Catalytic Process for the Conversion of Synthesis gas to Ethanol for Use as an Alternative Fuel

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CATALYTIC PROCESS FOR THE CONVERSION OF SYNTHESIS GAS TO ETHANOL FOR USE AS AN ALTERNATIVE FUEL

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agriculture and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Gordon A. and Mary Cain Department of Chemical Engineering

By
Nitin Kumar
B.Sc.(Engg.), B.I.T. Sindri, 1997
December, 2011
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ABSTRACT

Higher alcohols are increasing as a proportion of the transportation fuel market, and can be used as neat fuels, or as blends with conventional fuels. For a number of reasons, these \( \text{C}_2^+ \)-alcohols will be of interest in the foreseeable future.

Large-scale production of higher alcohols will likely be carried out via syngas, which can be produced from a number of feedstocks, including coal, natural gas and biomass. Rhodium-based catalysts have been found to be the most active/selective for higher alcohols. However, the literature shows that the yields of \( \text{C}_2^+ \)-alcohols that can be achieved with current catalysts, even the most active/selective, are not practical, typically less than 10%. Also, due to the high cost of rhodium, the production of ethanol from Rh-based catalysts is not economically feasible at industrial scale.

This research is based on development of non-rhodium based catalysts for conversion of synthesis gas to \( \text{C}_2^+ \)-alcohols, with focus on ethanol. The work reported here aims to identify active catalysts, synthesize them using advanced methods that allow atomic-level control of the surface, and characterize them using state-of-the-art facilities, such as LSU’s synchrotron beam line and in-situ FTIR.

Studies on cobalt-rhenium catalysts showed that precursors have a significant effect on the catalyst characteristics. Cobalt acetate precursor catalyst was found to be highly dispersed compared to the nitrate precursor catalyst. The nitrate precursor catalyst was found to be more active for CO hydrogenation compared to the acetate precursor catalyst, but selectivity towards oxygenates was lower. In-situ FTIR results showed that CO adsorption takes place relatively weakly on the acetate precursor catalyst, owing to its high dispersion, as compared to the nitrate
precursor catalyst. The weakly adsorbed CO on the acetate precursor catalyst is believed to be responsible for higher oxygenates selectivity.

Studies on cobalt-palladium catalysts showed that they are active for CO hydrogenation. A 2 wt% cobalt catalyst was found to be more selective towards oxygenates formation as compared to 10 wt% cobalt catalyst, both having same loading of 2 wt% palladium. In-situ DRIFTS results showed that the active sites for CO hydrogenation were terminal (for 10%Co) and bridge-type (for 2%Co).
CHAPTER 1: INTRODUCTION

1.1. RESEARCH OBJECTIVE

To develop cobalt-based catalysts for the selective conversion of coal, biomass or natural gas derived synthesis gas to oxygenates, particularly ethanol.

1.2. ENGINEERING RELEVENCE OF PROJECT

Developing low-cost sustainable fuels, such as ethanol, is receiving much attention due to rising energy cost, depletion of fossil fuel resources, national security, and environmental issues. The use of ethanol for transportation fuel has been increasing, since it can be used as a neat fuel, fuel additive or blend with the conventional fuel. The ethanol-based fuels are a promising alternative to the petroleum based fuels 1-4. This has led to an increased research on improving production of ethanol from various sources for both ecological and economic reasons, primarily for its use as an alternative to petroleum based fuels.

1.3. CATALYSTS FOR SYNGAS TO OXYGENATES PRODUCTION

Catalysts for ethanol synthesis from syngas can be broadly grouped into four categories 1:

1. Rh-based catalysts
2. Modified methanol synthesis catalysts (based on Cu)
3. Modified Fischer-Tropsch catalysts
4. Modified Mo-based catalysts

1.3.1. Rh-Based Catalysts

Rh-based catalysts are the most widely studied catalysts for synthesis of ethanol from syngas 5-13. The position of Rh in the periodic table is interesting because it lies between metals that dissociate CO to form hydrocarbons (e.g., Co, Fe) and those which do not dissociate CO to
produce oxygenates (e.g., Pd, Pt, Ir). The selectivity of alcohols on a supported Rh-based catalyst depends on many parameters including, but not limited to, support, promoter and reaction conditions \(^{14-21}\). The literature shows that commercially practical selectivities to ethanol can be obtained over several catalysts, but only at impractically low conversions \(^2\). Net yields reported are typically well below 10%. Methane and methanol yields are high in some of the catalysts. Table 1.1 presents the activities and selectivities of selected Rh-based catalysts used for conversion of syngas to ethanol.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Experimental Conditions</th>
<th>X(_{\text{CO}}) (%)</th>
<th>Carbon Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RhCoFeK/SiO(_2)(d)</td>
<td>Temp. 281 (°C), Pr. 900 (psig), GHSV 3000 (h(^{-1})), H(_2)/CO 1.0</td>
<td>6.8</td>
<td>HC: 41.9, CO(_2): 14.7, C(_1)-OH: 8.6, C(_2)-OH: 15.8</td>
</tr>
<tr>
<td>RhCe/SiO(_2)</td>
<td>Temp. 350 (°C), Pr. 1 atm, GHSV 300 (h(^{-1})), H(_2)/CO 1.7</td>
<td>NA</td>
<td>HC: 50.9, CO(_2): NA, C(_1)-OH: 3.0, C(_2)-OH: 45.0</td>
</tr>
<tr>
<td>RhMo/ZrO(_2)(e)</td>
<td>Temp. 210 (°C), Pr. 300 (psig), GHSV 2400 (h(^{-1})), H(_2)/CO 1.0</td>
<td>10</td>
<td>HC: 34.0, CO(_2): 20.0, CO: NA, C(_2)-OH: 16.0</td>
</tr>
<tr>
<td>1%Rh/V(_2)O(_5)</td>
<td>Temp. 220 (°C), Pr. 1 atm, GHSV NA (h(^{-1})), H(_2)/CO 1.0</td>
<td>4.5</td>
<td>HC: 50.5, CO(_2): 6.0, C(_1)-OH: 6.2, C(_2)-OH: 37.2</td>
</tr>
<tr>
<td>1%Rh/ZrO(_2)</td>
<td>Temp. 220 (°C), Pr. 1 atm, GHSV NA (h(^{-1})), H(_2)/CO 1.0</td>
<td>2.0</td>
<td>HC: 31.5, CO(_2): 2.3, C(_1)-OH: 15.4, C(_2)-OH: 50.8</td>
</tr>
</tbody>
</table>

\(a\) X\(_{\text{CO}}\) = CO conversion; HC = total hydrocarbons including methane; C\(_1\)-OH = methanol; C\(_2\)-OH = ethanol; NA = data not available. \(b\) Carbon selectivity is defined as the selectivity of all the carbon-containing products formed from converted carbon. \(c\) HC = hydrocarbon selectivity calculated from the alcohol selectivity data. This may include CO\(_2\) selectivity. \(d\) Other products include C\(_2\)-C\(_6\) acetaldehydes and esters. \(e\) Other products are oxygenates.

### 1.3.2. Modified Methanol Synthesis Catalysts (Cu-Based)

Copper-based modified methanol synthesis catalysts have been studied by many researchers \(^{22-32}\). The higher alcohol yield was found to be depending upon the promoter, H\(_2\)/CO ratio and the reaction conditions. However, in all the cases, methanol was found to be the major product on these catalysts \(^{23}\). The reason for low ethanol selectivity can be attributed to the chain
growth mechanism for the formation of higher alcohols. The mechanism involves formation of ethanol from methanol via a slow difficult reaction, while it quickly converts to higher alcohols via a faster chain growth mechanism \(^1\). The activities and selectivities of Cu-based modified methanol synthesis catalysts have been presented in Table 1.2.

Table 1.2: Performance of Cu-based catalysts for conversion of syngas to ethanol \(^2\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Experimental Conditions</th>
<th>(X_{CO})^a (%)</th>
<th>Space time yield (mg/(g cat h))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(C_1)-OH</td>
</tr>
<tr>
<td>3Cs-Cu-ZnO-Cr(_2)O(_3)</td>
<td>Temp. (°C)</td>
<td>Pr. (psig)</td>
<td>GHSV (h(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>325</td>
<td>1100</td>
<td>5450</td>
</tr>
<tr>
<td>3Cs-Cu-ZnO-Cr(_2)O(_3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>325</td>
<td>1100</td>
<td>18000</td>
</tr>
<tr>
<td>4Cs-Cu-ZnO-Cr(_2)O(_3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>1100</td>
<td>3200</td>
</tr>
<tr>
<td>Cu(<em>{1.0})Co(</em>{1.0})Mn(<em>{0.8})K(</em>{0.12})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>870</td>
<td>4000</td>
</tr>
<tr>
<td>Cu(<em>{1.0})Co(</em>{1.0})Fe(<em>{0.8})K(</em>{0.12})</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a\) \(X_{CO}\) = CO conversion; \(C_1\)-OH = methanol; \(C_2\)-OH = ethanol; \(\sum\text{alcohol}\) = sum of all the alcohols; NA = data not available.\(^b\) \(H_2/(CO+CO_2)\).

1.3.3 Modified Fischer-Tropsch Catalysts

Another approach to making higher alcohols has been based on the modified Fischer-Tropsch catalysts, where researchers have added a promoter to the conventional Co, Ru and Fe-based Fischer-Tropsch catalysts \(^33-39\). The basic philosophy is to produce the active sites that adsorb CO both, associatively and dissociatively \(^1\). The alcohols and oxygenates selectivities on these catalysts depends greatly on the type of promoter, method of catalyst preparation and, reaction conditions \(^40,41\). Although the selectivities towards oxygenated compounds were found to have increased, the hydrocarbon selectivity remained high in all the studies. Table 1.3 presents the performance of selected modified Fischer-Tropsch catalysts for conversion of syngas to ethanol.
1.3.4. Modified Mo-Based Catalysts

Works on modified molybdenum-based catalyst\textsuperscript{42-46} have resulted in formation of mixed alcohols from syngas. The products were found to be shifted from hydrocarbons to alcohols as a result of alkali promotion on these catalysts\textsuperscript{2}. The main mechanism for oxygenates formation is believed to proceed via CO insertion into the metal–CH\textsubscript{x} bond\textsuperscript{1,47,48}. The performances of modified Mo-based catalysts have been presented in Table 1.4.

Table 1.3: Performance of modified Fischer-Tropsch catalysts for conversion of syngas to ethanol\textsuperscript{2}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Experimental Conditions</th>
<th>(X_{\text{CO}})\textsuperscript{a} (%)</th>
<th>Carbon Selectivity (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp. (°C)</td>
<td>Pr. (psig)</td>
<td>GHSV (h\textsuperscript{-1})</td>
</tr>
<tr>
<td>Co-Re-Sr/SiO\textsubscript{2}</td>
<td>250</td>
<td>305</td>
<td>2000</td>
</tr>
<tr>
<td>Co-Ru-Sr/SiO\textsubscript{2}</td>
<td>250</td>
<td>305</td>
<td>2000</td>
</tr>
<tr>
<td>Co-Ir-Sr/SiO\textsubscript{2}</td>
<td>220</td>
<td>305</td>
<td>2000</td>
</tr>
<tr>
<td>KLaCo\textsubscript{0.7}Cu\textsubscript{0.3}O\textsubscript{3,6}</td>
<td>275</td>
<td>1000</td>
<td>5000</td>
</tr>
</tbody>
</table>

\(X_{\text{CO}}\) = CO conversion; HC = total hydrocarbons including methane; C\textsubscript{1}-OH = methanol; C\textsubscript{2}-OH = ethanol; NA = data not available. Carbon selectivity is defined as the selectivity of all the carbon-containing products formed from converted carbon. HC = hydrocarbon selectivity calculated from the alcohol selectivity data. This may include CO\textsubscript{2} selectivity.

Table 1.4: Performance of modified Mo-based catalysts for conversion of syngas to ethanol\textsuperscript{2}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Experimental Conditions</th>
<th>(X_{\text{CO}})\textsuperscript{a} (%)</th>
<th>Carbon Selectivity (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp. (°C)</td>
<td>Pr. (psig)</td>
<td>GHSV (h\textsuperscript{-1})</td>
</tr>
<tr>
<td>1%K-Co\textsubscript{1}Mo\textsubscript{4}</td>
<td>300</td>
<td>870</td>
<td>10000</td>
</tr>
<tr>
<td>K-β-Mo\textsubscript{2}C</td>
<td>300</td>
<td>1160</td>
<td>2000</td>
</tr>
<tr>
<td>KRhMoS\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>327</td>
<td>1450</td>
<td>4800</td>
</tr>
<tr>
<td>LaKNiMoS\textsubscript{2}</td>
<td>320</td>
<td>1160</td>
<td>2500</td>
</tr>
</tbody>
</table>

\(X_{\text{CO}}\) = CO conversion; HC = total hydrocarbons including methane; C\textsubscript{1}-OH = methanol; C\textsubscript{2}-OH = ethanol; NA = data not available. Carbon selectivity is defined as the selectivity of all the carbon-containing products formed from converted carbon. HC = hydrocarbon selectivity calculated from the alcohol selectivity data. This may include CO\textsubscript{2} selectivity.
1.4. SYNTHESIS OF CATALYSTS

Cobalt-based modified Fischer-Tropsch catalysts were synthesized for the present study. Two different promoters were used: rhenium and palladium. The Co-Re series of catalysts were synthesized by Chevron Energy Technology Company using conventional sequential co-impregnation method. The initial silica support was modified by ZrO₂ for these catalysts before impregnating the cobalt and rhenium salts.

The silica supported Co-Pd catalysts were synthesized at LSU with two different cobalt loadings: 2 wt% and 10 wt%. The Pd loading in these catalysts was kept constant (2 wt%). These catalysts were synthesized by conventional incipient wetness impregnation method.

1.5. RATIONALE FOR SELECTING Co-Re CATALYST

Cobalt is a well-known Fischer-Tropsch catalyst. The promotion of cobalt by rhenium has been found to improve selectivity toward oxygenated compounds, mainly ethanol. Matsuzaki et. al. studied the effect of Re addition to silica supported cobalt catalysts and found that the activity of cobalt derived from cobalt acetate precursor is dramatically increased towards ethanol after rhenium promotion. They attributed the increase in ethanol selectivity to high dispersion of the catalyst. Rhenium has also been found to activate the cobalt sites in the catalyst by reducing the oxidized cobalt species to metallic cobalt during the reaction. The reduction mechanism is believed to be due to H₂ spillover from reduced rhenium to the neighboring cobalt atom. Vada et.al. found that the CO hydrogenation rate was significantly increased over an Al₂O₃ supported cobalt catalyst modified by Re, as compared to non-promoted catalyst.

1.6. RATIONALE FOR SELECTING Co-Pd CATALYST

As a Fischer-Tropsch catalyst, cobalt produces hydrocarbons through CO hydrogenation by
C-O bond dissociation \(^{40}\). On the other hand, CO adsorption on Pd has been reported to be associative \(^{51-55}\). Since formation of ethanol requires both these types of adsorbed CO, it is expected that addition of Pd would increase the catalyst selectivity towards ethanol. Many studies have indicated that addition of Pd to a silica supported cobalt catalyst enhanced the formation of oxygenated compounds and increased the CO hydrogenation activity \(^{56,57}\). However, it is critical that cobalt and palladium exist in atomic proximity in order to facilitate the formation of oxygenated compounds.

1.7. OUTLINE OF THE DISSERTATION

**Chapter 1** introduces the need and advantages to convert synthesis gas to oxygenated compounds, various catalysts used for this reaction, and rationale for this project.

**Chapter 2** presents the literature review on this subject. It summarizes the works done by researchers in this area, their results, and conclusions. It also gives justification for the catalytic systems chosen in this work.

**Chapter 3-6** are written in journal style. **Chapters 3** \(^{58}\) and **4** \(^{59}\) have been published in peer-reviewed journals. **Chapter 5** has been submitted to ACS Catalysis for publication. **Chapter 6** has been submitted to Journal of Catalysis for publication. Each journal chapter has its own introduction, experimental methods, results and discussion, followed by references. There could be some duplication in the introduction and experimental methods used, however the results and data analysis are unique and address the objective of the research. **Chapter 3** examines the effect of cobalt precursors (cobalt nitrate and cobalt acetate) on CO adsorption behavior over a rhenium promoted, silica supported catalyst. It suggests that the formation of oxygenated compounds requires CO to adsorb relatively weakly on the surface, and within a narrow range of wavenumber. **Chapter 4** focuses on the characterization of cobalt-rhenium
catalyst by various methods in order to understand the reduction behavior. The characterization techniques used are in-situ XRD, in-situ XANES and TPR, where the reduction of catalyst is studied when temperature is ramped under hydrogen flow. Chapter 5 presents in situ DRIFTS studies on cobalt-rhenium catalyst for the effect of H₂ preadsorption on CO adsorption behavior. A comparison of CO and syngas adsorption has been made over bare and H₂ preadsorbed surfaces at different temperatures. The results for CO adsorption/hydrogenation on cobalt-palladium based catalyst are described in Chapter 6. The catalytic activities and selectivities have been correlated to the active sites found by in-situ DRIFTS study.

Chapter 7 is the summary of conclusions of the work described in Chapters 3-6. A recommendation for future work is also given.

1.8. REFERENCES


47. Smith, K. J.; Herman, R. G.; Klier, K. Chemical Engineering Science 1990, 45, 2639.


CHAPTER 2: LITERATURE REVIEW

Direct conversion of syngas to oxygenates has been a topic of interest for many researchers due to potential application in energy systems. There are a large number of publications dedicated to this topic in the literature, mostly dealing with CO hydrogenation, where researchers have identified potential catalysts and tried to understand the reaction mechanisms. This review summarizes works on catalytic conversion of syngas to ethanol.

2.1. ETHANOL

Ethanol enriched fuel has been shown to be cleaner burning by increasing the efficiency of combustion process and reduce the emission of greenhouse gases \(^1\textsuperscript{-}\textsuperscript{8}\). Ethanol blended with gasoline enhances the octane number and decreases the CO, NOx, hydrocarbons and particulate emissions from combustion \(^9\textsuperscript{,}10\). Being a liquid fuel, the storage and dispensing of ethanol is similar to that of gasoline. Ethanol can be also converted into a hydrogen-rich gas for use in an energy conversion device such as fuel cell \(^11\textsuperscript{-}\textsuperscript{13}\). This conversion is usually done by steam reforming \(^14\textsuperscript{-}\textsuperscript{20}\). It has the advantage of containing significant stoichiometric quantities of hydrogen. Many studies \(^21\textsuperscript{,}22\) report the use of ethanol in the fuel cells. With the increasing shortage of petroleum, urban air pollution and accumulation of CO\(_2\) in the atmosphere, ethanol is expected to play a more significant role in the future \(^6\textsuperscript{,}23\).

Ethanol can be produced in several ways, including fermentation of sugars derived from corn or sugar cane, hydration of petroleum-based ethylene, and catalytic conversion of syngas derived from different sources. Fig. 2.1 shows the different sources of carbon-containing feedstocks from which ethanol can be produced by using different synthesis methods \(^24\).

Large-scale formation of ethanol by ethylene hydration is not attractive because the cost is
dependent on the crude oil prices and imported oil. The production of fuel-grade ethanol by fermentation route is also expensive and energy-inefficient because the process involves energy-intensive distillation steps\textsuperscript{24} and its limitation to metabolize 5-carbon pentose sugars, which is a significant portion of sugars derived from lignocellulose or woody biomass\textsuperscript{25}. The syngas route is an attractive one, as syngas can be produced from various sources, including coal, natural gas, biomass etc\textsuperscript{26-30}. This route from syngas to ethanol will give us flexibility to produce ethanol from any of these sources.

While syngas can be produced from any carbon based feedstock (hydrocarbons, coal, petroleum, biomass), the lowest cost routes to syngas so far are based on natural gas\textsuperscript{31,32}. Although US coal reserves are greater and coal remains available at lower prices than
hydrocarbons, the investment in a coal-based syngas plant is ca. 3 times that required for a natural gas-based plant. The advantage of using natural gas as a major feedstock for syngas has also been emphasized in the literature. Methane is the main component in the natural gas and, almost all options for methane utilization involve its initial conversion to syngas according to the following reaction:

\[ CH_4 + H_2O \rightarrow CO + 3H_2, \quad \Delta H_{298}^{\circ} = +206 \text{ kJ/mol} \]

This reaction is highly endothermic and is carried out at 900°C and 15-30 atm. It also gives H₂-rich syngas with H₂:CO ratio of 3:1. Reverse water-gas shift reaction is used in order to adjust the H₂:CO ratio to the desired value of 2:1.

\[ CO_2 + H_2 \rightarrow CO + H_2O, \quad \Delta H_{298}^{\circ} = +41 \text{ kJ/mol} \]

The natural gas to syngas conversion technology is well established by using steam reforming of methane as a primary route. Autothermal reforming (ATR) is a preferred technology, both economically and technically, for natural gas to syngas conversion.

Although ethanol demand is rising, and it is expected to do so in the near future because of its many advantages discussed above, the literature shows that the conversion of syngas into ethanol is plagued by poor selectivity. Methane, CO₂ and methanol are the main undesirable products that are formed during the reaction over a catalytic system.

