3.1.4 Activation Study of Precipitated Iron Fischer-Tropsch Catalysts

ABSTRACT

Slurry phase Fischer-Tropsch Synthesis (FTS) was conducted with two precipitated iron catalysts (100Fe/3.6Si/0.71K and 100Fe/4.4Si/1.0K, atomic % relative to Fe) at 543K, 1.31MPa and a synthesis gas (H_2/CO=0.7) space velocity of 3.1 NL h^{-1} g Fe^{-1}. The impact of activation gas (CO, H_2/CO=0.7 or H_2/CO=0.1), temperature (543K or 573K) and pressure (1.31MPa or 0.10 MPa) on the long term (>500 h) activity and selectivity of the catalysts were explored. Pretreatment with CO under the conditions employed gave highly active and stable catalysts. Catalyst performance when synthesis gas activation was used was found to be dependent upon the partial pressure of hydrogen in the activating gas with low hydrogen partial pressures resulting in the highest catalyst activity. X-ray diffraction results indicate that carbon monoxide activations and synthesis gas activations with low hydrogen partial pressure result in the formation of the carbides χ-Fe_5C_2 and ϵ'-$Fe_{2.2}C$ while activation with synthesis gas with high hydrogen partial pressure results in the formation of only Fe_3O_4. It was found that treating the 100/3.6Si/0.71K catalyst activated with synthesis gas at 1.31 MPa and 543K, with carbon monoxide caused the activity to increase dramatically and the Fe_3O_4 to be partially converted to iron carbides. It is concluded that Fe_3O_4 is relatively inactive for FTS while the presence of some bulk iron carbide is necessary for high FTS activity to be achieved.

INTRODUCTION

The activation procedure used for iron based Fischer-Tropsch synthesis (FTS) catalysts has a great influence on their activity and selectivity [1]. Reduction of fused magnetite catalysts with hydrogen at high temperatures (>673K) and high linear flow rates is necessary to produce a substantial surface area necessary for good activity; however, reduction with synthesis gas or carbon monoxide is ineffective [2]. In contrast, activation of precipitated iron catalysts is not understood as well. Precipitated catalysts have been reported to be successfully activated with carbon monoxide [3,4] hydrogen [2,5] or synthesis gas [6-8].

Several research groups have reported that pretreatment of precipitated iron oxide with carbon monoxide is the preferred activation procedure. Bukur et al. have reported that pretreatment of doubly promoted Fe/Cu/K catalysts with carbon monoxide or synthesis gas (H_2:CO~0.7 or 2.0) results in higher initial activity and a heavier product than activation with hydrogen; however, hydrogen pretreatments were reported to result in more stable catalysts [4,5]. Pennline et al. found that activation of a precipitated iron-manganese catalyst with carbon monoxide was superior to activation with hydrogen or synthesis gas at 15 MPa and 548 K; furthermore, they report little temperature or pressure affects when activating with carbon monoxide [9]. During the initial German work on FTS, the Kaiser Wilhelm Institute favored pretreating catalysts with carbon monoxide at subatmospheric pressure [10]. In addition, Huang et al. have reported that an ultrafine iron oxide catalyst has superior activity when pretreated with carbon monoxide than with hydrogen or synthesis gas (H_2:CO=1.0) at 533 K and 0.79 MPa [11].

Although pretreatment of precipitated iron catalysts with carbon monoxide leads to active catalysts, hydrogen pretreatment is more favorable on an industrial scale, because it is less expensive and easier to purify. In general, pure hydrogen can be prepared from synthesis gas using a membrane separation process that allows only hydrogen to pass; however, this separation will not lead to pure carbon monoxide, but instead will produce a carbon monoxide rich synthesis gas. SASOL utilizes hydrogen pretreatment of precipitated iron catalysts used in its commercial FT reactors [2]. In addition, much of the early German work utilized hydrogen pretreatment, i.e., Ruhrchemie AG, IG Farbenindustrie AG and Lurgi [10]. Hydrogen pretreatment has the disadvantage that the metallic iron that is formed is susceptible to sintering. High flow rates are needed to keep the partial pressure of water low and low temperatures are necessary to insure that a high surface area is maintained [2,5].

The development of a pretreatment procedure utilizing synthesis gas that would consistently lead to active catalysts would be attractive, because pretreatments could be performed with the same gas that is used in the FTS, thereby eliminating the need for a pure hydrogen or carbon monoxide stream. Kölbel and Ralek [6] and Mobil [7,8] have reported high activity and good stability with precipitated Fe/Cu/K catalysts in laboratory and demonstration plant slurry reactors using *in situ* synthesis gas activation. Pretreatment conditions appear to be crucial in determining the ultimate FT activity of synthesis gas activated catalysts. Kolbel and Ralek report that the temperature of the synthesis gas pretreatment is critical to the final activity and selectivity of the catalyst; too high a temperature will result in “supercarbonization” and too low a temperature will prevent activation [6]. In addition, pressure may also affect the ultimate activity; many of the German companies preferred activation at a low pressure when using synthesis gas pretreatments [10].

