

EFFECT OF PRETREATMENT ON CATALYST ACTIVITY AND SELECTIVITY DURING FISCHER-TROPSCH SYNTHESIS IN A SLURRY REACTOR

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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 synthesis (FTS) at SASOL in South Africa¹. However, the purpose of pretreatment for iron FT catalysts is not clearly understood. Reduction in H₂ 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^{2,3}. At high syngas conversions, a reaction mixture becomes more oxidizing and magnetite is also formed^{1,4,5}. During FTS, 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^{1,5}. Other pretreatments have been also employed, such as CO activation, synthesis gas pretreatment or induction, and/or H₂ reduction followed by CO treatment or vice versa^{4,6}.

Also, there has been a large number of related studies on model iron catalysts dealing with an issue of the role of iron phases in FTS. However, this issue still remains to be a controversial one. Briefly, some workers consider the surface carbides, with an underlying iron carbide bulk structure, to be the active phase^{2,7}. In the so-called competition model of Niemantsverdriet and van der Kraan⁸ iron atoms at the surface are considered as the active sites. In the latter model both bulk carbidation and FTS (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 Fe₃O₄ (magnetite) is the active phase in FTS^{9,10}. Validity of the latter proposal was questioned¹¹, but some evidence in its support was also presented^{12,13}.

In this paper we describe new results from our on-going studies¹⁴⁻¹⁷ on the effect of pretreatment procedures on activity and selectivity of precipitated iron catalysts. Results illustrating both the initial and steady state behavior of a catalyst with nominal composition 100 Fe/3 Cu/6 K/16 SiO₂ (on mass basis) during FTS are presented, and activity/selectivity data are correlated with iron phases in the working catalyst under conditions representative of industrial practice.

EXPERIMENTAL

The reactor used in this study was a 1 dm³ stirred tank reactor (Autoclave Engineers). Detailed description of the reactor system and operating procedures was provided elsewhere^{17,18}. The feed gases (H₂>99.5% purity, and CO>99.3% purity) or a premixed gas passed through a series of traps to remove impurities. The feed gas flow rate was controlled using calibrated mass flow controllers, and the feed was introduced into the reactor below a flat blade impeller, used to agitate the slurry. After leaving the reactor, the exit gas passed through a series of product collection traps. All products collected in the steady state traps were analyzed by gas chromatography after physical separation into an aqueous and organic phase. The reactants and noncondensable products leaving ice traps were analyzed on an on-line gas chromatograph (Carle AGC 400). Powder X-ray diffraction (XRD) patterns of the catalyst samples withdrawn from the reactor were obtained on a Scintag XDS2000 system using Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$).

Catalyst preparation involved three steps: preparation of the iron-copper precursor, incorporation of binder/support (silicon oxide), and finally potassium impregnation. The preparation procedure was described in detail previously¹⁹. In brief, 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. Impregnation with SiO₂ binder/support was accomplished by addition of the appropriate amount of dilute K₂SiO₃ solution to undried, reslurried Fe/Cu co-precipitate. After a vacuum drying step, the potassium promoter was added as aqueous KHCO₃ solution via an incipient wetness pore filling technique. Dried catalyst was calcined in air at 300°C for 5 h, and then crushed and sieved to a diameter less than 270 mesh (53 μm). Durasyn - 164 oil (a hydrogenated 1 - decene homopolymer, -C₃₀ obtained from Albemarle Co.) was used as the initial slurry liquid medium.

All pretreatments were conducted in situ at 0.8 MPa. In runs designated SA-0946 and SA-1626 the catalyst was pretreated at 280°C, 750 cm³/min for 8 h in CO and syngas (H₂/CO = 0.67), respectively. In run SB-2145 the catalyst was reduced with hydrogen at 240°C, 7500 cm³/min for 2 h, whereas in run SB-2486 the catalyst was exposed to reaction conditions, without any

pretreatment (unreduced catalyst). After the pretreatment, the catalyst was tested initially (baseline conditions) at 260°C, 1.48 MPa, 2.3 NL/g-cat/h (1.4 NL/g-cat/h in run SB-2145 only) and syngas feed with $H_2/CO = 0.67$ (molar feed ratio). In addition to baseline conditions, the catalyst was tested at different gas space velocities and reaction pressure, but these results are not reported here.

