

Shape Selective Catalysts for F-T Chemistry

Interim Report: January 2001 – December 2002

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Prepared by

D. C. Cronauer, Chemical Technology Division

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Summary

Argonne National Laboratory (ANL) is carrying out a research program to create, prepare, and evaluate catalysts to promote Fischer-Tropsch (F-T) chemistry, specifically the reaction of hydrogen with carbon monoxide to form long-chain hydrocarbons. In addition to F-T catalysts needing high activity, it is desirable that they have high selectivity and stability with respect to both mechanical strength and aging properties. In this project, selectivity is directed toward the production of diesel fraction components and avoiding excess yields of both light hydrocarbons and heavy waxes. Shape-selective catalysts have the potential to both limit the formation of long-chain products and yet retain the active metal sites in a protected "cage." This cage also restricts their loss by attrition during use in slurry-bed reactors.

Experimentation has included evaluation of samples of (1) iron-based F-T catalysts prepared at Argonne National Laboratory, (2) iron-based F-T catalysts prepared by B.H. Davis of the Center of Applied Energy Research (CAER), (3) the Davis catalyst that were sized by differential gravity separation, and (4) the Davis catalyst onto which inorganic or catalytic "shells" were deposited. The ANL-prepared samples had a wide range of particle size and were irregular in shape. A sizeable portion of the samples provided by Davis were spherical, because they had been prepared by spray-drying. To compare the catalytic activities of the samples, we used a micro-scale fixed-bed reactor system for F-T runs of low conversion to avoid thermal and mass transfer effects. In summary, the highest activity was that of the original Davis catalyst; additional research must be carried out to generate more permeable surface cages. A number of approaches that have been published for other applications will be tested.

Introduction

Fischer-Tropsch (F-T) chemistry involves the reaction of hydrogen with carbon monoxide to form long-chain hydrocarbons. Even though this process was invented in Germany in 1923, there has been a continuing development of catalysts, the most common of which are based upon iron, cobalt, and ruthenium. It has been directed that research in this project center upon iron-containing catalysts.

The available literature on these catalysts is very extensive, and it is well beyond the scope of this project to prepare another literature survey. Only recent literature dealing with specific problem areas will be cited when appropriate. For reference, a very extensive and recent series of articles on the F-T process has been edited by Hans Schulz and Michael Claeys and published as "Special Issue: Recent Advances in Fischer-Tropsch Synthesis" in *Applied Catalysis A: General* 186 (1999) pages 1 through 433.¹ See also C.N. Satterfield, *Heterogeneous Catalysis in Industrial Practice*, 2nd Ed., Krieger Publ. Co., Malabar, FL, 1996.² B. H. Davis has carried out an extensive study of F-T catalysis under DOE contracts; reference is made to the Final Technical Report³ of Contract No. PC90056 and interim reports of PC94055.

Iron is the least expensive F-T catalyst. It is typically promoted with alkali (i.e., 0.5 wt% K₂O) for activity and stability. It is proposed² that potassium donates electrons to the iron, weakens the CO bond, strengthens the Fe-C bond, and weakens the Fe-H bond, so the quantity of CO adsorbed increases and that of H₂ decreases. For reference, the fixed-bed reactors at SASOL (South African Synthetic Oil Limited) operate at about 220°C and 2.7 MPa using a precipitated iron catalyst heavily promoted with potassium. The entrained-bed reactors operate at about 320°C and 2.2 MPa with a reduced fused magnetite catalyst of considerably lower potassium content.

CuO is added to the Fe catalyst to lower the reduction temperature of Fe₂O₃. This addition reduces sintering and apparently does not affect catalyst selectivity. SiO₂ and Al₂O₃ may be added for structural strength; however excessive levels reduce catalyst activity.

Because alkalinized iron catalysts demonstrate water gas activity, they are of particular interest when the feed stream has low hydrogen content (i.e. H₂/CO ratio of about 1.0 for coal or heavy oil gasification versus 2.0 for methane gasification). It has been reported¹ that the activity of iron catalysts is affected through the interaction with water. When using these iron catalysts, water must be removed from recycle streams along with heavy hydrocarbon products. Typical ratios of recycle to fresh feed rates are about 2.