The catalyst phase that exists is strongly dependent on the activation procedure employed. Activation with hydrogen, carbon monoxide or synthesis gas generally result in the rapid formation of Fe_3O_4 [3]. With additional time, the Fe_3O_4 is converted to metallic iron in the case of hydrogen pretreatment or various iron carbides (usually χ-

Fe_5C_2 or ϵ'-$Fe_{2.2}C$) with carbon monoxide or synthesis gas pretreatment [1-3,5]. During synthesis, metallic iron is rapidly converted to iron carbide and with longer times on stream the iron carbide may be oxidized to Fe_3O_4 [1-3,5]. Several studies have been made to correlate catalyst composition with activity [3,12-15]. Some reports claim iron carbides are active for FTS [12] while others claim an oxide species is responsible for activity [16]. In contrast, it has also been reported that a correlation between catalyst activity and bulk phase composition cannot be made [1-3].

The present study is aimed at providing a better understanding of the relationship between pretreatment, FTS activity and the phase composition of precipitated iron catalysts used in a slurry reactor. A comparison is made between pretreatment with carbon monoxide and synthesis gas (H_2:CO=0.7 or 0.1) with particular attention being paid to the affect of temperature and pressure used during the activation procedure on the resulting FTS activity.

EXPERIMENTAL

Catalysts were prepared by continuous precipitation of amorphous ferric oxyhydroxide from aqueous iron(III) nitrate nonahydrate (1.17M) and concentrated ammonium hydroxide (15.6M) in a continuous stirred tank reactor at pH 9.5. Hydrolyzed tetraethyl orthosilicate was added to the iron(III) nitrate solution to give the desired level of silicon. The catalyst slurry was filtered continuously with one or more six inch rotary drum vacuum filters. The resulting catalyst cake was washed and filtered twice with a volume of distilled deionized water equal to the volume of the previous filtrate. A 5 kg catalyst batch was precipitated in this manner, oven dried in flowing air at 393 K and crushed to -300 mesh. The composition of this catalyst in terms of atomic percent relative to Fe is 100Fe/3.6Si. During loading into the slurry reactor, the catalyst was treated with sufficient potassium *t*-butoxide to make the composition 100Fe/3.6Si/0.71K. A large 75 kg catalyst batch was also prepared; however, this catalyst was prepared by adding potassium nitrate to the slurry, spray dried and calcined in air at 623 K. The composition of this catalyst was 100Fe/4.4Si/1.0K.

All FTS runs were conducted in a one liter autoclave operating as a continuous stirred tank reactor (CSTR). Catalysts were suspended in Ethylflo 164 hydrocarbon oil (Ethyl Corporation) which is reported to be a C_{30} 1-decene homopolymer. All catalysts loadings were 10 weight per cent unless otherwise noted. A schematic of the reactor system is shown in Figure 1. Hydrogen and carbon monoxide feed gas flow rates were controlled by two mass flow controllers (Brooks Instruments) with the resulting synthesis gas composition regulated by adjusting the flow rate of the appropriate gas. The synthesis gas, after passing through a 2 L mixing vessel, was delivered to the catalyst slurry through a dip tube that extended to below the impeller blade. The reactor effluent exited the reactor and passed sequentially through two traps maintained at 333 K and 273 K. Accumulated reactor wax was removed daily through a tube fitted with a porous metal filter (0.5 µm). Uncondensed effluent was sent to an on-line Carle gas analyzer for determination of carbon monoxide, hydrogen, carbon dioxide, methane and C_2-C_4 alkanes and alkenes. An on-line Hewlett-Packard 5790 GC equipped with a Porpack-Q column was utilized for C_4-C_9 quantification. Liquid samples were analyzed with a Hewlett-Packard 5890 GC equipped with a 60 m DB-5 capillary column. The reactor was also equipped with a tube that extended below the liquid level which permitted catalyst slurry samples to be withdrawn periodically.

Catalysts were pretreated with carbon monoxide or activated with synthesis gas with a hydrogen:carbon monoxide ratio of 0.7 or 0.1. In general, the activation gas flow was started at ambient conditions, the necessary reactor pressure was set and the reactor was ramped to the desired temperature at 2 K min^{-1}. After reaching the activation temperature, the conditions were maintained for 24 h. Following the activation treatment, the reactor was brought to reaction conditions: hydrogen:carbon monoxide ratio of 0.7, 3.1 NL h^{-1}g^{-1}(Fe) (NL corresponds to 273 K, 0.10 MPa) 543 K and 1.31 MPa.

Catalyst samples were Soxhlet extracted according to the method of McCartney et al., [17] to remove accumulated wax and then analyzed by X-ray diffraction. Powder X-ray diffraction patterns of the catalysts were obtained using a Philips APD X-ray diffraction spectrometer equipped with a Cu anode and Ni filter operated a 40Kv and 20Ma (CuKα=1.5418 Å). Iron phases were identified by comparing diffraction patterns of the catalyst samples with those in the standard powder X-ray diffraction file compiled by the Joint Committee on Powder Diffraction Standards published by the International Center for Diffraction Data.

