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**Design, Synthesis, and Mechanistic Evaluation of Iron-Based Catalysis  
for Synthesis Gas Conversion to Fuels and Chemicals**

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## ABSTRACT

This project extends previously discovered Fe-based catalysts to hydrogen-poor synthesis gas streams derived from coal and biomass sources. These catalysts have shown unprecedented Fischer-Tropsch synthesis rates and selectivities for synthesis gas derived from methane. During the first reporting period, we certified a microreactor, installed required analytical equipment, and reproduced synthetic protocols and catalytic results previously reported. During the second reporting period, we prepared several Fe-based compositions for Fischer-Tropsch Synthesis and tested the effects of product recycle under both subcritical and supercritical conditions. During the third and fourth reporting periods, we improved the catalysts preparation method, which led to Fe-based materials with the highest FTS reaction rates and selectivities so far reported, a finding that allowed their operation at lower temperatures and pressures with high selectivity to desired products ( $C_{5+}$ , olefins). During the fifth and sixth reporting period, we studied the effects of different promoters on catalytic performance, specifically how their sequence of addition dramatically influenced the performance of these materials in the Fischer-Tropsch synthesis. We also continued our studies of the kinetic behavior of these materials during the sixth reporting period. Specifically, the effects of  $H_2$ ,  $CO$ , and  $CO_2$  on the rates and selectivities of Fischer-Tropsch Synthesis reactions led us to propose a new sequence of elementary steps on Fe and Co Fischer-Tropsch catalysts. Finally, we also started a study of the use of colloidal precipitation methods for the synthesis small Co clusters using recently developed methods to explore possible further improvements in FTS rates and selectivities. We found that colloidal synthesis makes possible the preparation of small cobalt particles, although large amount of cobalt silicate species, which are difficult to reduce, were formed.

During this seventh reporting period, we have explored several methods to modify the silanol groups on  $SiO_2$  by using either a homogeneous deposition-precipitation method or surface titration of  $Si-OH$  on  $SiO_2$  with zirconium (IV) ethoxide to prevent the formation of unreduceable and unreactive  $CoO_x$  species during synthesis and FTS catalysis. We have synthesized monometallic  $Co/ZrO_2/SiO_2$  catalysts with different Co loadings (11-20 wt%) by incipient wetness impregnation methods and characterized the prepared Co supported catalysts by  $H_2$  temperature-programmed reduction ( $H_2$ -TPR) and  $H_2$ -chemisorption. We have measured the catalytic performance in FTS reactions and shown that although the hydroxyl groups on the  $SiO_2$  surface are difficult to be fully titrated by  $ZrO_2$ , modification of  $ZrO_2$  on  $SiO_2$  surface can improve the Co clusters dispersion and lead to a larger number of exposed Co surface atoms after reduction and during FTS reactions.

During this seventh reporting period, we have also advanced our development of the reaction mechanism proposed in the previous reporting period. Specifically, we have shown that our novel proposal for the pathways involved in CO activation on Fe and Co catalysts is consistent with state-of-the-art theoretical calculations carried out in collaboration with Prof. Manos Mavrikakis (University of Wisconsin-Madison). Finally, we have also worked on the preparation of several manuscripts describing our findings about the preparation, activation and mechanism of the FTS with Fe-based catalysts and we have started redacting the final report for this project..

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## EXECUTIVE SUMMARY

This project exploits our recent discovery of catalyst compositions and synthesis and activation protocols leading to iron-based catalysts with Fischer-Tropsch synthesis (FTS) rates and selectivities similar to those on cobalt-based catalyst at low temperatures required to form olefins and large hydrocarbons using stoichiometric synthesis gas. These materials are being extended to the conversion of substoichiometric streams to explore whether the unprecedented activities and selectivities with streams derived from natural gas can be realized with more demanding coal-derived synthesis gas ratios. Fe catalysts convert streams derived from coal and biomass, because O-atoms are rejected as CO<sub>2</sub> instead of H<sub>2</sub>O, but they tend to be much less active than Co catalysts, which reject O-atoms as H<sub>2</sub>O. Higher FTS rates, lower CO<sub>2</sub> selectivities, and greater structural stability remain critical hurdles in converting H<sub>2</sub>-poor streams to high-value fuels and chemicals. During the first reporting period, we certified a microreactor, installed required analytical tools, and reproduced previous synthetic protocols and catalytic results. During the second reporting period, we prepared several Fe-based compositions and tested the effects of product recycle under both subcritical and supercritical conditions. During the third reporting period, we improved catalyst synthesis protocols, and achieved the highest FTS reaction rates and selectivities so far reported at low temperatures. During the fourth reporting period, we studied the effect of different promoters on catalytic performance, finding that the sequence of addition dramatically influences the performance of these materials in the FTS. During the fifth reporting period, we continued our studies of the kinetic behavior of these materials during the sixth reporting period. Specifically, the effects of H<sub>2</sub>, CO, and CO<sub>2</sub> on the rates and selectivities of FTS led us to propose a new sequence of elementary steps on Fe and Co catalysts. We also started a study of the use of colloidal precipitation methods for the synthesis small Co clusters using recently developed methods to explore possible further improvements in Fischer-Tropsch synthesis rates and selectivities. Colloidal syntheses allow the preparation of small cobalt particles, although large amount of cobalt silicate species, which are difficult to reduce, were formed.

