# Fischer-Tropsch synthesis catalysts based on Fe oxide precursors modified by Cu and K: structure and site requirements

Senzi Li[a], George D. Meitzner[b], and Enrique Iglesia[a]

[a]Department of Chemical Engineering, University of California, Berkeley, CA 94720

[b]Edge Analytical, Inc., 2126 Allen Blvd., Middleton, WI 53562

The reduction, carburization, and catalytic properties of Fischer-Tropsch synthesis (FTS) catalysts based on Fe-Cu were examined using kinetic and spectroscopic methods at reaction conditions. $Fe_2O_3$ precursors reduce to $Fe_3O_4$ and then carburize to form a mixture of $Fe_{2.5}C$ and $Fe_3C$ in both CO and $H_2$/CO mixtures at 540-720 K. Oxygen removal initially occurs without FTS reaction as $Fe_2O_3$ forms inactive O-deficient $Fe_2O_3$ species during initial contact with synthesis gas at 523 K. FTS reactions start to occur as $Fe_3O_4$ forms and then rapidly converts to $FeC_x$. The onset of FTS activity requires only the conversion of surface layers to an active structure, which consists of $FeC_x$ with steady-state surface coverages of oxygen and carbon vacancies formed in CO dissociation and O-removal steps during FTS. The gradual conversion of bulk $Fe_3O_4$ to $FeC_x$ influences FTS rates and selectivity weakly, suggesting that the catalytic properties of these surface layers are largely independent of the presence of an oxide or carbide core. The presence of Cu and K increases the rate and the extent of $Fe_3O_4$ carburization during reaction and the Fischer-Tropsch synthesis rates, apparently by decreasing the size of the carbide crystallites formed during reaction.

## 1. INTRODUCTION

Fe, $FeC_x$, $FeO_y$ can co-exist when Fe oxides are activated in reactive gases or used in Fischer-Tropsch synthesis (FTS) reactions [1]. The relative abundance of these phases depends on reaction conditions and it can influence catalytic properties. The presence and role of these phases remain controversial [2], because the detection of active sites is usually indirect and the results tend to provide infrequent snapshots of the catalyst structures as a function of time on stream, instead of a continuous record of structural transformations during FTS reactions. The present study addresses the characterization of the structure and stoichiometry of active phases formed from Fe oxide precursors during FTS using a combination of isothermal transient kinetic methods, *in situ* X-ray absorption spectroscopy, and steady-state FTS rate and selectivity measurements.

## 2. EXPERIMENTAL

Fe oxide precursors were prepared by precipitation of an aqueous solution of $Fe(NO_3)_3$ (Aldrich, 99.99%, 3.0 M) or a mixture of $Fe(NO_3)_3$ and $Zn(NO_3)_2$ (Aldrich, 99.99%, 1.4 M) with $(NH_4)_2CO_3$ (Aldrich, 99.9%, 1 M) at 353 K and at constant pH of 7.0. The precipitates were treated in dry air at 393 K for 12 h and then at 643 K for 4 h. X-ray diffraction measurements confirmed that the crystal structure of resulting Fe oxides was $Fe_2O_3$. Fe oxide powders were impregnated with an aqueous solution of $Cu(NO_3)_2$ (Aldrich, 99.99%, Cu/Fe=0.01) and/or $K_2CO_3$ (Aldrich, 99.99%, K/Fe=0.02) using incipient wetness methods. The dried material was treated in air at 673 K for 4 h. Detailed descriptions of these synthesis procedures are reported elsewhere [3]. The Cu-promoted oxide hereafter is designated as $Fe_2O_3$-Cu, and after K addition, as $Fe_2O_3$-K-Cu.

