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Fischer–Tropsch Synthesis: Effect of Water Over Iron-Based Catalysts

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Abstract The effect of water on the performance of potassium-promoted precipitated iron catalyst was investigated during Fischer–Tropsch synthesis (FTS) using a continuously stirred tank reactor (CSTR) at two different reaction temperatures. Water was added in such a manner as to replace an equivalent amount of inert gas so that all other reaction conditions (e.g., reactant partial pressure, space velocity) remained the same before, during, and after water addition. The externally added water had a positive effect on CO conversion at 270 °C whereas, for the reaction carried out at 230 °C, the added water decreased CO conversion and deactivated the catalyst. From these findings, the addition of water at 230 °C oxidized the catalyst, transforming the iron carbide to the Fe_3O_4 phase. When the reaction was carried out at 270 °C, severe oxidization did not take place and a carbide phase was retained. The loss in activity and the rate of deactivation were more pronounced at 230 °C compared to the 270 °C condition for the same catalyst. Mössbauer spectroscopic measurements revealed that for the reaction carried out at 230 °C, the catalyst had 85% of the iron present as Fe_3O_4 and the remaining as Hägg carbide (χ-Fe_5C_2), whereas at the higher temperature reaction condition the catalyst had about 66% of the iron present as ε'-$Fe_{2.2}C$, with the remaining as Fe_3O_4. These findings were also supported by XANES analysis, where a high white line intensity was observed for the sealed used catalyst sample for the low temperature reaction condition, indicating a higher extent of oxidation. A low white line intensity was recorded for the used sample for the high temperature reaction condition, indicative of a higher extent of reduction.

Keywords Fischer–Tropsch synthesis · Iron catalyst · Water effect · Mössbauer · XANES · Effect of temperature

1 Introduction

Fischer–Tropsch synthesis (FTS) offers the possibility of converting a mixture of hydrogen and carbon monoxide (synthesis gas or syngas) to ultra-clean hydrocarbons, virtually free of sulfur. This syngas is usually produced from natural gas or coal, and typically (though not always, depending on gasifier type) exhibits a lower H_2/CO ratio in the case of coal gasification. In the FTS process, hydrocarbons are produced from CO and H_2, and the reaction can be expressed as:

$$n\ CO + (2n+1)\ H_2 \rightarrow C_nH_{2n+2} + n\ H_2O$$

Although several metals are active for FTS, only iron and cobalt catalysts appear to be economically viable on an industrial scale. The higher water–gas shift activity of iron makes it a good candidate for converting hydrogen lean syngas derived from coal. Controlling selectivity is an important aspect of FTS catalyst development. Typical cobalt catalysts have a high activity for hydrogenation and tend to produce linear alkanes. Iron catalysts are more versatile than cobalt catalysts, produce less methane, and can be geared toward the production of alkenes, oxygenates, and branched hydrocarbons depending on the promoters and process conditions employed. When an iron catalyst is

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used to carry out the FTS reaction, the water–gas shift (WGS) reaction also occurs. This side reaction consumes CO and water produced during the FTS reaction to produce additional hydrogen, rejecting CO_2 in the process:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Water is produced during FTS and will always be present in varying quantities during the reaction. A fraction of the water, formed as a primary product, is converted on an iron catalyst to carbon dioxide by the simultaneous occurrence of the WGS reaction. For iron catalysts, addition of water to the feed during FTS affected the CO and hydrogen partial pressures inside the reactor by increasing the WGS rate [1–3]. The effect of water on the FTS rate has a long history. In 1950, Exxon workers provided data to show that the addition of steam to a fluidized bed reactor containing an iron catalyst increased the amount of oxygenates that were formed [4]. Later, researchers at Mobil showed that exposure of an iron catalyst to steam induced an effect (labeled selectivation) which caused an increase in the selectivity for liquid hydrocarbons relative to that of the catalyst prior to steam addition [5]. Karn et al. [2] reported that 10–30% H_2O added to syngas with a 1:1 H_2/CO ratio had relatively little effect on CO conversion using a fixed bed reactor and a 6–8 mesh fused iron nitride catalyst. In slurry-phase FTS, Satterfield et al. [3] performed water co-feeding experiments on iron FTS catalysts employing inlet H_2/CO ratios of 0.96 and 0.52. Using an inlet H_2/CO ratio of 0.96, the additional water accelerated the deactivation rate during FTS. However, in the case of an inlet H_2/CO ratio of 0.52, the addition of 20 mol% water to the feed exhibited no influence on the FT reaction rate. Reymond et al. [6] reported that in studies at atmospheric pressure and differential conversion, addition of only 0.6% H_2O to syngas having a 9:1 H_2/CO ratio produced about a threefold drop in rates of both CH_4 and CO_2 production.