RESULTS AND DISCUSSION

Catalyst Activation

Early in our efforts to develop an effective activation procedure for precipitated iron catalysts, we found that a 24 h treatment with carbon monoxide at 543 K and 1.31 MPa consistently resulted in highly active and stable catalysts (Figures 2a and 3). Initial carbon monoxide conversion for the 100Fe/3.6Si/0.71K and 100Fe/4.4Si/1.0K catalysts activated in this manner were 92% and 85%, respectively, with corresponding deactivation rates of 4.8% and 1.0% per week, respectively. Hydrocarbon productivities typically were in the range of 160-170 g m^{-3} (CO+H_2 feed) with greater than 80% being C_3 and higher. The reproducibility of this activation procedure has facilitated screening large numbers of catalysts so that reliable data concerning optimum promoter levels can be determined. Much of this work is directed at developing a process for catalyst preparation that is suitable for scale-up to pilot plant scale.

The use of pure carbon monoxide as an activation gas is acceptable for small laboratory reactors; however, it is cost prohibitive for a pilot plant. As a result, it is economically attractive and operationally more facile to be able to activate catalysts *in situ* with the same synthesis gas as used during the FTS. Activity and selectivity results of our initial efforts using synthesis gas activation are shown in Table 1. Treatment of either 100Fe/3.6Si/0.71K or 100Fe/4.4Si/1.0K catalysts with synthesis gas (H_2:CO=0.7) at 3.1 NL $h^{-1}g^{-1}$(Fe), 543 K and 1.31 MPa resulted in poor FTS activity. Carbon monoxide conversions were typically below 30% and did not increase appreciably with time on stream. Kölbel and Ralek have reported successful synthesis gas activations with a precipitated Fe/Cu/K catalyst at 0.8-1.5 MPa and at a “formation” temperature 15-30 K above the FTS temperature (~573 K); however, they report that at too high a temperature carbon will form and at too low a temperature the formation will not take place and the catalyst will be inactive [6]. In contrast, we have found that increasing the activation temperature to 573 K while maintaining the pressure at 1.31 MPa has little affect on conversion during synthesis with catalysts activated with synthesis gas.

During the Reichsamt comparative experiments conducted in Germany in 1943, the Kaiser Wilhelm Institute, Brabag and Rheinpreussen all activated their iron catalysts with synthesis gas or water gas at atmospheric or subatmospheric pressure [10]. To explore the possible affect of pressure on synthesis gas activation, both 100Fe/3.6Si/0.71K (Figure 3) and 100Fe/4.4Si/1.0K (Figure 2c) catalysts were treated with synthesis gas (H_2:CO=0.7) at 3.1 NL $h^{-1}g^{-1}$(Fe), 0.10 MPa and 543 K for 24 h. A dramatic increase in activity was observed as compared to when the same activation was conducted at 1.31 MPa. For both the 100Fe/3.6Si/0.71K and 100Fe/4.4Si/1.0K catalysts, the initial carbon monoxide conversion was greater than 85% which is comparable to that obtained when pretreating with carbon monoxide at 543 K and 1.31 MPa. In fact, the 100Fe/4.4Si/1.0K catalyst had an initial conversion of 92% and displayed remarkable stability, deactivating at an average rate of only 0.59% per week for over 2700 h. In addition, the 100Fe/4.4Si/1.0K catalyst was also activated with synthesis gas (H_2:CO=0.7) at 573 K and 0.10 MPa. As was found when activating with synthesis gas at 1.31 MPa, increasing the temperature had little affect on the initial carbon monoxide conversion (Figure 2d); however, the deactivation rate was higher at 1.6% per week.

It is interesting to note that no such pressure dependence was observed with carbon monoxide pretreatment (Figure 2b). Pretreating the 100Fe/4.4Si/1.0K catalyst with carbon monoxide for 24 h at 543 K and 1.31 MPa resulted in an initial conversion slightly lower than when activating at 0.10 MPa; however, after 72 h at synthesis conditions, the conversions were essentially the same in both cases.

Selectivity data at high conversion for the 100Fe/4.4Si/1.0K catalyst activated with carbon monoxide or synthesis gas are presented in Table 2. In general, carbon monoxide activations resulted in the production of less methane and more liquid products than activations with synthesis gas. At comparable conversions, the catalyst activated with carbon monoxide at either 543 K/1.31 MPa or 543 K/0.10 MPa produced up to twice as much C_{12}+ as when activated with synthesis gas at 0.10 MPa. In contrast, Bukur et al. reported similar selectivities for a doubly promoted Fe/Cu/K catalyst that was activated with carbon monoxide or with synthesis gas [5].

The fact that pretreatment with carbon monoxide at either 0.10 or 1.31 MPa results in similar FTS activity suggests that the pressure dependence of synthesis gas activation is due to the presence of hydrogen. To test this possibility, the 100Fe/3.6Si/0.71K catalyst was treated with a synthesis gas low in hydrogen (H_2:CO=0.1) for 24 h at 2.1 NL $h^{-1}g^{-1}$(Fe), 543 K and 1.31 MPa. The initial carbon monoxide conversion was approximately 65% which is intermediate between activation with pure carbon monoxide and synthesis gas with a hydrogen:carbon monoxide ratio of 0.7. As shown in Figure 4, there is a clear correlation between the partial pressure of hydrogen in the activating gas and the carbon monoxide conversion obtained during the early synthesis period.