A rapid switch transient method was used to determine the extent and rate of reduction and carburization of Fe oxide precursors and the rate of FTS reactions during the initial stages of the catalytic reaction. Samples (0.2g) were pretreated in He (100 $cm^3$/min) up to 573 K and then cooled to 523 K. A $H_2$/CO/Ar stream (40/20/40 %, 1 atm, Matheson, 99.99%) was then introduced and the concentrations of gas products in the effluent stream were monitored using on-line mass spectrometry. Here, $CH_4$ formation rate was used as a surrogate measure of hydrocarbon formation rates because it can be measured accurately and changes with time on stream in parallel with the formation rates of other hydrocarbons. A pre-reduced $Fe_3O_4$-Cu sample was prepared by treating $Fe_2O_3$-Cu (0.2g, Cu/Fe=0.01) in 20 % $H_2$/Ar (100 $cm^3$/min) while increasing the temperature to 533 K at 0.167 $Ks^{-1}$. The $Fe_3O_4$ sample was then cooled to 523 K in He (100 $cm^3$/min) before exposing it to the $H_2$/CO/Ar stream. A $FeC_x$-Cu sample ($Fe_{2.5}C$ and $Fe_3C$ mixture) was also prepared by treating $Fe_2O_3$-Cu (0.2g, Cu/Fe=0.01) in 20 % CO/Ar (100 $cm^3$/min, Matheson, 99.99%) while heating to 673 K at 0.083 $Ks^{-1}$. The presence of $Fe_3O_4$ and $FeC_x$ phases was confirmed by X-ray diffraction and by detailed oxygen removal and carbon introduction measurements [4].

X-ray absorption spectra were obtained at the Stanford Synchrotron Radiation Laboratory using a wiggler side-station (beamline 4-1). Fe K-edge X-ray absorption spectra were acquired during FTS in synthesis gas using an *in situ* X-ray absorption cell [5]. A precursor oxide sample (8 mg; diluted to 10 wt.% Fe with graphite) was placed within a thin quartz capillary. Synthesis gas ($H_2$/CO=2) was passed through the sample at 523 K and a space velocity of 30,000 $h^{-1}$. The spectra were recorded *in situ* as the structure of the catalysts developed with time on stream after exposure to synthesis gas (~14 h). In order to capture the phase evolution of the Fe oxide precursors during initial contact with synthesis gas, XAS spectra were also measured after rapidly cooling samples to room temperature while flowing He through the powder bed. The relative concentrations of Fe carbides and Fe oxides in the samples were obtained using principal component analysis and a linear combination of X-ray absorption near-edge spectra (XANES). The spectra of reference materials, $Fe_2O_3$, $Fe_3O_4$, and $FeC_x$, were fitted to the catalyst XANES in the region between 7.090 and 7.240 keV.

## 3. RESULTS AND DISCUSSION

Figure 1 shows the temperature-programmed reduction profile of $Fe_2O_3$-Cu in $H_2$ and its reduction/carburization in CO. The amount of oxygen removed as a function of temperature indicates that the reduction of $Fe_2O_3$-Cu in $H_2$ proceeds in two steps: $Fe_2O_3$ reduced to $Fe_3O_4$ (<600 K); then, $Fe_3O_4$ reduced to Fe at 600-950 K. The oxygen removal and carbon introduction rates as a function of temperature for the $Fe_2O_3$-Cu sample in CO suggest that reduction/carburization occurred also in two sequential steps, except that reduction started at ~80 K higher temperature in CO than in $H_2$. It appears that CuO reduced in $H_2$ at 470 K to form $H_2$ dissociation sites that increase $Fe_2O_3$ reduction rates. Carburization did not start until 550 K, as $Fe_3O_4$ started to reduce. The formation of Fe carbides occurred concurrently with the reduction of $Fe_3O_4$. X-ray diffraction of samples treated in CO at 550 K and 750 K confirmed that reduction and carburization of Fe oxides in CO proceeds via two sequential steps: $Fe_2O_3$ reduces to $Fe_3O_4$, $Fe_3O_4$ reduces and carburizes to form a mixture of $Fe_{2.5}C$ and $Fe_3C$.

Mass spectrometric analysis of initial products formed on $Fe_2O_3$-Cu, $Fe_3O_4$-Cu and $FeC_x$-Cu after exposure to synthesis gas at 523 K was used in order to measure the rate of initial reduction and carburization of Fe oxides as well as the FTS rates. Figure 2 shows the oxygen removal by $H_2$ and CO forming $H_2O$ and $CO_2$ and the $CH_4$ formation rates during the initial reduction/carburization in $H_2$/CO and during subsequent steady-state FTS on $Fe_2O_3$-Cu at 523 K. During the initial 60 s, oxygen was removed from $Fe_2O_3$-Cu; reduction occurred without the concurrent formation of $CH_4$ or other hydrocarbons. The oxygen removed under the first sharp peak arises from the reduction of CuO to Cu. The rest of the oxygen removed during the induction period corresponds to an average stoichiometry of $Fe_2O_{2.8}$. This indicates that O-deficient $Fe_2O_3$ is not active for FTS reaction. $CH_4$ formation rates started to increase after this induction period and reached steady-state values after removal of only about 1-2 equivalent layers of O-atoms (assuming that a monolayer consists of $10^{19}$ O-atom/$m^2$) in $Fe_2O_3$, suggesting the facile formation of active sites, which rapidly reached their steady-state site density.