Numerous articles have indicated that iron catalysts are active for F-T synthesis only when in the carbide state. A recent review article⁴ of Van Der Laan and Beenackers provides a good summary of pertinent references; see also Bukur et al.⁵ Numerous articles have demonstrated the importance of catalyst pre-conditioning treatment of fresh catalyst with CO to establish the active carbide surfaces; for example, see Shroff, et al.⁶ The procedure used by Davis³ is as follows:

“The catalyst was pretreated in CO; the sample was heated from 110 to 270°C during a period of about 2 (2°C/min.) hours and then held at 270°C in a CO flow of 2 NL/g Fe/hr for 22 hours.”

The strength of iron-based catalysts is of concern, particularly when used in slurry-bed catalytic reactors. Espinoza, et al⁷ of SASOL states, “The main difficulty with the commercial application of the SPR (Slurry Phase Reactor) is the separation of the wax product from the catalyst. This is especially true for the relatively friable precipitated iron catalysts.” D. S. Kalakkad et al.⁸ studied the attrition and phase transformation of precipitated iron F-T catalysts. They found that spray-dried particles (agglomerates) of about 30 μm diameter easily fragmented to particles of about 1 μm size. In addition, phase transformation resulted in size reductions to about 20 μm. The recent presentation of Gormley, Deffenbaugh and Zarochard⁹ also points out the difficulty of catalyst attrition with the subsequent problems of cleaning up the resulting F-T wax product stream.

Goals/Objectives

The goal of this project is to create, prepare, and evaluate catalysts to promote Fischer-Tropsch (F-T) chemistry. Emphasis will be placed upon iron-containing catalysts that are preferred for syn-gases because of low ratios of H₂/CO. Emphasis will also be placed upon shape-selective catalysts that have the potential to limit long-chain products and retain the active metal sites in a protected “cage” to restrict their loss during use in slurry-bed reactors.

Experimentation and Results

Experimental

A continuous-flow catalytic-bed unit has been modified and used for this study. A flow schematic is given in Figure 1.

The feed blend consists of CO and H₂. The blend is passed through a preheater/reactor that consists of a 1/2-in.-O.D. (3/8" I.D.) tube of about 36 in. length. Gaseous flow is downward through the following zones:

1. An empty (quartz wool) zone to serve as preheater,
2. Inert packing consisting of low-surface α -Al₂O₃ to ensure radial flow dispersion,
3. Supported catalyst that is blended with inert filler,
4. Additional α -Al₂O₃ packing, and
5. A bottom zone made up of a low-internal-diameter tube so that the catalyst is in the temperature-controlled region of the tube.

The preheater/reactor has a total of six internal and two external thermocouples. The reactor temperature is controlled using the thermocouple at the center of the catalyst bed.

The reactor effluent is cooled in air and then passed through wet-ice- and dry-ice/ethanol-cooled traps. The latter traps are set up for parallel operation so that periodic condensate samples can be recovered for weighing and sampling. The pressure of the off-gas is controlled and subsequently metered and sampled.

Catalyst Preparation

Samples of iron-based F-T catalyst have been prepared using procedures similar to those reported by Davis.³ Samples were made by mixing ferric nitrate with concentrated ammonia at temperatures maintained at about 55°C. Selected batches were made with the addition of tetraethyl orthosilicate (TEOS) prior to the precipitation with ammonia in order to observe if there were changes of precipitate properties.

Two samples of F-T catalyst were also obtained from B. H. Davis of CAER. The first consisted of the bulk spray-dried catalyst designated “RLS 4.4 Si/150 Cyclone Iron Catalyst,” and the second was freshly prepared catalyst designated “RJO 290 100Fe/4.6Si/1.44K.”

Selected CAER catalyst samples were separated by differential settling to isolate fractions of different particle diameter. Specifically, 10 g of CAER catalyst was mixed with 98 g water plus 2 g of ethanol (serving as a wetting agent). After being well agitated, the slurry was allowed to settle for various times, and various amounts of the upper liquid were siphoned off. The slurry samples were filtered through Whatman No. 50 hardened paper and dried in a vacuum oven.

Selected samples of the treated and untreated CAER catalyst samples were contacted with aqueous/ethanol solutions of tetraethylorthosilicate (TEOS) followed by the drop-wise addition of 30 wt% ammonium hydroxide solution (maintaining a pH of about 11.0). This procedure should generate a silica gel coating on the catalyst particles. The depth and thickness of the coating into the particles should have been influenced by the concentrations, rates of addition, etc. Selected blends were also made with limited levels of tetraethyl ammonium hydroxide (TEOH -- 20 wt% in water). The resulting catalyst samples were dried in a vacuum oven and calcined (400°C for 4 hr).

