enhanced Ethanol Selectivity, Activity and Stability for the Catalytic HDO of Acetic Acid Using Tin-Platinum and Tin-Ruthenium Supported on Carbon at Mild Conditions

5.1 Introduction

Organic biomass generated by plants and animals has the potential to be used as a renewable energy source. When subjected to fast pyrolysis, which involves heating in the absence of oxygen, biomass produces a crude black liquid called bio-oil. A major component of this bio-oil are carboxylic acids. From these acids, acetic acid is the most abundant [20] and it can be catalytically hydrogenated to produce hydrocarbons and ethanol [107]. This overall process of converting highly oxygenated molecules into hydrocarbons is called hydrodeoxygenation (HDO). In the past, HDO has primarily been facilitated using monometallic heterogeneous catalysts [27, 45, 48, 49, 52]. These catalysts carry out different mechanistic pathways, which produce different selectivity and activity depending on the metal, support, and experimental set-up. For example, HDO of cresol (a biomass component) over a Pt/Al₂O₃ catalyst results in mainly methylhexane and methylhexanol, whereas platinum supported on mesoporous zeolite (Pt/ZM-5) produces mainly methylcyclohexane [108]. Another example is HDO of anisole, which produced different selectivity depending on the type of catalyst employed (e.g., Mo/Al₂O₃, Ni/SiO₂, Pt/Inconel, among others [109,
For the HDO of acetic acid, there have been a few studies using monometallic catalysts. Catalysts such as Pt [25], Ru and MoOx [52] have been using in the past. Also, in our previous work (Chapter 4) we saw that the main product for the HDO of acetic acid on Pt, Pd, Ru and Rh supported on activated carbon was methane. With these catalysts, the C-C bond tends to cleave promoting the decarbonylation and decarboxylation pathways. These pathways resulted in the formation of C₁ products.

Researchers have shown that bimetallic catalysts in hydrogenation reactions can be used to achieve unique pathways that may exhibit more desirable selectivity and/or activity for a target compound. For the HDO of acetic acid, it would be desirable to promote the hydrogenation pathway to produce ethanol. A common parent metal in bimetallic catalysts used for these reaction is platinum, which, by itself, generally affords low selectivity to ethanol [29, 51]. Thus, Pt does not favor the addition of hydrogen to carbon-oxygen bonds because of its high hydrogenolysis activity that produces H₂O, CO and CH₄. Rachmady and Vannice examined the bimetallic catalyst Pt-Fe/SiO₂ at different loadings [48]. They demonstrated that both platinum [45] and iron [27, 49] have high selectivity and activity to ethanol or acetaldehyde. Zhang et al. [29] added tin to platinum to produce a bimetallic catalyst. They prepared several PtSn catalyst supported on different materials (e.g., ZrO₂, TiO₂, SiC, SiO₂), and they found that a carbon nanotube-supported catalyst had the highest activity and selectivity to ethanol. In a more focused study, Zhang et al. [50] added Sn to Pt supported on Al₂O₃. They found that the addition of Sn in different molar ratios increased the selectivity towards ethanol. Another second metal that has been added to Pt/Al₂O₃ is indium [51], which resulted in enhanced acetic acid activity and ethanol selectivity by effectively eliminating the decarbonylation pathway. Onyestyak and co-workers [51] believe that In promotion results from the formation of an alloy phase or intermetallic platinum-indium compound. The change in selectivity and activity of a parent metal upon addition of a second metal can be attributed to several
different phenomena, typically classified as geometric, electronic, and bifunctional effects. The addition of a second metal that alters the size or shape of the active sites of the catalyst is classified as a geometric effect. The addition of a second metal that modifies the active site electronic properties by transferring electrons between the two metals is classified as an electronic effect. Finally, a bifunctional effect involves each individual metal carrying out different functions in the reaction mechanism [111]. An example of the geometric effect was demonstrated by Zhang et al. by adding different amounts of Sn to surface Pt in a SnPt/ZSM-5 structure for propane dehydrogenation. Zhang discovered that the addition of Sn decreased the size of Pt clusters on the catalyst surface, with the increased presence of surface Sn affording higher selectivity to propene. An optimal amount of Sn was determined that maximized the yield and selectivity of propene, although too much Sn reduced propane conversion [112]. The present study focuses on the hydrodeoxygenation (HDO) of acetic acid (AA) using Sn-bimetallic catalysts supported on carbon using 20%H<sub>2</sub>/He with a total pressure of 1 atm. These conditions differ from much of the relevant research on bimetallic catalysts for this reaction, in that they were conducted in a higher H<sub>2</sub> pressure range [29, 50, 113]. The parent metals chosen here are Pt and Ru, since they were the most active and stable monometallic catalysts investigated in our prior study (see Chapter 4). Molar compositions of SnPt, Sn<sub>2</sub>Pt, SnRu and Sn<sub>2</sub>Ru were thus compared to their monometallic Pt, Ru and Sn counterparts for comparison. The catalytic activity, stability, product selectivity, reaction kinetics, and activation energy for each catalyst were determined to better understand the reaction mechanism.

5.2 EXPERIMENTAL

5.2.1 CATALYSTS SYNTHESIS

The carbon support was an activated carbon from BASF (Cp-97 SBET=615m<sup>2</sup>/g). Two bimetallic SnPt/Cp-97 and two bimetallic SnRu/Cp-97 with different molar
ratios (Sn:M, 1:1 and 2:1 where M=Pt or Ru), and a 6%Sn/Cp-97, were synthesized by incipient wetness. The base catalysts for the bimetallic syntheses were Pt/Cp-97 and Ru/Cp-97 (both 5wt%) commercial catalysts from BASF. The precursor used for the synthesis of the 6%Sn/Cp-97 and the bimetallic catalysts was Tin (II) chloride dehydrate (SnCl\(_2\)-2H\(_2\)O). The catalysts were written as SnM for 1:1 ratio and Sn\(_2\)M for 2:1 ratio for Sn and Pt, respectively. M represent the base catalyst (i.e. Pt or Ru).

5.2.2 Catalyst Characterization

Temperature Program Reduction (TPR)

All catalyst samples were loaded in a custom reactor capable of performing temperature-programmed flow experiments. An Inficon Transpector 2 Mass Spectrometer was used to analyze gas composition as a function of time during temperature ramps. Temperature programmed reduction (TPR) of oxygen-pretreated SnPt, Sn\(_2\)Pt, SnRu and Sn\(_2\)Ru surfaces was conducted to know the temperature to be used for pulse chemisorption experiments. Samples were reduced at 400 °C (350 °C for 6%Sn) at a ramp rate of 10 °C/min for two hours in a stream of 10% H\(_2\)/balance in Ar (20 sccm) followed by a purge for one hour in flowing Ar (20 sccm) at the reduction temperatures. After that, samples were cooled to ambient temperature (40 °C) in flowing Ar and then exposed to a gas stream of 10% O\(_2\)/balance He for 30 minutes to cover each catalyst surface with a layer of chemisorbed oxygen atoms. Next, remaining gas O\(_2\) was removed flowing Ar for 30 minutes (until no O\(_2\) signal was seen). Finally, for the TPR experiment, 20 sccm of 10% H\(_2\)/balance in Ar was flowed from 25-450 °C at a ramp rate of 5 °C/min. Spectrum from 1 to 50 amu were recorded with a focus on H\(_2\) signal.
**Pulse H$_2$ Chemisorption**

The metal dispersions of the catalysts were determined by pulsed hydrogen titration of oxygen pre-covered sites using a Micromeritics 2920 AutoChem II Analyzer equipment. The bimetallic catalysts were reduced at 400 °C, at 350 °C for 6%Sn and 250 °C for 5%Pt and 5%Ru in 10% H$_2$ for two hours. Then, the gas was changed to argon to flush the hydrogen out for 1 hour, followed by cooling to 40 °C. For all the catalysts a flow of 50 sccm of 10% O$_2$/Ar was added and then 30 minutes of Ar to remove any O$_2$ (at 40 °C). Then, 10% H$_2$/Ar at 40 °C for Pt, at 250 °C for Ru (since there is no H$_2$ adsorption at 40 °C [83]), at 400 °C for SnRu, Sn$_2$Ru, Sn$_2$Pt and at 300 °C for SnPt (since at higher temperatures H$_2$ titrates O$_2$ evidenced by H$_2$-TPR found in the supporting information section) was added until there were no more uptake of H$_2$. This was repeated at least three times for reproducibility for each catalyst.

**X-ray Diffraction (XRD)**

X-ray diffraction (XRD) patterns were recorded using a Rigaku MiniFlex II diffractometer system with a D/tex Ultra detector with Cu Kα radiation (λ = 1.54 Å). Data were collected from 20-80° 2θ with a step size of 0.04° and a scan rate of 2°/min. XRD was used to determine if there were any particle size on the fresh and after reaction samples. Particle sizes were estimated using the Scherrer equation with PDXL 2 as a reference for instrumental broadening. For curve fitting, Rigaku’s Fityk 0.9.8 [114] was used for background subtraction and particle size measurement.

**X-ray Photoelectron Spectroscopy**

X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos AXIS Ultra DLD XPS system with a monochromatic Al Kα source operated at 15 keV and 150W, using a hemispherical energy analyzer. The X-rays were incident at an angle of 45° with respect to the surface normal. Analysis was performed at a
pressure below $1 \times 10^{-9}$ mbar. High resolution core level spectra were measured with a pass energy of 40 eV and analysis of the data was carried out using XPSPEAK41 software. The XPS experiments were performed while using an electron gun directed on the sample, for charge neutralization. The XPS system was equipped with a catalyst treatment cell directly attached to the analysis chamber. The catalysts were transferred in the catalysis cell from ultrahigh vacuum and back, without exposure to the atmosphere. The in-situ treatments in the cell were performed under flow conditions, of a 5% $H_2$/Ar for 2 hours at 200 °C for Pt and Ru, at 350 °C for Sn, SnPt and Sn$_2$Pt and at 400 °C for SnRu and Sn$_2$Ru.

