VIII Catalyst Characterization

The goals of this task are to: (a) provide basic characterization of all catalyst prepared (atomic absorption analysis, surface area, X-ray diffraction); (b) determine bulk iron phases after the pretreatment and during Fischer-Tropsch synthesis in fixed bed and/or slurry reactors by XRD and Mössbauer effect spectroscopy (at University of Kentucky); and (c) study reduction behavior of iron F-T catalysts by isothermal and temperature programmed reduction (TPR). These studies may lead to activity-structure relationships, and better understanding of the factors which influence catalyst activity, selectivity and longevity.

Results obtained under this task are described in Chapters III-VII and Chapter IX of this report, in sections titled Catalyst Characterization Studies.

IX Testing of Alternative Catalysts

Although catalysts B and C have desirable activity and selectivity characteristics, they may not have a sufficient mechanical strength and attrition properties required for utilization in commercial bubble column slurry reactors. This task has been undertaken with the objective to test catalysts with potentially improved mechanical and attrition properties. Four supported catalysts were synthesized (see Appendix 1 for details) by conventional impregnation of two commercial supports (silica - Davison grade 952; and alumina - Vista B). Nominal compositions (on mass basis) of synthesized catalysts are: (1) 100 Fe/5 Cu/6 K/139 SiO_2 (2) 100 Fe/10 Cu/6 K/134 SiO_2, (3) 100 Fe/5 Cu/6 K/139 Al_2O_3 and (4) 100 Fe/10 Cu/6 K/134 Al_2O_3. The corresponding weight % of iron (as metal) in the prepared catalysts is about 33.8%.

Reduction behavior of the four supported catalysts was studied by both temperature programmed and isothermal reduction in hydrogen, and by isothermal reduction in CO at 280°C. Also, two precipitated promoted iron catalysts, containing aluminum oxide as a binder, were characterized by isothermal reduction in the TGA unit with hydrogen at 240°C and 280°C. Nominal compositions of these two catalysts are: 100 Fe/5 Cu/4.2 K/20 Al_2O_3 and 100 Fe/5 Cu/4.2 K/31.6 Al_2O_3. These catalysts were synthesized earlier in our laboratory during DOE contract DE-AC22-85PC80011 using the procedure described in Appendix 1. Composition of these two catalysts is similar to our catalysts C and B, except that aluminum oxide was used as a binder instead of silicon oxide. Results from catalyst characterization studies are described in section IX-1, whereas results from three slurry reactor tests of catalysts 100 Fe/5 Cu/4.2 K/20 Al_2O_3 (run SA-0097), 100 Fe/5 Cu/6 K/139 SiO_2 (SB-0627) and 100 Fe/5 Cu/9 K/139 Al_2O_3 (SB-2337) are described in section IX-2.

IX-1 Catalyst Characterization Studies

Elemental Analysis and BET Surface Area Measurements

Elemental compositions of the four catalysts prepared by impregnation of the two supports, determined by Huffman Laboratories, Inc., are listed in Table IX-1.1. In general, amounts of promoters (Cu and K), relative to metallic iron, are in good agreement with their intended (nominal) amounts. However, experimentally determined amounts of silica and alumina are in all cases less than the expected amounts, which is due to experimental errors (incomplete dissolution of these two oxides and errors in their quantification).

The BET surface areas of calcined supports (air at 500°C for 5 h) were 308 m^2/g (Davison silica support) and 195 m^2/g (Vista B alumina support), whereas the corresponding pore volumes were 0.7 cm^3/g and 0.45 cm^3/g (Table IX-1.1).

The surface areas of impregnated supports (after calcination at 300°C for 5 h) determined by single point BET method in the Pulse Chemisorb 2705 unit are also summarized in Table IX-1.1. The BET surface area of silica supported catalysts (100 Fe/5 Cu/6 K/139 SiO_2 and 100 Fe/10 Cu/6 K/134 SiO_2) is about 94-103 m^2/g, and that of alumina supported catalysts (100 Fe/5 Cu/6 K/139 Al_2O_3 and 100 Fe/5 Cu/6 K/134 Al_2O_3) is 94-136 m^2/g. Comparing the BET surface areas of supports before and after the impregnation it is observed that the surface areas of both supports (252 m^2/g for silica and 213 m^2/g for alumina) is reduced markedly (to about 94-136 m^2/g) after the addition of iron, copper, and potassium. The decrease in surface area of the supports is attributed to the pore filling and/or pore blocking of mesopores during the impregnation step.

Temperature Programmed Reduction (TPR)

Results from TPR measurements (peak positions and degree of reduction) of the four supported catalysts are summarized in Table IX-1.2.

Figure IX-1.1 illustrates TPR profiles of 100 Fe/x Cu/ 6 K/y SiO_2 catalysts (where x= 5 or 10; y = 134 or 139) prepared by impregnation of the Davison silica support. The peak positions for the catalyst having smaller amount of copper promoter (5 pbw of Cu per 100

Table IX-1.1 Elemental Analysis and Textural Properties of Supports and Supported Catalysts

Catalyst or Support	Composition by AAS# 100 Fe/x Cu/y K/z SiO_2	Surface area*, m^2/g		Pore Volume, cm^3/g
		Single Point	BET Plot	
Silica (Davison, grade 952)**	-	252	308	0.70
Alumina (Vista B)**	-	213	195	0.45
100 Fe/5 Cu/6 K/139 SiO_2	100 / 5 / 5.6 / 125	100		
100 Fe/10 Cu/6 K/134 SiO_2	100 / 8.9 / 5.7 / 122	94		
100 Fe/5 Cu/6 K/139 Al_2O_3	100 / 4.8 / 5.7 / 119	136		
100 Fe/10 Cu/6 K/134 Al_2O_3	100 / 8.3 / 5.4 / 97	94		

* Samples were degassed at 200°C in He flow (50 cm^3/min) for 2.5 hours.
** Calcined in air at 500°C for 5 h.
# measurements conducted at Huffman Laboratories, Inc.

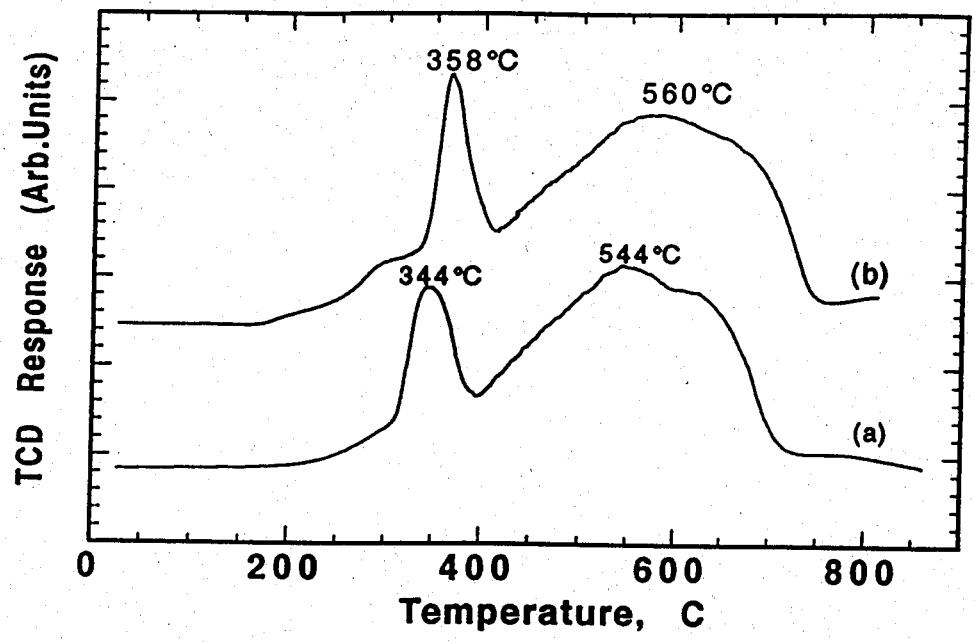

Figure IX-1.1 Effect of copper addition on the TPR behavior of silica supported iron catalysts: (a) 100 Fe/5 Cu/6 K/139 SiO_2; and (b) 100 Fe/10 Cu/6 K/134 SiO_2.