Catalyst Characterization

Catalyst slurry samples were removed from the reactor for the series of runs with the 100Fe/3.6Si/0.71K catalyst. X-ray diffraction analysis of the catalyst following pretreatment with CO (Figure 5a) or synthesis gas at 0.10 MPa (Figure 5b) shows the presence of Fe_3O_4 and the carbides χ-Fe_5C_2 and ϵ'-$Fe_{2.2}C$. In addition, X-ray diffraction data for the catalyst activated with hydrogen lean synthesis gas (H_2:CO=0.1) (Figure 5c) showed Fe_3O_4 and small amounts of iron carbides. In contrast, X-ray diffraction analysis of the catalyst activated with synthesis gas at 1.31 MPa showed only Fe_3O_4 (Figure 5d).

As discussed above, the carbon monoxide conversion of the 100Fe/3.6Si/0.71K catalyst activated with synthesis gas (H_2:CO=0.7) at 1.31 MPa and 543 K never rose above 12%. After 96 h of synthesis, the hydrogen flow was stopped and the catalyst was treated with carbon monoxide under the same operating conditions for 22 h. Following the carbon monoxide treatment, the hydrogen flow was resumed and the activity of the catalyst was found to rapidly increase (Figure 6). The ultimate activity of catalyst was similar to that obtained for the carbon monoxide pretreated catalyst. X-ray diffraction analysis shows that the catalyst consists of only Fe_3O_4 prior to the carbon monoxide treatment; however, following the carbon monoxide treatment, the catalyst consists of a mixture of Fe_3O_4, χ-Fe_5C_2 and ϵ'-$Fe_{2.2}C$ (Figure 7). These results are consistent with the Fe_3O_4 phase being relatively inactive for FTS while χ-Fe_5C_2 and ϵ'-$Fe_{2.2}C$ are necessary for high FTS activity. This does not necessarily imply that χ-Fe_5C_2 and ϵ'-$Fe_{2.2}C$ are active phases for FTS, in fact, previous works have shown that there is no correlation between the amount of bulk iron carbide present and the activity of the catalyst [2,3]. It is possible; however, that the presence of a bulk iron carbide is necessary to serve as a support for an active surface species. In considering the above results and discussion, it should be kept in mind that the characterization is based upon XRD; therefore, only bulk phases are detected.

The overall Fischer-Tropsch Synthesis with iron catalysts can be approximated as the sum of the hydrogenation of carbon monoxide to methylene groups and the water-gas shift reaction.

$$x\mathrm{CO} + 2x\mathrm{H_2} \rightarrow x(\text{-}\mathrm{CH_2}\text{-}) + x\mathrm{H_2O} \tag{1}$$

$$y\mathrm{H_2O} + y\mathrm{CO} \rightarrow y\mathrm{CO_2} + y\mathrm{H_2} \tag{2}$$

$$(x+y)\mathrm{CO} + (2x-y)\mathrm{H_2} \rightarrow x(\text{-}\mathrm{CH_2}\text{-}) + (x-y)\mathrm{H_2O} + y\mathrm{CO_2} \tag{3}$$

For iron based catalysts, whether the catalyst exists as a carbide or as an oxide depends on the reducing behavior of the atmosphere present in the reactor. During Fischer-Tropsch synthesis, the catalyst is exposed to an atmosphere of hydrogen, carbon monoxide and the reaction products: water and carbon dioxide. It is well known that water and carbon dioxide will oxidize metallic iron and iron carbides to Fe_3O_4 [1,2].

Thermodynamic data on the metallic iron/iron oxide system show that at a $H_2O:H_2$ ratio > 0.03 or a $CO_2:CO$ ratio > 2.8 oxidizing conditions exist and Fe_3O_4 is the stable phase compared to metallic iron [18]. Equation 3 can be used to calculate the $H_2O:H_2$ and $CO_2:CO$ ratios based on the carbon monoxide and hydrogen conversions. During activation of the 100Fe/3.6Si/0.71K catalyst with synthesis gas at 1.31 MPa, the $H_2O:H_2$ ratio was 0.16 and the $CO_2:CO$ ratio was 0.022. The water level clearly was high enough to make Fe_3O_4 the thermodynamically stable phase during the activation which would explain why no iron carbides could be detected by XRD. This conclusion requires that the formation of iron carbides results from an iron species that is lower-valent than is present in Fe_3O_4. In contrast, synthesis gas activation of the same catalyst at 0.10 MPa had a much lower $H_2O:H_2$ ratio of 0.0070 and a $CO_2:CO$ ratio of 0.90. These water and carbon dioxide levels were low enough to enable the catalyst to be reduced to form active iron carbides. It appears that by decreasing the hydrogen partial pressure, reaction 1 is suppressed enough during the activation that active iron carbides can be formed. An alternate method of activation with synthesis gas would be to operate at high linear flow rates (low conversion) to suppress water formation and to rapidly remove it from the reactor as is usually done when activating with pure hydrogen [2,5].

