Executive Summary

CAER

Both cobalt and iron catalysts were used in the initial study of catalyst-wax filtrations. For both systems, the filters studied were internally placed in the 1000 mL continuous stirred tank reactors. For the supported cobalt catalysts based on silica, alumina, and titania support material, wax has been successfully removed from the reactor during operations of up to five months. Wax separations from the catalyst slurry is not a problem using a fine (2 to 5 micron) porous metal filter. Operations of the laboratory reactors with wax production of 100 g/day or higher can be accomplished.

Two filters manufactured by the Pall Corporation installed in 1000mL continuous stirred tank reactors to study wax-catalyst separations for a high alpha Fe catalyst (100Fe/4.6Si/2.0Cu/5.0K). One filter used a material called Rigimesh (filter A) which is a sintered woven wire mesh of different sizes. The other filter tested is composed of PMM medium (filter B) which is a thin sintered matrix of stainless steel powder within the pores of sintered stainless steel mesh. Both of the filters were studied using the same catalyst and run conditions. Filter A was more effective than filter B. The run using filter B had to be terminated after 1000 hours of operation due to the filter plugging. However, with filter A, the run was voluntarily terminated after 1500 hours of successful operations. It was also determined that the activity decline is at approximately the same rate as the loss of catalyst and that the loss of activity is clearly lower than the DOE target of 1% CO conversion per week. Therefore, we consider this to be a demonstration of our ability to operate the CSTR so that we can now define the activity, selectivity and catalyst deactivation characteristics for both intermediate and high alpha catalysts.

A study of the impact of potassium on the activation energy of precipitated iron catalysts was started this quarter. Five catalysts, with atomic composition 100Fe/4.6Si, 100Fe/4.6Si/0.36K, 100Fe/4.6Si/0.71K, 100Fe/4.6Si/1.4K and 100Fe/4.6Si/2.2K were used in this study. All runs were conducted in 1000 mL continuous stirred tank reactors. In general, the activation energy ranged between 64 $kJmole^{-1}$ and 82 $kJmole^{-1}$. The activation energy decreased from 79 kJ mol^{-1} for the catalyst with no potassium to 64 kJ mol^{-1} for the catalyst with 0.36K; however, additional potassium caused the activation energy to increase up to 82 kJ mol^{-1} for the 2.2K catalyst. The activation energy for the 0K catalyst was essentially the same for the duplicate runs; however, additional runs with the 0.36K and 2.2K catalyst will be completed before any conclusions can be reached about the effect (if any) of potassium on activation energy. No reason that the activation energy should have a minimum with respect to potassium loading is apparent. It may be that we are only seeing the effects of experimental error from the catalysts being incompletely activated (activity always increased after completing the series of temperature reductions and then returning to the original conditions). This is an important aspect and work continues on this.

UC/B

During this reporting period, we have completed the *in-situ* X-ray absorption spectroscopy (XAS) studies at the Stanford Synchrotron Radiation Laboratory (SSRL) with emphasis on Fe K-edge measurements of the initial structure and the long-term phase evolution during reduction and carburization of Fe oxides. The results showed that the K addition to Fe_2O_3-Cu significantly decreased the reduction and carburization time because K increases carburization rates and Cu catalyses oxygen removal from Fe_2O_3. In this reporting period, we have started quantitative measurements the number of active sites in order to confirm some of the

structure-function rule that we have developed during our previous studies. Our initial efforts have focused on counting the active sites and investigating the chemisorption behavior of probe molecules H_2, CO, and H_2/CO mixtures using mass spectroscopy. The temperature-programmed desorption (TPD) of chemisored titrants showed that H_2 and CO competitively adsorb on Fe sites. CO occupies two Fe sites while chemisorbing alone. However, in the presence of H_2, a portion of CO absorbs molecularly on Fe sites. We have also prepared K- and Re-promoted Fe-Si catalysts and investigated the reduction and carburization process and catalytic activity in an attempt to find alternative catalysts with higher FTS rates, lower CO_2 formation rates, and higher C_{5+} and olefinic selectivity. However, no significant promotion effects were observed for K or Re promoted Fe-Si oxides, because a large fraction of the K titrates the SiO_2 component and Re was not completely reduced during FTS reactions.

Fischer-Tropsch synthesis reactions were carried out on Fe-Si-K catalyst samples (100 Fe/4.6 Si/1.4 K) at two different temperatures and pressures (220 ºC, 30 atm and 235 ºC, 21.4 atm). The reaction results at 235ºC were compared with those for Fe-Zn-Cu-K catalyst studied previously at similar CO space velocities. The CO conversions were higher on Fe-Si-K (~15% higher at a CO space velocity of 5 NL/hr.g-Fe). The CO_2 selectivities were higher for Fe-Zn-Cu-K than Fe-Si-K (~15% higher at 20% CO conversion). The slopes of the CO_2 selectivity versus reciprocal space velocity curves were identical in both cases, suggesting the increase in the CO_2 selectivity is due to a higher primary CO_2 formation rate (*via* the removal of surface oxygen by CO to form CO_2). CH_4 selectivities were higher for Fe-Zn-Cu-K than Fe-Si-K (~3% higher at 40% CO conversion). The C_{5+} hydrocarbon selectivity was higher over Fe-Zn-Cu-K than Fe-Si-K (~8% higher at 40% CO conversion).