The differences among these studies may be attributed to differences in reactor type or catalyst used. Studies of water addition revealed relatively small changes in the reaction rates [2, 3]; additional CO_2 was produced but synthesis of FT products was inhibited. However, these trends became less pronounced as the conversion increased. In contrast, reactions carried out under differential conversion [6] displayed much greater effects of water addition on the catalytic activity but had no clear impact on selectivity.

Potassium has been used extensively as the promoter compared to other Group I alkali metals. One claim is that potassium enhances adsorption of CO and decreases the relative pool of adsorbed hydrogen. In this view, potassium decreases secondary hydrogenation of alkenes. The results were explained based on the perspective that potassium donates electrons to iron and facilitates the dissociative chemisorption of CO, which tends to accept electrons from iron [7, 8]. Hydrogen at higher surface coverage, however, is prone to act as an electron donor to iron. Thus, the presence of potassium may actually weaken the strength of the Fe–H bond [9, 10] and influence its adsorption rate in that manner. Ribeiro et al. [11] demonstrated a plausible electronic effect by conducting TPR-EXAFS/TPR-XANES experiments, where a systematic increase in the carburization rates of Fe:Si:alkali catalysts were observed as a function of increasing alkali promoter basicity (i.e., moving down the column). Potassium salts are widely used as the most effective promoter in iron-based catalysts; however, the readiness to form an alkali compound with common catalyst supports or structural promoters, such as alumina or silica, complicates the situation. Li et al. [12–14] concluded that potassium promotes the formation of an increased number of active sites during reduction and carburization of iron oxides by facilitating the rapid formation of nucleation sites, resulting in the formation of smaller iron carbide crystallites.

The purpose of the present work was to study the effect of water over a potassium-promoted precipitated Fe catalyst, which was investigated by directly adding varying amounts of water into the feed gas but carefully maintaining a constant flow rate and reactant partial pressures using an inert balancing gas; the impact of reaction temperature was also explored. Thus, in these studies, the added water replaced an equivalent amount of inert gas so that all other reaction conditions remained the same before, during, and after water addition. The CSTR is well-suited to this type of experiment because ideally all catalyst particles experience the same gas composition during each set of conditions (i.e., better uniformity in temperature and concentration distributions). To characterize the oxidation state changes, used catalysts sealed in their in-situ state by the wax product, were withdrawn from the reactor and characterized by XANES analysis at the synchrotron at Brookhaven National Laboratory.

2 Experimental

2.1 Catalyst Preparation

Precipitated iron catalysts were prepared using a ferric nitrate solution obtained by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ in deionized water, and then tetraethylorthosilicate was added to provide the desired Fe:Si ratio. The mixture was stirred vigorously until the tetraethylorthosilicate had hydrolyzed. A flow of the tetraethylorthosilicate and iron nitrate mixture was added to a CSTR precipitation vessel together with a stream of 30% ammonium hydroxide that was added at a rate to maintain a pH of 9.0. By maintaining the slurry pH at 9.0 and an average residence time of 6 min, a base catalyst material containing iron and silicon was obtained. The slurry from the CSTR was filtered using a vacuum drum filter and the solid was washed twice with deionized water. The final filter cake was dried for 24 h in an oven at 110 °C with flowing air. For this study, the Fe:Si catalyst base powder was then impregnated with the proper amount of aqueous KNO_3 and $Cu(NO_3)_2$ solution to produce the desired composition of Fe:Si:K:Cu = 100:4.6:5.0:2.0 (atomic ratio). The catalyst was dried at 110 °C overnight with good mixing followed by impregnation and calcination at 350 °C in an air flow for 4 h.

2.2 BET Surface Area

Surface area measurements were conducted using a Micromeritics Tristar 3000 gas adsorption analyzer. In each test, a weight of approximately 0.25 g of sample was used. Nitrogen physisorption was performed at its boiling temperature.

2.3 Mössbauer Spectroscopic Measurements

Mössbauer spectra were collected in a transmission mode by a standard constant acceleration spectrometer (MS-1200, Ranger Scientific). A radiation source of 30 mCi ^{57}Co in Rh matrix was used and spectra were obtained using a gas detector. The catalyst samples collected from the CSTR were in the rewax matrix that was a solid at room temperature. This solid matrix was mounted in plexiglass compression holders that present a thin aspect to the γ-ray beam. All samples were investigated at cryogenic temperatures, typically over a velocity range of ±10 mm/s. For the low temperature measurements, the samples were placed inside a vibration free closed cycle cryostat (Cryo-Industries of America). The structural analysis of the samples was done by least-squares fitting of the Mössbauer spectra to a summation of hyperfine sextets. The least-square fitting procedure was done with user defined functions within the PeakFit program. The parameters for each sextet in the fit consisted of the position, width and height of the first peak, the hyperfine magnetic field, and the quadrupole electric field. These parameters were allowed to vary freely to obtain the best fit of the experimental data. Errors in the determined percent Fe values are about ±3% for well resolved spectra; in those that contain several iron oxide and carbide phases the uncertainty increases with the complexity of the spectrum (i.e., depending on the degree of overlapping and the weakness of the signal). However, these complex spectra are obtained during the course of change from a predominantly iron carbide or iron oxide phase and conform to a greater trend.

