

Executive Summary

CAER

A series of Fe-Al (0-25% Al) and Fe-Si (0-8% Si) catalysts were prepared to study the effect of structure promoters on iron FTS catalysts. BET data show that as the quantity of the promoter is increased, the surface area increased. In addition, as the calcination temperature increases, the surface area decreases. XRD analysis shows that Al promoted catalysts are not very crystalline at loadings greater than approximately 7 atom %. In contrast, the Si promoted catalysts are amorphous, with crystallinity being evident only for the small atomic fraction. It appears that Si retards the crystallization of Fe_2O_3 to a much greater degree than Al. In order to make accurate lattice parameter determinations, the catalysts were calcined at 600°C for 24 hours prior to additional XRD determinations. In all cases, Fe_2O_3 was identified as the only species present. At the higher levels of Al, 17.9% and 24.22%, there is evidence of another species that has not been identified. The XRD analysis of the catalysts showed that as the quantity of the promoter increased, there was a shift in all 2θ to higher values indicating that the promoter had entered the hematite lattice and was influencing its dimensions.

Iron Fischer-Tropsch synthesis (FTS) catalysts promoted with potassium or beryllium showed a superior deactivation property. Potassium promoted iron FTS catalyst showed a low deactivation rate of 0.59% CO conversion/week after passing an initial conditioning period of 300 hours. Beryllium promoted iron catalyst produced an even more stable activity than potassium. A deactivation rate as low as 0.43% CO conversion/week was obtained from beryllium promoted catalyst. Higher temperature generated a shorter conditioning period for potassium promoted catalyst. The FTS activity began to decrease when the bulk phase of the catalyst changed from 100% carbide to iron oxides. Although the initial activity changed rapidly, little change occurred in the bulk phase of the catalyst. For potassium promoted catalyst, FTS activity, CO_2 selectivity, hydrocarbon productivity and water gas shift activity

showed the same conditioning period of 300 hours of time on stream after passing a peak value at about 120 hours of reaction time. A higher water gas shift activity, higher CO₂ and CH₄ selectivity by beryllium promoted catalyst than those by potassium were also found in an FTS process. Beryllium promoted catalyst also showed a superior regenerability when either H₂ or CO was utilized. When rejuvenated with CO a better activity recovery was achieved than that with H₂.

We are continuing to study the impact on reducibility of cobalt oxides by the use of different supports and by the incorporation of different promoters and additives to supported cobalt catalysts. The reduction of Co₃O₄, which is present on the catalyst after calcination, is a two step process which passes through an intermediate CoO phase before reduction to the metal. In our previous investigations, we found by temperature programmed reduction that a 15%Co/Al₂O₃ displayed a broad second peak attributed to the reduction of cobalt species interacting with the support. In agreement, hydrogen chemisorption with pulse reoxidation revealed that the unpromoted catalyst displayed poor percentage reduction of only 30% after reduction at 623K, the standard activation temperature of Co FTS catalysts. While promotion of supported Co catalysts with the noble metal promoters Pt and Ru had a similar effect on catalyzing both reduction steps of Co₃O₄ to Co metal, Re only aided in catalyzing the second step when a significant interaction of the Co species with the support was present, such as found on Al₂O₃ supported catalysts. After reduction at 623K, therefore, the number of Co active sites increases remarkably with the addition of noble metal promoter, thereby increasing the initial activity under reaction testing.

We have investigated the possibility of a synergism between Pt and Re on the reducibility of supported Co oxides, and are testing the catalysts in the CSTR to draw conclusions as to the effect of Pt-Re promotion and synergism on the catalyst stability.

In this report we describe SBCR pilot plant results and operating experiences using an improved catalyst/slurry filtration system. The following improvements to the filtration system were included: an enlarged let-down valve trim, an automatic differential pressure controller for the filter media and a by-pass for the let-down valve. Further filtration tests were conducted using a high alpha iron-based F-T catalyst. During the activation, problems were encountered with the gas sparger in several pilot runs. Catalyst had infiltrated the sintered metal sparger causing an excessive pressure drop. A new activation procedure was developed to minimize sparger plugging.

As in previous reported pilot-scale experiments, conversion results of the high alpha catalyst in the SBCR were compared to that of CSTR experiments. A method for estimating the SBCR recirculation rate is also described.

The effect of water on iron FTS catalysts has been widely studied and it is well known that water may reoxidize these catalysts during synthesis. The effect of water on Co FTS catalysts is less well understood. In a previous study the effect of water on the catalytic properties of a Pt promoted Co/Al₂O₃ was studied. These previous results were compared to the results of this study using a Co/SiO₂ catalyst. In order to determine the effect of water addition time on the catalytic activity, the smaller or larger amount (5 or 25 vol%) was continuously added for 96 hours. It was found that the longer time addition of the smaller amount of water did not show a significant effect on the CO conversion and the catalyst deactivation rate. However, for the addition of the larger amount of water, CO conversion increased for the initial 24 hours and for the long time addition resulted in the irreversible deactivation of the catalyst. The effect of the water partial pressure was also studied. Methane selectivity decreased and CO₂ and olefin ratios increased with increasing water partial pressure.

UC/B

During this reporting period, $^{13}\text{CO}_2$ addition experiments were initiated on a Fe-Zn-Cu-K catalyst in order to determine the extent of participation of CO_2 in chain initiation and growth. The experiments are carried out at 508 K and 0.8 MPa, i.e., at conditions where the water gas-shift reaction is far from equilibrium. Prior to these experiments, the sampling system at the outlet of the reactor system (after the gas chromatograph) was modified in order to allow the separation of light hydrocarbons ($>\text{C}_4$) from CO , N_2 and H_2 , and hence enhance the sensitivity of analysis of the former.

The preparation and revision of three manuscripts describing the site requirements and the effect of promoters (K, Cu and Ru) on the structure, reduction/carburization behavior and the catalytic performance of Fe- or Fe-Zn-based catalysts, begun during the previous reporting period, were completed and submitted to peer-reviewed journals. One manuscript titled "Spectroscopic and transient kinetic studies of site requirements in iron-catalyzed Fischer-Tropsch Synthesis" was submitted to the *Journal of Physical Chemistry B*. Another manuscript titled "Promoted iron-based catalysts for the Fischer-Tropsch Synthesis: Design, synthesis, site densities, and catalytic properties", prepared during the previous reporting period, was submitted to the *Journal of Catalysis*, and a third manuscript titled "Effects of Zn, Cu and K promoters on the structure, reduction/carburization behavior, and performance of Fe-based Fischer-Tropsch Synthesis catalysts" was submitted to *Catalysis Letters*. Another manuscript describing the effects of K and Cu promoters and the effect of CO_2 addition on CO_2 formation during Fe-based FTS reactions is currently under preparation.

In addition, a manuscript titled "Structure and site evolution of iron oxide catalyst precursors during the Fischer-Tropsch Synthesis" was accepted for publication in the *Journal of Physical Chemistry B*, and a manuscript titled "Structural analysis of unpromoted Fe-based

Fischer-Tropsch catalysts using X-ray absorption spectroscopy”, submitted jointly with the University of Kentucky to *Applied Catalysis*, has also been accepted for publication.

In this reporting period, a new transient experimental setup was developed. An improved gas inlet manifold and a new micro fluidized reactor were also constructed. This system is capable of performing isotopic switch experiments at steady-state conditions. It will be used to study the surface carbon capacities at working conditions by the help of $^{12}\text{CO}/^{13}\text{CO}$ isotopic switch.

Switching experiments have been performed on Co/SiO_2 under FTS reaction during this quarter. These studies involved switches between synthesis gas and hydrogen at 453 K and 0.5 MPa (FT conditions) in order to quantify the number of active sites during the reaction. A set of experiments were conducted in order to investigate the effect of CO conversion, at constant pressure and temperature, on the number of active sites on the catalyst, identified by the active carbon adsorbed on the surface. The data showed a slight increase in the number of active adsorbed carbon; however this increase was not significant.

Task 1. Iron Catalyst Preparation

The objective of this task is to produce robust intermediate- and high- α catalysts.