5.3 Catalyst Evaluation

5.3.1 Acetic Acid Reaction

The HDO of acetic acid was carried out in a single pass, packed bed, plug flow reactor system [40, 84]. The catalysts were reduced in situ for 1 h at 250 °C for Pt, Ru, at 350 °C for Sn and at 400 °C for all the bimetallic catalysts studied. The concentration feed of AA (VWR, 99%) was 1.1% and 20% for $H_2$ balanced with He, with a total flow of 50 sccm. The total pressure was 1 atm. For the Temperature-dependence studies, the temperature studies were 200, 250, 300, 350 and 400 °C. For kinetic experiments, AA and $H_2$ mole fractions ranged from $X_{AA}$ ~0.0016-0.051 and $X_{H_2}$ ~0.20-0.99 at 200 °C, while the total flows ranged from 50-200 sccm to ensure no external mass transfer limitations for every catalysts (Figure B.1) and differential conversion (i.e. <10%). All products were analyzed by an in-line Hewlett-Packard 5890 gas chromatograph (GC) equipped with a flame ionization detector (FID) for analysis of organic products (including unreacted AA), and a thermal conductivity detector (TCD) for analysis of small gas molecules such as CO and CO$_2$. 
5.3.2 Acetaldehyde Reaction

The concentration feed of Acetaldehyde (VWR, 99%) was 4% and 20% H₂ balanced with He, with a total flow of 50 sccm. The reaction rates studies were done from 200-300 °C at a total pressure of 1 atm. The reaction was performed in the same reactor as with the acetic acid reaction.

5.4 Catalyst Characterization

5.4.1 X-ray Diffraction

X-ray diffraction patterns were acquired to determine the particle size of the fresh and after reaction samples for every catalyst. Figure B.2a summarizes all XRD peaks for: 5%Pt, 6%Sn, SnPt, Sn₂Pt and Cp-97 at the full spectrum studied, while Figure 5.1 shows a zoomed in region for 5%Pt, SnPt and Sn₂Pt. For the bimetallic catalysts there are two distinctive peaks that are missing from monometallic platinum, that is when 2θ is at around 41.5 ° and 43.8 °. Based results from Zhang et al. [29], those peaks arise from a PtSn phase (could be alloy in the bulk) (PDF Card No.: 00-025-0614 Quality: I). In both SnPt and Sn₂Pt, there are monometallic Pt, Sn, SnO₂ and PtSn phases (Table B.1). Table 5.1 summarizes average particle size from XRD and Table B.1 shows the distinctive phases that the Pt-based bimetallic catalysts contains. For 5%Pt the metal particle size is 3.0 nm. On the other hand, for the 6%Sn, the average particle size is large (16.4 nm), while this catalyst also contains three types of tin oxides: SnO, SnO₂ and Sn₃O₄ which particle sizes are big as well.
Figure 5.1  XRD zoom in profile showing the PtSn phase in the bulk for SnPt and \( \text{Sn}_2\text{Pt} \) at \( 2\theta = 41.5 \) and 43.8°.

Table 5.1  Summary of particle size using XRD for 5%Pt, 6%Sn, SnPt, Sn\(_2\)Pt, 5%Ru, SnRu and Sn\(_2\)Ru for the fresh and the after reaction catalysts.

<table>
<thead>
<tr>
<th>Catalyst supported on Cp-97</th>
<th>( D_v (\text{nm})^a )</th>
<th>( D_v (\text{nm})^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%Pt</td>
<td>3.0</td>
<td>3.5</td>
</tr>
<tr>
<td>6%Sn</td>
<td>16.4</td>
<td>10.7</td>
</tr>
<tr>
<td>SnPt</td>
<td>7.6</td>
<td>5.6</td>
</tr>
<tr>
<td>Sn(_2)Pt</td>
<td>5.4</td>
<td>5.6</td>
</tr>
<tr>
<td>5%Ru, SnRu &amp; Sn(_2)Ru</td>
<td>&lt;1.5</td>
<td>&lt;1.5</td>
</tr>
</tbody>
</table>

\( a^a \) Fresh sample  
\( b^b \) After reaction sample
Interestingly, when looking at the SnPt sample, the average particle size increased to 7.6 nm, although the Pt metal particle size is small (1.5 nm), the Sn and SnO₂ particles are considerably smaller than monometallic Sn, and the bulk PtSn phase is 11.7 nm. For the Sn₂Pt sample, the monometallic Sn, SnO₂ and Pt particles are about the same size than the SnPt sample, but the PtSn phase is half the size. It seems that the addition of Sn is helping disperse Pt on both catalysts [112]. For Ru in the bimetallic samples (Figure B.2b) the particle sizes must be very small (< 1.5 nm), since no associated peaks for Ru (expected at 2θ = 38.5, 42.3 and 44.1 °) are clearly visible in the raw patterns. In addition, no RuSn phase (e.g., Ru₃Sn₇ nanoclusters [115]) (highest peak expected at 2θ = 42 °) are observed. The addition of Sn to Ru does not increase the particle size of Ru, on the contrary, it keeps the Ru, Sn and SnO₂ particles very small (<1.5 nm). The combination of Ru and Sn creates a synergy that significantly decrease the possibility of particle aggregation.

5.4.2 H₂-Pulse Chemisorption

H₂-TPR on oxygen pre-covered sites was performed (Figure B.3) to determine the optimal temperature for the H₂-titration experiment for the bimetallic catalysts. H₂ titration of pre-covered oxygen was performed to obtain the dispersion in the monometallic and the bimetallic catalysts. There was no H₂ chemisorption for 6%Sn at any of the conditions that were studied, consistent with the literature observations for this metal [50]. For 5%Pt the pulse chemisorption was done in ambient temperature (40 °C) revealing a dispersion of 24%. There was no H₂ uptake for the bimetallic catalysts (Pt and Ru based) at ambient temperature, suggesting that Sn covers the base metal active sites. Thus, H₂-pulse chemisorption was performed at higher temperatures and are displayed in Table 5.2.
Table 5.2  Chemisorption dispersion with the corresponding H\textsubscript{2} titration conditions for: 5\%Pt, SnPt, Sn\textsubscript{2}Pt, 5\%Ru, SnRu and Sn\textsubscript{2}Ru.

<table>
<thead>
<tr>
<th>Catalyst on Cp-97</th>
<th>H\textsubscript{2}-Conditions (°C)</th>
<th>Dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Pt</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>SnPt</td>
<td>300</td>
<td>30</td>
</tr>
<tr>
<td>Sn\textsubscript{2}Pt</td>
<td>400</td>
<td>21</td>
</tr>
<tr>
<td>5% Ru</td>
<td>250</td>
<td>12</td>
</tr>
<tr>
<td>SnRu</td>
<td>400</td>
<td>11</td>
</tr>
<tr>
<td>Sn\textsubscript{2}Ru</td>
<td>400</td>
<td>10</td>
</tr>
</tbody>
</table>

For the SnPt sample, at 300 °C the dispersion of Pt was 30\%. This is significantly higher than that of the monometallic based catalyst (5\%Pt) since with the appropriate amount of Sn added to Pt, more Pt can be exposed in the surface [50, 112]. With further addition of Sn in the Sn\textsubscript{2}Pt catalyst, the opposite effect was observed, with the exposed Pt being less at 21\% dispersion. This is attributes to the Sn covering some active sites even after high temperature treatment, which is consistent with the available literature [112]. Ruthenium monometallic catalyst chemisorbs H\textsubscript{2} in pre-covered O\textsubscript{2} surface at 250 °C [83]. For both bimetallic catalysts, the H\textsubscript{2} pulse chemisorption temperature was 400 °C, with a metal Ru dispersion close to that of 5\% Ru. There is a disagreement between XRD and chemisorption for all the catalysts studied due to carbon decoration, explained in detail elsewhere [86]. This support (Cp-97) covers the metal particle sites, reducing exposure in the surface, thus the disagreement with XRD data.

5.4.3 X-ray Photoelectron Spectroscopy

The catalysts were characterized by X-ray Photoelectron Spectroscopy (XPS) after ex-situ reduction with H\textsubscript{2} in a furnace (fresh catalysts in Fig. B.4) and after in-situ
reduction with $\text{H}_2$ in a catalysis cell, attached to the XPS system (reduced catalysts). Since the catalytic evaluation for the hydrogenation of acetic acid was performed on the reduced catalysts, their chemical state after in-situ reduction, was the focus of our study. For the reduced 5\%Pt sample in Figure 5.2a, the Pt 4f spectrum peak consists of two peak components (which have doublets), recorded at 71.3 eV and 74.5 eV Binding Energy (BE), which are consistent with the presence of metallic platinum and oxidized Pt (IV) \[87, 116\], respectively. After in-situ reduction of the SnPt and Sn$_2$Pt catalysts, there is no oxidized Pt on the surface and a very slight shift in the BE of the Pt 4f peak of the metallic state at 71.6 eV can be observed. This suggests only a weak (if any) electronic interaction between the two metals \[117\].

Following the oxidation state of tin (Figure 5.2b) on 6\%Sn, SnPt and Sn$_2$Pt catalysts, it was found that the Sn 3d spectrum can be deconvoluted into two peaks at around 485.0 eV and 485.9 eV BE for all catalysts. The higher BE peak (485.0 eV) can be assigned to metallic tin (Sn$^0$) \[116\] and the 485.9 eV peak can be attributed to Sn (IV) or Sn (II) \[118\]. This data shows that even in a reductive environment, Sn is not completely reduced, which is in agreement with previously reported work \[113\].

However, following the contribution of each Sn state in the Sn 3d spectrum Table 5.3, it is observed that after in-situ reduction, the ratio of metallic to oxidized tin on the catalyst increases from 60\% (6\%Sn sample) to 69\% on Sn$_2$Pt and 75.0\% for SnPt. This observation leads to the conclusion that the amount of Pt on the surfaces contributes to the amount of metallic tin that is recorded by XPS after reduction. Thus, the high $\text{H}_2$ dissociation ability of Pt to produce atomic hydrogen facilitates the reduction the tin oxide on the surface. This suggests an intimate bimetallic interaction between Pt and Sn, as will be confirmed in the catalytic evaluation. Table 5.4 presents the Pt/Sn surface atomic ratio as measured by XPS. It is observed that the Pt/Sn ratio increases after reduction for both SnPt and Sn$_2$Pt. This can be explained by diffusion of tin towards the bulk of the nanoparticles \[112\].

