Task 11. University of California, Berkeley (Subcontract)

Final Research Report

October 1, 1998 to September 30, 2001

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

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 have proposed that surface iron atoms are responsible for FTS activity [6], while some others considered surface carbides or a mixture of carbides [7,8] and metallic iron [9] to be the active phase. There are several 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.

This project is aimed at building on our previous research on structure-function roles for FTS reactions on catalysts based on Co [13,14] and Fe [15,16]. It addresses the characterization of the structure and function of the active sites involved in the Fischer-Tropsch synthesis on these multi-component Fe-based catalysts. It involves the use of characterization techniques such as X-ray absorption spectroscopy, X-ray diffraction, and temperature programmed reaction, monitoring of isothermal product transients under FTS reaction conditions using mass spectrometry, as well as activity and product selectivity measurements in a high pressure reactor under FTS conditions, in order to obtain a complete picture of the structure-function relationships of the active sites on Fe catalysts. In Section 2, we address the structure and site evolution of iron oxide precursors during FTS. The effect of Zn, Cu, K as promoters for FTS is discussed in Section 3 while the effects of Cu and Ru as well as surface area of precursors, as site density enhancers are illustrated in detail in Section 4. We also demonstrate that the high activity Fe-Zn-Cu-K catalysts are comparable in performance with typical Co/SiO₂ catalysts at low temperatures.

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 an apparent modifier of the adsorption enthalpies of H₂ and CO, increases the selectivity to desired C_{5+} products [18]. Copper promotes the carburization processes and decreases the temperature required for the activation of iron oxide. Here, our initial 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 have examined 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. Finally, as part of our attempt to design a high activity Fe-based FTS catalyst, we have also investigated the use of Ru as a promoter in place of Cu, based on the high activity of Ru-based catalysts for CO hydrogenation reactions [19], as well as by the synthesis of higher surface area Fe-Zn precursors. The performance of Fe catalysts thus prepared, have been evaluated at conditions typically used for Co-FTS reactions (473 K and 2 MPa) for comparison with a typical Co/SiO₂ catalyst.

2. Synthesis Procedures for Fe-Zn-K-Cu(Ru) Samples

Fe-Zn oxide precursors were prepared by co-precipitation from a mixed solution of Fe and Zn nitrates using ammonium carbonate using a procedure reported previously [16]. A solution containing Fe(NO₃)₃ (Aldrich, 99.9+%, 3.0 M) and Zn(NO₃)₂ (Aldrich, 99.9+%, 1.4 M) at a Zn/Fe atomic ratio of 0.1 was added into a large flask containing deionized water at 353 K (~100 cm³) at a rate of 120 cm³h⁻¹ using a liquid pump. (NH₄)₂CO₃ (Aldrich, 99.9%, 1 M) was added separately to this flask at the rate required to maintain the pH at a constant value of 7.0±0.1, measured by a pH meter (Omega, PHB-62). The precipitates (~20 g) were washed five times with doubly distilled deionized water (~ 200 cm^{3}/g each time), dried in ambient air at 393 K overnight, and then treated in flowing dry air at 623 K for 1 h. The K, Cu, and Ru promoters were added to these Fe-Zn oxide precursors by incipient wetness impregnation with aqueous solutions of K₂CO₃ (Aldrich, 99.99%, 0.16 M), Cu(NO₃)₂ (Aldrich, 99.99%, 0.16 M), or ruthenium (III) nitrosyl nitrate $[Ru(NO)(NO_3)_x(OH)_y (x+y=3)]$ (Aldrich, dilute nitric acid solution, Ru 1.5%) at the concentrations required to obtain the desired K/Fe, Cu/Fe, or Ru/Fe atomic ratios (K/Fe=0.02, Cu,Ru/Fe=0.01). The impregnated samples were then dried 373 K in ambient air. Finally, the samples were treated in flowing dry air at 673 K for 4 h. The resulting oxide precursors are denoted throughout as Fe-Zn-K₂, Fe-Zn-K₂-Cu₁ and Fe-Zn-K₂-Ru₁, respectively. The subscripts denote the atomic content of the corresponding promoter divided by the Fe atomic content and multiplied by 100. These catalysts were pressed at 443 MPa into pellets, lightly crushed, and then sieved to retain the 80 - 140 mesh fraction for FTS reaction. Pure Fe oxide precursors were prepared in an identical manner and promoted with Cu and K for the initial characterization studies.

High surface area Fe-Zn-K-Cu oxide precursors were prepared using surface-active components, such as alcohols, in order to minimize pore mouth pinching as intrapore liquids with high surface tension are removed by drying. These processes lead to a decrease in pore volume and surface area. Fe-Zn-K₄-Cu₂ oxides were prepared by the procedure described above, except that alcohols (isopropanol or ethanol) were used to replace the water retained within pores during precipitation before the drying step. After co-precipitation, the powders were washed with isopropanol or absolute ethanol (Fischer Chemical) five times (~200 cm³/g each time) at ambient temperature. Magnetic stirring was used during alcohol washing in order to increase the rate at which liquid water within

pores was replaced by the alcohol. In order to maintain similar promoter surface densities on these higher surface area oxides, proportionally higher concentrations of K (K/Fe=0.04) and Cu (Cu/Fe=0.02) were introduced by incipient wetness impregnation.

3. Structure and site evolution of iron oxide catalyst precursors during the Fischer-Tropsch Synthesis

3.1. Methodology

Several of the Fe phases described in Section 1 have been detected in freshly activated or used Fe-based FTS catalysts. Most of these phases have been proposed at various times to be the active species for FTS reactions. The relative abundance of these phases depends on reaction conditions. Even after many ex situ characterization studies, the composition of Fe-based FTS catalysts during reaction and the identity of the active phase remain controversial. Fe-based catalysts have been investigated by Mössbauer spectroscopy [7,20]; the time resolution of Mössbauer spectroscopy (>1 h for typical samples) precludes its use for *in situ* transient measurements during initial phase transformations. Also, Mössbauer spectroscopy is sensitive only to the recoil-free fraction, which depends on the structure of the Fe-containing phase. This recoil-free fraction must be accurately measured as a function of temperature for precise structural assessments using Mössbauer spectroscopy. X-ray diffraction (XRD) cannot detect inorganic structures without long-range periodicity; as a result, it is not sensitive to amorphous or well-dispersed Fe species, which tend to account for a large fraction of the surface area and the active sites available for FTS. X-ray photoelectron spectroscopy (XPS) [11,21] has been used to examine catalytic solids before and after reaction, but it cannot be used during FTS. It requires quenching and catalyst cleansing procedures that influence the state of the surface layers meant to be probed by XPS. Recent high resolution transmission electron microscopy (HRTEM) studies have addressed the active phase of working Fe catalysts after different activation and reaction treatments; these studies have provided useful, but occasionally misleading insights about the nature of the working Fe catalysts [22,23]. However, none of these measurements were performed during reaction or even within the FTS reactor. Therefore, the relevant catalytic surfaces may have become restructured or contaminated, even with careful handling and controlled passivation, as a result of the indispensable quenching and cleansing procedures.

X-ray absorption spectroscopy (XAS) can probe the local structure of inorganic structures, even as catalytic reactions occur, by using *in situ* spectroscopic cells with realistic and well-defined hydrodynamics. The X-ray absorption near-edge spectrum (XANES) is sensitive to the oxidation state and to the symmetry of the absorber atom [24]. Comparisons between these features and those in compounds with known local structure can be used to quantify the fraction of each absorber present within each type of local coordination environment using principal component analysis (PCA) [25] and linear combination [26] methods. The region beyond the absorption edge contains oscillations in absorbance, which arise from the scattering of the emitted photoelectrons by the atoms surrounding the absorber. This extended X-ray absorption fine structure (EXAFS) region

of the spectrum contains information about the identity and the location of neighboring atoms coordinated to the absorber directly or through other atoms [24]. Therefore, X-ray absorption methods are ideally suited for *in situ* characterization of Fe-based FTS catalysts. We are not aware of its previous use for the structural characterization of Fe catalysts during FTS. Several reaction cells have been reported previously for *in situ* XAS measurements [27,28]. Here, we report a cell design based on modifications of one of these previously described cells [28], and use it to probe the local structure of Fe catalysts derived from Fe₂O₃ precursors during FTS. This study focuses on the evolution of the Fe₂O₃ component in the precursor materials during FTS reactions, on the effect of various promoters (Cu, K), and on the extent and rate of structural transformations occurring as Fe oxide catalyst precursors activate during contact with synthesis gas and as FTS reactions approach steady-state.

3.2. X-ray absorption sample preparation

Fe K-edge X-ray absorption spectra were measured for reference compounds with known local structures and for catalyst precursors consisting of Fe-K-Cu oxides (K/Fe=0.02, Cu/Fe=0.01) during their reduction and carburization in CO and in synthesis gas. Fe₂O₃ (Alfa AESAR, 99.998%), Fe₃O₄ (Alfa AESAR, 99.997%), and FeO (Alfa AESAR, 99.5%) were used as reference crystalline oxides. Fe₃C, which can form during FTS reactions, was prepared by temperature-programmed reaction (0.167 K/s) of Fe₂O₃ up to 973 K using CO (Matheson, 99.99%, 107 mol CO/g-atom Fe-h) as the reduction and carburization agent [3]. The resulting Fe₃C powder was passivated in flowing 1 % O₂/He (Matheson, 99.999%, 0.05 mol/h) at room temperature (RT) for 1 h before removing from the synthesis cell. X-ray diffraction measurements confirmed the exclusive presence of Fe₃C in this sample.

The Fe₂O₃ used for *in situ* XAS measurements was prepared by precipitation from an aqueous solution of Fe(NO₃)₃ (Aldrich, 99.99%, 3.0 M) with $(NH_4)_2CO_3$ (Aldrich, 99.9%, 1 M) at 353 K and a constant pH of 7.0. The precipitate was dried at 393 K overnight and treated in dry air at 643 K for 4 h. These oxide precursors were impregnated with aqueous solutions of K₂CO₃ (Aldrich, 99.99%,) and/or Cu(NO₃)₂ (Aldrich, 99.99%) to incipient wetness in order to give K/Fe and Cu/Fe atomic ratios of 0.02 and 0.01, respectively. These compositions were found to give the best catalytic performance in the Fischer-Tropsch synthesis described in subsequent sections.

All samples used in spectroscopic measurements were diluted to 10 wt.% Fe using graphite powder (Alfa AESAR, 99.9995%, $S_g < 1 m^2/g$), pressed at 10 MPa, sieved to retain 180-250 µ particles, and placed within a quartz capillary cell [29]. The inertness of graphite was tested by flowing H₂ over Fe oxides mixed with graphite up to 873 K without any detectable formation of FeC_x. Also, no carbon oxide products were detected by mass spectrometry, indicating that neither FeO_x nor the Fe metal formed during reduction reacted with graphite at typical FTS temperatures (473-773 K). The maximum sample thickness was set by the inner diameter of the quartz capillary (0.8 mm). Reference compounds were also diluted with graphite to 10 wt.% Fe and held using a ProleneTM film against an Al plate containing a beam slit.



3.3. In situ X-ray absorption microreactor cell



Figure 1. X-ray absorption cell: (A) picture, (B) front view, (C) top view with the heating unit removed.

An *in situ* X-ray absorption reaction cell was designed as a modified version of a previously reported reaction cell [29]. The modifications consisted of a finned heated block designed to replace the temperature control by heated air used in the earlier design. The cell consists of a quartz capillary (0.8 mm inner diameter, 0.1 mm wall thickness, 100 mm length) mounted horizontally into a stainless steel base using metal fittings and graphite ferrules (Figure 1). Samples with 180-250 μ particles formed a dense bed through which gas flows with negligible pressure drop and plug-flow hydrodynamics. Heat is supplied by four cartridges heaters mounted into a finned copper block. The copper block was insulated using a ceramic foam casing. A 20×4 mm beam path was cut into the finned copper block and the ceramic insulation in order to provide a clear path for the X-ray beam (10×0.2 mm) at a 45° angle through the middle section of the capillary.

Gases were introduced into the cell from lecture bottles mounted in a portable gas manifold unit with built-in gas purifiers (O₂ remover; 13X molecular sieve; Matheson) and mass flow controllers (Porter Instruments). Features of this XAS cell include small sample loadings (1-10 mg), low flow rates (1.3-13.4 mmol/h), and plug-flow hydrodynamics, as well as the ability to attain conversions and space velocities similar to those typical of laboratory tubular microreactors. The capillary microreactor can reach temperatures of ~973 K and pressures up to 1.0 MPa. It also provides efficient heat transfer and accurate temperature control and measurement. A thermocouple (0.5 mm outer diameter) inserted into the outlet side of the capillary using a metal T-union provides accurate temperature measurements and prevents the sample from being dislodged from the capillary by the flowing gas. Temperature uniformity was confirmed by measuring the temperature profile along the sample bed under conditions identical to those used for the *in situ* experiments. The typical temperature variation along the sample bed is within ± 0.5 K. During *in situ* measurements, the cell temperatures can be controlled within ± 0.5 K in either temperature-programmed or isothermal modes using a temperature controller (Series 982, Watlow). For the quench experiments described below, the capillary cell can be cooled to ambient temperature within a few seconds by simply sliding the heating block away from the capillary cell.

3.4. Measurements of X-ray absorption spectra, FTS rates and data analysis

Fe K-edge X-ray absorption spectra were measured at the Stanford Synchrotron Radiation Laboratory (SSRL) on a wiggler side-station (beamline 4-1). During these measurements, the storage ring was operated at 30-100 mA and 3.0 GeV. Two Si (111) crystals were used in the monochromator, which was detuned by 20% in order to eliminate harmonics from the monochromatic beam. Three N₂-filled ion chambers were used in order to measure the intensity of the X-ray beam incident on the sample (I₀), after the sample (I₁), and after a 5 μ Fe calibration foil (I₂). In this manner, the sample spectrum (I₀/I₁) and a reference spectrum (I₁/I₂) were obtained simultaneously. The most restrictive aperture along the beam path was the 0.2×12 mm slit within the hutch, which provided a resolution better than 2 eV at the Fe K-edge (7.112 keV) [30].

In order to achieve the required time resolution for spectrum measurements during temperature-programmed reduction and carburization in CO, a slow heating rate was used (0.017 K/s) and only the near-edge spectra were measured (6.900-7.350 keV; 120 s per spectrum). After isothermal exposure to synthesis gas for 8-14 h, the spectra were recorded in the full energy range (6.900-8.120 keV; 0.33 h per spectrum) in order to measure accurate spectra in both the near-edge and the fine structure regions.

X-ray absorption data were analyzed using WinXAS (version 1.2) [31]. Raw spectra were shifted in energy in order to align the first inflection point in the Fe foil calibration spectra with the known absorption energy of Fe metal (7.112 keV) [30]. Linear fits to the pre-edge region (6.900-7.100 keV) were subtracted from the spectra, and the spectra were normalized by a sixth-order polynomial fit of the post-edge region (7.240-8.120 keV). Principal component analysis [25] and linear combination methods [26] were used to calculate the relative abundance of the various Fe phases using the near-edge spectral region between 7.090 and 7.240 keV for each sample and for the Fe reference compounds.

The approach used to identify chemical species and to measure their relative abundance involves using linear combinations of the spectra from reference compounds, which include the structures thought to be present in the sample, in order to fit the experimental near-edge spectra of each sample. In the present case, it is difficult to anticipate which of the many possible Fe carbides, oxides, and oxycarbides may be formed during reactions with CO or with synthesis gas. Moreover, some species may be stable only under FT synthesis conditions. Thus, they are not necessarily available as structurally pure references. In view of this, we have used principal component analysis (PCA) in order to identify sets of spectral features that increase or diminish in synchrony as the spectral series progresses. These sets of features comprise contributions from the spectra of chemical species that change in concentration as the sample evolves under *in situ* treatments.

During the reduction and carburization of Fe oxides in CO or in synthesis gas, PCA identified three major components involved in the phase changes; these components were Fe_2O_3 , Fe_3O_4 and a carbide resembling Fe_3C . Therefore, *in situ* spectra were described using a linear combination of the near-edge spectra of these three reference compounds. Fe and FeO were specifically rejected by the PCA analysis, and their presence in linear combinations did not improve the spectral fits, suggesting that Fe and FeO do not occur as intermediates during reduction and carburization of Fe_2O_3 precursors. The target-transform application of the PCA led to an excellent fit quality to Fe_3C , using components generated from our catalyst spectra. The analysis of the fine structure, however, indicated that the carburized Fe catalyst did not achieve sufficient long-range order to be rigorously described as a specific crystallographic phase of Fe carbide; therefore, we refer to it only as FeC_x throughout the rest of this report.

Isothermal transient experiments to measure rates of product formation at FTS conditions similar to those for *in situ* XAS measurements, were carried out using on-line mass spectrometric analysis. A 0.2 g sample diluted with graphite (0.5 g, 180-250 μ , Alfa

AESAR, 99.998%) was loaded into a quartz microreactor and treated in He (Matheson, 99.999%, 0.268 mol/h) at temperatures up to 573 K and cooled under the same flow of He to 523 K. The He stream was switched to a flow of synthesis gas in Ar (H₂/CO/Ar=40/20/40 kPa, Matheson, 99.999%, total molar rate 0.268 mol/h) at 523 K. The resulting isothermal transients in the rate of evolution of several FTS products (CH₄, H₂O and CO₂, etc.) were measured as a function of time using on-line mass spectrometry (Leybold Inficon, Transpector Series). The rate of formation of CH₄ was used as a surrogate measure of the total FTS rates, because it can be measured accurately and changes with time on stream in parallel with the rate of formation of other hydrocarbon products. CH₄ selectivities change with time on stream by less than 5%; therefore, CH₄ formation rates accurately reflect the total rate of hydrocarbon synthesis.

3.5. Fe K-edge XANES of reference compounds

Figure 2 shows the near-edge spectra for the Fe₃C, FeO, Fe₃O₄, and Fe₂O₃ reference compounds. The absorption edge at \sim 7.120 keV is caused by the ejection of Fe *1s* electrons after absorption of a photon. The measured absorption edge energies for all reference compounds are listed in Table 1. These binding energies of *1s* electrons increase with increasing Fe valence. The weak pre-edge features in the spectra of Fe oxides reflect electronic transitions from *1s* atomic orbitals to unoccupied *p*-*d* hybrid molecular orbital final states; these transitions are dipole-forbidden in non-centrosymmetric structures.



Figure 2. Normalized Fe K-edge X-ray absorption spectra for Fe oxides and carbide.

Table 1. Absorption edge energies for Fe compounds with known structure and oxidation state.

Compound	Fe	Fe ₃ C	FeO	Fe ₃ O ₄	Fe ₂ O ₃
Binding Energy (keV)	7.112	7.112	7.119	7.123	7.124

3.6. In situ Fe K-edge XANES during reactions of Fe oxide precursors with CO

Figure 3 shows Fe near-edge spectra for the Fe_2O_3 sample during exposure to CO. No detectable changes in the spectra occurred below 450 K. Gradual changes occurred at temperatures between 450 K and 600 K, but the spectra then remained unchanged at higher temperatures. Thus, it appears that the formation of a stable compound is complete by ~600 K. A qualitative comparison of the reference spectra (Figure 2) with those of the samples after exposure to CO (Figure 3) suggests that structural transformations involve the intermediate formation of Fe₃O₄ and its ultimate conversion to FeC_x.



Figure 3. In situ Fe K-edge XANES spectra for Fe oxide in CO as a function of temperature. (1 mg precipitated Fe_2O_3 , CO flow rate=107 mol/g-atom Fe h)

A more quantitative assessment of these transformations is shown in Figure 4, which shows the relative abundances of the various phases required to describe the experimental near-edge spectra during reduction and carburization of Fe₂O₃ in CO. The reduction of Fe₂O₃ did not start until ~450 K. Above 450 K, the relative abundance of Fe₃O₄ increased, and then it decreased above 550 K, as Fe₃O₄ was converted to FeC_x. The concentration profiles for Fe₂O₃, Fe₃O₄, and FeC_x suggest that these transformations occurred in a sequential manner. The evidence for the rapid conversion of Fe₃O₄ to FeC_x (Figure 4) was provided by detailed temperature-programmed reduction and carburization studies of Fe₂O₃ in CO (Section 5) with concurrent measurements of the amounts of CO₂ evolved and of CO consumed using mass spectrometry. The reduction and carburization of Fe₂O₃ in synthesis gas (H₂/CO=2) followed the same reaction sequence as in CO, except that all structural changes occurred at slightly higher temperatures (~20 K).



Figure 4. In situ evolution of Fe_2O_3 in CO as a function of temperature. Fe_2O_3 (dot), Fe_3O_4 (square), FeC_x (triangle). (1 mg precipitated Fe_2O_3 , CO flow rate=107 mol/g-atom Fe h)

3.7. In situ Fe K-edge XANES of Fe-K-Cu oxide precursors in synthesis gas

Previous studies have shown that both K and Cu markedly increase FTS and water-gas shift reaction rates [1,4]. K also increases the olefin content and the molecular weight of FTS products [18,32]. The evolution of the Fe near-edge spectral features in Fe and Fe-K-Cu oxide precursors during exposure to synthesis gas was used in order to examine the effects of H_2 in modifying the structural details detected during carburization in CO, as

well as the role of the K and Cu on the rate and products of the transformation that occurs during the initial exposure of these oxide precursors to synthesis gas.

Figure 5 shows the near-edge spectra for Fe, Fe-Cu, Fe-K, and Fe-K-Cu oxide precursors measured *in situ* after contact with synthesis gas at 523 K for 5 h. The absorption edge energy was lower and the spectra resembled the Fe carbide spectrum (Figure 2) more closely when K or Cu was present in the sample. These effects of Cu or K were even stronger when both promoters were present.



Figure 5. In situ Fe K-edge spectra of Fe-K-Cu oxides in synthesis gas at 523 K for 5 h. (1 mg precipitated Fe_2O_3 , $H_2/CO=2$, synthesis gas flow rate=107 mol/g-atom Fe h).

3.8. *Effects of K and Cu on catalyst structure and on FTS rates*

The spectra of Fe, Fe-Cu, Fe-K, and Fe-K-Cu oxide precursors during exposure to synthesis gas at 523 K were described by linear combinations of the near-edge spectra of reference compounds. The structural evolution of unpromoted Fe₂O₃ as a function of time is shown in Figure 6. The Fe₃O₄ and FeC_x contributions approached constant values of ~70% and ~30%, respectively, after ~4 h. Carburization rates then decreased as the remaining Fe oxides became covered by a dense Fe carbide coating, which appears to inhibit the rate-determining oxygen diffusion step required for carburization processes. At 543 K, the FeC_x contribution increased to ~45% after 4 h, apparently because of faster oxygen diffusion at higher temperatures. Previous studies have suggested that the reduction and carburization (or nitridation) of transition-metal oxides are limited by the bulk diffusion of oxygen in the lattice of the corresponding oxide [33,34]. This was

inferred from the excellent agreement between the activation energies for the synthesis of transition-metal carbides or nitrides and those for the diffusion of oxygen in the oxides. The absence of Fe metal or FeO in the near-edge spectra of these samples confirms the rate-determining nature of oxygen diffusion steps. If the removal of oxygen atoms at crystallite surfaces or at oxide-carbide interfaces had occurred without the immediate availability of carbon to react with the resulting reduced species, nucleation of Fe metal and FeO crystallites would have occurred and such phases would have been detectable by X-ray absorption.



Figure 6. Phase evolution of Fe_2O_3 with time on stream after exposure to synthesis gas at 523 K (1 mg precipitated Fe_2O_3 , $H_2/CO=2$, synthesis gas flow rate=107 mol/g-atom Fe h).

Figure 7 shows the structural evolution of Fe-Cu oxide precursors (Cu/Fe = 0.01) during exposure to synthesis gas (H₂/CO=2) at 523 K for 14 h. These data show that Fe₂O₃ converts to Fe₃O₄, and subsequently to FeC_x more rapidly than for the pure Fe oxide samples (Figure 6). CuO reduces to Cu readily in H₂ at 523 K; once reduced, it provides sites for H₂ dissociation, which in turn lead to adsorbed hydrogen species that reduce Fe₂O₃ to Fe₃O₄ at lower temperatures than for unpromoted Fe₂O₃.

The ultimate extent of carburization after long contact times (8 h) was also higher for Fe-Cu oxides (~45%; Figure 7) than for unpromoted Fe oxide samples (~30%; Figure 6). The more complete carburization of Cu-containing Fe₂O₃ precursors would be unexpected without changes in the size of the crystalline structures, because carburization rates become ultimately controlled by the rate of oxygen diffusion. Oxygen diffusion rates cannot be influenced by the mere presence of Cu metal sites at the surface of such structures. Instead, it appears that the presence of Cu metal species at Fe₂O₃ surfaces leads to the simultaneous formation of a larger number of Fe_3O_4 or FeC_x nuclei, which then grow to consume a large fraction of the remaining Fe_2O_3 starting material. In contrast, the nucleation of these phases on pure Fe_2O_3 surfaces is likely to proceed through the formation of a uniform shrinking core of FeO_x encapsulated by a growing FeC_x layer or at least via the initial formation of a smaller number of nuclei. Our parallel XAS studies of the structural evolution of Fe_2O_3 during initial exposure to synthesis gas discussed in Section 5 have shown that Fe_2O_3 , once reduced to Fe_3O_4 , readily reduces and carburizes to FeC_x , at least in the near-surface regions, as indicated by the concurrent formation of Fe_3O_4 and FeC_x and the rapid attainment of steady-state FTS reaction rates.

The conversion of Fe₃O₄ to Fe₃C is accompanied by a substantial decrease in crystallite volume, because of the lower density of Fe₃O₄ (5.2 g/cm³) compared with FeC_x (7.7 g/cm³ for Fe₃C) [35]. The dense Fe carbide layers formed at pure Fe₃O₄ surfaces apparently provide an effective barrier to the diffusion of oxygen. In addition, the carburization of the shrinking oxide core cannot continue to completion without the nucleation of a void or the shattering of the carbide shell because of the density mismatch between the two phases. This shrinking core type of reduction is similar to the model proposed in previous studies, for the reduction behavior of transition-metal oxides [36].



Figure 7. Phase evolution of Fe-Cu oxide with time on stream after exposure to synthesis gas at 523 K (1 mg precipitated Fe₂O₃, Cu/Fe=0.01, H₂/CO=2, synthesis gas flow rate=107 mol/g-atom Fe h).

The simultaneous formation of a larger number of FeC_x nuclei on Cu-promoted Fe_2O_3 leads to the growth of smaller carbide regions, which avoid both the longer diffusion

paths and the void nucleation or shell breakup required in pure Fe₃O₄. This leads, in turn, to more complete carburization and to smaller FeC_x structures, with a higher surface area and a smaller oxygen diffusion distance, and with a larger density of sites for CO activation. The apparent correlation between FTS rates and the extent of carburization is not causal. Instead, both reflect the smaller size of the active carbide structures that form during FTS when Cu is present on the Fe₂O₃ precursors. This finding resolves the puzzling observed correlation between the extent of carburization and FTS rates, even when the formation of only a few near-surface layers of FeC_x is apparently sufficient to achieve steady-state FTS reaction rates. Although only the incipient conversion of Fe₃O₄ to FeC_x is required for Fe₂O₃ or Cu-containing Fe₂O₃ precursors to become active in FTS reactions, the smaller and more extensively carburized structures formed when Cu is present lead to the higher FTS rates observed on Cu-containing Fe₂O₃ precursors than on pure (Section 5). As we describe immediately below, K has a similar effect as Cu on FTS rates and on the rate and extent of carburization of Fe₂O₃ precursors.



Figure 8. Phase evolution of Fe-K oxide with time on stream after exposure to synthesis gas at 523 K (1 mg precipitated Fe₂O₃, K/Fe=0.02, H₂/CO=2, synthesis gas flow rate=107 mol/g-atom Fe h).