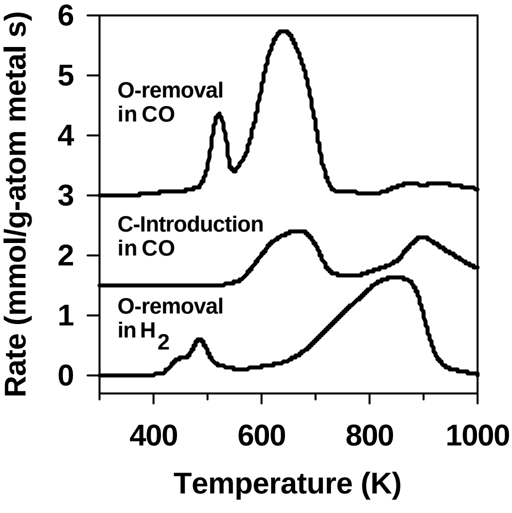

Fig. 1. Temperature-programmed reaction of $Fe_2O_3$-Cu in $H_2$ and CO (0.2 g sample; Cu/Fe=0.01, 0.167 $Ks^{-1}$; 20 % $H_2$ or CO in Ar; 100 $cm^3$/min total flow rate).

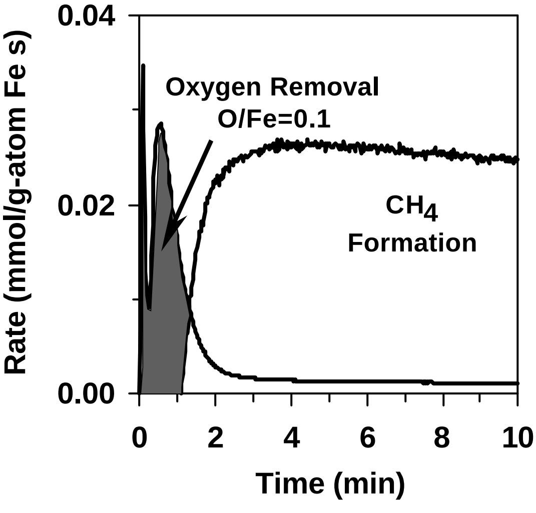

Fig. 2. Mass spectrometric product transients on $Fe_2O_3$-Cu with time on stream after exposure to synthesis gas at 523 K (0.2 g sample; Cu/Fe=0.01; $H_2$/CO=2, 100 $cm^3$/min total flow rate).

Figure 3 shows the results of linear combinations of Fe K-edge XANES for reference compounds ($Fe_2O_3$, $Fe_3O_4$ and $FeC_x$) as a description of the spectra measured for $Fe_2O_3$-Cu after exposure to synthesis gas at 523 K for various times. $Fe_2O_3$ rapidly disappeared during the induction period and $Fe_3O_4$ and Fe carbides formed concurrently; the extent of reduction and carburization increased with time on stream. $Fe_3O_4$ alone was never detected during FTS reactions, indicating its facile conversion to Fe carbides. Fe metal was not detected at any time during exposure to synthesis gas at 523 K.

The structural changes from $Fe_2O_3$ to $Fe_3O_4$, the subsequent facile conversion of $Fe_3O_4$ to Fe carbides, and the concurrent increase in FTS rates suggest that FTS reactions first occur as $Fe_3O_4$ is formed and then rapidly converted to $FeC_x$. The extent of carburization continued to increase with time on stream, without a detectable increase in FTS reaction rates, indicating that only the incipient conversion of $Fe_3O_4$ to $FeC_x$ was required for FTS reactions to occur at steady-state rates. In effect, only surface layers of Fe carbides appear to be required to form FTS active sites, irrespective of the structure and composition of the bulk phase. The catalytic properties of Fe carbides appear not to be influenced by a remaining Fe oxide core or by its ultimate conversion to $FeC_x$.