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Figure 5.2  XPS data for oxidation states of 6%Sn, SnPt and Sn₄Pt, b) Sn 3d spectra (6%Sn, SnPt and Sn₄Pt), b) Ru 3d spectra (5%Ru, SnRu and Sn₂Ru) and d) Sn 3d spectra (6%Sn, SnRu and Sn₂Ru). Blue represent the metal, magenta represent the oxides and garnet represents a Sn-based phase.
Table 5.3  XPS data for oxidation states of 6%Sn, SnPt, Sn$_2$Pt, SnRu and Sn$_2$Ru.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fresh Sample</th>
<th>In-situ reduction</th>
<th>Fresh Sample</th>
<th>In-situ reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MO$_2$</td>
<td>M°</td>
<td>MO$_2$</td>
<td>M°</td>
</tr>
<tr>
<td>6%Sn/Cp-97</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>SnPt/Cp-97</td>
<td>29%</td>
<td>71%</td>
<td>0%</td>
<td>100%</td>
</tr>
<tr>
<td>Sn$_2$Pt/Cp-97</td>
<td>14%</td>
<td>86%</td>
<td>0%</td>
<td>100%</td>
</tr>
<tr>
<td>6%Sn/Cp-97</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>SnRu/Cp-97</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
<td>100%</td>
</tr>
<tr>
<td>Sn$_2$Ru/Cp-97</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
<td>100%</td>
</tr>
</tbody>
</table>

M- Pt or Ru

Table 5.4  Pt/Sn and Ru/Sn ratios for fresh and in-situ reduced samples of SnPt, Sn$_2$Pt, SnRu and Sn$_2$Ru.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fresh Sample</th>
<th>In-situ reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M/Sn</td>
<td>M/Sn</td>
</tr>
<tr>
<td>SnPt/Cp-97</td>
<td>0.22</td>
<td>0.57</td>
</tr>
<tr>
<td>Sn$_2$Pt/Cp-97</td>
<td>0.18</td>
<td>0.63</td>
</tr>
<tr>
<td>SnRu/Cp-97</td>
<td>0.38</td>
<td>0.33</td>
</tr>
<tr>
<td>Sn$_2$Ru/Cp-97</td>
<td>0.30</td>
<td>0.33</td>
</tr>
</tbody>
</table>

M- Pt or Ru

Figure 5.2c shows the BE of Ru 3d peak for 5%Ru, SnRu and Sn$_2$Ru catalysts. The BE of 280.4 eV is attributed to the presence of metallic Ru (Ru°) [91], while the 279.5 eV peak corresponds to a bimetallic SnRu phase [119], representing (unike for Pt) a clear electron transfer from Sn to Ru [119, 120]. Figure 5.2d shows the Sn 3d peaks obtained by XPS for the 6%Sn, SnRu and Sn$_2$Ru catalysts. Again, the Sn 3d peak at lower BE peak (485.0 eV) corresponds to metallic Sn, while the second peak (486.5 eV) corresponds to Sn (IV). By following the contribution of each Sn state in the Sn
3d spectrum Table 5.3 for those catalysts, it is observed that after in-situ reduction, the ratio of metallic tin on the catalyst increases from 56% (6%Sn sample) to 66.0% (SnRu sample) and only to 52% in the Sn<sub>2</sub>Ru sample. This observation leads to the conclusion that the amount of Ru on the surfaces contributes to the reduction of tin, but when Sn is in excess (2:1 Sn:Ru) the oxide reduction is less. The bimetallic effect again can be explained, by considering the high H<sub>2</sub> dissociation probability by Ru to atomic hydrogen, which can then reduce the tin on the surface. In Table 5.4 it is observed that the Ru/Sn surface atomic ratio as measured by XPS is almost constant, before and after reduction, for both SnRu and Sn<sub>2</sub>Ru catalysts. This observation leads to the conclusion that that there are few (if any) geometric differences on SnRu bimetallic catalysts before and after reduction. Thus, a strong electronic interaction and possible bifunctional effects might be expected in the catalytic evaluation.

5.4.4 Catalytic Evaluation of Tin-Platinum and Tin-Ruthenium

Temperature-dependent conversion and selectivity plots for the Pt-based catalysts are shown in Figure 5.3. The selectivity is on the left Y-axis and is represented by bars, the ratio of CO production to the sum of CO and CO<sub>2</sub> production (if there is decarbonylation reaction) is on the right Y-axis and is represented by open circles, and conversion is indicated on the top X-axis. For the Pt-based catalysts, the highest conversions over all temperatures were observed for the monometallic 5%Pt, followed by SnPt, Sn<sub>2</sub>Pt and finally 6%Sn. As seen in the literature [29], for 5%Pt (Fig. 5.3a), methane is the most selective product through the temperature range since it is easy for the C-C bond of acetic acid to cleave over Pt (refer to 4 for more details). The main pathway for the entire temperature range for this catalyst is decarbonylation followed by ketonization (with the production of acetone), with only some decarboxylation and hydrogenation. At 300 °C there is a trace amount of ethanol.
Figure 5.3  Temperature-dependent conversion and selectivity for HDO of AA on: a) 5%Pt, b) 6%Sn, c) SnPt and d) Sn$_2$Pt. (Black) methane, (blue) ethane, (orange) ethanol, (green) acetone, (red) acetaldehyde, (gray) ethyl acetate and (black circle) CO ratio on the Y-right axis.

For 6%Sn (Fig. 5.3b), the selectivity is mostly towards acetaldehyde, acetone and some methane, making the hydrogenation pathway the dominant pathway from 250-400 °C (there is no measurable activity at 200 °C). As the temperature increases, the selectivity increases for acetone and decreases for acetaldehyde, until at 400 °C, there is around 45% selectivity towards acetaldehyde and around 40% towards acetone, with the rest being methane. Thus, the selectivity trend and activity are very different from that of 5%Pt. For SnPt (Fig. 5.3c) from 200-350 °C there is significant selectivity towards ethanol, which was not present with 6%Sn and only showed up in a trace amount at 300 °C in 5%Pt. From 200-250 °C the main pathway was hydrogenation
producing ethanol, followed by acetaldehyde (a likely intermediate product). In this
temperature range there was also some ethyl acetate (ethanol reacting with AA) [29]
and some methane from the decarbonylation pathway. Similar studies were conducted
by Zhang et al. where they tested several PtSn bimetallic catalysts supported on
alumina at 275 °C with a pressure of 2MPa and a H₂/AA ratio of 10 and a LHSV=0.6 h⁻¹ [50]. A comparable catalyst to our SnPt/Cp-97 is their 10Pt10Sn/Al₂O₃ catalyst,
where the selectivity towards ethanol was 54%, ethyl acetate 38%, acetaldehyde 1%,
methane 4% and ethane 1%. This was the highest ethanol selectivity for any catalyst
studied at 275 °C, and very similar to our results although their pressure was higher.
When the temperature goes higher (350-400 °C) the selectivity trend looks more
like a combination of monometallic 6%Sn and 5%Pt since H₂ reduction helps the
development of metal Sn and Pt on the surfaces. For Sn₂Pt (Fig. 5.3d) at 200 °C
the main product is ethanol with trace amounts of ethyl acetate formed. Ethanol is
only produced from 200-300 °C, since as the temperature increases, ethanol decreases
and acetaldehyde increases until there is no ethanol produced. This suggest that
ethanol and acetaldehyde are produce from different pathways, more on this will be
discussed at a later section. At higher temperatures (350-400 °C) acetone starts to
be produced with acetaldehyde and methane, looking more like monometallic 6%Sn.
Zhang et al. argue [50] that the formation of a PtSn phase (perhaps an alloy) and Pt-
SnOₓ species prevent significant Pt monometallic sites on the surface. They therefore
attribute the high ethanol selectivity at lower temperatures to the presence of PtSn
and Pt-SnOₓ. Our XRD and XPS experiments provide proof about SnOₓ presence
and an XPS peak at 76.4 eV that might be that of a PtSn phase on (or near) the
surface. One hypothesis by Homs et al. is that the C=O bond of AA adsorbs
on the SnOₓ moieties that act as electrophilic or Lewis acid sites to improve the
hydrogenation of the AA carbonyl group [121]. Also, Zhang et al. suggests that the
formation of PtSn "alloy" [50] could change the electronic properties of Pt through a
decrease in the Pt ensemble size at the surface (geometric effect). This in turn might retard the C-C and C-O bond cleavage that forms methane and ethane. However, the XPS evidence in our work shows only a very weak electronic effect at best, so a primarily geometric effect is more likely. Also, as the temperature increases, the amount of ethanol decreases because more Pt sites are exposed on the surface (thus negating the lower temperature geometric ensemble effect), as was implied by the H₂ pulse chemisorption experiments. These differences in selectivity between the SnPt and Sn₂Pt and the parent Pt catalyst further agree with the XPS data, and suggest that a bifunctional effect is taking place. Indeed, the selectivity at low temperatures from the bimetallic catalysts is completely different from the monometallic catalyst, strongly suggesting this effect.

For Ru-based bimetallic catalysts, the order of activities (based on conversion) was Ru>SnRu~Sn₂Ru>Sn. For 5%Ru in Figure 5.4a (more details in Chapter 4) the main product was methane from the whole temperature range, and this is due to Ru promoting C-C bond cleavage [28, 97]. The main pathway is decarboxylation, ketonization and hydrogenation (ethane) from 200-250 °C. At higher temperatures the main pathway is decarbonylation. The selectivity using SnRu (Fig. 5.4b) changes generally to acetaldehyde through the whole temperature range. At 200 °C, the main product is acetaldehyde followed by methane and some ethyl acetate. At 250 °C the main pathway is hydrogenation with acetaldehyde as the main product, followed by ethanol (~28%), then esterification forming ethyl acetate, decarbonylation forming methane and some traces of acetone through ketonization. For Sn₂Ru (Fig. 5.4c) the same trend is observed with the hydrogenation pathway dominating the temperature range, but this time with less methane and acetone. Also, this is the only catalyst that shows ethanol being produced over the entire temperature range, although the selectivity is less than 20% at all of the temperatures. Like with the Pt-based bimetallic catalysts, ethanol production reduces as the temperature increases since Ru and
Sn are more present in the surface. The addition of Sn to Ru catalysts forms a RuSn phase as seen with XPS.

Figure 5.4 Temperature-dependent conversion and selectivity for HDO of AA on: a) 5%Ru, b) SnRu and c) Sn$_2$Ru. (Black) methane, (blue) ethane, (orange) ethanol, (green) acetone, (red) acetaldehyde, (gray) ethyl acetate and (black circle) CO ratio on the Y-right axis.

This is likely responsible for the change in selectivity of SnRu and Sn$_2$Ru, as has been observed for similar catalysts during hydrogenation of furfurals [119]. From the literature [115], we know that the SnO$_x$ and RuSn phase improve the hydrogenation pathway. The stability of the bimetallic catalysts was tested and can be seen in Figure fig5:p2. The activity was measured in TOF (1/min) based of the chemisorption estimates of site densities at 200 °C, then 300 °C, 200 °C, 300 °C, 400 °C, 300 °C and finally back to 200 °C to see if the activity changed at 200 °C when going back and
forward to higher temperatures. For every Pt and Ru bimetallic catalyst, the TOF remained relatively constant through this experiment. At 400 °C these catalysts seem to deactivate, but it does not affect the activity when going back to 200 °C. When looking at the particle size using XRD in Table 5.1, it was revealed that the particle size of these catalyst did not increase dramatically, including those of the PtSn phase. Therefore, sintering is not an issue when adding Sn to Pt or Ru. Also, it seems that the PtSn[29, 50, 122] and RuSn [119] phases stabilize the corresponding catalysts.

