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Development of Precipitated Iron Fischer-Tropsch Catalysts

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~~Draft~~ Final Technical Report

Texas Engineering Experiment Station Project 32525-44580

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Richard E. Tischer, Project Manager (PETC)

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Abstract

Despite the current worldwide oil glut, the United States will ultimately require large-scale production of liquid (transportation) fuels from coal. Slurry phase Fischer-Tropsch (F-T) technology, with its versatile product slate, may be expected to play a major role in production of transportation fuels via indirect coal liquefaction.

Some of the F-T catalysts synthesized and tested at Texas A&M University under DOE Contract No. DE-AC22-89PC89868 were more active than any other known catalysts developed for maximizing production of high molecular weight hydrocarbons (waxes). The objectives of the present contract were to demonstrate repeatability of catalyst performance and reproducibility of preparation procedures of two of these catalysts on a laboratory scale. Improvements in the catalyst performance were attempted through the use of: (a) higher reaction pressure and gas space velocity to maximize the reactor productivity; (b) modifications in catalyst preparation steps; and (c) different pretreatment procedures.

Repeatability of catalyst performance and reproducibility of catalyst synthesis procedure have been successfully demonstrated in stirred tank slurry reactor tests. Reactor space-time-yield was increased up to 48% by increasing reaction pressure from 1.48 MPa to 2.17 MPa, while maintaining the gas contact time and synthesis gas conversion at a constant value. Use of calcination temperatures above 300°C, additional CaO promoter, and/or potassium silicate as the source of potassium promoter, instead of potassium bicarbonate, did not result in improved catalyst performance. By using different catalyst activation procedures we were able to increase substantially the catalyst activity, while maintaining low methane and gaseous hydrocarbon selectivities. Catalyst productivity in runs SA-0946 and SA-2186 was 0.71 and 0.86 gHC/g-Fe/h, respectively, and this represents 45-75% improvement in productivity relative to that achieved in Rheinpreussen's demonstration plant unit (the most successful bubble column slurry reactor performance to date), and sets new standards of performance for "high alpha" iron catalysts.

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I EXECUTIVE SUMMARY

Slurry phase Fischer-Tropsch (F-T) processing is a very promising alternative to conventional vapor phase processes, but additional improvements are needed in the catalyst performance (higher activity, minimization of methane and low molecular weight hydrocarbon yields, and better catalyst stability) in order to accelerate commercialization of this technology. This can be achieved in several ways: (a) through development of new improved catalysts; (b) use of novel reactor configurations; (c) use of suitable catalyst pretreatment (activation) procedures or through combination of these methods, as demonstrated in studies at Texas A&M University (TAMU) sponsored by DOE (Contracts DE-AC22-85PC8011 and DE-AC22-89PC89868). Some of the iron based catalysts synthesized and tested at TAMU, have proven to be more active than any other known iron F-T catalysts developed for maximizing production of high molecular weight hydrocarbons (Bukur et al., 1994).

The overall objectives of this contract are to: (1) demonstrate repeatability of performance and preparation procedure of two high activity, high alpha iron F-T catalysts synthesized at TAMU during the DOE Contract DE-AC22-89PC89868; and (2) seek potential improvements in the catalyst performance through variations in process conditions, pretreatment procedures and/or modifications in preparation steps (e.g. means of introduction of promoters and calcination conditions). The major accomplishments are summarized here.

Repeatability of Performance of Baseline Catalysts

The objective of this task is to verify repeatability of results obtained in stirred tank slurry reactor (STSR) tests of two catalysts designated B (100 Fe/5 Cu/6 K/24 SiO_2 containing 55.4 wt% of iron) and C (100 Fe/3 Cu/4 K/16 SiO_2 containing 59.7 wt% of iron) during the previous DOE Contract DE-AC22-89PC89868. These two catalysts were chosen due to their excellent performance (high syngas conversion and low methane and gaseous hydrocarbons selectivities) in slurry reactor tests. The catalysts from the same preparation batch and the same pretreatment and process conditions, were employed as in the previous slurry reactor tests of these two catalysts.

