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Steady state Fischer–Tropsch synthesis in fixed-bed and stirred tank slurry reactors

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Abstract

A precipitated iron catalyst (100 Fe/0.3 Cu/0.8 K) was tested in a fixed-bed reactor and a stirred tank slurry reactor at 250–260°C, 1.48 MPa, 2 Nl g-cat^{-1} h^{-1}, and H_2:CO = 2:3. Two different pretreatment procedures were employed (hydrogen reduction at 250°C and synthesis gas activation at 280°C) in each of the two reactor types. The activity of the hydrogen reduced catalyst was stable with time-on-stream, and it produced more methane and gaseous hydrocarbons than the syngas pretreated catalyst. Secondary reactions (olefin hydrogenation and isomerization) were more pronounced in tests with the hydrogen reduced catalyst. Hydrocarbon distribution shifted toward lower-molecular-weight products with time-on-stream in the stirred tank slurry reactor tests, but the total olefin content of C_2 to C_{15} hydrocarbons remained constant during the tests which lasted 300 hours.

1. Introduction

Fischer–Tropsch (FT) hydrocarbon synthesis from coal derived synthesis gas is practised on a commercial scale at SASOL plants in South Africa in fixed- and fluidized-bed reactors. The circulating fluidized-bed (Synthol) reactors have high selectivity to gasoline range products, whereas fixed-bed (ARGE) reactors produce predominantly diesel fuel and hydrocarbon waxes. This variation in product distribution is achieved through the use of different process conditions and catalysts. Potassium-promoted iron catalysts are used in both reactors, but the quantitative information on performance of these catalysts is limited, since activities and selectivities are often reported as relative quantities and the process conditions under which the results were obtained are not stated [1].

In recent years several studies were conducted with an alkali-promoted fused iron catalyst, used commercially in ammonia synthesis, which is similar to that used in synthol reactors at SASOL [2–4], and with a precipitated iron catalyst synthesized by Ruhrchemie, which was used originally in ARGE reactors at SASOL [5–8]. Precipitated iron catalysts promoted with copper and potassium were used in some of the most successful slurry bubble column reactor tests [9,10]. Data on performance of precipitated iron catalysts (activity, selectivity and stability) during Fischer–Tropsch synthesis (FTS) under steady-state conditions are scarce. Here, we report results from a study with a precipitated iron catalyst in a fixed-bed and a stirred tank slurry reactor. Reported results provide information on the effects of pretreatment procedures (H_2 vs. synthe-

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sis gas), reactor type (fixed-bed vs. stirred tank slurry reactor) and time-on-stream on the catalyst activity, stability and product distribution (hydrocarbon selectivity and olefin selectivities as a function of carbon number).

2. Experimental

A detailed description of our fixed-bed reactor (FBR) and stirred tank slurry reactor (STSR) systems used in this study was given elsewhere [7,8,11,12]. The FBR was constructed of 1 cm i.d. stainless steel tube with an effective bed volume of 28 cm^3, whereas a 1 dm^3 reactor (Autoclave Engineers) was used as the STSR. The feed gas flow-rate in both systems 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. High-molecular-weight hydrocarbons (wax), collected in the high pressure trap (FBR) or withdrawn from a slurry reactor through a porous cylindrical sintered metal filter, and liquid products, collected in the low pressure ice trap, were analyzed by gas chromatography. The reactants and noncondensible products leaving the ice traps were analyzed on an on-line GC (Carle AGC 400) equipped with multiple columns and both flame ionization and thermal conductivity detectors. Further details on the product analysis system can be found elsewhere [11,12]. Mass balance closures were typically $100 \pm 3\%$.

A precipitated iron catalyst used in this study was synthesized in a continuous co-precipitation unit [11,12]. Briefly, the catalyst precursor was continuously precipitated from a flowing aqueous solution containing iron and copper nitrates at the desired Fe/Cu ratio, using aqueous ammonia. After filtering and washing, Fe/Cu co-precipitate was vacuum dried, and potassium promoter was added as aqueous $KHCO_3$ solution via an incipient wetness pore filling technique. The nominal catalyst composition is 100 Fe/0.3 Cu/0.8 K (on mass basis). Dried catalyst was calcined in air at 300°C for 5 h, and then crushed and sieved to about 0.25 to 0.50 mm (30 to 60 mesh), for tests in the fixed-bed reactor, or to less than 53 μm (270 mesh) for the tests in the slurry reactor. A purified n-octacosane was used as the liquid medium in the slurry reactor.

