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X-RAY ABSORPTION SPECTROSCOPY APPLIED TO MIXED-METAL IRON-BASED FISCHER-TROPSCH CATALYSTS

A Dissertation

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

in

The Gordon A. and Mary Cain Department of Chemical Engineering

By
Andrew Allen Campos
B.S., University of Florida, 2005
May 2010
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Abstract

Synthetic fuels derived from methane, coal or biomass are essential in addressing future transportation fuel demands which are expected to exceed petroleum-derived capacities. The Fischer-Tropsch synthesis (FTS) is the most studied technique for the conversion of coal or biomass-derived syngas into transportation fuels. Fe-based catalysts are typically used for the FTS of biomass and/or coal-derived syngas due to: the relatively low cost of iron, water-gas shift activity, and low methane selectivity at industrial FTS conditions.

Fe/Cu/SiO$_2$ Fischer-Tropsch catalysts promoted with Cr, Mn, Mo, W, or Zr were studied in-situ, using Fe K-edge TPR XANES (temperature programmed reduction X-ray absorption near-edge structure), which was collected during reduction under flowing syngas. XANES analysis indicates that the phase transformations under syngas reduction are similar among the Fe/Cu/SiO$_2$-containing catalysts. LCF (linear combination fitting) used an expanded model (original model: Fe$_2$O$_3$ → Fe$_3$O$_4$ → Fe$_x$C) which included Fe$^{2+}$ phases: FeO and Fe$_2$SiO$_4$. This expanded model was found to more closely account for the Fe-containing phases under syngas reduction.

Fe K-edge XANES spectra were also collected during in-situ H$_2$ reduction (25-300°C, 2° C/min; 300°C, 2 hr), followed by a syngas reaction (2:1 H$_2$:CO ratio, 300°C, 4 hr) of a Cr-promoted, Mn-promoted, and an unpromoted catalyst. XANES analysis indicates that the Fe phase transitions under flowing H$_2$ (where bulk α-Fe is not observed) or syngas (before observable Fe$_x$C formation) are very similar. During H$_2$ reduction, it was shown from the Cr K-edge XANES analysis that Cr substituted as a trivalent species into Fe$_3$O$_4$, corresponding to the Fe$_3$O$_4$-Cr$_2$O$_3$ phase. Mn K-edge XANES analysis indicates that Mn substituted as a divalent species into Fe$_3$O$_4$, corresponding to a composition of (Fe$_{1-y}$Mn$_y$)$_3$O$_4$. The differences in the oxidation state of the substituted promoter (i.e., divalent Mn vs. trivalent Cr substitution into...
Fe$_3$O$_4$ likely contributed to the differences in the steady state activity of the catalyst. Mn promotion inhibited carbon deposition and had a higher steady state activity relative to the unpromoted catalyst. The deactivation of the Cr-promoted to the steady state CO hydrogenation levels of the unpromoted catalyst suggests that the formation of the Fe$_3$O$_4$-Cr$_2$O$_3$ phase does not prevent carbon deposition.
Chapter 1: Introduction

1.1. Research Objective

To use X-ray absorption spectroscopy (XAS), X-ray diffractometry (XRD), and mass spectrometry (MS) to study the effects of a transition metal addition (i.e., Mn, Zr, Cr, etc.) with iron-based Fischer-Tropsch catalysts. The overall objective is to determine whether transition metals formed mixed metal carbides or oxides with iron during activation or during CO hydrogenation conditions.

1.2. Engineering Relevance of Project

There is an increasing interest in the United States to develop alternative fuels and it is apparent that using domestic resources is the most attractive way to become energy independent. The United States has approximately three times the energy in coal reserves than the entire Middle East in oil and natural gas reserves combined\(^1\). Although there are engineering issues with coal-to-liquid (CTL) processes, rising prices in petroleum as well as innovative research is creating a favorable environment for large-scale implementation of CTL Fischer-Tropsch in the US\(^2,3\).

1.3. Iron-based Fischer-Tropsch Catalysts

Coal-derived synthesis gas typically has a H\(_2\):CO ratio between 0.5-0.7:1\(^4\), which requires a catalyst with water-gas shift activity to carry out the reaction. The catalyst most widely used for the Fischer-Tropsch reaction of coal-derived synthesis gas is iron-based due to its water-gas-shift activity (to improve H\(_2\) efficiency), low cost, and low methane selectivity (necessary for higher selectivity of liquid fuels).

1.4. Synthesis of Iron-based Catalysts

The studied catalysts were synthesized at Clemson University using co-precipitation methods and adding a third transition metal (different from Fe or Cu) to an iron-based catalyst to improve catalytic activity, stability\(^5\), and selectivity due to iron-transition metal interactions.
1.5. Using XAFS to Characterize the Catalysts

Changes in catalyst activity due to changes in the local environment of iron require a characterization technique such as XAFS (X-ray absorption fine structure), which gives unique information about the local structure of a central atom (i.e., Fe, Cr, etc.) that is not possible with other characterization techniques. In-situ XAFS is used to determine how the transition metals affected the local environment of iron during activation and reaction, which will complemented the activity, selectivity, and SSITKA (steady-state isotopic transient kinetic analysis) studies at Clemson University.

1.6. Rationale for This Research

The United States has approximately three times the energy in coal reserves than the entire Middle East in oil and natural gas reserves combined, which is shown in Table 1.1. This, combined with increasing per capita energy consumption, high dependency on domestic energy imports (as of August 2009: 33% of total energy is imported; 56.9% of net petroleum imported), and rising oil prices signals the necessity for the cost-effective conversion of domestic resources into clean fuels.

<table>
<thead>
<tr>
<th>Table 1.1: Fossil fuel reserves by location.</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity</td>
<td>Energy equivalent (BTUs)</td>
</tr>
<tr>
<td>262.7 billion short tons of coal in the US</td>
<td>$2.0 \times 10^{19}$</td>
</tr>
<tr>
<td>746 billion barrels of oil in the Middle East</td>
<td>$4.3 \times 10^{18}$</td>
</tr>
<tr>
<td>2549 trillion cubic feet in natural gas in the Middle East</td>
<td>$2.6 \times 10^{18}$</td>
</tr>
</tbody>
</table>

The most developed technology for the conversion of coal-to-liquid (CTL) fuels is the Fischer-Tropsch synthesis (FTS), which converts coal-derived synthesis gas (syngas) into primarily linear hydrocarbons as in Equation (1.1):

$$\text{(2}n \text{+ 1)}\text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O} \quad (1.1)$$
Since coal-derived synthesis gas has a low ratio of hydrogen to carbon monoxide\textsuperscript{4}, the water-gas-shift activity provided by the iron increases the hydrogen efficiency. Other factors such as the relatively low cost of iron, and low methane selectivity (necessary for a higher selectivity of liquid fuels) also makes iron-based catalysts optimal for CTL FTS.

1.6.1. Improvement of Catalyst Selectivity

Despite a great deal of research into iron-based Fischer-Tropsch catalysts, the products of the reaction are usually a highly variable mixture of alkanes, olefins, and oxygenates (Figure 1.1); therefore improvement of the catalytic selectivities are needed before commercialization of coal-based FTS in the US.

\begin{equation}
\ln \left( \frac{w_n}{n^{\alpha}} \right) = n \times \ln(\alpha) + \left( \ln(1 - \alpha)^2 - \ln(\alpha) \right)
\end{equation}  (1.2)

where \( w_n \) is the weight fraction of product containing \( n \) number of carbons, and \( \alpha \) is the chain growth probability\textsuperscript{12}. Figure 1.2 clearly shows that the hydrocarbon product distribution (which
is analogous to selectivity, depending on the definition of desired products) is a strong function of the chain growth probability, $\alpha$.

![Diagram](image)

Figure 1.2: Hydrocarbon product wt. fraction as a function of chain growth probability$^{12,13}$.

1.6.2. Low Sulfur, High Cetane Number FT Diesel

Petroleum diesel (diesel consists of primarily linear hydrocarbons in the C$_{10}$-C$_{20}$ range) has a cetane number 40-55 (analogous to octane for gasoline) compared with Fischer-Tropsch diesel which has a cetane number 73-75$^{13}$. The higher cetane number means it burns cleaner and causes fewer pollutants in the atmosphere. Fischer-Tropsch diesel is virtually sulfur free (due to sulfur removal in the gasification process); therefore, partial oxidation of FT diesel is desirable for hydrogen generation for fuel cell applications (due to low sulfur tolerance of PEMFCs and the low concentration of sulfur-containing groups in FT diesel)$^{14,15}$.

1.6.3. Thermodynamics of Diesel Formation

The Fischer-Tropsch reaction is highly exothermic, making heat removal an issue. Therefore, a reactor that removes heat efficiently and effectively such as a slurry bubble column reactor (SBCR) is the most promising for commercial applications. In a SBCR, an inert liquid phase maintains optimum reaction conditions (20 atm, 260-280°C) due to its ability to remove
heat quickly. Equation (1.3) shows the thermodynamics for C\textsubscript{16}H\textsubscript{34} (cetane, a component in diesel)\textsuperscript{16},
\[ 33 \text{H}_2 + 16 \text{CO} \rightarrow \text{C}_{16}\text{H}_{34} + 16 \text{H}_2\text{O}; \Delta H_{\text{rxn}}^\circ = -2475 \text{kJ mol}^{-1}; \Delta G_{\text{rxn}}^\circ = -181 \text{kJ mol}^{-1} \tag{1.3} \]
which shows that the reaction is spontaneous (from the negative Gibbs free energy of reaction) as well as exothermic.

1.6.4. Attrition Properties of Iron-based Fischer-Tropsch Catalysts

Slurry bubble column reactors are advantageous for the heat removal required for the Fischer-Tropsch reaction, however in commercial processes the high gas flow rates cause the catalyst particles to collide and then break into smaller particles or attrite\textsuperscript{5,17}. When the fine particles are downstream, the following problems can occur: 1) filter blockages (causing a reactor shut down); 2) difficult separation process (the iron-based catalyst is made of primarily iron which has a similar density to the hydrocarbon waxes); 3) increases in slurry viscosity slowing reaction kinetics (mass-transfer limitations, causing a reactor shut down)\textsuperscript{17}.

In the field of steel alloying, the microstructure of (Fe, Cr)\textsubscript{23}C\textsubscript{6} was studied by Fan et al., showing that the mixed metal carbide has advantageous wear-resistant properties\textsuperscript{18}. Other studies have also shown that the wear-resistant properties of various steel alloys are greater than without the alloy additions\textsuperscript{19,20}. Therefore, if the secondary metal forms an alloy with iron during the FT reaction, then the microstructure effects of alloying should also correlate to improvements in the mechanical properties at the microstructure level, thus increasing attrition resistance. While this research did not address the attrition properties of the transition metal promoted catalysts, it is an interesting field of research that should be pursued further.

1.7. Synthesis of Iron-based Catalysts

The synthesis of the iron-based Fischer-Tropsch catalysts were based on the novel idea of adding a transition metal to the catalyst in order to improve the stability of the carbide phase (i.e.,
a Fe-Cr-C phase is more stable than $\theta$-Fe$_3$C$^{21}$, as well as the activity, selectivity, and attrition resistance of the catalyst$^{22}$. The mol.-based compositions of the catalysts are presented in Equation (1.4).

$$(100 - x)\text{Fe}/x\text{Me}/5\text{Cu}/17\text{SiO}_2; \text{Me} = \text{Cr, Mn, Mo, Zr, W}; \quad x \leq 20 \quad (1.4)$$

Within the Fischer-Tropsch community, there is speculation about the active phase of iron during the reaction; however, the current consensus is some form of the iron carbide is the active phase$^{23, 24}$.

Catalytic activity changes during the FTS are due to carburization on the surface of the catalyst. This activity increase occurs until an inactive graphitic layer forms on the surface, causing a decrease in H$_2$ and CO diffusion to the active iron carbide$^{25}$. Since iron-based mixed metal carbides are more stable than $\theta$-Fe$_3$C$^{21}$, a transition metal alloy with iron should improve the stability of the active carbide, thus inhibiting inactive carbon build-up on the catalyst that renders it inactive$^{26}$.

### 1.8. Experimental Objectives of Research

XAS characterization of the transition metal promoted catalysts had several goals: 1) determining the effects of transition metal promotion on the reducibility of Fe (i.e., metal-loading effects and comparing different transition metals); 2) determining the site-location of the transition metal additions on the as-prepared catalyst, as well as during reduction and reaction; 3) to study the catalyst under a reactive environment, and give a phase speciation during reduction and reaction conditions; 4) to study the effluent gases of the in-situ experiments (residual gas analysis via mass spectrometry). The latter two objectives would give a side-by-side comparison of the phases and effluent gases during reduction and reaction.
1.9. Outline of the Dissertation

Chapter 1 introduces the concept of the Fischer-Tropsch synthesis, a reaction which converts coal- or biomass-derived synthesis gas into liquid fuels. The rationale for this research is based on the high domestic coal resources, limited domestic petroleum capacity, and the drive for energy independence in the US. It is described why the iron-based catalyst is generally preferred for the conversion of gasified coal into liquid fuels, as well as why improvements in catalytic performance with transition metal additions are necessary for the domestic commercialization of this process.

Chapter 2 describes X-ray absorption spectroscopy and how it can be applied to catalytic systems. Specifically, this work is focused on studying the effects of transition metal promotion of Fe-based Fischer-Tropsch catalysts with XAS. The limited studies of XAS for Fe-based Fischer-Tropsch catalysts, especially for the transition metal promotion of Fe/Cu/SiO₂-based catalysts is discussed.

Chapters 3-5 are written in journal style. Chapter 3 has been published in a peer-reviewed journal; Chapters 4 and 5 will be submitted for publication. These stand-alone chapters have some overlap in the introduction and experimental methods used, however the results are unique and address various aspects of the experimental objectives. Chapter 3 is an activity and ex-situ XANES study on the effects of Mn promotion on an Fe-based Fischer-Tropsch catalyst. The work in Chapter 3 mainly deals with three catalysts: 100Fe/5Cu/17SiO₂, 95Fe/5Mn/5Cu/17SiO₂, 80Fe/20Mn/5Cu/17SiO₂, and determines the effect of Mn promotion on the CO hydrogenation activity, as well as carbon deposition. In addition, the Fe phase composition of the fresh and reacted catalyst is investigated in conjunction with the Mn-site location of the spent catalyst. Chapter 4 is an in-situ Fe K-edge XANES study of the reduction of 95Fe/5Me/5Cu/17SiO₂ (Me = Cr, Mn, Mo, W, Zr) compared to the unpromoted
100Fe/5Cu/17SiO₂ catalyst. The XANES spectra were collected while reducing the catalyst in flowing syngas to determine the effect of the transition metal on Fe reduction and CO hydrogenation. A quadrupole mass spectrometer was used to measure the outlet gas composition under the same conditions (temperature ramp rate, catalyst mass, syngas composition, and flow rate) as the in-situ TPR XANES experiments. This work gave a side-by-side comparison of the effluent gases and the Fe phase composition during CO hydrogenation conditions. **Chapter 5** is an in-situ Fe K-edge XANES study which focuses on the effects of Cr or Mn-promotion on an Fe-based Fischer-Tropsch catalyst during H₂ activation and syngas reaction. Additionally, the in-situ Cr and Mn K-edge XANES were studied during H₂ reduction and CO hydrogenation conditions to determine how the local environment of these promoters affected the initial and steady state CO hydrogenation catalytic activity.

**Chapter 6** offers a summary of the body of work encompassed in **Chapters 3-5**. A recommendation for future work is also given.

### 1.10. References


21. B.-J. Lee, Calphad, 1992, 16(2), 121-149.


Chapter 2: Literature Review

2.1. X-ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) is an interesting characterization technique that uses synchrotron radiation in order to probe local structure of a specified element. XAS has the advantage of being able to determine the local environment of nearly all elements of interest in the Fischer-Tropsch synthesis (for example, contrasted with Mössbauer spectroscopy, which is limited to elements that exhibit the Mössbauer effect).

Synchrotron facilities provide high fluxes in the X-ray region of the electromagnetic spectrum, sufficient for XAS studies. One example of a synchrotron facility is the Center for Advanced Microstructures and Devices (CAMD) located in Baton Rouge, Louisiana. CAMD uses a bending magnet to accelerate packets of electrons approaching the speed of light in a storage ring\textsuperscript{1,2}. The accelerated electrons emit a spectrum of energy, from which a double crystal monochromator filters a single wavelength from the spectrum by rotating the crystal; this is shown in Figure 2.1.

![Flow diagram of synchrotron radiation from storage ring to transmission chamber.](image)

Figure 2.1: Flow diagram of synchrotron radiation from storage ring to transmission chamber.

When the X-ray photons travel through the sample, fractions of the electrons absorb the energy. The photon energy required to free an electron that is bound to a central atom is called
the edge (a list of edge energies are tabulated). This edge is a pseudo-binding energy that is dependent on the atomic number and oxidation state of the atom, as well as the distance and angular momentum of the electron. The $1s$ shell is the closest to the nucleus; therefore, it has the highest edge energy, which is the K-edge. The $2s, 2p_{1/2}, 2p_{3/2}$ shells are the next highest in energy, which are the L$_{I}$, L$_{II}$, L$_{III}$ edges, respectively.

If the energy of the photon absorbed by the electron is greater than its edge energy, the electron will exit the core hole it was occupying and behave as a wave with a kinetic energy equaling the difference between the photon energy and the binding energy; this is the photoelectron. The photoelectron wave has a final state of $\ell \pm 1$ (where $\ell$ refers to angular momentum) of what it had when it occupied the core shell [i.e., the excitation of the $1s$ shell ($\ell = 0$), will have an angular momentum of $\ell = 1$, or p-type symmetry)]$^4$. The wavelength of the photoelectron is given by Equation (2.1):

$$\lambda = \frac{\hbar}{p}$$  \hspace{1cm} (2.1)

where $\hbar$ is Dirac’s constant, $\lambda$ is the wavelength, and $p$ is the momentum of the photoelectron$^5$. The momentum of the photoelectron is given by Equation (2.2):

$$\frac{p^2}{2m} = h\nu - E_0$$  \hspace{1cm} (2.2)

where $m$ is the mass of an electron, $E_0$ is the binding energy of the photoelectron, and $\nu$ is the frequency$^5$.

Neighboring atoms cause interference, also called backscattering, with the wave which either result in constructive or destructive interference$^5,6$. A spectrum of the backscattering phenomenon is better known as X-ray absorption fine structure (XAFS). Three common methods for collecting XAFS spectra are: total electron-yield (contains surface-specific information) as well as fluorescence and transmission (contains bulk information)$^7$. 
2.1.1. XANES and EXAFS

XANES (X-ray absorption near-edge structure) and EXAFS (extended X-ray absorption fine structure) are the two regions in an XAFS (X-ray absorption fine structure) spectrum. XANES spectra range from -20 eV to 30 eV past the edge [the point of inflection on the $\chi \mu(E)$ vs. E graph shown in Figure 2.2]. The XANES region contains information about the oxidation state and the local structure of the absorbing atom$^5,8$.

![Normalized (defined later) K-edge of a Mo$_2$C std. in transmission (taken at the NSLS).](image)

EXAFS spectra range from approximately 30 eV to 1000 eV past the edge. EXAFS spectra contain information about bond distances, coordination numbers and type of neighboring atoms, as well as the Debye-Waller factor (a measurement of bond disorder)$^9,10$.

The Debye-Waller ($\sigma$) factor has two contributions: (1) from thermal disorder (which is due to vibrations of the molecules); (2) structural disorder, which is due to differences in the distances of a given coordination shell (a coordination shell is defined as atoms that are sufficiently separated so that their Fourier transform in R-space shows separate peaks$^5$). Therefore, if a coordination shell has complete homogeneity with all atoms at a specific distance, the structural contribution to the Debye-Waller factor would be minimal.
Basic understanding of XAS theory is necessary before extracting meaningful structural parameters from an EXAFS spectrum. The theory is based on the interference of the photoelectron by neighboring atoms; the atomic number and distance of the neighboring atoms correlate to the magnitude of the interference. The principle that the photoelectron acts as a wave as it is backscattered is the premise for the EXAFS formula \[ \text{See Equation (2.1)} \]\(^7,\text{10}\). XAFS theory began by the work of Lytle, Sayers and Stern, who discovered that structural information can be obtained by applying a Fourier transform (a frequency filter) to an EXAFS spectrum\(^11,\text{12}\).

The signal for transmission is given by Equation (2.3), which states the product of absorption (\(\mu\)) and sample thickness (\(t\)) is equal to the natural logarithm of the ratio of the flux transmitted by the sample (\(I\)) divided by the flux colliding with the sample (\(I_0\)).

\[
\mu(E)t = -\ln \left( \frac{I}{I_0} \right) \quad (2.3)
\]

The next step in data reduction is the removal of the background from the data as well as identifying the location of the point of inflection (also referred to as the edge, which is the point at which the photoelectron is said to have zero kinetic energy), which XAFS analysis software such as Athena evaluates\(^13\). The normalized signal (\(\chi\)) has no dependence on sample thickness and treats the summation of all signals as a single scattering event (or one atom).

Equation (2.4) states that the normalized signal is a dimensionless ratio of the absorption (\(\mu\)) minus the background (\(\mu_b\)), both of which are divided by the step size (\(\Delta \mu_0\)) shown in Figure 2.3. The step size (\(\Delta \mu_0\)) is halfway between the peak and the trough of the first oscillation past the point of inflection.

\[
\chi(E) = \frac{\mu(E) - \mu_b(E)}{\Delta \mu_0(E_0)} \quad (2.4)
\]

Background subtraction is the approximation of a central atom with no nearest neighbors (GUI programs such as Athena do this approximation after the analyst specifies certain
criteria\cite{14}; since subsequent equations use Equation (2.4), the importance of the background subtraction cannot be understated\cite{4,5,14}. A foil standard gives the best possible signal-to-noise ratio (due to a lack of the structural disorder contribution of the Debye Waller factor), which determines how far past the edge, or point of inflection, that a scan can provide usable data\cite{4}.

Figure 2.3: $\chi \mu (E)$ vs. E for the Zn foil (taken at CAMD); location of the edge and $\Delta \mu_0$ indicated.

When absorption occurs at the K-edge, the photoelectron from the 1s shell has zero kinetic energy (applicable at other core shells such as the $2p_{3/2}$ at the L$_{III}$ edge)\cite{4,5}. Using quantum mechanics, the kinetic energy (or wave number) of the photoelectron is given by Equation (2.5):

$$k (\text{nm}^{-1}) = \frac{\sqrt{2m_e(E - E_0)}}{h}$$  \hspace{1cm} (2.5)

where $m_e$ is the mass of an electron, $\hbar$ is Dirac’s constant, $E$ is the energy of the photon, and $E_0$ is the edge energy\cite{4,5,14}. Using Equation (2.5), the wavenumber of a photoelectron 1000 eV past the edge is calculated.

$$k = \sqrt{\frac{2 \times 9.109 \times 10^{-31} \text{ kg} \times 1000 \text{ eV} \times \frac{1.6021 \times 10^{-19} \text{ J}}{1 \text{ eV}}}{\frac{6.6261 \times 10^{-34} \text{ m}^2 \times \text{ kg/s}}{2\pi}} \times \frac{1 \text{ m}}{10^9 \text{ nm}}} = 162.0 \text{ nm}^{-1}$$
As shown from the calculation above, the photoelectron wavelengths that are of interest in an EXAFS spectrum are small, and therefore give short-ranged order information about the central atom. Converting from energy-space to wave number (Figure 2.4) gives the kinetic energy of the photoelectron over various distances from the central atom.