2.2. THERMODYNAMICS

The CO hydrogenation reaction leading to formation of ethanol is as follows:

\[ 2CO + 4H_2 \rightarrow C_2H_5OH + H_2O, \]

\[ \Delta H_{298}^{\circ} = -61.1 \text{ kcal/mol} \]

\[ \Delta G_{298}^{\circ} = -29.3 \text{ kcal/mol} \]
Despite the fact that the hydrogenation of CO to ethanol is thermodynamically favorable, thermodynamics also tells us that if methane is allowed as a product, free energy minimization starting with a typical syngas mixture results in a product mixture containing virtually no ethanol. Figure 2.2 (Spivey et. al. 40) shows the thermodynamic equilibrium concentrations of products as a result of CO hydrogenation to ethanol, when methane is not allowed (a), and when methane is allowed (b) as a product. The simulations were done at 30 bar pressure with 49% H$_2$, 26% CO, 21% CO$_2$ and 4% H$_2$O as initial reactants. This shows that the formation of methane, which is thermodynamically favored, must be kinetically limited if ethanol yield is to be significant 40.

Figure 2.2: Concentration profiles of CO and CO$_2$ hydrogenation to ethanol. (a) No Methane allowed, (b) Methane allowed. Reaction at 30 bar, initial reactants: H$_2$ = 49%, CO = 26%, CO$_2$ = 21%, H$_2$O = 4%, calculated using AspenPlus® software 40.
2.3. REACTION MECHANISM FOR SYNGAS TO ETHANOL

Many studies have been carried out to find the mechanism of CO hydrogenation \(^{41-47}\). It is generally agreed that the reaction mechanism leading to ethanol formation consists of four basic steps \(^{48}\):

a) Dissociative adsorption of CO and H\(_2\),

b) Formation of surface hydrocarbon \((\text{CH}_x)_{\text{ads}}\) and hydroxyl \((\text{OH})_{\text{ads}}\) species, and

c) CO insertion into the C-H bond of \((\text{CH}_x)_{\text{ads}}\)

d) Hydrogenation of the resulting oxygenated intermediate

Fig. 2.3: Simplified sequence of ethanol formation by CO hydrogenation \(^{40}\)
Figure 2.3 shows the simplified sequence of steps leading to ethanol formation by CO hydrogenation. Methane and hydrocarbons are formed by the hydrogenation of \((\text{CH}_x)_{\text{ads}}\), suggesting that ethanol formation is favored by a catalyst that selectively promotes the CO insertion reaction instead of the hydrogenation of the \((\text{CH}_x)_{\text{ads}}\) species (step 7 instead of step 6 in Fig. 2.3). One key is to increase the surface concentration of CO in order to promote the CO insertion step [step (c) above] in preference to the hydrogenation of the \((\text{CH}_x)_{\text{ads}}\) species to form methane. This would require a catalyst that preferentially adsorbs CO associatively.

2.4. COBALT-RHENIUM CATALYSTS FOR CONVERSION OF SYNGAS TO ETHANOL

Cobalt-based catalysts are found to be advantageous for converting syngas to liquid fuels because of their low costs, high CO hydrogenation activity, and low water-gas shift activity\(^49,50\). These catalysts, when modified by noble metals, give rise to increased activity and selectivity towards oxygenates. Many studies conclude that addition of even a very small amount of noble metals into cobalt-based catalysts changes significantly their physicochemical and catalytic properties\(^51-55\).

Literature suggests that addition of Re to cobalt increases the reducibility of cobalt and enhances the activity of the catalyst towards C\(_2\) oxygenates\(^51,54,56-59\). Rhenium promotes the activation of the cobalt sites via reduction of oxidized cobalt species while keeping the cobalt highly dispersed\(^57,60,61\). It has been found that reduced Re activates hydrogen and reduce cobalt particles by a H\(_2\)-spillover mechanism\(^51,57\). Re is also found to help improve selectivity towards oxygenates, especially ethanol\(^57\). Cobalt catalysts promoted by small amounts of Re have been found to significantly increase the amount of adsorbed CO on cobalt and thus CO hydrogenation rates\(^61\). However, some researchers have proposed the active sites for CO hydrogenation to be the highly dispersed cobalt sites only\(^56,57\). Addition of Re increases the dispersion and
reducibility of cobalt and decreases the size of cobalt crystallites, thereby increasing the number of active sites \(^{51,54}\). For example, one study showed that the active site density of a 1% Re/cobalt catalyst was found to be more than twice that of the unpromoted catalyst \(^{62}\).

**2.4.1. Reducibility of Catalyst**

The activity of cobalt-based catalyst depends on various factors, including the preparation method, support and promoters. Since the oxidized form of the catalyst is not active for CO hydrogenation, it is important to reduce the catalyst before the reaction, and to maintain it in a reduced state during the reaction \(^{63}\). The activity of cobalt-based catalysts is reported to depend mainly on the number of active metal sites formed by reduction \(^{64}\).

Cobalt is found to be easier to reduce when supported on SiO\(_2\) than on Al\(_2\)O\(_3\) \(^{51}\). However, in most cases, large crystalline Co\(_3\)O\(_4\) is formed which does not favor oxygenates formation \(^{57}\). Therefore, cobalt must exist in a highly dispersed form in order to facilitate the formation of oxygenates. The synthesis of catalysts with highly dispersed cobalt requires the initial Co\(_3\)O\(_4\) phase to be highly dispersed on the support, which requires strong interaction between the support and cobalt precursor \(^{49,64}\). These strong interactions usually result in cobalt species that are difficult to reduce. If a higher reduction temperature is applied to reduce the catalyst, it may result in sintering of the highly dispersed crystallites, which in turn can adversely affect the activity and dispersion of the catalyst. To address the competing effect of dispersion versus reducibility, generally a promoter is added to the catalyst, which increases the reducibility of the catalyst while keeping the active metal highly dispersed \(^{63}\).

**2.4.2. Mechanism of Rhenium Promotion of Cobalt**

The mechanism of how rhenium promotes cobalt has not been clearly understood yet. There are two proposed theories for increased activity of cobalt catalyst as a result of Re addition: (1) Re facilitates the reduction of cobalt oxide phases by hydrogen spillover from Re to
cobalt and, (2) direct interaction between cobalt and rhenium, resulting in formation of bimetallic particles. A large group of researchers, however, agree with the \( \text{H}_2 \) spillover mechanism for promotion of cobalt catalysts by rhenium. In this process, the molecular hydrogen is first activated on rhenium, undergoes dissociative adsorption, and migrates to the neighboring cobalt atom. The migrating hydrogen is generally believed to be in the form of \( \text{H}^+ \), \( \text{H}^- \) and \( \text{H}^* \), depending on the conditions. The bridge for this spillover is formed by surface \( \text{OH}^- \) groups.

The fact that rhenium promotion increases the reducibility of cobalt catalysts has been observed by many researchers. Temperature programmed reduction spectra of mono-and bimetallic catalyst samples were found to be shifted by 200 °C towards the low temperature region as a result of rhenium promotion. Hilmen et. al. compared the TPR results of an intimate and loose mixtures of \( \text{Co/Al}_2\text{O}_3 + \text{Re/Al}_2\text{O}_3 \) with that of co-impregnated \( \text{Co-Re/Al}_2\text{O}_3 \) catalysts. They found that the intimate mixture of \( \text{Co/Al}_2\text{O}_3 + \text{Re/Al}_2\text{O}_3 \) showed the promoting effects of rhenium on the reduction of cobalt similar to that of the co-impregnated catalyst, while this was not observed for the loose mixture. However, when the loose mixture was pretreated with \( \text{Ar} \) saturated with water vapor, a promoting effect was observed. Based on this they concluded that a direct contact between Re and Co atoms is not necessary for the reduction of cobalt by \( \text{H}_2 \) spillover.

2.4.3. Modification of Support by Zr

Zirconia has been proposed as an important promoter for \( \text{Co/SiO}_2 \) catalysts. Addition of \( \text{ZrO}_2 \) as promoter can modify and improve the catalyst texture and porosity, help the reduction of oxidized Co species to metallic cobalt, increase the dispersion of cobalt, and improve the chemical stability of the support. Pre-impregnated zirconia is believed to form a protecting layer over the silica support to prevent the reaction between silica and cobalt that may lead to the
formation of inert cobalt silicates \(^{68,71}\). Modification of silica support by zirconium reduces the strong interaction between cobalt and silica \(^{69}\). Weakening of cobalt-support interaction helps improve the reducibility of cobalt. The mechanism is believed to be due to the formation of cobalt-zirconium species, which are more reducible than cobalt silicate and cobalt hydrosilicate species, which are formed with interaction of silica \(^{69,72-76}\). However, the cobalt crystallite size was found to have increased with increasing zirconium loading \(^{69}\).

Literature is divided on the effect of Zr on the activity of cobalt catalysts. Some authors report that increasing Zr loading resulted in increased CO conversion and increased C\(_{5+}\) selectivity \(^{77-79}\), and attributed these effects to increase in metallic cobalt available under reaction conditions \(^{69}\). Other authors \(^{80,81}\) found no specific effect of Zr addition on the activity of cobalt catalysts.

### 2.5. COBALT-PALLADIUM CATALYSTS FOR CONVERSION OF SYNGAS TO ETHANOL

It is clear from the mechanism leading to ethanol formation from syngas (Fig. 2.3) that it is necessary to have both associative and dissociative adsorption of CO over the surface of the catalyst. Rh has been found to have both of these CO adsorption species on its surface \(^{40}\). Due to high cost of Rh, it is not economically feasible to use it in the commercial reactors. Thus emphasis has been on the cheaper metals to get the same (or higher) selectivity towards ethanol.

The unique combination of cobalt and palladium can be used to achieve this goal. Cobalt is a well-known Fischer-Tropsch catalyst, known for dissociative adsorption of CO and promote the formation of C-C bonding in higher alcohols synthesis \(^{57}\). On the other hand, it is generally agreed that under these conditions CO adsorption on palladium is associative (linear or multi-fold bridge) and not dissociative \(^{82-87}\). Poutsma et. al. \(^{86}\) observed that methane is the main
product over supported palladium catalysts at 260-350 °C and 150-16000 psig pressure. Addition of Pd to a silica supported cobalt catalyst has been found to increase the CO hydrogenation activity and enhance the formation of oxygenated compounds. It would be expected for a cobalt-palladium system that CO adsorption takes place both, associatively (on Pd) and dissociatively (on Co). Such a catalyst would therefore be expected to show more selectivity towards oxygenated compounds, and could be used the same way as Rh. However, it is critical that cobalt and palladium are in close contact with each other so as to facilitate the formation of these oxygenated compounds.

2.5.1. Mechanism of CO Hydrogenation Over Palladium

An example of CO hydrogenation on Pd (111) surface is presented in Figure 2.4, which is constructed from the activation energies of elementary reaction steps determined using the Bond-Order-Conservation (BOC) method. BOC method has been used by Bell to calculate the activation energies of elementary steps involved in the CO hydrogenation to methane and methanol, as well as the heats of adsorption of all the relevant reaction intermediates. It is claimed that this method is provides the heat of adsorption for molecular species, which are in very good agreement with the experimental values. Figure 2.4 shows three possible mechanisms of reaction networks for CO hydrogenation over Pd (111) surface. For pathway A, the CO$_s$ undergoes dissociative adsorption by C-O bond rupture as soon as it is adsorbed. The activation barrier for this is 100 kcal/mol. For pathway B, the adsorbed CO$_s$ undergoes hydrogenation without the C-O bond rupture to form HCO$_s$. If the C-O bond rupture takes place for HCO$_s$ species, the required activation energy is 88 kcal/mol, which is lower than pathway A. For pathway C, the HCO$_s$ species undergo hydrogenation to form H$_2$CO$_s$ species which again undergo hydrogenation to form CH$_3$O$_s$ species. The bond rupture of H$_2$CO$_s$ species is also
Figure 2.4: Potential energy diagram for CO hydrogenation on Pd (111).
possible, but the corresponding activation energy is significantly larger than that for the hydrogenation of \( \text{H}_2\text{CO}_3 \) and \( \text{CH}_3\text{O}_3 \). Once the \( \text{CH}_3\text{O}_3 \) species are formed, there are two competing steps: (1) it can undergo further hydrogenation to give \( \text{CH}_3\text{OH} \), or (2) the rupture of C-O bond takes place. Comparison of pathways B and C shows that the activation energy for HCO\(_3\) dissociation is 16 kcal/mol greater than that for HCO\(_3\) hydrogenation. This results in a higher probability of HCO\(_3\) hydrogenation as compared to HCO\(_3\) dissociation. For pathway C, the activation energy for step 1 is 5 kcal/mol lower than that of step 2. Consequently, the formation of \( \text{CH}_3\text{OH} \) is more favorable than C-O bond rupture on Pd(111). The pathways A and B are unlikely to occur because of the large difference in activation energies. Thus it can be concluded that pathway C is the most favorable step and oxygenates can be easily formed on Pd as compared to methane.

### 2.5.2. Synthesis of Cobalt-Palladium Catalysts

Co-Pd/SiO\(_2\) catalysts were synthesized using a conventional incipient wetness impregnation method with two different cobalt loadings: 2 wt% and 10 wt% (represented as 2Co-2Pd and 10Co-2Pd respectively). The Pd loading in both the catalysts was kept the same as 2 wt%. The SiO\(_2\) support was obtained from Alfa Aesar (Surface Area = 300 m\(^2\)/g, Pore Volume = 1 cc/g). The precursors used for cobalt and palladium were cobalt nitrate and palladium (II) 2,4-pentanedionate \([\text{Pd(\text{CH}_3\text{COCHCOCH}_3)}_2]\) respectively. These salts were dissolved in a calculated amount of ethanol before impregnating over SiO\(_2\). The catalyst was dried overnight at 110 °C followed by calcination under air for 2 h at 450 °C using a temperature ramp of 1°C per minute.

### 2.6. REFERENCES


3.1. INTRODUCTION

The increasing demand for clean fuel has led to increased research interest in the production of liquid fuels from sources other than petroleum. The conversion of coal- or biomass-derived syngas to ethanol is a promising alternative. Cobalt-based catalysts have been found to be advantageous for the conversion of syngas to liquid fuels because of their low costs, low water-gas shift activity and high activity for CO hydrogenation.

Carbon monoxide adsorption and hydrogenation on supported cobalt catalysts has been studied extensively, e.g., where CO is used as probe to identify the nature of adsorption sites. An understanding of this adsorption/hydrogenation process at the molecular level is important in order to understand the syngas reactions on various supported metal catalysts. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) can be used to probe the active sites, adsorbed species, and intermediates on the catalyst surface. Song et.al. used this technique to study CO adsorbed on Co/SiO\textsubscript{2} catalysts with different pore sizes and found different CO adsorption sites which changed with changing pore sizes. They also observed that the intensities of linear and bridge-type CO adsorption changed significantly with pore size.

Heal et.al. used IR to study CO adsorbed on Co/SiO\textsubscript{2} at different temperatures and correlated the observed shift in spectra to the change in bond strength of C-O adsorbed on the surface, which is influenced by the C-metal bond strength. They also attributed methane formation to linearly adsorbed CO.

Addition of Re to Co/SiO₂ catalysts has been found to improve selectivity towards oxygenates, especially ethanol. Re has been found to promote activation of the cobalt site in the catalyst via reduction of oxidized cobalt species to the metallic state and keeping the cobalt highly dispersed. Small amounts of Re have been found to significantly increase the amount of adsorbed CO on cobalt and thus CO hydrogenation rates.

Zirconia has been proposed as an important promoter for Co/SiO₂ catalysts. Addition of ZrO₂ promoter can modify and improve the catalyst texture and porosity, assist in the reduction of oxidized Co species to metallic cobalt, increase the dispersion of cobalt, and improve the chemical stability of the support. Pre-impregnated zirconia is believed to form a protecting layer to prevent the reaction between silica and cobalt to form inert cobalt silicates.

Cobalt precursors have a significant effect on the activity of catalysts and product distribution, and their role has been investigated by several researchers. One study showed a higher total catalytic activity when using a cobalt nitrate precursor relative to a cobalt acetate precursor. It is important to understand the surface phenomenon in order to explain this precursor effect.

The objective of the work reported here is to investigate different active sites for cobalt catalysts prepared from acetate and nitrate precursors and to correlate those sites with CO adsorption/hydrogenation activity in order to understand the reaction mechanism on these catalysts, particularly the formation of oxygenates.

### 3.2. EXPERIMENTAL

#### 3.2.1. Catalyst Preparation

Co-Re/SiO₂ based catalysts were synthesized using a conventional incipient wetness impregnation method. Cobalt-rhenium catalysts prepared from cobalt nitrate and cobalt acetate
precursors (designated as CoRe(N) and CoRe(A) respectively) were prepared using a SiO$_2$ support obtained from Alfa Aesar (Surface Area = 300 m$^2$/g, Pore Volume = 1 cc/g) which was modified with 2% Zr by impregnation. Zirconium(IV) oxynitrate hydrate ZrO(NO$_3$)$_2$$\cdot$6H$_2$O, was used as the Zr precursor. The modified support was dried for 2 hrs at 120°C and calcined in air for 2 hrs at 500°C. A mixture of cobalt and rhenium salts was simultaneously impregnated on the Zr-modified support. Perrhenic acid, Re$_2$O$_7$(OH)$_2$ was used as the Re precursor, cobalt(II) nitrate hexahydrate, Co(NO$_3$)$_2$$\cdot$6H$_2$O and cobalt(II) acetate tetrahydrate, Co(CH$_3$COO)$_2$$\cdot$4H$_2$O were used as cobalt precursors. The catalyst was dried for 2 hrs at 120°C and calcined under air flow for 2 hrs at 300°C at a ramp rate of 1°C per minute. Both catalysts contain 10 wt% cobalt (as metal Co) and 4 wt% Re.

3.2.2. Temperature Programmed Reduction (TPR)

Temperature programmed reduction (TPR) profiles of the calcined catalysts were recorded using Altamira AMI 200-R-HP unit equipped with a thermal conductivity detector (TCD). The catalyst samples were first purged in a fixed bed micro reactor system under flowing argon at 150°C for 1 hour to remove traces of water and then cooled to 25°C. TPRs were performed using a 10% H$_2$/Ar mixture at a flow rate of 50 cm$^3$/min while the temperature was linearly ramped from 25°C to 750°C using a ramp rate of 10°C/min.

3.2.3. X-Ray Diffraction (XRD)

XRD measurements were carried out with Bruker/Siemens D5000 automated powder X-ray diffractometer using Cu K$_\alpha$ radiation ($\lambda = 1.5406$Å). Fresh calcined catalysts were used for the XRD measurements.

3.2.4. Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES)

The trace element determinations were performed on a Varian Vista AX CCD simultaneous
ICP-OES. Varian ICPExpert version 4.0 was used by ICP-OES.

3.2.5. Catalyst Activity Test

CO hydrogenation reactions at differential conversions were carried out in a ¼” glass-lined stainless steel fixed bed micro-reactor system at different temperatures (230°C, 270°C) and total pressure of 10 bar. Prior to reaction, the catalyst was reduced in-situ for 4 hrs at 400°C in flowing H₂/He mixture (50% H₂). CO hydrogenation reactions were carried out with a H₂:CO ratio of 2:1. For these experiments the syngas was diluted with helium to reduce heat effects within the bed and to ensure that the conversion was low enough to keep the oxygenated products in the vapor state for online GC/MS analysis. The GC/MS system used for the outlet product gas analysis (Agilent Technologies 6890N/5975B) is equipped with two thermal conductivity detectors (TCD). The line from the reactor exit to the sampling valve is heat traced to prevent products from condensing upstream of the GC/MS. The sampling valves are placed in an isothermal oven and maintained at a temperature of 250°C. Oxygenates and C₂-C₄ hydrocarbons analysis were done using the mass selective detector (MSD), while CO, H₂ and CH₄ were analyzed on the TCD. All selectivities are reported in terms of carbon efficiency defined as:

\[
\text{Selectivity of A (\%) = } \frac{n \times c_{n\ A}}{\text{Total CO reacted}} \times 100
\]

Where \( n \) is the number of carbons in A and \( c_{n\ A} \) is mol fraction of A.

3.2.6. In-situ Diffuse Reflectance FTIR Spectroscopy (DRIFTS)

FTIR spectra were collected with a Nexus 870 model (Thermo Nicolet) spectrometer equipped with a MCT-A detector cooled by liquid nitrogen. KBr beamsplitter was used to obtain spectra in the range of 4000–650 cm⁻¹. In-situ measurements were carried out in a ceramic sample holder equipped with a thermocouple. Provisions were made to the cell for gas inlet,
outlet, heating and cooling. A sample holder was used to hold ~20 mg of catalyst. DRIFTS spectra were collected by using series collection for 15 min. For each spectrum 32 scans at a resolution of 4 cm$^{-1}$ were used.

Before each experiment the catalyst was heated in helium at 150°C for 30 min to remove any moisture and gases. The catalyst was reduced by flowing a mixture of hydrogen and helium (4% H$_2$ in He) for 2 hrs at 350°C. The cell was then flushed with helium and temperature was brought back to 25°C. Backgrounds were collected at desired temperatures (270°C, 230°C and 25°C) during the cooling process after the system is allowed to equilibrate for 15 min at that temperature. Difference spectra were obtained by subtracting the background from the subsequent spectra. Two series of experiments were performed at each temperature: CO adsorption and CO hydrogenation. Each series was set for 15 min and was divided into three parts. In the first part helium was flowed for 20 sec followed by flowing CO + He for 7 min in the second part. The third part consisted of flushing with helium (for CO adsorption studies) or flowing H$_2$ + He (for CO hydrogenation studies) for the rest of the time. 2% CO/2% Ar/He was used for CO adsorption/hydrogenation. The experiments were carried out at 25°C, 230°C and 270°C and performed at atmospheric pressure.

