Manganese Promoted CO Hydrogenation Catalysts: A

Study of Metal Promoter Interaction Effects

By

JINGJING LIU
B.S., Sichuan University, Chengdu, Sichuan, China, 2009

THESIS

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Defense Committee:

Randall J. Meyer, Chair and Advisor, Chemical Engineering
Brian P. Chaplin, Chemical Engineering
Robert F. Klie, Physics
Christopher L. Marshall, Argonne National Laboratory
Jeffrey T. Miller, Argonne National Laboratory
This thesis is dedicated to my dear Mother, Father, and Summer
my inspiration to every achievement in my life
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-J.L
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<td>DI</td>
<td>Dry Impregnation</td>
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<tr>
<td>EDX</td>
<td>Energy-Dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
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<tr>
<td>FT</td>
<td>Fischer-Tropsch</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma spectroscopy</td>
</tr>
<tr>
<td>IE</td>
<td>Ion Exchange</td>
</tr>
<tr>
<td>IWI</td>
<td>Incipient Wet Impregnation</td>
</tr>
<tr>
<td>PZC</td>
<td>Point of Zero Charge</td>
</tr>
<tr>
<td>SEA</td>
<td>Strong Electrostatic Adsorption</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature Programmed Reduction</td>
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<td>UV-Vis</td>
<td>Ultraviolet-Visual Spectroscopy</td>
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<td>XANES</td>
<td>X-ray Absorption Near-Edge Structure</td>
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<td>WI</td>
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SUMMARY

The aim of the work described in this thesis is to investigate the rational design of promoted metal catalysts for CO hydrogenation reactions. The main body of this work focuses on the use of simple techniques and common elemental precursors to improve the interactions in between a promoter and active metal. One of the many ways of achieving this is through the use of Strong Electrostatic Adsorption (SEA). Special attention to the surface charging parameters of mixed oxide as a function of solution pH can create a driving force to selectively adsorb a precursor complex onto a single phase of a binary mixture.

The use of promoters is ubiquitous in CO hydrogenation reactions to increase active metal’s activities as well as the selectivity towards desired products. Although, the precise active site of promoters in reactions and how they interact with active metals to react the reactants require many more studies, it is agreed that a key design objective is to increase the metal-promoter interactions. This work demonstrates a procedure to achieve this with Mn promoter catalysts.

In Chapter 1, we present an introduction and a brief review of CO hydrogenation catalysts for both the conversion of syngas to alcohols (particularly ethanol) and, additionally the conversion of syngas to long-chained hydrocarbons in a typical Fischer-Tropsch (FT) reaction. In Chapter 2, the fundamentals of the Transmission Electron Microscope (TEM) and its applications on catalysis related projects are presented. Chapter 3 gives a detailed discussion for rational design to selectively adsorb a [MnO₄]⁻ promoter precursor over a Rh₂O₃/SiO₂ supported catalyst. Various techniques (ICP,
STEM-EELS, XANES, EXAFS, TPR) were utilized to study the intrinsic properties of the catalysts and how the different catalysts preparation method could affect the metal-promoter interactions. The alcohol (ethanol) synthesis reactivity measurement also gave us key insight to the role of the promoter as a function of metal-promoter interactions. In Chapter 4, we focus on the rational design of the selective adsorption of a [MnO₄⁻] precursor over a Co₃O₄/TiO₂ supported catalyst, in this study, catalysts with three metal-promoter interactions (namely Mn monolayer coverage on Co, Mn partial coverage on Co and least Mn interaction with Co) were made and the different metal-promoter interactions were visualized by the STEM-EELS analysis, the F-T reactivity results demonstrated that the catalyst which has the strongest Mn-Co interaction (Mn monolayer coverage on Co) has the highest selectivity towards C₅⁺ hydrocarbons (desired product).

In Chapter 5, we continue discussing the CO hydrogenation for alcohol synthesis (especially ethanol). However in this chapter, we studied the metal-promoter interaction effects over Mn promoted Rh catalysts supported on multi-walled carbon nanotubes (CNTs) by just using the normal impregnation (DI, dry impregnation) catalysts preparation method. The enhanced Mn interaction with Rh particles was achieved by increasing the Mn loading (2 wt% Mn vs 1 wt% Mn loading), and the enhancement was visualized and quantified by STEM-EELS analysis due to the virtue of CNTs support (low Z number of C). Once again, in the reactivity results, the catalyst with stronger Mn-Rh interactions exhibited higher selectivity towards ethanol.

This thesis ends with main conclusion that the key of rational catalysts design is to enhance the metal-promoter interactions, which can be achieved by either selectively adsorbing promoter onto the active metal or simply increasing the promoter loading by
impregnation method. By focusing the intrinsic principles of catalyst preparation, this concept of stronger metal-promoter interactions can be applied to a wide range of catalytic materials to help define the promoter’s precise roles in various catalytic reactions.
1. INTRODUCTION

1.0 Background of Catalysis

In 1835 Jons Jacob Berzelius (1779-1848, one of the most famous Swedish chemist) discovered a chemical change in which one agent was involved in a reaction without itself being changed to another species[1]. This observation is considered as the very first description of catalysis and a milestone in the scientific history. In the early part of the last century, the knowledge and research of catalysis started to bloom, as catalysts were heavily utilized in industrial processes, which related to the production of fuels and commodity chemicals (eg. NH₃). For these processes, heterogeneous catalysts are employed whereby the catalyst is in the solid phase and the reactants and products are either liquids or gases. Heterogeneous catalysts are often composed of metal (eg. Fe, Rh, Pt) nanoparticles dispersed upon high surface area inert substrates (Al₂O₃, SiO₂, C) in order to achieve maximum usage of the metal and maintain good thermal and mechanical properties. Over time characterization techniques utilizing X-Rays and electrons helped to define surface characteristics and electronic states of the active metals have allowed us to correlate the atomic structure of the catalysts with their reactivity[2]. Using a combination of advanced experimental techniques and computational capability the method of catalyst preparation can now be linked to the creation of specific active sites where the reaction takes place. However, even though great advances have been made to boost our understanding of catalysis, big challenges still exist in front of us. Although the features of active catalysts are generally known, the tuning of selectivity to achieve 100% yield and the development of robust catalysts, which resist deactivation, remain elusive goals.
Most importantly, the identity of the active site is a question of fundamental importance to how heterogeneous catalysts work. However, despite this importance, in many complex cases, we still have little idea exactly how reactants interact with the surface and what are the exact roles of promoters. For example, even the best catalysts for alcohol synthesis found to date produce large amounts of unwanted products (such as methane and other oxygenates). Therefore, it is hoped that through our work, substantial gains can be made through a detailed investigation of active sites, which are responsible for highly selective and active conversion of syngas into alcohol and long chain hydrocarbons.

1.1 Catalysts Preparation

This work focuses on supported metal catalysts, and there are many ways to produce them, but among the most prevalent methods is impregnation where a high surface area oxide or carbon support is contacted with a liquid solution containing a precursor, typically a metal salt dissolved in solution[3]. In addition to impregnation precipitation, and adsorption are the other primary methods to support metals. In each case, the support is chosen based on certain desirable characteristics: (1) inertness, (2) mechanical properties, such as resistance, hardness, and compressive strength, (3) stability under reaction and regeneration conditions, (4) surface area, (5) porosity, and (6) low cost[4]. Supports such as Alumina, silica, titania, and carbons are the most wildly used in industry. Besides the classical techniques, there are also specialized techniques of supported metal catalysts synthesis such as atomic layer deposition (ALD), in which precursors react with a surface one at a time in a sequential, self-limiting, manner. By exposing the precursors to the growth surface repeatedly, a thin film is deposited[5]. In
all cases, once the precursor is adsorbed, the catalyst is generally subjected to a series of calcination (oxidation) and reduction treatments to convert the precursor into metal atoms, which form nanoparticles. In this thesis, we primarily utilized impregnation and adsorption as the catalyst synthesis methods.

1.1.1 Impregnation

Impregnation is among one of the most prevalent methods in preparing catalysts, and it contains two categories, which are named as dry (incipient wetness) impregnation and wet impregnation. In Dry Impregnation (DI) or Incipient Wetness Impregnation (IWI), a sufficient amount of metal solution is added to just fill the pore volume of the catalyst support. An advantage of the method is that the metal content or metal loading is fixed, so it requires no filtering making it the simplest method to employ. Moreover, the DI or IWI method is simple and straightforward, so it’s highly efficient and scalable[6]. However, it also comes with some major disadvantages in producing an efficient catalyst. As the precursor is randomly added onto the support or supported catalyst, so there is no guarantee in the interaction between the precursor and the support or the precursor and the supported metal (e.g. promoter and the active metal), and the precursor coverage is generally considered to be uneven which often results in a very broad particle size distribution.

In Wet Impregnation (WI), the contacting solution has a volume which is substantially larger than the pore volume of the support or the supported catalyst. After contact the solution is stirred constantly to ensure a more homogenous metal distribution. However, as the metal precursor is added into the excessive volume of solution, not all of the metal precursor is deposited on the support surface.
1.1.2 Adsorption

Adsorption is, in effect, wet impregnation, but with strong (electrostatic) interactions that occur between the support and a cationic or anionic metal complex. Strong Electrostatic Adsorption (SEA) takes into consideration the charging parameters of the support as a function of pH. As depicted in Figure 1.1, hydroxyl groups on the surface of the oxide can either be protonated (positively charged) when solution pH is below the point of zero charge (PZC) or deprotonated (negatively charged) when the solution pH is above the PZC. The pH at which the hydroxyl groups are neutral is termed the point of zero charge (PZC).

![Diagram of adsorption mechanism](image)

**Figure 1.1** The three regimes of the electrostatic adsorption mechanism[7].


The simplest and most accurate method of determining the PZC of a support is by measuring the equilibrium pH at high oxide surface loading (e.g. 10,000 m²/L) after the
oxide has been in contact with solutions of varying initial pH. Surface loading, which is the amount of support surface per liter of solution, can be calculated by the following equation:

\[
\text{Surface loading (m}^2/\text{L}) = \frac{\text{mass of solid (g)} \times \text{oxide surface area (m}^2/\text{L})}{\text{Volume of solution (L)}}
\]

If we also know the volume of solution and the surface area of the oxide, then we can calculate the weight of oxide needed to conduct this experiment for a particular surface loading (e.g. 1,000 m\(^2\)/L).

The result of experimental PZC measurement of various types of SiO\(_2\) is showed in Figure 1.2a. All the data follow a curved line, which demonstrates a plateau at a pH of about 4.1, which corresponds to the PZC value of all types of silica. Below the PZC, the hydroxyl groups protonate (forming positively charged \(-\text{OH}^+\)), so the surface can adsorb anionic metal complexes such as permanganate as [MnO\(_4\)]\(^-\). Above the PZC, the hydroxyl groups deprotonate (forming negatively charged \(-\text{O}^-\)), and cations such as platinum tetraammine as [(NH\(_3\))\(_4\)Pt]\(^{2+}\) can be strongly adsorbed onto the surface[8]. Figure 1.2b shows a typical uptake experiment on the various kinds of silica where the concentration of the precursor in solutions with different initial pH is measured respectively before and after contacting the precursor solutions to the silica support. For each initial pH, the difference of the concentration of the precursor solution before and after the contact is the amount of the precursor absorbed onto the support at that initial pH. In Figure 1.2b, we can see at low pH there is negligible uptake of the cationic precursor ([NH\(_3\))\(_4\)Pt]\(^{2+}\) on the SiO\(_2\) surface. However as the pH increases, the amount of the absorbed precursor also increases until a maximum uptake is reached at a pH of about 11. As the pH further
increases, the ionic strength of the solution increases, and the competitive adsorption between metal precursor and solution cations at extremely high pH eventually results in a decrease in the adsorption. In some cases, extreme pH conditions can cause redox reactions between the metal precursors and the ionic solution or degradation of the support material[7].

Figure 1.2 Experimental and RPA modeled results: (a) PZC determination of various kinds of silica, (b) [(NH3)4Pt]2+ uptake on various kinds of silica[7].


The theory of SEA can be further applied to promoted and bimetallic systems where the intimate contact between the metal and promoter is fundamentally important. Pioneering research began with Schwarz et al.[9, 10], who showed promising results for selective adsorption. This technique of controlling the surface charging parameters for the purpose of promoted metal system is critical for the catalysts synthesis in this work. Figure 1.3 shows the difference of a high PZC oxide and a low PZC oxide in terms of
surface parameters in different pH solutions[11]. Based on this theory our strategy of having an intimate metal-promoter interaction catalyst is described as follows: If a low PZC oxide (e.g. TiO$_2$ and SiO$_2$ with a low PZC of about 4) is used as a support for a high PZC oxide (e.g. Co$_3$O$_4$ and Rh$_2$O$_3$ with a PZC of 8 and 8.75 respectively), then the density of protonated hydroxyl groups on the surface of the high PZC oxide (such as Rh$_2$O$_3$) would be much higher than those on the low PZC supports (such as SiO$_2$) in an acidic solution. Therefore, under such a circumstance, if we introduce an anionic metal precursor (such as [MnO$_4$]$^-$) into the mixture solution, the anionic precursor would be selectively adsorbed onto the Rh$_2$O$_3$ rather than the SiO$_2$. Successful examples of applying the SEA method to make efficient CO hydrogenation catalysts can be found in the previous research results from our group[11-14].

![Figure 1.3 Schematic of proposed selective adsorption[11].](image)

1.2 CO Hydrogenation Catalysis for Alcohol Synthesis

1.2.1 Motivation and Background

One of the largest societal challenges of our day is the quest for alternative fuel resources that will reduce our current greenhouse gas emission and dependence on foreign crude oil. The International Energy Agency estimates that the world marketed energy consumption will increase from 524 quadrillion Btu in 2010 to 630 quadrillion Btu in 2020 and 820 quadrillion Btu in 2040 and that the majority of this energy will be produced from fossil fuels, especially from coal and oil[15-17]. Ethanol is one potential alternative synthetic fuel for use in automobiles, and the use of ethanol as a gasoline additive is already in practice both in the U.S. and internationally. For example, almost every oil company is blending about 10% ethanol in volume with the gasoline at their gas stations in the state of Illinois[18]. In addition to its application as an additive in transportation fuels, renewable ethanol from biomass can also serve as a feedstock for the synthesis of a variety of industrial chemicals and polymers including plasticizers and detergents [19, 20].

Currently there are two major ways of producing ethanol: 1) fermentation of sugars derived from corn or sugar cane, 2) hydration of petroleum-based ethylene. However, traditional fermentation routes to alcohols are often slow and inefficient. Although fermentation is commercially practical, and the primary route for manufacture, the production of fuel-grade ethanol is still expensive (as reported in early 2013[21], the total cost of E-100, pure ethanol, from Brazil is $2.92/gallon which includes shipping and
tax and possesses a lower power density than gasoline) and energy-inefficient because the process contains energy intensive distillation steps[22]. In addition, using crops for fuel grade alcohol production is controversial due to doubts about its overall energy efficiency and its effect on food prices[23]. On the other hand, chemical routes to alcohols (hydration of ethylene) are dominated by acid catalyzed processes which generate significant waste and rely on petrochemical feedstocks. Indirect liquefaction, which consists of gasification of the entire biomass components (including hemicellulose and lignin), into syngas followed by the catalytic conversion of syngas to liquid fuels provides an alternative which avoids drying, utilizes biomass sources and avoids acid waste [24-26]. Research on the catalytic conversion of syngas to alcohols has been conducted for many decades[24, 27-44]. Substantial amount of research work[26] has been conducted for syngas conversion process development, which is to produce higher alcohols containing a mixture of oxygenates such as methanol and isobutanol as precursors for methyl tertiary butyl ether (MTBE), which has been recommended as an octane blend in the past. However, because MTBE has been recently replaced by ethanol, the interest in the synthesis of ethanol from biomass- and coal-derived sygas conversion is growing substantially. The overall chemical reaction for ethanol production from synthesis gas can be described as following two equations based on different stoichiometry with \( \text{H}_2: \text{CO} \) ratios varying between 1 to 2.

\[
2 \text{ CO} + 4 \text{ H}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}
\]

\[
3 \text{ CO} + 3 \text{ H}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{CO}_2
\]
1.2.2 The Choice of Active Metals

The heterogeneous catalysts[26] used for the ethanol and higher alcohols synthesis can be generally classified into two categories: (1) noble metals-based and (2) Non-noble metals-based. The noble metals-based catalysts are usually supported rhodium (Rh) catalysts while the non-noble metals-based catalysts include modified methanol synthesis catalysts, modified Fischer–Tropsch synthesis catalysts, and MoS$_2$-based catalysts [26, 31]. In V. Subramani et al.’s review work[26], the authors depict various scenarios (reproduced here as Figure 1.4) where syngas is converted to different products over different catalysts.

![Figure 1.4 Syngas conversion to different products over different types of catalysts[26].](image)


By far the most widely studied catalysts for the hydrogenation of CO to oxygenates are based on rhodium (Rh) and the ability of rhodium catalysts to selectively
covert syngas to oxygenated products has been recognized for decades[33, 45, 46]. Among all of the transition metal catalysts, Rh catalysts are often considered as the best catalysts for producing oxygenates from syngas. It appears that Rhodium’s unique activity for oxygenated products must stem from the intermediate position of its d-electrons relative to the metals which do not dissociate CO (Ir, Pd, Pt) and thus favor methanol production and those which easily dissociate CO under reaction conditions (Co, Rh, Fe) and therefore favor production of higher hydrocarbons[31, 47-49]. In another words, Rhodium provides a balance between CO dissociation and CO insertion. However, the majority of CO hydrogenation studies using unpromoted Rh have observed a strong selectivity for methane with a low oxygenates selectivity. Thus, the addition of promoters as additives is not only necessary but will also greatly improve the catalytic performance of Rh catalysts.

1.2.3 Promotion Effects

The direct conversion of syngas to ethanol has been reported by Union Carbide Company as early as 1975 over SiO₂ supported Rh catalyst promoted by metal ions, such as Fe, Mo, Mn, W, Th, and U, in a stirred autoclave reactor[50-53]. In this study, the authors found that catalysts containing only Rh produce acetaldehyde and acetic acid as the principal non-methane products. While the addition of Fe (up to 35% of the Rh on a per mole basis) did not change the rate of syngas conversion greatly, both acetaldehyde and acetic acid disappeared and were replaced by C₂H₅OH. At 300 C° and 72 bar total pressure of H₂/CO, a 2.5% Rh/SiO₂ catalyst promoted with 0.05% Fe produced 31.4% ethanol but the rates of ethanol production were about 50 L/g cat hr. In contrast to Fe, Mn
was found to have little effect on the product distribution, but greatly enhanced the conversion of syngas.

Following this early work, there are several reports on the conversion of syngas to ethanol using Rh supported on various oxides supports with addition of various promoters. These studies have successfully shown the product distribution obtained from syngas conversion could be altered in favor of ethanol by modifying the supports or by promotion, in general the sources for promoters could come from a broad spectrum, from transition metals such as Mn, Fe, V, Ti, and Zr, as well as rare earth/alkali elements such as La, Ce, Li, and K[33, 43, 46, 47, 54-70]. Chuang et al.[46] created a chart (showed here as Figure 1.5) which summarizes the promoter and support effects on C₂ oxygenate synthesis on supported Rh catalysts by classifying the promoters as to their perceived role in facilitating one of the three key reactions in alcohol synthesis (C-O dissociation, C-C formation, C-H formation). For example, Fe is believed to promote hydrogenation, and Mn is suggested to promote the CO dissociation while V and Ti promote both the CO dissociation and CO insertion processes.
Figure 1.5 Support and promoter effects on C₂ oxygenate synthesis on supported Rh catalysts[46].


Burch et al.[57] demonstrated in their work the differences in CO hydrogenation products distribution between using unpromoted and promoted Rh supported catalysts on SiO₂. With a syngas feed with a 1:1 H₂:CO ratio, and a total pressure of 20 bar at 270 °C, 2 wt% Rh on SiO₂ produced primarily methane and the selectivity towards ethanol is only about 0.7% with a conversion of 1.5%. However, the selectivity towards ethanol improved significantly, when the catalysts were promoted by different metals such as Fe, Mn, Ce, Li and Ir. For example, a 1wt% Fe-2%Rh/ SiO₂ catalyst demonstrated 39% selectivity to ethanol at 4.5% CO conversion. J. Gao et al.[68] investigated the combined promotion effects of V and La for CO hydrogenation at 230 °C and 1.8 bar. In their work, the two promoters were co-impregnated onto the 1.5 wt% Rh on SiO₂ catalysts with different promoter weight loadings. In the cases where the loading of La was fixed at 2.6
wt%, increasing the loading of V from 0.75 wt% to 3.7% wt%, the author found that the selectivity to ethanol increased from 16% to 21% and the CO conversion rate remained nearly constant across the range of V weight loading. The authors also compared the results of the Rh-La-V/SiO₂ catalysts with unpromoted Rh/SiO₂ and singly promoted Rh-La/SiO₂ and Rh-V/SiO₂ catalysts, and showed improved reactivity (3×) and better ethanol selectivities indicating that the promoters are operating in some synergistic fashion. Lin et al. [71] employed Mn as a promoter to 1% Rh/SiO₂ catalyst with a Rh/Mn weight ratio of 1:1 and performed the CO hydrogenation at 310 °C and 60 bar continuously for about 1000 hr. The selectivity towards ethanol, acetic acid and acetaldehyde were found to be 34.8%, 30.7%, and 19.2% respectively with low selectivities for other oxygenates.

Subramani et al. [26] summarized the promoted Rh catalyst literature in Figure 1.6 by relating the promoter type (i.e. position on the periodic table) to both the catalytic activity and selectivity for ethanol formation over Rh-supported SiO₂ catalysts. As can be seen in the figure, promoters such as Zr, Ti, and V exhibit higher catalytic activity for ethanol formation, whereas La, Ce, Y show higher ethanol selectivity. However, to some extent, this summary of comparison depicted in Figure 1.6 could be misleading since different researchers used different catalyst preparations and tested their catalysts in different reaction conditions (i.e. temperature, pressure or syngas ratio). Consequently, one has to be cautious in interpreting the reactivity comparison for different promoters in this graph. In order to study the promoter effect in more detail, one could pick any of the many promoters shown in this figure. Our goal is to examine the relationship between the physical structure, electronic state and catalytic selectivity for a single promoter to try to deduce how the promoter participates in the reaction. In this thesis, Manganese (Mn)
was selected as the promoter to be studied. From previous research in our group[11, 12], we have observed that Mn can be used successfully to promote CO hydrogenation and the catalysts preparation methods are known to some degree. Detailed research results will be discussed in specific chapters in this thesis.