2.4 X-ray Absorption Near Edge Spectroscopy

Used catalyst samples, suspended in their in-situ state by extraction from the reactor under inert gas and rapidly cooling in the wax product (*ca.* 1 min), were retrieved from the reactor and analyzed by X-ray absorption near edge spectroscopy (XANES) at Brookhaven National Laboratory. XANES spectra were recorded near the Fe K edge (7.112 keV) in the transmission mode at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), Upton, New York, Beamline X-18b. The beamline is equipped with a Si(111) channel cut monochromator. A crystal detuning procedure was used to help minimize glitches. The X-ray ring at the NSLS has a flux of 1×10^{10} photons per second at 8 keV, and the usable energy range at X-18b is from 5.8 to 40 keV. Sample thickness was determined by calculating the amount in grams per square centimeter of sample, D, by utilizing the following thickness equation:

$$\mathrm{D} = \ln(\mathrm{I_o}/\mathrm{I_t})/\mathrm{sum}\left\{(\mathrm{m}/\mathrm{r})_\mathrm{j}\cdot\mathrm{w_j}\right\}$$

where, m/r is the total cross section (absorption coefficient/density) of element "j" in the sample at the absorption edge of the XANES element under study in cm^2/g, w_j is the weight fraction of element j in the sample, and $\ln(I_o/I_t)$ was taken over a typical range of 1–2.5. An average value of D from inputting both values was employed. Based on the calculation for D and the cross-sectional area of the pellet, the grams were calculated. For each XANES analysis, spectra were normalized to the height of the edge jump and truncated over the range 7.090–7.215 keV using the WinXAS [15] software and qualitatively compared.

2.5 In-situ Activation of Catalysts

In this study, the potassium promoted iron catalysts were pretreated with CO at 270 °C for 24 h in the CSTR while suspended in the start-up wax. Carbon monoxide activation was carried out at 1.3 MPa. The reduction of Fe_2O_3 with CO occurs in at least two steps:

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$

$$5Fe_3O_4 + 32CO \rightarrow 3Fe_5C_2 + 26CO_2$$

However, for high surface area materials, Fe_3O_4 may be a short-lived intermediate.

2.6 Reactor System

The FTS experiments were conducted in a 1 L CSTR equipped with a magnetically driven stirrer with turbine impeller, a gas-inlet line, and a vapor outlet line with a stainless steel (SS) fritted filter (2 µm) placed external to the reactor. A tube fitted with a SS fritted filter (0.5 μm opening) extending below the liquid level of the reactor was used for withdrawing reactor wax (i.e., rewax, which is solid at room temperature), thereby maintaining a relatively constant liquid level in the reactor. Separate mass flow controllers were used to control the flow rates of hydrogen and carbon monoxide. Carbon monoxide was passed through a vessel containing lead oxide on alumina to remove any traces of iron carbonyl. The gases were premixed in an equalization vessel prior to entering the reactor. The mixed gases entered the CSTR below the stirrer, which was operated at 750 rpm. The reactor temperature was maintained constant (±1 °C) by a temperature controller. After the activation period, the synthesis gas mixture (28.8% H_2, 41.2% CO) and inert balancing gas (30%) was introduced.

A series of measurements was conducted so that the pressure of carbon monoxide and hydrogen in the feed remained constant and was 70% of the total pressure, with the remainder being inert gas. A Teledyne ISCO Model 500 D syringe pump with Series-D pump controller was used to add water to the reactor. When water was added, the flow rate of inert gas was lowered such that a fraction of the inert gas was replaced by an equivalent volume of water. Thus, the sum of water added plus inert gas partial pressure was always 3.9 atm (0.38 MPa). The added water is expressed in one of two ways; in the first case the water added to the feed is expressed as the percentage of the total feed and in the second it is expressed as the partial pressure in the reactor.