FTS reaction studies on Fe-Si (100 Fe/4.6 Si) and Fe-Si-K (100 Fe/4.6 Si/1.4 K) catalysts showed that the addition of K to the Fe-Si catalyst does not significantly promote FTS reactions. In fact, the CO conversions obtained at both conditions (235 ºC, 21.4 atm and 220 ºC, 30 atm) were slightly higher on Fe-Si than Fe-Si-K. These results are in contrast to those obtained previously on Fe-Zn-Cu catalysts, which showed that K strongly promoted the FT activity of the catalyst. The CO_2 selectivities increased slightly (from ~4.6% to ~9.3% at 20% CO conversion at 235 ºC); these changes were much higher in the case of the Fe-Zn-Cu systems. In addition, CH_4 selectivities decreased (from ~11% to ~5%) and the C_{5+} selectivities increased (from ~60% to ~75%) at 235 ºC with the addition of K to the Fe-Si catalyst. These changes were much smaller than those observed for CH_4 selectivities (from ~11% to ~3%) and C_{5+} selectivities (from ~63% to ~83%) at 235 ºC on Fe-Zn-Cu-K.

As part of our continued efforts to certify a with a re-designed microreactor in the Co-FTS unit, space-velocity runs and water addition runs were conducted with a 21.9% Co/SiO_2 catalyst at 200ºC and 20 atm. While site-time yields were identical in both cases, the CH_4 selectivities were higher and the C_{5+} selectivities were lower than those reported on a similar catalyst in an earlier report [1Q' FY99]. In addition, the α–olefin to *n*-paraffin ratios were slightly lower indicating that the catalyst in the latter case exhibited a higher hydrogenation activity. To check if the difference in the data was due to incomplete reduction of the catalyst, the FTS runs were conducted after reduction at 325 ºC and 350 ºC. The site-time yields were similar, but differences in the selectivities remained. Currently, attempts are being made to identify and eliminate the causes for these discrepancies. Work also continues on an efficient code to evaluate the suitability of specific mechanism-based rate expressions to describe the complex

experimental dependence of FTS rates and selectivities on reactant and product concentrations and the critical role of primary and secondary reactions in catalyst performance.

Task 1. Iron Catalyst Preparation

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

No scheduled activity to report. If the filtration of the fine (1-3 micron) particle is successful as early results suggests, robust catalysts may not be required.

Task 2. Catalyst Testing

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

2.1. Impact of Potassium on the Activation Energy of Precipitated Iron FTS Catalysts

Several kinetic models have been proposed for iron based Fischer-Tropsch catalysts. Anderson (1) proposed a rate expression in which water inhibits the FT rate:

$$-R_{CO+H_2} = \frac{kP_{H_2}P_{CO}}{P_{CO} + bP_{H_2O}} \tag{1}$$

Anderson noted that at syngas conversion below 60%, the FT rate was first order with respect to hydrogen and zero order with respect to carbon monoxide (equation 2).

$$-R_{CO+H_2} = kP_{H_2} \tag{2}$$

Huff and Satterfield proposed a rate expression based on the carbide mechanism in which the rate limiting step was the hydrogenation of a surface carbide species (2). This model also accounted for inhibition by water (equation 3).

$$-R_{CO+H_2} = \frac{kP_{CO}P^2{}_{H_2}}{P_{CO}P_{H_2} + bP_{H_2O}} \tag{3}$$

Ledakowicz has proposed two rate expressions (3) in which the FT rate is inhibited by CO_2 adsorption (equation 4).

$$-R_{CO+H_2} = \frac{kP_{CO}P_{H_2}}{P_{CO} + cP_{CO_2}} \tag{4}$$

and a general rate expression which accounts for both H_2O and CO_2 inhibition (equation 5).

$$-R_{CO+H_2} = \frac{kP_{CO}P_{H_2}}{P_{CO} + aP_{H_2O} + cP_{CO_2}}$$

Using these and other rate equations, the activation energy of the FT reaction with iron catalysts has been determined to fall within a broad range of 71 to 103 kJ mol^{-1}. The impact of promoters on the activation energy has not been reported. Satterfield has reported an activation energy of 83 kJ mol^{-1} for a fused iron catalyst promoted with K, Ca, Si, and Al (2). Bukur has reported activation energies of for precipitated iron catalysts promoted with K, Cu and SiO_2 (4). A systematic study of the effect of potassium on the FT activation energy has not been reported. Potassium can either increase or decrease the activity of iron-based catalysts depending on the H_2/CO ratio of the syngas and the range of syngas conversion studied. Furthermore, the CO conversion increases, attains a maximum, and then decreases as the amount of potassium in the catalyst is increased. As a consequence it is possible that potassium will impact the activation energy of the FT reaction.

Experimental

Five catalysts with atomic composition 100Fe/4.6Si, 100Fe/4.6Si/0.36K, 100Fe/4.6Si/0.71K, 100Fe/4.6Si/1.4K and 100Fe/4.6Si/2.2K were studied. 15.0 g of catalyst and 290 g of C_{30} oil were loaded into 1000 ml autoclaves. The catalysts were activated with CO at

$270^{O}C$ and 175 psig for 24 h. Initial FTS conditions were $270^{O}C$, 175 psig, $H_2/CO=0.67$ and ghsv=5.0 sl h^{-1} g-Fe^{-1}. After the syngas conversion stabilized, the temperature was lowered to $250^{O}C$ for 24 hours and then to $230^{O}C$ for 24 hours. The temperature was then increased to $270^{O}C$ to determine whether catalyst deactivation had occurred.