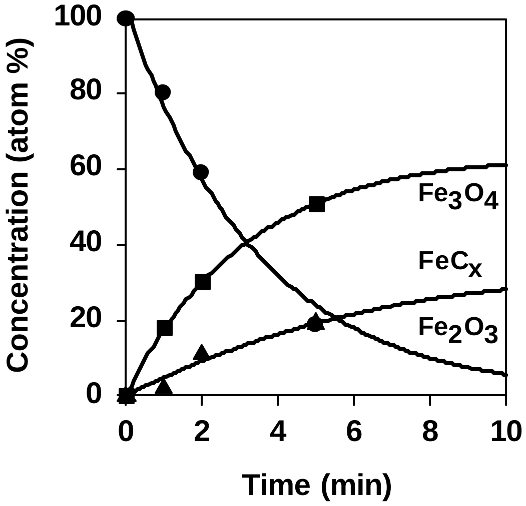

Fig. 3. Fe K-edge X-ray absorption measurements of the phase evolution of $Fe_2O_3$-Cu oxide with time on stream after exposure to synthesis gas at 523 K (1 mg, precipitated $Fe_2O_3$, Cu/Fe=0.01, $H_2$/CO=2, 30000 $h^{-1}$).

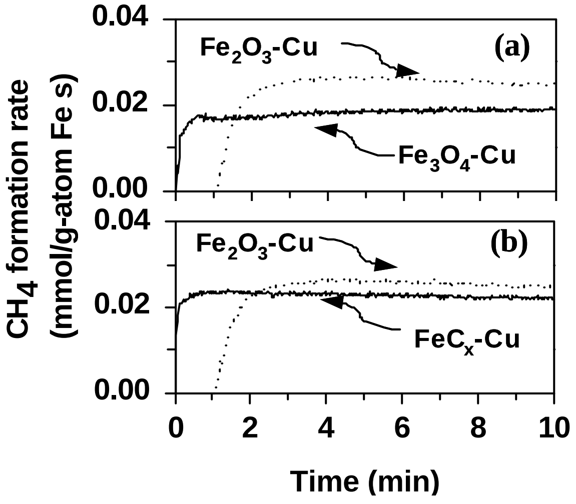

Fig. 4. Mass spectrometric product transients on (a) $Fe_3O_4$-Cu and (b) $Fe_xC$-Cu with time on stream after exposure to synthesis gas at 523 K (0.2 g sample; Cu/Fe=0.01; $H_2$/CO=2, 100 $cm^3$/min total flow rate).

Figure 4 shows the initial $CH_4$ transients on pre-carburized Fe carbides ($FeC_x$-Cu) and pre-reduced Fe oxides ($Fe_3O_4$-Cu) at 523 K during exposure to synthesis gas. Steady-state reaction rates were reached on both $Fe_3O_4$-Cu and $FeC_x$-Cu immediately upon contact with $H_2$/CO mixtures and without the induction period observed on $Fe_2O_3$ precursors. FTS rates remained constant even as the gradual removal of oxygen and the introduction of carbon continued to occur on $Fe_3O_4$-Cu. This indicates that the formation of an active surface occurred only after a few FTS turnovers, irrespective of the initial presence of $Fe_3O_4$ or $FeC_x$. This active surface is likely to consist of Fe carbides with a steady-state mixture of surface vacancies and adsorbed C and O atoms formed in the CO dissociation and O-removal steps required to complete a FTS catalytic turnover. The relative concentrations of these species are rapidly established by FTS elementary steps; they depend on the redox properties of the gas phase, on the reaction temperature, and on the presence of any surface promoters that modify the redox properties of the surface.

Figure 5 shows steady-state hydrocarbon formation rates as a function of CO conversion on $Fe_2O_3$-Zn-Cu and $Fe_2O_3$-Zn-K-Cu (508 K, 21.4 bar, $H_2/CO=2$). ZnO species in these samples act as a structural promoter to increase FTS rates by inhibiting sintering of the oxide precursors during synthesis. The steady-state reaction data showed that the presence of Cu and K significantly increased FTS rates, suggesting that K and Cu increased the density of active sites formed during activation in $H_2$/CO mixtures.