During this seventh reporting period, we have explored several methods to modify the silanol groups on SiO<sub>2</sub> by using either a homogeneous deposition-precipitation method or surface titration of Si-OH on SiO<sub>2</sub> with zirconium (IV) ethoxide to prevent the formation of unreduceable and unreactive CoO<sub>x</sub> species during synthesis and FTS catalysis. We have synthesized monometallic Co/ZrO<sub>2</sub>/SiO<sub>2</sub> catalysts with different Co loadings (11-20 wt%) by incipient wetness impregnation methods and characterized the prepared Co supported catalysts by H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) and H<sub>2</sub>-chemisorption. We have measured the catalytic performance in FTS reactions and shown that although the hydroxyl groups on the SiO<sub>2</sub> surface are difficult to be fully titrated by ZrO<sub>2</sub>, modification of ZrO<sub>2</sub> on SiO<sub>2</sub> surface can improve the Co clusters dispersion and lead to a larger number of exposed Co surface atoms after reduction and during FTS reactions. During this seventh reporting period, we have also advanced our development of the reaction mechanism proposed in the previous reporting period. Specifically, we have shown that our novel proposal for the pathways involved in CO activation on Fe and Co catalysts is consistent with state-of-the-art theoretical calculations carried out in collaboration with Prof. Manos Mavrikakis (University of Wisconsin-Madison). Finally, we have drafted several manuscripts describing our findings and started redacting the final report for this project.

# Design, Synthesis, and Mechanistic Evaluation of Iron-Based Catalysis for Synthesis Gas Conversion to Fuels and Chemicals

## Description of Tasks

### Task One (Years 1 and 2)

Extension of synthesis and activating protocols for Fe-based catalysts prepared by precipitation, treatment with surface-active agents, activation in synthesis gas, and promotion by Ru to materials suitable Fischer-Tropsch synthesis with coal- and biomass-derived synthesis gas.

### Task Two (Years 1 and 2)

Characterization of carbide-oxide phase transformations and their impact on catalyst mechanical integrity using electron microscopy and in situ X-ray absorption protocols.

### Task Three (Years 2 and 3)

Exploratory studies of the effects of CO<sub>2</sub> and light hydrocarbon recycle on the rate and selectivity of FTS reactions at low H<sub>2</sub>/CO ratios on optimized Fe-based catalysts (developed in part (i)).

## Objectives and Specific Tasks

Fe-based catalysts are typically preferred for converting coal or biomass derived synthesis gas streams with low H<sub>2</sub>/CO ratios (H<sub>2</sub>/CO = 0.7-1) because their significant water-gas shift activity (H<sub>2</sub>O + CO → CO<sub>2</sub> + H<sub>2</sub>) leads to rejection of excess carbon as CO<sub>2</sub>. Fe-based catalysts typically show much lower catalytic activities than Co-based catalysts and lower mechanical stability, as a result of their tendency to interconvert between oxide and carbide phases as the redox properties change within catalytic reactors. Fe-based catalysts with higher Fischer-Tropsch Synthesis (FTS) activity and greater structural integrity remain significant obstacles to their use in the synthesis of high-value fuels and petrochemicals.

Iron-based catalysts with FTS activities and selectivities similar to those on cobalt-based catalyst using stoichiometric H<sub>2</sub>/CO streams derived from natural gas were recently reported by our research group. Novel synthesis methods based on supercritical and subcritical drying of powders after precipitation at a constant pH led to significant improvements in the surface area of oxide precursors, while activation and promotion protocols led to active Fe carbide clusters with high surface areas and mechanical strength. These gave in turn unprecedented activity and C<sub>5+</sub> selectivity during use with stoichiometric synthesis gas (H<sub>2</sub>/CO = 2).