Fe₂O₃ precursors modified by K (K/Fe = 0.02) reduce and carburize even more rapidly than Cu-promoted Fe₂O₃ (Figure 8), consistent with our reduction and carburization kinetic measurements on these samples using both CO and H₂/CO reactants. The similar reduction-carburization promotion introduced by K in both CO and H₂/CO suggests that the role of K is to increase the rate of CO activation on Fe₂O₃ surfaces (Section 5). In contrast, the effect of Cu is most evident when H₂ is also present with CO, because of the

role of Cu surfaces as H_2 dissociation sites. The presence of dispersed K species, probably as carbonates, also leads to the rapid incipient formation of multiple Fe₃O₄ and FeC_x nuclei and to the ultimate formation of smaller crystallites with carbided surfaces. In this manner, we reconcile the similar directional effects of Cu and K on FTS reaction rates and the apparent contradiction between the positive effects of the higher extents of carburization induced by K and Cu and the rate increase for FTS reactions, which appear to require only the near-surface conversion of Fe oxides to FeC_x (Section 5). During the incipient conversion of Fe oxides to carbides upon contact with synthesis gas, CH₄ formation rates initially increased rapidly as a layer of FeC_x formed, and then they increased at a slower rate as the surface area of the FeC_x structures continued to increase gradually with increasing extent of carburization (Section 5). Ultimately both the FeC_x content and the FTS rates reached their respective steady-state values.



Figure 9. Phase evolution of Fe-K-Cu oxide with time on stream after exposure to synthesis gas at 523 K (1 mg precipitated Fe₂O₃, K/Fe=0.02, Cu/Fe=0.01, H₂/CO=2, synthesis gas flow rate=107 mol/g-atom Fe h).

Reduction and carburization processes were even faster when both Cu and K were present (Figure 9), than when samples were promoted by either K or Cu (Figures 7 and 8). Apparently, the presence of a larger number of "activation sites" provided by the combined contributions of both Cu and K at Fe_2O_3 surfaces, leads to an even larger number of incipient nucleation points than when only one of these promoters is present. The resulting higher density of FeC_x nuclei ultimately grow into even smaller crystallites, which provide a larger number of sites for CO and H₂ activation, leading to even faster

reduction and carburization, shorter diffusion distances required for complete carburization, and higher FTS reaction rates than on singly-promoted samples.

3.9. *CO chemisorption and surface area measurements*

Precipitated Fe oxides (0.2 g; diluted with graphite) were treated in flowing He (0.268 mol/h) up to 573 K and then cooled down to 523 K. The He stream was switched to a $H_2/CO/Ar$ stream (40/20/40 kPa; 0.268 mol/h) at 523 K for 1 h and flushed with He (0.268 mol/h) at this temperature for 1 h in order to remove any reversibly adsorbed species. The samples were then cooled to RT before CO chemisorption and BET surface area measurements.

Two sets of temperature-programmed desorption (TPD) experiments were performed. In one experiment, a flow of CO/Ar stream (20/80 kPa; 0.268 mol/h) was passed through the sample for 0.5 h. Physisorbed species were removed by flushing the sample using Ar (0.268 mol/h) for 0.5 h. The amount of carbon species CO_x (CO+CO₂) evolved as the samples were heated in Ar flow (0.268 mol/h) at 0.167 K/s to 1000 K was measured by mass spectrometry. Another set of experiments followed the same protocol but without a CO chemisorption after FTS reaction. The difference between the peak areas under these two TPD curves was taken as a measure of the availability of active sites capable of chemisorbing CO reversibly at FTS temperatures. This method allows us to subtract from the total CO evolved those CO species formed from irreversibly adsorbed carbon species during FTS, as well as the CO_x produced from reaction of FeC_x with residual Fe oxides at temperatures much higher than those of the FTS reaction.

BET surface area measurements were carried out on samples after FTS reaction at 523 K and quenching to RT by passivating catalyst samples in flowing 1 % O_2 /He at RT. N_2 physisorption measurements were performed at its normal boiling point (77 K) using an Autosorb 6 system (Quantachrome, Inc.). Surface areas were calculated using the BET method.

The formation of smaller crystallites and of a higher density of active sites when K and/or Cu are present during activation is consistent with measurements of the BET surface area and the CO chemisorption capacity after FTS reactions for 1 h (H₂/CO=2, 523 K; Table 2). BET surface areas were higher on samples containing K and/or Cu, consistent with the formation of active catalysts containing smaller crystallites. CO chemisorption uptakes increased with increasing BET surface area. The site density available for CO chemisorption was higher on K- or Cu-containing samples. Chemisorption uptakes reached their highest value for samples prepared from the Fe-K-Cu oxide precursors. These values correspond to about one monolayer (~15 CO/nm²) of chemisorbed CO. This suggests that K and/or Cu promote the formation of smaller Fe carbide crystallites, which in turn increase the number of sites available for CO adsorption/dissociation and consequently for the initial reduction and carburization and for steady-state FTS turnovers.

Oxide precursor	Fe	Fe-Cu	Fe-K	Fe-K-Cu
Surface area (m^2/g)	13	17	18	23
Amount of CO _x desorbed before CO chemisorption (mmol/g-atom Fe)	12.2	14.1	23.4	56.9
Amount of CO _x desorbed after CO chemisorption (mmol/g-atom Fe)	20.3	27.9	40.9	95.7
Amount of CO chemisorbed (mmol/g-atom Fe)	8.1	13.8	17.5	38.8
CO chemisorption site density (molecule /nm ²)	5	6	7	13
FeC _x concentration ^a (atom %)	28.8	32.4	60.8	88.0
CH ₄ formation rate ^b (mmol/g-atom Fe s)	0.061	0.070	0.11	0.19

Table 2. The surface area and CO chemisorption results after 1 h FTS reactions; Fe carbide concentrations obtained from *in situ* XAS, and CH₄ formation rates from transient experiments, after 5 h FTS reactions.

^aFeC_x concentration measured after exposure to synthesis gas at 523 K for 5 h (1 mg precipitated Fe₂O₃, K/Fe=0.02, Cu/Fe=0.01, H₂/CO=2, synthesis gas flow rate=107 mol/g-atom Fe h).

^bCH₄ formation rates measured after exposure to synthesis gas at 523 K for 5 h (0.2 g precipitated Fe₂O₃, K/Fe=0.02, Cu/Fe=0.01, H₂/CO=2, synthesis gas flow rate=64.3 mol/g-atom Fe h).

In order to explore the relation between the structure of the working catalysts and their catalytic performance, FTS rates were measured during exposure to synthesis gas at the same conditions (H₂/CO=2, 523 K) as the XAS experiments. Figure 10 shows the Fe carbide concentrations obtained from *in situ* XAS and the CH₄ formation rates measured in the corresponding transient FTS experiments on unpromoted precipitated Fe₂O₃ as a function of time. The rate of formation of CH₄ increased with increasing FeC_x content. This indicates that Fe carbide (FeC_x) is the stable Fe phase during FTS and provides the active surfaces required for FTS turnovers. On samples containing K and/or Cu (Table 2), FTS rates increased proportionally with the observed increase in FeC_x content (at long contact times) and in CO chemisorption uptakes. This supports the conclusion that the effect of K and Cu on the structure of catalysts is to provide a larger number of active Fe carbide sites for FTS reactions. The chemical promotion effects by K and/or Cu do not appear to be necessary in order to account for the increase in reaction rates observed

when Fe_2O_3 precursors are impregnated with these components. Cu does not influence the selectivity; the effects of K on FTS selectivity will be discussed in the next Section.



Figure 10. Fe carbide concentration (dots) obtained from XAS (H₂/CO=2, 523 K, synthesis gas flow rate=107 mol/g-atom Fe h), and CH₄ formation rate as function of time on unpromoted precipitated Fe₂O₃ (H₂/CO=2, 523 K, synthesis gas flow rate=64.3 mol/g-atom Fe h).

Clearly, K and Cu lead to the formation of FeC_x structures with higher specific surface area and smaller size. A consequence of their smaller size is their more complete carburization, which is not the direct cause of the higher FTS rates observed in the presence of K and/or Cu. Their more complete carburization reflects the shorter diffusion paths for lattice oxygen species in the smaller crystallites, but the attainment of steadystate FTS rates appears to require only the formation of FeC_x near surface layers, the FTS activity of which does not depend on the existence or chemical identity of a separate oxide phase residing within the carbide shell.

4. Effect of Zn, Cu and K on the reduction/carburization and catalytic performance of Fe catalysts

4.1. Methodology

We examine here a series of co-precipitated Fe and Zn oxides containing Zn, Cu and K (Zn/Fe=0-0.4, K/Fe=0-0.04, Cu/Fe=0-0.02; atomic ratios) in order to probe the roles of these additives on the structure, reduction/carburization behavior, and catalytic properties of Fe oxides. The surface area, bulk structure, and reduction and carburization behavior were systematically investigated using BET surface area measurements, X-ray diffraction (XRD) and temperature-programmed reaction (TPR) studies. In parallel, steady-state FTS rates and selectivities were measured as a function of the Zn, K and Cu contents at typical FTS conditions (493 K, 3.16 MPa) using a tubular reactor with plug-flow hydrodynamics in order to relate the observed catalytic promotion to the active structures formed during activation of the oxide precursors in H_2/CO mixtures.

4.2. Crystal structure

Powder X-ray diffraction (XRD) measurements were carried out using a Siemens Diffractometer D-5000 and Cu K α radiation ($\lambda = 1.5406$ Å). X-ray powder diffraction patterns for Fe₂O₃-Zn precursors with Zn/Fe atomic ratios of 0-0.4 are shown in Figure 11. These diffraction data indicate that rhombohedral hematite (Fe₂O₃) with a corundumtype structure, forms in samples with Zn/Fe < 0.2, while a $ZnFe_2O_4$ phase with a cubic franklinite spinel-type structure appears along with hematite at higher Zn/Fe ratios. Fe₂O₃ and ZnFe₂O₄ co-exist at intermediate Fe/Zn ratios. ZnFe₂O₄ is the only detectable phase in the sample with the highest Zn/Fe ratio (0.4); its broad diffraction peaks reflect the Zndeficient nature of the Fe-Zn spinel structure, which requires a Zn/Fe ratio of 0.5 for the formation of stoichiometric ZnFe₂O₄. Precipitated Fe-Zn oxides appear to be present in the form of a mixture of Fe_2O_3 and $ZnFe_2O_4$. The only Zn-containing phase is $ZnFe_2O_4$, and it acts as a textural promoter that increases the surface area of Fe₂O₃-Zn precursors, as shown in the next section. At low Zn concentrations (Figure 11; patterns a-c), Zn is detected only as small ZnFe₂O₄ crystallites, which appear to inhibit the sintering of Fe₂O₃ at high temperatures (623-673 K). At higher Zn contents (Figure 11; patterns d and e), it is likely that ZnFe₂O₄ crystallites provide a matrix for the isolation of individual Fe₂O₃ crystallites. Zn also titrates Fe by forming ZnFe₂O₄, a less reducible compound than Fe_2O_3 ; this tends to weaken the structural promotion by Zn by preventing the reduction of some of the Fe and its contribution to the pool of active sites. Thus, intermediate Zn/Fe ratios are likely to lead to optimum catalytic performance. The impregnation of potassium and copper and the subsequent treatment in air did not influence the crystalline phases detected by X-ray diffraction. This shows that Fe-Zn oxide structures, once formed, remain stable during subsequent aqueous impregnation and thermal treatment.



Figure 11. X-ray diffraction patterns of Fe_2O_3 -Zn samples with different Zn/Fe ratios. (a) 0, (b) 0.05, (c) 0.1, (d) 0.2, and (e) 0.4.

4.3. Surface areas of Fe₂O₃-Zn-K-Cu oxide precursors

The textural promotion effects of $ZnFe_2O_4$ on the surface area of Fe oxide precursors were examined by N₂ physisorption measurements for K- and/or Cu-promoted Fe₂O₃-Zn samples. BET surface areas were measured using N₂ physisorption at its normal boiling point, after evacuating the samples at 393 K for 3 h. The BET surface area of Fe₂O₃-Zn-K-Cu increased monotonically with increasing Zn/Fe ratio (Figure 12). The surface area for the sample with a Zn/Fe ratio of 0.4 is almost twice that for Zn-free Fe₂O₃ (96 vs 53 m²g⁻¹). The addition of K and/or Cu to Fe-Zn oxides did not influence surface areas, suggesting that K and Cu reside at Fe oxide crystallite surfaces and that they do not influence the structure or the dispersion of the previously established Fe oxide phase. These data suggest that Zn, as a ZnFe₂O₄ phase, inhibits the sintering of Fe oxides, by keeping Fe oxides from migrating, and hence preventing sintering during treatments at high temperatures or by providing anchoring or nucleation sites for Fe oxides during precipitation or thermal treatment. However, it is not clear if this increase in surface area alone accounts for the higher FTS rates observed on Zn-promoted samples [16] or what the optimum Zn/Fe ratio is; therefore, the catalytic behavior of on K- and Cu-promoted Fe oxides with different Zn/Fe ratios was examined in order to establish a suitable Zn concentration for maximum FTS reaction rates.



Figure 12. BET Surface areas of K- and/or Cu-promoted Fe₂O₃-Zn (K/Fe=0.02; Cu/Fe=0.01) samples as a function of Zn/Fe ratios: (•) Fe₂O₃-Zn-K₂-Cu₁ sample, (\bigcirc) Fe₂O₃-Zn-Cu₁ sample, (\bigcirc) Fe₂O₃-Zn-Cu₁ sample, (\bigcirc) Fe₂O₃-Zn-K₂ sample.

4.4. Zn promotion effects on Fischer-Tropsch Synthesis rates and selectivity

Steady-state FTS rates and selectivities (493 K, 3.16 MPa) on Fe₂O₃-Zn-K-Cu catalysts with a constant K and Cu content (K/Fe=0.02, Cu/Fe=0.01) but different Zn contents, were determined in a fixed-bed single-pass flow reactor with plug-flow hydrodynamics. This reactor was held within a three-zone furnace controlled by three temperature controllers (Watlow, Series 982 and 988). The tubular reactors were constructed of stainless steel (SS 304, 1.27 cm outer diameter and 1 cm inner diameter). Axial temperature profiles were measured using a type K movable thermocouple contained within a 0.32 cm thermowell. The temperatures at all bed positions were within ± 0.5 K of the average bed temperature. All lines after the reactor were kept at 433-553 K and a vessel placed immediately after the reactor was held at 408 K to collect liquid products. Another vessel was placed at ambient pressure and temperature after a sampling valve,

which collected gaseous components (at ambient pressure and 523 K) for injection into a gas chromatograph.

The catalysts (100-180 μ , 0.4 g) were diluted with 11 g of quartz granules (100-180 μ) in order to avoid temperature gradients. These quartz granules were washed with concentrated nitric acid and treated in air at 973 K before use. The Fe catalysts were activated using flowing synthesis gas (H₂/CO=2) at 0.1 MPa by increasing the temperature from 298 K to 423 K at a rate of 0.167 K/s and from 423 K to 543 K at 0.017 K/s. The catalyst was held at 543 K for 1 h, following which the reactor was set to the desired operating conditions.

Sample	Zn/Fe=0	Zn/Fe=0.1	Zn/Fe=0.4	
Surface area (m ² /g)	53	65	96	
CO conversion rate (mol CO/h.g-at.Fe)	1.52	2.40	2.63	
CO ₂ formation rate (mol CO/h.g-at.Fe)	0.19	0.30	0.21	
Hydrocarbon formation rate (mol CO/h.g-at.Fe)	1.33	2.10	2.52	
CO ₂ selectivity (%)	12.3	12.3	7.6	
CH_4 selectivity (%) ^a	1.7	1.8	2.3	
C_{5^+} selectivity (%) ^a	86.6	87.6	85.6	
$1-C_5H_{10}/n-C_5H_{12}$ ratio	1.9	1.8	2.0	

Table 3. Effect of Zn loading on the surface area and the steady state performance of a Fe_2O_3 -K-Cu catalyst (K/Fe=0.02, Cu/Fe=0.01; H₂/CO=2, 493 K, 3.16 MPa, CO conversion=16-18%).

^a CH_4 and C_{5+} selectivities are reported on a CO_2 -free basis.

A H₂/CO/N₂ mixture with N₂ being the internal standard (0.62/0.31/0.07 mole; Praxair: 99.9% H₂, 99.9% CO, 99.99% N₂) was used as the reactant. This reactant mixture was purified using activated carbon (Sorb-Tech RL-13) to remove metal carbonyls and a molecular sieve trap (Matheson, Model 452A) to remove water. All flows were metered using electronic mass flow controllers (Porter, Model 201-AFASVCAA). Reactant and product streams were analyzed on-line using a gas chromatograph (Hewlett Packard, Model 5890 Series II) equipped with a 10-port sampling valve and two sample loops. The contents of one sample loop were injected into a cross-linked methyl silicone capillary column (HP-1, 50 m × 0.32 mm; 1.05 μ film). The contents of the other loop were

injected into a Porapak Q (15.2 cm \times 0.318 cm) packed column. Ar, N₂, CO, CO₂, and light hydrocarbons eluting from the packed column were analyzed using a thermal conductivity detector (TCD). A flame ionization detector (FID) was used to analyze all hydrocarbon products as they eluted from the capillary column. The concentrations of all hydrocarbons up to C₁₅ were measured using these chromatographic protocols.

These results are shown in Table 3 at similar CO conversion levels. The presence of Zn at a Zn/Fe atomic ratio of 0.1 increased CO conversion rates (from 1.5 to 2.4 mol CO/h.g-at. Fe), but additional increases in the Zn/Fe ratio from 0.1 to 0.4 did not lead to higher FTS rates. The additional increase in surface area brought about by these higher Zn contents occurs at the expense of the reaction of some of the Fe oxide precursor to form less reducible ZnFe₂O₄. FTS selectivities (CH₄, C₅₊, and *1*-pentene/*n*-pentane ratios) were almost unchanged by the presence of Zn. It appears that Zn acts only as a textural promoter and that a Zn/Fe atomic ratio of ~0.1 provides an optimum balance between a higher surface area and a decrease in the fraction of the Fe that is activated during contact with synthesis gas at FTS conditions. Therefore, a Zn/Fe atomic ratio of 0.1 was chosen to study the effects of Cu and K on FTS reaction rates and selectivities.

4.5. Reduction kinetics of Fe_2O_3 -Zn-K-Cu precursors in H_2

The rates of reduction and carburization of K- and/or Cu-promoted Fe₂O₃-Zn were measured by using temperature-programmed reaction (TPR) methods with H₂ or CO as the reactant. Samples (0.2 g) were placed in a quartz cell (10 mm i.d.) and first treated in 20% O₂ in Ar (0.268 mol/h) to 673 K at 0.33 K/s, held at 673 K for 900 s, and then cooled to ambient temperature in Ar. The flow was then switched to 20% H₂ or 20% CO in Ar (0.268 mol/h) and the reactor temperature was increased to 1000 K at 0.167 K/s. The concentrations of reactants and products were measured using a mass spectrometer (Leybold Inficon Instruments Co., Inc.) equipped with a differentially pumped sampling system.

Figure 13 shows the rates of removal of lattice oxygen atoms during treatment of Fe_2O_3 -Zn-K-Cu precursors using H₂ as the reductant. The areas under these reduction peaks were calibrated using CuO. The respective amounts of oxygen in the two reduction peaks in Figure 13 show that Fe₂O₃ reduces in two steps. Fe₃O₄ is first formed and then reduced to form Fe metal. The presence of Cu in Fe-Zn oxides (Zn/Fe=0.1) causes the reduction of Fe₂O₃ to Fe₃O₄ to occur at temperatures ~140 K lower than in Cu-free samples (Figure 13b); these reduction processes occur at temperatures identical to those required for the reduction of CuO to Cu metal (Figure 13a). As CuO reduces, Cu crystallites nucleate and provide H₂ dissociation sites, which in turn lead to reactive hydrogen species capable of reducing Fe oxides at relatively low temperatures. Potassium, shown to be present as a carbonate by X-ray absorption spectroscopy [37], does not influence the reduction of Fe₂O₃, but it weakly inhibits the reduction of Fe₃O₄ to Fe metal. When both Cu and K are present, the reduction profile resembles that for Fe₂O₃-Zn-Cu; Fe₂O₃ reduces at temperatures characteristic of CuO reduction (~470 K), except for a small fraction of the Fe₂O₃, which is not affected by Cu, apparently because of inefficient contact between some of the Fe₂O₃ precursor and the CuO promoter. The presence of Cu or K does not strongly influence the reduction of Fe₃O₄ to Fe, because thermodynamics and the

nucleation of a new crystal structure, and not H_2 dissociation steps, control reduction rates at these higher temperatures [36,38]. The effects of Cu on the kinetics of removal of lattice oxygen from Fe-Zn oxides suggest that Cu increases the initial rate of nucleation of reduced Fe oxide phases. Consequently, a larger number of nuclei become available for crystallization of reduced FeO_x and FeC_x crystallites; as a result higher FTS rates would be expected when precursor activation occurs in synthesis gas in the presence of these promoters.



Figure 13. Oxygen removal rates of Fe_2O_3 -Zn-K-Cu (Zn/Fe=0.1) in H₂. (a) CuO, (b) Fe_2O_3 -Zn (c) Fe_2O_3 -Zn-Cu₁, (d) Fe_2O_3 -Zn-K₂, (e) Fe_2O_3 -Zn-K₂-Cu₁ (0.2 g sample, 0.167 K/s ramping rate, 20% H₂/Ar, 0.268 mol/h flow rate).

4.6. Reduction and carburization kinetics of Fe₂O₃-Zn-K-Cu in CO

The rates of oxygen removal and of carbon introduction using CO were measured as a function of temperature on Fe_2O_3 -Zn-K-Cu oxides by monitoring the concentrations of CO and CO₂ in the effluent stream. Two general stoichiometric reactions are involved in the carburization of Fe oxides. The removal of lattice oxygen occurs via the stoichiometry given by:

$$Fe_xO + CO = Fe_x + CO_2$$

Initially Fe oxides reduce to form CO_2 and a Fe center with valence lower than in Fe₂O₃. In a sequential or alternate step, CO carburizes Fe oxides to form CO_2 and Fe carbides:

$$Fe_xO + 2CO = Fe_xC + CO_2$$

In this step, oxygen removal and carbon deposition occur concurrently. The excess amount of CO consumed relative to that of CO_2 produced provides a measure of the extent of carbon deposited. The different CO and CO_2 stoichiometries associated with these two steps, allows to decouple oxygen removal and carbon deposition steps using the following equations:

$$R_0 = Oxygen Removal Rate = 2 R_{CO2} - R_{CO}$$
 (1)

$$R_{\rm C}$$
 = Carbon Introduction Rate = $R_{\rm CO}$ - $R_{\rm CO2}$ (2)

where, R_{CO2} is the rate of formation of the CO₂ product and R_{CO} is the rate of consumption of the CO reactant. We note that this approach remains rigorous even if the actual reactions do not proceed as written, because equations (1) and (2) merely reflect an oxygen and a carbon balance, respectively. Together with the structures detected by X-ray diffraction at various stages during reaction with CO, this approach probes the temperatures required, the rates of reduction and carburization, as well as the structure and stoichiometry of the carbides formed.



Figure 14. Rates of CO consumption (solid line) and CO₂ formation (dashed line) for the Fe_2O_3 -Zn-K₂-Cu₁ sample (Zn/Fe=0.1) during the reduction and carburization in CO (0.2 g sample, 0.167 K/s ramping rate, 20% CO/Ar, 0.268 mol/h flow rate). Temperatures (dotted line) at which reactions were terminated for XRD measurements (Figure 15).

CO consumption and CO₂ formation rates are shown in Figure 14 for Fe₂O₃-Zn-K-Cu samples as a function of temperature. The stoichiometries for oxygen removal and carbon introduction measured from the areas under these peaks indicate that the reduction-carburization of Fe oxides proceeds in two sequential steps. Fe₂O₃ first reduces to Fe₃O₄ at ~543 K; then, Fe₃O₄ concurrently reduces and carburizes to a mixture of Fe_{2.5}C and Fe₃C in the 543-723 K temperature range. Above 723 K, CO disproportionation occurs via the Boudouard reaction, with the formation of excess amorphous carbon; this amorphous carbon is not present in the carbide structures prevalent at temperatures below 723 K. X-ray diffraction patterns at various stages in these processes (Figure 15) confirmed the sequential nature of the structural evolution from Fe₂O₃ to Fe₃O₄ and then to mixtures of Fe_{2.5}C and Fe₃C. Figure 6 shows oxygen removal and carbon introduction rates as a function of temperature for Fe₂O₃-Zn-K-Cu samples using CO as the reactant. The areas under the oxygen removal peaks for Fe₂O₃-Zn confirm that Fe₂O₃ is first converted to Fe₃O₄ without any detectable carburization.



Figure 15. X-ray diffraction patterns showing the phase evolution of the Fe_2O_3 -Zn-K₂-Cu₁ oxide (Zn/Fe=0.1) during the reduction and carburization in CO at (a) 560 K, (b) 730 K, and (c) >730 K (0.2 g sample, 0.167 K/s ramping rate, 20% CO/Ar, 0.268 mol/h flow rate).

The temperatures required and the areas under the carbon introduction peaks show that reduced Fe_3O_4 species are then concurrently carburized to form FeC_x (Figure 16a). The addition of K and/or Cu to Fe_2O_3 did not influence this reduction-carburization sequence,

but the reduction-carburization rates increased and the required temperatures decreased when these promoters were present (Figure 16b-d). Cu increased oxygen removal rates and decreased the temperature required for the reduction and concurrent carburization of Fe₃O₄ by ~50 K. This effect of Cu on reduction rates was weaker than that observed when H₂ was used as the reductant, apparently as a result of the slower activation of CO relative to H₂ on Cu metal surfaces. The addition of K to Fe₂O₃ shifted the oxygen removal peak to higher temperatures (Figure 16c), but the rate of incipient carburization, indicated by the low-temperature shoulder in the carbon introduction peak, was slightly lower than on the unpromoted Fe oxide (Figure 16a). This may merely reflect a catalytic effect of K-promoted Fe oxides on CO activation rates or just the faster nucleation of FeC_x crystallites on oxide surfaces promoted with K carbonate. When both K and Cu were present in the catalyst, the combined effect of Cu in promoting the oxygen removal and K in CO activation leads to the highest reduction/carburization and Fe carbide nucleation rates, as indicated by the markedly lowered temperatures required for oxygen removal and carbon introduction (Figure 16d).



Figure 16. Oxygen removal and carbon introduction rates for the Fe_2O_3 -Zn-K-Cu (Zn/Fe=0.1) samples in CO. (a) Fe_2O_3 -Zn (b) Fe_2O_3 -Zn-Cu₁, (c) Fe_2O_3 -Zn-K₂, (d) Fe_2O_3 -Zn-K₂-Cu₁ (0.2 g sample, 0.167 K/s ramping rate, 20% CO/Ar, 0.268 mol/h flow rate)

In summary, K and Cu increased the rates of reduction and carburization of Fe-Zn oxide precursors when CO is used as the reactant. These faster rates of nucleation reflect a larger number of nuclei, which ultimately lead to smaller crystallites and to higher catalytic surface areas as determined by *in situ* X-ray absorption measurements shown in Section 3. These promotional effects of K and Cu, which appear to be mostly textural in nature, are confirmed by the FTS catalytic data described in the next section.

4.7. Effects of K and Cu on Fischer-Tropsch Synthesis rate and selectivity

The promotional effects of Cu and K on the behavior of Fe-Zn FTS catalysts were examined using a tubular reactor with plug-flow hydrodynamics. Fe₂O₃-ZnO catalysts (Zn/Fe=0.1) with varying K (K/Fe=0, 0.02 and 0.04) and Cu (Cu/Fe=0, 0.01, 0.02) contents were used to convert H₂/CO mixtures at 493 K and 3.16 MPa. FTS rates and selectivities are shown in Table 4.

Table 4. Steady state performance of Fe_2O_3 -Zn catalysts (Zn/Fe=0.1) with different loadings of K and Cu (H₂/CO=2, 493 K, 3.16 MPa, CO conversion = 14-18%).

K/Ea atomia ratio						
(×100)	0	0	2	2	2	4
Cu/Fe atomic ratio (×100)	0	1	0	1	2	1
CO conversion rate (mol CO/h.g-at.Fe)	0.70	0.87	1.23	2.40	2.43	2.49
CO ₂ formation rate (mol CO/h.g-at.Fe)	0.02	0.06	0.10	0.30	0.32	0.30
Hydrocarbon formation rate (mol CO/h.g-at.Fe)	0.68	0.81	1.13	2.10	2.11	2.19
CO ₂ selectivity (%)	2.3	6.5	8.5	12.3	12.9	12.1
CH_4 selectivity (%) ^a	4.8	10.2	1.8	1.8	2.0	2.5
C_{5^+} selectivity (%) ^a	81.9	62.1	87.5	87.6	86.7	85.2
<i>1</i> -C ₅ H ₁₀ / <i>n</i> -C ₅ H ₁₂ ratio	1.9	1.7	1.8	1.8	1.8	2.0
<i>1</i> -C ₁₀ H ₂₀ / <i>n</i> -C ₁₀ H ₂₂ ratio	0.4	0.4	1.7	1.8	1.7	1.7

^a CH_4 and C_{5+} selectivities are reported on a CO_2 -free basis.