Three tests were conducted with each of the two catalysts. In the original tests conducted in 1991 (SB-1931 with the catalyst B, and SB-0261 with the catalyst C) n-octacosane was used as the initial medium. In the four tests conducted during the current contract, Ethylflo 164 oil (a hydrogenated 1-decene homopolymer liquid - C_{30}, obtained from Ethyl Co.) was used as the start-up fluid, due to problems encountered in three initial tests using n-octacosane as the start-up liquid (low activity in all three tests). The effect of reactor set-up (slurry A vs. slurry B reactor system) was investigated in two recent tests with the catalyst C (runs SB-0045 and SA-0705). In general, reproducibility of results in multiple tests of the same catalyst may be regarded as quite satisfactory. The catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) was more stable in the original test (SB-1931) than in the two recent tests (SB-3354 and SB-0665), whereas the opposite trend was observed in tests with the catalyst C (100 Fe/3 Cu/4 K/16 SiO_2). Hydrocarbon product distributions and olefin selectivities in multiple tests with the same catalyst were reproducible.

Performance of catalysts B and C is comparable to, or exceeds, that obtained in the two most successful bubble column slurry reactor (BCSR) tests conducted by Mobil (Kuo, 1985) and Rheinpreussen (Kölbel et al., 1955). In Mobil's run CT-256-13 at synthesis gas conversion of 82%, methane and C_1+C_2 selectivities were 2.7 and 5.6 wt%, respectively, whereas the catalyst productivity was about 0.26 g HC/g-cat/h (Test conditions: 257°C, 1.48 MPa, 2.3 Nl/g-Fe/h, $H_2/CO = 0.73$). In Rheinpreussen's demonstration plant unit the C_1+C_2 selectivity was 6.8% at the synthesis gas conversion of 89%, and the catalyst productivity was about 0.33 g HC/g-cat/h (Test conditions: 268°C, 1.48 MPa, 3.1 Nl/g-Fe/h, $H_2/CO = 0.67$).

In run SB-3354 with catalyst B (TOS = 97 h) the following results were obtained at 260°C, 1.48 MPa, 3.2 Nl/g-Fe/h, $H_2/CO = 0.67$: Methane and C_1+ C_2 selectivities were 3.2 and 5.3 wt%, respectively, and the catalyst productivity was 0.26 g HC/g-cat/h at the synthesis gas conversion of 71.5%. The catalyst performance in the original test of the catalyst B (run

SB-1931) was even better, i. e. higher activity and lower methane and gaseous hydrocarbon selectivities were obtained (Bukur et al., 1994).

The performance of catalyst C in run SB-0045 at the reaction pressure of 1.48 MPa and 215 hours on stream, was very similar to that obtained in Mobil's run CT-256-13. However, the productivity of catalyst C was improved at reaction pressure of 2.17 MPa and gas space velocity of 3.4 Nl/g-Fe/h (TOS = 336 h). Methane and C_1+C_2 selectivities were 2.6 and 5.4 wt%, respectively, and the catalyst productivity was 0.36 g HC/g-cat/h at the synthesis gas conversion of about 80%. The latter productivity is higher than productivity's obtained in Mobil's and Rheinpreussen's bubble column slurry reactor tests, primarily due to the use of higher reaction pressure and higher gas space velocity in the present study.

Reproducibility of Catalyst Preparation Procedure

Repeatability of performance of catalysts B and C was demonstrated in multiple tests with catalysts from different preparation batches. Three STSR tests were conducted with catalyst B, and four tests with catalyst C. In general, catalysts from different preparation batches had similar performance (activity and selectivity) and reproducibility of catalyst preparation procedure is regarded as satisfactory.