The principal objectives of this project are to:

1. optimize synthesis protocols to prepare Fe-based catalysts with FTS rates and hydrocarbon product distributions similar to those of Co-based materials using surface-active compounds and supercritical conditions and explore the use of Ru as activation promoter,
2. evaluate the performance of prepared catalysts in synthesis gas streams derived from coal or biomass ( $H_2/CO = 0.7-1.0$ ) and optimize activation protocols for high activity, selectivity and mechanical integrity,
3. determine the effects of Ru loading and mode of addition on the concentration of active sites and on the intrinsic activity and selectivity of such active sites,
4. establish the extent and dynamics of carbide-oxide transformations during reactions of synthesis gas mixtures with varying redox potential and their influence on the structural integrity and stability of Fe-based catalysts.

### **Technical Activities and Accomplishments (FY 2006)**

During the seventh reporting period, we have prepared, characterized and measured the FTS activity of monometallic Co supported catalysts. We have also carried out theoretical calculations about the FTS mechanism. These studies have:

- (1) explored several methods to terminate the silanol groups on  $SiO_2$  support by use either a homogeneous deposition-precipitation method or surface titration reaction (using zirconium (IV) ethoxide reacting with Si-OH on the  $SiO_2$  in ethanol),
- (2) prepared monometallic  $Co/ZrO_2/SiO_2$  catalysts with different Co loading (11-20 wt%) by incipient wetness impregnation method,
- (3) demonstrated that  $ZrO_2$  modification has only a weak influence on  $CoO_x$  reduction rates but leads to an improvement in Co dispersion,
- (4) evaluated the impact of  $ZrO_2$  modification on FTS rates and selectivities,
- (5) supported the involvement of hydrogen species in the mechanism of CO dissociation over Fe and Co catalysts.

The detailed results, findings, and conclusions are included in the last part of this report as sections:

- 2.1. Fischer-Tropsch Synthesis with Fe-based catalysts.
- 2.2. Mechanistic and kinetic study of the Fischer-Tropsch Synthesis with Fe-based catalysts.
- 2.3. Effect of  $ZrO_2$  modification on  $SiO_2$  surface silanol groups
- 2.4. Effect of  $ZrO_2$  modification on Co-supported catalysts.

### **Immediate Next Steps and Research Plans**

During the next reporting period, we will improve and optimize the monometallic Co colloid preparation procedure by using other kind of surfactants. We will explore a new method to reduce the  $\text{CoO}_x$  species and to decompose the protective organic molecules at low temperature in order to obtain clean and small Co metal particles, as well as to prevent the formation of irreducible  $\text{CoO}_x$  species. We will complete the experimental and theoretical work on the mechanism of FTS reactions on Co and Fe. Finally, we will complete the writing of three manuscripts and the final report.

## Detailed results, findings and conclusions

### 1. Experimental details

#### 1.1. Catalysts preparation.

##### *A. Preparation of ZrO<sub>2</sub>/SiO<sub>2</sub> via homogeneous deposition-precipitation*

SiO<sub>2</sub> (6.0 g, Davison Grace 62, 287 m<sup>2</sup> g<sup>-1</sup>, treated in dry air at 873 K for 16 h before use), zirconyl nitrate (2.8 g, Aldrich, 99.99 %) and urea (1.0 g, ACROS, 99 %) were added into 50 cm<sup>3</sup> of deionized and doubly-distilled water (DDI) under vigorous stirring at ambient temperature. The suspension was stirred at 363 K for 5 h. After water evaporation at 373 K, the samples were treated in flowing dry air (Praxair, extra dry, 1.67 cm<sup>3</sup> s<sup>-1</sup>) by increasing the temperature from ambient to 773 K at 0.17 K s<sup>-1</sup> and holding for 3 h.

