### Quarterly Research Report

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### Structural and Catalytic Characterization of the Mechanism and Site Requirements in Fischer-Tropsch Synthesis on Fe and Co Catalysts

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### I. FISCHER-TROPSCH SYNTHESIS ON IRON CATALYSTS

### 1. Background

### 1.1. Structure and Function of Active Phases in Fischer-Tropsche Synthesis

Fe-based oxides have been used as commercial catalysts for Fischer-Tropsch synthesis (FTS) to produce a large variety of paraffin and olefin products, ranging from methane to high molecular weight waxes [1]. During activation by synthesis gas and subsequent FTS reaction, several phases including metallic iron, iron carbides and iron oxides are known to co-exist at steady-state conditions [2-5]. The distribution and amounts of these phases depend on exposure to various activation and reaction conditions, leading to different catalytic performances in FTS. Some researchers [6] have proposed that surface iron atoms are responsible for FTS activity, while some others considered surface carbides or a mixture of carbides [7,8] and metallic iron [9] to be the active phase. There are also some reports that suggest that magnetite  $Fe_3O_4$  is the active phase in FTS [10-12]. Although these studies have each provided some evidence to support their specific proposals about the active phase, the available information remains phenomenological, and a method to identify the active phase during reaction and to count the number of active sites has not yet been established.

Based on the previous research on Co [13,14] and Fe catalysts [15,16] for FTS as well as our last quarterly work on TPSR of Fe oxides in  $H_2$ , our characterization during this research period involves temperature-programmed reactions of Fe-based catalysts with flowing streams of CO or  $H_2$ -CO mixtures. We monitored the gas phase concentrations throughout the reduction and carburization processes by means of an on-line mass spectrometer, and followed the evolution of bulk phases and crystal size by X-ray diffraction and of surface area by nitrogen physisorption measurements. In this way, we can determine the temperature required for the formation of Fe carbides as well as the stoichiometry and structure of such carbides. Our goal is to develop a new synthesis method to improve the compositional and structural purity of Fe carbides formed, and consequently to refine the structure-function relationships that we have previously proposed to interpret the catalytic behavior of Fe-based catalysts.

### 1.2. Effect of Zn, K and Cu

Many components have been added to Fe catalysts in order to improve their mechanical and catalytic properties. Our previous studies have shown that zinc, alkali and copper [16,17] promote the catalytic properties of Fe oxides. Zinc oxide, as a non-reducible oxide in FTS conditions, appears to stabilize the surface area of Fe oxide. Alkali, as a modifier of the adsorption enthalpies of  $H_2$  and CO, increases the selectivity to desired  $C_{5+}$  products. Copper promotes the carburization processes and decreases the temperature required for the activation of iron oxide. Here, our efforts have focused on Fe-Zn-K-Cu catalysts. We have prepared a series of Zn and Fe co-precipitated oxides with varied Zn/Fe ratios and then introduced varying amounts of K and Cu. We are examining the surface area, bulk structure, required reduction and carburization temperatures as well as the catalytic behavior of these catalysts, in order to identify optimum Zn/Fe ratios and Cu and K contents that give maximum site density and catalytic activity.

### 2. Synthesis Procedures for Fe-Zn-K-Cu Oxides

All catalysts were prepared by co-precipitation of zinc and iron nitrates at a constant pH of 7.0 in order to to form porous mixed oxides. Then, these oxide precursors were impregnated with an aqueous solution of potassium and copper salts using incipient wetness methods. The Zn/Fe oxide precursors were prepared first. Fe nitrate (1.4 M) and Zn nitrate (3.0 M) solutions were mixed at a given atomic Zn/Fe ratio. A solution of ammonium carbonate (1 M) was prepared separately. Deionized water (ca. 50 ml) was added into a large flask, which was heated on a hot plate with a magnetic stirrer and held at 80 °C throughout the preparation process. The mixed Zn/Fe solution was added at 2  $cm^{3}/min$  flow into the flask through a feeding pump. At the same time, the ammonium carbonate solution was fed separately, and its flow was controlled to maintain the slurry pH at 7±0.1, as monitored by a pH meter. The resulting precipitates were washed several times with about 1 l water per gram of catalyst, dried at 120 °C overnight, and then calcined at 350 °C for 1 h. The calcined material was promoted with 2 at.% K using K<sub>2</sub>CO<sub>3</sub> solution (0.16 M) by incipient wetness and then dried. The same process was repeated in order to promote samples with 1 at.% Cu using  $Cu(NO_3)_2$  solutions (0.16 M). Finally, the dried material was treated in dry air at 400 °C for 4 h. This final calcination temperature was chosen from temperature-programmed oxidation data, which showed that this temperature is sufficient to decompose all metal nitrates and carbonates except K<sub>2</sub>CO<sub>3</sub>. The catalysts contain CuO, ZnO, Fe<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>. These catalysts were pressed at 443 MPa into pellets, lightly crushed, and then sieved to retain the 80 - 140 mesh fraction for FTS reaction.

### 3. Catalyst Characterization

### 3.1. Protocols for the Characterization of Fe-based FTS Catalysts

This research program addresses the synthesis and the structural and catalytic characterization of the active sites of Fe-based catalysts for FTS. We have designed a matrix of samples that contains a systematic range of multi-components catalysts in order to determine the number and type of surface sites present on fresh catalysts and the samples after FTS reaction (Table 1.1). Our objective is to develop rigorous relationships between the synthesis methods, the resulting catalyst structures, and their function in FTS reactions.

### 3.2. Surface Area

The surface areas of Fe-Zn oxides calcined at different temperatures and promoted with K and Cu are shown in Table 1.2. The calcination temperatures we used for Fe-Zn oxides and for K or Cu promoted Fe-Zn oxide samples were 350 °C and 400 °C, respectively. The surface area measurements on Fe-Zn oxide (Zn/Fe=0.1) at 350 °C and 400 °C gave similar values (56 vs 53 m<sup>2</sup>g<sup>-1</sup>), indicating that the calcination temperature does not influence the surface area at the investigated temperature region. The lower surface areas (ca. 20%) for K or Cu promoted samples were caused by the presence of K or Cu species.

Composition of the Catalysts		Characterization		
Zn/Fe mole ratio	K (at.%)	Cu (at.%)	FTS	FIS reaction
	0	0		
0		0		
0	2	1		
		2		
	4	1		
	0	0	XRD	Effect of
0.05	2	1		reaction
	4	2	Surface area	condition
	0	0	<b>.</b>	220 °C
	0	1	XAS	21.4 atm
0.1		0		235 °C
0.1	2	1	H <sub>2</sub> -TPR	21.4 atili
		2		270 °C 5 atm
	4	1	CO-TPR	5 ann
	0	0		Effect of CO <sub>2</sub> addition
0.2	2	1	(H <sub>2</sub> +CO)-TPR	
	4	2		
	0	0		
	0	1		
0.4		0		
0.4	2	1		
		2		
	6	1		

Table 1.1 Matrix of Fe-Zn-K-Cu samples and characterization methods for FTS reaction

Composition	Without	K and Cu	1 at.% Cu	2 at.% K
Calcination Temperature (°C)	350	400	400	400
$S_{g} (m^{2}g^{-1})$	56	53	44	40

Table 1. 2. Surface areas  $(m^2g^{-1})$  of Fe-Zn-K-Cu samples (Zn/Fe=0.1)

### 3.3. Temperature-Programmed Surface Reaction (TPSR) of Fe-Zn and Fe-Zn-K-Cu Oxides in CO

Temperature-programmed reduction and carburization of Fe-Zn oxides in CO have been carried out during this reporting period. Since CO either reduces metal oxides releasing  $CO_2$  or carburizes metallic Fe forming carbide, we can quantitatively analyze the amount of Fe being reduced and carburized from the amount of CO consumption and  $CO_2$  formation from the following formulas:

 $Fe_xO + CO = Fe_xC + CO_2 + C$  (graphite)

Amount of oxide reduced =  $2(CO_2 \text{ formation}) - (CO \text{ consumption})$ Amount of carbide or free carbon formed = (CO consumption) - (CO<sub>2</sub> formation)

Combined with XRD measurements, these data allow us to get information about the temperatures and rates at which carbides are formed, about the amount of Fe oxide that is reduced or carburized, and about the stoichiometry of the carbides formed. We used several samples of typical composition from the catalyst matrix (Table 1.1) to test the effects of Zn, K and Cu on the reduction and carburization behavior of Fe oxide.