Four tests were conducted in the fixed-bed and the stirred tank slurry reactors, which lasted between 140 and 300 hours. In two of the tests the catalyst was reduced in-situ with hydrogen at 250°C for 2 hours (FBR test FB-0403, and STSR test SA-0791). Two tests were conducted after synthesis gas (H_2:CO = 2:3) pretreatments at 280°C for 8 h (FBR test FB-0352) or 12 h (STSR test SB-2262). After the pretreatments the catalyst was tested at: 250°C, 1.48 MPa, $H_2/CO = 0.67$ and 2 Nl/g-cat^{-1} h^{-1} (where, Nl h^{-1}, denotes volumetric gas flow-rate at standard temperature and pressure) in the fixed-bed reactors, whereas the reaction temperature was 260°C (the other conditions being the same) in the test SA-0791. During the first 80 h on stream in the slurry reactor test SB-2262 the reaction temperature was 250°C, and 260°C for the remainder of the test. The catalyst from the same preparation batch (C0308-3) was used in the two fixed-bed reactor tests and in the test SA-0791, whereas the catalyst from another batch (C0308-1) was used in the test SB-2262.

3. Results and discussion

3.1. Catalyst characterization results

The catalyst was characterized after various stages of pretreatment and usage in the FT synthesis reaction by BET-N_2 surface area measurements, X-ray diffraction (XRD) and/or Mössbauer effect spectroscopy (MES). Results of these measurements are summarized in Table 1. Elemental analysis of catalyst samples from two preparations by atomic absorption spectroscopy

Table 1
Summary of catalyst characterization results — 100 Fe/0.3 Cu/0.8 K catalyst (batch C0308-3)

Characterization of calcined catalyst samples by BET and XRD[a]		
SA (m^2/g)	130	(151)
Pore volume (cm^3/g)	0.36	(0.26)
Average pore diameter (nm)	11	(6.9)
Phases	α-Fe_2O_3	(α-Fe_2O_3)
Average particle size (nm)	14	(17)
Characterization of catalyst samples by BET and MES after pretreatment in the fixed-bed reactor		
Pretreatment conditions	H_2, 250°C, 2 h	$H_2/CO = 0.7$, 280°C, 8 h
SA (m^2/g)	21	34
Pore volume (cm^3/g)	0.28	0.3
Average pore diameter (nm)	38	35
Phases	100% α-Fe	16% Spm; 84% χ-Fe_5C_2
Phases identified by MES after FT synthesis in the fixed-bed reactor		
	Run FB-0403, TOS = 140 h	Run FB-0352, TOS = 150 h
Top	13% Spm; 64% χ-Fe_5C_2; 23% α-Fe	6% Spm; 94% χ-Fe_5C_2
Bottom	8% Spm; 14% Fe_3O_4; 7% χ-Fe_5C_2; 71% ϵ'-$Fe_{2.2}C$	9% Spm; 59% Fe_3O_4; 32% ϵ'-$Fe_{2.2}C$
Phases identified by MES and XRD during FT synthesis in the stirred tank slurry reactor		
	Run SA-0791	Run SB-2262 (C0308-1 batch)
		TOS = 0 h: 8% Spm; 38% Fe_3O_4; 54% ϵ'-$Fe_{2.2}C$
		TOS = 54 h: 7% Fe_3O_4; 86% ϵ'-$Fe_{2.2}C$; 7% χ-Fe_5C_2
		XRD: Fe_3O_4; ϵ'-$Fe_{2.2}C$; χ-Fe_5C_2
	TOS = 290 h	TOS = 284 h: 7% Spm; 93% χ-Fe_5C_2
	XRD: ϵ'-$Fe_{2.2}C$	XRD: χ-Fe_5C_2

[a] Data in parenthesis are for the catalyst from batch C0308-1.
Spm = superparamagnetic phase; TOS = time-on-stream.