2.7 Product Sampling and Analysis

The conversions of CO and H_2 were obtained by gas chromatographic analysis (micro-GC equipped with thermal conductivity detectors) of the product gas mixture. The reaction products were collected in three traps maintained at different temperatures: a hot trap (200 °C), a warm trap (100 °C), and a cold trap (0 °C). The products were separated into different fractions (wax, oil, and an aqueous phase) for quantification. For example, the oil product from the warm and cold traps was combined prior to GC analysis. Hydrogen, carbon monoxide and syngas conversion were obtained by using the following formula (N = moles of gas)

$$\text{Conversion}(\%) = \left(\frac{N_{\text{in}} - N_{\text{out}}}{N_{\text{in}}}\right) \times 100$$

3 Results and Discussion

Results of surface area measurements by adsorption of nitrogen at 77 K (Table 1) shows a lower BET surface area for potassium and copper promoted catalyst in comparison to the base catalyst, which has a surface area 176 m^2/g. For the promoted catalyst (100 Fe:4.6 Si:5.0 K:2.0 Cu), if the promoter oxides do not contribute to the surface area, the expected surface area would have been around 168 m^2/g. The actual measured surface area for the promoted catalyst is much lower, ~96 m^2/g. This indicates some pore blockage in the promoted catalyst due to the promoter oxide clusters blocking of a fraction of pores from the adsorbing gas. The pore size distributions of the base and promoted catalysts are shown in Fig. 1. The promoted catalyst displayed a wider average pore size, suggesting that the narrower pores were more significantly affected.

Water co-feeding to the iron FT synthesis was performed by Satterfield et al. [3] in a well-mixed slurry reactor; Karn et al. [2] also studied the effect of water but used a fixed bed reactor. However, unlike the current study, no adjustments were made to the reactor system (partial pressures) during periods of co-feeding of water. This means that the co-fed component significantly diluted the reaction medium. For iron catalysts, reaction rate may be very sensitive to the syngas partial pressure [16]. We explored the effect of water on FTS over the potassium promoted precipitated Fe catalyst by co-feeding different amounts of water (5.0–25 mol%) added into the feed gas at two different reaction temperatures. The partial pressures of the inlet hydrogen and carbon monoxide were kept constant during all periods by use of an inert gas. After every interval whereby co-fed water was added, the water was switched off and replaced by 30% of volume added inert gas to return to the reference conditions (i.e., baseline Fischer–Tropsch synthesis excluding co-fed water); thus, a trend could be developed regarding the effect of varying

Table 1 BET surface area, pore volume and pore radius values of base catalyst and alkali promoted catalyst

Catalyst	Surface area[a] (m^2/g)	Pore volume[a,b] (single point) (cm^3/g)	Pore volume[a,c] (BJH adsorp) (cm^3/g)	Average pore radius (nm)
Fe:Si (100:4.6)	176	0.27	0.28	2.74
Fe:Si:K:Cu (100:4.6:5.0:2.0)	96.1	0.15	0.16	2.79

[a] Calculated from N_2 adsorption measurements

[b] Single point adsorption average pore volume

[c] BJH adsorption cumulative pore volume

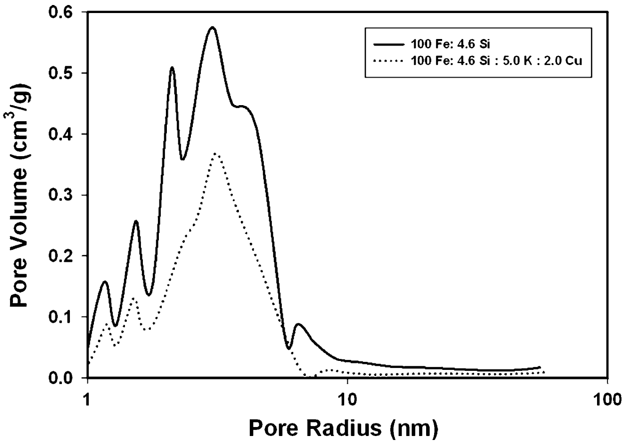

Fig. 1 BJH pore size distribution curves of the base catalyst and potassium promoted iron catalyst

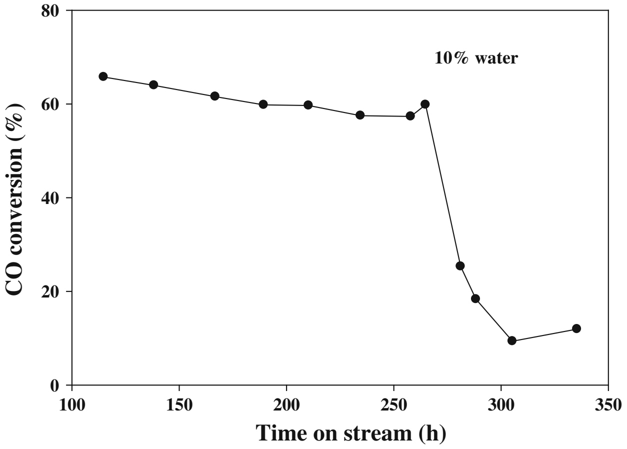

Fig. 3 Effect of water on CO conversion for potassium promoted iron catalyst at higher conversion level. ($T = 230$ °C, $P = 13$ atm (1.31 MPa), $H_2/CO = 0.7$, SV = 2 SL/g Fe/h)

amounts of water on the FT rate while at the same time the catalyst deactivation rate could also be monitored.