Catalyst Particle Size/Shape Determination

Selected samples of the catalysts mentioned in the preceding section were examined using a JEOL JSM6400 Scanning Electron Microscope. The experimental technique and results were described in the previous report.¹¹ In summary, the samples prepared at ANL were highly irregular, and they ranged widely in size (2 through 600 μm). There were also large chunks and even solid chips that averaged about 150 μm . The sample of the spray-dried CAER catalyst was also examined. This material consisted of a blend of fine particles (1 to 5 μm) and spherical agglomerates in the range of 20 to 40 μm . This is consistent with a description stated by B. H. Davis that the spray-drying had not been as effective as desired. The addition of TEOS prior to precipitation and spray-drying did not insure uniform particle size. The sample of freshly prepared CAER catalysts designated "RJO 290 100Fe/4.6Si/1.44K" was also scanned using the SEM. This catalyst was also irregular in size, ranging between 2 and 30 μm .

Results

Considering that the goal of this project is to create, prepare, and evaluate catalysts to promote Fischer-Tropsch (F-T) chemistry, with emphasis on iron-containing and shape-selective catalysts, initial experimentation was directed toward preparing and evaluating selected prepared catalysts. The results of the experiments are summarized in Figures 2 through 4 and Tables 1 through 7.

The first F-T experiment was undertaken using the preheater and reactor charged with only $\alpha\text{-Al}_2\text{O}_3$ to ensure that there was no or only limited background catalytic activity due to the "inert" filler. Runs 85A, 85C, 87C and 85F were made at mid-bed temperatures ranging between 265 and 290°C, pressures averaging 13.1 MPa (190 psia), a CO/H₂ molar ratio of 1.0, and a gas feed rate of about 40 mL/min. For reference, this gas feed rate would be equivalent to a space velocity (SV) of 3.4 NL/Hr-g with a desired F-T catalyst charge of 0.7 g. This SV was used in the demonstration runs of CAER.³

As shown in Tables 1 and 7, there was only a nominal level (<0.05 %) of methane generated in one of

the runs in the first experiment; 0.02 % and less was observed in the other runs. These levels are indicative of background error, apparently generated by gas chromatograph switching at about the column elution time. No other hydrocarbons or carbon dioxide were detected at levels at or above 0.01%. In summary, the α -Al₂O₃ was essentially inert at the desired reaction conditions.

A sample of as-received CAER F-T catalyst, which was labeled “RLS 4.4 Si/150 Cyclone Iron Catalyst,” was used in Runs 100 and 101. These runs were made using the overall conditions described above and mid-bed temperatures of 268 and 284°C (Runs 100 and 101, respectively). The resulting product gas analyses are given in Tables 3 and 4, and summarized in Table 7. This catalyst was active with 35 and 57% CO conversion levels at mid-bed temperatures of 268 and 284°C, respectively. Based upon an overall carbon material balance, the selectivity of converted CO to hydrocarbons averaged 56%, with the remainder going to form CO₂.

A sample of the as-received CAER F-T catalyst was separated into coarse and fine fractions using differential settling in an ethanol/water solution. The coarse sample was dried at about 100°C and calcined at 400°C for 4 hours. The resulting catalyst, which was designated 72 CAER, was used for F-T reactions at reaction temperatures between 270 and 290°C in Runs 90 through 96.

As shown in Tables 2 and 7 and Figures 2 and 3, the activity of the 72 CAER catalysts demonstrated an activity equivalent to that of as-received CAER sample with the exception that nominally more CO₂ was generated with the 72 CAER catalysts. The distributions of generated hydrocarbons were also similar with the exception that nominally lower levels of C₄ and C₅₊ hydrocarbons were observed; see Figure 4. In summary, the separation and calcination did not greatly change the activity of the iron F-T catalyst, so it will serve as a reference and base catalyst for future runs.

