

Executive Summary

CAER

Formation of an iron carbide is necessary for high activity with precipitated iron catalysts. A precipitated iron catalyst (100Fe/4.6Si/2.7Cu/1.0K) which was activated with hydrogen at 220°C and ambient pressure was partially reduced to metallic iron and Fe₃O₄. Metallic iron was not stable under FT conditions and exposure to syngas (H₂/CO=0.7) at 270°C and 1.3 MPa converted all of the metallic iron to ϵ' -Fe_{2.2}C. Catalysts activated with carbon monoxide (unpromoted iron and 100Fe/8.9Cu/1.9K/67kaolin) or syngas with low hydrogen partial pressure (100Fe/3.6Si/0.7K) at 270°C produced predominantly χ -Fe₅C₂ and had high initial syngas conversion. Activation with syngas at 270°C and 1.3 MPa partially reduced the 100Fe/3.6Si/0.7K catalyst to 100% Fe₃O₄ which resulted in low FT activity. Iron carbides produced by carbon monoxide and syngas activation of promoted catalysts were partially oxidized to Fe₃O₄ during the first 24 hours of FT synthesis; however, these catalysts deactivated slowly. There was no difference in the activity, stability or deactivation characteristics of ϵ' -Fe_{2.2}C and χ -Fe₅C₂ under the FT conditions employed in this study. Catalysts with stable activity maintained a constant iron carbide level. An unpromoted iron catalyst deactivated more rapidly than iron catalysts promoted with potassium, copper and a nonreducible metal oxide. The deactivation of the unpromoted iron catalyst was caused by oxidation of active iron carbide to inactive/less active Fe₃O₄.

The presence of iron carbides and Fe₃O₄ together can be explained by inhomogeneity of gases within individual catalyst particles. Water and carbon dioxide produced by conversion of syngas within catalyst particles can cause the environment inside a particle to be oxidizing while the surface is exposed to reducing conditions of the reactor atmosphere. This would result in the formation of a Fe₃O₄ core and an iron carbide outer layer. Another possibility is that under typical FT conditions the redox potential of the reactor atmosphere lies within the narrow region of the C/H/O/Fe phase diagram where Fe₃O₄ and iron carbides can coexist.

UC/B

During this reporting period, we have continued to investigate the temperature-programmed surface reaction (TPSR) of Fe-Zn and Fe-Zn-K-Cu oxides with CO in order to determine the temperatures required for the reduction and carburization of the oxides, the rates at which Fe carbides are formed and the amount of Fe oxide that is reduced or carburized. Generally, the reduction and carburization of the oxides proceeded in three steps: Fe₂O₃ was first reduced to Fe₃O₄ at about 270°C; Then, Fe₃O₄ was reduced to metallic Fe followed by carburization to a mixture of χ -Fe_{2.5}C and Fe₃C between 270 ~ 450°C. Above 450°C, CO disproportionation (Boudouard reaction) occurred, leading to the formation of excess free carbon. X-ray diffraction measurements showed that a phase transformation from χ -Fe_{2.5}C to Fe₃C occurred at about 450°C.

The TPSR studies on the effects of Zn, K and Cu on the reduction and carburization of the Fe oxides showed that Zn did not appreciably influence the reduction and carburization of Fe oxides at low Zn contents (<0.2). However, the reduction and carburization on the sample with high Zn content (e.g., 0.4 Zn/Fe) shifted to higher temperatures because ZnFe₂O₄ is more stable against reduction than Fe₂O₃; K slightly inhibited both the reduction and carburization of Fe

oxides; Cu decreased not only the temperature required for the reduction but also that for carburization. Cu appeared to facilitate the incorporation of carbon within Fe to form Fe carbides.

In-situ X-ray absorption studies on Fe-based catalyst were conducted at the Stanford Synchrotron Research Laboratory (SSRL) during this reporting period. X-ray absorption near-edge spectra (XANES) and extended X-ray absorption fine structure spectra (EXAFS) at Fe K-edge for Fe-Zn-K-Cu oxide (Zn/Fe = 0.1, 2 at.% K, 1 at.% Cu) were recorded in flowing H₂, CO and synthesis gas at different temperatures. Fe K-edge spectra for the Fe-Zn-K-Cu oxide in CO showed progressive shifts of the edge energy from 7123 eV (Fe³⁺) to 7112 eV (Fe⁰) along with changes in the near-edge and fine structure regions while increasing the temperature up to 500°C. A principal component analysis of the near-edge spectra is being carried out in order to quantify the relative concentration of various oxide, carbide and metal phases during FTS.

The effects of potassium on Fischer-Tropsch synthesis (FTS) were examined on Fe-based catalysts (Zn/Fe = 0.1, 1 at.% Cu) with different K contents (0 ~ 4 at.%). The addition of potassium (2 ~ 4 at.%) increased FTS and water-gas shift reaction rates, decreased the selectivity to methane and increased selectivities to high molecular weight hydrocarbons and to olefins. Potassium levels above 2 at.% had only small effects on FTS rates and selectivities. Also, the promotion effect of K was more evident at 235°C and 21.4 atm than at 270°C and 5 atm for all K contents.

The effects of CO₂ addition on the rate of water-gas shift reaction and on the selectivities to CO₂ and hydrocarbons were investigated by adding CO₂ on a K-free sample (Zn/Fe = 0.1, 1 at.% Cu) at 270°C and 5 atm. Addition of CO₂ inhibited the formation of CO₂ via water-gas shift but did not affect the FTS reaction because both the CO conversion rate and CO₂ net formation rate decreased when CO₂ was added but FTS rates did not depend on CO₂ pressure. The inhibit effect of CO₂ on the water-gas shift reaction was less evident on a K-containing sample (Zn/Fe = 0.07, 2 at.% K and 1 at.% Cu) for FTS that was run at 235°C and 21.4 atm since the water-gas shift reaction is more thermodynamically favorable at lower temperatures. Although addition of CO₂ can be used to decrease CO₂ yields during FTS, the elimination of net CO₂ formation may well require levels of CO₂ that are impractical because of separation and re-compression costs.

Co catalysts were prepared by incipient wetness impregnation of SiO₂ with Co nitrate solution (12.7 wt.% and 21.9 wt.%). FTS reaction rates and selectivities at different space velocities showed that CO conversion and C₅₊ selectivity increased while CH₄ selectivity and α -olefin to *n*-paraffin ratio decreased with increasing bed residence time. FTS reaction rates also increased with increasing bed residence time. Water, one of the reaction products, appeared to have an accelerating effect on FTS rates. Water effects on FTS rates and selectivities were examined by adding H₂O (2 ~ 8 atm) to synthesis gas feeds at low CO conversions. CO conversion rates increased with increasing water partial pressure. The selectivity to desired C₅₊ products increased and the olefin content in products also increased with increasing water partial pressure. The beneficial effect of water on the FTS rate and product distribution reflects an increase in the rate of chain growth and in chain termination to α -olefins.

D₂O tracer studies are being carried out on Co catalysts by co-feeding 2 atm D₂O with 20 atm synthesis gas (13.8 % D in the feed). The D contents in the primary products (C₄-C₈) and in the H₂ isotopomers increased as the bed residence time increased. This indicates that water dissociation is not quasi-equilibrated in the Co-catalyzed FTS. The kinetic isotope effect (KIE) was also studied by comparing the FTS rates in flowing H₂/CO/N₂ (62/31/7) and D₂/CO/N₂ (62/31/7). The ratio of methane formation rate ($k_{\text{CH}_4}/k_{\text{CD}_4}$) was 1.34, suggesting the involvement

of hydrogen dissociation in the rate-determining step. In contrast, KIE were less than worthy for steps leading to the formation of higher molecular weight olefins, suggesting that chain termination to olefins is larger for deuterium containing chains. In the next report, we will discuss the mechanistic implications of these findings.

Task 1. Iron Catalyst Preparation

The objective of this task is to produce robust intermediate- and high- α catalysts.
No scheduled or further activity to report.

Task 2. Catalyst Testing

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

No scheduled or further activity to report.

Task 3. Catalyst Characterization

The objective of this task is to obtain characterization data of the prepared catalysts using routine and selected techniques.