CONCLUSIONS

CO pretreatment of precipitated Fe/Si/K catalysts consistently results in high FTS activity because active carbide phases are readily formed. In the case of syngas activation, there is a relationship between the hydrogen partial pressure in the activation gas and the initial FTS activity. During activation with syngas, the catalyst is exposed to carbon dioxide and water as well as carbon monoxide and hydrogen. It has been found that during activations with high partial pressures of hydrogen, enough water is formed to prevent the catalyst from being reduced to active iron carbide phases and only relatively inactive Fe_3O_4 is formed. The results of this study indicate that the formation of an iron carbide (χ-Fe_5C_2 and/or ϵ'-$Fe_{2.2}C$) is necessary for high FTS activity; however, based on previous Mössbauer spectroscopy experiments, the activity of iron catalysts is not related to the amount of bulk iron carbide present [3]. These results indicate that a layer of surface carbide may be responsible for FTS activity.

ACKNOWLEDGMENT

This work was supported by the U. S. Department of Energy, contract no. DE-AC22-94PC94055 and the Commonwealth of Kentucky.

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Table 1

Results of Syngas Activations at 1.31 MPa

Catalyst	100 Fe/3.6 Si/0.71 K						100 Fe/4.4 Si/1.0 K	
Activation Conditions	H_2/CO = 0.7, 1.31 MPa, 543K		H_2/CO = 0.7, 1.31 MPa, 573K		H_2/CO = 0.1, 1.31 MPa, 543K		H_2/CO = 0.7, 1.31 MPa, 543K	
Time-on-Stream, h	46	92	46	119	47	139	48	192
Conversion/%								
CO	12	12	15	21	62	60	22	33
H_2	22	26	21	26	58	54	28	35
CO + H_2	16	18	18	23	61	57	25	34
H_2:CO Usage Ratio	1.3	1.5	0.98	0.87	0.65	0.63	0.89	0.74
CO_2 Selectivity/mol %	37	43	35	34	46	46	38	43
Hydrocarbon Productivity								
g HC Nm^{-3} feed gas	27	25	37	51	126	120	52	70
g C_3 + Nm^{-3} feed gas	22	20	31	44	108	103	44	59
g HC g^{-1}(Fe)h^{-1}	0.084	0.078	0.11	0.16	0.39	0.37	0.16	0.21
Alkene Selectivity/mol %								
C_2	58	74	62	67	23	16	75	63
C_3	92	91	84	89	69	62	83	81
C_3	83	84	81	84	76	76	86	84

Table 2
FTS Results for Catalysts at High Activity

Pretreatment	CO/543 K/1.31 MPa		CO/543 K/0.10 MPa		H_2:CO = 0.7/543K/0.10 MPa		H_2:CO = 0.7/573K/0.10 MPa	
Time-on-Stream/h	336	1992	360	1016	312	2852	312	1836
Space Velocity/NL $h^{-1}g^{-1}$(Fe)	3.4	3.4	3.1	3.1	3.1	3.1	3.1	3.1
Conversion/%								
CO	84	74	84	79	87	74	84	68
H_2	76	65	75	73	77	67	76	67
CO + H_2	81	70	80	76	83	71	81	67
WGS								
CO_2/mol %	46	42	45	44	50	46	47	44
H_2:CO Usage	0.63	0.61	0.63	0.65	0.62	0.64	0.62	0.68
K_{app}	14	7.2	16	12	40	30	16	4.4
Productivity								
g HC Nm^{-3} feed gas	167	159	168	162	162	146	165	140
g C_3+Nm^{-3} feed gas	142	132	142	134	130	110	136	116
g HC g^{-1}(Fe)h^{-1}	0.62	0.58	0.52	0.50	0.50	0.45	0.50	0.42
Selectivity/wt.% (alkene)								
C_1	8.1	8.7	8.2	8.7	11	15	9.6	8.3
C_2-C_4	26(57)	28(61)	27(57)	29(57)	32(48)	37(53)	30(54)	33(65)
C_5-C_{11}	34(58)	27(66)	36(60)	32(60)	46(54)	34(56)	34(59)	40(68)
C_{12}+	32	36	29	31	11	15	26	19