Figure 1.6 Effect of the nature of the promoter on catalytic activity and selectivity for ethanol from syngas over Rh/SiO₂ catalysts[26].

Also a brief summary of the alcohol productivity over various kinds of promoted Rh catalysts from many previous researches is presented here in Table 1.1.

**Table 1.1** A literature summary of the previous alcohol synthesis research on various kinds of promoted Rh catalysts.

<table>
<thead>
<tr>
<th>Source and Author</th>
<th>Catalysts</th>
<th>Selectivity (EtOH)</th>
<th>Activity, Conversion or TOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burch et al.[57]</td>
<td>2Rh/SiO2</td>
<td>0.70%</td>
<td>Conversion 1.52%</td>
</tr>
<tr>
<td>Same as above</td>
<td>2Rh/Fe/SiO2</td>
<td>39.00%</td>
<td>Conversion 4.45%</td>
</tr>
<tr>
<td>Same as above</td>
<td>2Rh/0.1Fe/SiO2</td>
<td>24.00%</td>
<td>Conversion 2.28%</td>
</tr>
<tr>
<td>Same as above</td>
<td>2Rh/Mn/SiO2</td>
<td>19%</td>
<td>Conversion 1.68%</td>
</tr>
<tr>
<td>Same as above</td>
<td>2Rh/Fe/SiO2</td>
<td>21%</td>
<td>Conversion 1.15%</td>
</tr>
<tr>
<td>Same as above</td>
<td>2Rh/0.034Li/SiO2</td>
<td>25% at 300°C</td>
<td>Conversion 1.11%</td>
</tr>
<tr>
<td>Same as above</td>
<td>2Rh/0.37Ir/SiO2</td>
<td>3.30%</td>
<td>Conversion 1.15%</td>
</tr>
<tr>
<td>Schunemann et al.[58]</td>
<td>RhFe/NaY NaOH</td>
<td>34%</td>
<td>Conv. 1.7%</td>
</tr>
<tr>
<td>Kienemann et al.[59]</td>
<td>5% Rh-0.5% Ce/SiO2</td>
<td>34%</td>
<td>Conv. 1.7%</td>
</tr>
<tr>
<td>Same as above</td>
<td>5% Rh-2% Ce/SiO2</td>
<td>36%</td>
<td>Conv. 2.2%</td>
</tr>
<tr>
<td>Same as above</td>
<td>5% Rh-5% Ce/SiO2</td>
<td>45%</td>
<td>Conv. 1.7%</td>
</tr>
<tr>
<td>Same as above</td>
<td>5% Rh/CeO2</td>
<td>38%</td>
<td>Conv. 1.2%</td>
</tr>
<tr>
<td>Burch et al.[60]</td>
<td>2Rh/2Fe/Al (Rh aq.)</td>
<td>27%</td>
<td>Conv. 1.8%</td>
</tr>
<tr>
<td>Same as above</td>
<td>2Rh/6Fe/Al</td>
<td>45%</td>
<td>Conv. 3.0%</td>
</tr>
<tr>
<td>Same as above</td>
<td>2Rh/10Fe/Al</td>
<td>49%</td>
<td>Conv. 3.8%</td>
</tr>
<tr>
<td>Holy et al.[44]</td>
<td>Co-Fe-Rh/SiO2</td>
<td>30%</td>
<td>Conv. 6%</td>
</tr>
<tr>
<td>Yu et al.[43]</td>
<td>4.5CeO2-2Rh/SiO2</td>
<td>48%</td>
<td>TOF 2.4 per h</td>
</tr>
<tr>
<td>Hu et al.[61]</td>
<td>6Rh-1.5Mn/SiO2</td>
<td>44.50%</td>
<td>Conv. 40.5%</td>
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<td>Same as above</td>
<td>6Rh-1.5Mn/SiO2</td>
<td>44.40%</td>
<td>Conv. 32.1%</td>
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<td>Same as above</td>
<td>6Rh-1.5Mn/SiO2</td>
<td>34.80%</td>
<td>Conv. 18.7%</td>
</tr>
<tr>
<td>Same as above</td>
<td>6Rh-1.5Mn/SiO2</td>
<td>40.90%</td>
<td>Conv. 35.4%</td>
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<tr>
<td>Mazzocchia et al.[72]</td>
<td>1Rh/ZrO2</td>
<td>50.80%</td>
<td>Conv. 2%</td>
</tr>
<tr>
<td>Fan et al.[73]</td>
<td>RhMnLiFe/CNTs (Carbon Nanotubes)</td>
<td>52.4% (C2+)</td>
<td>Oxygenates</td>
</tr>
<tr>
<td>Same as above</td>
<td>RhMnLiFe/CNTs (Carbon Black)</td>
<td>59% (C2+)</td>
<td>Oxygenates</td>
</tr>
<tr>
<td>Same as above</td>
<td>RhMnLiFe/CMK-3 (Mesoporous C)</td>
<td>39.6% (C2+)</td>
<td>Oxygenates</td>
</tr>
<tr>
<td>Same as above</td>
<td>RhMnLiFe/AC (Active Carbon)</td>
<td>26.8% (C2+)</td>
<td>Oxygenates</td>
</tr>
<tr>
<td>Gao et al.[63]</td>
<td>1%Rh/SiO2</td>
<td>15.60%</td>
<td>SS Rate 0.03 µmol/g/s</td>
</tr>
<tr>
<td>Same as above</td>
<td>1.5%Rh-2.6%La/SiO2</td>
<td>21.50%</td>
<td>SS 0.07</td>
</tr>
<tr>
<td>Same as above</td>
<td>1.5%Rh-1.5%V/SiO2</td>
<td>13.60%</td>
<td>SS 0.09</td>
</tr>
<tr>
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<td>1.5%Rh-0.8%Fe/SiO2</td>
<td>19.40%</td>
<td>SS 0.11</td>
</tr>
<tr>
<td>Mazzocchia et al.[64]</td>
<td>1.4%Rh/ZrO2</td>
<td>30%</td>
<td>Conv. 4.2%</td>
</tr>
<tr>
<td>Same as above</td>
<td>1.4%Rh/ZrO2</td>
<td>4%</td>
<td>Conv. 34.7%</td>
</tr>
<tr>
<td>Catalyst</td>
<td>1.4%Rh/ZrO₂</td>
<td>1.4%Rh/ZrO₂</td>
<td>1.4%Rh/ZrO₂</td>
</tr>
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<td>----------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Koerts et al.[65]</td>
<td>3%Rh/SiO₂</td>
<td>18.90%</td>
<td>Conv. 0.27 mmol CO/Surface Metal</td>
</tr>
<tr>
<td>Same as above</td>
<td>V-3%Rh/SiO₂</td>
<td>22.80%</td>
<td>Metal Atom/sec</td>
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<td>Bhasin et al.[33]</td>
<td>2.5%Rh/SiO₂</td>
<td>31.40%</td>
<td>Rate 0.27 µmol/g/s</td>
</tr>
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<td>Haider et al.[67]</td>
<td>2%Rh/SiO₂</td>
<td>21.80%</td>
<td>Rate 0.27 µmol/g/s</td>
</tr>
<tr>
<td>Chuang et al.[66]</td>
<td>3%Rh/TiO₂(Anatase)</td>
<td>16.70%</td>
<td>SS Rate 0.27 µmol/g/s</td>
</tr>
<tr>
<td>Mo et al.[69]</td>
<td>2.6%La/1.5%V/SiO₂</td>
<td>19.40%</td>
<td>SS 0.12</td>
</tr>
<tr>
<td>Same as above</td>
<td>6%La/1.5%V/SiO₂</td>
<td>18.30%</td>
<td>SS 0.17</td>
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<td>1.5%Rh-0.8%Fe/SiO₂</td>
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<td>5.80%</td>
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</tr>
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<td>2.6%La/SiO₂</td>
<td>22.30%</td>
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<td>2.6%La/SiO₂</td>
<td>5.30%</td>
<td>SS 0.05</td>
</tr>
<tr>
<td>Catalyst Composition</td>
<td>Activity</td>
<td>Conversion</td>
<td>Notes</td>
</tr>
<tr>
<td>----------------------</td>
<td>----------</td>
<td>------------</td>
<td>-------</td>
</tr>
<tr>
<td>Same as above 1.5%Rh-0.5%Cu/SiO2 2%Rh-0.6%Cu-SiO2</td>
<td>16.70%</td>
<td>SS 0.002</td>
<td></td>
</tr>
<tr>
<td>Same as above 2.6%La/SiO2</td>
<td>13.10%</td>
<td>SS 0.09</td>
<td>Activity 0.0879 mmol CO/mol Rh/s (Overall conversion was kept below 5%)</td>
</tr>
<tr>
<td>Beutel et al.[74] 3%Rh-V/SiO2</td>
<td>44.60%</td>
<td>41%</td>
<td>Activity 0.0522</td>
</tr>
<tr>
<td>Same as above 3%Rh-V/SiO2</td>
<td>45.20%</td>
<td>Activity 0.0409</td>
<td></td>
</tr>
<tr>
<td>Same as above 3%Rh-Nb/SiO2</td>
<td>33.10%</td>
<td>Activity 0.17</td>
<td></td>
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<tr>
<td>Same as above 3%Rh-Nb/SiO2</td>
<td>47.40%</td>
<td>Activity 0.138</td>
<td></td>
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<tr>
<td>Same as above 3%Rh-Ta/SiO2</td>
<td>34%</td>
<td>Activity 0.078</td>
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<tr>
<td>Same as above 3%Rh-Ta/SiO2</td>
<td>42.60%</td>
<td>Activity 0.128</td>
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<td>49.60%</td>
<td>Activity 0.088</td>
<td></td>
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<tr>
<td>De Jong et al.[70] 2.1%Rh/SiO2</td>
<td>25% C2 oxygenates</td>
<td>TON 60/s</td>
<td></td>
</tr>
<tr>
<td>Same as above 2%Rh/2.1%MnO/SiO2</td>
<td>27% C2 oxygenates</td>
<td>TON 110/s</td>
<td>Rate (10^{-1} mol CO g^{-1} Rh h^{-1}) 4.28</td>
</tr>
<tr>
<td>Prieto et al.[75] 2.5%Rh-7.9%Fe/Al2O3</td>
<td>23% Oxygenates (86% alcohols)</td>
<td>Rate 1.93</td>
<td></td>
</tr>
<tr>
<td>Same as above 2.5%Rh-10.3%V/Al2O3</td>
<td>12% Oxygenates (55% alcohols)</td>
<td>Rate 1.69</td>
<td></td>
</tr>
<tr>
<td>Same as above 2.5%Rh-15.1%Nb/Al2O3</td>
<td>20% Oxygenates (46% alcohols)</td>
<td>Rate 2.1</td>
<td></td>
</tr>
<tr>
<td>Same as above 2.5%Rh-23.5%Ta/Al2O3</td>
<td>27% Oxygenates (41% alcohols)</td>
<td>Rate 1.65</td>
<td></td>
</tr>
<tr>
<td>Same as above 2.5%Rh-6.8%Ti/Al2O3</td>
<td>36% Oxygenates (71% alcohols)</td>
<td>Rate 0.64</td>
<td></td>
</tr>
<tr>
<td>Same as above 2.5%Rh-12.1%Y/Al2O3</td>
<td>51% Oxygenates (72% alcohols)</td>
<td>Rate 0.53</td>
<td></td>
</tr>
<tr>
<td>Same as above 2.5%Rh-17%Pr/Al2O3</td>
<td>49% Oxygenates (79% alcohols)</td>
<td>Rate 0.44</td>
<td></td>
</tr>
<tr>
<td>Same as above 2.5%Rh-Nd/Al2O3</td>
<td>59% Oxygenates (83% alcohols)</td>
<td>Rate 0.39</td>
<td></td>
</tr>
<tr>
<td>Same as above 2.5%Rh-Sm/Al2O3</td>
<td>32% Oxygenates (35% alcohols)</td>
<td>Rate 2.2</td>
<td></td>
</tr>
<tr>
<td>Same as above 2.5%Rh-Li-Ta/Al2O3</td>
<td>31%</td>
<td>Conv. 9.28%</td>
<td></td>
</tr>
<tr>
<td>Gogate et al.[76] 2%Rh-2.5%Fe/TiO2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Although the exact roles promoters play are still unclear, there are still a handful of possible mechanisms that have been proposed. For example, Wang et al.[77] have employed various techniques (CO-TPD, TPSR and XPS) to examine the mechanisms of ethanol formation on Mn promoted Rh catalysts. They proposed that the structure for the active site involves the presence of both metallic and oxidic Rh (as showed in Figure 1.7). The tilt adsorbed CO species (i.e. CO adsorbed in a configuration that is not perpendicular to the surface) is the main precursor for both CO dissociation and the formation of ethanol and methanol. Ethanol is formed by direct hydrogenation of the tilt-adsorbed CO molecules, followed by CH₂ insertion into the surface CH₂-O species.

![Figure 1.7 The proposed mechanism of ethanol formation on the Rh-Mn/SiO₂ catalyst.](Reprinted from Y. Wang, Luo, H.Y., Liang, D.B., Bao, X.H., Different Mechanisms for the Formation of Acetaldehyde and Ethanol on the Rh Based Catalysts, Journal of Catalysis, 196 (2000) 46-55. Copyright (2000), with permission from Elsevier.)


Ethanol synthesis via the acetaldehyde formation followed by fully hydrogenation (an acetate mechanism) has also been known as another pathway over Mn promoted Rh-based catalyst[77]. According to Wang et al., acetaldehyde is formed through CO insertion into the surface CH₃–Rh species followed by hydrogenation (the pathway of
acetaldehyde formation is shown as Figure 1.8). After which, ethanol can be formed via the fully hydrogenation of formed acetaldehyde. The role of Mn promoter is this case was described to stabilize the surface acetyl species (as intermediate).

![Figure 1.8](image)

**Figure 1.8** The pathway of acetaldehyde formation over Mn promoted Rh based catalyst[77].


In addition, if methanol is formed, it can also be a source for ethanol and it is found to decompose to formaldehyde on many kinds of metals such as Mg and Cu and can be converted to ethanol[78-80]. Formaldehyde and adsorbed formyl act as intermediates in the ethanol synthesis from methanol coupling (see Figure 1.9 for the scheme). However, although the formaldehyde and formyl intermediates can be produced directly from CO hydrogenation, it is still a relatively slow step compared to their formation via the condensation of two methanol molecules[81].
Figure 1.9 The mechanism of ethanol synthesis from methanol condensation on Cs promoted Cu catalysts[31].

Note: Reproduced from J.J. Spivey, A. Egbebi, Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas, Chemical Society Reviews, 36 (2007) 1514-1528. Copyright (2007), with permission from Royal Society of Chemistry.

1.2.4 The Choice of Supports

Just like promoters, supports can play an important role in Rh catalysts to improve the selectivity to oxygenates and activities for syngas conversion to alcohols. The support affects the Rh dispersion, which in turn affects the nature of the CO adsorption. The supports can be oxides or carbons. SiO₂ is a ubiquitous metal oxide support used for Rh based syngas conversion catalysts, and has been well recognized for its high surface area, high porosity and its stability[44, 54, 82]. Other metal oxide supports include TiO₂, Al₂O₃, ZnO, MgO, V₂O₃ and etc[26, 31]. CO hydrogenation is a prominent reaction for exhibition of SMSI (strong metal support interaction) effects, particularly for metals supported on TiO₂, as a migration of reduced species from the support during the high-temperature reduction can occur resulting in decoration of the supported nanoparticles [83, 84]. Various kinds of carbon are also considered as a potential support for Rh based
catalysts because of their high surface area and it lack of interaction with the metal. [73]. For instance, Fan et al.[73] have studied the effects of carbon supports for syngas conversion into C₂ oxygenates over Rh based catalysts. The carbon supports used in their work include carbon nanotubes, carbon black, mesoporous carbon and active carbon. With an elemental ratio of Rh:Mn:Li:Fe =1:1:0.075:0.05 under the reaction condition of 320 °C and 30 bar, they found that the catalyst supported on carbon black generated the highest C₂⁺ oxygenate selectivity of 59% at a CO conversion of 4%. The authors also noted that the graphitized structure combined with the tubular morphology of carbon nanotubes likely play an important role. As the channels of CNTs do not only exert spatial restriction limiting the aggregation of metal particles, but also possibly modifying the metal catalyst properties (such as the redox properties of metal and metal oxide particles) due to the unique electron structure of the curved graphene walls[85].

1.2.5 Reaction Conditions

CO hydrogenation activity and selectivity can also be influenced by the reaction conditions, including temperature, pressure, gas composition, and flow rate[61], Hu et al., examined the effects of reaction conditions for syngas conversion to ethanol over 6 wt% Rh- 1.5 wt% Mn/SiO₂ by varying the pressure from 38 bar to 54 bar at a constant reaction temperature at 300 °C. Although the CO conversion remained constant (44.5%), the selectivity to ethanol increased from 32.1% to 40.5%. The H₂/CO ratio was also varied from 1:1 to 3:1 at constant temperature (300 °C) and pressure (38 bar), resulting in a maximum in ethanol selectivity at a ratio of 2:1 (ethanol selectivity: 40.9%, 44.4% and 34.8% respectively) while the CO conversion increased from 18.7% to 35.4% with increasing H₂:CO ratio. Lowering the temperature to 265 °C at a H₂:CO ratio of 2
resulted in an increase in the ethanol selectivity to 61.4%, but a decrease in conversion to 25.4%. The authors also noted that the formation of undesired product, methane, can be suppressed under conditions of low temperature, high pressure and low H₂/CO ratio.

1.3 CO Hydrogenation Catalysis for Fischer-Tropsch Synthesis

1.3.1 Background

As has been discussed in the previous session, CO hydrogenation can be used for alcohol (primarily ethanol) synthesis; the CO hydrogenation can also be used for the production of another important alternative fuels, namely as the Fisher-Tropsch (FT) process. The FT process is the catalytic conversion of syngas, mixtures of CO and H₂, to more desirable long-chain hydrocarbons, the reaction is described as: \( n \text{CO} + (2n+1) \text{H}_2 \rightarrow C_n \text{H}_{2n+2} + n \text{H}_2 \text{O} \).

In 1922, Hans Fischer and Franz Tropsch proposed the Synthol process under high pressure (>100 bar) at 673 K, which gave a mixture of aliphatic oxygenated compounds via reaction of carbon monoxide with hydrogen over alkalized iron chips. The product was then heated under pressure and then transformed into a mixture of hydrocarbons[86]. In 1926, Hans Fischer and Franz Tropsch published their first report of hydrocarbon synthesis[87]. In 1934, the FT process was licensed by Ruhrchemie and reached industrial maturity in 2 years. In April 1936[88], the first large-scale FT plant was operated in Braunkohle-Benzin. Then Germany had a capacity of 660,000 tons of primary products per year in 1938. After World War II, ARGE (Arbeitsgemeinschaft Ruhrchemie und Lurgi) developed a large-scale process with a fixed bed FT reactor. However, commercial development largely stalled due to the availability of cheap crude.
In South Africa, however, due to the availability of coal and the lack of liquid based hydrocarbon resources, Sasol commercialized the F-T processes by building FT plants for diesel fuel production in three phases in 1955, 1980 and 1982 respectively. In June 2006, the Sasol Oryx 34 000 bpd plant was inaugurated. In the last decade Shell and Sasol signed an agreement to build 140 000 bpd GTL-FT plants in Qatar. Thus, after several decades of research and development, FT technology has finally come to the stage of full-scale industry and worldwide commercialization[88]. The revival of FT research is also reflected in the current output of peer reviewed FT research papers, which has tripled since 1995[89], we now see the advantages of present-day new technology to improve the benchmark research of the past. However, challenges such as high selectivity towards the desired C_{10}-C_{20} paraffins for detergents or gasoline free of aromatics or C_2-C_5 olefins still remain, novel ideas and improved techniques are needed for the next F-T innovation.

1.3.2 The Choice of Active Metal

In general, all group VIII metals have noticeable activity in the hydrogenation of carbon monoxide to hydrocarbons, Ruthenium followed by iron, nickel, and cobalt are the most active metals for the CO hydrogenation reaction[88]. Vannice et al.[48] showed that the average molecular weight of hydrocarbons produced from FT synthesis decreased in the sequence of Ru > Fe > Co > Rh > Ni > Ir > Pt > Pd. Consequently ruthenium, iron, cobalt, rhodium and nickel have desirable catalytic activity, which can be considered for commercial production. Ni catalysts under commercial conditions produce too much methane. Ruthenium and Rhodium are too expensive and Rh is better for producing oxygenates. Therefore Cobalt and Iron are the metals which have been used in industrial FT hydrocarbon synthesis. In general, Cobalt catalysts exhibit both
higher activity and selectivity than their iron counterparts. Although Cobalt catalysts are more expensive, they exhibit more resistant to deactivation. In Khodakov et al.[88]’s review work of FT catalysts, the authors made a brief comparison of Cobalt and iron catalysts for FT synthesis, which is showed here as Table 1.2.

Table 1.2 Comparison of Cobalt and Iron Catalysts for FT synthesis[88].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Cobalt catalysts</th>
<th>Iron catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>cost and lifetime</td>
<td>more expensive resistant to deactivation</td>
<td>less expensive less resistant to deactivation</td>
</tr>
<tr>
<td>activity at low conversion</td>
<td>higher; less significant effect of water on the rate of carbon monoxide conversion</td>
<td>lower; strong negative effect of water on the rate of carbon monoxide conversion</td>
</tr>
<tr>
<td>productivity at high conversion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>maximal chain growth probability</td>
<td>0.94</td>
<td>0.95</td>
</tr>
<tr>
<td>water gas shift reaction</td>
<td>not very significant; more noticeable at high conversions</td>
<td>significant</td>
</tr>
<tr>
<td>$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>maximal sulfur content</td>
<td>&lt;0.1 ppm</td>
<td>&lt;0.2 ppm</td>
</tr>
<tr>
<td>flexibility (temperature and pressure)</td>
<td>less flexible; significant influence of temperature and pressure on hydrocarbon selectivity</td>
<td>flexible; methane selectivity is relatively low even at 613 K</td>
</tr>
<tr>
<td>attrition resistance</td>
<td>Good</td>
<td>not very resistant</td>
</tr>
</tbody>
</table>


1.3.3 Promoter and Support Effects

A broad spectrum of elements has been employed to promote Co FT catalysts. Weckhuysen et al.[90] have summarized and compared the promotion effects of different types of promoters in his review work for cobalt based FT catalysts (Table 1.3).
Table 1.3 Summary of promotion effects of different elements used for the Co based FT catalysts[90].