![Figure 2.4](image)

Figure 2.4: $\chi(k)$ vs. $k$ for $k_w = 2$ for the Ti foil std. [taken at CAMD; $k_w$ refers to the power of $k$ that $\chi(k)$ is multiplied by to emphasize the signal at higher $k$-values (i.e., $k^3 \chi(k)$ refers to $k_w = 3$)].

The usable EXAFS parameters in Equation (2.6) can be derived using advanced quantum mechanics (using Fermi’s Golden Rule), which has the usable parameters for which an EXAFS experimenter can extract information from a spectrum\(^5\).

$$\chi(k) = \sum_i \frac{s_i^2 N_i F_i(k)}{k R_i^2} \sin[2kR_i + \varphi_i(k)] \exp(-2\sigma_i^2 k^2) \exp\left(-\frac{2R_i}{\lambda(k)}\right) \quad (2.6)$$

Built into the code of XAFS fitting software Artemis\(^1\), is IFEFFIT which calculates the mean-free path ($\lambda$), scattering amplitude ($F_i$), and phase-shift ($\varphi_i$) based on the atomic number of the neighboring atom. Fitting a standard with a known atomic configuration (i.e., $\alpha$-Fe foil) is a common approach for solving for the electronic relaxation factor ($s_0^2$) for use in EXAFS fitting of the unknown spectrum. From Equation (2.6), the useful parameters from EXAFS are the
average coordination number \( (N_i) \), bond distance \( (R_i) \), and Debye-Waller factor \( (\sigma_i^2) \). Although the EXAFS parameters can be fit using the k-space data (Figure 2.4), a Fourier Transform (a frequency filter) is commonly used to convert the energy space into a pseudo-radial distribution (Figure 2.5). The pseudo-radial distribution (shifted from actual distances by \( \sim - 0.5\text{Å} \)) allows for better spatial recognition for fitting since the peaks (often referred to as shells) typically correspond to different atoms. Therefore, with the R-space it is possible to fit individual shells, as opposed to fitting the summation from all sine waves (Figure 2.4).

![Figure 2.5: \( \chi(R) \) vs. R for \( k_w = 2 \) for the Ti foil std.](image)

Since the XANES is -20 to 30 eV relative to the edge, the photoelectron has a low kinetic energy, which suggests that there is a long mean-free path and multiple-scattering occurring. The multiple-scattering phenomenon is due to the interference by more than one nearest neighbor before the photoelectron returns to the initial state. Therefore, obtaining additional information in the XANES region such as bond angles and local geometry (i.e., octahedral vs. tetrahedral coordination) are possible after thorough analysis.
2.2. XANES Spectroscopy and Catalysis

X-ray absorption spectroscopy is a powerful characterization tool in catalysis. Since the mean free path of the photoelectron is several angstroms, information of the element-specific fine structure is available\textsuperscript{5, 6, 14}.

With XANES, it is possible to study gradual changes in a transient structure with scan times as low as 10 minutes at CAMD. With special devices such as the Lytle Cell\textsuperscript{17, 18}, it is possible to study catalysts in-situ, which is useful since XAS can study amorphous materials in ways that no other characterization technique can.

A XANES spectrum is similar to a fingerprint of a sample; therefore, it is possible to determine the relative phase composition of a specific element within a sample (i.e., 20% Fe\textsubscript{2}O\textsubscript{3}, 40% Fe\textsubscript{3}O\textsubscript{4}, 40% Fe\textsubscript{x}C) by fitting the sample’s spectrum with a linear combination of the standards’ spectra\textsuperscript{4, 19}. This method for analysis generally requires some knowledge about the sample, since fitting the wrong standards sometimes results in fits that appear good but are chemically unreasonable\textsuperscript{19, 20}. In addition, fitting amorphous samples with non-stoichiometric phases can introduce errors into the fits\textsuperscript{19, 20}.

In addition to linear combination fitting, qualitative and quantitative information can be derived from a XANES spectrum. Based on the edge location (i.e., shift to right suggests a higher oxidation state), pre-edge features (generally are 1s $\rightarrow$ 3d transitions, which are exhibited on the K-edge spectra of transition metal oxide-type phases), and post-edge features (i.e., location of first major peak, double peaks vs. single peak, peak width, etc.), various information about the sample can be obtained\textsuperscript{5}. Efforts to simulate the XANES environment using calculations based on the principles of real-space multiple-scattering (RSMS) theory have been made by Rehr et al., who have developed the FEFF software (current version: FEFF 8.4)\textsuperscript{21}. This software is available for the simulation of the XANES environment for any structural
arrangement, up to 300 atoms\textsuperscript{21}. Therefore, with FEFF it is possible to simulate the XANES of theoretical structures (i.e., simulate a spectrum of a non-stoichiometric phase such as $\epsilon'$-Fe$_{2.2}$C$^{22}$), and compare the calculated results with experimental ones.

A quantitative analysis of the oxidation state is possible by making a linear calibration plot of the oxidation state vs. edge position from standards (i.e., Mn$^0$, MnO, Mn$_2$O$_3$, MnO$_2$)$^{23-25}$. The position of the edge, as previously discussed, is generally defined as the maximum of the first derivative of an XAFS spectrum$^5,23$. Then, the oxidation state of a sample is calculated after determining the edge position$^{23-25}$.

Principal Component Analysis (PCA) is often useful since this technique allows the user to determine the minimum required standards to fit the data$^{26,27}$. PCA is a linear algebra technique that handles each XANES spectrum as a vector; a series of XANES spectra are inputted into a matrix$^{27}$. An orthogonal linear transform returns the eigenvectors of the matrix. Ideally, the eigenvectors that do not appear to be noise correspond to an additional phase that is present in the data. If each phase were truly orthogonal it would be possible to determine which standards correspond to an eigenvector, but it is not that simple. It is sometimes possible to determine phases that are present from the eigenvectors by calculating a target transform of the standards. The target transform essentially is an attempt to reproduce the standard XANES spectrum from a linear combination of the eigenvectors. If a chemically justified standard is able to be reproduced by the target transform, it is said to be a phase in the sample; otherwise it is likely that the phase is not present in the bulk of a sample$^4,27$. Unfortunately, if the XANES of the samples are distorted due to amorphous and non-stoichiometric phases, it is difficult to include and exclude phases based on the target transform. However, it is possible to determine how many phase changes the sample goes through from the initial PCA (or sometimes referred to as the orthogonal linear transform).
2.3. Iron Catalyst Evolution

Iron-based FT catalysts are interesting since one of the reacting components, CO, activates the catalyst by carburization\(^{28}\). The observed increases in catalytic activity with time on stream for CO and H\(_2\)/CO activated catalysts is most likely due to the formation of various carbide phases\(^{22,29}\). Although the path to the carbide phase varies depending on the activation gas used (Figure 2.6), the Fe\(_2\)O\(_3\) phase eventually reduces to iron carbide (Fe\(_x\)C) with sufficient temperature.

![Diagram of catalyst evolution](image)

Figure 2.6: Iron catalyst evolution in Fischer-Tropsch synthesis\(^{28}\).

Studies of the Fischer-Tropsch synthesis reaction, have led to the identification of several iron carbide phases: \(\chi\)-Fe\(_5\)C\(_2\)\(^{30,31}\), \(\theta\)-Fe\(_3\)C\(_3\), \(\varepsilon\')-Fe\(_{2.2}\)C\(^{22}\), and \(\varepsilon\)-Fe\(_2\)C\(_3\)\(^{34}\). Li et al. performed a TPR XANES experiment, shown in Figure 2.7, on a precipitated Fe\(_2\)O\(_3\) catalyst (the catalyst was impregnated with Cu and K, following the precipitation). Linear combination fits of the XANES spectra are shown in Figure 2.8, which demonstrates that Fe\(_2\)O\(_3\) is being reduced to Fe\(_3\)O\(_4\), before it reduces to the Fe\(_x\)C phase; this is consistent with the phase evolution proposed by Xu et al. (Figure 2.6) for CO reduction\(^{28,35}\).
Figure 2.7: Fe K-edge TPR XANES in CO at various temperatures (1 mg precipitated Fe$_2$O$_3$, promoted with Cu, K).

2.4. Previous Studies Using Transition Metal Addition with Iron-based Fischer-Tropsch Catalysts

Iron-cobalt alloys under FTS conditions show a higher activity than can be explained by Fe and Co alone; there is also evidence of a layering effect of the carbide phases on the surface ($\chi$-Fe$_5$C$_2$ on top of Co$_2$C)$^{36}$. Two other likely explanations of the higher observed activity: 1) iron catalyzed the water-gas shift reaction [Equation (2.7)], allowing for more cobalt activity (since cobalt is more active than iron, increasing the hydrogen concentration from the WGS reaction could create more activity from Co); 2) the mixed carbide formation is a more active Fischer-Tropsch catalyst.

Figure 2.8: Atomic concentration of the Fe$_2$O$_3$, Fe$_3$O$_4$, and Fe$_x$C, as determined from linear combination fitting of the XANES data from Figure 2.7.$^{35}$
\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]  \hspace{1cm} (2.7)

Other works related to the metal oxide promotion of formulations similar to the industrial Ruhrchemie catalyst (mass basis: 100Fe/5Cu/4.2K/25 SiO$_2$\textsuperscript{33,37}) are discussed here. Büssemeier et al. previously reported testing Fe/K/kieselguhr\textsuperscript{1} (a mineral that consists mainly of SiO$_2$) catalysts promoted with either Ti, V, Mo, W, and Mn (promotion levels, synthesis technique, nor pretreatment discussed); tested at industrially relevant conditions (10-20 atm, 250-360°C, H$_2$:CO ratio between 0.6-1:1)\textsuperscript{38}. Büssemeier et al. discussed that the transition metal promoted catalysts exhibited lower overall catalytic activity, but had higher selectivities towards lower olefins\textsuperscript{38}. However, it was mentioned that a precipitation method for synthesis could negate activity drops\textsuperscript{38}. Dry discussed the effects of transition metal oxide promotion (Cr, Ti, V; as well as alkali and alkaline promotion) to the precipitated Fe/Cu/K/SiO$_2$ catalyst (exact composition, catalyst pretreatment, nor reaction conditions specified), and found transition metal oxide promotion slightly lowered the catalytic activity and wax selectivity\textsuperscript{33}. With few exceptions most other works related to the transition metal oxide promotion of the Fe-based FT (or WGS) catalysts deal with catalysts that are not Cu- and SiO$_2$-promoted: Cr\textsuperscript{39-46}, Mn\textsuperscript{34,41,47-66}, Mo\textsuperscript{67-69}, W (no other references found), Zr\textsuperscript{70-72}.

Characterizing the transition metal promoted catalysts with in-situ techniques such as SSITKA and XAFS are advantageous since the active carbides are mainly on the surface and can oxidize under ambient conditions\textsuperscript{28}. While passivation (~1% O$_2$/He in ambient conditions) preserves the bulk structure of the catalyst, it is likely that the surface layer that contains the active catalyst would also be oxidized; therefore, in-situ characterizations would still contain information about the active surface layer and therefore are more useful.

\footnote{While kieselguhr is mentioned as the support of choice in the Büssemeier et al. study, there is also mention of alumino silicate, aluminum oxide, or molecular sieves as other possible supports for the iron-based Fischer-Tropsch catalyst. This ambiguity is believed to be intentional as it is well-known that the science of industrial catalysis is a well-kept secret.}
2.5. Rationale for Using X-ray Absorption Spectroscopy to Study the Effects of Transition Metal Promotion of Cu, SiO$_2$-promoted Fe-based Fischer-Tropsch Catalysts

Hydrogenation of CO to higher hydrocarbons has been known since Fischer and Tropsch published their works in 1926$^{73-75}$. Despite the long history of research in Fe-based FTS since then, a recent critical review by de Smit et al. has pointed out that there are a limited number of truly in-situ studies for the Fe-based FT catalyst$^{76}$. Currently, the only commercialized production of liquid hydrocarbons from coal gasification is Sasol, which is based in South Africa. Sasol currently uses a precipitated synthesis of 100Fe/5Cu/4.2K/25 SiO$_2$ (mass basis) as the catalyst of choice for this reaction$^{33, 37, 77}$.

The limited number of published studies related to the transition metal promotion of Cu- and SiO$_2$-promoted Fe-based Fischer-Tropsch catalysts is described in Section 2.4. The limited number of in-situ studies for the Fe-based Fischer-Tropsch catalyst provides opportunities for novel research in this area, despite Fe-based Fischer-Tropsch being considered one of the most well-studied areas in heterogeneous catalysis$^{76}$. The flexibility of XAS described in Section 2.2 for studying the element-specific local environment (i.e., of either Fe, or the Me of interest) in either an ex-situ or in-situ environment (at catalytically relevant pressures) is therefore pursued in this work.

2.6. References


39. T.C. Bromfield and R. Visagie, Use of a source chromium with a precipitated catalyst in a Fischer-Tropsch reaction, USPO, Editor. 2005: US.
Chapter 3: An Activity and XANES Study of Mn-promoted Fe-based Fischer-Tropsch Catalysts*

3.1. Introduction

Increasing petroleum prices have created renewed interest in coal-to-liquid (CTL) research. The Fischer-Tropsch Synthesis (FTS) is currently the most developed technology for the conversion of gasified coal into liquid fuels. However cost barriers require additional research before this process is commercially viable\(^1\)\(^2\); SASOL in South Africa is currently the only company using FTS for commercial CTL processes.

Recent studies of Mn additions in Fe-based FT catalysts have focused on increases in catalytic activity\(^3\)\(^,\)\(^4\). Temperature programmed reduction (TPR) with different Mn loadings has shown increased Fe-Mn interaction with increased Mn promotion\(^4\). Mössbauer studies have shown that iron-manganese oxide phases can form during high temperature (500°C) calcination\(^5\)\(^-\)\(^7\). A study by Jaggi et al.\(^8\) (2:1 H\(_2\):CO ratio, 10 atm) suggested that in cases where iron was a majority component, the iron-manganese oxide is reduced in a step-wise sequence similar to that observed for Fe\(_2\)O\(_3\): α-(Fe\(_{1-x}\)Mn\(_x\))\(_2\)O\(_3\) → (Fe\(_{1-y}\)Mn\(_y\))\(_3\)O\(_4\) → (Fe\(_{1-z}\)Mn\(_z\))O → Fe\(_x\)C + MnO.

Most of the studies related to Mn-promotion of Fe-based FT catalysts focus on formulations which did not include SiO\(_2\) or Cu\(^3\)\(^-\)\(^25\). Other than recent studies by Lohitharn et al.\(^26\)\(^-\)\(^29\), the authors are only aware of relatively few studies on catalysts which contained either Cu and/or SiO\(_2\) for Mn-promoted catalysts\(^30\)\(^-\)\(^33\). The limited number of studies on the effects of Mn-promotion on SiO\(_2\) and/or Cu-promoted Fe-based FT catalysts include Kuznetsov et al. who studied the Mn, SiO\(_2\) (but not Cu) promotion of an Fe-based FT catalyst and found significant increases in activity relative to the catalyst without Mn\(^30\).

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*Reproduced with the permission of Elsevier. This chapter has been published as A. Campos, N. Lohitharn, A. Roy, E. Lotero, J.G. Goodwin Jr., and J.J. Spivey, Applied Catalysis A: General, 2010, 375(1), 12-16.
Whether Cu affects the product selectivity is less certain\textsuperscript{33-35}. Briefly, the role of Cu is generally believed to enhance the reducibility of Fe due to the lower temperature of reduction of Cu (CuO $\rightarrow$ Cu\textsuperscript{0}) relative to Fe (Fe\textsubscript{2}O\textsubscript{3} $\rightarrow$ α-Fe)\textsuperscript{36}, and is not addressed here.

The role of Si\textsubscript{2}O\textsubscript{2} in the chemistry of Fe is also not completely understood\textsuperscript{37-39}. However, it is generally accepted that Si\textsubscript{2}O\textsubscript{2} decreases the reducibility of Fe, limits the crystallization of the Fe\textsubscript{2}O\textsubscript{3} phase during synthesis (resulting in smaller Fe\textsubscript{2}O\textsubscript{3} crystallites after calcination), and increases the basicity of the surface\textsuperscript{36}.

XANES is used here to study the subtle differences in the oxidation state, electronic structure, and the local structures of Fe and Mn. We are aware of only one XANES study on a Mn-promoted Fe-based FT catalyst\textsuperscript{19}. This study examined an equimolar Fe/Mn catalyst supported on γ-Al\textsubscript{2}O\textsubscript{3} used for FT synthesis at 2 MPa, 200°C, and a 2:1 H\textsubscript{2}:CO ratio for 4 hours. The catalyst was studied ex-situ using both XANES and EXAFS scans. Mn promotion increased CO hydrogenation activity and iron dispersion (relative to no Mn promotion); in addition, it was found that some Fe reduced to the zero oxidation state (although not explicitly stated, it is likely this was a mixture of iron carbide phases) whereas Mn\textsuperscript{0} was not observed\textsuperscript{19}. This study did not focus on the formation of a mixed iron-manganese oxide or the effect of Mn-metal loading on iron reducibility, which are the subjects of the work presented here.

3.2. Experimental

3.2.1. Catalyst Preparation

Catalyst formulations of (100-x)Fe/xMn/5Cu/17Si (on an atomic basis), where x is 0, 5, or 20, were prepared by a pH precipitation method\textsuperscript{40}. Detailed catalyst preparations have been described elsewhere\textsuperscript{29}. Briefly, Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O, Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O, and Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} were used for the unpromoted catalyst and Mn(NO\textsubscript{3})\textsubscript{2} for the Mn-promoted Fe-based catalyst, which were mixed and precipitated with NH\textsubscript{4}OH. The precipitate was washed, dried and calcined at 300°C.
for 5 h. A 50-100 mg sample of the calcined catalyst was H₂ pretreated in-situ (30 cc/min, 280°C, 1 atm) for 12 hours prior to the reaction at 1.8 atm, 280°C; with a 2:1 ratio of a H₂:CO mixture (10 cc/min H₂, 5 cc/min CO, and 45 cc/min He for 6 hrs). Following the reaction, the catalyst was passivated in a 2% O₂/He mixture to preserve the bulk structure of the catalyst for XANES studies. A related study has shown that the catalyst is almost completely XRD amorphous²⁹, so XRD was not used for identifying unique phases present.

### 3.2.2. XANES Experiments

The Fe XANES required a θ-Fe₃C standard which was synthesized using a CO TPR of an Fe₂O₃ standard (details of the TPR are given elsewhere⁴¹). Other Fe standards used were Fe₂O₃ (99.85+% metals basis Alfa Aesar), Fe₃O₄ (99.95% metals basis Alfa Aesar), FeO (99.5% metals basis Alfa Aesar), Fe₂SiO₄ (Alfa Aesar), and a 7.5 µm thick α-Fe foil placed after the transmission chamber for calibration. Standards used for the Mn XANES were Mn₂O₃ (98% metals basis Alfa Aesar), MnO₂ (99.997% metals basis Alfa Aesar), MnO (99.99% metals basis Alfa Aesar), and Mn⁰ (400-mesh) for calibration. The XANES scanning parameters are in Table 3.1. Mn and Fe K-edge studies were carried out at the DCM (Double Crystal Monochromator) beamline at LSU’s synchrotron facility, the J. Bennett Johnston Sr. Center for Advanced Microstructures and Devices (CAMD, Baton Rouge, LA). The synchrotron was operated with an electron energy of 1.3 GeV, a current between 100-230 mA; Ge(220) crystals were used to calibrate the DCM beamline (~2 eV resolution at the scanned energies) for the Fe and Mn K-edges. The powdered samples were prepared on Kapton tape; for the Fe transmission studies and Mn standards the tape was folded to obtain a ln(I₀/Iₜ) ratio of 1 and then scanned at ambient conditions.
Table 3.1: Scan parameters for Fe, Mn XANES.

<table>
<thead>
<tr>
<th>Element (edge KeV)</th>
<th>Mn (6.540)</th>
<th>Fe (7.112)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scan interval (eV, rel. to foil)</td>
<td>-100, -15, 50, 150</td>
<td>-100, -15, 50, 150</td>
</tr>
<tr>
<td>Step size (eV)</td>
<td>2, 0.3, 1</td>
<td>2, 0.3, 1</td>
</tr>
<tr>
<td>Integration time (s)</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>Data acquisition type</td>
<td>Fluorescence (stds. in transmission, 1s int. time)</td>
<td>Transmission</td>
</tr>
</tbody>
</table>

3.2.3. Data Analysis

The unreduced catalyst spectra were used in a Principal Component Analysis (PCA) with the ‘PC Analysis’ component of the SixPACK (v. 0.53) software. No noticeable glitches were present and the reference foil calibration show no detectable energy shifts. Following the PCA, standards were fit using the Target Transform to determine which phases from the standards were present in the data set. Data reduction for the least squares fitting (sometimes referred to as linear combination fitting) of Fe was performed using Origin 8; the spectra were normalized by dividing by the average of the first post-edge peak and trough, which is shown in Figure 3.1. Following normalization, the data were fit using the ‘Least Sq. Fitting’ program from SixPACK with three components from the Fe PCA (Fe$_2$O$_3$, Fe$_3$O$_4$, θ-Fe$_3$C). Normalization and least squares fitting were repeated using Athena to refit the results.

A series of ab initio XANES calculations using FEFF 8.4 for the Mn K-edge were used to simulate spectra. The crystal structure data were obtained from the Inorganic Crystal Structure Database (ICSD) with the FindIT program. The Mn FEFF calculations used were specific to the XANES region, using the phases: Fe$_{2.7}$Mn$_{0.3}$C (23818-ICSD), Mn$_7$C$_3$ (31017), Fe$_2$MnO$_4$ (9092, 155275), MnO (9864), Mn$_2$O$_3$ (9090), Fe$_2$O$_3$ (15840), Fe$_3$O$_4$ (27899, 28664), and FeO (27856). Iron oxide phases required Mn-substitution for Fe-sites to be used in this analysis; the crystal structures were input into Atoms (v. 3.0.1) and the FEFF cards were modified for XANES ab initio calculations.
Figure 3.1: Fe K-edge XANES of Fe/Mn post-reaction catalysts and Fe standards.

