

# DEVELOPMENT OF IRON FISCHER - TROPSCH CATALYSTS

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## **Introduction and Objectives**

Improvements in the catalyst performance (activity, selectivity and/or stability) are needed to accelerate commercialization of Fischer-Tropsch (FT) technology based on coal derived synthesis gas. Some of iron based catalysts synthesized and tested at Texas A&M University (TAMU) during the DOE Contract DE-AC22-89PC89868, had higher activity than other known iron FT catalysts developed for maximizing production of high molecular weight hydrocarbons (Bukur et al., 1993; 1994). The objectives of the current contract are to: (1) demonstrate repeatability of performance and preparation procedure of two high activity, high alpha iron Fischer-Tropsch catalysts synthesized at TAMU; (2) seek improvements in the catalyst performance through variations in process conditions, pretreatment procedures and/or modifications in catalyst preparation steps; (3) investigate performance of catalysts in a small scale bubble column slurry reactor, and (4) investigate feasibility of producing catalysts on a large scale in collaboration with a catalyst manufacturer.

## **Repeatability of Catalyst Performance and Preparation Procedures**

Repeatability of performance of the two catalysts with nominal compositions (mass basis) 100 Fe/5 Cu/6 K/24 SiO<sub>2</sub> (catalyst B) and 100 Fe/3 Cu/4 K/16 SiO<sub>2</sub> (catalyst C) was demonstrated in multiple tests (three tests with each of the two catalysts from batch 1) under the same process conditions in a stirred tank slurry reactor (Figures 1 and 2). Also, the catalysts from different batches had a similar performance during the first 120 h of testing, as shown in Figures 1 and 2. Activity of the catalyst C was similar in all seven tests. For example, syngas conversions (Figure 1a) were between 78 and 84 % (i.e., 81 ± 3%). Methane (Figure 1b) and C<sub>1</sub> + C<sub>2</sub> selectivities (not shown) were also similar in all seven tests. At about 100 h on stream, a mean value of methane selectivity from all seven tests is 2.6 %, whereas the minimum value is 2.1 % (run SA-2715) and maximum 3.1 % (runs SB-2145 and SA-0705). Also, a mean value of C<sub>1</sub> + C<sub>2</sub> selectivity at about 100 h on stream was 5.7 %, whereas the minimum and the maximum were: 4.8 % (SA-2715) and 6.5 % (SA-0705), respectively. Lower methane and gaseous hydrocarbon selectivities obtained in tests with catalysts from batches 1-3, in comparison to the catalyst from batch 4, are consistent with higher potassium loadings of these catalysts. High syngas conversions and low gaseous hydrocarbon selectivities were obtained in all tests. For example, in run SA-1665 with the catalyst C at 300 h on stream (260°C, 2.17

MPa, 3.4 NI/g-Fe/h and  $H_2/CO = 0.67$  feed gas), the syngas conversion was 77%, methane selectivity (mol% C basis) was 2.7%, and selectivity of  $C_2$  hydrocarbons (ethane + ethylene) was 3.5%.

Syngas conversions in all six tests of catalyst B are within 10% of the mean value of the conversion, i.e.  $71 \pm 6$  % (Figure 2a). Catalyst from batch 5 (run SB-2585) was the least active (66-71 % conversion), whereas the catalyst from batch 4 (SA-2615) was the most active (74-77 % conversion). Similar values of methane selectivities were obtained in all three tests of the catalyst from batch 1 (runs SB-1931, SB-3354, and SB-0665), and in run SB-2585 with batch 5 catalyst, whereas higher values were obtained in tests with batch 3 (SB-1295) and batch 4 (SA-2615) catalysts (Figure 2b). A possible reason for higher methane and  $C_1+C_2$  selectivities obtained in run SB-1295 is that potassium content of batch 3 catalyst is lower than that of the other batches (5.2 K per 100 Fe (batch 3) vs. 6.2 - 7.8 K per 100 Fe in other batches). However, the catalyst from batch 4 (SA-2615) had higher potassium loading (6.5 K per 100 Fe) than the catalyst from batch 3, and yet its methane and  $C_1+C_2$  selectivities were higher.

In general, catalysts from different preparation batches had similar performance (activity, selectivity and deactivation rates), and reproducibility of catalyst preparation procedure may be regarded as satisfactory.

### **Effects of CaO Promoter and Source of Potassium Promoter**

We have synthesized and tested four catalysts with two levels of CaO promotion, which represent modifications of our baseline catalysts B and C. Nominal compositions of these catalysts are: 100 Fe/3 Cu/4 K/x Ca/16 SiO<sub>2</sub> and 100 Fe/5 Cu/5 K/x Ca/24 SiO<sub>2</sub>, where  $x = 2$  or 6. Results from screening fixed bed reactor tests showed that the addition of small amounts of CaO promoter ( $x = 2$ ) results in the catalyst performance (activity and gaseous hydrocarbon selectivity) similar to that of the baseline catalysts, whereas the addition of a larger amount of CaO ( $x = 6$ ) results in markedly lower catalyst activity in comparison to baseline catalysts. Selectivity of the two catalysts with  $x = 6$ , was similar to that of the corresponding baseline catalysts. On the basis of these results it was decided to evaluate the two catalysts with  $x = 2$  in stirred tank slurry reactors (STSR's). Results illustrating performance of the 100 Fe/3 Cu/4 K/2 Ca/16 SiO<sub>2</sub> catalyst are shown in Figure 3.