A. Effect of Structural Promoters on Iron Catalysts

Synthesis of the Catalysts

The Fe-Al samples were prepared by co-precipitation of iron and aluminum from nitrate solutions at constant pH of 8.5. Iron nitrate (1.3M) and aluminum nitrate (1.43M) solutions were mixed to yield a given Al/Fe ratio. Ammonium hydroxide (30% NH_3) was used as the precipitant. About 100 cm^3 deionized water was placed in a large beaker and heated to 85°C using a magnetic stirrer/hotplate. The pH was adjusted to 8.5 by addition of an appropriate quantity of NH_4OH . The temperature was held at 85 °C throughout the precipitation procedure. The solution of Fe^{3+} and Al^{3+} ions was added slowly to the beaker with continuous stirring. Simultaneously, the NH_4OH was added at a rate such that the pH was maintained at a constant value of 8.5. The resulting precipitate was filtered using vacuum filtration and washed with deionized water until the pH of the filtrate was measured to be in the range 7.0 to 7.5. The precipitate was subsequently dried in an oven overnight at 110°C followed by calcination in static air at 400°C for 10 hours. Samples were prepared that contained from 0% to ~25% Al. The samples were analyzed for iron content following calcination using ICP. The iron content by weight in the unpromoted samples was found to contain 70% Fe (average of 3 analyses) which agrees very well with the theoretical value of 69.994% in Fe_2O_3 , confirming that the sample was hematite. XRD analysis also provided further proof that the samples contained hematite. Table 1 lists the compositions of the promoted iron catalysts.

The Fe-Si samples were already available in the lab. They were prepared by hydrolyzing an appropriate quantity of tetraorthosilicate (TEOS) in the acidic $\text{Fe}(\text{NO}_3)_3$ solution followed by precipitation using NH_4OH . They had silicon contents of up to ~8% Si, had been calcined at

400°C and were used without any further treatment. Their compositions are summarized in Table 2.

XRD analysis of the samples showed that as the degree of loading of the promoter increased the samples became more amorphous. The samples were then treated in an oven at 600°C for 24 hours to improve crystallinity.

BET Surface Area Measurements

Nitrogen sorption isotherms were measured using a Micromeritics TriStar 3000 instrument. Prior to analysis each sample was outgassed at 160°C for at least 12 hours to a pressure less than 100 mTorr. The results of the analyses for the samples calcined at 400°C and 600°C are presented in Tables 3 and 4. It can readily be seen that as the quantity of the promoter is increased the surface area also increases. Also, as the temperature of the calcination is increased the surface area decreases. Representative plots illustrating the trend in change of surface area with increasing atomic percent of structural promoter for both the Al and Si additions are shown in Figures 1 and 2, respectively.

XRD Analysis

The samples containing varying atom percentages of the structural promoters Al or Si were prepared in order to investigate whether they are capable of entering into solid solution with the hematite and hence be well dispersed throughout the oxide mass. Whether or not these promoters had entered into solid solution was determined from their effect on the lattice parameters of the magnetite. Powder X-Ray Diffraction was used to determine the unit cell dimensions of the hematite. Hematite has a hexagonal structure and thus two cell dimensions, a_0 and c_0 , had to be determined. X-Ray Diffractograms were obtained for all samples. Figures 3 and 4 show the diffractograms obtained for the Al and Si promoted iron oxide samples calcined at 400°C. It can be seen that the Al promoted samples are not very crystalline at loadings greater

than about 7 atom%. In contrast, the Si promoted samples are quite amorphous to X-Rays, crystallinity only evident for the very small atomic fractions. It appears that the Si retards the crystallization of the Fe_2O_3 to a much greater degree than the presence of the Al. In order to make accurate lattice parameter determinations a greater degree of crystallinity is required so all the samples were heated in an oven to 600°C for 24 hours and the resulting diffractograms are shown in Figures 5 and 6. In all cases Fe_2O_3 was identified as the only species present. At the higher levels of Al addition, 17.9% and 24.22%, there is evidence of another species present but this has yet to be identified. The ten most intense peaks of the diffractograms were each analyzed individually using the fitting program WINFIT to determine accurate peak locations in terms of 2θ . These 2θ values together with their corresponding Miller indices were input to the program UnitCell to calculate the lattice parameters for the hexagonal Fe_2O_3 . It was found that as the quantity of the promoter increased there was a shift in all 2θ to higher values indicating that the promoter had entered the hematite lattice and was influencing its dimensions. These shifts in the lattice dimensions are shown as a function of the promoter concentration in Figures 7 to 10. The shift to higher 2θ values resulted in a decrease in both a_0 and c_0 lattice parameters. This is to be expected as the ionic radii of both Al^{3+} and Si^{4+} , 0.5\AA and 0.41\AA , respectively, are both less than that of Fe^{3+} (0.64\AA), and would lead to a contraction of the unit cell. The shifts in the lattice dimensions are taken as evidence that the cations have entered into the hematite lattice.

Table 1		
Al Content of the Samples		
Sample	Al/Fe	Atom % Al
8A	---	0
10A	0.0118	1.17
3A	0.02	1.96
4A	0.044	4.21
5A	0.0706	6.6
6A	0.1335	11.77
7A	0.218	17.9
9A	0.3197	24.22

Table 2		
Si Content of the Samples		
Sample	Si/Fe	Atom % Si
FeSiO	---	0
FeSi ₂	0.02	1.96
FeSi ₄	0.044	4.21
FeSi ₈	0.08	7.41

Table 3

Results of BET Analysis of Samples Treated at 400°C

Sample	BET S.A. m ² /g	Pore Volume cm ³ /g	Average Pore Radius nm
8A	33.44	0.19	11.4
10A	133.5	0.24	3.6
3A	46.19	0.2	8.5
4A	19.05	0.13	13.6
5A	99.6	0.25	4.9
6A	176.6	0.25	2.8
7A	232.6	0.24	2.1
9A	215.3	0.22	2.1
FeSiO	23.7	0.18	12.0
FeSi ₂	78.9	0.2	5.1
FeSi ₄	163.2	0.24	2.9
FeSi ₈	193.5	0.24	2.5

Table 4

Results of BET Analysis of Samples Treated at 600°C

Sample	BET S.A. m ² /g	Pore Volume cm ³ /g	Average Pore Radius nm
8B	9.95	0.11	22.6
10B	11.6	0.12	20.9
3B	15.2	0.14	18.5
4B	14.9	0.11	14.4
5B	25.4	0.2	15.9
6B	36.4	0.22	11.9
7B	44.0	0.18	8.3
9B	52.9	0.18	6.6
FeSiOB	4.3	0.03	13.5
FeSi ₂ B	36.8	0.19	10.4
FeSi ₄ B	64.3	0.2	6.2
FeSi ₈ B	98.3	0.21	4.2

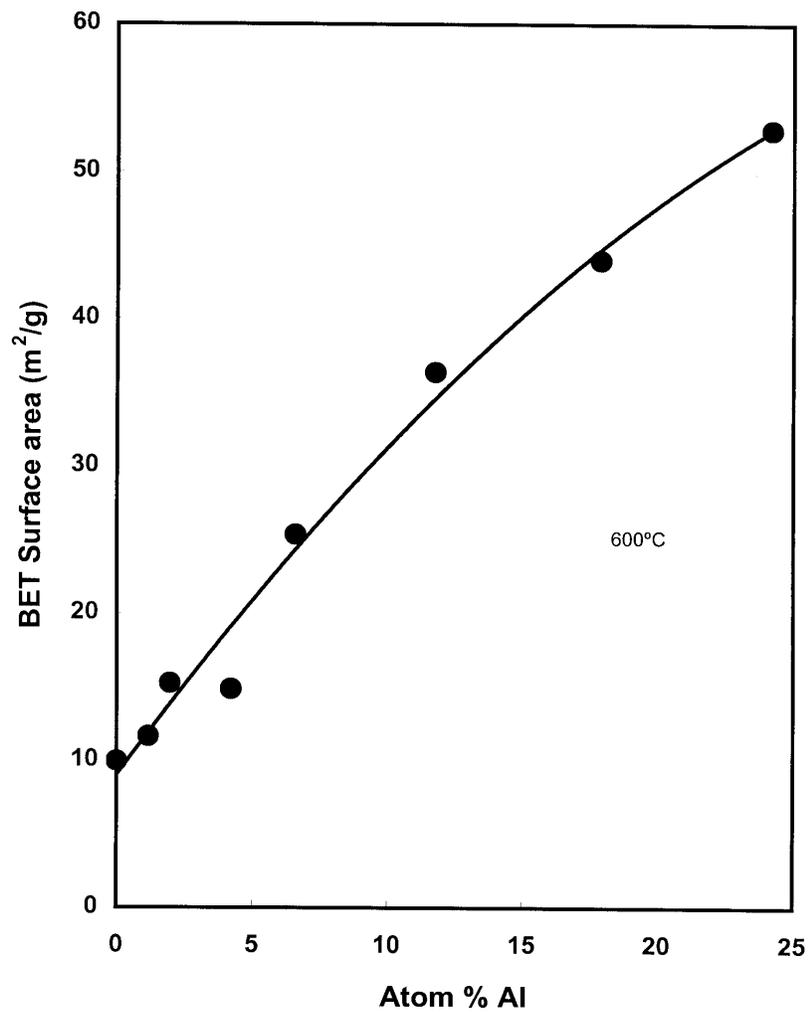


Figure 1. Variation of BET surface area with increasing atomic percent of Al. All samples were calcined at 600°C.

