Technology Development for Iron and Cobalt Fischer-Tropsch Catalysts

Quarterly Report

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Abstract

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The effects of copper on Fischer-Tropsch activity, selectivity and water-gas shift activity were studied over a wide range of syngas conversion. Three catalyst compositions were prepared for this study: (a) 100Fe/4.6Si/1.4K, (b) 100Fe/4.6Si/0.10Cu/1.4K and (c) 100Fe/4.6Si/2.0Cu/1.4K. The results are reported in Task 2.

The literature review for cobalt catalysts is approximately 90% complete. Due to the size of the document, it has been submitted as a separate report labeled Task 6.

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Fe-Zn-K-Cu catalysts with different Zn/Fe ratios (0 ~ 0.4) were prepared using co-precipitation method and then promoted with potassium (2 at.%) and copper (1 at.%). Only Fe_2O_3 is detected in samples with lower Zn loadings (Zn/Fe < 0.2) and $ZnFe_2O_4$ at the high Zn loading (Zn/Fe = 0.4). Both Fe_2O_3 and $ZnFe_2O_4$ phases were detected at intermediate Fe/Zn ratios. It appears that the $ZnFe_2O_4$ phase resists sintering during calcination at 350^{o}C, and that its effect becomes increasingly critical as the required calcination temperature increases (400^{o}C). Carburization of Fe oxides with CH_4/H_2 mixtures leads to the formation of Fe carbides with significant residual Fe metal. Potassium inhibits the reduction of Fe oxides in H_2 and Cu decreases the reduction temperature. The presence of Zn appears not to influence the reduction of Fe oxides in H_2. Fischer-Tropsch synthesis studies using a well-studied Fe-Zn catalyst gave reaction rates and product distributions in excellent agreement with literature data. These results were obtained in order to certify the operation of our new microreactor system. The addition of CO_2 decreases water gas shift reaction rates and CO_2

selectivity during Fischer-Tropsch synthesis on Fe-Zn catalysts. The rate of hydrocarbon formation is not affected by the CO_2 partial pressure. Fischer-Tropsch synthesis at different temperatures and H_2 and CO concentrations on Fe-Zn-K-Cu catalysts shows that low temperatures and high total reactant pressures favor the formation of heavier and more paraffinic hydrocarbons. The selectivity to CO_2 selectivity and to olefinic products increased with increasing reaction temperature. Reaction rates on our Fe-Zn-K-Cu catalyst (Zn/Fe = 0.1, 2 at.% K, 1 at.% Cu) between 220^{o}C and 270^{o}C are similar to those obtained on Co/SiO_2 catalyst (12.7 wt.%) at slightly low temperature (200^{o}C), while selectivities to C_4-C_{12} (32 % at 220^{o}C and 235^{o}C, and 50% at 270^{o}C) on our Fe-Zn-K-Cu catalyst are higher than that on Co/SiO_2 (21%). A multi-compartment kinetic model of catalytic surfaces is being developed in order to allow the deconvolution and analysis of isotopic transients and exchange dynamics during the Fischer-Tropsch synthesis on Fe and Co catalysts.

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