##### *B. Preparation of ZrO<sub>2</sub>/SiO<sub>2</sub> by using zirconium (IV) ethoxide*

First, 10 g of SiO<sub>2</sub> (Davison Grace 62, 287 m<sup>2</sup> g<sup>-1</sup>, treated in dry air at 873 K for 16 h before use) was dried in ambient air at 398 K for 6 h. 4 g of zirconium (IV) ethoxide (Alfa Aesar, 99 %), 2 cm<sup>3</sup> of acetic acid (Fischer, 99.8 %) and 10 g of pretreated SiO<sub>2</sub> were added into 140 cm<sup>3</sup> of ethanol (Aldrich, 99.5 %) at ambient temperature in a dry box. The resulting suspension was stirred at ambient temperature for 12 h. After filtering and washing with ethanol solution, the samples were treated in flowing dry air (Praxair, extra dry, 1.67 cm<sup>3</sup> s<sup>-1</sup>) by increasing the temperature from ambient to 953 K at 0.17 K s<sup>-1</sup> and holding there for 3 h [1].

##### *C. Preparation of Co supported catalysts via incipient wetness impregnation*

A Co/SiO<sub>2</sub> (11 wt.%) was prepared by incipient wetness impregnation of SiO<sub>2</sub> (Davison Grace 62, 287 m<sup>2</sup> g<sup>-1</sup>, treated in dry air at 873 K for 16 h before use) with Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Aldrich, 99.999 %) in DDI water. Impregnation was carried out in air at 373 K. The catalyst was treated in flowing dry air (Praxair, extra dry, 1.67 cm<sup>3</sup> s<sup>-1</sup>) by increasing the temperature from ambient to 673 K at 0.17 K s<sup>-1</sup> and holding it there for 4 h. The Co/ZrO<sub>2</sub>/SiO<sub>2</sub> catalysts with different Co loading (11 wt.%, 20 wt.%) were prepared by incipient wetness impregnation of ZrO<sub>2</sub>/SiO<sub>2</sub> (3.2 Zr nm<sup>-2</sup>) with Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Aldrich, 99.999 %) in DDI water. Impregnation was carried out in air at 373 K. The catalysts were treated in flowing dry air (Praxair, extra dry, 1.67 cm<sup>3</sup> s<sup>-1</sup>) by increasing the temperature from ambient to 673 K at 0.17 K s<sup>-1</sup> and holding there for 4 h.

#### 1.2. Catalysts characterization.

Surface areas were measured with a Quantasorb apparatus (Quantasorb 6 Surface Analyzers, Quantachrome Corp.) by adsorption of N<sub>2</sub> at its normal boiling point. Prior to N<sub>2</sub> adsorption-desorption measurement, samples were treated in dynamic vacuum (0.1 Pa) at 473 K for 3 h. The samples specific surface areas were calculated on the basis of the Brunauer, Emmett and Teller theory (BET). Powder X-ray diffraction (XRD) characterization was measured with a Siemens D5000 diffraction-meter by using a CuK<sub>α</sub> radiation. XRD patterns were recorded for 20° < 2θ < 70° by step-scanning at 0.05° increments. Temperature-programmed reduction (TPR) experiments were operated in a flow unit equipped with a thermal conductivity detector (QS-10, Quantachrome Corp.).

The sample was put inside a U-type quartz reactor and treated in 20% H<sub>2</sub> [Praxair, 20 % H<sub>2</sub>, 80 % Ar, 1.33 cm<sup>3</sup> s<sup>-1</sup>] by heating to 1123 K at 0.17 K·s<sup>-1</sup>. H<sub>2</sub> concentrations were calibrated by reducing CuO. Chemisorption data were collected with a Quantachrome 1C Autosorb apparatus. The samples were reduced in pure hydrogen (Praxair, 99.999 %) at 673 K for 1 h and then evacuated at this temperature for 10 min to remove the chemisorbed hydrogen on the surface. The hydrogen chemisorption was carried out at 373 K (Quantasorb chemisorption analyzer). Adsorption isotherms were extrapolated to zero pressure to obtain the chemisorption uptakes. Dispersion values were calculated from hydrogen uptake and cobalt content assuming a 1:1 stoichiometry of H to surface cobalt atoms. The crystal diameter was calculated from  $d/nm=96/D$  (D=dispersion), which assumes hemispherical crystallites with random surface orientation exposing low-index crystal planes.

