TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSTS

Robert J. O'Brien, Ajoy Raje, Robert L. Spicer, Liguang Xu, Shiqi Bao, Scott Lambert and
Burtron H. Davis
DAVIS@ALPHA.CAER.UKY.EDU
Phone: (606) 257-0251
Fax: (606) 257-0302
Center for Applied Energy Research
University of Kentucky
2540 Research Park Drive
Lexington, KY 40511

OBJECTIVE

The objective of this research project is to develop the technology for the production of physically robust iron-based Fischer-Tropsch catalysts that have suitable activity, selectivity and stability to be used in the slurry phase synthesis reactor development work. The catalysts that are developed shall be suitable for testing in the Advanced Fuels Development Facility at LaPorte, Texas, to produce either low- or high-alpha product distributions. Studies will be conducted to define the chemical phases present at various stages of the activation and synthesis and to define changes that occur during these stages. The oxidation/reduction cycles that are anticipated to occur in large, commercial reactors will be studied at the laboratory scale. Catalyst performance will be determined for catalysts synthesized in this program for activity, selectivity and aging characteristics.

SUMMARY OF RESULTS

A. CATALYST ACTIVATION

A.1. Activation with Hydrogen. Hydrogen reduction results in the reduction of Fe_2O_3 to Fe_3O_4 and then to metallic Fe. Metallic iron has a propensity to sinter so that catalysts prepared by this technique have low surface areas if temperatures in the range of 400^oC are employed.

A.2. Activation with CO. An easy and reproducible procedure for catalyst activation involves treating the iron catalyst with CO at 270^oC during a 24 hour period. In this reaction, the reduction of iron is effected by the production of CO_2. At the same time, the carbide may be formed using the carbon deposited by the Boudourd Reaction.

Based upon the rate of formation of CO_2, the reduction leads to the formation of Fe_2O_3 to Fe_3O_4 and then to a mixture of iron carbides. This procedure produces carbon during a 24 hour period

that is in excess of that needed to form iron carbide. This method is especially attractive since the presence of traces of sulfur in the catalyst does not result in the formation of H_2S which is a severe catalyst poison.   The CAER has obtained very similar curves of the extent of reduction/carbide formation versus time for conversion in 1-liter CSTRs and in a 2"x6' bubble column reactor; the CAER data was subsequently confirmed by an activation run with approximately 1,000 pounds of catalyst in the DOE LaPorte pilot plant. The disadvantage of this procedure is that in a typical syngas plant there is not a stream of pure CO. Furthermore, whereas hydrogen can be obtained in high purity from a syngas stream using membrane diffusion processes, it is not possible to easily separate pure CO from a syngas stream.

A.3. Activation with Syngas. There are conflicting reports of the success in activating a catalyst in syngas at medium or high pressure reaction conditions. When success has been reported, the catalyst was usually contacted with lower temperatures and low flow rates and then the temperature was gradually elevated to the desired reaction temperature. In work at the U.S. Bureau of Mines in the late 1940s-early 1950s, they would adjust the flow of syngas to maintain about 20 vol.% CO_2 in the exit gas. In some cases, it would require several days until the maximum conversion was obtained with this activation procedure. For activation at reaction pressure, we find that there is nearly a linear relationship between the mole fraction of hydrogen in the activation gas and the conversion of CO; i.e., the higher the fraction of hydrogen in the synthesis gas the lower the CO conversion. Even after 24 hours of activation in synthesis gas with a low mole fraction of hydrogen, the conversion may increase during a three to five day period. It appears that the ultimate activity of the iron catalyst is directly related to the partial pressure of hydrogen and that the activity declines as the hydrogen partial pressure increases. On the other hand, if activation with syngas is effected at atmospheric pressure, the presence of hydrogen does not appear to have an impact so that comparable activities can be obtained for activations conducted with only CO or with syngas.

A.4. Role of Copper. Copper may be an important component of an iron catalyst. The copper provides a very beneficial effect if the catalyst is to be reduced in hydrogen during the activation procedure.   Since the addition of copper allows the reduction to be effected at a lower temperature, the resulting surface area following reduction of an iron catalyst containing copper is higher than one which does not contain copper. Even when the reduction/carbiding is conducted with CO, it appears that the copper allows these operations to be conducted at a slightly lower temperature. It appears that the presence of copper (in the 1-4 wt% range) does not alter the product selectivity from that of a catalyst with the same composition without copper.