CO conversion rates increased with K (K/Fe=0.02) or Cu (Cu/Fe=0.01) addition, suggesting that the promotion of carburization and reduction rates by these species led to either a larger number of active sites or to sites with a higher intrinsic activity. These rates were higher on the sample containing both K and Cu (Fe₂O₃-Zn-K₂-Cu₁) than on Cu-promoted (Fe₂O₃-Zn-Cu₁), K-promoted (Fe₂O₃-Zn-K₂), or unpromoted (Fe₂O₃-Zn) catalysts. The effects of K and Cu on the doubly promoted sample are nearly additive, suggesting an almost independent effect of each promoter. The previously reported decrease in FTS rates with increasing K content on Fe-Si oxide precursors [18], was not observed in catalysts made from Fe-Zn precursors, possibly because of the higher surface of the precursors or the more dispersed nature of the promoter in the latter samples. For Fe-Zn oxide precursors, no detectable changes in FTS rates or selectivities were observed upon increasing the atomic K/Fe ratio above 0.02 (Table 2). Similarly, an increase in Cu/Fe atomic ratios from 0.01 to 0.02 did not influence reaction rates or product selectivities (Table 2). Thus, a Cu/Fe ratio of 0.01 and a K/Fe ratio of 0.02 led to optimum FTS catalytic properties. It appears that the surface density of promoters or the extent to which they contact the Fe oxide precursors does not continue to increase as the Cu or K contents increased above a threshold value. This threshold value is most rigorously expressed as a promoter surface density and it corresponds to $\sim 1 \text{ Cu/nm}^2$ and $\sim 2 \text{ K/nm}^2$.

Hydrocarbon formation rates (in mol CO converted/h.g-at. Fe) are shown in Figure 17 for the various promoted Fe_2O_3 -ZnO catalysts as a function of CO conversion. The effects of increasing CO conversion were similar on all catalysts, suggesting that these catalysts show similar kinetic dependences on reactant and product concentrations.



Figure 17. Hydrocarbon formation rates on Fe₂O₃-Zn (•), Fe₂O₃-Zn-Cu₁ (\blacktriangle), Fe₂O₃-Zn-K₂(\blacklozenge), and Fe₂O₃-Zn-K₂-Cu₁ (\blacksquare) catalysts (493 K, 3.16 MPa, H₂/CO=2).

CO₂ selectivities are shown as a function of CO conversion in Figure 18 and compared at a similar CO conversion value (14-18%) in Table 4. CO₂ selectivities increased with increasing CO conversion on all four catalysts (Figure 18); they were higher on Fe₂O₃-ZnO promoted by both Cu and K than on unpromoted or singly promoted samples at all conversion levels. H₂O, which forms as a primary product during FTS reactions on Fe catalysts, reacts with CO to give CO₂ via secondary water gas shift reactions. The local slope of the curves in Figure 18 reflect the contributions from secondary reactions (predominately water gas shift), while CO₂ selectivities extrapolated to zero conversion reflect the relative rates at which chemisorbed oxygen, formed in CO activation steps, is removed by adsorbed CO (as CO_2) or by adsorbed hydrogen (as H_2O). The slopes of the CO₂ selectivity curves in Figure 18 are similar for K-promoted Fe₂O₃-Zn-Cu₁ and Fe₂O₃-Zn catalysts, consistent with similar secondary water gas shift rates. Fe₂O₃-Zn and Fe₂O₃-Zn-Cu₁ catalysts without K resemble each other in their secondary water gas shift rates, which are lower than those measured on K-containing samples. This lack of effect of Cu is unexpected, in view of the high water gas shift rates reported on Cu-based catalysts [39]. The presence of Cu predominately influences the intrinsic oxygen removal selectivity by promoting the removal of oxygen using CO. On the other hand, Fe₂O₃-Zn-K₂ and Fe₂O₃-Zn-K₂-Cu₁ showed significantly larger slopes than K-free samples, indicating that the presence of K increases secondary water gas shift rates, as also reported for Fe-Si oxide precursors [18], without influencing the primary oxygen removal selectivity.



Figure 18. CO₂ selectivities on Fe₂O₃-Zn (\bullet), Fe₂O₃-Zn-Cu₁ (\blacktriangle), Fe₂O₃-Zn-K₂ (\blacklozenge), and Fe₂O₃-Zn-K₂-Cu₁ (\blacksquare) catalysts (493 K, 3.16 MPa, H₂/CO=2).

The presence of K in Fe₂O₃-Zn catalysts led to lower CH₄ selectivities (Table 4, Figure 19) and higher C_{5+} selectivities (Table 4, Figure 20), apparently by decreasing the availability of H* atoms required for termination of growing chains via hydrogen addition reactions to form paraffins. In contrast, the addition of Cu to Fe₂O₃-Zn increased CH₄ selectivities and decreased C₅₊ selectivities (Table 4, Figure 20). When Cu and K are both present, the tendency of Cu to decrease product molecular weight almost disappeared. Potassium also inhibits secondary reactions of α -olefins, such as isomerization to internal or branched olefins and hydrogenation to n-paraffins, by titrating acid sites or uncarbided sites on Fe₂O₃-Zn. The titration of these sites and the apparent decrease in the availability of adsorbed hydrogen also lead to lower rates of secondary hydrogenation reactions. *1*-Pentene/*n*-pentane ratios are shown in Figure 21 on various catalysts, and also compared in Table 4 at similar CO conversions. The olefin content in the K-promoted catalysts increased slightly with CO conversion. This is likely to reflect an inhibiting effect of H₂O or CO₂ on the termination of growing chains by hydrogen addition, as reported previously [16]. The intrinsic olefin/paraffin ratios (extrapolated to zero CO conversion) are actually higher on catalysts without K, but the tendency of K-free catalysts to hydrogenate olefins leads to a marked decrease in olefin content with increasing residence time. Similarly, 1-decene/n-decane ratios (Figure 22, Table 4) are significantly higher in the presence of K and the effects of K are much stronger for the larger olefins, because of their greater propensity for secondary reactions.



Figure 19. CH₄ selectivities on Fe₂O₃-Zn (\bullet), Fe₂O₃-Zn-Cu₁ (\blacktriangle), Fe₂O₃-Zn-K₂ (\blacklozenge), and Fe₂O₃-Zn-K₂-Cu₁ (\blacksquare) catalysts (493 K, 3.16 MPa, H₂/CO=2).



Figure 20. C_{5+} selectivities on Fe₂O₃-Zn (•), Fe₂O₃-Zn-Cu₁ (\blacktriangle), Fe₂O₃-Zn-K₂ (•), and Fe₂O₃-Zn-K₂-Cu₁ (•) catalysts (493 K, 3.16 MPa, H₂/CO=2).



Figure 21. $1-C_5H_{10}/n-C_5H_{12}$ ratios on Fe₂O₃-Zn (•), Fe₂O₃-Zn-Cu₁ (\blacktriangle), Fe₂O₃-Zn-K₂ (•), and Fe₂O₃-Zn-K₂-Cu₁ (\blacksquare) catalysts (493 K, 3.16 MPa, H₂/CO=2).


Figure 22. $1-C_{10}H_{20}/n-C_{10}H_{22}$ ratios on Fe₂O₃-Zn (•), Fe₂O₃-Zn-Cu₁ (•), Fe₂O₃-Zn-K₂ (•), and Fe₂O₃-Zn-K₂-Cu₁ (•) catalysts (493 K, 3.16 MPa, H₂/CO=2).

5. Design of high activity Fe Fischer-Tropsch Synthesis catalysts by promotion with Cu, Ru and by synthesis of high surface area Fe-Zn precursors

5.1. Introduction

Fe-based catalysts provide an attractive complement to Co-based catalysts for the Fischer-Tropsch synthesis (FTS). They lead to more olefinic products and to lower CH₄ selectivities than Co-based catalysts over a wide range of temperatures and H₂/CO ratios, including synthesis gas with low H₂/CO ratios derived from coal or biomass [1]. Cobalt catalysts are typically more active than Fe-based catalysts, but they require low reaction temperatures (470-490 K), because the selectivity to desired C_{5+} hydrocarbons and the quality of the diesel range products becomes unacceptably low at higher temperatures [40]. The lower apparent FTS rates on Fe-based catalysts reflect to some extent the lower dispersion of their active component. Thus, an increase in the surface area and in the density of active sites during synthesis and during the initial stages of use in synthesis gas may bring Fe-based catalysts into the range of productivity and reaction conditions typical of Co-based catalysts [41]. The resulting opportunities for using Fe-based catalysts at lower temperatures may also lead to even heavier products and to lower CO₂ selectivities. Such active Fe-based catalysts would also allow direct comparisons of FTS turnover rates on Fe and Co catalysts at similar conditions. Such comparisons require reliable measurements of the number of exposed active components in both catalysts. These measurements are available for Co catalysts, but not for Fe-based catalysts, which activate to form complex mixtures of oxide and carbide phases only during Fischer-Tropsch synthesis reactions.

Here, we report the design and synthesis of Fe-based catalysts with hydrocarbon synthesis productivities (per catalyst mass) similar to those on Co-based materials. We also report direct comparisons of turnover rates on these two types of catalysts. These comparisons exploit a method developed to titrate the number of CO binding sites on Fe catalysts after activation and FTS reaction. Our studies of the catalytic properties of Fe (Section 3) and Fe-Zn (Section 4) catalysts have shown that FTS rates increased with K or Cu addition, and that the rate was highest when both K and Cu were present [16]. These promotional effects reflect predominately the formation of Fe carbides with higher dispersion when K or Cu is present. Our initial attempt to improve the density of active sites in these materials and to decrease the CO₂ selectivity led us to replace Cu, the active component in the best available water-gas shift (WGS) catalysts [39], with Ru. Ru was chosen because it does not introduce undesired methanation side reactions and it is an active, but impractical, FTS catalyst [42], and a promoter for Co-based catalysts [43]. Ru increased FTS rates more effectively than Cu at similar atomic contents without detectable changes in chain growth selectivity. As in the case of Cu, Ru predominately increased the density of active sites by favoring the nucleation of smaller Fe carbide and Fe₃O₄ domains as Fe₂O₃ precursors convert to active catalysts during the initial stages of FTS reactions. This conclusion was confirmed by surface area, CO chemisorption, and isothermal transient experiments. These smaller crystallites, in turn, provided higher surface areas, shorter bulk diffusion distances, more complete carburization of Fe₂O₃ precursors, and higher steady-state FTS rates.

Higher FTS rates were also achieved by synthetic protocols leading to higher precursor surface areas. These led to a higher Fe_2O_3 dispersion, which was maintained during catalyst activation in synthesis gas, especially when decomposition and activation procedures were designed in order to minimize the subsequent sintering of these high surface area oxide precursors. FTS rates and selectivities were measured on these materials at operation conditions typical of Co catalysts (H₂/CO=2, 2.0 MPa, 473 K) on a high surface area Fe-Zn-K-Cu oxide catalyst and on a Co/SiO₂ catalyst. The obtained results show that turnover rates are higher on exposed Co surface atoms than on Fe-based active sites. Fe-based catalysts designed with a high density of CO binding sites, however, can lead to similar and even higher hydrocarbon synthesis productivities and to lower CH₄ selectivities than Co-based FTS catalysts.

5.2. Comparison of the Reduction and Carburization Behavior of Fe-Zn-K oxides Promoted with Ru or Cu



Figure 23. Oxygen removal rates for Fe-Zn-K-Cu(Ru) oxides in H₂. (a) Fe-Zn-K₂, (b) Fe-Zn-K₂-Cu₁, and (c) Fe-Zn-K₂-Ru₁. (0.2 g sample; K/Fe=0.02, Cu(Ru)/Fe=0.01; 0.167 K/s ramping rate; 20% H₂/Ar, 0.268 mol/h flow rate).

Figure 23 shows oxygen removal rates for Fe-Zn-K-Cu and Fe-Zn-K-Ru oxides as a function of temperature during exposure to H_2 . The amounts of oxygen removed in each of the two major reduction peaks indicate that the reduction of Fe-Zn-K-Cu(Ru) oxides

follows the same sequential reduction steps observed for Fe_2O_3 discussed in Section 4. Fe_2O_3 reduces to Fe_3O_4 and then to Fe in two steps with distinct kinetics. The addition of Cu to Fe-Zn-K oxides led to incipient reduction at ~130 K lower temperatures than on Cu-free samples (Figures 23a and 23b), as a result of H₂ dissociation sites formed by reduction of CuO to Cu metal at low temperatures. Ru had similar but stronger effects on the temperature required for reduction of Fe_2O_3 to Fe_3O_4 and of Fe_3O_4 to Fe (by an additional 50 K and 100 K, respectively). It appears that Ru, because of its higher metal dispersion, lower reduction temperature, or higher H₂ dissociation turnover rate, leads to hydrogen dissociation at lower temperatures than for oxide precursors with similar atomic Cu content.



Figure 24. Oxygen removal and carbon introduction rates for Fe-Zn-K-Cu(Ru) samples in CO. (a) Fe-Zn-K₂, (b) Fe-Zn-K₂-Cu₁, and (c) Fe-Zn-K₂-Ru₁. (0.05 g sample; K/Fe=0.02, Cu(Ru)/Fe=0.01; 0.167 K/s ramping rate; 20% CO/Ar, 0.268 mol/h flow rate).

Figure 24 shows oxygen removal and carbon introduction rates for Fe-Zn-K-Cu and Fe-Zn-K-Ru oxides as a function of temperature using CO as the reducing and carburizing reagent. Fe-Zn-K-Cu(Ru) oxides convert via reduction/carburization steps identical to those for pure Fe₂O₃ (Section 4). Fe₂O₃ reacts with CO to form Fe₃O₄ and the latter simultaneously reduces and carburizes to form a mixture of Fe_{2.5}C and Fe₃C, confirmed by X-ray diffraction and denoted here as FeC_x (Section 4). The temperature required for these reduction-carburization processes is lowest for Fe-Zn-K₂-Ru₁ and highest for the sample without either Cu or Ru (Fe-Zn-K₂). Ru-promoted samples reduced and carburized at a temperature ~30 K lower than the Cu-containing samples. The promoting effects of Ru and Cu on the reduction and carburization of Fe-Zn oxide precursors by CO were weaker than their respective effects when H₂ was used as the reductant, but Cu, and especially Ru, clearly increased the rate of oxygen removal using CO as the reductant. The effects of Ru and Cu on the rate of reduction and carburization of Fe-Zn oxide precursors suggest that these components increase the initial rate of nucleation of reduced Fe-containing phases (Fe₃O₄, FeC_x). The resulting larger number of nuclei then lead to a

better dispersion of these reduced phases, as shown earlier (Section 3), and to a larger number of active sites for Fischer-Tropsch synthesis reactions. This expectation was confirmed by the catalytic measurements reported in the next section.

5.3. Effect of Ru and Cu on Fischer-Tropsch Synthesis rate and selectivity

Fischer-Tropsch synthesis rates were measured on Fe-Zn-K₂, Fe-Zn-K₂-Cu₁, and Fe-Zn-K₂-Ru₁ samples at 508 K and 2.14 MPa. Measurements were conducted at different CO space velocities; steady-state hydrocarbon formation rates (mol CO/h.g-at.Fe) are shown as a function of the resulting extent of CO conversion in Figure 25a. These rates were higher on the Ru-promoted sample (Fe-Zn-K₂-Ru₁) than on Cu-promoted (Fe-Zn-K₂-Cu₁) or unpromoted (Fe-Zn-K₂) catalysts. The effects of increasing conversion on FTS rates were similar on all samples, suggesting similar kinetic dependencies on reactant and product concentrations on all catalysts. Ru and Cu appear to increase the number of active sites available on catalysts derived from Fe-Zn oxide precursors, without any detectable changes in turnover rates, in the kinetics of chain growth or CO hydrogenation on active sites, or in the pathways available for these reactions. This is consistent with the nearly identical selectivities to C₅₊ (Figure 25c) and CH₄ (compared in Table 5 at similar CO conversions), and with the similar α -olefin/*n*-paraffin ratios (Figure 25d) on all catalysts at all conversion levels.

 CO_2 selectivities increased with CO conversion on all three catalysts (Figure 25b). They were higher on Cu- or Ru-promoted Fe-Zn-K oxides than on unpromoted catalysts at all conversion levels. The slopes of the CO₂ selectivity-CO conversion curves in Figure 25b are similar on all three catalysts, suggesting that the rate of secondary water-gas shift reactions are not influenced by these promoters, even though high water-gas shift rates have been reported on Cu-containing catalysts [39]. The extrapolated y-intercepts in Figure 25b reflect the relative rates of removal of chemisorbed oxygen atoms, formed in CO dissociation steps, using either CO or hydrogen. Cu and Ru increase slightly the value of this intercept in Figure 25b, suggesting an increase in the probability of oxygen removal via reactions with CO when these promoters are present. Another possible explanation for these higher intercepts is the presence of intrapellet H₂O concentration gradients caused by diffusional restrictions, which can become more severe within liquidfilled pores as volumetric productivities become higher in the presence of Cu or Ru promoters.

The catalytic properties of Fe-Zn-K₂, Fe-Zn-K₂-Cu₁, and Fe-Zn-K₂-Ru₁ are compared in Table 5 at similar CO conversions. The addition of Cu or Ru to Fe-Zn oxide precursors led to two-fold and four-fold increases in hydrocarbon synthesis rates, respectively. These promotion effects cannot be explained by the FTS activity of the Ru promoter, which, even if atomically dispersed, would account for only about 20% of the rate increase observed upon Ru addition, based on reported FTS turnover rates on Ru [19].



Figure 25. Steady-state FTS rates and selectivities on promoted Fe oxide catalysts as a function of CO conversion (H₂/CO=2, 508 K and 2.14 MPa). (a) Hydrocarbon formation rate, (b) CO₂ selectivity, (c) C₅₊ selectivity, and (d) *1*-C₅H₁₀/*n*-C₅/H₁₂ ratio. (**■**) Fe-Zn-K₂, (•) Fe-Zn-K₂-Cu₁, and (•) Fe-Zn-K₂-Ru₁.

 C_{5+} formation rates increased proportionately with the observed increase in hydrocarbon synthesis rates, leading to nearly identical C_{5+} selectivities on all catalysts. The slightly lighter products formed on samples promoted with Cu or Ru reflects the lower surface density of the potassium promoter at the higher surface areas prevalent in metal-promoted samples, as discussed below. Ru, and to a lesser extent Cu, appear to increase the number of FTS active sites formed during the activation of Fe-Zn oxide precursors. This proposal is confirmed below by measurements of the structural evolution of the active phases during reaction and by surface area and CO chemisorption measurements after catalyst activation and Fischer-Tropsch synthesis.

Sample	Fe-Zn-K ₂	Fe-Zn-K ₂ -Cu ₁	Fe-Zn-K ₂ -Ru ₁
CO conversion rate (mol CO/h.g-at. Fe)	1.7	3.5	7.2
CO_2 formation rate (mol CO/h.g-at. Fe)	0.2	0.7	1.1
Hydrocarbon formation rate (mol CO/h.g-at. Fe)	1.5	2.8	6.0
CO ₂ selectivity (%)	11.5	20.2	16.8
CH ₄ selectivity (%) ^a	2.0	2.4	2.8
C_{5^+} selectivity (%) ^a	88.2	85.3	85.0
$1-C_5H_{10}/n-C_5H_{12}$ ratio	2.3	2.5	2.5

Table 5. Steady-state Fischer-Tropsch synthesis rates and selectivities on Fe-Zn-K₂, Fe-Zn-K₂-Cu₁, and Fe-Zn-K₂-Ru₁ samples (atomic ratios: Zn/Fe=0.1, K/Fe=0.02, Cu(Ru)/Fe=0.01; H₂/CO=2, 508 K, 2.14 MPa, CO conversion is 13-16%).

^a $\overline{\text{CH}_4}$ and $\overline{\text{C}_{5^+}}$ selectivities are reported on a $\overline{\text{CO}_2}$ -free basis.

5.4. Surface areas and CO chemisorption site densities on fresh and activated Fe-Zn-K-Cu(Ru) oxides

Table 6 shows BET surface areas and CO chemisorption uptakes (measured as illustrated in Section 3.9) on Fe-Zn-K₂, Fe-Zn-K₂-Cu₁, and Fe-Zn-K₂-Ru₁ oxide precursors after FTS reactions for 1 h at the conditions indicated. BET surface areas are also reported for the oxide precursors after thermal treatment in air at 673 K for 4 h, but before FTS reactions. Before reaction, BET surface areas were not affected by the presence of Cu or Ru promoters. After FTS reactions for 1 h, surface areas were higher on the metalpromoted samples than on unpromoted samples, suggesting that smaller Fe₃O₄ and FeC_x crystallites form when Cu or Ru are present during *in situ* activation of Fe-Zn oxide precursors.

Sample	Fe-Zn-Ka	Fe-Zn-K ₂ -	Fe-Zn-K ₂ -
Sumple		Cu ₁	Ru ₁
Surface area before FTS (m^2/g)	56	65	63
Surface area after FTS^{a} (m ² /g)	23	31	39
Amount of CO_x desorbed before CO chemisorption (mmol/g-at. Fe)	11.3	65.3	68.4
Amount of CO _x desorbed after CO chemisorption (mmol/g-at. Fe)	31.6	109.9	124.5
Amount of CO chemisorbed (mmol CO/g-at. Fe)	20.3	44.6	58.1
FeC_x concentration ^b (atom %)	11.8	23.6	57.1
CH ₄ formation rate ^c (mmol/s.g-at. Fe)	0.173	0.262	0.372

Table 6. BET surface areas and CO chemisorption uptakes on Fe-Zn-K₂, Fe-Zn-K₂-Cu₁, and Fe-Zn-K₂-Ru₁ samples after FTS reactions ($H_2/CO=2$, 523 K, 1 h); Fe carbide concentrations were obtained from *in situ* XAS measurements; CH₄ formation rates were obtained from isothermal transient experiments.

^aSurface areas measured after exposure to synthesis gas at 523 K for 1 h (0.2 g sample, K/Fe=0.02, Cu/Fe=0.01, $H_2/CO=2$, synthesis gas flow rate=64.3 mol/h.g-at. Fe).

^bFeC_x concentration measured after exposure to synthesis gas at 523 K for 5 h (1 mg precipitated Fe₂O₃, K/Fe=0.02, Cu/Fe=0.01, H₂/CO=2, synthesis gas flow rate=107 mol/h g-at. Fe).

^cCH₄ formation rates measured after exposure to synthesis gas at 523 K for 1 h (0.2 g sample, K/Fe=0.02, Cu/Fe=0.01, H_2 /CO=2, synthesis gas flow rate=64.3 mol/h.g-at. Fe).

CO chemisorption uptakes on activated samples were significantly higher when Cu or Ru were present, suggesting the presence of a larger number of CO adsorption sites when Fe-Zn oxide precursors are activated in the presence of Cu or Ru. Chemisorption uptakes were higher on the Ru-promoted sample than on the Cu-promoted sample, a trend also observed for hydrocarbon synthesis rates. This apparent correlation between FTS rates and CO chemisorption uptakes was also observed on Zn-free Fe-K-Cu samples (Section 3). It is consistent with Cu and Ru leading to the formation of smaller Fe carbide crystallites, which in turn provide a higher density of sites for CO chemisorption and for FTS reaction turnovers. Thus, it appears that these reduction-carburization promoters increase the rate of catalyst activation by providing a large number of nucleation sites, which favor the formation of smaller FeC_x and Fe₃O₄ crystallites. These smaller crystallites, and the faster carburization kinetics introduced by Cu and Ru, were probed directly during activation of Fe-Zn oxide precursors using *in situ* X-ray absorption spectroscopy, as described in the next section.

5.5. Structural characterization of Fe-Zn-K-Cu(Ru) catalysts during Fischer-Tropsch Synthesis using X-ray absorption spectroscopy

In situ Fe K-edge X-ray absorption spectroscopy was used to monitor the structural evolution of Fe-Zn oxides during activation and FTS reactions and the effects of Cu and Ru on the kinetics of formation and on the relative abundance of species formed as Fe-Zn oxide precursors undergo activation during contact with synthesis gas. Fe₂O₃, Fe₃O₄, and FeC_x were identified by principal component analysis and the sample spectra were described as linear combinations of these standard compounds as a function of time in contact with synthesis gas. FeC_x concentrations are reported as Fe atomic fractions as a function of contact time in Figure 26. The reduction and carburization rates and the extent of carburization of these materials are smaller than for the Zn-free samples reported in Section 3, because Zn species, in the form of ZnFe₂O₄, inhibit the rate of reduction/carburization processes (Section 4). The structure evolves, however, in a manner similar to that previously found for Zn-free samples - via the initial formation of Fe_3O_4 and the rapid subsequent transformation of this phase into FeC_x . Since the details of such transformations are very similar for Fe and Fe-Zn oxide precursors, we restrict our discussion here to the extent and kinetics of FeC_x formation and to the effect of Cu and Ru on these properties for Fe-Zn oxide precursors.



Figure 26. The evolution of Fe carbides during *in situ* XAS measurement of Fe-Zn-K-Cu(Ru) samples in synthesis gas. (a) Fe-Zn-K₂, (b) Fe-Zn-K₂-Cu₁, and (c) Fe-Zn-K₂-Ru₁. (1 mg sample, K/Fe=0.02, Cu(Ru)/Fe=0.01, H₂/CO=2, synthesis gas flow rate=107 mol/h.g-at. Fe).

Figure 26 shows that Cu, and especially Ru, increased carburization rates and the steadystate extent of carburization of Fe-Zn oxide precursors promoted also with K. The faster carburization kinetics of oxides promoted with Ru or Cu using synthesis gas is similar to their promotion effect reported above using either H_2 or CO as the reducing agents. As shown in Figure 26, the extent of carburization is also higher on samples promoted with Ru or Cu than on the Fe-Zn-K sample. The FeC_x content, however, reached a nearly constant value after ~8 h on stream at the conditions of this study (Figure 26). Thus, while faster carburization may lead to the more rapid attainment of steady-state FTS reaction rates, it should not lead to higher steady-state FTS reaction rates, which are measured after contact with synthesis gas for more than 24 h. Also, it is not obvious how the greater extent of carburization achieved when Cu or Ru are present would lead to higher steady-state FTS rates, because previous studies using Fe₂O₃ precursors have shown that the carburization of one or two near-surface layers is sufficient to attain steady-state FTS reaction rates. We conclude that the extent of carburization is controlled by the diffusion path for the removal of lattice oxygen from the core of Fe oxide precursors. Thus, the shorter diffusion path within the smaller crystallites formed during activation on promoted samples is responsible for the greater extent of carburization on the promoted samples. In this manner, both the higher FTS rates and the faster and more extensive carburization find a common cause in the role of promoters in nucleating Fe active phase as smaller crystallites. No causal relationship between the extent of carburization and the observed FTS reaction rates is warranted by these observations.

5.6. Isothermal transient analysis of reduction, carburization, and Fischer-Tropsch Synthesis products during activation of Fe-Zn-K-Cu(Ru) catalysts

Fischer-Tropsch synthesis rates were measured during exposure to synthesis gas at the same conditions as those used to measure X-ray absorption spectra of these samples (H₂/CO=2, 523 K) in order to relate the observed structural evolution to the rate of hydrocarbon formation as Fe oxide catalyst precursors activate during FTS. CH₄ formation rates on Fe-Zn-K oxide precursors promoted with Cu or Ru are shown in Figure 27 as a function of time. For unpromoted Fe-Zn-K oxides, a short induction period was observed upon initial contact with synthesis gas. CH₄ was immediately detected, however, on Fe-Zn oxides promoted with Cu or Ru. CH₄ formation rates during initial contact with synthesis gas and at steady state were higher on promoted catalysts. The initial increase in CH_4 formation rates is accompanied by the formation of an excess amount of CO_2 and H_2O_2 , indicative of the removal of lattice oxygen during the initial reduction and carburization of the oxide precursors. These reduction-carburization processes are faster on Ru-containing samples than on Cu-containing or unpromoted Fe-Zn-K samples. Steady-state FTS rates were attained after ~1 h in contact with synthesis gas, even though X-ray absorption spectra detected a continuing increase in FeC_x content up to ~ 8 h. These data confirm the previous proposal that FTS reactions are influenced only by the density of active carbide sites in near-surface layers, irrespective of the presence of a remaining Fe oxide core. These data are also consistent with FTS data obtained at higher pressures and reported above, and with a role of Cu or Ru in nucleating smaller and more easily carburized structures from Fe-Zn-K oxide precursors.

