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Activation Studies with a Precipitated Iron Catalyst for Fischer–Tropsch Synthesis

II. Reaction Studies

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Effects of pretreatment conditions on catalyst performance (activity, selectivity, and stability with time) during Fischer–Tropsch (FT) synthesis were studied in a fixed-bed reactor using a commercial precipitated iron catalyst (100 Fe/5 Cu/4.2 K/25 SiO_2 on a mass basis). The catalyst activity increased slightly with time-on-stream after hydrogen reductions, which was accompanied with conversion of metallic iron and part of iron oxides to ε′-carbide (ε′-$Fe_{2.2}C$). Initial activity of the H_2-reduced catalyst at 280°C for 8 or 24 h was markedly lower than that obtained in other tests. This is attributed to slow carburization of large oxide particles and partial poisoning of catalyst sites by migration of sulfur from the bulk to the surface of the catalyst during the reduction. Pretreatments with carbon monoxide and syngas resulted in partial conversion of Fe_2O_3 to χ-carbide (χ-Fe_5C_2). During FT synthesis the CO- and the syngas-pretreated catalyst deactivated slowly with time-on-stream, due to partial conversion of χ-carbide to less active iron oxide phases and buildup of carbonaceous deposits which block the active sites. The hydrogen-reduced catalyst at 280°C, for 1–24 h, produced more methane and gaseous hydrocarbons than the CO- or the syngas-pretreated catalyst and favored secondary reactions (1-olefin hydrogenation, isomerization, and readsorption). © 1995 Academic Press, Inc.

INTRODUCTION

Promoted iron catalysts, reduced with hydrogen, have been used in commercial fixed-bed and entrained fluid bed reactors for synthesis gas conversion to transportation fuels via Fischer–Tropsch (FT) synthesis at SASOL in South Africa (1). However, the purpose of pretreatment for iron FT catalysts is not clearly understood. Reduction in H_2 may lead to a zero-valent state, but upon exposure to a synthesis gas the metallic iron is rapidly converted to a carbide phase or a mixture of iron carbides (1–4). At high syngas conversions, a reaction mixture becomes more oxidizing and magnetite is also formed (1, 5–7). During FT synthesis, the bulk iron may be distributed among several phases, e.g., carbides, oxides, and metallic iron, which often results in a lack of correlation between the catalyst bulk composition and its activity and/or selectivity (1, 6). Other pretreatments have been also employed, such as CO activation, synthesis gas pretreatment or induction, and/or H_2 reduction followed by CO treatment or vice versa (5, 8).

Also, there has been a large number of related studies on model iron catalysts dealing with the issue of the role of iron phases in FT synthesis. However, this issue remains a controversial one. Briefly, some workers consider the surface carbides, with an underlying iron carbide bulk structure, to be the active phase (2, 9). In the so-called competition model of Niemantsverdriet and van der Kraan (10) iron atoms at the surface are considered as the active sites. In this model both bulk carbidation and FT synthesis (hydrocarbon formation) have a common surface carbidic precursor. In addition to these two postulates concerning the nature of the active phase, Teichner and co-workers proposed that Fe_3O_4 is the active phase in FT synthesis (11, 12). Validity of this proposal has been questioned (13), but some evidence in its support has also been presented (14–16).

In recent years, there has been a renewed interest in the effect of activation (pretreatment) conditions on performance of precipitated iron catalysts in fixed-bed and slurry reactors under reaction conditions representative of industrial practice (14, 17–22). Studies at the U.S. Department of Energy, Pittsburgh Energy Technology Center were conducted in a stirred tank slurry reactor (STSR) with iron–manganese and iron catalysts promoted with copper and potassium (17–19). In studies with precipitated iron–

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manganese catalysts Pennline *et al.* (17) found that pretreatments with H_2 or $H_2/CO = 1$ syngas at 275°C resulted in completely inactive catalysts during the synthesis. Activations with CO were more successful, and changes in activation temperature or pressure had some effect on catalyst activity and selectivity. Zarochak and McDonald (18, 19) employed activations with syngas ($H_2/CO = 0.7$ or 1) and CO in studies with (Fe/ Cu/ K_2O) catalysts. Following activation, catalysts deactivated with time-on-stream. Deactivation rate was affected both by pretreatment and reaction conditions during FT synthesis.

Researchers from Exxon (14) reported results from a study in which they compared performance of an iron oxide catalyst in the form of the spinel of Fe_3O_4 and a catalyst derived from this precursor by carburization with syngas ($H_2/CO = 1$) at 350°C for 24 h. Fischer–Tropsch synthesis was carried out in a STSR at 270°C and 600 kPa using syngas with $H_2/CO = 2$ (conversion of about 50%). After 60 h of FT synthesis under these conditions both the iron oxide and iron carbide catalyst retained their original bulk phase identity, as determined by X-ray diffraction. The authors found that carbided iron surface produces a more olefinic and higher molecular weight product than an oxide surface. This was attributed to higher acidity of the oxide surface.

Davis and Tungate (20) studied pretreatment effects on a commercial sample of a high surface area ultrafine iron oxide (United Technologies, surface area 270 m^2/g) in a STSR at 260°C, 0.8 MPa, $H_2/CO = 1$ at a gas space velocity of 2.9 Nl/g-cat/h, for 50–100 h on stream. Prior to FT synthesis the catalyst was pretreated with H_2, CO, or syngas ($H_2/CO = 1$) at 260°C for 24 h. It was found that activation with CO resulted in activity which was three times higher than that of the H_2- or syngas-pretreated catalyst. After 10 h of FT synthesis, methane and CO_2 selectivities were the same, regardless of the pretreatment procedure employed. Magnetite was the only iron phase found in the used catalyst samples withdrawn from the reactor after 10–48 h of synthesis.