Results

Syngas conversion profiles for each potassium loading are shown in Figures 1-5. Syngas conversion stabilized after about 120 hours on steam for each catalyst. After decreasing the temperature to $250^{O}C$ and then $230^{O}C$, the temperature was increased to $270^{O}C$. In each case the conversion was higher than before the temperature reductions. This occurred even after most of the catalysts appeared to be deactivating slightly before the initial temperature reductions. In order to insure consistency, kinetic data were obtained from the initial temperature reductions. Syngas conversion as a function of potassium loading at each temperature is shown in Figure 6. The syngas conversion increased slightly when going from 0K to 0.36K at each temperature; however, there was essentially no effect on conversion with increasing potassium loading beyond 0.36K.

For the sake of simplicity the reaction was assumed to be first order in H_2 and zero order in CO (equation 2).

$$-R_{CO+H_2}=kP_{H_2}$$

Rate constants at each temperature for each potassium loading are shown in Table 1. There is approximately 5% relative error for the rate constant of the duplicate runs using 0K loading.

Table 1						
	k (mol h^{-1} g-Fe^{-1} kPa^{-1})					
T (^{O}C)	**0K**	**0K**	**0.36K**	**0.72K**	**1.44K**	**2.18K**
230	1.32×10^{-4}	1.18×10^{-4}	1.93×10^{-4}	1.58×10^{-4}	1.36×10^{-4}	1.23×10^{-4}
250	2.79×10^{-4}	2.56×10^{-4}	3.37×10^{-4}	3.33×10^{-4}	2.88×10^{-4}	2.80×10^{-4}
270	5.31×10^{-4}	4.90×10^{-4}	6.17×10^{-4}	5.67×10^{-4}	5.64×10^{-4}	5.38×10^{-4}

Arrhenius plots for the different catalysts are shown in Figure 7. Activation energy as a function of potassium loading is shown in Figure 8. In general, the activation energy ranged between 64 kJ mol^{-1} and 82 kJ mol^{-1}. The activation energy decreased from 79 kJ mol^{-1} for the catalyst with no potassium to 64 kJ mol^{-1} for the catalyst with 0.36K; however, additional potassium caused the activation energy to increase up to 82 kJ mol^{-1} for the 2.2K catalyst. The activation energy for the catalyst without K was essentially the same for the duplicate runs; however, additional runs which repeat the runs with 0.36K and 2.2K should be completed before any conclusions can be reached about the effect (if any) of potassium on activation energy. No reason that the activation energy should have a minimum with respect to potassium loading is apparent. It may be that we are only seeing the effects of experimental error from the catalysts being incompletely activated (activity always increased after completing the series of temperature reductions and then returning to the original conditions). This is an important aspect and work continues on this.

References

1. Anderson, R. B. In "Catalysis," Vol. 4; Emmett, P. H., Ed. Reinhold: New York, 1956.
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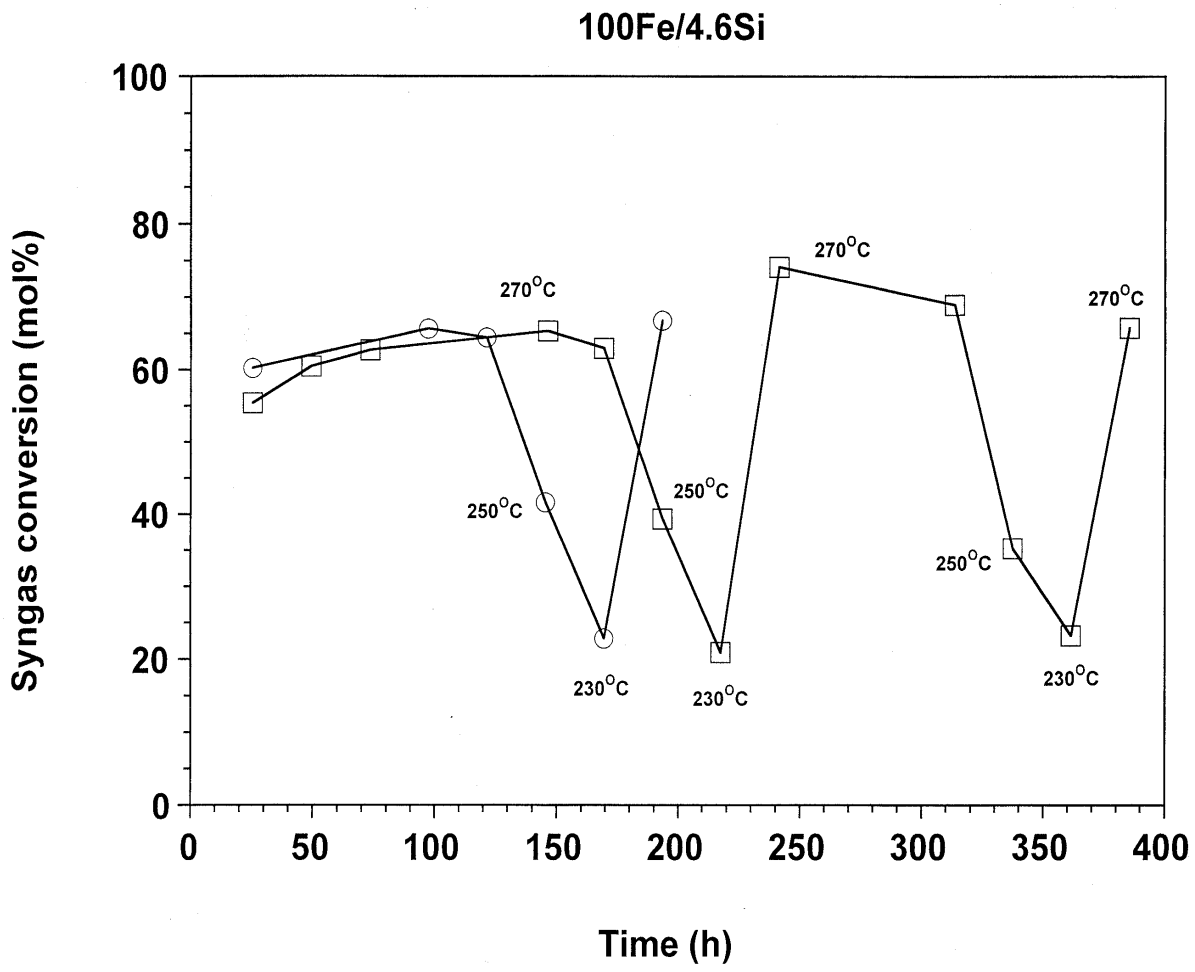
100Fe/4.6Si
Syngas conversion (mol%)
Time (h)
0
20
40
60
80
100
0
50
100
150
200
250
300
350
400
270°C
250°C
230°C
270°C
250°C
230°C
270°C
250°C
230°C
270°C

