

Technology Development for Iron and Cobalt Fischer-Tropsch Catalysts

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Abstract

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The use of alkali promoters has been widely practiced. However, data to compare various promoters is limited for the iron-based catalysts and much of the available data were obtained at low pressure or under a variety of reaction conditions. The importance of the alkali promoter in determining catalytic activity, stability and selectivity merits a comparison of the promoters under suitable reaction conditions. The present study utilizes medium pressure synthesis conditions to compare the alkali promoters under the same reaction conditions and over a wide range of conversion levels.

Iron-based Fischer-Tropsch (FT) catalysts undergo a series of phase transformations during activation and use. Activation with carbon monoxide or syngas typically results in the conversion of Fe_2O_3 to Fe_3O_4 and ultimately to one or more carbides. During FT synthesis, iron carbides can be oxidized to Fe_3O_4 if the $\text{H}_2\text{O}/\text{H}_2$ or CO_2/CO ratios are high enough. There has been considerable debate about the active phase of the FT synthesis. Some studies have indicated an active oxide species while most have supported a carbide species. Mössbauer spectroscopy has proven to be an effective technique for the analysis of iron-based FT catalysts. *In situ* Mössbauer studies have been reported; however, these studies have been performed at low pressure and low conversions. Studies performed at industrially relevant conditions have generally involved removing the catalyst from the reactor followed by passivation which, if not performed properly, will oxidize the catalyst. Herein are reported the Mössbauer results obtained on an unpromoted precipitated iron catalyst that was activated and reacted in a slurry phase, continuous stirred tank reactor at high conversion and under industrially relevant conditions.

Strict measures were observed to prevent oxidation of the catalyst samples. The Fe-Si, Fe-K, Fe-Si-K catalysts were all studied using the same methods.

We have studied and are continuing to study the impact on reducibility of cobalt by the use of different supports and by the incorporation of different promoters and additives to supported cobalt catalysts. Although the use of different supports and promoters is well documented, what is less well understood are the reasons for the differences in deactivation rates of these catalysts. Only by rigorous characterization can the properties of the catalysts brought about by differences in preparation, support, and degree and type of promoter be linked to the resulting catalytic properties under reaction. We therefore have spent considerable attention on the characterization of not only the fresh catalysts, but also the spent catalysts sampled after many days on stream in the continuously stirred tank reactor. With this approach, it is our goal to understand what properties are required for high initial activity and, just as importantly, for the maintaining of high stability, and how to achieve them in the catalyst preparation and activation steps. Interestingly, while addition of promoters can markedly improve the reducibility of cobalt FTS catalysts, leading to more available catalytic sites for reaction, these catalysts often display significantly high rates of deactivation. This raises many questions, which should be able to be addressed through careful characterization. To address these questions, we are employing several characterization techniques, including temperature programmed reduction (TPR), hydrogen chemisorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), and in the near future, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and X-ray absorption spectroscopy methods (XAS) such as extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES).

Currently, the CAER is utilizing the Prototype Integrated Process Unit (PIPU) system for scale-up research of the Fischer-Tropsch Synthesis (FTS).

The PIPU is a pilot plant system built in the early 1980s for studying a multitude of synthetic fuel/chemical processes. In the mid 1990s, a direct coal liquefaction reactor within the PIPU plant was reconfigured as a SBCR for FTS studies. The reactor was originally designed to operate with coarse catalyst pellets ($>500 \mu\text{m}$). Consequently, the reactor system did not contain a wax separation system sufficient for smaller catalyst particles that are typically used in FTS. Therefore, a slurry accumulator and a batch wax filtration system were installed.

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Treatment temperatures play a major role in determining the surface area of Fe-Zn oxides. H_2O removal is critical in preparing high surface area Fe-Zn precursors. Decreasing the surface tension of liquids during drying processes and increasing the space velocity of dry air in subsequent treatment processes can significantly increase the surface area of catalyst precursors. Each impregnation slightly decreases the surface area of Fe-Zn precursors. However, the previous impregnation history on Fe-Zn precursors does not appear to influence the ultimate surface area of promoted Fe-Zn oxides at a given treatment temperature. High surface area Fe-Zn-K₄-Cu₂ oxide (Zn/Fe=0.1, K/Fe=0.04, Cu/Fe=0.02) reduces at slightly higher temperatures in H_2 but reduces and carburizes at lower temperatures ($\sim 30 \text{ K}$) in CO than on Fe-Zn-K₂-Cu₁ oxide (Zn/Fe=0.1, K/Fe=0.02, Cu/Fe=0.01), suggesting its slightly higher surface K/Cu ratio than on Fe-Zn-K₂-Cu₁ oxide. CO chemisorption on Fe-Zn-K-Cu oxides after FTS reaction showed that the amount of CO adsorbed is proportional to the surface area of each sample. Zn, Cu and K promoter lead to higher surface area Fe carbides, which provide a higher density of binding sites for adsorption and also for FTS reactions. Fixed bed reactor studies with high surface area Fe-Zn-Cu-K samples showed that

an increase in surface area led to proportionally higher FTS rates with negligible changes in the product selectivity. This effect is attributed to an improvement in dispersion of the active Fe_xC structure upon increase in surface area. Similarly, the addition of Ru to Fe-Zn-K also increases FTS rates by improving the availability of active sites on the catalyst surface. Tests conducted with increased surface hydrogen coverage on Fe-based catalysts showed an increase in the paraffin content and a decrease in the product molecular weight at conditions normally utilized for Co-based catalysts. Similarly, when a Co/SiO_2 catalyst is operated at higher CO surface coverages and at conditions utilized for Fe-based catalysts, an increase in the olefin content and lower CH_4 selectivity were observed. The primary difference between FTS reactions on Fe and Co catalysts appear to be due to the lack of secondary olefin readsorption reactions in the case of the former, which could explain the observed differences in product selectivity. Studies with a Co/SiO_2 catalyst at different reaction pressures showed the existence of the autocatalytic water effect even at lower pressures (i.e., 5 atm).

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