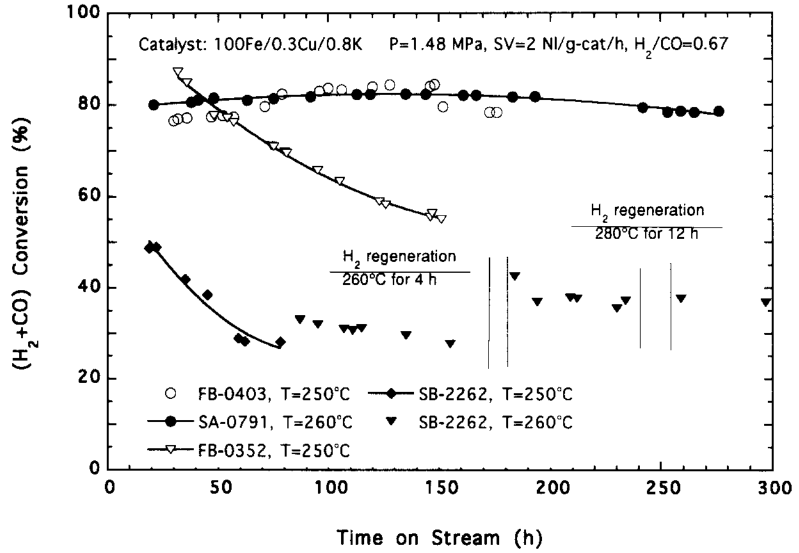

Fig. 1. Effect of pretreatment procedures on synthesis gas conversion and catalyst stability. Reduction conditions: H_2, 250°C for tests FB-0403 and SA-0791; $H_2/CO = 0.7$, 280°C for tests FB-0352 and SB-2262.

gave the following results: 100 Fe/0.27 Cu/0.95 K (C0308-1 batch) and 100 Fe/0.33 Cu/0.84 K (C0308-3 batch). The actual compositions are close to each other and to the nominal catalyst composition. After calcination the catalyst from batch C0308-1 had larger surface area and smaller pore volume than the catalyst from batch C0308-3 (Table 1). The catalyst from both batches was in the form of crystalline hematite (α-Fe_2O_3) with particle sizes of 14–17 nm after calcination at 300°C. In general, the physical properties of the catalyst samples from the two batches were not markedly different.

After pretreatments with H_2 at 250°C or syngas at 280°C in the FBR both the BET surface area and the pore volume of the catalyst had decreased, and the average pore diameter increased relative to the calcined catalyst. The catalyst was completely reduced to α-Fe after the H_2 reduction. The most dominant iron phase in the syngas pretreated catalyst was monoclinic χ-Fe_5C_2 carbide (84%), the remainder being the phase exhibiting superparamagnetic properties (iron oxide or carbide). After the FT synthesis in the FBR there were differences in the nature of and/or relative amounts of bulk iron phases among the samples taken from the top part (near the reactor inlet) and the bottom part of the reactor, due to the presence of redox gradients in the gas composition along the reactor [13]. The reducing atmosphere prevails in the top part, whereas the gas environment is more oxidizing in the bottom part due to the presence of H_2O and CO_2 formed during the FTS reaction. Thus, the samples from the top part of the reactor contain iron carbides and/or α-Fe, whereas magnetite (Fe_3O_4) is present in samples from the bottom part of the reactor (see Table 1).

In the catalyst sample withdrawn from the slurry reactor after the syngas pretreatment at 280°C for 12 h (Run SB-2262) the following phases were identified: ϵ'-carbide (54%), Fe_3O_4 (38%), and superparamagnetic iron phase (8%). The degree of iron reduction in the STSR was lower than that in the FBR, and different iron carbide phases were formed in different types of reactors (χ-carbide in the FBR; ϵ'-carbide in the STSR). It is not clear whether this is due to: (a) use of different reactors, (b) differences in the pretreatment conditions (duration and gas flowrate per gram of Fe in the catalyst); or (c) use of catalyst from two preparation batches. After 54 h of FTS the relative amount of the carbide phases (ϵ'-carbide + χ-carbide) increased from 54% to 93%, whereas the amount of oxide phases decreased. This shows that progressive carburization of the catalyst occurred under FTS conditions. At 284 h on stream the ϵ'-carbide was completely converted to χ-carbide (Table 1). There were two regeneration procedures carried out with hydrogen prior to this sampling; one after 162 h (at 260°C for 4 h), and the other one after 244 h on stream (at 280°C for 12 h).