A typical TPSR of Fe-Zn-K-Cu oxides in CO is shown in Figure 1.1(A). Generally, the reduction/carburization of the oxides proceeds in three steps: Fe<sub>2</sub>O<sub>3</sub> is first reduced to Fe<sub>3</sub>O<sub>4</sub> at about 270 °C; Then, Fe<sub>3</sub>O<sub>4</sub> is reduced to metallic Fe followed by carburization to a mixture of  $\chi$ -Fe<sub>2.5</sub>C and Fe<sub>3</sub>C between 270 ~ 450 °C; Above 450 °C, CO disproportionation (Boudouard reaction) occurs, leading to the formation of excess free carbon. XRD measurements (Figure 1.1(B)) showed that a phase transformation from  $\chi$ -Fe<sub>2.5</sub>C to cementite (Fe<sub>3</sub>C) occurs at about 450 °C during carburization in CO (Figure 1.1). The excess free carbon formed in this phase transformation may act as nucleation sites for the subsequent deposition of free carbon via the Boudouard reaction.



Figure 1.1 (A) TPSR of Fe-Zn-K-Cu oxide (Zn/Fe=0.1, 2 at.% K and 1 at.% Cu) in CO (0.2 g samples; 10 °C/min ramping rate; 100 cm<sup>3</sup>/min, 20% CO/Ar). (B) XRD showing the phase transformation from  $\chi$ -Fe<sub>2.5</sub>C to cementite Fe<sub>3</sub>C during the TPSR in CO.

Figure 1.2 shows the reduction (A) and carburization (B) of Fe-Zn oxides with different Zn/Fe ratio in CO. Stoichiometric calculations show that  $Fe_2O_3$  is first reduced to  $Fe_3O_4$  at around 270 °C and further reduced to metallic Fe at temperatures between 270~500 °C. The carburization of metallic Fe occurs at 350 °C, and the carburization rate increases dramatically following the marked increase of the reduction rate of  $Fe_3O_4$ .



Figure 1.2 The reduction (A) and carburization (B) of Fe-Zn oxides with different Zn/Fe ratio in CO (0.2 g samples;  $10 \,^{\circ}$ C/min ramping rate;  $100 \, \text{cm}^3$ /min,  $20\% \, \text{CO/Ar}$ ).

At low Zn contents (<0.2), Zn does not significantly influence the reduction/carburization of Fe oxides because of the small amount of Zn that exists in amorphous  $ZnFe_2O_4$  form. However, at high Zn contents (e.g., Zn/Fe=0.4), ZnFe<sub>2</sub>O<sub>4</sub> is the predominant bulk phase and there is small amount of Fe<sub>2</sub>O<sub>3</sub> in amorphous form, leading to the detection of three reduction peaks. The first small peak can be ascribed to the reduction of amorphous Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>; the second peak appears to reflect the reduction of ZnFe<sub>2</sub>O<sub>4</sub> to a mixture of Fe<sub>3</sub>O<sub>4</sub> and ZnO, and the third peak is due to the reduction of the oxide mixture. ZnFe<sub>2</sub>O<sub>4</sub> is reduced and carburized at about 50 °C higher temperature than Fe<sub>2</sub>O<sub>3</sub>. The slight shifts of reduction/carburization steps to higher temperatures in high Zn loading samples are reasonable because ZnFe<sub>2</sub>O<sub>4</sub> is more thermodynamically stable than Fe<sub>2</sub>O<sub>3</sub>. The residual ZnO seems to act as the sites for the Boudouard reaction, leading to more carbon deposition on samples with higher Zn contents.

### 3.3.2 Effects of K and Cu on the Reduction and Carburization of Fe Oxides in CO

Figure 1.2 shows the effect of K and Cu on the reduction and carburization behavior of Fe oxides in CO. It is found that Cu slightly decreases the temperature required to reduce  $Fe_2O_3$  to  $Fe_3O_4$  but markedly decreases that required to reduce  $Fe_3O_4$  to metallic Fe. Also, Cu decreases the temperature required for carburization. For example, 1 at.% Cu decreases the carburization temperature about 50 °C. K slightly inhibits the reduction of Fe oxide. On the 4 at.% K sample, in spite of promotion with 1 at.% Cu, the reduction temperature increases about 50 °C compared with that of pure Fe<sub>2</sub>O<sub>3</sub>.

On the pure  $Fe_2O_3$  samples, initial rates of carburization are fast, but beyond this initial stage, carburization remains at a constant rate until the Boudouard reaction begins to occur at higher temperatures. This suggests that the incorporation of carbon within Fe becomes slower as soon as surface carbide forms, and that the carburization rate is limited by the diffusion of carbon into Fe interstices.

For the Fe oxide samples promoted with 1 at.% Cu or (2 at.% K + 1 at.% Cu), the carburization of Fe occurs in such a way that reduction and carburization take place simultaneously, that is, Fe is carburized as soon as Fe<sub>3</sub>O<sub>4</sub> is reduced. It seems that Cu dissociates CO at high temperatures (>270  $^{\circ}$ C), and this helps the reduction of Fe<sub>3</sub>O<sub>4</sub> to metallic Fe. Fe may then react with dissociated carbon forming Fe carbide. However, the formed carbide appears to inhibit the diffusion of carbon species into the inner interstices. Here, Cu probably acts as a fast "transfer station" for carbon species between the outer and the inner interstitial positions, because the addition of Cu appear to facilitate the incorporation of C with Fe as well as the diffusion of C into Fe lattice interstices. This reminds us the fact that a topotactic reaction route is required in preparation for high surface area molybdenum nitride and carbides [20]. It seems that such a topotactic reaction is also required to produce high surface area Fe carbide, i.e., carbon should incorporate with Fe as soon as oxygen is removed from  $Fe_3O_4$  and fill the vacancy left by the leaving oxygen. Although it is not clear why Fe oxide promoted with (2 at.% K+1 at.% Cu) shows a lower reduction/carburization temperature than those promoted with K and Cu separately, there seems to exist synergism between K and Cu components.



Figure 1.3 The reduction (A) and carburization (B) of Fe oxides with different K and Cu contents (0.2 g samples,  $10 \,^{\circ}$ C ramping rate;  $100 \, \text{cm}^3/\text{min}$ ,  $20\% \, \text{CO/Ar}$ ).