Syngas conversions, methane and C_1+C_2 selectivities obtained in tests with catalysts B and C were similar to those obtained in two tests conducted in slurry bubble column reactors (Mobil's and Rheinpreussen's tests). However, the catalyst productivity in two tests with catalyst C (runs SA-1665 and SB-0045), at 2.17 MPa, was even higher (0.53 or 0.60 g HC/g-Fe/h) than that obtained in Rheinpreussen's test (0.49 g HC/g-Fe/h), whereas at the reaction pressure of 1.48 MPa the catalyst productivity of our catalysts B and C (0.38-0.42 g HC/g-Fe/h) was similar to that obtained in Mobil's study (0.39 g HC/g-Fe/h). Due to complete reactor backmixing in our experiments (stirred tank reactor) it may be expected that the catalyst productivity under the same process conditions would be even higher in a reactor with partial fluid mixing (e.g., bubble column slurry reactor). ✓

The Effect of Basic Oxide Promoter and Source of Potassium

Four catalysts containing CaO promoter with nominal compositions 100 Fe/3 Cu/4 K/x Ca/16 SiO_2 and 100 Fe/5 Cu/5 K/x Ca/24 SiO_2, where $x = 2$ or 6, were synthesized and tested in fixed bed reactors. The major findings from these tests are 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 B and C, whereas the addition of a larger amount of CaO ($x = 6$) results in markedly lower catalyst activity in comparison to the baseline catalysts. Selectivity of the two catalysts with $x = 6$, is similar to that of the corresponding baseline catalysts. On the basis of these results it was decided to evaluate two catalysts with $x = 2$ in stirred tank slurry reactors.

The 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 catalyst was tested in run SA-2405, and its performance was compared to that of the baseline catalyst B in run SB-1295, whereas results from run SB-3115 with the 100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 catalyst were compared with results obtained with the catalyst C in run SA-1665. General trends in tests with the CaO containing catalysts showed some similarities, as well as differences. For example activity of the 100 Fe/5 Cu/5 K/2 Ca/24 SiO_2 catalyst (run SA-2405) was nearly the same as that of the baseline catalyst B (run SB-1295) but its stability with time (deactivation rate) was better, whereas the 100 Fe/3 Cu/4 K/2 Ca/16 SiO_2 catalyst (run SB-3115) was less active (about 15%) than the baseline catalyst C (run SA-1665) and its deactivation rate was higher. At 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 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 (at a constant P/SV ratio to maintain a constant value of the gas residence time at different pressures). The addition of CaO promoter did not result in improved performance of the baseline catalysts, but the CaO promoted catalysts may be suitable for operation at higher reaction pressures. Finally, it is possible that the performance of CaO promoted catalysts may be improved with the use of different pretreatment procedures, but this has not been investigated in the present study.

Some differences in catalyst performance were observed in fixed bed tests of catalysts B (runs FA-1725 and FB-1715) and C (runs FA-1605 and FB-1985) prepared by different methods. In both cases, the activity and methane selectivity of catalysts prepared using potassium silicate as the source of potassium promoter were higher than those of the corresponding baseline catalysts prepared by incipient wetness impregnation using $KHCO_3$ as the source of potassium promoter. On the other hand, in two slurry reactor tests of catalyst B (SB-1295 - K from $KHCO_3$, and SA-3155 - K from K_2SiO_3) it was found that the activity of the catalyst prepared from K_2SiO_3 is about 15 % lower than that of the catalyst prepared by $KHCO_3$ impregnation, whereas gaseous hydrocarbon selectivities were similar after about 140 h on stream.

On the basis of these results we conclude that the baseline procedure utilizing impregnation of Fe-Cu-SiO_2 precursor with the aqueous solution of $KHCO_3$ is the preferred method of catalyst preparation. The second procedure, which avoids the impregnation step, provides satisfactory results, and may be used as an alternative.

Pretreatment Effect Research

The effect of different pretreatment procedures on the performance of catalyst C (100 Fe/3 Cu/4 K/16 SiO_2, batch-4) was studied in a STSR. Seven different pretreatment procedures were employed: three with hydrogen as reductant at different temperatures (240-280°C), CO and synthesis gas ($H_2/CO = 0.67$) pretreatments at 280°C for 8 hours, TAMU pretreatment, and no pretreatment before testing at 1.48 MPa, 260°C, 1.4-2.3 Nl/g-cat/h with synthesis gas with H_2/CO molar feed ratio of 0.67.