B. CATALYST AGING

One of the targets for the CAER work was to prepare a catalyst that would have an initial CO conversion of 90% and a decline in CO conversion that was less than 1% per week of operation. These two targets were to be met using reaction conditions that were identical to those utilized

by Kölbel and coworkers in the German work using slurry reactors (1) except that the flow rate of the reactant gases was to be 50% greater than the German worker utilized. It has been shown that the CAER produced catalysts attained the initial CO conversion and the slow deactivation rate during up to about 4,000 hours (166 days; 5.5 months) of continuous operation. Several tests have been conducted for 2,000 hours or longer and each attained a catalyst deactivation rate of 1% CO conversion/week or less.

Catalyst aging data have been obtained for a pure iron catalyst and three catalysts containing promoters. It is evident that all four catalysts had a similar high activity during the initial 200 hours of testing. Only after this period did differences in aging become apparent. The iron catalyst containing potassium aged more rapidly than the one that contained only iron. On the other hand, the addition of silicon to the iron catalyst caused the aging to occur at a slightly slower rate than for the pure iron catalyst. There is a strong synergism between iron, potassium and silicon since this combination produces a catalyst with outstanding long-term stability.

Various reasons have been offered to account for the gradual loss in activity of the catalysts. However, we have been unable to identify a single factor that could account for the different catalyst aging treads for the four catalysts. For example, water vapor provides an oxidizing atmosphere; however, the partial pressure of water vapor in contact with the catalyst cannot account for the different aging rates. Likewise, carbon deposition, as measured by total carbon content, cannot account for the difference in the aging rates. Loss of surface area cannot account for the aging rate differences since all catalyst's surface areas **increase** with time on stream, most likely due to the deposition of carbon. This data indicates that it is necessary to conduct reasonably long-term testing of the catalyst if significant differences in stability are to be elucidated.

C. CATALYSTS CHARACTERIZATION - TRENDS WITH TIME

While the composition of the catalyst following activation depends upon the activation procedure, in general the catalyst will contain a significant fraction of iron carbide. Activation in pure CO or in a syngas mixture at atmospheric pressure produces the highest fraction of iron carbides following 24 hours of activation. However, during the course of the synthesis, the composition of the catalyst gradually changes to produce a higher fraction of Fe_3O_4. Thus, the iron catalyst undergoes significant phase and chemical composition changes during use for synthesis.

The characterization has been conducted using X-ray diffraction, Mössbauer spectroscopy, surface area, elemental analysis, scanning electron microscopy and transmission electron microscopy, including high resolution transmission electron microscopy. In general, we have not found the changes in activity to be directly related to the phase or chemical composition of the catalyst.

D. PRODUCT SELECTIVITY

Both types of promoters impact selectivity although the alkali promoter has a greater impact than the structural promoter (silica or alumina). It appears that alumina impacts the product selectivity by the production of **more oxygenates** and a **higher alkene content of the higher carbon number hydrocarbons**. The production of more oxygenates (essentially an equilibrium value of the primary alcohol and corresponding aldehyde or the secondary alcohol and the corresponding ketone) with the alumina promoter is surprising since free aluminium oxide is a far better alcohol dehydration catalyst than silica. At least in the fresh, oxide catalyst form, both aluminium and silicon are substituted into the Fe_2O_3 as judged by the shifts of the iron oxide X-ray diffraction peak positions. This result implies that the Al and Si are not present as the metal oxide even in the carbided catalyst.

The potassium (and other alkalis to a smaller extent) affect both the molecular weight distribution of the products (and indirectly the methane production) and the amount of alkenes in each carbon number fraction. In general, a higher potassium content produces higher weight products. Thus, whereas the value of alpha (the ratio of chain propagation to chain termination) is about 0.7 for unpromoted iron or a catalyst containing up to about 0.5 wt.% potassium, the value of alpha can be increased to greater than 0.9 with catalysts containing higher amounts of potassium.

For conversions at $270^{\circ}C$, the ethene/(ethane + ethene) ratio is very dependent upon the potassium content, ranging from about 0.3 for no potassium to about 0.7 for potassium 0.1 K/Fe. For the C_3 and C_4 fraction, the alkene will account for 80% or greater of the product for as little as 0.07 K/Fe. For the C_5-C_{12} fraction, 65% or greater of the hydrocarbon products are alkenes for 0.07K/Fe. The fraction of alkenes decrease with increasing carbon number and the rapidity of the decline depends upon the alkali level in the catalyst. The alpha-olefin content of the C_4-fraction is usually 0.8 or higher, and decreases with increasing CO conversion and carbon number fraction. In general, decreasing the reaction temperature and the CO conversion level leads to a higher alkene content and a higher alpha-olefin content.