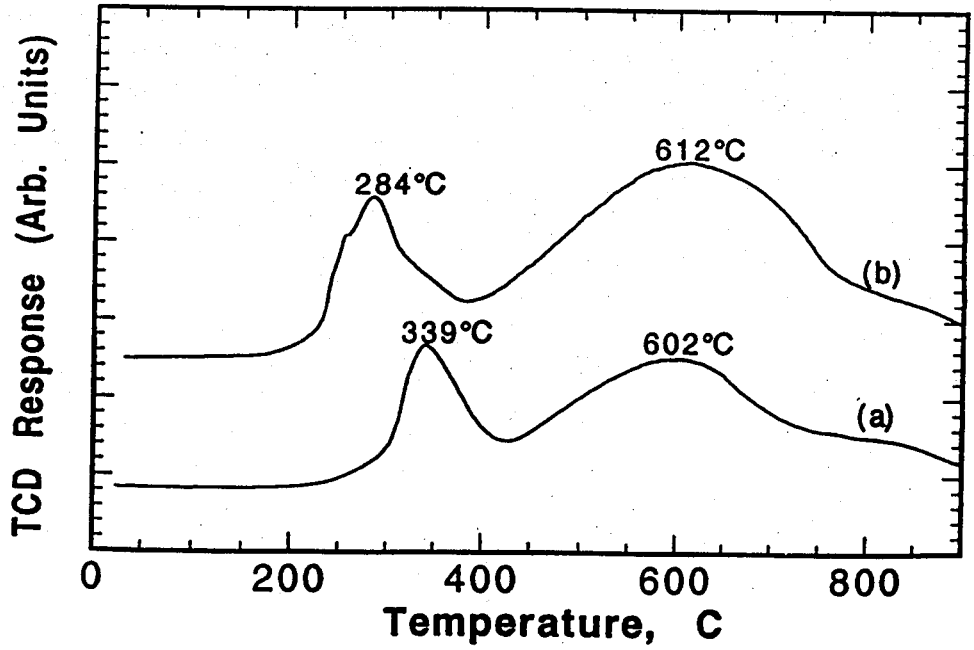

Figure IX-1.2 Effect of copper addition on the TPR behavior of alumina supported iron catalysts: (a) 100 Fe/5 Cu/6 K/139 Al_2O_3; and (b) 100 Fe/10 Cu/6 K/134 Al_2O_3.

Table IX-1.2 TPR Results for Supported Fischer-Tropsch Catalysts

Sample	Reduction Temperature Range, °C	Peak Position, °C		Degree of Reduction, (%) (#)	
		First Stage	Second Stg.	First stage	Total*
100 Fe/5 Cu/6 K/139 SiO_2	RT to 800	344	544	21	85
100 Fe/10 Cu/6 K/134 SiO_2	RT to 800	358	560	27	102
100 Fe/5 Cu/6 K/139 Al_2O_3	RT to 900	339	602	20	73
100 Fe/10 Cu/6 K/134 Al_2O_3	RT to 900	284	612	26	103

* The %degree of reduction are for the temperature range of RT to 800°C.

\# Sample wt = 20 mg, reducing gas = 5%H_2/95%N_2, flow rate = 40 cm^3/min, ramp = 20°C/min, temperature range = room temperature to 800 - 900°C.

pbw of Fe) are lower (344°C and 544°C) than the corresponding values (358°C and 560°C) observed for the catalyst having 10 pbw of copper per 100 pbw of Fe, which is not consistent with the role of copper as promoter which facilitates iron reduction. However, the degree of reduction for both the first and second stage of the reduction increased with the increasing amount of copper promoter. The degree of reduction values for the first stage of iron oxide reduction are 21% and 27%, respectively for the catalysts having 5 and 10 parts of copper. Also, the total degree of reduction values (at the end of TPR) for these two catalysts are 85% and 102%, respectively. These results are consistent with the expected effect of copper promotion on the reduction of iron oxides.

TPR profiles of 100 Fe/x Cu/ 6 K/y Al_2O_3 catalysts (where x= 5 or 10; y = 134 or 139) are shown in Figure IX-1.2. The peak positions for the first stage of reduction are 284°C and 339°C for the catalysts having 10 and 5 parts of copper, respectively. These results are consistent with the expected effect of copper promotion on the reduction of iron oxide. However, the peak positions (602°C and 612°C) for the second stage of reduction are not consistent with the expected promotional effect of copper. The degree of reduction values (Table IX-1.2) for the first stage of reduction are 20% and 26% for the catalysts having 5 and 10 parts of copper, respectively, whereas the expected degree of reduction corresponding to complete conversion of iron oxide (Fe_2O_3) into magnetite (Fe_3O_4) for these two catalysts is 10.8% and 10.5%, respectively. These results indicate that some of the magnetite is reduced to metallic iron during the first stage of the reduction. Total degree of reduction values for these two catalysts are 73% and 103%, respectively. These results clearly show that the addition of copper promotes the reduction of iron.

Isothermal Reduction

Results from isothermal reduction experiments in thermogravimetric analysis (TGA) unit are summarized in Table IX-1.3, and Figures IX-1.3 to IX-1.5.

Degree of reduction of 100 Fe/5 Cu/4.2 K/20 Al_2O_3 catalyst (Figure IX-1.3a) increased rapidly during the first 70 minutes of reduction, and then slowly at both reduction

Table IX-1.3 Summary of isothermal reduction experiments with alternative F-T catalysts in the TGA unit

Catalyst	Reduction Temperature, °C	% Degree of Reduction
100 Fe/5 Cu/4.2 K/20 Al_2O_3	240 280	59 69
100 Fe/5 Cu/4.2 K/31.6 Al_2O_3	240 280	28 42
100 Fe/5 Cu/4.2 K/100 SiO_2	280 240	38 33
100 Fe/5 Cu/6 K/139 SiO_2	280	43
100 Fe/10 Cu/6 K/134 SiO_2	280	79
100 Fe/5 Cu/6 K/139 Al_2O_3	280	35
100 Fe/10 Cu/6 K/134 Al_2O_3	280	51

Reduction conditions: Reducing gas = H_2 (100 cm^3/min), ramping in He = 5°C/min, sample wt = ~ 20 mg, and total reduction time = ~ 8 h. The sample was dried at 280°C in He (100 cm^3/min) for 30 minutes.