Figure 1.

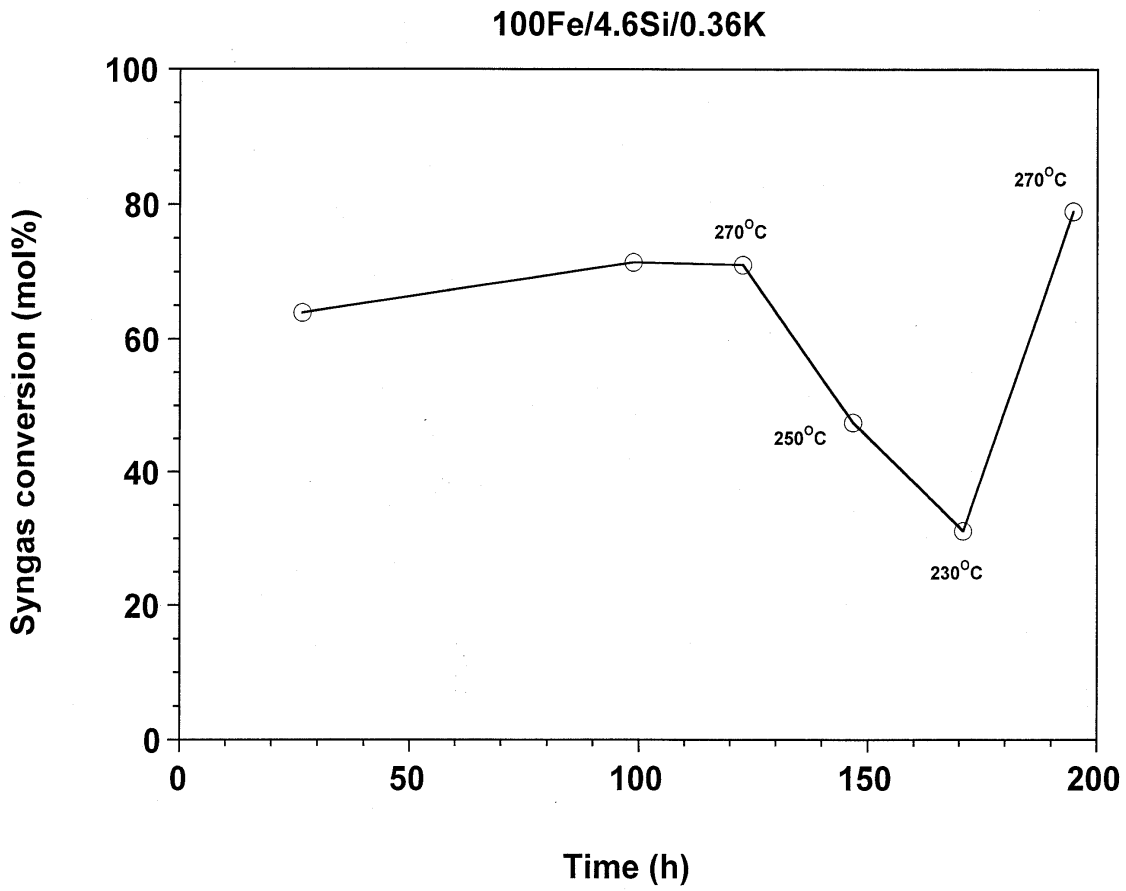
100Fe/4.6Si/0.36K
Syngas conversion (mol%)
Time (h)
0
20
40
60
80
100
0
50
100
150
200
270°C
270°C
250°C
230°C

Figure 2.