### 3.3.3 Comparison of the Reduction of Fe-Zn-K-Cu Oxides in H<sub>2</sub> and CO

Figure 1.4. shows the TPSR of Fe-Zn-K-Cu oxides in  $H_2$  and in CO. As presented in our last report, Cu decreases the reduction temperature of Fe oxides in  $H_2$ , while K inhibits the reduction of Fe oxides. The reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> is separated into two parts because  $H_2$  dissociates on Cu. Those Fe oxide crystallites that are in contact with Cu can

be readily reduced as soon as CuO is reduced. Those that are not near Cu, will not be reduced at those lower temperatures. In CO, Cu slightly decreases the temperature in the first reduction step but not as strongly as with  $H_2$  as the reductant. This reflects the fact that CO dissociates on Cu at higher temperatures than  $H_2$ . As a result, Fe<sub>2</sub>O<sub>3</sub> is reduced at lower temperatures in  $H_2$  than in CO. However, Cu significantly decreases the temperature required for the second reduction/carburization step in the presence of CO (ca. 100 °C lower in CO than in H<sub>2</sub>). K also appears to slightly inhibit the reduction of Fe oxides in CO but not as strongly as in H<sub>2</sub>.



Figure 1.4 The comparison of TPSR of Fe-Zn-K-Cu oxide (Zn/Fe=0.1, 2 at.% K and 1 at.% Cu) in CO and H<sub>2</sub>. (0.2 g samples, 10 °C ramping rate; 100 cm<sup>3</sup>/min, 20% CO or H<sub>2</sub>/Ar).

### 3.4. In-Situ X-ray Absorption (XAS) Studies on Fe Catalysts

X-ray adsorption near edge (XANES) and extended X-ray adsorption fine structure (EXAFS) analyses of X-ray absorption spectra are very powerful techniques to determine the oxidation state and the local structure of Fe, Cu, Zn and K in FTS catalysts, especially at the beginning of carburization and reduction processes when metal or carbides are present in amorphous or microcrystalline phases. In-situ X-ray absorption studies during the FTS reaction can establish a relationship between the catalytic activity and the structural phases of the catalysts. In-situ X-ray absorption studies on Fe-based catalysts are currently being carried out at the Stanford Synchrotron Radiation Laboratory.

*In-situ* treatments were carried out in a XAS cell of our design (Figure 1.5). This cell consists of a 0.8mm internal diameter quartz tube with 0.1mm-wall thickness connected to a gas manifold. Cartridge heaters placed in a finned copper block are used to heat the cell. The copper block is placed inside an insulating ceramic chamber. A 20mm by 4mm beam path is machined out of the copper and ceramic to allow the X-rays (6mm by

0.2mm beam) to pass through the heated zone. This design also accommodates rapid cooling of the quartz cell to room temperature by simply sliding the heated zone back from the cell. A flow trough was added beneath the copper block to rapidly cool the copper heat sink and ceramic insulation using flowing air or flowing liquid  $N_2$ .



Figure 1.5 XAS cell. (a) quartz capillary cell and holder, (b) copper block, (c) Insulator (not to scale).

Our preliminary XAS studies focused on the structural evolution of Fe species during the reduction and carburization process in FTS. The catalysts we used for FTS reaction generally contain more than 60 wt.% Fe, which is too high a concentration for the acquisition of unbiased spectra. Therefore, we diluted the samples with graphite powder (surface area of ca. 1 m<sup>2</sup>/g), which was shown to be inactive in synthesis gas up to 600 °C. The optimum concentration of Fe for XAS measurement was found to be 7 wt.%.

Fe K-edge spectra were recorded on a typical Fe-Zn-K-Cu oxide sample (Zn/Fe=0.1, 2 at.% K and 1 at.% Cu) in CO at different temperatures. The normalized near edge spectrum at the Fe K-edge is shown in Figure 1.6. Fe K-edge spectrum of Fe-Zn oxide shows a sharp increase in absorbance at 7123 eV, caused by the excitation of Fe 1s electrons. As the carburization temperature increases, the edge energy progressively shifts from 7123 eV to 7112 eV, which is the absorption edge of metallic Fe. A principal component analysis of the near edge spectra is being carried out in order to quantity the relative concentration of various oxide, carbide and Fe metal phases during FTS. We also performed the in-situ XAS measurements for the Fe-Zn-K-Cu oxide in H<sub>2</sub> and synthesis gas. These spectra are currently being analyzed.



Figure 1.6 Normalized Fe K-edge spectra showing the shifts of the edge energy on Fe-Zn-K-Cu sample (Zn/Fe=0.1, 2 at.% K, 1 at.% Cu) during the carburization in CO. (8 mg samples with 7 wt.% Fe;  $1.5 \text{ cm}^3/\text{min}$  CO).

### 4. Fischer-Tropsch Synthesis on Fe-Based Catalysts

### 4.1. Investigation of Potassium Effects during FTS Reaction

The addition of potassium has been found to affect the catalytic activity for both the Fischer-Tropsch synthesis and the concurrent water-gas shift reaction and the hydrocarbon selectivity on Fe-based catalysts. During this reporting period, the potassium effects on methane and higher hydrocarbon selectivities, the rates of the water-gas shift and Fischer-Tropsch synthesis and the olefin selectivity were measured on Fe-based catalysts (Zn/Fe = 0.1, 1 at.% Cu) with atomic K contents of 0%, 2% and 4% in a fixed-bed reactor at different temperatures and pressures using synthesis gas with a H<sub>2</sub>/CO ratio of 2:1.



#### 4.1.1 Effects of Potassium on the Fischer-Tropsch Synthesis Activity

Fig. 1.7. CO conversion as a function of reciprocal space velocity on the catalysts (Zn/Fe = 0.1, 1 at.% Cu) with various potassium loading levels at 235 °C and 21.4 atm, H<sub>2</sub>/CO=2

Fig. 1.8. CO conversion as a function of reciprocal space velocity on the catalysts (Zn/Fe = 0.1, 1 at.% Cu) with various potassium loading levels at 270 °C and 5 atm,  $H_2/CO=2$ 

CO conversion is a rough measure of FTS activity. CO conversions for the three levels of potassium loading studied at 235 °C and 21.4 atm are shown in Fig. 1.7. The K-free catalyst showed a very low activity for CO conversion. At the same space velocity, much higher CO conversions were obtained on the K promoted catalysts (2 at.% K and 4 at.% K) than on the K-free catalyst. This result is in agreement with previous reports [16, 21]. Potassium can increase CO chemisorption and decrease  $H_2$  chemisorption on Fe-based catalysts [22]. Potassium donates electrons to iron, facilitating CO chemisorption,

because CO tends to accept electrons from iron. On the other hand, hydrogen donates electrons to iron (electron affinity decreases upon  $H_2$  chemisorption), and the presence of electron-donating alkali would be expected to weaken the iron-hydrogen bond. The net result of potassium promotion is the strengthening of the Fe-C bond and the weakening of the C-O and Fe-H bonds [23]. The weakening of C-O bond favors its dissociation and the removal of oxygen by hydrogen to form the monomer CH<sub>2</sub>, which is an essential step in FTS. Therefore, potassium improves FTS activity.

However, the catalyst with 4 at.% K did not exhibit a further increase in FTS activity. As shown in Fig. 1.7, CO conversion was almost the same on the catalyst with 4 at.% K as on the catalyst with 2 at.% K. This suggests that high concentrations of K may cover the active sites for FTS reaction and that an increase in potassium favors carbon deposition, which can block the active surface area, leading to a further decline in the activity [21]. As a result, the promotion effects of potassium are reduced or offset at high K levels. Therefore, the FTS activity did not increase with increasing potassium concentration.