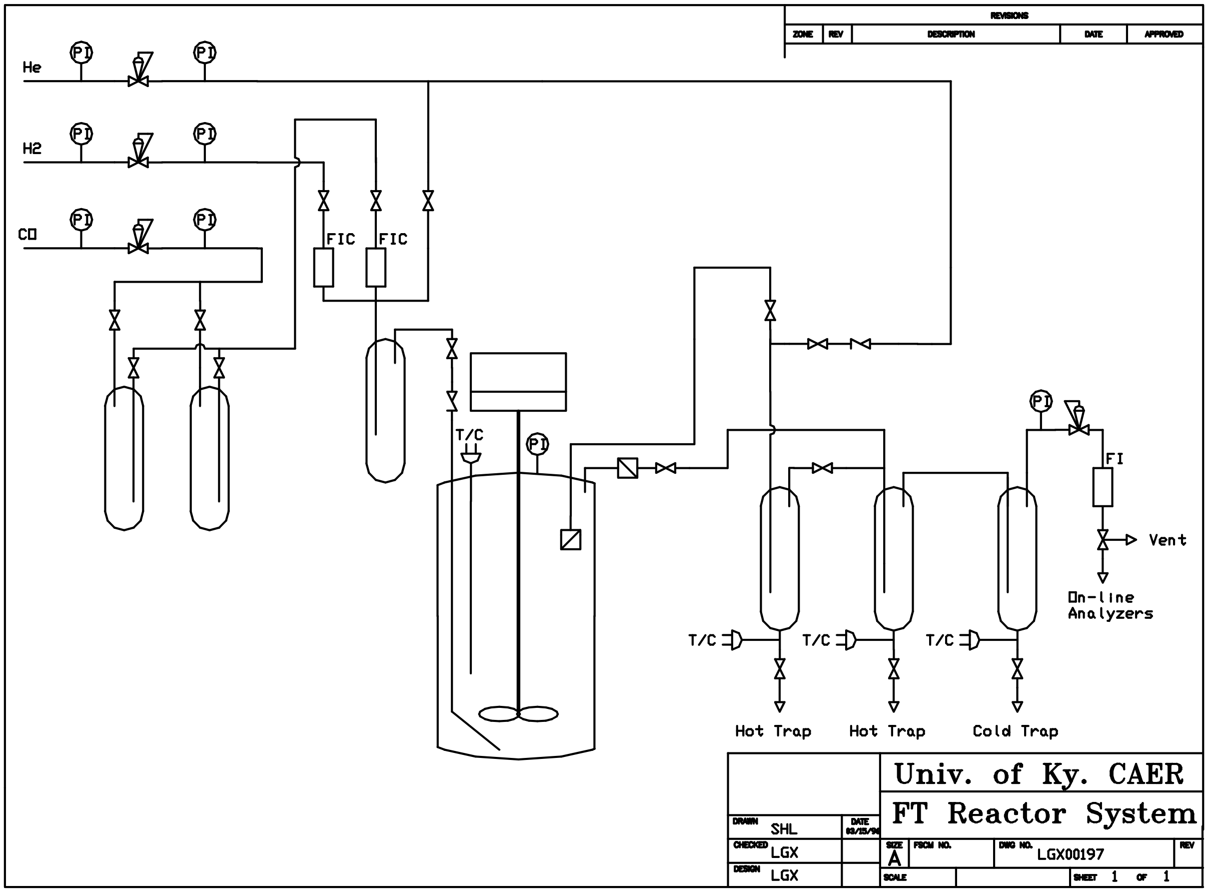

Figure 1. Schematic of the one liter continuous stirred tank reactor system.

