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Deoxygenation properties of Ru-based phosphide catalysts

Bo Carrillo
Western Washington University

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DEOXYGENATION PROPERTIES OF Ru-BASED PHOSPHIDE CATALYSTS

By

Bo Carrillo

Accepted in Partial Completion

Of the Requirements for the Degree

Master of Science

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DEOXGENATION PROPERTIES OF Ru-BASED PHOSPHIDE CATALYSTS

A Thesis

Presented to

The Faculty of

Western Washington University

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science

by

Bo Carrillo

July 2014
Abstract

Bio-oil derived from fast pyrolysis of bio-mass is becoming a more viable option for addressing the growing demand for oil while being more environmentally friendly than fossil fuels. However, bio-oils have poor chemical stability and high acidity due to their high oxygen content. Metal phosphides such as ruthenium phosphide (Ru₂P) have been investigated by the Bussell group to catalytically upgrade compounds contained in bio-oil, but further optimization is required before their commercial viability can be accessed. In current research, less expensive, more abundant metals (Co or Ni) are being used to replace some of the ruthenium, which is both expensive and rare.

Cobalt-ruthenium phosphides (CoₓRu₂₋ₓP, 0 ≤ x ≤ 2) and nickel-ruthenium phosphides (NiₓRu₂₋ₓP, 0 ≤ x ≤ 2) supported on silica at a fixed P/M molar ratio (M = Co + Ru or Ni + Ru) of 0.72 were prepared from hypophosphite-based precursors and their properties for furan deoxygenation were investigated. The deoxygenation properties of the Co-Ru and Ni-Ru phosphides were compared with those of Co-Ru/SiO₂ and Ni-Ru/SiO₂ catalysts having the same metal composition as well as an industrial Co-Mo/Al₂O₃ hydrotreating catalyst. The deoxygenation activities were observed to be strongly influenced by the metal content of the catalysts with the highest activity observed for M-rich MₓRu₂₋ₓP/SiO₂ catalysts, suggesting a synergistic effect as their deoxygenation activities were significantly higher than either Ru₂P/SiO₂ or MₓP/SiO₂. The product selectivities of the metal phosphide (e.g. Co₁.₀₀Ru₁.₀₀P/SiO₂) and metal catalysts (e.g. Co₁.₀₀Ru₁.₀₀/SiO₂) differed significantly. The metal phosphides showed a much higher selectivity for C₃ hydrocarbons, while the metal catalysts showed high selectivity towards methane. The observed trends in deoxygenation activity and selectivity of the metal phosphide catalysts will be discussed.
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Western Washington University Chemistry Department

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Chapter 1: Introduction

1.1 Biofuels vs Fossil Fuels

Fossil fuels have been the driving force of the world economy for over 100 years. Global petroleum usage has continued to grow steadily since the early 1980s and is expected to continue to do so.\textsuperscript{1,2} Much of the demand growth comes from the developing countries China and India rapidly adopting modern conveniences, specifically automobiles.\textsuperscript{2} With fossil fuel demand steadily increasing and supplies finite, we are tasked with the responsibility of finding fossil fuel alternatives. A viable substitute will need to include a liquid fuel so that the existing distribution infrastructure such as pipelines and fueling stations can be used. Also, this substitute for fossil fuels needs to be renewable. A renewable source of liquid fuel will have a lower carbon footprint and limit our demand for foreign oil and its associated conflict.\textsuperscript{3}

Currently there are two classifications of biofuels. First generation biofuels are those that come from a food source feedstock. These include biodiesel from feedstocks such as vegetable oils and bio-ethanol from corn kernels or sugar cane. These are the two most widely used forms of biofuels, but account for only 1.5% of the total liquid fuel produced worldwide.\textsuperscript{2} Biofuels that are derived from a food source have unwanted consequences for the global food market as well as being an unpredictable and unreliable feedstock. When there is high demand for a food-based feedstock, the price will rise. This may not adversely affect wealthy nations, but can have dramatic consequences for third-world nations due to food shortages. Food crops also tend to be energy intensive to cultivate and their production relies heavily on the weather. A serious drought can easily disrupt the global food market and cause food shortage issues around the world. Second
generation biofuels are those that come from a non-food source feedstock. These include biodiesel from algae, bio-ethanol from cellulose, and bio-oil from a biomass resource such as wood chips, sawdust or municipal waste. Second generation biofuels are still in an early development and testing phase and are not yet a commercially viable replacement for fossil fuels. Feedstocks for second generation biofuels are inherently more reliable than those for first generation biofuels since they do not participate in the global market for food crops. Cellulose and lignin-rich feedstocks are generally easier and quicker to grow than food crops, allowing them to be grown in areas unsuitable for food crops. Bio-oil is a diverse fuel source that can be used to produce diesel, aviation fuel, and gasoline without disrupting food crops.

1.2 Bio-Oil

Bio-oil is a dark liquid composed of a mixture of free-flowing, highly oxygenated organic compounds. Bio-oil can be used for a number of applications. Raw bio-oil can be used directly as fuel to run an engine, turbine, or boiler but this is generally not done because of the corrosive properties and low energy content of raw bio-oil. In most cases, the bio-oil needs to be upgraded and contaminants removed in a similar manner as is done for crude oil. It can then be converted to gasoline, diesel, or any other liquid fuel type needed. The biofuels produced via upgrading bio-oil are similar to those derived from crude oil and can be used with our existing fuel infrastructure and vehicles. Other uses for bio-oil relate to its use as a feedstock for bio-based chemicals.

Bio-oil is typically produced via a process known as fast pyrolysis, which depolymerizes the cellulose, hemicellulose, and lignin fractions in biomass. The biomass is first dried to reduce the moisture content to less than 10 wt% unless the feedstock is naturally dry. The dried biomass is then rapidly heated in a pyrolyzer to ~500 °C in the absence of oxygen, causing the long chain
polymers (cellulose, hemicellulose, and lignin) to depolymerize. The resulting products are of three fractions: non-condensable gases, bio-oil, and bio-char. The non-condensable gases are typically fed back to a gas burner to aid in the heating process. The bio-char is a carbon-rich solid that can be used either to fuel a boiler or, more likely, as a soil amendment. The third fraction is the bio-oil itself, a mixture of water, guaiacols, catechols, syringols, vanillins, furanarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, and other carboxylic acids. Other major oxygenated compounds include hydroxyaldehydes, hydroxyketones, sugars, and phenolics. Typical bio-oil yields range from ~60-95 wt% of the pyrolysis products depending on the feedstock used.

Figure 1.1 Biomass fast pyrolysis flow diagram (adopted from the U.S. Department of Agriculture)

1.2.1 Contaminants

There are several properties of bio-oil that set it apart from petroleum including high oxygen and low sulfur contents, low energy content, aging, poor phase stability, and corrosiveness. Table 1.1 shows the physical properties of bio-oil as compared to heavy fuel oil. Bio-oil differs in nearly all respects from petroleum-based fuel oil. Bio-oil properties are also extremely variable, depending on the biomass used.
Table 1.1 Typical properties of wood pyrolysis bio-oil and of heavy fuel oil

<table>
<thead>
<tr>
<th>physical property</th>
<th>bio-oil</th>
<th>heavy fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>moisture content, wt%</td>
<td>15-30</td>
<td>0.1</td>
</tr>
<tr>
<td>pH</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>higher heating value MJ/kg</td>
<td>16-19</td>
<td>40</td>
</tr>
<tr>
<td>viscosity (at 50 °C), cP</td>
<td>40-100</td>
<td>180</td>
</tr>
<tr>
<td>elemental composition, wt%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>54-58</td>
<td>85</td>
</tr>
<tr>
<td>H</td>
<td>5.5-7.0</td>
<td>11</td>
</tr>
<tr>
<td>O</td>
<td>35-40</td>
<td>1.0</td>
</tr>
<tr>
<td>N</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>S</td>
<td>trace</td>
<td>0.5-3.0</td>
</tr>
<tr>
<td>ash</td>
<td>0-0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Unlike petroleum, bio-oils contain significant amounts of oxygen; for example, ~35-40 wt% oxygen content for bio-oil derived from wood. Woody biomass is composed of highly oxygenated compounds including the polymer, cellulose (Figure 1.2), copolymers (hemicellulose) that are made up of many different building blocks such as glucomannan (Figure 1.3), and a complex polymer, lignin (Figure 1.4). The oxygen present in the woody biomass is transferred over to the bio-oil. The high oxygen content is responsible for many of the differences between petroleum fractions and bio-oil including energy density, stability, and corrosiveness.

Figure 1.2 Chemical structure of cellulose

Figure 1.3 Chemical structure of glucomannan, a component of hemicellulose
Figure 1.4 Lignin building blocks

The water content in bio-oils varies considerably depending upon the biomass feedstock used and comes from the original moisture in the feedstock as well as dehydration reactions that occur during pyrolysis. Water content has an impact on the viscosity and energy density of bio-oils. Water reduces the viscosity and improves flow, a beneficial characteristic for combustion. However, water drastically reduces the energy content of the bio-oil. Table 1.1 shows that the energy density (higher heating value) of bio-oil is half that of heavy fuel oil. The viscosity of bio-oil is lower than that of heavy fuel oil which is beneficial. However, over time it has been observed that the viscosity of bio-oils increases. This “aging” process is believed to result from polymerization reactions occurring within the bio-oil itself as well as possible reactions with air. Another byproduct of high oxygen content is acidity. The formic acid and acetic acid in bio-oil cause the pH to be very low (pH ~2.5). This high acidity results in a corrosive oil that can damage engines, turbines, and storage vessels. Common construction materials, carbon steel and aluminum, have been shown to be corroded by bio-oil.

1.2.2 Hydrotreating

Following pyrolysis, bio-oil is typically upgraded to lower the oxygen content. Reducing the oxygen content has the benefit of lowering the acidity, improving stability, and increasing the
energy content of the resulting fuel. Deoxygenation of bio-oil can occur through three different pathways as shown in Figure 1.5. These pathways may or may not involve reaction with hydrogen, but its presence is necessary to limit catalyst coking.

![Chemical reactions](image)

**Figure 1.5** Hydrotreating deoxygenation pathways. a) hydrodeoxygenation b) decarbonylation c) decarboxylation

Hydrodeoxygenation, or HDO (Figure 1.5a), is generally the preferred reaction pathway because the oxygen is selectively removed by cleavage of the C-O bond with \( \text{H}_2 \). By cleaving the C-O bond, all of the carbon is retained in the hydrocarbon product. However, there is substantial \( \text{H}_2 \) consumption and the hydrogenation of aromatics is likely under reaction conditions.

Decarbonylation (Figure 1.5b) and decarboxylation (Figure 1.5c) remove the oxygen through cleavage of C-C bonds to produce CO and CO\(_2\), respectively. These pathways can be beneficial because hydrogenation of the aromatics is less likely, resulting in lower hydrogen consumption. However, because of the loss of carbon in the hydrocarbon product, there will be a lowering of the energy content. The CO produced during deoxygenation can be used to make methane via methanation (Figure 1.6a). Similarly, CO\(_2\) can be converted to CO via the reverse water-gas shift reaction (Figure 1.6b) and then be converted into syngas (CO + \( \text{H}_2 \)). Syngas can then be used to make other fuel products such as diesel or gasoline. However, there can be unwanted consequences of
producing CO during deoxygenation. CO can poison the active sites on HDO catalysts, making the catalyst less active over time.\textsuperscript{16} In addition, reactions 1.6a and 1.6b result in substantial H\textsubscript{2} consumption.

\begin{align*}
\text{a.} & \quad \text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \\
\text{b.} & \quad \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}
\end{align*}

\textbf{Figure 1.6} Secondary reaction pathways: a) methanation b) reverse water-gas shift

The removal of impurities such as sulfur, nitrogen, and oxygen from fuel feedstocks requires the use of a heterogeneous catalyst. Many deoxygenation studies have used the commercial Co-Mo/Al\textsubscript{2}O\textsubscript{3} and Ni-Mo/Al\textsubscript{2}O\textsubscript{3} catalysts employed in hydrotreating crude oils.\textsuperscript{17-19} These catalysts are treated with a sulfiding agent prior to use, yielding a phase similar to molybdenum disulfide (MoS\textsubscript{2}).\textsuperscript{20, 21} These catalysts, used extensively for the removal of sulfur and nitrogen from crude oil feedstocks, require sulfur to be present in the reactor feed to maintain the sulfide structure of the catalysts. Because bio-oils contain only trace amounts of sulfur, a sulfiding agent must be added to the reactor feed to maintain the catalyst phase and activity. Sulfur must be removed from the product stream in a later step to yield an ultralow sulfur transportation fuel. Metal sulfides also contain low active site densities (Figure 1.7a) because the molybdenum atoms are sandwiched between two layers of sulfur. Only the edge molybdenum atoms are available for catalysis.
To avoid having to introduce sulfur into a nearly sulfur-free feedstock and to increase active site densities, new catalysts must be developed to suit the needs of bio-oil hydrotreatment. Other classes of catalysts used for deoxygenation of bio-oil compounds include noble metals and metal phosphides. Noble metals (Figure 1.7b) are excellent hydrogenation catalysts and have much higher active site densities than metal sulfides (Figure 1.7a). However, noble metal catalysts are expensive and susceptible to active site poisoning over time and, therefore, their prospects for use in commercial hydrotreatment of bio-oils is low. Metal phosphides also have higher active site densities than metal sulfides because of high metal atom exposure at the surface of these materials (Figure 1.7c). They have shown higher activity than metal sulfides and noble metals for hydrodesulfurization, while still exhibiting excellent stability.

1.3 Deoxygenation and Noble Metal Phosphides

There has been recent interest in metal phosphides for deoxygenation of bio-oil feedstocks, including studies of molybdenum phosphide (MoP), nickel phosphide (Ni$_2$P), tungsten phosphide (WP), cobalt phosphide (Co$_2$P), and iron phosphide (Fe$_2$P). Metal phosphides have been shown to be more active than both commercial metal sulfides and supported noble metal catalysts in a few cases. Metal phosphides have the benefit of exhibiting metallic
properties with less tendency to deactivate by site poisoning than metal catalysts. Bimetallic phosphides have been explored for hydrotreating with the goal of tuning the properties of the catalysts to optimize activities and selectivities.

Noble metal catalysts, including ruthenium, palladium, rhodium, and platinum, have been shown to be more active than conventional hydrotreating catalysts for deoxygenation of bio-oil feedstocks. In an effort to increase activity and lower susceptibility to poisoning, noble metal phosphides (Ru₂P, Rh₂P, Pd₃P₂, Pd₃P, PdP₂) are being investigated and tested for heteroatom removal reactions. The noble metal phosphides have been shown to be promising catalysts for hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO). However, noble metals are both expensive and rare. To improve sustainability, cost efficiency, and selectivity, bimetallic catalysts of noble metals and their phosphides are being explored for HDS and HDN properties. To our knowledge, there have been no published studies in the area of bimetallic noble metal phosphides and their application to deoxygenation of bio-oil feedstocks.

1.4 Thesis Research Goals

The goals of this thesis research were to synthesize and characterize a series of MₓRu₂₋ₓP/SiO₂ (M = Co, Ni) catalysts to explore their deoxygenation properties. The bimetallic phosphide catalysts were tested for furan deoxygenation activity and selectivity and compared to a commercial Co-Mo/Al₂O₃ catalyst. The most active catalysts were further investigated to gain a better understanding of phase, particle size and surface composition, and how these properties affect activity and selectivity.
Chapter 2: Experimental Methods

2.1 Catalyst Preparation

All reagents except the fumed silica (SiO$_2$) were used as received. Prior to use, silica (Cabot, Cab-O-Sil, M-7D, 200 m$^2$/g, 99.9%+) calcined in air by heating from room temperature to 773 K at 40 K min$^{-1}$, and holding at that temperature for 3 h. After calcination, the SiO$_2$ was stored in a 383 K oven to avoid hydration with water. Gases used for synthesis and characterization were purified with 5 Å molecular sieve moisture traps (Alltech) and oxygen purification traps (Oxy-Clear, Alltech).

2.1.1 Synthesis of Ruthenium Catalysts

*Supported ruthenium chloride precursor (RuCl$_3$/SiO$_2$)*

A silica supported ruthenium chloride precursor having a metal loading equivalent to 15 wt% Ru$_2$P (13.3 wt% Ru) was prepared as follows. RuCl$_3$·3H$_2$O (0.7917 g, Pressure Chemical Co.) was dissolved in ~10 mL of nanopure H$_2$O. The dark aqueous solution was added dropwise to 2.0000 g of the calcined silica support by incipient wetness impregnations followed by drying in an oven at 388 K. This process was repeated until all of the solution was impregnated to the support followed by multiple washes of ~1 mL of nanopure H$_2$O. The resulting supported ruthenium chloride precursor was then stored in vials to be used for subsequent catalyst preparation.