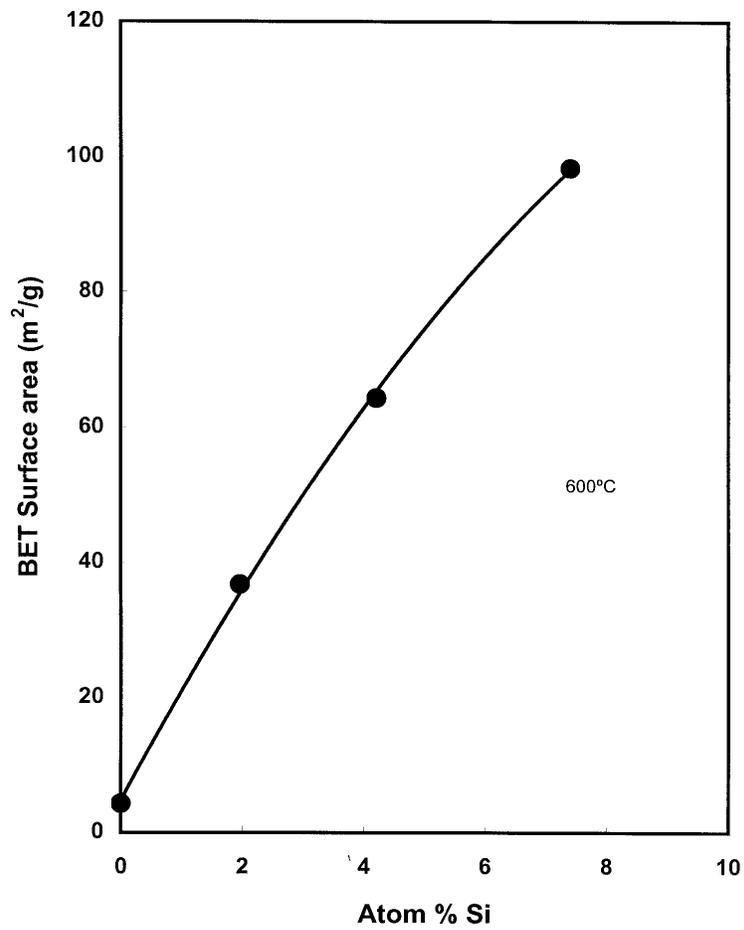


Figure 2. Variation of BET surface area with increasing atomic percent of Si. All samples were calcined at 600°C.

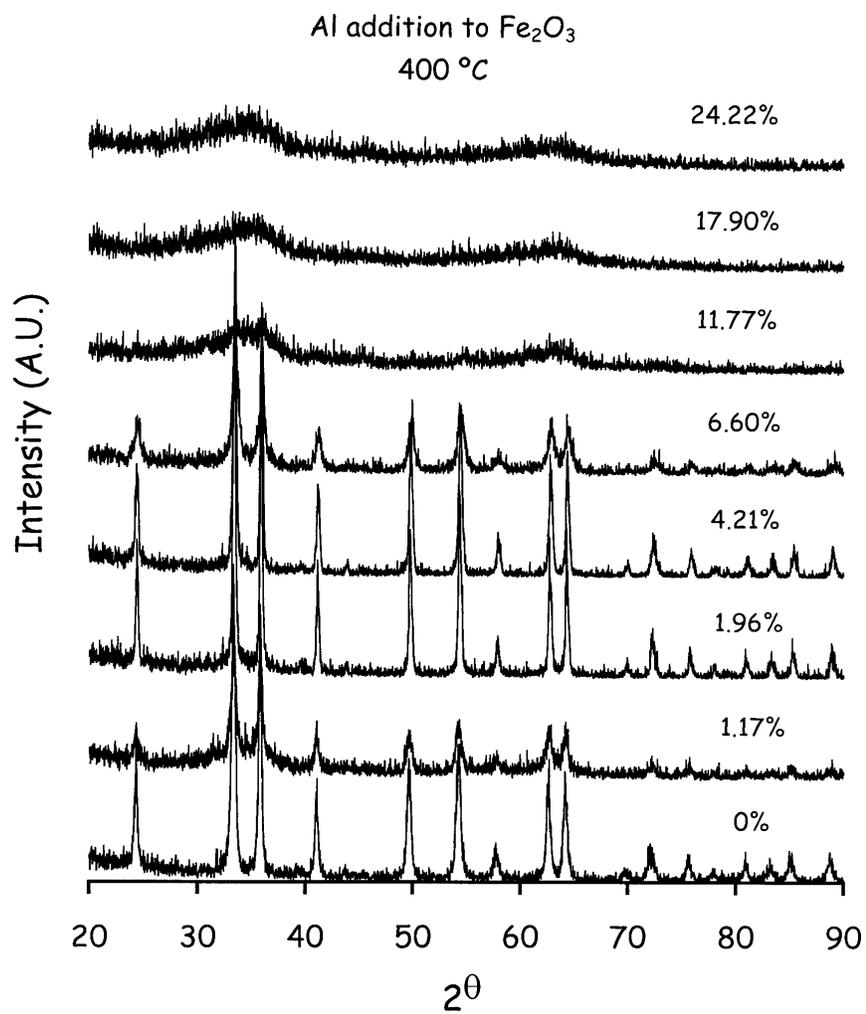


Figure 3. X-ray diffractograms of Al promoted hematite samples calcined at 400°C.

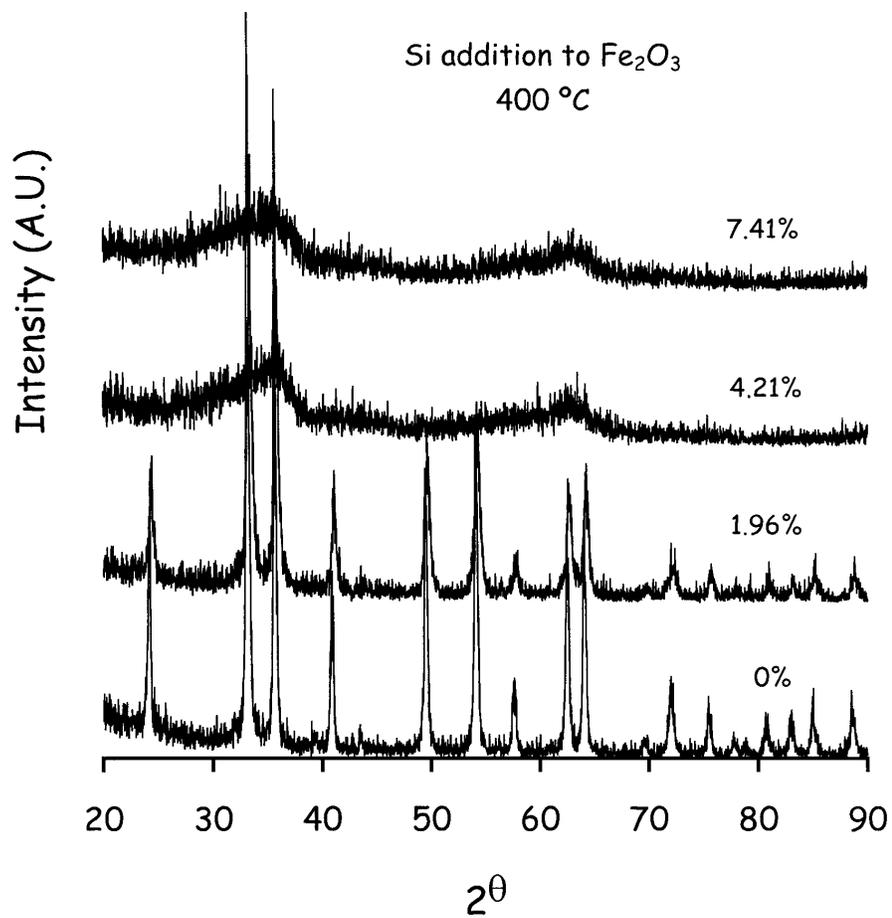


Figure 4. X-ray diffractograms of Si promoted hematite samples calcined at 400°C.