<table>
<thead>
<tr>
<th>Promotion type</th>
<th>Promotion mode</th>
<th>Activity</th>
<th>Selectivity</th>
<th>Stability</th>
<th>Element reported in literature to play a role in this promotion effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structural</td>
<td>Support stabilization</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>Mg, Si, Zr, Nb, Rh, La, Ta, Re, Pt</td>
</tr>
<tr>
<td></td>
<td>Cobalt gluing</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>B, Mg, Zr</td>
</tr>
<tr>
<td></td>
<td>Cobalt dispersion increase</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>Ti, Cr, Mn, Zr, Mo, Ru, Rh, Pd, Ce, Re, Ir, Pt, Th</td>
</tr>
<tr>
<td>Electronic</td>
<td>Decorating cobalt surface</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>B, Mg, K, Ti, V, Cr, Mn, Zr, Mo, La, Ce, Gd, Th, Ni, Cu, Ru, Pd, Ir, Pt, Re</td>
</tr>
<tr>
<td>Synergistic</td>
<td>Watergas shift</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>B, Mn, Cu, Ce</td>
</tr>
<tr>
<td></td>
<td>Hydrogenation/dehydrogenation</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>Ni, Zr, Gd</td>
</tr>
<tr>
<td></td>
<td>Coke burning</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>Ni, Zr, Gd</td>
</tr>
<tr>
<td></td>
<td>H₂S adsorption</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>B, Mn, Zn, Zr, Mo</td>
</tr>
</tbody>
</table>


Among the oxide promoters, ZrO₂[91, 92], La₂O₃[93, 94], and MnO[95-98] have been most often used. These promoters could modify the porosity and texture of the catalyst, reduce formation of hardly reducible cobalt mixed oxides, increase cobalt dispersion, reducibility, and fraction of different cobalt metal crystalline phases, enhance mechanical and attrition resistance of cobalt FT catalysts, and improve the chemical stability of the support[88]. Mn has been described as a perspective promoter, which
could enhance both the carbon monoxide conversion rate and hydrocarbon selectivity. Using Mn as a promoter for unsupported Co catalyst for FT synthesis was first reported by van der Riet et al.[99] and the authors found the selectivity of C3 hydrocarbons was improved while suppressing the methane productivity. Based on this early research, Hutchings et al.[100] proposed a reaction mechanism of C-C bond formation, which involves α-hydroxylated metal-alkyl as an important intermediate, and the formation of this intermediate involves the coupling of electrophilic and nucleophilic C1 surface intermediates. Zhang et al.[101] found that the addition of small amounts of Mn can improve the dispersion of cobalt metals and the formation of bridged type adsorbed CO is favored. Martinez et al.[102] used SBA-15 silica as a catalytic support to prepare Mn-promoted Cobalt catalysts. It was found that promotion of cobalt with 2 wt% Mn significantly enhanced cobalt dispersion, but decreased its reducibility (Mn can retard the cobalt oxide reduction). The Mn-promoted catalysts were less active (about 2/3 less) than the unpromoted ones. Voβ et al.[103] have investigated the Mn promotion effects over Co/TiO₂ catalyst, and by XPS characterization the authors noticed that the dispersion of Mn is higher than that of Co in the catalyst system, and there was no noticeable Co 2p XPS binding energy shift. The authors also noted the Mn was present as MnO in the reduced catalyst but did not invoke any participation of MnO in the reaction mechanism. Morales et al.[104] found the catalyst preparation methods can have a huge impact on the location of the Mn promoter in the MnCoTiO₂ FT catalysts. Using the IWI synthesis method, was dispersed on the TiO₂ surface as small MnO₂ particles as revealed by the elemental EELS mapping prior to reduction. In contrast, using homogeneous deposition precipitation, the majority of the MnO₂ species were found on top of the Co₅O₄ particles.
These authors also found that based on their EXAFS and STEM-EELS results, after reduction in hydrogen, the Mn promoter might either exist as MnO phase or in the form of Ti$_2$MnO$_4$ which mainly segregated at the exterior surface of the titania support. The authors claimed that the interaction of MnO and metallic Co could induce an electronic promotion to enhance the FT selectivity towards higher hydrocarbons, while the Ti$_2$MnO$_4$ compound only behaved as spectator species. Bezemer et al.[105, 106] studied the promotion effects of MnO over a Co/CNF (carbon nanofiber) FT synthesis catalyst. Their XPS and STEM-EELS results showed that the MnO was in close association with Co species before and after reduction in hydrogen. The authors then tested their catalysts for FT performance at 1 and 20 bar syngas pressure, the reactivity data showed lower MnO loading resulted in a higher TOF value, and at 20 bar reaction pressure, the C$_5^+$ hydrocarbon selectivity was about 78 wt% at a 0.03 wt% MnO loading. However, although the promotion effect of Mn is prominent, many researchers[11, 105-108] have reported Mn promoter can hinder the reducibility of Co species (and metallic Co is considered to be the active phase for FT synthesis) during the reduction process. In this thesis, we applied Mn as a promoter for FT synthesis, and details would be discussed in Chapter 5.

The FT catalytic performance of Cobalt based catalysts is greatly depended on the catalytic support. The primary function of a support in this case is to disperse Co species and to stabilize Co particles. Moreover, a suitable support should also be able to enhance the mechanical properties of Co FT catalysts, because the catalyst solidity is an important concern for slurry FT reactors[109]. Cobalt catalysts are mainly supported on alumina[110, 111], silica[112] or Titania[113] and, more recently, carbons[114]. Reuel et
al. [115] have proposed the following activity trend for Co based FT catalyst as a function of support: Co/TiO₂ > Co/Al₂O₃ > Co/SiO₂ > Co only > Co/MgO. However, Iglesia et al. [116] pointed out that at the reaction condition when the pressure is greater than 5 bar and under high CO conversions, the support would have little influence on the C₅⁺ hydrocarbon selectivity. The strong metal-support interactions (SMSI [117, 118]) can affect the reducibility of the cobalt and for example, in the case of titania supported cobalt catalysts, higher methanation turnover rates was observed because the TiOₓ overlayers were formed during the reduction pretreatments, which influenced CO and H₂ adsorption thermodynamics [119] (the SMSI effect is also shown in Figure 1.10). In addition, being a strong Louis acid [120], titania forms Lewis-acid base complex with adsorbed CO or H₂CO at the metal-support interface, facilitating the breaking of the C=O bond. In this thesis, we chose Titania as the support for the FT thesis work, and will be discussed in details in later chapter.

**Figure 1.10** The strong metal-support interaction effect [90].


In this Chapter 1, a short review and introduction of CO hydrogenation catalysis is discussed. And this thesis will organize as follows. Chapter 2 explains the critical role of STEM-EELS in the elemental analysis of nanostructures.
2. THE APPLICATION OF ELECTRON MICROSCOPY IN CATALYST CHARACTERIZATION

2.0 Transmission and Scanning Transmission Electron Microscopy (TEM/STEM)

Under the condition of sufficient illumination, the smallest distance our human eye can resolve (the distance between two points) is about 0.1~0.2 mm. This distance is defined as the resolution or the resolving power of our eyes. So any instrument that can ‘see’ things better than our eyes (show us pictures revealing detail smaller than 0.1 mm) could be described as a microscope, and its highest useful magnification is governed by its resolution[121]. Figure 2.1 illustrates the size ranges for various types of microscopes and what type of objects that they can image.

Figure 2.1 A comparison of the resolution between the human eye and various types of microscopes, illustrating their vast utility in science. copyright by UIC RRC.
From Figure 2.1, we now have the ability to image objects on the scale of individual atoms using the most powerful transmission electron microscopes (TEM). The TEM is a fascinating instrument because it utilizes electrons to resolve the details of matter. As electrons are smaller than atoms, this tool can be used to help us ‘see’ details well below the atomic level. Here, one must be careful regarding the word ‘see’, as it is the interaction of the electrons with the surrounding matter, such as atoms with a certain fixed pattern, that is converted into an image that is seen by our human eyes. Specifically an electron directed at the object to be imaged will be redirected by its interaction with the object, or will be scattered. Generally speaking, electron scattering is probably the most essential theory behind the microscope. There are several kinds of electron scattering involved in the TEM, in the classical TEM textbook by Williams and Carter[121], the authors summarized the electron scattering in the TEM by the following picture showed here as Figure 2.2.
As has been seen in the above figure, when the sample is thin enough, the coherent incident beam would pass through the sample, and the transmitted beam is subcategorized by direct beam, elastic scattered electrons and inelastic scattered electrons. In elastic scattering, the kinetic energy of a particle is conserved in the center-of-mass frame, but their direction of propagation is modified, so the electron beam in which the incident electrons lost no energy as they traversed the specimen. On the other hand, inelastic scattering is often termed energy-loss scattering and electron beam in which the incident
electrons lost energy as they travelled through the specimen. Simply speaking, the transmitted beam is used for bright field imaging, elastic scattered electrons are used for dark field imaging, and signals generated by inelastic scattered electrons can be used for electron energy loss spectroscopy (EELS), energy dispersive X-ray spectroscopy (EDXS) and so on. One thing we need to be cautious here is that the samples inserted into the TEM have to be thin, so that the electron beam can be forward scattered and be collected as signals on the detector, the thicker the samples are, the less forward scattered electrons we will get, and eventually all the incident beam would become backward scattered electrons. The back scattering phenomenon caused by bulk samples can also be used to generate as microscopy images by using scanning electron microscope (SEM). However, in this thesis, we will focus on TEM imaging.
Figure 2.3 A detailed set up diagram of the JEOL 3010 transmission electron microscope, copyright by JEOL.

Figure 2.3 shows the detailed set up of a transmission electron microscope (specifically that for the JEOL model 3010, other models will have highly similar
configurations). The electrons are first generated by the electron gun on the top, either by thermionic emission or by field emission. Any material will emit electrons when heated to a particular temperature (i.e. the material has sufficient energy to overcome the natural barrier that prevents electrons from leaking out from the surface) W and LaB$_6$ are two major sources of these types of emission. The JEOL 3010 TEM at UIC uses this type of emission. In contrast, field emission relies upon the application of a strong electric field to the gun tip, which is very fine and sharp, to extract electrons from the tip material (typically W). The JEOL ARM-200CF at UIC uses this type of emission. After the electron emission from the electron gun, the electrons are accelerated to obtain certain energy in the acceleration tube (basically an electric field). Then, the electron beams are focused by passing through several magnetic coils (think these coils as lenses in an optical microscope). The intensity of the aligned electron beam can be adjusted by inserting apertures with different sizes. After alignment, the beam would pass the specimen holder where the sample is loaded, and the transmitted beams would then continue traveling through another sets of coils such as objective lens coil and projector lens coil to have the desired magnification and focus. Finally, the scattered beam is captured by detectors and presented as an image in the computer. For a more detailed explanation of the function of the TEM, please refer to Williams and Carter’s *Transmission Electron Microscopy* [121].

The Scanning Transmission Electron Microscope (STEM) is intrinsically operates like a TEM, but there are three major differences. First, unlike a TEM, which uses a static electron beam to probe the samples, a STEM (just its name implies) uses a scanning convergent electron beam to probe the samples. In addition, the probe size of the
convergent beam is generally smaller than TEM, and thus leads to higher resolution. Second, the degree of magnification of a STEM is governed by the size of the scanning area, for example, if the scanned area on the specimen is 1cm×1cm, and the resultant image is displayed on a CRT with an area 10cm×10cm then the magnification is 10×. If the scan dimension is reduced to 1mm, the magnification is 100×. Finally, the STEM collects the high angle scattered electrons to form a dark field image (or Z contrast image[122]) and is also capable of doing bright field imaging, while the TEM normally collects the direct beam to form a bright field image. The principle of the formation of Z contrast imaging (or high angle annular dark field) with the STEM is still based on electron scattering. A highly focused electron beam (convergence angle α ~15-35 mrad) is rastered across the surface of the sample material and the high-angle scattering (40-100 mrad at 200kV) is collected on an annular dark field detector (as depicted in Figure 2.4.). Detecting the scattered intensity at these high angles and integrating over a large angular range effectively averages coherence effects between neighboring atomic column to residual correlations between nearest neighbors[123]. Therefore, in the approximation of large collection angles, each atom can now be considered an independent scatter with scattering cross-sections approaching ~Z², where Z is the atomic number. This cross section effectively forms an objective function that is strongly peaked at the atom sites. The heavier the element, the stronger the electron scattering intensity will be, thus allowing us to see the heavier elements as bright features in the image. However, when there are two elements with similar Z numbers in the same system such as Fe (Z=26) and Co (Z=27), we can actually not distinguish them just from a STEM image. Under such
circumstances, that we employ Electron Energy Loss Spectroscopy (EELS)[124] to aid our analysis.

**Figure 2.4** A brief schematic of STEM operation.

The physical principle behind EELS[124] relates to the interaction of the electrons with the sample to cause either collective excitations of electrons in the conduction band (low loss EELS), or discrete transitions between atomic energy-levels, e.g. 1s-2p transitions (core loss EELS). Here, core loss EELS will be used since the
transitions of highly localized core electrons into unoccupied states above the Fermi level allow the degree of hybridization between atomic orbitals to be determined. A key aspect of this research is the ability to correlate the spectrum with a structural feature image. EELS can provide information about the local electronic environment of the probed atom. This technique will aid in our identification of the location and state of the promoter particularly at the interface with the active metal.

2.1 STEM/EELS Application in Catalysis

In the past, many studies have relied on traditional methods for characterizing catalysts which suffer from an ‘information gap’ between the extensive information that can be extracted from the conventional spectroscopic techniques (without the ability to define and location), and what can be obtained from traditional microscopy techniques (without the ability to characterize composition and bonding). The combination of atomic resolution Z contrast imaging and electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) can directly address these issues by measuring the local changes in atomic structure and correlated them directly with the size and elemental composition of the metal cluster. Here some representative examples of using STEM/EELS to characterize the catalytic properties would be presented.

Wang et al.[125] made catalysts with multi-metallic composition for the oxygen reduction reaction by depositing a monolayer of Pt on Pd or Pd₃Co nanoparticles and characterized the catalysts by the STEM/EELS technique. The authors confirmed that the desired structures had been created by examining the STEM intensity profiles as well as acquiring an elemental map of the clusters (see Figure 2.5). These catalysts showed between 5 and 9 fold enhancements in activity even when compared to slightly smaller
(or higher dispersion) 3 nm Pt nanoparticles. Based on their DFT results, the authors concluded that part of this enhancement was caused by lattice-mismatch induced contraction of the (111) facets.

Figure 2.5 Pt–Pd nanoparticles characterized by STEM, e-chem (particle simulation) and EELS elemental map (right bottom, green is Pt and red core is Pd) [125].


Liu et al. [126, 127] made bimetallic catalysts of 2 wt% Pd and 1wt% Ni supported on TiO$_2$. Figure 2.6a shows a HAADF image revealing a large particle supported on the TiO$_2$ powder. When the 0.2-nm electron probe was placed right on the
edge of the particle (circle 1 in Figure 2.6a), the corresponding EELS spectrum (Figure 2.6b) showed only the presence of Pd without any detectable Ni signal. To verify the finding, the authors performed additional EELS measurements examining the edge regions of the Pd-Ni nanoparticle and from areas just inside the surface of the particle. Two of the spectra are presented in Figure 2.6c of the Pd M-edges and in Figure 2.6d of the Ni L-edges. These spectra demonstrated that the outmost surface layer of the Pd-Ni bimetallic nanoparticle consists of Pd only whereas the inner particles contain both Pd and Ni. The authors also claimed detailed analysis of many EELS spectra obtained from different regions of the nanoparticle can provide information about the thickness of the Pd skin layer and how the composition of the nanoparticle varies with the distance from the edge of the particle. However the authors did not have any EELS elemental map to present a more straightforward ‘grape’ structure of their Pd-Ni catalyst (Pd thin layer as the skin, and bimetallic Pd-Ni as core).
**Figure 2.6** a: HAADF image of a Pd-Ni/TiO$_2$ bimetallic catalyst; b, c, d: EELS spectra obtained from the edge with respect to the different circle numbers (e.g. b: Pd M edge spectra in circle area 1) in the HAADF image[126, 127].


Bezemer et al.[106] investigated the promoter effects of manganese oxide on carbon nanofiber-supported cobalt catalysts for Fischer–Tropsch synthesis. Using STEM-EELS as a characterization tool, the authors demonstrated that the Mn promoter were always closely associated or mixed with Co particles before and after the reduction (Figure 2.7). The authors also explained that in the drying step (catalyst preparation, before reduction), MnO was deposited on the cobalt particles, due to its tendency to form
a stable mixed compound with Co. After reduction, the MnO remained close to the cobalt particles, because the support material lacked sites with significant interaction with MnO.

**Figure 2.7** STEM-EELS characterization of MnCoCNF FT catalysts, A is before reduction and B is after reduction. In the images, from left to right are HAADF image, CNF support, elemental map of Co (yellow) and Mn (red)[106].


In comparison with Bezemer’s, which is described above, Feltes et al.[128] (which stems from our own research group and is the predecessor to the current work) have also investigated the Mn promoted Co catalysts supported on TiO$_2$ (as opposed to
CNF) for Fischer Tropsch synthesis. In this work, Feltes et al. found that while before reduction, the Mn was evenly associated with Co particles (Figure 2.8), after reduction, the Mn promoter tended to migrate towards the metal-support interface. Feltes et al. also speculated that this migration phenomena results from the higher surface free energy of metal-support interface, so MnOₓ migrates off the Co particle towards this interface to lower the total surface free energy of the system. Morales et al.[107] also observed migration of MnOₓ in their promoted FT catalysts (also Mn/Co/TiO₂). From their STEM-EELS results, the authors demonstrated before calcination, MnOₓ species were located preferentially with the Co₃O₄ particles. It appears as if a mixed compound between Co and Mn (Mn^{n+} cations are likely to replace either the octahedral or tetrahedral sites in the Co₃O₄ structure, leading to the formation of a mixed spinel compound of the type MnₓCo_{3-x}O₄) was formed and/or that MnOₓ species cover the surface of Co₃O₄. After reduction and passivation, Mn is no longer mixed with the Co⁰ particles. Instead, the MnO is dispersed over the TiO₂ support and is concentrated close to the Co⁰ particles. The authors also concluded under certain conditions, the Mn promoter would migrate to reach a more energetically favorable state.
Figure 2.8 EELS elemental maps (Blue–Ti, Red–Co, Green–Mn) for the Mn_{SEA}/Co/TiO_{2} catalyst (a) calcined and (b) reduced [128].


In this thesis, we will heavily utilize the STEM-EELS characterization for our CO hydrogenation catalysts (for both alcohol synthesis and FT synthesis) in order to exploit how the degree of metal-promoter interactions would affect the catalytic reactivity. Detailed work will be presented in following chapters.
3. SELECTIVE ADSORPTION OF MANGANESE ONTO RHODIUM FOR OPTIMIZED ALCOHOL SYNTHESIS CATALYSTS

3.0 Introduction

Ethanol is one potential alternative synthetic fuel for use in automobiles, and the use of ethanol as a gasoline additive is already in practice both in the U.S. and internationally. Renewable ethanol can also serve as a feedstock for the synthesis of variety of industrial chemicals and polymers[19]. However, traditional fermentation routes to alcohols are often slow and inefficient. In addition, using crops for fuel grade alcohol production is controversial due to doubts about its overall energy efficiency and its effect on food prices[23].

Several previous studies show that ethanol can be produced from syngas hydrogenation over various kinds of supported metal catalysts, such as Co[129, 130], Cu[131], and Pd[132]. However, among late d-band transition metals, rhodium has been shown to be the best metal for selective conversion of syngas to oxygenated products like alcohols[45, 46, 57]. It appears that Rhodium’s unique activity for oxygenates products likely stems from the intermediate position of its d-electron relative to metals that do not dissociate CO (Ir, Pd, Pt) and thus favor methanol production and those which easily dissociate CO under reaction conditions (Co, Fe) and, therefore, favor production of higher hydrocarbons[47-49]. However, the majority of CO hydrogenation studies using unpromoted Rh have observed a strong selectivity for methane with minimal selectivity to oxygenates[26, 31]. It is now well established that the addition of promoters as additives will greatly improve the catalytic performance of Rh catalysts resulting in moderate selectivities for specific oxygenates such as ethanol[61, 62, 77]. In this work,
we focus on one such promoter, Mn, to examine if a better, more intimate promoter-metal interaction can increase the rate and selectivity for higher alcohol production.

Among the most common methods in producing the promoted catalyst is impregnation of the promoter, which can be classified as dry (incipient wettess) or wet impregnation. In incipient wettess impregnation (IWI), a sufficient amount of metal solution is added to just fill the pore volume of the catalyst support or supported catalyst. However, this often results in poor to moderate interaction between active metal and promoter because the promoter will be randomly distributed across the surface of the support. Therefore, a key design objective is to increase the promoter–metal interaction to maximize its effectiveness. One possibility for potential improvement of the promoter–metal interaction is the use of the strong electrostatic adsorption (SEA) method, which has been refined by Regalbuto et al.[3, 7] following Schwarz’s original proposal about the electrostatic interactions between a metal ion and a charged support[9, 10]. The method of synthesis relies upon the naturally occurring hydroxyl groups (-OH) on the oxide surfaces that can become protonated or deprotonated when the contacting solution is acidic or basic, respectively. The density of the charged hydroxyl groups on the oxide at a given pH depends on its point of zero charge (PZC, the pH at which the hydroxyl groups remain neutrally charged). Metal oxides with a basic PZC (such as Al₂O₃, its PZC is ~8.5) will have greater density of protonated hydroxyl groups (-OH₂⁺) than metal oxides with a acidic PZC (such as TiO₂, its PZC is ~3.7) in acid environment (solution) and will adsorb anionic complex or metal precursor and vice versa. This can be expanded to preferential adsorption of a promoter on the metal oxide of the active metal at a pH at which it will not adsorb substantially on the support. In this study, MnO₄⁻ is selectively
adsorbed on Rh$_2$O$_3$, which has a high PZC (~8.75) under acidic pH in the presence of the SiO$_2$ support, which has a low PZC (~4). A schematic of the process is depicted in Figure 3.1.

![Schematic Diagram](image)

**Figure 3.1** Schematic shows the selective adsorption of Mn promoter onto supported rhodium catalysts in acidic solution.