3.3. RESULTS AND DISCUSSION

3.3.1. Temperature Programmed Reduction (TPR)

TPR results in Figure 3.1 show a small peak at around 335°C on both catalysts due to reduction of large crystalline Co$_3$O$_4$ $^{23}$. This peak is very small in case of CoRe(A), indicating that only a small amount of large crystalline Co$_3$O$_4$ is present. The shoulder peak found in CoRe(N) at around 400°C is due to the reduction of rhenium oxide $^{24}$. The reduced Re promotes the reduction of cobalt by hydrogen spillover from Re to cobalt oxide $^{14,24}$. The peak at around
415°C on both catalysts is due to the reduction of highly dispersed cobalt oxide \textsuperscript{24}. For CoRe(A), the peak due to reduction of this dispersed cobalt oxide phase overlaps with the peak due to reduction of rhenium oxide at around 405°C. The fact that both rhenium and highly dispersed cobalt reduce at same temperature suggests that Re is in the immediate vicinity of cobalt, facilitating its reduction by hydrogen spillover \textsuperscript{14,25}.

![Figure 3.1: Temperature Programmed Reduction of CoRe(N) and CoRe(A)](image)

3.3.2. X-ray Diffraction (XRD)

The XRD results for CoRe(N) and CoRe(A) are shown in figs. 3.2 and 3.3 respectively. No XRD peaks were observed for CoRe(A), indicating that any cobalt crystallites are less than ~2 nm, in agreement with the results reported by Matsuzaki \textit{et.al.} \textsuperscript{14} for a 5% Co-5% Re/SiO\textsubscript{2}
catalyst prepared from cobalt acetate precursor. Matsuzaki et.al. \(^{14}\) reported observing a diffraction pattern for rhenium metal in their XRD, but the XRD pattern was not provided. The only obvious difference, other than slightly higher Re loading compared to our catalysts (5% vs. 4%) is the fact that they used ammonium perrhenate (NH\(_4\)ReO\(_4\)) as the Re precursor, while we used perrhenic acid, Re\(_2\)O\(_7\)(OH\(_2\))\(_2\). The absence of a Re peak for both the catalysts indicate that Re is highly dispersed. The fact that we do not see any Co\(_3\)O\(_4\) phase peaks in XRD for CoRe(A) also indicates that cobalt clusters are also highly dispersed after modification with Re. The CoRe(N) catalyst gives peaks corresponding to a crystalline Co\(_3\)O\(_4\) phase. This result is in agreement with Matsuzaki et.al.\(^{14}\) for an unpromoted 5% Co/SiO\(_2\) catalyst and Martinez et.al.\(^{26}\), who reported a crystalline Co\(_3\)O\(_4\) phase for 1% Re/20% Co/SBA-15 prepared from a cobalt nitrate precursor.

![XRD results for CoRe(N)](image_url)

Figure 3.2: XRD for catalyst CoRe(N)
3.3.3. ICP-OES

The results for ICP-OES are presented in Table 3.1. The figures indicate metal wt%. The metal loadings are close to their intended values. There is a small, but statistically significant difference in Co and Re contents.

Table 3.1: ICP metal analysis results for catalysts CoRe(N) and CoRe(A) *

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co</th>
<th>Re</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoRe(N)</td>
<td>9.37</td>
<td>4.88</td>
<td>1.93</td>
</tr>
<tr>
<td>CoRe(A)</td>
<td>8.65</td>
<td>4.70</td>
<td>1.89</td>
</tr>
</tbody>
</table>

* Errors in reported values are within ±1%

3.3.4. Catalyst Activity Tests

The results of CO hydrogenation tests for CoRe(N) and CoRe(A) are presented in Table 3.2.
Table 3.2: Selectivities of products of CO hydrogenation reaction at different temperatures for CoRe(N) and CoRe(A) †

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp (°C)</th>
<th>EtOH %</th>
<th>MeOH %</th>
<th>CH₄ %</th>
<th>C₂⁺ Oxy % *</th>
<th>C₂⁺ HC % #</th>
<th>CO Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoRe(N)</td>
<td>230</td>
<td>3.0</td>
<td>1.4</td>
<td>39.5</td>
<td>3.6</td>
<td>47.8</td>
<td>4.1</td>
</tr>
<tr>
<td>CoRe(A)</td>
<td>230</td>
<td>15.9</td>
<td>5.7</td>
<td>45.2</td>
<td>1.3</td>
<td>23.5</td>
<td>0.3</td>
</tr>
<tr>
<td>CoRe(N)</td>
<td>270</td>
<td>0.4</td>
<td>0.3</td>
<td>45.9</td>
<td>2.1</td>
<td>42.0</td>
<td>29.4</td>
</tr>
<tr>
<td>CoRe(A)</td>
<td>270</td>
<td>15.9</td>
<td>7.8</td>
<td>34.2</td>
<td>5.2</td>
<td>29.3</td>
<td>3.7</td>
</tr>
<tr>
<td>CoRe(N)</td>
<td>300</td>
<td>0.1</td>
<td>0.1</td>
<td>46.8</td>
<td>1.1</td>
<td>32.2</td>
<td>47.0</td>
</tr>
<tr>
<td>CoRe(A)</td>
<td>300</td>
<td>9.5</td>
<td>3.2</td>
<td>43.5</td>
<td>2.8</td>
<td>33.9</td>
<td>10.2</td>
</tr>
</tbody>
</table>

† Pressure = 10 bar, 2H₂/CO, Catalyst wt. = 50 mg, Space Velocity = 72,000 scc.hr⁻¹ g.cat.⁻¹
* includes higher oxygenates other than methanol and ethanol
# includes higher hydrocarbons other than methane

These results show that CoRe(N) is more active for CO hydrogenation (indicated by the higher CO conversion) compared to CoRe(A). The results discussed in the in-situ DRIFTS section gives some insight about the differences in activity. It is interesting to see that even in case of similar CO conversion (e.g., compare CoRe(N) at 230˚C to CoRe(A) at 270˚C), the CoRe(A) catalyst produces less methane, even though the higher temperature should lead to higher methane selectivity. However, the selectivity towards oxygenates is much greater for CoRe(A) as compared to CoRe(N) at all temperatures. For example, the ethanol selectivity at 270˚C is 15.9% for CoRe(A) versus 0.4% for CoRe(N). This can be attributed to the presence of highly dispersed cobalt with very small crystallite size for CoRe(A), as suggested by XRD results. A similar effect of metal cluster size on oxygenates selectivity for Pd/SiO₂ catalysts has
been reported where increased selectivities towards oxygenates are attributed to smaller Pd cluster sizes in the range 5 nm to 19 nm. Also, the presence of Re in close proximity to cobalt for CoRe(A), suggested by the TPR results, also increases oxygenates selectivity. This result is in agreement with Matsuzaki et.al. who found that a Co-Re/SiO₂ catalyst prepared from cobalt acetate precursor had a far greater ethanol selectivity than a nominally identical catalyst prepared from cobalt nitrate precursor. They attribute the increase in ethanol/oxygenates selectivity to the presence of small cobalt clusters that are more easily reduced by hydrogen spillover from rhenium. Comparison of our results on the CoRe(N) and CoRe(A) catalysts show a similar trend – higher ethanol/oxygenates selectivity for CoRe(A), which we also attribute to the smaller cobalt cluster size on the CoRe(A) catalyst. Further, our results show that hydrocarbon formation on CoRe(A) is suppressed as compared to CoRe(N), in agreement with Matsuzaki et.al.

3.3.5. In-situ DRIFTS - CO Adsorption at 25°C

The DRIFTS spectra of the carbonyl region for CoRe(A) as a function of time are shown in Figure 3.4. These spectra were taken after the catalyst was reduced in-situ with H₂. The peak observed at 2059 cm⁻¹ during the start of CO flow can be assigned to linearly coordinated CO to a Co(0) center on the surface of the catalyst. This peak shifts to higher
wavenumbers (2059 cm\(^{-1}\) → 2079 cm\(^{-1}\) → 2088 cm\(^{-1}\)) with time reflecting a decrease in \(\pi\)-backbonding from the Co atoms to the carbonyl ligands. As more CO coordinates to the surface there are fewer cobalt atoms without electron-withdrawing CO ligands that can donate electron-density to nearby cobalt atoms that have CO’s coordinated. The increase in electron-withdrawing \(\pi\)-backbonding carbonyls causes a general decrease in surface electron-density resulting in the steady shift to higher CO stretching frequencies and weaker cobalt-carbonyl bonding.

The peak at 2176 cm\(^{-1}\) is higher than free CO (2143 cm\(^{-1}\)) indicating that there is no \(\pi\)-backbonding taking place between the metal center and carbonyl ligand. When CO acts as a simple \(\sigma\)-donor, the carbonyl stretching frequency increases above 2143 cm\(^{-1}\). This points to CO coordinating to higher oxidation state Co(II)/Co(III) centers, probably from Co\(_3\)O\(_4\) nanoclusters formed during calcining that weren’t fully reduced upon subsequent H\(_2\) treatment. Busca and coworkers\(^{28}\) studied the coordination of CO to Co\(_3\)O\(_4\) and found a relatively strong carbonyl band near 2180 cm\(^{-1}\). They also found that CO rapidly reduces Co\(_3\)O\(_4\) to form Co(II) and Co(I) oxidation state centers at room temperature.

The peak that grows in at 2125 cm\(^{-1}\) can most likely be assigned to CO coordinated to Co(I) centers generated from the CO-induced reduction of Co\(_3\)O\(_4\). Busca also observed this as the appearance of a CO band at 2120 cm\(^{-1}\)\(^{28}\). It can be seen from the CO band growth pattern that CO preferentially coordinates to the most electron-rich Co(0) sites in a linear fashion at the beginning of CO flow (peak at 2059 cm\(^{-1}\)). Coordination to higher oxidation state Co(II)/Co(III) centers initially produces the 2176 cm\(^{-1}\) band, followed almost immediately by CO-induced reduction of some of the Co(II)/Co(III) centers to Co(I) leading to growth of the Co(I)-CO species at 2125 cm\(^{-1}\).
When the CO flow is stopped and helium flow started, the more weakly coordinated CO ligands with the 2176 and 2125 cm\(^{-1}\) bands are preferentially removed causing those bands to decrease in intensity first, but some of the CO coordinated to Co(II)/Co(III) and Co(I) remains even after flushing with helium for 30 min. The persistence of these higher wavenumber bands indicates nanoporous Co\(_3\)O\(_4\) where some of the coordinated CO is partially protected in nanocracks or holes and not as easily lost as one would expect for a simple surface bound CO with such a high stretching frequency.

A comparison of CO adsorption at 25°C between catalysts CoRe(N) and CoRe(A) after 7 min of helium flushing is shown in Figure 3.5. No Co(II)/Co(III)-CO (~2175 cm\(^{-1}\)) or Co(I)-CO (2119 cm\(^{-1}\)) bands are observed for CoRe(N). The peak at 2057 cm\(^{-1}\), as with CoRe(A), is due to linearly adsorbed CO to a Co(0) center. This lower stretching frequency points to more electron-rich cobalt centers relative to the CoRe(A) catalyst system where a 2076 cm\(^{-1}\) value is seen.

The 1942 cm\(^{-1}\) shoulder on CoRe(N) can either be assigned to a bridged metal carbonyl (M\(_2\)-CO) \(^{29}\) or to a terminal carbonyl on an even more electron-rich metal center. There is considerable disagreement in the heterogeneous surface literature about what CO

![Figure 3.5: FT-IR spectra for CO adsorption at 25°C and 230°C at 1 atm for catalysts CoRe(N) and CoRe(A) after helium flushing for 7 min](image)

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stretching frequencies indicate bridging CO’s. A majority of authors cite values below 2000 cm\(^{-1}\) as indicating bridging CO’s, with values below 1900-1850 cm\(^{-1}\) indicating triply bridging CO’s.\(^8,9,12,13,30-33\)

Molecular carbonyls, sometimes referred to as polycarbonyls in the heterogeneous literature, point to a very different story with doubly bridging CO’s for cobalt complexes having frequencies, for example, between 1720 cm\(^{-1}\) for Co\(_2(\mu\text{-CO})_2\text{(CO)}_2\text{(et,ph-P4)}\), where et,ph-P4 = (Et\(_2\)PCH\(_2\)CH\(_2\))(Ph)PCH\(_2\)P(Ph)(CH\(_2\)CH\(_2\)PEt\(_2\)), a strongly donating tetraphosphine ligand,\(^34\), to 1866 cm\(^{-1}\) for Co\(_2(\mu\text{-CO})_2\text{(CO)}_6\)\(^35\). Triply bridging carbonyls in molecular complexes lie even lower in the 1622 cm\(^{-1}\) to 1693 cm\(^{-1}\) range.\(^36\)

Perhaps influenced by CO stretching frequencies in well-characterized molecular complexes, there is a smaller camp of authors that generally limit assignments of bridging carbonyls to bands below 1900 cm\(^{-1}\) and down to about 1750 cm\(^{-1}\), although triply-bridging carbonyl assignments often start appearing at the lower end of this wavenumber regime.\(^1,9,37\) DFT calculations also support the assignment of terminal CO bands down into the upper 1800 cm\(^{-1}\) region, depending on the nature of the metal atom it is coordinated.\(^32\) As one example of the confusion as to where terminal and bridging CO bands should occur, Song and coworkers\(^12\) cite Rygh’s paper\(^32\) as evidence for bridging CO bands occurring in the mid-1900 cm\(^{-1}\) region even though Rygh concludes otherwise.

The 1942 cm\(^{-1}\) band is very small or non-existent on CoRe(A). The presence of CO bands greater than 2100 cm\(^{-1}\) for CoRe(A), especially the high 2175 cm\(^{-1}\) band, points to the CoRe(A) catalyst having a greater quantity of higher oxidation state Co(I), Co(II), and Co(III) centers. The terminal Co(0)-CO band is shifted by 19 cm\(^{-1}\) lower wavenumbers for CoRe(N) as compared to CoRe(A). This indicates a stronger CO adsorption on CoRe(N) as compared to CoRe(A). This
is also an indication of a larger cobalt cluster size for CoRe(N) compared to CoRe(A). Earlier IR studies 27 on the effect of cluster size on CO peak shifts suggest that as the cluster size decreases, the peak shifts from strongly bound surface species to less strongly bound surface species, i.e., CO adsorption is stronger on larger clusters. This result is consistent with the XRD results (Figures 3.2 & 3.3) where the CoRe(A) catalyst exists as particles with sizes less than about 2 nm. Since CoRe(A) is more selective towards oxygenates, it can be inferred that less strongly adsorbed carbonyls are involved in CO hydrogenation and oxygenate formation.

### 3.3.6. CO Adsorption at 230°C

The results for CO adsorption for CoRe(N) and CoRe(A) at 230°C are also shown in Figure 3.5. CO is adsorbed almost exclusively in the linear mode (2073 cm\(^{-1}\)) on CoRe(A). The amount of CO adsorbed on the Co(II)/Co(III) (2175 cm\(^{-1}\)) and Co(I) sites (2119 cm\(^{-1}\)) decreases at 230°C compared to 25°C, showing that CO is weakly bonded to these surface sites as expected from their higher CO frequencies.

For CoRe(N), the CO adsorption at 1942 cm\(^{-1}\) is reduced at 230°C as compared to 25°C. More linearly adsorbed CO sites are found in CoRe(N) than CoRe(A), which is consistent with the higher CO reaction rates on CoRe(N) compared to CoRe(A), as shown in Table 3.2. Similar results have been reported on Co/SiO\(_2\) catalysts prepared using these same two precursors 14,22, where the nitrate precursor catalysts (both promoted and unpromoted) were found to have higher rates of CO conversion than those prepared from an acetate precursor. Also, for CoRe(N) the CO peak at 2053 cm\(^{-1}\) (Figure 3.5) is more strongly adsorbed relative to the 2073 cm\(^{-1}\) peak for CoRe(A), which leads to higher selectivities for hydrocarbons. Similar conclusions were drawn for CO adsorption on Pd catalysts 27 where weakly adsorbed CO on small Pd crystallites was
found to be responsible for higher methanol selectivity, while more strongly adsorbed CO was responsible for methane (hydrocarbon) selectivity.

It has been reported $^{5,38}$ that the probability of C-O bond dissociation depends mainly on the strength of the metal-carbon (M-C) bond. Strong M-C bonds are favored by electron-rich metal centers due to $\pi$-backbonding, which at the same time weakens the C=O triple bond leading to lower carbonyl stretching frequencies. The lower the CO stretching frequency, the weaker the C-O $\pi$-bonds and the greater the rate of C-O bond cleavage and hydrogenation relative to CO insertion. This decreases selectivity towards oxygenates and favors the formation of hydrocarbons $^{38}$ because CO insertion is a key step in the proposed mechanism for $C_2^+$ oxygenates formation $^5$. The higher $C_2^+$ oxygenates selectivity observed for the CoRe(A) catalyst (Table 3.2) corresponds to the presence of more weakly coordinated CO, consistent with these earlier results.

It is interesting that the TPR results showed similar amount of reduced cobalt for both catalysts. The IR data is clearly indicating that the CoRe(A) catalyst has more surface-accessible Co in +1, +2, and +3 oxidation states. The larger particle size for the CoRe(N) catalyst means that the oxidized cobalt (+2/+3 oxidation states) present for that system is buried under a Co/Re shell and not available to either influence the surface cobalt centers or for coordinating CO. The ~2 nm CoRe(A) particles, on the other hand, have exposed Co(II)/Co(III) centers, probably in the form of $Co_3O_4$, that reduces the overall electron-density on the nearby surface Co(0) centers leading to higher CO stretching frequencies.

3.3.7. CO Hydrogenation at 230°C for CoRe(N)

The DRIFTS results for CO hydrogenation (flowing $H_2 + He$ over catalyst pre-adsorbed with CO at 230°C) for CoRe(N) is presented in Figure 3.6. These spectra are taken at different
times after starting H$_2$ flow (t = 0 sec).

On comparing the spectra at t = 0 and t = 28 sec, the linearly adsorbed CO peak height is reduced, but the lower energy band increases in a relative sense. This could indicate that some of the linearly adsorbed CO’s are transforming to bridge-type sites under the flow of hydrogen.

There could be three possibilities for CO hydrogenation in this case:

1. CO hydrogenation taking place on linearly adsorbed CO sites.
2. CO hydrogenation taking place on bridge-type adsorbed CO sites.
3. CO hydrogenation taking place on both types of sites.

Based on these results it cannot be concluded which of the three possibilities applies for CO hydrogenation for the CoRe(N) catalyst. CO hydrogenation activities of linear and bridged-
type sites are not fully understood. Bridging CO’s have been found to react more readily with hydrogen than the linearly adsorbed CO on promoted cobalt catalysts similar to those reported here\textsuperscript{8,9}. It has also been reported\textsuperscript{8} that a low density of bridging carbonyls results in a low chain growth probability and low C\textsubscript{5+} hydrocarbon selectivity. However, Song et. al.\textsuperscript{12} found that both linear and bridging CO’s were equally reactive on an unpromoted Co/SiO\textsubscript{2} catalyst at reaction conditions comparable to those studied here.

What does appear clear is that lower CO stretching frequencies (bridging or terminal) on cobalt promote CO hydrogenation to form hydrocarbon products. Re is important here in helping to activate H\textsubscript{2} and allow it to readily migrate to the Co centers. For the CoRe(N) catalyst the lower wavenumber bands (1990-1920 cm\textsuperscript{-1}) could indicate that linearly coordinated CO is transforming to a doubly-bridging mode on the Co surface and hydrogenation is taking place on these sites (case 2). A possible site transformation mechanism is presented in Figure 3.7. The spillover of hydrogen from Re to Co causes the linearly adsorbed CO to shift to a neighboring cobalt atom forming a bridge-type structure, which then undergoes hydrogenation.

![Figure 3.7: Proposed mechanism for transformation of linearly adsorbed CO to bridge-type](image-url)
3.3.8. CO Hydrogenation at 230°C for CoRe(A)

The DRIFTS results for CO hydrogenation for CoRe(A) is presented in Figure 3.8. This series of spectra are quite different from that seen for CoRe(N) in Figure 3.6. The 2183 cm⁻¹ high frequency band associated with Co(II)/Co(III)-CO coordination is lost fairly quickly most likely due to reduction to Co(0) sites.

![Figure 3.8: FTIR spectra for CO hydrogenation at 230°C and 1 atm pressure for CoRe(A) at different times (in seconds) after starting H₂ flow (t=0 corresponds to when H₂ flow started)](image)

The site transformation from linear to bridged is not observed for CoRe(A). One possible explanation for this could be because of highly dispersed cobalt clusters, the possibility of having a neighboring cobalt atom is low. In other words, the presence of Co-Co type structure is negligible. This also indicates that Re and Co exist in close proximity to each other, which agrees with the TPR results.
For CoRe(A) there is little doubt that the Co-CO linear sites are the active sites for CO hydrogenation. The shift in the CO peak (2074 cm\(^{-1}\) \(\rightarrow\) 2047 cm\(^{-1}\)) probably reflects, in part, reduction of the electron-deficient Co(I), Co(II), and Co(III) sites producing a somewhat more electron-rich Co(0) surface, but still electron-deficient enough to favor oxygenate production. Lower CO surface coverage, as discussed previously, can also account for the shifting of CO stretching frequencies to lower wavenumbers.

3.3.9. Comparison of CO Adsorption for CoRe(N) and CoRe(A) at Different Temperatures

A comparison of CO adsorption for CoRe(N) at 25°C, 230°C and 270°C is presented in Figure 3.9. The peak shifts towards lower wavenumbers (red shift) with increasing temperature. This indicates that only strongly adsorbed surface species remain on the surface with increasing temperature, as expected. Also, the amount of linearly adsorbed CO is higher at 230°C as compared to 25°C and decreases with further increase in temperature to 270°C, which shows an activated chemisorptions phenomenon. The peak at 1943 cm\(^{-1}\) is clearly seen at 25°C, but decreases in intensity as the temperature increases. This is curious since this band is
assigned to either a bridging CO or a terminal carbonyl on a more electron-rich metal center. Neither should be lost more readily than a terminal Co(0)-CO.