Similar promotion effects of potassium were observed at 270 °C and 5 atm. Interestingly, K promotion effects became smaller, compared to the results at 235 °C and 21.4 atm (Fig. 1.8). As discussed in the previous section, potassium favors carbon deposition. Higher temperatures (270 °C) also favor carbon deposition too. More carbon is deposited at higher temperature than at lower temperature on the K-promoted catalysts. As a result, a larger fraction of the active sites in the K-promoted catalyst may be blocked at 270 °C than at 235 °C. The promotion effects of potassium thus become smaller at 270 °C.



Fig. 1.9. CO conversion rate as a function of CO conversion on the catalysts (Zn/Fe = 0.1, 1 at.% Cu) with various potassium loading level at 235 °C and 21.4 atm,  $H_2/CO=2$ 



Fig. 1.10. Hydrocarbon formation rate as a function of CO conversion on the catalysts (Zn/Fe = 0.1, 1 at.% Cu) with various potassium loading level at 235 °C and 21.4 atm, H<sub>2</sub>/CO=2

Figs. 1.9 and 1.10 show CO conversion rates and hydrocarbon formation rates at 235  $^{\circ}$ C and 21.4 atm as a function of CO conversion. At the same CO conversion, the CO conversion rates are much higher on the K-promoted catalysts than on the K-free catalysts, confirming the promotion effect of potassium. It is also noted that the trends in CO conversion rates depend on the CO conversion level. At low CO conversions, a higher CO conversion rate was obtained on the catalyst with 2 % K than on the catalyst with 4 % K but the opposite trend was observed at high CO conversions.

Similar trends were observed for hydrocarbon formation rates as a function of potassium loading level (Fig. 1.10)

### 4.1.2. Effects of Potassium on Water-Gas Shift Reaction

Water is the primary oxygenate product, and  $CO_2$  forms via a subsequent water-gas shift. Higher  $CO_2$  selectivity means that more  $CO_2$  is produced from water and CO, indicating that the catalyst is more active for water-gas shift reaction.



Fig. 1.11. CO<sub>2</sub> selectivity as a function of CO conversion on the catalysts (Zn/Fe = 0.1, 1 at.% Cu) with various potassium loading levels at 235 °C and 21.4 atm,  $H_2/CO=2$ .

Fig. 1.11 shows CO<sub>2</sub> selectivity as a function of CO conversion with various potassium loading level at 235 °C and 21.4 atm. CO<sub>2</sub> selectivity increased with CO conversion at all K loadings. This is expected if more water is produced at the higher CO conversion. CO<sub>2</sub> selectivity was considerably increased after potassium was introduced into the catalyst. For example, at 20% CO conversion, CO<sub>2</sub> selectivity was about 9% on the K-free catalyst while it was as high as 27% on the catalyst with 2 at.% K, indicating that potassium increased the activity of the catalyst for the water-gas shift reaction. This is in agreement with many other previous studies [16, 21].

#### 4.1.3. Effects of Potassium on Hydrocarbon Selectivity and 1-Olefin to n-Paraffin Ratio

Fig. 1.12 shows methane selectivity as a function of CO conversion on the catalysts (Zn/Fe = 0.1, 1 at.% Cu) with various potassium loading levels at 235 °C and 21.4 atm. Methane selectivities were almost independent of CO conversion on all three catalysts. This is expected since  $H_2/CO$  ratio just slightly increased with increasing CO conversion. It is clearly seen from Fig. 1.12 that potassium can inhibit the formation of methane. For example, methane selectivity was about 10% on K-free catalyst while it was only 3% on the catalyst promoted with 2 at.% K.  $C_{5+}$  selectivities were 62% and 82.5% on these two catalysts, respectively (Fig. 1.13). The inhibition effect on the methane formation and the promotion effect of chain growth of potassium are in agreement with the results obtained in several earlier studies on Fe-based catalysts [16, 19]. The decrease in methane selectivity and the increase in  $C_{5+}$  selectivity are due to the increased CO and lower hydrogen surface coverage in the presence of potassium, as discussed before. Low hydrogen surface concentration also reduce the probability of chain termination to paraffins and increase the possibility of the olefin formation since chain growth can terminate either by  $\beta$ -hydrogen abstraction to form  $\alpha$ -olefin or by H-addition to form paraffins [24, 25]. Therefore, the addition of K can increase 1-olefin to n-paraffin ratio (Fig. 1.14).



Fig. 1.12. Methane selectivity as a function of CO conversion on the catalysts (Zn/Fe = 0.1, 1 at.% Cu) with various potassium loading levels at 235 °C and 21.4 atm,  $H_2/CO=2$ .



Fig. 1.13.  $C_{5+}$  selectivity as a function of CO conversion on the catalysts (Zn/Fe = 0.1, 1 at.% Cu) with various potassium loading levels at 235 °C and 21.4 atm, H<sub>2</sub>/CO=2.



Fig. 1.14. 1-olefin to n-paraffin ratio as a function of CO conversion on the catalysts (Zn/Fe = 0.1, 1 at.% Cu) with various potassium loading levels at 235 °C and 21.4 atm,  $H_2/CO=2$ .

#### 4.2. CO<sub>2</sub> Addition Effects

The effects of CO<sub>2</sub> addition on the rate of water-gas shift reaction and on CO<sub>2</sub> and hydrocarbon selectivities were investigated by adding CO<sub>2</sub> at 270 °C and 5 atm on the K-free catalyst (Zn/Fe=0.1, 1 at.% Cu). The partial pressure of synthesis gas was maintained constant as the CO<sub>2</sub> pressure was varied. Fig. 1.15 shows CO conversion as a function of the added CO<sub>2</sub> pressure. Fig. 1.16 shows CO conversion rate, CO<sub>2</sub> net formation rate and hydrocarbon formation rate against the added CO<sub>2</sub> pressure. It is seen from Fig. 1.16 that the net CO<sub>2</sub> formation rate decreased with CO<sub>2</sub> pressure, suggesting that addition of CO<sub>2</sub> can inhibit CO<sub>2</sub> pressure (Figs. 1.15 and 1.16). However, hydrocarbon formation rate was almost independent of CO<sub>2</sub> pressure, indicating that the addition of CO<sub>2</sub> did not affect Fischer-Tropsch synthesis reactions.



Fig. 1.15. CO conversion as a function of  $CO_2$  pressure on the K-free catalyst (Zn/Fe=0.1, 1 at.% Cu) at 270 °C and 5 atm, H<sub>2</sub>/CO=2.

However, even when the CO<sub>2</sub> partial pressure was 4 atm, which was much higher than CO pressure in feed (1.55 atm), some CO<sub>2</sub> was still produced during FTS reactions. This is in agreement with our calculations, which indicate that at these reaction conditions, a CO<sub>2</sub>/CO ratio of about 7.4 in the feed (e.g. CO<sub>2</sub> partial pressure about 11.4 atm) would be required by thermodynamics in order to avoid any net CO<sub>2</sub> formation via water-gas shift reactions. It shows that although CO<sub>2</sub> addition can be used to decrease CO<sub>2</sub> yields during FTS, the elimination of net CO<sub>2</sub> formation may well require levels of CO<sub>2</sub> that are impractical because of separation and re-compression costs.



Fig. 1.16. CO conversion rate, hydrocarbon formation rate and net  $CO_2$  formation rate as a function of  $CO_2$  pressure on the K-free catalyst (Zn/Fe=0.1, 1 at.% Cu) at 270 °C and 5 atm, H<sub>2</sub>/CO=2.