Two comprehensive studies on the effect of pretreatment conditions were conducted in our laboratory with precipitated iron catalysts having nominal compositions 100 Fe/3 Cu/0.2 K (21) and 100 Fe/0.3 Cu/0.8 K (22). Eleven pretreatment procedures were employed in a study with 100 Fe/3 Cu/0.2 K catalyst, and five were employed in a study with 100 Fe/0.3 Cu/0.8 K catalyst to determine the effects of reductant type (H_2, CO, and syngas), pretreatment temperature, and duration. Following activation the catalysts were tested in a fixed-bed reactor at 250°C, 1.48 MPa, 2 Nl/g-cat/h, and syngas feed with $H_2/CO = 1$ (100 Fe/3 Cu/0.2 K catalyst) or $H_2/CO = 0.67$ (100 Fe/0.3 Cu/0.8 K). Results from both studies showed that activation parameters have a significant effect on catalyst activity, stability (deactivation), and selectivity during FT synthesis. Catalysts activated with CO or syngas produced less gaseous hydrocarbons and more high molecular weight hydrocarbons (wax) than the H_2-reduced catalysts. However, the CO and syngas activations usually led to faster catalyst deactivation during FT synthesis. Hydrogen-reduced catalysts had a constant or gradually increasing FT activity during 100–200 h of testing. Activity of the hydrogen-reduced catalysts was a strong function of pretreatment conditions (temperature, duration, and flow rate) and generally decreased with increase in reduction temperature and/or duration of reduction.

All these studies (5, 6, 14, 17–22) were conducted with precipitated iron catalysts which do not contain silica as a binder. Here we report results from pretreatment effect studies with a commercial precipitated iron catalyst, obtained from Ruhrchemie AG (Oberhausen–Holten, Germany). This catalyst was initially used in fixed-bed reactors at SASOL (1), and in addition to copper and potassium promoters it contains silica as the binder/promoter. The addition of silica is known to inhibit reduction of iron (23, 24) and improves catalyst stability during FT synthesis (24, 25). Activation (pretreatment) parameters investigated in the present study are reductant type (H_2, CO, and syngas), temperature, and duration of pretreatment. Results from the catalyst characterization studies reported in the accompanying paper (26) are used here to explain some of the activity/selectivity trends.

EXPERIMENTAL

A detailed description of our downflow fixed-bed reactor and product analysis systems used in this study is given elsewhere (21, 27). Briefly, the fixed-bed reactor was constructed of 1-cm-i.d. stainless steel tube with an effective bed volume of 28 cm^3. The feed gas flow rate was adjusted with a mass flow controller and passed through a series of oxygen removal, alumina, and activated charcoal traps to remove trace impurities. The feed was preheated before entering the reactor. After leaving the reactor, the exit gas passed through a series of high- and low- (ambient) pressure traps to condense liquid products. During mass balance periods liquid products were allowed to accumulate in high- and low-pressure mass balance traps, and their mass was recorded at the conclusion of the mass balance period. High molecular weight hydrocarbons (wax) and liquid products, collected in the high- and low-pressure traps, were analyzed by gas chromatography. The reactants and gaseous products were analyzed on a Carle AGC 400 gas chromatograph, equipped with multiple columns and flame ionization and thermal conductivity detectors. Mass balance closures were typically 100 ± 3%.

Nominal composition of the Ruhrchemie catalyst is 100 Fe/5 Cu/4.2 K/25 SiO_2 (28). The as-received catalyst was calcined in air at 300°C for 5 h and then crushed and sieved

TABLE 1

Pretreatment Conditions and Test Designations

Test (ID)	Temperature (°C)	Reductant	Duration (h)	Pressure (MPa)	Flow rate (cm^3/min)
FA-0643	220	H_2	1	0.1	4,000
FB-0183	280	H_2	1	0.1	4,000
FB-1593	280	H_2	8	0.1	175
FB-1733	280	H_2	24	0.1	175
FB-2290	310	$H_2/CO = 2.0$	6	0.1	1,200
FB-1588	280	CO	12	0.1	170

to about 0.25 to 0.50 mm (32 to 60 mesh). Calcined catalyst was diluted 1:5 by volume with glass beads of the same size range and then loaded into the reactor. Following the catalyst pretreatment, flow was switched to helium and the reactor temperature was decreased to 190–200°C. The reactor system was then pressurized to 1.48 MPa (200 psig), the helium flow was stopped, and synthesis gas ($H_2/CO = 0.67$) was introduced at a gas space velocity of 2.0 Nl/g-cat/h. The reactor temperature was then increased gradually to 250°C. This is referred to as the conditioning period. After achieving the desired process conditions of 250°C, 1.48 MPa, 2.0 Nl/g-cat/h and $H_2/CO = 0.67$, the catalyst was tested over a period of 70 to 130 h. Test designations and pretreatment conditions are listed in Table 1. Test FB-1588, with the CO-pretreated catalyst, lasted over 630 h (25), but here we report only results from the first 170 h of testing.

RESULTS

Catalyst Activity and Stability

Change in catalyst activity, measured by volumetric gas contraction, during the conditioning period is shown in Fig. 1. Volumetric gas contraction, defined as 100 × (inlet flow rate − outlet flow rate)/(inlet flow rate), is a convenient measure of catalyst activity, since it changes nearly linearly with syngas ($H_2 + CO$) conversion. At temperatures of 220°C and above, the activity of the H_2-reduced catalyst varied with reduction conditions and increased in the following order: FB-1593 (280°C, 8 h) < FB-1733 (280°C, 24 h) < FA-0463 (220°C, 1 h) ≤ FB-0183 (280°C, 1 h). The CO-pretreated catalyst had higher activity than the H_2-reduced catalyst, regardless of the reduction conditions, during the conditioning period (for $T \geq 220°C$).

After about 70 h on stream (including the 30-h conditioning period) differences in the syngas conversions after different pretreatments were relatively small (Fig. 2). The highest conversion was obtained in Run FB-0813, after the H_2-reduction at 280°C for 1 h at a flow rate of 4,000 cm^3/min (63–65%). When the catalyst was reduced at 280°C using a markedly lower H_2 flow rate (corresponding to a gas space velocity of 3.0 Nl/g-cat/h) for 8 and 24 h (Runs FB-1593 and FB-1733, respectively) the syngas conversions were significantly lower during initial periods of FT synthesis at 250°C. In Run FB-1593 the initial syngas conversion (1 h at the process conditions) was only 47%, whereas in Run FB-1733 it was 54%. In both tests the conversion increased with time, reaching 62% at 154 h on stream in Run FB-1593 and 58% in Run FB-1733. The syngas conversion values obtained in Run FA-0643, on the catalyst reduced with H_2 at 220°C for 1 h at a flow rate of 4,000 cm^3/min, were between 59 and 63%. All four H_2 reduction procedures led to gradually increasing catalyst activity during FT synthesis at 250°C.