A comparison of CO adsorptions for CoRe(A) is also presented in Figure 3.9. The red shift of the primary 2076 cm\(^{-1}\) band is similar with increasing temperature to that found in CoRe(N). The 2175-2180 cm\(^{-1}\) band associated with Co(II)/Co(III) sites persists at 230°C, but disappears at 270°C. These higher oxidation sites should be gradually reduced by CO and eventually disappear. The Co(I)-CO band proposed to be at 2125 cm\(^{-1}\) is found to be reducing in intensity with increasing temperature, consistent with the weaker cobalt carbonyl bonding.

3.3.10. Comparison with Co/Re/\(\gamma\)-Al\(_2\)O\(_3\) Fischer-Tropsch Catalyst

Figure 3.10 shows a comparison of the DRIFTS spectra under CO and H\(_2\)/CO conditions for CoRe(N), CoRe(A), and the 12% Co/1% Re/\(\gamma\)-Al\(_2\)O\(_3\) Fischer-Tropsch catalyst system studied by Rygh and Nielsen. Although there are certainly some differences in exact band positions between Rygh’s catalyst system and CoRe(N), there are a number of similarities. The fact that CoRe(N) functions mainly like a Fischer-Tropsch catalyst fits with the spectral analogies to

**Figure 3.10:** a) Rygh’s 1-4 FT-IR spectra at 250°C immediately before H\(_2\) addition. b) after 35 mins of H\(_2\) exposure. c) after 18 hrs followed by evacuation. d) proposed Re-CO bands from CO only study. e) CoRe(N) CO-only spectrum at 230°C. f) 111 sec of H\(_2\). g) 129 sec of H\(_2\). h) 397 sec of H\(_2\) (vertically expanded). i) CoRe(A) catalyst after 360 sec of H\(_2\).
Rygh’s catalyst. It is clear that the CoRe(A) catalyst, however, is quite different in that it lacks most of the lower frequency CO bands associated with Fischer-Tropsch activity.

Rygh has assigned a series of broad CO bands between 2020 and 1920 cm$^{-1}$ (Figure 3.10d) as arising from linear Re-carbonyls. This could be responsible for or contribute to the 1943 cm$^{-1}$ shoulder seen for the CoRe(N) catalyst. Re is less electronegative relative to Co, the Re 5d orbitals overlap better with the CO $\pi^*$-antibonding orbitals, so Re should engage in more $\pi$-backbonding to a terminal carbonyl, leading to lower CO stretching frequency. The presence of larger Re clusters, which are likely on the larger CoRe(N) catalyst particles could lead to these types of Re-CO bands. The lack of them in the CoRe(A) catalyst is, once again, generally consistent with the smaller particle size and more atomically dispersed Re centers.

The proposed larger and more isolated Re clusters on the CoRe(N) catalyst are consistent with the TPR results, where a shoulder is observed for the case of CoRe(N) catalyst. This shoulder is likely due to reduction of rhenium oxide and cobalt oxide in contact with each other. The peak observed after the shoulder would then be due to the slower reduction of cobalt oxide not in contact with Re. This is not observed for the CoRe(A) catalyst due to the more highly dispersed Re and much smaller Re(0) clusters that result.

3.3.11. CO Desorption Rate

CO desorption rates were calculated for CoRe(N) based on decrease in peak height with respect to time. The results for 230°C and 270°C are presented in Figures 3.11 and 3.12 respectively.

The surface CO desorption rate is faster in presence of hydrogen than that of helium at both temperatures. This result is expected, as CO adsorbed on the surface depletes faster because of hydrogenation reactions at these temperatures.
Figure 3.11: CO desorption rates for CoRe(N) at 230°C and 1 atm pressure during helium and hydrogen flow.

Figure 3.12: CO desorption rates for CoRe(N) at 270°C and 1 atm pressure during helium and hydrogen flow.
A comparison of Figures 3.11 and 3.12 shows that the CO desorption rate is faster at higher temperatures, for both helium and hydrogen flow conditions, which is also an expected result.

3.4. CONCLUSIONS

Experimental results showed significant differences in catalyst behavior and physical properties for two nominally identical Re-promoted cobalt catalysts prepared from cobalt nitrate [CoRe(N)] and cobalt acetate [CoRe(A)] precursors. XRD showed no peaks for the CoRe(A) catalyst, indicating that cobalt is present in clusters less than 2 nm in size. CO hydrogenation activity/selectivity results on these two catalysts showed that while the rate of CO reaction on CoRe(N) was greater than CoRe(A), the selectivities towards ethanol and oxygenates were far higher for the CoRe(A) catalyst. This appears to be due in part to the smaller cluster size of highly dispersed cobalt and rhenium phases for CoRe(A).

FT-IR DRIFTS studies demonstrate considerably different metal carbonyl coordination sites for both catalysts. The CoRe(N) catalyst system showed carbonyl bands with lower stretching frequencies (2057 cm\(^{-1}\)) relative to CoRe(A) and distinct similarities to Co/Re/Al\(_2\)O\(_3\) Fischer-Tropsch catalysts characterized by Rygh and Nielsen\(^1\). The CoRe(A) catalyst, in marked contrast, had a higher frequency band assigned to Co(0)-CO (2074 cm\(^{-1}\)) and extremely high frequency bands at 2175-2183 cm\(^{-1}\), assigned to Co(II)/Co(III)-CO (due to Co\(_3\)O\(_4\)), and 2125 cm\(^{-1}\) assigned to Co(I)-CO resulting from CO (or H\(_2\)) reduction of the Co(II)/Co(III) centers. While carbonyl bands around 1950 cm\(^{-1}\) were found on CoRe(N), which could be assigned to either bridging CO’s or terminal Re-carbonyls, few such sites were found on CoRe(A). CO hydrogenation results for CoRe(N) demonstrate that lower frequency carbonyls undergo hydrogenation to form far more hydrocarbon products, in analogy with related Fischer-Tropsch systems. For CoRe(A) the linear sites are found to be the active sites for CO
hydrogenation and production of higher amounts of desired oxygenated products. A stronger interaction of CO with the surface was observed for CoRe(N) compared to CoRe(A) at all temperatures, which is an indication of larger cobalt cluster size. Sites on CoRe(A) that adsorb CO linearly and relatively weakly (i.e., higher CO stretching frequencies) are responsible for higher selectivity towards oxygenates. Red shifts of linearly adsorbed CO peaks were observed for both the catalysts with increasing temperature.

The differences in catalyst behavior between CoRe(N) and CoRe(A) are tied into the electronic differences indicated by the metal carbonyl FT-IR spectra. The more electron-rich bulk-like Co & Re centers in the CoRe(N) catalyst causes it to behave more like a traditional Fischer-Tropsch catalyst system. The larger particle size of the CoRe(N) catalyst has the oxidized Co$_3$O$_4$ crystallites buried beneath the Co/Re metallic surface, since any significant amounts of exposed Co$_3$O$_4$ would coordinate CO and produce higher frequency carbonyl bands, which are not observed. The 1942 cm$^{-1}$ band for CoRe(N) (and general band intensity between 2000 and 1900 cm$^{-1}$) can be tentatively assigned to bridged CO on cobalt and terminal Re-CO’s. The Re-CO bands, if present, indicate larger clusters of Re on the surface.

In marked contrast, the CoRe(A) catalyst has very small ~2 nm sized particles with exposed Co$_3$O$_4$ and more atomically dispersed Co(0) and Re(0) centers. The higher Co(0)-CO stretching frequency arises from the smaller Co cluster size and presence of nearby Co$_3$O$_4$ species that are electron-withdrawing and reduce the electron-density on the Co(0) centers. If the observation of Re(0) cluster linear carbonyls in the 2000-1920 cm$^{-1}$ region is correct for the CoRe(N) catalyst system, the lack of bands in this region for CoRe(A) indicates that the more atomically dispersed Re centers may not be as effective in activating H$_2$ and providing H atoms to the Co sites. The presence of surface accessible Co$_3$O$_4$ on the CoRe(A) catalyst indicates that
H₂ reduction is more difficult than we anticipated, providing support for the lack of significantly-sized Re clusters.

The selectivity of the CoRe(A) catalyst for oxygenates appears to be clearly tied into its lower hydrogenation activity. The current results indicate that it may be possible to maintain the oxygenate selectivity while increasing the overall catalyst activity for CoRe(A) by increasing the amount of Re used and experimenting with longer H₂ catalyst reduction conditions. Maintaining nanosized catalyst particles and highly dispersed Re (or other H₂-activating metal) appears to be a critical feature for oxygenate selectivity based on this study.

3.5. REFERENCES


CHAPTER 4: COMBINED IN-SITU XRD AND IN-SITU XANES STUDIES ON THE REDUCTION BEHAVIOR OF RHENIUM PROMOTED COBALT CATALYST *

4.1. INTRODUCTION

Increase in crude oil prices, depletion of fossil fuel resources, and increasing demand for clean fuel has led to increased research interest in alternative energy resources; particularly the production of liquid fuels from sources other than petroleum. The conversion of coal- or biomass-derived syngas to ethanol is a promising alternative \(^1\)-\(^4\). Ethanol offers many advantages, including its use in present internal combustion engines and fuel infrastructure with minor changes \(^1\).

Cobalt-based catalysts have been found to be advantageous for the conversion of syngas to liquid fuels because of their low costs, low water-gas shift activity and high activity for CO hydrogenation \(^5\),\(^6\). The catalytic activity, however, depends on various factors including, the method of preparation, type of support, and promoters. The oxidized form of catalyst is not active for CO hydrogenation, and therefore it is important to reduce the catalyst before the reaction and to maintain the catalyst in a reduced state during the reaction. The activity of cobalt catalysts depends mainly on the number of active metal sites which are formed by reduction \(^7\).

It is well known that cobalt is easier to reduce when supported on SiO\(_2\) than supported on Al\(_2\)O\(_3\) \(^8\). However, in most cases, cobalt is present as large crystalline Co\(_3\)O\(_4\), which do not favor oxygenates production \(^9\). Cobalt must be in a highly dispersed form in order to facilitate oxygenates production.

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* Reproduced by permission of the PCCP Owner Societies. This chapter has been published as Kumar, N.; Payzant, E.A.; Jothimurugesan, K.; Spivey, J. J. Physical Chemistry Chemical Physics 2011, 13, 14735.
To synthesize catalysts with highly dispersed cobalt, the initial Co$_3$O$_4$ phase should also be highly dispersed on the support, which requires strong interaction between the support and cobalt precursor. However, these strong interactions result in cobalt species that are difficult to reduce. If a higher reduction temperature is applied to the catalyst, it may result in sintering of the highly dispersed crystallites, which in turn can adversely affect the dispersion and activity of the catalyst. To address this problem, generally a promoter is added to the catalyst, which increases the reducibility of the catalyst while keeping the active metal highly dispersed.

Addition of rhenium to Co/SiO$_2$ catalysts has been found to promote activation of the cobalt sites in the catalyst via reduction of oxidized cobalt species while keeping the cobalt highly dispersed. Reduced Re is found to activate hydrogen and reduce cobalt particles by a H$_2$-spillover mechanism. Re also helps improve selectivity towards oxygenates, especially ethanol. Small amounts of Re have been found to significantly increase the amount of adsorbed CO on cobalt and thus CO hydrogenation rates. However, the active sites for CO hydrogenation has been proposed to be the highly dispersed cobalt sites only.

Zirconia has also been proposed as an important promoter for Co/SiO$_2$ catalysts. Addition of ZrO$_2$ promoter can modify and improve the catalyst texture and porosity, assist in the reduction of oxidized Co species to metallic cobalt, increase the dispersion of cobalt, and improve the chemical stability of the support. Pre-impregnated zirconia is believed to form a protecting layer to prevent the reaction between silica and cobalt that leads to formation of inert cobalt silicates.

It has been observed experimentally and confirmed by theoretical studies that the behavior of Co-based supported catalyst in FT synthesis depends on the characteristics of the metallic phase (i.e. fcc or hcp), showing that FTS reaction is structure sensitive and that Co-hcp
phase is more active. The objective of the work reported here is to investigate the reduction behavior of Re-promoted silica supported cobalt catalyst and understand the role of promoters in the reduction of catalyst.

4.2. EXPERIMENTAL

4.2.1. Catalyst Preparation

Co-Re/(Zr/SiO$_2$) based catalyst was synthesized using a conventional incipient wetness impregnation method. SiO$_2$ support obtained from Alfa Aesar (Surface Area = 300 m$^2$/g, Pore Volume = 1 cc/g) was modified with 2% Zr by impregnation. Zirconium(IV) oxynitrate hydrate ZrO(NO$_3$)$_2$$\cdot$6H$_2$O, was used as the Zr precursor. The modified support was dried for 2 h at 120 °C and calcined in air for 2 h at 500 °C. A mixture of cobalt and rhenium salts was simultaneously impregnated on the Zr-modified support. Perrhenic acid, Re$_2$O$_7$$(\text{OH})_2$ was used as the Re precursor and cobalt(II) nitrate hexahydrate, Co(NO$_3$)$_2$$\cdot$6H$_2$O was used as cobalt precursor. The catalyst was dried for 2 h at 120 °C and calcined under air flow for 2 h at 300 °C at a ramp rate of 1 °C per min. The catalyst contains 10 wt% cobalt (as metal Co), 4 wt% Re and 2 wt% Zr.

4.2.2. Temperature Programmed Reduction (TPR)

Temperature programmed reduction (TPR) profiles of the calcined catalyst were recorded using an Altamira AMI 200-R-HP unit equipped with a thermal conductivity detector (TCD). The catalyst sample was first purged in a fixed-bed micro-reactor system under flowing argon at 150 °C for 1 h to remove traces of water and then cooled to 25 °C. TPR was performed using a 10% H$_2$/Ar mixture at a flow rate of 50 cm$^3$/min while the temperature was linearly ramped from 25 °C to 750 °C using a ramp rate of 10 °C/min. H$_2$ consumption during reduction was measured
by analyzing effluent gases with TCD. Calibration of TCD was done by reduction of different weights of Ag₂O powder. A four point calibration was done and the actual H₂ consumption was calculated based on an equation fitting these points.

### 4.2.3. In-situ X-Ray Diffraction (XRD)

In-situ XRD experiments were carried out at Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL). These experiments were done with PANalytical X’Pert Pro MPD X-ray diffractometer using Cu Kα radiation (λ = 1.5406Å). The sample was mounted in an Anton Paar XRK hot stage, which can go up to 900 °C and 10 bar pressure and has the provision for gas flow. Fresh calcined catalyst was used for the in-situ XRD experiments.

The gases used for the experiments are:

1. 2% CO, 2% Ar, balance He
2. 4% H₂, balance He

The catalyst was crushed to fine powder (~200 mesh) before loading in the sample chamber. The sample chamber is provided with gas inlet and outlet lines. Scans were taken in flowing H₂/He (50 sccm) or flowing syngas (CO:H₂ = 1:2; total flow = 50 sccm). The time taken for one scan was approximately 30 min and the angle was varied from 15 ° to 70 ° (step size = 0.0167113 °).

The catalyst was held at the intended scan temperature during the 30 min scan.

The catalyst was reduced at 400 °C for 2 h in flowing H₂/He. The temperature was ramped from room temperature to 400 °C at a rate of 20 °C/min. Scans were taken at room temperature, 100 °C, 200 °C, 300 °C and 400 °C in flowing H₂/He. At each temperature the system was held for approximately 30 min for scanning. The catalyst was reduced at atmospheric pressure in H₂/He, but the syngas experiments were carried out at 5 bar pressure.
Particle sizes for different phases were calculated using Scherrer formula on the basis of FWHM and taking into account the correction for instrumental broadening. Calculation of theoretical X-ray powder patterns and data analysis was done using the software X’Pert HighScorePlus(v3.0).

4.2.4. In-situ X-ray Absorption Near Edge Structure (XANES)

In-situ XANES experiments were carried out at Center for Advanced Microstructures and Devices (CAMD) at Louisiana State University, USA. This synchrotron light source operates the storage ring at 1.3 GeV with a ring current between 100 and 200 mA. The storage ring contains bending magnets for generation of synchrotron x-rays. A double crystal monochromator with Ge(220) crystals was used for selection of energy. The absorption spectra were collected at Co K-edge in transmission mode at the DCM beamline using ion chambers that were filled with helium. The photon energy was calibrated to the K-edge (taken as the maximum in the first derivative) of cobalt foil at ~2 eV resolution. XANES spectra were collected in the range -50 eV to +100 eV relative to the cobalt K-edge energy. A cobalt foil was kept after the sample and data were collected simultaneously for both, the catalyst sample and the cobalt foil in transmission mode. A special design Lytle Cell was used for in-situ experiments. The cell contains a sample chamber with the provision for gas flow through the sample chamber. Design of the Lytle cell allows the maximum operating temperature of 362 °C and pressure of 1 atm. The catalyst was placed into the sample chamber and sealed with Kapton tape. Following gas mixtures were used for the experiments:

1. 10% H₂, balance Ar for in-situ reduction
2. 10% syngas (CO:H₂= 1:2), balance He for in-situ CO hydrogenation

The flow of gases in the chamber was maintained at 50 sccm. Temperature was ramped from room temperature to 362 °C at the rate of 2 °C/min. Scans were taken (~10 min/scan)
during temperature ramping. The temperatures reported are the temperatures just before start of scans. Data was analyzed by using XAS data analysis software, Athena. The E-shift was calculated by fitting a curve to the first derivative of the spectrum of the cobalt foil, locating the maximum of the curve near the cobalt K-edge, and subtracting it from the theoretical cobalt K-edge value (7709 eV). Appropriate pre-edge and post-edge lines were selected and the spectra were normalized. The software allows for least square fitting of the unknown samples with the standards. Spectra of various standards were obtained in the beamline prior to the in-situ experiments. Standards used were metallic cobalt foil, CoO and Co$_3$O$_4$. The spectra obtained over the catalytic sample were fit into these standards using linear combination fitting, to find out the relative compositions of these components. The fitting range was -20 eV to +30 eV and the sum of the coefficients was forced to 1.

### 4.3. RESULTS AND DISCUSSION

#### 4.3.1. ICP-OES

The results for ICP-OES are presented in Table 4.1. The figures indicate metal wt%. The metal loadings are close to their intended values.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Re</td>
<td>Zr</td>
</tr>
<tr>
<td>Component</td>
<td>9.37</td>
<td>4.88</td>
<td>1.93</td>
</tr>
</tbody>
</table>

*Errors in reported values are within ±1%*
4.3.2. Temperature Programmed Reduction

The TPR result is shown in fig. 4.1. The shoulder peak at around 400 °C (peak 3) is due to the reduction of rhenium oxide. Some contribution to this peak is also due to the reduction of highly dispersed Co$_3$O$_4$ in close proximity of rhenium oxide.

Figure 4.1: Temperature Programmed Reduction of calcined Co-Re/(Zr/SiO$_2$) catalyst under H$_2$ flow. Peaks are indicated as 1, 2, 3 and 4.

It is widely accepted that the reduced rhenium promotes the reduction of cobalt by hydrogen spillover from Re to cobalt oxide. The peak at around 415 °C (peak 4) is due to the reduction of highly dispersed cobalt oxide by the spillover mechanism. The reduction is at a little higher temperature as compared to peak 3 because these highly dispersed cobalt oxides are not in close proximity with rhenium. Reduction of large crystalline Co$_3$O$_4$ is observed as two
well resolved peaks around 230 °C (peak 1) and 335 °C (peak 2)\textsuperscript{21,22}. These peaks correspond to two steps reduction of cobalt oxide (Co\textsubscript{3}O\textsubscript{4} \rightarrow CoO \rightarrow Co\textsuperscript{0}). Peak 1 is due to reduction of large crystalline Co\textsubscript{3}O\textsubscript{4} to CoO \textsuperscript{21,23,24} and peak 2 is due to reduction of CoO to Co\textsuperscript{0}. Schanke et al.\textsuperscript{21} found two well-resolved peaks corresponding to these steps at 327 °C and 397 °C with their areas ratio as 1:3 for unpromoted Co/SiO\textsubscript{2} catalyst. They also observed Co\textsubscript{3}O\textsubscript{4} to be the only cobalt phase detected by XRD, which is similar to what we observe here (see the \textit{in-situ} XRD section). The fact that Schanke et al.\textsuperscript{21} observed the reduction of large crystalline cobalt oxides at temperatures higher than ours could be because our catalyst surface was modified with 2\% Zr, which may have increased the reducibility of large crystalline cobalt oxides \textsuperscript{14,15}. Pre-impregnated zirconia is believed to form a protecting layer to prevent the reaction between silica and cobalt to form inert cobalt silicates\textsuperscript{13,16}.

An attempt to quantify the H\textsubscript{2} consumption at these temperatures was made by peak fitting and calculating the corresponding areas under the peak. But peak 1 is so small that it could not be fitted within reasonable error. So another TPR was carried out with larger amount of catalyst and higher TCD gain. We observed the TCD signal saturation for the larger peaks (peaks 3 and 4), but peaks obtained at 1 and 2 were large enough to fit a curve. The area calculated for peak 2 was found to be three times the area calculated for peak 1, which is consistent with the stoichiometry of the corresponding reductions. This strongly suggests that the large crystalline Co\textsubscript{3}O\textsubscript{4} undergoes a two-step reduction, with CoO being an intermediate. This, however, is not the case with the highly dispersed Co\textsubscript{3}O\textsubscript{4}, which reduces at higher temperature (415 °C) as a single unresolved peak (peak 4). This is because the reduction of highly dispersed Co\textsubscript{3}O\textsubscript{4} is facilitated by reduced Re (which reduces at 400 °C as peak 3), thereby making the two steps faster and resulting in unresolved single peak at 415 °C.
The H₂ consumption calculated by area under the TPR curve for all the four peaks is presented in Table-4.2(a). The peaks in the TPR curve were de-convoluted for this calculation.