On samples containing Cu or Ru (Table 6), FTS rates increased proportionally with the observed increase in FeC_x content and in CO chemisorption uptakes. All these results clearly show that Cu and Ru favor the formation of a more dispersed active phase, and that chemical promotion effects, such as an increase in the turnover rate of FeC_x sites, are unnecessary in order to account for the observed increase in FTS rates when Cu or Ru are present during the activation of Fe-Zn oxide precursors. These conclusions, taken together with the previous observation that higher surface area precursors prepared by incorporating ZnO during the precipitation of Fe₂O₃ also led to higher FTS reaction rates [16], led us to attempt the synthesis of more highly dispersed active carbide phases by using Fe oxide precursors with higher surface areas.



Figure 27. CH₄ formation rate as a function of reaction time in contact with synthesis gas (H₂/CO=2, 523 K, synthesis gas flow rate=107 mol/h.g-at.Fe). (a) Fe-Zn-K₂, (b) Fe-Zn-K₂-Cu₁, and (c) Fe-Zn-K₂-Ru₁ sample.

5.7. Synthesis of Fe-Zn-K-Cu oxide precursors with high surface area

Our efforts to improve the dispersion and site density of the FeC_x structures formed during reaction included the use of specific synthetic protocols designed to increase the surface area of Fe-Zn oxide precursors and to minimize the sintering that occurs during drying and impregnation with Cu(Ru) and K. In this section, we examine the promoter concentrations required in order to optimize catalysts prepared from precursors with varying surface area. We also show that the surface density of the Cu and K promoters (~2 K/nm² and 1 Cu/nm²), and not their atomic content, are the relevant controlling variables in determining the dispersion and catalytic properties of FeC_x structures.

Several factors, such as the drying processes after precipitation or impregnation and the temperature and time of thermal treatments designed to decompose precursors, influence the surface area of Fe-Zn oxide precursors. These factors were systematically examined in order to increase catalyst surface areas and FTS reaction rates. The effect of precipitation pH was examined previously; it was found that a pH of 7.0 held constant during precipitation, led to the highest precursor surface areas [44]. The effect of Zn/Fe ratio on the performance of Fe-Zn-K catalysts for FTS reactions was also previously examined and a Zn/Fe atomic ratio of 0.1 was found to give highest FTS reaction rates (Section 4). Sintering of porous materials often occurs as a result of pore pinching during the final stages of drying, even at low temperatures. This process is particularly severe with water, because of its high surface tension (γ =72 mN/m at 298 K). Alcohols have lower surface tensions (e.g. γ =22 mN/m for ethanol and isopropanol at 298 K); they also act as surface-active agents that decrease the surface tension of aqueous solutions [35]. Therefore, the water contained within the pores in Fe-Zn oxide precipitates was replaced before drying by extensive washing with either ethanol or isopropanol in an attempt to inhibit sintering of Fe-Zn oxide precursors during drying.

Figure 28. BET surface areas of Fe-Zn and Fe-Zn-K₂-Ru₁ samples dried with various intrapore liquids as a function of thermal treatment temperature. (a) Fe-Zn precursor washed by intrapore water (\blacksquare), (b) Fe-Zn precursor washed by intrapore ethanol (\bullet), (c) Fe-Zn precursor washed by intrapore isopropanol (+), (d) Fe-Zn precursor washed by ethanol and subsequently promoted with K and Ru (\bullet) (K/Fe=0.02, Ru/Fe=0.01). (All the samples were treated in dry air at the stated temperature for 4 h).

Figure 28 shows the surface area of Fe-Zn oxide precursors with different intrapore liquids after thermal treatment at various temperatures (Figure 28a-c). After drying at 398 K for 12 h, precipitates washed with ethanol or isopropanol showed higher Fe-Zn oxyhydroxide surface areas than precipitates dried without replacing intrapore water with alcohols (215 vs. 148 m²/g). The similar precursor surface areas obtained with isopropanol and ethanol are consistent with the similar surface tension of these two liquids. All other precipitation variables were kept constant; therefore, it appears that the drying step and the surface tension of the intrapore liquids during drying strongly influence the pore structure and the surface area of the Fe-Zn oxide precursors. Our data show that a high space velocity of dry air (~2000 cm³/h.g-cat.) is also required in order to minimize sintering during the decomposition of these oxyhydroxide precursors. The replacement of H₂O with lower surface tension liquids during drying and the rapid removal of H₂O as it forms during oxyhydroxide decomposition at higher temperatures are critical in preserving the initial surface area of these precipitated precursors.

The temperature and time of the final thermal treatment in air also influenced Fe-Zn oxide surface areas. After drying oxyhydroxide precipitates with different intrapore liquids at 398 K for 12 h, they were treated in flowing dry air at various temperatures for 4 h in order to identify optimum treatment protocols. All samples showed the expected decrease in surface area with increasing treatment temperature, but the higher surface area samples obtained by drying alcohol-containing precipitates were more sensitive to this treatment temperature. X-ray diffraction confirmed that Fe-Zn hydroxides formed poorly crystalline Fe₂O₃ at ~543 K. Zn, possibly as the ZnFe₂O₄ phase detected in samples with higher Zn/Fe ratio (>0.2) and treated at higher temperatures (~673 K), was well dispersed and not detected in these alcohol-washed samples. It appears that thermal treatment at 543 K provides a compromise between structural purity and a high surface area in Fe₂O₃, and that the surface area of the resulting oxide is highest when intrapore water is replaced with lower surface tension liquids, such as alcohols.

The effects of impregnation with K and Cu promoters on surface areas were also investigated. Fe-Zn oxyhydroxide precursors were impregnated with K carbonate (K/Fe=0.02) and dried at 393 K for 12 h. Ru (Ru/Fe=0.01) was then added as Ru nitrosyl nitrate using similar impregnation procedures. The addition of K to Fe-Zn hydroxide precursors decreased its surface area (220 vs. 192 m²/g), apparently because of pore collapse caused by the removal of high surface tension intrapore liquids. Similarly, the subsequent impregnation of the Fe-Zn-K with Ru led to an additional decrease in its surface area. Each impregnation and subsequent drying decreased the surface area by 10-20%. Ru-promoted Fe-Zn-K hydroxides were then treated at different temperatures in order to examine the effect of treatment temperature on surface area (Figure 28d). The effects of temperature on the surface area of Fe-Zn-K-Ru oxides were similar to those found in Fe-Zn oxides. The surface area of Ru-promoted Fe-Zn-K oxides decreased from 142 to 96 m²/g as thermal treatment temperatures increased from 523 to 623 K.

Based on these surface areas for Fe-Zn hydroxides and Fe-Zn-K-Ru oxide precursors prepared by different methods, we selected a procedure for maximizing the surface area of Fe-Zn-K-Cu samples. Fe-Zn hydroxide precursors were first prepared by co-

precipitation at a constant pH of 7.0 and the precipitates were thoroughly washed with ethanol in order to replace intrapore water. Fe-Zn hydroxide precursors were then treated at 543 K for 4 h in flowing dry air (2000 cm³/h.g-cat). The resulting Fe-Zn oxide precursors were impregnated with K and Cu using incipient wetness impregnation method and aqueous solutions of Cu nitrate and K carbonate. The amounts of K (K/Fe=0.04) and Cu (Cu/Fe=0.02) were chosen so as to maintain the K and Cu surface densities at the levels previously shown to lead to maximum FTS reaction rates on conventionally prepared samples (~2 K-atom/nm²; 1 Cu-atom/nm²). The surface area of the resulting Fe-Zn-K₄-Cu₂ oxides was 120 m²/g, almost twice that of the Fe-Zn-K₂-Cu₁ oxide samples. As a result, the K and Cu content were chosen to be about twice as high as those in the conventionally prepared Fe-Zn-K₂-Cu₁ sample. A Fe-Zn-K₂-Cu₁ sample prepared from high surface area Fe-Zn oxide precursors led to lower FTS rates and to significantly lighter products than a sample with the higher promoter concentrations (Fe-Zn-K₄-Cu₂), suggesting the presence of sub-optimum levels of K and Cu and confirming the relevant role of atomic surface density as the defining variable in the design of these promoted catalytic materials.

5.8. Site density of active species and promoters and effects on the Fischer-Tropsch Synthesis

The relevance of improvements in surface area to the catalytic performance of these materials in FTS reactions was confirmed by the FTS rate and selectivity measurements on a high surface area Fe-Zn-K₄-Cu₂ oxide (120 m²/g) and on a lower surface area Fe-Zn-K₂-Cu₁ oxide prepared *via* conventional methods (65 m²/g). The amounts of K and Cu in the Fe-Zn-K₄-Cu₂ sample were chosen in order to maintain the same surface density of promoters as in the Fe-Zn-K₂-Cu₁ sample prepared from Fe-Zn oxide precursors with lower surface area. Steady-state FTS rates and selectivities at 508 K and 2.14 MPa are shown as a function of CO conversion in Figure 29. Hydrocarbon synthesis rates are about two-fold higher on Fe-Zn-K₄-Cu₂ than on Fe-Zn-K₂-Cu₁, a difference that parallels the difference in surface area for their respective Fe-Zn oxide precursors. The similarities between these two samples in CO₂ and C₅₊ selectivities, in α -olefin/*n*-paraffin ratios, and in their kinetic response of FTS rates to changes in conversion, suggest that the synthetic protocols used to increase the precursor surface areas led to a larger number of active sites in working catalysts, without detectable changes in chain growth pathways.

Figure 30 shows FeC_x concentrations obtained from XAS measurements of the structural evolution of these oxide precursors during FTS reactions. Figure 31 shows the corresponding CH₄ formation rates on these two samples at the same conditions used for the X-ray absorption experiments. Both the extent of carbide formation and the steady-state CH₄ formation rate are significantly higher on Fe-Zn-K₄-Cu₂ than on Fe-Zn-K₂-Cu₁. The consistent correlation between the Fe carbide concentration and FTS rates is again not causal, but it confirms that promoters (Ru, Cu, K) and higher surface area precursors increase the density of active sites in the Fe carbide structures prevalent during steady-state Fischer-Tropsch synthesis. Accordingly, we examined next whether further increases in the surface density of these promoters leads to additional improvements in active site density and in FTS rates.



Figure 29. Comparison of the FTS activity of (•) Fe-Zn-K₂-Cu₁, and (\blacktriangle) Fe-Zn-K₄-Cu₂ as a function of CO conversion at steady-state reaction conditions (H₂/CO=2, 508 K and 2.14 MPa). (a) Hydrocarbon formation rate, (b) CO₂ selectivity, (c) C₅₊ selectivity, and (d) *1*-C₅H₁₀/*n*-C₅/H₁₂ ratio.



Figure 30. FeC_x concentrations as a function of time on (a) Fe-Zn-K₂-Cu₁ and (b) Fe-Zn-K₄-Cu₂ samples as a function of reaction time during *in situ* X-ray absorption measurements in synthesis gas (1 mg precipitated sample, H₂/CO=2, synthesis gas flow rate=107 mol/h.g-at. Fe).



Figure 31. CH₄ formation rates as a function of time in contact with synthesis gas at the conditions of X-ray absorption measurements shown in Figure 8 (H₂/CO=2, 523 K, synthesis gas flow rate=107 mol/h.g-at.Fe). (a) Fe-Zn-K₂-Cu₁ sample, (b) Fe-Zn-K₄-Cu₂ sample.

We prepared a Fe-Zn-K-Cu sample using the same Fe-Zn oxide precursor and treated the sample at the same conditions as the Fe-Zn- K_2 -Cu₁ sample but added a higher K concentration (Fe-Zn- K_4 -Cu₁).

Table 7. Steady-state FTS rates and selectivities ($H_2/CO=2$, 508 K, 2.14 MPa, CO conversion is 13-16%), and the characterization results for Fe-Zn-K₂-Cu₁, Fe-Zn-K₄-Cu₁ and Fe-Zn-K₄-Cu₂ samples after FTS reactions.

Sample	Fe-Zn-K ₂ -Cu ₁	Fe-Zn-K ₄ -Cu ₁	Fe-Zn-K ₄ -Cu ₂	
CO conversion rate (mol CO/h.g-at. Fe)	3.5	3.6	6.8	
CO ₂ formation rate (mol CO/h.g-at. Fe)	0.7	0.8	1.4	
Hydrocarbon formation rate (mol CO/h.g-at. Fe)	2.8	2.8	5.4	
CO ₂ selectivity (%)	20.2	22.4	20.5	
CH_4 selectivity (%) ^a	vity (%) ^a 2.4		3.8	
C_{5+} selectivity (%) ^a	85.3	85.5	80.8	
$I-C_5H_{10}/n-C_5H_{12}$ ratio	2.5	2.5	2.7	
Surface area before FTS (m^2/g)	65	58	120	
Surface area after FTS^b (m ² /g)	31	26	43	
Amount of CO_x desorbed before CO chemisorption (mmol/g-at. Fe)	65.3	72.0	75.2	
Amount of CO _x desorbed after CO chemisorption (mmol/g-at. Fe)	109.9	112.3	141.1	
Amount of CO chemisorbed (mmol CO/g-at. Fe)	44.6	40.3	65.9	
FeC _x concentration ^c (atom %)	23.6	-	69.2	
CH ₄ formation rate ^d (mmol/s.g-at. Fe)	0.262	0.289	0.527	

 $^{a}CH_{4}$ and C_{5+} selectivities are reported on a CO₂-free basis.

^bSurface areas measured after exposure to synthesis gas at 523 K for 1 h (0.2 g sample, K/Fe=0.02, Cu/Fe=0.01, $H_2/CO=2$, synthesis gas flow rate=64.3 mol/h g-at. Fe).

^cFeC_x concentration measured after exposure to synthesis gas at 523 K for 5 h (1 mg precipitated Fe₂O₃, K/Fe=0.02, Cu/Fe=0.01, H₂/CO=2, synthesis gas flow rate=107 mol/h g-at. Fe).

 d CH₄ formation rates measured after exposure to synthesis gas at 523 K for 1 h (0.2 g sample, K/Fe=0.02, Cu/Fe=0.01, H₂/CO=2, synthesis gas flow rate=64.3 mol/h g-at. Fe).

Table 7 compares FTS performance, surface area, CO chemisorption uptake, and the extent of carburization for Fe-Zn-K₂-Cu₁, Fe-Zn-K₄-Cu₁ and Fe-Zn-K₄-Cu₂ catalysts. Fe-Zn-K₂-Cu₁ and Fe-Zn-K₄-Cu₁ samples have similar surface areas, but different potassium contents and surface densities (2 vs. 4 K/nm²); yet, similar FTS reaction rates, CO chemisorption uptakes, and extents of carburization were obtained. This suggests that the higher K surface density did not lead to a further increase in the number of active sites, possibly because excess potassium leads to larger promoter domains without a significantly better contact between the promoter and the Fe oxide precursors or a higher actual surface density of potassium species. We have observed that increasing Cu or K concentrations beyond those required to achieve surface densities of 1 and 2 atom/nm², respectively, did not increase FTS reaction rates on conventionally prepared samples. Fe-Zn-K₂-Cu₁ and Fe-Zn-K₄-Cu₂ samples have different BET surface areas but similar apparent surface densities of K and Cu on the available surface area. The Fe-Zn-K₄-Cu₂ sample with the higher surface area shows higher FTS rates and a higher density of CO binding sites, indicating that higher precursor surface areas lead to proportionately higher FTS rates and active site densities, as long as the promoter surface densities are kept above a threshold level. These results suggest that promoter concentrations are more appropriately defined in terms of surface density in designing catalysts with similar and optimum promoter contents as the surface areas of Fe oxide precursors are changed by modifying precipitation, drying, and promoter impregnation protocols. The parallel increases in FTS rates, surface area, CO adsorption site availability, and steady-state concentration of Fe carbides suggest that higher FTS activity can be achieved by the design and appropriate promotion of high surface area oxide precursors.

5.9. Fischer-Tropsch Synthesis Rates and Selectivities on Fe-based catalysts – A comparison

The apparent low Fischer-Tropsch synthesis rates on Fe-based catalysts at reaction conditions typically used for Co-based catalysts (473 K-488 K) has led to their predominant use at higher temperatures (500 K-543 K). Here, we compare FTS reaction rates and selectivities on a Fe-Zn-K₄-Cu₂ catalyst with those on previously reported Febased catalysts.

The Fe-Zn-K₄-Cu₂ sample is compared with previously reported Fe-based catalysts in Table 8 for nearly stoichiometric reactants (H₂/CO=1.7-2.0) and at relatively high CO conversions (~50%). The results from the low-surface area Fe-Zn-K₂-Cu₁ sample are representative of the catalyst reported in reference [16]. The CO conversion rate and the hydrocarbon synthesis productivity on Fe-Zn-K₄-Cu₂ are about twice that of the Ruhrchemie AG catalyst (Fe-SiO₂-K_{5.9}-Cu_{4.4}) [45], and nearly three times higher than that of the Fe-Zn-K₂-Cu₁ catalyst, even though our Fe-Zn-K₄-Cu₂ catalyst was tested at lower temperatures (508 K vs. 523-543 K). Fe-Zn-K₄-Cu₂ also compares well with a Fe-Si_{4.6}-K_{1.4} catalyst tested at 543 K [18,46]. CO₂ selectivities are lower on Fe-Zn-K₄-Cu₂ than on the other catalysts, predominately because of the lower reaction temperatures made possible by its high surface area and FTS activity. The proper design of synthesis, promotion, and activation protocols that increase the density of FTS active sites have led

to additional improvements in hydrocarbon synthesis productivities, even after several decades of active research on Fe-based FTS catalysts.

Catalyst	Fe-Zn-K ₄ - Cu ₂	Fe-Zn-K ₂ - Cu ₁	Fe-Si _{4.6} - K _{1.4} [18,46]	Fe-SiO ₂ -K _{5.9} - Cu _{4.4} [Ruhrchemie LP33/81] [45]
Reactor Type	Fixed-Bed	Slurry	Slurry	Spinning Basket
Temperature (K)	508	543	543	523
Pressure (MPa)	2.14	0.50	1.31	2.40
H ₂ /CO ratio	2.0	2.0	1.7	2.0
CO space velocity (NL/h.g- cat)	3.4	1.4	5.7	2.4*
CO conversion (%)	50.8	55.5	50.0*	52.7
CO rate (mol CO/h.g-cat)	0.08	0.03	0.12*	0.05*
Hydrocarbon productivity (g/h.kg-cat)	765	258	1008*	404
CO ₂ selectivity (%)	31.7	48.6	40.0*	42.3*

Table 4. Steady-state FTS performance of various Fe-based catalysts using natural gasderived synthesis gas ($H_2/CO=1.7-2.0$)

*- Values calculated based on reported data or graphs

6. Comparison of the performance of a Fe-Zn-K-Cu and Co/SiO₂ catalysts at Co conditions

The high surface area Fe-Zn-K₄-Cu₂ sample discussed in the previous section was also compared with a Co/SiO₂ catalyst at conditions typical of Co-based FTS catalysts (Table 5). Fe-based catalysts typically require higher temperatures, while Co-based catalysts must be operated within a very narrow range of temperature (473-500 K), pressure (~2 MPa), and synthesis gas stoichiometry (H₂/CO~2), because of their predominant methanation activity at higher temperatures, lower pressures, or higher H₂/CO ratios.

The Co/SiO₂ catalyst (21.9 wt.% Co) used for comparison purposes, was prepared by incipient wetness impregnation of SiO₂ (Grace-Davison; grade 62) with a solution of cobalt nitrate (Aldrich, 98%, 2.5 M), dried in ambient air at 333 K, and treated in H₂ using previously reported procedures [13]. This sample showed a Co dispersion of 4.6% using H₂ chemisorption methods. Its FTS turnover rate at standard conditions (473 K, 2.0 MPa) was 46-73 h⁻¹. This performance places it among the Co-based catalysts with the highest reported turnover rates at these reaction conditions [14].

The hydrocarbon synthesis productivity, CH₄ selectivity, C₅₊ selectivity, and *1*-pentene/*n*pentane and 1-decene/n-decane ratios are shown as a function of CO conversion on Fe- $Zn-K_4-Cu_2$ and Co/SiO_2 in Figures 32a-e. Table 9 provides a summary of these comparisons at similar CO conversions (18-21%). Hydrocarbon synthesis productivities are very similar on these two catalysts (Table 9, Figure 32a). Hydrocarbon synthesis turnover rates estimated from the number of sites available on Co/SiO₂ (using H₂) chemisorption before reaction) and on Fe-Zn-K₄-Cu₂ (using CO chemisorption after reaction) are higher on the former catalyst [Co; 60.9 h⁻¹; Fe; 19.8 h⁻¹] (Table 9). FTS rates increased slightly with CO conversion on Co catalysts, because of a promoting effect of the water formed in FTS reactions [14]. CH_4 selectivities (Figure 32b) were lower on Fe than on Co catalysts, but C_{5+} selectivities (Figure 32c) were very similar on the two catalysts, because of higher C₂-C₄ olefin selectivities on Fe (Fe: 6.4%; Co: 4.4%). The 1pentene/n-pentane ratios are similar on the two catalysts (Figure 32d and Table 9). Larger hydrocarbons are essentially paraffinic on Co catalysts, because of extensive readsorption and chain initiation by larger α -olefins formed in primary chain termination steps, as shown by the lower *1*-decene/n-decane ratios on Co than on Fe catalysts (Figure 32e, Table 9).

In summary, hydrocarbon synthesis rates (per g) on Fe-Zn-K₄-Cu₂ catalysts prepared via the synthesis, promotion, and activation protocols reported here are nearly identical to those observed on Co/SiO₂ catalysts representative of the state-of-the-art. The lower apparent turnover rates on Fe-based catalysts are compensated by a larger density of active sites per gram of catalyst to yield similar hydrocarbon synthesis rates per gram of catalyst. The higher bed density of Fe oxide precursors relative to Co/SiO₂ leads to much higher volumetric productivities on Fe-Zn-K₄-Cu₂ (0.188 g-hydrocarbons/cm³-catalyst.h) than on Co/SiO₂ (0.061 g-hydrocarbons/cm³-catalyst.h), an advantage that can be used to decrease the reactor volumes required in packed bed or bubble column reactors. These Fe-based catalysts, with their lower CH₄ selectivities and more olefinic products, provide attractive alternatives to Co-based catalysts. These Fe-based catalysts also show a much weaker dependence of selectivity on temperature, pressure, and synthesis gas ratio than Co catalysts. Their higher CO_2 selectivity, even at low temperatures, continues to inhibit their use in the conversion of natural gas-derived synthesis gas. Additional decreases in CO_2 selectivities on Fe catalysts will require even lower reaction temperatures or the internal recycle of some CO_2 to the inlet of FTS reactors or synthesis gas generation units.

Figure 32. Comparison of the performance of the Fe-Zn-K₄-Cu₂ (•), and 21.9 wt.% Co/SiO₂ (•) catalysts for the FTS reactions (473 K and 2.14 MPa, H₂/CO=2). (a) Hydrocarbon productivity, (b) CH₄ selectivity, (c) C₅₊ selectivity, (d) $1-C_5H_{10}/n-C_5H_{12}$ ratio, and (e) $1-C_{10}H_{20}/n-C_{10}/H_{22}$ ratio.





Table 9. A comparison of the Steady-state FTS performances between Fe and Co catalysts (473 K, 2.0 MPa, $H_2/CO=2$) at CO conversion range of 18~21% (atomic ratios: Zn/Fe=0.1, K/Fe=0.04, Cu/Fe=0.02; 21.9 wt.% Co/SiO₂).

Catalyst	Fe-Zn-K ₄ -Cu ₂	Co/SiO ₂
Total available metal sites for FTS ($\times 10^{-4}$ mol/g-cat.)	7.4	1.7
Hydrocarbon synthesis turnover rate (h ⁻¹)	16.7	59.6
Hydrocarbon synthesis productivity (g/h.kg-cat)	171	143
Hydrocarbon synthesis volumetric productivity (g-hydrocarbons/cm ³ -catalyst.h)	0.188	0.061
CO ₂ selectivity (%)	15.8	0.3
$ ext{CH}_4 \left(\%\right)^{ ext{a}}$	2.0	6.8
$C_2-C_4 (\%)^a$	8.9	6.4
C_{5+} (%) ^a	89.1	86.8
$1-C_5H_{10}/n-C_5H_{12}$ ratio	2.1	2.0
$1-C_{10}H_{20}/n-C_{10}H_{22}$ ratio	1.6	0.3

 $^{a}\overline{\rm CH_{4}}$ and $\rm C_{5+}$ selectivities are reported on a CO₂-free basis.

7. Structural analysis of unpromoted Fe-based FTS catalysts using X-ray absorption and Mössbauer emission spectroscopy

7.1. Introduction

The activation of Fe-based precursors in synthesis gas is a complex process, which is difficult to follow as it occurs. The effects of the structural changes that occur during activation on the catalytic behavior of these materials remain unclear. For example, as the partial pressure of hydrogen increases relative to that of CO during activation, at otherwise similar conditions, the ultimate steady-state FTS rates decrease [47]. Promoters, such as Cu and K, shorten the time required for the conversion of Fe oxide precursors into active catalysts. After the initial activation, the structure of Fe-based FTS catalysts continues to evolve with increasing time-on-stream [48].

X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) methods provide unique information about the oxidation state and local environment of each absorber element in complex multi-component materials. In this study, these techniques were used in order to determine the structure of Fe catalysts after they catalyze FTS reactions for various periods of time. In the studies reported here, which were conducted in collaboration with the University of Kentucky, an unpromoted precipitated iron catalyst was used in order to avoid the complexity introduced by chemical and structural promoters. The X-ray absorption results were compared with previous Mössbauer spectroscopy data [48,49] on similar Fe catalysts and the results of these two structural characterization techniques are taken together with their catalytic properties at a given time-on-stream in order to infer the nature of the active species and the chemical and structural changes that accompany deactivation during FTS reactions.

7.2. Catalyst preparation

One sample of the unpromoted Fe oxide precursor (Sample 0) and samples of this precursor after activation (Sample 1) and after use for various lengths of time (Samples 3, 5, 7, 10, 13, 19 and 20) were examined. The Fe oxide precursor was prepared by precipitation from an aqueous solution of $Fe(NO_3)_3$ ·9H₂O (Johnson Matthey Co., >98% metals basis, 1 M; 2.6 cm³/s) using concentrated NH₄OH (VWR, reagent grade, 28-30 wt.%; 1.2 cm³/s). The pH of the slurry was kept constant at 9.3 and the residence time in the reactor was 300 s. This resulted in a total slurry volume of 34.4 l. After initial filtration, the precipitates were washed by re-slurring twice with 34.4 l of deionized water with intervening filtration using rotary drum filters. The washed precipitates were dried in air at 373 K overnight. The dried materials were ground using a mortar and pestle in order to obtain particles with ~0.15 mm diameter and then treated in stagnant dry air at 623 K for 4 h.

7.3. Activation and FTS reactions

All FTS experiments were carried out in a 1-liter continuous stirred tank reactor (CSTR). The catalyst precursor (64.44 g) was suspended in C-30 oil (Ethylflow, decene trimers;

Ethyl Corp., 290 g) and pretreated with CO at 543 K and 1.22 MPa for 24 h. The CO flow (58.7 sl/h. g-Fe) was started at ambient conditions (298 K and 0.1 MPa), the pressure was raised to 1.22 MPa, and the temperature of the reactor was then increased to 543 K at 0.033 K/s and maintained at this temperature for 24 h. After this activation treatment, the reactor was brought to reaction conditions (543 K; 1.22 MPa; H₂/CO=0.68; $3.1 \text{ sl}(\text{CO+H}_2)/\text{h. g-Fe}$) by introducing H₂ into the CO stream over a period of ~3 h.