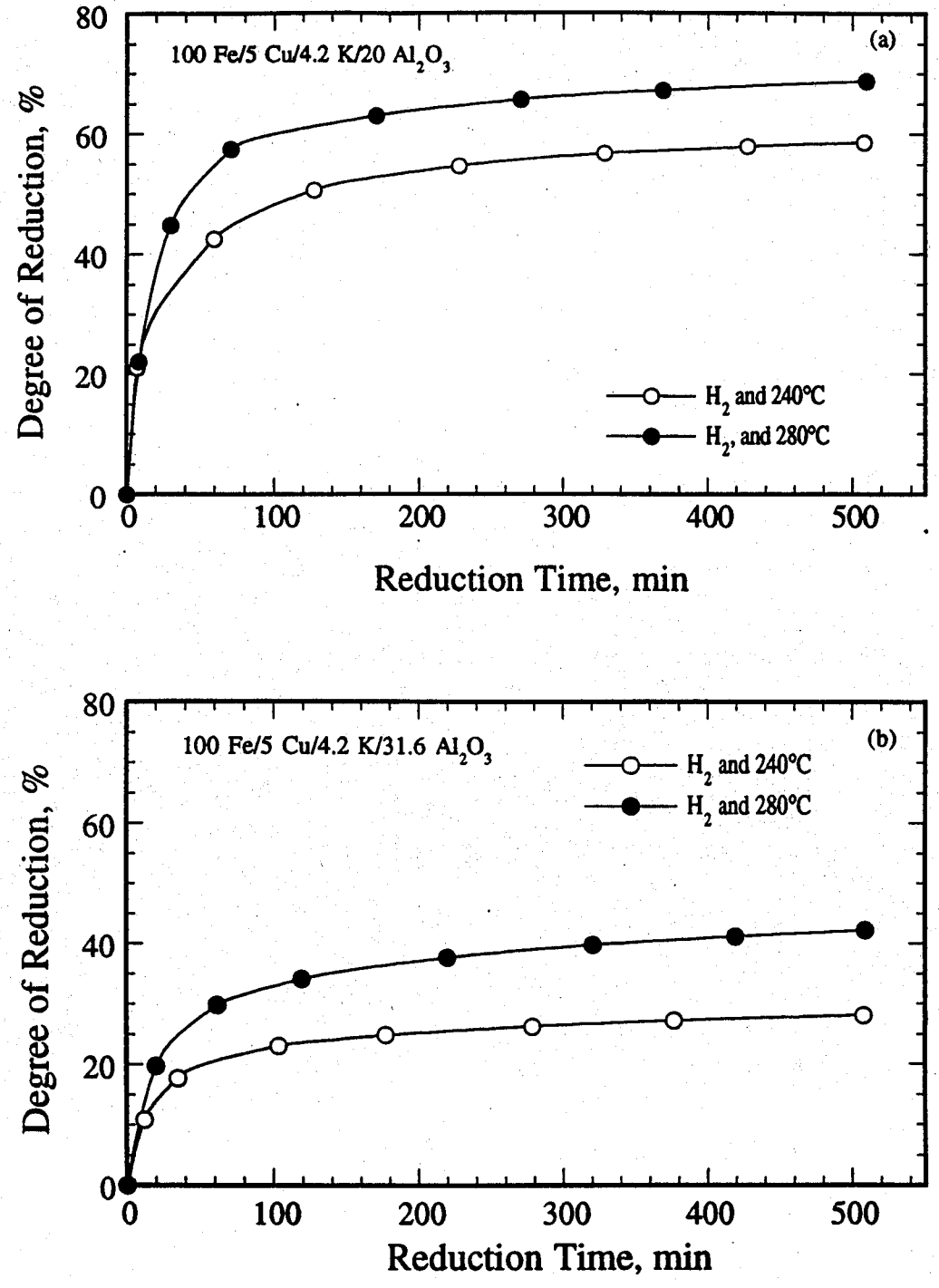

Figure IX-1.3 Effect of alumina content and reduction temperature on the reduction behavior of promoted Fischer-Tropsch catalysts in hydrogen: (a) 100 Fe/5 Cu/4.2 K/20 Al_2O_3; (b) 100 Fe/5 Cu/4.2 K/31.6 Al_2O_3.

temperatures (240°C and 280°C). The degree of reduction values (Table IX-1.3) at the end of 8 h reduction period are about 59% and 69%, for the reduction temperatures of 240°C and 280°C, respectively.

Degree of reduction of 100 Fe/5 Cu/4.2 K/31.6 Al_2O_3 catalyst (Figure IX-1.3b) increased rapidly during the first 100 minutes of reduction, and then continued to increase slowly at both reduction temperatures (240°C and 280°C). At the end of the reduction period the degree of reduction values are about 28% and 42%, at the reduction temperatures of 240°C and 280°C, respectively. These results show that the reduction is inhibited by the addition of aluminum oxide, which is indicative of interactions between the iron and the alumina.

Degree of reduction of 100 Fe/5 Cu/6 K/139 SiO_2 catalyst increased gradually during the first 220 minutes of reduction, and then very slowly (Figure IX-1.4). After 8 h of reduction with hydrogen at 280°C the final degree of reduction is about 43%. The degree of reduction of 100 Fe/10 Cu/6 K/134 SiO_2 catalyst increased rapidly during the first 50 minutes of reduction (to about 70%), and then very slowly reaching 79% after 8 hours of reduction in hydrogen at 280°C. These results clearly show that the reduction of iron in silica supported catalysts increases with the increasing amount of Cu promoter.

The alumina supported catalysts (100 Fe/5 Cu/6 K/139 Al_2O_3 and 100 Fe/10 Cu/6 K/134 Al_2O_3) exhibited the same type of behavior as the two silica supported catalysts (Figure IX-1.5). At the end of 8 h reduction period at 280°C, the degrees of reduction were about 35% and 51%, for the catalysts containing 5 and 10 parts pbw of Cu per 100 pbw of Fe. These results again show that the addition of copper promotes the reduction of iron oxide. Also, it appears that the interactions between iron and alumina support are stronger than on the silica support, resulting in lower reducibility of iron on alumina.

Reduction behavior of the silica and alumina supported catalysts in CO at 280°C is shown in Figures IX-1.6 and IX-I.7, respectively. The two silica supported catalysts lost about 2% of the initial weight during heating in helium from room temperature to 280°C, due