The catalyst from run SA-0791 was only characterized by XRD at the end of the run (TOS = 290 h). The pseudo-hexagonal ϵ'-carbide was the only crystalline iron phase found in this sample. At the end of STSR tests iron carbides were the most dominant phases in the used catalyst, regardless of the pretreatment procedures employed. The hydrogen reduced catalyst was carburized to ϵ'-carbide, whereas the syngas pretreated catalyst was carburized to χ-carbide during the FTS.

3.2. Catalyst activity and stability

Changes of (H_2 + CO) conversion with time-on-stream (TOS) for all four tests are shown in Fig. 1. After hydrogen reductions the syngas conversion was about 80% in both fixed-bed and STSR tests. During the STSR test SA-0791 at about 200 h on stream there was flow interruption resulting in temperature drop, and no measurements were taken during the next 40 h. After the synthesis was resumed the conversion was slightly lower, and the test was terminated at 300 h on stream.

After the synthesis gas pretreatments, the syngas conversion declined with time in both fixed-bed (FB-0352) and STSR tests (SB-2262). The syngas conversion in the FBR was initially higher (88% at 30 h on stream) than that of the hydrogen reduced catalyst, but at 150 h it was only 55%. The conversions in the STSR test SB-2262 were significantly lower than those in the FBR test FB-0403. The (H_2+CO) conversion decreased from an initial value of 49% to 28%, during the first 60 h of testing. Reaction temperature was then increased to 260°C, which was accompanied by increase in conversion to about 35% followed by slow deactivation. At about 162 h on stream the catalyst was regenerated with H_2 at 260°C for 4 h, which resulted in increase in conversion to about 43% at 170 h, followed by decrease to 37% at 240 h on stream. Another regeneration was attempted at 244 h using more severe reduction conditions (280°C for 12 h), but the conversion remained nearly the same (about 37%) and the test was terminated at 300 h on stream.

Comparisons of catalyst activities in terms of (H_2+CO) conversion are not meaningful when the reaction conditions are not the same and/or when the experiments are done in different types of reactors. In such cases an apparent reaction rate constant provides a better basis for comparison of catalyst activity. In this study the apparent reaction rate constant was calculated assuming that the reaction rate has a first-order dependence on hydrogen partial pressure and its units are: mmol (H_2+CO) converted h^{-1} g-Fe^{-1} MPa^{-1} of H_2. Calculation of the apparent rate constant in the STSR is quite straightforward if one assumes that it behaves as a perfectly mixed flow reactor. On the other hand, in the FBR the reaction rate varies with position along the reactor and estimation of the apparent rate constant is not so straightforward. In this case, the rate constants were estimated using a procedure described by Zimmerman et al. [14], and calculated values are listed in Table 2. Data obtained at 260°C (STSR) were converted to 250°C using the activation energy of 90 kJ/mol, which is typical for FTS over iron catalysts [7]. The average values of the apparent rate constant at 250°C after H_2 reductions in the FBR and the STSR were nearly the same, i.e.: 233 and 247 (mmol h^{-1} g-Fe^{-1} MPa^{-1}), respectively.

With the syngas pretreated catalyst the corresponding values of the apparent reaction rate constant at 250°C were: 134–177 (FBR), and 46–68 mmol h^{-1} g-Fe^{-1} MPa^{-1} (STSR) during the mass balance periods shown in Table 2. The