### **1.3. Fischer-Tropsch Synthesis activity and selectivity**

Fischer-Tropsch Synthesis (FTS) rates and selectivities were measured by using a fixed-bed single-pass flow reactor with plug-flow hydrodynamics. The temperature of the catalyst bed was measured by a *K*-type thermocouple (Omega, 0.05-cm diameter, 46-cm length) located within a center thermowell. The flow rates of H<sub>2</sub> [Praxair, 99.999%] and synthesis gas (Praxair, 62 % H<sub>2</sub>, 31 % CO and 7 % N<sub>2</sub> internal standard) were controlled by mass flow controllers (Porter Inc.). The catalyst (0.56 g, 105-177  $\mu$ m particle size) was diluted with 1.4 g of SiO<sub>2</sub> (Davison Grace, 62, 105-177  $\mu$ m particle size) in order to avoid temperature gradients. Before reaction, the catalyst was reduced in pure H<sub>2</sub> [Praxair, 99.999 %, 2.14 cm<sup>3</sup> (g-catalyst s)<sup>-1</sup>] within the reactor by heating to 673 K at 0.17 K·s<sup>-1</sup> and holding for 5 h. FTS reactions were carried out at 473 K using the synthesis gas (Praxair, 62 % H<sub>2</sub>, 31 % CO and 7 % N<sub>2</sub> internal standard) at pressure of 2.15 MPa. Reactant and product streams were online analyzed by a gas chromatograph (Agilent, 6890N) equipped with a cross-linked methyl silicone capillary column (HP-1) and a Porapak Q packed column, respectively [2].

## **2. Results and Discussion**

### **2.1. Fischer-Tropsch Synthesis with Fe-based catalysts.**

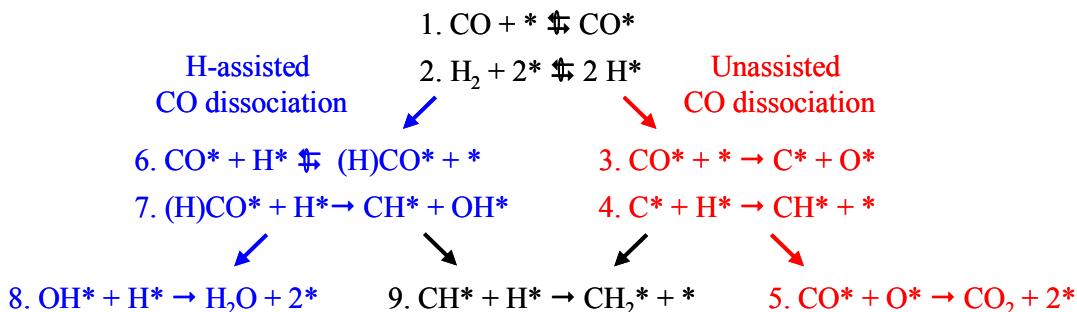
Two manuscripts have been prepared during this reporting period. The first manuscript describes an optimum experimental procedure for promoters addition (K, Cu, Ru) to Fe-based catalysts. As presented in a previous reporting period, the order of promoter addition drastically affects the catalytic performance. Thus, when acidic solutions of Cu and Ru are added to Fe-Zn-K, potassium is dissolved into the impregnating solutions and finally large KNO<sub>3</sub> patches are deposited over the catalyst surface. As a consequence, K promotion is less effective and the catalytic activity decreases when compared with the solid prepared by adding Cu or Ru in a first step.

The second manuscript describes the optimum activation protocol, as well as the structural evolution of Fe-based catalysts during this activation step. In summary, we have studied the activation procedure, which involves reduction and carburization of oxide precursors during the early stages of contact with synthesis gas. We describe also the analysis of the evolution of oxide, carbide, and metal phases of the active iron components

during initial contact with synthesis gas using advanced synchrotron techniques based on X-ray absorption spectroscopy.

## 2.2. Mechanistic and kinetic study of the Fischer-Tropsch Synthesis with Fe-based catalysts.

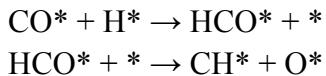
Several different elementary steps (direct CO dissociation, hydrogenation of C\* or CH\* species) have been proposed to be kinetically-relevant in previous studies to explain the measured dependence of hydrocarbon synthesis rates on CO and H<sub>2</sub> pressures. These proposals, however, cannot account for the relative rates at which oxygen is removed as H<sub>2</sub>O or CO<sub>2</sub> as H<sub>2</sub> and CO pressures vary. In the previous reporting periods, we investigated the kinetics of the FTS with Fe-based catalysts. Mechanistically, we proposed a set of elementary steps in which we considered two different pathways for CO activation: unassisted and H-assisted. The unassisted dissociation leads to O\* removal exclusively as CO<sub>2</sub>; the other path dissociates CO after H-addition and leads to the direct formation of OH\*, which is removed as H<sub>2</sub>O (Scheme 1). Both routes ultimately form a CH<sub>x</sub> monomer required for chain growth. A *pseudo*-steady-state analysis of this set of elementary steps accurately describes the rates of formation of hydrocarbons, CO<sub>2</sub> and H<sub>2</sub>O as a function of H<sub>2</sub> and CO pressures on Fe catalysts.