The 100 Fe/3 Cu/4 K/2 Ca/16 SiO<sub>2</sub> catalyst (run SB-3115) was less active (about 15%) than the baseline catalyst C (run SA-1665) and its deactivation rate was higher (Figure 3a). At the reaction pressure of 1.48 MPa, selectivity of gaseous hydrocarbons on CaO containing catalysts was higher than that of the corresponding baseline catalysts. However, at the reaction pressure of 2.17 MPa the gaseous hydrocarbon selectivity decreased on the CaO containing catalysts, and was nearly the same as that of the baseline catalysts at 1.48 MPa. It appears that the selectivity of the CaO promoted catalysts improves at higher reaction pressures, whereas the selectivity of the catalyst C is essentially independent of reaction pressure (see Figure 3b for methane selectivity).

Two catalysts (B and C) were prepared using two different methods of potassium promotion. Baseline catalysts were prepared by incipient wetness impregnation of Fe-Cu-SiO<sub>2</sub> precursor with an aqueous solution of KHCO<sub>3</sub> (Bukur et al., 1990). In a modified procedure, aqueous solution of potassium silicate is added to the Fe-Cu precursor as a source of silicon oxide, and then the excess amount of potassium is removed by washing to get a desired level of potassium promotion.

Catalyst B synthesized using aqueous solution of potassium silicate as the source of potassium was less active (Figure 4a), and syngas conversions in run SA-3155 were about 15 % lower than those obtained in run SB-1295 (baseline catalyst). Methane and gaseous hydrocarbon selectivities in run SA-3155 were significantly lower during the first 100 h on stream, but these differences in selectivity diminished with time and the catalyst selectivities in the two tests were nearly the same after 140 h (Figure 4b, methane selectivity).

The above results indicate that the baseline catalyst synthesis procedure which utilizes impregnation of Fe-Cu-SiO<sub>2</sub> catalyst precursor with aqueous solution of KHCO<sub>3</sub> as the source of potassium promoter is preferred to the alternative method in which the potassium is added in the form of aqueous potassium silicate solution.

### **Effect of Calcination Temperature**

Effect of catalyst calcination temperature in air at 300-500°C for 5 h, on the performance (activity and selectivity) of catalysts B and C in a fixed bed reactor was found to be insignificant. Rapid calcination at 700°C for 1h resulted in lower catalyst activity, but the gaseous hydrocarbon selectivities were similar to those obtained in tests of catalysts calcined at 300-500°C. Two STSR tests of catalysts B and C calcined at 700°C for 1 h were conducted, and representative results from one of these tests (run SB-0376 with catalyst C) are shown in Figure 5.

Catalyst C calcined at 700°C for 1h (SB-0676) had significantly lower activity (apparent reaction rate constant based on the first order dependence on hydrogen partial pressure) than the catalyst calcined at 300°C for 5h (run SA-1665). This is in agreement with the findings from the fixed bed reactor tests, and lower activity is mainly due to the loss of surface area during high temperature calcination. Methane selectivity was higher on the catalyst calcined at 700°C during testing at 1.48 MPa, but it became similar to that obtained in run SA-1665 at 1.48 MPa, when the reaction pressure was increased to 2.17 MPa (Figure 5b).

### **Effect of Pretreatment Procedures**

Four pretreatment procedures have been studied with the catalyst C in slurry reactor tests. They are: (1) standard or baseline procedure with H<sub>2</sub> at 240°C for 2 h (runs SA-1665 and SB-2145); (2) H<sub>2</sub> at 250°C for 4 h (SB-3425); (3) H<sub>2</sub> at 280°C for 8 h (SA-0376); and (4) CO at 280°C for 8h (SA-0946). Activity of the catalyst reduced with H<sub>2</sub> at 280°C for 8h was similar to those observed in runs SA-1665 and SB-2145 following the standard reduction procedure (the lowest reduction temperature and the shortest

duration), but was markedly lower than the activity in run SB-3425 (Figure 6a). Previous studies in our laboratory with iron based catalysts without silicon oxide, have shown that the use of more severe reduction conditions may result in very low catalyst activity (Bukur et al., 1989; 1995). Methane selectivities in run SA-0376 were similar to those obtained in run SB-3425, and slightly higher than those in runs SA-1665 and SB-2145. Initial activity of the CO pretreated catalyst was similar to that of hydrogen reduced catalysts at 240°C for 2h, and 280°C for 8h, but it increased with time and at 100 h on stream it became higher than that of the hydrogen reduced catalyst at 250°C for 4 h. Methane selectivity in run SA-0946 was initially higher than that of the hydrogen reduced catalysts, but it decreased with time and at about 240 h on stream it became lower than that of the hydrogen reduced catalysts. After the pretreatment the crystalline phases of iron, determined by X-ray diffraction, were: magnetite and  $\alpha$ -Fe (runs SA-0376 and SB-3425), magnetite (runs SA-1665 and SB-2145), and magnetite plus iron carbides ( $\epsilon'$  and  $\chi$  - carbides).

The above results show that the catalyst activity and selectivity can be controlled to some extent through variations in the pretreatment conditions.

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