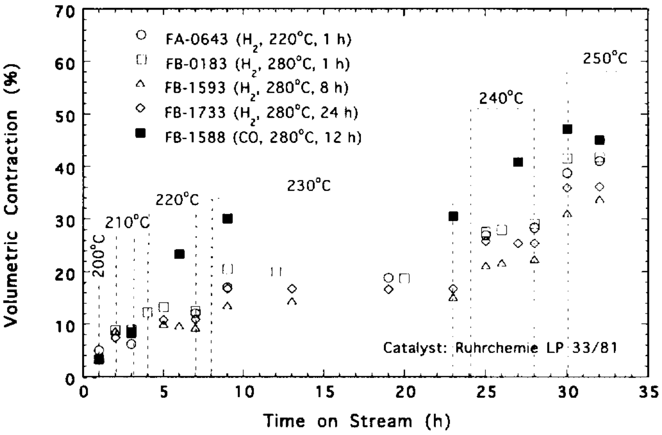

FIG. 1. Volumetric contraction during conditioning period (process conditions: 1.48 MPa, 2 Nl/g-cat/h, $H_2/CO = 0.67$, 200–250°C).

Initial ($H_2 + CO$) conversion at 250°C on the CO-pretreated catalyst (FB-1588) was 66% and then decreased with time to 55% at 160 h on stream. The conversion continued to decline slowly with time, but at a lower rate, and

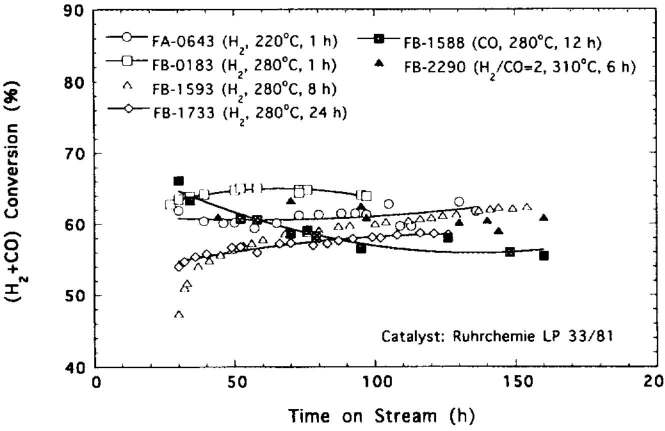

FIG. 2. Effect of pretreatment conditions on synthesis gas conversion and catalyst stability.

TABLE 2

Ruhrchemie Catalyst Activity and Selectivity

Test designation	FA-0643		FB-0183	FB-1593		FB-1733		FB-2290		FB-1588	
Time-on-stream (h)	65	93	71	72	144	71	116	73	157	71	167
CO conversion (%)	59.7	61.8	66.4	61.2	64.9	58.7	60.7	61.1	57.9	56.4	51.6
(H_2 + CO) conversion (%)	60.5	61.2	64.7	59.2	62.5	57.3	58.7	63.3	60.9	58.6	54.4
STY (mmol/g-cat/h)	54.0	54.8	58.2	53.0	55.9	51.0	52.1	56.8	55.0	52.0	49.1
k (mmol/g-Fe/h/MPa)[a]	207	216	215	192	205	187	190	225	216	201	187
(H_2/CO) usage ratio	0.67	0.66	0.67	0.64	0.63	0.66	0.64	0.75	0.78	0.76	0.78
(H_2/CO) exit ratio	0.65	0.68	0.79	0.78	0.81	0.75	0.78	0.60	0.57	0.60	0.60
$K_p = P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$	9.9	10.2	12.5	13.0	16.0	11.1	11.0	2.28	1.71	2.20	2.00
mmol CH_4/g-Fe/h	1.83	1.98	2.98	2.43	2.69	2.33	2.36	2.04	1.94	1.41	1.33
Hydrocarbon selectivity (wt.%)											
CH_4	7.0	7.7	10.4	9.4	10.0	9.0	8.6	7.0	6.9	5.6	5.6
C_2–C_4	17.7	19.8	24.2	22.5	23.2	25.3	23.0	22.7	23.3	22.7	22.8
C_5–C_{11}	25.0	27.0	32.8	29.6	31.7	32.9	31.6	22.4	31.7	18.6	20.2
C_{12^+}	50.3	45.5	32.6	38.5	35.1	32.8	36.8	47.9	38.1	53.1	51.4
Olefin content (wt.%)											
C_2–C_4	66.3	65.8	64.7	63.8	63.3	65.6	65.5	75.9	76.8	77.6	80.8
C_5–C_{11}	70.5	70.9	68.1	68.6	68.7	69.4	69.5	77.4	74.2	77.2	77.1

Note. Process conditions: 250°C, 1.48 MPa, 2.0 Nl/g-cat/h, $H_2/CO = 0.67$.

[a] Apparent reaction rate constant for a first-order reaction in hydrogen, based on measured usage ratio.

at 460 h on stream it was 50% (25). Activity of the syngas-pretreated catalyst (FB-2290) was fairly stable between 50 and 160 h on stream, and the (H_2 + CO) conversion was about 62%.

An apparent reaction rate constant, which is an alternate measure of catalyst activity, was calculated from experimental data by assuming that the reaction rate has a first-order dependence on hydrogen partial pressure (29). Calculated values of the apparent rate constant are listed in Table 2, and, in some cases, they do not follow the same trend as the syngas conversions, due to differences in H_2-to-CO usage ratios. The apparent reaction rate constant of the syngas-pretreated catalyst (216–225 mmol/g-Fe/h/MPa) was slightly greater than the corresponding rate constants of the H_2-reduced catalyst (187–216 mmol/g-Fe/h/MPa). The apparent rate constant in Run FB-1588, the CO-pretreated catalyst, declined from 201 mmol/g-Fe/h/MPa at 71 h to 187 mmol/g-Fe/h/MPa at 167 h on stream, due to catalyst deactivation.