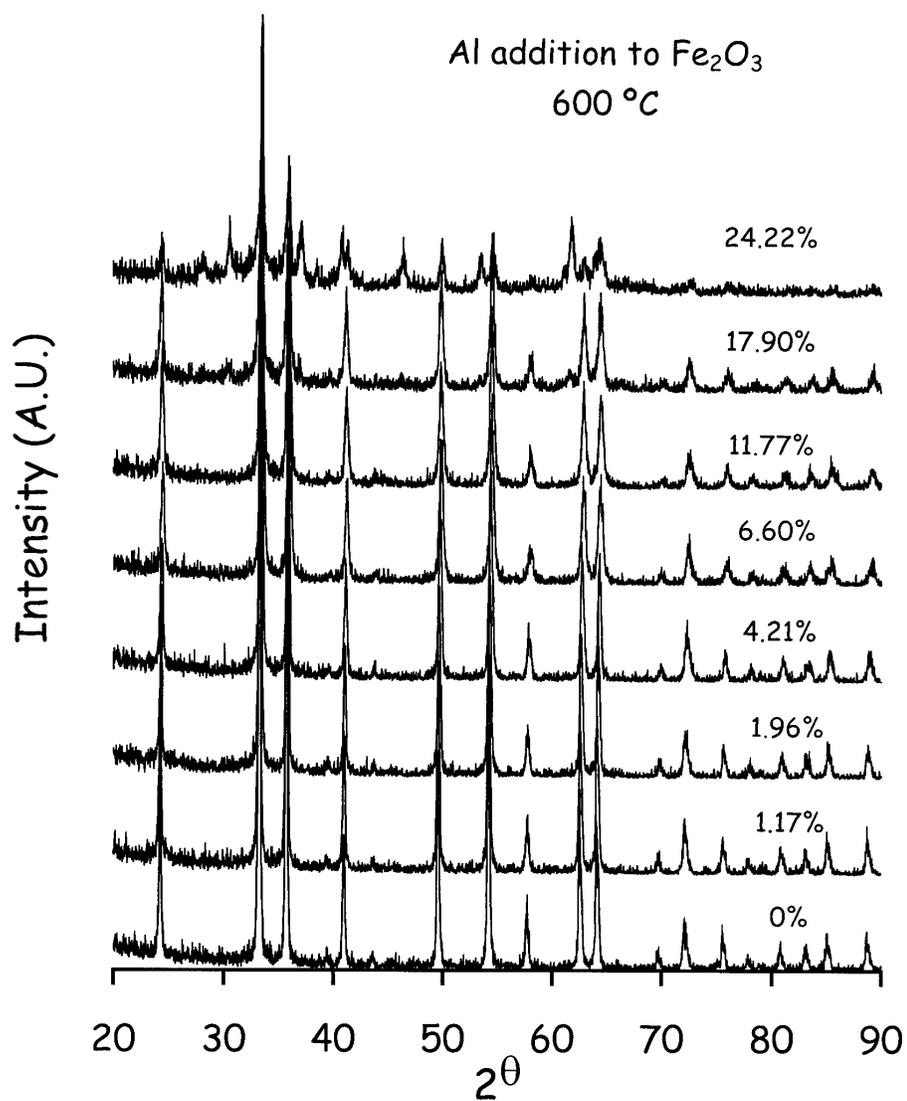


Figure 5. X-ray diffractograms of Al promoted hematite samples calcined at 600°C.

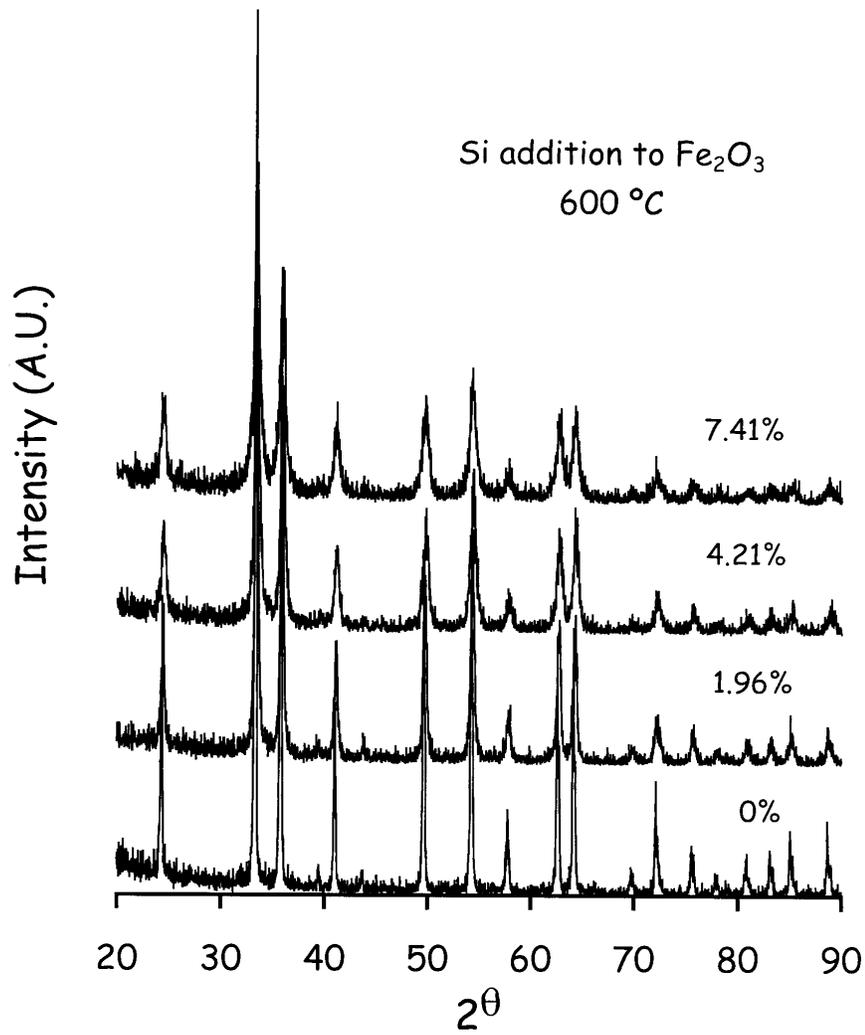


Figure 6. X-ray diffractograms of Si promoted hematite samples calcined at 600°C.

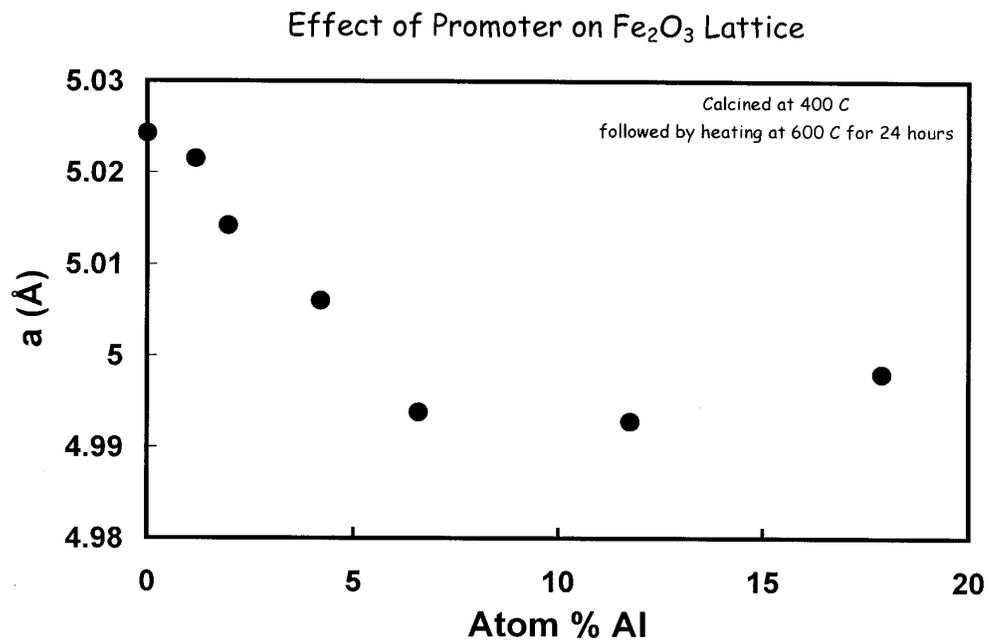


Figure 7. Variation of unit cell parameter a_0 with concentration of Al promoter.