Reaction products were analyzed using gas chromatography. Gas products were analyzed using a Hewlett-Packard Quad-Series Refinery Gas Analyzer (QRGA). The analysis of the aqueous phase collected after the reactor was carried out using a Hewlett-Packard 5790 gas chromatograph equipped with a thermal conductivity detector and a Porapak Q-column. Oil and wax were combined and analyzed with a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and a 60 m DB-5 column. The wax products were analyzed using a Hewlett-Packard 5890 high temperature gas chromatograph using flame ionization detection and a 30 m alumina clad HT-5 column.

Catalyst samples were extracted from the autoclave during reaction using a dip tube blanketed with an inert gas. All subsequent handling of the used catalysts was carried out under inert gas within a glove box. A total of 20 samples were withdrawn from the reactor during the 452 h experiment. The conversions have not been corrected for the decline in the amount of catalyst withdrawn from the reactor. Based upon the initial solid content of the slurry, the initial slurry volume, and the amount of sample removed from the reactor, catalyst removal would account less than a 15% decrease in CO conversion by the end of the experiment.

7.4. *Mössbauer emission spectroscopy measurements*

The Mössbauer experiments used a constant acceleration spectrometer. The radioactive source consisting of 50 mCi of 57 Co in a Rh matrix. Samples 1, 3, 10 and 20 in powdered form were loaded into Plexiglass compression holders presenting a thin sample to the beam. Spectra collected from Samples 1, 3 and 10 were analyzed by least squares fitting the data to a summation of five sextets, while the spectrum collected from Sample 20 was fitted to the sum of two sextets. Hyperfine parameters extracted from the fits were used to estimate the composition of the samples. The two sextets having the highest hyperfine magnetic field were found to correspond to Fe at the tetrahedral and the octahedral sites of Fe₃O₄. The remaining three sextets were found to correspond to Fe centers located at the three crystallographic sites in the Hägg carbide (Fe₅C₂).

7.5. Mössbauer structural analysis

Table 10 shows the catalyst composition and the relative areal fraction of their sextets obtained from the Mössbauer spectra as a function of time-on-stream. It is worth noting here that these areal fractions measured at room temperature were not corrected by using the recoil-free fraction ratio of the different Fe sites. Therefore, the fractional composition of the samples might be slightly different from the areal fractions. The Fe₅C₂ phase was established from the measured hyperfine parameters, although the measured

atomic ratio, Fe(I):Fe(II):Fe(III), did not conform to the expected ratio of 2:2:1. In largecrystal Fe carbide samples, the ratio frequently differs from 2:2:1 because of the variable concentration of carbidic carbon. Here, however, the deviation is stronger and indicates that crystallization is incomplete. In spite of this, Fe_5C_2 is the only iron carbide that can be discerned from the Mössbauer measurements. The Mössbauer data (Table 10) show that the extent of carburization was nearly complete after the 24 h activation period in contact with flowing CO, and then decreased with time-on-stream. After 452 h, only Fe_3O_4 was detected.

	Sample			
	1	3	10	20
FTS reaction time (h)	0	23	168	452
Fe ₅ C ₂ (at.%)	94	83	42	0
Fe ₃ O ₄ (at.%)	6	17	58	100

Table 10. Mössbauer structural analysis results

7.6. Fe K-edge XANES

Figure 33 shows X-ray absorption near-edge spectra (XANES) for Samples 0, 5, 7, 13 and 19. All spectra show weak pre-edge peaks, indicating the presence of some residual Fe oxides. The absorption edge energy, defined at the first inflection point in the absorption edge, shifts to lower energies for Samples 5 and 7, suggesting the formation of Fe species with lower oxidation states than in Fe₃O₄. The absorption edge energy shifts back to higher values for Samples 13 and 19. The higher absorption edge energies on the catalyst precursor (Sample 0) and in Samples 13 and 19 and the more intense pre-edge features and first maximum in the absorbance spectrum, in the near-edge region indicate the more prevalent presence of Fe oxides in these samples compared to the other used samples.

Principal component analysis (PCA) indicated the presence of two species, identified as Fe_3O_4 and FeC_x in Samples 5-19. The near-edge spectra for these samples can be described as a combination of the standard spectra for Fe_3O_4 and FeC_x ; the relative amounts of these two phases can be obtained using least square error minimization techniques [26]. Fe_2O_3 , FeO and Fe were excluded from the fittings because they were rejected by PCA and because their presence failed to improve fits.

The XAS spectra of the catalyst precursor before activation cannot be fitted to combinations of Fe_2O_3 and Fe_3O_4 spectra. The EXAFS of this sample (Sample 0)

suggests the presence of FeO(OH), apparently as a result of the incomplete crystallization of the oxides during calcination at relatively low temperatures. These temperatures (623 K) are generally sufficient to decompose FeO(OH), but the short treatment time and the stagnant nature of the ambient air within and above the sample bed appeared to inhibit water removal and dehydration, and led to amorphous Fe oxides. Therefore, Sample 0 contained hydrated Fe oxides, which did not crystallize fully during synthesis. X-ray diffraction (XRD) and Mössbauer analyses of other samples that received a similar activation did not detect crystalline Fe compounds in these samples.



Figure 33. Normalized Fe K-edge XANES for (A) Sample 0, (B) Sample 5, (C) Sample 7, (D) Sample 13 and (E) Sample 19.

Table 11 shows the relative abundances of standard compound structures corresponding to the best fits of the experimental spectra for each sample. Figure 34 presents a typical fit to the spectrum for Sample 5. All the fits were excellent. The results from linear combination fits show a monotonic decrease in the relative abundance of Fe carbides with increasing time-on-stream (Samples 5, 7 and 13). After FTS reactions for 432 h, the only detectable phase was Fe_3O_4 (Sample 19), as also found by Mössbauer emission spectroscopy.

7.7. *Fe K-edge fine structure*

Figure 35 shows the Fourier transforms of the Fe K-edge EXAFS for each sample and for the standard Fe compounds. The radial structure function for the catalyst precursor (Sample 0) is poorly resolved, indicating a disordered or non-uniform geometry around Fe absorbers. The radial structure functions for Samples 5 and 7 appear to reflect the combined contributions of Fe_3O_4 and FeC_x . The relative contributions of these two structures suggest that Sample 5 has a higher Fe carbide fraction than Sample 7. After

264 h on-stream, the catalyst (Sample 13) shows a fine structure similar to that of pure Fe_3O_4 ; after 432 h, the fine structure features in Sample 19 are identical to those in pure Fe_3O_4 . The evolution of the radial structure function with increasing time-on-stream is consistent with the changes in structure detected from the linear combination analysis of the near-edge spectra.

	Sample				
	0	5	7	13	19
FTS reaction time (h)	-	71	121	264	432
FeC_x (at.%)	0	52	35	2	0
Fe ₃ O ₄ (at.%)	-	48	65	98	100



Figure 34. Experimental and the linear combination XANES fit for Sample 5.

7.8. Comparison of the results from Mössbauer emission and X-ray absorption spectroscopy

The quantitative phase compositions obtained from Mössbauer emission and X-ray absorption spectroscopies differ (Figure 36). The compositional trends obtained by the two techniques, however, are very similar. Both techniques show that the carbide phase is more prevalent in the earlier stages of contact with synthesis gas and that the Fe carbide content decreases with increasing reaction time. After about 400 h, the only detectable phase is Fe₃O₄. Both techniques indicate that the decrease in the amount of Fe carbide parallels the observed decrease in catalytic activity (Figure 36). Two possible explanations can be proposed for the quantitative differences in the samples used for X-ray absorption spectroscopic measurements were stored for ~2 years. The samples were

stored in the wax FTS product and under an inert gas blanket, but it is possible that some of the carbides were oxidized during storage, leading to the lower carbide fraction detected by XAS. Another possibility is that the Mössbauer technique overestimated the amount of the carbide phase present in the samples. The measured fractions of the oxide and the carbide were calculated from the areas of their sub-spectra divided by the area of the main spectrum, which included all sub-spectra. Corrections were not made for the fraction of the solid sampled by the Mössbauer technique, because such corrections require literature data for the recoil-free fraction of the oxide and carbide phases. Literature values are available for large crystals of these phases, but the small crystals present in FTS catalyst samples make such corrections non-rigorous.



Figure 35. Fe K-edge EXAFS for (A) Sample 0, (B) Sample 5, (C) Sample 7, (D) Sample 13, (E) Sample 19, and standard compounds Fe₂O₃ (triangle), Fe₃O₄ (plus), FeC_x (dot).

7.9. Discussion

Integral FTS rates decreased by almost a factor of 10 leading to a decrease in CO conversion from 86 to 12% after 452 h on-stream (Figure 36). Clearly, the high conversions in the early stages of the reaction lead to much higher H_2O/H_2 and CO_2/CO ratios than those present at the low conversions prevalent at later reaction times. Thus, the oxidizing potentials of the reactant-product mixtures in the gas phase and in the liquid

phases in equilibrium with this gas phase are significantly higher during the early stages of the experiment. Yet Fe carbides were the predominant Fe species at these conditions, although they decreased in relative abundance as the reaction proceeded for longer periods of time. In spite of the fact that CO_2 can lead to the oxidation of Fe carbides, the presence of added CO_2 ($CO_2/CO=0.3$) in the feed gas did not influence CO conversion rates or apparently alter the structure of the catalytic phases. Thus, CO_2 was essentially inert at our reaction conditions. The addition of water at H₂O/CO ratios up to 0.3 also did not influence the rate of hydrocarbon formation, but increased the rate of water gas shift [50]. However, the lack of impact of added CO_2 and H₂O was studied only for an iron catalyst containing silica (4.4 at.% Si to 100 at.% Fe) and potassium (1.0 at.% K to 100 at.% Fe). Thus, the extrapolation of these results to the unpromoted catalyst used in this study may not be appropriate.



Figure 36. FTS rates measured from the CSTR (543 K; 1.22 MPa; $H_2/CO=0.68$; 3.1 litres (CO+ H_2)/h g Fe), and the Fe carbide concentrations obtained from the Mössbauer and the XAS measurements as a function of reaction time.

It appears that individual iron particles undergo re-oxidation rather uniformly. If only the surfaces of each catalyst particle were rapidly oxidized during deactivation, and this initial process were followed by the slower oxidation of the bulk carbide phase, the CO conversion would decline much more rapidly than the concentration of the active Fe carbide phase. The experimental evidence indicates that both decline to a similar extent as deactivation occurs. Thus, it appears that catalyst particles start to re-oxidize via the nucleation of an oxide phase either at the surface or within their core, and ultimately re-oxidize completely, while other particles remain essentially as iron carbide. One possible explanation for this unusual behavior would be a distribution of carbide crystallites and a size-dependent thermodynamic propensity to re-oxidize, but data supporting such effects are not available and such particle size dependence would be unexpected for the large crystallites of Fe phases detected by X-ray diffraction. In any event, the bulk phase composition and specifically the relative abundance of Fe carbides in the unpromoted

iron catalyst directly influence CO conversion rates (Figure 36). This is most readily explained if the catalyst system is composed of a mixture of catalyst particles whose surface resembles either iron oxide or iron carbide phases, and whose distribution favors less active Fe oxides over more active Fe carbides as the catalyst deactivates.

A tenuous balance among several concurrent processes determines the surface and bulk composition of a catalyst during steady-state FTS. First, there must be a balance between the amount of CO that is converted to products in the Fischer-Tropsch and the water-gas shift reactions, and the amount of CO that is dissociated on the catalyst surface in a form that maintains the carbide phase. Any imbalance between these rates would lead to the net introduction or removal of carbon or oxygen atoms into the inorganic structure, and to the interconversion of Fe oxides and Fe carbides. If the removal of the carbon and oxygen atoms using hydrogen or CO becomes imbalanced, the surface chemical potential of either carbon or oxygen becomes higher than in the contacting gas phase. This can lead to the formation of bulk structures in thermodynamic equilibrium with the steady-state surface chemical potential. On unpromoted iron catalysts, it appears that deactivation leads to the preferential inhibition of oxygen removal pathways over those leading to the removal of carbon to form CH_x species and ultimately hydrocarbons. The concomitant depletion of the surface carbon pool leads to the nucleation of Fe₃O₄ patches, which dissociate CO and catalyze FTS with very low reaction rates. If only the surface were oxidized, to resemble Fe₃O₄, however, the catalytic activity would change much more rapidly than the Fe oxide content in the catalysts and the catalyst would recarburize in the presence of the carburizing synthesis gas mixture present at low conversions. The catalytic activity declines at about the same rate as the bulk carbide phase. This eliminates the possibility of just surface oxidation causing the compositional changes defined by the Mössbauer and the X-ray absorption spectroscopy measurements and influencing FTS reaction rates.

In the case of the unpromoted Fe catalysts of this study, the re-oxidation may be caused, or at least initiated, by changes in the relative rates of oxygen formation in CO activation steps and of oxygen removal by reaction with hydrogen or CO to form water and CO₂, respectively. Such changes occur concurrently with the observed decrease in the rate of the reaction, apparently because of the common need for H₂ activation steps for both monomer formation and for oxygen removal in FTS reaction catalyzed by Fe carbide particles. Thus, re-oxidation reflects changes in the surface chemical potential of C*, O*, and H* adsorbed species, instead of corresponding changes in chemical potential within the contacting gas phase. In turn, this suggests that the removal of oxidizing species, such as adsorbed H₂O^{*}, OH^{*}, or O^{*}, occurs via steps that are not quasi-equilibrated during FT synthesis, and that their surface concentrations can significantly exceed those that would be in equilibrium with the contacting gas phase. The non-equilibrated nature of water desorption steps has been recently demonstrated during FTS reactions on Co catalysts by the very low HD and D₂ concentrations among hydrogen molecules and by the low Dcontent in the hydrocarbon formed from CO/H₂/D₂O reactant mixtures as discussed in Section 5 in the discussion on Co-FTS catalysts.

The data in Figure 36 suggest a direct relationship between the FTS rates and the concentration of Fe carbides during reaction. It appears that catalytically active species reside on carbided surfaces. We have shown in Section 4 and 5 that Fe_3O_4 crystallites become almost immediately active in FTS reactions after exposure to synthesis gas and that only the incipient conversion of near surface oxide layers to Fe carbides is required for steady-state FTS rates. Thus, the observed deactivation with time-on-stream is unlikely to reflect merely the bulk re-oxidation of a particle core to Fe_3O_4 , because such particles would immediately re-activate to give high FTS reaction rates, as they initially do when Fe oxides precursors are activated in synthesis gas. Instead, it appears that the observed oxidation and deactivation of Fe carbides are concurrent processes caused by changes in the carbide surface, which render the oxidation potential of adsorbed species high enough to form Fe_3O_4 surfaces. These surfaces exhibit a structure or composition that prevents their re-carburization at FTS reaction conditions, even at the low conversion levels and reducing conditions prevalent as conversion decreases during catalyst deactivation.

7.10. Conclusions

Mössbauer and XAS measurements of the phase composition of unpromoted Fe catalysts sampled at various periods of FTS reactions showed a consistent decrease in the Fe carbide concentration with time-on-stream. The CO conversion decreased by a factor of 10 during the structural evolution of the catalysts from initial nearly pure Fe carbides after activation in CO, to their gradual oxidation with increasing reaction time, and their ultimate transformation to pure Fe₃O₄ after 450 h on-stream. It appears that the observed oxidation and deactivation of Fe carbides are concurrent processes caused by changes of chemical potential of absorbed species at the carbide surface, which render higher concentrations of oxidizing species on the surface than in the contacting gas phase. These conditions, in turn, lead to the oxidation of Fe carbides even in the reducing environments prevalent as conversion decreases during catalyst deactivation.

8. Pathways for CO₂ Formation and Conversion during FTS reactions on Iron-Based Catalysts

8.1. Introduction

The removal of chemisorbed oxygen atoms (O*) formed in the CO dissociation steps required for monomer formation during FTS can occur *via* reactions of O* with coadsorbed hydrogen (H*) or carbon monoxide (CO*). These reactions lead to the formation of H₂O and CO₂, respectively, as the oxygen carrier. In this manner, H₂O and CO₂ both form as primary FTS products. CO₂ and H₂O can also form *via* secondary reactions, but thermodynamic constraints lead to the net formation of CO₂ and the net depletion of H₂O at typical FTS reaction conditions. This occurs with the overall stoichiometry of the water-gas shift (WGS) reactions on Fe-based FTS catalysts [51-53]. Fe, Zn and Cu oxides can also provide active sites for these CO₂-forming reactions [52-54], which are useful for coal-derived synthesis gas streams (H₂/CO ~ 0.7), because oxygen rejection by excess CO reactants allows more efficient use of these CO-rich streams. For synthesis gas streams derived from natural gas, CO₂ formation leads to high H₂/CO ratios along the reactor bed and to lower olefin and C₅₊ selectivities. The control of oxygen removal *via* both primary removal and secondary oxygen removal pathways remains a critical issue in the design and use of Fe-based catalysts for FTS reactions.

The mechanism of CO_2 formation and the role of CO_2 in chain growth remain controversial. Some studies propose that FTS and WGS reactions proceed on different sites [20,54,55] with carbide sites involved in FTS and Fe₃O₄ as the active phase for WGS reactions involving surface formate (HCOO*) intermediates [45]. The rapid dynamic interconversion between FeC_x and Fe₃O₄ during FTS discussed in Section 3 makes the site assignments for these two reactions difficult to support with definitive experimental evidence. Most studies, however, do not consider primary CO₂ formation routes at all during FTS. The non-zero CO₂ selectivity observed at low CO conversions and low H₂O concentrations, and the expected presence of O* and CO* during FTS, show that CO₂ can also form as a primary product. Yet another CO₂ formation route involves the synthesis and decomposition of organic acids [56-58]. CO₂ can form via decarboxylation of organic acids formed from FTS alcohol products. The addition of ¹⁴CH₃OH [56] or 1-pentanol [1-¹⁴C] [57] to $H_2/^{12}CO$ led to higher ¹⁴C contents in CO₂ than in CO, suggesting an intermediate role of alcohols in CO₂ formation. The absence of ¹⁴C in C₁-C₄ products during the addition of *1*-pentanol $[1-^{14}C]$ suggests that CO₂ is not formed via direct alcohol decomposition, but rather via oxidation of alcohol to carboxylic acids followed by subsequent decarboxylation to form CO₂ and an olefin [57].

Another important aspect of CO₂ chemistry during FTS is its potential role in monomer formation and chain initiation. The addition of ${}^{14}CO_2$ (1.4% mol) to $H_2/{}^{12}CO$ (1:1) did not lead to detectable ${}^{14}C$ contents on fused Fe catalysts (501 K, 0.1 MPa, H₂/CO=1) [58]. More recent studies by Xu *et al.* [59,60], however, detected almost identical radioactivity per mole in CO₂ and in hydrocarbons on a Fe-Si-K catalyst (543 K, 0.8 MPa, H₂/CO=0.7), suggesting that each hydrocarbon molecule contained one ${}^{14}C$ from ${}^{14}CO_2$. These latter results are surprising in view of the isotopic and chemical equilibration

detected between CO and CO_2 in the effluent stream, which would render the chemical source of the carbon atoms indeterminate.

In this section, we describe the role of CuO and K_2CO_3 promoters on primary and secondary CO₂ formation pathways during FTS and probe the relative rates of primary oxygen removal *via* reaction with adsorbed hydrogen (to form H₂O) or with adsorbed CO (to form CO₂). ¹³CO₂ addition studies at conditions far from water-gas shift equilibrium are used to show that CO₂ is essentially inert in chain growth or initiation reactions and that its chemical conversion to hydrocarbons occurs *via* surface or gas phase CO intermediates. Finally, a reversible reaction kinetic analysis approach is developed in order to describe the effects of CO₂ recycle on CO₂ selectivity. As suggested previously [16], the presence of CO₂ inhibits the net rate of WGS during Fischer-Tropsch synthesis on Fe-based catalysts. The addition or recycle of CO₂ decreases the net rate of CO₂ formation and increases the fraction of the oxygen atoms in CO removed as H₂O, an important practical issue in the use of Fe-based catalysts for H₂/CO mixtures derived from natural gas.

8.2. Experimental Methods

¹²CO₂ and ¹³CO₂ addition experiments were carried out on the low surface area Fe-Zn-K₂-Cu₁ catalyst and the high surface area Fe-Zn-K₄-Cu₂ catalyst respectively. An equimolar ¹²CO₂/Ar mixture (Linde, Air Products Co.) was used in ¹²CO₂ addition experiments carried out to simulate recycle conditions. The pressure of ¹²CO₂ was varied while maintaining a constant synthesis gas pressure. ¹³CO₂ addition experiments were carried out in order to probe the role of CO₂ in chain initiation and growth by adding 0.1 MPa ¹³CO₂ (Cambridge Isotope Laboratories Inc., 99% isotopic purity) at 508 K, 0.8 MPa synthesis gas pressure, and a H₂/CO ratio of 2.0. The ¹³C content in the products of ¹³CO₂/¹²CO/H₂ mixtures was measured using a mass selective detector (Hewlett Packard, Model 5890; Series II/5791A) and separating the products with a HP-1 capillary column (cross-linked methyl silicone, 50 m × 0.32 mm × 1.05 µm). The ¹³C contents in reactants and products were measured from mass ion intensities using deconvolution techniques that account for natural abundance and mass fragmentation patterns [61].

8.3. Role of CuO and K_2CO_3 promoters on CO_2 formation pathways

 CO_2 selectivities on Fe-Zn, Fe-Zn-Cu₁, Fe-Zn-K₂ and Fe-Zn-K₂-Cu₁ are shown as a function of CO conversion for stoichiometric synthesis gas (H₂/CO=2) at 508 K and 2.14 MPa in Figure 37a and at 543 K and 0.5 MPa in Figure 37b. These data were obtained by changing the CO space velocity at constant temperature and H₂ and CO partial pressures. CO_2 selectivities increased with decreasing space velocity (and increasing reactor residence time and CO conversion) on all catalysts. This increase in CO_2 selectivity reflects the formation of CO_2 by reactions of water with CO-derived intermediates in secondary reactions with the stoichiometry of the water-gas shift reaction. In these reactions, H₂O formed in primary oxygen removal steps readsorbs on sites where it can dissociate and its extent of readsorption and reaction increases, as the concentration of water increases with increasing CO conversion and decreasing space velocity. The

dependence of CO_2 selectivity on reactor residence time weakens at higher CO conversion levels, as CO_2 -forming reactions approach equilibrium on all catalysts.



Figure 37. CO₂ selectivity as a function of CO conversion on the different Fe catalysts at (a) 508 K, 2.14 MPa, H₂/CO=2, and (b) 543 K, 0.5 MPa, H₂/CO=2. (\blacktriangle): Fe-Zn, (\blacklozenge): Fe-Zn-Cu₁, (\blacksquare): Fe-Zn-K₂, and (\blacklozenge): Fe-Zn-K₂-Cu₁.



Figure 38. Oxygen selectivity to H₂O as a function of CO conversion on the different Fe catalysts at (a) 508 K, 2.14 MPa, H₂/CO=2, and (b) 543 K, 0.5 MPa, H₂/CO=2. (\blacktriangle): Fe-Zn, (\blacklozenge): Fe-Zn-Cu₁, (\blacksquare): Fe-Zn-K₂, and (\bullet): Fe-Zn-K₂-Cu₁. Dashed line: Oxygen selectivity to H₂O at WGS equilibrium.

 CO_2 selectivities are higher on promoted Fe catalysts than on unpromoted samples at all CO conversion levels. The slope of these CO_2 selectivity curves at different points (Figure 37) (or more rigorously the slopes of the CO_2 formation rates shown later) gives a measure of the rate of secondary CO_2 -forming reactions. These slopes are very similar for Fe-Zn-K₂ and Fe-Zn-K₂-Cu₁ catalysts at 508 K (Figure 37a). Similarly, Fe-Zn and Fe-Zn-Cu₁ catalysts also show nearly identical slopes, indicating that the addition of Cu to Fe-Zn-K₂ or Fe-Zn does not increase the rate of WGS reactions. Figures 38a and 38b show the oxygen selectivities to H₂O on all four catalysts at the two reaction conditions of this

study. This oxygen selectivity is defined as the percentage of the oxygen in the converted CO that appears as a given product, in the case of Figure 38 as H_2O . The oxygen selectivity to H_2O decreases with increasing CO conversion as water readsorbs and finds additional opportunities to react and approach equilibrium, which favors CO_2 as the oxygen removal carrier at these reaction conditions. These H_2O selectivities extrapolate to high values as CO conversion decreases, consistent with a high primary selectivity for oxygen removal as water. The readsorption of water and its subsequent probability of reaction with CO-derived intermediates to form CO_2 , leads to a decrease in the H_2O selectivity with increasing CO conversion (Figure 38).

The CO₂ selectivities extrapolated to low CO conversion levels are non-zero, consistent with these primary pathways for oxygen removal as both CO₂ and H₂O. Cu increases this primary selectivity to CO₂ and thus the propensity for O* removal as CO₂ on Fe-Zn catalysts. In contrast, K increases the rate of the secondary WGS reaction without influencing primary CO₂ selectivities (Figures 37 and 38). It appears that K promotion does not influence the relative abundance of CO* and H* species available for oxygen removal, even though previous studies have suggested that K effects on hydrocarbon selectivity and FTS rates reflect an increase in the binding energy of adsorbed CO relative to that of hydrogen [4,16]. The higher CO₂ selectivity on Cu-containing catalysts suggests that Cu increases the availability of CO* for O* removal in primary pathways. but that Cu does not increase the rate of secondary CO₂-forming reactions (see slopes in Figure 37), even though previous reports have attributed higher CO₂ selectivities on Cupromoted samples to Cu-catalyzed WGS reactions [62]. The primary CO₂ selectivity is lower at 508 K and 2.14 MPa (Figure 37a) than at 543 K and 0.5 MPa (Figure 37b) on all catalysts, suggesting that O* removal as H₂O has a lower activation energy than parallel pathways leading to CO₂.

The slope of the CO₂ selectivity data in Figure 37 may also include other secondary routes for the formation of CO₂, such as the conversion of alcohol primary products to acids and their subsequent decarboxylation [57,59]. These pathways are unlikely to contribute appreciably to CO₂ at the conditions of our experiments (508-543 K, 0.5-2.14 MPa, and H₂/CO=2), because alcohol selectivities, and their observed changes with space velocity, are much smaller than the changes in CO₂ selectivity shown in Figure 37 and than the changes in alcohol selectivities reported previously at lower H₂/CO ratios (0.7) [18,20]. Water-gas shift reactions, possibly on sites that also catalyze CO dissociation and chain growth as part of FTS catalytic sequences, appear to provide the predominant secondary route for CO₂ formation at the conditions of our experiments.

8.4. Effects of CO_2 addition to synthesis gas on Fe-based catalysts

Water-gas shift reactions approach equilibrium with increasing residence time and temperature during FTS (Figure 37). This approach to equilibrium and its kinetic consequences can be rigorously described by a parameter η , given by the concentration ratio in equation (1) divided by the equilibrium constant at the reaction temperature:
$$\eta = \frac{1}{K_{WGS}} \left(\frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \right)$$
(1)

In Equation (1), P_j is the partial pressure of species j and K_{WGS} is the WGS equilibrium constant. The value of η ranges from 0 to 1 as chemical reactions approach equilibrium. Figures 39a and 39b show this value for the two experimental conditions used to obtain the data in Figures 37a and 37b. These values suggest that reverse WGS reaction rates are significant. Therefore, the addition of CO₂ to synthesis gas feeds can lead to lower net rates of CO₂ formation and of O* removal as CO₂ during FTS.



Figure 39. The approach to equilibrium parameter (η) for water-gas shift reaction as a function of the amount of CO₂ added on the Fe-Zn-K₂-Cu₁catalyst; (a) 508 K, 2.14 MPa, H₂/CO=2, and (b) 543 K, 0.5 MPa, H₂/CO=2.