Effect of pretreatment procedure on water–gas–shift (WGS) activity, measured by H_2-to-CO usage ratio and partial pressure quotient K_p, is illustrated in Table 2. The partial pressure quotient values during FT synthesis following H_2 reductions were about five times greater than those obtained after the CO and syngas pretreatments. The usage ratio was stable with time-on-stream in all tests (0.63–0.67 after the H_2 reductions and 0.76–0.78 following the CO and/or syngas pretreatments). Thus, the WGS activity of the Ruhrchemie catalyst was higher (smaller usage ratio, greater K_p) after the H_2 reductions than after the CO and the syngas activations.

Reproducibility of Results

Before describing results on catalyst selectivity, we shall address an important issue of reproducibility of experimental data reported in this paper. In our study, the complete mass balances (analysis of tail gas, liquid products, and wax collected in high-pressure trap) were made two or three times between 65 and 170 h on stream, except in Run FB-0183, where only one mass balance was made at 71–79 h on stream. Selected results from two mass balances for five of the six tests are shown in Table 2 (hydrocarbon selectivities and olefin contents in C_2–C_4 and C_5–C_{11} hydrocarbons). These results clearly show that variations of selectivities with time-on-stream are insignificant and that they are small in comparison with differences in selectivities arising from the use of different pretreatment procedures (e.g., CO and syngas pretreatments vs hydrogen reductions). As a further illustration of the fact that selectivities do not vary with time-on-stream, total olefin and 2-olefin selectivities obtained in tests FB-1588 (CO pretreatment) and FB-1593 (H_2 reduction at 280°C for 8 h) are presented in Fig. 3. Also, selectivities obtained between 65 and 170 h are not affected by differences in the syngas conversion, since the range of variations of the latter (54–65%) is too small to have a significant impact on selectivity (24, 25).

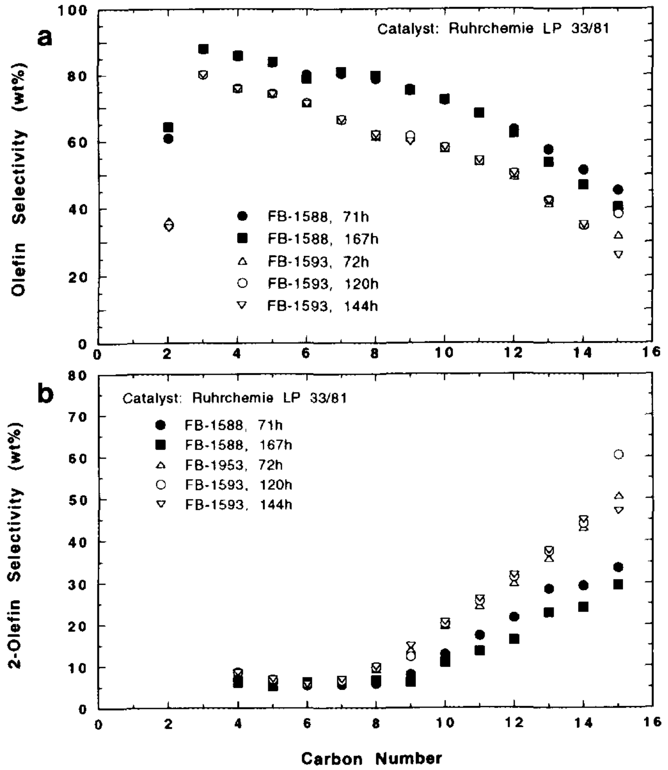

FIG. 3. Effect of time-on-stream on (a) olefin selectivity and (b) 2-olefin selectivity, in tests FB-1588 (CO pretreatment) and FB-1593 (H_2 reduction at 280°C for 8 h).

Multiple tests with the Ruhrchemie catalyst using the same pretreatment procedure were also conducted in our laboratory in conjunction with this and related studies (30). Two tests (including FB-0183) were made using hyrogen reduction at 280°C for 1 h and the syngas conversion between 30 and 100 h on stream was virtually the same in both tests (62–65%). Four tests (including FA-0643) were made using hydrogen reduction at 220°C for 1 h. A mean value of syngas conversion at about 70 h on stream was 60.2%, with a standard deviation of 1.2%. This corresponds to an experimental error (defined as 100 × standard deviation/mean value) of only 2%. The corresponding mean values and standard deviations for hydrocarbon selectivities were $CH_4 = 6.5 \pm 1.1\%$; $(C_2–C_4) = 17.8 \pm 1.2\%$; $(C_5–C_{11}) = 23.4 \pm 3.3\%$; $C_{12^+} = 51.5 \pm 4.6\%$ (where the results are shown in the form mean value ± standard deviation). This corresponds to experimental errors ranging from 7% (C_2–C_4 hydrocarbons) to 18.5% (methane selectivity). Experimental errors in olefin selectivities were between 1 and 5% for hydrocarbons with carbon numbers C_3 to C_{14}, whereas the ethylene selectivity was the least reproducible (error of 12%). Experimental errors for 2-olefin selectivities were somewhat greater (typically 10% for C_6–C_{15} hyrocarbons and about 25% for C_4 and C_5 hydrocarbons), largely due to analytical errors in the product analysis. Results from these multiple tests, using hydrogen reduction at 220°C for 1 h, clearly show that the combined effect of experimental errors arising from repeatability of reaction tests and errors in product analysis is small.

The above results indicate that differences in activities and selectivities observed in the present study are caused by the use of different pretreatment procedures, rather than by experimental errors and artifacts. Also, due to the absence of significant variations of product selectivities with time-on-stream the average values from multiple mass balances will be used to illustrate the effect of activation procedures on catalyst selectivity.