3.3. Results and Discussion

3.3.1. Reactivity Results

The CO hydrogenation (C\textsubscript{1}-C\textsubscript{8} hydrocarbon formation) activity of the 100Fe and Mn-promoted catalysts, adapted from the Lohitharn et al. study\textsuperscript{26}, is shown in Figure 3.2. The initial and steady-state FTS activity was clearly enhanced by Mn promotion and unaffected by increasing Mn content; indicating strong Fe-Mn interactions, since Mn is not an active FT metal. Lohitharn et al. has shown for the specific catalysts and conditions of interest in this study that the C\textsubscript{2}-C\textsubscript{4} olefin selectivity increased with Mn-promotion\textsuperscript{26}.

The chain growth probability, \( \alpha \), was approximately 30\% higher for the 95Fe5Mn catalyst than the 100Fe catalyst at the peak FTS activity\textsuperscript{29}. However, at steady-state conditions (5 hrs TOS) the 95Fe5Mn and 100Fe catalysts had an \( \alpha \) of 0.35\textsuperscript{26,29}. The 80Fe20Mn catalyst had a steady-state (5 hr TOS) \( \alpha \) of 0.33\textsuperscript{26}. While industrial FTS conditions (>20 bar, ~220-280°C) would produce \( \alpha \) in the 0.85-0.90 range for a silica supported, Fe-based catalyst\textsuperscript{36,47}, the
observed values for $\alpha$ were based on the reaction pressures of 1.8 atm. The modest pressures used in this study maintained the products in the gaseous state, which allowed for semi-continuous quantification of essentially all hydrocarbon products, preventing liquid and wax products from clogging the reactor.

Figure 3.2: Activity of Fe catalyst at 280°C, 1.8 atm, H$_2$:CO = 2:1, total flow rate = 60 cc/min, 50-100 mg of catalyst. (The catalyst was reduced in-situ at 280°C with 30 cc/min of H$_2$)$^{26}$.

3.3.2. Fe XANES

Principal Component Analysis shows four phases present within the spectra of the calcined and reacted catalyst, three of which are readily identified as Fe$_2$O$_3$, Fe$_3$O$_4$, and $\theta$-Fe$_3$C, which is consistent with the literature at the reaction conditions tested (1.8 atm and 280°C)$^{48,49}$.

The least squares analysis of iron in Table 3.2 shows that the Fe$_x$C concentration decreases as the Mn loading in the catalyst increases (Figure 3.1). The increases in observed Fe$_3$O$_4$ concentration are likely due to the formation of an iron-manganese mixed metal oxide phase, which stabilizes the Fe$_3$O$_4$ phase through Mn substitution for iron. Jaggi et al.$^8$ postulated several iron manganese oxide FT phases which exist either after calcination at 500°C, such as $\alpha$-
(Fe$_{1-x}$Mn$_x$)$_2$O$_3$ or reduction such as (Fe$_{1-y}$Mn$_y$)$_3$O$_4$, (Fe$_{1-x}$Mn$_x$)O. However, the XANES spectra of the calcined catalysts in the results reported here do not suggest mixed metal oxide formation, given the agreement between calcined spectra for Mn K-edge with Mn$_2$O$_3$ and Fe$_2$O$_3$ for Fe K-edge.

Table 3.2: Least squares fitting for iron (error bars correspond to 1σ based on the fitting error).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Fe$_2$O$_3$</th>
<th>Fe$_3$O$_4$</th>
<th>Fe$_x$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Fe – post-rxn.</td>
<td>3.8% ± 0.4%</td>
<td>53.5% ± 0.6%</td>
<td>42.7% ± 0.7%</td>
</tr>
<tr>
<td>95Fe5Mn – calcined</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>95Fe5Mn – post-rxn.</td>
<td>0% ± 0%</td>
<td>61.3% ± 0.5%</td>
<td>38.7% ± 0.5%</td>
</tr>
<tr>
<td>80Fe20Mn – calcined</td>
<td>100%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>80Fe20Mn – post rxn.</td>
<td>5.9% ± 0.6%</td>
<td>69.6% ± 1.0%</td>
<td>24.6% ± 0.8%</td>
</tr>
</tbody>
</table>

*Note:* (Fe$_{1-y}$Mn$_y$)$_3$O$_4$ phase may affect fitting

Evidence of (Fe$_{1-y}$Mn$_y$)$_3$O$_4$ formation in this study indicates this phase prevents further reduction of Fe from the oxide phase to the active carbide phase. However, the activity study of the catalysts in Figure 3.2 as well as the activity and selectivity studies by Lohitharn et al. have shown an increase in catalytic activity with Mn promotion. A Mössbauer and XRD study by Herranz et al. (1.01 MPa, 300°C reaction conditions) has shown a lower initial CO conversion when syngas is used to activate the catalyst. However, a higher activity was observed with either H$_2$ activation, as used in the present study, or CO activation. These two activation steps also led to a higher $\alpha$ value relative to the catalyst without Mn promotion.

Although the surface of the iron carbide phase is generally accepted as the active phase in the FTS, surface characterizations using TEM and HRTEM imaging have shown that graphitic layers can form on the surfaces of larger iron carbide crystals, which cause catalyst deactivation. The results reported here indicate that Mn substitution for Fe-sites in the Fe$_3$O$_4$ lattice lowers the reducibility of the iron, limiting the formation and crystallization of the Fe$_x$C phase, creating a more active and stable catalyst.
3.3.3. Carbon Balance on Mn-promoted Catalysts

Figure 3.3 shows the carbon balances of the 80Fe20Mn, 95Fe5Mn catalysts compared to the 100Fe catalyst (Lohitharn et al.\textsuperscript{29}). The carbon balance was calculated using Eq. (3.1), solving for \( C\text{\textsubscript{catalyst}} \) (carbon deposited on the catalyst at any time), which was subsequently integrated over the entire run to find the total carbon shown in Figure 3.1:

\[
\text{CO}_{\text{converted}} = \text{CO}_2 + \text{Hydrocarbons\textsubscript{total}} + C\text{\textsubscript{catalyst}} \quad (3.1)
\]

The \( C\text{\textsubscript{catalyst}} \) is assumed to be in two forms: 1) an iron carbide phase (active for FTS)\textsuperscript{6,48,50-52}; 2) inert carbon (graphite) deposited on the catalyst\textsuperscript{53,54}. The carbon balance assumed negligible liquid and wax products within the pores of the catalyst, which is valid for the \( \alpha \) values in this study. The carbon contribution of the iron carbide phase in the bulk (as determined from the XANES) is also included in Figure 3.3, which assumed all iron carbide has the same carbon:iron ratio as \( \theta\text{-Fe}_3\text{C} \).

Figure 3.3 clearly shows that Mn-promotion decreases the amount of carbon deposited on the catalyst, which is consistent with the limited \( \text{Fe}_3\text{C} \) formation observed in the Fe XANES spectra. In addition, the total carbon deposited on the catalyst reached a steady-state value at approximately 90 minutes, with significantly less carbon deposited on the Mn-promoted catalysts. The majority of the carbon deposition (Figure 3.3) and deactivation (Figure 3.2) occurred at the beginning of syngas exposure, which is consistent with previous studies\textsuperscript{50,51}.

3.3.4. Mn XANES

The PCA of the Mn spectra has shown that there are two Mn-containing phases in the calcined and reacted catalyst, one of which is Mn\textsubscript{2}O\textsubscript{3}. Phases which were excluded from the PCA were MnO, MnO\textsubscript{2}, Mn\textsubscript{3}O\textsubscript{4}, Mn\textsuperscript{0}. The spectra of the 95Fe5Mn and 80Fe20Mn catalysts (shown in Figure 3.4) indicate that there is a mixture of the Mn\textsuperscript{2+} and Mn\textsuperscript{3+} oxidation states, since the white lines of the reacted catalysts are between that of the Mn\textsubscript{2}O\textsubscript{3} and MnO spectra. Using the first
Figure 3.3: Integrated carbon balance for the 100Fe, 95Fe5Mn, and 80Fe20Mn catalysts. The Fe₅C contribution assumed all the iron carbide was in the same carbon:iron ratio as θ-Fe₃C²⁶, ²⁹.

The pre-edge region of the FEFF calculations where Mn substituted for octahedral sites (Fe³⁺) in Fe₂O₄ (28664-ICSD) are in general agreement with the post-reaction 95Fe5Mn and 80Fe20Mn spectra shown in Fig. 3.6. A Mn K-edge XANES study by Farges⁵⁵ determined the pre-edge feature is related to 1s → empty 3d level transitions, which are sensitive mainly to local rather than long-range order, indicating this method is useful in determining the cation distribution (tetrahedral vs. octahedral sites) for Mn.
Figure 3.4: Mn K-edge XANES of 95Fe/5Mn, 80Fe/20Mn post-rxn. and MnO, Mn$_2$O$_3$ stds.

The sharper peak of the 95Fe5Mn post-reaction spectrum suggests that Mn is completely substituted in Fe$_3$O$_4$. The broad peak in the 80Fe20Mn post-reaction spectrum suggests it is a mixture of the two phases from the PCA, the (Fe$_{1-x}$Mn$_x$)$_3$O$_4$ phase and Mn$_2$O$_3$. The fact that some of the Mn is not incorporated into the Fe$_3$O$_4$ phase is believed to cause the limited increases in activity as Mn concentration increased (Figure 3.3), since alone it is not an active FT metal.

The Mn oxidation state of the post-reaction 80Fe20Mn and 95Fe5Mn catalysts (Figure 3.5) are lower than what would be predicted by the average oxidation state of Fe in Fe$_3$O$_4$ (+2.67). The data suggest that Mn preferentially occupies octahedral sites and is predominantly in the bivalent state (Figure 3.5), indicating a partially inverted spinel with a high degree of inversion$^{56}$. It has been previously suggested that there is an inverse relationship between the particle size and the degree of inversion$^{56-58}$, which is consistent with the small particle sizes found from previous XRD work on the 95Fe5Mn catalyst.
Figure 3.5: Average Mn oxidation state as a function of edge energy (The edge energy, as measured by the second peak of the first derivative; error bars based on 95% confidence interval of linear fit).

Figure 3.6: Mn K-edge XANES of 95Fe/5Mn, 80Fe/20Mn post-rxn and Mn-substitution for Fe\(^{2+}\) (tetrahedral), Fe\(^{3+}\) (octahedral) sites in Fe\(_3\)O\(_4\) FEFF calculation.
3.4. Conclusions

Mn-promotion of the Fe-based FT catalyst activated in H₂ significantly increased the C₁-C₈ FTS activity at 1.8 atm, 280°C, 2:1 H₂:CO ratio. The iron XANES PCA indicated four phases, three of which are Fe₂O₃, Fe₃O₄, and θ-Fe₃C; the Mn PCA indicated two phases, one of which can be identified as Mn₂O₃. The FEFF calculations imply that Mn is selectively substituting for octahedral sites in Fe₃O₄, corresponding to the composition of (Fe₁₋ₓMnx)₃O₄, which explains the additional phase observed in the Fe and Mn PCA.

The mixed metal oxide is believed to decrease the reducibility of iron through a stabilization of the Fe₃O₄ phase [reducibility: (Fe₁₋ₓMnx)₃O₄ < Fe₃O₄], which is a precursor for Fe₃C₃₆,₄₈. Fe-based FT catalysts deactivate when carbon deposition occurs on larger iron carbide clusters. This study has shown less carbon deposition, Fe₃C formation, and higher CO hydrogenation activity with the Mn-promoted catalysts. This indicates that the (Fe₁₋ₓMnx)₃O₄ phase was responsible for the formation of smaller clusters of Fe₃C which were more active for CO hydrogenation and were less prone to deactivation through carbon deposition.

3.5. References

34. I. E. Wachs, D. J. Dwyer, and E. Iglesia, Applied Catalysis, 1984, 12(2), 201-217.

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Chapter 4: An In-situ XANES Study of Promoted Fe-based Fischer-Tropsch Catalysts: Effect of Transition Metal Promoters on Fe Reduction and CO Hydrogenation

4.1. Introduction

The global demand for transportation fuels, specifically in emerging economies, is projected to outpace the petroleum-derived fuel capacity\(^1\). Transportation fuels derived from unconventional (non-petroleum based) feedstocks such as coal or biomass are expected to contribute significantly to the increased production of fuels\(^1, 2\).

The Fischer-Tropsch synthesis (FTS) is the most studied technique for the conversion of coal or biomass-derived syngas into transportation fuels\(^3\)-\(^5\). Fe-based catalysts are typically used for the FTS of biomass and/or coal-derived syngas for several reasons: the relatively low cost of iron, water-gas shift (WGS) activity to convert the hydrogen-lean syngas typical of coal or biomass gasification, and low methane selectivity (especially at industrial FTS conditions)\(^3\), \(^4\), \(^6\), \(^7\).

This work focuses on the XANES (X-ray absorption near edge structure) characterization of the transition metal promotion of Fe-based, FTS catalysts with a mol-based formula of 95Fe/5Me/5Cu/17SiO\(_2\) (Me = Cr, Mn, Mo, W, Zr) compared to unpromoted 100Fe/5Cu/17SiO\(_2\). Previously, Lohitharn et al. characterized these catalysts using SEM/EDX (scanning electron microscopy/energy-dispersive X-ray spectroscopy)\(^8\)-\(^10\), SSITKA (steady state isotopic transient kinetic analysis)\(^8\), \(^9\), \(^11\), \(\text{H}_2\) TPR\(^10\), BET surface area\(^10\), and also measured the selectivity and activity of CO hydrogenation and WGS\(^8\), \(^10\). Briefly, this study has shown that:

- \(\text{H}_2\) TPR – transition metal additions affected the catalyst reducibility, especially for the \(\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4\) transition, except for W which did not appear to affect the catalyst reducibility\(^10\).
- BET surface area – the as-prepared catalyst had a high surface area (>300 m\(^2\)/g), which was not greatly affected by adding different transition metals\(^10\).
- SEM/EDX, ICP-OES (inductively coupled plasma optical emission spectrometry) – the as-prepared catalyst had a uniform composition (approximately constant Fe:Me ratio on the surface and in the bulk)\textsuperscript{8, 10}.
- Catalytic activity – transition metals increased the CO hydrogenation and WGS activities compared to the unpromoted catalyst; especially for the Mn or Zr-promoted catalyst\textsuperscript{8, 10}.
- SSITKA and ITKA [isotopic transient kinetic analysis (non-steady state)] – Mn or Zr-promotion increased the number active surface intermediates, while turnover frequency was not affected (indicating that the active sites are likely similar regardless of the promoter used)\textsuperscript{8, 9, 11}.

This study reports in-situ Fe K-edge XANES results during a syngas TPR (temperature-programmed reduction) followed by CO hydrogenation, as well as determining the temperature-resolved Fe phase speciation for 95Fe/5Me/5Cu/17SiO\textsubscript{2} and 100Fe/5Cu/17SiO\textsubscript{2} catalysts\textsuperscript{12, 13}. We are not aware of directly comparable real-time, in-situ studies for Fe-based FTS catalysts which correlate the bulk Fe phase composition to the catalytic activity, especially for the transition metal promotion of Fe/Cu/SiO\textsubscript{2}-containing catalysts. The study most closely related to this work was performed by de Smit et al. on the effects of Cu and Cu/K/SiO\textsubscript{2} on a co-precipitated Fe-based FTS catalyst, which was characterized using TPR XANES (as well as isothermal conditions to study the reaction), WAXS (wide-angle X-ray scattering), and catalyst reaction testing\textsuperscript{14}. The main focus of the de Smit et al. study was to compare the promotional effects of Cu and Cu/K/SiO\textsubscript{2} on the short-range (XANES) and long-range (WAXS) order of the catalyst and relate it to catalytic performance\textsuperscript{14}. However, the work presented here focuses on a direct comparison between the Fe phase composition during syngas reduction (TPR XANES) and real-time catalytic activity.
4.2. Materials and Methods

4.2.1. Catalyst Synthesis

Mol-based catalyst formulations of 95Fe/5Me/5Cu/17Si and 100Fe/5Cu/17Si were prepared by a pH precipitation method\textsuperscript{15}, where Me = Cr, Mn, Mo, W, or Zr. Detailed catalyst preparations have been described elsewhere\textsuperscript{10}. Briefly, aqueous solutions of Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O, Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O, and Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} were mixed with the nitrate precursor of a third transition metal (Cr, Mn, or Zr; MoO\textsubscript{3} and WCl\textsubscript{6} were used for Mo and W, respectively). The solution was mixed and precipitated with NH\textsubscript{4}OH at 83°C to a pH between 8 and 9. The precipitate was aged (room temperature, 17 hrs), washed, dried (110°C, 18-24 hrs), and calcined (300°C, 5 hrs).

Any future reference in this work to the fresh, calcined catalyst refers to the co-precipitated catalyst after the synthesis procedures details described above, including calcination. In addition, a shorthand nomenclature for the catalyst is used in the figures: i.e., 95Fe5Zr corresponds to the mol-based composition 95Fe/5Zr/5Cu/17Si.

4.2.2. Catalyst Characterization

4.2.2.1. Fe K-edge XANES

In-situ TPR XANES studies for the Fe K-edge were carried out at the DCM beamline at LSU’s synchrotron facility, the J. Bennett Johnston Sr. Center for Advanced Microstructures and Devices (CAMD, Baton Rouge, Louisiana). The synchrotron was operated with an electron energy of 1.3 GeV and a current between 100-230 mA. The DCM is used with Ge(220) crystals calibrated with a 7.5 µm thick α-Fe foil, which was placed after the sample to maintain the calibration. The Lytle cell (EXAFS Company, Basic furnace/Cryostat unit), described elsewhere\textsuperscript{16}, is used for the TPR XANES experiments. The samples were prepared to obtain an optimum step-size [ln(\(\mu_0/\mu\)) = 1.0-1.4], which was found to be approximately 0.02 g catalyst mixed with 0.02 g SiO\textsubscript{2} (99.9% metals basis, amorphous, Alfa Aesar). The powder sample was
enclosed between two pieces of Kapton tape, which was then made gas-tight after aluminum spacers were screwed into place.

The XANES scanning parameters are in Table 4.1: Fe K-edge TPR XANES scanning parameters. The standards used were: Fe₂O₃ (99.99% metals basis, Alfa Aesar), Fe₃O₄ (99.95% metals basis, Alfa Aesar), FeO (99.5% metals basis, Alfa Aesar), Fe₂SiO₄ (Stock# 44278, Alfa Aesar), θ-Fe₃C (synthesized via syngas-TPR of the Fe₂O₃ standard; detailed elsewhere¹⁷,¹⁸), ZrFe₂ (Product# 693812-1G, Sigma Aldrich), and FeSi (99.9% metals basis, Alfa Aesar). Figure A.1 shows the Fe K-edge spectra of the standards (available in Appendix A). The in-situ XANES experiments were performed on the following catalysts: 95Fe/5Me/5Cu/17Si (Me = Cr, Mn, Mo, W, Zr), 100Fe/5Cu/17Si, and the Fe₂O₃ standard.

Table 4.1: Fe K-edge TPR XANES scanning parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scan interval relative to edge</td>
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<td>Energy step size (eV)</td>
<td>1, 0.5, 1</td>
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<tr>
<td>Integration time (s)</td>
<td>1</td>
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<tr>
<td>Fe K-edge (7.122 KeV)</td>
<td></td>
</tr>
</tbody>
</table>

Data reduction and linear combination fitting of the derivative of the normalized XANES spectra were performed using the Athena software (v. 0.8.056), following a similar procedure described by Calvin et al. for fitting Fe nanoparticles¹⁹-²¹. Prior to the linear combination fitting (LCF), each spectrum (including the standards) was calibrated using the maximum of the first derivative of the Fe foil spectrum which was measured independently each run. Following edge identification, pre-edge subtraction and determining the normalization range, then linear combination fitting was used to quantitatively describe the spectra.

4.2.2.2. Syngas TPR

TPR under flowing syngas experiments were carried out at the DCM beamline at CAMD using the Lytle cell. Gas flow was maintained using rotameters (Model FM-1050, Matheson
Trigas), the temperature was maintained using a Variac (10 amp, Model 3PN1010B, Staco) with a custom-built temperature controller (using an Omega CN7500 PID controller), and X-ray alignment was made with an XYZ stage. The furnace was purged with He (UHP, Capitol Welders) to prevent the heating element from burning out. The Lytle cell had a syngas flow (5.00% Ar/16.5% CO/33.0% H₂/bal. He, Airgas) of approximately 12 sccm (measured at the exit of the Lytle cell with an ADM2000 Agilent flow meter), and the exhaust gas was vented. The temperature controller was set to raise the temperature from 25-362°C (using the Simon Bare temperature correlation for the Lytle cell\(^\text{16}\)) at a ramp rate of 2°C/min. This allowed for continuous scans throughout the TPR; each scan approximately took 740s, corresponding to one scan every 25°C. After each TPR experiment, the catalyst was allowed to cool down to room temperature and was passivated in a 2% O₂/bal. He mixture (Airgas) for approximately 15 minutes for use in XRD measurement.

**4.2.2.3. Mass Spectrometry**

An Ametek Dycor Quadlink Residual Gas Analyzer / Quadrupole Mass Spectrometer (RGA/QMS) was used to measure the outlet gas composition under similar conditions [temperature ramp rate, weight hourly space velocity ( WHSV), syngas composition] from an Altamira 200R-HP system. The catalyst mass used was approximately 0.1 grams of the fresh calcined catalysts that were run for the in-situ Fe K-edge experiments [i.e., \([95\text{Fe}/5\text{Me}/5\text{Cu}/17\text{Si} (\text{Me} = \text{Cr, Mn, Mo, W, Zr}), 100\text{Fe}/5\text{Cu}/17\text{Si}, \text{and the Fe}_2\text{O}_3 \text{ standard}]\). The flow rates used were: 30 sccm He (UHP, Airgas), 20 sccm H₂ (UHP, Airgas), and 10 sccm CO (UHP, Airgas), to repeat the same WHSV as was done for the XANES experiments. The MS signals of interest for analysis were: m/z=15 for CH₄, m/z=18 for H₂O, and m/z=44 for CO₂\(^{22}\).
4.2.2.4. XRD

XRD scans were performed at the XPD (X-ray Powder Diffraction) beamline at LSU’s CAMD with catalysts prepared on a Si(510) zero-background sample holder with Co K\textsubscript{a} excitation (6.9030 KeV) tuned with Ge(220) crystals; the 2\theta was varied from 20° to 80°, with a step size of 0.05°, and a 3s integration time. The fresh calcined and post-syngas TPR catalysts from the XANES experiments were also examined by XRD. Since the catalysts were SiO\textsubscript{2}-diluted prior to the syngas TPR, the amorphous SiO\textsubscript{2} std. was also tested.