Mössbauer Spectroscopy of Iron-Based Fischer-Tropsch Catalysts: Impact of Activation Procedure

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Abstract

The impact of activation procedure on the phase composition of precipitated iron Fischer-Tropsch (FT) catalysts has been studied. Catalyst samples taken during activation and FT synthesis have been characterized by Mössbauer spectroscopy. Formation of iron carbide is necessary for high FT activity. Hydrogen activation of precipitated iron catalysts results in reduction to predominantly metallic iron and Fe_3O_4 . Metallic iron is not stable under FT conditions and is rapidly converted to ϵ' - $\text{Fe}_{2.2}\text{C}$. Activation with carbon monoxide or syngas with low hydrogen partial pressure reduces catalysts to χ - Fe_5C_2 and a small amount of superparamagnetic carbide. Exposure to FT conditions partially oxidizes iron carbide to Fe_3O_4 ; however, catalysts promoted with potassium or potassium and copper maintain a constant carbide content and activity after the initial oxidation. An unpromoted iron catalyst which was activated with carbon monoxide to produce 94% χ - Fe_5C_2 , deactivated rapidly as the carbide was oxidized to Fe_3O_4 . No difference in activity, stability or deactivation rate was found for χ - Fe_5C_2 and ϵ' - $\text{Fe}_{2.2}\text{C}$.

Introduction

Iron Fischer-Tropsch (FT) catalysts undergo numerous phase changes which may have profound effects on catalyst activity (1-3), selectivity (4), attrition (5) and deactivation (6). Precipitated and fused iron catalysts are typically oxides before use and need to be activated by reducing to the zero valent state. The activation procedure generally involves reducing with hydrogen to metallic iron or with carbon monoxide or syngas to various iron carbides. Metallic iron, produced by hydrogen activation, is rapidly converted to iron carbides when exposed to syngas under FT conditions (2,3). Additional phase transformations may occur during FT synthesis. Water is a primary product of the FT synthesis and may reach concentrations high enough to oxidize iron carbides to Fe_3O_4 (7). In addition, carbon dioxide produced by the water-gas shift reaction can reach oxidizing concentrations at high conversion (7). A thermodynamic study of the iron carbide/oxide system under typical FT conditions has shown that both Fe_3O_4 and iron carbide are thermodynamically favored (8).

Several iron carbides have been identified in active iron FT catalysts. Among these are: $\chi\text{-Fe}_5\text{C}_2$, $\epsilon'\text{-Fe}_{2.2}\text{C}$, $\theta\text{-Fe}_3\text{C}$ and Fe_7C_3 . The thermal stability of $\chi\text{-Fe}_5\text{C}_2$, $\epsilon'\text{-Fe}_{2.2}\text{C}$, and $\theta\text{-Fe}_3\text{C}$ carbides with increasing temperature has been reported to be: $\epsilon'\text{-Fe}_{2.2}\text{C} \leq \chi\text{-Fe}_5\text{C}_2 < \theta\text{-Fe}_3\text{C}$ (9, 10). Conducting FT synthesis at moderate to low temperatures ($<270^\circ\text{C}$) generally results in $\chi\text{-Fe}_5\text{C}_2$ and/or $\epsilon'\text{-Fe}_{2.2}\text{C}$ formation (2, 3). The $\theta\text{-Fe}_3\text{C}$ and Fe_7C_3 carbides have been reported at high temperature FT synthesis with fused iron catalysts (7). The role of iron carbides in FT synthesis has been debated since Fischer and Tropsch proposed hydrocarbons were formed by the hydrogenation of bulk iron carbide (11). Emmett demonstrated that hydrocarbons synthesized over a ^{14}C labeled iron carbide catalyst had lower radioactivity than the catalyst thereby demonstrating that bulk iron carbide does not directly participate in hydrocarbon production; however, Emmett did not rule out the possibility that a surface carbide was involved in hydrocarbon production (12). Subsequent studies with ^{13}C tracers have verified that carbon on the surface of carbided catalysts does become incorporated in FT products (13).

In addition to iron carbides, Fe_3O_4 (magnetite) is generally found in used iron FT catalysts. Magnetite has been reported to be both active (14) and inactive for FT synthesis (1). The discrepancy may be due to oxidation of iron carbides by improper passivation prior to analysis (15). Metallic iron has also been proposed to be active for FT synthesis (5). This is unlikely because thermodynamic data predict metallic iron will either be oxidized to Fe_3O_4 or converted to iron carbide(s) depending on the conversion level (8).

Herein, the impact of hydrogen, carbon monoxide and syngas activation on the phase composition of precipitated iron catalysts will be presented. Correlations between phase composition and FT activity and deactivation will be discussed.

Experimental

Catalysts with atomic composition 100Fe/4.6Si/1.0K, 100Fe/4.6Si/2.7Cu/1.0K, 100Fe/3.7Si/0.7K and an unpromoted catalyst were prepared by continuous precipitation and incipient wetness impregnation of promoters as previously described (1). A commercially prepared catalyst with mass composition 100Fe/8.9Cu/1.9K/67kaolin was obtained from United Catalysts Inc. Catalyst and Ethlyflo 164 (Ethyl) C_{30} oil were charged into a one liter autoclave operated as a continuous stirred tank reactor (cstr). Hydrogen activation was conducted by heating the reactor to 220°C at 120°C/h with hydrogen flow of 120 l h^{-1} (STP) at ambient

pressure; conditions were maintained for 24 hours. Activation with carbon monoxide was conducted at 270°C for 24 hours at 1.3 MPa pressure with a space velocity of 2 l h⁻¹ g-Fe⁻¹ (STP). Syngas activations were conducted at 270°C for 24 hours with H₂/CO=0.7 and space velocity of 3.1 l h⁻¹ g-Fe⁻¹ (STP) at either ambient pressure or 1.3 MPa. Fischer-Tropsch synthesis was conducted at 270°C, H₂/CO=0.7, space velocity=3.1 l h⁻¹ g-Fe⁻¹ (STP) and 1.3 MPa pressure.

Catalyst/slurry samples were removed from the reactor periodically during activation and throughout FT synthesis. Mössbauer spectra were obtained with a conventional constant acceleration spectrometer using 30 mCi ⁵⁷Co in rhodium matrix. Catalyst compositions are given as percent of total iron. For example, 80% Fe₅C₂ refers to 80% of the total iron in the catalyst being in Fe₅C₂.

Results

Hydrogen activation

Mössbauer spectroscopy data of 100Fe/4.6Si/2.7Cu/1.0K catalyst during hydrogen activation are shown in Figure 1. Exposure of the catalyst to hydrogen at 220°C for 2 hours resulted in the catalyst being partially reduced to 20% Fe₃O₄ with the remaining 80% a superparamagnetic species. During the course of the activation, the Fe₃O₄ phase increased at the expense of the superparamagnetic species. Metallic iron (10%) was first detected after 10 hours of activation and after 24 hours of activation the catalyst composition was 65% Fe₃O₄, 24% metallic iron and 11% superparamagnetic species.

Exposure of the hydrogen activated catalyst to syngas at FT conditions caused rapid phase changes. Within 3 hours of starting FT synthesis, the superparamagnetic species had disappeared, the metallic iron decreased to 4% and ε'-Fe_{2.2}C (34%) was formed. Following 20 hours of FT synthesis, the Fe₃O₄ had decreased slightly to 59% and the remainder of the catalyst was ε'-Fe_{2.2}C. Catalyst composition and syngas conversion as a function of time on stream are shown in Figure 3. The catalyst had high initial syngas conversion (85%) and deactivated slowly at the rate of 0.9% per week. The catalyst was run for over 3500 hours during which the catalyst composition remained constant at approximately 60% Fe₃O₄ and 40% ε'-Fe_{2.2}C.

Carbon monoxide activation

Phase changes for a typical iron-based catalyst during carbon monoxide activation are shown in Figure 4 (16). The 100Fe/8.9Cu/1.9K/67kaolin catalyst was initially α-Fe₂O₃ as determined by XRD and Mössbauer spectroscopy. The catalyst was reduced to 100% Fe₃O₄ during the heating from ambient temperature to 270°C (2 hours) under carbon monoxide. Iron carbide phases began to appear after 4.5 hours of activation. The first carbide phase detected was a superparamagnetic carbide; this phase increased to approximately 10% of the iron and remained constant throughout the activation. χ-Fe₅C₂ (26%) was first detected after 10 hours of activation and continued to increase at the expense of Fe₃O₄. The catalyst composition after 26 hours of activation was 90% χ-Fe₅C₂ and 10% superparamagnetic carbide. Carbon dioxide production as a function of time on stream is also plotted in Figure 4. Carbon dioxide can be produced by the reduction of α-Fe₂O₃ to Fe₃O₄ (equation 1), reduction of Fe₃O₄ to iron carbide (equation 2) and from the Boudouard reaction (equation 3).