Table 2
Comparison of catalyst performance in fixed-bed and slurry reactor tests

Test designation	FB-0403		SA-0791			FB-0352		SB-2262[b]		
Temperature (°C)	250	250	260	260	260	250	250	250	260	260[a]
SV (Nl g-cat^{-1} h^{-1})	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Time-on-stream (h)	67	116	39	111	266	72	144	44	92	212
CO conversion (%)	86.4	89.5	86.1	86.8	82.4	76.8	59.7	30.0	32.8	38.8
(H_2+CO) conversion (%)	81.4	84.3	81.8	82.6	78.7	70.7	55.7	28.7	31.3	36.7
k (mmol g-Fe^{-1} h^{-1} MPa^{-1})	218	229	347	365	326	177	134	68.6	77.0	93.0
Usage ratio (H_2/CO)	0.61	0.61	0.60	0.60	0.61	0.59	0.59	0.61	0.60	0.57
Exit ratio (H_2/CO)	1.30	1.54	1.20	1.22	1.04	1.18	0.86	0.71	0.72	0.73
$K_p=P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$	77.0	78.1	33.2	42.2	39.6	20.0	17.8	26.0	10.4	12.7
Hydrocarbon selectivity (wt.-%)										
CH_4	9.1	8.4	5.5	6.0	6.8	4.3	5.0	6.2	7.4	7.0
C_2–C_4	26.5	24.4	19.0	21.3	24.0	18.6	20.6	15.6	19.9	20.5
C_5–C_{11}	41.3	41.7	30.0	38.5	41.0	23.1	24.0	14.5	14.8	15.3
C_{12+}	23.1	25.5	45.5	34.2	28.2	54.0	50.4	63.7	57.9	57.2

$P=1.48$ MPa, $H_2/CO=0.67$ for all tests.
[a] Following H_2 regeneration.
[b] Catalyst from C0308-1 batch.

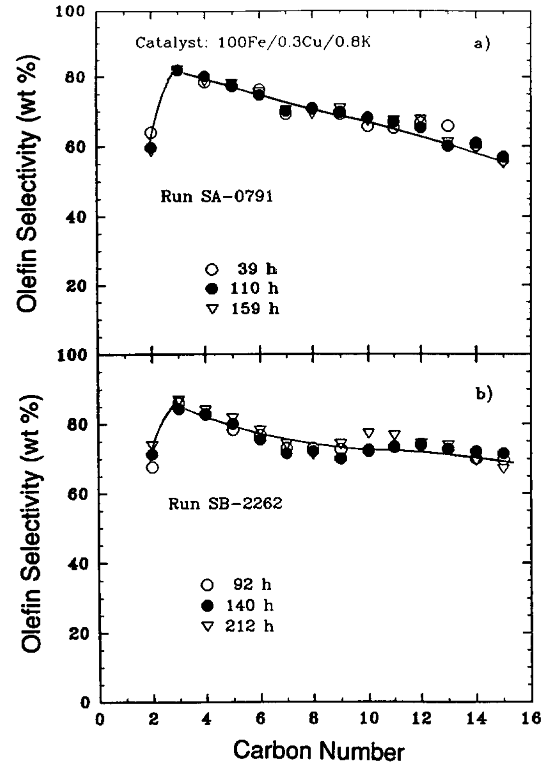

Fig. 2. Effect of time-on-stream on olefin selectivity in the slurry reactor tests: (a) run SA-0791; (b) run SB-2262.

apparent rate constant in the fixed-bed reactor test FB-0352 at 30 h on stream was 218 (mmol h^{-1} g-Fe^{-1} MPa^{-1}), which is only about 10% less than that of the H_2 reduced catalyst. The intrinsic catalyst activity was significantly lower in the STSR than in the FBR, which is probably due to the use of catalysts from two different batches and differences in the pretreatment procedures.

The FTS reaction on iron catalysts is accompanied by a reversible water-gas-shift (WGS) reaction, with water being the primary product of the FTS reaction while CO_2 is formed as a secondary product during the course of the WGS reaction. Values of the (H_2/CO) usage ratio, UR, and partial pressure quotient, $K_p = P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$, provide relative measures of the water-gas-shift activity. The equilibrium values of the partial pressure quotient at 250 and 260°C are: 83.6 and 70.9, respectively [15]. The hydrogen reduced catalyst had higher WGS activity than the syngas activated catalyst (see Table 2).