Figure 5.5 Activity measurements as TOF (1/min) at 1) 200 °C, 2) 300 °C, 3) 200 °C, 4) 300 °C, 5) 400 °C, 6) 300 °C and 7) 200 °C for SnPt, Sn2Pt, SnRu and Sn2Ru. Red bars (200 °C) are 10 times the original activity value.

When comparing the TOF at (200 °C since at this temperature the measured conversions are differential (i.e., < 10%)) the activity trend goes as follows: Sn2Ru > SnPt ~ Sn2Pt ~ SnRu at 200 °C.
5.4.5 Ethanol Formation

Figure 5.6 shows the reaction rate of ethanol from the acetaldehyde reaction and acetic acid reaction. This plot shows that acetaldehyde as an intermediate from the hydrogenation of acetic acid to form ethanol for SnPt and Sn$_2$Pt is highly unlikely.

![Graph showing ethanol reaction rates](image)

Figure 5.6  Ethanol reaction rate from the acetaldehyde reaction and ethanol reaction rate from the acetic acid reaction for Pt, Ru, SnPt, Sn$_2$Pt, SnRu and Sn$_2$Ru from 200-300 °C. The concentration of acetaldehyde was 4% and that of acetic acid 1%. For both reaction the hydrogen content was 20%/He.

However, Luo et al. shows that for the SnRu catalysts, ethanol is produced from the hydrogenation of acetaldehyde [115]. Liu et al. did a DFT study of acetic acid hydrogenation on Cu$_2$In (100) [123] and found different possible intermediates that could then produce ethanol. The most favorable step involved acetaldehyde as an intermediate. However, intermediates coming from bond formation and bond breaking of acetic acid such as hydroxyalkyl $\rightarrow$ hydroxy-ethyldyne $\rightarrow$ 1-hydroxyethyl...
to ethanol, could be the steps to forming ethanol from Pt-based bimetallic catalyst. DFT studies on the catalysts studied here should be performed to see if this is the case, but our experimental results suggest that acetaldehyde is not an intermediate to form ethanol in the Pt-based bimetallic catalysts.

5.4.6 Reactant Kinetics and Apparent Activation Energy Studies

Reactant reaction order studies were conducted at 200 °C since it allowed the reaction to be carried out at very low differential conversion, ensuring that true kinetics could be measured. The concentration of AA or hydrogen was changed, while holding all other parameters constant. External mass transfer limitations were eliminated for each catalyst by choosing an appropriate flow rate from 50-200 sccm (Fig. B.1). Internal mass transfer limitation calculations were performed using the Weisz-Prater criterion discussed elsewhere [99, 100] and in Appendix A, with values of 8.26x10^-2, 5.22x10^-2, 8.10x10^-3 and 1.11x10^-1 found for SnPt, SnPt, SnRu and SnRu, respectively. Since these values are significantly less than 0.3, it is concluded that there were no pore diffusion limitations at these conditions. The kinetics were modeled by a power rate law \( r_A = k[P_{AA}]^\alpha[P_{H_2}]^\beta \). Figures 5.7a and 5.7b showing ln(rA) plotted versus the mole fraction of AA and H\(_2\), respectively, for each Pt-based catalyst. The slopes of the lines indicate the reaction orders of each reactant. The AA reaction order (\( \alpha \)) was found to be 0.21 ± 0.08, 0.22 ± 0.04 and 0.11 ± 0.05 for Pt, SnPt and SnPt, respectively. For H\(_2\), the reaction order (\( \beta \)) was found to be 0.61 ± 0.12, 0.36 ± 0.09 and 0.43 ± 0.09 for Pt, SnPt and SnPt, respectively. The addition of Sn did not have much impact on either of the AA or H\(_2\) reaction orders. The low reaction orders might suggest that there are different sites of adsorption, since two species should not be strongly adsorbed on the same site.
Figure 5.7  Power rate law for the kinetic dependencies of AA (20% H2/balance) for: a) 5%Pt, SnPt and Sn$_2$Pt and c) 5%Ru, SnRu and Sn$_2$Ru and for the kinetic dependencies of H$_2$ (1.1% AA) for: b) 5%Pt, SnPt and Sn$_2$Pt and d) 5%Ru, SnRu and Sn$_2$Ru. Reactor conditions: 200 $^\circ$C and 1 atm pressure. Total flow: 5%Pt-150 sccm, PtSn-50 sccm, Sn$_2$Pt-200 sccm, 5%Ru-50 sccm, SnRu-200 sccm and Sn$_2$Ru-200 sccm.

For Ru-based catalysts (Fig. 5.7c), the AA reaction order was 0.09 ± 0.09, 0.03 ±0.10 and 0.20 ± 0.04 for Ru, SnRu and Sn$_2$Ru, respectively. Like with Pt-based bimetallic catalysts, the low reaction orders suggest strong adsorption of AA on these catalysts. For H$_2$, the reaction order (Fig. 5.7d) was as follows: 0.40 ± 0.08, 0.95 ± 0.13 and 0.97 ± 0.14 for Ru, SnRu and Sn$_2$Pt, respectively. The addition of Sn made the reaction order increase to ~1, suggesting that the H$_2$ adsorption has weakened significantly.

Apparent activation energy experiments were examined over the range 200-240
These values were obtained through an Arrhenius analysis, as shown in Figure 5.8.

![Arrhenius plots](image)

Figure 5.8 Arrhenius apparent activation energies for a) 5%Pt, SnPt and Sn$_2$Pt and c) 5%Ru, SnRu and Sn$_2$Ru.

For Pt-based catalysts (Fig. 5.8a) the apparent activation energy (Ea) values were found to be 23.6 ± 2.8, 16.6 ± 2.0 and 13.3 ± 0.8 kcal/mol for Pt, SnPt and Sn$_2$Pt, respectively. In Figure 5.8b, Ea values equal to 21.8 ± 2.0, 20.4 ± 2.8 and 14.6 ± 0.6 kcal/mol were found for Ru, SnRu and Sn$_2$Ru, respectively. Thus, for both catalyst families, the addition of Sn decreases the overall apparent activation energies. For the HDO reaction of AA there is not much literature in activation energies.
especially in bimetallic catalyst. However it is known that Ea values depends on product distribution and reactant partial pressures [45].

5.5 Conclusion

In conclusion, the addition of Sn to Pt and Ru helps improve the activity, selectivity towards ethanol and stability at the studied conditions. As the temperature increases, for all the bimetallic catalysts, the selectivity towards ethanol goes down. Characterization methods such as XPS and XRD with temperature dependence experiments shows that there is a PtSn (for SnPt and Sn$_2$Pt) and a RuSn (for SnRu and Sn$_2$Ru) phase that with SnO$_{x}$ that is assumed to helps the production of oxygenated products such as ethanol from 200-300 °C. Also, XPS data shows that Pt-based bimetallic catalyst has strong bifunctional and geometrical effects, while weak electronic effect. On the contrary, for Ru-based catalyst it was shown that it contains strong electronic and bifunctional effects, while no geometrical effect. The comparison between the acetaldehyde reaction and acetic acid reaction suggest that for SnRu and Sn$_2$Ru there is an acetaldehyde intermediate that hydrogenates to produce ethanol. On the other hand, for SnPt and Sn$_2$Pt there is another intermediate involved rather than acetaldehyde. Kinetic experiments showed that AA reaction orders and H$_2$ reaction orders for Pt-based bimetallic catalysts were small, suggesting different sites for adsorption. For Ru-based catalysts however, the AA reaction order were low, but those of H$_2$ ~1, suggesting a strong adsorption from AA and not from H$_2$. Also, the activation energy reduces with the addition of Sn when comparing with the parent metal.
Chapter 6

Phosphorous Diffusion Through Nickel

Phosphide—Low Energy Diffusion Path and its Unique Local Structure

6.1 Abstract

Phosphorous (P) diffusion in bulk Ni$_2$P was investigated by density functional theory (DFT) to find the origin of the low temperature P diffusion into the surface. The Ni$_2$P bulk structure consists of two types of layers, Ni$_3$P$_2$ and Ni$_3$P stacked along the $[0001]$ direction. Two types of P vacancies in Ni$_2$P were studied: V$_{1P}$ (P deficient in Ni$_3$P$_2$), and V$_{2P}$ (P deficient in Ni$_3$P). V$_{1P}$ was a somewhat more stable point defect than V$_{2P}$ by 0.20 eV. The P diffusions to vacancies (V$_{1P}$ and V$_{2P}$) had large diffusion barriers of more than 1 eV, except the P diffusion path along $[0001]$ direction through an interstitial site in Ni$_3$P$_2$ ($I_{1\rightarrow2}$) and then to V$_{1P}$ which showed the lowest energy barrier of about 0.18 eV. The DFT calculations suggested that the two adjacent vacancies (both V$_{1P}$) allow the local rearrangement of the structure to form a tetrahedral structure at the intermediate state. We have proposed a new diffusion mechanism in the intermetallic compound named interstitial-vacancy diffusion mechanism.

6.2 Introduction

Ni$_2$P is an intermetallic compound whose bonding has covalent, ionic and metallic character and shows unique properties especially in catalysis. Over the past decade,
the catalysis of Ni$_2$P has been investigated for a variety of industrially important reactions, including hydrodesulfurization (HDS) [53, 54, 58, 124–127], hydrodenitrogenation (HDN) [53, 128], hydrodeoxygenation (HDO) [55–57] and the electrocatalytic hydrogen evolution reaction (HER) [59, 129]. Although operando spectroscopies have provided information about the catalytic active sites [124, 126, 130, 131] the detail structure and activity relation requires surface scientific investigation using single crystal surfaces and surface science techniques such as XPS, LEED, STM and DFT [61–64, 132–145]. The Ni$_2$P single crystal surfaces showed interesting features [145]. The phosphorus-poor surface created by Argon sputtering recovers original Ni$_2$P stoichiometry by diffusion of phosphorus at low temperature (177 °C) [64]. Further high temperature annealing induced the segregation of the phosphorus to produce a phosphorus-rich well-defined reconstructed surface [61–63, 145]. The surface-segregated phosphorus atom termination stabilizes the reconstructed surfaces, which is related to the reduction of the density of state at the Fermi level by the P adsorption on the Ni dangling bond [62, 63]. The P segregation and the P diffusion to the surface occur from the bulk at relatively low temperature (~177 °C). However, little is known about diffusion in bulk Ni$_2$P. The diffusion of atoms through materials is mainly discussed in three mechanisms [146]: interstitial, vacancy and interstitialcy mechanism. The interstitial mechanism requires a large diffusion barrier and occurs at the higher temperature. Vacancy model is the easiest way for the diffusion. However, in Ni$_2$P the simple vacancy model rarely occurs because the P vacancy is only surrounded by Ni atoms. In binary compounds, another vacancy diffusion process called the ”six-jump cycle mechanism” has been proposed for vacancy diffusion (See Fig. C.1 in Appendix C) [147, 148]. To understand the low temperature P diffusion in Ni$_2$P the diffusion process was investigated by density function theory (DFT) calculations. The present work provides a new insight on P low temperature diffusion where intermediate interstitial structure is stabilized by the local reconstruction
to create tetrahedral structure around Ni atoms that reduces the activation energy tremendously.