*Supported ruthenium metal (Ru/SiO$_2$)*

A 0.5000 g portion of the dried supported ruthenium chloride precursor was placed into a quartz U-tube fitted inside of a furnace (Figure 2.1) and subjected to a temperature programmed reduction (TPR). The TPR procedure consisted of first degassing the sample in a 60 mL/min flow of
He (Airgas, 99.999%) for 30 min, then reduction in a 100 mL/min flow of H₂ (Airgas, 99.999%) while the temperature was increased from room temperature to 773 K at a rate of 5 K min⁻¹ and then held at that temperature for an additional 1 h. Following the reduction process, the samples were cooled to room temperature in a continued flow of H₂ (100 mL/min), and then flushed with He (60 mL/min) for 30 min. The sample was subsequently passivated in a 1.0 mol% O₂/He (Airgas, 99%) mixture (60 mL/min) for 2 h at room temperature to prevent rapid oxidation of the Ru metal particles upon exposure to air.

**Figure 2.1** Atmospheric pressure flow system for reduction of catalyst precursors.

*Supported ruthenium phosphide (Ru₂P/SiO₂)*

To prepare Ru₂P/SiO₂ catalysts, a 0.5000 g portion of the supported ruthenium chloride precursor was used. The dried precursor was impregnated with a 0.0344 g solution of NH₄H₂PO₂ (Fluka, >97%) dissolved in ~2 mL of nanopure H₂O using successive incipient wetness impregnations
and dryings as described for the precursor synthesis. However, dryings were done at 338 K to prevent the decomposition of the hypophosphite. Once fully impregnated and dried, the material was reduced by TPR and passivated using the methods described earlier for the Ru/SiO$_2$ synthesis.

### 2.1.2 Synthesis of Bimetallic Ruthenium Catalysts

**Supported cobalt-ruthenium salt precursor (Co-Ru/SiO$_2$)**

Silica-supported cobalt-ruthenium precursors with metal loadings corresponding to 15 wt% $M_2P$ ($M = \text{Co + Ru}$) were prepared. As-prepared metal loadings for the Co-Ru/SiO$_2$ catalyst series are shown in Table 2.1.

**Table 2.1 As-prepared loadings for the Co-Ru/SiO$_2$ catalyst series**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/SiO$_2$</td>
<td>13.3</td>
</tr>
<tr>
<td>Co$<em>{0.25}$Ru$</em>{1.75}$/SiO$_2$</td>
<td>13.2</td>
</tr>
<tr>
<td>Co$<em>{0.50}$Ru$</em>{1.50}$/SiO$_2$</td>
<td>13.1</td>
</tr>
<tr>
<td>Co$<em>{0.75}$Ru$</em>{1.25}$/SiO$_2$</td>
<td>13.0</td>
</tr>
<tr>
<td>Co$<em>{1.00}$Ru$</em>{1.00}$/SiO$_2$</td>
<td>12.9</td>
</tr>
<tr>
<td>Co$<em>{1.25}$Ru$</em>{0.75}$/SiO$_2$</td>
<td>12.8</td>
</tr>
<tr>
<td>Co$<em>{1.50}$Ru$</em>{0.50}$/SiO$_2$</td>
<td>12.6</td>
</tr>
<tr>
<td>Co$<em>{1.75}$Ru$</em>{0.25}$/SiO$_2$</td>
<td>12.4</td>
</tr>
<tr>
<td>Co/SiO$_2$</td>
<td>12.3</td>
</tr>
</tbody>
</table>

The silica-supported cobalt-ruthenium precursors were prepared as follows. The first step was an incipient wetness impregnation of the calcined silica support with an aqueous solution containing selected amounts of Co(NO$_3$)$_2$·6H$_2$O (Alfa Aesar, ACS grade) and RuCl$_3$·3H$_2$O (Table 2.2) in ~10 mL nanopure H$_2$O, followed by washes with ~1 mL of nanopure H$_2$O. The material was then dried at 388 K.
Table 2.2 Reagent masses for 15 wt% Co$_{x}$Ru$_{2-x}$P/SiO$_2$ (P/M = 0.72) assuming 2.0000 g SiO$_2$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co(NO$_3$)$_2$·6H$_2$O (g)</th>
<th>RuCl$_3$·3H$_2$O (g)</th>
<th>NH$_4$H$_2$PO$_2$ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru$_2$P/SiO$_2$</td>
<td>0.0000</td>
<td>0.7917</td>
<td>0.1810</td>
</tr>
<tr>
<td>Co$<em>{0.25}$Ru$</em>{1.75}$P/SiO$_2$</td>
<td>0.1154</td>
<td>0.7256</td>
<td>0.1896</td>
</tr>
<tr>
<td>Co$<em>{0.50}$Ru$</em>{1.50}$P/SiO$_2$</td>
<td>0.2422</td>
<td>0.6528</td>
<td>0.1990</td>
</tr>
<tr>
<td>Co$<em>{0.75}$Ru$</em>{1.25}$P/SiO$_2$</td>
<td>0.3823</td>
<td>0.5724</td>
<td>0.2094</td>
</tr>
<tr>
<td>Co$<em>{1.00}$Ru$</em>{1.00}$P/SiO$_2$</td>
<td>0.5379</td>
<td>0.4832</td>
<td>0.2210</td>
</tr>
<tr>
<td>Co$<em>{1.25}$Ru$</em>{0.75}$P/SiO$_2$</td>
<td>0.7116</td>
<td>0.3836</td>
<td>0.2339</td>
</tr>
<tr>
<td>Co$<em>{1.50}$Ru$</em>{0.50}$P/SiO$_2$</td>
<td>0.9069</td>
<td>0.2716</td>
<td>0.2484</td>
</tr>
<tr>
<td>Co$<em>{1.75}$Ru$</em>{0.25}$P/SiO$_2$</td>
<td>1.1279</td>
<td>0.1448</td>
<td>0.2648</td>
</tr>
<tr>
<td>Co$_2$P/SiO$_2$</td>
<td>1.3803</td>
<td>0.0000</td>
<td>0.2835</td>
</tr>
</tbody>
</table>

**Supported cobalt ruthenium metal (Co-Ru/SiO$_2$)**

Co-Ru/SiO$_2$ catalysts were prepared with metal loadings (Co + Ru) equivalent to that of the 15 wt% Co$_{x}$Ru$_{2-x}$P/SiO$_2$ catalysts of similar composition. A portion of the dried precursor was subjected to a temperature-programmed reduction (TPR) procedure in which the precursor was first degassed in a 60 mL/min flow of He for 30 min, then reduced in a 100 mL/min flow of H$_2$ while the temperature was increased from room temperature to 773 K in 1 h, 40 min and then held at that temperature for an additional 1 h. Following the reduction process, the samples were cooled to room temperature in a continued flow of H$_2$ (100 mL/min) then flushed with He (60 mL/min) for 30 min. The Co-Ru/SiO$_2$ samples were then passivated in a 1.0 mol% O$_2$/He mixture (60 mL/min) for 2 h at room temperature.

**Supported cobalt-ruthenium phosphide (Co$_{x}$Ru$_{2-x}$P/SiO$_2$)**

To synthesize the Co$_{x}$Ru$_{2-x}$P/SiO$_2$, 0.5 g portions of the dried Co-Ru/SiO$_2$ precursors were impregnated by incipient wetness with a selected amount of NH$_4$H$_2$PO$_2$ (P/M = 0.72) in ~2 mL nanopure H$_2$O solution, followed by washes with ~0.5 mL nanopure H$_2$O. The material was then
dried at 338 K. Once fully impregnated and dried, the material was then reduced by TPR and passivated using the methods described earlier for the Co-Ru/SiO$_2$ synthesis.

On a mole basis of M$_2$P, the amount of metal and P varied as shown in Table 2.3. This variation is due to the molar mass of cobalt (58.93 g/mol) being less than the molar mass of ruthenium (101.07 g/mol). To compensate for this difference, activity is reported per mole of M$_2$P.

**Table 2.3** Molar quantities for 15 wt% Co$_x$Ru$_{2-x}$P/SiO$_2$ catalysts assuming 2.0000 g of SiO$_2$ and M$_2$P stoichiometry

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Moles</th>
<th>Co</th>
<th>Ru</th>
<th>P</th>
<th>M$_2$P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru$_2$P/SiO$_2$</td>
<td>0.0000</td>
<td>0.0030</td>
<td>0.0015</td>
<td>0.00151</td>
<td></td>
</tr>
<tr>
<td>Co$<em>{0.25}$Ru$</em>{1.75}$P/SiO$_2$</td>
<td>0.0004</td>
<td>0.0028</td>
<td>0.0016</td>
<td>0.00159</td>
<td></td>
</tr>
<tr>
<td>Co$<em>{0.50}$Ru$</em>{1.50}$P/SiO$_2$</td>
<td>0.0008</td>
<td>0.0025</td>
<td>0.0017</td>
<td>0.00166</td>
<td></td>
</tr>
<tr>
<td>Co$<em>{0.75}$Ru$</em>{1.25}$P/SiO$_2$</td>
<td>0.0013</td>
<td>0.0022</td>
<td>0.0018</td>
<td>0.00175</td>
<td></td>
</tr>
<tr>
<td>Co$<em>{1.00}$Ru$</em>{1.00}$P/SiO$_2$</td>
<td>0.0018</td>
<td>0.0018</td>
<td>0.0018</td>
<td>0.00185</td>
<td></td>
</tr>
<tr>
<td>Co$<em>{1.25}$Ru$</em>{0.75}$P/SiO$_2$</td>
<td>0.0024</td>
<td>0.0015</td>
<td>0.0020</td>
<td>0.00196</td>
<td></td>
</tr>
<tr>
<td>Co$<em>{1.50}$Ru$</em>{0.50}$P/SiO$_2$</td>
<td>0.0031</td>
<td>0.0010</td>
<td>0.0021</td>
<td>0.00208</td>
<td></td>
</tr>
<tr>
<td>Co$<em>{1.75}$Ru$</em>{0.25}$P/SiO$_2$</td>
<td>0.0039</td>
<td>0.0006</td>
<td>0.0022</td>
<td>0.00221</td>
<td></td>
</tr>
<tr>
<td>Co$_2$P/SiO$_2$</td>
<td>0.0047</td>
<td>0.0000</td>
<td>0.0024</td>
<td>0.00237</td>
<td></td>
</tr>
</tbody>
</table>

**Supported nickel-ruthenium salt precursor (Ni-Ru/SiO$_2$)**

Silica-supported nickel-ruthenium precursors with metal loadings corresponding to 15 wt% M$_2$P (M = Ni + Ru) were prepared. As-prepared metal loadings for the Co-Ru/SiO$_2$ catalyst series are shown in Table 2.4.

**Table 2.4** As-prepared loadings for the Ni-Ru/SiO$_2$ catalyst series

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>wt%</th>
<th>Catalyst</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/SiO$_2$</td>
<td>13.3</td>
<td>Ni$<em>{1.25}$Ru$</em>{0.75}$/SiO$_2$</td>
<td>12.7</td>
</tr>
<tr>
<td>Ni$<em>{0.25}$Ru$</em>{1.75}$/SiO$_2$</td>
<td>13.2</td>
<td>Ni$<em>{1.50}$Ru$</em>{0.50}$/SiO$_2$</td>
<td>12.6</td>
</tr>
<tr>
<td>Ni$<em>{0.50}$Ru$</em>{1.50}$/SiO$_2$</td>
<td>13.1</td>
<td>Ni$<em>{1.75}$Ru$</em>{0.25}$/SiO$_2$</td>
<td>12.4</td>
</tr>
<tr>
<td>Ni$<em>{0.75}$Ru$</em>{1.25}$/SiO$_2$</td>
<td>13.0</td>
<td>Ni/SiO$_2$</td>
<td>12.3</td>
</tr>
<tr>
<td>Ni$<em>{1.00}$Ru$</em>{1.00}$/SiO$_2$</td>
<td>12.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The silica-supported nickel-ruthenium precursors were prepared as described below. The first step was an incipient wetness impregnation of the calcined silica support with an aqueous solution containing selected amounts of Ni(NO$_3$)$_2$·6H$_2$O (Fluka, >97%) and RuCl$_3$·3H$_2$O (Table 2.5) in ~10 mL nanopure H$_2$O, followed by washes with ~1 mL of nanopure H$_2$O. The material was then dried at 388 K.

**Table 2.5** Reagent masses for 15 wt % Ni$_x$Ru$_{2-x}$/SiO$_2$ (P/Me = 0.72)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni(NO$_3$)$_2$·6H$_2$O (g)</th>
<th>RuCl$_3$·3H$_2$O (g)</th>
<th>NH$_4$H$_2$PO$_4$ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru$_2$/SiO$_2$</td>
<td>0.0000</td>
<td>0.7917</td>
<td>0.2508</td>
</tr>
<tr>
<td>Ni$<em>{0.25}$Ru$</em>{1.75}$/SiO$_2$</td>
<td>0.1153</td>
<td>0.7258</td>
<td>0.2627</td>
</tr>
<tr>
<td>Ni$<em>{0.50}$Ru$</em>{1.50}$/SiO$_2$</td>
<td>0.2421</td>
<td>0.6532</td>
<td>0.2759</td>
</tr>
<tr>
<td>Ni$<em>{0.75}$Ru$</em>{1.25}$/SiO$_2$</td>
<td>0.3823</td>
<td>0.5730</td>
<td>0.2904</td>
</tr>
<tr>
<td>Ni$<em>{1.00}$Ru$</em>{1.00}$/SiO$_2$</td>
<td>0.5381</td>
<td>0.4838</td>
<td>0.3065</td>
</tr>
<tr>
<td>Ni$<em>{1.25}$Ru$</em>{0.75}$/SiO$_2$</td>
<td>0.7122</td>
<td>0.3842</td>
<td>0.3245</td>
</tr>
<tr>
<td>Ni$<em>{1.50}$Ru$</em>{0.50}$/SiO$_2$</td>
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<td>0.2721</td>
<td>0.3448</td>
</tr>
<tr>
<td>Ni$<em>{1.75}$Ru$</em>{0.25}$/SiO$_2$</td>
<td>1.1299</td>
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<td>0.3678</td>
</tr>
<tr>
<td>Ni$_2$/SiO$_2$</td>
<td>1.3836</td>
<td>0.0000</td>
<td>0.3941</td>
</tr>
</tbody>
</table>

**Supported nickel-ruthenium metal (Ni-Ru/SiO$_2$)**

Ni-Ru/SiO$_2$ catalysts were prepared with metal loadings (Ni + Ru) equivalent to that of the 15 wt% Ni$_x$Ru$_{2-x}$/SiO$_2$ catalysts of similar composition. A portion of the dried nickel-ruthenium precursor was subjected to a TPR procedure in which the precursor was first degassed in a 60 mL/min flow of He for 30 min, then reduced in a 100 mL/min flow of H$_2$ while the temperature was increased from room temperature to 773 K in 1 h, 40 min and then held at that temperature for an additional 1 h. Following the reduction process, the samples were cooled to room temperature in a continued flow of H$_2$ (100 mL/min) then flushed with He (60 mL/min) for 30 min. The samples were then passivated in a 1.0 mol% O$_2$/He mixture (60 mL/min) for 2 h at room temperature.
**Supported nickel ruthenium phosphide (Ni\textsubscript{x}Ru\textsubscript{2-x}P/SiO\textsubscript{2})**

To synthesize the Ni\textsubscript{x}Ru\textsubscript{2-x}P/SiO\textsubscript{2}, 0.5 g portions of the dried Ni-Ru/SiO\textsubscript{2} precursors were impregnated by incipient wetness with a selected amount (P/Me = 0.72) of NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4} in ~2 mL nanopure H\textsubscript{2}O solution, followed by washes with ~0.5 mL nanopure H\textsubscript{2}O. The material was then dried at 338 K. Once fully impregnated and dried, the material was then reduced by TPR and passivated using the methods described earlier for the Ni-Ru/SiO\textsubscript{2} synthesis.

On a mole basis of M\textsubscript{2}P, the amount of metal and P varied as shown in Table 2.6. This variation is due to the molar mass of nickel (58.69 g/mol) being less than the mass of ruthenium (101.07 g/mol). To compensate for this difference, activity is reported per mole of M\textsubscript{2}P.