The kinetic consequences of this approach to equilibrium and of the addition of CO_2 can be described by considering how forward rates $r_{f,i}$, and reverse rates $r_{r,i}$, of each elementary step i in the WGS reaction:

$CO + H_2O \Leftrightarrow CO_2 + H_2$

depend on the affinity of that step (A_i) , as given by the De Donder equation [63] of nonequilibrium thermodynamic treatments of chemical kinetics:

$$\frac{r_{f,i}}{r_{r,i}} = \exp\left(\frac{A_i}{RT}\right)$$
(2)

The affinity is the negative of the Gibbs free energy of step i:

$$A_i = -\Delta G_i \tag{3}$$

and it is related to standard affinity for that step A_i^o by:

$$A_{i} = A_{i}^{o} + RT \ln \left(\frac{P_{CO_{2}} P_{H_{2}}}{P_{CO} P_{H_{2}O}} \right)$$
(4)

The net rate of the overall reaction is then given by:

$$r = r_f - r_b = r_f \left(1 - \exp\left(\frac{-A}{\sigma RT}\right) \right)$$
(5)

in which, σ is the average stoichiometric number for the catalytic sequence. This number is unity for overall reactions, such as WGS, in which every elementary steps occurs only once in the complete catalytic sequence [64]. Equation (5) then becomes:

$$r = r_f - r_r = r_f \left(1 - \exp\left(\frac{-A}{RT}\right) \right)$$
(6)

The affinity of the overall reaction (A) depends on the standard reaction affinity A^o and on the partial pressures of reactants and products:

$$A = A^{o} + RT \ln \left(\frac{P_{CO_{2}} P_{H_{2}}}{P_{CO} P_{H_{2}O}} \right)$$
(7)

The standard affinity A^o equals the negative of the standard Gibbs free energies for the reaction and it is related to the equilibrium constant:

$$A^{\circ} = -\Delta G^{\circ} = RT \ln K_{WGS} \tag{8}$$

Combining Equations (5) and (6), we obtain:

$$A = RT \ln \frac{1}{K_{WGS}} \left(\frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \right)$$
(9)

and then from Equations (1), (6) and (9) we obtain an expression for the net rate of a chemical reaction as it approaches equilibrium in terms of the parameter η that measures the extent of this approach to equilibrium:

$$r = r_f \left(1 - \frac{1}{K_{WGS}} \left(\frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \right) \right) = r_f (1 - \eta)$$
(10)

The forward WGS rate can then be calculated from the measured net rate of CO_2 formation divided by (1- η), where the latter is evaluated at the average partial pressures for each reactant and product in the reactor. The forward rate estimated in this manner is shown in Figures 40a and 40b as a function of CO conversion along with the net CO_2 formation rate for the two reaction conditions used in this study. For the catalysts promoted with K, the CO_2 forward rate increases with increasing conversion, indicating that K increases the rate of the secondary CO_2 forming reactions reaction involving a water co-reactant, which increases in concentration with increasing CO conversion. Cu promotes the removal of O* by CO* rather than H*, but the nearly constant forward CO_2 rate with increasing CO conversion suggests that it does not introduce active sites for secondary water-gas shift reactions. Next, we examine the effects of addition of CO_2 to synthesis gas using this formalism for estimating the effects of CO_2 on the net rate and on the rate of the forward CO_2 formation reactions.

The effects of CO_2 addition on FTS rates and selectivities were examined on Fe-Zn-K₂-Cu₁ at the two reaction conditions used for the space velocity data in Figure 37 (508 K, 2.14 MPa H₂/CO and 543 K, 0.5 MPa H₂/CO). CO conversion rates and hydrocarbon and net CO₂ formation rates are shown as a function of the average CO₂ pressure in the

reactor (the average of the inlet and outlet CO_2 pressures in the reactor) in Figures 41a and 41b. The CO conversion rates and the net CO_2 formation rates decreased with increasing CO_2 pressure, but hydrocarbon formation rates were not affected. This shows that the presence of CO_2 in the synthesis gas feed decreases the net rate of CO_2 formation without any influence in the rate of formation of hydrocarbon chains. The effect of CO_2 on the net rate of CO_2 formation is stronger at higher temperatures, apparently because of the faster forward WGS rates and the less favorable equilibrium as temperature increases. The observed decrease in the net rate of CO_2 formation or merely an increase in the reverse rate of these reactions as they approach equilibrium. The relative importance of these two effects can be discerned by applying the formalism derived above to these kinetic data.



Figure 40. CO₂ forward rate as a function of CO conversion on the different Fe catalysts at (a) 508 K, 2.14 MPa, H₂/CO=2, and (b) 543 K, 0.5 MPa, H₂/CO=2. (\blacktriangle): Fe-Zn, (\blacklozenge): Fe-Zn-Cu₁, (\blacksquare): Fe-Zn-K₂, and (\blacklozenge): Fe-Zn-K₂-Cu₁.



Figure 41. CO conversion rate (•), hydrocarbon formation rate (\blacksquare) and CO₂ formation rate (\blacktriangle), as a function of the average CO₂ pressure on the Fe-Zn-K₂-Cu₁ catalyst at (a) 508 K, 2.14 MPa, H₂/CO=2, and (b) 543 K, 0.5 MPa, H₂/CO=2.



Figure 42. Forward WGS rates (•), net WGS CO₂ formation rates (•), and the approach to equilibrium parameter, η (\diamond), as a function of CO₂ pressure on the Fe-Zn-K₂-Cu₁ catalyst at 543 K, 0.5 MPa, H₂/CO=2.

Figure 42 shows that forward CO₂ formation rates $[r_f = r/(1-\eta)]$ at 543 K are nearly unchanged as the average CO₂ pressure (and hence η) increases. Thus, the presence of CO₂ merely increases the rate of conversion of CO₂ to CO *via* reverse WGS reactions in the exact manner predicted by Equation 10. The net rate of CO₂ formation decreases without detectable changes in the rate of the forward reaction and without the appearance of pathways that use CO₂ directly to form hydrocarbons.

Net CO₂ formation rates in Figure 42 extrapolate to zero net rates at CO₂ pressures of ~0.85 MPa (CO₂/CO = 5.5). At this CO₂ pressure, *all* of the O* species formed *via* CO dissociation would be removed as H₂O during FTS at 543 K. The required CO₂/CO ratio predicted from Equation 10 and the equilibrium constant for WGS at 543 K (K=63.6) is 5.2, in close agreement with the value of 5.5 obtained from the experimental data shown in Figure 42. At 508 K, the effects of CO₂ addition on the net rate of CO₂ formation were much smaller owing to the fact that the WGS reaction was significantly away from equilibrium (Figure 38a). The use of K_{WGS} values for this temperature and Equation 10 leads to a predicted value of ~2.7 MPa (CO₂/CO=4.4).

Net CO₂ selectivities and CH₄ and C₅₊ selectivities (on a CO₂-free basis) are shown as a function of the average CO₂ pressure in Figures 43a and 43b for the two reaction conditions used in these experiments. At 543 K, CO₂ leads to a slight increase in C₅₊ selectivity and to a concomitant decrease in CH₄ selectivity (Figure 43b); these effects are not detectable at lower temperatures (Figure 43a). These selectivity effects appear to reflect small changes in the H₂/CO usage ratio as the O* is increasingly removed as water (using H₂) instead of CO₂ (using CO) as the CO₂ concentration increases. They lead to slightly lower average H₂/CO ratios throughout the catalyst bed (Figures 44a and 44b), especially at higher temperatures, for which oxygen removal selectivities depend on the presence and concentration of CO₂ in the synthesis gas. H₂ and CO chemisorption are generally assumed to be quasi-equilibrated during FTS; therefore, these changes in the H₂/CO ratio lead to a concomitant increase in the surface coverages of CO* relative to

H* and to a increase in the probability of chain growth and in the average molecular weight of the products formed. These changes become detectable only at higher temperatures, for which significant reverse rates lead to appreciable changes in the synthesis gas composition. The α -olefin/*n*-paraffin ratios on Fe-Zn-K₂-Cu₁ also increase with increasing CO₂ pressure (Figures 44a and 44b) for chains of all sizes at 543 K, while the effects were very small at 508 K. These changes are also consistent with the lower H₂/CO ratios and the lower expected surface H* concentrations prevalent when CO₂ is added to the synthesis gas stream.



Figure 43. Product selectivities as a function of the average CO₂ pressure on the Fe-Zn-K₂-Cu₁ catalyst at (a) 508 K, 2.14 MPa, H₂/CO=2, (b) 543 K, 0.5 MPa, H₂/CO=2; (•): C₅₊, (\blacksquare): CO₂ and (\blacktriangle): CH₄.



Figure 44. α -Olefin/*n*-paraffin ratio for different hydrocarbon chain sizes as a function of the average CO₂ pressure on the Fe-Zn-K₂-Cu₁ catalyst at (a) 508 K, 2.14 MPa, and (b) 543 K, 0.5 MPa, H₂/CO=2; (\bullet): C₃H₆/C₃H₈, (\blacksquare): *1*-C₅H₁₀/*n*-C₅H₁₂, (\blacktriangle): *1*-C₁₁H₂₂/*n*-C₁₁H₂₄, and (\circ): Average H₂/CO ratio in the reactor.

These results show that the extent to which O^* is removed as CO_2 during FTS can be controlled by the addition or recycle of CO_2 and that the required CO_2 concentrations can be accurately estimated using a rigorous kinetic treatment of reversible reactions as such reactions approach equilibrium. At temperatures and reaction conditions for which WGS reactions are far away from equilibrium, the complete inhibition of CO_2 formation requires large CO_2/CO ratios. However, at higher temperatures, which lead to higher forward WGS rates and to less favorable WGS thermodynamics, the CO_2/CO ratios required to eliminate CO_2 formation become small enough for potential use of CO_2 recycle when H_2/CO mixtures derived from natural gas are used on Fe-based FTS catalysts.

8.5. The role of CO_2 in the initiation and growth of hydrocarbon chains

As WGS reactions approach equilibrium during FTS, CO and CO₂ become kinetically indistinguishable, because their interconversion is much faster than chain initiation and growth steps required for hydrocarbon formation. Then, a significant fraction of the C-atoms in CO₂ can contribute towards the formation of hydrocarbons, but *via* the formation of CO intermediates in reverse WGS reactions. A direct role of CO₂ in chain initiation and propagation was proposed by Xu *et al.* [57,60], but it is unclear how such conclusions could be reached from isotopic experiments influenced by significant chemical (and isotopic) interconversion of CO and CO₂ *via* WGS reactions.

Here, we report the results of experiments in which 0.1 MPa ${}^{13}CO_2$ was added to synthesis gas (P_{CO}=0.25 MPa, P_{H2}=0.50 MPa and P_{N2}=0.05 MPa) at conditions far removed from the WGS equilibrium (η =0.025). The CO conversion and product selectivities are listed in Table 12. The ${}^{13}C$ contents in hydrocarbons chains of a given size were measured in order to probe the relative contributions of ${}^{13}CO_2$ and ${}^{12}CO$ to chain initiation and chain growth. These results were not corrupted by any isotopic or chemical equilibration between the CO and CO₂ components in the reactant stream. As shown in Figure 45, the ${}^{12}CO$ reactant exiting the reactor retains the ${}^{12}C$ isotopic purity, while the initially pure ${}^{13}CO_2$ reactants retain ${}^{13}C$ fractions greater than 0.5.

The ¹³C contents in CO₂, CO, hydrocarbons, oxygenates (aldehydes + alcohols) are shown in Figure 45. No¹³C was detected in CO, suggesting that dilution of the CO reactant by CO molecules formed from CO₂ via reverse WGS reactions was negligible at these reaction conditions, consistent with the low value of η (=0.025). The fraction of ¹³C in CO2 was 0.533, because CO2 formed during O* removal using CO or via WGS reactions dilutes the isotopically pure ${}^{13}CO_2$ reactants. The ${}^{13}C$ fraction in all C₁-C₁₀ paraffins, C_2 - C_{10} olefins, and C_1 - C_8 oxygenates are much lower than in CO₂, and in most cases, well below the detection limit (~0.02-0.03) of our analytical methods. Clearly, no preferential incorporation of CO₂ is detected in any of the hydrocarbon products; exclusive chain initiation by CO_2 , as proposed earlier [57,60], would have led to significant isotopic enrichment of the smaller products and to a decrease in the ¹³C content with increasing chain size, neither of which was experimentally observed in our study (Figure 45). Also, the reactivity of CO_2 in chain initiation and growth would have to be at least five times lower than that of CO, because the average ¹³C fraction in the combined CO/CO_2 pool is about 0.25, while that in the pool of hydrocarbon formed is less than 0.05, and for most of the hydrocarbons below the detection limit. Thus, the participation of CO₂ is no greater than that of CO in either the formation of monomers or the initiation of chains, and probably much smaller. CO_2 is also not involved in alcohol formation, because the ¹³C content in alcohols was also very low and similar to that found in hydrocarbons.

Temperature (K)	508
Synthesis Gas Pressure (MPa) (H ₂ /CO=2)	0.8
¹³ CO ₂ pressure (MPa)	0.1
CO conversion (%)	21.1
CO ₂ selectivity (%)	35.9
η^*	0.025
Selectivity (CO ₂ -free, %)	
CH_4	3.5
C ₅₊	81.8

Table 12. Conditions for ${}^{13}CO_2$ addition experiments performed on the Fe-Zn-K₄-Cu₂ catalyst, reaction parameters and ${}^{13}C$ content in different components.

*: as defined in Equation 1





In summary, an investigation of the CO₂ formation and reaction pathways during Fischer-Tropsch synthesis (FTS) has been carried out on a co-precipitated Fe-Zn catalyst promoted with Cu and K. The removal of adsorbed oxygen formed during CO dissociation steps can occur by primary and secondary pathways. Primary pathways for oxygen removal include reactions with adsorbed hydrogen to form H₂O and with adsorbed CO to form CO₂. The relative probability of oxygen removal either as H₂O or CO_2 is determined by the reaction temperature and the presence of promoters (Cu and K). H₂O formed by primary pathways can undergo readsorption followed by its subsequent reaction with CO-derived intermediates leading to the formation of CO₂. The forward rate of CO₂ formation increases with an increase in residence time, while the net CO₂ formation rate decreases due to the approach towards WGS reaction equilibrium. CO₂ addition during FTS does not influence CO₂ forward rates, but increases the rate of their reverse steps leading to the attainment of WGS equilibrium; and hence it can result in the minimization of CO₂ formation during FTS and to the preferential removal of oxygen as H_2O . CO_2 addition also results in lower H_2/CO ratios in the reactor, which in turn resulted in higher C_{5+} selectivities and olefin content. From our experimental data and the predictions from our thermodynamic treatment, it was found that at 543 K, the addition of 0.85 MPa CO₂ to synthesis gas (H₂/CO=2, 0.50 MPa) could eliminate CO₂ formation during FTS and lead to the complete removal of dissociated oxygen formed during FTS as H₂O. These studies also suggest that the recycle of CO₂ formed during FTS can be used as a tool to improve the carbon efficiency on Fe catalysts, which in turn adds to their advantage of being cheaper and more flexible than Co catalysts. Finally, the addition of 13 CO₂ to H₂/ 12 CO reactants showed that the hydrocarbon products had a negligible 13 C content, indicating that CO₂ is much less reactive than CO towards chain initiation and growth. Our studies also show that except at WGS reaction equilibrium, where CO and CO₂ become kinetically indistinguishable from each other, CO₂ does not appear to compete with CO towards chain initiation and growth reactions.

9. Investigation of the kinetic isotope effects during FTS Reactions on Fe catalysts

Isotope effects were determined by performing FTS reactions on the Fe-Zn-K₂-Cu₁ catalyst with CO/H₂/N₂ (31/62/7) and CO/D₂/N₂ (31/62/7) mixtures (H₂/CO=D₂/CO=2.0) at 508 K and 2.14 MPa. The deuterium content in hydrocarbon products (up to C₈) and in water were measured by a Hewlett-Packard 5890 gas chromatograph coupled with a 5972 A mass selective detector, while the D content in hydrogen isotopomers was determined by online mass spectrometry (Leybod Inficon Instruments Co., Inc.). The D contents were calculated using matrix techniques that correct for ion fragmentation [61].

9.1. H_2/D_2 effects on FTS rates

Figures 46 and 47 show hydrocarbon formation rates and CO_2 formation rates as a function of CO conversion on the Fe-Zn- K_2 -Cu₁ catalyst. Hydrocarbon formation rates were much higher with D_2/CO than with H_2/CO . In contrast, CO_2 formation rate was lower with D_2/CO than with H_2/CO . It has been proposed previously that the formation of higher molecular weight hydrocarbons on Fe-based catalyst during FTS reactions is initiated by the addition of a methyl group to a methylene group and that further chain growth occurs by the reaction of the methylene group with adsorbed alkyl groups. The alkyl groups then react to form olefins and paraffins via either hydrogen elimination or addition. Consistent with these views of CO hydrogenation, one would expect to observe a normal isotopic effect if D_2 were used instead of H_2 .



Figure 46. Hydrocarbon formation rate as a function of CO conversion on the Fe-Zn- K₂-Cu₁ catalyst (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 508 K, 2.14 MPa, H₂/CO=D₂/CO=2.

However, we observed an inverse isotopic effect as D_2 was used instead of H_2 . The overall isotopic effect for CO hydrogenation could arise from a combination of kinetic and equilibrium isotope effects, the former favoring the reaction of H_2 and the latter favoring the reaction of D_2 . If the chemisorption characteristics of H_2 and D_2 on Co were

to be different so as to result in a higher surface coverage of D* than H*, this would lead to a thermodynamic isotope effect that would be opposite in magnitude to the kinetic isotope effect. The inverse isotopic effects of our observations suggested a dominant role of the thermodynamic effects.



Figure 47. CO_2 formation rate as a function of CO conversion on the Fe-Zn- K_2 -Cu₁ catalyst (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 508 K, 2.14 MPa, H₂/CO=D₂/CO=2.

The isotopic effect can be expressed by the ratio of r_H/r_D , where r_H and r_D are FTS rates for H₂ and D₂ respectively, at the same CO conversion. Since experimental values for both r_H and r_D were not obtained at the same CO conversion, these values were obtained by extrapolation from the respective rate vs CO conversion curves. A reaction rate expression proposed [65] for FTS is

$$-r_{CO+H_2} = \frac{kP_{CO}P_{H_2}^2}{P_{CO}P_{H_2} + bP_{H_2O}}$$

Where b is the adsorption parameter and k is the rate constant. Based on this rate expression, hydrocarbon formation rate $(-r_{CO+H_2})$ increases almost linearly with hydrogen pressure at low CO conversions. Since the surface hydrogen concentration is determined by hydrogen pressure (*i.e.* H₂ dissociation is quasi-equilibrated), higher surface hydrogen concentrations result in higher hydrocarbon formation rates. Therefore, hydrocarbon formation rates were higher with D₂ at the same CO conversion, as shown in Figure 46. The lower CO₂ formation rates with D₂ were also due to the higher surface deuterium concentration since hydrogen is one of the products of the water-gas shift reaction (Figure 47). The higher surface D₂ concentration is due to its larger adsorption equilibrium coefficient. This result is in agreement with previous studies. Soller [66] observed that the adsorption of D₂ was about 1.4 times higher than that of H₂ on Cu powder at 398 K. Larger adsorption coefficients were also obtained for D₂ than for H₂ on Ni during the hydrogenation of acetylene [67] and of CO₂ [68].

Figure 48 shows the r_H/r_D ratios for CO conversion, hydrocarbon and CO₂ formation as a function of CO conversion. The r_H/r_D ratio for hydrocarbon formation was about 0.5 and

slightly decreases with increasing CO conversion. The isotope effect (r_H/r_D) for CO consumption is about 0.6, and independent of CO conversion. This value is similar to that reported by Sakharov and Dokukina [69]. The r_H/r_D ratio for CO₂ formation was greater than 1. The inverse isotopic effect for hydrocarbon formation $(r_H/r_D < 1)$ and the normal isotopic effect for CO₂ formation $(r_H/r_D > 1)$ are expected because higher surface hydrogen concentration was present when D₂ was used. The slight decrease in the r_H/r_D ratio for hydrocarbon formation could be associated with small changes in the partial pressure of hydrogen with CO conversion.



Figure 48. r_H/r_D ratios for CO conversion, hydrocarbon and CO₂ formation as a function of CO conversion for H₂/CO or D₂/CO reactants on the Fe-Zn- K₂-Cu₁ catalyst (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 508 K and 2.14 MPa.

9.2. H_2/D_2 effects on α -olefin/n-paraffin ratios

Figure 49 shows α -olefin/n-paraffin ratios as a function of the carbon number. The increase in surface H₂ or D₂ concentration on the catalyst increases the probability of hydrogen addition of the adsorbed alkyl to form paraffins and decrease the probability of hydrogen elimination of the adsorbed alkyl to form olefins. Hence, lower α -olefin/n-paraffin ratios are observed with D₂ than H₂. The isotopic effect for *1*-butene and *n*-butane is illustrated in Figure 50. The r_H/r_D ratios for *1*-butene were higher than that for *n*-butane, suggesting that the inverse isotopic effect is more evident for paraffins than for olefins. This is because the probability of paraffin formation increased due to higher surface hydrogen concentrations when D₂ was used.



Figure 49. α -Olefin/*n*-paraffin ratio as a function of CO conversion for H₂/CO or D₂/CO reactants on the Fe-Zn-K₂-Cu₁ catalyst (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 508 K and 2.14 MPa.



Figure 50. r_H/r_D ratios for *1*-butene, *n*-butane and total C₄ as a function of CO conversion for H₂/CO or D₂/CO reactants on the Fe-Zn-K₂-Cu₁ catalyst (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 508 K and 2.14 MPa.

II. FISCHER-TROPSCH SYNTHESIS ON COBALT CATALYSTS

1. Background

In contrast with Fe, Co catalysts work at relatively lower reaction temperatures and pressures with slightly higher selectivity to linear paraffins in the C₅₊ range and much lower water-gas-shift activity [4]. We have previously developed a reaction-transport model [13] of chain growth and termination for FTS with Co and Ru-based catalysts. The aim of this project at Berkeley is to utilize a combination of activity and selectivity measurements in a high-pressure reactor along with in situ characterization tools such as FTIR and X-ray absorption spectroscopies, as well as the use of isotopes in order to investigate mechanistic implications of FTS reactions on Co-based catalysts. In contrast to Fe catalysts, H₂O is the primary oxygenate product on Co catalysts. The commercial practice of FTS requires that Co catalysts withstand long-term operation at high conversions, where water concentrations can approach their saturation levels and even condense within catalyst pores. This warrants a detailed study of its effects on the FTS rates and selectivities, as well as the chemical characteristics of the Co surface. In this project, we have utilized silica- and titania-supported Co catalysts in order to probe the kinetics of the FTS reaction as well as the effect of water on the FTS performance of Co catalysts. We have also utilized isotopic mixtures in order to test the reversibility of hydrogen and water dissociation steps in the proposed FTS mechanisms and to determine if water participates in the kinetically relevant steps of CO activation and hydrocarbon chain growth.

2. Catalyst synthesis and characterization

The Co/SiO₂ catalysts (12.7 and 21.9 wt.%) and Co/TiO₂ (15 wt.%) were prepared by incipient wetness impregnation of an aqueous solution of Co nitrate (Aldrich 98%) onto SiO₂ support (PQ Co. CS-2133; treated in dry air at 673 K for 3 h) and TiO₂ (Degussa; treated in dry air at 673 K for 3 h) respectively. These samples were dried at 333 K in ambient air for 24 h and treated in flowing H₂ (1.2 x 10^4 cm³/h.g-cat) by increasing the temperature from 293 K to 423 K at 0.17 K/s and from 423 K to 623 K at 8.3 x 10^{-3} K/s and then holding at 623 K for 1 h. The samples were then passivated in a 1% O₂/He at ambient temperature before exposure to ambient air. Cobalt dispersions were measured using H₂ chemisorption (AutoSorb-1; Quantachrome) at 373 K, after passivated samples were reduced in H₂ at 598 K, evacuated to < 10^{-3} Pa at 598 K, and cooled to 373 K. A 1:1 H/Co titration stoichiometry was used to calculate cobalt dispersions, which were found to be 6.3% and 4.2% for 12.7% Co/SiO₂ and 21.9% Co/SiO₂, respectively [70].

3. FTS activity and selectivity measurements

FTS reaction rates and selectivities were measured at 473 K and 2 MPa using a singlepass fixed-bed reactor (SS 304, 0.95 cm O.D. and 0.5 cm I.D.), held within a three-zone furnace and controlled by three temperature controllers. Axial temperature profiles were measured using a type K movable thermocouple contained within a 0.32 cm thermowell, and they were within ± 0.5 K of the average bed temperature. All lines were heat-traced to 433-553 K and two vessels, one at 408 K after the reactor to collect liquid products, and the other at ambient pressure and temperature to collect water and light fractions were used. Analysis of reactants and products were conducted using a HP 5890 GC-Series II and the procedure is described in detail in Section 4.4. Flow of synthesis gas (62% H₂, 31% CO, 7% N₂ internal standard; Praxair: 99.9% H₂, 99.9% CO, 99.99% N₂) and hydrogen (Bay Air gas: 99.999%) were metered using mass flow controllers (Brooks, Model 5850-CAB1AF1A3). H₂/D₂ kinetic isotope effects were studied by running FTS with mixtures of CO/N₂ (Matheson, UHP, 81.5/18.5, molar ratio) with H₂ or D₂ (Cambridge Isotope Laboratories, Inc., 99.8%). Studies were also conducted with the addition of H₂O to synthesis gas using a ISCO 400D pump.

4. Effect of water on FTS rate and selectivities on Co catalysts

The Co site-time yields for the 12.7 and 21.9 wt.% Co/SiO_2 catalysts at 473 K and 2 MPa are shown as a function of the average water pressure in Figure 1. These data points include both space velocity and water addition runs (0.2, 0.4 and 0.8 MPa) at the lowest CO conversion. These data indicate that both indigenous and added water enhances FTS rates.



Figure 1. Water effects on FTS reaction rate (Co/SiO₂ catalysts, 473 K, 2 MPa, $H_2/CO=2$; Open symbols: space velocity runs; Filled symbols: water addition runs at the lowest CO conversions; water partial pressure is the average of the inlet and the exit values).

These results are consistent with those observed previously on Co/SiO₂ and Co/TiO₂ [14,71], and Co-Mg-Th-Aerosil [72]. However this behavior is in contrast to results reported on Co supported on Mn and Al oxides, which showed that water inhibits FTS rates [73-75]. Higher water concentrations also led to lower CH₄ and higher C₅₊ selectivities on Co-based catalysts as shown in Figures 2 and 3 and also as previously reported [14, 71-72, 76-78]. Iglesia *et al.* proposed that FTS rate and C₅₊ selectivity enhancements might reflect higher CO diffusion rates through a water-rich intrapellet phase stabilized by capillary effects [14].

The evidence considered was indirect and based on the influence of the support pore structure on these water effects and on the well-documented effects of intrapellet transport restrictions on FTS chemistry. Large pores would require larger H₂O concentrations to form a water-rich condensed phase, while smaller pores could stabilize such a phase even at all water concentrations prevalent in the experimental CO conversion range covered in these studies [14]. On TiO₂-supported Co catalysts, TiO_x overlayers can form during pre-reduction; these overlayers are removed in more oxidizing environments [78]. Thus, a role of water on such catalysts may be to remove TiO_x overlayers at high water concentrations. Such overlayers, however, do not form on silica, which also show water enhancement effects on large-pore supports. It is also

possible that water may: (1) participate in kinetically relevant steps in the reaction mechanism, or (2) enhance the active site density. In this project, we have tested both these hypotheses. The first approach involves the formulation of reaction mechanisms that involve water participating in the rate-determining steps, followed by fitting the reaction data obtained using non-linear regression to the obtained rate expressions.



Figure 2. Water effects on CH₄ selectivity (Co/SiO₂ catalysts, 473 K, 2 MPa, H₂/CO=2; Open symbols: space velocity runs; Filled symbols: water addition runs at the lowest conversions; water partial pressure is the average of the inlet and the exit values)



Figure 3. Water effects on C_{5+} selectivity (Co/SiO₂ catalysts, 473 K, 2 MPa, H₂/CO=2; Open symbols: space velocity runs; Filled symbols: water addition runs at the lowest conversions; water partial pressure is the average of the inlet and the exit values)

5. Kinetic studies to explore effect of water on the reaction mechanism

5.1. H_2 - D_2 Exchange and D_2O Tracer Experiments

 D_2 -H₂ exchange was carried out by performing FTS reactions at 473 K and 2 MPa with a CO/H₂/D₂/N₂ mixture (31% CO, 31% D₂, 31% H₂, 7% N₂). The deuterium content in hydrocarbon products (up to C₈) 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 [61]. The formation rate of the HD was compared to the rate of hydrogen converted to hydrocarbons (Figure 4). The isotopic exchange rates presented here have been calculated by subtracting those measured in a blank run using SiO₂. Hydrogen exchange rate decreased from 450 h⁻¹ to 200 h⁻¹ as the CO conversion increased from 6% to 15% (by decreasing bed residence time), while the rates of hydrogen conversion to hydrocarbons were less than 50 h⁻¹. At zero CO conversion, the D₂-H₂ exchange rate (590 h⁻¹) is almost 20 times larger than the conversion rate (30 h⁻¹). It is also observed that the isotopic exchange nearly reaches equilibrium at CO conversions of 6-15%. Therefore, the results of these H₂-D₂ exchange experiments show that the H₂ dissociation step is quasi-equilibrated during FTS.