6.3 Computational Method

The DFT calculations were performed using the Vienna ab initio Simulation Package code (VASP 5.4.1) [71, 72]. The Perdew-Burke-Ernzerhof exchange-correlation functional with a generalized gradient approximation was used [73, 74]. Projector-augmented wave approach [75, 76] has been used together with plane wave basis sets with a 4x4x4 k-points mesh Brillouin-zone integration to obtain the optimized structures and a 8x8x12 k-points mesh for the density of state (DOS) calculation. Spin-polarized calculations were performed for all the systems with an energy convergence tolerance of 1x10^{-8} eV/atom. The density of states for α and β spins did not show any differences, and thus the spin effect on diffusion was not discussed in this paper. The transition and intermediate steps were analyzed with the climbing-image nudged-elastic-band (cNEB) method [77]. The optimized bulk Ni$_2$P lattice constants were a = b = 0.589 nm, c = 0.337 nm, α = β = 90°, γ = 120°. These are consistent with the previous work (Table C.2) [64, 132, 138]. The unit cell was increased to a 2x2x3 supercell with a = b = 1.178 nm, c = 1.011 nm for the present studies. The formation energies for each structure are defined as:

$$E_f^i(Ni_{72}P_{35}) = E_{tot}(Ni_{72}P_{35}) + \frac{1}{4}E_{tot}(P_4) - E_{tot}(Ni_{72}P_{36})$$  \hspace{1cm} (6.1)

where $E_{tot}$ (Ni$_{72}$ P$_{35}$), $E_{tot}$ (Ni$_{72}$ P$_{36}$) and $E_{tot}$ (P$_4$) are the total energies for the supercell with a phosphorus vacancy, of the perfect Ni$_2$P and a gas-phase P$_4$ molecule, respectively.
6.4 Results and Discussion

6.4.1 Stable Structures of P Vacancies

The Ni$_2$P crystal has a space group $P6_2m$ [149]. Figure 6.1a illustrates the Ni$_2$P of (2x2x3) supercell. Two types of layers are alternatively stacked along the [0001] direction; one is called as "Ni$_3$P$_2$ layer" (Figure 6.1b) and the other is "Ni$_3$P layer" (Figure 6.1c).

![Figure 6.1 Ni$_2$P Structure: a) supercell containing 72 Ni and 36 P atoms, b) Ni$_3$P$_2$ layer with tetrahedral structure, c) Ni$_3$P layer with square-base pyramid, d) vacancy in Ni$_3$P$_2$ layer and e) Ni$_3$P layer. Local structure with the corresponding P and Ni for: f) Perfect structure, g) V$_P^1$, h) V$_P^2$. Diffused P is in red, Ni$_3$P$_2$ and Ni$_3$P vacancies are in pink and orange dotted circles, respectively.](image)

The coordinates of all atoms are listed in Table C.1 in the supporting information. A
set of different Ni and P sites in each layer are named Ni(1) and P(1) (blue and pink spheres in Fig. 6.1b) for the Ni$_3$P$_2$ layer and Ni(2) and P(2) (green and orange spheres in Fig. 6.1c) for the Ni$_3$P layer. Nickel atoms in the Ni$_3$P and Ni$_3$P$_2$ layers have different local structures. Ni(1) in Ni$_3$P$_2$ layer has a near-tetrahedral P coordination while Ni(2) in Ni$_3$P has a square-base pyramidal P coordination, as shown in Figs. 6.1b and c. The Ni-P distances in crystallographic data were well reproduced by DFT calculations shown in Table C.3. Since sputtering selectively removes P [64], the discussion in this paper is only about P vacancy and P diffusion. There are two types of P vacancies in Ni$_2$P: V$_{P1}$ (P(1) deficient, pink dotted circle in Figure 6.1d) and V$_{P2}$ (P(2) deficient, orange dotted circle in Figure 6.1e). The formation energies in Table 6.1 show that the V$_{P1}$ was energetically more favorable than V$_{P2}$ by 0.20 eV.

Table 6.1  Defect formation energy and relative energy barrier for structures.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formation energy/ eV</th>
<th>Relative energy / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$_{P1}$</td>
<td>1.25</td>
<td>-</td>
</tr>
<tr>
<td>V$_{P2}$</td>
<td>1.45</td>
<td>0.20</td>
</tr>
<tr>
<td>T$_{P1}$</td>
<td>3.06</td>
<td>1.81</td>
</tr>
<tr>
<td>T$_{P2}$</td>
<td>4.33</td>
<td>3.08</td>
</tr>
<tr>
<td>T$_{P1}$</td>
<td>1.43</td>
<td>0.18</td>
</tr>
<tr>
<td>T$_{P2}$</td>
<td>6.31</td>
<td>5.06</td>
</tr>
<tr>
<td>T$_{SP1}$</td>
<td>3.06</td>
<td>1.81</td>
</tr>
</tbody>
</table>

The local structures of the perfect Ni$_2$P structure and vacancies (V$_{P1}$, V$_{P2}$) are shown in Figure 6.1f, 6.1g and 6.1h, respectively. Numbers at subscripts were given to identify the different Ni and P sites, while the number in parentheses indicated the different types of Ni and P in Ni$_3$P$_2$ and Ni$_3$P layers. Removal of the P$_{20}$ (1) atom generates the vacancy, V$_{P1}$, as shown in Figure 6.1g. Figure C.2 shows the displacement directions of the Ni atoms around the vacancy. The vacancy was surrounded by
9 Ni atoms. The three Ni in the lower Ni$_3$P (in this case Ni$_{16,17,18}(2)$) and the three Ni atoms in the upper Ni$_3$P layer (Ni$_{40,41,42}(2)$) moved away from the vacancy V$_1^P$, as shown in Figure C.2. The three Ni atoms in the same plane (Ni$_3P_2$; Ni$_{37,38,39}(1)$) also moved away from the V$_1^P$, although only a small degree. Interestingly, Ni(2) atoms around the V$_1^P$ which originally had the square-base pyramid geometry became a near-tetrahedral (tetrahedrality was 0.028 discussed later). In contrast, the V$_2^P$ (Figure 6.1h) that is created by the lack of P(2) showed smaller displacements than 0.1 Å of the Ni(2) (the same layer) or Ni(1) in adjacent layers (Table C.4). The most significant displacement was the Ni$_{40}(2)$ where Ni$_{40}(2)$-P(1) distances reduced to 2.42 Å from 2.47 Å. The $I^P_1 \rightarrow 1$ and $I^P_2 \rightarrow 2$ were unstable with a relative energy of 1.81 eV and 3.08 eV, respectively. Since the relative energies are so high, in-plane diffusions are less likely. The shortest distances between the diffusing P and the surrounding P atoms in the intermediate states are 3.20 Å and 2.41 Å for $I^P_1 \rightarrow 1$ and $I^P_2 \rightarrow 2$, respectively, which are smaller than the sum of van der Waals radius and result in the large diffusion barrier. Other P-P distances ($d_{pp}$) are summarized in the supporting information (Table C.5).

6.4.2 In-plane Diffusion

First, we considered the in-plane diffusion of P. The intermediate states of P diffusion to the V$_1^P$ or V$_2^P$ were denoted as $I^P_1 \rightarrow 1$ and $I^P_2 \rightarrow 2$, shown in Figures 6.2a and 6.2b, respectively, which corresponded to the interstitial sites surrounded by Ni atoms. Red balls in these figures are diffusing P atoms which are denoted as P(1’) and P(2’) hereafter.

6.4.3 Inter-plane Diffusion

Three phosphorus inter-plane (or interlayer) diffusion paths between P(1) and P(2) were considered for this work. One type of interlayer diffusion path is the P vertical
diffusion along [0001] direction from P(1) and P(2) site to another corresponding P site, denoted as $I^P_{1\rightarrow 2}$ and $I^P_{2\rightarrow 1}$, respectively.

Figure 6.2  a)Intermediate state P diffusion in Ni$_3$P$_2$  b)intermediate state P diffusion in Ni$_3$P  c)intermediate state P diffusion from Ni$_3$P$_2$ to Ni$_3$P  d)intermediate state P diffusion from Ni$_3$P to Ni$_3$P$_2$. Diffused P is in red, Ni$_3$P$_2$ and Ni$_3$P vacancies are in pink and orange doted circles, respectively. Local structure with the corresponding P and Ni for: e)$I^P_{1\rightarrow 2}$, f)TS$^P_{2\rightarrow 1}$ and g) cNEB diffusion energy barrier for TS$^P_{2\rightarrow 1}$ and $I^P_{2\rightarrow 1}$ (with a zoom in of the $I^P_{1\rightarrow 2}$). Arabic numbers represent the points and diffusion path of TS$^P_{2\rightarrow 1}$, Roman number indicates the points and diffusion path of $I^P_{1\rightarrow 2}$ (see Fig. C.1).

The energy difference between the initial state $V^P_2$ and the intermediate state
$I_{2\rightarrow1}^P$ is 4.86 eV, in which the P(2) diffuses through a P-rich Ni$_3$P$_2$ layer. Here, the diffusing P(2') interacts repulsively with the surrounding P(1) atoms in Ni$_3$P$_2$ layer at the intermediate $I_{2\rightarrow1}^P$ step, where the $d_{pp}$ was found at 2.70 Å. In contrast, the energy difference was 0.18 eV for the diffusion from P(1) to the intermediate state $I_{1\rightarrow2}^P$, where the shortest $d_{pp}$ was 3.41 Å. We calculated the energy change along the diffusion path through the $I_{1\rightarrow2}^P$ using the cNEB method as shown in Figure 6.2g. The Roman numbers in Figure 6.2g correspond to the P pathway in $I_{1\rightarrow2}^P$ (Roman numbers) in of Figure C.1. The diffusion barrier between $I_{1\rightarrow2}^P$ and $V_{1}^P$ was a little more than 0.18 eV, indicating the easy diffusion path of the P(1).