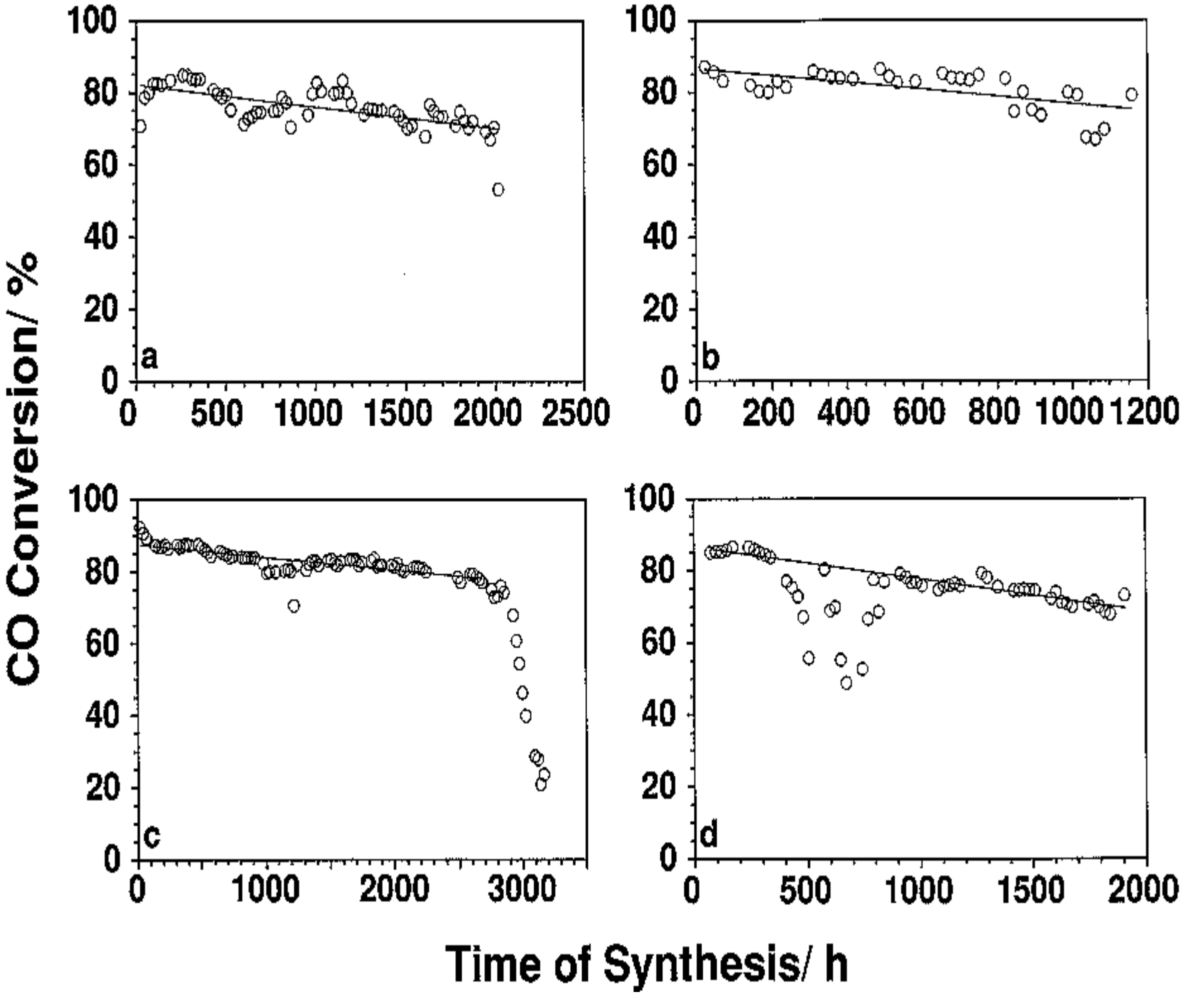

Figure 2. Carbon monoxide conversion for 100Fe/4.4Si/1.0K catalyst pretreated for 24 h at with (a) carbon monoxide at 543 K an 1.31 MPa, (b) carbon monoxide at 543 K and 0.10 MPa, (c) synthesis gas (H_2:CO=0.7) at 543 K and 0.10 MPa, and (d) synthesis gas (H_2:CO=0.7) at 573 K and 0.10 MPa.

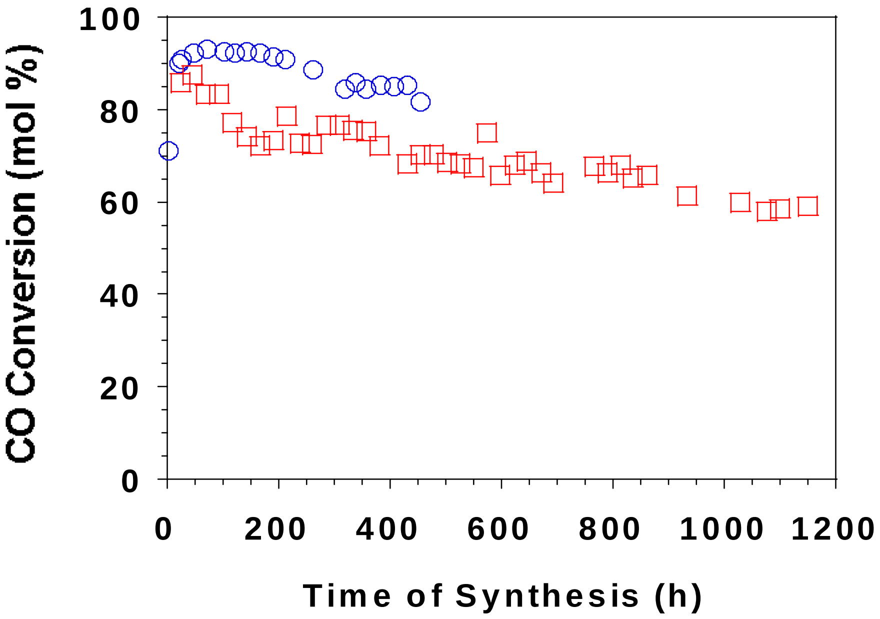

Figure 3. Carbon monoxide conversion for 100Fe/3.6Si/0.71K catalyst pretreated for 24 h with (○) carbon monoxide at 543 K and 1.31 MPa and (□) synthesis gas (H_2:CO=0.7) at 543 K and 0.10 MPa.

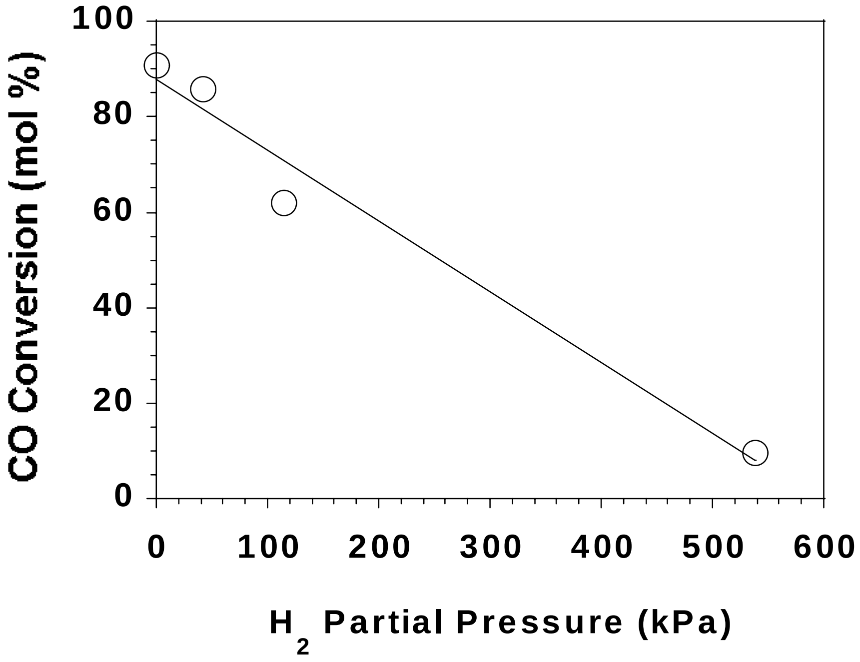

Figure 4. Initial carbon monoxide conversion as a function of the partial pressure of hydrogen in the pretreatment gas for the 100Fe/3.6Si/0.71K catalyst.