Catalyst Selectivity

The effect of pretreatment conditions on hydrocarbon product distribution is illustrated in Table 2 and Fig. 4. Hydrocarbon products in both Table 2 and Fig. 4 are lumped into four groups: C_1 (methane), C_2–C_4 (light gases), C_5–C_{11} (gasoline fraction), and C_{12^+} (diesel fuel and hydrocarbon wax). The CO-activated catalyst had the lowest methane selectivity (~5.6 wt.%). The catalyst reduced with H_2 at 220°C for 1 h also had relatively low methane selectivity (7.3%) and had the lowest selectivity to C_2–C_4 hydrocarbons (18.8%). These two pretreatment procedures resulted in relatively high C_{12^+} selectivities, about 47.9% (H_2 at 220°C) and 52.2% (CO activation). Hydrocarbon selectivities were similar after the hydrogen reductions at 280°C. In all three tests, methane selectivity was relatively high (8.8 to 10.4%), whereas C_{12^+} selectivity was relatively low (32 to 36%). Hydrocarbon selectivities on the syngas-pretreated catalyst were between values obtained on the CO-pretreated catalyst and on the H_2-reduced catalyst at 280°C; e.g., methane selectivity was 7%, while C_{12^+} selectiv-

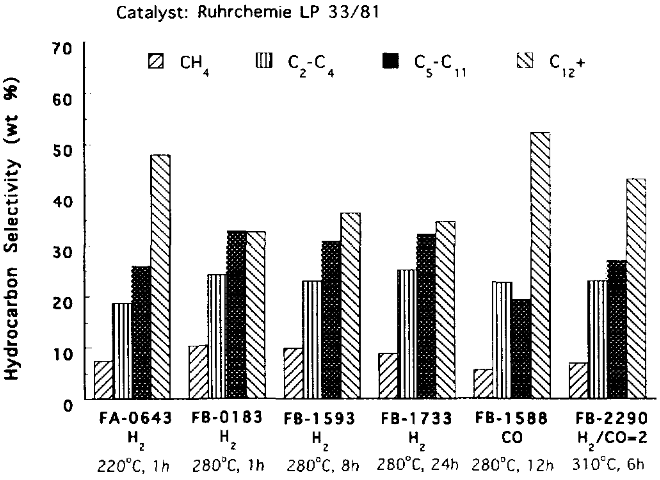

FIG. 4. Effect of pretreatment conditions on hydrocarbon product distribution.

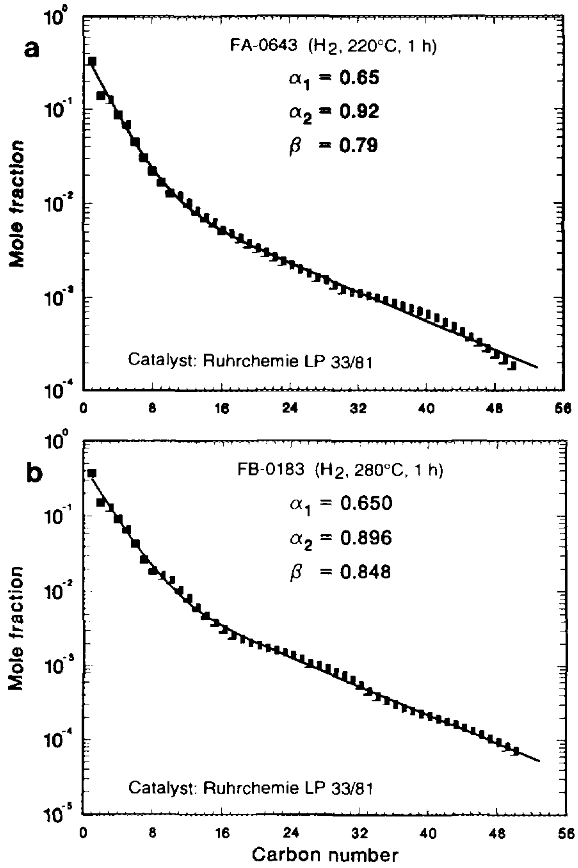

FIG. 5. Carbon number product distribution for selected pretreatment conditions: (a) run FA-0643 (93 h on stream); (b) run FB-0183 (71 h on stream).

ity was 43%. Methane production rate (per gram of iron in the catalyst) follows the same trends as the methane selectivity (mass fraction of methane in total hydrocarbons), as shown in Table 2.

Representative carbon number product distributions are presented in Fig. 5 in the form of Anderson–Schulz–Flory (ASF) plots. The data were fitted well with a three-parameter (double alpha) model of Huff and Satterfield (31). The model parameters (chain growth parameters, α_1 and α_2, and the fraction of type 1 sites, β) were estimated by a nonlinear regression. The fraction of high molecular weight products were higher in Run FA-0643 than in Run FB-0183, which is reflected in a higher value of α_2 parameter and a lower value of β. This is consistent with hydrocarbon product distributions shown in Table 2 and Fig. 4.

Primary products of FT synthesis are 1-olefins and, to a smaller extent, *n*-alkanes (1, 5, 32). The 1-olefin may subsequently be hydrogenated to the *n*-alkane, isomerized to the 2-olefin, or readsorbed to initiate further chain growth. The total olefin content (selectivity), defined as 100 × olefin/(olefin + paraffin), obtained in tests FB-1588 (CO pretreatment) and FB-1593 (H_2 reduction at 280°C for 8 h) is shown in Fig. 3a for carbon numbers up to C_{15}. The CO-pretreated catalyst had higher olefin content than the H_2-reduced catalyst. For example, the olefin contents of the CO-pretreated catalyst, in C_2–C_4 and C_5–C_{11} ranges, were about 10–15 wt.% higher than on the hydrogen-reduced catalyst (Table 2). The total olefin content in all four tests employing the H_2 reductions was nearly the same (not shown in Fig. 3a) in spite of differences in reduction conditions (temperature or duration). The olefin selectivity after the syngas pretreatment (FB-2290) was between values obtained in tests after the CO and the H_2 pretreatments. The olefin selectivity, in Fig. 3a, passes through a maximum at C_3, which is due to secondary reactions. Ethylene is more reactive than other low molecular weight olefins, whereas a decrease in olefin content with increase in molecular weight has been attributed to greater adsorptivities (5, 32) and/or lower diffusivities (33) of high molecular weight 1-olefins, as well as to readsorption of 1-olefins and subsequent chain termination to paraffins (34).

