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**TECHNOLOGY DEVELOPMENT FOR COBALT F-T CATALYSTS RECEIVED**

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## EXECUTIVE SUMMARY

The investigation of the effect of certain promoters (Fe, Pd, and Ru) on the deactivation characteristics of Co catalysts during F-T synthesis was continued during this reporting period. All catalysts were tested first at 220°C, then at higher temperatures from 240 to 280°C, while monitoring their deactivation. The choice of these promoters was based on their intrinsic ability to enhance the hydrogenation reactions while slowing down the Boudouard reaction under the conditions used in F-T synthesis. Olefin hydrogenation and CO dissociation reactions were used individually to investigate further the nature of the deactivation process of these catalyst during F-T synthesis. Hydrogenation of isobutene (IB) was carried out in the presence of CO between 120 and 180°C and atmospheric pressure. CO dissociation activities of the catalysts were measured using a pulse technique at 2.5 atm and at temperatures between 180 and 280°C with intermittent H<sub>2</sub> bracketing at 350°C. Promotion with high loadings of Fe or Pd resulted in catalysts with relatively lower activity and higher methane selectivity. The deactivation process and rate for catalysts containing Pd or Fe were similar to those of the non-promoted or Ru-promoted alumina-supported Co catalysts tested previously. The only exception was Co.068 with 1% Pd which had adequate activity and selectivity as well as lower deactivation rate at the various temperatures tested.

Promotion of Co catalyst with Ru doubled the isobutene hydrogenation activity at 120°C and more than tripled it at 180°C. Addition of Fe to CoRu almost completely reversed the effect of Ru and was more pronounced with increasing Fe concentration. The addition of Pd, however, led to a dramatic increase in the hydrogenation activity by more than an order of magnitude compared with the plain Co catalyst and still by a factor of 8 compared with CoRu catalysts. The results of the Boudouard reaction indicate that addition of increasing amounts of Fe to CoRu also gradually

decreased the CO dissociation activity. However, the promotion with 1% Pd instead of Ru showed practically no influence on CO<sub>2</sub> formation. Using 2% Pd, however, reduced the CO dissociation activity by a factor of 2.

During this reporting period, a number of runs were performed in the slurry bubble column reactor in order to evaluate the effect of certain promoters (Fe and Pd) on the deactivation characteristics of Co catalysts during F-T synthesis. The reaction was performed under standard conditions followed by high temperatures up to 300°C in order to evaluate the catalyst resistance to deactivation. The results indicate that the addition of Fe to cobalt catalysts can prevent their fast deactivation at high temperature. However, this promoter results in low overall activity catalysts with high selectivities for methane.

Another aging run was carried out successfully for ca. 850 h using Co/Al<sub>2</sub>O<sub>3</sub> as the second catalyst selected for its low methane selectivity and adequate activity in the SBCR system. The reaction was carried out at 220°C and very little deactivation was observed under these conditions.

A series of four SBCR runs was made with an iron catalyst supplied by DOE/PETC that had been used in the F-T Run II at LaPorte, Texas, in 1995. The F-T synthesis was carried out under similar or close to conditions used at Laporte in order to evaluate the catalyst performance and see whether some of the problems encountered during the Laporte run could have been predicted from a bench scale reactor run.

Finally, four Co catalysts were run in a one liter autoclave at the Center for Applied Energy Research of the University of Kentucky, Lexington, Kentucky. Their performance in the CSTR was comparable to that observed previously in the SBCR.

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