Figure 4 shows that enough carbon dioxide was produced after 8 hours to account for 100% carbiding of the catalyst; however, Mössbauer data reveal that the catalyst was approximately 10% iron carbide at this time. By the end of carbon monoxide activation, there was approximately 60% more carbon dioxide produced than was needed to completely carbide the catalyst. This indicates that a large amount of Boudouard carbon was produced.

Figure 5 shows that the iron carbide was partially oxidized to Fe_3O_4 (8%) after 20 hours of FT synthesis. Over the remainder of the run (140 h), the Fe_3O_4 content grew to 16% with the balance a mixture of $\chi\text{-Fe}_5\text{C}_2$ and superparamagnetic carbide. Catalyst activity remained high during the run with carbon monoxide conversion greater than 65%.

An unpromoted iron catalyst was also activated with carbon monoxide under identical conditions to the catalyst described above. The catalyst was reduced to 94% $\chi\text{-Fe}_5\text{C}_2$ and 6% Fe_3O_4 after 24 hours of activation; no superparamagnetic carbide was detected. This catalyst initially had high FT activity with syngas conversion of 84%; however, the catalyst was not stable and deactivated at the rate of 3.7% syngas conversion per day. The catalyst composition changed significantly during the deactivation; as the conversion decreased, the amount of $\chi\text{-Fe}_5\text{C}_2$ decreased and the amount of Fe_3O_4 increased. The catalyst was 100% Fe_3O_4 after 450 hours of FT synthesis and the syngas conversion had decreased to 18%.

Syngas activation

Catalyst composition and syngas conversion for the 100Fe/3.6Si/0.7K catalyst activated at FT synthesis conditions, syngas ($\text{H}_2/\text{CO}=0.7$) at 270°C and 1.3 MPa, are shown in Figure 6 (16). Initial syngas conversion was 6% and it increased slowly to only 18% after 92 hours on stream; the catalyst was composed of 100% Fe_3O_4 during this time. Since the conversion was low, the catalyst was treated with carbon monoxide for 19 hours at 1.3 MPa and 270°C. The catalyst was partially reduced to 42% $\chi\text{-Fe}_5\text{C}_2$ and superparamagnetic carbide after the carbon monoxide treatment. Fischer-Tropsch synthesis was resumed and the syngas conversion increased rapidly to the same level obtained for another FT run when the catalyst was activated with carbon monoxide (Figure 6). This run was continued for 430 hours during which the syngas conversion remained close to 80% and the catalyst composition was approximately 40% $\chi\text{-Fe}_5\text{C}_2$ and superparamagnetic carbide with the remainder Fe_3O_4 .

Figure 7 shows the composition and syngas conversion for the 100Fe/3.6Si/0.7K catalyst after activation with syngas ($\text{H}_2/\text{CO}=0.7$) at ambient pressure and 270°C for 24 hours (16). In contrast to activation with syngas at 1.3 MPa, activation at ambient pressure resulted in a catalyst with high syngas conversion (82%). The catalyst composition after activation was 68% $\chi\text{-Fe}_5\text{C}_2$ and superparamagnetic carbide and 32% Fe_3O_4 . The total iron carbide content decreased to 53% during the first 24 hours and then slowly decreased to 40% after 400 hours. The remainder of the catalyst was Fe_3O_4 . Syngas conversion decreased slowly to 65% after 400 hours.

Discussion

Activation of the 100Fe/4.6Si/2.7Cu/1.0K catalyst with hydrogen at 220°C for 24 hours partially reduced the catalyst to 24% metallic iron, 11% superparamagnetic species and 65% Fe₃O₄. Exposing the activated catalyst to FT conditions caused the conversion of all of the metallic iron and superparamagnetic species and a small amount of Fe₃O₄ to ϵ' -Fe_{2.2}C. Throughout 3500 hours of FT synthesis, the catalyst composition remained constant at 40% ϵ' -Fe_{2.2}C and 60% Fe₃O₄. The catalyst had high initial activity with syngas conversion greater than 80% and a deactivation rate of only 0.9% syngas conversion per week. In contrast, activation with carbon monoxide resulted in greater than 90% of an unpromoted iron catalyst and a 100Fe/8.9Cu/1.9K/67kaolin catalyst being reduced to χ -Fe₅C₂ and a small amount of superparamagnetic iron carbide. The superparamagnetic carbide was not identified because Mössbauer data were collected at room temperature; however, this may be small particle ϵ' -Fe_{2.2}C (9). Activation with hydrogen lean syngas at ambient pressure was very similar to activation with carbon monoxide. The catalyst was composed of 68% χ -Fe₅C₂ and superparamagnetic carbide following activation.

Activation with hydrogen, carbon monoxide or syngas can result in high activity if the appropriate promoters and conditions are applied (Figure 8). Activation with hydrogen requires that the catalyst be promoted with copper to lower the reduction temperature and prevent sintering; catalysts activated with hydrogen that do not contain copper generally have lower activity and require a long induction period (17). In addition, a high space velocity of hydrogen is required to maintain a low water partial pressure in the reactor and thereby prevent sintering of metallic iron (7). In the case of syngas activation, a low hydrogen partial pressure is required to minimize the water concentration in the reactor which if too high prevents Fe₃O₄ from being reduced to χ -Fe₅C₂ (1). If the activation procedure is conducted properly, hydrogen, carbon monoxide or syngas activated catalysts will have similar activity. There does not seem to be a difference in the activity of hydrogen activated catalysts where the carbide phase of the active catalyst is ϵ' -Fe_{2.2}C and the activity of carbon monoxide or syngas activated catalysts where the predominant carbide phase is χ -Fe₅C₂. Likewise the deactivation characteristics of hydrogen, carbon monoxide and syngas activated catalysts are very similar over the span of at least 1000 hours (8). This is surprising because it has been reported that ϵ' -Fe_{2.2}C is not as active as χ -Fe₅C₂ and the transformation of ϵ' -Fe_{2.2}C into χ -Fe₅C₂ has been identified as a cause of deactivation of iron catalysts (6). Although there is no difference in activity of ϵ' -Fe_{2.2}C and χ -Fe₅C₂, a strong correlation between iron carbide content and FT activity has been observed. An unpromoted iron catalyst immediately following carbon monoxide activation was composed of 92% χ -Fe₅C₂ and 8% Fe₃O₄. The catalyst gradually oxidized to Fe₃O₄ during FT synthesis and after 450 hours was 100% Fe₃O₄. Catalyst activity, as measured by syngas conversion, decreased linearly from 84% to 19% as the catalyst was oxidized. Although the syngas conversion was 19% after the catalyst had been oxidized to Fe₃O₄, it is possible that the low activity was due to a small amount of iron carbide not detectable by Mössbauer spectroscopy (<5%) and not Fe₃O₄.

Catalysts which had stable activity were composed of 40% to 85% iron carbide and 60% to 15% Fe₃O₄ throughout FT synthesis. The question of how a catalyst can be partially and not completely oxidize during FT synthesis can be answered by thermodynamic analysis of the C/H/O/Fe system (8). A phase diagram of the C/H/O system is shown in Figure 9. The diagram is a ternary plot on the basis of mole % of C, H and O of the gases in the reactor atmosphere (CO, CO₂, H₂, H₂O and CH_x) at 300°C and 1.5 MPa. Iron carbide and carbon are the stable phases in

Region A, iron carbide, Fe_3O_4 and carbon are the stable phases in Region B, Fe_3O_4 and carbon are the stable phases in Region C and Fe_3O_4 is the stable phase in region D. Composition of the reactor atmosphere at syngas conversion ranging from 29% to 84% are shown on the phase diagram for a typical FT catalyst. The gas composition of the reactor atmosphere over this range of conversions lies close to the boundary of iron carbide/carbon and iron carbide/ Fe_3O_4 /carbon regions. Another possible explanation for the presence of both iron carbide(s) and Fe_3O_4 is inhomogeneity within catalyst particles. The ultimate particle size of a precipitated iron catalyst is on the order of 200 Å and these particles form agglomerates which can be smaller than 1 μm or as large as 250 μm. Conversion of carbon monoxide and hydrogen to carbon dioxide, water and hydrocarbons in the interior of these agglomerates can cause the water and carbon dioxide concentrations within the particles to be higher than at the surface of the agglomerate which is exposed to the bulk gas phase. This could lead to the formation of particles with a Fe_3O_4 core and an iron carbide surface.