4.3. Results and Discussion

4.3.1. XRD

Figure 4.1 shows the X-ray diffraction spectra of both the calcined and post-syngas TPR catalysts. These XRD spectra were compared with the diffraction patterns of the Fe\textsubscript{2}O\textsubscript{3} standard, as well as the Fe\textsubscript{2}O\textsubscript{3} standard post-syngas TPR spectrum. The XRD spectra of calcined catalysts show two broad diffraction peaks in the 2\theta ranges of 30-45° and 60-80°, while the SiO\textsubscript{2} std. shows a broad diffraction peak at a 2\theta of 20-30°. This is consistent with the catalyst being highly amorphous, which is likely due to the combination of the co-precipitation synthesis method used as well as SiO\textsubscript{2} limiting the crystallization of Fe\textsubscript{2}O\textsubscript{3} during calcination\textsuperscript{14, 23, 24}. As expected, the unreacted Fe\textsubscript{2}O\textsubscript{3} std. shows strong diffraction peaks at 2\theta values which exclusively correspond to α-Fe\textsubscript{2}O\textsubscript{3} (rhombohedral hematite) phase (JCPDS 87-1165).

The XRD spectra of the post-syngas TPR catalysts show one broad diffraction peak at 2\theta ranges of 20-30°, which is consistent with the SiO\textsubscript{2}-dilution prior to the syngas TPR. Another weak, broad diffraction line in the 2\theta range of 47.6-51.3° is similar to that of χ-Fe carbide formed at relatively low temperatures\textsuperscript{25}. Vasireddy et al. reported that the XRD spectra of CO-activated Fe catalysts treated at 280°C also show the χ-Fe\textsubscript{2.5}C phase, which is consistent with a study by Zhao et al.\textsuperscript{26, 27}. A characteristic diffraction line corresponding to either α-Fe or γ-Fe was not
Figure 4.1: XRD data for the calcined and syngas (TPR) reduced Fe$_2$O$_3$ std., 100Fe/5Cu/17Si, and 95Fe/5Me/5Cu/17Si (Me= Cr, Mn, Mo, W, Zr) catalysts.

observed in either the calcined or the post-syngas TPR catalysts. Following the syngas TPR, the Fe$_2$O$_3$ std. shows diffraction lines corresponding to primarily Fe$_3$O$_4$ (magnetite) along with α-Fe$_2$O$_3$. This result is somewhat surprising since the post-syngas TPR Fe$_2$O$_3$ std. was passivated, however the XRD spectrum indicates that any Fe$_x$C formed during the syngas reduction was oxidized and therefore the passivation procedure was ineffective. Generally the observation of a small exotherm after the introduction of a dilute O$_2$/inert mixture is an indicator of passivation taking place\textsuperscript{10, 28}; however this is cannot be detected with the in-situ equipment used since the thermocouple is not in direct contact with the catalyst.
Figure 4.2: Normalized Fe K-edge XANES for the syngas TPR reduction of the Fe$_2$O$_3$ std., 100Fe/5Cu/17Si, and 95Fe/5Me/5Cu/17Si (Me = Cr, Mn, Mo, W, Zr).
4.3.2. Fe K-edge XANES

The normalized Fe K-edge XANES spectra are shown in Figure 4.2. In order to develop the LCF model, several methods have been used: 1) empirical observation of the XANES spectra; 2) chemical knowledge of the system; 3) statistical treatment to determine whether increasing the complexity of the model is justified\textsuperscript{20,29}.

4.3.2.1. Empirical Observation of Fe K-edge XANES Results

There are some clear differences between the reduction profile (from Figure 4.2) of the Fe/Cu/SiO\textsubscript{2}-containing catalysts and the Fe\textsubscript{2}O\textsubscript{3} standard. For example, the temperature of reduction of the Fe\textsubscript{2}O\textsubscript{3} std. is higher than the Fe/Cu/SiO\textsubscript{2}-containing catalysts. Also, the Fe/Cu/SiO\textsubscript{2}-containing catalysts reduce gradually with increasing temperature, whereas the reduction of the Fe\textsubscript{2}O\textsubscript{3} std. is noticeably more rapid. Differences among the Fe/Cu/SiO\textsubscript{2}-containing catalyst are more subtle relative to the reduction profile for the Fe\textsubscript{2}O\textsubscript{3} std. This is to be expected since there are several differences between the Fe/Cu/SiO\textsubscript{2}-containing catalysts and the Fe\textsubscript{2}O\textsubscript{3} standard: 1) Cu promotion; 2) preparation method (the catalysts were prepared by precipitation, and thus have smaller particle sizes, even if neglecting SiO\textsubscript{2} promotion\textsuperscript{14}); 3) SiO\textsubscript{2} promotion; 4) transition metal promotion (not including Cu); however the 100Fe/5Cu/17SiO\textsubscript{2} catalyst was not promoted with a third transition metal.

4.3.2.2. Chemical Knowledge of Fe/Cu/SiO\textsubscript{2} Catalysts

Previous in-situ studies of SiO\textsubscript{2}-supported Fe-based FTS catalysts have shown evidence of Fe\textsuperscript{2+} phase(s) (not including Fe\textsubscript{3}O\textsubscript{4}) following reduction and/or reaction\textsuperscript{14,22,24,30-34}. In-situ Fe K-edge XANES studies of precipitated Fe/Cu, Fe/Cu/K, and/or Fe catalysts (without SiO\textsubscript{2} promotion) reduced in H\textsubscript{2}, CO, or syngas, under reaction conditions have not shown an observable Fe\textsuperscript{2+} phase\textsuperscript{14,18,35}. Information regarding the Fe\textsuperscript{2+} phase(s) is rather limited. The studies that have found evidence of Fe\textsuperscript{2+} phases have indicated octahedral symmetry for Fe, and
generally strong Fe-Si interactions\textsuperscript{14,22,30,32}. Another possible phase was discussed by Lund and Dumesic for Fe\textsubscript{3}O\textsubscript{4} and SiO\textsubscript{2} combining to form: \([\text{Si}_2^{4+}, \square](\text{Fe}_2^{2+}, \text{Fe}_4^{3+})\text{O}_{12}\), with an average Fe oxidation state of 2.67+\textsuperscript{36}. There is not a complete consensus as to whether Fe and Si form a single phase (under FTS conditions) as Jin et al. has studied Fe/Cu/SiO\textsubscript{2}/K using electron energy loss spectroscopy (EELS) and found that iron and silicon were two separate phases\textsuperscript{37}.

![Image](image.png)

Figure 4.3: (a) A comparison of the Fe syngas reduction at three different temperatures for the 100Fe/5Cu/17Si catalyst: 25°C, 300°C, 362°C. (b) A comparison between the iron oxide phases used to fit the data and the 100Fe/5Cu/17Si catalyst.

Figure 4.3a shows three spectra of the 100Fe/5Cu/17SiO\textsubscript{2} catalyst at: 25°C, 300°C, and 362°C. This figure demonstrates that SiO\textsubscript{2}-promotion resulted in the formation of (a) stabilized Fe\textsuperscript{2+} phase(s). This is based on the spectrum at 300°C, which is not similar to any of the spectra observed during reduction of the Fe\textsubscript{2}O\textsubscript{3} std. from Figure 4.2. In other words, since the Fe\textsubscript{2}O\textsubscript{3} std. was reduced more completely than other catalysts in the study, it would be expected to have exhibited a reduction profile similar to the 100Fe/5Cu/17SiO\textsubscript{2} catalyst. However, since the Fe\textsubscript{2}O\textsubscript{3} std. did not appear to have a similar reduction profile as the 100Fe/5Cu/17SiO\textsubscript{2} catalyst, intermediate phase(s) for the 100Fe/5Cu/17SiO\textsubscript{2} catalyst must be considered.
The sensitivity of XANES to the mean oxidation state is used to compare the 100Fe/5Cu/17SiO$_2$ catalyst spectrum at 300°C to the Fe$^{2+}$ standards (Fe$_2$SiO$_4$ and FeO) and Fe$_3$O$_4$ (having a 2.67 mean oxidation state) in Figure 4.3b. Assuming negligible zero valent Fe at these conditions (which the pre-edge feature at 7.112 KeV indicates), there appears to be a significant contribution of the 2+-oxidation state to the 100Fe/5Cu/17SiO$_2$ spectrum at 300°C.

4.3.2.3. Choosing the Model for LCF

In-situ Mössbauer studies by Xu et al. (for evaporative deposited Fe/SiO$_2$, FePt/SiO$_2$ and FePtK/SiO$_2$) and in-situ Fe K-edge XANES studies by Li et al. (for precipitated Fe, Fe/Cu, Fe/Cu/K) describe the currently accepted reduction pathway for Fe-based FTS catalysts in syngas: Fe$_2$O$_3$ → Fe$_3$O$_4$ → Fe$_x$C$^{18, 22}$. Recent studies on a Fe/Cu/K/SiO$_2$ using in-situ scanning transmission X-ray microscopy (STXM) and in-situ Fe K-edge XANES studies have shown direct evidence of a Fe$^{2+}$ phase(s)$^{14, 31, 32}$. The work presented here quantifies the contribution from these phases by modifying the currently accepted model to account for the observed Fe phase changes during syngas reduction. Based on the XRD analysis, current understanding of the Fe phase changes, and empirical observations of the XANES data the following phases are used for LCF of the Fe K-edge XANES spectra: Fe$_2$O$_3$, Fe$_3$O$_4$, FeO, Fe$_2$SiO$_4$, and Fe$_x$C.

Modifications of the model are based on the amorphous nature of the Fe/Cu/SiO$_2$-containing catalysts since only the Fe$_2$O$_3$ and Fe$_x$C phases are indicated from the XRD spectra (Figure 4.1), whereas Fe$_3$O$_4$ was observed in the post-reduced Fe$_2$O$_3$ std. Despite no direct evidence of a Fe$^{2+}$ phase(s) from the XRD analysis, a previous study using in-situ WAXS collected in parallel with in-situ Fe K-edge XANES on a precipitated Fe/Cu/K/SiO$_2$ FTS catalyst did not find any crystalline formation of Fe$^{2+}$ phase(s); however the Fe$^{2+}$ phase was determined to be present in the Fe K-edge XANES data$^{14}$. This would suggest that even in-situ XRD would not have shown the presence of Fe$^{2+}$ phase(s) in precipitated catalysts with similar formulations. In
addition, Niemantsverdriet et al. have shown that a Fe$^{2+}$ phase(s) formed during FTS conditions was unstable under ambient conditions$^{30}$. Since the XRD samples in the present study were exposed to ambient conditions, a XRD analysis would be unlikely to reveal the presence of Fe$^{2+}$ phases. Two Fe$^{2+}$ phases are used for the LCF of the XANES spectra: FeO and Fe$_2$SiO$_4$. This was done because more Fe$^{2+}$ was present in the spectra than can be explained solely by Fe$_2$SiO$_4$ and Fe$_3$O$_4$. By calculation, the maximum contribution of Fe$^{2+}$ would be 57% of Fe atoms if all SiO$_2$ in the 95Fe/5Me/5Cu/17SiO$_2$ catalyst was present in the Fe$_2$SiO$_4$ phase with the remaining Fe present as Fe$_3$O$_4$. The inclusion of two Fe$^{2+}$-containing phases is also supported in the statistical treatment of the LCF data presented in section 4.3.2.4 below.

4.3.2.4. LCF of Fe K-edge XANES Spectra

During the LCF, it was difficult to distinguish between the Fe$_2$O$_3$ and Fe$_3$O$_4$ phases (Figures A.2-3, available in Appendix A) because of the amorphous structure of the catalyst and the similarities in the local structures of the two phases (similar XANES spectra at the resolutions scanned, ~2 eV). Therefore these two phases (Fe$_2$O$_3$ and Fe$_3$O$_4$) were modeled (or fit) as a single phase. The difficulty of fitting Fe oxide phases of similar local structures of nanoparticles or amorphous materials is also discussed in the literature$^{21,38}$. It is therefore an implied assumption that while the Fe$_2$O$_3$ and Fe$_3$O$_4$ were indistinguishable when fitting a XANES spectrum of an amorphous material, the FeO and Fe$_2$SiO$_4$ spectra could be differentiated. The XANES spectra between FeO and Fe$_2$SiO$_4$ are distinct. Specifically, there are differences in the pre-edge feature, white line intensities, and the intensity of the main 1s $\rightarrow$ 4p transition, due to significant differences in their local structures. A comparison of these two spectra (FeO and Fe$_2$SiO$_4$) are shown in Figure 4.3b and Figure A.1 (Appendix A).

Kelly et al. explain a statistical approach for determining whether adding complexity to the LCF model (i.e., an additional phase) improves the goodness-of-fit parameter, $\chi^2_v$. The
results for using different models for the LCF of the 100Fe/5Cu/17SiO₂ catalyst at 362°C is presented in Table 4.2. The models are listed in order of decreasing $\chi^2_v$ values (lower $\chi^2_v$ correspond to better fits). The $\chi^2_v$ values are given in the relative ratio to the optimum model, which achieved the minimum value for $\chi^2_v$. Model 1 uses the currently accepted phases for the reduction in syngas to model the 100Fe/5Cu/17SiO₂ spectrum at 362°C: Fe₂O₃/Fe₃O₄ and Fe₄C. This model was found to have a poor fit. This finding is consistent with a significant presence of Fe³⁺ phases (see section 4.3.2.1).

Table 4.2: 100Fe/5Cu/17Si at 362°C, a comparison of goodness-of-fit parameter for different models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Fe₂O₃/Fe₃O₄</th>
<th>FeO</th>
<th>Fe₂SiO₄</th>
<th>Fe₄C</th>
<th>$\chi^2_{\text{if}} / \chi^2_{\text{if}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25% ± 5%</td>
<td>--</td>
<td>--</td>
<td>75% ± 8%</td>
<td>19.5</td>
</tr>
<tr>
<td>2</td>
<td>--</td>
<td>100%</td>
<td>--</td>
<td>--</td>
<td>9.22</td>
</tr>
<tr>
<td>3</td>
<td>29% ± 2%</td>
<td>71% ± 2%</td>
<td>--</td>
<td>--</td>
<td>2.71</td>
</tr>
<tr>
<td>4</td>
<td>25% ± 1%</td>
<td>56% ± 2%</td>
<td>19% ± 2%</td>
<td>--</td>
<td>1.20</td>
</tr>
<tr>
<td>5</td>
<td>20% ± 2%</td>
<td>45% ± 3%</td>
<td>20% ± 2%</td>
<td>14% ± 3%</td>
<td>1.00</td>
</tr>
</tbody>
</table>

The subsequent model starts with the best fit for a single phase (using either: Fe₂O₃/Fe₃O₄, FeO, Fe₂SiO₄, or Fe₄C) and incrementally increase the number of phases (i.e., Model 2 had the best fit for a 1 component model; Model 3 had the best fit for a 2 component model; etc.). It was found that the $\chi^2_v$ for Model 2 (9.22) was lower than Model 1 (19.5). This indicates that the LCF model using solely FeO to fit the spectrum produces a better fit than Model 1, which is fitted with both Fe₂O₃/Fe₃O₄ and Fe₄C components. Model 5, which included the Fe₂O₃/Fe₃O₄, FeO, Fe₂SiO₄, and Fe₄C phases, improved the fit by a factor of 19.5, relative to the model which only had fit Fe₂O₃/Fe₃O₄ and Fe₄C. The results in Table 4.2 give a statistical basis for the inclusion of both the FeO and Fe₂SiO₄ phases for fitting the 100Fe/5Cu/17SiO₂ catalyst.

This approach is followed for the 95Fe/5Me/5Cu/17SiO₂ catalysts at 362°C and the results are summarized in Tables A.1-5 in Appendix A. The comparatively low $\chi^2_v$ values
support the four component model to fit the Fe/Cu/SiO$_2$-containing catalysts. Even though Fe$_2$O$_3$ and Fe$_3$O$_4$ are separate phases, since they were modeled as a single phase, they are considered to contribute 'one component' to this model. Also, the $\chi^2_v$ for the 95Fe/5W/5Cu/17SiO$_2$ catalyst at 362°C was not improved with the inclusion of Fe$_x$C (Table A.4, Appendix A), and therefore a three component LCF model was used for this catalyst.

The error associated with the fits in Table 4.2, as well as Tables A.1-12 are solely from the 1σ error. However, contributions from other factors are more significant such as: 1) the fact that the standards are not representative of the phases in the sample (i.e., in Fe nanoparticles or amorphous Fe oxide phases the standards do not always represent phases in the sample$^{21,38}$); 2) determining the proper edge-step for normalization; 3) sample inhomogeneities are introduced in preparation (i.e., sample thickness effects); 4) there may be small variations of sample composition during the scan; 5) using a single spectrum to model the Fe$_2$O$_3$/Fe$_3$O$_4$ phases, or the θ-Fe$_3$C std. to model all Fe$_x$C contributions (this latter assumption has been made previously in the literature$^{27,35,39,40,20,21}$). The ideal case for LCF is when the spectra of the standards are well-represented in the spectrum of the analyte$^{20}$. In addition, the ideal analyte for LCF would have a well-defined phase composition$^{20}$. Studies which have investigated ideal systems have found errors between ±4-8% on the basis of concentration of the analyte (i.e., ±8% error for 45% FeO would corresponds to a mol. based phase composition of 45% ± 8%)$^{20,41}$. For a system as complex as the Cu, SiO$_2$, and transition metal-promoted Fe-based FTS catalyst, where the phase structure is not well-defined, the reported errors for the optimum fit are likely in the range of ±10-15%. Direct assignment of the error bars for each fit is not attempted in this work. As stated previously, Table 4.2 and Tables A.1-12 (Appendix A) report the 1σ errors associated with the fit, which is underrepresented error associated with the LCF.
Figure 4.4: Linear combination fitting of the XANES spectra (Figure 4.2) for syngas TPR reduction of Fe$_2$O$_3$ std., 100Fe/5Cu/17Si, and 95Fe/5Me/5Cu/17Si (Me = Cr, Mn, Mo, W, Zr) catalysts. The y-axis is the mol. fraction of Fe distributed in the Fe$_2$O$_3$/Fe$_3$O$_4$, FeO, Fe$_2$SiO$_4$, and Fe$_3$C phases.
The LCF results for the syngas reduction of the Fe$_2$O$_3$ std., 100Fe/5Cu/17SiO$_2$, and 95Fe/5Me/5Cu/17SiO$_2$ catalysts are given in Figure 4.4. Additional details on the fits are available in Tables A.6-12 in Appendix A. The reduction profile for the Fe$_2$O$_3$ std. is consistent with the currently accepted model for Fe reduction: Fe$_2$O$_3$ → Fe$_3$O$_4$ → Fe$_x$C (where Fe$_3$O$_4$ formation is consistent with the XRD analysis).

The LCF results for the Fe/Cu/SiO$_2$-containing catalysts show the formation of FeO before the Fe$_2$SiO$_4$ phase in all catalysts, with the exception of the 95Fe/5Zr/5Cu/17SiO$_2$ where the onset of FeO and Fe$_2$SiO$_4$ formation is observed simultaneously. After the observable formation of the Fe$^{2+}$ phases, the LCF results (Figure 4.4) consistently show significantly more FeO formation than Fe$_2$SiO$_4$. Since SiO$_2$ promotion is responsible for the formation of Fe$^{2+}$ phases, it is likely that the FeO phase is interacting strongly with the SiO$_2$ and/or the Fe$_2$SiO$_4$ phase. Otherwise, the bulk FeO formation would not be observed. This was the case of the reduction of Fe$_2$O$_3$ std. which exhibited significant Fe$_x$C but no observable bulk FeO formation.

The Fe/Cu/SiO$_2$-containing catalysts also exhibit Fe$_x$C formation. This can be seen by comparing the spectra for the 100Fe/5Cu/17SiO$_2$ catalyst between 300$^\circ$C and 362$^\circ$C in Figure 4.3a, which shows increased reduction in the 362$^\circ$C spectrum relative to 300$^\circ$C. The statistical analysis showed a 20% improvement when Fe$_x$C was allowed to be included in the LCF model for the 100Fe/5Cu/17SiO$_2$ catalyst at 362$^\circ$C (Table 4.2 - Model 4 vs. 5). Therefore, the LCF model included: Fe$_2$O$_3$/Fe$_3$O$_4$, FeO, Fe$_2$SiO$_4$, and Fe$_x$C. The Fe/Cu/SiO$_2$-containing catalysts demonstrated significant Fe$^{2+}$ phases. Further work, including high resolution in-situ Fe K-edge XANES or STXM, would give insight into these Fe$^{2+}$ bulk phases. To date, few studies have unambiguously identified the Fe$^{2+}$ phases that this study models, especially for formulations similar to the industrially relevant catalyst formulation discussed by Dry - 100Fe/5Cu/5K$_2$O/25SiO$_2$ (mass basis)$^{23}$. The improvement in the fitting results in Figure 4.5
indicates that this modified model more closely describes the bulk Fe phase changes during syngas reduction at 1 atm for the 95Fe/5Me/5Cu/17Si and 100Fe/5Cu/17Si catalysts than a model which only includes Fe$_2$O$_3$, Fe$_3$O$_4$, and Fe$_x$C.

Figure 4.5: Comparison of LCF results: Model 1 (using Fe$_2$O$_3$/Fe$_3$O$_4$, Fe$_x$C phases) and Model 4 (using Fe$_2$O$_3$/Fe$_3$O$_4$, Fe$_x$C phases) for the 100Fe/5Cu/17Si catalyst, measured at 300°C during syngas TPR (2:1 H$_2$:CO ratio, 362°C, 1 atm). The normalized $\chi\mu(E)$ is shown since it is visually difficult to distinguish the derivative of normalized $\chi\mu(E)$, despite it being fit using the derivative.

**4.3.2.5. Effects of Transition Metal Promotion on Fe/Cu/SiO$_2$**

The differences between the reduction profile for the Fe$_2$O$_3$ std. and the 100Fe/5Cu/17SiO$_2$ catalyst are more significant than between the 95Fe/5Me/5Cu/17Si and 100Fe/5Cu/17Si catalysts. During syngas reduction, the Fe/Cu/SiO$_2$-containing catalysts followed the phase evolution given in Figure 4.6, except for the 95Fe/5W/5Cu/17Si catalyst.
where bulk Fe₅C formation was not observed. The results presented in Figure 4.4 shows that the 95Fe/5Zr/5Cu/17Si and 95Fe/5Mn/5Cu/17Si catalysts had increased reducibilities relative to the 100Fe/5Cu/17Si catalyst. This is based on the higher Fe₅C concentrations observed in 95Fe/5Zr/5Cu/17Si (23%, observed at 362°C) and 95Fe/5Mn/5Cu/17Si (27%, observed at 362°C), relative to the 100Fe/5Cu/17Si (14%, observed at 362°C) catalyst. A comparison of the spectra is given in Appendix A, Fig A.4. While it is discussed that the errors associated with the compositions are likely in the range of ±10-15%, the lower intensity of the main peak (1s → 4p transition) is consistent with increased Fe₅C content in the 95Fe/5Zr/5Cu/17Si and 95Fe/5Mn/5Cu/17Si catalyst relative to 100Fe/5Cu/17Si. Previous activity studies of the
95Fe/5Zr/5Cu/17Si and 95Fe/5Mn/5Cu/17Si catalysts exhibited the highest initial and steady state CO hydrogenation activity relative to the other 95Fe/5Me/5Cu/17Si or 100Fe/5Cu/17Si catalysts, albeit with H2 activation and at slightly higher reaction pressures (1.8 atm)10. The LCF results for the 100Fe/5Cu/17Si catalyst and the 95Fe/5Cr/5Cu/17Si or 95Fe/5Mo/5Cu/17Si were not significantly different, especially for the formation of the FexC phase. Within the error of the LCF, there was no observable bulk FexC formation for the 95Fe/5W/5Cu/17Si catalyst.