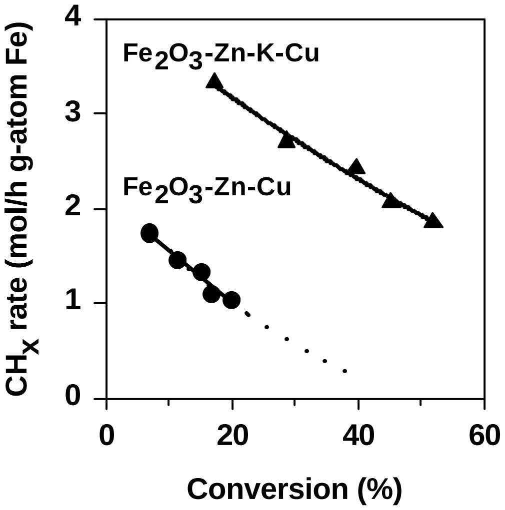

Fig. 5. Hydrocarbon formation rates as a function of CO conversion at steady-state FTS conditions (0.4 g sample; Zn/Fe=0.01, K/Fe=0.02, Cu/Fe=0.01, $H_2/CO=2$; 508 K, 21.4 atm).

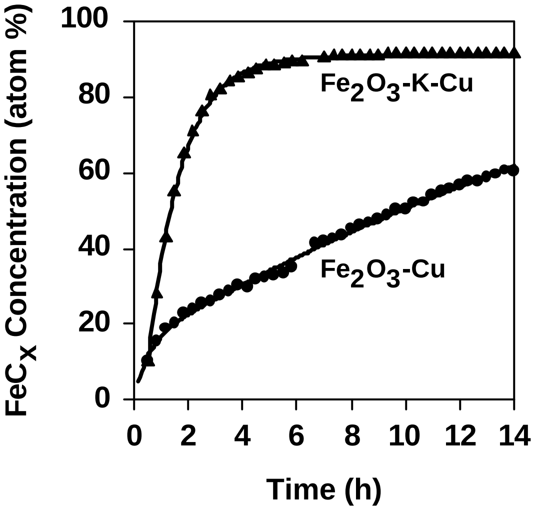

Fig. 6. *In situ* linear combination fits to Fe K-edge XANES of $Fe_2O_3$-K-Cu and $Fe_2O_3$-Cu as a function of time in synthesis gas at 523 K (1 mg sample; Cu/Fe=0.01, K/Fe=0.02; $H_2/CO=2$, 30000 $h^{-1}$).

The presence of Cu and of K increased the rate and the extent of $Fe_3O_4$ carburization during FTS reactions. The correlation between the rate and extent of carburization of these catalysts and their FTS rates appears to reflect the fact that K and Cu decrease the size of the carbide crystallites formed during reaction and thus increase the number of active sites. Our surface area and CO chemisorption measurements on the samples after FTS reactions confirmed that the surface areas and the amount of CO chemisorbed on the K- and Cu-containing samples are higher than on the samples without K and Cu. This supporting evidence will be described in a separate paper [6]. It appears that the smaller size of the crystallites formed in K- and Cu-containing samples account for their more complete carburization during FTS. It is not, however, their more complete carburization, but their higher surface area that accounts for higher FTS rates obtained on K and Cu promoted catalysts.

## 4. CONCLUSIONS

Porous $Fe_2O_3$ precursors sequentially reduce to $Fe_3O_4$ and then carburize to a mixture of Fe carbides ($Fe_{2.5}C$ and $Fe_3C$) in CO or in synthesis gas. The incipient conversion from $Fe_3O_4$ to Fe carbides occurs rapidly, at least in near surface layers, at FTS conditions. Oxygen removal initially occurs without FTS reaction as $Fe_2O_3$ forms inactive O-deficient $Fe_2O_3$ species during contact with synthesis gas. FTS reactions occur as $Fe_3O_4$ is formed and rapidly converted to $FeC_x$. FTS reactions require only the incipient conversion of surface layers to an active structure, which consists of $FeC_x$ with a steady-state surface coverage of carbon and oxygen vacancies. The catalytic properties of Fe catalysts are not influenced by the gradual conversion of bulk $Fe_3O_4$ to $FeC_x$ and its ultimate carburization at FTS conditions. The presence of Cu and of K increases the rates and extent of $Fe_3O_4$ carburization during reaction and the Fischer-Tropsch synthesis rates, apparently by providing multiple nucleation sites that lead to higher surface area $FeC_x$ crystallites during reaction.

## 5. REFERENCES

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