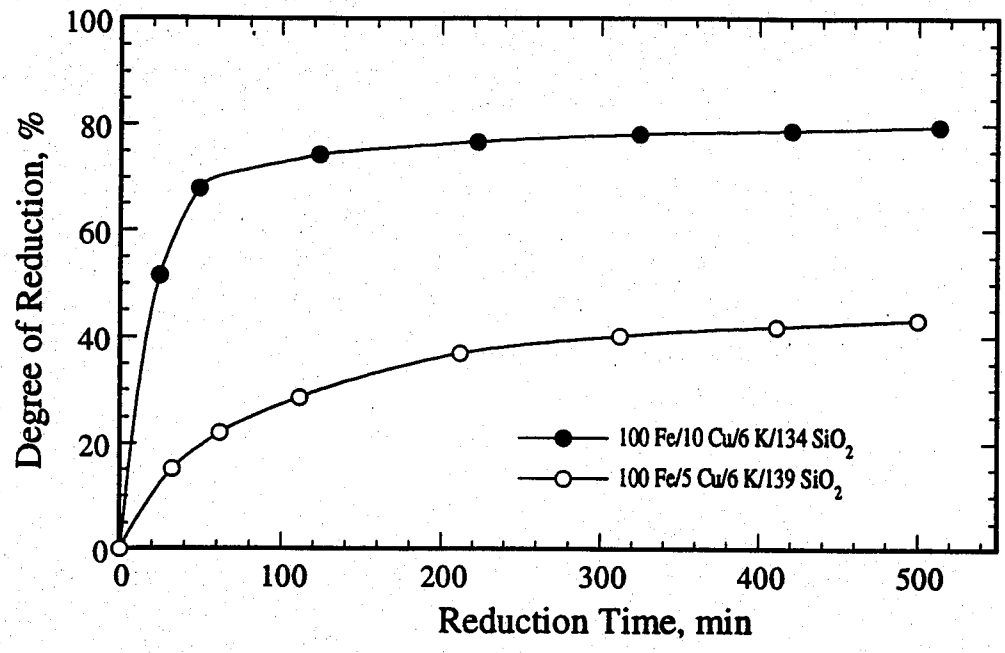

Figure IX-1.4 Effect of copper promotion on the degree of reduction of silica supported iron catalysts in hydrogen at 280°C.

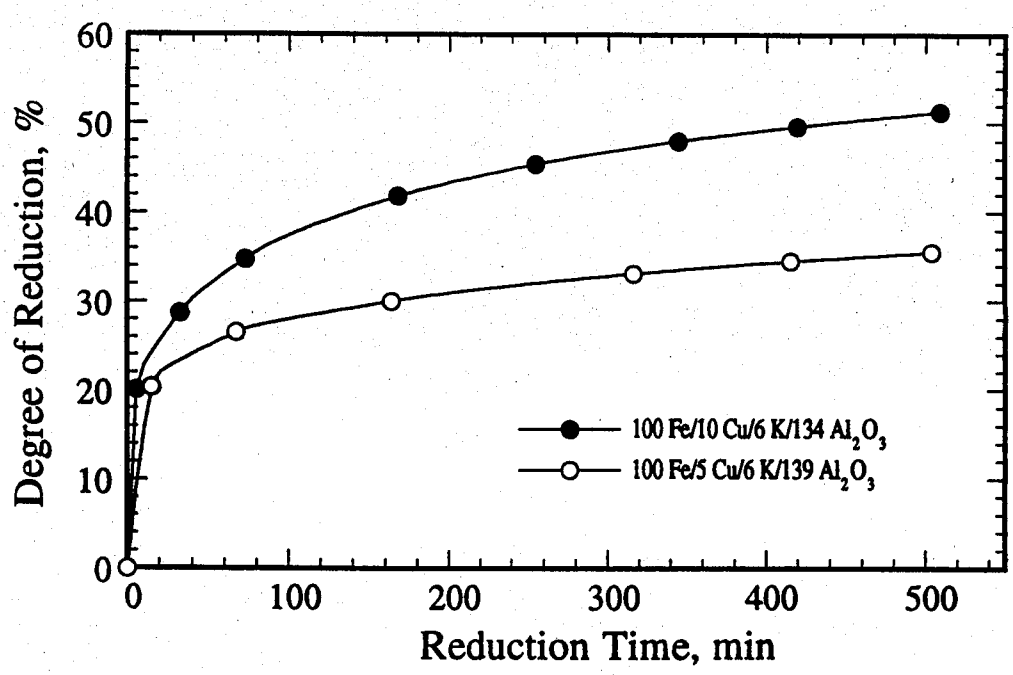

Figure IX-1.5 Effect of copper promotion on the degree of reduction of alumina supported iron catalysts in hydrogen at 280°C.

to removal of the adsorbed moisture. The weight loss was fairly rapid during the first 100 minutes of exposure to CO. After 200 minutes, both catalysts started to gain weight. Interestingly, the weight loss of both catalysts is almost the same during the entire reduction period. As shown above (Figure IX-1.4) the degree of reduction in hydrogen (at 280°C) of the catalyst having 10 parts of copper was significantly higher than that of the catalyst having 5 parts of copper. Hence, the relatively low weight loss of the catalyst having 10 parts of copper during CO reduction suggests that carburization (formation of iron carbides) and carbon deposition are dominant processes from the very beginning of the catalyst exposure to CO.

Alumina supported catalysts had lost about 6% of the initial weight during heating in helium from room temperature to 280°C, due to removal of adsorbed moisture. The weight loss was rapid during the first 60 minutes of exposure to CO. After 200 minutes of reduction, the weight remaining began to increase slowly with time. The weight loss during the first 60 minutes of reduction was slightly higher for the catalyst having 5 parts of copper compared to the catalyst having 10 parts of copper. Again, this suggests that carburization and/or carbon deposition are dominant processes on the catalyst having higher copper content.

The observed changes in weight for all four catalysts during the CO reduction are the net result of three competing reactions: (a) reduction of iron oxides; (b) carbon deposition (2 $CO \rightarrow CO_2 + CO$); and (c) carbide formation (i.e. carburization). For all four catalysts, the theoretical weight loss corresponding to formation of χ-carbide ($Fe_2O_3 \rightarrow \chi\text{-}Fe_5C_2$) is about 14%, whereas the theoretical weight loss for formation of magnetite ($Fe_2O_3 \rightarrow Fe_3O_4$) is about 2.4%. After 100 minutes of CO reduction, the experimental weight loss was about 5-7% on all four catalysts, suggesting that oxide reduction and carburization are the dominant reactions, and that carburization is incomplete. During the later stages of reduction a gradual

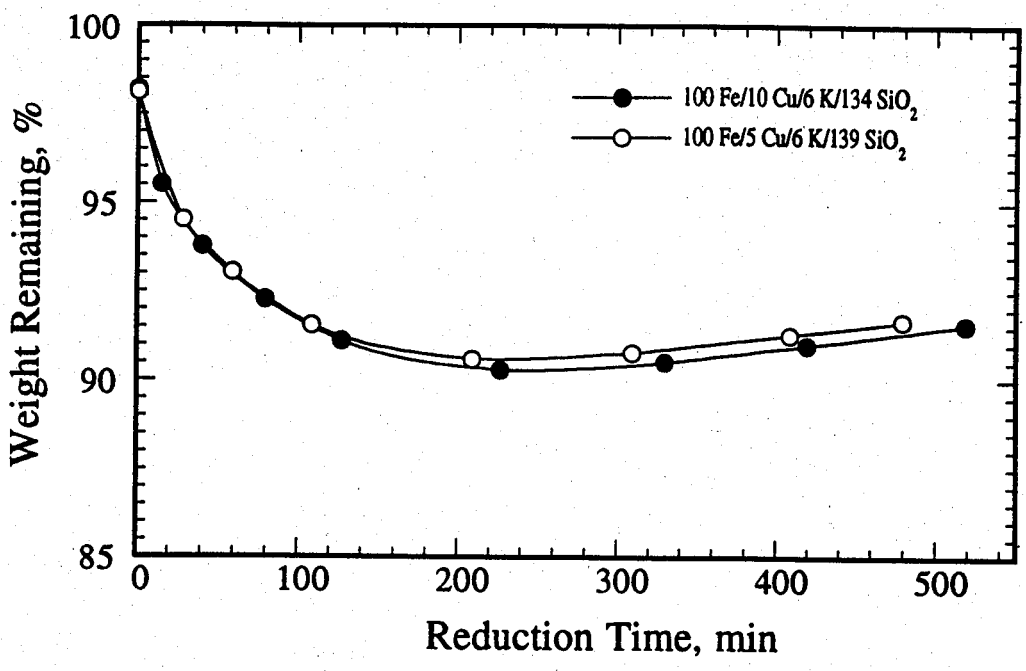

Figure IX-1.6 Effect of copper promotion on the reduction behavior of silica supported iron catalysts in CO at 280°C.