**Scheme 1.** Proposed elementary steps for hydrocarbons (CH<sub>2</sub>\* species), water and primary carbon dioxide formation from CO and H<sub>2</sub>.

We found that the H-assisted pathway (steps 6 and 7) is preferred under typical reaction conditions. The validity of the proposed mechanism was examined by comparing the experimental and the calculated rates of hydrocarbons, primary CO<sub>2</sub> and water formation respectively. A good agreement was found between the reaction rates calculated with the kinetic expressions derived from our model and the experimental values.

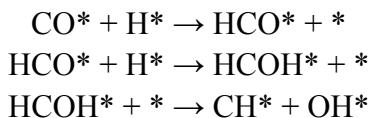
These results were preliminary confirmed with theoretical slab calculations performed about the Fischer-Tropsch Synthesis mechanism in close collaboration with Prof. Manos Mavrikakis (University of Wisconsin, Madison). These calculations showed that the H-assisted CO dissociation pathway is energetically possible on a Fe(110) surface. According to these calculations, the most probable intermediates are surface formyl species. Next, these species are dissociated according to the following expressions:



The maximum energy barrier in this sequence is *ca.* 1.1 eV (=110 kJ mol<sup>-1</sup>).

These calculations support our proposal about the importance of the assistance of hydrogen species (H<sup>\*</sup>) in the CO dissociation event. However, surface O<sup>\*</sup> species are formed from the H-assisted CO dissociation, which is in contrast with our experimental results regarding the O<sup>\*</sup> removal selectivity. The disagreement is related to the fact that the theoretical calculations were carried out considering a low surface CO coverage ( $\theta_{\text{CO}^*}=0.25$ ).

In this reporting period, we have extended these calculations at high CO coverage, which are more realistic conditions. Again, we have found that the H-assisted CO dissociation possess a lower energetic barrier than the unassisted pathway on a Fe(110) surface. But more importantly, we have determined that the surface formyl species does not dissociate directly to form oxygen surface species (O<sup>\*</sup>), probably because the probability of the presence of adjacent empty active sites at these conditions is very low. Consequently, surface formyl species dissociate with the assistance of surface hydrogen atoms to form CH<sup>\*</sup> and OH<sup>\*</sup> species:



The maximum energy barrier in this sequence is *ca.* 0.9 eV (=90 kJ mol<sup>-1</sup>).

Therefore, the FTS mechanism that we have proposed is not only supported by the experimental results, but also by the theoretical calculations carried under those reaction conditions closer to the experiments. Currently, we are preparing a manuscript describing our experimental observations and the mechanism proposed.

### 2.3. Effect of ZrO<sub>2</sub> modification on SiO<sub>2</sub> surface silanol groups

Loading a layer of ZrO<sub>2</sub> on SiO<sub>2</sub> surface provides a simple but effective approach to terminate the hydroxyl groups on SiO<sub>2</sub>, an approach that may weaken the oxide-support interactions that inhibit the reduction of supported metal oxides (CoO<sub>x</sub> in this study) [3]. In this report, Zr surface densities are expressed as the number of Zr atoms per BET surface area (Zr nm<sup>-2</sup>). Figure 1 shows the IR spectra of SiO<sub>2</sub> and ZrO<sub>2</sub>/SiO<sub>2</sub> samples treated in flowing helium at 673 K for 0.5 h to remove the physisorbed water. The SiO<sub>2</sub> spectrum is dominated by an intense sharp band at 3735 cm<sup>-1</sup>, characteristic of isolated non-interacting surface silanol groups [4,5]. After ZrO<sub>2</sub> deposition, each ZrO<sub>2</sub>/SiO<sub>2</sub> sample exhibited the same isolated silanol band in the IR spectra but with lower intensity relative to pure silica. Also, the intensities of silanol groups decreased with increasing Zr density on ZrO<sub>2</sub>/SiO<sub>2</sub> surfaces (Table 1).