One measure of the distance of the water-gas shift reaction from equilibrium can be obtained by the following ratio,

$$\eta = \frac{\left(\frac{P_{CO_2}P_{H_2}}{P_{CO}P_{H_2}}\right)}{K} \tag{1}$$

where K is equilibrium constant for water-gas shift reaction. As shown in Fig. 1.17, the value of  $\eta$  is very small when no CO<sub>2</sub> was added into the synthesis gas and increased to about 0.5 as 4 atm CO<sub>2</sub> was added into the synthesis gas. The value of 0.5 means water-gas shift reaction remained far from equilibrium. That is the reason why CO<sub>2</sub> was still produced via water-gas shift even when 4 atm CO<sub>2</sub> was added into synthesis gas.

 $CO_2$  formation rate via water-gas shift depends on the  $CO_2$  forward rate  $\mathbf{r}_f$  and reverse reaction rate  $\mathbf{r}_b$ .  $CO_2$  formation rate r can be expressed as the following equation,

$$\mathbf{r} = \mathbf{r}_{f} - \mathbf{r}_{b} = k_{1} f(\mathbf{P}_{j}) - k_{-1} g(\mathbf{P}_{i})$$
(2)

where  $k_1$  is the rate constant for the water-gas shift reaction and  $k_{-1}$  the rate constant for the reverse reaction. Since  $\mathbf{r}_f = \mathbf{r}_b$  at equilibrium, the reaction rates must satisfy  $\frac{f(P_j)}{g(P_i)} = \frac{P_{CO_2}P_{H_2}}{P_{co}P_{H_2O}}$ . Then from equations (1), (2), and  $\mathbf{K} = k/k_{-1}$ , we can obtain the following equation.

$$r = k_1 f(P_j) (1 - \frac{k_{-1}}{k_1} \frac{f(P_j)}{g(P_i)}) = r_f (1 - \eta)$$
(3)

Fig. 1.18 shows the CO<sub>2</sub> forward rate  $r_f (= r/(1-\eta)$  as a function of  $\eta$ . It is seen that CO<sub>2</sub> forward rate  $r_f$  was almost not changed with  $\eta$  within the experimental error. Therefore, the reduction in CO<sub>2</sub> net formation rate is caused by the increase in the reverse rate of water-gas shift reaction after addition of CO<sub>2</sub>.



Fig. 1.17. The value of  $\eta$  as a function of CO<sub>2</sub> pressure on the K-free catalyst (Zn/Fe=0.1, 1 at.% Cu) at 270 °C and 5 atm, H<sub>2</sub>/CO=2.



Fig. 1.18.  $CO_2$  forward rate as a function of  $\eta$  on the K-free catalyst (Zn/Fe=0.1, 1 at.% Cu) at 270 °C and 5 atm, H<sub>2</sub>/CO=2.

### II. FISCHER-TROPSCH SYNTHESIS ON COBALT CATALYSTS

### 1. Background

In contrast with Fe, Co catalysts may work at relatively low reaction temperatures and pressures with slightly higher selectivity to linear paraffins in the  $C_{5+}$  range and much lower water-gas-shift activity [4]. We have developed a *reaction-transport model* [13] of chain growth and termination for FTS with Co and Ru-based catalysts. During this reporting time, we prepared some silica-supported Co catalysts. We explored the effects of bed residence time and of water concentration on Co-catalyzed FTS. We also explored the reversibility of hydrogen and water dissociation steps by performing D<sub>2</sub>O tracer and kinetic isotope effect run.

### 2. Preparation of Cobalt Catalysts

Co catalysts were prepared by incipient wetness impregnation of SiO<sub>2</sub> (PQ Co. CS-2133) with Co nitrate (Aldrich 98%) solution (Table 2.1) [26]. The samples were dried at 60°C for 24 h. Temperature-programmed reduction (TPR) was carried out in order to determine required pretreatment conditions for all catalyst precursors. The TPR results (Figure 2.1) showed that the supported cobalt nitrate decomposes at about 160°C. The resulting cobalt oxide species reduce completely below 300°C. Thus, the catalyst precursors were pretreated following the procedures:

- (1) reduced in flowing H<sub>2</sub> (20 ml min<sup>-1</sup> g<sup>-1</sup> cat) by increasing the temperature from 20°C to 150°C at 10°C min<sup>-1</sup> and from 150°C to 350°C at 30°C h<sup>-1</sup> (This low heating rate minimizes the deleterious effect of the water formed during the decomposition of Co nitrate and during the reduction of Co oxides, and it leads to higher Co dispersion [26])
- (2) held at 350°C in flowing  $H_2$  for 1 h
- (3) passivated in a 1%  $O_2$ /He at 25°C before exposure to ambient air

Co content (wt%) <sup>a,b</sup>	Co Dispersion (%) <sup>a,c</sup>	Co content (wt%) <sup>[c,d]</sup>	Co Dispersion (%) <sup>[c,d]</sup>
12.7	5.8	13.0	6.3
21.9	4.6	24.8	4.2

Table 2.1.	Characterization	of Co/SiO <sub>2</sub>	catalysts
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<sup>a</sup> this work

<sup>b</sup> confirmed by ICP

<sup>c</sup> from  $H_2$  chemisorption, measured at 100°C

<sup>d</sup> previous work [13]



Figure 2.1. Temperature-programmed reduction of Co/SiO<sub>2</sub> catalysts  $(10\% \text{ H}_2/\text{Ar}, 10 \text{ }^\circ\text{C min}^{-1})$ 

### 3. Hydrogen Chemisorption

Co dispersion was measured by  $H_2$  chemisorption at 100°C assuming a 1:1 H:Co surface stoichiometry. These measurements were carried out in a glass volumetric adsorption unit capable of 10<sup>-4</sup> Pa dynamic vacuum. Pre-reduced and passivated catalysts were rereduced in flowing  $H_2$  by increasing the temperature from 20°C to 300°C at 10°C min<sup>-1</sup> and then holding for 10 min, evacuated at 300°C to less than 10<sup>-3</sup> Pa, and cooled to 100°C. The chemisorption isotherms were measured at five  $H_2$  pressures between 0 and 500 Torr. These isotherms (Figure 2.2) were extrapolated to zero pressure in order to calculate chemisorption uptakes. The Co dispersions calculated from the  $H_2$ chemisorption uptakes are presented in Table 2.1. The dispersions of the two Co/SiO<sub>2</sub> catalysts were very similar to those reported after similar pre-treatments in the literature [13].



Figure 2.2. Hydrogen chemisorption on Co/SiO<sub>2</sub> catalysts (measured at 100°C)

### 4. Fischer-Tropsch synthesis on Cobalt Catalysts

### 4.1. Catalytic Reaction Unit

Catalyst studies were performed in a fixed-bed, single-pass flow reactor, hereafter referred to as the FTS unit (FTSU) (Appendix 2.1). It consists of six feed streams, one of which introduces syngas into the reactor after passing through gas purifiers (Matheson, Model 454 and 452) for the removal of metal carbonyls and of water. Flow rates were metered using mass flow controllers (Brooks 5850). A three-zone split tube furnace was controlled with three temperature controllers (IEPS Co.). The system pressure was maintained using a back-pressure regulator (Mity Mite, Model S-91xw). Liquid reactants were introduced using a high-pressure syringe pump (Isco, Inc., Model 500D). In addition, the FTSU was equipped with an automatic six-port switching valve, which enabled the unit to carry out isotopic switch transient and temperature programmed studies.