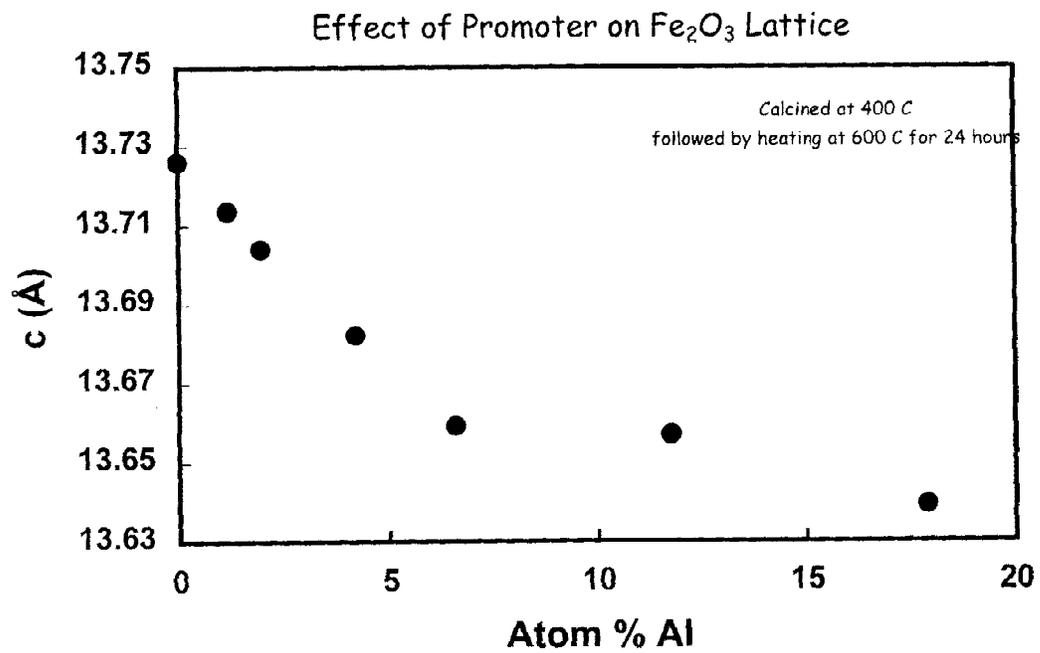


Figure 8. Variation of unit cell parameter c_0 with concentration of Al promoter.

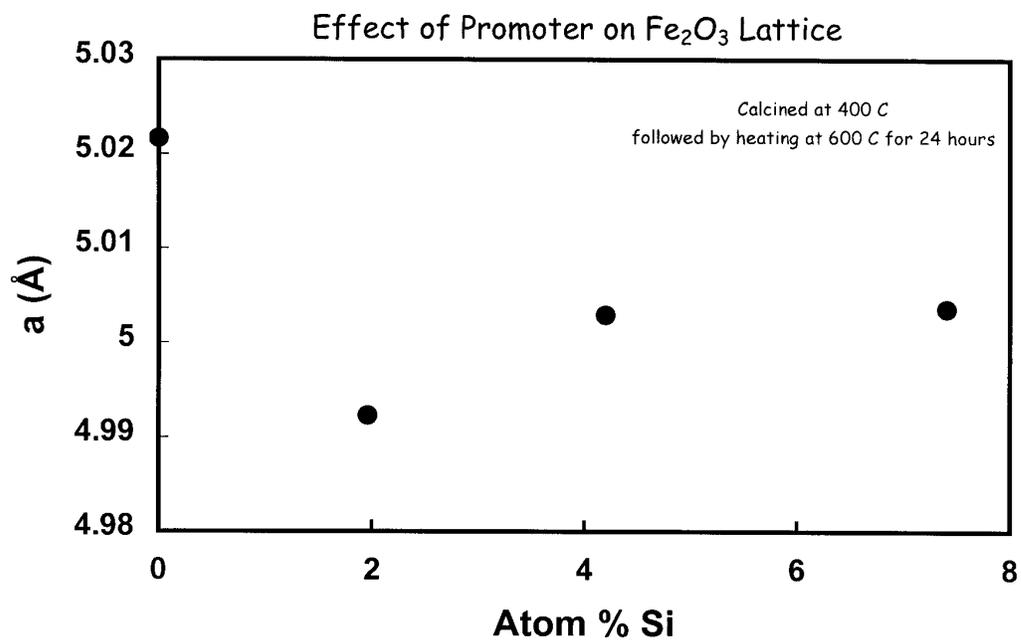


Figure 9. Variation of unit cell parameter a_0 with concentration of Si promoter.

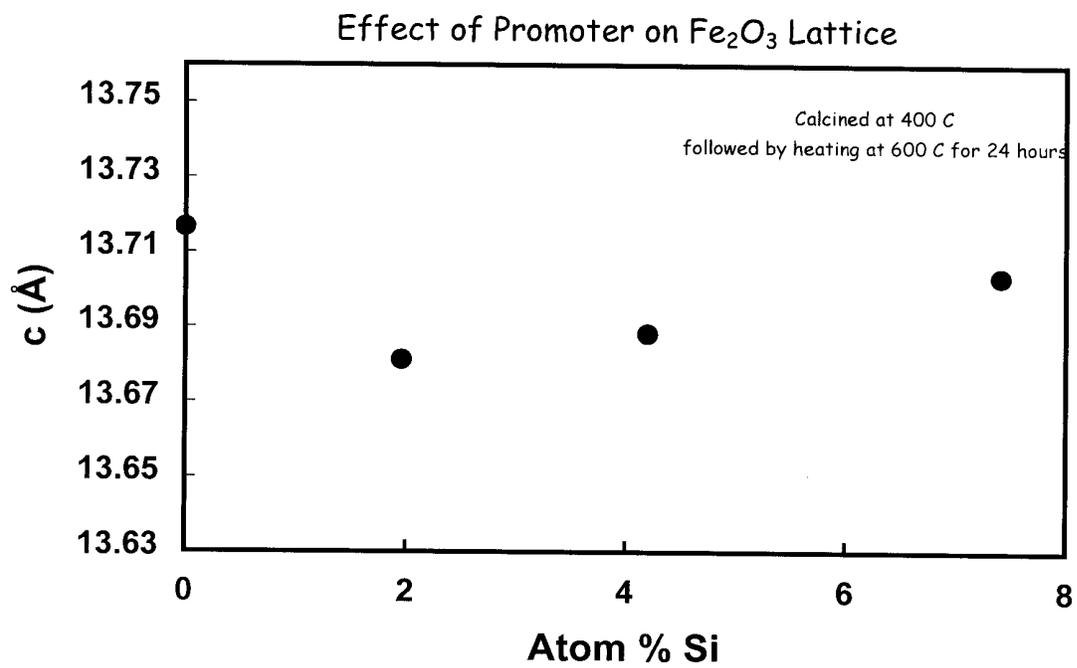


Figure 10. Variation of unit cell parameter c_0 with concentration of Si promoter.

Task 2. Catalyst Testing

The objective of this task is to obtain catalyst performance on the catalysts prepared in Task 1.

A. Deactivation and Regeneration of Alkali Metal Promoted Iron Fischer-Tropsch Synthesis Catalysts

Abstract

Iron Fischer-Tropsch synthesis (FTS) catalysts promoted with potassium or beryllium showed a superior deactivation property. Potassium promoted iron FTS catalyst showed a low deactivation rate of 0.59% CO conversion/week after passing an initial conditioning period of 300 hours. Beryllium promoted iron catalyst produced an even more stable activity than potassium. A deactivation rate as low as 0.43% CO conversion/week was obtained from beryllium promoted catalyst. Higher temperature generated a shorter conditioning period for potassium promoted catalyst. The FTS activity began to decrease when the bulk phase of the catalyst changed from 100% carbide to iron oxides. Although the initial activity changed rapidly, little change occurred in the bulk phase of the catalyst. For potassium promoted catalyst, FTS activity, CO₂ selectivity, hydrocarbon productivity and water gas shift activity showed the same conditioning period of 300 hours of time on stream after passing a peak value at about 120 hours of reaction time. A higher water gas shift activity, higher CO₂ and CH₄ selectivity by beryllium promoted catalyst than those by potassium were also found in an FTS process. Beryllium promoted catalyst also showed a superior regenerability when either H₂ or CO was utilized. When rejuvenated with CO a better activity recovery was achieved than that with H₂.