In addition to the impregnation method, surface titration (using zirconium (IV) ethoxide reacting with Si-OH on the SiO<sub>2</sub> in ethanol) and homogeneous deposition-

precipitation methods were also used to terminate silanol groups, respectively. Although the intensities of hydroxyl groups on  $\text{ZrO}_2/\text{SiO}_2$  prepared by the homogeneous deposition-precipitation process are weaker than in  $\text{ZrO}_2/\text{SiO}_2$  prepared by impregnation (Table 1), some hydroxyl groups still exist on the surface. These data indicate that the hydroxyl groups on the  $\text{SiO}_2$  surface are difficult to be fully titrated by  $\text{ZrO}_2$  modification, perhaps because of steric factors or the difficulty in anchoring Zr precursors irreversibly on single isolated silanol OH groups.

Table 1. Si-OH intensities of various  $\text{ZrO}_2/\text{SiO}_2$  samples

Sample	Preparation method	Si-OH intensity
$\text{SiO}_2$	-	1.03
$\text{ZrO}_2/\text{SiO}_2$ (0.8 $\text{Zr nm}^{-2}$ )	Impregnation of zirconium(IV) oxynitrate	0.91
$\text{ZrO}_2/\text{SiO}_2$ (3.2 $\text{Zr nm}^{-2}$ )	Impregnation of zirconium(IV) oxynitrate	0.68
$\text{ZrO}_2/\text{SiO}_2$	Zirconium (IV) ethoxide titrate	1.20
$\text{ZrO}_2/\text{SiO}_2$ (3.2 $\text{Zr nm}^{-2}$ )	Homogeneous deposition-precipitation	0.48

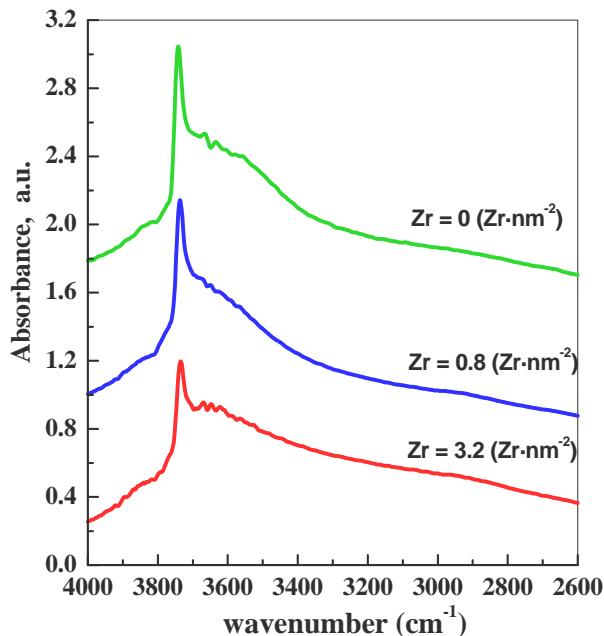


Figure 1. IR spectra of  $\text{SiO}_2$  and  $\text{ZrO}_2/\text{SiO}_2$  samples

#### 2.4. Effect of $\text{ZrO}_2$ modification on Co supported catalysts

Monometallic cobalt supported catalysts were prepared by incipient wetness impregnation methods on  $\text{SiO}_2$  and  $\text{ZrO}_2/\text{SiO}_2$  supports. The reduction behavior of  $\text{CoO}_x/\text{SiO}_2$  and  $\text{CoO}_x/\text{ZrO}_2/\text{SiO}_2$  precursors were examined by  $\text{H}_2$  temperature-programmed reduction ( $\text{H}_2\text{-TPR}$ ). Figure 2 shows their  $\text{H}_2\text{-TPR}$  profiles. There are two main  $\text{H}_2$  consumption peaks in every profile with temperature ranges of 500-600 K and

600-700 K. Previous studies [6] have shown that  $\text{Co}_3\text{O}_4$  reduces to Co metal in two steps (Equations 1-2), leading to distinct peaks in the TPR profile. Therefore, the reduction peaks within 500-600 K can be attributed to reduction of  $\text{Co}_3\text{O}_4$  to  $\text{CoO}$ , and the  $\text{CoO}$  formed is then reduced subsequently to Co metal at higher temperatures resulting in broader peaks in the TPR profiles (Figure 2). We have also observed that  $\text{CoO}_x/\text{ZrO}_2/\text{SiO}_2$  samples exhibit similar reduction behavior as  $\text{CoO}_x/\text{SiO}_2$ . Also, the calculated  $\text{H}_2/\text{Co}$  ratios are close to the theoretical values ( $\text{H}_2/\text{Co}=1.33$ ), indicating that most of the  $\text{CoO}_x$  species can be reduced to cobalt metal within a temperature range of 400-700 K in these samples.