Significant improvements in the catalyst activity were obtained through the use of different pretreatment procedures. Our standard reduction procedure with the catalyst C (hydrogen reduction at 240°C for 2 hours) resulted in the initial activity, expressed in terms of the apparent reaction rate constant, of about 250 mmol/g-Fe/MPa/h. The activity decreased with time and at about 400 h the apparent rate constant reached the value of 220 mmol/g-Fe/MPa/h (run SA-1665) or 140 mmol/g-Fe/MPa/h (run SB-2145). The initial activity of the catalyst reduced with hydrogen at 250°C for 4 hours (run SB-3425) was about 350 mmol/g-Fe/MPa/h, which represents a 40% increase relative to the standard reduction procedure. However, the catalyst activity decreased with time and at about 300 h the apparent rate constant was 250 mmol/g-Fe/MPa/h (similar to the value obtained in run SA-1665).

The CO pretreatment (SA-0946), syngas pretreatment (SA-1626) and TAMU pretreatment (SA-2186) also resulted in improved catalyst activity, relative to the standard reduction procedure. The initial values of the apparent reaction rate constant, after these pretreatments, were 300-400 mmol/g-Fe/MPa/h, corresponding to 20-60% increase in activity relative to the standard procedure. Activity of the CO and TAMU pretreated catalysts increased with time, and at 400 hours the values of the apparent reaction rate constants were 360 and 430 mmol/g-Fe/MPa/h, respectively. As the result of the improvement in the catalyst activity, while maintaining low methane and gaseous hydrocarbon selectivities, the catalyst productivities in these two tests were markedly higher than those obtained in Mobil's and Rheinpreussen's slurry bubble column reactor tests. The catalyst productivity in Rheinpreussen test was 0.49 gHC/g-Fe/h, and those obtained in runs SA-0946 and SA-2186 were 0.71 and 0.86 gHC/g-Fe/h, respectively. This represents 45-75% improvement in catalyst productivity relative to that achieved in Rheinpreussen's demonstration plant unit, and sets new standards of performance for "high alpha" iron catalysts. We believe that the performance of our catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) can be also improved through the use of better pretreatment procedures.

Calcination Effect Research

We have conducted six fixed bed reactor tests, and two slurry reactor tests to investigate the effect of calcination temperature on performance of catalysts B and C during F-T synthesis. Both catalyst B (100 Fe/5 Cu/6 K/24 SiO_2) and C (100 Fe/3 Cu/4 K/16 SiO_2) were tested in fixed bed reactors after calcinations at 400°C and 500°C for 5 h, and after flash calcination at 700°C for 1 h, and in a stirred tank slurry reactor after flash calcination at 700°C for 1 h.

In fixed bed reactor tests, activities, as well as gaseous hydrocarbon selectivities, of catalysts B and C calcined at 400°C and 500°C, were similar to those of catalysts calcined at 300°C (baseline calcination temperature). Catalysts calcined at 700°C for 1 h had lower activity, than the catalysts calcined at temperatures of 300-500°C. Gaseous hydrocarbon selectivity of catalyst C, was not strongly affected by the use of different calcination temperatures, whereas the catalyst B calcined at 700°C had higher gaseous hydrocarbon selectivity than the catalysts calcined at lower temperatures.

The main findings from slurry reactor tests are: (1) The activity of catalysts B and C calcined at 700°C is lower than that of these two catalysts calcined at 300°C; (2) Gaseous hydrocarbon selectivities are higher on catalysts calcined at 700°C; (3) Alpha olefin selectivity of C_{10}+ hydrocarbons was markedly higher on catalysts calcined at 700°C; and (4) Oxygenates yields were about four times higher on the catalysts B and C calcined at 700°C, than on the catalysts calcined at 300°C.

Testing of Alternative Catalysts for Slurry Reactors

Although catalysts B and C have desirable activity and selectivity characteristics, they may not have a sufficient mechanical strength and attrition properties required for utilization in commercial bubble column slurry reactors. This work has been undertaken with the objective to test catalysts with potentially improved mechanical and attrition properties.

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

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

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