The 1-olefin isomerization activity, measured by a 2-olefin content (selectivity), varied markedly with pretreatment conditions. As shown in Fig. 3b, the isomerization of C_{8^+} olefins was higher in Run FB-1593 (H_2 reduction) than in Run FB-1588 (CO pretreatment). The 2-olefin content of the syngas-pretreated catalyst (FB-2290) was nearly the same as that of the CO-pretreated one, and the 2-olefin selectivity in tests FA-0643 and FB-1593 was essentially the same as that in FB-1593. The 2-olefin selectivity of C_{8^+} hydrocarbons in Run FB-0183 (H_2 reduction at 280°C for 1 h) was greater than that obtained in the other three tests employing H_2 reductions reaching 75% at C_{15} (not shown in Fig. 3b). An increase in the 1-olefin isomerization with increase in carbon number (molecular weight) was observed in all six tests and is due to the same factors which affect the total olefin selectivity. A longer residence time of high molecular weight 1-olefins either on the catalyst surface or in the pores increases probability for secondary hydrogenation, isomerization, and readsorption reactions.

DISCUSSION

Major findings from reaction tests following six different pretreatment procedures are as follows. (1) After the CO pretreatment the catalyst activity was high initially and then gradually decreased with time. The catalyst deactivation rate was moderate. (2) Initial catalyst activity in tests after H_2 reductions at 280°C using a flow rate of 175 cm^3/min for 8 or 24 h was low. Steady state activities in these two tests were slightly lower than those obtained after H_2 reductions at 220°C and 280°C for 1 h, using a flow rate of 4,000 cm^3/min. (3) Catalyst activity increased with time in all four tests where H_2 reductions were employed. (4) The WGS activity was higher on the H_2-reduced catalyst, than on the CO- or the syngas-pretreated catalyst. (5) Secondary reactions were higher in tests on the hydrogen-reduced catalyst. (6) The CO and, to a lesser extent, the syngas pretreatments favored production of higher molecular weight products as compared to the H_2 reductions at 280°C. The catalyst reduced with H_2 at 220°C produced less gaseous hydrocarbons (C_2–C_4) than either the CO- or the syngas-pretreated catalyst, and its C_{12^+} selectivity was only slightly lower than that of the CO-pretreated catalyst.

Most of these observations are in a qualitative agreement with those made in our previous studies with precipitated iron catalysts having nominal compositions 100 Fe/3 Cu/0.2 K (21) and 100 Fe/0.3 Cu/0.8 K (22). A possible explanation for these observations on the basis of results from characterization studies and previous FT reaction studies on the effects of promoters, binders, and bulk iron phases on catalyst activity and selectivity are given below.

Catalyst Activity and Stability—CO and Syngas Activations

After pretreatments with the CO and the syngas, the bulk iron phases identified by Mössbauer spectroscopy were Hägg carbide (χ-Fe_5C_2), 54% in both cases, and iron oxide or carbide phases which exhibit superparamagnetic behavior (26). The catalyst surface area (118 and 99 m^2/g after the CO and syngas pretreatments, respectively) and the pore volume were also similar after these two pretreatments. During the subsequent FT synthesis, no significant differences in the catalyst activity and selectivity were observed in tests with the CO- and the syngas-pretreated catalysts. This represents a good correlation between the catalytic behavior and the bulk iron phases and textural properties of the catalyst after the pretreatment. A moderate decrease of catalyst activity with time after the CO or the syngas pretreatment coincides with partial conversion of the Hägg carbide to magnetite (26), which is consistent with the carbide model for FT synthesis (2, 9). Catalyst deactivation may also be due to blocking of active sites by carbonaceous deposits (1, 35). The observed losses in activity are small in comparison to those observed in some of our tests of precipitated iron catalysts without silica as a binder (21, 22). On an unsupported catalyst the active sites are close to each other, which facilitates a crystallite size growth by sintering, and carbonaceous deposits can cover a larger fraction of the surface, both of which contribute to catalyst deactivation. In contrast, the active sites are more isolated in the presence of silica binder on the Ruhrchemie catalyst. As a result, an inactive carbon layer covers a smaller number of active sites, and the growth of iron crystallites is hindered during FT synthesis, and thus the catalyst deactivation is slower than on a low surface area unsupported catalyst.

Catalyst Activity and Stability—Comparison of CO, Syngas, and H_2 Activations

After all four H_2 reductions, the initial catalyst activity during the conditioning period at temperatures between 220 and 250°C was lower than that of the CO-pretreated catalyst (Fig. 1). This is consistent with the competition model of Niemantsverdriet and van der Kraan (10). According to this model, during an early period of FT synthesis on the H_2-reduced catalyst some of the active surface carbon is consumed to form bulk carbides, and thus the rate of FT synthesis is initially lower relative to a precarbided catalyst. As the time progresses, the χ-carbide, formed after the CO and the syngas pretreatments, is gradually oxidized to magnetite, whereas α-Fe and a fraction of iron oxide phases, formed after H_2 reductions, are converted to ε'-$Fe_{2.2}C$ iron carbide (26). As a result of these changes in the catalyst bulk and surface compositions, differences in the catalyst activity after about 60 h on stream were smaller (less than 15%).

Catalyst Activity and Stability—H_2 Reduction

Four H_2 reduction procedures were employed to study effects of the reduction temperature (FA-0643 vs FB-0183) and the duration of reduction (FB-1593 vs FB-1733) and the combined effect of duration and flow rate (FB-0183 vs FB-1593 or FB-1733). We specifically address the following observations: (1) Similarities of FT activities in tests FA-0643 (reduction at 220°C for 1 h) and FB-0183 (reduction at 280°C for 1h); (2) low initial activities (during the conditioning period at reaction temperatures 220–240°C, and during early periods of synthesis at 250°C) in tests FB-1593 and FB-1733, after H_2 reductions at 280°C for 8 and 24 h, respectively; and (3) absence of catalyst deactivation in all four tests during the first 100–150 h on stream.

