Technology Development for Iron and Cobalt Fischer-Tropsch Catalysts

Quarterly Report

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Abstract

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The influence of process parameters on Fischer-Tropsch synthesis over alkali metal promoted iron catalysts was studied. This study was to investigate the effects of reaction temperature, pressure and space velocity on Fischer-Tropsch synthesis (FTS) product selectivity, reaction conversions and productivity. Three alkali metal promoted iron catalysts, two with potassium and other with beryllium, were used in this study. Factorial experimental design was applied to reduce number of reaction runs and to detect the single effect and the interaction effect of temperature, pressure and space velocity. A mathematical model is being developed to further analyze and optimize the process.

Fresh and spent unpromoted and noble metal promoted 15%Co/Al_2O_3 catalysts were analyzed by XANES to provide insight into catalyst deactivation. XANES analysis of spent unpromoted and Ru promoted Co/Al_2O_3 catalysts gave evidence of oxidation of a fraction of the cobalt by water produced during the reaction. From analysis of the pre-edge feature, the oxidized clusters showed evidence of a tetrahedral environment, indicating that either Co_3O_4 and/or Co aluminate was formed. Comparison of XANES derivative spectra to references and LC fitting suggested that some form of Co aluminate species was formed. Because bulk oxidation of Co by water is not permitted thermodynamically under FTS conditions, it is concluded that the smaller clusters interacting with the support and deviating from bulklike behavior undergo oxidation in the presence of water. Promotion with Ru or Pt allowed for the reduction of smaller clusters interacting with the support, yielding more active sites and a higher initial rate of activity. Since these clusters deviated more from the bulk and generated a higher water partial pressure due to enhanced activity, the rate of deactivation was faster for the promoted catalysts.

In this report we describe results and operating experiences for two SBCR pilot plant runs completed during this reporting period. For the first time since overhauling the SBCR plant, a high alpha iron-based F-T catalyst run was completed. The objective of the run was to test the efficiency of the new catalyst/wax filtration system for removing heavier F-T products. Conversion and catalyst activity decline of the high alpha catalyst in the SBCR were compared to that of CSTR experiments. The activity decline measured in the SBCR system was shown to be similar to that of the CSTR experiments.

A catalyst attrition study was conducted using a spray-dried iron catalyst. Attrition of the catalyst particles occurred in two stages: 1) a rapid breakdown during catalyst loading and activation and 2) after two days time on stream an exponential decay period. SEM images of the particles indicate that breakdown of the particles was more physical than chemical in nature. During the end of the attrition test, the effect of syngas composition was investigated by changing the H_2/CO ratio from 0.7 to 2.0. After changing the H_2/CO ratio to 2.0, the trend of losing reactor slurry level (as shown from a previous SBCR run) was verified. The cause of the slurry level decrease was found to due to a decreased gas hold-up with the reactor vessel.

A study to determine the effectiveness of H_2O as a hydrogen source was begun. This work used D_2O as a probe to study the deuterium distribution of the FT products. The H/D ratio of the products gave an indication of the surface H-D pool and a quantitative measure of the effectiveness of H_2O as a hydrogen source. These initial results suggest that as a hydrogen source, water can be effective as H_2 using the reaction conditions studied.

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Experiments were carried out with a Fe-Zn-Cu-K catalyst at 473 K with varying H_2/CO ratios in order to understand the effect of H*/CO* ratios on the reaction rates as well as the growth and termination of hydrocarbon chains.. The FT rates increased with hydrogen partial pressure suggesting a positive dependence of the former on the latter. An increase in H* surface concentration led to lower CO_2 selectivities (owing to increased rate of the reverse water-gas shift reaction) led to an increase in the intrinsic termination of hydrocarbons at lower carbon numbers and decreased the olefin content in the products. A manuscript describing the systematic catalyst design route for FTS reactions, via a study of the promoter effect of Cu and Ru, on the site density and catalytic performance of Fe-Zn catalysts, has been prepared. *In situ* FTIR spectroscopic experiments conducted on a Co/SiO_2 catalyst indicated a small and irreversible increase in the number of CO adsorption site upon addition of water, which indicated that the significant promotion of the steady state FTS rates by water cannot merely reflect an increase in the total number of CO adsorption sites alone. This suggests the participation of water as a reactant in kinetically relevant steps in the FTS reaction. Switching experiments were carried out on the Co unit under FTS conditions (high temperature and high pressure) in order to estimate the number of active sites on the catalyst during the reaction. An experimental technique for collecting and analyzing data was developed during this quarter, which led to reproducible results.

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