Table 4.2: Hydrogen consumption calculation on the basis of 100 mg Co-Re/(Zr/SiO₂) catalyst. (a) Actual H₂ consumption in the TPR experiment, (b) Theoretical H₂ consumption calculation based on the complete reduction of species as per the stoichiometries indicated. The metal loadings are taken from Table-4.1.

(a)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Temperature (°C)</th>
<th>Species Reduced</th>
<th>Actual H₂ Consumed (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>230</td>
<td>Co₃O₄ → CoO</td>
<td>1.52x10⁻⁵</td>
</tr>
<tr>
<td>2</td>
<td>335</td>
<td>CoO → Co</td>
<td>4.68x10⁻⁵</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
<td>Re₂O₇ → Re Co₃O₄ → Co</td>
<td>1.34x10⁻⁴</td>
</tr>
<tr>
<td>4</td>
<td>415</td>
<td>Co₃O₄ → Co</td>
<td>1.45x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td>3.42x10⁻⁴</td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
<tr>
<th>Stoichiometry</th>
<th>Theoretical H₂ consumption (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₃O₄ + 4H₂ → 3Co + 4H₂O</td>
<td>2.12x10⁻⁴</td>
</tr>
<tr>
<td>Re₂O₇ + 7H₂ → 2Re + 7H₂O</td>
<td>9.18x10⁻⁵</td>
</tr>
<tr>
<td>Total</td>
<td>3.04x10⁻⁴</td>
</tr>
</tbody>
</table>

66
The theoretical H₂ consumption based on complete reduction of metals is also presented in Table-4.2(b). The calculation is based on 100 mg catalyst and using the metal loadings from ICP analysis (Table-4.1). The H₂ consumption corresponding to peak 3 is found to be higher than that required for the reduction of rhenium oxide to metallic rhenium. This suggests that a part of the peak is due to the reduction of highly dispersed Co₃O₄ in close contact with rhenium. The total experimental H₂ consumed is around 11% higher as compared to the theoretical H₂ consumption. This can be attributed due to the experimental errors and the errors in curve fitting.

The TPR results indicate that the catalyst contains two types of cobalt: (a) large crystalline Co₃O₄, and (b) highly dispersed Co₃O₄ interacting with the support. Using the metal loadings from the ICP analysis (Table-4.1), an estimate of the relative amounts of the two types of cobalt can be made by comparing the corresponding sum of areas under peaks 1 and 2 (complete reduction of large crystalline Co₃O₄) to the sum of the areas under peak 4 and a part of peak 3 (complete reduction of highly dispersed Co₃O₄). The fraction of large crystalline Co₃O₄ was calculated to be around 25% of total Co₃O₄.

4.3.3. In-situ X-ray Diffraction (XRD)

To study the effect of reduction treatment under H₂ and to monitor the crystal phase formation of cobalt with temperature, we carried out in-situ XRD experiments. Figure 4.2 shows the results as the catalyst was heated at different temperatures under H₂/He flow. The room temperature profile is similar to that at 100 °C and thus has not been presented here. A discussion on XRD at room temperature is given in our previous work 19.

The XRD patterns have a moderately low signal to noise ratio because of the low amount of crystallinity in the catalyst. This is consistent with the TPR results (Figure 4.1), where we see
a small peak at 335 °C corresponding to the reduction of large crystalline Co$_3$O$_4$. Reduction of highly dispersed Co$_3$O$_4$ is not observed in the XRD, but is seen in the TPR at 415 °C.

Figure 4.2: In-situ XRD results for Co-Re/(Zr/SiO$_2$) catalyst at different temperatures under H$_2$/He flow and atmospheric pressure

For the case of 100 °C and 200 °C, the peaks appearing at 31.1 °, 36.7 °, 44.7 °, 59.1 ° and 65 ° correspond to (022), (113), (004), (115) and (044) reflections of the Co$_3$O$_4$ phase respectively, which is the only phase observed till 200 °C. The absence of Re-oxide phase could be due to small amount of Re present in the system and/or due to highly dispersed Re. With increasing temperature (300 °C), new peaks corresponding to the CoO phase appear. There is a
mixture of Co$_3$O$_4$ and CoO phase at 300 °C. Peaks at 36.4°, 42.5° and 61.5° correspond to (111), (002) and (022) reflections of CoO phase respectively and peaks at 31° and 36.4° are due to reflections from (022) and (113) planes of Co$_3$O$_4$ respectively. When the temperature is increased to 400 °C, the peaks corresponding to Co$_3$O$_4$ and CoO disappear and three peaks appear at 41.4°, 44.1° and 47°. These peaks can be ascribed to reflections from (010), (002) and (011) planes of hcp-Co phase. The fact that peak at 44.1° is larger than the expected peak ratios of the hcp-Co phase suggests the presence of fcc-Co phase $^{17}$, which has the most significant peak reflection from (111) plane at that position. The next most abundant peak for fcc-Co appears at 51.2°, which we see as very low intensity at that position, given the noise in the data. This could indicate that this catalyst contains mostly hcp-Co as compared to fcc-Co.

Related in-situ XRD studies suggest the formation of bcc-Co phase $^{25}$ along with fcc-Co under syngas flow after ~60 h over Co and Co/MnO catalysts. Initially, they found only fcc-Co and attributed the formation of metastable bcc-Co after long times-on-stream in syngas due to the presence of interstitial carbon formed as a result of dissociation of CO.

Presence of fcc-Co and hcp-Co depends on the catalytic composition as well as reduction environment. Some researchers observed only the fcc-Co phase for an unpromoted cobalt catalyst supported on silica when reduced under H$_2$ $^{26}$, but the reduction under syngas or CO resulted in both the phases (fcc-Co and hcp-Co). A number of researchers have observed the formation of both hcp-Co and fcc-Co phases after reduction in H$_2$ using in-situ XRD $^{27-29}$. It has been shown experimentally that the Fischer-Tropsch synthesis activity can be related to the characteristics of the metallic cobalt phase (fcc or hcp) $^{17,29-31}$. Amariglio et al. $^{30}$ found that the rate of methanation produced by the hcp-Co phase was higher than that produced by the fcc-Co phase. Srinivasan et al. $^{29}$ also found the higher activity of the hcp-Co and attributed this to
stacking faults in the hcp-Co, which resulted in reduced particle size of the hcp-Co phase as compared to the fcc-Co phase. We calculated the particle sizes for various phases and found that the mean particle sizes for Co$_3$O$_4$ and CoO are in the range 10-12 nm and that for hcp-Co are in the range 3-4 nm. The particle size for fcc-Co phase could not be calculated because of its most significant peak coincides with the reflection from (002) hcp-Co phase. This catalyst has been reported $^{19}$ to be active for CO hydrogenation with methane as the main product. Thus we can attribute the activity of the catalyst mainly to the presence of hcp-Co phase. This seems reasonable because there is more hcp-Co phase present than the fcc-Co phase in the reduced state of catalyst.

The introduction of syngas to the reduced catalyst at 270 °C and 5 bar did not result in any noticeable change in the XRD pattern even after 2 h, and thus these diagrams have not been presented here. We do not see the presence of Co$_2$C phase, perhaps because of the short time-on-stream, although Co$_2$C phase has been observed after flowing syngas for much longer time (180 h). $^{16,28}$

4.3.4. In-situ X-ray Absorption Near Edge Structure (XANES)

XANES spectra for the standards (Co$_3$O$_4$, CoO, Co-metal) were taken before running the catalyst, and the results are presented in figure 4.3. The peak height decrease and the changes in the pre-edge feature can be seen for the standards, going from higher oxidation state to lower oxidation state.

Figure 4.4 shows in-situ XANES results under H$_2$ flow at different temperatures. The pre-edge feature, typical for partially tetrahedral coordinated cobalt (which is the case for bulk Co$_3$O$_4$), gradually decreases with increasing temperature. The broadening of the peak indicates
the transformation to octahedrally coordinated cobalt as in CoO. Thus it can be inferred that the catalyst is gradually reduced as the temperature is increased. The catalyst also reduces with time when left under hydrogen flow at a constant temperature of 362 °C (shown as bold curves in Figure 4.4). A linear combination fit of these results is presented in Figure 4.5 using Co₃O₄, CoO and Co-metal as standards. The choice of these standards seems chemically reasonable, since these phases are expected to be present in the sample under H₂ reduction. The error bars are also plotted and they seem to be in a reasonable limit. It can be seen that the Co₃O₄ begins to reduce to CoO (Co⁺³ to Co⁺²) after 200 °C. This is consistent with the TPR result, where the 230 °C peak (peak 1) is due to the reduction of Co⁺³ to Co⁺². It is evident from Figure 4.5 that Co₃O₄ undergoes a two-step reduction from Co⁺³ to Co⁺² to Co⁰.

![Figure 4.3: Normalized cobalt K-edge XANES results for cobalt standard compounds, Co₃O₄, CoO, and Co foil](image)

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Figure 4.4: Normalized cobalt K-edge XANES results for Co-Re/(Zr/SiO$_2$) catalyst as a function of temperature programmed reduction under H$_2$ flow. The bold curves represent the spectra at a constant temperature of 362 °C.

The values reported in Fig. 4.5 are the mole fractions of different species present at that temperature. From the stoichiometry of reduction, 3 mol of CoO is produced for every mole of Co$_3$O$_4$ converted (reduced). The fraction of Co$_3$O$_4$ reduced was calculated at each temperature using the XANES results shown in Fig. 4.5. These fractions are listed in Table-4.3.
Figure 4.5: Linear combination fit results obtained from in-situ XANES data during temperature programmed reduction for Co-Re/(Zr/SiO$_2$) catalyst under H$_2$ flow

Table 4.3: Fraction of Co$_3$O$_4$ converted at different temperatures, calculated using data from Fig. 4.5.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>219</th>
<th>237</th>
<th>255</th>
<th>290</th>
<th>362</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Co$_3$O$_4$ Reduced</td>
<td>6.4</td>
<td>18.2</td>
<td>20.8</td>
<td>25.7</td>
<td>33.0</td>
</tr>
</tbody>
</table>

It can be seen that at 290 °C, where Fig. 4.1 indicates that all the large crystalline Co$_3$O$_4$ should be in a reduced state (CoO, Co), the fraction of Co$_3$O$_4$ reduced is 25.7%. This is in good agreement with that calculated from TPR (25%) by taking the deconvoluted areas under the curve.
The linear combination fit shows that Co₃O₄, CoO and Co-metal phases are present at 300 °C (Figure 4.5). However, the in-situ XRD results at 300 °C (Figure 4.2) do not show metallic cobalt phase. One possible reason for this could be due to very small amount of metallic cobalt present at that temperature. This, and the lack of a clear crystalline peak in the XRD data, probably explains why there is no peak corresponding to metallic cobalt phase.

![Graph showing mole fraction of Co, CoO, and Co₃O₄ over time at 362 °C](image)

Figure 4.6: Linear combination fit results for Co-Re/(Zr/SiO₂) catalyst obtained from in-situ XANES data at constant temperature of 362 °C under H₂ flow

Figure 4.6 shows the linear combination results obtained from XANES experiments after keeping the catalyst at constant temperature of 362 °C in flowing H₂/He mixture. The proportion of metallic cobalt increases with time, with a corresponding decrease in CoO and Co₃O₄. The fraction of Co₃O₄ reduced was calculated at different times and listed in Table-4.4.
Table 4.4: Fraction of Co$_3$O$_4$ converted at different times at a constant temperature of 362 °C, calculated using data from Fig. 4.6.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>12</th>
<th>23</th>
<th>35</th>
<th>47</th>
<th>60</th>
<th>70</th>
<th>83</th>
<th>96</th>
<th>110</th>
<th>120</th>
<th>140</th>
<th>184</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Co$_3$O$_4$ Reduced</td>
<td>33.0</td>
<td>32.0</td>
<td>40.5</td>
<td>49.7</td>
<td>43.9</td>
<td>44.6</td>
<td>50.1</td>
<td>51.8</td>
<td>52.0</td>
<td>46.4</td>
<td>55.5</td>
<td>53.7</td>
</tr>
</tbody>
</table>

Figure 4.7: In-situ XANES results for Co-Re/(Zr/SiO$_2$) catalyst at different temperatures and different times under H$_2$ and syngas flow (bold)
It can be seen from Table 4.4 that around 55% Co$_3$O$_4$ reduces at 362 °C with time on stream, whereas the fraction of large crystalline Co$_3$O$_4$ is calculated from TPR to be only 25%. This indicates that some of the highly dispersed Co$_3$O$_4$ also reduces at 362 °C, when kept for longer time (TPR results in Fig. 4.1 shows that highly dispersed Co$_3$O$_4$ reduces at 400 °C as peak 3). It also suggests the reduction of a fraction of rhenium oxide which reduces at the same temperature (400 °C, peak 3 in Fig. 4.1) and facilitates the reduction of Co$_3$O$_4$. However, it is not possible to calculate the fraction of reduced rhenium from these data.

The effect of syngas flow over a partially reduced catalyst is seen in figure 4.7, which shows the XANES analysis of data. Initially, the catalyst was kept at 362 °C in flowing H$_2$/He for 184 min. The temperature was then reduced to 219 °C and syngas was introduced. The temperature was increased to 300 °C under syngas flow. The bold curves represent the XANES results during syngas flow. The catalyst oxidizes in the presence of syngas, particularly at 219 °C, and starts to reduce when temperature is increased to 300 °C. The linear combination fit results for these XANES data are presented in figure 4.8. It clearly shows a sharp drop in the metallic cobalt from about 65% to 10% under syngas flow (figure 4.8b).

The oxidation of reduced cobalt under Fischer-Tropsch reaction conditions has been observed by many researchers. Van Berge et al. $^{32}$ found similar results, even though the oxidation of bulk metallic cobalt to either CoO or Co$_3$O$_4$ is not allowed thermodynamically under these conditions. This oxidation of catalyst can be attributed to be due to the formation of metal-oxygen bonds as a result of CO hydrogenation reactions at these conditions $^{32,33}$. These metal-oxygen bonds are stronger than those in bulk cobalt, making the oxidation of surface cobalt possible. Another argument for the observed oxidation is that the thermodynamics can be influenced by metal-support interaction, which in turn can result in oxidation of small metal
clusters under conditions where bulk metal oxidation is not possible. Another possibility in our case is due to redox reaction between cobalt metal and rhenium oxide (Re$_2$O$_7$).

The partial oxidation of catalyst under syngas flow is not observed in the \textit{in-situ} XRD experiments, and there is no significant change in the patterns under H$_2$ flow at 400 °C and under syngas flow at 270 °C. This can be explained as follows: The reduction temperature for in-situ XRD experiments is 400 °C, where rhenium reduction takes place (see figure 4.1). When temperature is reduced to 270 °C under syngas flow, the reduced rhenium helps keep the cobalt in metallic phase; which otherwise could have been oxidized by the phenomenon described earlier. Hence we do not observe oxidation of metallic cobalt, and the XRD patterns do not
change for these cases. On the other hand, for the in-situ XANES, the reduction temperature is 362 °C, which is too low for the complete reduction of rhenium oxide. In such a system, the H₂ spillover phenomenon is very less as compared to the system where rhenium is completely reduced. Thus in the absence of sufficient amount of reduced rhenium, cobalt oxidation takes place under syngas flow (see the 219 °C point in Fig. 4.8b). These results demonstrate the importance of reduced rhenium on the reduction behavior of cobalt oxide. It can be concluded that rhenium must be in a reduced state under Fischer-Tropsch reaction conditions in order to keep the cobalt in reduced state.

In the case of in-situ XANES experiments the fact that we observe around 10% metallic cobalt at 219 °C (where metallic cobalt would not be expected) suggests that some rhenium is in the reduced state. This is supported by the fact that there is a higher fraction of metallic cobalt present at 362 °C under H₂ flow.

4.4. CONCLUSIONS

Experimental results showed two step reduction of the large crystalline cobalt clusters in Co-Re/(Zr/SiO₂) catalyst from Co₃O₄→CoO→Co⁰. The intermediate CoO phase is observed in in-situ XRD under hydrogen temperature programmed reduction experiments. The metallic cobalt formed under hydrogen flow consists of both Co-hcp and Co-fcc phases. However, the Co-hcp phase was more abundant, and is thought to be more active phase as compared to Co-fcc phase. In-situ XANES results are consistent with those obtained from TPR and in-situ XRD. The catalyst is increasingly reduced as a function of time when left under hydrogen flow at 362 °C. This increase in reduction with time suggests that some rhenium is also reduced at that temperature, facilitating the reduction of cobalt oxide. The flow of syngas over a partially
reduced catalyst resulted in a lesser degree of reduction, with the metallic cobalt converting mostly to CoO. The oxidation of the catalyst could be attributed due to the CO hydrogenation reaction at these conditions. The presence of reduced rhenium is found to facilitate the reduction of cobalt oxide under flow of syngas.

4.5. REFERENCES


CHAPTER 5: EFFECT OF H₂ PRE ADSORPTION ON CO ADSORPTION OVER CO-BASED CATALYST: IN SITU DRIFTS STUDY

5.1. INTRODUCTION

Cobalt-based catalysts are highly active for CO hydrogenation. The mechanism is generally thought to be one involving coadsorption of CO and H₂ on the surface. The adsorption of CO is significantly different in the presence of hydrogen than when CO is the sole adsorbate. Therefore, it is important to understand the interaction between H₂ and CO on metal surfaces because this affects the catalysis of reactions such as Fischer-Tropsch or higher oxygenates synthesis.

Many researchers have studied the interaction of H₂ and CO over single crystals. For a Ni(100) surface on which hydrogen was preadsorbed at 150 K, Politano et al. found weakly bonded CO phase with no transformation of adsorption sites between bridge-type and atop sites. On a Pd(110) surface, Conrad et al. found that CO displaces adsorbed H₂ completely, but H₂ does not displace adsorbed CO. They attributed this mainly to the higher adsorption energy of CO. Morkel et al. found a temperature-dependent site blocking effect on Pd(111) surface. They observed that preadsorbed H₂ was able to hinder the CO adsorption at low temperature (100 K), while at higher temperature (150 K), H₂ was replaced by CO. Merrill et al. observed site blocking by hydrogen on a H₂ presaturated Fe(100) surface and showed that adsorbed hydrogen strongly affects CO adsorption. CO adsorption was found to be significantly enhanced over a Co/SiO₂ catalyst in the presence of preadsorbed H₂. In view of all these, it is important to study the effect of hydrogen preadsorption on CO adsorption.

Infrared spectroscopy has made a considerable contribution in determining various adsorbed species and their reactivity. Adsorption of CO as a probe molecule has been widely used to
characterize metal sites and surface structure because CO is one of the best characterized diatomic molecules in experimental spectroscopy. However, to the best of our knowledge, no work has been done comparing CO and CO/H$_2$ adsorption over bare and H$_2$ preadsorbed surfaces at different temperatures. Our recent work on Co-Re/(Zr/SiO$_2$), showed that this is an active catalyst for CO hydrogenation $^{13}$, suggesting that the interaction of CO and H$_2$ on this catalyst is important in understanding the mechanism of reaction. Here we use in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to compare the adsorption of CO on reduced Co-Re/(Zr/SiO$_2$) from two gas compositions: (a) CO only, and (b) CO from a CO/H$_2$ mixture. For each gas composition, two catalyst surfaces were used for these experiments: (a) a reduced and adsorbate-free surface and (b) a hydrogen preadsorbed surface.

5.2. EXPERIMENTAL

5.2.1. Catalyst Preparation

Co-Re/(Zr/SiO$_2$) based catalyst was synthesized using a conventional incipient wetness impregnation method. The synthesis method has been described in our previous work $^{14}$.

5.2.2. In-situ Diffuse Reflectance FTIR Spectroscopy (DRIFTS)

FTIR spectra were collected with a Nicolet 6700 model (Thermo Scientific) spectrometer equipped with a MCT-A detector cooled by liquid nitrogen. KBr beamsplitter was used to obtain spectra in the range of 4000–650 cm$^{-1}$. In-situ measurements were carried out in a specially designed environmental chamber (Harrick) equipped with a thermocouple. Provisions were made to the cell for gas inlet, outlet, heating and cooling. A sample holder was used to hold ~20 mg of catalyst. DRIFTS spectra were collected by using series collection for 30 min. For each spectrum 32 scans at a resolution of 4 cm$^{-1}$ were used.
Before each experiment the catalyst was heated in flowing helium at 150 °C for 30 min to remove any moisture and gases. The catalyst was reduced by flowing a mixture of hydrogen and helium (10% H₂ in He) for 2 hrs at 400 °C. The catalyst was subjected to four different sets of experiments after the reduction:

i. Cooling down in H₂ to the desired temperature (300 °C, 270 °C, 230 °C and 25 °C) followed by CO adsorption experiments (CO adsorption on H₂ preadsorbed surface)

ii. Cooling down in H₂ to the desired temperature followed by syngas experiments (syngas on H₂ preadsorbed surface)

iii. Cooling down in helium to the desired temperature followed by CO adsorption experiments (CO adsorption on bare surface)

iv. Cooling down in helium to the desired temperature followed by syngas experiments (syngas on bare surface)

When the catalyst was cooled under helium flow after reduction, the preadsorbed H₂ was removed completely, giving rise to a bare surface. For the case when the catalyst was cooled under H₂ flow, a considerable amount of H₂ remained on the catalyst before introduction of CO/syngas. Backgrounds were collected at each temperature during the helium/H₂ flow for use in the experiments. Difference spectra were obtained by subtracting the background from the subsequent spectra. The catalyst was kept in H₂/helium for 30 min at the desired temperature before starting the experiment. In a typical CO/syngas experiment, CO/syngas flow was started over the reduced catalyst and continued for 5 min followed by helium flow for 25 min. 5% CO/He and 10% H₂/He was used for these experiments. The experiments were carried out at 25 °C, 230 °C and 270 °C and performed at atmospheric pressure.
5.3. RESULTS AND DISCUSSION

5.3.1. CO Adsorption at 25 °C

The DRIFTS spectra of the carbonyl region for CO adsorption over the reduced, adsorbate-free bare catalyst surface of Co-Re/(Zr/SiO₂) at 25 °C is shown in Figure 5.1. The spectra in the figure are taken after start of helium flow. The peak at 2055 cm⁻¹ can be assigned to CO linearly adsorbed on a Co⁰ center, although a part of this peak could be due to CO linearly adsorbed on Re sites. Rygh and Nielsen found that both Co and Re carbonyls show distinct bands in this region, but they ascribe the intensity increase (as a result of temperature rise) to an increase in the amount of Co carbonyl species (and not the Re carbonyl species) on the catalyst surface.