The activity trends observed in the present study with the 100 Fe/0.3 Cu/0.8 K catalyst are consistent with results from our studies with precipitated iron catalysts with nominal compositions 100 Fe/3 Cu/0.2 K and 100 Fe/5 Cu/4.2 K/25 SiO_2 (Ruhrchemie catalyst), which showed that the hydrogen reduced catalysts have higher WGS activity and are more stable than the CO or syngas pretreated catalysts [11,16].

3.3. Hydrocarbon product distribution

Hydrocarbon selectivities, as a function of TOS, obtained in all four tests are given in Table 2. Gradual shift towards lower-molecular-weight products (CH_4, C_2–C_4, C_5–C_{11}) accompanied with decrease in the C_{12}+fraction, was clearly evident in STSR tests, which lasted longer than the FBR tests. The syngas pretreated catalyst produced less gaseous hydrocarbons (C_1–C_4) and more C_{12}+products than the H_2 reduced catalyst. Hydrocarbon product distribution in test SB-2262 was unusual in that low C_2–C_4 and high

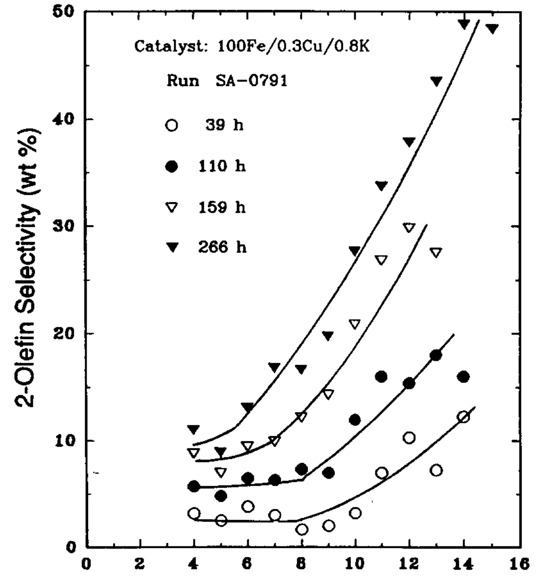

Fig. 3. Variation of 2-olefin selectivity with time-on-stream (run SA-0791).

C_{12} + selectivities were accompanied by relatively high methane selectivity. In the tests with the H_2 reduced catalyst methane selectivity in the slurry reactor (SA-0791) varied from 5.5 to 6.5% (before the operational accident), and was markedly lower than that in the fixed-bed reactor (about 9%), even though the reaction temperature was 10°C higher in the STSR. This is probably due to a much better temperature control in the STSR, and/or due to differences in the catalyst composition (iron phases) during the FTS.

3.4. Olefin selectivity

The consensus from many studies with iron FT catalysts is that 1-olefins and, to a smaller extent, n-alkanes are the primary products of FTS [1,5,19,20]. The 1-olefin may subsequently be hydrogenated to the n-alkane or isomerized to the 2-olefin. The effect of time-on-stream on total olefin content and 2-olefin selectivity is shown in Figs. 2 and 3, for the two STSR tests. Total olefin content remained constant with time (Fig. 2), whereas 2-olefin selectivity, defined as 100 × (2-olefin)/(1-olefin + 2-olefin), increased with time in the test SA-0791. The 2-olefin selectivity was low (4–15%), and did not vary with time-on-stream in the test SB-2262.

As can be seen in Fig. 2, the olefin content dependence on carbon number of hydrocarbon products passes through a maximum. This is believed to be due to secondary hydrogenation of 1-olefins [17,18]. Ethylene is more reactive than other low-molecular-weight olefins, whereas the decrease in olefin content with increase in molecular weight has been attributed to their greater adsorptivity [18,19], higher solubility resulting in longer residence time in a slurry reactor [5,20], and/or lower diffusivities [21]. The increase in olefin isomerization activity with increase in carbon number is due to the same factors which affect the olefin hydrogenation activity. The longer residence time of high-molecular-weight 1-olefins either in the catalyst pores or in the reactor itself increases probability for secondary hydrogenation and isomerization reactions.

The effects of pretreatment conditions and the reactor type on olefin selectivity are shown in Fig. 4. In both the FBR and the STSR, the olefin content was higher on the syngas pretreated catalyst than on the H_2 reduced catalyst. Hydrogenation activity was higher in the STSR than in the FBR after the syngas pretreatments, even though the conversion was lower in the former than in the latter.