Figure 4. Hydrogen conversion rate to hydrocarbons (\blacklozenge), HD formation rate (\Box), and expected rate for equilibrium HD formation (Δ) in the D₂-H₂ exchange reaction at FTS conditions on a 21.9 wt.% Co/SiO₂ catalyst (473 K, 2 MPa, H₂/D₂/CO = 1/1/1).

In order to explore the reversibility of water dissociation step during FTS, D_2O tracer studies were carried out by co-feeding 0.2 MPa D_2O with 2 MPa syngas (13.8% D in the feed) using a ISCO 400D series pump. The deuterium content in hydrocarbon products (up to C₈) and in water were measured by a Hewlett-Packard 5890 gas chromatograph coupled with a 5972 A mass selective detector, while the D content in hydrogen isotopomers was determined by online mass spectrometry (Leybod Inficon Instruments Co., Inc.). The D contents were calculated using matrix techniques that correct for ion fragmentation as mentioned earlier. The results are shown in Figure 5. The D content in water decreases with increase in the bed residence time, because more H_2O formed at longer bed residence times, *i.e.*, at higher conversions. The D contents in all the primary products (C₄-C₈) and in the H₂ isotopomers increase with increasing bed residence time, suggesting the D content in surface H-D pool increases with bed residence time. The water dissociation steps during FTS are as follows:

- 1. $O^* + H^* \leftrightarrow OH^* + *$
- 2. $OH^* + H^* \leftrightarrow OH_2^* + *$
- 3. $OH_2^* \leftrightarrow H_2O + *$



Figure 5. Deuterium content in FTS products (21.9 wt% Co/SiO₂ catalysts, 473 K; $H_2/CO/N_2 = 62/31/7$, 2 MPa; D₂O added, 2 atm)

These may influence the H/D ratio on surface. Assuming the step (3) is quasiequilibrated, at least one of the steps (1) and (2) must be away from equilibrium. Otherwise, the D content in all hydrocarbons and H₂ isotopomers would be independent of bed residence time. Also, extrapolating the data in Figure 5 to zero bed residence time, we find that the D content in hydrocarbons and H₂ isotopomers are ~0.03. This is an indication that water dissociation is reversible, but not quasi-equilibrated during FTS. In the following section, we propose a series of reaction mechanisms that could involve the participation of water in monomer formation pathways. A set of kinetic data was obtained using the procedure described in Section 6.3, where in the partial pressure of

CO, H_2 or H_2O was varied holding the pressures of the other two components to a constant value at 473 K and 2 MPa on a 21.9 wt.% Co/SiO₂ catalyst. We also fit our kinetic data to the rate expressions obtained using non-linear multivariate regression.

5.2. Formulation of reaction mechanisms and derivation of rate expressions

The Fischer-Tropsch synthesis is a polymerization reaction, although the mechanism and the nature of the intermediates remain a subject of active discussion [13,79,80]. The surface carbide mechanism, which was originally proposed by Fischer and Tropsch [2], is

the currently accepted route for the formation of monomers. This mechanism assumes that CO dissociates on surface metal sites to form carbon adatoms. Subsequently, carbon adatoms undergo hydrogenation to form surface CH_x groups, which are the monomers in chain growth processes leading to hydrocarbons (olefins, paraffins and oxygenates) with a broad range of chain length and functionality.

Reference	Catalyst	Overall kinetic expression*
van der Baan, <i>et al.</i> , [81]	Co/Al ₂ O ₃	$-\mathbf{r}_{\rm CO} = a P_{\rm H2} P_{\rm CO}^{1/2} / (1 + b P_{\rm CO}^{1/2})^3$
Wojciechowsky, et al., [82]	Co/Kieselguhr	$-\mathbf{r}_{\rm CO} = a P_{\rm H2}{}^{1/2} P_{\rm CO}{}^{1/2} / (1 + b P_{\rm H2}{}^{1/2} + c P_{\rm CO}{}^{1/2})^2$
Satterfield, et al., [83]	Co/MgO/SiO ₂	$-r_{\rm CO+H2} = aP_{\rm H2}P_{\rm CO}/(1+bP_{\rm CO})^2$
Pannell, et al., [84]	Co/La ₂ O ₃ /Al ₂ O ₃	$-\mathbf{r}_{\rm CO+H2} = a P_{\rm H2}^{0.55} P_{\rm CO}^{-0.33}$
Yang, et al., [85]	Co/CuO/Al ₂ O ₃	$-r_{\rm CO+H2} = aP_{\rm H2}P_{\rm CO}^{-0.5}$

Table 1. Kinetic rate expressions of the FTS on cobalt-based catalysts

* a, b, and c in these equations are temperature-dependent constants.

Some kinetic rate expressions FTS reported in the literature for cobalt-based are shown in Table 1. According to these studies, the FTS rates exhibit a positive order in H_2 , while the influence of CO varies from negative to mildly positive depending on the CO concentration. However, none of these rate expressions contain a water partial pressure term, implying that these authors did not notice an effect of water. In addition, none of these expressions can be obtained rigorously by pseudo-steady state analyses of a set of elementary steps.

In our studies, the Langmuir-Hinshelwood type rate expressions were obtained by assuming that the rate-determining step involves the formation of surface methylene groups (CH₂*) from adsorbed C* and H^{*}. We observed the enhancement of the synthesis rate by water on cobalt catalysts. To explain the positive water effect, an additional pathway for C* consumption must be considered and this pathway must be influenced by gas phase water. From the D₂O tracer study, we know that the concentration of surface OH₂* depends on the relative amount of water in the gas mixture. It is expected that surface C* may react with OH₂* to form CHOH* species. The latter species may be hydrogenated or may react with partially hydrogenated Cn* species. In fact, the presence of species containing C-O-H bands on cobalt FTS catalysts has been confirmed by IR spectroscopy [86]. Of course, other pathways may also lead to species containing C-O-H bands. The concentration of OH₂* will increase with water partial pressure, increasing the C* consumption through the proposed water-aided pathway. However, the hydrogenation of C* using hydrogen remains operative and it is the dominant route when the water concentration is low. The corresponding elementary steps for FTS on cobalt are as follows:

Mechanism 1:

- 1. $H_2 + 2^* \leftrightarrow 2H^*$
- 2. $CO + 2^* \leftrightarrow C^* + O^*$
- 3. $C^* + H^* \rightarrow CH^* + *$
- 4. $C^* + OH^* \rightarrow COH^* + *$
- 5. $O^* + H^* \leftrightarrow OH^* + *$
- 6. $OH^* + H^* \leftrightarrow OH_2^* + *$
- 7. $OH_2^* \leftrightarrow H_2O + *$

The dissociative H_2 adsorption (Step 1) is a quasi-equilibrated step (based on the results of D_2 - H_2 exchange). In addition, it is not likely to be a rate-determining step because the FTS rate has a positive order in CO partial pressure for low CO concentrations [82], which would not be present if hydrogen dissociation on free sites were to be the only kinetically relevant step. CO chemisorbs molecularly and then dissociates to produce adsorbed C and O, respectively. The extent to which these processes are reversible remains unresolved [79]. Here, we assume that CO adsorption (Step 2) is also quasiequilibrated. We also conceive two parallel pathways that consume surface C*, namely,

C* reacting with H* (Step 3) and with OH_2^* (Step 4). We have the synthesis rate, $\Gamma_{-CO} = k_3[C^*][H^*] + k_4[C^*][OH_2^*]$. We assume that the important surface species are unoccupied sites and adsorbed C*, O*, OH_2^* and H*. Other species, though present, are not important in the stoichiometric balance of surface sites. Applying the pseudo-steady state approximation to step 1 through 7 leads to a Langmuir-Hinshelwood type expression.

$$\mathbf{r}_{-CO} = \mathbf{a} \mathbf{P}_{CO}^{1/2} \mathbf{P}_{H2}^{1/4} (\mathbf{b} \mathbf{P}_{H2}^{1/2} + \mathbf{c} \mathbf{P}_{H2O})^{1/2} / (1 + \mathbf{d} \mathbf{P}_{H2}^{1/2} + \mathbf{e} \mathbf{P}_{H2O} + \mathbf{f} \mathbf{P}_{CO}^{1/2})^2, \text{ in which,}$$

$$\mathbf{a} = (\mathbf{K}_1^{1/2} \mathbf{K}_2 \ k_5)^{1/2}$$

$$\mathbf{b} = \mathbf{K}_1^{1/2} \mathbf{k}_3$$

$$\mathbf{c} = k_4 \mathbf{K}_{-7}$$

$$\mathbf{d} = (\mathbf{K}_1)^{1/2}$$

$$\mathbf{e} = \mathbf{K}_{-7}$$

$$\mathbf{f} = (\mathbf{K}_2 (k_5 / k_3 + k_3 / k_5))^{1/2}$$

Since CO adsorption is much stronger than the adsorption of H_2 and water on cobalt [13,82], the term in the denominator containing CO partial pressure becomes much larger than the others if the CO partial pressure in the gas phase is not too low. Then, the rate expression simplifies to

$$\mathbf{r}_{-CO} = a \mathbf{P}_{CO}^{-1/2} \mathbf{P}_{H2}^{1/4} (b \mathbf{P}_{H2}^{1/2} + c \mathbf{P}_{H2O})^{1/2}, \text{ in which,}$$

$$a = k_1^{1/4} k_5^{1/2} / (\mathbf{K}_2^{1/2} (k_5/k_3 + k_3/k_5))$$

$$b = \mathbf{K}_1^{1/2} k_3$$

$$c = k_4 \mathbf{K}_{-7}$$

Another mechanism was also considered to account for the positive water effects. Earlier studies suggest that the Co surface is covered almost entirely by non-dissociated CO during FTS [4,79]. Hydrogen-assisted CO dissociation has also been considered as a rate-

limiting step in FTS [86]. Here, we have assumed that both H_2 and H_2O can react with adsorbed CO. Then, we have the follow elementary steps.

Mechanism 2

- 1. $H_2 + 2^* \leftrightarrow 2H^*$
- 2. $CO + * \leftrightarrow CO^*$
- 3. $CO^* + H^* \rightarrow C^* + OH^*$
- 4. $CO^* + OH_2^* \rightarrow C^* + 2OH^*$
- 5. $O^* + H^* \leftrightarrow OH^* + *$
- 6. $OH^* + H^* \leftrightarrow OH_2^* + *$
- 7. $OH_2^* \leftrightarrow H_2O + *$

A rate expression was obtained according to the proposed mechanism by applying the pseudo-steady state hypothesis with quasi equilibrium assumptions.

$$\mathbf{r}_{-CO} = (aP_{CO}P_{H2}^{1/2} + bP_{CO}P_{H2O})/(1 + cP_{H2}^{1/2} + dP_{H2O} + eP_{CO})^2$$
, where,

$$a = K_1^{1/2} K_2 k_3$$

$$b = K_2 k_4 (K_7)^{-1}$$

$$c = K_1^{1/2}$$

$$d = (K_7)^{-1}$$

$$e = K_2$$

A modification of the second mechanism was also considered by including an additional step that allows the formation of CH* directly during hydrogen-assisted CO dissociation as shown below.

Mechanism 3:

- 1. $H_2 + 2^* \leftrightarrow 2H^*$
- 2. $CO + * \leftrightarrow CO^*$
- 3. $CO^* + H^* \rightarrow C^* + OH^*$
- 4. $CO^* + H^* \rightarrow CH^* + O^*$
- 5. $CO^* + OH_2^* \rightarrow COH^* + 2OH^*$
- 6. $COH^* + * \rightarrow C^* + OH^*$
- 7. $O^* + H^* \leftrightarrow OH^* + *$
- 8. $OH^* + H^* \leftrightarrow OH_2^* + *$
- 9. $OH_2^* \leftrightarrow H_2O + *$

The parallel pathways for CO dissociation are described by the steps 3, 4 and 5. Using similar procedures as above, this mechanism led to the following rate expression:

$$r_{\rm CO} = \frac{\left(aP_{\rm CO}P_{\rm H_2}^{1/2} + bP_{\rm CO}P_{\rm H_2O}\right)}{\left(1 + cP_{\rm H_2}^{1/2} + dP_{\rm H_2O} + eP_{\rm CO} + \frac{fP_{\rm CO}P_{\rm H_2O}}{P_{\rm H_2}^{1/2}}\right)^2}$$

where the rate is given in h⁻¹ and the individual pressures in atm. The experimental data was also used to test the above expression in the regression program and determine the various constants.

5.3. Kinetic studies and mathematical fitting of data to rate expressions

FTS kinetic data were obtained over a broad range of H₂/CO ratios (1.3 to 8.5) and pressures (1.3 to 3.3 MPa) and space velocities, and with different concentration of H₂O, at 473 K and 2 MPa on the 21.9 wt.% Co/SiO₂ catalyst. The experimental results are presented in Table 2. For this set of data, it was difficult to do a regression using only the two adjustable parameters, P_{CO}, P_{H2}. Thus, it was decided that the rate expression should also include P_{H2O}. These data were first fitted using a multilinear regression, leading to a power law rate expression: $\mathbf{r}_{.CO} = 56.3 \text{H}_2^{0.43} \text{CO}^{-0.53} \text{H}_2 \text{O}^{0.38}$.



Figure 6. A comparison of predicted rates from Mechanism 2 with the measured rates for a 21.9% Co/SiO₂ catalyst at 473 K and 2 MPa, $H_2/CO=2$.

Figure 7. A comparison of predicted rates from Mechanism 3 with the measured rates for a 21.9% Co/SiO₂ catalyst at 473 K and 2 MPa, $H_2/CO=2$.

A sample of this data was then regressed using nonlinear least squares method and fitted to the above proposed mechanisms in order to obtain the best possible fit. A comparison between the measured rates and predicted rates is plotted for the above-mentioned mechanisms 2 and 3 are shown in Figures 6 and 7. In both cases, the predicted rates are within 95% of the measured rates and hence both the mechanisms are consistent with the FTS reaction kinetics on Co/SiO_2 and can explain the positive water effect on these catalysts. The parameters obtained in both these cases are listed in Table 3.

No	Par	rtial press	ure	СО	СО	CH ₄	C ₅ +
		(atm)		conversion	conversion	formation	synthesis
					rate	rate	rate
	H_2	СО	H_2O	(%)	(h^{-1})	(h^{-1})	(h^{-1})
1	11.6	5.4	0.5	17.2	48.3	4.6	41.8
2	11.6	5.7	0.3	8.7	36.9	4.2	28.7
3	9.3	6.0	0.2	7.7	29.9	2.8	24.1
4	18.3	6.0	0.1	4.5	32.3	5.8	17.8
5	17.2	5.1	0.6	20.4	64.7	8.8	53.7
6	17.9	5.9	0.2	8.0	42.5	6.6	29.8
7	24.0	5.3	0.5	16.6	70.4	12.1	51.1
8	25.0	6.0	0.2	7.6	50.1	10.0	29.3
9	11.9	5.8	0.2	7.4	41.8	5.2	32.2
10	11.3	5.3	0.6	21.3	59.7	5.2	50.8
11	11.9	5.9	0.2	6.6	37.2	5.2	27.5
12	10.8	2.6	0.3	20.4	57.2	7.3	42.7
13	11.5	2.8	0.1	7.7	43.9	8.0	30.8
14	10.2	2.3	0.5	32.9	68.6	9.4	58.1
15	11.8	5.8	0.2	5.3	30.1 4.4		22.2
16	11.4	5.5	0.5	17.1	54.0 4.9		43.4
17	11.2	5.2	0.6	21.5	60.4 5.4		50.4
18	11.4	1.4	0.1	10.0	57.0	13.1	
19	10.6	1.3	0.2	23.1	64.7	12.6	
20	9.7	1.2	0.3	38.5	80.3	16.4	60.4
21	11.3	5.2	0.6	20.4	57.2	5.3	47.5
22	11.6	8.7	0.2	4.8	27.4	3.2	20.6
23	11.3	8.6	0.3	6.6	30.4	3.0	22.9
24	11.7	5.4	0.5	18.0	50.5	5.1	42.5

Table 2. Experimental results of FTS kinetic study over 21.9 wt.% Co/SiO₂ catalyst*

* Reaction conditions: 473 K, H_2/CO ratios from 1.3 to 8.5, pressures from 13 to 33 atm, water partial pressure is the average of water pressures at the reactor inlet and outlet.

Parameter	Mechanism 2	Mechanism 3		
a (atm ^{-3/2} hr ⁻¹)	59.8	45.3		
$b (atm^{-2} hr^{-1})$	527.1	443.4		
c (atm ^{-1/2})	$2.3*10^{-14}$	8.8*10 ⁻⁸		
$d (atm^{-1})$	1.8	$1.5*10^{-8}$		
$e(atm^{-1})$	1.0	0.9		
$f(atm^{-3/2})$	-	1.0		

Table 3. Values of Parameters in rate expressions, obtained by best fit for two mechanisms listed above.

6. Determination of the Kinetic isotope Effect (KIE) during FTS on Co catalysts

Isotope effects were determined by performing FTS reactions with $CO/H_2/N_2$ and $CO/D_2/N_2$ mixtures. Rates of CO consumption as a function of the average H₂O partial pressure within the reactor are shown for experiments with both CO/H_2 and CO/D_2 over the 21.9 wt.% Co/SiO_2 catalyst in Figure 8. In both cases, the FTS rate increases with increasing CO conversion (and hence water concentration). The isotope effects (r_H/r_D) for overall CO consumption were obtained by comparing the synthesis rate with CO/H_2 to that using CO/D_2 at each conversion level (Figure 9). The isotope effect (r_H/r_D) for CO consumption is about 0.8, and independent of CO conversion. This value is almost identical to that reported by Sakharov and Dokukina [65]. If C-H bond formation is a rate-determining step, this will result in a normal isotope effect ($k_H/k_D > 1$). On the other hand, if the chemisorption characteristics of H₂ and D₂ on Co were to be different so as to result in a higher surface coverage of D* than H*, this would lead to a thermodynamic isotope effect that would be opposite in magnitude to the kinetic isotope effect. Hence, the inverse isotope effect observed can reflect on a combination of kinetic and equilibrium isotope effects.



Figure 8. Rate of CO consumption versus CO conversion: \blacklozenge H₂, \Box D₂ (21.9 wt% Co/SiO₂, 473 K, 2 MPa, H₂/CO or D₂/CO = 2).

The fact that the observed isotope effect is almost independent of which hydrogen isotope is used indicates that it is unlikely for water to play a direct kinetic role that would account for the observed rate enhancement. This is because at higher CO conversions, the water concentration is larger and would lead to a greater contribution of H₂O-mediated pathways and to a different KIE value than at the low H₂O concentrations that prevail at low CO conversions. This result indicates that H₂O does not play a role in the reaction mechanism and hence the turnover rate enhancement due to an increase in the H₂O concentration could reflect instead an increase in the active site density (either CObinding sites or the total amount of active carbon on the catalyst surface). We test this hypothesis in the next section.



Figure 9. Isotope effect for CO consumption versus CO conversion (21.9 wt% Co/SiO₂, 200°C, 20 atm, H₂/CO or D₂/CO = 2).

7. Possible effects of water on the number of CO-binding sites available during FTS

7.1 *Introduction*

The isotopic studies discussed in the previous section have failed to detect, however, any shift in CO activation pathways when H₂O is present. H₂O can also influence FTS rates by increasing the number of exposed Co surface atoms available for CO adsorption and for monomer formation and chain growth during FTS. This could be possible due to water possibly removing or preventing the formation of less reactive forms of C-containing intermediates. Previous studies have shown that H₂O inhibits FTS reaction rates in some cases [73-75] and XPS studies [73] detected surface oxidation processes on Co/Al₂O₃ samples exposed to high H₂O concentrations during FTS. Bulk oxidation to CoO or Co₃O₄ is not thermodynamic feasible, but metal-oxygen bonds at metal surfaces are significantly stronger than in bulk oxides and small Co clusters strongly interacting with Al₂O₃ may show a greater tendency to oxidize than large Co crystallites. None of these studies however, have probed structural and compositional changes *during* Fischer-Tropsch synthesis.

In this section, we apply two techniques well suited for the detection of any such changes during reaction with the specific objective to measure changes in the oxidation state and in the availability of Co surface sites as H₂O concentrations change during FTS. In situ infrared spectra of CO adsorbed during FTS on Ru, Co and Fe have been reported, but typically at low pressures and high temperatures, which lead to methane as the predominant reaction product [87-91]. Stretching modes for linearly adsorbed CO, for -CH₂ and -CH₃ groups, and for surface formates were detected on Ru/Al₂O₃ [87]. A bridged CO adsorbed species was also detected on Ru/SiO₂ [88]. The -CH₂ and -CH₃ groups arise from growing chains [88,89] and from hydrocarbons physisorbed or condensed within catalyst pores. These adsorbed species have also been reported in less detailed infrared studies of Co/Al₂O₃ catalysts [90,91]. These previous infrared studies did not address the effect of reaction conditions, and specifically of H₂O concentration, on the surface coverage or frequency of these adsorbed species. The surface of Co catalysts is covered mostly by adsorbed CO during FTS [92]. Therefore, the intensity of the CO infrared bands reflects the number of Co surface atoms capable of chemisorbing CO during FTS.

X-ray absorption spectroscopy (XAS) can probe the local structure in solids during catalytic reactions. It has been used to examine the structure of Co [93,94], Co-Ru [43,95] and Co-Re [96] FTS catalysts. We present here the results of *in situ* characterization studies of Co/SiO₂ catalysts using infrared and X-ray absorption spectroscopy at various H_2O concentrations in the synthesis gas reactant stream. These studies probed a possible role of water in increasing the fraction of the Co surface atoms available for reactions and in changing the oxidation state of the Co metal crystallites initially present in supported Co catalysts after pre-treatment and before FTS reactions.

7.2. FTS activity and selectivity measurements at 0.5 MPa

At first, FTS activity and selectivity measurements were carried out at 0.5 MPa and 473 K, because these conditions are more accessible during in situ infrared and X-ray absorption spectroscopy studies. The Co site-time yields shown in Figure 10 as a function of the average water partial pressure in the reactor confirmed the presence of similar H₂O effects at these lower synthesis gas pressures. As in the case of the 2.0 MPa runs shown in Section 4, space velocity and water addition results fall in a single curve in the data shown in Figure 10. CH₄ selectivities decreased and C₅₊ selectivities increased with increasing water concentration at these lower pressures (Figure 11, Table 4). Water addition at these lower pressures also decreased the paraffin and internal olefin contents in FTS products (Figure 12, Table 4).

Several plausible roles of H_2O in FTS have been proposed [14]. For example, an intrapellet water phase, favored at high H_2O partial pressures, can increase transport rates for CO, because the solubility and diffusivity of CO is higher in water than in hydrocarbon liquids [97]. Intrapellet CO concentration gradients lead to lower FTS rates and C_{5+} and olefin selectivity; thus, an increase in CO diffusion rates could lead to the concurrent changes in rates and selectivities observed at high H_2O partial pressures. Higher transport rates mediated by intrapellet aqueous or water-rich phase, which prevails at higher H_2O pressures within the pores of the support, would be consistent with the observed effects of H_2O on FTS rates and selectivity. They would also account for the unexplained effect of support structure on the magnitude of the rate enhancements [14] and for the contradictory reports of the effect of water on rates (but not on selectivity) from various research groups. For example, the addition of water catalysts did not influence reactions rates on Co-Ru/ZrO₂/Aerosil [72], but led to lower rates on Co-Re/Al₂O₃ [73]. Co/SiO₂ catalysts with larger pores showed marked rate enhancements with H_2O , while rates on Co supported on SiO₂ with smaller pores were unaffected [14].



Figure 10. Cobalt site-time yield (h^{-1}) as a function of the average water partial pressure on a 12.7% Co/SiO₂ catalyst at 473 K, 0.5 MPa, H₂/CO=2. (Open symbols: Space velocity runs, Filled symbols: Water addition runs).



Figure 11. CH₄ selectivities (\bigcirc, \bullet) and C₅₊ selectivities (\Box, \blacksquare) as a function of the average water partial pressure on a 12.7% Co/SiO₂ catalyst at 473 K, 0.5 MPa, H₂/CO=2. (Open symbols: Space velocity runs, Filled symbols: Water addition runs).



Figure 12. *1*-pentene/*n*-pentane ratios (\bigcirc, \bullet) and *1*-octene/*n*-octane ratios (\Box, \blacksquare) as a function of the average water partial pressure on a 12.7% Co/SiO₂ catalyst at 473 K, 0.5 MPa, H₂/CO=2. (Open symbols: Space velocity runs, Filled symbols: Water addition runs).

In the next section, we explore the effects of water on the density of CO-binding sites by collecting infrared spectra during FTS reaction using synthesis gas reactants with and without added water.

Space velocity cm ³ /g.s	Average H ₂ O Pressure MPa	CO conversion (%)	Co site-time yield h ⁻¹	CH ₄ selectivity %	C ₅₊ selectivity %	$I-C_5H_{10}/n-C_5H_{12}$ ratio	l-C ₈ H ₁₆ / n - C ₈ H ₁₈ ratio	$I-C_5H_{10}/2-C_5H_{10}$ ratio
0.08	0.07	56.8	16.9	6.4	88.2	0.46	0.10	2.1
0.17	0.02	26.7	16.8	7.1	86.4	0.80	0.17	3.8
0.25	0.02	18.2	16.6	7.4	85.9	1.12	0.24	5.4
0.35	0.01	13.1	16.8	7.3	86.3	1.47	0.32	7.3
0.50	0.01	9.8	17.8	7.4	84.9	1.69	0.38	8.4
0.50	0.06	10.2	18.5	5.9	87.2	2.77	0.84	19.5
0.50	0.11	11.4	20.8	5.6	87.6	3.52	1.23	34.4
0.50	0.16	13.5	24.6	5.2	89.2	3.36	1.20	31.0
0.50	0.21	14.1	25.7	3.4	92.3	3.74	1.56	38.1
0.50	0.26	13.9	25.3	3.2	92.9	3.78	1.64	41.0

Table 4. Effect of water concentration on the performance of a 12.7% Co/SiO₂ catalyst at 473 K, 0.5 MPa and H₂/CO=2.

7.3. In situ infrared spectra during FTS

In situ infrared spectra were acquired using a Mattson RS-18000 Spectrometer in the transmission mode at a resolution of 2 cm^{-1} using a stainless steel cell (Figure 10). The sample consisted of a thin wafer held in the beam path by a holder. The optical path was minimized by using packed CaF₂ windows on both sides of the pellet, which also minimized the dead volume in the flow manifold. The cell temperature was held constant using a resistive heater surrounding the cell; the cell windows were kept to 353 K using a continuous water flow. The reaction temperature was monitored with a K-type thermocouple (Omega, 0.08 cm diameter, 10 cm length) placed within 1 mm of the center of the sample wafer. Wafers (20 x 1 mm) were prepared by pressing a mixture of Co/SiO₂ (0.07 g, 12.7 wt.%) and Al₂O₃ (Alon, 0.03 g) at ~100 MPa. The sample was treated in O₂/He flow (3.6 x 10^3 cm³/h) at 623 K for 0.5 h in order to remove any species adsorbed during exposure to ambient air. The cell was then flushed briefly with He at 623 K and the sample wafers reduced in H₂ (3.6 x 10^3 cm³/h) at 623 K for 2 h. The temperature of the cell was then decreased to 473 K in H₂ and a background spectrum was collected. Synthesis gas (H₂:CO=2:1, 4.8 x 10^3 cm³/h) was introduced and the cell was pressurized to 0.5 MPa. Spectra were collected at 453 K and 473 K with and without external H₂O addition. Water was added by using an Isco 500D pump. All heating and cooling cycles were carried out at 0.082 Ks⁻¹ in order to prevent damage to the CaF₂ windows. All spectra were corrected for gas phase CO contributions by subtracting the spectrum obtained without a catalyst wafer at each temperature.