Figure 5.1: CO desorption under helium flow over Co-Re/(Zr/SiO₂) catalyst at 25 °C. The catalyst was reduced at 400 °C for 2 h followed by helium flush for 30 min at 25 °C before introducing CO (bare surface)
This peak shifts towards lower wavenumbers (2055 cm\(^{-1}\) to 2034 cm\(^{-1}\)) with helium flush, indicating an increase in \(\pi\)-backbonding from the Co atoms to the carbonyl ligands. As the CO population decreases with time under helium flow, less CO coordinates to the surface and there are more cobalt atoms available (without electron-withdrawing CO ligands) that can donate electron-density to nearby cobalt atoms coordinated to CO. The increase in electron density for the CO coordinated cobalt atoms results in increased \(\pi\)-backbonding from the Co atoms to the carbonyl ligands, thereby shifting the wavenumbers towards a lower value. In other words, a decrease in electron-withdrawing \(\pi\)-backbonding carbonyls causes a general increase in surface electron-density resulting in the steady shift to lower CO stretching frequencies and stronger cobalt-carbonyl bonding.

The DRIFTS spectra of the carbonyl region for the CO adsorbed over H\(_2\) preadsorbed catalyst surface of Co-Re/(Zr/SiO\(_2\)) catalyst at 25 °C is shown in Figure 5.2. As in Figure 5.1, the spectra in the figure are taken after start of helium flow so that a direct comparison of CO adsorption on the bare surface (Figure 5.1) and the same surface on which H\(_2\) was preadsorbed (Figure 5.2) can be made.

A comparison of Figure 5.1 and Figure 5.2 shows that:

i. The saturated chemisorbed CO (at t=0) appears at 2055 cm\(^{-1}\) in Figure 5.1 (bare surface) compared to 2034 cm\(^{-1}\) in Figure 5.2 (H\(_2\) preadsorbed surface).

*Possible explanation:* On the bare surface, CO adsorption takes place initially on sites that offer higher \(\pi\)-backbonding, corresponding to higher energy sites (and thereby lower wavenumbers). Once these sites are occupied, CO adsorption starts to shift towards the lower energy sites, where it is weakly adsorbed (and thereby shifting towards higher wavenumbers). In the case of H\(_2\) preadsorbed surface, while CO can replace H\(_2\) at higher
energy sites, the lower energy sites are still occupied by H\textsubscript{2}. Therefore, the peak in Figure 5.2 does not shift to higher wavenumbers as compared to Figure 5.1. This also results in low surface coverage of CO in case of H\textsubscript{2} preadsorbed surface, as compared to the bare surface (compare the peak heights of these two figures). This indicates that the sites that adsorb CO are the same as the sites that adsorb H\textsubscript{2} at room temperature. This also indicates a lack of interaction between CO and H\textsubscript{2} at room temperature. Similar results have been obtained by Bridge et al.\textsuperscript{16} on Co(001) at room temperature where they found that preadsorbed H\textsubscript{2} reduces the CO sticking probability significantly as compared to a

![Figure 5.2: CO desorption under helium flow over Co-Re/(Zr/SiO\textsubscript{2}) catalyst at 25 °C. The catalyst was reduced at 400 °C for 2 h and kept under H\textsubscript{2} flow for 30 min at 25 °C before introducing CO (H\textsubscript{2} preadsorbed surface)
bare surface. They attribute this behavior to displacement of H\textsubscript{2} by CO at room temperature.

ii. The peak shift to lower wavenumbers as a result of helium flow is much larger in Figure 5.1 (2055 to 2034 cm\textsuperscript{-1}) compared to that of Figure 5.2 (2034 to 2032 cm\textsuperscript{-1}).

Possible explanation: CO adsorption takes place over a wide wavenumber range on the bare surface (Figure 5.1) because of availability of sites having wide range of adsorption energies. With H\textsubscript{2} preoccupying some (perhaps all) of the sites (Figure 5.2), CO adsorption takes place over those sites that adsorb CO preferentially as compared to H\textsubscript{2}. These sites are expected to be higher energy sites, thereby giving a lower wavenumber (2034-2032 cm\textsuperscript{-1}). On comparing the peak width of linearly adsorbed CO in both the cases, we see that in the case of the bare surface (Figure 5.1), the peak is much wider as compared to the H\textsubscript{2} preadsorbed surface (Figure 5.2). This indicates that CO adsorption takes place over a wide range of wavenumber for the bare surface as compared to H\textsubscript{2} preadsorbed surface, where the CO adsorption takes place over a narrow range of wavenumbers. These sites adsorb CO preferentially compared to H\textsubscript{2}. In Figure 5.2, only the peak height drops with flowing helium, without the peak shifting too much, which shows that CO is adsorbed on sites having similar energy of adsorption. These are the sites that preferentially adsorb CO compared to H\textsubscript{2}.

iii. The bridge-type adsorption (peak at 1938 cm\textsuperscript{-1}) is reduced in Figure 5.2 compared to Figure 5.1, but the peak shift is not observed.

Possible explanation: With H\textsubscript{2} occupying some of the higher energy sites in Figure 5.2, lesser bridged adsorption is expected. However, the peak shifting is not observed because there is no change in the energy of adsorption corresponding to bridged species as a result of H\textsubscript{2} preadsorption.
5.3.2. CO Adsorption at Higher Temperatures

The DRIFTS spectra of the carbonyl region for the bare and H₂ preadsorbed surfaces of Co-Re/(Zr/SiO₂) catalyst at 230 °C, 270 °C and 300 °C are shown in Figure 5.3, 5.4 and 5.5 respectively. These figures show a comparison of CO flow and syngas flow over a bare and H₂ preadsorbed surfaces. These spectra were taken after 5 minutes of CO/syngas flow over the reduced surface. This time (5 min) was sufficient to reach the steady state for all the cases.

The peak intensity of linearly adsorbed CO is found to be the lowest for the case of CO flow over the bare surface, and highest for that of the H₂ preadsorbed surface. This result is the opposite of the results at 25 °C, where a higher CO peak was seen for the bare surface, suggesting that the active sites for CO adsorption are modified by H₂ at higher temperature, resulting in more CO adsorption. Another possibility is the dissociative adsorption of CO over the catalyst surface forming M-C bond, which cannot be detected by DRIFTS. When CO is adsorbed over the bare catalyst surface at high temperature, some sites may adsorb CO associatively and some sites dissociatively. The associative adsorption of CO results in IR-active peaks. However, the dissociative adsorption resulting in the formation of M-C bonds cannot be detected by the infra-red in the regions studied.

At 25 °C, CO adsorption on cobalt takes place mainly associatively. The dissociative adsorption of CO increases with temperature. Therefore over a bare surface at 25 °C one might expect to see mostly associatively adsorbed CO. For the case of H₂ preadsorbed surface at 25 °C, the presence of H₂ would block some of the active sites, thereby resulting in less CO adsorption, as seen in the previous section. At higher temperatures on a H₂ preadsorbed surface, the active sites are modified by the presence of H₂. CO adsorption on these modified sites takes place
readily as compared to the bare surface, where dissociative adsorption of CO results in blocking some of the active sites by forming M-C bonds.

Figure 5.3: CO adsorption at 230 °C as a result of CO flow and syngas flow over bare and H\textsubscript{2} preadsorbed surfaces of Co-Re/(Zr/SiO\textsubscript{2}) catalyst

The effect of H\textsubscript{2} preadsorption has been studied by many researchers\textsuperscript{7,8,16,18,19}. There is a general agreement that CO adsorption is enhanced over H\textsubscript{2} preadsorbed surfaces at higher temperatures. It is suggested\textsuperscript{20,21} that the presence of preadsorbed H\textsubscript{2} caused CO molecules to migrate to different active sites. Another proposed possibility is that the electronic shift can occur on a catalyst surface, resulting in a change of the adsorption properties of metallic cobalt.
In the presence of preadsorbed H$_2$, Rodrigues et al. $^{19}$ found the formation of “hydrocarbonyl” on Co/SiO$_2$ catalyst. They ascribed its structure to HCo(CO), which forms when hydrogen undergoes dissociative adsorption over cobalt atom followed by CO adsorption (see Figure 5.6). The formation of hydrocarbonyl has also been reported by Kadinov et al. $^{22}$ when CO was co-adsorbed with H$_2$ on 5% Ru/Al$_2$O$_3$ catalyst. Kadinov et al. $^{18}$ also observed a band at 2060 cm$^{-1}$ when CO and H$_2$ co-adsorbed on Co/Al$_2$O$_3$ catalyst, which they attributed to hydrocarbonyl species. They claimed that hydrocarbonyl formation is a requisite step in the overall reaction between co-adsorbed CO and H$_2$. While conducting temperature programmed experiments on Rh$_2$Co$_2$/Al$_2$O$_3$ catalyst, Chen et al. $^{23}$ observed a new band at 2046 cm$^{-1}$ which
they ascribed to “carbonyl hydride”, an intermediate species formed during the reaction process by co-adsorption of CO and H$_2$ on Co$^0$ active sites.

Figure 5.5: CO adsorption at 300 °C as a result of CO flow and syngas flow over bare and H$_2$ preadsorbed surfaces of Co-Re/(Zr/SiO$_2$) catalyst.

The adsorption of H$_2$ over reduced cobalt has been widely studied and there is an agreement that at higher temperatures H$_2$ adsorption is activated, and it is adsorbed dissociatively over cobalt$^{24-26}$. When CO is adsorbed over such Co-H complexes, it forms the hydrocarbonyl structure (Figure 5.6). The formation of the hydrocarbonyl complex inhibits the CO bond dissociation, resulting in more linearly adsorbed CO over H$_2$ preadsorbed surface at higher temperatures. However, this does not hold true at 25 °C. Bartholomew$^{26}$ found that H$_2$ adsorption over supported cobalt catalyst at room temperature requires high activation energies, which severely limit the rate of adsorption. The formation of hydrocarbonyl species in such cases is not expected because of this limitation. This, in turn, limits the role of H$_2$ to occupying the
active sites and blocking them for further adsorption. Therefore we see a remarkable difference between the results at 25 °C and that at higher temperatures for CO adsorbed on a bare surface as compared to that on H₂ preadsorbed surface.

![Figure 5.6: Proposed scheme for formation of hydrocarbonyl species over reduced metallic cobalt](image)

The adsorption of CO from a CO+H₂ mixture follows a similar trend at all higher temperatures; i.e. more CO adsorption over H₂ preadsorbed surface than bare surface. When syngas is flowed on a bare surface, only some of the active sites are modified by H₂. Out of the remaining sites, which are occupied by CO, some sites may adsorb CO dissociatively. Therefore, in such a system some of the sites behave like the H₂ preadsorbed surface and the remaining like the bare surface. This explains why the peak intensity for such case is an intermediate between that of bare surface and H₂ preadsorbed surface.

It is interesting to note that the peak intensity for CO adsorption from syngas on H₂ preadsorbed surface is smaller than that of CO on H₂ preadsorbed surface for all the cases. It may be possible that two H-atoms adsorb on the same site in the presence of syngas, which inhibit CO adsorption on those sites. Under CO flow, two H-atoms can combine to form H₂, thereby
releasing the site for CO adsorption. Bridge et al. 16 observed the similar competitive adsorption behavior and concluded that the H₂ displacement rate depends directly on the CO adsorption rate. Our experiments at high temperatures showed that chemisorbed CO peak intensity was increased when H₂ flow was stopped for the system under CO+H₂ flow.

![Chart](image)

**Figure 5.7:** A comparison of linearly adsorbed CO peak intensities at different temperatures for the case of bare and H₂ preadsorbed surfaces

Fig. 5.7 compares the peak intensities of linearly adsorbed CO (2067-2074 cm⁻¹) at different temperatures for the bare surfaces and the H₂ preadsorbed surfaces. The CO peak intensity is maximum at 270 °C for both the surfaces. This behavior is typical of an activated
chemisorption process, where increasing temperature favor CO chemisorption until a temperature where the rate of CO dissociation exceeds the rate of CO chemisorption.

The large increase in CO peak intensity from 25 °C to 230 °C suggests the generation/activation of new sites at higher temperatures. A comparison of the relative peak positions (2034 cm\(^{-1}\) at 25 °C vs. 2074 cm\(^{-1}\) at 230 °C) suggests that CO is adsorbed more strongly at 25 °C than 230 °C. However, the amount of CO adsorbed is much lower at 25 °C than at 230 °C. This indicates that the newly activated sites at higher temperatures adsorb CO slightly more weakly, perhaps due to electron withdrawal from cobalt as a result of increased population of CO on the surface, thereby shifting the peak maxima towards higher wavenumbers (blue shift). Between 230 and 300 °C, the wavenumbers do not change with temperature (see Figs. 5.3, 5.4 and 5.5). This could reflect the balance between the two competing effects: blue shift due to generation/activation of new sites and red shift due to increasing temperature, which comes about because the strongly adsorbed CO is more stable at higher temperatures.

5.4. CONCLUSION

CO adsorption over a reduced, bare surface and H\(_2\) preadsorbed surface at 25 °C showed more CO adsorption on a bare surface than H\(_2\) preadsorbed surface. On a bare surface, CO was found to be adsorbed over a wide range of wavenumbers, whereas, CO adsorption over H\(_2\) preadsorbed surface was found to be on a narrow wavenumber range at room temperature. This indicates that sites of a particularly narrow energy range adsorb CO preferentially, and H\(_2\) blocks some of the CO adsorption sites at room temperature. The results at 230, 270 and 300 °C, however, were found to be opposite, i.e., much more adsorbed CO was found over a H\(_2\) preadsorbed surface than the bare surface, suggesting that the catalyst surface is modified by H\(_2\)
at higher temperatures such as to facilitate CO adsorption. Similar behavior is observed for the case of syngas flow over bare and H\textsubscript{2} preadsorbed surfaces.

5.5. REFERENCES


6.1. INTRODUCTION

Research on alternative energy has become more important in recent times due to continued depletion of conventional energy resources and climbing crude oil prices. Oxygenated compounds, such as ethanol are promising alternative fuels because of their biodegradability and renewability.1

A viable route for the production of ethanol is the catalytic conversion of synthesis gas, which can be obtained by several means including coal gasification, natural gas, or a renewable resource like biomass.2-5 The mechanism leading to ethanol formation requires CO to adsorb on the catalyst surface both, associatively and dissociatively. The CO insertion mechanism is proposed by many researchers 4,6-8 as the key step leading to the formation of oxygenated compounds. It is proposed that the hydrocarbon chain propagation involves stepwise addition of CHx--monomeric units. Alternatively, chain growth termination by CO insertion would form acyl intermediates, which can be hydrogenated to form oxygenates.

Cobalt based catalysts have been found to be advantageous for the conversion of syngas to oxygenated compounds because of their low cost, low water-gas shift activity, and high activity for CO hydrogenation.9-11 Cobalt is a well-known Fischer-Tropsch catalyst, producing primarily long chain hydrocarbons through CO hydrogenation by C-O bond dissociation.12 On the other hand, it is generally accepted that under conditions at which cobalt forms hydrocarbons, CO adsorption on Pd is associative (linear or multi-fold bridge) rather than dissociative.13-18 For example, Poutsma et. al.17 observed the formation of methanol over supported palladium
catalysts at 260-350 °C and 150-16000 psig pressure. Addition of Pd to a silica supported cobalt catalyst has been found to promote the CO hydrogenation activity and enhance the formation of oxygenated compounds \(^{19,20}\). It would be expected for a Co-Pd system that CO adsorption takes place both associatively (on Pd) and dissociatively (on Co). Such a catalyst would therefore be more selective towards oxygenated compounds. It is critical, however, that cobalt and palladium are in close contact to facilitate the formation of C\(_2^+\) oxygenated compounds.

The focus of present study is on the activity and selectivity of silica supported Co-Pd catalysts for the conversion of syngas to oxygenates. 2 wt\% Pd catalyst with two cobalt loadings (2 wt\% and 10 wt\%) were prepared, characterized, and tested for this purpose. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) technique was used to probe the surface species and the active sites for CO hydrogenation on these catalysts.

6.2. EXPERIMENTAL

6.2.1. Catalyst Preparation

Co-Pd/SiO\(_2\) based catalysts were synthesized using a conventional incipient wetness impregnation method to produce two catalysts, both with 2 wt\% Pd but different cobalt loadings: 2 wt\% and 10 wt\% (designated as 2Co-2Pd and 10Co-2Pd respectively). The SiO\(_2\) support was obtained from Alfa Aesar (Surface Area = 300 m\(^2\)/g, Pore Volume = 1 cc/g). The precursors used for cobalt and palladium were cobalt nitrate and palladium (II) 2,4-pentanedionate [Pd(CH\(_3\)COCHCOCH\(_3\))\(_2\)] respectively. These salts were dissolved in a calculated amount of ethanol before impregnating over SiO\(_2\). The catalysts were dried overnight at 110 °C and calcined under air for 2 h at 450 °C at a temperature ramp of 1°C per minute.
6.2.2. Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES)

The bulk elemental composition was measured using a Perkin Elmer 2000 DV ICP-optical emission spectrometer. A repeat sample analysis was carried out to estimate the experimental error.

6.2.3. Temperature Programmed Reduction (TPR)

Temperature programmed reduction (TPR) profiles of the calcined catalyst were recorded using an Altamira AMI 200-R-HP unit equipped with a thermal conductivity detector (TCD). The catalyst sample was first purged in a fixed-bed micro-reactor system under flowing argon at 150 °C for 1 h to remove traces of water and then cooled to 25 °C. TPR was performed using a 10% H₂/Ar mixture at a flow rate of 50 cm³/min while the temperature was linearly ramped from 25 °C to 750 °C at 10 °C/min.

6.2.4. In-situ X-Ray Diffraction (XRD)

In-situ XRD experiments were carried out at Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL). These experiments were done with PANalytical X’Pert Pro MPD X-ray diffractometer using Cu Kα radiation (λ = 1.5406Å). The sample was mounted in an Anton Paar XRK hot stage, which can go up to 900 °C and 10 bar pressure and has the provision for gas flow. Fresh calcined catalyst was used for the in-situ XRD experiments.

The gases used for the experiments are:

1. 2% CO, 2% Ar, balance He
2. 4% H₂, balance He

The catalyst was crushed to fine powder (~200 mesh) before loading in the sample chamber. The sample chamber is provided with gas inlet and outlet lines. Scans were taken in
flowing H₂/He (50 sccm). The time taken for one scan was approximately 30 min and the angle was varied from 15 ° to 70 ° (step size = 0.0167113 °). The catalyst was held at the intended scan temperature during the 30 min scan.

Scans were taken at room temperature, 150 °C, 200 °C, 250 °C and 300 °C in flowing H₂/He. Between scans, the temperature was increased at a rate of 20 °C/min. Data analysis and peak identification were done using the software X’Pert HighScorePlus(v3.0).

6.2.5. Catalyst Activity Test

CO hydrogenation reactions at differential conversions were carried out in a ¼” glass-lined stainless steel fixed bed micro-reactor system at different temperatures (230°C, 270°C) and total pressure of 10 bar. Prior to reaction, the catalyst was reduced in-situ for 2 h at 300°C in flowing H₂/He mixture (50% H₂). CO hydrogenation reactions were carried out with a space velocity of 24,000 scc.h⁻¹.g.cat⁻¹ and an H₂:CO ratio of 2:1. For these experiments the syngas was diluted with helium to reduce heat effects within the bed and to ensure that the conversion was low enough to keep the oxygenated products in the vapor state for online GC/FID analysis. In addition, the line from the reactor exit to the sampling valve was heat traced to prevent products from condensing upstream of the GC/FID. The sampling valves are placed in an isothermal (90°C) oven. The GC/FID system (Shimadzu GC-2014) is equipped with two thermal conductivity detectors (TCD), used to analyze CO, CO₂ and H₂. Oxygenates and hydrocarbons analysis are done using a Restek™ RT-Q Bond column (25 m) connected to the flame ionization detector (FID). Helium was used as a carrier gas for FID column and CO/CO₂ TCD column, while N₂ is used for the H₂ TCD column. The FID column oven was programmed to give the
best possible separation of the products without co-elution. All selectivities are reported in terms of carbon efficiency defined as:

\[
\text{Selectivity of A (\%)} = \frac{n \times C_n^A}{\text{Total CO reacted}} \times 100
\]

Where \(n\) is the number of carbons in A and \(C_n^A\) is mol fraction of A.