RESULTS AND DISCUSSION

Catalyst activity

Hydrogen reduced catalyst reached its steady state activity within 4 h from exposure to synthesis gas, and then its activity decreased slowly during the first 150 h of testing (Fig. 1). In the other three tests the time needed to reach a steady state activity was longer, about 20 h for the syngas pretreated and unreduced catalyst, and 80 h for the CO pretreated catalyst. Since the process conditions, including the gas space velocity, were the same in runs SB-2486, SA-1626 and SA-0946, the values of syngas conversion can be used as a measure of relative catalyst FTS activity. Initial activity of the unreduced catalyst (SB-2486) was the lowest, but at approximately 20 h on stream it was the same as that of the CO pretreated catalyst (SA-0946). After 20 h on stream the conversion (activity) of unreduced catalyst started to decline, whereas that of the CO pretreated catalyst continued to increase up to 80 h, and then became stable at about 76%. Initially, the conversion of the syngas pretreated catalyst was higher than that of the unreduced and the CO pretreated catalyst, and it reached its steady state value of ~70% at about 20 h. The steady state activity of the syngas pretreated catalyst was lower than that of the CO pretreated catalyst. Although, the conversion of the hydrogen reduced catalyst (SB-2145) up to 80 h on stream was higher than those obtained in the other three tests, this does not imply the highest catalyst activity, since the gas space velocity in run SB-2145 (1.4 NL/g-cat/h) was significantly lower than in the other three tests (2.3 NL/g-cat/h). In order to compare the activity of catalysts in tests under different process conditions, a simple model was used to estimate values of apparent rate constant²⁰. The apparent rate constant was calculated assuming that the reaction rate has a first-order dependence on hydrogen pressure, and that the reactor can be modeled as a perfectly mixed flow reactor. At 100 h on stream the estimated values of the apparent rate constant were, in the order of increasing activity, 230 (runs SB-2145 and SB-2486), 330 (SA-1626), and 360 mmol/g-Fe/h/MPa (run SA-0946).

Crystalline phases found in samples withdrawn after the pretreatment (Fig. 4) were as follows: magnetite (hydrogen reduced catalyst); χ -carbide and possibly small amount of magnetite (CO pretreated catalyst); iron carbides (χ -carbide and/or ϵ' -carbide) and magnetite (syngas pretreatment). Unreduced catalyst had an amorphous structure (iron oxide/oxyhydroxide). Dominant phase in the syngas activated catalyst (SA-1626) after 137 h on stream was ϵ' -carbide, whereas both ϵ' -carbide and magnetite were found in the hydrogen reduced catalyst and the unreduced catalyst at 145 h and 147 h on stream, respectively (Fig. 5). Crystalline phases in the CO pretreated catalyst after 113 h on stream were χ -carbide and possibly magnetite.

The FTS on iron catalysts is accompanied by a reversible water-gas-shift (WGS) reaction. Values of carbon dioxide selectivity (% of CO converted to CO_2) provide indication of the WGS catalyst activity. Carbon dioxide selectivity of 50% corresponds to complete conversion of water formed by FTS to carbon dioxide. After 20 h on stream, carbon dioxide selectivities in all four tests were about 48% (Fig. 2). Hydrogen and syngas reduced catalysts reached this value after about 5 h only, the unreduced catalyst at ~8 h, whereas the CO pretreated catalyst achieved its steady state carbon dioxide selectivity at ~20 h on stream. Carbon dioxide selectivity in all tests was never greater than 50%, which would indicate that carbon dioxide is also produced via the reaction between CO and iron oxides in the catalyst.