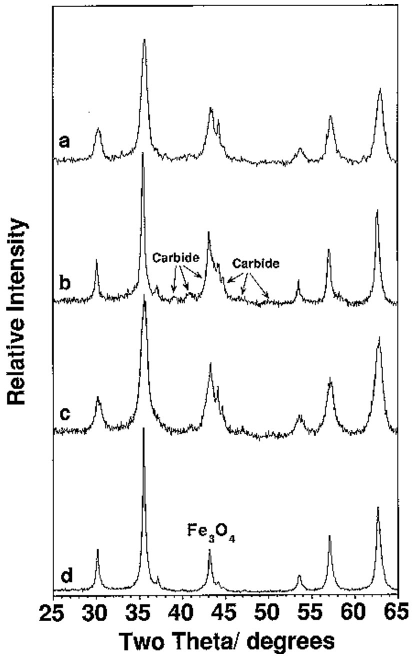

Figure 5. X-ray diffraction results for 100Fe/3.6Si/0.71K catalyst following 24 h pretreatment with (a) carbon monoxide at 543 K and 1.31 MPa, (b) synthesis gas (H_2:CO=0.7) at 543 K and 0.10 MPa, (c) synthesis gas (H_2:CO=0.1) at 543 K and 1.31 MPa, and (d) synthesis gas (H_2:CO=0.7) at 573 K and 1.31 MPa.

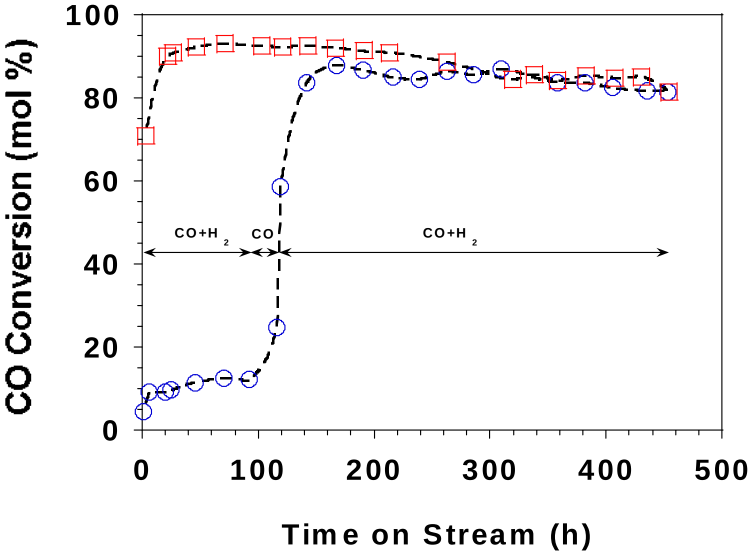

Figure 6. Carbon monoxide conversion for 100Fe/3.6Si/0.71K catalyst (○) activated with synthesis gas at 543 K and 1.31 MPa, followed by a carbon monoxide treatment at 543 K and 1.31 MPa after 96 hr of synthesis and (□) pretreated with carbon monoxide for 24 h at 543 K and 1.31 MPa.

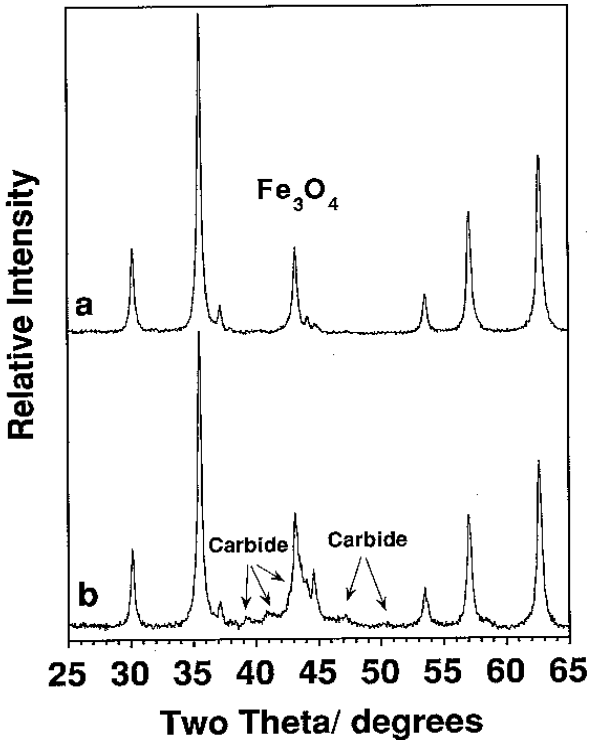

Figure 7. X-ray diffraction results for the 100Fe/3.6Si/0.71K catalyst (a) after 96 hr of exposure to synthesis gas at 543 K and 1.31 MPa and (b) followed by a 22 h exposure to carbon monoxide at 543 K and 1.31 MPa.