A sample of 72 CAER catalysts was mixed in an aqueous ethanol solution to which was added a small amount of tetraethylammonium hydroxide (TEAOH, 0.1 g with 2.0 g 72 CAER) with a brief contact time of 2 minutes. The objective was to have limited TENOH penetration into the iron catalyst particles. A dilute TEOS solution was added with subsequent drop-wise addition of NH₄OH solution to promote precipitation on the outside of the coarse F-T catalyst particles. The resulting slurry was held overnight, filtered, dried and calcined. The recovered catalyst was designated 77B.

An F-T experiment was carried out under the overall conditions and at temperatures of 270 and 288°C. The results are summarized in Tables 5 through 7 and Figures 2 through 4. In summary, this catalyst had about one-half to two-thirds the activity of the 72 CAER catalyst. The selectivity of CO conversion to the various hydrocarbons essentially followed that of the parent catalyst.

Interim Observations/Conclusions

The following interim observations/conclusions have been noted and are reported in both this and the previous interim report:

1. Iron-based catalysts can be prepared at ANL using the techniques outlined in the CAER reports, but a high degree of mixing must be introduced to generate more uniform particle sizes.

2. The spray-dried bulk catalyst sample of CAER contains a high level of dispersed fine particles. A portion of these fines can be removed by differential settling techniques.
3. A flow unit has been modified and demonstrated for use in this program.
4. Reaction conditions have been established such that reasonable levels of CO conversion can be achieved with an active catalyst. These conditions can be used as a basis to evaluate prepared catalyst samples.
5. The initial experiment carried out in an attempt to coat an active F-T catalyst and yet maintain activity was not as successful as desired, but there are a number of available approaches that will be evaluated in planned experimentation.

Planned Experimentation

Considering that DOE has requested that this program study iron-containing F-T catalysts, and that extensive literature has been published on the mechanisms, catalyst preconditioning, and product distributions of these catalysts, emphasis in this program will be centered upon the primary remaining problem of the formulation of an attrition-resistant iron-based catalyst.

Experimentation will continue using recovered coarse samples of CAER F-T onto which various agents will be used to form “cages” around the catalyst particles. The resulting catalysts are being tested in a differential reactor to isolate samples that have reasonable activity and porosity. Based upon past conversations with B. H. Davis concerning cooperative work, selected samples then will be tested for abrasion resistance. If successful, the resulting formulation will be presented to DOE and CAER for further evaluation.

Cited References:

1. H. Schulz and M. Claeys, “Special Issue: Recent Advances in Fischer-Tropsch Synthesis” in *Applied Catalysis A: General* 186 (1999) pages 1 through 433.
2. C. N. Satterfield, *Heterogeneous Catalysis in Industrial Practice*, 2nd Ed., Krieger Publ. Co., Malabar, FL, 1996.
3. B. H. Davis, *Technology Development for Iron Fischer-Tropsch Catalysts, Final Technical Report*, December 18, 1990--December 17, 1993, DE96005561, DOE/PC/90056--T17, 12/31/96.
4. G. van der Laan and A.A.C.M. Beenackers, *Catal. Rev.-Sci. Eng.*, 41(3&4), 255-318 (1999).
5. D. B. Bukur, et al., *Journal of Catalysis* 155, 353-365 (1995).
6. M. D. Shroff, et al., *Journal of Catalysis* 156, 185-207 (1995).

7. R. L. Espinoza, Steynberg, B. Jager, and A.C. Vosloo, *Applied Catalysis A: General* 186 (1999), 13-26.
8. D. S. Kalakkad, M. D. Shroff, S. Kohler, N. Jackson, and A. K. Datye, *Applied Catalysis A: General* 133 (1995), 335-350.
9. R. J. Gormley, P.W. Deffenbaugh, and M.F. Zarochar, "In-situ Filtration of Fischer-Tropsch Product Wax from Iron-based Catalysts," National Laboratory Catalysis Conference 2000, Argonne, IL, Oct. 12-13, 2000.
10. J. van de Loosdrecht, S. Barradas, E. A. Caricato, P. J. van Berge, and J. L. Visagie, "Support Modification of Cobalt Based Slurry Phase Fischer-Tropsch Catalysts," preprints 45(3), Div. Fuel Chem., ACS Nat. Meeting, Washington, DC, Aug 2000, 587-591.
11. D. C. Cronauer, "Shape Selective Catalysts for F-T Chemistry" Interim Report for the Period June 2000 through January 2001, Argonne National Laboratory, February 2001.