A very rapid achievement of steady state activity of the hydrogen reduced catalyst (SB-2145) indicates either that magnetite is active for FTS or that it rapidly converted to an active carbide phase. However, the conversion of magnetite to zero-valent iron is a slow step in reduction of iron oxide, and it is unlikely that it can occur to an appreciable extent after 2 h of exposure to syngas at 260°C. For example, the unreduced iron requires about 20 h of exposure to reach its steady state activity (SB-2486). Also, as carburization of iron oxide increases with time, the catalyst activity does not increase with time, but actually decreases slowly. Activity of the unreduced catalyst (largely Fe^{3+} iron) is low initially, and it increases during the first 25 h of synthesis, due to formation of magnetite and/or ϵ' -carbide, indicating that one or both of these phases are active for FTS. Activity of the CO reduced catalyst is rather low initially (χ -carbide), and increases gradually with time. This behavior is not entirely consistent with hypothesis that iron carbide is the active phase for the FTS. If the latter hypothesis was correct, one would expect the initial activity of the partially carbided catalyst to be markedly greater than that of the catalyst in the form of magnetite. Also, the catalyst in test SA-0946 had a long induction period, and its activity at ~20 h on stream was similar to that of the unreduced catalyst. Initial activity of the syngas activated catalyst (mixture of iron carbide and magnetite) was the highest, but it also

went through an induction period lasting approximately 25 h. Steady state activities, between 113 and 147 h on stream, of catalysts pretreated by CO and syngas were higher than those of the hydrogen and unreduced catalysts. Magnetite was virtually absent in the CO and syngas pretreated catalysts, whereas both hydrogen and unreduced catalyst contained both magnetite and ϵ -carbide. All these observations are consistent with hypothesis that both magnetite and iron carbides are active for FTS, and that iron carbides have higher FTS activity than magnetite.

Methane Selectivity

During the first 20 h on stream, methane selectivities (%CO converted to CH_4 /%CO converted to products other than CO_2) of the syngas and CO activated catalysts were significantly higher (3.5 - 6%) than those obtained on the hydrogen reduced catalyst and unreduced catalysts (1.5 - 2%). Methane selectivities of the CO and syngas pretreated catalysts decreased with time, whereas those of the hydrogen reduced and unreduced catalysts increased with time (Fig. 3). These data suggest that methane selectivity is low on iron oxides, and is higher on carbided catalysts. A possible reason for markedly higher methane selectivity on carbided catalysts during early periods of synthesis, is that part of methane is produced by reaction between hydrogen and surface carbon formed during the pretreatment.

SUMMARY

After pretreatments in hydrogen, carbon monoxide, syngas ($\text{H}_2/\text{CO} = 0.67$), and without pretreatment the precipitated iron catalyst was tested in a stirred tank slurry reactor at 260°C, 1.48 MPa, 1.4 or 2.3 Nl/g-cat/h and $\text{H}_2/\text{CO} = 0.67$. Hydrogen reduced catalyst quickly reached steady state activity (within 4 h), whereas the syngas, the CO activated and unreduced catalyst required longer time (up to 100 h for the CO pretreated catalyst). Initially, the CO and syngas activated catalysts, were slightly more active than the hydrogen reduced and unreduced catalyst. Methane selectivities of hydrogen reduced and the unreduced catalyst were initially significantly lower than those on the CO and syngas activated catalyst.

From these results and catalyst characterization by XRD it was concluded that both magnetite and iron carbides are active for FTS, however the activity is higher on partially carbided catalysts. Methane selectivity is lower on the catalyst which contains significant amounts of bulk iron oxides, than on partially carbided catalyst.

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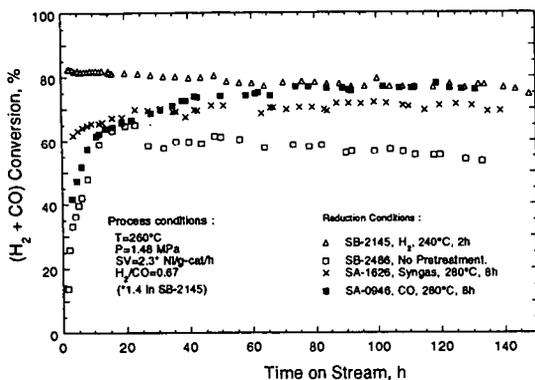


Figure 1. Effect of pretreatment conditions on synthesis gas conversion.

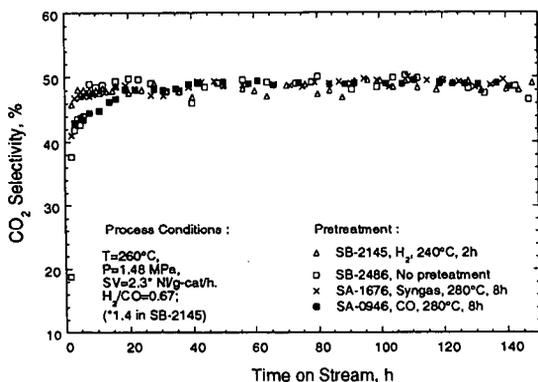


Figure 2. Effect of pretreatment conditions on carbon dioxide selectivity.