The feed gas and the reactor effluent were analyzed on-line using a gas chromatograph (Hewlett-Parkard, Model 5890 series II) equipped with a ten-port sample valve and two sample loops. One sample was injected into a capillary column (HP-1 cross-linked methyl silicone,  $50m \times 0.32mm \times 1.05\mu m$  film) while the other was injected into a packed column (Carboxen-1004,  $2m \times 1/16$ "). A TCD was used to analyze CO, N<sub>2</sub>, CO<sub>2</sub>, Ar, H<sub>2</sub>O, and light hydrocarbons (C<sub>1</sub>-C<sub>3</sub>). A FID analyzed all products except for permanent gases and water. A typical separation of reaction products is given in Appendix 4.1-4.3.

#### 4.2. FTS on Co/SiO<sub>2</sub> Catalysts

### 4.2.1. FTS conditions

FTS was running at 200°C using 20 atm syngas ( $H_2/CO/N_2 = 62/31/7$ ). Bed residence time was defined as catalyst volume divided by space velocity at standard conditions. Selectivity of hydrocarbon is based on carbon and CO<sub>2</sub>-free.

### 4.2.2. Space Velocity Effects

Space velocity effects on reaction rates and selectivities were examined by changing the syngas flow rate while maintaining other conditions constant. The results are shown in Figures 2.3 to 2.8. The two Co/SiO<sub>2</sub> catalysts exhibited similar behaviors in the space velocity run. The CO conversion increases with increasing bed residence time (Figure 2.3, 2.4), but surprisingly the apparent FTS reaction rate also increases with increasing bed residence time (Table 2.2). This is unusual in view of the fact that the partial pressures of CO and H<sub>2</sub> reactants decrease as CO conversion increases by increasing bed residence time. It appears that one of the reaction products  $(H_2O)$  has an accelerating effect on the FTS rate, since the water partial pressure is higher at higher conversion (Tables 2.2). The details of these unusual autocatalytic effects will be the subject of future studies. As shown in Figures 2.5 to 2.8, CH<sub>4</sub> selectivity decreases, C<sub>5+</sub> selectivity increases, and  $\alpha$ -olefin to *n*-paraffin ratio decreases with increasing bed residence time. These trends were previously attributed to a greater probability of olefin readsorption and growth as CO conversion and bed residence time increased [14]. Both the catalysts have very low CO<sub>2</sub> selectivities (Figure 2.5, 2.6), consistent with very low water-gas-shift reaction rates at the conditions. In general, the results of space velocity studies are in agreement with a reaction transport model [13]. This model proposes that diffusionenhanced olefin resorption increases the probability of chain growth and leads to heavier and more paraffinic products [13].

	Space	Bed	CO	Water partial	Site-time
Catalyst	velocity	residence	conv	pressure	yield
	$(ml g^{-1}min^{-1})$	time (s)	(%)	(atm) <sup>b</sup>	$(h^{-1})$
	11.4	15.8	49.0	2.2	34.1
12.7 wt%	17.1	10.5	29.0	1.1	30.3
Co/SiO <sub>2</sub>	34.2	5.3	12.8	0.4	26.8
	51.4	3.5	8.7	0.3	26.9
	30.0	6.2	54.9	2.6	71.4
	45.0	4.1	33.0	1.3	64.5
21.9 wt%	60.0	3.1	21.6	0.8	56.4
Co/SiO <sub>2</sub>	90.0	2.0	12.9	0.4	50.5
	180.0	1.0	5.7	0.2	44.7

Table 2.2. Effects of bed residence time on FTS rate<sup>a</sup>

<sup>a</sup> reaction conditions: 200°C, 20 atm,  $H_2/CO = 2.0$ <sup>b</sup> average of the inlet and the exit water pressures



Figure 2.3. Space velocity effect on CO conversion (12.7 wt% Co/SiO<sub>2</sub>, 200°C, 20 atm,  $H_2/CO = 2.0$ )



Figure 2.4. Space velocity effect on  $CH_4$ ,  $C_{5+}$ , and  $CO_2$  selectivities (12.7 wt% Co/SiO<sub>2</sub>, 200°C, 20 atm,  $H_2/CO = 2.0$ )



Figure 2.5. Space velocity effect on *a*-olefin to *n*-paraffin ratio (12.7 wt% Co/SiO<sub>2</sub>, 200°C, 20 atm,  $H_2/CO = 2.0$ )



Figure 2.6. Space velocity effect on CO conversion (21.9 wt% Co/SiO<sub>2</sub>, 200°C, 20 atm,  $H_2/CO = 2.0$ )



Figure 2.7. Space velocity effect on CH<sub>4</sub>,  $C_{5+}$ , and CO<sub>2</sub> selectivities (21.9 wt% Co/SiO<sub>2</sub>, 200°C, 20 atm, H<sub>2</sub>/CO = 2.0)



Figure 2.8. Space velocity effect on *a*-olefin to *n*-paraffin ratio (21.9 wt% Co/SiO<sub>2</sub>, 200°C, 20 atm, H<sub>2</sub>/CO = 2.0)

#### 4.2.3. Effects of Water on FTS Reaction Rate and Selectivity

So far, most of kinetic rate equations for Co-catalyzed FTS do not include the influence of water [27]. Water is usually considered to have little effect on the overall rate of CO consumption on Co catalysts [28]. But in the above space velocity studies, water has been found to promote the CO conversion rate. We have examined the water effects on FTS rate and selectivities by adding 2, 4, and 8 atm  $H_2O$  at low CO conversions while maintaining the H<sub>2</sub> and CO partial pressures constant. The results are shown in Figures 2.9 to 2.12. CO conversion rates increase with increasing water partial pressure (Figure 2.9). We suggest that water may affect FTS by changing the relative concentrations of kinetic-relevant species on surface. The nature of this kind of water effect is being studied by using D<sub>2</sub>O isotopic tracers. It should be noted that the high loading Co catalyst is deactivated when the water partial pressure reaches 8 atm (Figure 2.9). The deactivation is probably due to the high concentration of water, which could oxidize active Co sites. On the other hand, water has a positive effect on the product distribution. The methane selectivity decreases (Figure 2.10), the selectivity to desired  $C_{5+}$  increases (Figure 2.11), and the products become more olefinic (Figure 2.12) with increasing water partial pressure. All these beneficial modifications of FTS selectivities were reported previously [14] and they are consistent with the literature [28]. It appears that water inhibits all termination steps leading to paraffins (e.g., secondary hydrogenation) with a consequent increase in the selectivity of  $\alpha$ -olefins.  $\alpha$ -Olefins possess higher probability of readsorption and of chain growth, resulting in heavier products.