**Table 2.6** Molar quantities for 15 wt% Ni\textsubscript{x}Ru\textsubscript{2-x}P/SiO\textsubscript{2} catalysts assuming 2.0000 g of SiO\textsubscript{2} and exact M\textsubscript{2}P stoichiometry

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Moles</th>
<th>Ni</th>
<th>Ru</th>
<th>P</th>
<th>M\textsubscript{2}P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru\textsubscript{2}P/SiO\textsubscript{2}</td>
<td>0.0000</td>
<td>0.0030</td>
<td>0.0015</td>
<td>0.00151</td>
<td></td>
</tr>
<tr>
<td>Ni\textsubscript{0.25}Ru\textsubscript{1.75}P/SiO\textsubscript{2}</td>
<td>0.0004</td>
<td>0.0028</td>
<td>0.0016</td>
<td>0.00159</td>
<td></td>
</tr>
<tr>
<td>Ni\textsubscript{0.50}Ru\textsubscript{1.50}P/SiO\textsubscript{2}</td>
<td>0.0008</td>
<td>0.0025</td>
<td>0.0017</td>
<td>0.00167</td>
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</tr>
<tr>
<td>Ni\textsubscript{0.75}Ru\textsubscript{1.25}P/SiO\textsubscript{2}</td>
<td>0.0013</td>
<td>0.0022</td>
<td>0.0018</td>
<td>0.00175</td>
<td></td>
</tr>
<tr>
<td>Ni\textsubscript{1.00}Ru\textsubscript{1.00}P/SiO\textsubscript{2}</td>
<td>0.0018</td>
<td>0.0018</td>
<td>0.0018</td>
<td>0.00185</td>
<td></td>
</tr>
<tr>
<td>Ni\textsubscript{1.25}Ru\textsubscript{0.75}P/SiO\textsubscript{2}</td>
<td>0.0024</td>
<td>0.0015</td>
<td>0.0020</td>
<td>0.00196</td>
<td></td>
</tr>
<tr>
<td>Ni\textsubscript{1.50}Ru\textsubscript{0.50}P/SiO\textsubscript{2}</td>
<td>0.0031</td>
<td>0.0010</td>
<td>0.0021</td>
<td>0.00208</td>
<td></td>
</tr>
<tr>
<td>Ni\textsubscript{1.75}Ru\textsubscript{0.25}P/SiO\textsubscript{2}</td>
<td>0.0039</td>
<td>0.0006</td>
<td>0.0022</td>
<td>0.00222</td>
<td></td>
</tr>
<tr>
<td>Ni\textsubscript{2}P/SiO\textsubscript{2}</td>
<td>0.0048</td>
<td>0.0000</td>
<td>0.0024</td>
<td>0.00238</td>
<td></td>
</tr>
</tbody>
</table>

**2.2 X-Ray Diffraction**

X-ray diffraction (XRD) patterns of the catalysts prepared in this research were acquired using a PANalytical X’Pert Pro MRD x-ray diffractometer. The X-ray diffractometer used a Cu-\(K\alpha\) monochromatized radiation (\(\lambda = 1.5418\) Å) and operated at 45 kV and 40 mA with a stage setting of \(z = 8.380\). Samples were first mounted to a 4” x 1” glass microscope slide by placing ~10-50 mg of the
desired catalyst on the center of the glass slide. Methanol was dropped around and onto the sample until it was fully saturated and formed a paste. Using a metal spatula, the paste was then spread out to ~5 cm² and allowed to dry. Before being mounted into the instrument’s sample mounting stage, the slide was tapped on its sides to remove any loose sample.

Sample data were collected using X’Pert Data Collector software over a Bragg angle (2θ) range of 20-80°. Scans had a step size of 0.025° and a dwell time of 25 s. Data were then converted to ASCII format using X’Pert HighScore software. Reference XRD patterns were obtained from the JCPDS powder diffraction file database using X’Pert HighScore software. Experimental and reference XRD patterns were plotted for the determination of phase purity and average crystallite size (Dc) using Origin 9.0 software.

2.2.1 Crystallite Size Calculations

The average crystallite size was determined using the Scherrer equation (Equation 2.1) where $K = 1$ (assuming spherical particles), $\lambda$ = the wavelength of incident x-rays ($\lambda = 1.5418$ Å), $\beta$ = the width of the peak at half maximum in radians, and $\theta$ = the center angle of diffraction at maximum peak intensity.

$$D_c = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (2.1)

2.3 Chemisorption Measurements

Carbon monoxide (CO) and oxygen (O₂) chemisorption measurements were acquired using a Micromeritics PulseChemisorb 2700 instrument (Figure 2.2).
Figure 2.2 Schematic representation of a Micromeritics PulseChemisorb 2700 apparatus.

About 0.10 g of catalyst was placed in a dry quartz U-tube (U-tube was dried at 398 K) and degassed at room temperature in a 60 mL/min flow of He for a period of 30 min. Residual water and oxygen were removed from the He using 5 Å molecular sieve (Alltech) and O₂ purification traps (Oxi-Clear, Alltech). A loop in the tubing carrying the desired probe gas (CO or O₂) was placed in a liquid nitrogen/pentane slush (~142 K) to remove condensable impurities.

Prior to the measurements, the catalyst samples were reduced in-situ. A standard reduction began by heating a catalyst sample from room temperature to 650 K in 1 h and holding for 2 h in a 60 mL/min flow of H₂ in a 60 mL/min flow of He to 673 K in 5 min and holding at that temperature for 55 min. The catalyst sample was then cooled to room temperature.

The commercial hydrotreating catalyst (Co-Mo/Al₂O₃) was subjected to a sulfidation pretreatment by heating from room temperature to 650 K in 1 h and holding for 2 h in a 60 mL/min flow of 3 mol% H₂S/H₂ (Airgas). In a 60 mL/min flow of H₂, the sample was then cooled to 623 K in 5 min and held for 55 min. The sample was then ramped to 673 K in 5 min in a 60 mL/min flow of He and held at 673 K for 55 min. The catalyst sample was then cooled to room temperature.
2.3.1 CO Chemisorption Measurements

2.3.1.1 Experiment

CO chemisorption measurements were carried out in a 45 mL/min flow of He at ~273 K by pulsing a previously calibrated amount of pure CO (Advanced Specialty Gases, 99.99%) into the flowing He while recording the non-adsorbed CO. A calibration pulse was determined by measuring the peak area of a 5 s CO pulse while bypassing the sample. Calibration pulses were performed in triplicate.

Following the calibration pulses, the sample was cooled to ~273 K using an ice bath. Five second pulses in 1 min intervals were flowed over the cooled sample. The thermal conductivity detector (TCD) detected non-adsorbed CO. Pulses continued until three consecutive full pulses were detected as non-adsorbed. Once the TCD returned to baseline, the ice bath was removed and the sample was heated to 673 K to desorb any CO on the catalyst. The peak area was then recorded of the desorbed CO peak. The adsorbed and desorbed CO measurements were then averaged.

2.3.1.2 Theory and Calculations

The ideal gas law, pulse area, number of pulses, non-absorbed peak area (NAPA), desorbed peak area, and the sample mass were used to calculate the CO chemisorption capacity (µmol CO/g cat). To calculate the amount of probe gas injected per pulse, the ideal gas law was used (Equation 2.2).

\[
n = \frac{PV}{RT} = \frac{(1\text{ atm})(1.01 \times 10^{-4} L)}{(0.082057 \frac{L\text{ atm}}{mol K})(298 K)} = 4.131 \text{ µmol probe gas/pulse area} \tag{2.2}
\]
Measurements were conducted at atmospheric pressure (P = 1 atm) using an injection loop volume of 101 µL, where R is the ideal gas constant (0.082058 L atm/mol K), and T was 298 K. The absorbed peak area was calculated by multiplying the number of pulses by the peak area/pulse and subtracting the NAPA from the total (Equation 2.3).

\[
\text{Absorbed peak area} = (\text{# of pulses})(\text{peak area/pulse}) - \text{NAPA} \tag{2.3}
\]

The absorbed peak area, the µmol CO/pulse, and the sample mass were then used to calculate the adsorbed CO chemisorption capacity (Equation 2.4). The peak area was multiplied by the µmol CO/pulse and then divided by the sample mass after the measurement to give an active site density.

\[
\text{adsorbed CO chemisorption capacity} = \frac{(\text{absorbed peak area})(\mu\text{mol CO/pulse area})}{g \text{ catalyst}} \tag{2.4}
\]

The desorbed chemisorption capacity is calculated using the desorbed peak area, the µmol CO/pulse area, and the sample mass (Equation 2.5). The desorbed chemisorption capacity is then averaged with the adsorbed chemisorption capacity to determine the CO chemisorption capacity.

\[
\text{desorbed CO chemisorption capacity} = \frac{(\text{desorbed peak area})(\mu\text{mol CO/pulse area})}{g \text{ catalyst}} \tag{2.5}
\]

2.4 BET Surface Area

2.4.1 Experiment

Single-point BET surface area measurements were acquired using a Micromeritics PulseChemisorb 2700 instrument. About 0.10 g of catalyst was placed in a quartz U-tube (U-tube was dried at 398 K) and degassed at room temperature in a 60 mL/min flow of He for a period of 30
Residual water and oxygen were removed from the He using 5 Å molecular sieve (Alltech) and O₂ purification traps (Oxi-Clear, Alltech).

Following the degas procedure, the samples were reduced in-situ. A standard reduction began by heating the catalyst sample from room temperature to 650 K in 1 h and holding for 2 h in a 60 mL/min flow of H₂ followed by heating in a 60 mL/min flow of He to 673 K in 5 min and holding at that temperature for 55 min. The catalyst sample was then cooled to room temperature.

Single-point BET measurements were carried out in a 35 mL/min flow of 28.6 mol% N₂/He (Airco). First a calibration was performed by injecting known volumes (0.2, 0.6, and 1.0 mL) of pure N₂ gas using the headspace of a dewar of liquid nitrogen. A calibration curve could then be fitted to the three calibration points (Figure 2.3).

![Figure 2.3 Sample calibration curve for BET surface area measurements.](image)

The sample was cooled to 77 K using a liquid nitrogen bath. N₂ adsorption was found by detecting the deficit of N₂ in the 28.6 mol% N₂/He stream. Once the detector returned to baseline, the peak area was noted. Desorption was measured by heating the sample to room temperature.
and recording the N\textsubscript{2} desorbed from the catalyst sample by detecting the excess N\textsubscript{2} present in the N\textsubscript{2}/He stream. The adsorption and desorption measurements were then completed in triplicate and averaged.

### 2.4.2 Theory and Calculations

The surface area of a catalyst sample can be calculated by first assuming that N\textsubscript{2} adsorbs onto the surface with infinite layers, that there is no interaction between each adsorbed layer, and that the Langmuir theory can be applied to each layer, as is consistent with the Brunauer-Emmett-Teller (BET) method and the BET equation (Equation 2.8).\textsuperscript{44} The variables in the BET equation are as follows; \(V\) is the volume of N\textsubscript{2} adsorbed at standard conditions (\(T = 273\ \text{K}, \ P = 1\ \text{atm}\)), \(A\) is Avogadro’s number, \(N\) is the accepted value for the area of a solid surface occupied by an adsorbed nitrogen molecule, \(P\) is atmospheric pressure and is multiplied by the mol\% of gas in the mixture (28.6 mol\% N\textsubscript{2}/He), \(P_0\) is the saturation pressure of liquid nitrogen, and \(M\) is the molar volume of a gas at standard conditions. The temperature and pressure did not change during normal testing conditions and were considered constant (Equation 2.9), allowing calculation of a BET factor of 2.82 m\textsuperscript{2}/mL and simplification of the BET equation (Equation 2.10). The volume of N\textsubscript{2} adsorbed determined using the calibration curve (Figure 2.3) can then be converted to surface area using the simplified BET equation (Equation 2.10) and normalized by dividing by the sample mass (Equation 2.11).

\[
\text{surface area} = \frac{VAN(1 - \frac{P}{P_0})}{M} \quad (2.8)
\]

\[
C = AN \left[ \frac{1 - \frac{P}{P_0}}{M} \right] = \frac{(273.15 \text{ K}) \times (6.023 \times 10^{23} \text{ cm}^3 \text{ g}^{-1} \text{ mol}^{-1})\times (16.2 \times 10^{-20} \text{ Å}) 	imes \left(1 - \frac{0.286 \times 760 \text{ mmHg}}{775 \text{ mmHg}}\right)}{22.414 \times 10^3 \text{ cm}^3 \text{ g}^{-1} \text{ mol}^{-1}} = 2.82 \frac{\text{m}^2}{\text{mL}} \quad (2.9)
\]
\[
\text{surface area} = V \times 2.82 \frac{m^2}{ml}
\]  \hspace{1cm} (2.10)

\[
\text{surface area} = \left( \frac{\text{volume } N_2 (ml)}{\text{mass of catalyst } (g)} \right) \left( 2.82 \frac{m^2}{ml} \right)
\]  \hspace{1cm} (2.11)

2.5 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectra (XPS) were collected at the Surface Analysis Recharge Center at the University of Washington using a Surface Science Instruments S-probe spectrometer having a monochromatized Al K\textsubscript{\alpha} X-ray. The samples were dusted onto double sided tape and neutralized with a low energy electron flood gun prior to data collection. Spectra were collected with a spot size of 800 \mu m in an analytical chamber with a pressure less than 5 \times 10^{-9} \text{Torr} during spectral acquisition. High-resolution spectra were collected with a pass energy of 50 eV and a take-off angle of \(\sim 55^\circ\) (55\(^\circ\) take-off angle \(\approx 50 \text{ Å} \) sampling depth). The Service Physics Hawk Data Analysis software was used to analyze the spectra. The most intense C(1s) high-resolution peak was used as a reference at a binding energy of 285.0 eV.

2.6 Furan Deoxygenation Activity Measurements

Catalyst samples were pretreated and tested for furan deoxygenation using the atmospheric pressure flow reactor shown in Figure 2.4.
Figure 2.4 Flow reactor used for furan deoxygenation measurements at ambient pressure.

A catalyst sample (0.1000 g) was placed on a quartz wool plug (~0.1 g) fitted at the base of the quartz U-tube. The U-tube was then placed inside of a ceramic fiber furnace and attached to the apparatus and thermocouple as shown in Figure 2.4. Glass bubblers filled with furan (Alfa Aesar, 99%) were cooled to 250 K by a recirculating refrigerated bath (Thermo Haake, C30-P) filled with ethylene glycol (Prestone). Gas flow was controlled by a mass flow controller (MKS instruments, Type 1159B) connected to a four-channel readout (MKS instruments, Model 647C). Reduction temperatures were controlled using a ceramic fiber furnace (Watlow) attached to a microprocessor temperature controller (Omega, Type CN-2011K) and monitored by a Type K thermocouple mounted to the U-tube. A second thermocouple was placed inside the furnace to provide thermal over-limit protection. During activity measurements the reactor effluent was analyzed by an on-line
HP-5890 Series II gas chromatograph (GC) equipped with a pneumatic sampling valve (Valco) and fitted with parallel columns and detectors (Figure 2.5): an alumina column (Agilent, GS-Alumina) attached to a flame ionization detector (FID) and a carbon column (Agilent, GS-CarbonPlot) attached to a thermal conductivity detector (TCD).

![Diagram of gas chromatograph column and detector arrangement for furan deoxygenation measurements.](image)

Figure 2.5 Gas chromatograph column and detector arrangement for furan deoxygenation measurements.

The alumina column with FID allowed detection and separation of C$_1$-C$_{10}$ hydrocarbons, while the carbon column with TCD allowed detection and separation of CO, CO$_2$, and C$_3$ hydrocarbons. The GC and sampling valve were controlled by a personal computer using Agilent ChemStation software.

2.6.1 Deoxygenation Measurements

Furan Deoxygenation Measurements

Two types of activity measurements were carried out: 1) temperature-dependent activity measurements and 2) time-dependent activity measurements. Furan deoxygenation activity measurements were carried out at temperatures in the range of 423-723 K using a reactor feed consisting of an 8.2 mol% furan/H$_2$ mixture, prepared by passing a 50 mL/min flow of H$_2$ through
two glass bubblers containing furan at 250 K. The metal phosphide and metal catalysts were pretreated by degassing in He (50 mL/min) at room temperature for 30 min and then heating from room temperature to 650 K in 1 h in a 50 mL/min flow of H₂ and holding at 650 K for 2 h. Following pretreatment, the catalyst samples were cooled to 423 K and the flow was switched to the furan/H₂ reactor feed (50 mL/min). The gas effluent was sampled at 1 h intervals for over 12 h after the sample reached the desired temperature. The catalyst samples were then heated in 5 min to the next temperature (25 or 50 K increments) depending upon the observed activity. The sequence was repeated to a maximum temperature of 673 K. During the temperature-dependent activity measurements, the reactor effluent was analyzed by an on-line HP-5890 series II gas chromatograph (GC) equipped with a pneumatic sampling valve (Valco) and fitted an alumina column (Agilent, GS-Alumina) attached to a flame ionization detector (FID). The GC and sampling valve were both controlled by a personal computer using Agilent ChemStation software.

Furan deoxygenation activity measurements were carried out at a fixed reaction temperature of 573 K for 48 h using the reactor feed described previously. The metal phosphide and metal catalysts were pretreated by degassing in He (50 mL/min) at room temperature for 30 min and then heated from room temperature to 650 K in 1 h in a 50 mL/min flow of H₂ and holding at 650 K for 2 h. Commercial hydrotreating catalyst samples (Co-Mo/Al₂O₃) were sulfided by heating from room temperature to 650 K in 1 h and holding for 2 h in a 60 mL/min flow of 3 mol% H₂S/H₂ (Airgas).