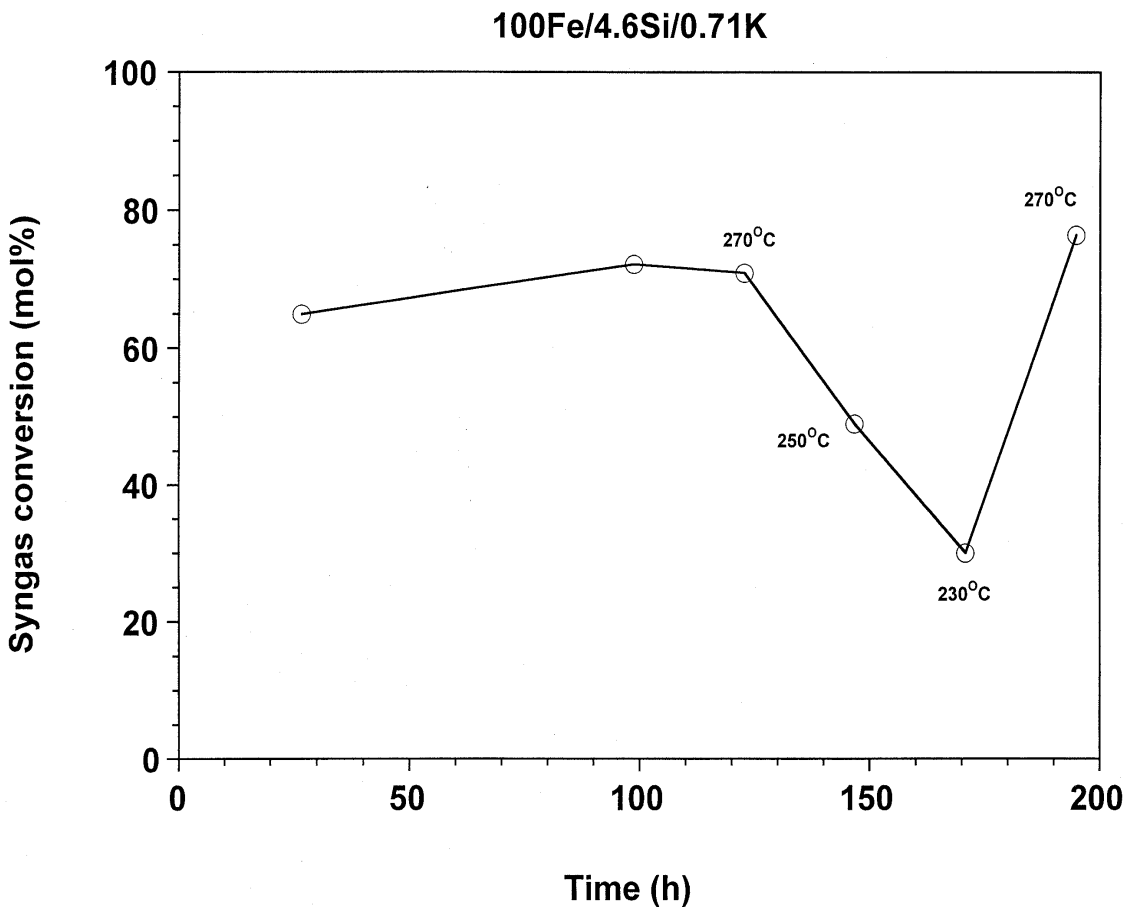
100Fe/4.6Si/0.71K
Syngas conversion (mol%)
Time (h)
0
20
40
60
80
100
0
50
100
150
200
270°C
270°C
250°C
230°C

Figure 3.

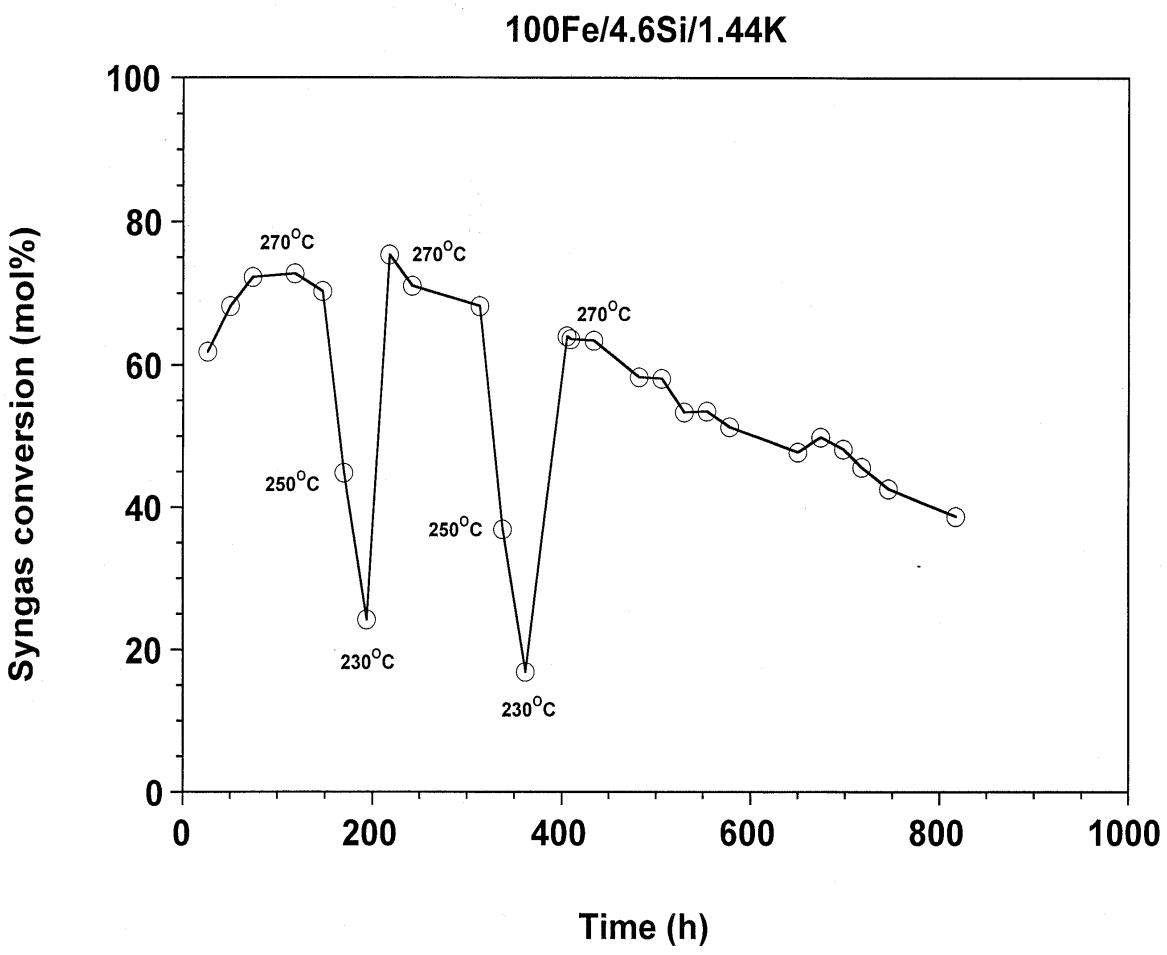
100Fe/4.6Si/1.44K
Syngas conversion (mol%)
Time (h)
0
20
40
60
80
100
0
200
400
600
800
1000
270°C
270°C
270°C
250°C
250°C
230°C
230°C