4.3.3 Mass Spectrometry

Reduction conditions used in the TPR XANES experiments were repeated in a microreactor to measure CO hydrogenation and WGS activity. Figure 4.7 shows the normalized intensity for the various reaction products: CO2 (m/z=44), H2O (m/z=18), and CH4 (m/z=15).

4.3.3.1. CO2

There are two main CO2 peaks for the Fe-containing catalysts, and only one for the Fe2O3 standard. Several reactions in the FTS produce CO2: the CO reduction of a transition metal oxide [i.e., CuO in this case (4.1)],

\[ \text{CO} + \text{CuO} \rightarrow \text{Cu}^0 + \text{CO}_2 \]  \hspace{1cm} (4.1)

the WGS (4.2) and Boudouard (4.3) reactions, as well as the formation of FexC (4.4).

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]  \hspace{1cm} (4.2)

\[ 2\text{CO} \rightarrow \text{CO}_2 + \text{C} \]  \hspace{1cm} (4.3)

\[ \text{xFeO} + (x+2)\text{CO} \rightarrow \text{Fe}_x\text{C} + (x+1)\text{CO}_2 \]  \hspace{1cm} (4.4)

A minor CO2 peak for the Fe/Cu/SiO2-containing catalysts is observed between 75-125°C. This minor peak is observed in the Fe/Cu/SiO2-containing catalysts but not in the Fe2O3 std. To determine whether this peak was due to the desorption of surface CO2 [since no catalyst pretreatment was performed before either this TPRS (temperature programmed reaction spectroscopy) or for the TPR XANES experiments] a He ramp of 2°C/min from 25-362°C was
Figure 4.7: Normalized MS signal for CH$_4$, CO$_2$, H$_2$O as a function of temperature for syngas (TPR) reduced Fe$_2$O$_3$ std., 100Fe/5Cu/17Si, and 95Fe/5Me/5Cu/17Si (Me = Cr, Mn, Mo, W, Zr) catalysts.
performed on the fresh calcined 95Fe/5W/5Cu/17Si catalyst. The results of this "blank" catalyst is shown for the three components of interest (H₂O, CO₂, CH₄) in Appendix A, in Fig. A.5. The CO₂ signal on the fresh calcined catalyst was insignificant relative to the CO₂ signal from the TPRS experiments. Since the precursors used for the synthesis of these catalysts were generally nitrates for the transition metals (Fe, Cu, and most of the Me promoters) or ethoxide (for Si), it is expected that the calcination of 300°C for 5hrs would have decomposed/vaporized the nitrate and ethoxide precursors. The low temperatures of this minor peak do not coincide with the expected temperatures for CuO reduction, WGS reaction, or Boudouard reaction. Therefore this minor CO₂ peak remains unassigned. After this minor peak, from 125-230°C the first major CO₂ peak is observed (the upper limit for the peak is 203°C and 247°C for the Cr or W-containing catalyst, respectively). This peak, especially in the interval near the peak maximum (approx. ±30°C) is assigned to the reduction of CuO. Hornés et al. found CO₂ evolution from the CO TPR of precipitated, unsupported CuO starting at temperatures of approximately 150°C, which is consistent with this result.

Since H₂O formation (from CO hydrogenation) is not observed in this temperature range, the WGS contribution to CO₂ formation is negligible. Büssemeyer et al. stated that the Boudouard reaction becomes thermodynamically favorable on Fe-based catalysts above 300°C, and therefore is not expected to contribute to the first major CO₂ peak. In addition, as this peak subsides, significant evolution of H₂O is observed which is consistent with the Fe K-edge XANES for observable Fe reduction. Therefore, it is not expected that the reduction of Fe contributes to this peak. In the case of the 95Fe/5W/5Cu/17Si catalyst there appears to be two peaks, and some overlap of CO₂ formation in addition to Fe reduction (from the XANES) and H₂O formation. This does not suggest that Cu₀ formation does not enhance Fe reduction, in fact, as the second half of this peak subsides, the H₂O peak (reduction of Fe) increases. This, in
addition to the first CO$_2$ peak decreasing before H$_2$O evolution is observed for the other Fe/Cu/SiO$_2$-containing catalysts, is consistent with Cu$^0$ formation increasing the reducibility of the Fe$_2$O$_3$. Furthermore, the reduction of the Fe$_2$O$_3$ std. (which is not Cu promoted) does not exhibit a lower temperature CO$_2$ peak from CuO reduction or a H$_2$O peak from Cu$^0$ enhancement of the reducibility of Fe$_2$O$_3$, and is therefore consistent with the literature which states that Cu$^0$ formation increases the reducibility of the Fe$_2$O$_3$ phase.$^{23,45}$

The second peak for CO$_2$ begins between 260$^\circ$C and 280$^\circ$C, and continues until the end of the TPSR at 362$^\circ$C for all samples, including the Fe$_2$O$_3$ std., in which case it is the first peak. Assignment of this peak is not trivial as there are several contributing factors to consider: 1) the Boudouard reaction becomes thermodynamically favorable in this temperature range; 2) H$_2$O is produced as a by-product of CO hydrogenation, and can react via the WGS reaction; 3) the formation of the Fe$_x$C is observed in all samples, except for the 95Fe/5W/5Cu/17Si catalyst. A comparison of the H$_2$O, CO$_2$, CH$_4$ peaks including baseline subtraction of the MS signal at 362$^\circ$C for the 100Fe/Cu/17Si catalyst for CO$_2$ ($3.7\times10^{-8}$), CH$_4$ ($3.2\times10^{-9}$) and H$_2$O ($3.5\times10^{-8}$) shows that the contribution from the WGS reaction cannot be neglected, even accounting for the relative sensitivities of these compounds. In addition, the LCF of the Fe K-edge XANES indicated formation of the Fe$_x$C phase (for all samples excluding the 95Fe/5W/5Cu/17Si catalyst), which necessitates some form of CO oxidation to form this phase.$^{46}$ The stoichiometry of this reaction likely involves some form of the forward reaction (4.4) and reverse of reaction (4.3). Moreover, the 'rustic' color of the fresh calcined catalysts changed to black when removed from the microreactor of the TPSR experiments (which were not passivated or diluted in amorphous SiO$_2$), indicating significant carbon disposition via the Boudouard reaction.

If the area under the first CO$_2$ peak corresponds solely to the CuO $\rightarrow$ Cu$^0$ transition, then the area under the first peak should be considerably less significant than the second peak, when
comparing the relatively low metal loadings of Cu to Fe. This is especially the case when considering that the second peak includes both bulk changes in Fe (via carbide formation) as well as graphitization of the catalyst (via the Boudouard reaction). The Fe K-edge XANES data alone may not explain this if some of the Fe reduction is occurring via the Fe$_2$O$_3 \rightarrow$ Fe$_3$O$_4$ transition but is non-distinguishable at the ~2eV resolution (for these amorphous catalysts).

4.3.3.2. H$_2$O

Since H$_2$O was not a component in the reactant gas, it is mainly formed by a combination of the WGS reaction (4.2), Fe$_3$O$_4$ reduction (4.5), and CO hydrogenation (4.6).

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (4.2)$$

$$\text{H}_2 + \text{Fe}_3\text{O}_4 \rightarrow \text{H}_2\text{O} + 3\text{FeO} \quad (4.5)$$

$$(2n + 1)\text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O} \quad (4.6)$$

The first major H$_2$O peak is shifted to higher temperatures relative to the first CO$_2$ peak for all Fe/Cu/SiO$_2$-containing catalysts. This is due to the lower temperature of reduction of CuO $\rightarrow$ Cu$^0$ (from CO$_2$), followed by the Cu$^0$ enhancement of the reduction of Fe. Since the first H$_2$O peak (Figure 4.7) is observed from ~220-280°C for the Fe/Cu/SiO$_2$-containing catalysts (~160-240°C for the 95Fe/5Cr/5Cu/17SiO2 catalyst), yet the Fe$_2$O$_3$ std. does not exhibit this peak, indicates that it likely corresponds to the reduction of Fe. This is consistent with the fitted XANES results in Figure 4.4, which show the reduction of Fe generally at the same temperatures as the first H$_2$O peak.

The second H$_2$O peak begins at approximately 285-300°C and continues to the end of the TPRS at 362°C. The reduction of the Fe$_2$O$_3$ std. begins at approximately 330°C, which correlates strongly with the formation of CH$_4$ (Figure 4.7). The extent to which the WGS reaction affects this peak is not known. However, the LCF results indicate for the Fe/Cu/SiO$_2$-containing catalysts that most of the Fe reduction to the 2+ oxidation state occurred within the same
temperature range as the first main peak of H\textsubscript{2}O, and implies that the reduction of Fe (from H\textsubscript{2}) is not a significant component of this peak. Therefore, it is likely that the second H\textsubscript{2}O peak mainly corresponds to the H\textsubscript{2}O by-product of CO hydrogenation, with some H\textsubscript{2}O consumed by the WGS reaction.

4.3.3.3. CH\textsubscript{4}

The onset of CH\textsubscript{4} formation was observed between 265-275°C for all Fe/Cu/SiO\textsubscript{2}-containing catalysts (Figure 4.7). The CH\textsubscript{4} signal increased with temperature, until the end of the reduction in flowing syngas. An interesting result is the CH\textsubscript{4} peak is not observed until after the first H\textsubscript{2}O peak subsides for the Fe/Cu/SiO\textsubscript{2}-containing catalysts (this corresponds the reduction of Fe\textsubscript{2}O\textsubscript{3}/Fe\textsubscript{3}O\textsubscript{4} phases to predominantly the Fe\textsuperscript{2+} oxidation state. CO hydrogenation activity is observed before the LCF data exhibit bulk Fe\textsubscript{x}C formation for most of the Fe/Cu/SiO\textsubscript{2}-containing catalysts, except for the 95Fe/5Zr/5Cu/17Si and 95Fe/5Mn/5Cu/17Si catalysts. In these two catalysts bulk Fe\textsubscript{x}C formation is first observed at the same temperature (300°C). For the Fe\textsubscript{2}O\textsubscript{3} std. the temperature at which CH\textsubscript{4} formation is observed (beginning at approximately 330°C) is higher than for the catalysts which were reduced at a lower temperature due to the Cu promotion.

4.3.3.4. Correlating CH\textsubscript{4} and Fe\textsubscript{x}C Formation

For the two catalysts that formed the greatest amount of Fe\textsubscript{x}C: 95Fe/5Zr/5Cu/17Si and 95Fe/5Mn/5Cu/17Si, the formation of bulk Fe\textsubscript{x}C formation correlated well with the formation of CH\textsubscript{4}. The trend between bulk Fe\textsubscript{x}C formation and CH\textsubscript{4} formation also correlated well for the reduction of the Fe\textsubscript{2}O\textsubscript{3} std, which formed the highest Fe\textsubscript{x}C phase fraction relative to any of the samples. However, for the other samples (i.e., 100Fe/5Cu/17Si, 95Fe/5Cr/5Cu/17Si, 95Fe/5Mo/5Cu/17Si) the correlation is only moderate, since CH\textsubscript{4} formation is observed before bulk Fe\textsubscript{x}C formation is detected. This is especially true for the 95Fe/5W/5Cu/17Si sample as there was no bulk Fe\textsubscript{x}C detected, yet CH\textsubscript{4} formation was observed. The minimum level of Fe\textsubscript{x}C
formation in any of the catalysts is 5%, which means for the current set of conditions this was approximately the limit of detection of the bulk Fe\textsubscript{x}C phase. The MS can detect CH\textsubscript{4} formation at conditions where XANES cannot detect Fe\textsubscript{x}C. For the LCF of the Fe K-edge XANES spectra, the limit of detection for bulk Fe\textsubscript{x}C is approximately 5%. Considering that two different types of catalysts (i.e., the Fe\textsubscript{2}O\textsubscript{3} std. and the 95Fe/5Zr/5Cu/17Si or 95Fe/5Mn/5Cu/17Si catalyst) there is a strong correlation between the bulk Fe\textsubscript{x}C phase fraction and CH\textsubscript{4} formation (Fig. 8) which is consistent with the literature with Fe\textsubscript{x}C as the active phase for CO hydrogenation. In the literature this is commonly referred to as the carbide model\textsuperscript{22, 28, 47, 48}. An obvious deficiency in using the carbide model to describe the catalytic activity with the LCF analysis is the relatively low Fe\textsubscript{x}C phase fraction (at the conditions studied) relative to the detectable limit of Fe\textsubscript{x}C.

Figure 4.8: Normalized (0, 1) comparison between the CO hydrogenation activity (Figure 4.7) of the 95Fe/5Zr/5Cu/17Si catalyst and Fe\textsubscript{2}O\textsubscript{3} std. to the TPR-syngas XANES linear combination fitting (Figure 4.4) results for Fe\textsubscript{x}C.
4.4. Conclusions

A modification of the currently accepted model for Fe reduction was necessary to accurately describe the Fe phase changes observed for Fe/Cu/SiO\textsubscript{2}-containing catalysts during a syngas TPR while scanning Fe K-edge XANES spectra. The addition of the Fe\textsubscript{2}SiO\textsubscript{4} and FeO phases to the current model (Fe\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{x}C) for LCF of the XANES spectra was able to account for the significant presence of bulk Fe\textsuperscript{2+} observed during reduction. These (bulk Fe\textsuperscript{2+}) phases were observed at the conditions studied (25-362°C, 2°C/min ramp, 2:1 H\textsubscript{2}:CO ratio, 1 atm) due to the complementary roles of Cu and SiO\textsubscript{2} promotion on the chemistry of Fe. The XANES analysis shows that Cu enhances the low temperature reduction of Fe, while SiO\textsubscript{2} forms stabilized Fe\textsuperscript{2+} phases that inhibit Fe\textsubscript{x}C formation. The syngas reduction of the Fe\textsubscript{2}O\textsubscript{3} std. did not form any observable Fe\textsuperscript{2+} phase (by LCF analysis of the XANES), forming mostly Fe\textsubscript{x}C. The LCF of the Fe K-edge XANES data revealed that during the syngas reduction, compared to the Fe\textsubscript{x}C formed in the 100Fe/5Cu/17Si catalyst: 1) 95Fe/5W/5Cu/17Si catalyst formed less Fe\textsubscript{x}C; 2) 95Fe/5Zr/5Cu/17Si, 95Fe/5Mn/5Cu/17Si, and the Fe\textsubscript{2}O\textsubscript{3} std. formed more Fe\textsubscript{x}C; 3) 95Fe/5Cr/5Cu/17Si and 95Fe/5Mo/5Cu/17Si formed approximately the same Fe\textsubscript{x}C.

Syngas TPRS results indicate CO is responsible for the CuO → Cu\textsuperscript{0} reduction, whereas H\textsubscript{2} is responsible for the Fe\textsubscript{2}O\textsubscript{3}/Fe\textsubscript{3}O\textsubscript{4} → FeO reduction. The reduction of CuO was observed at a lower temperature than the Fe\textsubscript{2}O\textsubscript{3}/Fe\textsubscript{3}O\textsubscript{4} → FeO reduction. This is consistent with Cu\textsuperscript{0} enhancing the reduction of Fe\textsubscript{2}O\textsubscript{3}/Fe\textsubscript{3}O\textsubscript{4} to lower oxidation states. For the Fe\textsubscript{2}O\textsubscript{3} std., the 95Fe/5Mn/5Cu/17Si, and 95Fe/5Zr/5Cu/17Si catalysts there a strong correlation between the mol. fraction of the Fe\textsubscript{x}C phase fraction and CH\textsubscript{4} formation, which is consistent with the carbide model. The other catalysts tested (95Fe/5Cr/5Cu/17Si, 95Fe/5Mo/5Cu/17Si, 100Fe/5Cu/17Si) formed less Fe\textsubscript{x}C, and also showed a less direct relationship between bulk Fe\textsubscript{x}C and CH\textsubscript{4} formation. The 95Fe/5W/5Cu/17Si catalyst formed CH\textsubscript{4} but had no detectable bulk Fe\textsubscript{x}C.
information. Although Fe₃C may be present in the 95Fe/5W/5Cu/17Si catalyst as well, it is below the XANES detectable limit.

4.5. References


Chapter 5: An In-situ XANES Study on the Effects of Cr or Mn Promotion on a H₂ Activated, Syngas Reacted, Fe/Cu/SiO₂ Fischer-Tropsch Catalyst

5.1. Introduction

Synthetic fuels derived from unconventional (nonpetroleum-based) feedstocks, such as methane, coal or biomass are becoming increasingly attractive for several reasons. Some of these are: political pressures for energy independence, volatility in petroleum prices, and future demand exceeding petroleum-derived capacities\(^1\). In order to address these issues, fuels derived from unconventional feedstocks must become economically viable\(^1,2\). An attractive medium for the synthesis of unconventional fuels is through indirect coal liquefaction technologies such as the Fischer-Tropsch synthesis (FTS). This reaction is currently the most studied technique for the conversion of methane, coal or biomass-derived syngas into transportation fuels\(^3-5\). The Fe-based catalyst is generally preferred for the FTS of coal and/or biomass-derived syngas due to the relatively low cost of iron, water-gas shift (WGS) activity, and low methane selectivity at industrial FTS conditions\(^3,4,6-9\).

The formulation of interest in this study is \((100 - x)\text{Fe}/x\text{Me}/5\text{Cu}/17\text{SiO₂}; \text{Me} = \text{Cr, Mn}; \ x \leq 20\), on an atomic basis. Related characterizations of these catalysts are available in the literature\(^10-13\). Briefly, Lohitharn et al. has shown significant improvements in the initial CO hydrogenation and WGS activities with the Cr- or Mn-promoted catalysts relative to the unpromoted catalyst (H₂ reduction: 280°C, 1.8 atm, 12 hrs; syngas rxn: 280°C, 1.8 atm, 2:1 H₂:CO ratio, 6 hrs)\(^10,12\). As the reaction progressed, the CO hydrogenation and WGS activities for the Cr-promoted catalyst declined to the steady state levels observed in the Fe/Cu/SiO₂ catalyst\(^10,12\). However, the Mn-promoted catalyst maintained a marked improvement relative to the Fe/Cu/SiO₂ catalyst\(^10,12\). The as-prepared catalyst had a BET surface area of >300 m²/g with insignificant variations for different levels of Cr or Mn promotion\(^10,12\). In addition, there were no
significant variations with respect to surface or bulk concentrations of Cr or Mn in the as-prepared catalyst\textsuperscript{10,12}.

Studies of Cr-promoted, Fe-based catalysts have generally been focusing on optimizing the water-gas shift (WGS) reaction\textsuperscript{14-22}. Fe\textsubscript{3}O\textsubscript{4} is generally believed to be the active Fe phase for the WGS reaction, which coexists with the active CO hydrogenation phase, Fe\textsubscript{x}C\textsuperscript{23,24}. The literature suggests that a Fe\textsubscript{3}O\textsubscript{4}-Cr\textsubscript{2}O\textsubscript{3} complex forms, resulting in increased WGS activity\textsuperscript{18,25}. Since Cr is believed to form a complex with the active WGS phase, it is important to further investigate the site-location of Cr in the as-prepared catalyst (i.e., substitution for tetrahedral vs. octahedral sites in Fe\textsubscript{3}O\textsubscript{4}), as well as during reduction and under CO hydrogenation conditions.

Mn-promoted, Fe-based FTS catalytic studies have focused on the effects of the Mn metal loading on the value of $\alpha$ (probability of chain growth), selectivity of lower olefins, catalytic activity, the effect on Fe-reducibility, and/or the characteristics of a Fe-Mn mixed metal oxide\textsuperscript{13,15,26-50}. Campos et al. studied the Fe and Mn K-edges using ex-situ XANES (X-ray absorption near edge structure) for the fresh calcined and post-reacted (H\textsubscript{2} reduced; syngas reacted; conditions described above) (100 – x)Fe/x Mn/5 Cu/17 SiO\textsubscript{2} mol. basis catalyst, where x=0, 5, 20\textsuperscript{13}. The Mn K-edge XANES analysis indicated that Mn in the as-prepared catalyst (300\textdegree C calcination) did not form a mixed metal oxide with Fe, and was present as Mn\textsubscript{2}O\textsubscript{3}\textsuperscript{13}. However, the post-reacted catalyst indicated that a mixed metal oxide corresponding to the composition of (Fe\textsubscript{1-x}Mn\textsubscript{x})\textsubscript{3}O\textsubscript{4} formed\textsuperscript{13}. The findings of the XANES study are contrasted with a Mössbauer study by Jaggi et al. which found that higher calcination temperatures (500\textdegree C) did form an $\alpha$-(Fe\textsubscript{1-x}Mn\textsubscript{x})\textsubscript{2}O\textsubscript{3} phase\textsuperscript{28}. The in-situ XANES experiments presented here give further insight as to whether a Fe-Mn mixed metal oxide forms during H\textsubscript{2} reduction or syngas reaction, for the 300\textdegree C calcined catalyst.
XANES is one of the few characterization techniques which requires no long-range order for measurement and is capable of obtaining truly in-situ bulk phase information at catalytically relevant pressures and temperatures\(^5\). Fe K-edge XANES is used in this present study to determine the bulk Fe phase composition during H\(_2\) activation and under syngas reaction. Additionally, the experimental conditions were repeated in order to study the local structures of Cr (using the Cr K-edge XANES) and Mn (using the Mn K-edge XANES). We are not aware of any study that has used in-situ XANES to determine the site-location of Mn or Cr promotion for the Fe-based FTS catalyst. The study most-closely related to this work collected in-situ Fe K-edge TPR XANES spectra while reducing under flowing syngas, which included three of the catalysts of interest in the study presented here: 100Fe/5Cu/17Si, 95Fe/5Mn/5Cu/17Si, and 95Fe/5Cr/5Cu/17Si. The TPR XANES study mainly focused on the phase composition of Fe during the syngas reduction, and the effect of the transition metal promoter on the Fe-reducibility. The work presented here studies the element-specific local structure and oxidation state of Cr and Mn under H\(_2\) reduction and under flowing syngas (CO hydrogenation conditions). In addition, this work studies the effect of different Cr or Mn promotion levels on the Fe reducibility during H\(_2\) reduction and the syngas reaction.