Table 2 shows the  $\text{H}_2$ -chemisorption data for supported cobalt catalysts. We have observed that the application of  $\text{ZrO}_2/\text{SiO}_2$  as a support improves the Co cluster dispersion, leading in that way to smaller Co cluster sizes than for  $\text{Co}/\text{SiO}_2$ . The above  $\text{H}_2$ -TPR and  $\text{H}_2$ -chemisorption results suggest that there is not strong interaction between the  $\text{SiO}_2$  support and the  $\text{CoO}_x$  when the  $\text{CoO}_x$  sizes are large ( $> 20\text{nm}$ ), because most of the  $\text{CoO}_x$  species can be reduced at low temperatures ( $< 700$  K).  $\text{ZrO}_2$  modification has only a weak influence on  $\text{CoO}_x$  reduction rates, but leads to an improvement in Co dispersion.

Table 2.  $\text{H}_2$ -chemisorption results of cobalt supported catalysts

Sample	Co dispersion (%)	Average Co size (nm)
11 wt.% $\text{Co}/\text{SiO}_2$	3.1	31
11 wt.% $\text{Co}/\text{ZrO}_2/\text{SiO}_2$ 3.2 ( $\text{Zr nm}^{-2}$ )	4.3	22
20 wt.% $\text{Co}/\text{ZrO}_2/\text{SiO}_2$ 3.2 ( $\text{Zr nm}^{-2}$ )	4.8	20

Table 3 shows the FTS results for monometallic Co supported catalysts. The Co-time yield is defined as the mole of CO converted per unit time per g-atom Co and Co site-time yield is defined as the mole of CO converted per unit time per surface Co atom (measured by  $\text{H}_2$  chemisorption) [6]. Since most of the  $\text{CoO}_x$  ( $> 90\%$ ) cannot be reduced at low temperatures ( $< 673$  K) on catalysts prepared by inverse micelle or homogeneous deposition-precipitation methods (please see previous report), these catalysts are not included in Table 3.

The use of  $\text{ZrO}_2/\text{SiO}_2$  as a support improves FTS rates (Co site-time yield and Co-time yield) and  $\text{C}_{5+}$  selectivity (from 76 to 86 %) while decreasing  $\text{CH}_4$  selectivity by a factor of  $\sim 2$  at the same Co content (Table 3). These data suggest that the modification of  $\text{ZrO}_2$  on  $\text{SiO}_2$  surface not only improves the Co clusters dispersion leading to more accessible sites, but also favors the formation of larger hydrocarbon molecules.

Table 3. FTS reaction results of monometallic Co supported catalysts

Catalyst	Co (wt.%)	Zr density (Zr nm <sup>-2</sup> )	Co size (nm)	Co-time yield [mol CO (g-atom Co h) <sup>-1</sup> ]	Co site-time yield [mol CO (g-atom Co h) <sup>-1</sup> ]	CH <sub>4</sub> selectivity (%)	C <sub>5+</sub> selectivity (%)
Co/SiO <sub>2</sub>	11	0	31	2.4	77.4	12.8	75.9
Co/ZrO <sub>2</sub> /SiO <sub>2</sub>	11	3.2	22	3.5	81.4	6.5	86.5

CO conversion is around 17-28%

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### Appendix B:

#### 1. Publications

1.1 A manuscript titled “Fischer-Tropsch synthesis on iron-based catalysts with hydrogen-poor synthesis gas” is currently in early draft form and will be submitted during the next and last reporting period.

1.2 A manuscript titled “Structure Evolution and Spectroscopic Studies of Site Requirements in Iron-Catalyzed Fischer-Tropsch synthesis” is currently in early draft form and will be submitted during the next and last reporting period.

1.3. A manuscript titled “A kinetic and mechanistic study of the Fischer-Tropsch Synthesis with Fe-based catalysts” is currently in early draft form and will be submitted during the next and last reporting period.

1.4 A first draft of the final project report is nearly complete.

#### 2. Presentations and Abstracts

2.1. M. Ojeda, A. Ishikawa, R. Nabar, A. Nilekar, M. Mavrikakis, E. Iglesia, “Fischer-Tropsch Synthesis catalysis: low-temperature Fe catalysts and the mechanism for CO dissociation on Fe and Co”, 20<sup>th</sup> North American Catalysis Society Meeting, Houston, Texas, June 17-22, 2007.