

Technology Development for Iron and Cobalt Fischer-Tropsch Catalysts

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## Abstract

### CAER

The impact of deuterium on the Fischer-Tropsch (FT) synthesis was studied with a precipitated iron catalyst in the slurry phase. Deuterium has been used by several research groups to better understand the mechanism of CO hydrogenation. Inverse ( $k_H/k_D < 1$ ), normal ( $k_H/k_D > 1$ ) and no isotope effect ( $k_H/k_D = 1$ ) have been reported. The conflicting results are thought to arise because rate of reaction is a combination of kinetic and equilibrium factors.

In summary, the presence of boron produced only minor changes on the properties of the cobalt catalyst. In earlier studies, it was shown that the presence of boron made the catalyst less susceptible to poisoning by sulfur.

Steady-state supercritical Fischer-Tropsch synthesis was studied in our work using a fixed-bed reactor and an unpromoted Co/SiO<sub>2</sub> catalyst. This serves as the baseline for promoted catalyst studies. A pentane-hexane mixture was used as the supercritical solvent. Overall reactor pressure, syngas partial pressure and contact time were kept constant to obtain a valid comparison of the impact of solvent density in the catalytic activity and selectivity. Three different partial pressures of the mixture were chosen based on the density-pressure curve in order to investigate the pressure tuning effect to Fischer-Tropsch synthesis near critical region.

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*In-situ* Fe K-edge X-ray absorption spectroscopic (XAS) measurement of Fe<sub>2</sub>O<sub>3</sub> in synthesis gas at 250°C showed that Fe<sub>2</sub>O<sub>3</sub> was converted to a mixture of Fe<sub>3</sub>O<sub>4</sub> and Fe carbides after 9 h. The linear combination of the X-ray absorption near edge spectroscopy (LC XANES) fit of the samples provided by the Center for Applied Energy Research (CAER) of the University of Kentucky showed that the samples used for various lengths of time for FTS contained both Fe carbides and Fe<sub>3</sub>O<sub>4</sub>, and the extent of carburization increased and reached a highest value and then decreased gradually with time on stream. After 432 h, all the Fe carbides were converted to Fe<sub>3</sub>O<sub>4</sub>. The isotopic effects using synthesis gases of D<sub>2</sub>/CO/N<sub>2</sub> and H<sub>2</sub>/CO/N<sub>2</sub> on an Fe-Zn catalyst (Zn/Fe=0.1, K/M=0.02, Cu/Fe=0.01) at 235°C and 21.4 atm showed that lower methane and CO<sub>2</sub> selectivities and a higher selectivity to C<sub>5+</sub> were obtained with H<sub>2</sub>/CO/N<sub>2</sub> than with D<sub>2</sub>/CO/N<sub>2</sub>. Inverse isotopic effects for CO conversion rate and hydrocarbon formation rate and a normal isotopic effect for CO<sub>2</sub> formation were observed when D<sub>2</sub> was used instead of H<sub>2</sub>. The  $k_H/k_D$  ratio for hydrocarbon formation decreased with increasing CO conversion and with increasing carbon number. The isotopic effects were more evident for the formation of hydrocarbons with higher molecular weight, and for the formation of paraffins than for olefins. Kinetic studies and the H<sub>2</sub>/D<sub>2</sub> isotope effects during FTS with both CO/H<sub>2</sub> and CO/D<sub>2</sub> were carried out over a 21.9 wt.% Co/SiO<sub>2</sub> catalyst at 200°C and 20 atm. The CO consumption rate data along with those obtained from the previous kinetic run were fitted to rate expressions on the basis of our proposed mechanisms with multivariable non-linear regression. The kinetic isotope effects for CO consumption and for individual hydrocarbons C<sub>1</sub>-C<sub>7</sub> were obtained by comparing the corresponding reaction rates with H<sub>2</sub> and D<sub>2</sub>. Inverse kinetic isotope effects were obtained for CO consumption ( $k_H/k_D = 0.8$ ) when the CO conversions were between 10% and 40%. The results showed that the isotope effects ( $k_H/k_D$ ) were generally inverse for paraffins whereas normal for olefins at low conversions when the effect of secondary reactions could be neglected. These isotope effects resulted from a combination of kinetic and equilibrium isotopic effects which may be associated with individual elementary steps.

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