The GC/FID system was calibrated with standard certified gas mixtures prior to the experiment. Different levels of concentration were used for the calibration and a curve fitting was done between the points obtained. The calibration was checked after each completed experiment to ensure the validity of the data reported.

### 6.2.6. In-situ Diffuse Reflectance FTIR Spectroscopy (DRIFTS)

FTIR spectra were collected with a Nicolet 6700 model (Thermo Scientific) spectrometer equipped with an MCT-A detector cooled by liquid nitrogen. KBr beamsplitter was used to obtain spectra in the range of 4000–650 cm\(^{-1}\). In-situ measurements were carried out in a specially designed environmental chamber (Harrick) equipped with a gas inlet, outlet, and a heating/cooling system. A sample holder was used to hold \(~20\) mg of catalyst. DRIFTS spectra were collected by using series collection for 30 min. For each spectrum 32 scans at a resolution of 4 cm\(^{-1}\) were used.

Before each experiment the catalyst was heated in helium at 150 \(^\circ\)C for 30 min to remove any moisture and gases. The catalyst was reduced by flowing a mixture of hydrogen and helium (10\% H\(_2\) in He) for 2 h at 300 \(^\circ\)C. The cell was then flushed with helium and brought to the desired reaction temperature (230 \(^\circ\)C and 270 \(^\circ\)C). Backgrounds were collected at desired temperatures after the system was allowed to equilibrate for 15 min at that temperature. Difference spectra were obtained by subtracting the background from the subsequent spectra.
Two series of experiments were performed at each temperature: CO adsorption and CO hydrogenation. Each series was set for 30 min and was divided into three parts. In the first part helium was flowed for 20 s followed by flowing CO + He for 5 min in the second part. The third part consisted of flushing with helium (for CO adsorption studies) or flowing H₂ + He (for CO hydrogenation studies) for the rest of the time. 5% CO/He was used for CO adsorption and 10% H₂/He for CO hydrogenation experiments. The experiments were carried out at 230 °C and 270 °C and performed at atmospheric pressure.

6.3. RESULTS AND DISCUSSION

6.3.1. ICP-OES

The results for ICP-OES are presented in Table 6.1. The numbers indicate metal wt%. The metal loadings are close to their intended values.

Table 6.1: ICP metal analysis results for catalysts 2Co-2Pd and 10Co-2Pd

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Co-2Pd</td>
<td>1.85 ± 0.02</td>
<td>1.72 ± 0.06</td>
</tr>
<tr>
<td>10Co-2Pd</td>
<td>8.82 ± 0.3</td>
<td>1.70 ± 0.08</td>
</tr>
</tbody>
</table>

6.3.2. Temperature Programmed Reduction

The TPR results are shown in Figure 6.1. The small peak below 100 °C can be attributed to the reduction of PdO to metallic Pd. Although, the reduction of PdO normally takes place below ambient temperature, this peak shift towards higher temperature indicates a strong interaction of PdO with cobalt and/or SiO₂. Pd-containing catalysts generally show a negative
peak around 80 °C, which is attributed to the decomposition of Pd hydride formed in the reduction of PdO under hydrogen before the start of ramp at room temperature. The absence of negative palladium hydride peak in both the catalysts suggests that palladium strongly interacts with cobalt.

Figure 6.1: Temperature programmed reduction of cobalt-based Pd promoted and unpromoted calcined catalysts under H₂ flow

The two step reduction of cobalt oxide is observed for 10Co-2Pd catalyst. The peak at 145 °C can be attributed to the reduction of Co₃O₄ to CoO and the peak at 310 °C is due to CoO
reduction to metallic cobalt $^{11,22,24}$. The area of peak at 310 °C was found to be approximately 4 times that of the peak at 145 °C. This does not agree with the stoichiometry of reduction of these species, suggesting that some Co$_3$O$_4$ may not have reduced under the 145 °C peak, and some contribution to the peak at 310 °C could be due to reduction of Co$_3$O$_4$ phase. It is possible that some Co$_3$O$_4$ may interact with the support, thereby decreasing its reducibility.

In order to confirm this, we conducted TPR experiments on a 10 wt% Co/SiO$_2$ catalyst (represented as 10Co) using the same support and prepared by the same method. The two peaks around 290 °C and 320 °C correspond to the two step reduction of Co$_3$O$_4 \rightarrow$CoO $\rightarrow$Co. The calculated area ratio of these peaks was 1:3, which corresponds to the stoichiometry of reduction of these species. The 145 °C peak is not found for this catalyst, indicating that Pd promotion increases the reducibility of the 10Co-2Pd catalyst. The TPR indicates that 10Co-2Pd catalyst behaves partly like promoted catalyst and partly like unpromoted catalyst, suggesting that some cobalt clusters are in contact with Pd, and some are not.

For 2Co-2Pd catalyst, the PdO reduction below 100 °C is similar to that of 10Co-2Pd catalyst. However, two broad peaks centered around 175 °C and 260 °C are found for the reduction of cobalt. The area ratio of these peaks is approximately 1:1, which does not correspond to the stoichiometry of two step reduction of cobalt oxide. It can therefore be concluded that there is a relatively intimate contact between cobalt and palladium in this catalyst, resulting in increased reducibility of cobalt.

6.3.3. **In-situ X-Ray Diffraction (XRD)**

The results of in-situ XRD for 2Co-2Pd and 10 Co-2Pd catalysts are presented in figures 6.2 and 6.3 respectively. These experiments were conducted under flowing H$_2$/He at selected temperatures.
For the case of 2Co-2Pd catalyst (Fig. 6.2), the cobalt oxide phase is not observed, indicating that it is well dispersed. Typically, cobalt oxide usually becomes more difficult to reduce as dispersion increases.\textsuperscript{9,25} In spite of that, the increased reducibility of this catalyst compared to 10Co-2Pd catalyst (see Fig. 6.1) shows the promoting effects of Pd in close contact with cobalt oxide. The PdO phase, found at 30 °C, converts to metallic Pd at 150 °C. This is consistent with the TPR, where the reduction of PdO takes place below 100 °C.

For the case of 10Co-2Pd catalyst (Fig. 6.3), both Co$_3$O$_4$ and PdO phases are observed at 30 °C. The crystalline PdO converts to metallic Pd by 150 °C, consistent with the TPR results. Also,
CoO phase appears at 150 °C and its peak intensity increases with increasing temperature before CoO starts to convert to metallic cobalt. The presence of both, CoO and Co$_3$O$_4$ phases at 150 °C indicates that the Co$_3$O$_4$ → CoO reduction is not complete at 150 °C. This is consistent with the argument given in the TPR discussion about the limited effect of palladium promotion for this catalyst. The CoO phase is found to increase with a corresponding decrease in Co$_3$O$_4$ phase as temperature is increased to 200 °C and 250 °C. Finally, the catalyst reduces completely at 300 °C, where the metallic cobalt and Pd phases are observed.

Figure 6.3: In situ XRD results for 10Co-2Pd catalyst at different temperatures under H$_2$/He flow and atmospheric pressure
6.3.4. Catalyst Activity Test

Both the catalysts were tested for their activity and selectivity for CO hydrogenation under similar conditions. The results are presented in Table 6.2.

Table 6.2: Selectivities of products of CO hydrogenation reaction at different temperatures for 2Co-2Pd and 10Co-2Pd †. The balance selectivity for all cases is due to CO₂

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp (°C)</th>
<th>EtOH %</th>
<th>MeOH %</th>
<th>CH₄ %</th>
<th>C₂+ Oxy %*</th>
<th>C₂₄ HC %#</th>
<th>CO Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Co-2Pd</td>
<td>230</td>
<td>6.6</td>
<td>14.9</td>
<td>11.7</td>
<td>5.3</td>
<td>55.1</td>
<td>0.05</td>
</tr>
<tr>
<td>10Co-2Pd</td>
<td>230</td>
<td>3.7</td>
<td>2.7</td>
<td>43.6</td>
<td>4.5</td>
<td>41.8</td>
<td>1.0</td>
</tr>
<tr>
<td>2Co-2Pd</td>
<td>270</td>
<td>5.6</td>
<td>18.8</td>
<td>41.1</td>
<td>3.1</td>
<td>25.8</td>
<td>0.18</td>
</tr>
<tr>
<td>10Co-2Pd</td>
<td>270</td>
<td>2.5</td>
<td>1.2</td>
<td>48.0</td>
<td>1.7</td>
<td>40.2</td>
<td>8.2</td>
</tr>
<tr>
<td>2Co-2Pd</td>
<td>270⁵</td>
<td>7.3</td>
<td>16.7</td>
<td>8.9</td>
<td>4.6</td>
<td>47.6</td>
<td>0.05</td>
</tr>
<tr>
<td>10Co-2Pd</td>
<td>270⁵</td>
<td>2.1</td>
<td>2.2</td>
<td>47.6</td>
<td>6.6</td>
<td>36.8</td>
<td>0.41</td>
</tr>
</tbody>
</table>

† Pressure = 10 bar, 2H₂/CO, Catalyst wt. = 150 mg, Space Velocity = 24,000 scc.h⁻¹g.cat.⁻¹
* includes higher oxygenates other than methanol and ethanol
# includes higher hydrocarbons other than methane
⁵ repeated experiment at 230 °C on the same catalyst after higher temperature experiments
† Errors in the reported values are ± 5.5% within 95% confidence interval

The results show that:

1. 10Co-2Pd catalyst is more active than 2Co-2Pd catalyst at all temperatures studied.
2. 10Co-2Pd catalyst is more selective towards total hydrocarbons as compared to 2Co-2Pd catalyst, which is more selective towards oxygenated compounds. The methanol selectivity, in particular, is much higher on 2Co-2Pd than on 10Co-2Pd catalyst.
3. The CO conversion for $^{10}\text{Co-2Pd}$ decreases (1.0% to 0.41%) when temperature is brought back to 230 °C, while for $^{2}\text{Co-2Pd}$ catalyst the corresponding CO conversion is unchanged (0.05%). The apparent deactivation of $^{10}\text{Co-2Pd}$ catalyst may be attributed to the oxidation of surface cobalt that is not in contact with Pd under reaction conditions. This isolated surface cobalt can deactivate by oxidation during the reaction in the absence of spillover of H$_2$ from neighboring Pd to cobalt, even though the oxidation of bulk metallic cobalt to either CoO or Co$_3$O$_4$ is not thermodynamically favored under these conditions $^{25-27}$. This oxidation can be attributed to be due to the formation of metal-oxygen bonds as a result of CO hydrogenation reactions at these conditions $^{26,27}$. These metal-oxygen bonds are stronger than those in bulk cobalt, making the oxidation of surface cobalt possible. Another argument is that the thermodynamics can be influenced by metal-support interaction, which in turn can result in oxidation of small metal clusters under conditions where bulk metal oxidation is not possible $^{27}$.

The fact that $^{2}\text{Co-2Pd}$ catalyst does not show any deactivation when the temperature is brought back to 230 °C could indicate a close contact between cobalt and Pd in this catalyst, so that the cobalt remains in the reduced state during the reaction by H$_2$ spillover from the neighboring Pd. This conclusion is consistent with the TPR and in situ XRD results and discussion.

Figure 6.4 (a) and (b) shows CO conversion as a function of time at different temperatures for $^{10}\text{Co-2Pd}$ and $^{2}\text{Co-2Pd}$ catalysts, respectively. The initial decrease in activity for $^{2}\text{Co-2Pd}$ catalyst at 230 °C (Fig. 6.4 (b)) shows that the catalyst takes some time to reach steady state activity, which is unchanged after the 270 °C experiment. For $^{10}\text{Co-2Pd}$ catalyst at 270 °C,
Figure 6.4: CO conversion at different temperatures as a function of time for (a) 10Co-2Pd and, (b) 2Co-2Pd catalysts. The order of temperature is 230 °C → 270 °C → 230 °C repeat.
the activity drops significantly and continuously with time, as seen in Fig. 6.4 (a), but the product selectivities remain constant (not shown). It can be argued that the apparent deactivation of 10Co-2Pd catalyst is due to high CO conversion compared to that of 2Co-2Pd catalyst, thereby leading to more carbon deposition on the active sites of the catalyst.

The 2Co-2Pd catalyst shows constant activity at each temperature without much deactivation. This also supports the arguments given above that there is close contact between cobalt and Pd in this catalyst.

6.3.5. In-situ Diffuse Reflectance FTIR Spectroscopy (DRIFTS)

In order to understand the activity/selectivity behavior of these catalysts, in-situ DRIFTS experiments were carried out at conditions similar to those of the CO hydrogenation reaction. Figure 6.5 presents the results of CO desorption at 230 °C under helium flow for 10Co-2Pd catalyst. The catalyst surface was preadsorbed with CO at 230 °C before the helium flow (see experimental protocol).

The doublets between 2300-2400 cm\(^{-1}\) and 2100-2200 cm\(^{-1}\) are due to gaseous CO\(_2\) and gaseous CO respectively, which disappear with helium flow. The linearly adsorbed CO peak can be seen in the range 2049-2061 cm\(^{-1}\). However, it cannot be concluded that CO is adsorbed solely on cobalt or Pd, because linear CO adsorption takes place on both the metals in this wavenumber range \(28^- {33}\).

The peak at around 2005 cm\(^{-1}\) can be attributed to compressed two fold bridging sites, and the peak in the wavenumber range of 1994-1909 cm\(^{-1}\) can be due to isolated two-fold bridging on Pd \(29,34^- {38}\). Finally, the peak at 1822 cm\(^{-1}\) is due to three-fold bridging on hollow Pd sites \(37,39,40\).
It can be seen that the peak intensity for all these adsorption sites decreases with time under helium flow.

![CO desorption graph](10Co-2Pd)

Figure 6.5: CO desorption at 230 °C as a result of helium flow over 10Co-2Pd catalyst. The surface was preadsorbed with CO before starting helium flow.

The result of CO hydrogenation at 230 °C for 10Co-2Pd catalyst is presented in Figure 6.6. The catalyst surface was preadsorbed with CO before starting H₂ flow. The peak intensity for bridging carbonyl (peak at 1984 cm⁻¹) increases initially before undergoing hydrogenation. Also, the linearly adsorbed CO (peak at 2053 cm⁻¹) disappears rapidly. It may be possible that some of the linearly adsorbed CO transforms to the bridged sites under H₂ flow, thereby increasing the intensity of bridge-type adsorbed CO at 1984 cm⁻¹. This transformation may occur as hydrogen adsorbs on sites already occupied by linear CO; the CO is then partially displaced and must
bridge to a neighboring metal atom \(^{31}\). The rapid decrease in the linearly adsorbed CO population indicates that this CO undergoes hydrogenation preferentially as compared to the bridge-type adsorbed CO.

Figure 6.6: CO hydrogenation at 230 °C as a result of hydrogen flow over 10Co-2Pd catalyst. The surface was preadsorbed with CO before starting hydrogen flow.

On comparing CO desorption (Fig. 6.5) and CO hydrogenation (Fig. 6.6), we see that the decrease in the peak intensity for linearly adsorbed CO (peak at 2053 cm\(^{-1}\)) is much faster in the case of CO hydrogenation. This can be attributed to two processes: (a) some linearly adsorbed CO transforms to bridge-type adsorbed CO and, (b) CO hydrogenation takes place mainly on the sites that adsorb CO linearly, thereby decreasing its peak intensity under hydrogen flow. While the evidence of process (a) is clearly seen because the bridged CO peak intensity is increased, the
much faster disappearance of linearly adsorbed CO peak (compare the decrease in 2053 cm\(^{-1}\) peak at \(t=0\) and \(t=1.4\) min vs. increase in 1984 cm\(^{-1}\) peak in Fig. 6.6) indicates that the linear sites are the most active sites for CO hydrogenation on 10Co-2Pd catalyst. Also, on comparing the 1960-1930 cm\(^{-1}\) peak intensities between \(t=5.7\) min and \(t=8\) min in Fig. 6.6, we see a relatively smaller decrease, clearly indicating that CO hydrogenation on bridged sites is much slower. Therefore, it is evident from Fig. 6.6 that the bridge-type adsorbed CO does not undergo hydrogenation and is more stable than the linearly adsorbed CO.

The results for CO desorption under helium and CO hydrogenation under H\(_2\) at 270 °C are similar to that at 230 °C, and therefore not produced here. Therefore, it can be concluded that at these temperatures linearly adsorbed CO sites are the main active site for 10Co-2Pd catalyst.

The results for CO desorption and CO hydrogenation at 230 °C for 2Co-2Pd catalyst are presented in Figures 6.7 and 6.8 respectively. For the case of CO desorption under helium flow (Fig. 6.7), we see that both linearly and bridge-type adsorbed CO peak intensities decrease with time. However, for the case of CO hydrogenation (Fig. 6.8), the bridge-type CO peak intensity initially increases and then the bridged species undergo hydrogenation. The site transformation from linear to bridge-type is seen here again (note the decrease in 2057 cm\(^{-1}\) peak intensity and corresponding increase in 1962 cm\(^{-1}\) peak intensity for \(t=0\) and \(t=1.2\) min in Fig. 6.8). However, we do not see a rapid decrease in the linearly adsorbed CO for this case, as we saw for 10Co-2Pd catalyst, suggesting that CO hydrogenation takes place on both linear and bridged sites simultaneously. But, the fact that the increase in bridged peak intensity between \(t=0\) and \(t=1.2\) in Fig. 6.8 is much more as compared to that between \(t=0\) and \(t=1.4\) in Fig. 6.6 indicates that the linearly adsorbed CO mainly transforms to bridged CO, which then undergoes hydrogenation. Therefore, it can be concluded that the active sites for 2Co-2Pd catalyst are bridge-type CO. The
linearly adsorbed CO only seems to migrate to bridged sites (although, some hydrogenation activity from the linearly adsorbed sites cannot be ruled out). The much larger increase in the peak area for bridged sites as compared to that of 10Co-2Pd catalyst supports this argument.

Figure 6.7: CO desorption at 230 °C as a result of helium flow over 2Co-2Pd catalyst. The surface was preadsorbed with CO before starting helium flow.

The results for CO desorption under helium and CO hydrogenation under H₂ at 270 °C are similar to that at 230 °C, and therefore not produced here. Therefore, it can be concluded that at these temperatures bridge-type adsorbed CO sites are the main active site for 2Co-2Pd catalyst.

There is a disagreement in the literature about the product formation and activities from hydrogenation of linear versus bridged CO. Morales et al. ⁴¹ proposed that in the presence of hydrogen, the bridged bonded CO species hydrogenate to hydrocarbons, because the bridge-
bonded CO molecule has a weaker C-O bond and thus can be more easily hydrogenated. Many other researchers \textsuperscript{11,42,43} have concluded that the linearly adsorbed CO are the active sites for the formation of oxygenated compounds, while the bridge-type adsorbed CO leads towards formation of hydrocarbon compounds. The activity of the bridge-type CO is also found to be greater than linearly adsorbed CO by these researchers. Zhang et. al. \textsuperscript{44} observed that the increase of bridged CO bands favored hydrocarbons formation and resulted in high overall CO hydrogenation activities. However, Song et. al. \textsuperscript{45} found similar activities for both, bridge-type CO and linearly adsorbed CO.

![Figure 6.8: CO hydrogenation at 230 °C as a result of hydrogen flow over 2Co-2Pd catalyst. The surface was preadsorbed with CO before starting hydrogen flow.](image)

Other researchers have expressed different opinions about the activities of linear and bridge-type adsorbed CO. On a bimetallic Cu-Co catalyst, Cao et. al. \textsuperscript{46} observed only linear
sites, and the bridging sites were absent. The fact that their catalyst was active towards both hydrocarbons and oxygenates led them to conclude that the ability to adsorb CO into a bridging configuration is not a prerequisite for the reactions leading to these products. It is proposed by Hindermann et. al. 47 that the first step to alcohols formation requires CO to be adsorbed in a linear or bridge form over a Cu-Co/SiO₂ catalyst, indicating that both the forms of adsorption can lead towards alcohol formation. Krishnamurthy and Chuang 48 found linear CO to be more active than the bridged CO in the formation of methane over Rh/SiO₂ catalyst. Matsuzaki et. al. concluded that the formation of oxygenated compounds is favored as the ratio of bridged to linear CO species increases 12. Arakawa et. al. 49 showed that linear CO species were responsible for high CO conversion and high selectivity towards hydrocarbons over a Co/SiO₂ catalyst prepared by using cobalt nitrate precursor. On increasing the Sr content for Re-Sr/Co(Ac)/SiO₂ catalyst, hydrocarbon formation decreased and selectivity of oxygenated compounds increased, while the CO conversion was decreased. The FT-IR results showed that with increasing Sr content, the linearly adsorbed CO decreased and bridged CO increased. Therefore they concluded that the bridged CO is responsible for the formation of oxygenated compounds.

Our activity results (Table-6.2) show that 10Co-2Pd catalyst is more selective towards hydrocarbons and 2Co-2Pd catalyst is towards oxygenated compounds. The reason for this seems to be that there are different active sites for these catalysts. The linearly adsorbed CO sites are the main active sites for CO hydrogenation for the case of 10Co-2Pd catalyst, and we believe that these sites undergo hydrogenation that leads mainly to hydrocarbon compounds. However, the bridged sites are the main active site for 2Co-2Pd catalyst, indicating that they are likelier to undergo hydrogenation to form oxygenated compounds. This raises the question: why are linear sites more active on one catalyst and bridging sites on the other? A possible answer is that the
active linear sites on 10Co-2Pd catalyst consist mainly of Co sites. These highly active sites are fewer in number on 2Co-2Pd catalyst, such that the reactivity of bridge-type CO increases in a relative sense.