Figure 4.

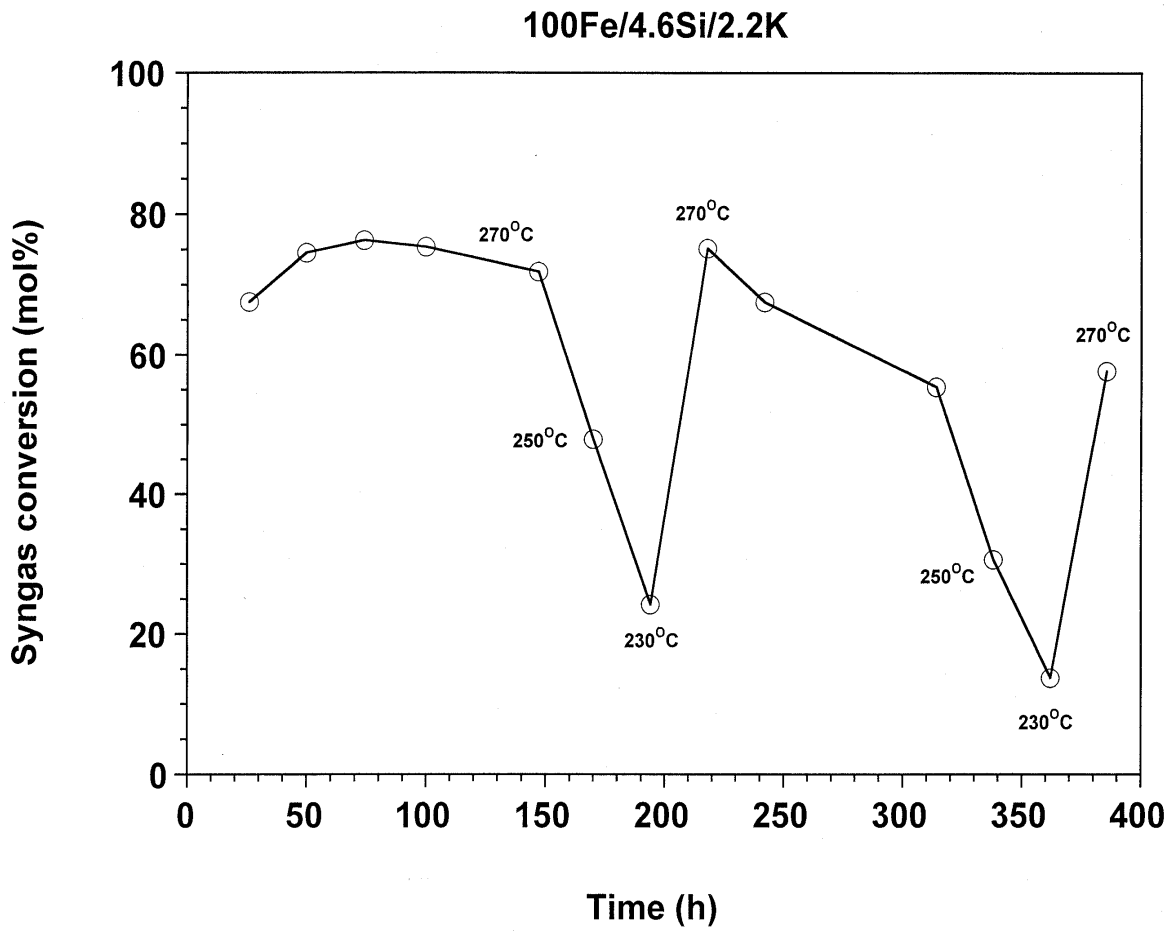
100Fe/4.6Si/2.2K
Syngas conversion (mol%)
Time (h)
0
20
40
60
80
100
0
50
100
150
200
250
300
350
400
270°C
250°C
230°C
270°C
250°C
230°C
270°C

Figure 5.