The effect of water on CO conversion for potassium promoted iron catalyst carried out at 230 °C is shown in Fig. 2. Steady state CO conversion ($\sim$45%) was reached during 210 h of time on-stream. After reaching the steady state conversion level, 10 vol% water was introduced to the feed gas by replacing an equal vol% of inert gas. The external addition of water caused a significant decrease in CO conversion; moreover, CO conversion did not recover when the water addition was terminated. The effect of water was also evaluated at high CO conversion levels ($\sim$60%) for the same catalyst at similar conditions as used for the earlier run, except at a lower space velocity of 2 SL/h/g_{Fe} (Fig. 3). Likewise, at this conversion level the addition of water caused a drastic decrease in CO conversion. Again, catalyst activity was not recovered after the addition of water was terminated, indicating that the catalyst had deactivated permanently. The catalyst is being subjected to a much higher water partial pressure than would be encountered during normal synthesis. The apparent negative influence of water on CO conversion may be ascribed to the competitive adsorption between water and CO on the catalyst surface. It is likely that the iron carbide was oxidized during exposure to the higher water partial pressure, which likely involves essentially complete transformation of iron carbide to magnetite (Fe_3O_4). In FTS H_2O/H_2 or CO_2/CO ratios are high enough, that iron carbides can be reoxidized to Fe_3O_4 [17, 18]. After the water addition, Fe_3O_4 was the major Fe phase, confirmed by Mössbauer and XANES experiments.

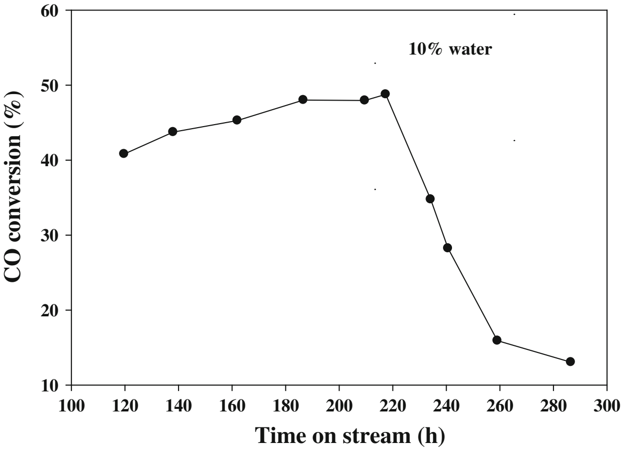

Fig. 2 Effect of water on CO conversion for potassium promoted iron catalyst at 230 °C. ($T = 230$ °C, $P = 13$ atm (1.31 MPa), $H_2/CO = 0.7$, SV = 6 SL/g Fe/h)

The effect of water on CO conversion for the same catalyst was carried out at 270 °C and results are shown in Fig. 4. Steady state CO conversion was reached in 130 h. The externally added water had a positive effect on CO conversion. CO conversion was found to increase with increasing vol% of co-fed water up to 15% and then there were slight decreases with further increases of water added to the feed gas. This effect was essentially reversible upon terminating water addition. That is, after terminating water addition, CO conversion was found to be about the same as before water addition. The added water to the reaction feed may react with CO (i.e., resulting in a decrease in the partial pressure of CO in the reactor) to produce CO_2 and hydrogen via the WGS reaction. The increase in the rate of CO consumption during FTS with water co-feeding was approximately equal to the increase in the rate of CO consumption by WGS. That is, the FT hydrocarbon production rate did not significantly change, but since the CO conversion rate changed, the relative rates of FTS and WGS did change.

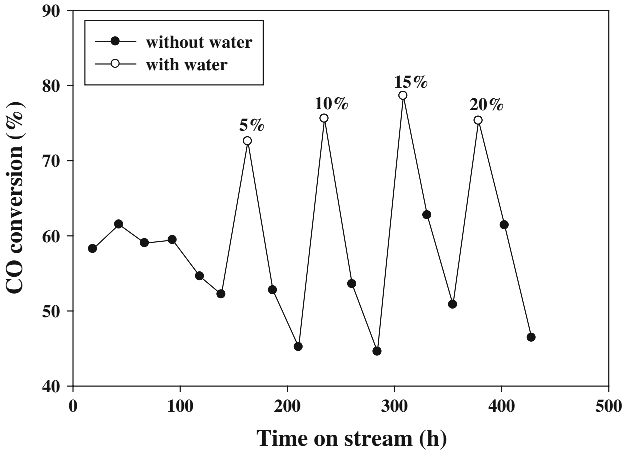

Fig. 4 Effect of water on CO conversion for potassium promoted iron catalyst at 270 °C. ($T = 270$ °C, $P = 13$ atm (1.31 MPa), $H_2/CO = 0.7$, SV = 3 SL/g Fe/h)