Another type of inter-plane diffusion was the P(2) diffusing to the $V_{1}^P$. The transition state (TS$_{2\rightarrow1}^P$) as shown in Figure 6.1f was calculated by cNEB method because it was difficult to determine the intermediate structure. The details of the diffusion pathway were illustrated in Figure C.1, corresponding to the Arabic numbers (1-6) in Figure 6.2g. Figure 6.1f shows the TS$_{2\rightarrow1}^P$ where the P$_{24}(2')$ diffused to an interstitial site in Ni$_3$P layer and then diffuses to $V_{1}^P$, and creating a new $V_{2}^P$. During the P$_{24}(2')$ diffusion, local structures were modified, especially, with a drastic displacement of P$_{32}(1)$ varying the P$_{32}(1) - Ni_{40}(2)$ distance from 2.47 Å to 3.40 Å at TS$_{2\rightarrow1}^P$, indicating the breaking of the bond as shown in Figure 6.2f. More details can be seen in Figure C.2d. The energy barrier for the diffusion path is 1.81 eV as shown in Table 6.1.

6.4.4 SIX-JUMP CYCLES DIFFUSION PATHWAY

The six-jump cycles diffusion pathway was considered as a possible mechanism for the diffusion of intermetallic compounds as shown in Fig.S1. First, $V_{1}^P$ or $V_{2}^P$ was filled with Ni instead of P, and the energy of Ni at $V_{1}^P$ or $V_{2}^P$ was low. However, the second step hardly occurred where Ni vacancy was filled with P. The P surrounded by 8 P atoms was quite unstable and its structures were unrealistic, therefore, the
six-jump cycles mechanism was ruled out as the diffusion pathway in Ni$_2$P.

6.4.5 Intermediate Structure of I$_{1\rightarrow 2}^P$ and Easy Diffusion Path

Here we discuss the high stability of the intermediate structure I$_{1\rightarrow 2}^P$ where the diffusing P$_{32}(1)$ (P$_{32}(1')$ for simplicity) is in between two vacancies. In the I$_{1\rightarrow 2}^P$ structure, we found Ni$_{40}(2)$ to form a new tetrahedral geometry during the P$_{32}(1')$ diffusion. The Ni$_{40}(2)$ – P$_{32}(1')$ distance was 2.17 Å, Ni$_{40}(2)$ – P$_{13}(1)$ and Ni$_{40}(2)$ – P$_{25}(1)$ decreased by 0.20 Å to be 2.17 Å and Ni$_{40}(2)$ – P$_{24}(2)$ remained the same distance (2.34 Å). The most considerable change in d$_{pp}$ is found with P$_{13}(1)$ – P$_{25}(1)$ and P$_{13}(1)$ – P$_{9}(2)$ in which the distance increases by about 0.44 Å and decreases about 0.10 Å, respectively, from the original structure. We calculated the tetrahedrality defined as

$$T = \frac{\sum_{i<j} (l_i - l_j)^2}{15\bar{l}^2} \tag{6.2}$$

where $l_i$ and $\bar{l}$ are the i-th edge of tetragon and the average 45. T=0 when it is perfect tetrahedral. T=0.18 when it is square planar. The original Ni(1) had a near-tetrahedral structure that gave the tetrahedrality as 0.0067. When V$_1^P$ was created, the Ni$_{40}(2)$ was surrounded by 4 P atoms and its tetrahedrality was 0.028. The tetrahedrality of Ni$_{40}(2)$ in the I$_{1\rightarrow 2}^P$ was 0.0046, therefore the tetrahedrality increased compared to the original Ni(1) near-tetrahedral structure. The original lattice positions of P$_{25}(1)$ and P$_{13}(1)$ made it possible for Ni$_{40}(2)$ to form the tetrahedral coordination. In addition, the tetrahedrality of Ni$_{37}(1)$ was 0.0077 in the I$_{1\rightarrow 2}^P$.

Ni$_{41}(2)$ and Ni$_{42}(2)$ had the same tetrahedrality as that of Ni$_{40}(2)$ with 0.0046. The rearrangement to tetrahedral local structures might be responsible of making the I$_{1\rightarrow 2}^P$ the most favorable diffusion path.

Local DOS (LDOS) and electron distributions were calculated in the tetrahedral local structure of the I$_{1\rightarrow 2}^P$. Figure 6.3a shows a total DOS of the I$_{1\rightarrow 2}^P$. The DOS from -0.6 to -4 eV were mostly composed of a Ni-Ni 3d band bonding (Figure C.3).
Figure 6.3  (a) Total DOS for the $I_{1\rightarrow 2}$ and LDOS for the d orbital of Ni$_{40}$(2) and p orbital of P$_{32}$(1'). (b) 3D representation of electron density around Ni$_{40}$ for Ni-P bonding region (-4 to -8 eV) for the $I_{1\rightarrow 2}$ structure, which show tetrahedral coordination. (c) 2D slice of (b) parallel to (0001) plane including Ni$_{40}$. Red circles represent the diffusing P.

The states of P3p and Ni3d from around -5 to -9 eV are mostly derived from the Ni-P bonds. Projected LDOS of P$_{32}$(1') p orbital and Ni$_{40}$(2) d orbital in the $I_{1\rightarrow 2}$ structure both have a bonding state at -4.7 eV. The energy indicates the Ni-P bonding in the $I_{1\rightarrow 2}$ structure is as stable as the Ni-P bonds in the perfect structure. Figure 6.3b shows an electron density distribution around Ni40 in the $I_{1\rightarrow 2}$ in the energy around -4.7 eV which indicates the formation of 4 Ni-P bonds in the tetrahedron. The bond state around P$_{32}$(1') is surrounded by 3 Ni(2) and making bonds with 3 Ni atoms illustrated in Figure 6.3c. In addition, the anti-bonding state of Ni$_{40}$(2) and P$_{32}$(1') exist higher than -0.6 eV (Figure 6.3 and S4). The present diffusion path is a combination of interstitial and vacancy diffusion mechanism, and thus is designated as the interstitial-vacancy diffusion mechanism. First, a P diffuses from a lattice site to an interstitial site, when a vacancy $V_{1}^{P}$ exists in another Ni$_{3}P_{2}$ layer.
Moreover, the $I_{1\rightarrow2}^P$ is largely stabilized because of the tetrahedral geometry formation. Our results showed the characteristic low diffusion barrier (about 0.18 eV) of the P in the interstitial-vacancy model. We have revealed an easy diffusion path of P vacancy along the [0001] direction. The diffusion process was accompanied by the local structure change to a tetrahedral arrangement. It has been shown that the Ni$_2$P (0001) surface is stabilized by P termination that forms tetrahedral coordination around the Ni [61].

6.5 Conclusion

We compared the stability of two types of vacancies and found that $V_{1}^P$ in the Ni$_3$P$_2$ layer was the most stable. When analyzing the different kinds of intermediate diffusion steps, $I_{1\rightarrow2}^P$ was the most favorable step studied, with a diffusion barrier of only 0.18 eV. Such a low barrier could explain the low temperature recovery of surface P concentration by the diffusion of P from the bulk [61, 64] observed in experiments. It was found that the type of diffusion mechanism taking place was an interstitial-vacancy diffusion mechanism, since a vacancy ($V_{1}^P$) was needed for the P to diffuse to an interstitial site and then to a lattice site. The low diffusion barrier and stability of the intermediate step structure seemed to be due to the reconstruction of the local structures into tetrahedral geometries. When the geometrical reconstruction took place in $I_{1\rightarrow2}^P$, the combination of the vacancies and P diffusion helped the Ni-P bonding to become dominant.
CHAPTER 7
CONCLUSION

In this work, an exploration of the gas-phase catalytic hydrodeoxygenation of biomass-derived molecule for upgrading bio-oil into valuable chemicals and fuels were investigated. Acetic Acid was chosen as the molecule to study since it is one of the most abundant carboxylic acids in bio-oils. The best possible products for this molecule is C₂ oxygenated products, specifically ethanol. Temperature-dependent conversion and selectivity were studied in a plug flow reactor at 1 atm from 200-400 °C. Monometallic and bimetallic catalysts were supported on activated carbon. Hydrogenation, decarbonylation and decarboxylation (HDO pathways) and side reaction such as ketonization and esterification pathways were discussed. For the monometallic catalysts (Pt, Pd, Ru and Rh) the main pathway for the gas-phase HDO of AA was decarbonylation/decarboxylation pathways. Over the entire temperature range, the main product was methane. The most active catalysts based on TOF for monometallic catalysts at 200 °C were as follow: Ru>Pt~Rh>Pd. Kinetic measurements revealed AA reaction orders < 0.4 and H₂ reaction orders < 0.6, suggesting relatively strong adsorption of both reactants on these metals. This may suggest that there are different sites for adsorption, since two species cannot both be strongly adsorbed on the same site. These results suggest that these monometallic catalysts are too active for C-C bond cleavage, which results in the formation of undesired C₁ products rather than C₂ oxygenates. Therefore, studies on bimetallic catalyst by adding Sn as a second metal were performed to see if it would promote the hydrogenation pathway. Platinum and ruthenium were chosen as the parent metal since they were the
most active and stable monometallic catalysts. The addition of Sn to Pt and Ru helped improved the activity, selectivity towards ethanol and stability from 200-300 °C. The selectivity towards ethanol decreased as the temperature increased for all the bimetallic catalysts. Characterization methods such as XPS and XRD with temperature dependence experiments shows that there is a PtSn (for SnPt and Sn\textsubscript{2}Pt) and a RuSn (for SnRu and Sn\textsubscript{2}Ru) phase that with SnO\textsubscript{x} that is assumed to help the production of oxygenated products such as ethanol from 200-300 °C. Also, XPS data shows that Pt-based bimetallic catalyst has strong bifunctional and geometrical effects, while weak electronic effect. In contrast, for Ru-based catalyst it was shown that it contains strong electronic and bifunctional effects, while no geometrical effect. Our studies suggest that for SnRu and Sn\textsubscript{2}Ru there is an acetaldehyde intermediate that hydrogenates to produce ethanol. On the other hand, for SnPt and Sn\textsubscript{2}Pt there is another intermediate involved rather than acetaldehyde. Kinetic experiments showed that AA reaction orders and H\textsubscript{2} reaction orders for Pt-based bimetallic catalysts were small, suggesting different sites for adsorption. For Ru-based catalysts however, the AA reaction order were low, but those of H\textsubscript{2} ~1, suggesting a strong adsorption from AA and not from H\textsubscript{2}. Also, the activation energy reduces with the addition of Sn when comparing with the parent metal. Overall, the most active and stable catalyst for the hydrogenation of acetic acid to ethanol at low temperature were the Pt-based bimetallic catalysts. Finally, a study about the defects and diffusion of phosphorous on nickel phosphide were performed. The stability of two types of vacancies were compared and found that a vacancy in the Ni\textsubscript{3}P\textsubscript{2} layer was the most stable. When analyzing the different kinds of intermediate diffusion steps, an intermediate state diffusion from a Ni\textsubscript{3}P\textsubscript{2} layer to an interstitial site in the Ni\textsubscript{3}P was the most favorable step studied, with a diffusion barrier of only 0.18 eV. This low barrier could explain the low temperature recovery of surface P concentration by the diffusion of P from the bulk observed in experiments. It was found that the type of diffusion mechanism
taking place was an interstitial-vacancy diffusion mechanism, since a vacancy was
needed for the P to diffuse to an interstitial site and then to a lattice site. The low
diffusion barrier and stability of the intermediate step structure seemed to be due to
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Appendix A

Supplementary Information for Chapter 4

Table A.1 Shows that the HDO CO$_2$ amount produced is significantly less than the theoretical CO$_2$ amount that the WGS reaction could produce, therefore there is no CO$_2$ produce from the WGS reaction at any temperature nor catalyst.