In the subsequent characterization, STEM and electron energy loss spectroscopy (EELS) were employed to observe the degree of metal–promoter interaction. In addition, X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) methods were used to investigate the information on the oxidation state and local geometry around the atom. Temperature-programmed reduction (TPR) was also used to study the reduction behavior of the promoted catalysts. Finally, the catalysts were tested in a plug flow reactor to determine the catalytic performance, that is, the rate and product selectivity. The results demonstrate higher ethanol selectivity with increasing metal–promoter interactions.
3.1 Experimental

3.1.1 Adsorption Experiments

The supported Rh$_2$O$_3$ on SiO$_2$ (Aerosil 300, BET surface area= 330m$^2$g$^{-1}$, pore volume=2.7mLg$^{-1}$, the BET data was measured on a Micromeritics ASAP 2020 at liquid nitrogen temperature by N$_2$ adsorption) was synthesized through IWI method by using rhodium nitrate, Rh(NO$_3$)$_3$ (Sigma–Aldrich, 10% Rh in > 5 wt% HNO$_3$). The precursor was dissolved in deionized water and then added drop wise to impregnate the support. The weight loading of Rh was controlled as 3wt%. The catalyst was dried in air at RT for 24 h followed by calcination at 500°C for 4 h (5°C min$^{-1}$ ramp) to convert the rhodium nitrate into rhodium oxide, Rh$_2$O$_3$. The PZC of SiO$_2$ was determined by measuring the equilibrium pH at a high oxide surface loading (10,000 m$^2$ L$^{-1}$) after SiO$_2$ has been in contact with solutions of varying initial pH, the resulting PZC of SiO$_2$ was 4. Owing to the expense of pure Rh$_2$O$_3$, the PZC and [MnO$_4$]$^-1$ uptake experiments had to be modified. The PZC of Rh$_2$O$_3$ was determined by single point analysis from 1g Rh$_2$O$_3$5H$_2$O (99.99%, Alfa Aesar) that was calcined at 350°C for 4h followed by copious washing in 0.01m HNO$_3$ and deionized water to remove any impurities. The resulting PZC=8.75 was measured using an Accumet spear-tip electrode at the point of incipient wetness with deionized water (pH$_i$ = 6.0).

Equilibrium adsorption experiments of the promoter were performed at a surface loading of 1000 m$^2$L$^{-1}$ in excess liquid to prevent large shifts in the solution pH caused by the oxide buffering effect[133]. The pH-adjusted solutions of KMnO$_4$ were contacted with SiO$_2$, and Rh$_2$O$_3$/SiO$_2$, and shaken for 1 h on a shaking bed, after which approximately 8mL of filtered solution were analyzed for Mn concentration by using a
PerkinElmer Inductively Coupled Plasma–Optical Emission Spectrometer (ICP–OES). Mn uptake was determined as the difference in concentration between the pre- and post-contacted solutions (in both adsorption experiments, the surface loading was controlled as 1000 m$^2$L$^{-1}$, and a 200 mgL$^{-1}$ Mn, permanganate solution was used). After the determination of the optimal uptake pH, the 3%Rh$_2$O$_3$/SiO$_2$ catalyst was loaded with 1wt% of Mn according to the adsorption experiments described above by using solutions with various pH and KMnO$_4$ as metal precursor. After filtration, the catalyst was dried overnight in the air at RT and then calcined at 350°C for 4 h. For the purpose of comparison, 1 wt % Mn using Mn(NO$_3$)$_2$ as the precursor was also put onto the 3 %Rh/SiO$_2$ catalyst by the IWI method.

3.1.2 Characterization

Scanning transmission electron microscopy (STEM) imaging was performed by using an aberration-corrected, cold-field emission gun microscope, JEOL JEM-ARM200CF, equipped with a post-column electron energy loss (EEL) spectrometer, and operated at 200 keV primary energy (See Figure 3.2). For high-angle annular dark-field imaging (HAADF), a spatial resolution of more than 70 pm can be achieved (as shown in Figure 3.3), whereas the energy of 350 meV is possible for EEL spectroscopy. Herein, we used HAADF imaging to determine the particle size distribution. The chemical composition of the catalyst particles was determined by using EELS spectrum imaging combined with mass contrast signals.
Figure 3.2 JEOL JEM-ARM200CF Scanning Transmission Electron Microscope equipped at UIC RRC.
**Figure 3.3** Atomic-resolution Z-contrast image of Si (110) clearly showing the Si dumbbell structure.

Transmission X-ray absorption spectroscopy (XAS) of the Rh K-edge of the in-situ reduced Rh/SiO₂ series catalysts were measured at Argonne national Laboratory’s (Argonne, IL) Advanced Photon Source (APS) on the Materials Research Collaborative Access Team’s (MRCAT) bending magnet beamline in sector 10-BM (Figure 3.4 showed a bird view of Argonne APS synchrotron). Catalysts samples were pressed into an in-situ cell and reduced at 210°C in H₂. After cooling to RT, the sample chamber was filled with He prior to measurements. The data fitting was done with the software WinXAS 97, version 3.0. A Rh foil was used as a reference for both XANES and EXAFS fitting (N_Rh= 12 which is the coordination number, and R= 2.69Å which is the bonding distance).
Figure 3.4 The Argonne Advanced Proton Source (APS) synchrotron radiation facility.

Temperature-programmed reduction (TPR) experiments were performed on a Micromeritics Autochem 2920 using a thermal conductivity detector (TCD) detector. After baseline stabilization, the reduction was performed in a 10% H₂/Ar flow at a heating ramp of 10°C min⁻¹.

3.1.3 CO Hydrogenation Reaction

Alcohol synthesis reactions of the SiO₂-supported Rh catalysts were investigated under isothermal plug flow conditions achieved by diluting the catalyst (0.15 g) with SiC (0.3 g, 70 mesh) in a half-inch diameter stainless steel reactor. Catalysts were reduced prior to reaction for 1 h at 300°C in H₂ (15% H₂ balanced in Ar). Reactions were performed at 20 bar, 285°C and a syngas flow ranging from 15 mLmin⁻¹ to 110 mLmin⁻¹ to compare the catalytic performance of all the catalysts at different CO conversions. The syngas feed had a composition of 32% CO, 64% H₂ (a 1:2 CO:H₂ ratio) and 4% N₂ as an
internal standard. The catalyst bed temperature was monitored by a thermocouple inserted within the catalyst bed. The reaction results reported here were generally obtained after 6 h reaction on-stream. A HP 6890 gas chromatograph equipped with one flame ionization detector (FID) and a TCD was integrated down-stream of the reactor to analyze the reaction products. A 30 m by 0.32 mm ID HP-Wax bonded polyethylene glycol capillary column (made by Restek) was used for analysis of the organic products (i.e., ethanol, acetaldehyde, propanol, acetic acid, etc.) through FID. Light inorganic gases (H₂, CO, CO₂, N₂, etc.) and methane as well as light hydrocarbons were separated on packed columns and quantified with TCD. The schematic chart of the reactor set up is presented here as Figure 3.5.

![Figure 3.5 CO hydrogenation reaction reactor configuration.](image-url)
3.2 Results and Discussion

3.2.1 Permanganate Adsorption

The permanganate adsorption results are shown in Figure 3.6. The data reveal that the amount of permanganate adsorbed onto SiO$_2$ support (PZC determination of SiO$_2$ is shown in Figure 3.7) was negligible in the uptake survey pH range. In comparison, if rhodium oxide (Rh$_2$O$_3$) was present on silica support, a considerable amount of Mn was absorbed on to the catalysts at acidic pH.

![Figure 3.6 Permanganate adsorption survey on pure SiO$_2$ support (black dot ●) and SiO$_2$ supported Rh$_2$O$_3$ (red square ■).](image-url)

Figure 3.6 Permanganate adsorption survey on pure SiO$_2$ support (black dot ●) and SiO$_2$ supported Rh$_2$O$_3$ (red square ■).
Figure 3.7 PZC determination results of SiO$_2$ at a surface loading of 10,000 m$^2$L$^{-1}$.

This experimental observation is consistent with the previous results of Feltes et al.\cite{11} who observed Mn uptake on TiO$_2$-supported Co catalysts using the same strategy of preferential adsorption (the PZC of TiO$_2$ is 3.7, the PZC of Co$_3$O$_4$ is 8). Specifically, at an initial pH of 1 the maximum Mn uptake on 3%Rh/SiO$_2$ is about 3 mmolL$^{-1}$ (~4.5 wt% loading) and 1 wt% (0.67 mmolL$^{-1}$) Mn uptake occurred if the initial pH was shifted to 2.3. Moreover, at extremely low pH, both the pre- and post-concentrations of permanganate solution decreased dramatically after a certain time and the concentration difference in between the pre- and post-solutions was almost zero. This observation implies that redox reactions occurred at extremely low pH (below pH 0.5), the speciation of KMnO$_4$ occurs in an acidic solution through the following pathways [Eqns. (1) and (2)]:

\[
\text{MnO}_4^- + 8\text{H}^+ + 5\text{Cl}^- \rightarrow \text{Mn}^{2+} + 2.5\text{Cl}_2 + 4\text{H}_2\text{O} \quad (1)
\]

\[
\text{MnO}_4^- + 4\text{H}^+ + 3\text{Cl}^- \rightarrow \text{MnO}_2 + 1.5\text{Cl}_2 + 2\text{H}_2\text{O} \quad (2)
\]
If the initial pH dropped below 0.5, precipitation of a brown solid (MnO$_2$) was observed and therefore catalyst synthesis at these conditions was avoided.

In comparison with Mn promotion of Co/TiO$_2$ Fischer–Tropsch catalysts[11], there were similar trends for Mn adsorption onto the catalysts: there was almost no Mn uptake onto pure titania support, but if Co oxide was present in the catalyst, significant uptake was observed between pH 0.5 and 2.5. The Mn uptake reached a maximum at a pH of approximately 1, just as we observed in the MnRh/SiO$_2$ system presented here.

3.2.2 Characterization of Mn-promoted Rh-based alcohol synthesis catalysts

Ertl et al.[134] proposed a maximum in the CO dissociation rate was reached in particles of approximately 3–4 nm, particles smaller or larger would lead to lower dissociation rate. As the synthesis of larger hydrocarbons (i.e., C$_x$H$_y$O$_z$; x>1) in the CO hydrogenation reaction requires an initial CO dissociation before catalysis can proceed, it is implied that this same particle size should maximize the reaction rate. Previously, Hanaoka et al.[135] have studied the effect of Rh particle size on CO hydrogenation products over Rh/SiO$_2$ catalyst. The authors found that as the Rh particle size increased, the overall products (oxygenates, hydrocarbons, etc.) from dissociated CO increased, but the portion of C$_2$ oxygenates decreased. A good balance in between these two functions can be achieved in a particle size range of approximately 3 nm. Therefore, we aimed at a particle size of approximately 3 nm in this study.

The dark-field STEM imaging of Mn-promoted Rh catalysts on SiO$_2$ are shown in Figure 3.8. The Rh particles exhibited small particle sizes. The particle size distribution
analysis is shown in Figure 3.9 with an average particle size of the catalyst promoted by SEA of 2.8±0.5 nm.

Figure 3.8 High resolution dark-field STEM imaging of 1 %MnSEA3%Rh/SiO₂ catalyst.

Figure 3.9 Particle size distribution of 1 %MnSEA3%Rh/SiO₂ catalyst, note that the particle sizes distribution chart here was made by analyzing multiple dark field images similar to the image shown above.
In addition to STEM imaging, EXAFS was used to confirm the average particle size. The magnitude of the Fourier transform of the EXAFS spectra of the Rh catalysts are plotted in Figure 3.10 along with that of a Rh foil as a reference. All three samples have a large central peak at approximately 2.5 Å with a smaller shoulder at approximately 1.8 Å indicating that the particles are metallic. In Table 3.1, we summarize the average particle sizes obtained by EXAFS and STEM for our promoted and unpromoted catalysts. The similarity of the EXAFS data indicated that the average Rh particle size of the three catalysts is very close and the estimated size from the coordination number is approximately 2–3 nm, consistent with the STEM particle size and close to the optimal size reported in Ertl et al.’s work[134]. The Rh catalysts promoted by the SEA method are slightly larger than those promoted by the IWI method from both the EXAFS and STEM results even though the Rh particles were the same size prior to promotion. The unpromoted Rh catalyst has an average size determined by EXAFS of 3.2±0.3 nm, which is almost the same as the average size for the catalyst promoted by the SEA method (~2.8 nm), but bigger than the one promoted using the IWI method (~1.9 nm). The reason for this is likely owing to the fact that the solution environments were different during promoter preparation (SEA was performed in acidic solution and IWI in deionized water) and therefore some redistribution of the metal may occur leading to different particle sizes. In summary, the particle sizes we obtained from EXAFS data, which represent the bulk average, are in agreement with the sizes we observed from the STEM data, which show the particle size distribution on a local scale.
Figure 3.10 Magnitude of the Fourier Transform of the EXAFS \( (k^2 = 2.5-12.5 \text{ Å}^{-1}) \) of Rh species present in the 3wt%Rh/SiO\(_2\) series of catalysts plotted with appropriate standards. In the plot the green is Rh foil, Red is 3%Rh/SiO\(_2\), Blue is 1%Mn\(_{\text{SEA}}\)3%Rh/SiO\(_2\), and black is 1%Mn\(_{\text{IWI}}\)3%Rh/SiO\(_2\).

Table 3.1 Particle size distribution of catalysts obtained by EXAFS and STEM.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Coordination Numbers[^{[a]}]</th>
<th>Bond Distance[^{[a]}]</th>
<th>(\sigma)^[^{[b]}]</th>
<th>Particle size by EXAFS (nm)</th>
<th>Particle size by STEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%Mn(_{\text{SEA}}) 3%Rh/SiO(_2)</td>
<td>7.6</td>
<td>2.68 Å</td>
<td>0.001</td>
<td>2.8±0.3</td>
<td>2.8±0.5</td>
</tr>
<tr>
<td>1%Mn(_{\text{IWI}}) 3%Rh/SiO(_2)</td>
<td>6.5</td>
<td>2.67 Å</td>
<td>0.001</td>
<td>1.9±0.2</td>
<td>2.0±0.4</td>
</tr>
<tr>
<td>3%Rh/SiO(_2)</td>
<td>8.2</td>
<td>2.69 Å</td>
<td>0.001</td>
<td>3.2±0.3</td>
<td>2.7±0.5</td>
</tr>
</tbody>
</table>

\[^{[a]}\] Value obtained from EXAFS data fitting; \[^{[b]}\] Disorder in the neighbour distance in EXAFS data fitting

EELS mapping has previously been used to analyze the distribution of the promoter phase on the catalyst surface\[^{[13]}\]. In Figure 3.11, we show the EELS mapping of Mn-promoted Rh/SiO\(_2\) catalysts (by SEA and IWI), the Mn K-edge energy loss signal
is used to locate the Mn composition, O K-edge energy loss signal is used to locate the support position, and the mass contrast imaging was used for Rh signals, because the Rh K-edge signal is not sufficient for EELS spectrum image analysis. As seen in Figure 3.11(a) for IWI samples, the promoter is not strongly associated with the metallic Rh particle, which is not surprising because through the IWI preparation method the Mn promoter was deposited randomly onto the catalyst without any special attraction with the Rh metal. On the other hand, the EELS mapping of our SEA-promoted catalyst (Figure 3.11b) exhibited a greater degree of promoter–active metal interaction, which is consistent with our initially proposed schematics (Figure 3.1) in catalyst preparation by the SEA method to achieve the selective Mn adsorption onto the Rh metal. In other words, this result suggests the creation of intimate interactions between Rh and Mn, which is believed to be the active sites for alcohol synthesis reaction, if we selectively directed the Mn promoter onto the supported Rh catalysts.
Figure 3.11 EELS elemental mapping of (a)1%MnIWI3%Rh/SiO₂ catalyst exhibiting intimate promoter–active metal interactions and (b)1%MnSEA3%Rh/SiO₂ catalyst. ■: Mn, ■: Rh, ■: silica.

XANES measurements after in situ reduction at 210°C reveal spectra (Figure 3.12) characteristic of metallic Rh for all the catalysts. Rh foil and rhodium oxide were used as standard references. Therefore, we can conclude that no matter how we add the promoters to the Rh catalysts, the Rh oxide present in the unreduced catalyst is reduced to metallic Rh after reduction. However, as shown by TPR, the reduction behaviors of IWI- and SEA-promoted catalysts are different.
Figure 3.12 XANES spectrum of Rh K-edge of 1 wt % Mn promoted 3 wt % Rh/ SiO2 catalysts plotted with appropriate standards: Rh$_2$O$_3$ reference (----), 1%Mn$_{\text{SEA}}$3%Rh/SiO$_2$ catalyst (—), 1%Mn$_{\text{IWI}}$3%Rh/SiO$_2$ catalyst (—), 3%Rh/SiO$_2$ catalyst (—), and Rh foil reference (—).

The TPR results for these catalysts are plotted in Figure 3.13. At first glance, the major reduction for unpromoted Rh/SiO$_2$ was observed at around 50°C, which corresponds to the reduction from Rh$_2$O$_3$ to metallic Rh. The low reduction temperature of rhodium oxide is consistent with that reported elsewhere[136]. For both the Mn-promoted Rh catalysts (those prepared by both IWI and SEA methods), Rh is completely reduced at low temperature, although the IWI-prepared catalyst has a slightly higher reduction temperature than the SEA-prepared catalyst. The TPR spectrum for the SEA prepared catalyst also exhibits a minor peak at approximately 200°C. This small peak at 200°C likely stems from the reduction of manganese oxide from a higher oxidation state.
(MnO₂) to a lower oxidation state (most likely MnO, as Mn₂O₃ is very unstable). Reduction to metallic Mn requires a reduction temperature above 1000°C[137], so the formation of metallic Mn (which could alloy with Rh) is highly improbable and the Rh EXAFS spectra (Figure 3.10) do not indicate the presence of the bimetallic RhMn nanoparticles either. In the case of the promoted catalyst prepared by use of IWI to deposit Mn, we see the major reduction temperature shift to a higher temperature (100°C), and the H₂ consumption decreased. This observation indicates that the way Mn interacted with Rh by IWI method makes it more difficult for Rh to be fully reduced. In other words, depositing promoters by SEA appears to have resulted in a higher degree of dispersion of the Mn species.

![Figure 3.13 TPR results of the 3%Rh/SiO₂ catalyst (---), 1%MnSEA3%Rh/SiO₂ catalyst (---), and 1%MnIWI3%Rh/SiO₂ catalyst (---).](image)

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3.2.3 Alcohol Synthesis Reactivity Results

The catalytic data is summarized in Table 3.2. Consistent with previous reactivity results, the unpromoted Rh/SiO\textsubscript{2} catalyst does not produce any oxygenates (including ethanol). The selectivity to higher hydrocarbons (the reaction produced 30% methane and 70% light hydrocarbons) was higher than that typically reported by Burch et al.\cite{57}. For example, they tested a 2\%wt Rh supported on silica catalyst for CO hydrogenation at 20 bar, 270°C and a 1:1 syngas ratio, and obtained a methane selectivity of 48\%, a light hydrocarbon selectivity of approximately 22\%, and the remaining 30\% share of the products contained primarily acid and acetaldehyde (which we did not observe in the products). The reaction pressure and temperature were almost identical to those in our system, but their H\textsubscript{2}/CO ratio of 1:1 decreased the amount of H\textsubscript{2} available and increased the CO partial pressure, which could shift the product distribution. In recent work by Haider et al.\cite{67} a 2 wt\% Rh catalyst supported on silica tested for CO hydrogenation at 20 bar, 300°C, and a 1:1 syngas ratio, gave a 51\% selectivity towards methane, and a light-hydrocarbon selectivity of approximately 47\% with no other products reported. In general, our result is consistent in product distribution with that by Haider et al. (only methane and light hydrocarbon were detected).

Both promoted catalysts produced ethanol as well as acetaldehyde, methane, C\textsubscript{3+} light hydrocarbons, acids, and C\textsubscript{3+} oxygenates. The SEA-promoted catalysts exhibited significantly higher (~3–4 times) ethanol selectivity than the IWI-promoted catalyst at each CO conversion (this trend is also presented in Figure 3.14). Moreover, at high CO conversion (>25\%) both the SEA and IWI promoted catalysts began to produce other products such as propanol, ethane, propylene, and CO\textsubscript{2}, which are not reported in Table
3.2. For example, at 40% CO conversion, the total production of these miscellaneous products summed to 5% for the SEA-prepared catalyst whereas these products amounted to 25% of the total products for the IWI-prepared catalyst.

Table 3.2 CO hydrogenation reactivity data of the promoted and unpromoted Rh/SiO₂ catalysts, reactions were performed at 20 bar, 285 °C and 2:1 H₂:CO syngas ratio.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO Conv. [%][a]</th>
<th>TOF s⁻¹[b]</th>
<th>E [a, c] %</th>
<th>A [a, d] %</th>
<th>M [a, c] %</th>
<th>L [a, f] %</th>
<th>O [a, g] %</th>
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</thead>
<tbody>
<tr>
<td>3%RhSiO₂</td>
<td>4.3</td>
<td>0.012</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>70</td>
<td>-</td>
</tr>
<tr>
<td>1%MnSEA</td>
<td>6.8</td>
<td>0.082</td>
<td>19.1</td>
<td>15.2</td>
<td>41.0</td>
<td>4.8</td>
<td>20.0</td>
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<tr>
<td>3%RhSiO₂</td>
<td>8.3</td>
<td>0.078</td>
<td>18.0</td>
<td>12.5</td>
<td>40.3</td>
<td>5.8</td>
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<td>11.0</td>
<td>0.085</td>
<td>18.0</td>
<td>10.0</td>
<td>44.1</td>
<td>6.6</td>
<td>21.9</td>
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<td>0.074</td>
<td>20.4</td>
<td>8.7</td>
<td>37.0</td>
<td>6.4</td>
<td>27.6</td>
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<td>0.080</td>
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<td>6.8</td>
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<td>0.080</td>
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<td>0.076</td>
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<td>3.9</td>
<td>50.2</td>
<td>1.6</td>
<td>18.1</td>
</tr>
<tr>
<td>1%MnIWI</td>
<td>7.5</td>
<td>0.058</td>
<td>4.8</td>
<td>8.4</td>
<td>17.5</td>
<td>51.2</td>
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</tr>
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<td>3%RhSiO₂</td>
<td>8.8</td>
<td>0.056</td>
<td>5.3</td>
<td>8.4</td>
<td>19.9</td>
<td>49.2</td>
<td>17.3</td>
</tr>
<tr>
<td></td>
<td>10.8</td>
<td>0.057</td>
<td>4.5</td>
<td>7.5</td>
<td>20.6</td>
<td>50.6</td>
<td>16.9</td>
</tr>
<tr>
<td></td>
<td>14.5</td>
<td>0.054</td>
<td>5.8</td>
<td>7.6</td>
<td>23.6</td>
<td>46.5</td>
<td>16.6</td>
</tr>
<tr>
<td></td>
<td>19.0</td>
<td>0.057</td>
<td>6.0</td>
<td>7.6</td>
<td>23.2</td>
<td>46.9</td>
<td>16.4</td>
</tr>
<tr>
<td></td>
<td>27.0</td>
<td>0.061</td>
<td>5.6</td>
<td>3.6</td>
<td>16.7</td>
<td>28.9</td>
<td>33.0</td>
</tr>
<tr>
<td></td>
<td>42.0</td>
<td>0.063</td>
<td>5.0</td>
<td>2.5</td>
<td>20.5</td>
<td>18.8</td>
<td>28.5</td>
</tr>
</tbody>
</table>

[a] The CO conversion were calculated by using Nitrogen gas as the internal standard, and follow the following equation:

\[
\text{%CO Conversion} = \frac{(M_{\text{CO feed}} - M_{N2 feed})}{M_{N2 product} \cdot M_{\text{CO product}}} \times 100\%
\]

The selectivity to product \(i\) is based on the total number of carbon atoms among the total products and is defined as:

\[
\text{%Select}_i = \frac{\sum n_i \cdot M_i}{(\sum n_i \cdot M_i)} \times 100\%.
\]

\(n_i\) is the carbon atoms number, \(M_i\) is the mole percent of product \(i\) detected downstream;

[b] The TOF is calculated as the active sites per second of 1g Rh, the Rh particles were assumed semispherical shape with radius obtained from EXAFS size, the Rh atoms were assumed closed packed cluster (diamond)
with distance obtained from EXAFS bonding distance;

\( ^c \) Selectivity for ethanol;
\( ^d \) Selectivity for acetaldehyde;
\( ^e \) Selectivity for methane;
\( ^f \) Selectivity for light hydrocarbons \( \text{C}_{3+} \);
\( ^g \) Selectivity for Acetic acids and \( \text{C}_{3+} \) Oxygenates.