The partial pressure of water is an important parameter, as it has been shown in many cases to inhibit the FT reaction rate, depending on catalyst formulation. The partial pressure of water (i.e., at steady state reaction conditions) in the reactor for a run carried out at 230 °C with low conversion (~45%) was found to be 0.35 bar. After the addition of water to the feed gas, the partial pressure of water increased to 1.09 bar. Similarly, for a high conversion level (~60%) run at steady state conversion the partial pressure of water was 0.61 bar. As a result of FTS, the partial pressure of water increases with increasing conversion to some level and then subsequently decreases. At a high conversion level, the deactivation rate was reasonably low. After the addition of water, the partial pressure of water in the reactor was 1.09 bar. In both the cases (i.e., high or low conversion levels), at this partial pressure of water, the catalyst deactivated and likely transformed to the Fe_3O_4 phase. Carrying out steady-state FTS at 270 °C, the partial pressure of water inside the reactor was found to be 0.1 bar. The partial pressure of water in the reactor is lower as the temperature increases due to consumption of water by WGS. The partial pressure of water inside the reactor is obviously increased by water co-feeding. The partial pressure of water in the reactor at 20 vol% was found to be 1.26 bar, obviously higher than that of the 10 vol% of water addition test at 230 °C. Under these higher water partial pressure conditions, the catalyst did not deactivate after the water addition for the reaction carried out at 270 °C. At the lower reaction temperature the partial pressure of the water reaches 1.03 bar, and the catalyst deactivated completely, irrespective of the conversion level. Thus, it is likely that at 270 °C the surface iron carbide may not be affected during the water addition.

The addition of external water at 230 °C was found to decrease CO conversion and deactivate the catalyst, whereas at 270 °C CO conversion increases with increasing amounts of vol% added water. When the reaction was carried out at low temperature (230 °C), the added water interacts with the surface carbide layer and it is oxidized to Fe_3O_4. Whereas for the reaction carried out at 270 °C, during the water addition the surface carbide phase may not be affected or both the oxidation as well as carburization reactions occur simultaneously. In our previous investigation [19], studies on the influence of activation gas type, activation temperature and pressure for a low alpha iron catalyst showed that, with increasing the activation temperature the CO conversion was found to increase.

The absolute rates of FT and WGS reactions as a function of water amount for potassium promoted iron catalyst are shown in Fig. 5. The impact of the added water is to increase the rate of the WGS reaction with increasing the water amount, leveling off at higher amounts of water. The relative rates (selectivity) of FT and WGS reactions as a function of water amount for the same catalyst are shown in Fig. 6. Prior to water addition (i.e., at baseline conditions), the catalyst exhibits less than 50% selectivity to CO_2. Without water co-feeding, FT selectivity is always at least as large as the WGS selectivity, and thus always greater than 50%. WGS reaction consumes CO and water, produced during the FTS reaction. FT selectivity decreases and WGS selectivity increases as the amount of water is increased. But, when we are adding the water amounts to the feed gas, the CO conversion was found to increase. In FT synthesis, selectivity depends on the conversion level and it is therefore important to compare the catalysts at constant CO conversion level. We cannot definitively compare the results at these different conversion levels, as it is not possible to maintain a constant conversion level during the addition of external water to syngas. It appears that if we were able to maintain a constant conversion level

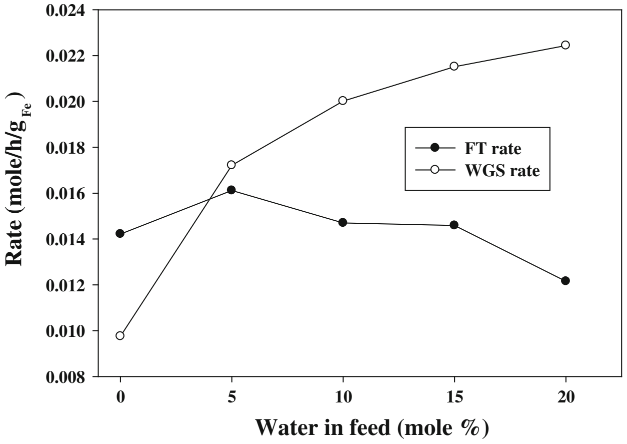

Fig. 5 Effect of water on FT and WGS reaction rates for the reaction carried out at 270. ($T = 270$ °C, $P = 13$ atm (1.31 MPa), $H_2/CO = 0.7$, SV = 3 SL/g Fe/h)