Table A.1 Maximum theoretical CO$_2$ amount that could be produce with the WGS reaction against the amount produced in the HDO reaction from 200-400 °C for the different catalysts.

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<th>5%Pt/Cp-97</th>
<th>5%Pd/Cp-97</th>
<th>5%Ru/Cp-97</th>
<th>5%Rh/Cp-97</th>
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<td></td>
<td>$Y_{CO2_{WGS}}$</td>
<td>$Y_{CO2_{HDO}}$</td>
<td>$Y_{CO2_{WGS}}$</td>
<td>$Y_{CO2_{HDO}}$</td>
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<td>5.25E-05</td>
<td>3.42E-03</td>
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</table>

Figure A.1 External mass transfer limitation experiment.
Figure A.1 shows the external mass transfer limitation experiment for the different catalysts. The reaction rate was observed as the flow rate was change from 50-200 sccm. To ensure no mass transfer limitation for 5%Pt the flow was 150 sccm, for 5%Pd it was 200 sccm, for 5%Ru it was 50 sccm and for 5%Rh the flow was 100 sccm.

Figure A.2  XPS patterns for in-situ reduced and fresh samples for: a) 5%Pt/Cp-97, b) 5%Pd/Cp-97, c) 5%Ru/Cp-97 and d) 5%Rh/Cp-97.
Figure A.2 shows the XPS data for the fresh catalyst sample (already reduced ex-situ) and in-situ reduced (in the XPS catalyst cell) sample for Pt, Pd, Ru and Rh. The blue curves represent the metal and the magenta represents an oxide.

Figure A.3 shows representative STEM images with the particle size distribution for Pt/Cp-97, Pd/Cp-97, Ru/Cp-97 and Rh/Cp-97. Here it can be seen that the particles are larger than when the catalyst is fresh (Fig.4.1) indicating sintering.

Internal mass transfer limitation using the Weisz-Prater [99, 100] criterion were calculated to ensure there were no pore diffusion limitations. The Weisz-Prater cri-
The reaction is as follows:

\[ N_{W-P} = \frac{R_{AA} \rho_C R_p^2}{C_s D_{eff}} \leq 0.3 \] (A.1)

where \( R_{AA} \) (moles/s-gecat) is the rate of reaction of acetic acid, \( \rho_C \) (gecat/m\(^3\)) is the catalyst pellet density, \( R_p \) (m) is the radius of the particle, \( C_s \) (moles/m\(^3\)) is the concentration of AA at the surface of the catalyst and \( D_{eff} \) (m\(^2\)/s) is the effective diffusion coefficient. The Weisz-Prater values for Pt, Pd, Ru and Rh supported on carbon were: 3.10x10\(^{-3}\), 1.21x10\(^{-3}\), 1.52x10\(^{-2}\) and 3.02x10\(^{-3}\), respectively, confirming that there are no internal mass transfer limitations for any of the catalysts.
Appendix B

Supplementary Information for Chapter 5

Figure B.1 shows the particle size for every phase found in each catalyst including oxides and bimetallic phases.

Table B.1  XRD particle size summary for every studied catalyst.

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<th>Sample</th>
<th>Catalyst</th>
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<th>MO</th>
<th>MO₂</th>
<th>MSn</th>
<th>Sn</th>
<th>SnO</th>
<th>SnO₂</th>
<th>Sn₃O₄</th>
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<tr>
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<td></td>
<td></td>
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<tr>
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M- Pt or Ru

Figure B.1 shows the external mass transfer limitation experiment for the different catalysts. The reaction rate was observed as the flow rate was change from 50-200 sccm. For SnRu- 50 sccm, Sn₂Pt, SnRu and Sn₂Ru-200 sccm to ensure no mass transfer limitation.
Figure B.1  External mass transfer limitation experiment for SnPt, Sn$_2$Pt, SnRu and Sn$_2$Ru supported on carbon.

Figure B.2  XRD Profiles from $2\theta = 20$-80 $^\circ$ for a) Pt-based catalysts (5%Pt, SnPt, Sn$_2$Pt), 6%Sn and b) for Ru-based catalysts (5%Ru, SnRu, Sn$_2$Ru).
Figure B.2 shows the complete XRD profiles for both Pt-based catalysts and Ru-based catalysts. It also shows the different Pt and Sn phases.

Figure B.3 shows the corresponding temperatures to perform chemisorption. For SnPt this temperature was 300 °C and for Sn$_2$Pt, SnRu and Sn$_2$Ru the temperature was 400 °C.

![Graph showing XRD profiles](image)

Figure B.3  H$_2$-TPR on oxygen pre-treated from 30-475 °C with a total flow of 20 sccm for: a) SnPt and Sn$_2$Pt: b) SnRu and Sn$_2$Ru.

Figure B.4 shows the XPS patterns for fresh samples that were reduced ex-situ. It can be observed that almost every peak is from an oxide. No electronic effects can be observed, since it is required the involvement of H$_2$. 

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Figure B.4  XPS patterns for fresh samples (ex-situ reduced) for: a) Pt 4f spectra (5%Pt, SnPt and Sn$_2$Pt), b) Sn 3d spectra (6%Sn, SnPt and Sn$_2$Pt), b) Ru 3d spectra (5%Ru, SnRu and Sn$_2$Ru) and d) Sn 3d spectra (6%Sn, SnRu and Sn$_2$Ru). Blue represent the metal and magenta represent the oxides.
APPENDIX C

SUPPLEMENTARY INFORMATION FOR CHAPTER 6

The coordinates derived from DFT calculations in perfect crystal Table C.1 shows the calculated coordinates of Ni and P in perfect crystal.

Table C.1 Coordinates of Ni and P in perfect crystal derived from the DFT calculation.

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<td>Ni58</td>
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<td>Ni59</td>
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<td>1.69</td>
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<td>5.10</td>
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<td>1.70</td>
<td>3.37</td>
<td>Ni63</td>
<td>2.94</td>
<td>5.10</td>
</tr>
<tr>
<td>Ni48</td>
<td>2.94</td>
<td>1.70</td>
<td>3.37</td>
<td>Ni64</td>
<td>2.94</td>
<td>5.10</td>
</tr>
<tr>
<td>Ni49</td>
<td>2.94</td>
<td>1.70</td>
<td>3.37</td>
<td>Ni65</td>
<td>2.94</td>
<td>5.10</td>
</tr>
</tbody>
</table>
Lattice parameter comparison Table C.2 show the lattice parameters from previous DFT and experimental studies. The lattice parameters of present study are in good agreement with those values.

Table C.2 Comparison of calculated and experimental lattice parameters.

<table>
<thead>
<tr>
<th>Functional</th>
<th>a=b/Å</th>
<th>c/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC²</td>
<td>5.859</td>
<td>3.382</td>
</tr>
<tr>
<td>DF-GGA²</td>
<td>5.855</td>
<td>3.339</td>
</tr>
<tr>
<td>GGA²</td>
<td>5.88</td>
<td>3.37</td>
</tr>
<tr>
<td>Experimental²</td>
<td>5.87</td>
<td>3.39</td>
</tr>
<tr>
<td>GGA²</td>
<td>5.89</td>
<td>3.37</td>
</tr>
</tbody>
</table>

a-[64], b-[132], c-[138], d-[149] and e-this work

Calculated and experimental distances of Ni-P and P-P Table C.3 shows the calculated and experimental distances of Ni and P for the two local structures, tetrahedral and square-base pyramid.

Table C.3 Comparison of calculated and experimental Ni-P and P-P distances for tetrahedral and Square-base pyramid structures.

<table>
<thead>
<tr>
<th>Local Structures</th>
<th>Parameters</th>
<th>Calculated / Å</th>
<th>Experimental / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedral</td>
<td>Ni (1)-P (1)</td>
<td>2.21</td>
<td>2.21</td>
</tr>
<tr>
<td></td>
<td>Ni (1)-P (2)</td>
<td>2.28</td>
<td>2.27</td>
</tr>
<tr>
<td></td>
<td>P (1)-P (1)</td>
<td>3.40</td>
<td>3.38</td>
</tr>
<tr>
<td></td>
<td>P (2)-P (2)</td>
<td>3.37</td>
<td>3.38</td>
</tr>
<tr>
<td></td>
<td>P (1)-P (2)</td>
<td>3.80</td>
<td>3.78</td>
</tr>
<tr>
<td>Square-base pyramid</td>
<td>Ni (2)-P (2)</td>
<td>2.34</td>
<td>2.37</td>
</tr>
<tr>
<td></td>
<td>Ni (2)-P (1)</td>
<td>2.47</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>P (2)-P (1)</td>
<td>3.80</td>
<td>3.78</td>
</tr>
<tr>
<td></td>
<td>P (1)-P (1)</td>
<td>3.40</td>
<td>3.38</td>
</tr>
</tbody>
</table>

Diffusion barrier calculations were obtained using cNEB [150] for the transient state $\text{TS}_{2 \rightarrow 1}^P$ and intermediate state $\text{I}_{1 \rightarrow 2}^P$ and are illustrated in Figure C.1 with the corre-
sponding pathways. This figure suggests how the P diffuses in both $\text{TS}_{2\rightarrow1}^P$ (Arabic numbers) and $I_{1\rightarrow2}^P$ (roman numbers). For $\text{TS}_{2\rightarrow1}^P$, the P(2) (red dot for better display) moves from the lattice site to different interstitial sites within Ni$_3$P, therefore forming a vacancy $V_{2}^P$.