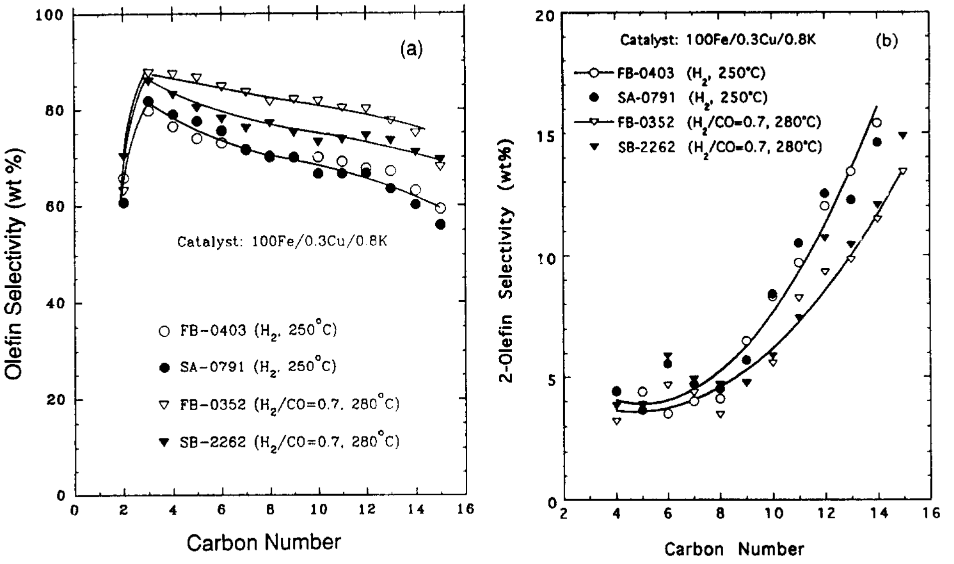

Fig. 4. Comparison of (a) olefin selectivities and (b) 2-olefin selectivities in fixed-bed and slurry reactor tests.

The initial (first 100 h on stream) 2-olefin selectivity was independent of the reactor type, as illustrated in Fig. 4b. The degree of 1-olefin isomerization was low in all tests, and slightly higher on the H_2 reduced catalyst.

4. Conclusions

The effects of pretreatment conditions and reactor type on the performance (activity, selectivity and stability with time) of the precipitated iron Fischer–Tropsch catalyst (100 Fe/0.3 Cu/0.8 K) were studied in the fixed-bed and the stirred tank slurry reactors. It was found that the hydrogen reduction results in stable or increasing catalyst activity with time-on-stream. Hydrogen reduced catalyst produces more methane and gaseous hydrocarbons than the syngas pretreated catalyst. Secondary reactions (olefin hydrogenation and isomerization) were more pronounced in tests with the hydrogen reduced catalyst.

Pretreatments with syngas at 280°C result in partial conversion of α-Fe_2O_3 to monoclinic χ-carbide (FBR) or pseudo-hexagonal ϵ'-carbide (STSR). The initial activity of the catalyst in the FBR was high but the catalyst deactivated fairly rapidly with time, possibly due to conversion of χ-carbide to less active iron oxide phases, and buildup of inactive carbonaceous species which block the active sites on the surface. The initial activity of the catalyst in the STSR (from a different batch than that used in the FBR) was low. It deactivated rapidly with time, and this was accompanied with increase in relative amount of iron carbide phases.

In the two slurry reactor tests hydrocarbon distribution shifted toward lower-molecular-weight products with time-on-stream, but the total olefin content did not vary with time. The increase in the 1-olefin isomerization with time was observed only in the STSR test SA-0791.

The results suggest that the surface hydrogen concentration is higher on the hydrogen reduced catalyst, which results in higher hydrogenation activity, production of low-molecular-weight hydrocarbons and better stability with time-on-stream. It is not possible to draw any meaningful correlations between the catalyst performance and the bulk iron phases in the working catalyst.

Acknowledgements

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