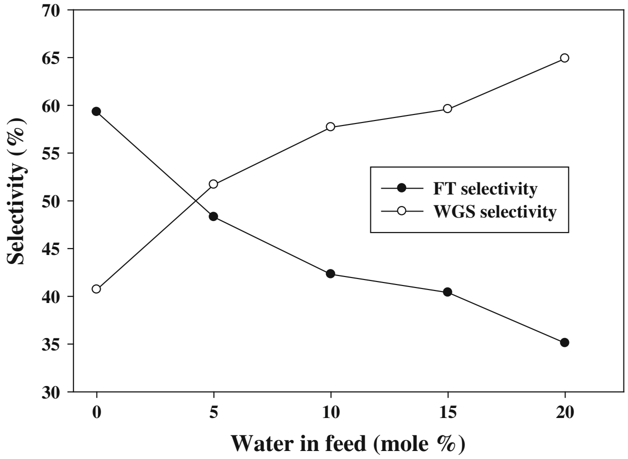

Fig. 6 Effect of water on selectivity for potassium promoted iron catalyst. ($T = 270$ °C, $P = 13$ atm (1.31 MPa), $H_2/CO = 0.7$, SV = 3 SL/g Fe/h)

before and during water addition, the relative rate of FT would be suppressed by increasing the water amount and that of WGS would increase. However, due to the increasing CO conversion during co-feeding the water, it is difficult to make a definitive conclusion regarding the active site for FT and WGS reactions (i.e., whether there is a common site or two sites). However, it appears that the reactions likely occur on a single site, since the relative rates of FT and WGS reactions change in the directions expected for a single site mechanism with water addition.

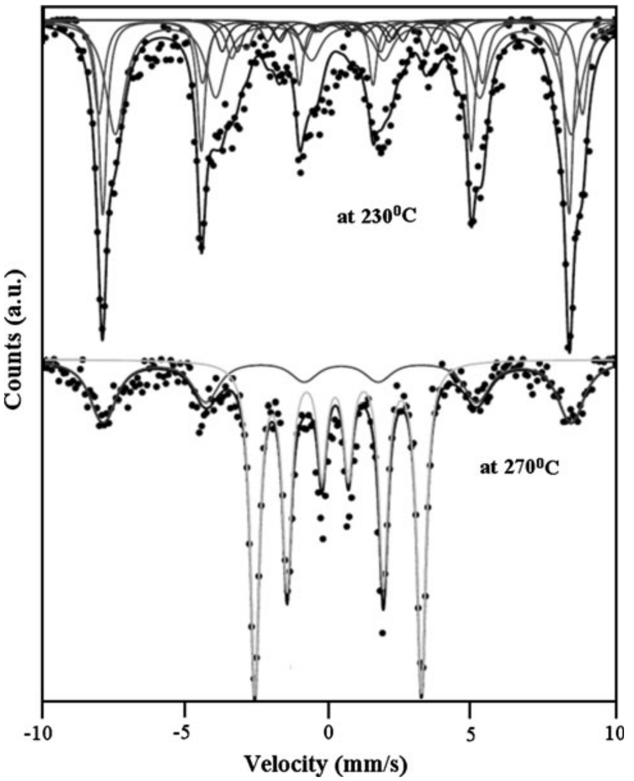

Fig. 7 Mössbauer spectra of used Fe catalysts for the reactions carried out at 230 and 270 °C

Mössbauer spectroscopy has proven to be an effective technique for the phase analysis of iron based FT catalysts. The effect of water on the Mössbauer spectra of the iron catalysts for the reaction carried out at 230 and 270 °C is shown in Fig. 7. The Mössbauer spectra in the present study represented a complex pattern comprised of magnetite, carbide and paramagnetic components. The extent of the resulting magnetic hyperfine splitting was in the range typical of the iron carbides [20]. The characteristic shape of the individual magnetic component indicates the presence of three distinct sextets. It is known that Mössbauer spectra of ε, χ, χ' and χ'' iron carbides contain three distinct sextets, while the Mössbauer patterns of ε' and θ iron carbides appear as a single sextet [21]. Reliable identification of different carbide phases was performed based on the number of constituent sextets, corresponding hyperfine magnetic fields, and their relative intensities. Compositional changes in terms of percent peak area of the different iron species were determined from curve fitting. For the reaction carried out at 230 °C, addition of 10% water caused a decrease in CO conversion and deactivated the catalyst. The low temperature (20 K) Mössbauer measurement of this catalyst revealed that about 85% of the iron in the catalyst was present as Fe_3O_4, with the remaining iron present as Hägg carbide (χ-Fe_5C_2). The addition of water at 270 °C increased the CO conversion with increasing amounts of water up to 20%. After 20% water addition, the catalyst sample corresponding to the higher FT temperature (270 °C) displayed about 66% of the iron as ε'-$Fe_{2.2}C$, with the remaining (34%) iron being Fe_3O_4. Thus, the presence of some fraction of iron carbide is necessary for a catalyst to exhibit high conversion.