Following pretreatment, the catalyst samples were cooled to the reaction temperature of 573 K and the flow was switched to the furan/H₂ reactor feed (50 mL/min). The gas effluent was sampled once the catalyst reached 573 K and was sampled at 1 h intervals for 48 h and analyzed by on-line GC as previously described in section 2.6.
2.6.1.1 Theory and Calculations

_Furan Deoxygenation Activity Analysis_

The flow rate of furan (nmol/s) in the reactor was calculated as follows. The furan vapor pressure at 250 K was determined using the Antoine equation (Equation 2.12) where \( P \) is pressure, \( A \) (unitless), \( B \) (K), and \( C \) (K) are component-specific constants, and \( T \) is temperature.\(^{45}\)

\[
P = 10^{A - \frac{B}{C + T}} \tag{2.12}
\]

The vapor pressure of furan (Equation 2.13) was then used to calculate the mol\% of furan in the reactant gas stream (Equation 2.14). Rearranging the ideal gas law (Equation 2.15) allowed for the calculation of the molar flow rate in mol/min at standard temperature and pressure (STP). Using the molar flow rate and the gas composition (8.15 mol\% furan), the furan flow rate was calculated as shown in Equation 2.16.

\[
\text{Furan Vapor Pressure (250 K)} = 10^{(6.9730 - \frac{1060.850}{227.750 - 25.000})} = 61.62 \text{ mmHg} \tag{2.13}
\]

\[
\text{mol} \% \text{ Furan} = \frac{61.62 \text{ mmHg}}{760 \text{ mmHg}} \times 100 = 8.15 \% \text{ Furan} \tag{2.14}
\]

\[
\text{Molar Flow Rate} = \left( \frac{1 \text{ atm} \times 50.0 \text{ ml}}{0.0821 \frac{L \text{ atm}}{K \cdot \text{mol} \times 273 K}} \right) \times \left( \frac{1 L}{1000 \text{ mL}} \right) = 0.00223 \frac{\text{mol s}}{\text{min}} \tag{2.15}
\]

\[
\text{Furan Flow Rate} = \left( 0.00223 \frac{\text{mol min}}{\text{min}} \right) \times \left( \frac{10^9 \text{ nmol}}{1 \text{ mol}} \right) \times \left( \frac{1 \text{ min}}{60 \text{ s}} \right) \times 0.815 = 3029 \frac{\text{nmol s}}{s} \tag{2.16}
\]

Furan deoxygenation activities were calculated using the relative peak area of the furan as detected by GC and reported in units of nanomoles of furan converted per second per gram of catalyst (nmol furan/s/g cat) as well as micromoles of furan converted per mole of \( \text{M}_2\text{P} \) (M = Co or
Ni + Ru) per second (μmol furan/s/mol M₂P). All peaks were integrated using ChemStation software to obtain the relative peak area. The relative peak area of furan was then used to calculate the percent furan converted to products using the known flow rate of furan.

_Furan Deoxygenation Selectivity Analysis_

Deoxygenation product concentrations were calculated using single-point response factors for each of the major products formed. Response factors were determined by flowing a known calibration gas mixture through the flow reactor apparatus. The calibration gas mixtures that were used were purchased from Scott Specialty Gases and provided by Air Liquide. Gas mixtures including item numbers, size, balance, project numbers, and accuracy are reported below in Table 2.7.
### Table 2.7 Scott Specialty Gas mixtures provided by Air Liquide

<table>
<thead>
<tr>
<th>Item #</th>
<th>Project #</th>
<th>Size (L)</th>
<th>Compound(s)</th>
<th>Balance</th>
<th>Accuracy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-04-234</td>
<td>01-68970-003</td>
<td>14</td>
<td>CO, CO₂, methane, ethane, propane, H₂, N₂, O₂</td>
<td>He</td>
<td>± 5</td>
</tr>
<tr>
<td>01-04-12</td>
<td>01-42819-003</td>
<td>14</td>
<td>Propylene</td>
<td>N₂</td>
<td>± 2</td>
</tr>
<tr>
<td>01-04-5557</td>
<td>01-58264-001</td>
<td>14</td>
<td>n-butane</td>
<td>N₂</td>
<td>± 2</td>
</tr>
<tr>
<td>01-04-4448</td>
<td>01-42819-004</td>
<td>14</td>
<td>propane</td>
<td>N₂</td>
<td>± 2</td>
</tr>
<tr>
<td>01-04-20</td>
<td>01-42819-005</td>
<td>14</td>
<td>trans-2-butene</td>
<td>N₂</td>
<td>± 2</td>
</tr>
<tr>
<td>01-04-25</td>
<td>01-42819-001</td>
<td>14</td>
<td>1-butene</td>
<td>N₂</td>
<td>± 2</td>
</tr>
<tr>
<td>01-04-19</td>
<td>01-42819-006</td>
<td>14</td>
<td>cis-2-butene</td>
<td>N₂</td>
<td>± 2</td>
</tr>
<tr>
<td>01-04-224</td>
<td>01-81860-001</td>
<td>14</td>
<td>n-butane, ethane, n-hexane, methane, n-pentane, propane, alkane</td>
<td>N₂</td>
<td>± 5</td>
</tr>
<tr>
<td>01-04-55</td>
<td>01-55572-001</td>
<td>48</td>
<td>1,3-butadiene, n-butane, 1-butene, cis-2-butene, ethyl acetylene, isobutene, isobutylene, trans-2-butene acetylene</td>
<td>N₂</td>
<td>± 10</td>
</tr>
<tr>
<td>01-04-54</td>
<td>01-63754-001</td>
<td>48</td>
<td>acetylene, n-butane, ethane, ethylene, methane, methyl acetylene, propane, propylene</td>
<td>N₂</td>
<td>± 10</td>
</tr>
</tbody>
</table>

Each calibration standard was measured by GC in triplicate for repeatability and integrated using ChemStation software. The resulting response area versus concentration was used to calculate
the response factor. The product response factors, retention times, and calibration gas concentrations are shown in Table 2.8.

**Table 2.8** GC calibration for deoxygenation products using a GS-Alumina column with a FID and a GS-CarbonPlot column with a TCD

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention Time (min)</th>
<th>Concentration</th>
<th>Response Factor</th>
<th>Detector</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>1.57</td>
<td>5.00 %</td>
<td>1.020</td>
<td>TCD</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.30</td>
<td>5.00 %</td>
<td>0.685</td>
<td>TCD</td>
</tr>
<tr>
<td>methane</td>
<td>1.30</td>
<td>1020 ppm</td>
<td>0.0412</td>
<td>FID</td>
</tr>
<tr>
<td>ethane</td>
<td>1.63</td>
<td>1010 ppm</td>
<td>0.0197</td>
<td>FID</td>
</tr>
<tr>
<td>ethylene</td>
<td>3.24</td>
<td>15.1 ppm</td>
<td>0.0199</td>
<td>FID</td>
</tr>
<tr>
<td>propane</td>
<td>3.82</td>
<td>1010 ppm</td>
<td>0.0131</td>
<td>FID</td>
</tr>
<tr>
<td>propylene</td>
<td>10.74</td>
<td>1003 ppm</td>
<td>0.01307</td>
<td>FID</td>
</tr>
<tr>
<td>n-butane</td>
<td>10.77</td>
<td>1010 ppm</td>
<td>0.00982</td>
<td>FID</td>
</tr>
<tr>
<td>trans-2-butene</td>
<td>14.84</td>
<td>0.95 %</td>
<td>0.00969</td>
<td>FID</td>
</tr>
<tr>
<td>1-butene</td>
<td>15.20</td>
<td>1002 ppm</td>
<td>0.00988</td>
<td>FID</td>
</tr>
<tr>
<td>cis-2-butene</td>
<td>15.32</td>
<td>1.01 %</td>
<td>0.01012</td>
<td>FID</td>
</tr>
<tr>
<td>isobutylene</td>
<td>15.82</td>
<td>15.1 ppm</td>
<td>0.00990</td>
<td>FID</td>
</tr>
</tbody>
</table>

Shown below in Figure 2.6 are sample FID and TCD GC traces for the furan deoxygenation of Co₁₅Ru₀.₅P/SiO₂ catalyst at 48 h on-stream. All of the peaks have been labeled and identified in Table 2.9. Peaks five and six correspond to propylene and n-butane. The GS-Alumina column with FID was unable to separate these two products, leaving the n-butane peak as a shoulder. However, reasonable separation was achieved with the GS-CarbonPlot column. Because the FID has greater sensitivity, the combined peak area (n-butane + propylene) is used from the FID trace. The ratio of propylene/n-butane from the TCD trace was then used to calculate individual peak areas for the FID trace.
Figure 2.6 FID and TCD GC traces for furan deoxygenation over a Co\textsubscript{1.5}Ru\textsubscript{0.5}P/SiO\textsubscript{2} catalyst at 48 h on-stream.

Table 2.9 GC peak identification for furan deoxygenation products over a Co\textsubscript{1.5}Ru\textsubscript{0.5}P/SiO\textsubscript{2} catalyst at 48 h on-stream.

<table>
<thead>
<tr>
<th>Peak #</th>
<th>Compound</th>
<th>Retention Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>methane</td>
<td>1.30</td>
</tr>
<tr>
<td>2</td>
<td>ethane</td>
<td>1.62</td>
</tr>
<tr>
<td>3</td>
<td>ethylene</td>
<td>3.16</td>
</tr>
<tr>
<td>4</td>
<td>propane</td>
<td>3.77</td>
</tr>
<tr>
<td>5</td>
<td>propylene</td>
<td>10.49</td>
</tr>
<tr>
<td>6</td>
<td>n-butane</td>
<td>10.58</td>
</tr>
<tr>
<td>7</td>
<td>trans-2-butene</td>
<td>14.93</td>
</tr>
<tr>
<td>8</td>
<td>1-butene</td>
<td>15.15</td>
</tr>
<tr>
<td>9</td>
<td>cis-2-butene</td>
<td>15.70</td>
</tr>
<tr>
<td>10</td>
<td>isobutylene</td>
<td>15.83</td>
</tr>
<tr>
<td>11</td>
<td>furan</td>
<td>23.35</td>
</tr>
<tr>
<td>12</td>
<td>CO</td>
<td>1.37</td>
</tr>
<tr>
<td>13</td>
<td>propylene</td>
<td>16.33</td>
</tr>
<tr>
<td>14</td>
<td>n-butane</td>
<td>17.21</td>
</tr>
<tr>
<td>15</td>
<td>furan</td>
<td>28.72</td>
</tr>
</tbody>
</table>
Chapter 3: Results

3.1 Catalyst Synthesis and Characterization

Silica-supported metal and metal phosphide catalysts were prepared as described in the experimental section. X-ray diffraction (XRD) was used to identify the crystalline phases present in the catalysts as well as to determine the average crystallite sizes. Reference patterns were obtained from the JCPDS database and compared with XRD patterns for the synthesized catalysts.\(^4\) BET surface area measurements were used to measure the microscopic surface area of the catalysts, while CO chemisorption capacities were measured to determine the density of active sites on the catalysts. BET surface areas were measured using N\(_2\) as the probe molecule and chemisorption capacities were measured at 273 K using CO as the probe molecule. X-ray photoelectron spectroscopy (XPS) was used to determine surface compositions and binding energies for selected catalysts.

*Supported ruthenium metal (Ru/SiO\(_2\)) catalysts*

Figure 3.1 shows the XRD pattern for an as-prepared 13.3 wt% Ru/SiO\(_2\) catalyst as well as for a sample of the catalyst after furan deoxygenation testing. The XRD pattern for the silica-supported Ru catalyst compares well with that of a Ru reference pattern (card no. 00-006-0663).\(^4\) The Scherrer equation and the \{100\} reflection at 44.1° were used to calculate the average crystallite sizes. No change in phase purity or average crystallite size was observed.
Figure 3.1 XRD patterns of a 13.3 wt% Ru/SiO₂ catalyst, before and after furan deoxygenation testing.

Supported ruthenium phosphide (Ru₃P/SiO₂) catalysts

Figure 3.2 shows the XRD pattern for an as-prepared 15 wt% Ru₃P/SiO₂ catalyst (13.3 wt% Ru) as well as for a sample of the catalyst after furan deoxygenation testing.
Figure 3.2 XRD patterns of a 15 wt% Ru$_2$P/SiO$_2$ catalyst, prepared using a P/Ru molar ratio of 0.72, before and after furan deoxygenation testing.

The XRD pattern for the silica-supported Ru$_2$P compares well with that of a Ru$_2$P reference pattern (card no. 01-089-3031). The Scherrer equation and the {112} reflection at 38.4° were used to calculate the average crystallite sizes. No change in phase purity or average crystallite size was observed.
An as-prepared sample of 15 wt% Ru$_2$P/SiO$_2$ was examined using XPS. Due to poor signal-to-noise, the XPS spectra provided limited surface chemical results. The binding energies of the Ru 3p$_{3/2}$ and the P 2p peaks were found to be 462.4 and 135.0 eV, respectively. The binding energy for Ru 3p$_{3/2}$ is higher than the binding energy range (461.1-462.2 eV) reported for ruthenium metal (Ru$^0$), but is below the reported binding energy for Ru$^{4+}$ in RuO$_2$ (463.2-464.8 eV), indicating the Ru in Ru$_2$P bears a positive charge (Ru$^{5+}$) close to +4. The P 2p binding energy is above the reported binding energy for elemental phosphorous (129.7 eV) and is similar to that of P$^{5+}$ in NaH$_2$PO$_4$ (134.1 eV). The Ru 3p$_{3/2}$ and the P 2p binding energies are consistent with Ru and P species present in the passivation layer of the Ru$_2$P particles. The peak areas of the Ru 3p$_{3/2}$ and the P 2p peaks were used to calculate the surface composition. Analysis of the XPS data indicated a phosphorous-rich surface composition of Ru$_{1.0}$P$_{1.7}$, but with a large error bar on this composition due to the poor signal-to-noise ratios.

Supported cobalt metal (Co/SiO$_2$) catalysts

Figure 3.3 shows the XRD patterns of an as-prepared 12.3 wt% Co/SiO$_2$ catalyst and a Co metal reference (card no. 01-070-2633). The XRD pattern for the silica-supported Co compares well with that of a Co reference pattern. The Scherrer equation and the {111} reflection at 44.3° were used to calculate the average crystallite sizes. Furan deoxygenation testing over a Co/SiO$_2$ catalyst resulted in substantial polymerization reactions in the reactor system so the measurement was not completed. For this reason there is not an XRD pattern for a tested Co/SiO$_2$ catalyst.
Figure 3.3 XRD pattern for an as-prepared 12.3 wt% Co/SiO₂ catalyst.

Supported cobalt phosphide (Co₃P/SiO₂) catalysts

Figure 3.4 shows the XRD pattern for an as-prepared 15 wt% Co₂P/SiO₂ catalyst as well as for a sample of the catalyst after furan deoxygenation testing. The XRD pattern for the silica-supported Co₃P compares well with a Co₂P reference pattern (card no. 00-006-0595).² The Scherrer equation
and the \{112\} reflection at 40.8° were used to calculate the average crystallite sizes. No change in phase purity or average crystallite size was observed.

**Figure 3.4** XRD patterns for a 15 wt% Co$_2$P/SiO$_2$ catalyst, prepared using a P/Co molar ratio of 0.72, before and after furan deoxygenation testing.

An as-prepared sample of 15 wt% Co$_2$P/SiO$_2$ was examined using XPS. Due to poor signal-to-noise, the XPS spectra provided limited surface chemical results. The binding energies of the Co 2p$_{3/2}$ and the P 2p peaks were found to be 782.4 and 134.1 eV, respectively. The binding energy for Co
2p_{3/2} is higher than the binding energy range (777.8-778.5 eV) for cobalt metal (Co^0) and the binding energy (778.2 eV) reported for Co_2P; it is closer to the reported binding energy range for CoO (Co^{2+}) of 780.0-781.2 eV. The P 2p binding energy is also above the reported binding energy (129.7 eV) for elemental phosphorous (P^0) and is similar to that of P^{5+} in NaH_2PO_4 (134.1 eV). The Co 2p_{3/2} and the P 2p binding energies are consistent with Co and P species present in the passivation layer of the Co_2P particles. The peak areas of the Co 2p_{3/2} and the P 2p peaks were used to calculate a surface composition. Analysis of the XPS data indicated a phosphorous-rich surface composition of Co_{1.5}P_{1.0}, but with a large error bar on this composition due to the poor signal-to-noise ratios.

**Supported cobalt-ruthenium metal (Co-Ru/SiO_2) catalysts**

Figure 3.5 shows the XRD patterns for selected catalysts in a series of as-prepared Co-Ru/SiO_2 catalysts having different metal compositions. The XRD patterns for silica-supported Co_{1.00}Ru_{1.00} and Co_{1.50}Ru_{0.50} catalysts compare well with that of a Ru reference pattern (card no. 00-006-0663), but the XRD peaks are shifted to higher Bragg angles. The Scherrer equation and the \{100\} reflection at 38.6-39.9° for Co_{1.00}Ru_{1.00}/SiO_2 and Co_{1.50}Ru_{0.50}/SiO_2 were used to calculate the average crystallite sizes reported in Table 3.1. The average crystallite sizes (10-13 nm) are similar to the value determined for Ru/SiO_2 (12 nm) and smaller than the value reported for Co/SiO_2 (30 nm).