Introduction

Hydrocarbons of various chain length can be produced from CO and H₂ in Fischer-Tropsch synthesis process, which can be expressed as



When an iron catalyst is used for FTS reactions, the water gas shift (WGS) reaction can also occur. This reaction consumes CO and water formed by the FTS reaction and produces additional hydrogen and carbon dioxide.



Potassium has long been used as a promoter for iron catalysts. It provides an increase in the alkene yield and a decrease in the CH₄ selectivity (1,2,3). Potassium can also increase the catalytic activity for FTS and water-gas shift (WGS) reactions (4). The influence of potassium on iron catalysts has been investigated by other researchers (e.g., 5-8). It is believed that alkali metals have significant effects on both FTS activity and product selectivity. As the most effective promoter, potassium salts are widely used in iron catalysts; however, the readiness to form an alkali compound with common catalyst supports, or structural promoters such as alumina or silica, complicates the situation. Although potassium enhanced the FTS activity and heavy fraction product distribution, high potassium loadings may cover too large of a fraction of the surface of the iron catalyst, resulting in a limited promotion effect or even a decrease in FTS conversions. Bonzel and Kerbs (9) claimed that potassium lowered the methane formation rate and increased the carbon deposition rate. It was also found that the deposited carbon was covered by potassium compounds rather than carbon sitting on top of the promoter. Huang et al. (6) studied the potassium promoted iron catalysts with XPS and found that two-thirds of the catalyst surface was covered by K₂O and SiO₂. Wang, et al. (7) applied the temperature programmed reduction (TPR) technique to study the effects of potassium. They suggested that potassium facilitates the desorption process of carbon monoxide and strengthens the Fe-C bond. Thus, potassium enhanced the selectivity of long-chain products; i.e., it resulted in a high alpha product distribution. Copper, as a secondary promoter, can facilitate the activation process.

Copper can therefore minimize the sintering of iron catalysts by lowering the reduction temperature (3).

Experimental

Catalyst

Two iron FTS catalysts with an atomic ratio of K:Fe=10:100 and Be:Fe=1.44:100 were prepared and utilized in this study. Precipitated iron catalysts were prepared using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ tetraethyl orthosilicate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and K_2CO_3 or $\text{Be}(\text{NO}_3)_2$ was used as the promoter precursor. Details of the preparation procedure was given elsewhere (5). The iron catalyst needs to be activated with H_2 , CO or synthesis gas. Activation procedures can have a significant effect on the selectivity and activity of iron catalyst (8,10). It was reported that catalysts activated with CO yielded higher amounts of long-chain hydrocarbons than catalysts activated with syngas or with H_2 . In addition, activation conditions may also influence the performance of the iron catalyst during the course of the run. In this study, the potassium promoted iron catalysts were pretreated with CO at 270°C and 1.2 MPa for 24 hours. The CO flowed through a catalyst slurry in 300 ml of Ethylflow oil. The reduction of Fe_2O_3 with CO occurs in two steps:



Reactor System

A one-liter continuous stirred tank reactor (CSTR) was used in this study. A sintered metal filter was installed to remove the wax samples from the catalyst slurry. The wax sample was extracted through the internal filter and collected in the hot trap held at 200°C. A warm trap (100°C) and cold trap (0°C) were used to collect light wax and the water plus oil samples, respectively, by condensing from the vapor phase that was continuously withdrawn from the reactor vapor space. CO and H_2 mass flow controllers were used to provide a simulated

synthesis gas of the desired composition. After the catalysts were activated with CO, syngas was introduced into the CSTR with a stirrer speed of 750 rpm. Reaction conditions were 1.2 Mpa, $H_2/CO = 0.67$, 230°C for potassium promoted catalyst and 270°C for beryllium promoted catalyst.

Product Sampling and Analysis

Daily gas, water, oil, light and heavy wax samples were collected and analyzed. A heavy wax sample was taken from the 200°C hot trap connected to the filter. The vapor phase above the slurry passed continuously to the warm (100°C) and the cold (0°C) traps outside the reactor. The light wax and water mixture was collected from the warm trap and an oil plus water sample from the cold trap. Tail gas from the cold trap was analyzed with an online HP Quad Series Micro GC, providing molar compositions of C_1 - C_7 olefins and paraffins as well as for H_2 , CO and CO_2 . Hydrogen and carbon monoxide conversions were calculated based on the gas product GC analysis results and the gas flow measured at reactor outlet. The oil and light wax samples were mixed before analysis with an HP 5790A GC. The heavy wax was analyzed with an HP5890 Series II Plus GC while the water sample was analyzed using an HP5890 GC.

Results and Discussion

Activation, conditioning and deactivation of potassium promoted catalyst

In this study, a potassium promoted iron FTS catalysts with an atomic ratio of Fe:K=100:10 was used. Reaction was carried out at 230°C, 1.2 MPa at a space velocity of 3.1 sl/h/g-iron. The results (Figure 1) show that a conditioning period, in which CO conversion increased from below 10% to a peak value of 45% at 120 hours of time on stream and then gradually decreased to a stable level at 300 hours of reaction time. As indicated in the figure, a deactivation rate of 0.827% per day was observed from the peak CO conversion during the conditioning period. Then a very low deactivation rate of 0.0834% per day was obtained following the initial conditioning period. Although CO conversion increased rapidly during the

initial conditioning phase, Mossbauer spectroscopy analysis shows that the bulk phase iron carbide did not change. Almost all iron was converted during the in-situ catalyst activation prior to the FTS reaction. As carbon monoxide conversion decreased from the maxima, Fe_3O_4 started to appear in the bulk phase of the catalyst. This result suggests that as both the FTS and WGS reactions proceed, increasing carbon dioxide and water partial pressure changed the reaction system to a more oxidizing environment and thus cause the formation of iron oxide, which subsequently cause the CO conversion decrease. A stabilized activity may be obtained after the iron oxides-carbides phase or the three-phase reaction system thermodynamic equilibrium was reached. Figure 1 also shows that a temperature increase caused a new conditioning period, in which CO conversion reached a maxima of 75% before it stabilized at about 57%. This new conditioning period (250°C) appeared more sharply than that over the fresh catalyst at 230°C, suggesting that at a higher temperature, the new equilibrium on the catalyst surface is easier to be established than that at a lower temperature.

Selectivity and productivity of potassium promoted iron catalyst

Figure 2 gives the CO_2 and CH_4 selectivity over the potassium promoted catalyst. Methane selectivity decreased from 3.5% at 24 hours of reaction time to a stable level of 1.6% in 300 hours of time on stream. While methane selectivity decreased monotonously, carbon dioxide went through a conditioning period similar to that of CO conversion. The CO_2 selectivity started from 23% at 24 hours of time on stream and decreased from its maxima of 43% to a stabilized level of 39% in 300 hours of time on stream. Hydrocarbon rate showed a similar trend to that of CO conversion and CO_2 selectivity, as indicated in Figure 3. The rate rapidly increased from below 0.1 g/h/g-iron to a peak value of 0.32 g/h/g-iron before reaching a stabilized level of 0.28 g/h/g-iron in 300 hours of time on stream.

Water gas shift activity over potassium promoted catalyst

When iron catalyst was utilized in an FTS process, water gas shift as expressed by equation [2] is always an important reaction involved. This property makes the iron catalyst more suitable for a carbon-rich syngas produced from coal. A water gas shift coefficient was calculated by the following equation to evaluate the WGS activity:

$$K_{WGS} = \frac{P_{[H_2]} \cdot P_{[CO_2]}}{P_{[CO]} \cdot P_{[H_2O]}} \quad [5]$$

Figure 4. gives the results of WGS coefficient and an initial conditioning period similar to the ones for CO conversion and CO₂ selectivity was found. The water gas shift activity rapidly increased from an initial value of 1.2 and then gradually decreased from its maxima of 2.8 to a stable level of 2.3. It indicates that potassium promoted iron catalyst showed a similar FTS and WGS activity trend.