Conclusions

Formation of an iron carbide is necessary for high activity with precipitated iron catalysts. A precipitated iron catalyst (100Fe/4.6Si/2.7Cu/1.0K) which was activated with hydrogen at 220°C and ambient pressure was partially reduced to metallic iron and Fe_3O_4 . Metallic iron was not stable under FT conditions and exposure to syngas ($\text{H}_2/\text{CO}=0.7$) at 270°C and 1.3 MPa converted all of the metallic iron to ϵ' - $\text{Fe}_{2.2}\text{C}$. Catalysts activated with carbon monoxide (unpromoted iron and 100Fe/8.9Cu/1.9K/67kaolin) or syngas with low hydrogen partial pressure (100Fe/3.6Si/0.7K) at 270°C produced predominantly χ - Fe_5C_2 and had high initial syngas conversion. Activation with syngas at 270°C and 1.3 MPa partially reduced the 100Fe/3.6Si/0.7K catalyst to 100% Fe_3O_4 which resulted in low FT activity. Iron carbides produced by carbon monoxide and syngas activation of promoted catalysts were partially oxidized to Fe_3O_4 during the first 24 hours of FT synthesis; however, these catalysts deactivated slowly. There was no difference in the activity, stability or deactivation characteristics of ϵ' - $\text{Fe}_{2.2}\text{C}$ and χ - Fe_5C_2 under the FT conditions employed in this study. Catalysts with stable activity maintained a constant iron carbide level. An unpromoted iron catalyst deactivated more rapidly than iron catalysts promoted with potassium, copper and a nonreducible metal oxide. The deactivation of the unpromoted iron catalyst was caused by oxidation of active iron carbide to inactive/less active Fe_3O_4 .

The presence of iron carbides and Fe_3O_4 together can be explained by inhomogeneity of gases within individual catalyst particles. Water and carbon dioxide produced by conversion of syngas within catalyst particles can cause the environment inside a particle to be oxidizing while the surface is exposed to reducing conditions of the reactor atmosphere. This would result in the formation of a Fe_3O_4 core and an iron carbide outer layer. Another possibility is that under typical FT conditions the redox potential of the reactor atmosphere lies within the narrow region of the C/H/O/Fe phase diagram where Fe_3O_4 and iron carbides can coexist.

Acknowledgment

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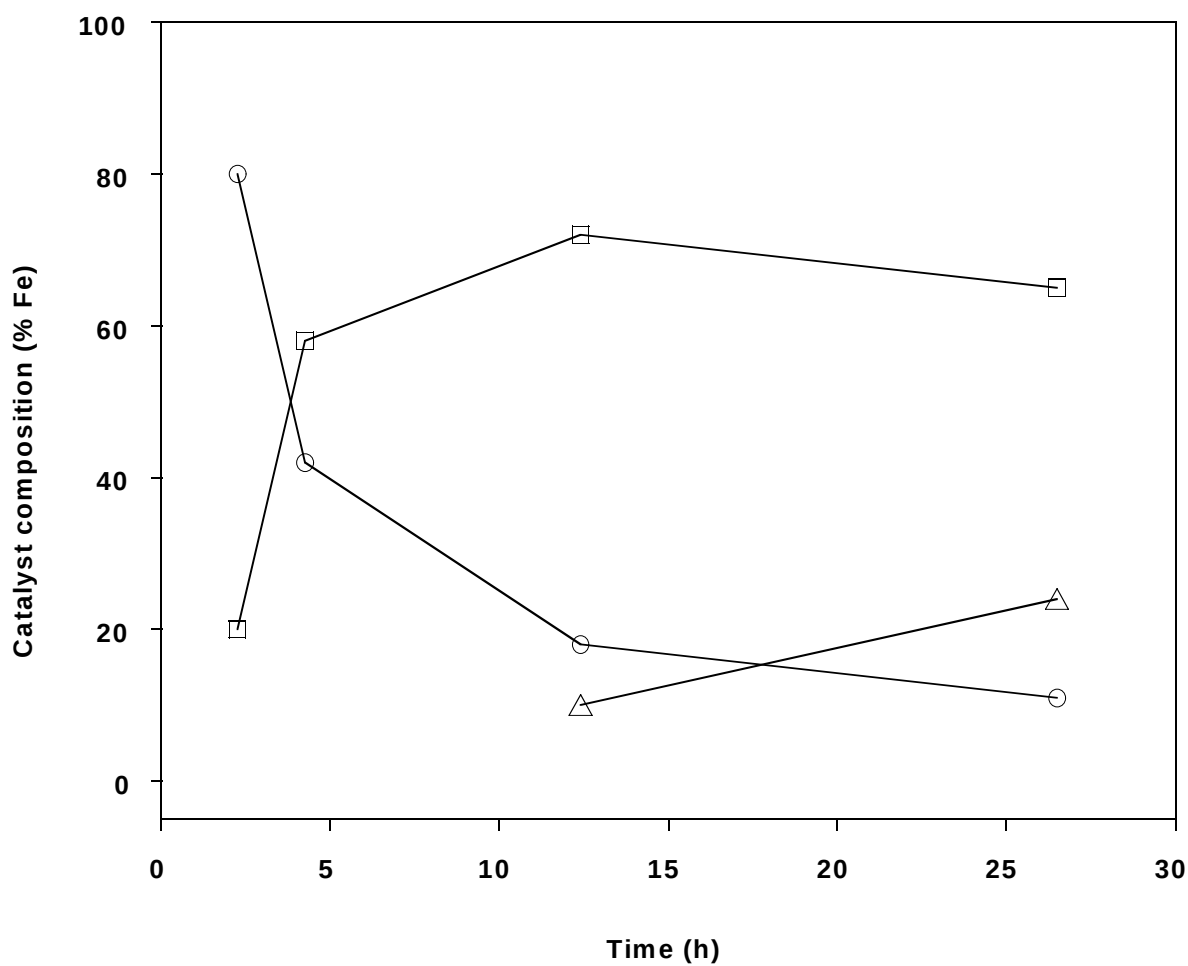


Figure 1. Phase composition changes of 100Fe/4.6Si/2.7Cu/1.0K catalyst during activation with H_2 at 220°C, 0.1 MPa. (○), superparamagnetic oxide; (□), Fe_3O_4 ; (△), Fe^0 .