**Table 3.1** Average crystallite sizes for as-prepared and deoxygenation tested Co-Ru/SiO_2 catalysts as well as BET surface areas and CO chemisorption capacities as-prepared.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average Crystallite Size (nm)</th>
<th>BET Surface Area (m^2/g cat)</th>
<th>Chemisorption Capacity (µmol CO/g cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>12</td>
<td>168</td>
<td>61</td>
</tr>
<tr>
<td>Co_{0.50}Ru_{1.50}</td>
<td>11</td>
<td>158</td>
<td>60</td>
</tr>
<tr>
<td>Co_{1.00}Ru_{1.00}</td>
<td>13</td>
<td>168</td>
<td>31</td>
</tr>
<tr>
<td>Co_{1.50}Ru_{0.50}</td>
<td>10</td>
<td>155</td>
<td>14</td>
</tr>
<tr>
<td>Co</td>
<td>30</td>
<td>----</td>
<td>34</td>
</tr>
</tbody>
</table>
Figure 3.5 XRD patterns of a series of as-prepared Co-Ru/SiO$_2$ catalysts having different metal compositions.
The Co-Ru/SiO₂ catalysts exhibited BET surface areas in the range 154-168 m²/g and CO chemisorption capacities in the 14-61 µmol CO/g range. A trend of decreasing CO chemisorption capacity with increasing Co content was observed.

**Supported cobalt-ruthenium phosphide (CoₓRu₂₋ₓP/SiO₂) catalysts**

The XRD patterns for a series of as-prepared 15 wt% CoₓRu₂₋ₓP/SiO₂ catalysts are shown in Figure 3.6. The XRD patterns for the bimetallic phosphide catalysts are similar to the reference pattern for Ru₂P, but the peaks are shifted to higher Bragg angles as the molar fraction of cobalt is increased. A peak at 31.3° in the XRD patterns for the Co₁.₅₀Ru₀.₅₀P/SiO₂ and Co₁.₇₅Ru₀.₂₅P/SiO₂ catalysts (noted by the asterisk symbol) indicates the presence of an impurity phase. The phase impurity is tentatively identified as CoP phase, as the CoP reference pattern has an intense peak at 31.5°. The Scherrer equation and the {112} reflection at 38.0-40.9° were used to calculate the average crystallite sizes reported in Table 3.2. The average crystallite sizes were in the 7-16 nm range with the exception of Co₂P (~30 nm). No changes in phase purity or crystallite size were observed after deoxygenation testing.
Figure 3.6 XRD patterns for a series of as prepared 15 wt% $\text{Co}_x\text{Ru}_{2-x}\text{P}/\text{SiO}_2$ catalysts.
Table 3.2 Average crystallite sizes for as-prepared and tested 15 wt% Co$_x$Ru$_{2-x}$P/SiO$_2$ catalysts as well as BET surface areas and CO chemisorption capacities.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>as-prepared</th>
<th>tested</th>
<th>BET Surface Area (m$^2$/g cat)</th>
<th>Chemisorption Capacity (µmol CO/g cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru$_3$P</td>
<td>13</td>
<td>12</td>
<td>132</td>
<td>88</td>
</tr>
<tr>
<td>Co$<em>{0.25}$Ru$</em>{1.75}$P</td>
<td>16</td>
<td>16</td>
<td>142</td>
<td>94</td>
</tr>
<tr>
<td>Co$<em>{0.50}$Ru$</em>{1.50}$P</td>
<td>8</td>
<td>10</td>
<td>148</td>
<td>146</td>
</tr>
<tr>
<td>Co$<em>{0.75}$Ru$</em>{1.25}$P</td>
<td>7</td>
<td>7</td>
<td>147</td>
<td>104</td>
</tr>
<tr>
<td>Co$<em>{1.00}$Ru$</em>{1.00}$P</td>
<td>7</td>
<td>8</td>
<td>148</td>
<td>132</td>
</tr>
<tr>
<td>Co$<em>{1.25}$Ru$</em>{0.75}$P</td>
<td>11</td>
<td>10</td>
<td>142</td>
<td>38</td>
</tr>
<tr>
<td>Co$<em>{1.50}$Ru$</em>{0.50}$P</td>
<td>12</td>
<td>11</td>
<td>144</td>
<td>62</td>
</tr>
<tr>
<td>Co$<em>{1.75}$Ru$</em>{0.25}$P</td>
<td>9</td>
<td>12</td>
<td>147</td>
<td>72</td>
</tr>
<tr>
<td>Co$_2$P</td>
<td>30</td>
<td>30</td>
<td>131</td>
<td>18</td>
</tr>
</tbody>
</table>

The BET surface areas and chemisorption capacities for the Co$_x$Ru$_{2-x}$P/SiO$_2$ catalysts are listed in Table 3.2. The catalysts exhibited similar BET surface areas near 140 m$^2$/g, only slightly lower than that of the Co-Ru/SiO$_2$ catalysts. There was an initial increase in CO chemisorption capacity for the Co$_x$Ru$_{2-x}$P/SiO$_2$ catalysts with increasing Co content followed by a sharp decrease as the Co content was increased beyond $x = 1.00$. The CO chemisorption capacities of the Co$_x$Ru$_{2-x}$P/SiO$_2$ catalysts were as much as five times larger than those of the Co-Ru/SiO$_2$ catalysts having similar metal compositions.

An as-prepared sample of 15 wt% Co$_{1.00}$Ru$_{1.00}$P/SiO$_2$ was examined using XPS. Due to poor signal-to-noise, the XPS spectra provided limited surface chemical results. The binding energies of the Ru 3p$_{3/2}$, Co 2p$_{3/2}$, and the P 2p binding energies were found to be 463.3, 782.1, and 134.7 eV respectively. The P 2p binding energy is similar to the reported binding energy of P$^{5+}$ in NaH$_2$PO$_4$ (134.1 eV). The Ru 3p$_{3/2}$, Co 2p$_{3/2}$, and the P 2p binding energies are above the range reported for elemental Ru (461.1-462.2 eV), Co (777.8-778.5 eV), and P (129.7 eV), indicating Ru, Co, and P are oxidized species in the passivation layer of the Co$_{1.00}$Ru$_{1.00}$P particles. Poor signal-to-noise made...
oxidation state information obtained from the binding energy of limited value. The peak areas of the Ru 3p$_{3/2}$, Co 2p$_{3/2}$, and the P 2p peaks were used to calculate the surface composition. Analysis of the XPS data indicated a metal-rich surface composition of Co$_{1.0}$Ru$_{1.5}$P$_{1.0}$, but with large error bars due to poor signal-to-noise.

**Supported nickel metal (Ni/SiO$_2$) catalysts**

Figure 3.7 shows the XRD pattern for an as-prepared 12.3 wt% Ni/SiO$_2$ catalyst as well as for a sample of the catalyst after furan deoxygenation testing.

**Figure 3.7** XRD patterns for a 12.3 wt% Ni/SiO$_2$ catalyst before and after furan deoxygenation testing.
The XRD pattern for the as-prepared Ni/SiO\textsubscript{2} catalyst compares well with that of a cubic Ni reference pattern (card no. 00-004-0850).\textsuperscript{43} The Scherrer equation and the \{111\} reflection at 44.6° were used to calculate the average crystallite size (28 nm) of the as-prepared Ni/SiO\textsubscript{2} catalyst. Following furan deoxygenation testing, a Ni phase change and increase in average crystallite size from 28 to 40 nm was observed for the Ni/SiO\textsubscript{2} catalyst. The XRD pattern for the tested Ni/SiO\textsubscript{2} catalyst compares well with that of a hexagonal Ni reference pattern (card no. 01-070-0989).\textsuperscript{43} The phase change occurred at a reaction temperature of 573 K, a temperature at which the formation of hexagonal Ni has been observed by others.\textsuperscript{48} The Scherrer equation and the \{100\} reflection at 39.6° were used to calculate the average crystallite size of the tested Ni/SiO\textsubscript{2} catalyst.

\textit{Supported nickel phosphide (Ni\textsubscript{2}P/SiO\textsubscript{2}) catalysts}

Figure 3.8 shows the XRD pattern for an as-prepared 15 wt\% Ni\textsubscript{2}P/SiO\textsubscript{2} catalyst as well as for a sample of the catalyst after furan deoxygenation testing. The XRD pattern for the Ni\textsubscript{2}P/SiO\textsubscript{2} catalyst compares well with that of a Ni\textsubscript{2}P reference pattern (card no. 03-065-1989).\textsuperscript{43} The Scherrer equation and the \{111\} reflection at 40.9° were used to calculate the average crystallite sizes. No change in phase purity or average crystallite size was observed.
Figure 3.8 XRD patterns of a 15 wt% Ni$_2$P/SiO$_2$ catalyst, prepared using a P/Ni molar ratio of 0.72, before and after furan deoxygenation testing.

Supported nickel-ruthenium metal (Ni-Ru /SiO$_2$) catalysts

Figure 3.9 shows the XRD patterns for selected catalysts in a series of as-prepared Ni-Ru/SiO$_2$ catalysts having different metal compositions.
Figure 3.9 XRD patterns of a series of as prepared Ni-Ru/SiO$_2$ catalysts having different metal compositions.

The XRD pattern for the silica-supported Ni$_{1.00}$Ru$_{1.00}$ catalyst compares well with that of a Ru reference pattern (card no. 00-006-0663). The XRD pattern for the silica-supported Ni$_{1.50}$Ru$_{0.50}$ catalyst exhibits peaks found in both the Ru (card no. 00-006-0663) and the Ni (card no. 00-004-0850) reference patterns. The XRD pattern for the silica-supported Ni catalyst compares well with that of a Ni reference pattern (card no. 00-004-0850). The Scherrer equation and the \{100\}
reflections at 38.5-39.7° for Ni<sub>1.00</sub>Ru<sub>1.00</sub> and Ni<sub>1.50</sub>Ru<sub>0.50</sub> were used to calculate the average crystallite sizes reported in Table 3.3. The as-prepared average crystallite sizes (10-13 nm) are similar to the value determined for Ru/SiO<sub>2</sub> (12 nm) and smaller than the value reported for Ni/SiO<sub>2</sub> (28 nm). No changes in phase purity or crystallite size were observed with the exception of an increased average crystallite size for the tested Ni/SiO<sub>2</sub> catalyst (40 nm).

**Table 3.3** Average crystallite sizes for as-prepared and tested Ni-Ru/SiO<sub>2</sub> catalysts as well as BET surface areas and CO chemisorption capacities.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average Crystallite Size (nm)</th>
<th>BET Surface Area (m&lt;sup&gt;2&lt;/sup&gt;/g cat)</th>
<th>Chemisorption Capacity (µmol CO/g cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>12 as-prepared, 13 tested</td>
<td>156</td>
<td>61</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;0.50&lt;/sub&gt;Ru&lt;sub&gt;1.50&lt;/sub&gt;</td>
<td>10 as-prepared, 10 tested</td>
<td>160</td>
<td>65</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;1.00&lt;/sub&gt;Ru&lt;sub&gt;1.00&lt;/sub&gt;</td>
<td>10 as-prepared, 11 tested</td>
<td>167</td>
<td>53</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;1.50&lt;/sub&gt;Ru&lt;sub&gt;0.50&lt;/sub&gt;</td>
<td>12 as-prepared, 5-10 tested</td>
<td>164</td>
<td>35</td>
</tr>
<tr>
<td>Ni</td>
<td>28 as-prepared, 40 tested</td>
<td>168</td>
<td>57</td>
</tr>
</tbody>
</table>

**Supported nickel-ruthenium phosphide (Ni<sub>x</sub>Ru<sub>1-x</sub>P/SiO<sub>2</sub>) catalysts**

The XRD patterns for a series of as-prepared 15 wt% Ni<sub>x</sub>Ru<sub>1-x</sub>P/SiO<sub>2</sub> catalysts are shown in Figure 3.10. The XRD patterns for the bimetallic phosphide catalysts are similar to the reference pattern for Ru<sub>2</sub>P, but the peaks shifted to higher Bragg angles as the molar fraction of cobalt increased. It should be noted that an impurity phase was observed in a few of the catalysts (indicated by the asterisk symbol). To our knowledge there is no reference pattern in the JCPDS database for RuP, however, the impurity peak at 46.0-46.3° compares well with an intense peak at 46.0° in the XRD pattern for unsupported RuP.28
Figure 3.10 XRD patterns for a series of as-prepared 15 wt% Ni$_x$Ru$_{2-x}$P/SiO$_2$ catalysts.
The Scherrer equation and the \{111\} reflection for Ni$_2$P and \{112\} reflection for Ru$_2$P at 38.0-40.9° were used to calculate the average crystallite sizes as reported in Table 3.4. The average crystallite sizes were in the 8-16 nm range.

**Table 3.4** Average crystallite sizes for as-prepared and tested 15 wt% Ni$_x$Ru$_{2-x}$P/SiO$_2$ catalysts as well as BET surface areas and CO chemisorption capacities.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>as-prepared</th>
<th>tested</th>
<th>BET Surface Area (m$^2$/g cat)</th>
<th>Chemisorption Capacity (µmol CO/g cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru$_2$P</td>
<td>13</td>
<td>12</td>
<td>132</td>
<td>88</td>
</tr>
<tr>
<td>Ni$<em>{0.25}$Ru$</em>{1.75}$P</td>
<td>13</td>
<td>15</td>
<td>146</td>
<td>120</td>
</tr>
<tr>
<td>Ni$<em>{0.50}$Ru$</em>{1.50}$P</td>
<td>13</td>
<td>13</td>
<td>152</td>
<td>134</td>
</tr>
<tr>
<td>Ni$<em>{0.75}$Ru$</em>{1.25}$P</td>
<td>8</td>
<td>9</td>
<td>155</td>
<td>115</td>
</tr>
<tr>
<td>Ni$<em>{1.00}$Ru$</em>{1.00}$P</td>
<td>8</td>
<td>8</td>
<td>152</td>
<td>111</td>
</tr>
<tr>
<td>Ni$<em>{1.25}$Ru$</em>{0.75}$P</td>
<td>13</td>
<td>13</td>
<td>159</td>
<td>81</td>
</tr>
<tr>
<td>Ni$<em>{1.50}$Ru$</em>{0.50}$P</td>
<td>16</td>
<td>15</td>
<td>140</td>
<td>97</td>
</tr>
<tr>
<td>Ni$<em>{1.75}$Ru$</em>{0.25}$P</td>
<td>13</td>
<td>15</td>
<td>158</td>
<td>88</td>
</tr>
<tr>
<td>Ni$_2$P</td>
<td>10</td>
<td>11</td>
<td>158</td>
<td>64</td>
</tr>
</tbody>
</table>

The BET surface areas and chemisorption capacities for the Ni$_x$Ru$_{2-x}$P/SiO$_2$ catalysts are listed in Table 3.4. The catalysts exhibited BET surface areas in the range 152-158 m$^2$/g. There was an initial increase in CO chemisorption capacity for the Ni$_x$Ru$_{2-x}$P/SiO$_2$ catalysts with increasing Ni content followed by a decrease as the Ni content was increased beyond $x = 1.00$. The BET surface areas and the trend in CO chemisorption capacities for the Ni-Ru phosphides were similar to those for the Co-Ru phosphides.

### 3.2 Furan Deoxygenation Activity

**Furan Deoxygenation Activity vs. Time Measurements**

The furan deoxygenation activities of selected metal and metal phosphide catalysts were measured at temperatures in the range 423-723 K. Shown below are the results for silica-supported
Ru (Figure 3.11) and Ru₂P (Figure 3.12) catalysts; furan conversion vs temperature measurements for Co₁.₀₀Ru₁.₀₀/SiO₂, Co₁.₀₀Ru₁.₀₀P/SiO₂, Co₂P /SiO₂, and Co/SiO₂ can be found in Appendix B. The furan conversion over Ru/SiO₂ was observed to be at its lowest level at 423 K (0.94%) and increased with temperature up to 523 K. The final furan conversion ranged from 11-15% in the 523-673 K range. The Ru/SiO₂ catalyst achieved its maximum initial furan conversion at 523 K; the conversion started at 38.3% followed by a sharp decline for ~5 h before slowly approaching a steady-state at ~15% conversion after ~5-12 h on-stream. A similar trend was observed for each temperature in the 523-673 K range.

Figure 3.11 Furan deoxygenation activity vs. time on-stream for a 13.3 wt% Ru/SiO₂ catalyst.
The Ru$_2$P/SiO$_2$ catalyst (Figure 3.12) achieved a maximum initial furan conversion of 48.4% at 673 K. The activity quickly declined over time for the 12 h period, yet the Ru$_2$P/SiO$_2$ catalyst was nearly twice as active as the Ru/SiO$_2$ catalyst after 12 h on-stream at this temperature. The sharp decline in activity over time was observed in the 673-723 K range. Activity at temperatures below 623 K approached steady-state after the first 3-5 h on-stream.

![Graph showing furan deoxygenation activity vs. time on-stream for a 15 wt% Ru$_2$P/SiO$_2$ catalyst.](image)

**Figure 3.12** Furan deoxygenation activity vs. time on-stream for a 15 wt% Ru$_2$P/SiO$_2$ catalyst.

Figure 3.13 shows the furan conversion vs. temperature for Ru/SiO$_2$ and Ru$_2$P/SiO$_2$ catalysts at the final hour of testing at each temperature. The Ru$_2$P/SiO$_2$ catalyst had its highest activity at 648 K and had higher activity than Ru/SiO$_2$ at temperatures ≥ 598 K. The Ru/SiO$_2$ catalyst was observed
to be more active than Ru$_2$P/SiO$_2$ at temperatures below 598 K and was most active at 523 K. Both Ru$_2$P/SiO$_2$ and Ru/SiO$_2$ had significantly higher furan conversions than an industrial Co-Mo/Al$_2$O$_3$ catalyst over the full range of temperatures.