Deactivation and Regeneration of beryllium promoted iron catalyst

A beryllium promoted iron catalyst with an atomic ratio of Fe:Be=100:1.44 was prepared and tested in this study. FTS was carried out at 270°C, 1.2MPa and 10 sl/h/g-iron. Table 1 gives the summary of results from the FTS reaction over beryllium promoted iron catalyst. At 270°C, a CO conversion of 51% and a CO₂ selectivity of 45% were obtained; however, a higher methane selectivity of 8.14% than that over the potassium promoted catalyst at 230°C. In addition, a higher hydrocarbon rate and higher water gas shift activity were produced over beryllium promoted catalyst at 270°C. Figure 5 gives the results of CO conversion and deactivation rate from the FTS reaction over the beryllium promoted iron catalyst. After passing an initial conditioning period, CO conversion stabilized at 50% in the first 500 hours of time on stream. As indicated in Figure 4, a deactivation rate as low as 0.0062% during the first 500 hours of time on stream, suggesting that a superior stability was achieved over beryllium promoted iron FTS catalyst.

The reaction was operated at a series of low space velocity at 500 hours and thus the catalyst deactivated significantly. Regeneration with hydrogen was carried out at the same temperature as the FTS but zero gauge pressure for 24 hours. As shown in the figure, CO conversion increased from 37.03% to 45.35% after hydrogen regeneration. Another regeneration with CO further improved the activity by almost 10% to 55.20%. This rejuvenated activity was maintained in the next 150 hours of time on stream. These results indicated that beryllium promoted catalyst showed a good regenerability and CO is a more efficient regeneration reagent than H₂.

Conclusion

Potassium promoted iron FTS catalyst showed a low deactivation rate of 0.083% per day after passing an initial conditioning period of 300 hours. Higher temperature generated a shorter conditioning period. The FTS activity began to decrease when the bulk phase of the catalyst changed from 100% carbide to iron oxides. Beryllium promoted iron catalyst produced an even more stable activity than potassium. A deactivation rate as low as 0.0062% per day was obtained from beryllium promoted catalyst. Although the initial activity changed rapidly, little change occurred in the bulk phase of the catalyst, suggesting only the surface change may attribute to the activity change in the initial conditioning period. For potassium promoted catalyst, FTS activity, CO₂ selectivity, hydrocarbon productivity and water gas shift activity showed the same conditioning period of 300 hours of time on stream after passing a peak value at about 120 hours of reaction time. Methane selectivity, however, showed a monotonous decrease from an initial maxima to a stable level of 1.6%.

Beryllium promoted iron catalyst showed a better deactivation property than potassium promoted catalyst, even operated at a higher reaction temperature than that over the potassium promoted catalyst. A higher water gas shift activity, higher CO₂ and CH₄ selectivity by beryllium promoted catalyst than those by potassium were also found in an FTS process.

Beryllium promoted catalyst also showed a superior regenerability when either H₂ or CO was utilized. Carbon monoxide rejuvenation generated a better CO conversion recovery than hydrogen.

Acknowledgment

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Table 1	
Productivity and Selectivity for Beryllium Promoted Catalysts	
Conversion (%)	
CO	51.21
H ₂	61.98
Syngas	55.53
Product distribution (%)	
C ₁	10.11
C ₂ -C ₄	35.61
C ₅ -C ₁₁	31.80
C ₁₂ -C ₁₈	11.56
C ₁₉₊	10.92
Hydrocarbon rate, g/hr/g-iron	1.08
Water-Gas Shift	
K _p ^a	1.76
H ₂ :CO usage ^b	0.81
Selectivity (%)	
CO ₂	45.00
CH ₄	8.14
a. $K_p = [P_{H_2} P_{CO_2}] / [P_{H_2O} P_{CO}]$.	
b. $Usage = r_{H_2} / r_{CO}$.	

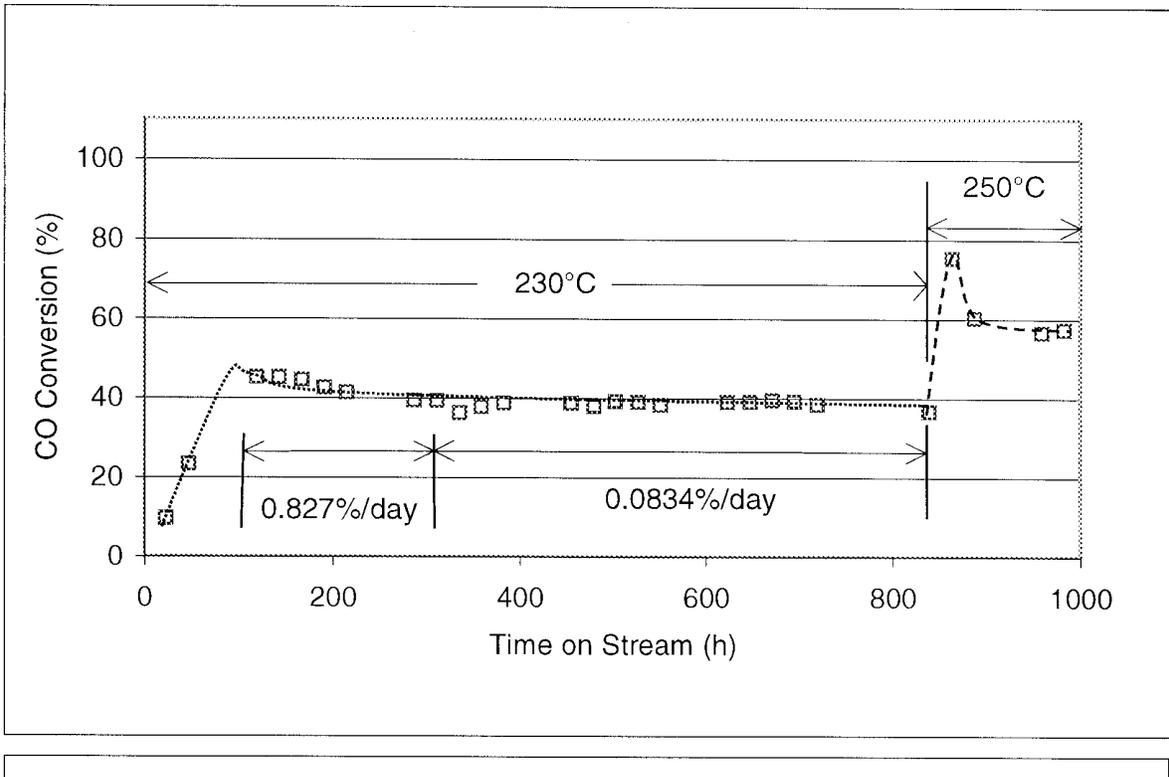


Figure 1. Deactivation rate over potassium promoted iron FTS catalyst.

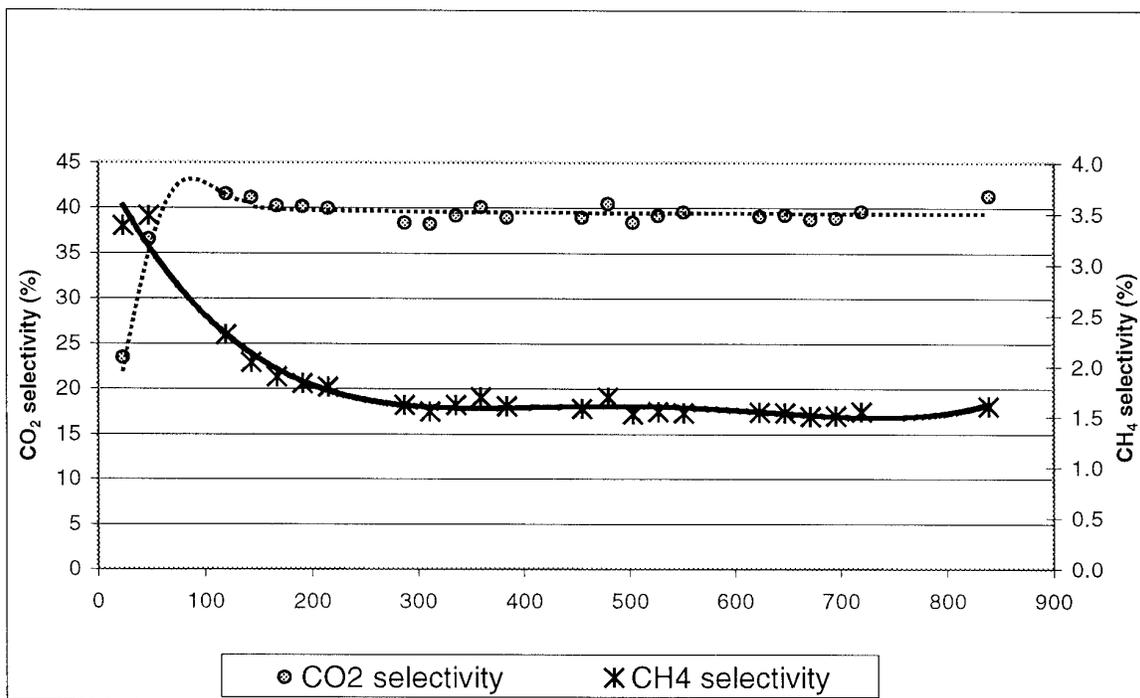


Figure 2. Methane and carbon monoxide selectivity over potassium promoted iron FTS catalyst.