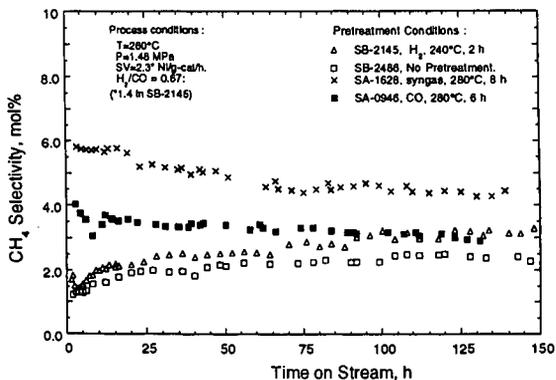


Figure 3. Effect of pretreatment conditions on methane selectivity.

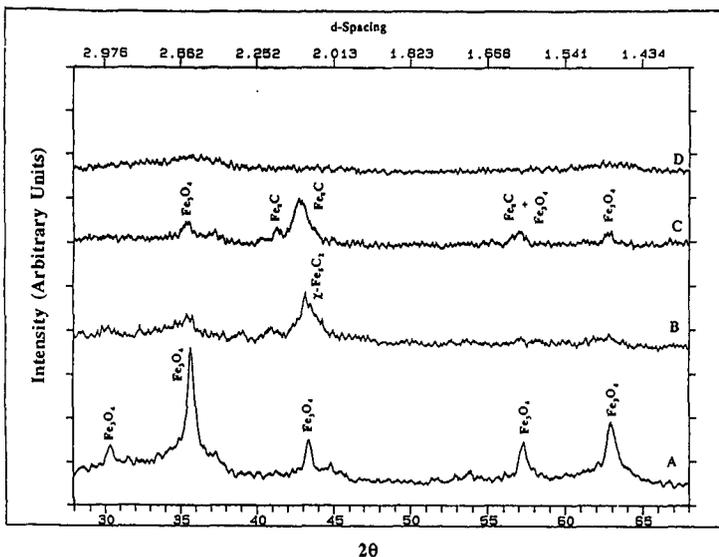


Figure 4. XRD patterns of reduced catalysts (TOS = 0 h) from slurry reactor tests: (A) SB-2145, H₂, 240°C, 2h, (B) SA-0946, CO, 280°C, 8h, (C) SA-1626, syngas, 280°C, 8h, and (D) SB-2486, No reduction.

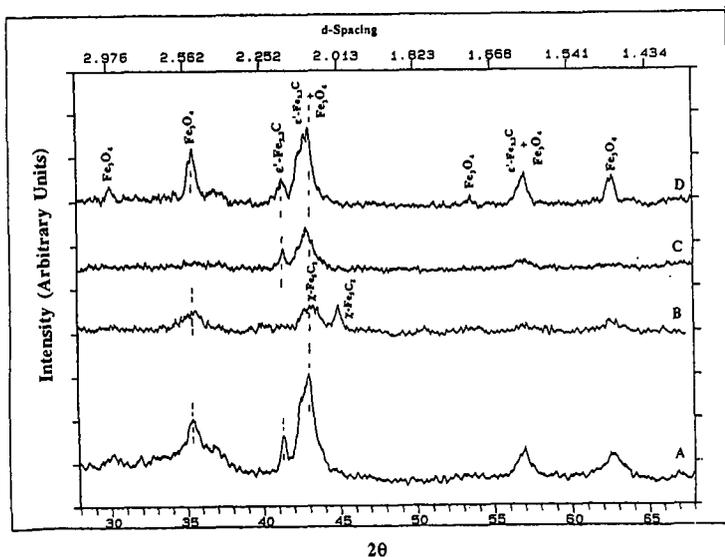


Figure 5. XRD patterns of used catalysts from slurry reactor tests: (A) SB-2145, TOS = 145 h, (B) SA-0946, TOS = 113 h, (C) SA-1626, TOS = 137 h, and (D) SB-2486, TOS = 147 h.