

Technology Development for Iron and Cobalt Fischer-Tropsch Catalysts

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## Abstract

### CAER

The impact of activation procedure on the phase composition of precipitated iron Fischer-Tropsch (FT) catalysts has been studied. Catalyst samples taken during activation and FT synthesis have been characterized by Mössbauer spectroscopy. Formation of iron carbide is necessary for high FT activity. Hydrogen activation of precipitated iron catalysts results in reduction to predominantly metallic iron and  $\text{Fe}_3\text{O}_4$ . Metallic iron is not stable under FT conditions and is rapidly converted to  $\epsilon'$ - $\text{Fe}_{2.2}\text{C}$ . Activation with carbon monoxide or syngas with low hydrogen partial pressure reduces catalysts to  $\chi$ - $\text{Fe}_5\text{C}_2$  and a small amount of superparamagnetic carbide. Exposure to FT conditions partially oxidizes iron carbide to  $\text{Fe}_3\text{O}_4$ ; however, catalysts promoted with potassium or potassium and copper maintain a constant carbide content and activity after the initial oxidation. An unpromoted iron catalyst which was activated with carbon monoxide to produce 94%  $\chi$ - $\text{Fe}_5\text{C}_2$ , deactivated rapidly as the carbide was oxidized to  $\text{Fe}_3\text{O}_4$ . No difference in activity, stability or deactivation rate was found for  $\chi$ - $\text{Fe}_5\text{C}_2$  and  $\epsilon'$ - $\text{Fe}_{2.2}\text{C}$ .

### UC/B

The temperature-programmed surface reaction (TPSR) of Fe-Zn and Fe-Zn-K-Cu oxides in CO showed that the reduction and carburization of Fe-Zn-K-Cu oxides proceeded in three steps:  $\text{Fe}_2\text{O}_3$  was first reduced to  $\text{Fe}_3\text{O}_4$ ; Then,  $\text{Fe}_3\text{O}_4$  was reduced to metallic Fe followed by carburization to a mixture of  $\chi$ - $\text{Fe}_{2.5}\text{C}$  and  $\text{Fe}_3\text{C}$ . The reduction and carburization of Fe oxides shifted to higher temperatures at higher Zn contents; K slightly inhibited both the reduction and carburization of Fe oxides; Cu decreased not only the temperature required for the reduction but also that for carburization. In-situ X-ray absorption studies at Fe K-edge for Fe-Zn-K-Cu oxide in CO showed progressive shifts of the edge energy from 7123 eV ( $\text{Fe}^{3+}$ ) to 7112 eV ( $\text{Fe}^0$ ) along with changes in the near-edge and fine structure regions while increasing the carburization temperature up to 500 °C. The Fischer-Tropsch synthesis (FTS) on Fe-Zn oxide showed that the addition of potassium (2 ~ 4 at.%) significantly increased FTS and water-gas shift reaction rates, decreased the selectivity to methane and increased selectivities to high molecular weight hydrocarbons and to olefins.  $\text{CO}_2$  addition experiments showed that the addition of  $\text{CO}_2$  inhibited the formation of  $\text{CO}_2$  via water-gas shift reactions but did not affect the FTS reaction. FTS reaction rates and selectivities at different space velocities on Co/ $\text{SiO}_2$  catalysts showed that CO conversion and  $\text{C}_{5+}$  selectivity increased while  $\text{CH}_4$  selectivity and  $\alpha$ -olefin to  $n$ -paraffin ratio decreased with increasing bed residence time. Also, FTS reaction rates increased with increasing bed residence time. Water increased FTS rates and selectivities to  $\text{C}_{5+}$  and olefins. CO conversion rates increased with increasing water partial pressure.  $\text{D}_2\text{O}$  tracer studies showed that water dissociation was not quasi-equilibrated in Co-catalyzed FTS. The kinetic isotope effect (KIE) experiments on Co catalysts suggested that hydrogen dissociation involved in the rate-determining step and that chain termination to olefins was larger for deuterium containing chains.

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