Figure 2.9. Water effect on FTS reaction rate (Co/SiO<sub>2</sub> catalysts, 200°C, H<sub>2</sub>/CO = 2.0; solid lines, space velocity runs, 20 atm; dash lines, water added at the lowest conversions; water partial pressure is the average of the inlet and the exit water pressures)



Figure 2.10. Water effect on CH<sub>4</sub> selectivity (Co/SiO<sub>2</sub> catalysts, 200°C, H<sub>2</sub>/CO = 2.0; solid lines, space velocity runs, 20 atm; dash lines, water added at the lowest conversions; water partial pressure is the average of the inlet and the exit water pressures)



Figure 2.11. Water effect on  $C_{5+}$  selectivity (Co/SiO<sub>2</sub> catalysts, 200°C, H<sub>2</sub>/CO = 2.0; solid lines, space velocity runs, 20 atm; dash lines, water added at the lowest conversions; water partial pressure is the average of the inlet and the exit water pressures)



Figure 2.12. Water effect on olefin to paraffin ratio (Co/SiO<sub>2</sub> catalysts, 200°C, H<sub>2</sub>/CO = 2.0; points, at the lowest conversion of each space velocity run, 20 atm; dash lines, water added at the lowest conversions; water partial pressure is the average of the inlet and the exit water pressures)

#### 4.2.4. D<sub>2</sub>O tracer and kinetic isotope effect studies

In order to explore the reversibility of water dissociation step during FTS, D<sub>2</sub>O tracer studies were carried out by co-feeding 2 atm D<sub>2</sub>O with 20 atm syngas (13.8% D in the feed). The deuterium content in hydrocarbon products (up to C<sub>8</sub>) and in water were measured by a GC-MS (Hewlett-Packard 5972), while the D content in hydrogen isotopomers was determined by mass spectrometry (Leybod Inficon Instruments Co., Inc.). The D contents were calculated using matrix techniques that correct for ion fragmentation [29]. The results are shown in Table 2.3 and in Figure 2.13. The D content in the water decreases with increase in the bed residence time, because more H<sub>2</sub>O formed at longer bed residence time, *i.e.*, higher conversion. The D contents in all the primary products (C<sub>4</sub>-C<sub>8</sub>) and in the H<sub>2</sub> isotopomers increase as increasing bed residence time, suggesting the D content in surface H-D pool changes with bed residence time. The water dissociation steps during FTS consist:

 $\begin{array}{ll} O^* + H^* \rightarrow OH^* + * & (1) \\ OH^* + H^* \rightarrow OH_2^* + * & (2) \\ OH_2^* \leftrightarrow H_2O + * & (3) \end{array}$ 

which may influence the H/D ratio on surface. Assuming the step (3) is quasiequilibrated, at least one of the steps (1) and (2) should be not quasi-equilibrated. Otherwise, D contents in the hydrocarbons and in the  $H_2$  isotopomers should be independent of bed residence time. Further, extrapolating the lines in Figure 2.13 to zero bed residence time, we find D contents in the hydrocarbons and in the H<sub>2</sub> isotopomers are around 3%. This is an evidence that water dissociation is reversible, although it is not quasi-equilibrated during FTS. Thus, water in the gas phase influences FTS probably by consuming surface vacant site (step 3). This will depress the dissociation of CO (forming the predominant species on surface) in which vacant sites are required. This may account for the CO conversion rate increasing with increase in the water partial pressure, since the rate is mildly negative order in CO partial pressure [13].

Bed 1	residence time (s)	1	1.5	3
Water	Frct of D (%)	0.37	0.29	0.25
	Dev from binomial	0.03	0.04	0.00
H <sub>2</sub> -iso	Frct of D (%)	0.05	0.06	0.09
	Dev from binomial <sup>b</sup>	0.00	0.00	0.01
$1-C_4H_8$	Frct of D (%)	5.2	6.3	9.3
	Dev from binomial	0.02	0.01	0.01
$n-C_4H_{10}$	Frct of D (%)	5.1	5.8	9.2
	Dev from binomial	0.04	0.01	0.02
$1 - C_5 H_{10}$	Frct of D (%)	5.5	6.2	9.6
	Dev from binomial	0.00	0.02	0.01
$n-C_5H_{12}$	Frct of D (%)	4.6	6.0	9.5
	Dev from binomial	0.01	0.01	0.02
$1 - C_6 H_{12}$	Frct of D (%)	4.3	6.0	9.7
	Dev from binomial	0.01	0.02	0.02
$n - C_6 H_{14}$	Frct of D (%)	4.7	5.8	8.8
	Dev from binomial	0.02	0.02	0.02
$1 - C_7 H_{14}$	Frct of D (%)	4.8	6.3	9.7
	Dev from binomial	0.02	0.02	0.02
$n-C_7H_{16}$	Frct of D (%)	4.4	5.7	8.6
	Dev from binomial	0.01	0.02	0.02
$\overline{I - C_8 H_{16}}$	Frct of D (%)	4.8	6.2	9.7
	Dev from binomial	0.03	0.01	0.02
$\overline{n-C_8H_{18}}$	Frct of D (%)	4.3	5.4	8.4
	Dev from binomial	0.02	0.02	0.03

Table 2.4. Deuterium content in hydrocarbon products, waterand hydrogen isotopomers<sup>a</sup>

<sup>a</sup> reaction conditions: 21.9 wt% Co/SiO<sub>2</sub> catalyst; 200°C; 20 atm syngas,  $H_2/CO = 2.0$ ; 2 atm D<sub>2</sub>O added;

<sup>b</sup> deviation from statistic distribution at each D content



Figure 2.13. Deuterium content in FTS products (21.9 wt% Co/SiO<sub>2</sub> catalysts, 200°C;  $H_2/CO/N_2 = 62/31/7$ , 20 atm; D<sub>2</sub>O added, 2 atm)

The kinetic isotope effect (KIE) was studied by comparing the rates of FTS using  $H_2/CO/N_2$  (62/31/7) and  $D_2/CO/N_2$  (62/31/7). All the conditions were same as those of the previous space velocity run. This KIE study can probe the reversibility of hydrogen dissociation steps and the role of hydrogen-containing species in the rate-determining step during FTS. As shown in Table 2.5, the ratio of CO conversion rate ( $k_{CO(H)}/k_{CO(D)}$ ) is 0.92. Since the CO conversion rate sums the formation of all carbon-based products, rigorous analysis of the formation rate of each primary product (non-deuterated and per-deuterated) is being performed in order to make conclusions about the mechanisms. First we consider the formation of methane during FTS, which involves the following steps: [28]

(1) (2) (3) (4) (5) (6)  $CO \leftrightarrow CO^* \leftrightarrow C^* \rightarrow CH^* \rightarrow CH_2^* \rightarrow CH_3^* \rightarrow CH_4$ 

CO dissociation (1, 2) is usually taken as a reversible step [13]. So the rate of methane formation depends on the subsequent hydrogen addition steps. If one of these steps is rate-determining, the methane formation rate should increase when we replace H<sub>2</sub> with D<sub>2</sub>. However, the observed ratio ( $k_{CH4}/k_{CD4}$ ) is 1.34, suggesting that none of the hydrogen addition steps are rate-determining. We may then infer the H<sub>2</sub> dissociation is rate-determining. If this is true, switching from H<sub>2</sub> to D<sub>2</sub> (with other conditions unchanged) would lower the surface D\* concentration compared with the H\* concentration, leading to the lower formation rate of CD<sub>4</sub>. Thus the preliminary results of the KIE run suggest the involvement of hydrogen dissociation in the rate-determining step.