![Graph showing furan conversion vs. temperature for different catalysts](image)

**Figure 3.13** Furan deoxygenation activity measurements vs. temperature for 13.3 wt% Ru/SiO$_2$, 15 wt% Ru$_2$P/SiO$_2$, and Co-Mo/Al$_2$O$_3$ catalysts.

The furan deoxygenation product selectivity was determined for Ru/SiO$_2$ and Ru$_2$P/SiO$_2$ over the temperature range 423-723 K. Shown below are the results for the silica supported Ru (Figure 3.14) and Ru$_2$P (Figure 3.15) catalysts; product selectivities for the Co$_{1.00}$Ru$_{1.00}$/SiO$_2$, Co$_{1.00}$Ru$_{1.00}$/SiO$_2$, and Co/SiO$_2$ catalysts can be found in Appendix B. The Ru/SiO$_2$ catalyst showed high selectivity for methane at all temperatures with longer chain hydrocarbons being only minor
products. These product selectivity measurements were carried out before the addition of the GS-CarbonPlot column and TCD detection, so propylene and n-butane were not resolved for product assignments and carbon monoxide detection was not possible. However, later studies with the GS-CarbonPlot and TCD system showed product selectivities to be 20.0 mol% propylene and 3.4 mol% n-butane for Ru/SiO$_2$ at 573 K, while Ru$_2$P/SiO$_2$ showed selectivities of 36.4 mol% propylene and 8.3 mol% n-butane at 573 K.

![Figure 3.14](image_url) Product selectivity vs. temperature for furan deoxygenation over a 13.3 wt% Ru/SiO$_2$ catalyst.

The Ru$_2$P/SiO$_2$ catalyst (Figure 3.15) showed high selectivity towards propane at temperatures in the range 423-473 K. At 523 K, selectivity shifted towards propylene/n-butane and
favored propylene/n-butane at temperatures ≥ 573 K. The propane selectivity decreased from 41.4 mol% to 9.6 mol% as the temperature was increased, while propylene/n-butane selectivity increased from 18.5 to 60.1 mol%. For further deoxygenation testing, 573 K was chosen as the reaction temperature because the Ru/SiO$_2$ and Ru$_2$P/SiO$_2$ catalysts showed significant activity that reached a steady-state after 40-48 h on-stream.

![Product selectivity vs. temperature for furan deoxygenation over a 15 wt% Ru$_2$P/SiO$_2$ catalyst.](image-url)

**Figure 3.15** Product selectivity vs. temperature for furan deoxygenation over a 15 wt% Ru$_2$P/SiO$_2$ catalyst.
3.2.1 Cobalt-Ruthenium Catalysts

Supported cobalt-ruthenium metal (Co-Ru/SiO₂)

Furan deoxygenation activity measurements were carried out at 573 K as a function of time on-stream for the Co-Ru/SiO₂ catalysts having different metal compositions. Shown in Figure 3.16 are plots of furan deoxygenation activity vs time on-stream for 15 wt% Ru/SiO₂, Co₀.₅₀Ru₁.₅₀/SiO₂, Co₁.₀₀Ru₁.₀₀/SiO₂, and Co₁.₅₀Ru₀.₅₀/SiO₂ catalysts, activity is reported in µmol furan/s/mol M₂P eq.

![Graph showing furan deoxygenation activity vs time on-stream for different Co-Ru/SiO₂ catalysts at 573 K.](image)

**Figure 3.16** Furan deoxygenation activity vs time for Ru/SiO₂, Co₀.₅₀Ru₁.₅₀/SiO₂, Co₁.₀₀Ru₁.₀₀/SiO₂, and Co₁.₅₀Ru₀.₅₀/SiO₂ catalysts at 573 K.
The furan deoxygenation activity decreased with time, but approached a steady-state at ~40-48 h on-stream. For this reason, activity comparisons are made at 48 h on-stream. Figure 3.17 shows a plot of furan deoxygenation activity at 48 h vs. Co content for selected Co-Ru/SiO₂ catalysts. A trend of initial increasing activity with Co content followed by a sharp decline in activity with increased Co content was observed, the catalyst having the composition Co₀.₅₀Ru₁.₅₀/SiO₂ was found to be the most active of the Co-Ru/SiO₂ catalysts.

![Figure 3.17](image)

**Figure 3.17** Furan deoxygenation activity at 48 h vs Co/(Co + Ru) molar ratio in the Co-Ru/SiO₂ catalyst precursors at 573 K.

The furan conversions, activities normalized by mass and mole of M₂P equivalent (M = Co + Ru), and the turnover frequencies (TOF) are listed below in Table 3.5 for the series of Co-Ru/SiO₂ catalysts.
Table 3.5 Furan deoxygenation activities and TOFs for Co-Ru/SiO₂ catalysts after 48 h on-stream at 573 K.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Furan Conversion</th>
<th>μmol furan/s/g cat</th>
<th>μmol furan/s/mol M₂P eq</th>
<th>TOF (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>6.6</td>
<td>2.01</td>
<td>3.06 × 10³</td>
<td>0.033</td>
</tr>
<tr>
<td>Co₀.₅₀Ru₁.₅₀</td>
<td>8.5</td>
<td>2.58</td>
<td>3.57 × 10³</td>
<td>0.043</td>
</tr>
<tr>
<td>Co₁.₀₀Ru₁.₀₀</td>
<td>3.6</td>
<td>1.10</td>
<td>1.38 × 10³</td>
<td>0.036</td>
</tr>
<tr>
<td>Co₁.₅₀Ru₀.₅₀</td>
<td>3.0</td>
<td>0.91</td>
<td>1.00 × 10³</td>
<td>0.065</td>
</tr>
<tr>
<td>Co₁.₇₅Ru₀.₂₅</td>
<td>3.4</td>
<td>1.04</td>
<td>1.07 × 10³</td>
<td>0.047</td>
</tr>
</tbody>
</table>

Supported cobalt-ruthenium phosphides (CoₓRu₂₋ₓP/SiO₂)

Furan deoxygenation activity measurements were carried out at 573 K as a function of time on-stream for the 15 wt% CoₓRu₂₋ₓP/SiO₂ catalysts. Shown in Figure 3.18 are the furan deoxygenation activity vs. time plots for 15 wt% Ru₂P/SiO₂, Co₁.₀₀Ru₁.₀₀P/SiO₂, Co₁.₅₀Ru₀.₅₀P/SiO₂, and Co₂P/SiO₂ catalysts.

Figure 3.18 Furan deoxygenation activity vs. time for 15 wt% Ru₂P/SiO₂, Co₁.₀₀Ru₁.₀₀P/SiO₂, Co₁.₅₀Ru₀.₅₀P/SiO₂, and Co₂P/SiO₂ catalysts at 573 K.
The Co,Ru$_{2-x}$P/SiO$_2$ catalysts showed only a slight increase or decrease in activity over the first few hours of testing and approached steady-state activity after ~5 h on-stream. The 15 wt% Co$_x$Ru$_{2-x}$P/SiO$_2$ catalysts showed similar activities after 48 h for catalysts having low Co content (Co/(Co + Ru) ratio below 0.5). Compared to the Co-Ru/SiO$_2$ catalysts, the Co$_x$Ru$_{2-x}$P/SiO$_2$ catalysts showed little to no deactivation over time, achieving steady-state activity after ~5 h on-stream. The Co$_x$Ru$_{2-x}$P/SiO$_2$ catalysts were significantly more active than the Co-Ru/SiO$_2$ catalysts after 48 h. The most active catalyst in the series, Co$_{1.50}$Ru$_{0.50}$P/SiO$_2$, had a Co/(Co + Ru) ratio of 0.75 as shown in Figure 3.19.

![Figure 3.19](image_url)  

**Figure 3.19** Furan deoxygenation activity at 48 h vs Co/(Co + Ru) molar ratio in the 15 wt% Co$_x$Ru$_{2-x}$P/SiO$_2$ catalysts at 573 K.

Catalysts with a Co/(Co + Ru) ratio above 0.75 showed a steep decline in activity with Co$_2$P/SiO$_2$ being the least active. A similar trend was observed with the TOFs, with the highest TOF at
Co/(Co + Ru) ratios above 0.50. The Co\textsubscript{1.50}Ru\textsubscript{0.50}P/SiO\textsubscript{2} catalyst was more than twice as active as Ru\textsubscript{2}P/SiO\textsubscript{2} and nearly 20 times more active than Co\textsubscript{2}P/SiO\textsubscript{2}.

The TOFs for the Co-Ru/SiO\textsubscript{2} and Co\textsubscript{x}Ru\textsubscript{2-x}P/SiO\textsubscript{2} catalysts are plotted in Figure 3.20. The TOFs for the Co-Ru/SiO\textsubscript{2} and Co\textsubscript{x}Ru\textsubscript{2-x}P/SiO\textsubscript{2} catalysts are steady with increased Co content until Co/(Co + Ru) > 0.5, when the TOFs increase substantially, then begin to drop at Co/(Co + Ru) > 0.75. The TOFs for the Co\textsubscript{x}Ru\textsubscript{2-x}P/SiO\textsubscript{2} catalysts start out lower than those of the Co-Ru/SiO\textsubscript{2} catalysts, but at Co/(Co + Ru) = 0.75, the TOF is 1.5 times higher than that of the Co-Ru/SiO\textsubscript{2} catalyst of a similar composition.

![Figure 3.20](image_url) Furan deoxygenation TOF at 48 h vs Co/(Co + Ru) molar ratio in the Co-Ru/SiO\textsubscript{2} and Co\textsubscript{x}Ru\textsubscript{2-x}P/SiO\textsubscript{2} catalysts at 573 K.

The furan conversions, activities normalized by mass and mole of M\textsubscript{2}P (M = Co + Ru), and the turnover frequencies are listed in Table 3.6 for the series of 15 wt% Co\textsubscript{x}Ru\textsubscript{2-x}P/SiO\textsubscript{2} catalysts.
Table 3.6 Furan deoxygenation activities for 15 wt% Co\textsubscript{\textit{x}} Ru\textsubscript{\textit{2-x}} P/SiO\textsubscript{2} catalysts after 48 h on-stream.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Furan Conversion</th>
<th>µmol furan/s/g cat</th>
<th>µmol furan/s/mol M\textsubscript{2}P</th>
<th>TOF (s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru\textsubscript{2}P</td>
<td>6.7</td>
<td>2.03</td>
<td>3.15 x 10\textsuperscript{3}</td>
<td>0.023</td>
</tr>
<tr>
<td>Co\textsubscript{0.25}Ru\textsubscript{1.75}P</td>
<td>6.0</td>
<td>1.83</td>
<td>2.72 x 10\textsuperscript{3}</td>
<td>0.019</td>
</tr>
<tr>
<td>Co\textsubscript{0.50}Ru\textsubscript{1.50}P</td>
<td>7.4</td>
<td>2.24</td>
<td>3.17 x 10\textsuperscript{3}</td>
<td>0.015</td>
</tr>
<tr>
<td>Co\textsubscript{0.75}Ru\textsubscript{1.25}P</td>
<td>5.9</td>
<td>1.80</td>
<td>2.42 x 10\textsuperscript{3}</td>
<td>0.017</td>
</tr>
<tr>
<td>Co\textsubscript{1.00}Ru\textsubscript{1.00}P</td>
<td>9.2</td>
<td>2.78</td>
<td>3.54 x 10\textsuperscript{3}</td>
<td>0.021</td>
</tr>
<tr>
<td>Co\textsubscript{1.25}Ru\textsubscript{0.75}P</td>
<td>12.8</td>
<td>3.90</td>
<td>4.69 x 10\textsuperscript{3}</td>
<td>0.103</td>
</tr>
<tr>
<td>Co\textsubscript{1.50}Ru\textsubscript{0.50}P</td>
<td>19.4</td>
<td>5.90</td>
<td>6.69 x 10\textsuperscript{3}</td>
<td>0.095</td>
</tr>
<tr>
<td>Co\textsubscript{1.75}Ru\textsubscript{0.25}P</td>
<td>11.3</td>
<td>3.45</td>
<td>3.66 x 10\textsuperscript{3}</td>
<td>0.048</td>
</tr>
<tr>
<td>Co\textsubscript{2}P</td>
<td>1.1</td>
<td>3.38</td>
<td>3.35 x 10\textsuperscript{2}</td>
<td>0.019</td>
</tr>
</tbody>
</table>

The product selectivities for the Co-Ru/SiO\textsubscript{2} and Co\textsubscript{\textit{x}} Ru\textsubscript{\textit{2-x}} P/SiO\textsubscript{2} catalysts are shown in Figure 3.21 and Figure 3.22, respectively.

![Figure 3.21](image-url) Product selectivity for furan deoxygenation over the Co-Ru/SiO\textsubscript{2} catalysts at 573 K.
The Co,Ru,P/SiO\textsubscript{2} catalysts yielded a mixture of C\textsubscript{3} and C\textsubscript{4} products, but favored the formation of C\textsubscript{3} hydrocarbons and CO while the Co-Ru/SiO\textsubscript{2} catalysts favored production of methane. Within the series of Co,Ru,P/SiO\textsubscript{2} catalysts, product selectivities were similar until the Co/(Co + Ru) fraction was above 0.50. Higher Co content catalysts showed lower propylene selectivity, while propane selectivity increased until the Co/(Co + Ru) ratio was above 0.75. Propylene production peaked for Co\textsubscript{2}P/SiO\textsubscript{2} while the C\textsubscript{4} production dropped off. For the series of Co,Ru\textsubscript{2-x}/SiO\textsubscript{2} catalysts, the product selectivities showed no significant changes with metal composition.

Figure 3.23 shows the selectivity differences between selected Co-Ru/SiO\textsubscript{2} and Co,Ru,P/SiO\textsubscript{2} catalysts. The Co-Ru/SiO\textsubscript{2} catalysts favored CH\textsubscript{4} while the Co,Ru\textsubscript{2-x}P/SiO\textsubscript{2} catalysts favored
longer chain hydrocarbons (C₃ and C₄). Little change was observed as Co was introduced into the Co-
Ru/SiO₂ catalysts, while increased Co content in the CoₓRu₂₋₄ₓP/SiO₂ catalysts showed higher
selectivity for propane and decreased selectivity for propylene.

![Selectivity Graph](image)

**Figure 3.23** Product selectivities for furan deoxygenation over silica-supported Ru, Ru₂P, Co₁.₅₀Ru₀.₅₀, and Co₁.₅₀Ru₀.₅₀P catalysts at 573 K.

### 3.2.2 Nickel-Ruthenium Catalysts

*Supported nickel-ruthenium metal (Ni-Ru/SiO₂) catalysts*

Furan deoxygenation activity measurements were carried out at 573 K as a function of time
on-stream for the Ni-Ru/SiO₂ catalysts having different metal compositions. Shown in Figure 3.24 are
plots of furan deoxygenation activity vs time on-stream for Ru/SiO₂, Ni₀.₅₀Ru₁.₅₀/SiO₂,
Ni₁.₀₀Ru₁.₀₀/SiO₂, Ni₁.₅₀Ru₀.₅₀/SiO₂, and Ni/SiO₂ catalysts.
Figure 3.24 Furan deoxygenation activity vs time for Ru/SiO₂, Ni/SiO₂, Ni₀.₅₀Ru₁.₅₀/SiO₂, Ni₁.₀₀Ru₁.₀₀/SiO₂, and Ni₁.₅₀Ru₀.₅₀/SiO₂ catalysts at 573 K.

The furan deoxygenation activities decreased with time, but approached steady-state values at ~40-48 h on-stream. For this reason, activity comparisons are made at 48 h on-stream. A trend of increasing activity with Ni content during the first few hours followed by a sharp decline in activity with increased Ni content was observed as shown in Figure 3.25. The Ni₀.₅₀Ru₁.₅₀/SiO₂ catalyst was found to be more than twice as active as Ni₁.₅₀Ru₀.₅₀/SiO₂ after 48 h on-stream. The furan conversions and activities normalized by mass and mole of M₂P equivalent (M = Co + Ru) are listed in Table 3.7 for the series of Ni-Ru/SiO₂ catalysts.
Figure 3.25 Furan deoxygenation activity at 48 h vs Ni/(Ni + Ru) molar ratio in the Ni-Ru/SiO₂ catalyst precursors at 573 K.