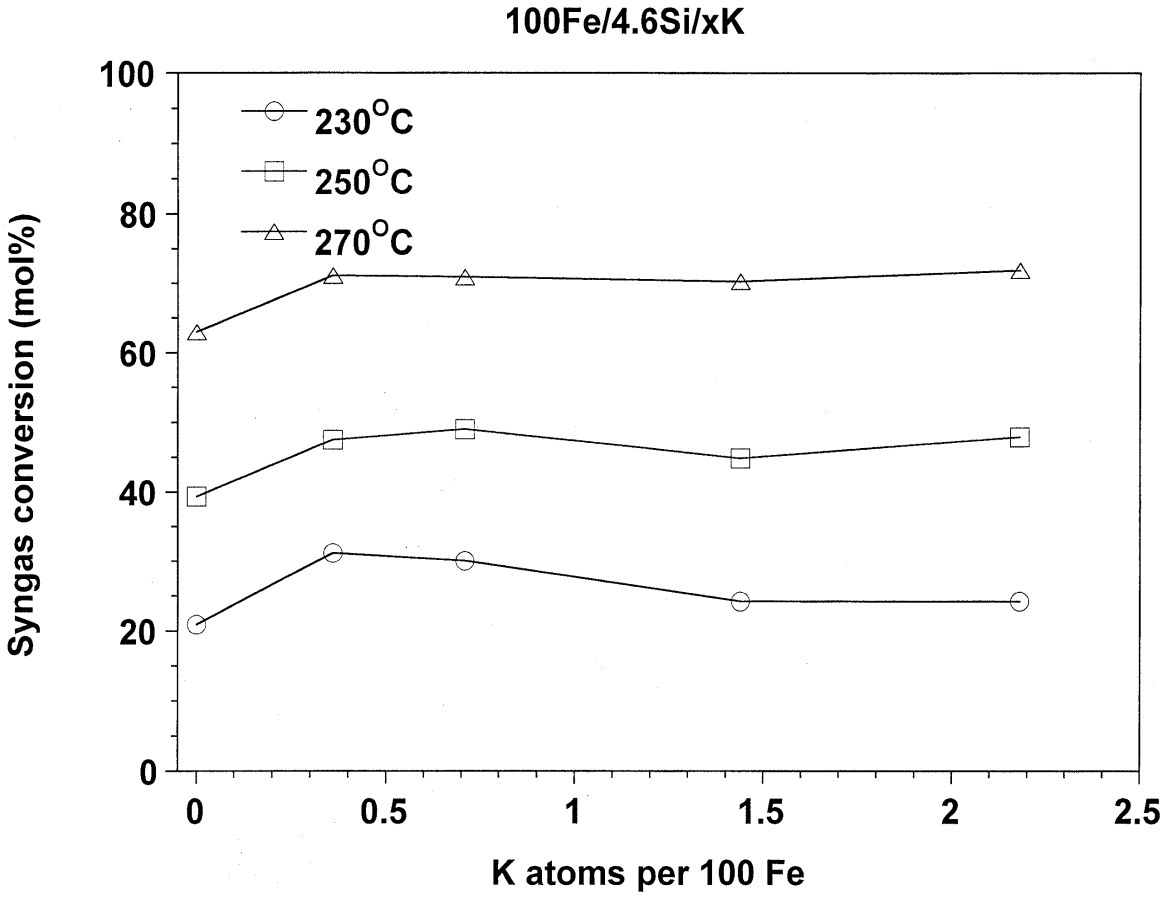
100Fe/4.6Si/xK
230°C
250°C
270°C
Syngas conversion (mol%)
K atoms per 100 Fe
0
20
40
60
80
100
0
0.5
1
1.5
2
2.5

Figure 6.

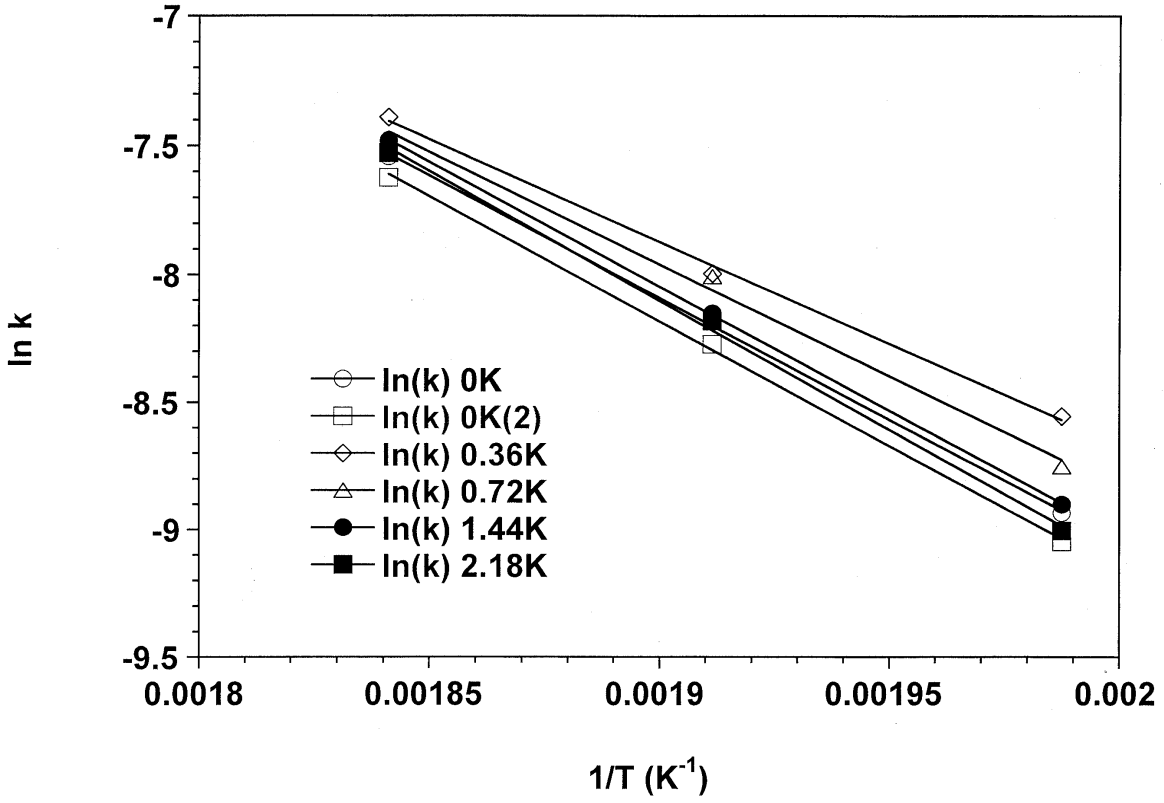
-7
-7.5
-8
-8.5
-9
-9.5
ln k
0.0018
0.00185
0.0019
0.00195
0.002
1/T (K-1)
ln(k) 0K
ln(k) 0K(2)
ln(k) 0.36K
ln(k) 0.72K
ln(k) 1.44K
ln(k) 2.18K