In situ infrared spectra collected on the 12.7 wt. % Co/SiO₂ catalyst at 473 K and 0.5 MPa ($H_2/CO=2$) are shown in Figure 11 as a function of time on stream. Several strong bands for adsorbed species were detected and their frequency and assignment resemble those reported in previous studies on Ru and Co catalysts [87-90]. The band at 1590 cm⁻¹ (symmetric –OCO- stretches) and a doublet at 1390 (-CH deformation mode) and 1377 cm^{-1} (asymmetric –OCO- stretching vibrations) obscured by intense hydroxyl SiO₂, bands, arise from surface formate species adsorbed on SiO₂. The 2067 cm⁻¹ band corresponds to linear CO species adsorbed on Co [87,89]. This band initially weakens and shifts slightly (to 2057 cm⁻¹) with time, and then reaches the steady-state intensity value in ~1 h. The two intense bands observed at 2927 cm⁻¹ and 2855 cm⁻¹ are assigned to symmetric and asymmetric C-H vibrations in methylene groups [87,88] and the band at 1450 cm⁻¹ arises from C-H bending modes in -CH₂ groups. The weak shoulder at 2959 cm⁻¹ is typical of symmetric C-H stretches; the antisymmetric modes are likely to be masked by the intense –CH₂ stretches [88-90]. As observed in Figure 11, these IR bands for methyl and methylene groups become more intense with time on stream, suggesting that they arise from growing chains or adsorbed hydrocarbons formed from synthesis gas; previous reports have shown that they are likely to be adsorbed growing chains because these bands are not observed when fresh samples are exposed to FTS hydrocarbon mixtures [88]. A very weak band was also detected in our samples at ~1900 cm⁻¹; this band is characteristic of bridged -CO- stretching vibrations on metal surfaces.



Figure 10. Schematic representation of the in situ FTIR spectroscopic cell



Figure 11. Evolution of FTIR spectra as a function of time under reaction conditions on a Co/SiO₂ catalyst at 473 K and 0.5 MPa (H₂/CO=2, $3.6 \times 10^3 \text{ cm}^3$ /h flow rate). (a) 1 min, (b) 10 min, (c) 20 min, (d) 40 min, and (e) 66 min.



Figure 12. Effect of water addition on steady state FTIR spectra under reaction conditions on a Co/SiO₂ catalyst, (473 K, 0.5 MPa, $H_2/CO=2$, 3.6 x 10³ cm³/h flow rate). (a) no water added, (b) 0.05 MPa H_2O , (c) 0.1 MPa H_2O , (d) H_2O stopped.



Figure 13. Effect of added water on the area of the CO adsorption peak at (a) 473 K, no water, (b) 473 K, 0.05 MPa H₂O, (c) 473 K, 0.1 MPa H₂O, (d) 473 K, H₂O stopped, (e) 453 K, no water, (f) 453 K, 0.05 MPa H₂O, and (g) 453 K, 0.1 MPa H₂O. (0.5 MPa, H₂/CO=2, 3.6×10^3 cm³/h flow rate).

Isotopic switch studies have shown than active Co and Ru surfaces are predominately covered by adsorbed CO during FTS, even near ambient pressures [92]. As a result, the adsorbed CO band intensity reflects the relative number of active sites involved in FTS turnovers. After steady-state spectra were collected at 473 K and 0.5 MPa, H₂O (0.05 MPa) was added and infrared spectra were acquired until CO infrared bands reached a constant intensity. The H₂O concentration was then increased to 0.1 MPa and infrared spectra were again collected until the intensity of all bands again reached constant values. After this, H₂O was removed from the synthesis gas stream and infrared spectra again collected until the system again reached steady state. The steady-state spectra for the initial and final dry synthesis gas experiments and for the two water concentrations are shown in Figure 12. The addition of water led to an initial slight decrease in the frequency of the adsorbed CO band (from ~ 2070 to ~ 2050 cm⁻¹) and to the appearance of an intense band at 1628 cm⁻¹, which corresponds to deformation vibrations in molecularly adsorbed water [88-91]. This band was also present on the pure SiO₂ support when water was added to the synthesis gas stream. The CO bands did not revert to their original frequency upon water removal, but adsorbed water bands disappeared gradually when H₂O was removed from the synthesis gas stream. After these experiments, the sample temperature was decreased to 453 K, spectra were collected, and H₂O (0.05 MPa) was added. The spectra and conclusions were similar to those obtained at 473 K. The area under the infrared CO band is shown in Figure 13 for the experiments described above.
At 473 K, the presence of H_2O (0.05 MPa) increased the initial CO band intensity by ~15% and then by another 5% when the H_2O pressure was increased to 0.1 MPa. These changes are much smaller in magnitude than the changes in FTS rates of 30% and 45% observed when these water concentrations were added to synthesis gas at 473 K and 0.5 MPa. Clearly, this rate enhancement cannot reflect a larger steady-state density of Co sites active for FTS when H₂O was added. The observed initial increase in CO band intensity upon H₂O does not appear to be related in fact to the FTS rate enhancements. These rate enhancements were fully reversed upon water removal, but the CO infrared band did not return to its initial intensity when H₂O was removed from the synthesis gas stream at 473 K (Figure 13). This band also did not change in intensity when 0.05 MPa H₂O was added during subsequent experiments at 453 K. The initial changes in the CO band intensities appear to reflect a gradual approach to a steady-state Co surface with a slightly lower adsorption capacity than fresh Co/SiO₂. High H₂O concentrations (0.25 MPa) led to a marked irreversible change in the CO infrared band. The infrared spectra before H₂O addition was not recovered upon removal of water from the synthesis gas stream. These high H₂O/H₂ ratios appear to lead to the surface oxidation of Co metal particles. Below these H₂O/H₂ ratios, the availability of CO binding sites was unchanged by H₂O partial pressures that markedly influenced FTS rates and selectivities.

These studies appear to rule a scavenging effect of H_2O on inactive adsorbed species or their precursors. They also cast some doubt on a role of water in removing transport restrictions, because the removal of these restrictions would have led to reversible effects of water on intrapellet CO concentrations and thus on the intensity of CO-related infrared bands. While inhibition of FTS rates caused by transport require very severe diffusional limitations, selectivity effects are noticeable even with very small intrapellet gradients, which would have not been detected in our on situ infrared studies. In the next section, we show that the structure and the oxidation state of the Co crystallites in Co/SiO₂ remain unchanged during FTS at 0.1 MPa H₂/CO, 0-0.015 MPa H₂O, and 473 K using *in situ* X-ray absorption spectroscopy.

7.4. In situ X-ray absorption spectroscopy during reactions of CO/H₂ and CO/H₂/H₂O on Co/SiO₂

X-ray absorption spectra were measured at the Co K-edge using a wiggler side-station (beamline 4-1) at the Stanford Synchrotron Radiation Laboratory (SSRL). The storage ring was operated at 30-100 mA and 3.0 GeV during the experiments. Two Si (111) crystals, detuned by 20% in order to minimize harmonics, were used as the monochromator. The X-ray beam intensities incident on the sample (I₀), leaving the sample (I₁), and after a 5 μ Co foil (I₂), were measured using three N₂-filled ion chambers, and the sample (I₀/I₁) and reference (I₁/I₂) spectra were collected simultaneously. The most restrictive aperture along the beam path was a 0.2×12 mm slit, which set an energy resolution of 2 eV at the Co K-edge (7.709 keV). Co₃O₄ (Alfa Aesar, 99.997%) was used as the reference. The catalyst sample (10 mg., 21.9 wt.% Co/SiO₂, 100-180 μ) was placed within a quartz capillary cell described in earlier sections and treated in H₂ by increasing the temperature to 608 K at 0.167 K/s, holding at 608 K for 1 h, and cooling to 473 K. Synthesis gas (Praxair: 62% H₂, 31% CO, 7% N₂; 3.6-7.4 x 10³

cm³/h.g-cat) was introduced and spectra were collected for 10 h during FTS. H₂O was then added to the synthesis gas reactants (H₂O/CO=0.05-0.1; 7.4 x 10^3 cm³/h.g-cat of synthesis gas) using a syringe pump (Cole Palmer, 74900 Series) and X-ray absorption spectra were collected during FTS reaction. X-ray absorption data were analyzed using the WinXAS code (version 1.2). Raw spectra were calibrated by aligning the first inflection point in spectrum for Co foil with the reported absorption energy for Co metal (7.709 keV). The background was subtracted using linear fits in the pre-edge region (7.840-8.720 keV). The fine structure spectra were analyzed after background subtraction and Fourier transform of k⁻¹-weighted data in the 3-16 A⁻¹ wavenumber range.



Figure 14. *In situ* XANES of a pre-reduced 21.9 wt.% Co/SiO₂ catalyst under (a) H₂ (12 x 10^3 cm³/h.g-cat), 608 K, (b) H₂/CO (7.5 x 10^3 cm³/h.g-cat), 473 K, (c) H₂/CO/H₂O (7.5 x 10^3 cm³/h.g-cat, H₂O/CO=10 %), 473 K, and (d) reference Co₃O₄.

Near-edge spectra for pre-reduced Co/SiO₂ (21.9 wt.% of Co) after treatment in H₂ (Figure 14a) and after exposure to synthesis gas without H₂O (Figure 14b) and with H₂O added (0.015 MPa H₂O, Figure 14c) are compared in Figure 14. Samples were treated in H₂ at 608 K for 1 h before exposure to synthesis gas. The reduced catalysts show lower absorption edge energy than Co₃O₄ (Figure 14d). During reduction in H₂, an absorption feature emerged at 7.709 keV along with the disappearance of the pre-edge feature present in Co₃O₄, indicating the formation of Co metal. No detectable spectral changes were detected after exposing the sample to synthesis gas (H₂/CO=2, 0.1 MPa; 1.02-2.05 cm³/g-s). The subsequent addition of H₂O to the synthesis gas (0.005-0.015 MPa) also did not lead to detectable changes in the near-edge spectra. These data clearly indicate that the structure, composition, and oxidation state of the Co metal crystallites present after reduction in H₂ are not changed during FTS and that the addition of amounts of water that lead to detectable change in FTS rates and selectivities also do not influence the nature of these Co metal particles. These conclusions are illustrated by the difference

spectra shown in Figure 15. In this figure, the spectrum of the reduced sample (Figure 14a) was subtracted from the spectra obtained in CO/H_2 (Figure 14b) and $CO/H_2/H_2O$ (Figure 14c) reactant mixtures. The nearly flat and identical difference spectra clearly show that Co metal particles retain their structure and oxidation state during reactions of synthesis gas with and without water added.



Figure 15. Difference X-ray absorption spectra of a 21.9% Co/SiO₂ catalyst under (a) H₂/CO and (b) H₂/CO/H₂O with respect to a reduced catalyst; 473 K, 0.1 MPa, H₂/CO=2, H₂O=0.01 MPa.

The analysis of the extended X-ray absorption fine structure (EXAFS) of these samples (Figure 16) confirms these conclusions. Figure 16 shows the radial structure functions of Co_3O_4 (Figure 16a), Co foil (Figure 16e), and of Co/SiO₂ after reduction in H₂ (Figure 16b) and during FTS with CO/H₂ (Figure 16c) and CO/H₂/H₂O (Figure 16d) reactant mixtures. The spectra of reduced Co catalysts resemble Co metal and do not change in synthesis gas and in the presence of H₂O. The consistent results with XANES and EXAFS analysis of Co catalysts coupled with our IR studies indicate that the chemical nature of the CO-binding Co sites are unchanged with increasing H₂O concentrations up to a threshold value.

Based on our IR and XAS results, it appears that water does not appear to modify the density of CO-binding sites during reaction as well as change their chemical characteristics. During FTS reactions on Co catalysts, the chemical environment near the catalyst surface is determined by hydrocarbon chains that are formed, as well as CO-binding sites. And since previous studies on CO hydrogenation reactions on Ru and Co catalysts have pointed out to the possible existence of active and inactive forms of carbon on the surface, it is conceivable that water could affect the relative concentrations of the different forms of carbon, which in turn would bring about an increase in the rate. In addition, a decrease in the CH_4 selectivity and increase in C_{5+} selectivity with increase in

 H_2O concentration can also explained by the possible difference in the ways chains terminate on these different forms of carbon. We have attempted to investigate this effect in a parallel study in which the CH_4 transient obtained during the switch of flow from synthesis gas (FTS conditions) at steady state to H_2 was utilized to obtain the total amount of active carbon on the catalyst surface, at different H_2O concentrations, as discussed in the next section.



Figure 16. In situ EXAFS of (a) reference Co_3O_4 and a pre-reduced 21.9 wt.% Co/SiO₂ catalyst under (b) H₂ (200 cm³/min, g-cat), 608 K, (c) H₂/CO (125 cm³/min g-cat), 473 K, (d) H₂/CO/H₂O (125 cm³/min g-cat, H₂O/CO=10 %), 473 K, and (e) Co foil.

7.5. Carbon coverage measurements during FTS

7.5.1. Introduction

An alternate unexplored explanation for the autocatalytic effect of water on Co/TiO₂ and Co/SiO₂ catalysts during FTS is that the presence of H_2O could affect the relative amounts of reactive and less reactive carbon on the catalyst surface. In the previous section we have shown with the help of *in situ* FTIR spectroscopy that the density of CO-binding sites was unchanged with changes in water concentration. In section, we present our studies in which we test whether water influences the concentration of carbonaceous species on the catalyst under reaction conditions.

Various researchers have presented techniques to estimate the amount of reactive carbon present on the catalytic surface. Winslow and Bell [98] determined the carbon coverage on a Ru/TiO₂ catalyst at 463 K and 0.08 MPa by titration with D₂, by following the

evolution of CD_4 (attributed to the hydrogenation of chemisorbed carbon) with time. Two CD₄ peaks were detected, the first one being representative of reactive carbon (named by the authors as Carbon α). The authors, following Bianchi *et al.* [99,100], who performed similar studies on an iron catalyst at atmospheric pressure, stated that the second peak is due to hydrogenation of a pool of less reactive carbon (Carbon β). In a different approach. Winslow and Bell [92] estimated the amount of carbon α from the decay with time of the flow rate of 13 CO after the feed of the reactor was changed from a 13 CO/H₂ mixture to a 12 CO/H₂ mixture; CD₄ that was observed upon feeding D₂ to the reactor after the first transient was completed, was attributed to hydrogenation of carbon β . A similar isotope exchange approach was also adopted by De Pontes et al. [101] on Ru/TiO₂ and Ru/SiO₂ to detect the presence of two pools of adsorbed carbon. Biloen et al. [102] presented data collected on an unsupported Co catalyst at 488 K, 0.3 MPa and a H₂/CO ratio of ~5:1, with ${}^{12}CO/H_2$ - ${}^{13}CO/H_2$ switch experiments, similar to the ones previously described. Finally, Mims and McCavendish [103] have also performed carbon coverage with an identical approach on a Co/SiO₂ catalyst. Despite the fact that Co is one of the most important and widely used catalyst for FTS, very few studies have been carried out at high-pressure reaction conditions to estimate the number of active carbon atoms during FTS on these catalysts. Here, we present our studies performed to determine if the observed rate enhancements by water would reflect an increase in the active carbon coverage on Co catalysts, based on switch transient measurements at high pressure conditions.

7.5.2. Catalyst synthesis and measurement of steady state and transient FTS kinetics

The 15 wt.% Co/TiO₂ sample was prepared by impregnation of standard solutions of CoNO₃·5H₂O onto TiO₂ (Degussa) respectively. The impregnated sample was dried in air at 333 K for 24 h. and subsequently reduced in flowing hydrogen (15 x 10^3 cm³/h, 0.0167 K/s from 313 K to 673K, hold for 16 h). The catalyst sample was then passivated with 1% O₂ in He for 1 h at ambient temperature.

The reactor setup was identical to the one used for all the other experiments listed in Sections 3-6. In addition, the flow of synthesis gas or H₂ was directed either to the reactor or to the vent with a 4-port valve, mounted close to the reactor inlet. A 1/16" capillary tube was positioned under the bed and was utilized to divert a part of the effluent stream (~10 %) into a differentially pumped atmospheric sampling system connected to a quadrupole mass spectrometer (Leybold Inficon Instruments Co., Inc.), allowing to continuously collect gas samples during the runs. This step minimized the total dead volume between the reactor and the mass spectrometer. Also, two needle valves were utilized in order to maintain the desired pressure drop between the reactor zone (at high pressure) and the tube to the mass spectrometer (under vacuum). Active carbon coverage measurements were conducted at steady state FTS conditions, by performing rapid switches of the feed to the reactor from synthesis gas to H₂ at high pressure, followed by monitoring of the transients of different components with the mass spectrometer.

The experiments performed on the Co/TiO_2 catalyst at 473 K and 2 MPa showed that the CO reaction rate increased significantly with increase in the average water partial

pressure in the reactor (Figure 17). An increase in water concentration decreased methane selectivities and correspondingly increased C_{5+} selectivities (Figure 18). The effect of the partial pressure of internally generated water on olefin selectivity is affected by the parallel effect of contact time. The combined result is reported in Figure 19 for *1*-pentane to *n*-pentane ratios; the observed decrease in olefin content with partial pressure of water produced is to be attributed to extensive readsorption of α -olefins into the growing chain mechanism at higher contact times [13]. The details related to calculation of the active carbon coverage are presented in the next section.



Figure 17. Rate of CO consumption as a function of the average water partial pressure. Full symbols: water internally generated, Open symbols: added water. (15 wt.% Co/TiO₂, 473 K, 2.0 MPa, $H_2/CO=2$).



Figure 18. Methane (\blacklozenge) and C₅₊ (\aleph) selectivities as a function of the average water partial pressure. Full symbols: water internally generated, Open symbols: added water. (15 wt.% Co/TiO₂, 473 K, 2.0 MPa, H₂/CO=2).



Figure 19. *I*-Pentene/*n*-pentane molar ratio as a function of the average water partial pressure. Filled symbols: water internally generated, Open symbols: added water. (15 wt.% Co/TiO₂, 473 K, 2.0 MPa, H_2 /CO=2).

7.5.3. Measurement and estimation of carbon coverage

When the reactor feed is changed from syngas to hydrogen, the carbon adsorbed on the surface of the catalyst during the reaction is hydrogenated mostly to methane; while at the same time, the flow rates of CO and Ar decrease to zero, and that of H_2 increases and reaches a steady value. The transients of CO, H_2 and CH_4 after a switch from syngas to hydrogen and back to syngas are presented in Figure 20. The hydrodynamics of the system is described by the following equation:

$$F(t) = F_1 + (F_2 - F_1) \cdot \left(1 - e^{-\frac{t - t_D}{\tau}} \right)$$
(1)

where: F(t) is the flow rate of an inert species as a function of the time t, F_1 is the flow rate of the same species before the switch to H_2 and F_2 is the flow rate when the transient is completed. Equation 1 results from the application of a non-stationary mass balance in the absence of reaction on a system that is combination of a plug flow reactor followed by a continuously stirred reactor. The Ar contained in the syngas mixture is the inert and internal hydrodynamic standard of the system: its flow rate transient is utilized to estimate the parameters t_D and τ in Equation 1. This model fits the decay profile of the Ar flow rate very well for all the experimental data collected as illustrated in Figure 21. Once a reliable model for the hydrodynamics of the system is devised, the peak of methane evolved from the catalyst surface is analyzed in order to deconvolute it into two contributions; one derived from hydrogen with a less active form of carbon on the catalyst.

In order to estimate only the amount of active carbon from the methane peak, Equation 1 is applied to the decay of methane after the attainment of the maximum value in the methane flow rate profile. In fact assuming that the kinetic of formation of methane is first order with the carbon coverage and with the hydrogen coverage, and supposing that after the maximum of methane flow rate, there is no change in the concentration of adsorbed hydrogen on the catalytic surface, the decay of methane with time should follow an exponential law with a time constant τ_{CH4} . However, when the linearized flow rate $\ln[(F(t)/(F_{peak}))]$ is plotted as a function of time (where F(t) is the actual methane flow rate, F_{peak} the rate corresponding to the maximum of the methane flow rate), two slopes are visible, for all the experiments conducted, corresponding to two different time constants for the consumption of adsorbed carbon. An example of the presence of two distinct slopes is presented in Figure 22; from the first part of the curve a time constant of 40 s is estimated, while from the second part, the resulting value of τ_{CH4} is 315 s. The first part of the curve can be attributed to hydrogenation of active carbon, whereas the second part derives from reaction of hydrogen with some form of less reactive carbon. Since in the absence of CO, secondary reactions of FTS products are inhibited on Co catalyst at high pressure, the methane detected likely derives from hydrocracking of heavy waxes contained in the catalyst pores. Once the time constant for hydrogenation of active carbon is calculated from the first part of the methane decay, Equation 1 can be used to extrapolate the curve until the transient is completed.

$$F_{\alpha}(t) = F_{peak} \cdot \left(\frac{1 - e^{-\frac{t - t_D}{\tau}}}{\tau} \right)$$
(2)

Here, $F_{\alpha}(t)$ is the methane flow rate thus calculated, and B(t) is the hydrodynamic decay that methane should follow in the absence of a reaction from F_{peak} to zero:

$$B(t) = F_1 \cdot \left(\begin{array}{c} -\frac{t-t_D}{\tau} \\ 1-e^{-\frac{\tau}{\tau}} \end{array} \right)$$
(3)

The amount of active carbon adsorbed on the catalyst at the time of the switch is determined from the area between $F_{\alpha}(t)$ and B(t) (Figure 23), after the transient is completed.

$$C^* = \int_{t_D}^{\infty} \left[F_{\alpha}(t) - B(t) \right] dt \tag{4}$$

If the Co loading and the dispersion of the catalyst are known, it is possible to calculate the percentage of the superficial Co sites occupied by active carbon.



Figure 20. Transient of CO, H₂ and CH₄ flow rates after switch from syngas to methane. (15 wt.% Co/TiO₂, 473 K, 2.0 MPa, H₂/CO=2, residence time = 1.7 sec, CO conversion = 6.3 %, CH₄ selectivity = 9.6 %).



Figure 21. Transient of Ar flow rate after switch from syngas to methane. (\blacklozenge): experimental, (no symbols): model. (15 wt. % Co/TiO₂, 473 K, 2.0 MPa, H₂/CO=2, residence time = 1.7 sec, CO conversion = 6.3 %, CH₄ selectivity = 9.6 %).



Figure 22. Normalized flow rate of CH₄ after switch from syngas to methane. (15 wt. % Co/TiO₂, 473 K, 2.0 MPa, H₂/CO=2, residence time = 1.7 sec, CO conversion = 6.3 %, CH₄ selectivity = 9.6 %).



Figure 23. Flow rate of CH₄ after switch from syngas to methane. (\blacklozenge): experimental, (no symbol): model; (15 wt.% Co/TiO₂, 473 K, 2.0 MPa, H₂/CO=2, residence time = 1.7 sec, CO conversion = 6.3 %, CH₄ selectivity = 9.6 %).

Data obtained from the carbon coverage measurements on the Co/TiO₂ catalyst are shown in Table 5. The estimates of the carbon coverage (θ_C) for which an effect on

selectivity was observed, estimated with the titration technique are between 15% and 24% and are of the same order of magnitude of the ones reported in the literature. For example, Winslow *et al.* [98] estimated a number of active carbon at steady state for a Ru/TiO₂ catalyst is $0.8 \cdot 10^{-7}$ mol, resulting in a coverage of superficial cobalt atoms by active carbon at steady state calculated by us of about 1.5%; the value obtained by Winslow *et al.* for the same catalyst [92] is 12%, whereas Mims *et al.* [103] obtained a value of 18500 mol_C/g_{cat} on a Co/SiO₂ catalyst leading to a coverage of superficial Co, from our calculations, of about 17%. Biloen *et al.* [102] also found the carbon coverage to be 4% on an unsupported Co catalyst and 14% on a Ru/ γ -Al₂O₃ catalyst.

In order to perform a more thorough statistical analysis, repeated measurements were collected at two different space velocities and by adding water at the higher space velocity: the results of these experiments are reported in Table 5. From those data it is evident that to an increase of the water partial pressure from 0.17 atm to 3.04 atm, at which the rate increases from 1.51 mmol/h/g to 2.83 mmol/h/g and the methane selectivity decreases from 9.1 % to 5.3 %, the active carbon coverage detected by the switch method does not change significantly. The hypothesis that the number of active carbon in the presence of water is greater than in dry conditions was also verified by a statistical test and rejected. These results suggest that both the higher activity and the changes in selectivity observed on the Co/TiO₂ catalyst cannot be attributed to a significantly greater number of active carbon adsorbed on the surface. The higher rate of CO consumption could hence be explained by hypothesizing a higher reactivity of the same amount of carbonaceous species, which may not be observed by the titration technique here adopted. Indeed, if water played a role in activating the carbon adsorbed on the surface during FTS, a switch to a pure hydrogen stream would not be able to detect it.

Alternatively, since the direct involvement of water into the mechanism of CO consumption was ruled out by the kinetic isotope effect experiments discussed in Section 6, the enhancement of the rate of CO consumption at high water partial pressure could derive from the easier transport of the reactants to the catalytic sites through the liquid waxes filling the pores. This phenomenon might be due to the formation of an aqueous phase, which would facilitate the transport of CO and H₂ [14]. Assuming a dependence of the CO consumption rate as $r_{CO} = k \cdot p_{H2}^{0.74} p_{CO}^{-0.24}$ [70], an equal increase of the amount of CO and H₂ dissolved in the liquid, due to a minor transport limitation of H₂ and CO, would positively affect the velocity, whereas the change in the concentration of adsorbed CO with respect to hydrogen could be such as to decrease the methane formation. The fact that the carbon coverage is not greatly affected by the presence of water might be explained if we consider that the amount of adsorbed carbon is much greater than the coverage by hydrogen. Hence, to a decrease of the number of carbon, to which the titration method here used may not be sensible enough, would correspond a significant increase of the adsorbed hydrogen, leading eventually to a higher rate. Still, further investigations are needed to understand the effect of water on activity and selectivity of cobalt catalysts.

Table 5. Results from the experiments on the 15 wt.% Co/TiO₂ catalyst at 2.0 MPa, 473K, $H_2/CO = 2$

	$SV = 36.3 \text{ min}^{-1}$	$SV = 28.2 \text{ min}^{-1}$	$SV = 36.3 \text{ min}^{-1}$
p _{H2O} (MPa)	$1.7 \cdot 10^{-2} \pm 2.4 \cdot 10^{-3}$	$2.0 \cdot 10^{-2} \pm 6.5 \cdot 10^{-3}$	$3.1 \cdot 10^{-3} \pm 2.9 \cdot 10^{-3}$
r _{CO} (mmol/h/g)	1.51 ± 0.20	1.35 ± 0.44	2.83 ± 0.22
CH ₄ selectivity (%)	9.11 ± 0.82	8.79 ± 1.27	5.31 ± 0.53
C [*] (µmol)	23.4 ± 3.31	24.8 ± 4.75	25.93 ± 5.10

8. Conclusions

Water enhances FTS rates, decreases CH₄ selectivity and increases product molecular weight and olefin content on Co-based FTS catalysts. We have carried out extensive studies with the use of isotopic tracers, in situ FTIR and XAS spectroscopies, and carbon coverage measurements based on site titration with H₂ switch, to investigate the possible causes of this positive water effect. Studies with CO/D₂ and CO/H₂ mixtures showed the existence of an overall inverse isotope effect, which resulted from a combination of kinetic and equilibrium isotope effects. The isotope effect was unchanged with changes in the average water pressure in the reactor, which pointed out to a lack of participation of water in the kinetically relevant steps in the FTS reaction mechanism. In situ FTIR spectroscopic measurements showed that increase in water concentrations in the reactor did not lead to a significant change in the total number of CO-binding sites, which points out the lack of existence of a correlation between FTS rates and site density. X-ray absorption spectroscopic measurements showed that the Co surface remains unoxidized under typical reaction conditions, contrary to what has commonly been reported in the literature. The carbon adsorbed on the surface during the reaction was measured by means of hydrogen titration at real FTS conditions (i.e. high temperature and pressure) on both catalysts. The amount of active carbon adsorbed on the catalytic surface was found to be independent of water partial pressure, according to our investigation. Therefore the autocatalytic effects of water on Co catalysts may not be attributed to a higher coverage of the surface by active carbon. The effect of water could derive either from a higher reactivity of the same number of carbon species, or from the formation of an intrapellet aqueous phase which would enhance the transport of the reactants to the catalytic sites. This we recommend as one of the few remaining avenues for research in the area of FTS reactions on Co-based catalysts.

III. APPENDIX

1. References

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