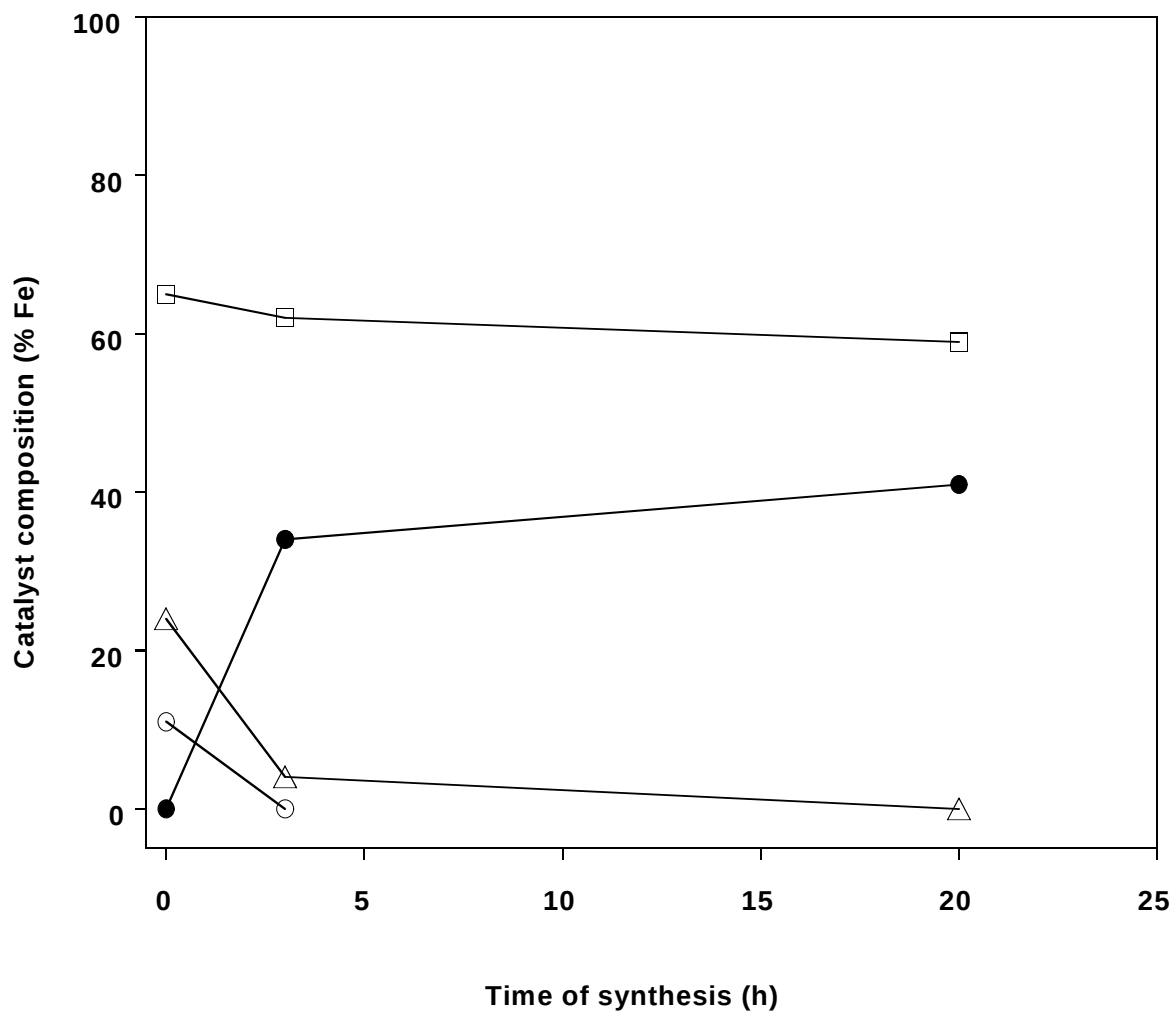


Figure 2. Phase composition changes of H₂ activated 100Fe/4.6Si/2.7Cu/1.0K catalyst during first 24 hours of FT synthesis (270°C, 1.3 MPa, H₂/CO=0.7, whsv=3.1 sl h⁻¹ g-Fe⁻¹). (○), superparamagnetic oxide; (□), Fe₃O₄; (△), Fe⁰; (●), ε'-Fe_{2.2}C.

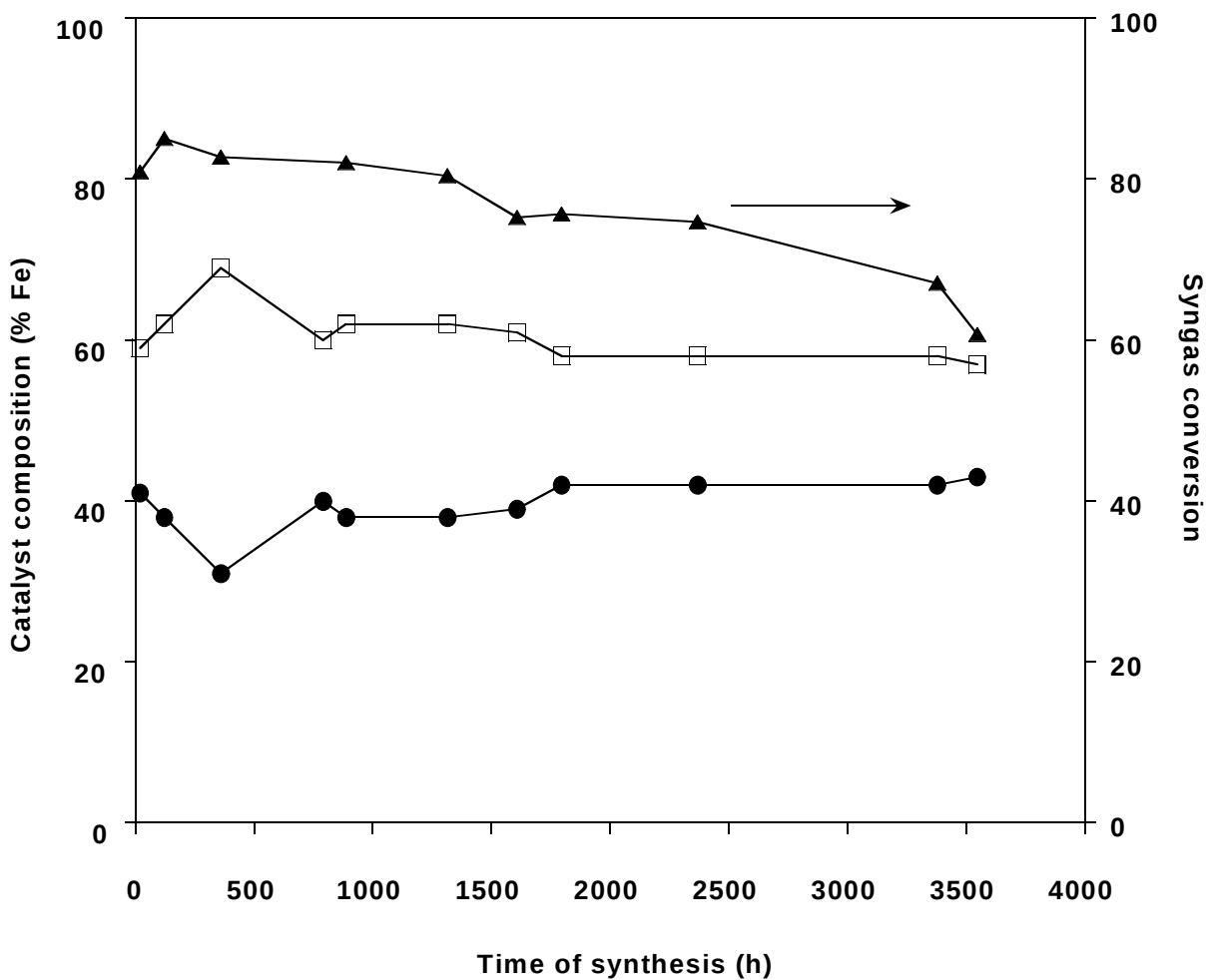


Figure 3. Long term phase composition of H_2 activated 100Fe/4.6Si/2.7Cu/1.0K catalyst during FT synthesis (270°C , 1.3 MPa, $\text{H}_2/\text{CO}=0.7$, $\text{whsv}=3.1 \text{ sl h}^{-1} \text{ g-Fe}^{-1}$). (□), Fe_3O_4 ; (●), ϵ' - $\text{Fe}_{2.2}\text{C}$; (▲), syngas conversion.