After the reduction with H_2 at 220°C for 1 h the BET surface area was 179 m^2/g, and bulk iron was in the form of oxides exhibiting superparamagnetic behavior. A fraction of iron oxides was in the form of magnetite with an average particle size of 5 nm, as determined by X-ray diffraction (26). The catalyst reduced at 280°C for 1 h had the BET surface area of 136 m^2/g, and bulk iron was partly in the form of α-Fe (13%), while the remainder was in the form of superparamagnetic oxides (Fe^{2+} and Fe^{3+}). The average particle size of α-Fe, determined by X-ray line broadening method, was 8 nm. The degree of iron reduction was lower after the H_2 reduction at 220°C, but the catalyst had higher surface area (i.e., smaller crystallite size) than the catalyst reduced at 280°C. As a result of these two opposing effects the initial activities in tests FA-0643 and FB-0183 were nearly the same. During FT synthesis in both tests the catalyst was partially carburized to ε'-carbide (20–42%), and the activity increased slightly with time.

Bulk iron phases in the catalyst reduced at 280°C for 8 h were α-Fe (8%) and superparamagnetic oxides (92%). (The catalyst was not characterized after the H_2 reduction at 280°C for 24 h.) The average α-Fe particle size after H_2 reduction at 280°C for 8 h was 10 nm (SA = 160 m^2/g). The increase in crystallite size in comparison to H_2 reductions at 220°C and 280°C for 1 h is due to a longer duration of reduction and the use of a low reductant flow rate. The latter results in an increase of the water partial pressure, which in turn enhances sintering of metal particles (1, 36). During FT synthesis at 250°C the catalyst reduced at 280°C for 8 or 24 h was also partially carburized to ε'-carbide. The fraction of bulk iron in the form of ε'-carbide in the used catalyst samples from Runs FB-1593 and FB-1733 varied between 31 and 52%, the remainder being in the form of superparamagnetic oxide/carbide phases. The bulk compositions of the used catalysts from these two tests were similar to those of the used catalysts in Runs FA-0643 and FB-0183, and consequently the steady state activities in all four tests were within 14% (based on values of the apparent rate constant).

The reasons for low initial activities in tests FB-1593 and FB-1733 are not completely understood. As stated above, the crystallite size after hydrogen reduction at 280°C for 8 h (FB-1593) was larger in comparison to H_2 reductions at 220 and 280°C for 1 h, and it is reasonable to expect that this would also be the case after 24 h reduction (FB-1733). The carburization of large particles is slower than that of the small ones (3); if we accept the postulate that iron carbides are more active for FTS than iron oxides, then we would expect lower activities in tests FB-1593 and FB-1733 in comparison to tests FA-0643 and FB-0183. Activity increases with time-on-stream with the extent of carburization of oxide particles, and the differences in activities in all four tests decrease with time (Fig. 2).

Also, lower activities in tests FB-1593 and FB-1733 may have been caused in part by migration of sulfur (the origin of which are bulk sulfate impurities present in the metal nitrates used to prepare the catalyst) from the bulk to the surface of the catalyst during the reduction. In a recent study at Sandia National Laboratory (37, 38) with a precipitated iron catalyst with nominal composition 100 Fe/3 Cu/0.2 K, it was found that the sulfur migration to the surface increases with both the reduction temperature and duration. These findings were used to explain results obtained in our study with this catalyst (21), which showed that the initial FT activity decreased markedly with increase in reduction temperature and/or duration of H_2 reduction. For example, initial (H_2 + CO) conversions after H_2 reductions were 30% (H_2 at 280°C for 24 h), 44% (H_2 at 280°C for 8 h), and 58% (H_2 at 250°C for 24 h), whereas initial conversions after the CO or syngas ($H_2/CO = 0.67$) pretreatments were about 80%. In this case, the decrease in activity could be correlated with increase in sulfur coverage. In the present study with the Ruhrchemie catalyst a decrease in activity with increase in duration of reduction at 280°C (1 h vs 8 or 24 h) was smaller than that observed in the study with the 100 Fe/3 Cu/0.2 K catalyst. According to Sault (37), this is to be expected since the BET surface area of the H_2-reduced Ruhrchemie catalyst (140–180 m^2/g) is much greater than that of the 100 Fe/3 Cu/0.2 K catalyst (5–10 m^2/g), and therefore the level of sulfur poisoning would be considerably smaller. Sault observed a trace amount of sulfur on hydrogen-reduced Ruhrchemie catalyst by Auger electron spectroscopy (AES), whereas, in our study employing X-ray photoelectron spectroscopy (XPS), we did not detect any sulfur during H_2 reduction at 280°C for 16 h (26). This discrepancy is probably due to greater sensitivity of the former technique. On the basis of these results one cannot rule out the possibility that sulfur poisoning had a detrimental effect on the FT catalyst activity in tests FB-1593 and FB-1733.

Activity of the H_2-reduced catalyst was stable with time or increased slightly during FT synthesis. This was also observed in our pretreatment effect studies with the 100 Fe/3 Cu/0.2 K and 100 Fe/0.3 Cu/0.8 K catalysts (21, 22). A possible explanation for this observation is that concentration of surface hydrogen during FT synthesis plays an important role in stabilizing the catalyst activity. It appears that the hydrogen concentration on the surface is higher on an H_2-reduced catalyst than on a fully (or partially) carbided catalyst following a CO or a syngas pretreatment. This could be due to the larger number of sites available for H_2 adsorption or to differences in strength of sites for hydrogen adsorption. When the concentration of surface hydrogen is sufficiently high, the rate of removal of surface carbon through hydrogenation is greater than or equal to the rate of CO dissociation. Consequently, the formation of carbonaceous or inactive carbon deposits is prevented or limited and the catalyst does not deactivate. Its activity may increase as a result of continued creation of active sites. In the present study this coincides with partial conversion of iron oxides to ε'-carbide, but does not necessarily imply that the ε'-carbide is the active phase for FT synthesis.

Water–Gas–Shift Activity

The WGS activity was higher over the catalyst reduced with the H_2 than on the catalyst pretreated with either the CO or the syngas. This observation is in agreement with results reported in several previous studies with precipitated iron catalysts (6, 21, 39). The nature of the active form of an iron catalyst for the WGS is still speculative and much of the evidence is circumstantial (7). It has been suggested that carbide phases are less active for the WGS reaction than metallic iron (39, 40) or that carbide phases are less active than magnetite (41). However, in a study by Satterfield *et al.* (7), with a fused iron catalyst, the WGS activity could not be correlated with a bulk concentration of magnetite. In the present study, we did not detect any α-Fe in the used catalysts and the relative amount of magnetite, determined by Mössbauer spectroscopy, in the used catalyst from Run FB-2290 (the syngas pretreatment) was greater than that in any of the used catalysts from tests with the H_2 reduction (26), but its WGS shift activity was lower. However, the nature of a significant fraction (45–80%) of iron in the used catalysts was not quantified, since it was in the form of small oxide/carbide particles exhibiting superparamagnetic behavior at room temperature.