E. CONVERSIONS IN 1-LITER CSTR AND 2"X6' BUBBLE COLUMN REACTOR

CAER personnel have made several runs in the 2"x6' slurry bubble column reactor (SBCR). The four initial runs were to activate an iron catalyst to be utilized in the DOE LaPorte, Texas pilot plant. The activation was conducted in CO and the four runs were conducted to obtain activated catalysts for filtration testing under the supervision of Air Products personnel. The catalyst had been spray dried to produce spherical particles in the 30-40 micron range. The four runs produced reproducible activation data with respect to the rate and extent of catalyst activation. The runs in the SBCR produced data that were in excellent agreement with runs at the CAER in CSTRs and at the LaPorte pilot plant run.

F.   PROCESS CONSIDERATIONS BASED ON CATALYST ACTIVITY/SELECTIVITY

Based upon the selectivity changes for the relative conversion of H_2 and CO, the catalyst productivity as a function of CO conversion, and the relative contribution of WGS and hydrocarbon production, a process based upon a series of smaller reactors rather than one large reactor or a process with low conversion and gas recycle is preferred.

The general feeling is that the FTS should be carried out at high syngas conversion. During the past 50 years significant increases have been made in developing catalysts with high activity. A comparison, based on assigning work at the Bureau of Mines using fused iron catalysts, is given in the following table.

		Relative Activity
1950	U.S. Bureau of Mines	1
1955	Kölbel	15
1980s	Mobil	13
1993	CAER	21
1996	CAER	43

Thus, there has been about a thirty fold increase in syngas conversion at high total conversion levels during the fifty years. However, there is a rapid increase in conversion with increasing contact time up to about 60% CO conversion levels; however, the increase in conversion becomes much slower above this 60% level. For example, it is possible to obtain a significantly higher hydrocarbon productivity per unit of catalyst by operating at a lower conversion level. At the higher conversion level (90% CO conversion), about 0.5 grams of hydrocarbon/g Fe/hr. are produced; however, at a conversion of 40% for CO, the hydrocarbon productivity becomes about 3 grams/g. Fe/hr. In addition, much less carbon is converted to CO_2 and the products contain a significantly higher content of alkenes.

Thus, based only on catalyst considerations, it is highly desirable to utilize several reactors in series. One scenario to do this would involve the use of smaller reactor sizes in the subsequent reactors. Another, and the preferred, method is to utilize the same size reactors. However, it should be noted that there is a conversion level where the composition of the exit gas is the same as the feed stream, a point that we refer to as the equivalence point. Thus, when the same size reactors are utilized, water would be removed between the reactors and makeup syngas would be added to make up for that which has been converted. Thus, all reactors would operate under identical conditions but the overall effect is to attain an equivalent high conversion using smaller, more productive reactors.

Another major problem is whether one should operate using a low or high alpha catalyst to produce transportation fuels. At Sasol, both options are utilized. The high temperature fluidized bed reactors produce products that are equivalent to a low alpha catalyst whereas the Arge and slurry reactors operate to produce high alpha products. Shell operates to produce high alpha products. When the high alpha catalyst is utilized, transportation fuels are produced from the high molecular weight products by hydrocracking. However, a plant that will emphasize transportation fuels must also convert the low molecular weight products to transportation fuels (3). The Mossgas operation in South Africa currently utilizes a Süde Chemie zeolite oligomerization catalyst to convert light olefins to transportation fuels. They report that the catalyst can be operated without separating the water and oxygenates from the alkene-rich stream.

It appears that the oligomerization route has appeal since this would permit one to operate with a low-alpha iron catalyst that would not produce a significant quantity of high molecular weight products. Thus, it would be possible to operate the slurry reactor without having to carry out catalyst/wax separation within the reactor in order to maintain an adequate inventory of catalyst in the reactor.

REFERENCES

1. H. Kölbel and M. Ralek, *Catal. Rev.-Sci. Eng.*, **21** 225 (1980).
2. P. R. Ellis, *Platinum Metals Rev.*, **47**, 7 (1997).
3. The COD Process. A new zeolite based process and catalyst for the conversion of olefins (COD) to diesel and gasoline, Süd-Chemie Group.