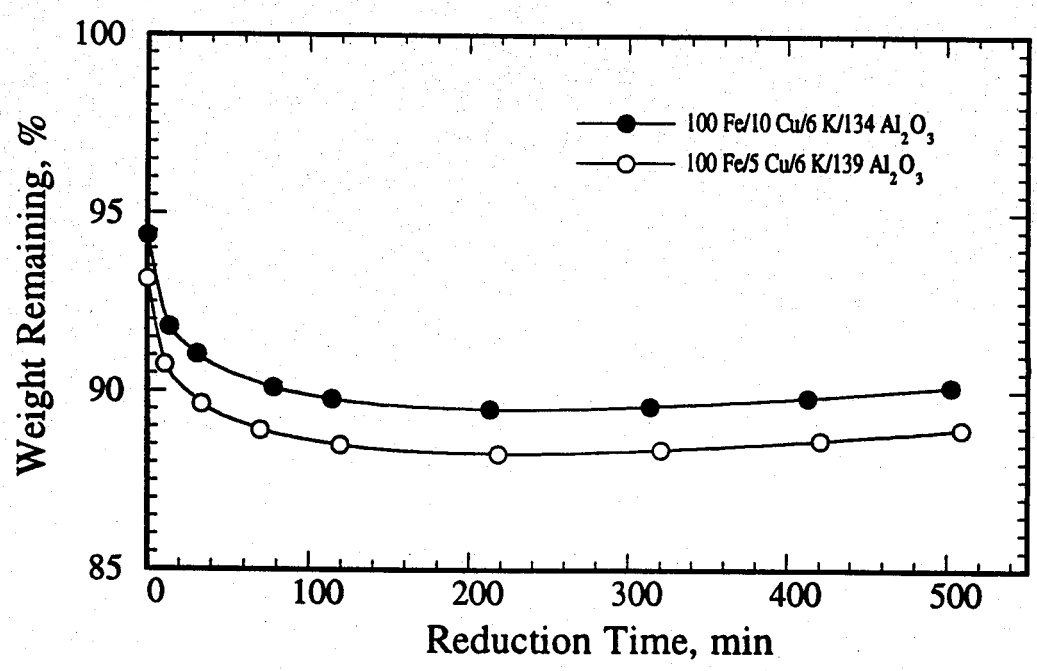

Figure IX-1.7 Effect of copper promotion on the reduction behavior of alumina supported iron catalysts in CO at 280°C.

increase in weight was observed with all four catalysts. This suggests that the carbon deposition is the dominant reaction, even though the carburization was not completed.

XRD Measurements

Results of XRD analysis of used catalysts from three slurry reactor tests are summarized in Table IX-1.4. As an illustration, the XRD patterns of catalysts withdrawn from the slurry reactor run SA-0097 with 100 Fe/5 Cu/4.2 K/20 Al_2O_3 catalyst are shown in Figure IX-1.8.

Magnetite (Fe_3O_4) and α-Fe were the major phases (Figure IX-1.8A) in the sample withdrawn immediately after the hydrogen reduction at 250°C for 4 hours (TOS = 0 h). During Fischer-Tropsch synthesis both magnetite and ε'-carbide ($Fe_{2.2}C$) were identified in samples withdrawn from the reactor between 4 and 308 hours on stream (Figure IX-1.8B to IX-1.8E. XRD patterns of samples withdrawn after 4 h (1-B) and 308 h (1-E) on stream are similar. The catalyst activity during this test decreased slowly with time (see section IX-2 of this chapter).

Used catalysts from runs SB-0627 (silica supported catalyst) and SB-2337 (alumina supported catalyst) contained magnetite and ε'-carbide (and possibly χ-carbide, as well). The increase in crystallinity of iron phases (i.e. increase in crystallite size) with time on stream was observed in catalyst samples from both runs. Catalysts deactivated with time in both tests (Section IX-2).

Table IX-1.4 Iron Phases in Used Catalyst Samples by X-ray Diffraction

Run Number	Catalyst	Time on Stream (TOS), h	Phases Identified by XRD
SA-0097	100 Fe/5 Cu/4.2 K/20 Al_2O_3	0	Fe_3O_4 and α-Fe
		4	Fe_3O_4 and ε'-$Fe_{22}C$
		24	Fe_3O_4 and ε'-$Fe_{22}C$
		162	Fe_3O_4 and ε'-$Fe_{22}C$
		308	Fe_3O_4 and ε'-$Fe_{22}C$
SB-2337	100 Fe/5 Cu/9 K/139 Al_2O_3	76	Fe_3O_4 and ε'-$Fe_{22}C$
		144	Fe_3O_4 and ε'-$Fe_{22}C$
		237	Fe_3O_4 and ε'-$Fe_{22}C$
SB-0627	100 Fe/5 Cu/6 K/139 SiO_2	150	Fe_3O_4, and ε'-$Fe_{22}C$
		306	Fe_3O_4, ε'-$Fe_{22}C$ and χ-Fe_5C_2 (?)

F-T process conditions in run SA-0097 were: T = 260°C, P = 1.48 - 2.17 MPa, H_2/CO = 0.67, SV = 1.4 - 2.1 Nl/g-cat/h.

F-T process conditions in run SB-2337 were: T = 260°C, P = 1.48 MPa, H_2/CO = 0.67, SV = 1.3 Nl/g-cat/h.

F-T process conditions in run SB-0627 were: T = 260°C, P = 1.48 - 2.17 MPa, H_2/CO = 0.67, SV = 1.4 - 2.0 Nl/g-cat/h.