5.2. Materials and Methods

5.2.1. Catalyst Synthesis

Catalysts with an atomic-basis formulation of 95Fe/5Cr/5Cu/17Si, 90Fe/10Cr/5Cu/17Si, 95Fe/5Mn/5Cu/17Si, 80Fe/20Mn/5Cu/17Si, and 100Fe/5Cu/17Si were prepared by a pH precipitation method\(^5\). Catalyst preparations have been previously detailed\(^1\). Briefly, the aqueous solutions of Fe(NO\(_3\))\(_3\)·9H\(_2\)O, Cu(NO\(_3\))\(_2\)·3H\(_2\)O, and Si(O\(_2\)H\(_5\))\(_4\) were mixed with the appropriate proportions of either Cr(NO\(_3\))\(_3\) or Mn(NO\(_3\))\(_2\); the 100Fe/5Cu/17Si catalyst was prepared without Cr or Mn. The mixed solution was precipitated with NH\(_4\)OH at 83\(^\circ\)C to a pH
between 8 and 9. Then, the precipitate was aged (room temperature, 17 hrs), washed, dried (110°C, 18-24 hrs), and calcined (300°C, 5 hrs).

References to the fresh, calcined catalyst refer to the co-precipitated catalyst after the synthesis procedures described, including calcination. A shorthand nomenclature for the catalyst is used in the figures: i.e., 80Fe20Mn corresponds to the atomic-based catalyst composition of 80Fe/20Mn/5Cu/17Si.

5.2.2. Catalyst Characterization

5.2.2.1. Fe, Cr, Mn K-edge XANES

In-situ XANES studies for the Fe, Cr, and Mn K-edges were carried out at the DCM beamline at LSU’s synchrotron facility, the J. Bennett Johnston Sr. Center for Advanced Microstructures and Devices (CAMD, Baton Rouge, LA). The synchrotron was operated with an electron energy of 1.3 GeV and a current between 100-230 mA. The DCM had Ge(220) crystals and was calibrated with either a 7.5 μm thick α-Fe foil, 2 μm α-Cr on Al foil, or cubic-Mn 400-mesh, for the respective element of interest for the in-situ XANES study. The foil standard was placed after the sample and measured independently to maintain energy calibration during the XANES scans.

XANES scans for the Fe, Cr, and Mn K-edges were performed in transmission mode using the Lytle cell (EXAFS Company, Basic furnace/Cryostat unit), which is described elsewhere. An optimum step-size [ln(μ/μ) = 1.0-1.4] was obtained for the Fe K-edge samples using approximately 0.02 g catalyst mixed with 0.02 g SiO2 (99.9% metals basis, amorphous, Alfa Aesar). After enclosing the sample between two pieces of Kapton tape, two aluminum spacers were screwed into place on each side to make the reactor cell gas-tight.

Rotameters (Model FM-1050, Matheson Trigas) maintained the gas flow, and the temperature was maintained using a Variac (10 amp, Model 3PN1010B, Staco) with a custom-
built temperature controller (using an Omega CN7500 PID controller). X-ray alignment was
made prior to running the experiments, with an XYZ stage. A He purge (UHP, Capitol Welders)
prevented the heating element from burning out.

The temperature profile for the in-situ H\textsubscript{2} reduction and CO hydrogenation of the catalyst
is summarized in Table 5.1. Each scan took approximately 740s, corresponding to scans every
25\degree C during the H\textsubscript{2}/He ramp. After each in-situ experiment, the sample was allowed to cool
down to room temperature and passivated in a 2.00\% O\textsubscript{2}, bal. He mixture (Airgas) for
approximately 15 minutes to allow for post-run ex-situ XRD measurement.

<table>
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<th>Temperature</th>
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<td>10\degree C/min</td>
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<td>120 min</td>
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<tr>
<td>300\degree C</td>
<td>240 min</td>
<td>H\textsubscript{2}/CO/Ar/He\textsuperscript{c}</td>
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</table>

\textsuperscript{a}UHP He (Capitol Welders)
\textsuperscript{b}10\% H\textsubscript{2}, bal. He (Airgas)
\textsuperscript{c}33.0\% H\textsubscript{2}, 16.5\% CO, 5.00\% Ar, bal. He (Airgas)

The XANES scanning parameters are in Table 5.2. The standards used were: Fe\textsubscript{2}O\textsubscript{3}
(99.99\% metals basis, Alfa Aesar), Fe\textsubscript{3}O\textsubscript{4} (99.95\% metals basis, Alfa Aesar), FeO (99.5\% metals
basis, Alfa Aesar), Fe\textsubscript{2}SiO\textsubscript{4} (Stock\# 44278, Alfa Aesar), θ-Fe\textsubscript{3}C (synthesized via a syngas TPR
of the Fe\textsubscript{2}O\textsubscript{3} standard; detailed elsewhere\textsuperscript{54, 55}), ZrFe\textsubscript{2} (Product\# 693812-1G, Sigma Aldrich),
FeSi (99.9\% metals basis, Alfa Aesar). The in-situ Fe K-edge XANES experiments were
performed on the following samples: 95Fe/5Cr/5Cu/17Si, 95Fe/5Mn/5Cu/17Si,
90Fe/10Cr/5Cu/17Si, 80Fe/20Mn/5Cu/17Si and 100Fe/5Cu/17Si. Standards used for the
calibration of the Mn K-edge were: Mn\textsubscript{2}O\textsubscript{3} (98\% metals basis Alfa Aesar), MnO\textsubscript{2} (99.997\% metals
basis Alfa Aesar), MnO (99.99\% metals basis Alfa Aesar), and the Mn\textsuperscript{0} (400-mesh) for
calibration. The standards used for the Cr K-edge were: Cr\textsubscript{2}O\textsubscript{3} (99.97\% metals basis Alfa Aesar),
Cr\textsubscript{7}C\textsubscript{3} (99.5% metals basis Alfa Aesar); the spectra of K\textsubscript{2}CrO\textsubscript{4} and K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} spectra were obtained from an open source XAFS database\textsuperscript{56}; CrO\textsubscript{3} and FeCr\textsubscript{2}O\textsubscript{4} spectra were obtained from Takaoka et al.\textsuperscript{57}.

Table 5.2: Fe, Cr, Mn K-edge TPR XANES scanning parameters.

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<th>Fe K-edge (7.122 KeV)</th>
<th>Cr K-edge (5.989 KeV)</th>
<th>Mn K-edge (6.539 KeV)</th>
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</tbody>
</table>

Data reduction for the Fe, Cr, or Mn K-edge XANES spectra were performed using the Athena software (v. 0.8.056)\textsuperscript{58}. Spectra are calibrated to account for shifts in (the maximum of the first derivative of) the foil which is measured independently for each scan. Following edge identification, pre-edge subtraction, and determining the normalization range, then linear combination fits (LCF) are done on the Fe K-edge XANES spectra. The LCF for this work follows a similar procedure described by Calvin et al. for the XANES fitting of Fe nanoparticles, where the fitting interval is 7092 to 7142 eV, using the derivative of the normalized XANES to fit the spectrum of the catalyst to a linear combination of Fe standards\textsuperscript{58-60}.

5.2.2.2. XRD

XRD scans were performed at the XPD (X-ray Powder Diffraction) beamline in CAMD. The samples were prepared on a Si(510) zero-background sample holder with Co K\textsubscript{α} excitation (6.9030 KeV) tuned with Ge(220) crystals; the 2θ was varied from 20° to 80°, with a step size of 0.05°, and a 3s integration time. The fresh calcined and post-reacted samples from the Fe K-edge XANES experiment was also run in XRD. Since the samples were diluted with amorphous SiO\textsubscript{2}, the amorphous SiO\textsubscript{2} std. was also tested.
5.3. Results and Discussion

5.3.1. XRD

X-ray diffraction spectra of the calcined and post-reacted catalysts are presented in Figure 5.1. Two broad diffraction peaks are observed in the spectrum of the calcined catalyst in the 2θ ranges of 30-45º and 60-80º; the SiO₂ std. shows a broad diffraction peak at a 2θ of 20-30º. These diffraction patterns are consistent with an amorphous catalyst due to the co-precipitation synthesis method used as well as SiO₂ limiting Fe₂O₃ crystallization during the calcination⁹, ⁶¹, ⁶².

Figure 5.1: XRD data for the calcined as well as the H₂ activated, syngas reacted catalysts (referred to in the figure as post-reaction): 95Fe5Cr, 90Fe10Cr, 95Fe5Mn, 80Fe20Mn, 100Fe catalysts.

A broad diffraction peak at a 2θ of 20-30º is observed in the post-reacted catalyst is consistent with SiO₂-dilution prior to the in-situ reduction/reaction XANES runs. A weak, broad
diffraction line in the 2θ range of 47.6-51.3º is similar to the χ-Fe carbide formed at relatively low temperatures, which is observed in the post-reacted 90Fe/10Cr/5Cu/17Si, 80Fe/20Mn/5Cu/17Si and 100Fe/5Cu/17Si catalysts. XRD spectra of CO-activated Fe-based catalysts treated at 280ºC also show the χ-Fe₂₅C phase. A characteristic diffraction line corresponding to α-Fe, γ-Fe is not observed in either the calcined or the post-reacted catalyst.

5.3.2. Fe K-edge XANES

The normalized Fe K-edge XANES spectra for the Fe/Cr/Cu/Si, Fe/Mn/Cu/Si, and Fe/Cu/Si catalysts during in-situ H₂ reduction and syngas reaction are shown in Figure 5.2. The Fe K-edge XANES reduction profiles during the hydrogen reduction and syngas reaction appear to be qualitatively similar to a previous in-situ Fe K-edge syngas TPR study. There is no detectable bulk Fe⁰ formation during H₂ reduction, however, under flowing syngas there appears to be continued reduction of the catalyst. This continued reduction under flowing syngas likely coincides with the formation of bulk Fe₅C. A model describing the Fe reduction under flowing the syngas reduction was proposed by Campos et al.: Fe₂O₃/Fe₃O₄ → FeO ↔ Fe₂SiO₄; FeO → Fe₅C (observed under flowing syngas); Fe₂O₃/Fe₃O₄ → Fe₅C (observed under flowing syngas), and is used in linear combination fitting of the normalized derivative Fe K-edge XANES spectra. That model is used in this present study since the Fe reduction profiles under flowing H₂ and syngas at the studied conditions for these catalysts are similar. The LCF results are given in Figure 5.3. The error bars associated with Figure 5.3 are solely associated with the 1σ error due to the fitting. Based on statistical studies for a model for a system where the chemistry is not well-defined (i.e., SiO₂- and Cu-promoted, amorphous, Fe-based catalyst) the errors associated with these fits are likely within the range of ±10-15% on an absolute basis (i.e., 10% error of a 40% mol.-basis concentration of FeO corresponds to a composition of 40 ± 10%).
Figure 5.2: Normalized Fe K-edge XANES for the H$_2$ reduction (2°C/min from 25-300°C and held at 300°C for 2hrs), followed by a syngas reaction (2:1 H$_2$:CO ratio, 4 hrs) for Mn, Cr, or unpromoted Fe-based FT catalysts.
Figure 5.3: Linear combination fitting of the Fe K-edge XANES spectra (Figure 5.2) during H₂ reduction and syngas reaction for Mn, Cr, or unpromoted Fe-based FT catalysts. Numbers on the figures correspond to: 0-1: H₂ reduction from 25-300°C, 2°C/min; 1-2: H₂ reduction at 300°C for 2hrs; 2-3: syngas reaction (2:1 H₂:CO ratio, 4 hrs).

The XRD spectra of the fresh and post-reacted catalyst are consistent with the formation of Fe₂O₃ and FeₓC phases, which are used in the LCF model. The absence of detectable Fe²⁺
phases in the XRD spectra are in agreement with in-situ XANES/WAXS (wide angle x-ray scattering) studies on a co-precipitated, SiO\textsubscript{2}- and Cu-promoted, Fe-based Fischer-Tropsch catalyst\textsuperscript{61}. The in-situ XANES/WAXS study has shown observable Fe\textsuperscript{2+} phase(s) from the XANES (short-range order characterization technique) analysis whereas the WAXS (long-range order characterization technique) analysis did not show observable formation of crystalline Fe\textsuperscript{2+} phase(s)\textsuperscript{61}. Additionally, Niemantsverdriet et al. has shown H\textsubscript{2} reduction of a FeRh/SiO\textsubscript{2} catalyst resulted in the formation of Fe\textsuperscript{2+} phase(s), however these Fe\textsuperscript{2+} phases were shown to oxidize in the presence of air\textsuperscript{67}. Considering that the XRD spectra in Figure 5.1 were collected under ambient conditions, and the these Fe\textsuperscript{2+} phases shown in the in-situ XANES spectra are air-sensitive and noncrystalline\textsuperscript{61, 67}, it is therefore not expected that the Fe\textsuperscript{2+} phases observed in the XANES would be detectable by XRD analysis.

\textbf{5.3.2.1. LCF Analysis of the Fe K-edge Spectra During H\textsubscript{2} Reduction}

LCF analysis of the H\textsubscript{2} reduction shown in Figure 5.3 ('0' to '2') are consistent with the formation of Fe\textsuperscript{2+} phase(s), which were fit using FeO and Fe\textsubscript{2}SiO\textsubscript{4}. Statistical justification for using two separate phases to model Fe\textsuperscript{2+} is given in a separate study\textsuperscript{11}. The results presented here for H\textsubscript{2} reduction at 300\textdegree C, 120 min, and 1 atm did not result in the bulk formation of \(\alpha\)-Fe. These results are consistent with a de Smit et al. study on a Fe/Cu/SiO\textsubscript{2}/K catalyst which has shown the formation of 6\% Fe\textsuperscript{0} (likely \(\alpha\)-Fe; mol.-basis phase fraction) after a H\textsubscript{2} TPR up to 350\textdegree C and 1 atm\textsuperscript{61}.

Lohitharn et al. performed quantitative H\textsubscript{2} TPRs on three of the catalysts of interest (100Fe/5Cu/17Si, 95Fe/5Mn/5Cu/17Si, 95Fe/5Cr/5Cu/17Si) and have shown ~33\% extent of reduction at 280\textdegree C, where Fe\textsubscript{2}O\textsubscript{3} \(\rightarrow\) \(\alpha\)-Fe was used as the basis for a 100\% extent of reduction\textsuperscript{12}. Since the XANES analysis presented here does not show observable formation of \(\alpha\)-Fe, this indicates a significant presence of Fe\textsuperscript{2+} phases in the bulk. If there was sole formation of FeO
and/or Fe$_2$SiO$_4$, this corresponds to a 33% extent of reduction when neglecting contributions from the reduction of the other transition metal oxides (i.e., Cu, Cr, or Mn).

Previous studies have attributed the presence of Fe$^{2+}$ phases to strong Fe-support interactions, where some of these studies have suggested that Fe-Si-O form a single phase [i.e., Fe$_2$SiO$_4$ or $[\text{Si}_2^{4+}, \Box (\text{Fe}_2^{2+}, \text{Fe}_4^{3+})_\text{O}_{12}]$]$^{23, 61, 62, 67-71}$. The study presented here, as well as related in-situ TPR XANES studies, have used Fe$_2$SiO$_4$ for the LCF of the Fe K-edge XANES spectra$^{11, 61}$. However, the study presented here shows more Fe$^{2+}$ than can be explained solely by Fe$_3$O$_4$ and Fe$_2$SiO$_4$, indicating an additional Fe$^{2+}$ phase which is fit (or modeled) using FeO$^{11}$.

The LCF for the H$_2$ reduction portion in Figure 5.3 indicates that the 100Fe/5Cu/17Si catalyst formed less Fe$_2$SiO$_4$ relative to the other studied catalysts, which is indicative that the 100Fe/5Cu/17Si catalyst formed weaker Fe-Si interactions. Lohitharn et al. studied the CO hydrogenation activity (C$_1$-C$_8$ hydrocarbons) for the catalysts of interest following H$_2$ activation (280ºC, 1.8 atm, 12 hr activation) and found that the 100Fe/5Cu/17Si catalyst exhibited a lower initial CO hydrogenation activity. Since SiO$_2$ is considered to increase the surface basicity of the catalyst$^4$, and H$_2$ activation resulted in lower initial CO hydrogenation activity$^{10, 12}$, then the decreased Fe-Si interactions (i.e., less surface basicity) in the 100Fe/5Cu/17Si catalyst likely contributed to the lower initial CO hydrogenation activity. A CO hydrogenation activity study of the catalysts of interest has shown that the Mn-promoted catalysts (95Fe/5Mn/5Cu/17Si and 80Fe/20Mn/5Cu/17Si) exhibited the highest initial CO hydrogenation activity relative to the other catalysts (Cr-promoted or unpromoted) in this present study$^{10, 12}$. Related studies of Mn-promoted Fe-based FTS catalysts have shown a positive correlation between the surface basicity (i.e., quantity of surface basic sites) and increasing levels of Mn promotion$^{42, 72, 73}$. The 100Fe/5Cu/17Si catalyst exhibited lower Fe$_2$SiO$_4$ formation and initial CO hydrogenation activity, while the Mn-promoted catalysts show a higher initial CO hydrogenation activity.
Therefore, differences in the surface basicity of the catalysts likely contributed to the changes in initial CO hydrogenation activity.

5.3.2.2. LCF Analysis of the Fe K-edge Spectra During Syngas Reaction

There was a slight oxidation of the catalyst (95Fe/5Cr/5Cu/17Si, 95Fe/5Mn/5Cu/17Si, 90Fe/10Cr/5Cu/17Si, 80Fe/20Mn/5Cu/17Si) between the reduction in flowing H₂ and the onset of the syngas reaction (Figure 5.3). The He purge appeared to partially oxidize the Fe²⁺ phases to Fe₂O₃/Fe₃O₄. Considering that exposure to an inert gas such as He partially oxidizes the Fe²⁺ phases indicates that these phases are metastable. Following the brief oxidation, the Fe phase composition during syngas reaction appears to return to the levels that were observed during the H₂ reduction. The He purge was used to analyze the phase composition following syngas exposure: 3, 15, and 27 min. This time interval was previously shown to have the largest variations in CO hydrogenation and WGS activity for the catalysts of interest. Significant differences in the bulk phase composition during this interval was not observed (i.e., instantaneous bulk FeₓC formation or variation in the XANES which would correspond to different bulk Fe phases).

The LCF results during the initial syngas reaction do not appear to show formation of bulk FeₓC (Figure 5.3). Flowing syngas following H₂ activation has previously shown immediate CO hydrogenation activity for the catalysts of interest. Surface FeₓC is generally considered the active Fe phase for CO hydrogenation, however the inability of LCF to detect low levels of FeₓC (< 5% mol.-basis Fe phase fraction in the bulk) is an obvious deficiency in describing the catalytic activity (surface phenomenon) with LCF XANES analysis (bulk characterization). Considering that the LCF indicates significant amounts of FeO and Fe₂SiO₄ in the bulk during H₂ reduction and syngas reaction is a unique finding and is difficult to determine using conventional methods since these phases are air-sensitive and noncrystalline.
Formation of the bulk Fe₃C phase is not observed until at least 51 min after the onset of the syngas reaction in the 95Fe/5Cr/5Cu/17Si and 95Fe/5Mn/5Cu/17Si catalysts. The other studied catalysts, with the exception of the 90Fe/10Cr/5Cu/17Si catalyst, have detectable bulk Fe₃C formation after 163 and 179 min for the 100Fe/5Cu/17Si and 80Fe/20Mn/5Cu/17Si catalysts, respectively. Once Fe₃C formation is detectable in the bulk, there appears to be a growth of this phase (i.e., crystallization) as the time on stream increases which is consistent with the literature.

The study presented here was performed at different conditions (1 atm, 300°C, 2 hr H₂ activation, 4 hr syngas reaction) relative to an ex-situ XANES study on the post-reacted (1.8 atm, 280°C, 12 hr H₂ activation, 6 hr syngas reaction) catalyst for the following compositions: 95Fe/5Mn/5Cu/17Si, 80Fe/20Mn/5Cu/17Si, and 100Fe/5Cu/17Si. The in-situ (presented here) and ex-situ (Campos et al.) studies significantly differ in the Fe K-edge XANES analysis: 1) Fe²⁺ phases were not observed in the ex-situ study; 2) the amounts of Fe₃C observed in the ex-situ study were significantly higher than the study presented here; 3) the ex-situ study showed increasing levels of Mn-promotion and had an inverse relationship with Fe₃C formation, whereas the study presented here have no clear correlation between the levels of Mn promotion and amounts of Fe₃C formation. Fe²⁺ phases were not observed in the LCF of the ex-situ XANES study, however this is not surprising considering that Niemantsverdriet et al. have shown that these phases are air-sensitive. The amounts of Fe₃C observed in the ex-situ study are likely higher due to the slightly greater pressure (1.8 atm vs. 1 atm) used to reduce and react the catalyst, as well as the longer H₂ reduction and syngas reaction times (i.e., the study presented

³Note the 90Fe/10Cr/5Cu/17Si catalyst was exposed to syngas for 183 min for the TPR XANES experiments. The light (X-ray source) was terminated before allowing for the full 240 min of syngas exposure but the syngas reaction was allowed to finish for collection of the XRD data. This discrepancy between 183 min of syngas exposure for the TPR XANES and 240 min of syngas exposure for the XRD experiments, likely accounts for the observation of a χ₁Fe₂.₅C peak in the XRD spectrum but not in the TPR XANES.
here shows that once Fe₃C is observed in the bulk, it increases proportional to the time under flowing syngas. The lack of a trend between levels of Mn promotion and Fe₃C formation in the study presented here, contrasted with an inverse trend between Mn promotion and Fe₃C formation observed in the ex-situ XANES study, is not clear.

5.3.2.3. Comparing Fe K-edge XANES to XRD Results

Based on the LCF results, the 95Fe/5Mn/5Cu/17Si catalyst resulted in the formation of Fe₃C in the bulk but was not observed in the XRD spectrum is indicative that the passivation procedure used was insufficient to maintain the bulk structure of the catalyst. However, the discrepancies between the Fe²⁺ phases observed in the XANES analysis for all catalysts studied, and lack of peaks in the Fe²⁺ in the ex-situ XRD spectra is attributed to the air sensitivity of these phases.

A criteria generally used for determining when passivation is occurring is the observation of a small exotherm after a dilute O₂/inert mixture is introduced which then slowly returns to room temperature, however since the thermocouple is not in direct contact with the catalyst with the XAFS in-situ cell used, an exotherm was not observed during passivation.

5.3.3. Cr K-edge XANES

The Cr K-edge XANES spectra collected during in-situ H₂ reduction and under syngas reaction for the 90Fe/10Cr/5Cu/17Si catalyst are given in Figure 5.4. A "fingerprint analysis" for the site-location and oxidation state of the Cr K-edge in the as-prepared and reduced 90Fe/10Cr/5Cu/17Si catalyst is given relative to Cr⁰, Cr³⁺, and Cr⁶⁺ standards in Figure 5.5. A sharp pre-edge (1s → 3d transition; 5.994 KeV) peak is observed in the as-prepared catalyst (25°C) and is consistent with a significant proportion of Cr⁶⁺ species (i.e., CrO₃, K₂CrO₄, or K₂Cr₂O₇). The calcination step (300°C, 5 hrs) during the catalyst synthesis likely resulted in the oxidation of the precipitated Cr³⁺ precursor. H₂ reduction after 125°C resulted in the Cr⁶⁺...
Figure 5.4: Normalized Cr K-edge XANES for the H₂ reduction (2°C/min from 25-300°C and held at 300°C for 2hrs), followed by a syngas reaction (2:1 H₂:CO ratio, 4 hrs) for the 90Fe10Cr catalyst.