Table 3.7 Furan deoxygenation activities for Ni-Ru/SiO₂ catalysts after 48 h on-stream.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Furan Conversion</th>
<th>µmol furan/s/g cat</th>
<th>µmol furan/s/mol M₂P eq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>6.6</td>
<td>2.01</td>
<td>3.06 × 10^3</td>
</tr>
<tr>
<td>Ni₀.₅₀Ru₁.₅₀</td>
<td>12.9</td>
<td>3.92</td>
<td>5.42 × 10^3</td>
</tr>
<tr>
<td>Ni₁.₀₀Ru₁.₀₀</td>
<td>10.1</td>
<td>3.06</td>
<td>3.80 × 10^3</td>
</tr>
<tr>
<td>Ni₁.₅₀Ru₀.₅₀</td>
<td>6.2</td>
<td>1.87</td>
<td>2.06 × 10^3</td>
</tr>
<tr>
<td>Ni₁.₇₅Ru₀.₂₅</td>
<td>4.3</td>
<td>1.30</td>
<td>1.34 × 10^3</td>
</tr>
<tr>
<td>Ni</td>
<td>11.9</td>
<td>3.62</td>
<td>3.47 × 10^3</td>
</tr>
</tbody>
</table>

Supported nickel-ruthenium phosphide (NiₙRu₂₋ₙP/SiO₂) catalysts

Furan deoxygenation activity measurements were carried out at 573 K as a function of time on-stream for the 15 wt% NiₙRu₂₋ₙP/SiO₂ catalysts. Shown below in Figure 3.26 are the furan deoxygenation activity vs. time plots for 15 wt% Ru₂P/SiO₂, Ni₀.₅₀Ru₁.₅₀P/SiO₂, Ni₁.₀₀Ru₁.₀₀P/SiO₂, Ni₁.₅₀Ru₀.₅₀P/SiO₂, and Ni₃P/SiO₂ catalysts.
Figure 3.26 Furan deoxygenation activity vs. time for 15 wt% Ru$_2$P/SiO$_2$, Ni$_{0.50}$Ru$_{1.50}$P, Ni$_{1.00}$Ru$_{1.00}$P/SiO$_2$, Ni$_{1.50}$Ru$_{0.50}$P/SiO$_2$, and Ni$_2$P/SiO$_2$ catalysts at 573 K.

A majority of the catalysts showed a slight increase or decrease in activity over the first few hours of testing. By ~30 h on-stream all catalysts achieved steady-state activity. Ni$_{1.50}$Ru$_{0.50}$P/SiO$_2$ was more than twice as active as Ru$_2$P/SiO$_2$ and nearly 90 times more active than Ni$_2$P/SiO$_2$. The furan conversions, activities normalized by mass and mole of M$_2$P (M = Ni + Ru), as well as the TOFs are listed in Table 3.8 for the series of 15 wt% Ni$_x$Ru$_{2-x}$P/SiO$_2$ catalysts.
Table 3.8 Furan deoxygenation activities for 15 wt% Ni<sub>x</sub>Ru<sub>2-x</sub>P/SiO<sub>2</sub> catalysts after 48 h on-stream.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Furan Conversion</th>
<th>μmol furan/s/g cat</th>
<th>μmol furan/s/mol M&lt;sub&gt;2&lt;/sub&gt;P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru&lt;sub&gt;2&lt;/sub&gt;P</td>
<td>6.7</td>
<td>2.03</td>
<td>3.15 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;0.25&lt;/sub&gt;Ru&lt;sub&gt;1.75&lt;/sub&gt;P</td>
<td>6.0</td>
<td>1.84</td>
<td>2.73 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;0.50&lt;/sub&gt;Ru&lt;sub&gt;1.50&lt;/sub&gt;P</td>
<td>3.2</td>
<td>9.61</td>
<td>1.36 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;0.75&lt;/sub&gt;Ru&lt;sub&gt;1.25&lt;/sub&gt;P</td>
<td>9.3</td>
<td>2.85</td>
<td>3.82 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;1.00&lt;/sub&gt;Ru&lt;sub&gt;1.00&lt;/sub&gt;P</td>
<td>6.8</td>
<td>2.07</td>
<td>2.63 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;1.25&lt;/sub&gt;Ru&lt;sub&gt;0.75&lt;/sub&gt;P</td>
<td>4.8</td>
<td>1.46</td>
<td>1.76 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;1.50&lt;/sub&gt;Ru&lt;sub&gt;0.50&lt;/sub&gt;P</td>
<td>22.0</td>
<td>6.69</td>
<td>7.57 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;1.75&lt;/sub&gt;Ru&lt;sub&gt;0.25&lt;/sub&gt;P</td>
<td>25.7</td>
<td>7.84</td>
<td>8.31 x 10&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;2&lt;/sub&gt;P</td>
<td>0.3</td>
<td>0.09</td>
<td>8.71 x 10&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

The 15 wt% Ni<sub>x</sub>Ru<sub>2-x</sub>P/SiO<sub>2</sub> catalyst series showed peak activity for the Ni/(Ni + Ru) ratio of 0.875 (Ni<sub>1.75</sub>Ru<sub>0.25</sub>P/SiO<sub>2</sub>) as shown in Figure 3.27. The Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst had very low activity relative to the catalysts containing Ru.

Figure 3.27 Furan deoxygenation activity at 48 h vs Co/(Co + Ru) molar ratio in the 15 wt% Co<sub>x</sub>Ru<sub>2-x</sub>P/SiO<sub>2</sub> catalysts at 573 K.
The TOFs for the Ni-Ru/SiO\textsubscript{2} and Ni\textsubscript{x}Ru\textsubscript{2-x}P/SiO\textsubscript{2} catalysts are plotted in Figure 3.28. The TOFs for the Ni\textsubscript{x}Ru\textsubscript{2-x}P/SiO\textsubscript{2} catalysts are steady with the addition of Ni content until Ni/(Ni + Ru) > 0.625, when the TOFs increase substantially, then drop for Ni/(Ni + Ru) > 0.875. The TOFs for the Ni-Ru/SiO\textsubscript{2} catalysts are highest at low Ni content (Ni\textsubscript{0.50}Ru\textsubscript{1.50}/SiO\textsubscript{2}) catalysts.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.28.png}
\caption{Furan deoxygenation TOF at 48 h vs Ni/(Ni + Ru) molar ratio in the Ni-Ru/SiO\textsubscript{2} and Ni\textsubscript{x}Ru\textsubscript{2-x}P/SiO\textsubscript{2} catalysts at 573 K.}
\end{figure}

The product selectivities for the Ni-Ru/SiO\textsubscript{2} and Ni\textsubscript{x}Ru\textsubscript{2-x}P/SiO\textsubscript{2} catalysts are shown in Figure 3.29 and Figure 3.30, respectively.
Figure 3.29 Product selectivity for furan deoxygenation over Ni-Ru/SiO$_2$ at 573 K.

Figure 3.30 Product selectivity for furan deoxygenation over 15 wt% Ni$_x$Ru$_{2-x}$/P/SiO$_2$ at 573 K.
The Ni$_x$Ru$_{2-x}$P/SiO$_2$ catalysts showed a mixture of C$_3$ and C$_4$ products, but favored the formation of C$_3$ hydrocarbons and CO. For the series of Ni$_x$Ru$_{2-x}$P/SiO$_2$ catalysts, the selectivities varied but always favored production of C$_3$ hydrocarbons. Higher Ni content caused propylene production to decrease while propane production increased until the Ni/(Ni + Ru) ratio was above 0.75, when propylene production increased and peaked, while C$_4$ production was at its lowest. The Ni-Ru/SiO$_2$ catalysts favored production of methane. For the series of Ni$_x$Ru$_{2-x}$/SiO$_2$ catalysts, product selectivities were similar and showed no significant changes with metal composition until Ni/SiO$_2$. The Ni/SiO$_2$ catalyst showed an increase in C$_3$ production and a decrease in methane and C$_2$ production relative to the catalysts containing Ru. Figure 3.31 shows the selectivity differences between selected Ni-Ru/SiO$_2$ and Ni$_x$Ru$_{2-x}$/SiO$_2$ catalysts.

Figure 3.31 Product selectivities for furan deoxygenation over silica-supported Ru, Ru$_2$P, Ni$_{1.50}$Ru$_{0.50}$, and Ni$_{1.50}$Ru$_{0.50}$P catalysts at 573 K.
The Ni-Ru/SiO$_2$ catalysts favored CH$_4$ while the Ni$_x$Ru$_{2-x}$P/SiO$_2$ catalysts favored longer chain hydrocarbons (C$_3$ and C$_4$). Little change was observed as Ni was introduced into the Ni-Ru/SiO$_2$ catalysts while increased Ni content in the Ni$_x$Ru$_{2-x}$P/SiO$_2$ catalysts resulted in substantially higher selectivity for propane and propylene selectivity decreased to 0.5 mol%. 
Chapter 4: Discussion

As the world’s demand for petroleum steadily increases, finite supplies and climate change concerns demand innovation in alternative and renewable transportation fuels. Bio-oil produced from the fast pyrolysis of biomass can alleviate some of the world’s demand for crude oil if its economical upgrading to transportation fuels can be accomplished.\(^6\),\(^32\),\(^33\),\(^49\)-\(^51\) Biomass contains many oxygen containing compounds including lignin, cellulose, and hemi-cellulose. Following fast pyrolysis, much of the oxygen from the biomass gets transferred to the bio-oil in the form of guaiacols, catechols, syringols, vanillins, acetic acid, formic acid and other oxygenated compounds.\(^5\),\(^7\) Oxygen containing compounds are undesirable in transportation fuel feedstocks because they are less energy dense than petroleum, and are also corrosive and unstable. The goal of this research was to synthesize, characterize, and evaluate new catalysts that are more effective and efficient at removing oxygen impurities from bio-oil feedstocks than current hydrotreating catalysts.

Alumina-supported Co-Mo and Ni-Mo sulfide catalysts have been used as industrial hydrotreating catalysts in the removal of sulfur and nitrogen impurities from crude oil feedstocks for decades.\(^9\),\(^33\),\(^39\) These sulfide catalysts have also been used in the deoxygenation of bio-oil; however, environmentally unwanted sulfur must be added to the feed to prevent deactivation.\(^51\) Noble metals (e.g., Ru, Pd, Pt, Re, and Rh) have been used as catalysts for the deoxygenation of bio-oil model compounds and show a marked improvement over industrial hydrotreating catalysts.\(^24\),\(^28\),\(^41\),\(^49\),\(^52\) Noble metals suffer from a number of drawbacks, however, including scarcity, deactivation, and high cost.

Ruthenium has been investigated as a potential catalyst for the hydrotreatment of bio-oil because of its higher activity compared to earth abundant metals (e.g., Ni, Co, Fe, and Mo) and
because it is more economically viable than other noble metals (e.g., Pt and Rh).\textsuperscript{24,53-56} Previous work in the Bussell group has shown ruthenium phosphides (RuP/SiO\textsubscript{2} and Ru\textsubscript{2}P/SiO\textsubscript{2}) to be more effective at removing oxygen than ruthenium metal (Ru/SiO\textsubscript{2}) and commercial Co-Mo/Al\textsubscript{2}O\textsubscript{3} hydrotreating catalysts for the deoxygenation of furan.\textsuperscript{28} An Ru\textsubscript{2}P/SiO\textsubscript{2} catalyst was found to be nearly three times more active than an Ru/SiO\textsubscript{2} catalyst and two to three times more active than an RuP/SiO\textsubscript{2} catalyst.\textsuperscript{28}

Early work on the deoxygenation of furan over industrial sulfided Co-Mo hydrotreating catalysts by Furimsky \textit{et al.} showed selectivity for butadiene, butenes, and propylene. Butenes are produced through the hydrodeoxygenation (HDO) pathway by cleavage of the C-O bond while propylene is produced through the decarbonylation pathway by selective cleavage of a C-C bond. The deoxygenation pathways proposed for furan are shown in Figure 4.1. The first pathway involves ring opening of furan (1a) followed by decarbonylation to give propylene (1b) or HDO to give butenes (1c), depending on the availability of surface hydrogen.\textsuperscript{57} The second pathway (2a) involves ring opening of the furan and C-O bond cleavage to form butadiene, which may or may not be further hydrogenated.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{reaction PATHWAYS.png}
\caption{Proposed reaction pathways for furan over sulfided Co-Mo catalysts.\textsuperscript{57}}
\end{figure}
Only a few furan deoxygenation studies have been carried out for noble metal catalysts. Furan deoxygenation over Pt nanoparticle catalysts was performed by Kliewer et al.\textsuperscript{58} Dihydrofuran (DHF), tetrahydrofuran (THF), butanol, and propylene were detected and propylene was observed to be the major hydrocarbon product at temperatures in the range 373 K to 413 K. The proposed reaction network is shown in Figure 4.2.

![Proposed deoxygenation reaction network for furan over Pt nanoparticle catalysts.\textsuperscript{58}](image)

**Figure 4.2** Proposed deoxygenation reaction network for furan over Pt nanoparticle catalysts.\textsuperscript{58}

The activity and selectivity of a catalyst can be tuned by changing its composition.\textsuperscript{59} Changing the composition has been shown to affect the geometric, magnetic, and electronic properties of a catalyst.\textsuperscript{23, 60, 61} For example, a change in lattice structure from hexagonal close packed to face centered cubic was observed for Co-Ru alloys with Co concentrations greater than 75 at. %.\textsuperscript{62} There has been significant interest in the catalytic properties of Co-Ru and Ni-Ru alloys.\textsuperscript{60, 63-71} Synergistic effects have been observed in Co-Ru and Ni-Ru catalysts that warrant investigation of bimetallic ruthenium and ruthenium phosphide catalysts for the deoxygenation of bio-oil.\textsuperscript{72-78} Huang et al reported rate enhancements of ethylene hydroformylation for Co-Ru catalysts and attributed them to synergistic effects between ruthenium and cobalt in supported catalysts.\textsuperscript{77} Rangan et al observed enhanced activity for the reforming of biomass gasification products over Ni-Ru catalysts compared to Ni.\textsuperscript{73} To optimize the properties of Ru\textsubscript{2}P/SiO\textsubscript{2} catalysts previously studied by the Bussell
group, this thesis research focused on the role of a second metal (Co or Ni) introduced to replace some of the expensive ruthenium, producing silica-supported M-Ru alloys and M-Ru phosphides (M = Co or Ni).

**Co-Ru and Ni-Ru alloys**

XRD analysis confirmed the synthesis of phase pure alloys in the M-Ru/SiO\(_2\) catalyst series. XRD patterns were consistent with an Ru phase for M/(M + Ru) ratios ≤ 0.75, and Co or Ni phases for ratios > 0.75. There was a distinct shift of XRD peak positions to higher Bragg angles with the introduction of the smaller Co or Ni atoms into the crystal lattice. The peaks shifted smoothly as the amount of Co or Ni increased for the Co-Ru/SiO\(_2\) and Ni-Ru/SiO\(_2\) catalyst series. This trend is consistent with the replacement of the larger Ru atoms with smaller Co or Ni atoms in the crystal lattice, allowing the lattice to contract, and was observed by Qadri *et al* in Co-Ru nanocrystalline alloys.\(^{62}\) The Scherrer equation was used to calculate the average crystallite sizes for the M-Ru/SiO\(_2\) catalysts, ranging from 10 to 13 nm with the exception of Co (30 nm) and Ni (28 nm). The crystallite sizes after furan deoxygenation testing were similar to the as-prepared crystallite sizes, indicating that little to no sintering occurred in reaction conditions.

CO chemisorption measurements were carried out to determine the active site densities of the as-prepared catalysts. Since no significant sintering was observed, CO chemisorption should be a good measure of active site densities on the catalysts during furan deoxygenation. CO chemisorption capacities were found to decrease with increased Co content for the Co-Ru/SiO\(_2\) and Ni-Ru/SiO\(_2\) catalyst series until the metal fraction (M/(M + Ru)) was above 0.75 as shown in Figure 4.3. Similar trends of decreased chemisorption capacity with increased Co or Ni content have been observed with Ni-Ru and Co-Ru catalysts supported on carbon.\(^{68}\) Huang *et al*. also observed a decrease of CO chemisorption capacity with the incorporation of Co content in Co-Ru/SiO\(_2\).
catalysts. No adsorption of CO onto Co/SiO₂ catalysts was observed at ~298 K and attributed the lower CO adsorption capacity of the Co-Ru/SiO₂ catalysts to a lower density of Ru sites on the bimetallic surfaces. Similarly, the Co/SiO₂ catalyst in this research was found to have a much lower CO chemisorption capacity (34 µmol CO/g cat) than the Ru/SiO₂ catalyst (61 µmol CO/g cat); however, it was greater than zero. This is likely due to our adsorption measurements being carried out at 273 K instead of at ambient temperature as was the case in the study by Huang et al.

![Graph showing CO chemisorption capacities for as-prepared M-Ru/SiO₂ catalysts.](image)

**Figure 4.3** CO chemisorption capacities for as-prepared M-Ru/SiO₂ catalysts.

Furan deoxygenation activity measurements were performed on a series of the M-Ru/SiO₂ catalysts to assess their ability for hydrotreating of bio-.oils. Preliminary furan deoxygenation
measurements were performed on Ru/SiO₂, Co₁₀₀Ru₁₀₀/SiO₂, and Co/SiO₂ catalysts at varying reaction temperatures to find the optimal reaction temperature for further reaction studies to probe the effects of catalyst composition. The Co-Ru/SiO₂ catalysts showed high selectivity towards methane at reaction temperatures in the range 423-673 K and showed steady deoxygenation activity between 523 K and 673 K. As a result, a reaction temperature of 573 K was selected for the composition studies.

