Fischer Tropsch Synthesis: A Comparison of Iron and Cobalt Catalysts

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The initial commercial production of Fischer-Tropsch products in Germany in the 1930-1940s was with a cobalt based catalyst. These catalysts, by today's standards, had a very low activity. In addition, much of the commercial work with the cobalt catalyst was done at atmospheric pressure and was therefore with a much lower average carbon number than the products produced today.

Following WW II, it appeared that there would be a severe shortage of crude oil so that U.S. organizations initiated work on Fischer-Tropsch synthesis (FTS). Over a ten year period, the U.S. Bureau of Mines was budgeted $85 million for work on direct and indirect coal liquefaction. These funds would represent more than a billion dollars in today's marketplace. A large (75 bbl/day) FTS pilot plant was built at Louisiana, MO but its operation was terminated after a few runs because the Middle-East oil reserves were recognized to be so large that conversion of coal to liquids would not be needed immediately. During the same time period, HRI led the effort to build a FTS plant in Brownsville, Texas that would be based on cheap natural gas and that used a fixed-fluid bed reactor and an iron catalyst. The operation was plagued with start-up problems and just about the time these were solved the price of natural gas significantly increased so the FTS activity was terminated.

The effort at Sasol in South Africa was initiated following WW II and has continued to today. The initial effort used both low-temperature FTS in fixed bed reactors and high temperature in FTS circulating fluid bed reactors. The effort was plagued by problems in the early stages but the support by the government allowed Sasol workers to overcome these problems. The efforts at Sasol have expanded to approach the production of 150,000 bbl/day; however, about 90% of the production is by high-temperature FTS. During the 1990s, PetroSA started up circulating fluid-bed reactors for FTS and now produce nearly 50,000 bbl/day. Thus the dominant production with the iron catalyst is at high temperature conditions in fluid bed reactors which dictates the production of gaseous products to prevent catalyst agglomeration and the loss of the ability to maintain the catalyst in a fluid bed.

The problems associated with iron catalysts that have received much attention were associated with the high temperature FTS and should not be compared to the cobalt catalyzed FTS which is carried out to produce high molecular weight products that cannot be kept in the vapor phase at the reaction temperature. Thus, the following comparison is based on low temperature FTS with both iron and cobalt catalysts.

In the following table we provide our version of the comparison of what we consider the current perception of the various properties of iron and cobalt catalysis for FTS and offer our version of the reality for the two catalysts.

CATALYST COMPARISON - PERCEPTION vs. REALITY				
Concept	Perception		Reality	
	Co	Fe	Co	Fe
Chain Growth Probability (α)	High	Low	Intermediate	Low to High
Activity	High	Low	High	High
Olefin Selectivity	Low	High	Low	High
H_2/CO Ratio for Feed	2+	0.5 to 2.5	1.0 to 2+	0.5 to 2+
Water-Gas-Shift, Activity and CO_2 Selectivity	Very Low	High	Very Low	Intermediate to High
Methane Selectivity	High	Low	Intermediate	Low to very low
Temperature	Only Low	Low to High	Only Low	Low to High
Temperature Sensitivity, Activation Energy	Very Sensitive	Slight	Slight	Slight
Temperature Sensitivity, Product Distribution	Sensitive	Slight	Very Sensitive	Very Slight
Pressure Sensitivity, Product Distribution	Very	Slight	Very	Slight
Sulfur Tolerance	Very Little	Very Little	Very Little	Intermediate
Stability, Life Time	Long	Short	Long	Long
Cost	Expensive	Cheap	Expensive	Cheap to Expensive
Separation from Wax	Easy	Difficult	Easy	Very Difficult
Robustness	Excellent	Poor	Excellent	Very Poor

The perception is that the cobalt catalyst has a higher chain growth probability. For many, many cobalt catalyst formulations from low to high cobalt loadings and promoted or unpromoted catalysts, we have consistently obtained an alpha value of 0.87 ± 0.02. For the iron catalyst, the alpha value depends upon the amount of alkali promoter. Thus, for a low loading of K, the alpha value may be around 0.7 but for a higher K loading the alpha value may be in the range of 0.90 to 0.95. Since the higher the alpha value, the higher the probability of chain growth to produce higher molecular weight products, the iron catalyst may in fact produce higher molecular weight products.

The current concept is that the cobalt catalyst is more active that the iron catalyst. This comparison is not straight forward. From a reactor productivity viewpoint, the productivity/catalyst loading is usually the important factor. Since the cobalt loading is usually in the 20% range with 80% support, the catalyst loading will the important factor. Because the cobalt catalyst has little water-gas shift (WGS) activity, the production of hydrocarbons by FTS is usually linearly related to the CO conversion. However, with the iron catalyst WGS occurs in addition to FTS and the ratio of the two reactions depends upon CO conversion. Data for the cobalt catalyst indicates that the productivity of hydrocarbons per gram of catalyst is about 1 g/g cat./hr. The productivity of an iron catalyst varies from about 0.5 g/g Fe /hr at high CO conversion to about 5 g/g Fe/hr at 30% CO conversion. Thus, considering that the iron catalyst contains only about 60% Fe, the productivity of the iron catalyst at 30% CO conversion is about 3 g/g cat/hr. Using this value for the productivity, the iron catalyst may be at least three times as active as a cobalt catalyst.