The proposal of deactivation by oxidation was tested by retrieving catalyst samples from the reactor after sealing the catalyst particles in their in-situ state by cooling them in the wax product. The XANES spectra at the Fe K-edge of the iron catalyst for the reaction carried out at 230 and 270 °C are shown in Fig. 8. As shown in Fig. 8, the trend in oxidation, as characterized by the intensity of the white line, agrees with the trend in deactivation rate observed with water addition. The sample corresponding to the higher FT temperature, 270 °C, and having the lowest deactivation rate, had the lowest white line intensity, indicating the highest extent of reduction. Recall that the catalyst corresponding to low temperature FT, 230 °C, and having the higher conversion of the two low temperature conditions (i.e., and thus a higher water partial pressure), exhibited the highest deactivation rate with water addition. It also displayed the highest white line intensity in XANES, corresponding to a higher extent of oxidation (Fig. 8). On

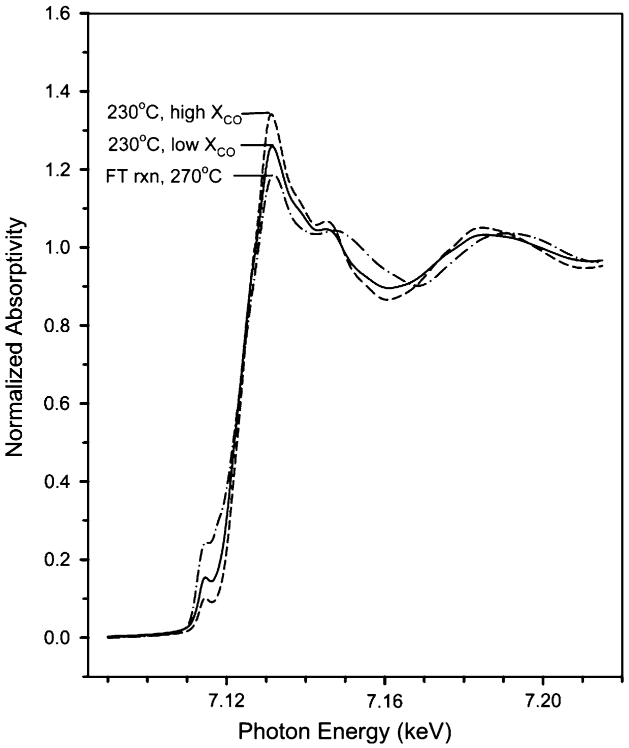

Fig. 8 Normalized XANES spectra at Fe K-edge of used catalyst for the reactions carried out at 230 and 270 °C

the other hand, the catalyst at the low temperature condition and having the lower conversion rate (i.e., not as high of a water partial pressure as the high conversion low temperature condition), exhibited intermediary deactivation and a corresponding intermediary degree of oxidation. These data confirm that the loss of the FT catalytic activity is due to conversion of the iron carbide to iron oxide. Furthermore, the data show that Fe_3O_4 has low, if any, activity for FT synthesis.

4 Conclusions

The effect of water on the activity of potassium promoted precipitated Fe catalyst has been investigated using a CSTR by adding varying amounts of water to the feed while employing an inert balancing gas during FTS at two different reaction temperatures. The addition of external water at 230 °C was found to decrease CO conversion and deactivate the catalyst, whereas at 270 °C the CO conversion increased with increasing levels of added water. Carbide appears to be the predominant phase of the working catalyst when the FTS reaction temperature is increased from 230 to 270 °C. Water co-feeding at the low reaction temperature favored oxidation over carburization, implying that the relative oxidation to recarburization rates favored oxidation at 230 °C but recarburization at 270 °C. Due to the increase in the conversion level by water co-feeding, it is difficult to make a definitive conclusion regarding the nature of the active sites for FT and WGS reactions; that is, whether FT and WGS occur on a single site or different sites. However, currently, it appears that the reactions may occur on a single site, since both the relative rates change with water addition. Mössbauer spectroscopy measurements of low and high temperature iron catalysts closely follow the catalytic activity. The oxidation state trends from XANES spectroscopy of the used catalyst samples were in agreement with the deactivation trends. That is, the catalyst sample corresponding to the higher temperature 270 °C condition displayed the highest extent of reduction (carbide phase).

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