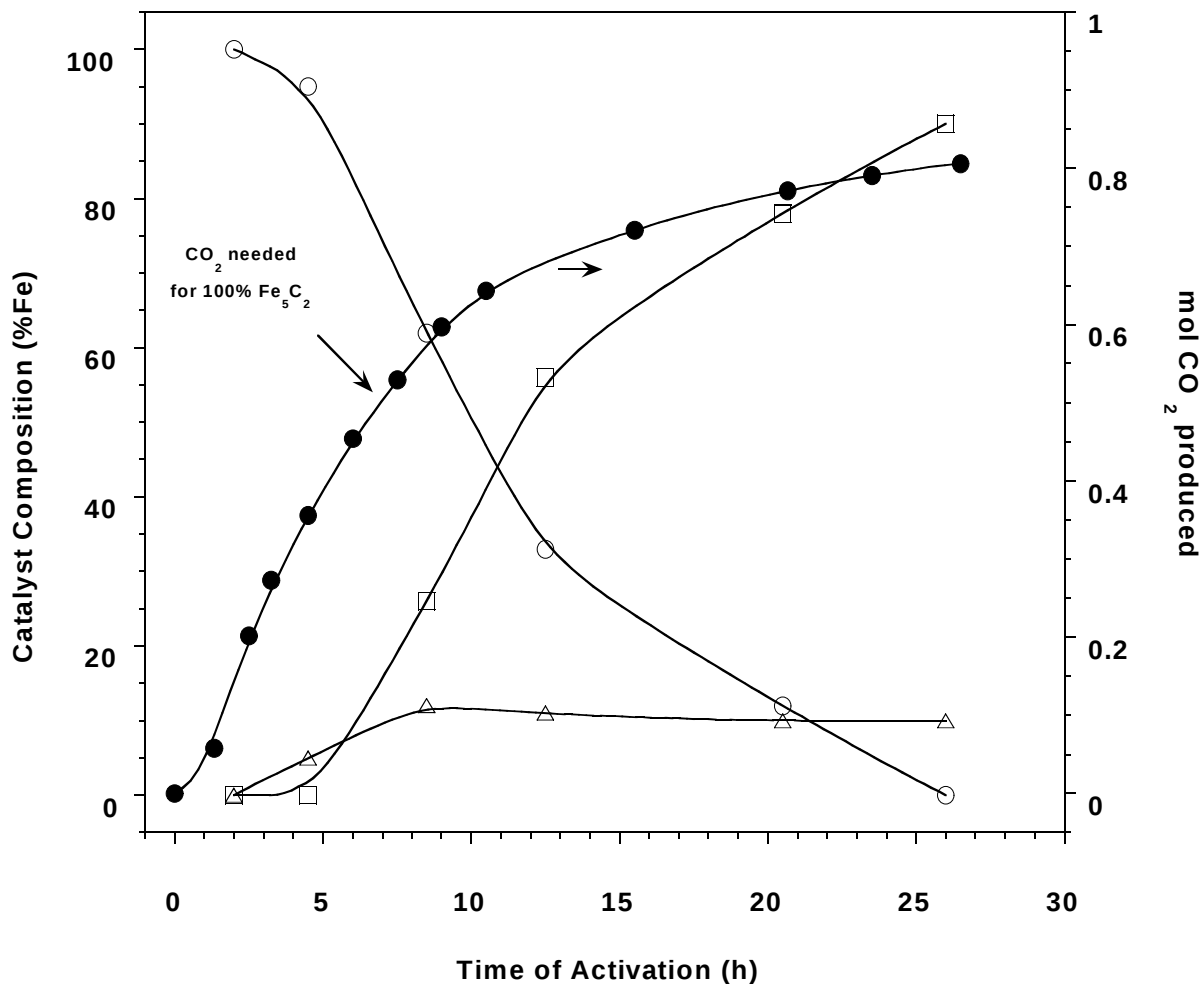


Figure 4. Phase composition changes of commercial 100Fe/8.9Cu/1.9K/67kaolin catalyst and moles of CO_2 generated during CO activation. ($\circ$), Fe_3O_4 ; ($\square$), $\chi\text{-Fe}_5\text{C}_2$; ($\triangle$), superparamagnetic carbide; ($\bullet$), moles of CO_2 . Mössbauer data from reference 16.

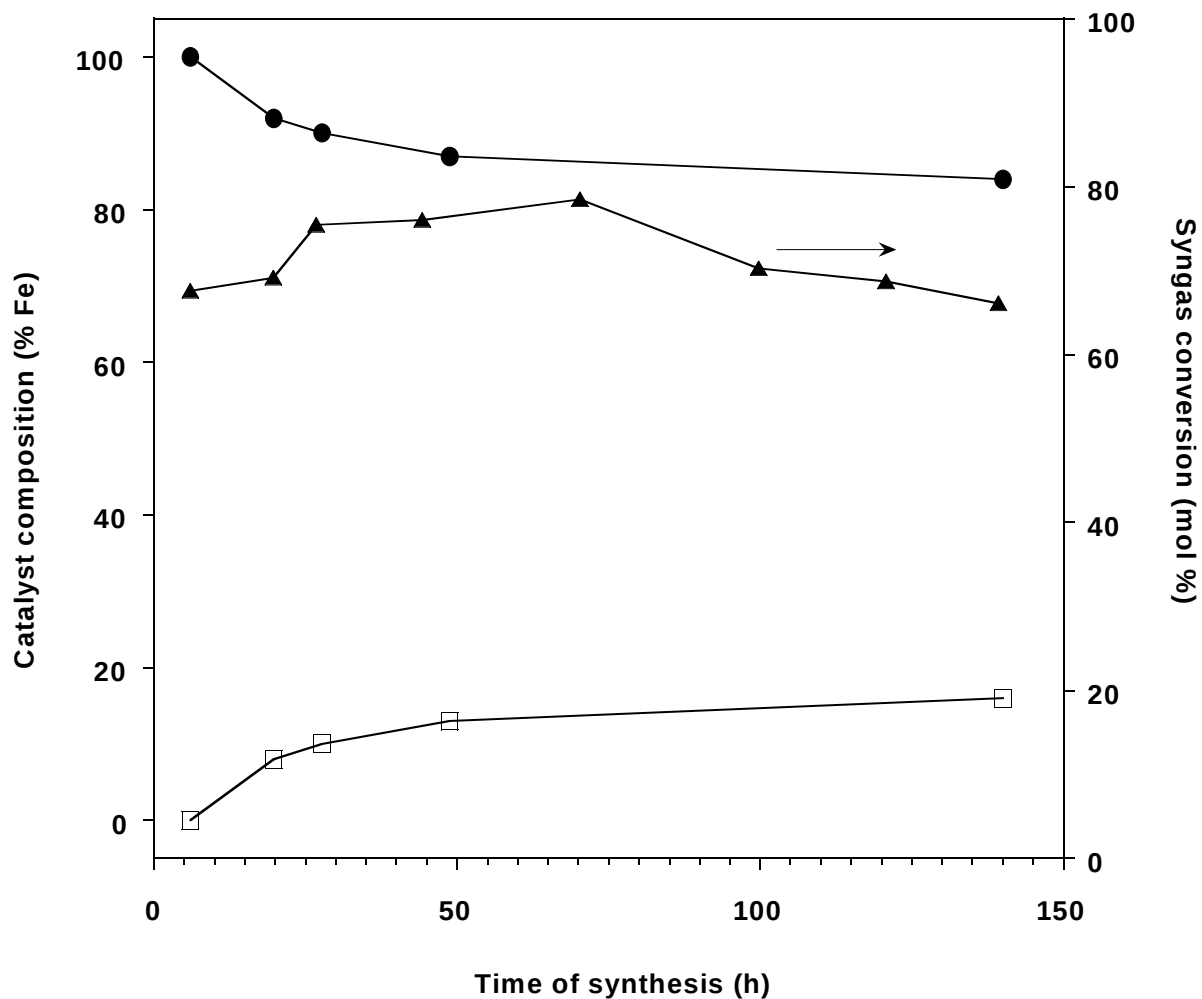


Figure 5. Phase composition of CO activated 100Fe/8.9Cu/1.9K/67kaolin catalyst during FT synthesis (270°C, 1.3 MPa, H₂/CO=0.7, whsv=3.1 sl h⁻¹ g-Fe⁻¹). (●), χ -Fe₅C₂ and superparamagnetic carbides; (□), Fe₃O₄; (▲), syngas conversion. Data from reference 16.