**Figure 3.14** Ethanol selectivity comparison at various CO conversion points for the 1%Mn\textsubscript{SEA}3%Rh/SiO\textsubscript{2} catalyst (red dots ●) and 1%Mn\textsubscript{IWI}3%Rh/SiO\textsubscript{2} catalyst (black squares ■).

The improvement in selectivity for the SEA-promoted catalyst over the IWI-promoted catalyst suggests that more intimate interaction of the Mn promoter with Rh increases the higher-alcohol selectivity. This is consistent with the previous proposal that the active sites for the CO hydrogenation to higher alcohols reaction are located at the interface of the active metal and the promoter[77]. In our catalysts synthesis, such an
intimate promoter–active metal interactions have been created by the SEA method so that there should be many more active sites available than for the catalysts prepared by the IWI method. The SEA catalyst also has a higher TOF than the IWI catalyst, which further indicates that stronger promoter–active-metal interactions improve the reaction rate for CO hydrogenation. From Table 3.2, it is observed that at lower conversion range (<10%) higher concentrations of acetaldehyde are produced (see this trend in Figure 3.15), which suggests that the acetaldehyde has not been fully hydrogenated to ethanol, and acetaldehyde is likely an intermediate product. If we take the ratio of ethanol/acetaldehyde for the two promoted catalyst at various CO conversion, there is always a higher ethanol/acetaldehyde ratio observed for the SEA-promoted catalysts suggesting Mn promotes the hydrogenation rate to give more ethanol.

**Figure 3.15** Acetaldehyde selectivity comparison at various CO conversion points for the 1%MnSEA3%Rh/SiO2 catalyst (red dots ■) and 1%MnIWI3%Rh/SiO2 catalyst (black squares ■).
However, the SEA-promoted samples also produced approximately 20% more methane, which is the primary unwanted byproduct for this reaction; and the IWI-promoted samples, on the other hand, produced higher amounts of C$_3$+ light hydrocarbons (~40% more). The IWI-promoted catalyst prevented the complete hydrogenation of the dissociated CO to form large quantities of methane just like SEA-promoted catalyst did during the reaction process, but instead allowed more carbon insertion to form C$_3$+ light hydrocarbons. In addition, both kinds of the promoted catalysts produced noticeable amount (~15–30%) of acids and some higher oxygenates (primarily acetic acid). In the work by Hu et al.[61] on CO hydrogenation reaction by using a Mn-promoted Rh catalyst supported on silica, at 39% CO conversion their primary products were ethanol (~54% selectivity) and methane (~40% selectivity). In addition, they produced trace amounts of CO$_2$, methanol, and C$_3$+ light hydrocarbons but did not quantify the formation of individual products such as ethane, and propane. The temperature in their reaction is similar (280°C) to that used in the current study, but Hu et al. used a much higher pressure at 5.4 MPa (54 bar). In comparison, at a CO conversion of 45 %, our major products from the SEA-promoted catalyst looked very similar to the products distribution from Hu et al. with major products as ethanol (14%) and methane (50%) and trace amounts of CO$_2$, propanol, and C$_3$+ light hydrocarbons. The SEA-promoted catalyst also produced significant amounts of acetic acid and C$_3$+ oxygenates (25%), which were not seen in Hu et al.’s work. The higher alcohol production is likely a result of the much higher pressure used in their work and which likely leads to higher CO coverage on the catalytic surface. However, the authors did not report their reaction products at low CO conversion. In contrast, Hanaoka et al.[135] studied the CO hydrogenation (260°C, 20
bar, and 1:1 CO/H$_2$ syngas ratio) by using Mn-promoted Rh/SiO$_2$ (1:1 Mn/Rh molar ratio, 1 wt% Rh) catalyst at low CO conversion (0.5%) with product distribution approximately 13% selectivity towards ethanol, approximately 43% to methane, approximately 9% to methanol, approximately 23% to acetic acid, and approximately 36% to C$_2$ oxygenates. Comparing these results to our results at low CO conversion, our SEA catalyst gave higher selectivity to ethanol production, and produced approximately the same amount of methane and acetic acid. Unlike Hanaoka et al. we did not observe any methanol formation but instead formation of noticeable amounts of light hydrocarbons (5%) and acetaldehyde (15%). Most recently, Huang et al.[138] found that very high selectivity to C$_{2+}$ oxygenates with a maximum of 74.5% at 270°C and 30 bar total pressure (1:2 CO:H$_2$) ratio could be achieved for Mn-promoted Rh nanoparticles encapsulated in a mesoporous silica nanoparticle framework (1.6 wt% Rh, 0.8 wt% Mn). Similar to our SEA-promoted catalyst, the primary C$_{2+}$ products were acetaldehyde and ethanol and neither methanol nor CO$_2$ was observed. The selectivity to methane reported by Huang et al. is lower than that presented here (only 25% as opposed to 40% at 10% conversion), but this may be a result of the higher pressure used by Huang et al., because this is also known to improve oxygenate selectivity and reduce methane production[31, 66, 72]. Although the synthesis strategy is different, Huang et al. note that the improved selectivity is tied to an intimate relationship between the Rh nanoparticles and Mn promoter.

3.3 Conclusion

Herein, Mn was selectively deposited by strong electrostatic adsorption (SEA) onto Rh oxide, which upon reduction created an intimate promoter–active-metal
interaction in the catalyst. By means of various characterization methods and CO hydrogenation reaction tests, the method of promoter addition was shown to be critical to the catalyst performance, because Mn-promoted Rh catalysts using the SEA method to add the Mn promoter were vastly more ethanol-selective than those using incipient wetness impregnation (IWI) to add Mn. Therefore, one can conclude that it is critical for targeted alcohol production to create a strong interaction between the active metal and promoter. Higher alcohol synthesis catalysts can be prepared by controlling the charging parameters of the active metal and support to selectively direct the promoter onto the active metal to achieve this intimate interaction. Furthermore, the selective adsorption method can be applied on other supports (TiO$_2$, Al$_2$O$_3$, etc.) and other promoters (V, La, etc.) to achieve the ideal metal–promoter interactions. For example, one can utilize the point-of-zero-charge difference between TiO$_2$ (~5) and Rh$_2$O$_3$ (8.75) to direct any anionic precursor onto the Rh metal and enhance the metal–promoter interaction (See Figure 3.16 for the preliminary permanganate adsorption results onto RhTiO$_2$ catalysts). Thus, significant potential exists for improvement of catalyst selectivity.
Figure 3.16 Preliminary Mn Uptake Survey on pure TiO$_2$ support (black dot ●) and TiO$_2$ supported Rh$_2$O$_3$ (red square ■).
4. CORRELATING THE DEGREE OF METAL-PROMOTER INTERACTION TO ETHANOL SELECTIVITY OVER MANGANESE PROMOTED RHODIUM CATALYSTS ON CARBON NANOTUBES

4.0 Introduction

Rhodium has been shown to be active for ethanol synthesis from syngas (CO, H₂ mixture gas) [26, 31, 57, 139, 140]. It has been suggested that Rhodium’s unique activity for oxygenates products stems from its intermediate position in the periodic table between metals which do not dissociate CO (Ir, Pd, Pt) and thus favor methanol production and those which easily dissociate CO under reaction conditions (Co, Fe) and therefore favor production of higher hydrocarbons [47-49]. However, using unpromoted Rh, previous CO hydrogenation studies have observed strong selectivity to methane with minimal selectivity to oxygenates [26, 31, 57, 67]. It is well known that the addition of promoters, such as K, Ti, V and Mn will greatly improve the catalytic performance of Rh catalysts resulting in moderate (i.e. ~10%) selectivities for specific oxygenates such as ethanol [46, 56, 67, 77, 141]. Kinetic studies by Gao et al.[63] have attempted to unravel the role of the promoter. However, even basic questions remain unanswered such as: what is the phase of the promoter? What is its physical relationship to the active metal site? Are unique active sites created at the metal-promoter interface? Here we focus on one such promoter, Mn, to attempt to identify the active phase in the promoter as well as to establish a relationship between reactivity (activity and selectivity) and promoter-metal interaction.
In previous studies, it was shown that the stronger metal-promoter interactions can enhance the selectivity to desired products [42, 60, 67, 106, 128, 142-144]. In this work, we explore a simple way to enhance the metal-promoter interactions by increasing the Mn promoter loading, so that more Rh particles have access to the Mn promoter. Multi-walled carbon nanotubes (MWCNTs) are chosen as the catalyst support in this work as many previous studies which used CNT supports, have shown exceptional catalytic performance [62, 145-149]. CNTs typically have high surface area (200–300 m²/g) [73, 150], good mechanical and electronic properties as well as high thermal stabilities [151]. Most importantly for our current study, carbon has a much lower Z number (Z=12) than other supports such as SiO₂ and TiO₂, so the direct visualization of the Mn promoter and its interactions with Rh particles can be achieved using atomic resolution STEM imaging. The catalysts were tested in a plug flow reactor to determine the catalytic performance, i.e. the rate and product selectivity. In addition, STEM and EELS characterization were employed to quantify the degree of metal-promoter interaction, the particle size distributions, the oxidation state of Rh and Mn, and the phase of Mn. XANES and EXAFS measurements are used to confirm these results, and demonstrate the enhanced selectivity to ethanol with increasing metal-promoter interactions.

4.1 Experimental

4.1.1 Catalyst Synthesis

Multi-walled carbon nanotubes (CNTs) were purchased from Cheap Tube Inc. (O.D. 10-20 nm, length 10-30 µm, pore volume=4ml/g). Raw CNTs were refluxed in concentrated HNO₃, 70 vol%, for 10 hr at 120 °C in a heating mantle while stirring. Then
the mixture was filtered and washed with deionized water 8 times, followed by drying at 80 °C for 8 hr. The supported Rh$_2$O$_3$ on CNTs was synthesized via Incipient Wetness Impregnation (IWI) using rhodium nitrate, Rh(NO$_3$)$_3$ (Sigma-Aldrich, 10% Rh in > 5 wt.% HNO$_3$). The precursor was dissolved in deionized water, and then added drop wise to impregnate the support. The weight loading of Rh is controlled at 3wt% (0.36 atomic %). The catalyst was dried in air at room temperature for 24 hr followed by calcination at 280 °C for 4 hr (5 °C /min ramp) to convert the rhodium nitrate into rhodium oxide, Rh$_2$O$_3$. The addition of Mn promoter were sequentially performed also by IWI using manganese nitrate (Sigma-Aldrich, Mn(NO$_3$)$_2$), onto the 3wt%RhCNTs (pore volume=1.5ml/g) which was synthesized in the first step. The loading of Mn is controlled as 1wt% (0.22 atomic %) and 2wt% (0.44 atomic %) respectively in order to vary the degree of metal-promoter interactions. In the end, a final calcination was performed at 250 °C for 4 hr.

4.1.2 Characterization

Scanning Transmission Electron Microscopy (STEM) imaging was performed on pre-reduced catalysts (All the catalysts were reduced in flowing H$_2$ at 300 °C for 2 hours before microscopy work) using an aberration-corrected, cold-field emission gun microscope, JEOL JEM-ARM200CF, equipped with a post-column electron energy-loss (EEL) spectrometer, and operated at a primary energy of 200 keV. For high-angle annular dark-field imaging (HAADF), a maximum spatial resolution of better than 70 pm can be achieved, while an energy resolution of 350 meV is possible for EEL spectroscopy. The probe size for HAADF imaging is 0.078nm and the aperture size is 30µm and for EELS mapping is 0.1nm and the aperture size is 40µm. The Gatan Enfina EELS
spectrometer is calibrated to ensure that the spectrometer dispersion plane is parallel to the long axis of the CCD detector and properly focused on the detector plane. In addition, the quadrupole and hexapole magnetic lenses in the spectrometer are used to minimize the spectrometer aberrations, in particular electrons entering the magnet at large angle with respect to the optical axis. The energy scale is calibrated using the focused zero-loss peak and a drift tube with well-defined potential offset. A convergence semi-angle of 22 mrad was used. The pixel dwell time for the EELS mapping is 0.2 s/pixel. The samples were prepared for microscopy by grinding a small amount of the reduced catalysts (~0.01 g) and then loading the ground sample (by the electrostatic force) onto a holey carbon copper grid.

In this work, HAADF images were used to determine the particle size distribution. The particle sizes were analyzed using the software Comptage de particule (V2). Roughly 500 particles from each sample were randomly chosen and counted for the particle size distribution plots. The elemental composition of the catalysts particles is determined using EELS spectrum imaging combined with mass contrast signals.

CO chemisorption measurements were performed at the Catalyst Testing Lab at Northwestern University using an Altamira Instruments BenchCAT 1000HP. Catalysts (0.2-0.3 g) were loaded into a U-shaped quartz reactor tube, which was weighed before and after sample addition to ensure an accurate weight measurement. This tube was then loaded into the furnace. Each catalyst was reduced at 300°C for 2 h (10°C/min ramp rate). And then flushed for 30 min in He. 5%CO/He was then pulsed (595 µL loop volume) into the system 15-20 times at 30°C to ensure the surface was saturated. Each spectrum was integrated to find the volume of CO remaining following adsorption. Any area less
than 20 pulses were considered to be complete adsorption. Surface saturation was typically reached within 10 pulses.

Transmission X-ray Absorption Spectroscopy (XAS) of the Rh K-edge and Mn K-edge of the \textit{in-situ} reduced MnRhCNTs catalysts were measured at Argonne National Laboratory’s Advanced Photon Source (APS) on the Materials Research Collaborative Access Team’s (MRCAT) bending magnet beamline in sector 10-BM. Catalysts samples were pressed into an \textit{in-situ} cell and reduced at 300 °C in H$_2$. After cooling to room temperature, the sample chamber was filled and sealed with He prior to measurements. The data fitting was done with the WinXAS software, version 3.0. A Rh foil was used as a reference for both XANES and EXAFS fitting (N$_{\text{Rh-Rh}}$=12, R=2.69 Å), and Mn metal, MnO, Mn$_2$O$_3$ and MnO$_2$ were measured as Mn standards for XANES in order to derive the Mn promoter phase.

4.1.3 \textit{CO Hydrogenation}

The CO hydrogenation performance of the Mn/Rh/CNTs catalysts was investigated under isothermal plug flow conditions by diluting 0.1g of the catalyst with 0.3g SiC (70 mesh) in a half-inch diameter stainless steel reactor. Catalysts were reduced prior to reaction for 1 hr at 300 °C in H$_2$ (~15% H$_2$ balanced in Ar). Reactions were performed at 20 bar, 290 °C and a syngas flow ranging from 15 ml/min to 110 ml/min in order to compare the catalytic performance of all the catalysts at different CO conversions. The syngas feed has a composition of 32% CO, 64% H$_2$ (a 1:2 CO:H$_2$ ratio) and 4% N$_2$ as an internal standard. The catalyst bed temperature was monitored by a thermocouple inserted within the catalyst bed. The reaction results reported here were generally obtained after 6 hours on-stream reaction. Catalyst activities and selectivities
were stable over an additional 6 hours of data collection. A HP 6890 gas chromatograph equipped with one flame ionization detector (FID) and a thermal conductivity detector (TCD) was integrated downstream of the reactor to analyze the reaction products. A 30 m by 0.32 mm ID HP-Wax bonded polyethylene glycol capillary column (made by Restek) was used for the analysis of the organic products (i.e. ethanol, acetaldehyde, propanol, acetic acid and etc.) via FID. Light inorganic gases (H₂, CO, CO₂, N₂ and etc.) and methane as well as light hydrocarbons were separated on packed columns and quantified with TCD.

4.2 Results and Discussion

4.2.1 Characterization

A series of Mn promoted and unpromoted Rh/CNTs catalysts were synthesized via the IWI synthesis method. The particle size distributions of the catalysts were obtained from STEM imaging (Figure 4.1), showing that the Rh particles are on average a little over 1 nm in size.
Figure 4.1 STEM HAAD images of (a) 3%Rh/CNTs, (b) 1%Mn3%Rh/CNTs, and (c) 2%Mn3%Rh/CNTs, and the particle size distribution of each catalyst.

The Rh K edge EXAFS spectrum of each sample was also obtained in order to estimate the particle size. The Fourier transformation in R space of the data taken on a
2%Mn promoted 3%Rh/CNTs as well as a Rh foil are shown in Figure 4.2. The other catalysts (3%Rh/CNTs and 1%Mn3%Rh/CNTs) gave almost identical spectra as the 2%Mn3%Rh/CNTs, so for simplicity those data are not shown here. From the EXAFS spectra, all the catalysts have large central peak at ~2.5 Å with a smaller shoulder at ~1.8 Å indicating that the particles are metallic with no formation of bimetallic RhMn nanoparticles in contrast to the results of Mei et al. [152], in which the authors proposed an alloy nanoparticle model wherein the promoter atom Mn existed in a binary alloy with Rh on the Mn promoted Rh/SiO₂ catalysts. Mei et al. used a co-precipitation technique to synthesize their catalysts followed by calcination at 400 °C and reduction at 260 °C so the synthesis technique by which the promoter is added could have a significant effect on the nature of the promoter and the subsequent catalytic behavior. By fitting the spectra with the Rh foil standard, the coordination number and bonding distance can be extracted.
Figure 4.2 Magnitude of the Fourier Transform of the EXAFS ($k^2=2.5$-$12.5$ Å$^{-1}$) of the 2%Mn3%Rh/CNTs (blue) plotted with the Rh foil standard (red).

Finally CO chemisorption was used as a probe of the available surface area for CO hydrogenation based on an assumption of a 1:1 CO:Rh surface site stoichiometry[153, 154]. Previous experiments from Yates and Sinfelt have revealed that the stoichiometry changes with particle size but in this work all samples had similar particle sizes based on TEM and EXAFS so the stoichiometry was assumed to be the same for all samples. For all 3 samples the CO chemisorption data indicated very similar available surface areas (54-58%). This indicates that the presence of Mn does not reduce the available surface area for adsorption of CO and no site blocking occurs. The particle sizes by EXAFS and STEM and the dispersions indicated by CO chemisorption for promoted and unpromoted catalysts are summarized in Table 4.1. Both the EXAFS and STEM indicated that the average Rh particle size of the three catalysts is about 1 nm while the CO chemisorption
indicated slightly less dispersion than expected for the particle sizes (which would indicate ~80 % dispersion) found via either EXAFS or STEM.

**Table 4.1** Particle size of catalysts obtained by STEM and EXAFS.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Coordination Number</th>
<th>Bond Distance (Å)</th>
<th>σ²</th>
<th>Particle size by EXAFS (nm)</th>
<th>Particle size by STEM (nm)</th>
<th>Dispersion % by CO Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%Rh/CNTs</td>
<td>4.9</td>
<td>2.67</td>
<td>0.003</td>
<td>1.2±0.1</td>
<td>1.3±0.4</td>
<td>58</td>
</tr>
<tr>
<td>1%Mn3%Rh/CNTs</td>
<td>5</td>
<td>2.67</td>
<td>0.003</td>
<td>1.2±0.1</td>
<td>1.1±0.4</td>
<td>54</td>
</tr>
<tr>
<td>2%Mn3%Rh/CNTs</td>
<td>4.8</td>
<td>2.67</td>
<td>0.003</td>
<td>1.1±0.1</td>
<td>1.2±0.4</td>
<td>57</td>
</tr>
</tbody>
</table>

*Debye Waller factor for the nearest neighbor distance in EXAFS data fitting*

As shown in Figure 4.3, XANES measurements after *in-situ* reduction at 300 C ° are characteristic of metallic Rh for 2%Mn3%Rh/CNTs. Using Rh foil and Rh₂O₃ were as standard references, the XANES result from 2%Mn3%Rh/CNTs matches the Rh metallic feature, in a similar fashion to the EXAFS spectra. Therefore, we can conclude that all the Rh particles after reduction would all exhibit Rh metallic phase in regardless of the amount of Mn loading. Previously [142] we found that Mn could shift the reduction temperature of Rh depending upon the method of Mn promotion. However, the reduction temperature of 300 C ° is sufficient to fully reduce the Rh in this case.
Figure 4.3 XANES spectra of the Rh K edge of 2%Mn3%Rh/CNTs (blue line) plotted with appropriate standards: Rh$_2$O$_3$ (dashed black line) and Rh foil (red line).