The cobalt catalyst produces at most 50% alkenes at about C_5 and decreases to essentially zero alkenes at about C_{10}. On the other hand, the iron catalyst can produce more than 60% alkenes in the C_2-C_{20} carbon number fraction with the actual fraction of alkenes depending on the reactor influence on hold-up time for the alkene. The longer the hold-up time, the greater the secondary hydrogenation reaction and the lower the alkene fraction.

It is considered that only the cobalt catalyst would be useful for a syngas derived from natural gas, where the H_2/CO ratio approaches 2, near the usage ratio for the FTS. However, the Lurgi gasifier used at Sasol produces a H_2/CO ratio approaching 2 and they operate using an iron catalyst. In the latter case, some hydrogen is removed from the syngas to be utilized in downstream processing prior to passing the syngas on to the FTS reactor. For this point, the syngas will have some ratio of C/H and the product witl have some ratio of C/H. When the ratio of C/H in the syngas does not match the C/H ratio of the products, with today's gasifiers it is because insufficient hydrogen is present in the feed gas. Thus, the issue becomes one of whether the C/H is adjusted by WGS prior to the FTS reactor as required by the cobalt catalyst or is adjusted in the FTS reactor as is possible with the iron catalyst. Actually, workers at Air Products ran a cobalt catalyst with a syngas with H_2/CO = 1 for months with very slow decline in catalytic activity; thus, it is not the cobalt catalyst property that limits the use of low H_2/CO syngas but the stoichiometry of the reaction. WGS is an important factor for FTS with an iron catalyst. While WGS is not considered to occur with the cobalt catalyst, it can become a factor at high CO conversion.

The cost of the cobalt catalyst is considered to be very high while that of the iron catalyst is very low. This is true if the iron catalyst is a by-product from steel making as has been practiced. However, when the iron catalyst is prepared by precipitation the advantage of cost for the iron catalyst over that of the cobalt catalyst narrows considerably. A recent announcement by Süd Chemie for the preparation of an iron catalyst directly from metallic iron using an organic acid may again provide a major cost advantage for the iron catalyst.

In operating at low-temperature, high wax conditions, the separation of the catalyst from the product may be a challenging problem. When operating with a fixed bed reactor, as Shell does, the separation of wax from the catalyst is essentially eliminated. However, the

maintenance of catalyst activity with the accumulation of wax within the catalyst pores and within the catalyst bed may be a problem that needs to be addressed. With the slurry liquid-phase operation, the separation of the catalyst offers a different problem. The support in most catalyst systems provides a robustness that significantly decreases the generation of small particles that make wax removal from the reactor a problem. However, the robustness of the iron catalyst is much lower, generating catalyst fines that make it difficult to obtain a clean wax from the reactor.

On the basis of initial catalytic activity and the lifetime of the catalytic activity, it appears that the catalysts based on iron or cobalt are similar. Because of the wide variation in the final catalyst that is determined by catalyst preparation and composition, a direct comparison on a quantitative basis is not possible.

For the production of high molecular weight products, the iron catalyst has the ability to produce much higher weight products when the comparison is made on the basis of the alpha value. For example, the average carbon number of the products for a cobalt catalyst with an alpha value of 0.87 is 7.7. For an iron catalyst with an alpha value of 0.95, the average carbon number of the products will be 20.

When one considers that in many locations the C_2-C_4 alkenes will be as, or more, valuable than transportation fuels, we consider the undesirable products as CO_2, CH_4 and C_2-C_4 alkanes. On this basis, the methane make for the cobalt catalyst is in the 8-10% range while for the iron catalyst it is in the 1.5-2% range. For the C_2-C_4 alkanes, there is a small advantage for the iron catalyst. The CO_2 production for the cobalt catalyst is 0.5% or less whereas for the iron catalyst it is difficult to operate so as to produce less than 15% CO_2. In the above, the percentage of the products is on a molar carbon converted basis. On the basis of undesirable products, cobalt is slightly preferred since it produces slightly less methane than iron produces carbon dioxide. However, these values for the iron catalyst depend upon the level of CO conversion and the ones provided are for CO conversion in the 30-40%/pass range. Operating at 70% CO single pass conversion will provide a larger advantage for the cobalt catalyst, primarily because the methane percentage will remain about the same but the carbon dioxide percentage will be considerably higher for the iron catalyst.