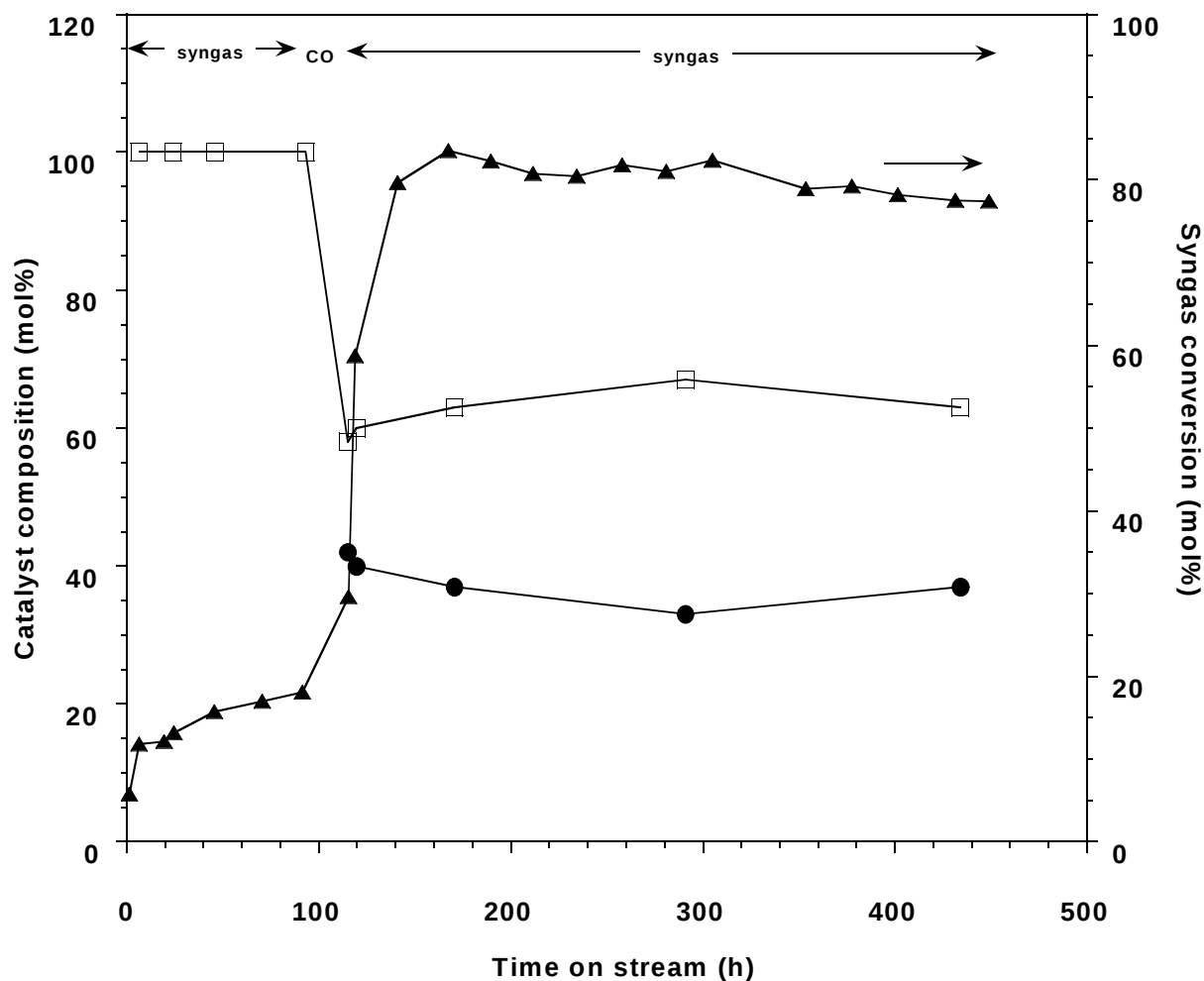


Figure 6. Phase composition of 100Fe/3.7Si/0.7K catalyst during syngas activation at 270°C, 1.3 MPa followed by CO treatment at 270°C, 1.3 MPa followed by FT synthesis (270°C, 1.3 MPa, H₂/CO=0.7, whsv=3.1 sl h⁻¹ g-Fe⁻¹). (□), Fe₃O₄ and superparamagnetic oxide; (●) χ-Fe₅C₂ and superparamagnetic carbides; (▲) syngas conversion. Data from reference 16.

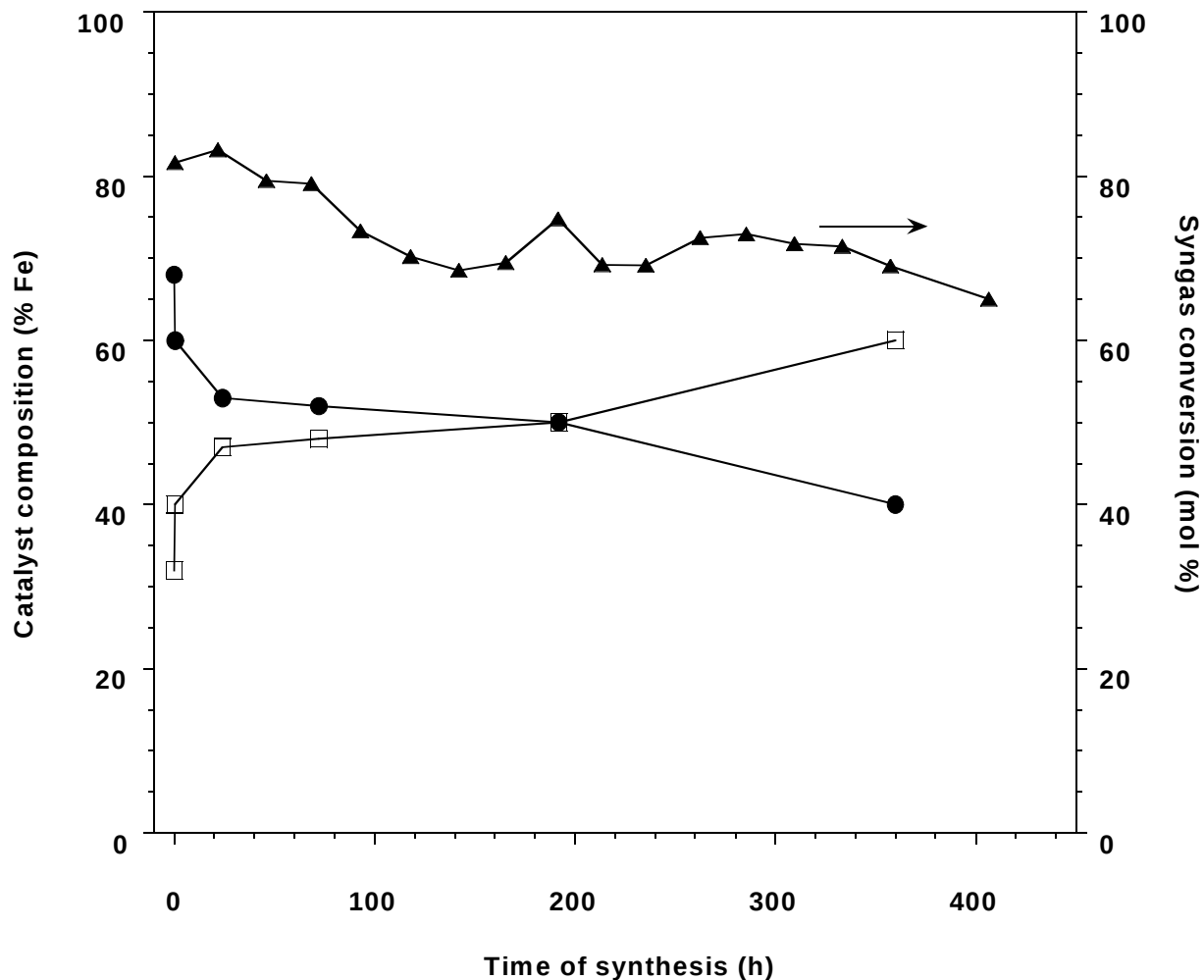


Figure 7. Phase composition of syngas activated ($H_2/CO=0.7$, 0.1 MPa, 270°C) 100Fe/3.7Si/0.7K catalyst during FT synthesis (270°C, 1.3 MPa, $H_2/CO=0.7$, $whsv=3.1 \text{ sl h}^{-1} \text{ g-Fe}^{-1}$). (●), χ -Fe₅C₂ and superparamagnetic carbides; (□), Fe₃O₄; (▲) syngas conversion. Data from reference 16.

