

Technology Development for Iron and Cobalt Fischer-Tropsch Catalysts

Quarterly Report

January 1, 2000 to March 31, 2000

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DE-FC26-98FT40308

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Abstract

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Both cobalt and iron catalysts were used in the initial study of catalyst-wax filtrations. For both systems, the filters studied were internally placed in the 1000 mL continuous stirred tank reactors. For the supported cobalt catalysts based on silica, alumina, and titania support material, wax has been successfully removed from the reactor during operations of up to five months. Wax separations from the catalyst slurry is not a problem using a fine (2 to 5 micron) porous metal filter. Operations of the laboratory reactors with wax production of 100 g/day or higher can be accomplished with the cobalt catalyst.

Two filters manufactured by Pall were studied using a high alpha iron catalyst. We were able to successfully operate for 1500 hours without the filter plugging using a Rigimesh filter. It was determined that the activity decline was at approximately the rate as the loss of catalyst and that loss of activity was lower than the DOE target of 1% CO conversion per week. Therefore, we consider this to be a demonstration of our ability to operate the CSTR so that we can now define the activity, selectivity and catalyst deactivation characteristics for both intermediate and high alpha catalysts.

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In-situ Fe K-edge X-ray absorption studies on Fe₂O₃-Cu and Fe₂O₃-Cu-K during 14 h FTS reaction confirmed the conversion sequence of Fe₂O₃ to Fe₃O₄ and then to Fe_xC and the continuous reduction and carburization even after FTS reaction rates reached steady-state. The addition of K to Fe₂O₃-Cu over a period of 14 h significantly decreased the reduction and carburization time because K increases carburization rates and Cu catalyzes the initial oxygen removal from Fe₂O₃. Using H₂, CO and H₂/CO mixture chemisorption measurements after FTS

reaction showed that H₂ and CO competitively adsorb on Fe sites. CO occupies two Fe sites while chemisorbing alone. In the presence of H₂, a portion of CO adsorbs molecularly on Fe sites. The structure, reduction and carburization behavior, and catalytic properties of Fischer-Tropsch synthesis (FTS) catalysts based on K- and Re-promoted Fe-Si oxides were also studied using transient reaction methods. No significant promotion effects were observed when K or ReO_x was added to Fe-Si oxides, because a large fraction of the K added titrates the SiO₂ component and because ReO_x was not completely reduced to Re metal during FTS. A comparison between the FTS reaction rates on Fe-Si-K and Fe-Zn-Cu-K catalysts showed that the Fe-Si-based catalyst has a higher FTS activity under the same conditions. However the Fe-Zn-Cu-K catalyst had a higher selectivity to C₅₊ hydrocarbons and a lower CH₄ selectivity. The Fe-Si-K catalyst also exhibited a lower CO₂ selectivity than the Fe-Zn-Cu-K counterpart, apparently because Cu, an excellent water-gas shift catalyst, is not present. Studies of the effect of K addition to Fe-Si oxides at different temperatures showed that K-promotion effects were smaller than observed for Fe-Zn-Cu oxides. Experiments conducted with a Co/SiO₂ catalyst unit in our attempts to certify a re-designed microreactor showed site-time yields identical to those obtained in earlier runs but higher CH₄ selectivities and lower C₅₊ selectivities were obtained. The discrepancies in the data are currently under investigation.

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