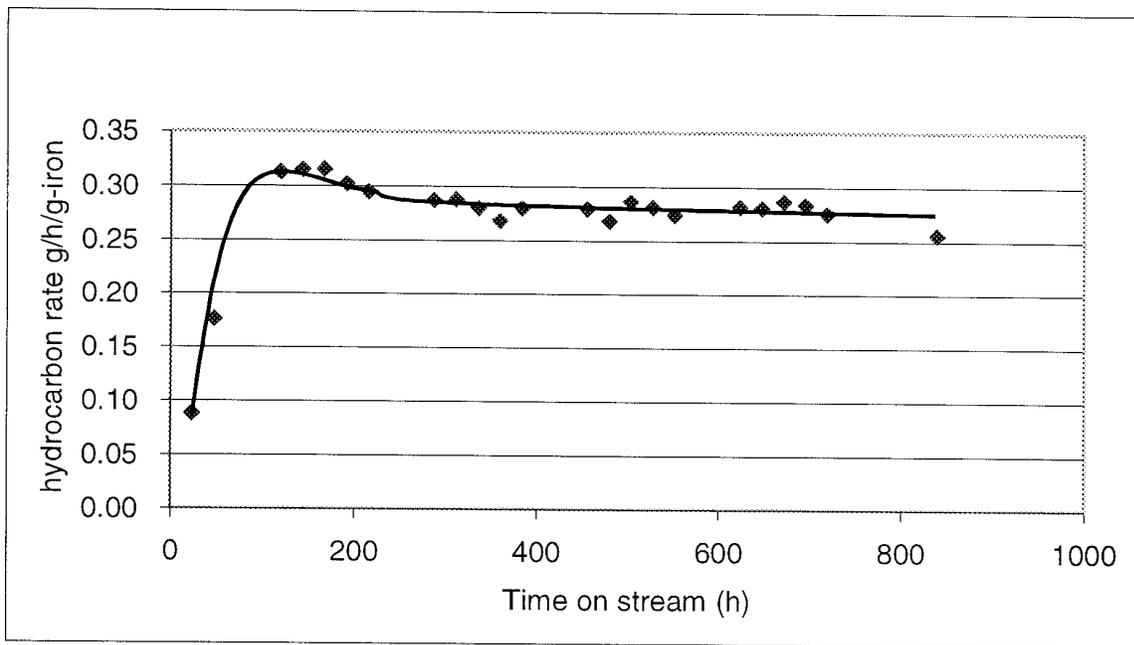


Figure 3. Hydrocarbon rate over potassium promoted iron catalyst.

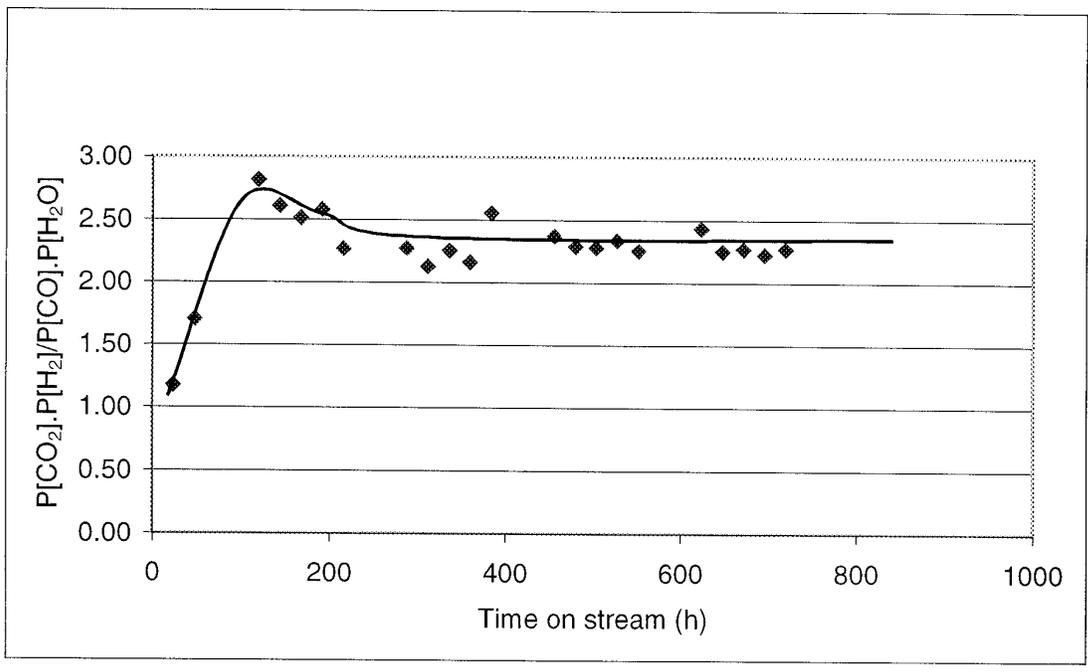


Figure 4. Water-gas shift coefficient over potassium promoted iron FTS catalyst.

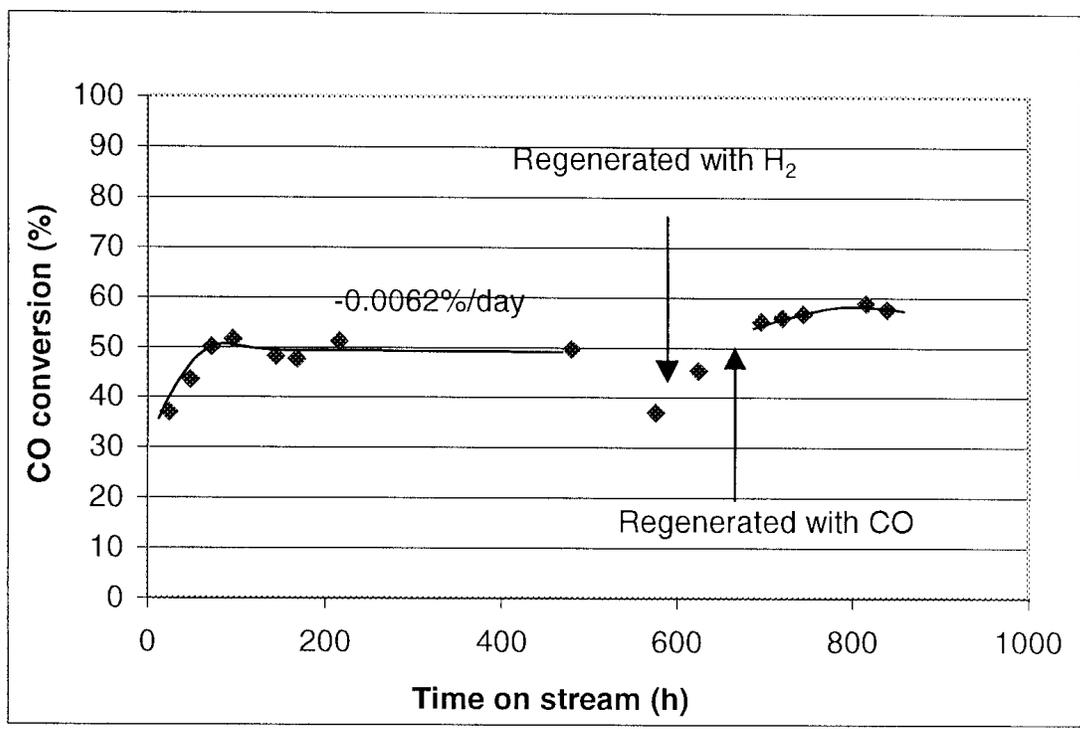


Figure 5. CO conversion over beryllium promoted iron catalyst.