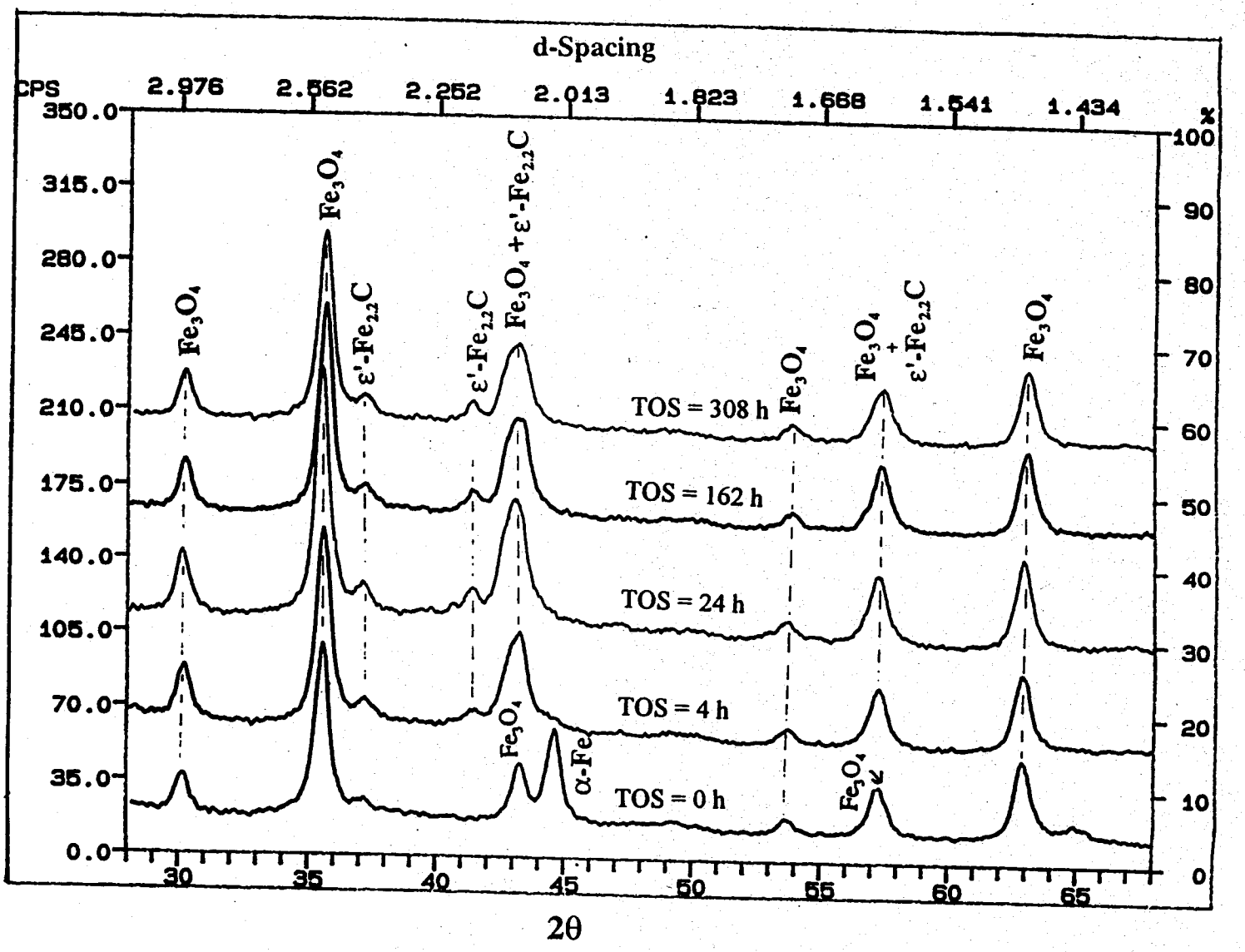

Figure IX-1.8 Changes in bulk iron phases with time on stream during run SA-0097 with the 100 Fe/5 Cu/4.2 K/20 Al_2O_3 catalyst.

IX-2 Reaction Studies

Three slurry reactor tests were conducted, and the reduction and process conditions employed in these tests are shown in Table IX-2.1. About 11-15 g of catalyst was used in these tests resulting in 3.8-5.1 wt% slurry. Durasyn 164-oil was used as the start-up liquid in all three tests. In run SA-0097 the catalyst which passed through a 270 mesh sieve (particles less than 63 micron in diameter) was loaded into the reactor, whereas in runs SB-0627 and SB-2337 the catalyst particle size was 45-63 microns (270-325 mesh).

Table IX-2.1 Reduction and Process Conditions in STSR Tests of Alternative Catalysts

Catalyst	Run ID	Reduction Conditions	Process Conditions [a]		
			TOS (h)	P (MPa)	SV (Nl/g/h)
100 Fe/5 Cu/4.2 K/20 Al_2O_3	SA-0097	H_2, 250°C, 0.8 MPa,	0-162	1.48	1.4
Iron content: 0.57 g-Fe/g-cat		4 h, 7500 cm^3/min	162-309	2.17	2.1
100 Fe/5 Cu/6 K/139 SiO_2	SB-0627	CO/He = 1/8, 0.8 MPa	0-150	1.48	1.4
Iron content: 0.34 g-Fe/g-cat		8 h, 7000 cm^3/min	150-306	2.17	2.0
100 Fe/5 Cu/9 K/139 Al_2O_3	SB-2337	CO/He = 1/5, 0.8 MPa	0-237	1.48	1.3
Iron content: 0.33 g-Fe/g-cat		8 h, 4000 cm^3/min			

[a] Other process conditions: T = 260°C, H_2/CO = 0/67.

The alumina containing catalyst (100 Fe/5 Cu/4.2 K/20 Al_2O_3) was pretreated using our standard reduction procedure for catalyst B, since its composition is similar to that of the catalyst B, except that aluminum oxide is used as binder instead of silicon oxide. The alumina and silica supported catalyst were reduced with CO, diluted with helium, at 280°C for 8 hours, since both catalysts responded well to CO pretreatment in the TGA unit (Section IX-1).

Catalyst Activity and Stability

Changes in synthesis gas conversion and H_2/CO usage ratio with time-on-stream at different process conditions for all three tests are shown in Figure IX-2.1. Results from run SA-1665 with catalyst C (100 Fe/3 Cu/4 K/16 SiO_2) are also shown for comparison.

The baseline catalyst C had the highest conversion (about 80%) and was very stable with time during testing at both 1.48 MPa and 2.17 MPa (Figure IX-2.1a). The alumina containing catalyst (SA-0097) had lower syngas conversion of about 60%, and was fairly stable during testing at 1.48 MPa (up to 162 h), but began to deactivate during testing at 2.17 MPa. The silica supported catalyst (SB-0627) was significantly more active than the alumina supported catalyst (SB-2337), but both catalysts deactivated fairly rapidly with time. For example the syngas conversion in run SB-0627 decreased from about 70% at 30 hours on stream to about 40% at 300 hours, whereas in run SB-2337 the maximum value of conversion was about 47% (at 32 h) and only 19% at 236 h.

The water-gas-shift (WGS) activity of the catalyst C was high (Figure IX-2.1b), as evidenced by low value of the usage ratio (about 0.57), whereas the silica supported catalyst (SB-0627) had relatively low WGS activity, particularly during testing at 2.17 MPa (usage ratio between 0.8 and 1). The WGS activity of the two alumina containing catalysts was relatively high (usage ratio of 0.60-0.64).

Changes in catalyst activity, expressed in terms of the apparent reaction rate constant for the first order reaction with respect to hydrogen, are shown in Figure IX-2.2. In addition to results obtained in three tests with alternative catalysts results from two tests with baseline catalysts B (run SB-1295) and C (run SA-1665) are also shown for comparison. Initially, the catalyst B and the silica supported catalyst (SB-0627) were the most active (k = 350-380 mmol/g-Fe/h/MPa), but both catalysts deactivated with time on stream. The apparent reaction rate constant in run SB-1295 (Catalyst B) reached a constant value of about 225 mmol/g-Fe/h/MPa at about 150 h on stream, whereas the silica supported catalyst (SB-0627) continued to deactivate with time and at 300 h its apparent reaction rate constant was 150