Catalyst Selectivity

The olefin content in the hydrocarbon product was lower and 2-olefin selectivity was greater in tests on the H_2-reduced catalyst than on the CO- or syngas-pretreated catalyst. This is consistent with the postulate that the surface hydrogen concentration is higher on the H_2-reduced catalysts than on the CO- or the syngas-pretreated catalysts. A higher hydrogen concentration enhances hydrogenation of olefins. According to Dictor and Bell (13) the olefin hydrogenation and isomerization reactions may occur via a common set of intermediates, and thus the olefin isomerization also increases with increase in hydrogen concentration. In tests after the H_2 reductions at 280°C (FB-0183, FB-1593, and FB-1733) methane and gaseous hydrocarbon selectivities were higher than those in tests following the CO and the syngas pretreatments (Fig. 4 and Table 2). Again, this is due to higher surface hydrogen concentration on the H_2-reduced catalyst, which favors methanation and chain termination reactions. However, the catalyst reduced with H_2 at 220°C (FA-0643) had the lowest gaseous hydrocarbon selectivity (C_2–C_4), and its C_{12^+} hydrocarbon selectivity was comparable to that of the CO-pretreated catalyst. Reasons for this type of behavior are not clearly understood, but may be related to the fact that this reduction procedure did not result in formation of any metallic iron. The ε'-carbide was found in all used catalyst samples in tests in which the hydrogen reductions were employed. It is possible that the surface affinity towards hydrogen or CO is not the same on the partially or completely reduced iron catalyst as on the catalyst which is in an oxide form after the reduction with hydrogen. Carburization of metallic iron proceeds very rapidly upon exposure to a synthesis gas (2, 3), but is slow on the Ruhrchemie catalyst in the oxide form (26), even at temperatures higher than those normally used in FT synthesis. This may result in differences in the surface composition of the working catalyst, which in turn has a large impact on the catalyst selectivity.

Differences in the surface composition may be rather subtle and difficult to detect by surface spectroscopic techniques. In the AES study of the Ruhrchemie catalyst after H_2 reductions at 220°C for 1 h, 280°C for 1 to 8 h, and CO pretreatment at 280°C, it was found that the surface compositions after these pretreatments are nearly identical (37, 38). Only partial reduction of iron to Fe_3O_4 or Fe_xO was observed on this catalyst, and no surface carbon deposition was observed. However, in our study by X-ray photoelectron spectroscopy of the Ruhrchemie catalyst after H_2 and CO pretreatments at 300°C for 4 h, it was found that the CO pretreatment leads to carbon deposition and greater degree of reduction to zero-valent iron than that obtained after the hydrogen reduction (26). The nature of the surface iron species on the CO-pretreated catalyst was not positively identified due to a close proximity of binding energies of metallic iron and surface carbide. Our data show that this type of surface inhibits hydrogenation reactions and promotes hydrocarbon chain growth.

SUMMARY

The effects of pretreatment conditions on the Ruhrchemie catalyst performance (activity, selectivity, and stability with time) during Fischer–Tropsch synthesis at 250°C, 1.48 MPa, 2.0 Nl/g-cat/h (3.8 Nl/g-Fe/h), and $H_2/CO = 0.67$ were studied in a fixed-bed reactor.

It was found that hydrogen reductions (four different pretreatments) result in stable or increasing catalyst activity with time-on-stream (up to 154 h of testing). Increase in FT activity coincides with conversion of metallic iron and part of iron oxides to pseudo-hexagonal ε'-carbide. The initial catalyst activity in tests after the H_2 reductions at 280°C for 8 and 24 h (tests FB-1593 and FB-1733) was markedly lower (up to 25%) than in tests after the H_2 reductions at 220 or 280°C for 1 h. This may be due to the fact that carburization of large iron oxide particles was significantly slower than that of the smaller particles under the reaction conditions employed in the present study. Also, there is some experimental evidence (37) that sulfur migrates from the bulk to the surface of the catalyst during the reduction at 280°C, and therefore the observed lower activities in tests FB-1593 and FB-1733 may have been caused in part by partial poisoning of the active sites by sulfur.

Pretreatments with carbon monoxide and syngas resulted in partial conversion of iron oxides to monoclinic χ-carbide. Initial activity of the CO-pretreated catalyst was higher than that of the hydrogen reduced catalyst, which is consistent with the competition model (10). Catalyst deactivation in these two tests was accompanied by partial conversion of χ-carbide to magnetite, in agreement with the hypothesis that an iron carbide is the active phase for FT synthesis (2, 9).

In tests following hydrogen reductions at 280°C (three different procedures) methane and gaseous hydrocarbon selectivities were higher than on the catalyst reduced at 220°C or on the CO- and the syngas-pretreated catalyst. Secondary reactions (1-olefin hydrogenation, isomerization, and readsorption) were more pronounced in tests on the hydrogen-reduced catalyst than on the CO- and the syngas-pretreated catalyst. The degree of both bulk iron reduction and surface reduction, determined by Mössbauer spectroscopy and X-ray photoelectron spectroscopy, was higher after the CO pretreatment (26). It appears that partially carbided surface (CO pretreatment) inhibits secondary reactions and promotes the hydrocarbon chain growth. On the metallic iron/iron oxide (Fe^{2+} and Fe^{3+}) surface the surface hydrogen concentration is higher, and this results in higher hydrogenation activity and chain termination reactions (i.e., increased selectivity of low molecular weight products) and better stability with time-on-stream (hydrogen reductions at 280°C).

The activity/selectivity trends observed in the present study with the Ruhrchemie catalyst are generally in a qualitative agreement with previous studies with promoted iron catalysts which do not contain the silica binder. Issues such as sulfur migration to the surface and its poisoning effect and underlying reasons for selectivity differences arising from the use of different reductants (H_2 vs CO) require further studies.

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