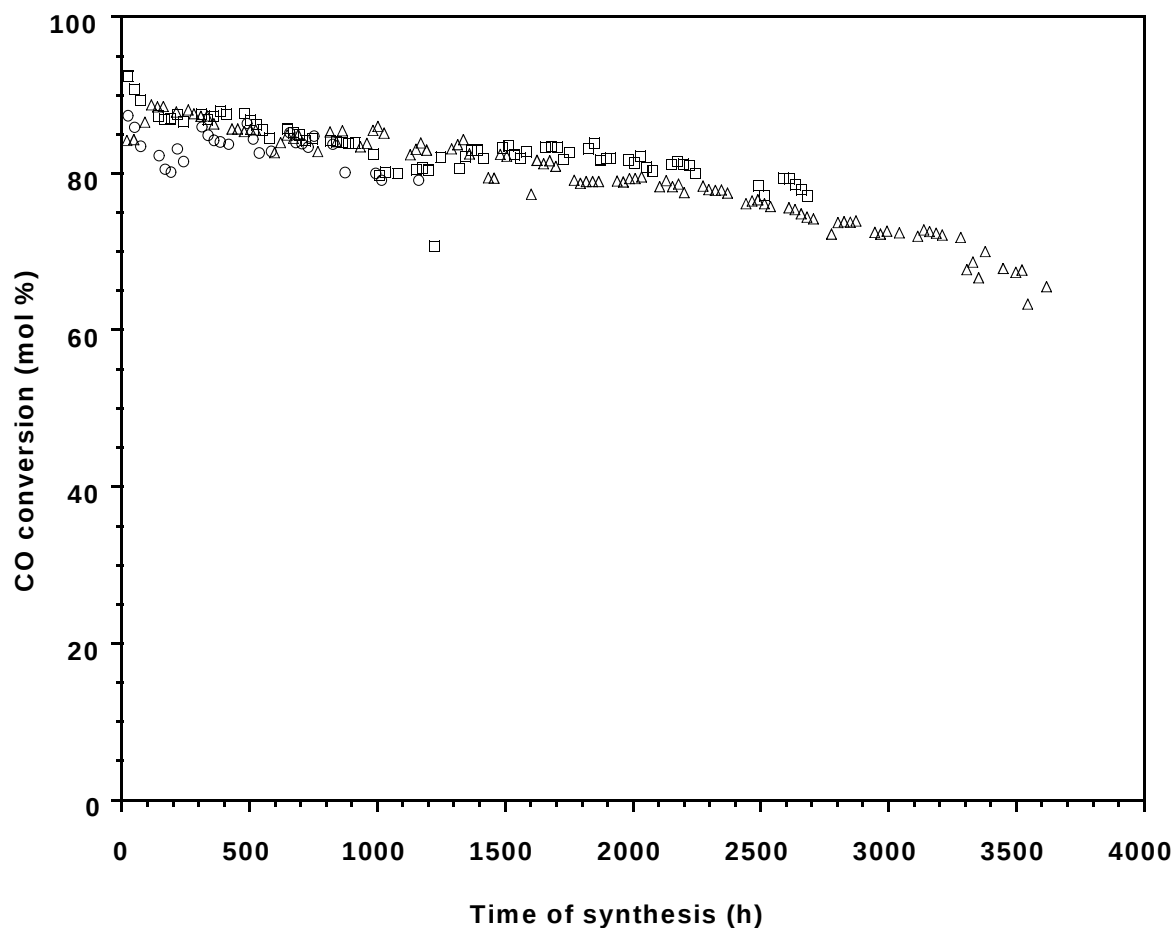


Figure 8. Comparison of CO conversion for (○), 100Fe/4.6Si/1.0K activated with CO at 270°C, 0.1 MPa; (□), 100Fe/4.6Si/1.0K, activated with syngas ($H_2/CO=0.7$) at 270°C, 0.1 MPa; and (△) 100Fe/4.6Si/2.0Cu/1.0K activated with H_2 at 220°C, 0.1 MPa. FT conditions: 270°C, 1.3 MPa, $H_2/CO=0.7$, $whsv=3.1 \text{ sl h}^{-1} \text{ g-Fe}^{-1}$).

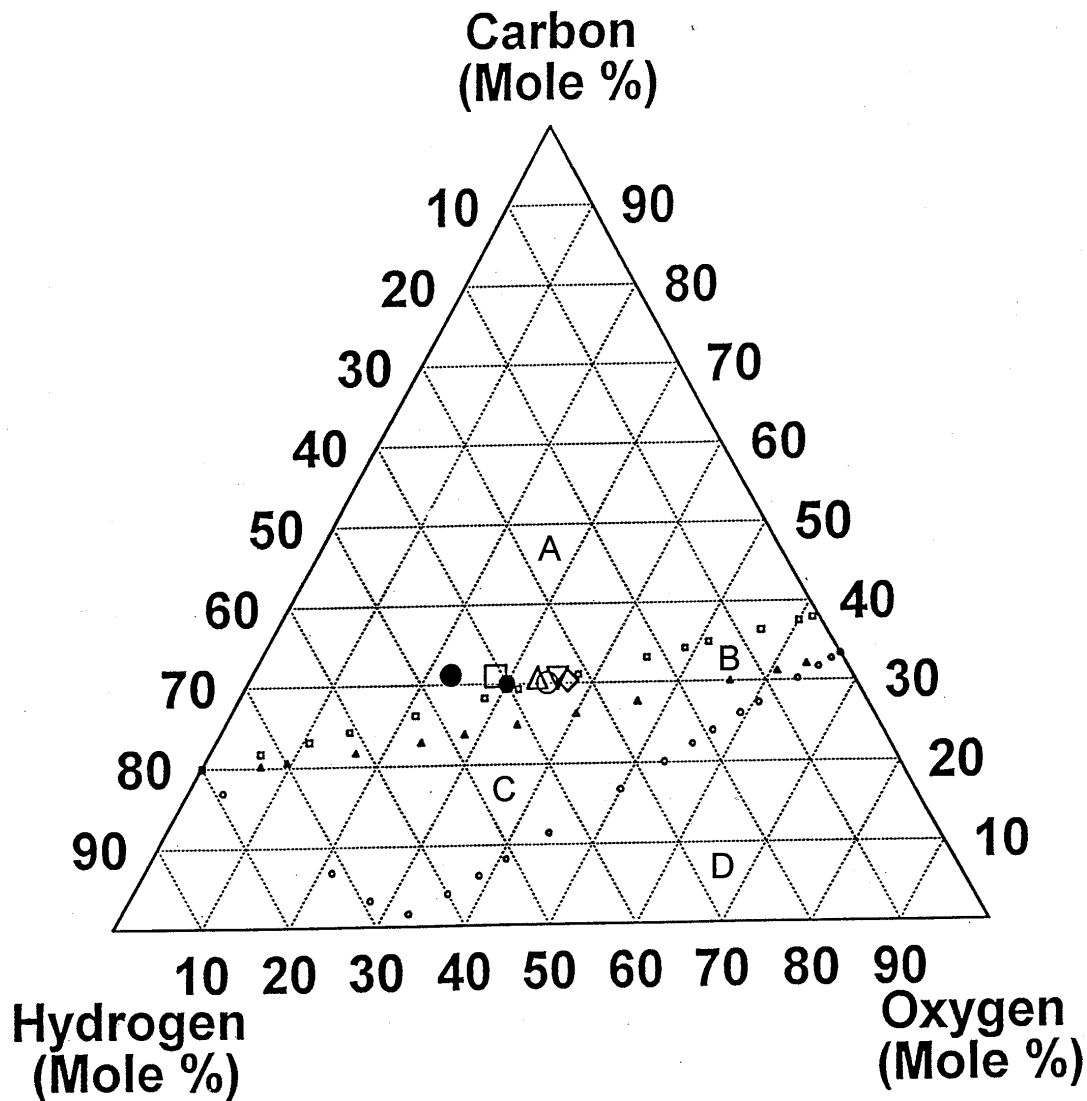


Figure 9. Ternary phase diagram for solid phase(s) present for graphite/gases (○), Fe/Fe₃O₄/gases (□) and Fe/Fe₃C/gases (△) at equilibrium at 300°C and 1.5 MPa. Region A: Fe₃C and C; Region B: Fe₃O₄, Fe₃C and C; Region C: Fe₃O₄ and C; Region D: Fe₃O₄. Gases = H₂O, CO, CO₂, H₂ and CH₄. Gas phase composition during FT synthesis (270°C, 1.3 MPa) at various conversions: CO=86%, H₂=80% (●); CO=78%, H₂=76% (□); CO=68%, H₂=69% (△); CO=46%, H₂=54% (◇); CO=32%, H₂=45% (∇); CO=23%, H₂=37% (○) and syngas composition of H₂/CO=0.67 (●).

Task 4. Wax/Catalyst Separation

The objective of this task is to develop techniques for the separation of catalysts from FT reactor slurries.

No scheduled or further activity to report.

Task 5. Oxygenates

The objective of this task is to obtain a better understanding of the factors that affects catalyst selectivity toward oxygenates for iron-based Fischer-Tropsch catalysts.

No scheduled or further activity to report.

Task 6. Literature Review of Prior Fischer-Tropsch Synthesis with Co Catalysts

The objective of this task is to prepare a critical review of prior work on cobalt Fischer-Tropsch catalysts.

This task is approximately 90% complete. Due to the size of the document, it has been submitted as a separate report to the AAD Document Control labeled Task 6.

Task 7. Co Catalyst Preparation

The objective of this task is to prepare a limited number of cobalt-based Fischer-Tropsch catalysts that can be used to obtain baseline data on cobalt-based Fischer-Tropsch synthesis.

No scheduled or further activity to report.

Task 8. Cobalt Catalyst Testing for Activity and Kinetic Rate Correlations

The objective of this task is to conduct initial screening of the cobalt catalysts prepared in Task 7 to select three baseline catalysts that will then be used to generate a data base on the performance of cobalt-based Fischer-Tropsch catalysts in slurry reactors.

No scheduled or further activity to report.

Task 9. Cobalt Catalyst Life Testing

The objective of this task is to obtain life data on baseline cobalt Fischer-Tropsch catalysts.

No scheduled or further activity to report.

Task 10. Cobalt Catalyst Mechanism Study

The objective of this task is to determine the impact of secondary reactions on the relationship of cobalt Fischer-Tropsch catalysts under conditions appropriate to slurry bubble column reactors.

No scheduled or further activity to report.

Task 11. University of California, Berkeley (Subcontract)

The objective of this task is the characterization of the structure and function of active sites involved in the synthesis of high molecular weight hydrocarbons from CO and H₂ on multi-component catalysts based on Fe as the active component.