It is apparent that the total amount of adsorbed CO on the 10Co-2Pd catalyst, which is equivalent to the integrated area under the absorbance curve (Fig. 6.6), is higher than that of 2Co-2Pd catalyst (Fig. 6.8). The higher activity of 10Co-2Pd catalyst can also be explained by the higher peak intensity of the active site (linearly adsorbed CO) in Fig. 6.6 as compared to that of the active site (bridged CO) for 2Co-2Pd catalyst (Fig. 6.8). The results also show that CO hydrogenation on 10Co-2Pd catalyst is much faster than on 2Co-2Pd. For example, after 25 min of hydrogen flow, the entire CO adsorbed on the catalyst surface is hydrogenated for 10Co-2Pd catalyst (Fig. 6.6), while for the case of 2Co-2Pd catalyst (Fig. 6.8), we still see a substantial population of linearly and bridge-type adsorbed CO on the surface. Earlier work on a 4.9% Pd/SiO$_2$ catalyst by Rabo et. al. $^{50}$ indicated that CO adsorption on palladium is nondissociative and the chemisorbed CO is less reactive to H$_2$ as compared to the metal-C species formed on cobalt, which is consistent with our results. Similar results were obtained at 270 °C for both the catalysts, except that the peak intensities decreased faster than that at 230 °C, indicating a higher activity at higher temperature, which is consistent with the activity results. This explains the higher activity of 10Co-2Pd catalyst as compared to 2Co-2Pd catalyst.

6.4. CONCLUSION

Silica supported Co-Pd catalysts prepared using different cobalt loadings show different characteristics. While TPR results show an intimate contact between cobalt and palladium for the catalyst with lower cobalt loading (2Co-2Pd), the same was not true for the higher cobalt loading
catalyst (10Co-2Pd). In situ XRD results confirmed the presence of highly dispersed cobalt for 2Co-2Pd catalyst. The addition of palladium increased the reducibility of cobalt for both the catalysts. Activity/selectivity studies on these catalysts showed contrasting behavior: 10Co-2Pd catalyst was more active but less selective towards oxygenated compounds, while 2Co-2Pd catalyst was less active and more selective towards these compounds. The hydrocarbon formation for 10Co-2Pd catalyst was significantly higher than 2Co-2Pd catalyst. 10Co-2Pd catalyst deactivated, while the 2Co-2Pd catalyst did not, probably due to close contact between cobalt and palladium in the 2Co-2Pd catalyst. The active sites for CO hydrogenation for 10Co-2Pd catalyst were those which adsorb CO linearly, while for the 2Co-2Pd catalyst the bridged sites were the main active sites leading towards the formation of oxygenated compounds.

6.5. REFERENCES


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7.1. CONCLUSIONS

Cobalt-based catalysts promoted with rhenium or palladium have been found to be active for CO hydrogenation. The product distribution is a strong function of cobalt precursor, cobalt dispersion and the proximity between cobalt and the promoting metal (Re or Pd).

Cobalt precursors have been found to affect the behavior, physical properties, activity, and selectivity of the catalyst significantly. Rhenium promoted cobalt prepared using cobalt nitrate [CoRe(N)] showed some crystallinity in the XRD patterns, while a nominally identical catalyst prepared from cobalt acetate [CoRe(A)] did not, suggesting that the CoRe(A) catalyst is highly dispersed with cobalt cluster size of less than 2 nm. CO hydrogenation results on these catalysts showed that while the rate of CO reaction for the CoRe(N) catalyst was greater than that of the CoRe(A) catalyst, the selectivities towards ethanol and oxygenates were far higher for the CoRe(A) catalyst. This could be attributed due to smaller cluster size of cobalt for CoRe(A) catalyst. In situ DRIFTS studies showed considerably different metal carbonyl coordination sites for these catalysts. Carbonyl bands around 1950 cm\(^{-1}\), which could be assigned to either bridged CO on cobalt or terminal CO on Re, were found for CoRe(N) catalysts, while few such sites were found for CoRe(A) catalyst. The linearly adsorbed CO on cobalt sites for CoRe(N) catalyst was found at lower wavenumbers compared to that of CoRe(A) catalyst, suggesting that CoRe(N) catalyst adsorbs CO relatively stronger than CoRe(A). This could explain why CoRe(N) catalyst is more selective towards hydrocarbons and CoRe(A) catalyst towards oxygenates.
TPR and in situ XRD results for CoRe(N) catalyst showed two step reduction with CoO as an intermediate \(^2\). The reduced cobalt was found to consist of both hcp and fcc phases. The Co-hcp phase, however, was more abundant, which is thought to be the more active phase as compared to the Co-fcc phase. The effect of rhenium on the oxidation of the catalyst under reaction conditions was studied and it was found that reduced rhenium facilitated the reduction of cobalt and helped keep cobalt in the reduced state.

CO adsorption studies on CoRe(N) catalyst over a reduced, bare surface and H\(_2\) preadsorbed surface at room temperature showed more CO adsorption on a bare surface than H\(_2\) preadsorbed surface. On a bare surface, CO was found to be adsorbed over a wide range of wavenumbers, whereas, over the H\(_2\) preadsorbed surface CO adsorption was found to be in a narrow wavenumber range at room temperature. This suggests that sites of a particularly narrow energy range adsorb CO preferentially, and H\(_2\) blocks some of the CO adsorption sites at room temperature. However, the results at 230, 270 and 300 °C were found to be opposite, i.e., much more adsorbed CO was found over a H\(_2\) preadsorbed surface than the bare surface, suggesting that the catalyst surface is modified by H\(_2\) at higher temperatures such as to facilitate CO adsorption. Similar behavior was observed for the case of syngas flow over bare and H\(_2\) preadsorbed surfaces.

The TPR results for palladium promoted cobalt catalyst showed an intimate contact between cobalt and palladium for the case of catalyst with lower cobalt loading (2Co-2Pd), while the same was not true for the higher cobalt loading catalyst (10Co-2Pd). The presence of highly dispersed cobalt for 2Co-2Pd catalyst was confirmed by in situ XRD results. The addition of palladium increased the reducibility of cobalt for both the catalysts. CO hydrogenation activity/selectivity studies on these catalysts showed contrasting behavior: 10Co-2Pd catalyst
was more active but less selective towards oxygenated compounds, while 2Co-2Pd catalyst was less active and more selective towards these compounds. The formation of hydrocarbon for 10Co-2Pd catalyst was significantly higher than 2Co-2Pd catalyst. The 10Co-2Pd catalyst deactivated, while the 2Co-2Pd catalyst did not, probably due to close contact between cobalt and palladium in the 2Co-2Pd catalyst, which helps keep cobalt in the reduced state. The active sites for CO hydrogenation for 10Co-2Pd catalyst were those on which CO is linearly adsorbed, while for the 2Co-2Pd catalyst the bridged sites were the main active sites leading towards the formation of oxygenated compounds.

7.2. RECOMMENDATIONS FOR FUTURE WORK

Based on the experiments done in this work and the results presented, the following are the recommendations for future work:

- High pressure in situ DRIFTS: The DRIFTS studies on these catalysts at high pressure and high temperature, that is similar to the reaction conditions, can give us more insight about the CO adsorption behavior and surface species responsible for oxygenates formation. Experiments at different pressures would be helpful to study the effect of pressure on the CO adsorption behavior for these catalysts.

- Labeled carbon isotope (C\textsuperscript{13}) experiments: The DRIFTS is sensitive to differentiate labeled carbon isotope C\textsuperscript{13} with C\textsuperscript{12}. This technique can be used for a mixture of labeled C\textsuperscript{13}O and non-labeled CO\textsubscript{2} to find out the source of carbon in various surface species. It would be helpful to understand, for example, whether both the carbons in ethanol come from CO, CO\textsubscript{2}, or one carbon from each.
• Synthesis and characterization of cobalt carbonyl precursor catalyst: Cobalt carbonyl precursor catalyst has been found to be active and selective for the conversion of syngas to oxygenates without any noble metal promotion \(^3\)\(^4\). An understanding of CO adsorption behavior on this catalyst using in situ DRIFTS to find out the surface species responsible for leading towards oxygenates will be useful. A comparison of these surface species with the ones that are observed in this study would be helpful to understand the mechanism of oxygenates formation on these cobalt-based catalyst.

• Study on syngas with impurities: The syngas coming out of gasifier or reformer typically contains CO\(_2\) and H\(_2\)O among other impurities \(^5\)\(^6\). It is important to study the effects of these feed impurities on the activity and selectivity of catalyst in order to have a more realistic view.

• Parametric study on activity/selectivity: The study of effects of pressure, temperature, syngas ratio, and space velocity on these catalysts is important in order to optimize the conditions for ethanol synthesis.

7.3. REFERENCES


APPENDIX A: GC/FID INSTRUMENT CONTROL PARAMETERS

This appendix contains the details about parameters used in GC/FID system (Shimadzu 2014).

Temperature: 200 °C
Injection Mode: Split
Sampling Time: 1 min
Carrier Gas: Helium
Flow Control Mode: Linear velocity
Pressure: 6.1 psi
Total flow: 49.7 mL/min
Column Flow: 8.11 mL/min
Linear Velocity: 61.7 cm/s
Purge Flow: 1.0 mL/min
Split ratio: 5.0

**Column Information**
Make: Restek®, RT-Q Bond
Length: 25 m
Film Thickness: 20 µm
Inner diameter: 0.53 mm
Temperature: 40 °C
Equilibration Time: 1 min
Column maximum temperature: 280 °C

<table>
<thead>
<tr>
<th>Ramp Rate (°C/min)</th>
<th>Temperature (°C)</th>
<th>Hold time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>40</td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>150</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>175</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>250</td>
<td>5</td>
</tr>
</tbody>
</table>

**Figure A1: Column oven temperature program**
Total program time: 29.88 min
<table>
<thead>
<tr>
<th><strong>LTCD</strong></th>
<th><strong>RTCD</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature: 250 °C</td>
<td>Temperature: 250 °C</td>
</tr>
<tr>
<td>Sampling rate: 240 ms</td>
<td>Sampling rate: 240 ms</td>
</tr>
<tr>
<td>Stop time: 29.88 min</td>
<td>Stop time: 29.88 min</td>
</tr>
<tr>
<td>Delay time: 0 min</td>
<td>Delay time: 0 min</td>
</tr>
<tr>
<td>Subtract detector: None</td>
<td>Subtract detector: None</td>
</tr>
<tr>
<td>Current: 100 mA</td>
<td>Current: 40 mA</td>
</tr>
<tr>
<td>Polarity: +(L-R)</td>
<td>Polarity: +(L-R)</td>
</tr>
<tr>
<td>Temperature (pre): 250 °C</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>FID</strong></th>
<th><strong>Additional Heater</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature: 250 °C</td>
<td>VHBOT: 90 °C</td>
</tr>
<tr>
<td>Sampling rate: 40 ms</td>
<td>VHTOP: 90 °C</td>
</tr>
<tr>
<td>Stop time: 29.88 min</td>
<td></td>
</tr>
<tr>
<td>Delay time: 0 min</td>
<td></td>
</tr>
<tr>
<td>Subtract detector: None</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Additional Flow</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>APC1 pressure: 76.5 psi</td>
</tr>
<tr>
<td>APC2 pressure: 55 psi</td>
</tr>
<tr>
<td>APC3 pressure: 44.5 psi</td>
</tr>
</tbody>
</table>
Figure A2: Schematic of valves and columns installed in the GC/FID system
APPENDIX B: ERROR ANALYSIS

Errors in the activity/selectivity data were analyzed based on repeat sampling at steady state. The error analysis was done as follows:

Calculation of average:

\[ x = \frac{x_1 + x_2 + x_3 + x_4 + \cdots}{n} \]

where \( n \) is number of data points.

Calculation of Standard Deviation:

\[ S = \frac{\sqrt{(x_1 - x)^2 + (x_2 - x)^2 + (x_3 - x)^2 + \cdots}}{n - 1} \]

95% confidence interval = [(\( x + 1.96 \times S \)), (\( x - 1.96 \times S \))]

Relative standard deviation (RSD) =

\[ \frac{S}{x} \times 100 \]
APPENDIX C: PERMISSION TO USE COPYRIGHT MATERIALS

C.1. Permission Letter for Chapter 3

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**Title:** In Situ FT-IR Study on the Effect of Cobalt Precursors on CO Adsorption Behavior

**Author:** Nitin Kumar et al.

**Publication:** The Journal of Physical Chemistry C

**Publisher:** American Chemical Society

**Date:** Feb 1, 2011

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C.2. Permission Letter for Chapter 4

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date Thu, Sep 29, 2011 at 3:19 AM
subject RE: Permission Request Form: Nitin Kumar

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In Situ FT-IR Study on the Effect of Cobalt Precursors on CO Adsorption Behavior

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Received: May 27, 2010; Revised Manuscript Received: August 6, 2010

Cobalt-rhenium based catalysts were prepared by coimpregnation from two different cobalt precursors: cobalt nitrate [CoRe(N)] and cobalt acetate [CoRe(A)]. They were characterized by H$_2$-TPR, ICP, XRD, DRIFTS, and activity/selectivity in CO hydrogenation. The results showed that precursors have a significant effect on the cluster size, dispersion, and CO adsorption/CO hydrogenation activities. XRD showed no bulk crystallinity for the CoRe(A) catalyst, whereas peaks corresponding to a CoO$_2$ phase were found for the CoRe(N) catalyst. TPR results suggested greater cobalt-rhenium contact for the CoRe(A) catalyst, with Re facilitating reduction of cobalt oxide by hydrogen spillover. Activity/selectivity studies showed that the CoRe(N) catalyst is more active for CO hydrogenation with high selectivity toward hydrocarbons, while the CoRe(A) catalyst has far higher selectivity to oxygenates (but considerably lower overall activity). DRIFTS studies at 25 °C show that CoRe(N) reacting with CoRe(A) showed lower frequency carbonyl bands (2057 and 1942 cm$^{-1}$), whereas CoRe(A) had CO bands at much higher frequencies (2183–2175, 2125, and 2074 cm$^{-1}$). The carbonyl bands in the 2183–2175 cm$^{-1}$ region are assigned to Co(II)/Co(III)–CO from the presence of nonreduced CO on the surface of the CoRe(A) catalyst. DRIFTS studies under CO hydrogenation conditions are also presented. Lower wavenumber IR bands seen between 1990 and 1920 cm$^{-1}$ for CoRe(N) are tentatively assigned to bridging COs on the cobalt and terminal carbonyls on Re(0) clusters. Only higher frequency COs are observed for CoRe(A) corresponding to less electron-rich cobalt centers, linear CO coordination, and oxygenate production. The presence of nanoparticle catalysts and highly dispersed Re on the CoRe(A) catalyst is proposed to be key factors in the high oxygenate selectivity. CO is weakly adsorbed on these sites facilitating the M–CO bond dissociation and increasing the CO insertion probability leading to the oxygenate formation.

Introduction

The increasing demand for clean fuel has led to increased research interest in the production of liquid fuels from sources other than petroleum. The conversion of coal- or biomass-derived syngas to ethanol is a promising alternative. Cobalt-based catalysts have been found to be advantageous for the conversion of syngas to liquid fuels because of their low costs, low water–gas shift activity, and high activity for CO hydrogenation. Carbon monoxide adsorption and hydrogenation on supported cobalt catalysts have been studied extensively, e.g., where Co is used as probe to identify the nature of adsorption sites. An understanding of this adsorption/hydrogenation process at the molecular level is important in order to understand the syngas reactions on various supported metal catalysts. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) can be used to probe the active sites, adsorbed species, and intermediates on the catalyst surface. Song et al. used this technique to study CO adsorbed on Co/SiO$_2$ catalysts with different pore sizes and found different CO adsorption sites which changed with changing pore sizes. They also observed that the intensities of linear and bridge-type CO adsorption changed significantly with pore size. Hagi et al. used IR to study CO adsorbed on Co/SiO$_2$ at different temperatures and correlated the observed shift in spectra to the change in bond strength of C–O adsorbed on the surface, which is influenced by the C-metal bond strength. They also attributed methylene formation to linearly adsorbed CO.

Addition of Re to Co/SiO$_2$ catalysts has been found to improve selectivity toward oxygenates, especially ethanol. Re has been found to promote activation of the cobalt site in the catalyst via reduction of oxidized cobalt species to the metallic state and keeping the cobalt highly dispersed. Small amounts of Re have been found to significantly increase the amount of adsorbed CO on cobalt and thus CO hydrogenation rate.

Zirconia has been proposed as an important promoter for Co/SiO$_2$ catalysts. Addition of ZrO$_2$ promoter can modify and improve the catalyst texture and porosity, assist in the reduction of oxidized Co species to metallic cobalt, increase the dispersion of cobalt, and improve the chemical stability of the support. Pretreated zirconia is believed to form a protective layer to prevent the reaction between silica and cobalt to form inert cobalt silicates.

Cobalt precursors have a significant effect on the activity of catalysts and product distribution, and their role has been investigated by several researchers. One study showed a higher total catalytic activity when using a cobalt nitrate precursor relative to a cobalt acetate precursor. It is important to understand the surface phenomenon in order to explain this precursor effect.

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Combined in situ XRD and in situ XANES studies on the reduction behavior of a rhenium promoted cobalt catalyst

Nitin Kumar, E. A. Payzant, K. Jothimurugesan and J. J. Spivey

Received 22nd March 2011, Accepted 17th June 2011 DOI: 10.1039/clsp0856

A 10% Co-4% Re(2% Zr:SbO₃) catalyst was prepared by co-impregnation using a silica support modified by 2% Zr. The catalyst was characterized by temperature programmed reduction (TPR), in situ XRD and in situ XANES analysis where it was simultaneously exposed to H₂ using a temperature programmed ramp. The results showed the two step reduction of large crystalline Co₃O₄ with CoO as an intermediate. TPR results showed that the reduction of highly dispersed Co₃O₄ was facilitated by reduced rhenium by a H₂-spillover mechanism. In situ XRD results showed the presence of both, Co-hcp and Co-fcc phases in the reduced catalyst at 400 °C. However, the Co-hcp phase was more abundant, which is thought to be due to the lower activity phase as compared to the Co-fcc phase for CO hydrogenation. CO hydrogenation at 270 °C and 5 bar pressure produces no detectable change in the phases during the time of experiment. In situ XANES results showed a decrease in the metallic cobalt in the presence of H₂CO, which can be attributed due to oxidation of the catalyst by reaction under these conditions.

Introduction

In crude oil prices, depletion of fossil fuel resources, and increasing demand for clean fuel have led to increased interest in alternative energy resources; particularly the production of liquid fuels from sources other than petroleum. The conversion of coal or biomass-derived syngas to ethanol is a promising alternative. Ethanol offers many advantages, including its use in present internal combustion engines and fuel infrastructure with minor changes.

Catalyst-based catalysts have been found to be advantageous for the conversion of syngas to liquid fuels because of their low costs, low water-gas shift activity and high activity for CO hydrogenation. The catalytic activity, however, depends on various factors, including the method of preparation, type of support, and promoters. The oxidized form of the catalyst is not active for CO hydrogenation, and therefore it is important to reduce the catalyst before the reaction and maintain the catalyst in a reduced state during the reaction. The activity of cobalt catalysts depends mainly on the number of active metal sites which are formed by reduction.

It is well known that cobalt is easier to reduce when supported on Sb₂O₃ than supported on Al₂O₃. However, in most cases, cobalt is present as large crystalline Co₃O₄, which do not favor oxygenates production. Cobalt must be in a highly dispersed form in order to facilitate oxygenates production. To synthesize catalysts with highly dispersed cobalt, the initial Co₃O₄ phase should also be highly dispersed on the support, which requires strong interaction between the support and the cobalt precursor. However, these strong interactions result in cobalt species that are difficult to reduce. If a higher reduction temperature is applied to the catalyst, it may result in sintering of the highly dispersed crystallites, which in turn can adversely affect the dispersion and activity of the catalyst. To address this problem, generally a promoter is added to the catalyst, which increases the reducibility of the catalyst while keeping the active metal highly dispersed.

Addition of Re to Co/Sb₂O₃ catalysts has been found to promote activation of the cobalt sites in the catalyst via reduction of oxidized cobalt species while keeping the cobalt highly dispersed. Reduced Re is found to activate hydrogen and reduce cobalt particles by a H₂-spillover mechanism. Re also helps improve selectivity towards oxygenates, especially ether. Small amounts of Re have been found to significantly increase the amount of adsorbed CO on cobalt and thus CO hydrogenation rates. However, the active sites for CO hydrogenation have been proposed to be the highly dispersed cobalt sites only.

Zirconia has also been proposed as an important promoter for Co/Sb₂O₃ catalysts. Addition of a ZrO₂ promoter can modify and improve the catalyst texture and porosity, assisting in the reduction of oxidized Co species to metallic cobalt, increase the dispersion of cobalt, and improve the chemical stability of the support. Pre-impregnated zirconia is believed...
VITA

Nitin Kumar, son of Arun Kumar and P.K. Devi, was born in 1974 in Patna (Bihar), India. He earned his bachelor’s degree in chemical engineering from Birsa Institute of Technology, Sindri (formerly known as “Bihar Institute of Technology”), in 1997. Following his graduation, he was selected for one year orientation course in “Nuclear Science and Engineering” at Bhabha Atomic Research Center, Mumbai, India, from 1997-1998. After successful completion of the training, he joined the research center as a scientific officer and worked for nine years in the area of process development, process design and engineering. He successfully completed several developmental projects at small and large scales. He joined Louisiana State University in August 2007 to pursue a doctorate in chemical engineering. He married Supriya Singh, daughter of Parshuram Prasad and Sharda Devi, in 2003. They are blessed with a son, Anmol, who was born in May 2010.