Figure 7.

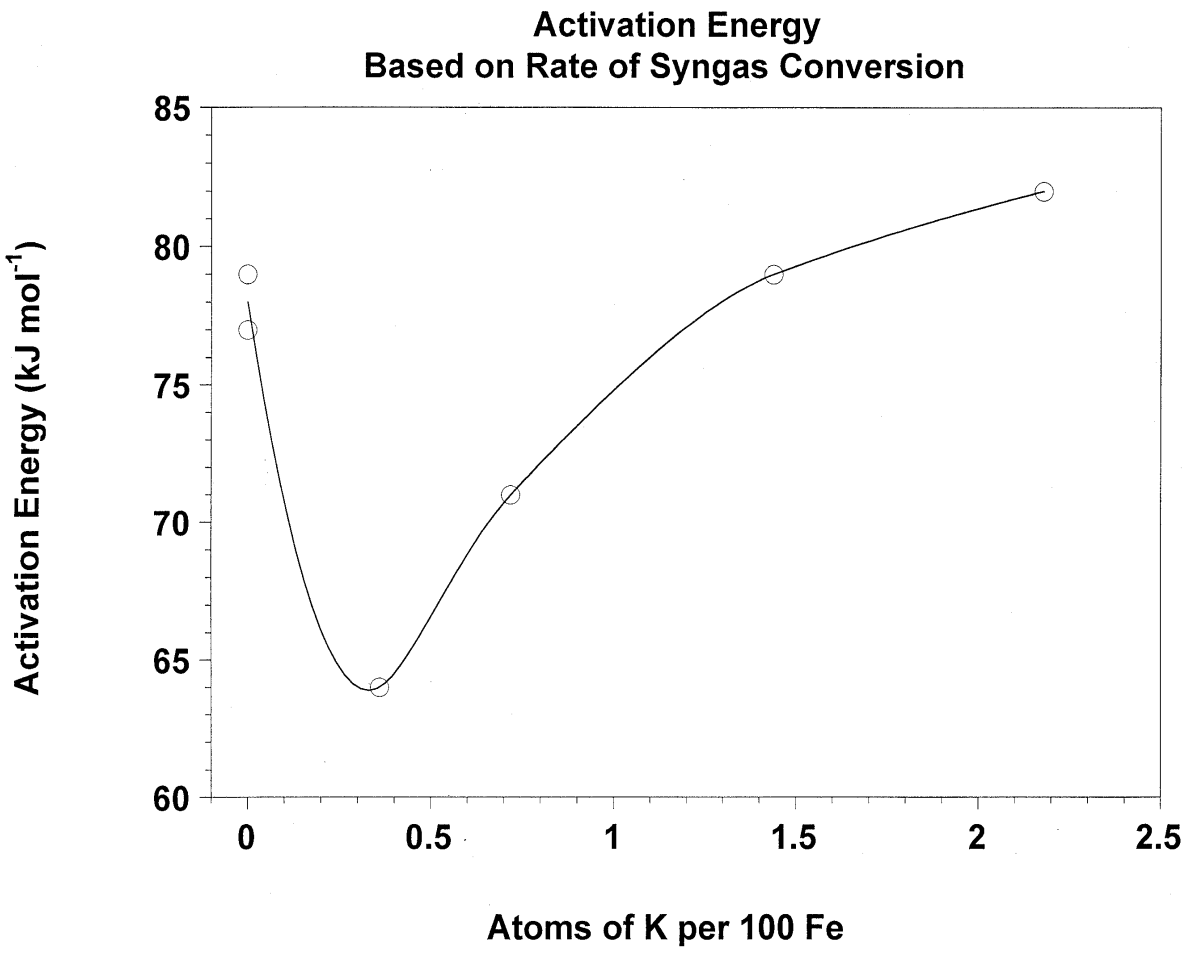
Activation Energy
Based on Rate of Syngas Conversion
Activation Energy (kJ mol-1)
85
80
75
70
65
60
0
0.5
1
1.5
2
2.5
Atoms of K per 100 Fe

Figure 8.