Although promoted Rh catalysts have been intensively studied previously for ethanol synthesis, the phase and location of the promoter to the metallic Rh nanoparticles are not thoroughly understood. XANES can be used to investigate the metal oxidation state and to help identify the promoter phase [155-158]. For example Bayram et al. [158] have investigated the transformation of cobalt coordination environment during ethanol steam reforming by comparing the XANES spectra of Co species under reaction condition with the XANES spectra of Co standards (Co, CoO, Co$_3$O$_4$), to determine Co phase at various reaction temperatures. Following this example, we first examined the XANES of various Mn standards (Mn, MnO, Mn$_2$O$_3$, MnO$_2$) as shown in Figure 4.4. The
Mn standards exhibit distinct features in the primary XANES peak between 6.55-6.57 keV that allows for straightforward discrimination between phases. Besides the major peak differences, the pre-edge of each spectra is another important feature to distinguish the Mn standards from each other. For example, the Mn metal has a pre-edge at ~6.451 keV, and the pre-edge of MnO₂ is shifted to ~6.453 keV. MnO and Mn₂O₃ have almost the same pre-edge at 6.45 keV, but the Mn₂O₃ sample has an extended shoulder right after its pre-edge peak and this feature is not observed with the MnO spectra. In Figure 4.5, the Mn K edge XANES spectra of 1%Mn3%RhCNTs and 2%Mn3%RhCNTs were plotted together with the MnO reference, both of the Mn promoted catalysts have the same pre-edge energy as the MnO reference at 6.54 keV, without an additional shoulder peak right after pre-edge peak. Moreover, both of the catalysts also exhibited similar XANES major peak as the MnO reference. Consequently, the promoter phase (oxidation state) is confirmed here as MnO. The assignment of the promoter as MnO has been previously made by, Wilson et al.[159] for Mn/Rh/SiO₂ catalysts, Morales et al.[160, 161] for Mn/Co/TiO₂ catalysts and Bezemer et al.[106] for Mn/Co/CNF catalysts.
Figure 4.4 XANES spectra of the Mn K edge of the Mn reference compounds: Mn metal (black), MnO (red), Mn$_2$O$_3$ (blue), and MnO$_2$ (green).
Figure 4.5 XANES spectra of the Mn K edge of the Mn promoted catalysts. 1%Mn3%RhCNTs (black) and 2%Mn3%RhCNTs (blue) are plotted together with the MnO reference (red).

Although the promoter phase has been identified as MnO regardless of loading, it is also necessary to determine the physical relationship between Rh and MnO and to determine how the local structure influences catalyst performance. STEM-EELS mapping has previously been used to successfully analyze the distribution of the promoter phase on the catalyst surface[14]. Figure 4.6 and Figure 4.7 show the high-resolution imaging and elemental composition of the two Mn promoted catalysts (2%Mn3%RhCNTs and 1%Mn3%RhCNTs). The Mn L-edge energy loss signal is used to map the Mn distribution, and mass contrast imaging was used for the Rh signal, since the Rh K-edge signal is not sufficient for EELS spectrum image analysis.
Figure 4.6 High-resolution STEM imaging and the EELS mapping of the different areas on 1%Mn3%RhCNTs catalyst. The Rh signal is shown in red and the Mn signal is shown in green, the orange and yellow color is caused by the overlap of Rh and Mn.
Figure 4.7 High-resolution STEM imaging and the EELS mapping of the different areas on 2%Mn3%RhCNTs catalyst. The Rh signal is shown in red and the Mn signal is shown
in green, the orange and yellow color is caused by the overlap of Rh and Mn. The C signal is neglected for the best visualization.

By combining the STEM-EELS results from Figure 4.6 and Figure 4.7, it is obvious that on multiple different areas of both catalysts, Rh particles were found to be associated with a thin layer of MnO. However, the degree of Mn-Rh (promoter-metal) interaction is different for these two Mn loadings. On the 2%Mn3%RhCNTs catalyst, MnO was found to have a higher degree of association with Rh particles than that on the 1%Mn3%RhCNTs catalyst. For instance, in Figure 4.6 it is common for the 1%Mn3%RhCNTs catalyst that a layer of MnO were only in contact with 1-2 Rh particles, but in Figure 4.7 it is common for the 2%Mn3%RhCNTs catalyst that a layer of MnO were normally in contact with 3-4 Rh particles. In addition to EELS mapping, additional EELS spectra were taken when the electron beam, which has a probe size of 1Å in diameter, was placed directly on or at the edge of the catalyst particles. In this way, one can directly tell if there is Mn associated with the analyzed Rh particles in the corresponding EELS spectrum. We analyzed ~150 particles and their vicinities for each catalyst to attempt to quantify the degree of metal-promoter interactions in the two promoted catalysts. For the 2%Mn3%RhCNTs catalyst, there are ~55% Rh particles are in contact with MnO, while for the 1%Mn3%RhCNTs catalyst, there are ~30% Rh particles are in contact with MnO. These results indicate that the higher the Mn loading the higher the degree of metal-promoter interactions.

EELS can also be used to confirm the oxidation state of the Mn promoter by looking at the Mn L edge energy loss spectrum. As shown in Figure 4.8, the Mn $L_2$-edge main peak was centered at 645 eV and the Mn $L_2$-edge main peak was centered at 657 eV, so the interval in between $L_3$ main peak and $L_2$ main peak is 12 eV. Laffont. et al.[162]
have used high-resolution electron energy loss spectroscopy to study the intrinsic properties of various Mn oxides (MnO, Mn$_2$O$_3$, MnO, MnO$_2$ and Mn$_3$O$_4$). In their results, the L$_3$ and L$_2$ edge peak difference for MnO is 12 eV as well (641.2 eV for L$_3$ main peak and 653.2 eV for L$_2$ main peak). The peak onset energy of the L$_3$, and L$_2$ peaks are shifted in our spectra. This chemical shift phenomenon might be caused by charge transfer between MnO and metallic Rh or even by the charge transfer in between the MnO and the CNTs support. Sun et al. also found this kind of chemical shift in their EELS of Pd-Cu/$\gamma$-Al$_2$O$_3$ bimetallic catalysts EELS study[163]. However, the L$_3$, L$_2$ peak difference is a fixed value and will not be affected by the shift, allowing us to confirm the presence of MnO (as opposed to Mn$_2$O$_3$ or MnO$_2$ for which the peak differences are 11 and 10 eV respectively). Consequently, we can conclude the Mn(II) oxide promoter phase from the EELS analysis is in agreement with the XANES spectra.
Figure 4.8 Mn L-edge energy loss spectrum, the $L_3$-edge main peak was centered at 645 eV and the $L_2$-edge main peak was centered at 657 eV.

4.2.2 CO hydrogenation

The CO hydrogenation reactivity results are summarized in Table 4.2. At ~3% CO conversion, the major products produced by the unpromoted Rh/CNTs catalyst are 10% ethanol, 51% methanol and 32% methane, small amount of light C$_2$+ hydrocarbons (5%) and acetaldehyde (2%) are also detected in the total products. Previously, in our examination of Rh catalysts supported on silica (3 wt% Rh, the average particle size is ~2.7 nm, reaction condition at 285 °C, 20 bar and 2:1 H$_2$:CO ratio, 4% CO conversion)[142], we found that the selectivity to methane was 30% with higher hydrocarbons as the only other products so the production of oxygenates by the
unpromoted catalysts has been significantly improved by the presence of the CNT support. From Table 2, it is also observed that with the increase of the CO conversion, the TOF of the Mn/3%Rh/CNTs remains nearly constant within some experimental error. the 2%Mn/3%Rh/CNTs decreases. This could indicate that a mass transfer limitation exists at the higher Mn loading, but it seems likely that the decrease in the TOF is due to a combination of random error in the measurement (which can be seen for the 1%Mn/3%Rh/CNT catalyst) and the fact that the rate is an integral rate as the conversion increases (i.e. the concentration of CO decreases).

These results here are similar to that of Egbebi et al.[141] in their study of 1wt%Rh/TiO$_2$ catalyst (the average size is ~1nm) for CO hydrogenation at 270 °C, 20 bar and 2:1 H$_2$:CO ratio in which they found the products contained 62% methane, 10% ethanol, 5.5% methanol, 9.2% acetaldehyde and the rest ~10% contained CO$_2$ and C$_2$ light hydrocarbons at 1% conversion of CO. Just as the TiO$_2$ support acts as a promoter, it appears to be the case for the CNT support as well, as the amount of ethanol produced from unpromoted catalysts is identical, while the selectivity to methane in our study is half that reported by Egbebi for Rh/TiO$_2$. The ability to produce oxygenates from TiO$_2$ supported Rh catalysts has been attributed to SMSI effects[83, 84, 164], where supports have strong interactions with active metal and act as a promoter. It seems here the support has an even better promoting effect than TiO$_2$ catalyst, but the mechanism of promotion must be different here since the CNTs cannot be reduced to a suboxide which then covers the metal nanoparticles as has previously been observed with Rh/TiO$_2$ [84]. Previous theoretical calculations[165, 166] have suggested that the CNT support may influence the
electronic structure of the metal nanoparticle, but the XANES does not offer any evidence to this effect.

**Table 4.2** CO hydrogenation reactivity data of the promoted and unpromoted Rh/CNTs catalysts, reactions were performed at 20 bar, 290 °C and 2:1 H₂:CO syngas ratio.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO Conv.ᵃ</th>
<th>TOFᵇ</th>
<th>EOHᶜ</th>
<th>Aᶜ</th>
<th>MOHᶜ</th>
<th>CH₄ᶜ</th>
<th>CO₂ᶜ</th>
<th>HCᶜ</th>
<th>Oxyᶜ</th>
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</thead>
<tbody>
<tr>
<td>3%Rh/CNTs</td>
<td>2.9</td>
<td>0.011</td>
<td>10.2</td>
<td>1.7</td>
<td>51.1</td>
<td>31.9</td>
<td>0</td>
<td>5.1</td>
<td>0</td>
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<tr>
<td>1%Mn3%Rh/CNTs</td>
<td>3.6</td>
<td>0.059</td>
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<td>2.9</td>
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<td>33.3</td>
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<td>2%Mn3%Rh/CNTs</td>
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<td>0.053</td>
<td>35.2</td>
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<td>6.5</td>
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<td>4.5</td>
<td>4.5</td>
<td>35.7</td>
<td>21.2</td>
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<td>0.036</td>
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<td>24.2</td>
<td>2.4</td>
<td>2.2</td>
<td>32.5</td>
<td>35.0</td>
<td>3.7</td>
<td>0</td>
</tr>
</tbody>
</table>

ᵃ Conversion of syngas over promoted and unpromoted Rh catalysts supported on CNTs.

Note: the CO conversion were calculated by using Nitrogen gas as the internal standard, and follow the following equation:

\[
CO \text{ Conv.} = \left( \frac{M_{CO\text{feed}} - M_{N2\text{feed}}}{M_{N2\text{product}} * M_{CO\text{product}}} \right) \times 100\%.
\]

ᵇ The TOF is calculated as the number of active sites per second. TOF calculated from the dispersion as determined by the CO chemisorption measurements are available in the supplementary material.

ᶜ The selectivity to product i is based on the total number of carbon atoms among the total products and is defined as: Select. %= \left( \frac{n_i * M_i}{\Sigma n_i * M_i} \right) * 100\%. ni is the carbon atoms
number of that product, $M_i$ is the mole percent of product $i$ detected downstream by GC. In the table, EOH is ethanol, A is acetaldehyde, MOH is methanol, HC is C$_2$ light hydrocarbons, Oxy is the bundle of acetic acid and C$_3$ oxygenates.

For the two Mn promoted catalysts, the TOF of the two samples is similar to one another, but the TOFs are increased by an order of magnitude as compared to the unpromoted catalyst, which could be due to a lowering of the activation barrier. Moreover the increase in the TOF could also be associated with the presence of new sites that are created by the promoter/metal interface. Using CO chemisorption as a probe of available surface for reaction, we observe that CO can at least adsorb to approximately the same number of metallic sites regardless of the promoter’s presence. In prior characterization discussion, the STEM-EELS measurements have demonstrated that the 2%Mn3%Rh/CNTs catalyst has a better Rh-Mn metal promoter interaction than the 1%Mn3%Rh/CNTs catalyst. The degree of metal-promoter interactions was found to be an important factor for the productivity of desired products in our previous studies[142]. Increasing the degree of the promoter-metal interaction results in a higher selectivity towards the desired products (i.e. ethanol). If this trend holds, the 2%Mn3%RhCNTs catalyst should have enhanced ethanol productivity compared with the 1%Mn3%RhCNTs catalyst due to its better metal-promoter interaction. As reported in Table 2, the selectivity toward ethanol is higher at all conversions. Furthermore, Table 2 indicates that the selectivity to ethanol decreases as the CO conversion increases. The origin of this decrease in selectivity stems from the production of a significant amount of CO$_2$. This result is anticipated because at a the syngas ratio (H$_2$:CO) of 2, an increase in ethanol production will result in a simultaneous production of water which serves as a source for the water gas shift reaction. Water gas shift has also been observed in our
previous CO hydrogenation study on MnRh/SiO$_2$ catalyst at high CO conversion (above 40%)[142]. Excluding CO$_2$ production, the selectivity to ethanol is actually seen to increase slightly as conversion increases as shown in Figure 9 with the 2%Mn3%Rh/CNTs catalyst always producing more ethanol (~10% higher selectivity) than the 1%Mn3%Rh/CNTs catalyst. The improvement in the ethanol selectivity for the 2%Mn3%Rh/CNTs catalyst here further demonstrates that more intimate interaction of the Mn promoter with Rh increases the alcohol selectivity. This is consistent with the previous proposal that the active sites for the CO hydrogenation to higher alcohols reaction are located at the interface of the active metal and the promoter[77]. The ethanol selectivity enhanced by better Rh-Mn interactions of this work is consequently in agreement with our previous results[142].

![Figure 4.9](image.png)

**Figure 4.9** Ethanol selectivity (excluding CO$_2$) comparison at various CO conversion for the 2%Mn3%Rh/CNTs catalyst (blue dots ●) and 1%Mn3%Rh/CNTs catalyst (red squares ■).
The work of Mei et al. [152] provides another interesting contrast. In their Mn/Rh/SiO\textsubscript{2} catalyst, the Mn and Rh are alloyed as opposed to Mn existing in an oxidized state. In their results, the catalyst produces similar amounts of CH\textsubscript{4} at the same temperature and conversion but produces significantly more C\textsubscript{2} oxygenates (other than ethanol) while producing no CO\textsubscript{2}. Accompanying DFT calculations show that the presence of Mn dramatically lowers the barrier for CH + CO to produce CHCO and increases CO insertion rates at the expense of hydrogenation events. Mei et al. also report very high barriers (> 1.6 eV) for CO\textsubscript{2} formation from oxidation of CO with either O or OH but this does not appear to be strongly affected by the presence of Mn so the suppression of water gas shift remains unclear.

As ethanol selectively increases, the acetaldehyde selectivity decreases (e.g. acetaldehyde produced by 2%Mn3%Rh/CNTs decreased from 6.5% to 2.4% when the CO conversion increased from 4% to 14%), suggesting that the acetaldehyde has not been fully hydrogenated to ethanol, and acetaldehyde is likely an intermediate product. If we take the ratio of ethanol/acetaldehyde for the two promoted catalysts at various CO conversions, there is always a higher ethanol/acetaldehyde ratio observed for the 2%Mn3%Rh/CNTs catalyst (e.g. at CO conversion ~4%, the ethanol/acetaldehyde ratio for 2%Mn3%Rh/CNTs is ~5.4, while for 1%Mn3%Rh/CNTs is ~4), suggesting better Rh-Mn interactions promote the hydrogenation rate to give more ethanol. This result is slightly surprising given that the role of the promoter is typically regarded as facilitating C-O bond cleavage and C-C bond formation as opposed to C-H bond formation as suggested by theoretical studies for CO hydrogenation by Rh based catalysts [152, 167, 168]. For example, in Zhao et al.’s [167] density functional theory calculations, the
authors find that the Rh-decorated Cu alloy catalyst has a significantly lower CO insertion barrier compared to pristine Rh(111) and Rh(553) surfaces, whereas the variation of CH₅ (x=1,2,3) hydrogenation barriers on the three surfaces is modest. Similarly, recent calculations of Li et al.[32] examining metallic Mn overlayers about Rh surfaces, suggest that the role of Mn is to lower the CO dissociation barrier as well as provide a lower barrier for CO insertion with the most favorable pathway occurring through formation of CH₃CO.

In addition, the 2%Mn3%Rh/CNTs catalyst produced no acetic acid nor C₃⁺ oxygenates products, while the 1%Mn3%Rh/CNTs catalyst produced considerable amounts of these products (e.g. ~22% at 3.6% CO conversion). As shown in Figure 4.10, the total production of oxygenates (excluding CO₂) remains relatively constant as CO conversion increases with the 1%Mn3%Rh/CNTs producing slightly more oxygenates due to the substantial difference in the production of acetic acid and other C₃⁺ oxygenates. Since acetic acid is an unwanted product in alcohol synthesis reaction, suppression of acid production by 2%Mn3%Rh/CNTs catalyst is considered to be another improvement for alcohol synthesis. However, the 2%Mn3%Rh/CNTs catalyst did produce higher selectivity to methane than the 1%Mn3%Rh/CNTs catalyst. For example, at 4% CO conversion, the 2%Mn3%Rh/CNTs catalyst had a ~49% selectivity to methane while the 1%Mn3%Rh/CNTs catalyst had a ~38% selectivity to methane. In the CO hydrogenation by Mn promoted Rh/CNTs catalyst by Pan et al.[62], the authors also observed that the methane selectivity was increased when the catalyst has a higher ethanol selectivity, specifically at 320 °C and 30 bar pressure (2:1 H₂:CO syngas ratio), the RhMn-in-CNTs catalyst (Mn promoted Rh catalyst deposited inside CNTs) produced ~25% ethanol and
~46% methane at a CO conversion of 18.8%, while the RhMn-out-CNTs catalyst (Mn promoted Rh catalyst deposited outside the CNTs) produced ~18% ethanol and ~27% methane at a CO conversion of 1.8%, Pan et al only compared the selectivity at two different CO conversions, so its not clear how the change in conversion would affect their selectivity ratio (presumably at higher conversion there is a higher selectivity to non-C\textsubscript{1} products) [142].

Figure 4.10 Total oxygenate selectivity (excluding CO\textsubscript{2}) comparison at various CO conversion for the 2%Mn3%Rh/CNTs catalyst (blue dots ●) and 1%Mn3%Rh/CNTs catalyst (red squares ■).
4.3 Conclusion

In this chapter, highly dispersed Rh/CNTs catalysts with and without a Mn promoter were synthesized. The average particle size of each catalyst was about 1nm. All catalysts are reduced to metallic Rh with no evidence of bimetallic RhMn nano-particle formation, Both XANES and EELS spectra show that the Mn promoter is present as MnO. EELS mapping showed the 2%Mn3%Rh/CNTs catalyst has a better metal-promoter interaction than the 1%Mn3%Rh/CNTs catalyst. Catalytic reactivity results show while both of the catalysts produced similar amount of total oxygenates (ethanol, methanol, acetaldehyde, acetic acid and C$_3^+$ oxygenates), the 2%Mn3%Rh/CNTs catalyst gave a higher ethanol selectivity which correlates with the higher degree of Rh-Mn interactions. Therefore, one can conclude that it is critical to create a high degree of interaction between the active metal and promoter to achieve high selectivity to ethanol.

In the next chapter (Chapter 5), we will discuss the FT synthesis Mn promoted Co catalysts supported on TiO$_2$, we will again link the FT reactivity results with the catalyst structure to examine the metal-promoter interaction effect.
5. THE INFLUENCE OF INTIMATE MANGANESE-COBALT INTERACTIONS IN THE ENHANCEMENT OF HIGHER MOLECULAR WEIGHT HYDROCARBONS IN FISCHER-TROPSCH CATALYSTS

5.0 Introduction

The unpredictable fluctuation in crude oil prices has revived interest in the Fischer Tropsch (FT) synthesis[6, 169-171], the catalytic conversion of syngas, a mixture of CO and H₂, to more desirable long chain hydrocarbons. This process can be expressed as:

\[ n\text{CO} + (2n+1)\text{H}_2 \rightarrow C_n\text{H}_{2n+2} + n\text{H}_2\text{O}. \]

Cobalt based FT catalysts are well known for their activity and stability[119, 170]. In general, cobalt catalysts exhibit both higher activity and selectivity to liquid hydrocarbons, e.g., C₅⁺ paraffins, than, for example, iron FT catalysts. For FT synthesis, early transition metals such as Mn are often used as a promoter for Co catalysts to increase the average molecular weight distribution of the products[90]. Recent work done with promoted Co catalysts[90, 104, 172, 173] has demonstrated the enhanced selectivity towards C₅⁺ hydrocarbons stemming from significant interaction between the promoter and Co species. The most common way to prepare promoted heterogeneous catalysts is Dry Impregnation (DI), where the promoter precursor is dissolved in an amount of water equal to the pore volume of the catalyst support either simultaneous to or subsequent to impregnation of the support with the active metal component. Using the DI method, the interaction between the active metal and promoter depends on the random distribution of promoter and the active metal on the catalytic support, and therefore the DI method is in general inefficient in maximizing the
promoter-metal interactions. In recent work, Strong Electrostatic Adsorption (SEA, which is discussed in details in Chapter 1 and 3) was utilized to steer the Mn promoter (using MnO$_4^-$ as the promoter precursor) selectively onto TiO$_2$ supported Co$_3$O$_4$ (Mn/Co molar ratio was approximately 0.3)[143]. This catalyst showed improvement in the C$_5+$ hydrocarbons selectivity (~10% greater) in comparison with Mn promoted catalysts for which the promoter was added by the DI method. However, in that work although intimate Mn-Co interactions were created, the Mn coverage on the surface of Co is still partial and uneven. In this current work, the SEA method is again utilized to selectively adsorb Mn onto Co$_3$O$_4$ supported on TiO$_2$, but through modification of the synthesis procedure we are able to create a monolayer of Mn surrounding the Co (Mn/Co ratio is approximately 0.1) and achieve improved interaction between the promoter and the active metal.