Feed	H <sub>2</sub> /CO/N <sub>2</sub> (62/31/7)	D <sub>2</sub> /CO/N <sub>2</sub> (62/31/7)
Bed residence time (s)	5.6	5.1
CO conversion (%)	48.6	47.4
CO conversion rate $(s^{-1})$	70.1	75.8
$k_{CO(H)}/k_{CO(D)}$	0.92	
Methane selectivity (%)	6.1	4.2
Methane formation rate $(s^{-1})$	4.3	3.2
k <sub>CH4</sub> /k <sub>CD4</sub>	1.34	

Table 2.5. Results of kinetic isotope effect run<sup>a</sup>

<sup>a</sup> reaction conditions: 21.9 wt% Co/SiO<sub>2</sub> catalyst; 200°C; 20 atm syngas, H<sub>2</sub>/CO = 2.0; 2 atm D<sub>2</sub>O added;

### III. APPENDIX

### 1. Reference

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### 2. Schematic Diagram of Experimental Apparatus

2.1. Catalytic Microreactor Unit (FTSU) for FTS on Co-based Catalyst



Appendix 2.1 Schematic diagram of the Fischer-Tropsch synthesis unit

## 3. Peak Identification on Gas-Chromatograph

Appendix 3.1. Gas chromatograph conditions and typical products of Co-based catalysts with retention time<sup>a</sup>

<sup>a</sup>Reaction conditions: 21.9 wt% Co/SiO<sub>2</sub> Catalyst, 200°C, 20 atm,  $H_2/CO/N_2 = 62/31/7$ 

TCD

Colum	1	Carboxen-1004, 2m × 1/16''		
	Initial Temperature (°C)	- 60	Initial Time (min)	3
Oven	Ramping Rate (°C/min)	10		
	Final Temperature (°C)	230	Final Time (min)	20
Detector Temperature (°C)		250	Injector Temperature (°C)	250
Inlet Pressure (atm)		4		
He Flow Rate (ml/min)		30	Reference Flow Rate (ml/min)	30

Index Number	Carbon Number	Products	Retention Time (min)
1		H <sub>2</sub>	0.87
2		N <sub>2</sub>	7.26
3	C1	СО	8.77
4	C1	CH <sub>4</sub>	13.57
5	C1	CO <sub>2</sub>	17.39
6		H <sub>2</sub> O	18.62
7	C2	C <sub>2</sub> H <sub>6</sub>	25.40
8	C3	C <sub>3</sub> H <sub>6</sub>	34.07
9	C3	C <sub>3</sub> H <sub>8</sub>	35.58

Column		HP-1, crosslinked methyl silicone, $50m \times 0.32mm \times 1.05\mu m$			
	Initial Temperature (°C)	- 60	Initial Time (min)	3	
Oven Ramping Rate (°C/min)		10	10		
	Final Temperature (°C)	230	Final Time (min)	20	
Detector Temperature (°C)		250	Injector Temperature (°C)	250	
Inlet Pressure (psi)		23.2	Split Ratio	25: 1	
He Flow Rate (ml/min)		100	Make-up He Flow Rate (ml/min)	20	
H <sub>2</sub> Flow Rate (ml/min)		30	Air Flow Rate (ml/min)	300	

Index Number	Carbon Number	Products	Retention Time
Index i tumber		Troducts	(min)
1	C1	CH <sub>4</sub>	2.25
2	C2	$C_2H_4$	2.53
3	C2	C <sub>2</sub> H <sub>6</sub>	2.76
4	C3	C <sub>3</sub> H <sub>6</sub>	5.02
5	C3	C <sub>3</sub> H <sub>8</sub>	5.23
6		unknown	8.07
7	C4	$1-C_4H_8$	8.77
8	C4	$1-C_4H_{10}$	9.04
9	C4	Cis-2-C <sub>4</sub> H <sub>8</sub>	9.45
10	C4	Trans-2-C <sub>4</sub> H <sub>8</sub>	9.91
11	C5	C <sub>5</sub> H <sub>10</sub> -isomer	10.86
12	C5	C <sub>5</sub> H <sub>12</sub> -isomer	11.38
13	C5	C <sub>5</sub> H <sub>12</sub> -isomer	11.49
14	C5	$1-C_5H_{10}$	11.82
15	C5	$1-C_5H_{12}$	12.13
16	C5	C <sub>5</sub> H <sub>10</sub> -internal	12.38
17	C5	C <sub>5</sub> H <sub>10</sub> -internal	12.58
18	C6	C <sub>6</sub> H <sub>12</sub> -isomer	13.57
19	C6	C <sub>6</sub> H <sub>14</sub> -isomer	14.08
20	C6	$1-C_6H_{12}$	14.49
21	C6	$1-C_6H_{14}$	14.77
22	C6	C <sub>6</sub> H <sub>12</sub> -internal	14.89
23	C6	C <sub>6</sub> H <sub>12</sub> -internal	15.11
24	C7	C <sub>7</sub> H <sub>14</sub> -isomer	15.99

25	C7	C <sub>7</sub> H <sub>16</sub> -isomer	16.55
26	C7	$1-C_7H_{14}$	16.86
27	C7	$1-C_7H_{16}$	17.11
28	C7	C <sub>7</sub> H <sub>14</sub> -internal	17.21
29	C7	C <sub>7</sub> H <sub>14</sub> -internal	17.40
30	C8	C <sub>8</sub> H <sub>16</sub> -isomer	18.20
31	C8	$1-C_8H_{16}$	19.00
32	C8	$1-C_8H_{18}$	19.23
33	C8	C <sub>8</sub> H <sub>16</sub> -internal	19.30
34	C8	C <sub>8</sub> H <sub>16</sub> -internal	19.47
35	С9	C <sub>9</sub> H <sub>18</sub> -isomer	20.23
36	С9	$1-C_9H_{18}$	20.96
37	С9	C <sub>9</sub> H <sub>18</sub> -isomer	21.08
38	С9	$1-C_9H_{20}$	21.18
39	С9	C <sub>9</sub> H <sub>18</sub> -internal	21.39
40	C10	C <sub>10</sub> H <sub>20</sub> -isomer	22.10
41	C10	$1-C_{10}H_{20}$	22.77
42	C10	C <sub>10</sub> H <sub>20</sub> -isomer	22.87
43	C10	$1-C_{10}H_{22}$	22.97
44	C10	C <sub>10</sub> H <sub>20</sub> -internal	23.17
45	C11	C <sub>11</sub> H <sub>22</sub> -isomer	23.84
46	C11	$1-C_{11}H_{22}$	24.45
47	C11	C <sub>11</sub> H <sub>22</sub> -isomer	24.52
48	C11	$1 - C_{11}H_{24}$	24.63
49	C11	C <sub>11</sub> H <sub>22</sub> -internal	24.82
50	C12	C <sub>12</sub> H <sub>24</sub> -isomer	25.46
51	C12	$1 - C_{12}H_{24}$	26.01
52	C12	C <sub>12</sub> H <sub>24</sub> -isomer	26.07
53	C12	$1-C_{12}H_{26}$	26.18
54	C12	C <sub>12</sub> H <sub>24</sub> -internal	26.36
55	C13	C <sub>13</sub> H <sub>26</sub> -isomer	26.98
56	C13	$1-C_{13}H_{26}$	27.48
57	C13	C <sub>13</sub> H <sub>26</sub> -isomer	27.52
58	C13	$1 - C_{13}H_{28}$	27.63
59	C13	C <sub>13</sub> H <sub>26</sub> -internal	27.81
60	C14	C <sub>14</sub> H <sub>28</sub> -isomer	28.40
61	C14	$1-C_{14}H_{28}$	28.85
62	C14	$1 - \overline{C_{14}H_{30}}$	28.99

63	C14	C <sub>14</sub> H <sub>28</sub> -internal	29.16
64	C15	C <sub>15</sub> H <sub>30</sub> -isomer	29.74
65	C15	$1-C_{15}H_{30}$	30.14
66	C15	$1-C_{15}H_{32}$	30.27
67	C15	C <sub>15</sub> H <sub>30</sub> -internal	30.44
68	C16	$1-C_{16}H_{34}$	31.48



Appendix 3.2. TCD chromatogram



Appendix 3.3. FID chromatogram



Appendix 3.3. FID chromatogram (continued)



Appendix 3.3. FID chromatogram (continued)



Appendix 3.3. FID chromatogram (continued)

# Task 12. Reporting/Project Management

Three monthly and one quarterly reports have been completed.