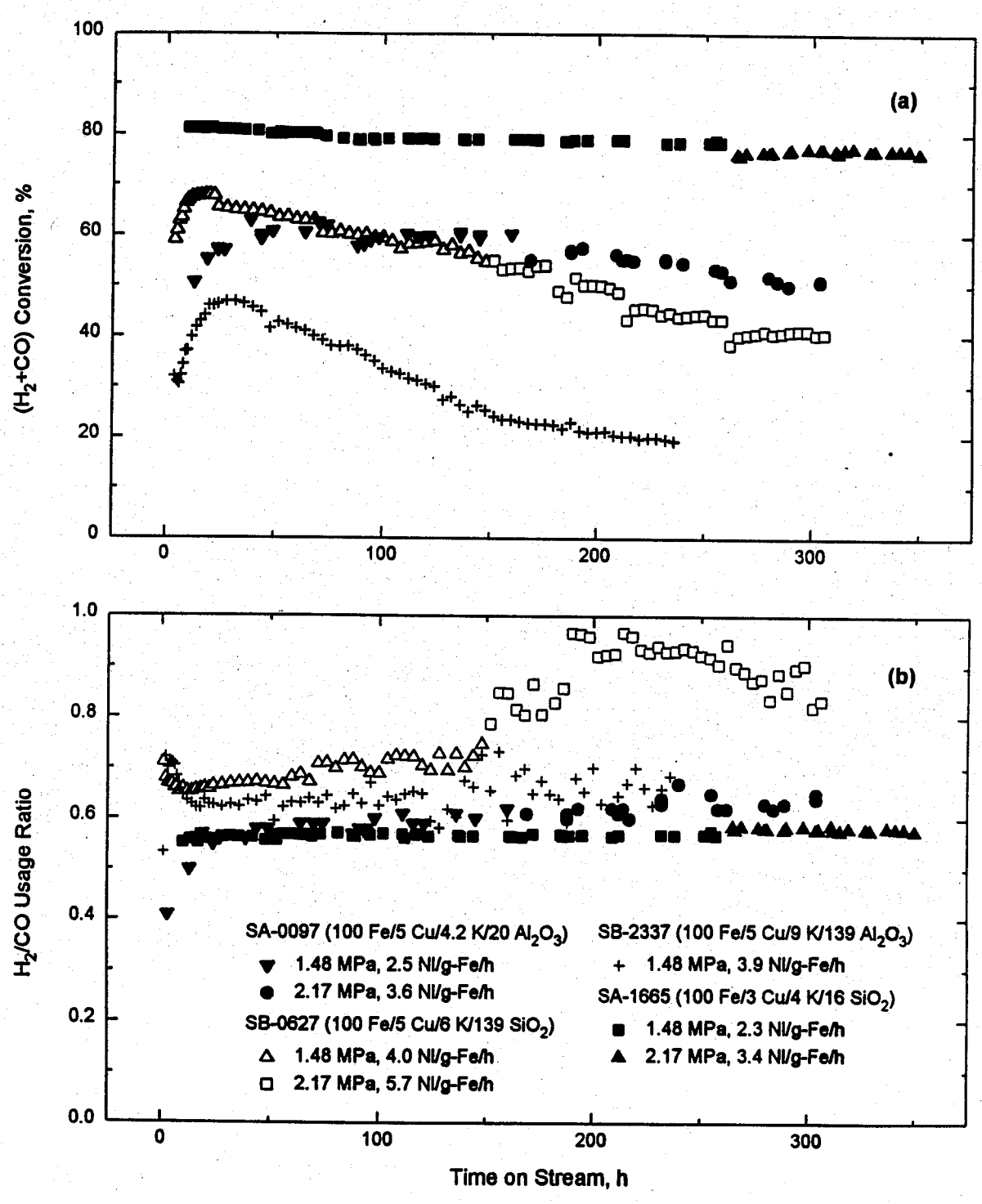

Figure IX-2.1 Synthesis gas conversion (a) and H_2/CO usage ratio (b) as a function of time for STSR tests of alternative catalysts and the baseline catalyst C.

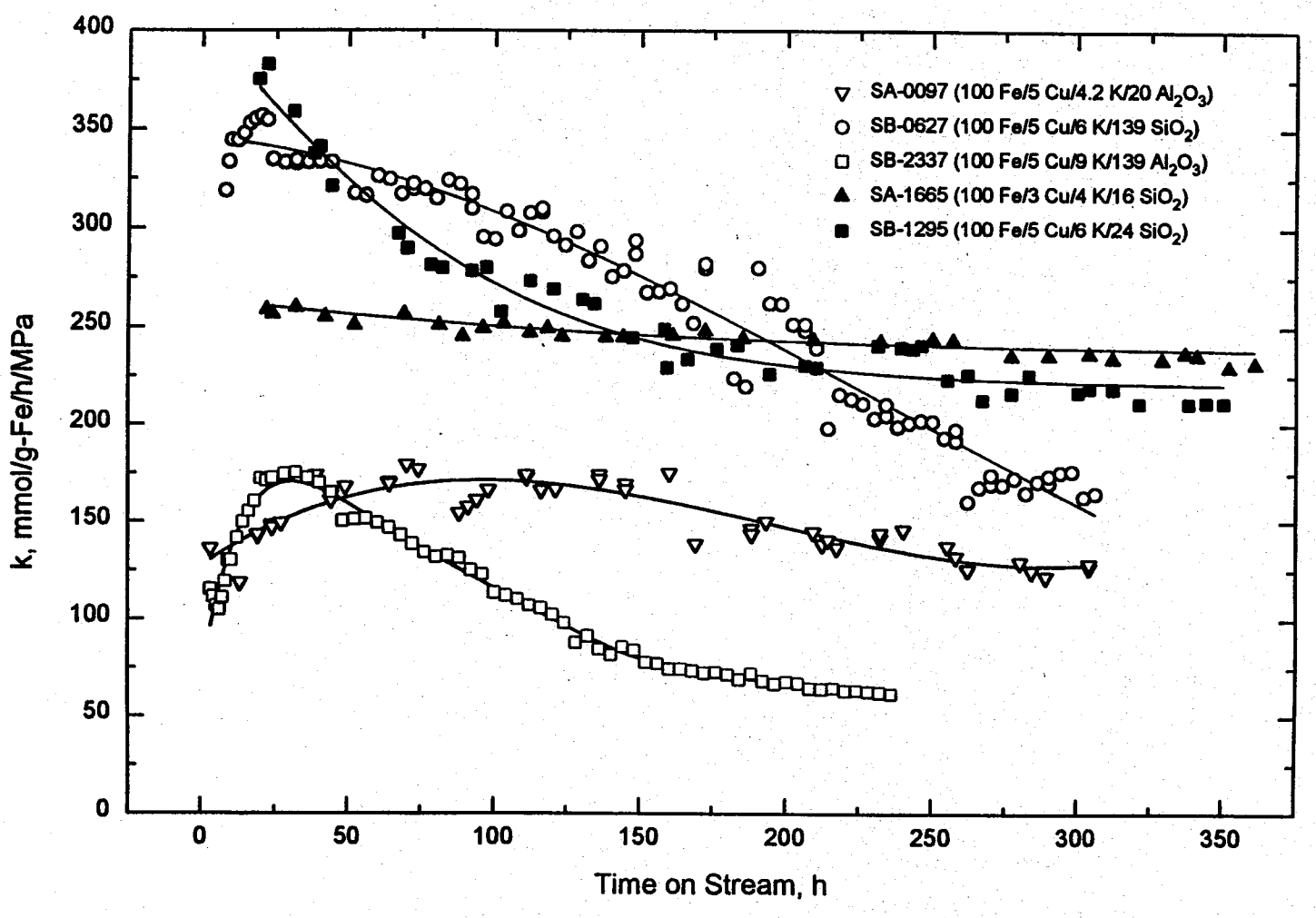

Figure IX-2.2 Apparent reaction rate constant as a function of time for STSR tests of alternative catalysts and the baseline catalysts B and C.

mmol/g-Fe/h/MPa. Catalyst C (SA-1665) was the most stable and its apparent reaction rate constant decreased from the initial value of about 250 mmol/g-Fe/h/MPa to about 225 mmol/g-Fe/h/MPa at 350 hours. The alumina containing catalyst (SA-0097) was markedly less active than the silica containing catalysts B and C, and its apparent reaction rate constant was between 125 and 175 mmol/g-Fe/h/MPa. The alumina supported catalyst was the least active and its apparent reaction rate constant was between 60 and 175 mmol/g-Fe/h/MPa.