5.1 Experimental

The Co/TiO$_2$ for this sample was prepared by dry impregnation of cobalt nitrate to achieve 10wt%Co on P25 and followed up by a calcination at 400 °C for 4 hrs (5°C/min ramp) in order to convert the Cobalt nitrate into Co$_3$O$_4$ (as determined by EELS and XRD, not shown). Using 1g of the Co/TiO$_2$, the Mn was deposited by adjusting 50ml of H$_2$O to a pH 1 (pH adjusted by titrating HCl solution), then adding in KMnO$_4$ (0.143g) to achieve a 200ppm Mn solution (This should result in ~1.1wt% Mn, 0.1 Mn/Co ratio, to achieve the monolayer in the reduced catalyst). The pH adjusted solution was shaken to ensure KMnO$_4$ is dissolved (<2min) and the pH is checked before adding the Co$_3$O$_4$/TiO$_2$. The resulting mixture is shaken for 1 hr before filtering the final catalyst material. The metal uptake was determined by ICP and was described in our previous work[11]). The
The Mn$^{\text{SEA, partial}}$/Co/TiO$_2$ catalyst is calcined at 400 °C for 4 hrs prior to reduction[12]. However, the Mn$^{\text{SEA, monolayer}}$/Co/TiO$_2$ catalyst is not calcined and is instead reduced at 350 °C. Figure 1 (the STEM-EELS) was acquired at Oak Ridge National Laboratory by using an aberration-corrected scanning transmission electron microscope, Nion UltraSTEM 100™ operated at 100 kV[174]. The EEL spectra were treated with the multivariate statistical analysis (MSA) package for Gatan Digital Micrograph[175]. The multivariate statistical analysis method is used to reduce the noise in the data and to increase the signal-to-noise ratio when the data is oversampling the sample, as done in this study. The FT catalytic testing was performed at Argonne National Laboratory, the reaction results reported here were generally obtained after 6 hours on-stream reaction in a half-inch diameter stainless steel reactor. A HP 6890 gas chromatograph equipped with one flame ionization detector (FID) and a thermal conductivity detector (TCD) was integrated downstream of the reactor to analyze the reaction products. A 30 m by 0.32 mm ID HP-Wax bonded polyethylene glycol capillary column (made by Restek) was used for analysis of the organic products (C$_2$-C$_4$ and C$_5$+ hydrocarbons) via FID. Light inorganic gases (H$_2$, CO, N$_2$, 4%N$_2$ used in the syngas feed as internal standard, so the gas mixture has a compositional ratio of H$_2$/CO/N$_2$=2:1:0.125) and methane were separated on packed columns and quantified with TCD. Catalysts were reduced prior to reaction for 2 h at 350 °C in H$_2$ (~15% H$_2$ balanced in Ar). The reaction was performed at 1 atm and 220 °C, the syngas flow rate was varied from 20 ml/min to 130 ml/min in order to achieve different CO conversion. All of the reactivity data were acquired after at least 6 hours’ on stream reaction.
5.2 Results and Discussion

The combination of Scanning Transmission Electron Microscopy (STEM) with Electronic Energy-Loss Spectroscopy (EELS) is a powerful tool for the direct visualization of the local placement of Mn promoter in the catalysts[176]. Figure 1a shows an atomic-resolution Z-contrast image of Mn promoted Co particles on TiO$_2$ support. The image shows a MnO coated Co nanoparticle about 9 nm in diameter, consistent with the average particle size of unpromoted Co/TiO$_2$ synthesized previously by Feltes et al.[11]. The EELS mapping shown in Figure 1b reveals that the Mn is present as a uniform monolayer covering the Co particle, thus providing clear evidence that the nanoparticles possess a core-shell structure. Furthermore, the Mn is not associated with the TiO$_2$ substrate, indicating that a highly preferential deposition of Mn onto Co has been achieved.
Figure 5.1 (a) Atomic resolution Z contrast imaging of monolayer Mn promoted Co catalyst supported on TiO₂. b) EELS mapping showed distinct elemental composition, in the graph, green is Mn, red is Co and blue is TiO₂.

In comparison, previous STEM-EELS mapping (Figure 5.2 a) of Mn/Co/TiO₂ with a higher Mn loading (0.3 Mn/Co ratio) showed significant areas of the Co surface which are not in contact with Mn and Mn aggregation was also observed[12]. When the DI method was used to perform the Mn promotion, even less interaction between the promoter and the active metal is present (Figure 5.2 b). In this study, we compare the Mn^{SEA_{monolayer}}/Co/TiO₂ catalyst to Mn^{SEA_{partial}}/Co/TiO₂ and Mn^{DI}/Co/TiO₂ catalysts from Feltes et al.
Figure 5.2 a) EELS mapping of Mn$^{\text{SEA, partial}}$/Co/TiO$_2$ catalyst, b) EELS mapping of Mn$^{\text{DI}}$/Co/TiO$_2$ catalyst, in the graph, green is Mn, red is Co and blue is TiO$_2$ [128].


The key to creation of the monolayer (as shown in Figure 5.1) appears to be a combination of using SEA as the method of promoter addition and removal of the calcination step. Previously, Feltes et al. demonstrated that use of DI to add the Mn promoter results in a random distribution of Mn across the support surface[12]. In contrast, more intimate contact between the promoter could be achieved by the SEA
method. However, Zhao et al. observed that after reduction, the MnO species are associated with the active metal to nearly the same degree, hence only a minor (10%) improvement in the selectivity[13]. In these experiments, the Mn deposited on the surface was first calcined at 400 °C resulting in the formation of MnO species which cover the surface. By removing the calcination step, we demonstrate that the SEA method provides a disperse (non-atomically dense) covering of the Co nanoparticle surface.

Previously, Morales et al.[96, 173] used XANES to identify the Mn promoter phase in Mn/Co/TiO₂ catalysts as Mn²⁺ (MnO). However, this result does not confirm the oxidation state of the active promoter in that XANES is a bulk technique which may not reveal the chemical state of minority interface sites for example. Therefore we have used the STEM-EELS spectra of the MnOₓ monolayer, shown in Figure 5.3, to help resolve this question. The Mn L₃-edge main peak is centered at 641.5 eV and the Mn L₂-edge main peak is centered at 653.5 eV, so the interval in between L₃ main peak and L₂ main peak is 12 eV. Previously Laffont. et al.[162] have used high-resolution electron energy loss spectroscopy to study the intrinsic properties of various Mn oxides (MnO, Mn₃O₃, MnO, MnO₂ and Mn₃O₄). In their results, the L₃ and L₂ edge peak difference for MnO is 12 eV as well (641.2 eV for L₃ main peak and 653.2 eV for L₂ main peak) which is a signature of the Mn²⁺ oxidation state, compared to 9.7 eV for Mn⁴⁺ or 10.9 eV for Mn³⁺. The difference in absolute peak energy can be attributed to the energy scale calibration. In our case, the O K-edge onset at 532 eV was used to calibrate the energy scale. Therefore, we confirm the results of Morales et al. and conclude that the monolayer promoter is indeed MnO (Mn²⁺), but since MnO₂ is never formed, there is little rearrangement of Mn on the surface and it remains associated with the Co nanoparticles.
Figure 5.3 Mn $L$-edge energy loss spectrum, the $L_3$-edge main peak was centered at $\sim 641.5$ eV and the $L_2$-edge main peak was centered at $\sim 653.5$ eV.

In order to assess how the structure of the catalyst affects its performance, the Mn$^{\text{SEAMonolayer}}$/Co/TiO$_2$ catalyst was tested for CO hydrogenation under identical conditions as previous Mn promoted Co catalysts tests ($220$ °C, 1 atm, 2:1 H$_2$/CO syngas ratio)\[11\]. The catalytic performance of Mn promoted catalysts in this and previous studies of Feltes and Morales et al.\[11, 12, 104\] are summarized in Table 5.1.
Table 5.1 FT reactivity results in comparison with previous catalytic studies.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sample</th>
<th>CO Conv. %</th>
<th>CH₄ wt%</th>
<th>C₂-C₄ wt%</th>
<th>C₅+ wt%</th>
<th>Act. c</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work²</td>
<td>Mn⁷⁷SEA_monolayer Co/TiO₂ (Mn/Co=0.1)</td>
<td>3.4 b</td>
<td>7</td>
<td>8</td>
<td>85</td>
<td>6.0</td>
</tr>
<tr>
<td>Feltes et al.[11]²</td>
<td>Co/TiO₂</td>
<td>2</td>
<td>26</td>
<td>37</td>
<td>37</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Mn⁷⁷SEA_partial Co/TiO₂ (Mn/Co=0.3)</td>
<td>2</td>
<td>18</td>
<td>21</td>
<td>61</td>
<td>0.6</td>
</tr>
<tr>
<td>Morales et al.[104]²</td>
<td>Mn⁷⁷DI/Co/TiO₂ (Mn/Co=0.3)</td>
<td>1</td>
<td>17</td>
<td>29</td>
<td>54</td>
<td>0.9</td>
</tr>
</tbody>
</table>

² The reaction conditions for all of the work in the table are the same: 220 °C, 1 atm and a 2:1 H₂/CO syngas ratio.

b The CO conversion in this work was calculated by using Nitrogen gas as an internal standard, and follow the following equation: \( \text{CO Conv.} = \left( \frac{M_{\text{COfeed}} - M_{\text{N₂feed}}}{M_{\text{N₂product}} \times M_{\text{COproduct}}} \right) \times \frac{100\%}{M_{\text{COfeed}}} \).

c Activity: \( 10^{-5} \text{ mol}_{\text{CO}} \cdot \text{g}^{-1} \cdot \text{Co}^{-1} \cdot \text{s}^{-1} \), calculated by \( r_{\text{CO}} = F_{\text{CO_feed}} \times X_{\text{CO}} / W_{\text{Co}} \). In this expression, \( F_{\text{CO_feed}} \) is the molar flow rate of CO at the reactor inlet, \( X_{\text{CO}} \) is CO conversion and \( W_{\text{Co}} \) is the weight of Co metal with the catalyst bed.

In both Feltes’ and Morales’ previous studies, the unpromoted Co supported on TiO₂ catalysts produced similar amounts of C₅+ hydrocarbons (37 wt%). After the addition of Mn promoter (by different methods), the selectivity of C₅⁺ hydrocarbons increased with a simultaneous decrease in the selectivity of methane. In addition, the Mn⁷⁷SEA_partial/Co/TiO₂ catalyst resulted in higher C₅⁺ hydrocarbons selectivity than the Mn⁷⁷DI/Co/TiO₂ catalyst. Feltes et al. previously attributed this to better contact between the Mn promoter phase and the Co nanoparticles. Here, we find that the selectivity is further improved to C₅⁺ products even at very low conversion (3.4 %) by the
Mn$^{\text{SEA_monolayer}}$/Co/TiO$_2$ catalyst. To determine the effect of conversion on selectivity, we evaluated the product distribution at conversions from 3-10% as shown in Figure 5.4. In contrast to the previous Mn-promoted catalysts synthesized by either SEA or DI which had methane selectivities of > 15%, the methane production decreased to below ~8 wt% (5.6 wt% the lowest) while simultaneously increasing the C$_5^+$ hydrocarbon selectivity above 82 wt% (87.6 wt% the highest).

Previous studies of Fischer Tropsch synthesis have also demonstrated a positive effect on selectivity by increased promoter-active metal interaction[107, 177] [106]. In Dinse et al.’s[177] recent study, unpromoted and Mn promoted Co/SiO$_2$ catalysts (synthesized via DI co-impregnation) were examined for FT synthesis at both low (1 atm) and high pressure (10 atm) at, 220°C with a 2:1 H$_2$/CO syngas ratio. Both the unpromoted and the Mn promoted catalysts at 10 atm showed high C$_5^+$ hydrocarbon selectivity (60% and 70% mole percent at 10% conversion for the unpromoted and Mn promoted catalysts, respectively). The higher selectivity at high pressure is attributed to the increase in CO:H surface coverage ratio, i.e., more surface CO and less H$_2$. Similarly, it was thought that the role of the Mn promoter was to increase C$_5^+$ hydrocarbon selectivity by increasing the CO:H coverage ratio. Dinse et al. also demonstrated that selectivity to C$_5^+$ increases from 70 to 85% as the conversion is increased from 10% to 50%. Therefore, it is likely that the Mn$^{\text{SEA_monolayer}}$/Co/TiO$_2$ may exhibit even higher selectivity as conversion and reaction pressure increases. Bezemer et al.[106] synthesized the Mn promoted Co/CNF (carbon nanofibers) catalyst using DI and examined their performance for FT, at 20 atm, 220 °C, and 2:1 H$_2$/CO ratio. The Mn promoted Co/CNF achieved a 78 wt% selectivity for C$_5^+$ hydrocarbons at 2% conversion. In their study of
C5+ selectivity as a function of Mn loading, Bezemer et al. found that the composition with the optimal selectivity changes as function of reaction conditions (eg. Total pressure), and that the changes in activity and selectivity are more dramatic at higher pressure. Moreover, the authors used STEM-EELS to show the Mn promoter were in association with the Co metal although the preparation method was Dry Impregnation. They attributed the preferential association of Mn with Co is due a lack of binding sites on the CNF to create interaction with the Mn precursor. The high selectivity in C5+ hydrocarbons in the work of Bezemer et al. can also be linked to the intimate Mn-Co interactions. Bezemer et al.’s result at 20 atm is very similar to our current result achieved by the core (Co) shell (Mn) structure catalyst despite the large difference in pressure, indicating the remarkable performance of the MnSEA_monolayer/Co/TiO2 catalyst despite the large difference in pressure, indicating its remarkable performance. In a recent study by Xiang et al.[144], both Cu and Mn were found to be enriched at the surface of promoted Co catalysts when Co, Mn and Cu nitrate precursors are precipitated as oxalates in a solution of oxalic acid using acetone as a solvent. The metal oxalates are then reduced by H2 at 350 °C to produce a mixed metal/metal oxide solid which had very high selectivity to higher alcohols at 240 °C, 6 MPa, 2:1 H2:CO. Like the current work, EELS mapping demonstrated that the Mn was present only at the surface of the promoted catalyst which suggests the creation of specific sites. In contrast to our result, Xiang et al., report that the promoting Mn overcoating was metallic in nature as opposed to Mn2+. When alloy nanoparticles of CuCo were deposited on a MnOx support, Xiang et al. found them to be less active and selective than their Mn monolayer catalysts.
Figure 5.4 Fischer-Tropsch selectivity results of Mn^{SEA_monolayer}/Co/TiO\textsubscript{2} catalyst at various CO conversion. Red • are C\textsubscript{5+} hydrocarbons, Green ♦ are C\textsubscript{2}-C\textsubscript{4} hydrocarbons, Black ■ are Methane.

Besides the higher C\textsubscript{5+} selectivity of the Mn^{SEA_monolayer}/Co/TiO\textsubscript{2} catalyst, its rate (or activity measured as CO converted per gram catalyst) is also much higher than the Mn^{SEA_partial}/Co/TiO\textsubscript{2} catalyst (as well as the unpromoted Co/TiO\textsubscript{2} catalyst) from Feltes et al.’s previous study as shown in Table 5.1. Dinse et al.[177] stated in their recent FT study that the increase in the activity of the Mn promoted catalyst could be related to an increase in the activity of Co sites located adjacent to Mn promoter (e.g. MnO) as a consequence of the promotion of CO dissociation from the Lewis acid-base interaction of Mn cations with the O atom of CO bound to Co through the C atom. Our results fit the explanation of Dinse et al. as well, since the Mn species have even and intimate interactions with Co metal on the surface on the Mn^{SEA_monolayer}/Co/TiO\textsubscript{2} catalyst which implies there are many more Co sites located adjacent to Mn promoters. In addition, the
creation of the monolayer allows for an optimal number of Mn-Co sites. As seen in Table 5.1, at a higher Mn loading. (0.3 as for the Mn$^{\text{SEA}\_\text{partial}}$/Co catalyst) the catalytic activity is lower than the unpromoted catalyst, since the number of exposed Co sites begins to decrease as the Mn/Co ratio increases beyond a certain point. This has also been shown by H$_2$ chemisorption measurements reported in Feltes et al. Similarly, Dinse et al. [177] report that the activity increased until reaching a maximum at an Mn:Co ratio of 0.05 and decreased at higher Mn:Co ratios. In Breejen et al.’s study[178] of Mn promoted Co/SiO$_2$ catalysts at 1atm, 220°C and 2:1 H$_2$/CO ratio, the catalysts calcined in nitrogen had an optimal activity at Mn/Co ratio of ~0.08. However, their catalysts calcined in air had a constant decrease in activity with increased Mn/Co ratio. As indicated by its name, the Mn$^{\text{SEA}\_\text{monolayer}}$/Co/TiO$_2$ appears to have complete coverage of the active metal. However, we speculate that the MnO overlayer is not atomically dense and acts instead as porous overcoat which allows transport of CO and H$_2$ to the catalytic surface. In contrast, the MnO phase partially covering the Co surface in the Mn$^{\text{SEA}\_\text{partial}}$/Co/TiO$_2$ catalyst is multilayer and dense and, therefore, reaction likely proceeds only at active metal sites. As observed by both Dinse et al. and Feltes et al., at very high loadings of Mn, the number of these sites decreases resulting a drop in activity.

### 5.3 Conclusion

In this study, a novel way of the synthesis of Fisher Tropsch catalysts is developed, and an even and uniform core-shell (Co core, Mn shell) structure is achieved by SEA synthesis method. We have demonstrated that significant improvement in performance (C$_5^+$ hydrocarbons selectivity and rate) is linked to creation of intimate contact between the promoter phase and the active metal in the form of a Mn monolayer
overcoating the Co nanoparticles. In another words, the higher the degree of metal-promoter interactions, the better selectivity towards desired products and the higher catalytic activity can be achieved, and this relationship in between catalyst structure and catalytic performance is also summarized in Figure 5.5.

**Figure 5.5** The trend of the FT catalytic performance as a function of the degree of metal-promoter interactions.

In the next Chapter (Chapter 6), we would present an additional brief session to this thesis, in which we would discuss how the in-situ XRD can be used to characterize the particle size of small (~1nm) Pt nanoparticles.
6. IN-SITU XRD CHARACTERIZATION OF SUPPORTED PT NANOPARTICLES

6.0 Introduction

Supported noble metal nanoparticles are widely used in heterogeneous catalysts for a various kinds of applications as we’ve discussed in previous chapters. To maximise the catalytic activity and due to the cost of noble metals (such as Pt, Rh), there is a strong desire to produce catalysts with the optimum catalytic activity per unit cost which typically requires synthesizing catalysts with very high dispersions (approaching 100%), corresponding to particle sizes close to 1 nm [179]. Important characteristics of interest for supported nanoparticle catalysts are the metal phase, the particle size distribution, bonding distances, oxidation states, and how these change under reaction conditions. Advanced material characterization techniques used to define these properties typically include X-ray absorption spectroscopy (XAS)[180], small angle X-ray scattering (SAXS)[181], X-ray photoelectron spectroscopy (XPS)[182], scanning transmission electron microscopy (STEM)[183] and X-ray Diffraction (XRD)[184]. XAS is conducive to in-situ studies and has become a vital tool to characterize oxidation state (XANES), bonding distance (EXAFS) and coordination numbers most adjacent to the scattering atom. Although XAS provides local structural details, the data reflect an average over all atoms making analysis of multiphase systems difficult. High-resolution STEM has developed significantly over the last 20 years allowing imaging of catalysts to sub-nanometer levels[127]. However the electron microscopes generally require high vacuum, which limits the ability to measure catalysts under realistic reaction conditions. XPS is a surface sensitive technique, which can provide the fraction of atoms in different oxidation
states, although many spectrometers are unable to generate data under reaction conditions. SAXS can provide particle morphology and size distributions, overcoming the limited sampling statistics of STEM, but yields little information about the catalyst phase assemblage, structure, or oxidation states.

Although XRD is prominent in characterization of the metal phase, and particle size, it is very challenging for XRD to obtain these material characteristics when the metal particle sizes are below 5nm, due to the absence of a sufficient lattices planes to effectively cancel incoherent scattering at angles close to the Bragg angle. Therefore, small particles exhibit significant peak broadening (as shown in Figure 6.1) which precludes accurate analysis [181, 185]. In fact, the lack of diffraction peaks in ex-situ XRD from metallic phases is sometimes used as evidence that the nanoparticles must be very small or amorphous [186].
However, numerical simulations have shown that Bragg diffraction peaks from Pt metal should be visible even for Pt clusters containing as few as 13 atoms [187]. These predictions raise an important question: Why does ex-situ experimental XRD characterization fail to demonstrate characteristic diffraction peaks? One hypothesis we can assert here is, that the conditions under which ex-situ XRD experiments are performed leads to formation of disordered oxide phases that obscure the presence of the metallic nanoparticles. Typically in an ex-situ XRD experiment pre-reduced metal nanoparticle samples are exposed to air, and some re-oxidation of the metal particles may occur, leading to formation of a layer of metal oxide encapsulating a metallic core. When the sizes of metal particles are big (>5nm), the thickness of an oxide layer is relatively thin comparing with the size of the nanoparticle, so enough metal is present in the metallic phase to generate detectable XRD peaks. However, when the particles are too

![Figure 6.1 XRD simulation of Pt nanoparticle with sizes ranging from 1-10 nm.](image)
small, the formation of the oxide layer would present as a significant fraction of the particle and therefore act as a huge hindrance for the inner metallic phase to be detectable.

A schematic of the surface reoxidation is illustrated in Figure 6.2.

**Figure 6.2** The illustration of metal oxide formation when metal particles are exposed in air.

Consequently, in order to perform XRD characterization on small metal particles, a primary concern that we must keep in mind, is that we must be certain that the metal particles remain in their metallic phase. Moreover, the catalytic support such as Al₂O₃ would generate XRD peaks as well, so careful subtraction of support background peaks from the overall data peaks is also important.

The purpose of the present study was to determine under what conditions 1-2 nm supported Pt nanoparticles could be analysed by conventional Bragg diffraction using both *in-situ* (i.e. flowing H2 to maintain metallic nanoparticles) and *ex-situ* XRD. We
have chosen Pt/Al₂O₃ as our probe system as supported Pt nanoparticles are one of the most widely studied heterogeneous catalysts due to their high catalytic activity for a number of catalytic reactions such as CO oxidation [188, 189], NOₓ reduction [190, 191], hydrocarbon hydrogenation [192, 193] and hydrogenolysis [194, 195]. In order to aid the interpretation of the in-situ XRD results, XAS and STEM results are also presented here.

6.1 Experimental

Supported platinum nanoparticles were prepared by atomic layer deposition (ALD). All the Pt samples were prepared in a continuous-flow stainless steel reactor operated under a base pressure of ~ 1 Torr [196]. Two types of supports were used, namely spherical alumina nanopowder (NanoDur™ mixture of delta and gamma Al₂O₃, Alfa-Aesar) and multi-walled carbon nanotubes (CNTs, O.D. 10-20 nm, length 10-30 µm, pore volume = 4 ml/g, Cheap Tube Inc.). Prior to ALD, the CNTs were activated by refluxing in conc. HNO₃, 70 vol%, for 10 h at 120 °C while stirring. The mixture was filtered and washed with deionized water eight times, followed by drying at 80 °C for 8 h. Al₂O₃ was used as-received. The supports, Al₂O₃ (500 mg) and CNTs (200 mg) were evenly spread into separated flat stainless steel trays and loaded into the ALD reactor. Pt ALD was performed using trimethyl (methylcyclopentadienyl) platinum (IV) (Pt(MeCp)Me₃, Sigma-Aldrich) and oxygen at 250 °C [197]. Three samples were prepared using 2 and 5 Pt ALD cycles over Al₂O₃ and 2 cycles over CNTs, marked as 2cPt-Al₂O₃, 5cPt-Al₂O₃ and 2cPt-CNT, respectively. After synthesis all three samples were reduced in 3.5 % H₂ at 250 °C for 1 h before being cooled to room temperature in He and then exposed to air for measurements.
Scanning Transmission Electron Microscopy (STEM) imaging was performed on pre-reduced catalysts using an aberration-corrected, cold-field emission gun microscope, JEOL JEM-ARM200CF, and operated at a primary energy of 200 keV. For high-angle annular dark-field imaging (HAADF), a spatial resolution of better than 70 pm can be achieved. In this work, HAADF images were used to determine the particle size distribution. The particle sizes were analyzed using the software Comptage de particule (V2). Approximately 500 particles from each sample were randomly chosen and counted for the particle size distribution plots.