Figure C.1  Diffusion Pathways for $\text{TS}_{2\rightarrow1}^P$ (a) and $I_{1\rightarrow2}^P$ (b) Arabic numbers represent the points and diffusion path of $\text{TS}_{2\rightarrow1}^P$, Roman number indicates the points and diffusion path of $I_{1\rightarrow2}^P$ and the red dotted atom represents the diffusive phosphorous for both structures. Layers change from Ni$_3$P to Ni$_3$P$_2$ between 4 and 5 in the Figure S1(a) (c) shows the "six-jump cycle mechanism" (d) and (e) shows the relative energy of each step of the "six-jump cycle mechanism".
Then, after the transient state "mountain", the P(2) goes to the vacancy \(V^P\) site in \(\text{Ni}_3P\). Nonetheless, for the diffusion path of the intermediate state \(I^P_{1\rightarrow2}\), it can be observed that the P(1) (red dot) goes from the lattice site in \(\text{Ni}_3P_2\) down to \(\text{Ni}_3P\) until it reaches the interstitial site in \(\text{Ni}_3P\) (\(I^P_{1\rightarrow2}\)), and since the difference between the "valley" (intermediate state) and the "mountain" (next point) is only 0.008 eV, the P(1) can then diffuse to the \(V^P\) site. These diffusion pathways and diffusion barriers provide good evidence that the \(I^P_{1\rightarrow2}\) might be the only possible path and therefore its relative energy is significantly lower than the \(\text{TS}^P_{2\rightarrow1}\) and the other intermediate states.

Displacements of Ni from the calculated perfect structure Table C.4 shows the difference in position of Ni with respect to the perfect structure. The equation used to calculate the displacements in Å is as follow:

\[
\sqrt{(X_1 - X_2)^2 + (Y_1 - Y_2)^2 + (Z_1 - Z_2)^2}
\]  

(C.1)

where, \(X_1, Y_1\) and \(Z_1\) are the position for the perfect structure, and \(X_2, Y_2\) and \(Z_2\) are the position for \(\text{Ni}_3P, \text{Ni}_3P_2, I^P_{1\rightarrow2}\) and \(\text{TS}^P_{2\rightarrow1}\). Ni displacements were significant (<0.1 Å) for all of the structures studied, except for \(V^P_2\).

Table C.4 Ni displacement for the different vacancies.

<table>
<thead>
<tr>
<th>Ni #</th>
<th>(V^P_1)</th>
<th>(V^P_2)</th>
<th>(I^P_{1\rightarrow2})</th>
<th>(\text{TS}^P_{2\rightarrow1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ni}_{16}) (2)</td>
<td>0.13</td>
<td>0.04</td>
<td>0.11</td>
<td>0.14</td>
</tr>
<tr>
<td>(\text{Ni}_{17}) (2)</td>
<td>0.13</td>
<td>0.02</td>
<td>0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>(\text{Ni}_{18}) (2)</td>
<td>0.13</td>
<td>0.01</td>
<td>0.11</td>
<td>0.20</td>
</tr>
<tr>
<td>(\text{Ni}_{21}) (1)</td>
<td>0.06</td>
<td>0.03</td>
<td>0.19</td>
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</tr>
<tr>
<td>(\text{Ni}_{26}) (1)</td>
<td>0.06</td>
<td>0.03</td>
<td>0.19</td>
<td>0.06</td>
</tr>
<tr>
<td>(\text{Ni}_{27}) (1)</td>
<td>0.06</td>
<td>0.08</td>
<td>0.19</td>
<td>0.20</td>
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<tr>
<td>(\text{Ni}_{31}) (1)</td>
<td>0.13</td>
<td>0.08</td>
<td>0.38</td>
<td>0.18</td>
</tr>
<tr>
<td>(\text{Ni}_{37}) (2)</td>
<td>0.13</td>
<td>0.02</td>
<td>0.38</td>
<td>0.12</td>
</tr>
<tr>
<td>(\text{Ni}_{38}) (2)</td>
<td>0.13</td>
<td>0.01</td>
<td>0.38</td>
<td>0.32</td>
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<tr>
<td>(\text{Ni}_{39}) (1)</td>
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<td>0.03</td>
<td>0.19</td>
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<tr>
<td>(\text{Ni}_{61}) (1)</td>
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<td>0.03</td>
<td>0.19</td>
<td>0.05</td>
</tr>
<tr>
<td>(\text{Ni}_{62}) (1)</td>
<td>0.01</td>
<td>0.08</td>
<td>0.19</td>
<td>0.06</td>
</tr>
<tr>
<td>(\text{Ni}_{63}) (1)</td>
<td>0.03</td>
<td>0.04</td>
<td>0.11</td>
<td>0.15</td>
</tr>
<tr>
<td>(\text{Ni}_{64}) (2)</td>
<td>0.03</td>
<td>0.02</td>
<td>0.11</td>
<td>0.14</td>
</tr>
<tr>
<td>(\text{Ni}_{65}) (2)</td>
<td>0.03</td>
<td>0.01</td>
<td>0.11</td>
<td>0.10</td>
</tr>
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</table>
Table C.5 shows the summary of P-P distances in $I_1^{P_{1\rightarrow 1}}$, $I_2^{P_{2\rightarrow 2}}$ intermediate structure.

Table C.5  Summary of P-P distances in-plane $I_1^{P_{1\rightarrow 1}}$, $I_2^{P_{2\rightarrow 2}}$ intermediate diffusion. Red represents the diffusive atom. For $I_1^{P_{1\rightarrow 1}}$ the vacancy is on $P_{20}(1)$, while $I_2^{P_{2\rightarrow 2}}$ is $P_{24}(2)$.

<table>
<thead>
<tr>
<th>Ni Reference</th>
<th>P-P</th>
<th>$I_{1^{P_{1\rightarrow 1}}}$ / Å</th>
<th>P-P</th>
<th>$I_{2^{P_{2\rightarrow 2}}}$ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni_{37}(1)</td>
<td>$P_{13}(1')-P_{21}(2)$</td>
<td>3.78</td>
<td>$P_{13}(1)-P_{21}(2')$</td>
<td>3.83</td>
</tr>
<tr>
<td></td>
<td>$P_{13}(1')-P_{6}(2)$</td>
<td>3.76</td>
<td>$P_{13}(1)-P_{6}(2)$</td>
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<tr>
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<td>$P_{21}(2)-P_{9}(2)$</td>
<td>3.44</td>
<td>$P_{21}(2')-P_{9}(2)$</td>
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<tr>
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<tr>
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<td>$P_{25}(1)-P_{33}(1)$</td>
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<td>$P_{20}(2)-P_{33}(1)$</td>
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<td>$P_{21}(2')-P_{33}(1)$</td>
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</tr>
<tr>
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<td>$P_{32}(1)-P_{13}(1')$</td>
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<td>$P_{21}(2')-P_{32}(1)$</td>
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<td>--</td>
<td>$P_{21}(2')-P_{32}(1)$</td>
<td>3.96</td>
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</table>

Nickel Phosphide structure and Displacement during the diffusion process. Figure C.2 the perfect structure supercell with the square-base pyramid and the tetrahedral local structures. Also, it shows the zoom in of the different Ni and P that are affected by $V_{1}^{P}$, $I_{1\rightarrow 2}$ and $T_{2\rightarrow 1}$. Figure C.2a shows the two local structures and some of the neighbor Ni and P from the 2nd layer to the 5th of the perfect structure. Figure C.2b illustrates substantial displacements of Ni atoms at Ni_{16−18}(2) and Ni_{40−42}(2) (both in Ni$_3$P), which move downward and upward, respectively, from the vacancy $V_{1}^{P}$. Likewise, Figure C.2c shows Ni displacement, but now for $I_{1\rightarrow 2}^{P}$. For this intermediate step, Ni$_{16−18}(2)$ move downward away from the vacancy (as we saw with $V_{1}^{P}$), but as a result of the $P_{32}(1')$ diffusion, Ni$_{40−42}(2)$ moves away in the same layer, to make space for $P_{32}(1')$. Also, at the same time Ni$_{64−66}(2)$ moves upward away from the other vacancy $V_{1}^{P}$. Ni$_{37−39}(1)$ move upward, and Ni$_{61−63}(1)$ downward, both toward the diffused $P_{32}(1')$. 
Figure C.2  Perfect structure supercell and a zoom in for the Ni and P near the tetrahedral and square-base pyramid structures, b) Ni displacement in $V^P_1$, c) $I^{P}_{1\rightarrow 2}$ and d) for $TS^{P}_{2\rightarrow 1}$. Pink and orange doted circles represent vacancy $V^P_1$ and $V^P_2$, black arrows represent the Ni displacements and the red P represent the diffusion phosphorous.

For $TS^{P}_{2\rightarrow 1}$ (Figure C.2d) shows that the diffusion makes some local distortions. Thanks to the $P_{24}(2)$ diffusion, the $P_{32}(1)$ bonding with $Ni_{40}(2)$ breaks. Basically, the $Ni_{40}$ moves upward, but at the same time $P_{32}$ moves upward as well. The phosphorous diffusion and the vacancy makes the local structure becomes a trigonal pyramidal. The $P_{24}(2)$ surrounding Ni ($Ni_{40-42}$) move upward and away of the diffused phosphorous. $Ni_{16-18}$ moves downward away of the vacancy, and $Ni_{64-66}$ move upwards. The only Ni on the fifth layer is $Ni_{61}$.

Partial density of states (PDOS) for a) Ni and b) P Figure C.3 shows the partial density of states (PDOS) for a) Ni and b) P. The d band consist mostly of $Ni_{3d}$ (Fig. C.3b), but also some of $P_{3p}$ (Fig. C.3a) and it is found from 1.3 to -4 eV, the delocalized band composed with $P_{3p}$ and $Ni_{3d}$ located from around -5 to -9 eV and the phosphorous s band (Fig. C.3b) from around -11 to -15 eV. Overall, the main d
band contribution comes from the Ni.

![Figure C.3 PDOs for a) Nickel and b) Phosphorous with the corresponding bands.](image)

Electron Density

![Figure C.4 Electron density distribution of $I_{1\rightarrow2}^P$ structure for the energy range of -0.6 to 0 eV.](image)