Gaseous Hydrocarbon Selectivities

Silica supported catalyst (SB-0627) had the highest methane (7-8 mol%) and C_1+C_2 selectivities (Figures IX-2.3a and IX-2-3b). Alumina containing catalyst (SA-0097) had methane selectivity between 5 and 6 mol%, which is high in comparison to our baseline catalysts C (2-3 mol%) and B (3-4 mol%, not shown in Figure IX-2.3a). Methane selectivity of the alumina supported catalyst was the lowest of the three alternative catalysts (about 3.5-3.8 mol%) which is consistent with its high potassium content (9 pbw of K per 100 pbw of Fe). However, the activity of this catalyst was very low and its deactivation rate was high (Figure IX-2.2). C_1+C_2 selectivities of the three alternative catalysts were high in comparison to the baseline catalyst C (Figure IX-2.3b).

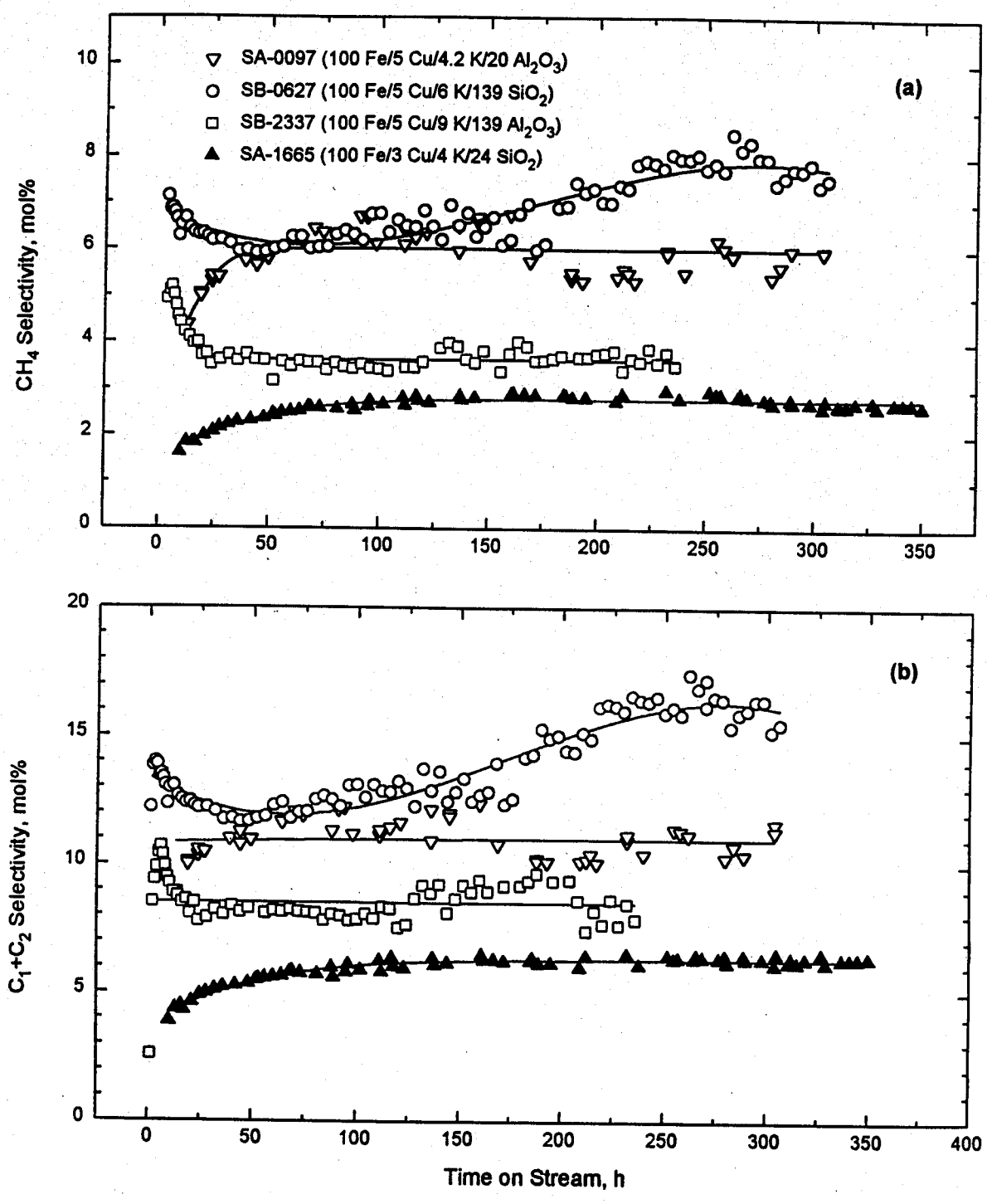

Figure IX-2.3 Methane selectivity (a) and (C_1+C_2) hydrocarbon selectivity (b) as a function of time for STSR tests of alternative catalysts and the baseline catalyst C.

Concluding Remarks on Alternative Catalysts

Three catalysts 100 Fe/5 Cu/4.2 K/20 Al_2O_3 (run SA-0097), 100 Fe/5 Cu/6 K/139 SiO_2 (SB-0627) and 100 Fe/5 Cu/9 K/139 Al_2O_3 (SB-2337) were evaluated in slurry reactor tests under this task. The alumina containing catalyst 100 Fe/5 Cu/4.2 K/20 Al_2O_3 was chosen, because of its similarity with our baseline catalysts B and C (similar promoter, Cu and K, and binder amounts, except that aluminum oxide was used as the binder instead of silicon oxide). The alumina and silica supported catalysts were chosen because they are expected to have high mechanical strength and high attrition resistance during testing in slurry reactors.

The alumina containing catalyst (SA-0097) was markedly less active and had higher methane and gaseous hydrocarbon selectivities than the baseline catalysts. The silica supported catalyst (100 Fe/5 Cu/6 K/139 SiO_2) deactivated fairly rapidly with time, and had markedly higher gaseous hydrocarbon selectivities than the baseline catalysts B and C. The alumina supported catalyst (100 Fe/5 Cu/6 K/139 Al_2O_3) was the least active, and deactivated rapidly with time-on-stream. Gaseous hydrocarbon selectivities were higher than those obtained in tests with the baseline catalysts B and C, but were lower than those obtained in tests of the other two alternative catalysts. The reasons for fairly rapid loss in activity in tests with the alumina and silica supported catalysts are not understood at the present time. In general the performance of the three alternative catalysts was inferior in comparison to our baseline catalysts.