Furan deoxygenation measurements were performed at 573 K for the Co-Ru/SiO₂ and Ni-Ru/SiO₂ series. Ni₀₅₀Ru₁₅₀/SiO₂ was found to be the most active M-Ru/SiO₂ catalyst, and was nearly twice as active as Ru/SiO₂ and more than 20 times as active as an industrial Co-Mo/Al₂O₃ catalyst. A similar synergistic effect has been observed for Pt-rich Ni-Pt catalysts for NO reduction while less dramatic effects were observed for Pt-rich Co-Pt catalysts. Furan deoxygenation in the Co-Ru/SiO₂ series, and was found to have 1.3 times higher activity than Ru/SiO₂. The plot in Figure 4.4 shows the linear relationship of furan deoxygenation activity and the number of active sites (CO chemisorption capacity) for the Co-Ru/SiO₂ catalyst series, indicating that the activity is proportional to the number of active sites. The slope of the straight line is the TOF. Since there is a linear relationship between activity and active site density, it can be concluded that the introduction of Co into the catalysts does not impart structural or electronic changes that significantly affect the properties of the active sites for furan deoxygenation.
The product selectivities after 48 h on-stream were determined in order to understand the furan deoxygenation reaction pathways for the M-Ru/SiO₂ catalysts. The M-Ru/SiO₂ catalysts showed high selectivity towards methane and C₂ hydrocarbons (31-52 mol%), indicating that hydrocarbon products of the deoxygenation pathways shown in Figure 4.1 or Figure 4.2 undergo further reactions in which C-C bonds are cleaved via hydrogenolysis to give CH₄ and C₂H₆. These hydrogenolysis reactions are undesirable for the purpose of creating a liquid fuel feedstock because gaseous hydrocarbons are produced. C₃ hydrocarbons were minor products (~20-32 mol%), created through the decarbonylation pathway.

**Figure 4.4** Furan deoxygenation activity vs. CO chemisorption capacity of Co-Ru/SiO₂ catalysts.
Co$_x$Ru$_{2-x}$P and Ni$_x$Ru$_{2-x}$P

There have been two reported studies of NiRuP and CoRuP, but focused only on their structural and magnetic properties.$^{60,81}$ Ohta et al reported that introducing Co or Ni into ruthenium phosphide reduced the magnetic susceptibility of Ru$_2$P.$^{60}$ NiRuP and CoRuP were found to have orthorhombic crystal structures with the lattice parameters listed in Table 4.1.$^{81}$

**Table 4.1** Lattice parameters and molecular volumes for Ru$_2$P, Co$_2$P, Ni$_2$P, and MRuP compositions.$^{81}$

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å$^3$)</th>
<th>V/c$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru$_2$P orth</td>
<td>5.902</td>
<td>3.859</td>
<td>6.896</td>
<td>39.26</td>
<td>0.683</td>
</tr>
<tr>
<td>CoRuP orth</td>
<td>5.688</td>
<td>3.691</td>
<td>6.756</td>
<td>35.45</td>
<td>0.705</td>
</tr>
<tr>
<td>NiRuP orth</td>
<td>5.717</td>
<td>3.656</td>
<td>6.838</td>
<td>35.74</td>
<td>0.731</td>
</tr>
<tr>
<td>Co$_2$P orth</td>
<td>5.646</td>
<td>3.513</td>
<td>6.608</td>
<td>32.75</td>
<td>0.755</td>
</tr>
<tr>
<td>Ni$_2$P hex</td>
<td>5.865</td>
<td>3.387</td>
<td>33.66</td>
<td>0.866</td>
<td></td>
</tr>
</tbody>
</table>

XRD analysis confirmed the synthesis of the M$_x$Ru$_{2-x}$P/SiO$_2$ catalysts from precursors having a P/M ratio of 0.72. Similar to the M-Ru/SiO$_2$ catalyst series, a shift of the peak positions to higher Bragg angles with the introduction of Co or Ni was observed for both the Co$_x$Ru$_{2-x}$P/SiO$_2$ and Ni$_x$Ru$_{2-x}$P/SiO$_2$ catalyst series. The Scherrer equation was used to calculate the average crystallite sizes for the catalysts, ranging from 7 to 16 nm with the exception of Co$_2$P (30 nm). The crystallite sizes were maintained after deoxygenation testing, implying that little to no sintering of the phosphide phase occurred.

CO chemisorption capacities were found to increase for low Co or Ni contents, then to decrease with increased Co or Ni content for (x ≥ 0.50) for the Co$_x$Ru$_{2-x}$P/SiO$_2$ and Ni$_x$Ru$_{2-x}$P/SiO$_2$ catalyst series as shown in Figure 4.5.
Figure 4.5 CO chemisorption capacities for as-prepared \( M_xRu_{2-x}P/SiO_2 \) catalysts.

Furan deoxygenation activity measurements were carried out for a series of 15 wt\% \( M_xRu_{2-x}P/SiO_2 \) (\( M = \text{Co, Ni} \)) catalysts to assess their ability for hydrotreating of bio-oils. Furan was selected as the model compound because it is a common building block of bio-oil compounds and because of its aromaticity; aromatic compounds are more difficult to deoxygenate than aliphatic compounds.\(^{49}\) Preliminary furan deoxygenation measurements were performed on 15 wt\% Ru\(_2\)P/SiO\(_2\), Co\(_{1.00}\)Ru\(_{1.00}\)P/SiO\(_2\), and Co\(_2\)P/SiO\(_2\) catalysts at varying reaction temperatures as described in Section 3.4. The Co\(_2Ru_{2-x}\)P/SiO\(_2\) catalyst showed the highest deoxygenation activity at high temperatures (~673 K) and high selectivity for propylene and n-butane at temperatures > 523 K. This is in contrast to the Ru/SiO\(_2\) and Co\(_{1.00}\)Ru\(_{1.00}\)/SiO\(_2\) catalysts that showed higher conversion at lower temperatures and showed high selectivity for CH\(_4\). As a mid-way point between the maximum furan conversion of
the Co-Ru/SiO₂ and Co₉Ru₂ₓP/SiO₂ catalysts, a reaction temperature of 573 K was selected for
detailed studies of the effects of catalyst composition.

Furan deoxygenation measurements were performed at 573 K for the 15 wt% MₙRu₂ₓP/SiO₂
catalyst series. Ni₁.₇₅Ru₀.₅₀P/SiO₂ was found to be the most active of the phosphide catalysts; it was
nearly three times as active as Ru₂P/SiO₂ and over 50 times more active than an industrial Co-
Mo/Al₂O₃ catalyst. The furan deoxygenation activities and CO chemisorption capacities are shown in
Figure 4.6 and Figure 4.7 for the CoₓRu₂ₓP/SiO₂ and NiₓRu₂ₓP/SiO₂ catalyst series,
respectively. The furan deoxygenation activities of the MₓRuₓP/SiO₂ catalysts do not correlate with
their CO chemisorption capacities as was observed for the M-Ru/SiO₂ series.

![Figure 4.6](image-url)  
**Figure 4.6** Furan deoxygenation activities at 573 K and CO chemisorption capacities for 15 wt%
Co₉Ru₂ₓP/SiO₂ catalysts.
While the CO chemisorption capacity reaches its maximum value at \( \frac{M}{(M + Ru)} = 0.25 \), the deoxygenation activity peaks at \( \frac{M}{(M + Ru)} = 0.75 \) for Co and 0.875 for Ni. When plotted as TOFs (Figure 3.20), a maximum TOF is achieved at \( \frac{Co}{(Co + Ru)} = 0.625 \), corresponding to a value more than five times higher than \( Ru_2P/SiO_2 \) or \( Co_2P/SiO_2 \). This supports the idea of synergy between the two metals since some of the bimetallic phosphide compositions have higher TOFs than either of the monometallic catalysts.

![Graph showing activity and chemisorption capacity for various compositions](image)

**Figure 4.7** Furan deoxygenation activities at 573 K and CO chemisorption capacities for 15 wt% \( Ni_xRu_{2-x}P/SiO_2 \) catalysts.

At 48 h on-stream, the most active \( Co_xRu_{2-x}P/SiO_2 \) catalyst (\( Co_{1.50}Ru_{0.50}P/SiO_2 \)) was more than six times as active as \( Co_{1.50}Ru_{0.50}P/SiO_2 \) and more than two times more active than the \( Ru/SiO_2 \) metal catalyst as shown in Figure 4.8. At 48 h on-stream \( Ni_{1.50}Ru_{0.50}P/SiO_2 \) was the most active \( Ni_xRu_2 \).
The P/SiO$_2$ catalyst, more than three times as active as Ni$_{1.50}$Ru$_{0.50}$/SiO$_2$ and nearly twice as active as the most active metal catalyst of the series (Ni$_{1.5}$Ru$_{1.5}$/SiO$_2$) as shown in Figure 4.9. The significant improvement in activity as well as its resistance to deactivation suggest a strong potential for M$_x$Ru$_2$-P/SiO$_2$ catalysts in the deoxygenation of bio-oil.

**Figure 4.8** Furan deoxygenation activity at 573 K vs. time for Ru/SiO$_2$, Co$_{1.50}$Ru$_{0.50}$/SiO$_2$, and Co$_{1.50}$Ru$_{0.50}$P/SiO$_2$ catalysts.
The Co$_{1.50}$Ru$_{0.50}$P/SiO$_2$ and Ni$_{1.50}$Ru$_{0.50}$P/SiO$_2$ catalysts exhibited little or no decrease in activity over time and while the Co$_{0.50}$Ru$_{1.50}$/SiO$_2$ and Ni$_{0.50}$Ru$_{1.50}$/SiO$_2$ catalysts exhibited substantial deactivation in the first 10-15 h of reaction. There are three main types of catalyst deactivation; chemical (e.g., poisoning), mechanical (e.g., coking), and thermal (e.g. sintering). The crystallite size stability confirmed by XRD rules out the possibility of sintering of the catalyst particles as the source of the deactivation. Previous studies have shown that there has been a relatively low carbon content for Ru$_2$P/SiO$_2$, Ru/SiO$_2$, and Ni$_2$P/SiO$_2$ catalysts following furan deoxygenation testing. Noble metals are known for being susceptible to poisoning by CO and S. While sulfur poisoning is
unlikely, it is possible that Ru deactivation by CO poisoning could be responsible for the trend of decreasing activity over time for the M-Ru/SiO₂ catalysts during furan deoxygenation.

Higher catalytic activity and improved stability of metal phosphide catalysts relative to metal catalysts having similar compositions has been observed before. In the case of the water-gas-shift reaction over Ni₂P(001), the O atoms deposited on the surface by dissociation of H₂O under reaction conditions preferentially interact with the P atoms, creating a Ni oxy-phosphide species that may inhibit the combination of Ni with O and enhance the oxidation resistance of Ni₂P.

Bussel et al. reported increased resistance to sulfur poisoning for noble metal phosphides (Rh₂P/SiO₂, Ru₂P/SiO₂) compared to the noble metals (Rh/SiO₂, Ru/SiO₂) for the hydrodesulfurization of dibenzothiophene. If active sites of the MₓRu₂₋ₓP/SiO₂ catalysts are more resistant to oxidation than in the M-Ru alloys, this may account for the relative stability of the MₓRu₂₋ₓP/SiO₂ catalysts compared to the M-Ru/SiO₂ catalysts.

The furan deoxygenation product selectivities after 48 h on-stream were calculated to determine the reaction pathways. The product selectivities of the MₓRu₂₋ₓP/SiO₂ catalyst series varied significantly from those of the M-Ru/SiO₂ catalysts. The MₓRu₂₋ₓP/SiO₂ catalysts showed high selectivity for C₃ and C₄ hydrocarbon products. Previous studies on the deoxygenation of furan over Co-Mo/Al₂O₃ found C₄s to be the primary products, specifically butadiene. The hydrogenation of furan over Pt(111) was found to favor butanol at a reaction temperature of 443 K, other detectable products were tetrahydrofuran and dihydrofuran. The CoₓRu₂₋ₓP/SiO₂ and NiₓRu₂₋ₓP/SiO₂ catalysts tested showed 15-19 mol% and 10-22 mol% selectivities for C₄ hydrocarbons, respectively, which are produced by cleavage of the C-O bond. This pathway is desirable because it retains energy density by keeping the carbon backbone intact. Interestingly, no butadiene, tetrahydrofuran, or dihydrofuran products were observed for any of the catalysts tested, which is likely due to the
higher reaction temperatures employed in this thesis research. In their studies of Co-Mo/Al₂O₃ catalysts, Schulz and Rahman observed that C₃ vs C₄ selectivity was dependent upon the H₂ pressure, which they attributed to increased availability of H₂ on the catalyst surface. The authors showed that the proportion of C₃S can be reduced by increasing H₂ pressure since the HDO pathway requires more H₂. All of the MₓRu₂₋ₓP/SiO₂ catalysts showed highest selectivity towards C₃ products (39-58 mol%), indicating that the preferred deoxygenation pathway is decarbonylation. While cleavage of C-C bonds is undesirable, this pathway does consume less hydrogen and CO can be used in syn-gas to prepare longer chain hydrocarbon products.
Chapter 5: Conclusion and Future Work

The goal of this thesis research was to synthesize, characterize, and evaluate a number of bimetallic phosphides of ruthenium for use in bio-oil processing. The silica-supported bimetallic phosphides (M\(_x\)Ru\(_{2-x}\)P/SiO\(_2\)) were synthesized using hypophosphite-based precursors with Co or Ni as the second metal and were tested for their furan deoxygenation properties. The M\(_x\)Ru\(_{2-x}\)P/SiO\(_2\) catalysts were compared with metal catalysts of similar compositions (M-Ru/SiO\(_2\)) and an industrial sulfided Co-Mo/Al\(_2\)O\(_3\) hydrotreating catalyst. Synergistic effects were observed for the Co- and Ni-rich M\(_x\)Ru\(_{2-x}\)P/SiO\(_2\) catalysts as their deoxygenation activities were significantly higher than either Ru\(_2\)P/SiO\(_2\) or M\(_2\)P/SiO\(_2\) (M = Co or Ni). The TOFs of the M\(_x\)Ru\(_{2-x}\)P/SiO\(_2\) catalysts reflected the high activities of these catalysts and they were also found to be more active and less susceptible to deactivation than the M-Ru/SiO\(_2\) catalysts of similar composition. The high furan deoxygenation activity of M\(_x\)Ru\(_{2-x}\)P/SiO\(_2\) catalysts provide evidence for their use in upgrading bio-oil to transportation fuels. M-Ru/SiO\(_2\) showed undesirable selectivity for CH\(_4\) through C-C hydrogenolysis.

Future research should include more extensive surface characterization of the M\(_x\)Ru\(_{2-x}\)P/SiO\(_2\) catalysts, including FTIR spectroscopy of adsorbed CO to probe the structure of the active sites. In this regard, XPS should also be used to measure the surface compositions and oxidation states of the as-prepared and deoxygenation-tested catalysts. The effect of increased H\(_2\) pressure on the deoxygenation pathways should be explored in order to optimize the selectivity towards C\(_4\) products. Finally, because bio-oil is a broad mixture of hydrocarbons, other bio-oil model compounds such as guaiacol and crotonaldehyde should be used to more fully assess the effectiveness of M\(_x\)Ru\(_{2-x}\)P/SiO\(_2\) catalysts for upgrading bio-oils to transportation fuels.
References


Appendix A: Calibration Standards

**Figure A.1** FID and TCD GC plots of a C$_1$-C$_6$ alkane calibration gas standard mix.
Figure A.2 FID and TCD GC plots of a C₄ hydrocarbon calibration gas standard mix.
Figure A.3 FID and TCD GC plots of a non-condensable gas calibration standard mix.
Figure A.4 FID and TCD GC plots of a propane calibration standard.

Figure A.5 FID and TCD GC plots of a propylene calibration standard.
Figure A.6 FID and TCD GC plots of a trans-2-butene calibration standard.

Figure A.7 FID and TCD GC plots of a 1-butene calibration standard.
Figure A.8 FID and TCD GC plots of a cis-2-butene calibration standard.
Appendix B: Supplemental Furan Deoxygenation Testing

Figure B.1 Furan deoxygenation activity measurements vs. time for an industrial Co-Mo/Al₂O₃ catalyst.
**Figure B.2** Furan deoxygenation activity measurements vs. temperature for 12.3 wt% Co/SiO$_2$, 15 wt% Co$_3$P/SiO$_2$, and Co-Mo/Al$_2$O$_3$ catalysts.

**Figure B.3** Furan deoxygenation activity measurements vs. temperature for 12.9 wt% Co$_{1.00}$Ru$_{1.00}$/SiO$_2$, 15 wt% Co$_{1.00}$Ru$_{1.00}$P/SiO$_2$, and Co-Mo/Al$_2$O$_3$ catalysts.
Figure B.4 Product selectivity vs. temperature for furan deoxygenation over a 12.3 wt% Co/SiO$_2$ catalyst.

Figure B.5 Product selectivity vs. temperature for furan deoxygenation over a 12.9 wt% Co$_{1.00}$Ru$_{1.00}$/SiO$_2$ catalyst.
Figure B.6 Product selectivity vs. temperature for furan deoxygenation over a 15 wt% \( \text{Co}_{1.00}\text{Ru}_{1.00}\text{P}/\text{SiO}_2 \) catalyst.