X-ray absorption measurements were acquired at the 10-BM beamline of the Materials Research Collaborative Access Team (MRCAT) at the APS, ANL. Data was acquired in transmission at the Pt L₃-edge (11.564 keV) in step-scan mode using ionization chambers optimized for the maximum current with linear response (~10¹⁰ photons detected/sec) with 10 % absorption in the incident ion chamber and 70 % absorption in the transmission X-ray detector. A Pt foil spectrum was acquired simultaneously with each sample measurement for energy calibration. Catalyst samples were pressed into a cylindrical sample holder consisting of six wells, forming a self-supporting wafer which was then placed in a quartz tube (1-in. OD, 10-in. length) sealed with Kapton windows by two Ultra-Torr fittings through which gas could be flowed. Measurements were first taken in air at room temperature on the pre-reduced catalysts before a flow of 3.5 % H₂/He was introduced and the samples reduced at 250 °C. The catalysts were then cooled in 3.5 % H₂/He and measurements performed at room temperature. The normalized, energy–calibrated absorption spectra were obtained using standard methods and standard data reduction techniques were employed to fit the data.
using the WINXAS 3.1 software. Linear combination fitting was used to estimate the fraction of Pt metal and PtO present in the samples measured in air, in each case using the appropriate fully reduced catalyst as the Pt metal reference and an oxidized Pt nanoparticle as the reference for PtO. The EXAFS parameters were obtained by a least square fit in $R$-space of the $k^2$-weighted Fourier Transform (FT) data. The Debye-Waller factor $\Delta \sigma^2$ was held constant at 0.002 for all fits.

*In-situ* XRD measurements were performed at the 11-ID-D beamline at the APS, ANL. Data was acquired in transmission using X-rays at 16 keV ($\lambda = 0.765334 \, \text{Å}$) and a Pilatus 2M detector with typical exposure times of 5-10 s. Samples were pressed into wafers and held inside a Linkam stage for *in-situ* measurement. Measurements were first taken in air at room temperature on the pre-reduced catalysts before a flow of 3.5 % H$_2$/He was introduced and the temperature was ramped to 250 °C, holding for 10 min. The catalysts were then cooled in 3.5 % H$_2$/He and measurements performed at room temperature. The corresponding supports were treated with the same procedure and the reference measurements taken at the same conditions. The 2-D scattering images were integrated to 1-D scattering intensity data using the Fit2D software [198] to yield plots of scattered intensity versus $2\theta$. The Le Bail method [199] was used to fit whole XRD patterns between $10^\circ$ and $56^\circ$ $2\theta$ by means of Materials Analysis Using Diffraction (MAUD), a Java based refinement software [200]. MAUD treats each parameter associated with line broadening separately and thus can be used to deconvolute the contributions from the instrument and from the microstructural features of the sample which broaden the diffraction peaks. The instrumental contribution to the observed peak shape was determined using a standard (CeO$_2$, NIST SRM 674b) by refinement of the
Cagliotti parameters which were then fixed for subsequent refinements of the catalyst samples. In addition to background polynomial, the following parameters were refined for each sample: lattice parameters, isotropic Del′ particle size and isotropic microstrain [201, 202]. Prior to Le Bail refinement, the background scattering from the supports were subtracted from the diffraction patterns from the catalysts using the PANalytical High Score Plus software. Where the support subtraction was not perfect, small regions were excluded from the refinement procedure.

6.2 Results and Discussion

The loading of Pt was determined by ICP and yielded Pt loadings of 2.82 %, 15.1 % and 9.82 % for 2cPt-Al₂O₃, 2cPt-CNT and 5cPt-Al₂O₃ respectively. In order to characterize the Pt particle size distributions after reduction and subsequent exposure to air, STEM measurements were performed. HAADF STEM images are shown in Figure 6.3. The imaging indicated approximately spherical morphology for all three samples and therefore the diameters of individual Pt particles were used to determine the Pt particle size for each sample. The particle size was dependent on the loading and the nature of the support with the average sizes of 2cPt-Al₂O₃, 2cPt-CNT and 5cPt-Al₂O₃ being 1.2 nm, 1.5 nm and 1.9 nm respectively. The standard deviations were similar for all catalysts.
Figure 6.3 STEM HAADF images and the corresponding particle sizes of (a) 2cPt-Al$_2$O$_3$, (b) 2cPt-CNT and (c) 5cPt-Al$_2$O$_3$.

EXAFS spectra measured in air and under H$_2$ are shown in Figure 6.4 and the fitted parameters are listed in Table 6.1. The EXAFS measurements of all three samples taken in air contained peaks at approximately 1.6 Å indicative of Pt-O scattering. The Pt-O coordination numbers are close to 4 which provides further evidence that the oxidized Pt species is PtO since many Pt(II) compounds are four coordinate [203]. In contrast, the spectra for the samples taken in flowing H$_2$ revealed peaks similar to the metallic foil showing the presence of fully reduced Pt. Compared to the fully reduced samples, measured in H$_2$, the peaks at 2.4-2.9 Å due to Pt-Pt scattering were much lower in
intensity. The Pt-Pt bond lengths of all three samples were slightly contracted by 0.01-0.02 Å relative to the foil. This phenomenon has been previously observed for small metallic nanoparticles [204-206]. On exposure to air, a fraction of the metal was oxidized, lowering the amount of metallic Pt in the sample and therefore the number of Pt atoms in the metallic phase able to contribute to Pt-Pt scattering. For example, for the 2cPt-Al₂O₃, where the average particle size by STEM was about 1.2 nm, the Pt nanoparticles were almost completely oxidized in the presence of air as indicated by its EXAFS spectra.

![Graph](image)

**Figure 6.4** Pt L₃-edge magnitude of the FT of the EXAFS of 2cPt-Al₂O₃ (green), 2cPt-CNT (blue) and 5cPt-Al₂O₃ (red) measured in (a) air and (b) H₂. Pt foil is shown for reference (black, dashed). $k^2$: $\Delta k = 3.0-11.4$ Å⁻¹.
Table 6.1 Fitted EXAFS data of the samples measured in air and in H\textsubscript{2} at the Pt L-edge.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scattering pair</th>
<th>$N^a$</th>
<th>$R$ (Å)$^a$</th>
<th>$E_0$ (eV)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na\textsubscript{2}Pt(OH)\textsubscript{6} (ref)</td>
<td>Pt-O</td>
<td>6.0</td>
<td>2.05</td>
<td>0.00</td>
</tr>
<tr>
<td>2cPt-Al\textsubscript{2}O\textsubscript{3} (air)</td>
<td>Pt-O</td>
<td>3.6</td>
<td>2.05</td>
<td>2.83</td>
</tr>
<tr>
<td>2cPt-CNT (air)</td>
<td>Pt-O</td>
<td>3.8</td>
<td>2.06</td>
<td>2.92</td>
</tr>
<tr>
<td>5cPt-Al\textsubscript{2}O\textsubscript{3} (air)</td>
<td>Pt-O</td>
<td>4.0</td>
<td>2.06</td>
<td>4.22</td>
</tr>
<tr>
<td>Pt foil (ref)</td>
<td>Pt-Pt</td>
<td>12.0</td>
<td>2.77</td>
<td>0.00</td>
</tr>
<tr>
<td>2cPt-Al\textsubscript{2}O\textsubscript{3} (H\textsubscript{2})</td>
<td>Pt-Pt</td>
<td>7.7</td>
<td>2.75</td>
<td>-3.54</td>
</tr>
<tr>
<td>2cPt-CNT (H\textsubscript{2})</td>
<td>Pt-Pt</td>
<td>8.2</td>
<td>2.75</td>
<td>-2.26</td>
</tr>
<tr>
<td>5cPt-Al\textsubscript{2}O\textsubscript{3} (H\textsubscript{2})</td>
<td>Pt-Pt</td>
<td>10.9</td>
<td>2.76</td>
<td>-2.16</td>
</tr>
</tbody>
</table>

$^a$ $N$ = coordination number; $R$ = bond distance; $\Delta\sigma^2$ Debye-Waller factor was 0.002 for all the samples; $E_0$ = energy offset.

The XRD patterns of the bare Al\textsubscript{2}O\textsubscript{3} support in air and 2cPt-Al\textsubscript{2}O\textsubscript{3} in air and H\textsubscript{2} are shown in Figure 6.5, illustrating that the diffraction patterns of 2cPt-Al\textsubscript{2}O\textsubscript{3} were dominated by peaks arising from the Al\textsubscript{2}O\textsubscript{3} support. The difficulty in detecting peaks from Pt is due to the low loading and high dispersion giving rise to extremely broad, low intensity diffraction peaks, which can easily go unidentified if only visual inspection of a powder pattern is performed. For this reason, a direct analysis of the Pt phase was not possible without further data processing. In order to isolate the diffraction features arising
from the Pt particles, the acquired diffraction pattern from the bare support was subtracted from the patterns of the Pt loaded catalysts and the resulting diffraction patterns are shown in Figure 6.6. Some parts of the subtracted diffraction patterns contained glitches where the subtraction of the support was non-perfect (see for example $2\theta = 22^\circ$ and $32^\circ$). This could be due to small changes in the Al$_2$O$_3$ support structure which could lead to shifts in the intensities or peak positions.

**Figure 6.5** XRD plots of bare Al$_2$O$_3$ support (top) and 2cPt-Al$_2$O$_3$ in air (middle) and in H$_2$ (bottom). Plots are offset for clarity.
Figure 6.6 XRD plots after subtraction of the support in air (top) and in H\(_2\) (bottom) of (a) 2cPt-Al\(_2\)O\(_3\) and (b) 2cPt-CNT and (c) 5cPt-Al\(_2\)O\(_3\).

Subtraction of the support contribution from the diffraction patterns of the Pt loaded samples allowed the peaks arising from metallic Pt to be fitted using Le Bail refinement which uses an iterative least squares method to fit a calculated diffraction
pattern to the observed data. The results of the refinements are shown in Table 6.2. From the XRD measurements in air it was not possible to extract any quantitative structural information from the 1.2 nm or 1.5 nm particles (STEM sizes) due to the lack of Pt metal peaks in the former case and the interference of the PtO phase with the Pt metal phase in the latter case preventing a satisfactory refinement of the Pt metal structure. Hence when measured in air the only sample where it was possible to calculate a Pt metal particle size was 5cPt-Al₂O₃, which yielded a value of 2.4 nm. When the measurement was performed under H₂, the particle size increased to 3.3 nm. Both 2cPt-Al₂O₃ and 2cPt-CNT contained smaller Pt metal particles than 5cPt-Al₂O₃ when measured in H₂ with values of 1.4 nm and 2.6 nm respectively. The general trend is in agreement with the particle size measurements from STEM.

Table 6.2 Results from Le Bail refinement of XRD data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phases detected</th>
<th>Lattice parameter, $a$ (Å)</th>
<th>Crystallite diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2cPt-Al₂O₃ (air)</td>
<td>PtO</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2cPt-CNT (air)</td>
<td>PtO + Pt</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5cPt-Al₂O₃ (air)</td>
<td>PtO + Pt</td>
<td>3.9355(09)</td>
<td>2.4</td>
</tr>
<tr>
<td>2cPt-Al₂O₃ (H₂)</td>
<td>Pt</td>
<td>3.8833(19)</td>
<td>1.4</td>
</tr>
<tr>
<td>2cPt-CNT (H₂)</td>
<td>Pt</td>
<td>3.8956(07)</td>
<td>2.6</td>
</tr>
<tr>
<td>5cPt-Al₂O₃ (H₂)</td>
<td>Pt</td>
<td>3.8997(04)</td>
<td>3.3</td>
</tr>
</tbody>
</table>
When the diffraction pattern was collected in H$_2$, measurable diffraction peaks from Pt metal observed for the 1.4 and 2.6 nm (XRD size) particles confirmed that the absence of peaks in air was due to oxidation of the nanoparticles and not a lack of sensitivity for the measurement of small nanoparticles. The presence of peaks shows that it is possible to observe very small particles (< 2 nm) by XRD provided the measurement is taken under conditions where oxidation cannot occur. This finding here highlights the importance of measuring small nanoparticles under *in-situ* conditions to correctly characterize the particle size. In addition to the particle size, the lattice parameter of the Pt phase was also calculated from the XRD pattern and provides further motivation for measurement under *in-situ* conditions. The lattice parameter calculated for the 2.4 nm particles in air was larger than bulk Pt and suggests that surface oxidation may cause disorder of the surface leading to an increase in the average (metallic) Pt-Pt bond distance and hence an increase in the size of the unit cell [207]. It is possible that the expanded lattice parameter results from the overlap of the peaks due to the PtO phase causing an apparent peaks shift to lower angle. When performed in H$_2$ the lattice parameters were in fact smaller than bulk, and the particles were fully reduced. This trend of a contraction in the Pt-Pt bond distance is consistent with the EXAFS data.

The approach to analysis taken here should be generally applicable to other supported metal nanoparticle systems. However support crystallinity is likely a key factor for the diffraction peaks from small metal nanoparticles to be differentiated from the support. Supports such as SiO$_2$ could be problematic since their poorly defined diffraction patterns make separation of support scattering from nanoparticle scattering more difficult. While those supports, which are typically more crystalline such as TiO$_2$,
would likely be more applicable to analysis due to the large difference in peak width compared to the metal nanoparticles.

6.3 Conclusion

Highly dispersed Pt nanoparticles with narrow distribution supported on Al$_2$O$_3$ and CNTs have been synthesized to investigate the conditions under which X-ray diffraction can be performed on small nanoparticles. This work has shown that in order to collect useful XRD data on very small (< 2 nm) metallic nanoparticles deposited on supports, measurements must be performed under an environment where the metal particles remain in their metallic phase. Otherwise, the formed metal oxide-capping layer may prevent the detection of the metallic peaks by XRD, especially when the metal particles are small (< 2 nm). For larger particles (> 2nm), although XRD performed in air can be used to observe the metal peaks, the remaining metal core after oxidation is still sufficiently large to be detected. However, the result may not be accurate and in-situ XRD is still required to obtain the correct sizes of the metal nanoparticles.
7. CONCLUDING REMARKS

The addition of promoters to enhance the overall catalytic activity and selectivity is important in both industry and academic research. The intimate metal-promoter interaction is often of vital importance to the catalyst’s performance. The identity of the active site is a question of fundamental importance to how heterogeneous catalysts work. However, despite this importance, in many cases, we still have little idea exactly how reactants interact with the surface. Moreover, the identities of the promoter phases in the promoted catalytic system are also unknown to many of us. This thesis has analyzed the fundamentals of catalyst preparation in an effort to increase the interaction of the promoter with the active metal, and the changes that we can observe for the catalytic performance of CO hydrogenation catalysts as a function of the degree of metal-promoter interactions. We have presented our results as a combination of catalysts synthesis, catalysts characterization by a various kinds of advanced techniques, and catalytic performance in a plug flow CO hydrogenation reactor.

Using the theory of Strong Electrostatic Adsorption (SEA), we have selectively deposited the Mn promoter onto the targeted active metal oxide on an oxide support. We have applied the selective adsorption methodology to examine the metal-promoter interaction effects on the catalytic performance of the CO hydrogenation catalysts for the conversion of synthesis gas (CO and H₂) to ethanol or longer-chain hydrocarbons for alternative fuel production.

In the first system, the MnO₄⁻ promoter precursor was selectively deposited onto the high PZC Rh₂O₃ as opposed to the low PZC silica support. Results by STEM-EELS
confirmed the creation of enhanced metal-promoter interactions when compared to its counterpart where Manganese nitrate was randomly deposited onto the Rh/SiO₂ catalyst by incipient wetness impregnation (IWI). The reactivity results indicate higher ethanol selectivity was achieved with the enhanced metal-promoter interactions. In the second system for the Mn promotion of a Co/TiO₂ catalyst for Fischer Tropsch synthesis, we further utilize the SEA synthesis method to examine the metal-promoter interaction effects on F-T productivity, here we have compared three types of FT catalysts, namely Mn^{SEA monolayer}/Co/TiO₂, Mn^{SEA partial}/Co/TiO₂ and Mn^{DI}/Co/TiO₂ catalysts. The reactivity results showed Mn^{SEA monolayer}/Co/TiO₂ catalyst has the highest selectivity (>80wt%) for C₅⁺ hydrocarbons, and the STEM-EELS characterization demonstrated the core-shell catalyst structure, where the Co particles were evenly coated by a monolayer of Mn promoter, was achieved during the synthesis process, thus leading to maximum metal-promoter interaction compared to the other two catalyst preparations. Moreover, the Mn promoter phase was found to be MnO by EELS spectrum.

Finally in another alcohol synthesis study over a Mn promoted Rh catalyst supported on carbon nanotubes (CNTs), we have once again linked significant improvement in catalytic performance (ethanol selectivity) to the creation of intimate contact between the promoter phase and the active metal as evidenced by the STEM-EELS characterization. However, due to the nature of CNTs, the SEA synthesis method is not practical for this catalytic system, the enhanced mental-promoter interaction was achieved by a higher Mn weight loading by impregnation method. Both XANES and EELS spectra show that the Mn promoter is present as MnO.
These are just three examples where we can achieve a better productivity from enhancing the metal-promoter interactions, and this idea will be promising in assisting us to define the precise roles of a promoter during a reaction. By focusing on the rational catalyst design, assisted by nowadays state of art characterization instruments and the fundamental studies from the computational calculations, we are bound to improve the overall efficiency of the world’s highly valued catalytic processes and find the solutions for the though industrial challenges.
[50] I. Catalytica Associates, Synthesis of methanol, glycols, higher alcohols and other oxygenates from CO/H2; Multiclient study No. 4162, in, 1983.


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Unit 2, Apt 24-2, Chongqing City, 400084, China email: jingjingmoon@gmail.com
Language: Chinese Mandarin and English

Education
B.S., Biochemical Engineering, 2009
Sichuan University, Chengdu, Sichuan, China

Ph.D., Chemical Engineering, 2014
University of Illinois at Chicago, Chicago, IL, USA

Research Experiences
University of Illinois at Chicago, 08/2009-05/2014
Department of Chemical Engineering, Chicago, IL
  ✔ Dissertation (Advisor: Prof. Randall Meyer): Manganese Promoted CO
      Hydrogenation Catalysts: A Study of Metal Promoter Interaction Effects.

University of Illinois at Chicago, 01/2011-05/2014
Department of Physics, Chicago, IL
  ✔ Research projects collaboration under the guidance of Prof. Robert Klie focusing
      on catalysts characterization by electron microscopy technique which includes
      TEM, STEM, and EELS.

Argonne National Laboratory, 03/2012- 03/2014
Chemical Science and Engineering Division, Heterogeneous Catalysis Group, IL
  ✔ Research collaboration under the guidance of Dr. Jeffrey Miller and Dr.
      Christopher Marshall for the following research projects:
      [1].In-situ synchrotron characterization of highly dispersed supported platinum
          nanoparticles.
      [2].Synthesis, Characterization and Reactivity Study of Highly Dispersed
          Mn/Rh/CNTs Catalyst for Enhanced Alcohol Production.
      [3].Reactivity Study of Mn/Co/TiO2 Fischer-Tropsch Catalysts with Different Co-Mn
          (metal-promoter) Interactions.
      [4].Reactivity Study of Selective Adsorption of Manganese onto Rhodium for
          optimized Mn/Rh/SiO2 Alcohol Synthesis Catalysts.

Sichuan University, 09/2008- 05/2009
Department of Chemical Engineering, Chengdu, Sichuan China
  ✔ Undergraduate thesis (Advisor: Prof. Liangyin Chu): Synthesis and
      Characterization of environmental responsive hydrogel.

Teaching Experience
Teaching Assistant:
Professional Skills

- Chemical Process Engineering: 1) Reactor design (High pressure, high heat, gas, liquid phase chemical reactions), build, optimization and trouble shooting. 2) Piping & Instrument Diagrams (P&IDs). 3) Process Flow Diagrams (PFDs). 4) Engineering design calculations, such as detailed equipment sizing.
- Chemical Product Analysis: On stream GC installation with Reactor, GC calibration (organic and inorganic) and products quantification, and GC-Mass Spectrometry.
- Catalysts Design and Synthesis: SEA and IWI synthesis methods (e.g. Impregnation of precious metal precursor onto oxide support such as SiO₂).
- Characterization Skills: 1) Transmission electron microscope (TEM/STEM). 2) EELS and EDXS for elemental composition analysis. 3) ICP-OES for metal loading quantification. 4) XAS analysis for metal oxidation state (XANES) and local geometry around the metal atoms (EXAFS). 5) XRD for metal phase and size confirmation. 6) TPR for reduction behavior study.
- Other PC Skills: Microsoft Office, Maple, ASPEN, FEFF, Matlab.

Publication


Conference Presentation

[2]. Gordon Research Conference (Catalysis 2012), New London, NH;
[3]. MSA (Microscopy Society of America) Conference (2012), Phoenix, AZ;
[4]. Microscopy for life: M3S Celebrates 55 Years (Invited talk, 2012), Baxter Headquarters, Deerfield, IL;
[5]. 23rd North American Catalysis Society Meeting (2013), Louisville, KY;
[6]. MSA (Microscopy Society of America) Conference (2013), Indianapolis, IN;
[7]. AICHE(2013), San Francisco, CA.

Award and Honor

- Chancellor’s Graduate Research Fellowship Award 2011-2012 and 2012-2013, UIC
- President of Graduate Student Association of Chemical Engineering (April 2010-May 2011), UIC
- Event Planner and coordinator in Chinese Student and Scholar Association at UIC. 2010-2011.
- Second Place of Western China division, National College Soccer League, 2006, Sichuan University

Memberships

- American Institution of Chemical Engineering (AIChE)
- North American Catalysis Society (NACS)
- Chicago Catalysis Club (CCC)