Figure 5.5: Normalized Cr K-edge XANES fingerprint analysis, a comparison of the 90Fe/10Cr/5Cu/17Si catalyst before and during reduction (the spectra of the catalyst were merged to reduce the noise). CrO₃ and FeCr₂O₄ were obtained from Takaoka et al.⁵⁷; K₂CrO₄ and K₂Cr₂O₇ were obtained from an open source XAFS database⁵⁶.
species reducing to the Cr$^{3+}$ oxidation state. At approximately 250ºC the sharp pre-edge completely disappears (Figure 5.4), with only Cr$^{3+}$ detected$^{77,78}$.

The XANES spectra in Figure 5.5 for the pre-reduced 90Fe/10Cr/5Cu/17Si catalyst indicates that it is a mixture of Cr$^{6+}$ and Cr$^{3+}$ based on the pre-edge to main (1s $\rightarrow$ 4p; 6.012 KeV) peak ratio. In the Cr$^{6+}$ standards there is a higher ratio of the pre-edge to the main peak$^{78}$.

The pre-edge feature of the reduced 90Fe/10Cr/5Cu/17Si spectrum (Figure 5.5) indicates a Cr$^{3+}$ phase (Figure 5.5), which is significantly different from the Cr$_2$O$_3$ standard. Furthermore, the spectrum of the reduced 90Fe/10Cr/5Cu/17Si catalyst more closely resembles the spectrum of the FeCr$_2$O$_4$ standard, which is in agreement with the formation of a Fe-Cr mixed metal oxide, with Cr in the 3+ oxidation state. This finding is consistent with the literature which indicated a Fe$_3$O$_4$-Cr$_2$O$_3$ spinel-type phase$^{18,25}$, where Dry has indicated that Cr goes into a solid solution with Fe$_3$O$_4$$^{15}$. This spinel-type phase is stable after its formation at approximately 250ºC (Figure 5.4), and has no detectable changes (i.e., reduction or oxidation) under either H$_2$ (300ºC, 2 hrs) or syngas (300ºC, 4 hrs).

The possibility of Cr forming a solid solution with FeO or Fe$_2$SiO$_4$ phases is unlikely considering that an ex-situ Cr K-edge post-reacted 90Fe/10Cr/5Cu/17Si spectrum (not shown) is almost identical to the in-situ 90Fe/10Cr/5Cu/17Si reduced (Figure 5.5) spectrum. Additionally, since $\alpha$-Fe is not observed during H$_2$ reduction, it is not possible for a $\alpha$-Fe/Cr$_2$O$_3$ type-phase to explain the reduced 90Fe/10Cr/5Cu/17Si spectrum. Therefore, the Fe$_3$O$_4$-Cr$_2$O$_3$ spinel-type phase formed during H$_2$ reduction (i.e., no evidence of a mixed metal oxide in the as-prepared catalyst) was stable during the remainder of the in-situ H$_2$ reduction and syngas reaction.

5.3.4. Mn K-edge XANES

The Mn K-edge XANES spectra collected during in-situ H$_2$ reduction and under syngas reaction for the 80Fe/20Mn/5Cu/17Si catalyst are given in Figure 5.6. This figure indicates that
H₂ reduction of Mn begins at 175°C and reaches a steady state structure at 275°C. Mn is in the 3+ oxidation state in the as-prepared catalyst, where the spectrum is in general agreement with Mn₂O₃ (i.e., Mn is not present as a mixed metal oxide in the as-prepared catalyst)¹³. The steady state structure of Mn is approximately in the 2+ oxidation state, but is not present as MnO, which is indicative of the formation of a mixed metal oxide formation.

Figure 5.6: Normalized Mn K-edge XANES for the H₂ reduction (2°C/min from 25-300°C and held at 300°C for 2hrs), followed by a syngas reaction (2:1 H₂:CO ratio, 4 hrs) for the 80Fe/20Mn/5Cu/17Si catalyst. The Mn K-edge results presented here are compared to a previous ex-situ Mn K-edge XANES study on the as-prepared and post-reacted 95Fe/5Mn/5Cu/17Si and 80Fe/20Mn/5Cu/17Si catalysts¹³. Similarities between the post-reacted 95Fe/5Mn/5Cu/17Si ex-situ Mn K-edge spectrum¹³ with the spectrum of the in-situ reduced 80Fe/20Mn/5Cu/17Si catalyst indicates that the local structures of Mn in these systems are similar. The ex-situ Mn K-edge XANES analysis of the 95Fe/5Mn/5Cu/17Si spectrum, which is almost identical to the in-situ reduced 80Fe/20Mn/5Cu/17Si spectrum, indicates that Mn²⁺ is substituting for octahedral sites in Fe₃O₄ in both cases¹³. This mixed metal oxide corresponds to a composition of (Fe₁₋ₓMnₓ)₃O₄.
\( \text{Mn}_3 \text{O}_4 \), which is an inverted spinel (i.e., a completely inverted spinel has 2+ species in octahedral sites and 3+ species in tetrahedral sites)\(^{13}\).

The 80Fe/20Mn/5Cu/17Si in-situ reduced spectrum is different from the previously analyzed 80Fe/20Mn/5Cu/17Si ex-situ spectrum\(^{13}\). These differences could be due to the disappearance of a more reduced phase iron-manganese oxide phase [i.e., \((\text{Fe}_{1-z}\text{Mn}_z)\text{O})\] after exposure to ambient air, which then forms separate phases of Mn\(_2\)O\(_3\) with Fe\(_2\)O\(_3\) and/or Fe\(_3\)O\(_4\). An alternative explanation could be that Mn was never fully reduced in the ex-situ XANES study, however, based on the Fe K-edge results presented here which shows that Fe is more reduced in the ex-situ study makes this explanation less reasonable\(^{13}\). Additionally, since the ex-situ Mn K-edge XANES analysis of the 95Fe/5Mn/5Cu/17Si spectrum shows that Mn is present as \((\text{Fe}_{1-z}\text{Mn}_z)\text{O}_4\) after exposure to air indicates that the \((\text{Fe}_{1-z}\text{Mn}_z)\text{O}_4\) phase is not air-sensitive.

### 5.3.5. Comparison of Mn and Cr K-edge XANES Analysis to Changes in CO Hydrogenation Activity\(^{10}\)

XANES analysis of the Cr and Mn K-edges suggest that these promoter have formed a mixed metal oxide with iron during H\(_2\) reduction and are stable (i.e., not further reduced) during reduction in syngas at 300\(^\circ\)C. The catalysts studied (Cr- or Mn-promoted) have previously shown increased initial CO hydrogenation activity relative to the 100Fe/5Cu/17Si catalyst\(^{10}\). As the time on stream progresses, the CO hydrogenation activity of the Cr-promoted catalyst approaches the 100Fe/5Cu/17Si catalyst, whereas the Mn-promoted catalysts maintained a significant activity improvement\(^{10}\). Both the Cr- and Mn-promoted catalysts substituted into the Fe\(_3\)O\(_4\) phase, while Mn substituted as a divalent species whereas Cr substituted as a trivalent species. While Fe\(_x\)C is generally considered to be the active phase for CO hydrogenation\(^{23,36,63,79,80}\), the crystallization of Fe\(_x\)C phases lead to graphitization of the catalyst\(^{75,76}\), resulting in catalyst deactivation\(^{63}\). Campos et al. have previously shown Mn promotion decreases the carbon deposition in the catalyst, and resulted in a higher steady state CO hydrogenation activity\(^{13}\). Since the Cr-
promoted catalysts had approximately the same steady-state CO hydrogenation activity relative to the 100Fe/5Cu/17Si catalyst, it is likely that the Fe$_3$O$_4$-Cr$_2$O$_3$ phase may have did not inhibit the carbon deposition.

5.4. Conclusions

LCF analysis is performed on the Fe K-edge XANES spectra collected during in-situ H$_2$ reduction (25-300°C, 2° C/min; 300°C, 2 hr) and syngas reaction (300°C, 4 hr) for Cr-promoted, Mn-promoted, and an unpromoted catalyst [base formula: (100 − x)Fe/x Me/5 Cu/17 SiO$_2$; Me = Cr, Mn; x ≤ 20]. The analysis indicated that Fe$^{2+}$ phases (i.e., FeO, Fe$_2$SiO$_4$) are a significant component of the Cu- and Si-promoted, co-precipitated catalyst. Additionally, LCF indicates that the reduction profile for Fe under flowing H$_2$ (where bulk α-Fe is not observed) is similar to a previous study on the reduction under flowing syngas (before Fe$_x$C formation is observed). Bulk Fe$_x$C formation is not observed until at least 51 min after syngas is introduced, indicating that CO hydrogenation activity occurs on a fraction of surface Fe$_x$C sites, before bulk Fe$_x$C is observed in the catalyst (LCF limit of detection for current study is ~5%).

XANES analysis for the Cr (90Fe/10Cr/5Cu/17Si) and Mn (80Fe/20Mn/5Cu/17Si) K-edges indicated that these promoters substituted into the Fe$_3$O$_4$ phase during H$_2$ reduction and are stable (i.e., not further reduced) during the syngas reaction (300°C, 4 hrs). It was found that Mn substituted in Fe$_3$O$_4$ as a divalent species, corresponding to a composition of (Fe$_{1-y}$Mn$_y$)$_3$O$_4$; Cr substituted as a trivalent species, which corresponds to a composition of Fe$_3$O$_4$-Cr$_2$O$_3$.

Previous CO hydrogenation activity results have shown that the initial (first 2 hrs) activity is improved with either Mn or Cr promotion, where the Cr-promoted steady state activity declined to the levels of the unpromoted (100Fe/5Cu/17Si) catalyst; the Mn-promoted catalyst maintained a marked improvement in steady state activity. The differences in the oxidation state of the substituted promoter (i.e., divalent Mn vs. trivalent Cr substitution into Fe$_3$O$_4$) likely
affects the surface chemistry of the catalyst (i.e., surface basicity which affects the amount of graphitization, and therefore deactivation of the catalyst). Mn promotion inhibiting carbon deposition has been previously shown\textsuperscript{13}; the deactivation of the Cr-promoted catalyst indicates that the formation of Fe\textsubscript{3}O\textsubscript{4}-Cr\textsubscript{2}O\textsubscript{3} likely has a minor effect on preventing deactivation via carbon deposition.

5.5. References


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Chapter 6: Conclusions and Recommendations for Future Work

6.1. Conclusions

The effects of the transition metal promotion of Fe/Cu/Si Fischer-Tropsch synthesis catalysts were investigated mainly using ex-situ and in-situ XANES spectroscopy, where the transition metal promoters studied included: Cr, Mn, Mo, W or Zr. The Mn-promoted catalysts (80Fe/20Mn/5Cu/17Si, 95Fe/5Cu/17Si) exhibited the maximum steady state CO hydrogenation activity\(^1,2\) and were more thoroughly characterized. Based on this investigation, it was determined that Mn forms a mixed metal oxide with Fe, where Mn substituted for octahedral sites in Fe\(_3\)O\(_4\) which corresponds to the composition of (Fe\(_{1-y}\)Mn\(_y\))\(_3\)O\(_4\). Moreover, it was found that Mn promotion inhibited the amount of carbon deposited on the catalyst; the carbon deposition inhibition likely resulted in the increase the steady state activity (in the Mn-promoted catalysts) relative to the 100Fe/5Cu/17Si catalyst. Related studies of Mn-promoted Fe-based FTS catalysts have shown a positive correlation between the surface basicity (i.e., quantity of surface basic sites) and increasing levels of Mn promotion\(^4-6\), when coupled with the formation of (Fe\(_{1-y}\)Mn\(_y\))\(_3\)O\(_4\) observed in the studies presented here, this gives an increased understanding as to the role of Mn and how it increases the steady state CO hydrogenation activity.

A refinement to the previously accepted reduction model: Fe\(_2\)O\(_3\) \(\rightarrow\) Fe\(_3\)O\(_4\) \(\rightarrow\) Fe\(_x\)C was made during the analysis of in-situ Fe K-edge TPR XANES (25-362\(^\circ\)C, 2\(^\circ\)/min ramp, 2:1 H\(_2\):CO ratio, 1 atm) spectra of 95Fe/5Me/5Cu/17Si (Me = Cr, Mn, Mo, W or Zr. The analysis indicated a significant amount of Fe\(^{2+}\) phases which exceeded what could be explained by the previous Fe reduction model; therefore, the FeO and Fe\(_2\)SiO\(_4\) phases were added to the LCF model and were found to give significant improvements to a reduced goodness-of-fit parameter, \(\chi^2\). FeO and Fe\(_2\)SiO\(_4\) were observed at the conditions studied due to the complementary roles of
Cu and SiO$_2$ promotion on the Fe chemistry, where Cu enhanced the low temperature reduction of Fe, and SiO$_2$ forms stabilized Fe$^{2+}$ phases that inhibited Fe$_x$C formation.

Fe K-edge XANES spectra collected during the in-situ H$_2$ reduction of the Cr- or Mn-promoted Fe/Cu/Si catalyst also showed a similar reduction profile relative to the syngas reduced catalyst (before detectable $\alpha$-Fe or Fe$_x$C formation are observed). It was determined that the as-prepared Cr (via Cr K-edge XANES analysis) and Mn (via Mn K-edge XANES analysis) were separate phases from Fe (i.e., there was no detectable Fe-Cr-O or Fe-Mn-O phases in the as-prepared catalyst). During H$_2$ reduction it was shown that Cr substituted as a trivalent species into Fe$_3$O$_4$, which corresponds to a composition of Fe$_3$O$_4$-Cr$_2$O$_3$; Mn substituted as a divalent species into Fe$_3$O$_4$, corresponding to a composition of (Fe$_{1-y}$Mn$_y$)$_3$O$_4$. The differences in the oxidation state of the substituted promoter (i.e., divalent Mn vs. trivalent Cr substitution into Fe$_3$O$_4$) likely affects the surface chemistry of the catalyst (i.e., surface basicity which affects the amount of inert carbon deposition, and therefore deactivation of the catalyst). Mn promotion inhibiting carbon deposition has been previously shown$^7$; the deactivation of the Cr-promoted catalyst indicates that the formation of Fe$_3$O$_4$-Cr$_2$O$_3$ has a minor effect on preventing deactivation via inert carbon deposition.

6.2. Recommendations for Future Work

Based on the results presented here, and considering the experiments previously performed in the literature, the followings are recommended:

- In-situ XPS: determining whether there is migration of promoters to the surface or bulk during reduction and reaction is important in understanding the chemistry of Fe. The three steps at which XPS should be collected: 1) as-prepared catalyst; 2) H$_2$ reduced catalyst; 3) syngas reacted catalyst following H$_2$ reduction. Due to the air sensitivity of Fe$^{2+}$ phases, these experiments ideally would prevent exposure to air.
• CO₂ TPD: the effect of the promoters on the surface basicity should be compared at different metal loadings and compared with other surface characterizations [i.e., 1) FT-IR: if CO is adsorbed stronger or weaker on Fe; 2) effect of basicity on activity/selectivity; 3) effect of basicity on carbon deposition; 4) if a promoter migrates to the surface such as Mn, and an increase in surface basicity it observed].

• High pressure (>10 atm) in-situ Fe K-edge XANES measurements - Dry⁸ has indicated that the H₂ reduced catalyst at industrially relevant conditions is present solely as α-Fe before syngas is introduced. This indicates that the studies presented here (1 atm) have significantly different chemistries at industrially relevant conditions (20 atm). A study showing the effect of pressure on the Fe reduction as well as a studying the edge of the promoter would be interesting.

• Effects of different activation gases (i.e., H₂, CO, or syngas) on the catalytic activity and selectivity.

• In-situ FT-IR: Determining the effect of different promoters (i.e., Cr, Mn, Zr) on the strength of CH bonds is important, the stronger the C–H bond, the weaker the Fe-C bond. These results would also be complementary to activity/selectivity studies.

• BET surface area measurements following H₂ reduction: Considering that Fe₂SiO₄ forms during H₂ reduction, when exposed to air these phases appear to separate. This phase separation phenomenon will likely result in a lower surface area.

6.3. References


Appendix A: Supplemental Data of an In-situ XANES Study of Promoted Fe-based Fischer-Tropsch Catalysts: Effect of Transition Metal Promoters on Fe Reduction and CO Hydrogenation

Figure A.1: Normalized Fe K-edge XANES of Fe stds. scanned, compared with the 95Fe/5Mn/5Cu/17Si sample before and after reduction in flowing syngas.
Figure A.2: A comparison of the Fe$_2$O$_3$ and Fe$_3$O$_4$ normalized Fe K-edge XANES spectra (below); the Fe$_3$O$_4$ std. with the 100Fe/5Cu/17SiO$_2$ spectrum.

Figure A.3: A comparison of the derivatives of the normalized XANES spectra from Figure A.2. (note: a change in the scale of the x-axis).
Figure A.4: Fe K-edge XANES for the 95Fe/Zr/5Cu/17Si, 95Fe/5Mn/5Cu/17Si, 100Fe/5Cu/17Si catalysts at 362°C, shown relative to the XANES of the 100Fe/5Cu/17Si catalyst at 300°C.
Figure A.5: A comparison of He ramp and syngas TPRS for 95Fe/5W/5Cu/17SiO$_2$ catalyst: (a) CH$_4$; (b) H$_2$O; (c) CO$_2$. (d) An additional perspective is given for the normalized TPRS results for the 95Fe/5W/5Cu/17SiO$_2$ catalyst.
Figure A.6: XRD spectrum for the synthesized $\theta$-Fe$_3$C std. (from the syngas TPR of the Fe$_2$O$_3$ std. to 550$^\circ$C) with the peaks identified from Cu K$_\alpha$. 

**Key**
- Graphite
- Fe$_3$O$_4$
- $\theta$-Fe$_3$C
Table A.1: 95Fe/5Cr/5Cu/17SiO₂ at 362°C, a comparison of goodness-of-fit parameter for different models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Fe₂O₃/Fe₂O₄</th>
<th>FeO</th>
<th>Fe₃SiO₄</th>
<th>Fe₃C</th>
<th>X²ᵣ / X²ᵣf</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27% ± 5%</td>
<td>--</td>
<td>--</td>
<td>73% ± 8%</td>
<td>10.6</td>
</tr>
<tr>
<td>2</td>
<td>--</td>
<td>100%</td>
<td>--</td>
<td>--</td>
<td>5.89</td>
</tr>
<tr>
<td>3</td>
<td>31% ± 2%</td>
<td>69% ± 2%</td>
<td>--</td>
<td>--</td>
<td>2.01</td>
</tr>
<tr>
<td>4</td>
<td>27% ± 2%</td>
<td>52% ± 3%</td>
<td>21% ± 2%</td>
<td>--</td>
<td>1.07</td>
</tr>
<tr>
<td>5</td>
<td>23% ± 2%</td>
<td>43% ± 4%</td>
<td>22% ± 2%</td>
<td>12% ± 2%</td>
<td>1</td>
</tr>
</tbody>
</table>

Table A.2: 95Fe/5Mn/5Cu/17SiO₂ at 362°C, a comparison of goodness-of-fit parameter for different models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Fe₂O₃/Fe₂O₄</th>
<th>FeO</th>
<th>Fe₃SiO₄</th>
<th>Fe₃C</th>
<th>X²ᵣ / X²ᵣf</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22% ± 5%</td>
<td>--</td>
<td>--</td>
<td>78% ± 7%</td>
<td>9.80</td>
</tr>
<tr>
<td>2</td>
<td>--</td>
<td>100%</td>
<td>--</td>
<td>--</td>
<td>4.08</td>
</tr>
<tr>
<td>3</td>
<td>28% ± 2%</td>
<td>72% ± 2%</td>
<td>--</td>
<td>--</td>
<td>2.11</td>
</tr>
<tr>
<td>4</td>
<td>25% ± 2%</td>
<td>60% ± 4%</td>
<td>15% ± 3%</td>
<td>--</td>
<td>1.58</td>
</tr>
<tr>
<td>5</td>
<td>16% ± 2%</td>
<td>39% ± 4%</td>
<td>18% ± 2%</td>
<td>27% ± 4%</td>
<td>1</td>
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</tbody>
</table>
Table A.3: 95Fe/5Mo/5Cu/17SiO$_2$ at 362$^\circ$C, a comparison of goodness-of-fit parameter for different models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Fe$_2$O$_3$/Fe$_3$O$_4$</th>
<th>FeO</th>
<th>Fe$_2$SiO$_4$</th>
<th>FeC</th>
<th>$\chi^2_{sf}/\chi^2_{if}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22% ± 6%</td>
<td>--</td>
<td>--</td>
<td>78% ± 5%</td>
<td>10.1</td>
</tr>
<tr>
<td>2</td>
<td>--</td>
<td>100%</td>
<td>--</td>
<td>--</td>
<td>4.10</td>
</tr>
<tr>
<td>3</td>
<td>25% ± 2%</td>
<td>75% ± 2%</td>
<td>--</td>
<td>--</td>
<td>1.70</td>
</tr>
<tr>
<td>4</td>
<td>21% ± 2%</td>
<td>63% ± 3%</td>
<td>21% ± 2%</td>
<td>--</td>
<td>1.20</td>
</tr>
<tr>
<td>5</td>
<td>15% ± 2%</td>
<td>50% ± 4%</td>
<td>17% ± 2%</td>
<td>18% ± 4%</td>
<td>1</td>
</tr>
</tbody>
</table>

Table A.4: 95Fe/5W/5Cu/17SiO$_2$ at 362$^\circ$C, a comparison of goodness-of-fit parameter for different models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Fe$_2$O$_3$/Fe$_3$O$_4$</th>
<th>FeO</th>
<th>Fe$_2$SiO$_4$</th>
<th>FeC</th>
<th>$\chi^2_{sf}/\chi^2_{if}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>29% ± 6%</td>
<td>--</td>
<td>--</td>
<td>71% ± 9%</td>
<td>13.3</td>
</tr>
<tr>
<td>2</td>
<td>--</td>
<td>100%</td>
<td>--</td>
<td>--</td>
<td>3.82</td>
</tr>
<tr>
<td>3</td>
<td>26% ± 2%</td>
<td>74% ± 2%</td>
<td>--</td>
<td>--</td>
<td>1.83</td>
</tr>
<tr>
<td>4</td>
<td>20% ± 2%</td>
<td>59% ± 3%</td>
<td>20% ± 2%</td>
<td>--</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>20% ± 2%</td>
<td>59% ± 3%</td>
<td>20% ± 2%</td>
<td>1% ± 4%</td>
<td>1.01</td>
</tr>
</tbody>
</table>
Table A.5: 95Fe/5Zr/5Cu/17SiO$_2$ at 362°C, a comparison of goodness-of-fit parameter for different models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Fe$_2$O/Fe$_3$O$_4$</th>
<th>FeO</th>
<th>Fe$_2$SiO$_4$</th>
<th>Fe$_x$C</th>
<th>$\chi^2_{df} / \chi^2_{df}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25% ± 5%</td>
<td>--</td>
<td>--</td>
<td>75% ± 5%</td>
<td>8.74</td>
</tr>
<tr>
<td>2</td>
<td>--</td>
<td>100%</td>
<td>--</td>
<td>--</td>
<td>5.38</td>
</tr>
<tr>
<td>3</td>
<td>30% ± 2%</td>
<td>70% ± 2%</td>
<td>--</td>
<td>--</td>
<td>1.87</td>
</tr>
<tr>
<td>4</td>
<td>27% ± 2%</td>
<td>57% ± 4%</td>
<td>16% ± 3%</td>
<td>--</td>
<td>1.33</td>
</tr>
<tr>
<td>5</td>
<td>20% ± 2%</td>
<td>39% ± 4%</td>
<td>19% ± 2%</td>
<td>23% ± 4%</td>
<td>1</td>
</tr>
</tbody>
</table>
Table A.6: Fe$_2$O$_3$ std. Fe K-edge XANES calibration and linear combination fitting parameters during reduction in flowing syngas.

<table>
<thead>
<tr>
<th>Temp. ($^\circ$C)</th>
<th>$\Delta E_0$ to calibrate</th>
<th>Fe$_2$O$_3$/Fe$_3$O$_4$ (mol. fraction, % basis)$^a$</th>
<th>$\Delta E_0$ (eV)$^b$</th>
<th>FeO (mol. fraction, % basis)$^a$</th>
<th>Fe$_2$SiO$_4$ (mol. fraction, % basis)$^a$</th>
<th>Fe$_3$C (mol. fraction, % basis)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.17</td>
<td>100%</td>
<td>-0.04</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>50</td>
<td>0.14</td>
<td>100%</td>
<td>0.15</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>75</td>
<td>0.12</td>
<td>100%</td>
<td>0.11</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>100</td>
<td>0.13</td>
<td>100%</td>
<td>0.07</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>125</td>
<td>0.18</td>
<td>100%</td>
<td>0.19</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>150</td>
<td>0.11</td>
<td>100%</td>
<td>0.08</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>175</td>
<td>0.11</td>
<td>100%</td>
<td>0.10</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>200</td>
<td>0.11</td>
<td>100%</td>
<td>0.08</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>225</td>
<td>0.12</td>
<td>100%</td>
<td>0.11</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>250</td>
<td>0.14</td>
<td>100%</td>
<td>0.07</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>275</td>
<td>0.13</td>
<td>100%</td>
<td>0.02</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>300</td>
<td>0.18</td>
<td>100%</td>
<td>0.07</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>325</td>
<td>0.19</td>
<td>100%</td>
<td>-0.02</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>350</td>
<td>0.19</td>
<td>54% ± 2%</td>
<td>0.08</td>
<td>--</td>
<td>--</td>
<td>46% ± 2%</td>
</tr>
<tr>
<td>362</td>
<td>0.17</td>
<td>46% ± 3%</td>
<td>0.08</td>
<td>--</td>
<td>--</td>
<td>54% ± 4%</td>
</tr>
</tbody>
</table>

$^a$Rounded to the nearest %

$^b$$\Delta E_0$ fitted parameter for the Fe$_2$O$_3$/Fe$_3$O$_4$ phase, this is calculated after sample calibration.
Table A.7: 100Fe/5Cu/17SiO$_2$ Fe K-edge XANES calibration and linear combination fitting parameters during reduction in flowing syngas.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$\Delta E_0$ to calibrate the sample w/ foil (eV)</th>
<th>Fe$_2$O$_3$/Fe$_3$O$_4$ (mol. fraction, % basis)$^a$</th>
<th>$\Delta E_0$ (eV)$^b$</th>
<th>FeO (mol. fraction, % basis)$^a$</th>
<th>Fe$_2$SiO$_4$ (mol. fraction, % basis)$^a$</th>
<th>Fe$_x$C (mol. fraction, % basis)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-1.21</td>
<td>100%</td>
<td>0.38</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>50</td>
<td>-1.28</td>
<td>100%</td>
<td>0.39</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>75</td>
<td>-1.29</td>
<td>100%</td>
<td>0.39</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>100</td>
<td>-1.28</td>
<td>100%</td>
<td>0.37</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>125</td>
<td>-1.25</td>
<td>100%</td>
<td>0.36</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>150</td>
<td>-1.21</td>
<td>100%</td>
<td>0.35</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>175</td>
<td>-1.22</td>
<td>100%</td>
<td>0.31</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>200</td>
<td>-1.18</td>
<td>100%</td>
<td>0.32</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>225</td>
<td>-1.17</td>
<td>92% ± 1%</td>
<td>0.36</td>
<td>8% ± 1%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>250</td>
<td>-1.12</td>
<td>71% ± 1%</td>
<td>0.36</td>
<td>22% ± 2%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>275</td>
<td>-1.08</td>
<td>45% ± 2%</td>
<td>0.36</td>
<td>37% ± 3%</td>
<td>18% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>300</td>
<td>-1.00</td>
<td>31% ± 2%</td>
<td>0.36</td>
<td>47% ± 3%</td>
<td>22% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>325</td>
<td>-1.01</td>
<td>24% ± 1%</td>
<td>0.36</td>
<td>54% ± 2%</td>
<td>22% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>350</td>
<td>-0.92</td>
<td>21% ± 2%</td>
<td>0.36</td>
<td>46% ± 3%</td>
<td>23% ± 1%</td>
<td>10% ± 4%</td>
</tr>
<tr>
<td>362</td>
<td>-0.89</td>
<td>20% ± 2%</td>
<td>0.36</td>
<td>45% ± 3%</td>
<td>20% ± 2%</td>
<td>14% ± 3%</td>
</tr>
</tbody>
</table>

$^a$ Rounded to the nearest %

$^b$ $\Delta E_0$ fitted parameter for the Fe$_2$O$_3$/Fe$_3$O$_4$ phase, this is calculated after sample calibration.
Table A.8: 95Fe/5Cr/5Cu/17SiO$_2$ Fe K-edge XANES calibration and linear combination fitting parameters during reduction in flowing syngas.

<table>
<thead>
<tr>
<th>Temp. ($^\circ$C)</th>
<th>$\Delta E_0$ to calibrate the sample w/ foil (eV)</th>
<th>Fe$_2$O$_3$/Fe$_3$O$_4$ (mol. fraction, % basis)$^a$</th>
<th>$\Delta E_0$ (eV)$^b$</th>
<th>FeO (mol. fraction, % basis)$^a$</th>
<th>Fe$_2$SiO$_4$ (mol. fraction, % basis)$^a$</th>
<th>Fe$_2$C (mol. fraction, % basis)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-0.70</td>
<td>100%</td>
<td>0.64</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>50</td>
<td>-0.75</td>
<td>100%</td>
<td>0.54</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>75</td>
<td>-0.74</td>
<td>100%</td>
<td>0.58</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>100</td>
<td>-0.74</td>
<td>100%</td>
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<td>--</td>
<td>--</td>
</tr>
<tr>
<td>125</td>
<td>-0.76</td>
<td>100%</td>
<td>0.52</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>150</td>
<td>-0.77</td>
<td>100%</td>
<td>0.46</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>175</td>
<td>-0.79</td>
<td>100%</td>
<td>0.41</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>200</td>
<td>-0.74</td>
<td>94% ± 2%</td>
<td>0.53</td>
<td>6% ± 2%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>225</td>
<td>-0.74</td>
<td>82% ± 1%</td>
<td>0.53</td>
<td>12% ± 2%</td>
<td>6% ± 3%</td>
<td>--</td>
</tr>
<tr>
<td>250</td>
<td>-0.78</td>
<td>66% ± 1%</td>
<td>0.53</td>
<td>28% ± 2%</td>
<td>5% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>275</td>
<td>-0.78</td>
<td>45% ± 2%</td>
<td>0.53</td>
<td>37% ± 3%</td>
<td>17% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>300</td>
<td>-0.71</td>
<td>29% ± 2%</td>
<td>0.53</td>
<td>43% ± 3%</td>
<td>28% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>325</td>
<td>-0.74</td>
<td>27% ± 2%</td>
<td>0.53</td>
<td>46% ± 3%</td>
<td>27% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>350</td>
<td>-0.73</td>
<td>24% ± 2%</td>
<td>0.53</td>
<td>46% ± 4%</td>
<td>25% ± 2%</td>
<td>5% ± 4%</td>
</tr>
<tr>
<td>362</td>
<td>-0.68</td>
<td>23% ± 2%</td>
<td>0.53</td>
<td>43% ± 4%</td>
<td>22% ± 2%</td>
<td>12% ± 4%</td>
</tr>
</tbody>
</table>

$^a$Rounded to the nearest %

$^b$\(\Delta E_0\) fitted parameter for the Fe$_2$O$_3$/Fe$_3$O$_4$ phase, this is calculated after sample calibration
Table A.9: 95Fe/5Mn/5Cu/17SiO$_2$ Fe K-edge XANES calibration and linear combination fitting parameters during reduction in flowing syngas.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$\Delta E_0$ to calibrate the sample w/ foil (eV)</th>
<th>Fe$_2$O$_3$/Fe$_3$O$_4$ (mol. fraction, % basis)$^a$</th>
<th>$\Delta E_0$ (eV)$^b$</th>
<th>FeO (mol. fraction, % basis)$^a$</th>
<th>Fe$_2$SiO$_4$ (mol. fraction, % basis)$^a$</th>
<th>Fe$_3$C (mol. fraction, % basis)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-1.16</td>
<td>100%</td>
<td>-0.47</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>50</td>
<td>-1.10</td>
<td>100%</td>
<td>-0.42</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>75</td>
<td>-1.10</td>
<td>100%</td>
<td>-0.46</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>100</td>
<td>-1.13</td>
<td>100%</td>
<td>-0.55</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>125</td>
<td>-1.06</td>
<td>100%</td>
<td>-0.51</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>150</td>
<td>-0.99</td>
<td>100%</td>
<td>-0.53</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>175</td>
<td>-1.02</td>
<td>100%</td>
<td>-0.60</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>200</td>
<td>-1.01</td>
<td>100%</td>
<td>-0.66</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>225</td>
<td>-0.94</td>
<td>90% ± 2%</td>
<td>-0.52</td>
<td>10% ± 2%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>250</td>
<td>-0.81</td>
<td>27% ± 2%</td>
<td>-0.52</td>
<td>48% ± 4%</td>
<td>25% ± 3%</td>
<td>--</td>
</tr>
<tr>
<td>275</td>
<td>-0.81</td>
<td>24% ± 2%</td>
<td>-0.52</td>
<td>53% ± 3%</td>
<td>23% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>300</td>
<td>-0.91</td>
<td>20% ± 2%</td>
<td>-0.52</td>
<td>51% ± 4%</td>
<td>20% ± 2%</td>
<td>8% ± 4%</td>
</tr>
<tr>
<td>325</td>
<td>-0.88</td>
<td>17% ± 2%</td>
<td>-0.52</td>
<td>45% ± 4%</td>
<td>19% ± 2%</td>
<td>19% ± 4%</td>
</tr>
<tr>
<td>350</td>
<td>-0.70</td>
<td>15% ± 2%</td>
<td>-0.52</td>
<td>40% ± 3%</td>
<td>17% ± 2%</td>
<td>28% ± 3%</td>
</tr>
<tr>
<td>362</td>
<td>-0.70</td>
<td>16% ± 2%</td>
<td>-0.52</td>
<td>39% ± 4%</td>
<td>18% ± 2%</td>
<td>27% ± 4%</td>
</tr>
</tbody>
</table>

$^a$Rounded to the nearest %

$^b$$\Delta E_0$ fitted parameter for the Fe$_2$O$_3$/Fe$_3$O$_4$ phase, this is calculated after sample calibration
Table A.10: 95Fe/5Mo/5Cu/17SiO$_2$ Fe K-edge XANES calibration and linear combination fitting parameters during reduction in flowing syngas.

<table>
<thead>
<tr>
<th>Temp. ($^\circ$C)</th>
<th>$\Delta E_0$ to calibrate the sample w/ foil (eV)</th>
<th>$\Delta E_0$ (eV)$^b$</th>
<th>Fe$_2$O$_3$/Fe$_3$O$_4$ (mol. fraction, % basis)$^a$</th>
<th>FeO (mol. fraction, % basis)$^a$</th>
<th>Fe$_2$SiO$_4$ (mol. fraction, % basis)$^a$</th>
<th>Fe$_3$C (mol. fraction, % basis)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.52</td>
<td>0.46</td>
<td>100%</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>50</td>
<td>0.48</td>
<td>0.46</td>
<td>100%</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>75</td>
<td>0.45</td>
<td>0.44</td>
<td>100%</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>100</td>
<td>0.36</td>
<td>0.35</td>
<td>100%</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>125</td>
<td>0.39</td>
<td>0.40</td>
<td>100%</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>150</td>
<td>0.40</td>
<td>0.31</td>
<td>100%</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>175</td>
<td>0.40</td>
<td>0.29</td>
<td>100%</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>200</td>
<td>0.34</td>
<td>0.23</td>
<td>100%</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>225</td>
<td>0.38</td>
<td>0.37</td>
<td>94% ± 2%</td>
<td>6% ± 2%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>250</td>
<td>0.35</td>
<td>0.37</td>
<td>86% ± 1%</td>
<td>14% ± 1%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>275</td>
<td>0.34</td>
<td>0.37</td>
<td>71% ± 1%</td>
<td>26% ± 2%</td>
<td>3% ± 1%</td>
<td>--</td>
</tr>
<tr>
<td>300</td>
<td>0.33</td>
<td>0.37</td>
<td>32% ± 2%</td>
<td>51% ± 3%</td>
<td>17% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>325</td>
<td>0.30</td>
<td>0.37</td>
<td>21% ± 2%</td>
<td>60% ± 3%</td>
<td>19% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>350</td>
<td>0.39</td>
<td>0.37</td>
<td>19% ± 2%</td>
<td>52% ± 4%</td>
<td>18% ± 2%</td>
<td>10% ± 4%</td>
</tr>
<tr>
<td>362</td>
<td>0.41</td>
<td>0.37</td>
<td>15% ± 2%</td>
<td>50% ± 4%</td>
<td>17% ± 2%</td>
<td>18% ± 4%</td>
</tr>
</tbody>
</table>

$^a$Rounded to the nearest %

$^b$$\Delta E_0$ fitted parameter for the Fe$_2$O$_3$/Fe$_3$O$_4$ phase, this is calculated after sample calibration
Table A.11: 95Fe/5W/5Cu/17SiO$_2$ Fe K-edge XANES calibration and linear combination fitting parameters during reduction in flowing syngas.

<table>
<thead>
<tr>
<th>Temp. ($^\circ$C)</th>
<th>$\Delta E_0$ to calibrate the sample w/ foil (eV)</th>
<th>Fe$_2$O$_3$/Fe$_3$O$_4$ (mol. fraction, % basis)$^a$</th>
<th>$\Delta E_0$ (eV)$^b$</th>
<th>FeO (mol. fraction, % basis)$^a$</th>
<th>Fe$_2$SiO$_4$ (mol. fraction, % basis)$^a$</th>
<th>Fe$_x$C (mol. fraction, % basis)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-0.85</td>
<td>100%</td>
<td>-0.41</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>50</td>
<td>-1.26</td>
<td>100%</td>
<td>-0.74</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>75</td>
<td>-1.35</td>
<td>100%</td>
<td>-0.77</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>100</td>
<td>-1.35</td>
<td>100%</td>
<td>-0.77</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>125</td>
<td>-1.37</td>
<td>100%</td>
<td>-0.80</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>150</td>
<td>-1.47</td>
<td>100%</td>
<td>-0.90</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>175</td>
<td>-0.90</td>
<td>100%</td>
<td>-0.55</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>200</td>
<td>-1.12</td>
<td>100%</td>
<td>-0.69</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>225</td>
<td>-1.05</td>
<td>97% ± 2%</td>
<td>-0.74</td>
<td>3% ± 2%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>250</td>
<td>-1.03</td>
<td>77% ± 2%</td>
<td>-0.74</td>
<td>21% ± 2%</td>
<td>2% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>275</td>
<td>-1.06</td>
<td>55% ± 2%</td>
<td>-0.74</td>
<td>37% ± 3%</td>
<td>8% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>300</td>
<td>-0.99</td>
<td>31% ± 2%</td>
<td>-0.74</td>
<td>50% ± 3%</td>
<td>18% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>325</td>
<td>-1.03</td>
<td>20% ± 2%</td>
<td>-0.74</td>
<td>60% ± 3%</td>
<td>19% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>350</td>
<td>-0.93</td>
<td>21% ± 2%</td>
<td>-0.74</td>
<td>57% ± 4%</td>
<td>22% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>362</td>
<td>-0.94</td>
<td>20% ± 2%</td>
<td>-0.74</td>
<td>59% ± 3%</td>
<td>20% ± 2%</td>
<td>--</td>
</tr>
</tbody>
</table>

$^a$Rounded to the nearest %

$^b$Δ$E_0$ fitted parameter for the Fe$_2$O$_3$/Fe$_3$O$_4$ phase, this is calculated after sample calibration
Table A.12: 95Fe/5Zr/5Cu/17SiO₂ Fe K-edge XANES calibration and linear combination fitting parameters during reduction in flowing syngas.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>∆E₀ to calibrate the sample w/ foil (eV)</th>
<th>Fe₂O₃/Fe₃O₄ (mol. fraction, % basis)</th>
<th>∆E₀ (eV)b</th>
<th>FeO (mol. fraction, % basis)b</th>
<th>Fe₃SiO₄ (mol. fraction, % basis)b</th>
<th>Fe₃C (mol. fraction, % basis)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.57</td>
<td>100%</td>
<td>0.43</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>50</td>
<td>0.58</td>
<td>100%</td>
<td>0.45</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>75</td>
<td>0.57</td>
<td>100%</td>
<td>0.40</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>100</td>
<td>0.30</td>
<td>100%</td>
<td>0.30</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>125</td>
<td>0.30</td>
<td>100%</td>
<td>0.34</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>150</td>
<td>0.34</td>
<td>100%</td>
<td>0.23</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>175</td>
<td>0.30</td>
<td>78% ± 2%</td>
<td>0.36</td>
<td>11% ± 2%</td>
<td>11% ± 3%</td>
<td>--</td>
</tr>
<tr>
<td>200</td>
<td>0.35</td>
<td>50% ± 2%</td>
<td>0.36</td>
<td>32% ± 3%</td>
<td>20% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>225</td>
<td>0.37</td>
<td>35% ± 2%</td>
<td>0.36</td>
<td>45% ± 3%</td>
<td>22% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>250</td>
<td>0.33</td>
<td>28% ± 2%</td>
<td>0.36</td>
<td>49% ± 4%</td>
<td>24% ± 3%</td>
<td>--</td>
</tr>
<tr>
<td>275</td>
<td>0.35</td>
<td>23% ± 2%</td>
<td>0.36</td>
<td>52% ± 3%</td>
<td>26% ± 2%</td>
<td>--</td>
</tr>
<tr>
<td>300</td>
<td>0.39</td>
<td>21% ± 2%</td>
<td>0.36</td>
<td>50% ± 4%</td>
<td>24% ± 2%</td>
<td>5% ± 4%</td>
</tr>
<tr>
<td>325</td>
<td>0.49</td>
<td>19% ± 3%</td>
<td>0.36</td>
<td>48% ± 5%</td>
<td>23% ± 3%</td>
<td>10% ± 5%</td>
</tr>
<tr>
<td>350</td>
<td>0.42</td>
<td>16% ± 2%</td>
<td>0.36</td>
<td>44% ± 4%</td>
<td>20% ± 2%</td>
<td>20% ± 2%</td>
</tr>
<tr>
<td>362</td>
<td>0.46</td>
<td>20% ± 2%</td>
<td>0.36</td>
<td>39% ± 4%</td>
<td>19% ± 2%</td>
<td>23% ± 4%</td>
</tr>
</tbody>
</table>

aRounded to the nearest %
b∆E₀ fitted parameter for the Fe₂O₃/Fe₃O₄ phase, this is calculated after sample calibration
Appendix B: In-situ XAFS Gas Flow Diagram and Pictures of Set Up

Figure B.1 - Gas flow diagram of the in-situ XAFS experiments at CAMD (dashed lines refer to He purge).
Figure B.2 - View of the in-situ XAFS setup at CAMD from just outside of the main DCM hutch
Figure B.3 - Close-up view of the in-situ (Lytle) XAFS cell
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An activity and XANES study of Mn-promoted, Fe-based Fischer–Tropsch catalysts

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1. Introduction

Increasing petroleum prices have created renewed interest in coal-to-liquid (CTL) research. The Fischer–Tropsch Synthesis (FTS) is currently the most developed technology for the conversion of gaseous coal into liquid fuels. However, cost barriers require additional research before this process is commercially viable [1,2]. Sasol in South Africa is currently the only company using FTS for commercial CTL processes.

Recent studies of Mn additions in Fe-based FT catalysts have focused on increased activity in catalytic Fischer–Tropsch reactions [3,4]. Temperature programmed reduction (TPR) with different Mn loadings has shown increased Fe–Mn interaction with increased Mn promotion [4]. Mådebäck et al. have shown that iron–manganese oxide phases can form during high temperature (500 °C) calcination [5–7]. A study by Jaggi et al. [8] (2:1 H2/CO ratio, 10 bar) suggested that in cases where iron was a majority component, the iron–manganese oxide is reduced in a step-wise sequence similar to that observed for Fe2O3: FeMn3O4 → Fe3O4 + MnO → Fe3O4 + Mn2O3. Most of the studies related to Mn-promotion of Fe-based FT catalysts focus on formulations which did not include SiC or Cu [3–25]. Other than recent studies by Lohitharn et al. [26–29], the authors are only aware of relatively few studies on catalysts which contained either Cu or Mn and/or Mn-promoted catalysts [30–32]. The limited number of studies on the effects of Mn-promotion on SiO2 and/or Cu-promoted Fe-based FT catalysts include Kuznetsova et al. who studied the Mn, Si, Cu (but not Ca) promotion of an Fe-based FT catalyst and found significant increases in activity relative to the catalyst without Mn [29].
Vita

Andrew Allen Campos was born in April, 1983, in Plantation, Florida. He earned his Bachelor of Science in Chemical Engineering at the University of Florida in August 2005. He is earning his Doctor of Philosophy in chemical engineering on May 2010 at Louisiana State University for his work in X-ray absorption spectroscopy applied to transition metal promoted iron-based Fischer-Tropsch catalysts.