

Role of cobalt catalyst porosity in the reaction of hydrocarbon synthesis from CO and H₂

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Abstract

Synthesis gas is a key feedstock for wide variety of chemicals as well as a source of pure hydrogen and carbon monoxide. Nowadays, one of the most promising and intensively developed route for syngas utilization is its catalytic conversion into long-chain hydrocarbons so called Fisher-Tropsch synthesis (FT). Synthetic fuel fractions produced via FT synthesis over cobalt catalysts are of high value due to extremely low sulphur and nitrogen content and absence of aromatics. Moreover, FT naphtha is superior feed for steam crackers and FT diesel have extremely high cetane number of about 70.

Effect of surface properties on catalyst performance is challenging problem for FT synthesis. There is currently a consensus that CO and hydrogen convert into hydrocarbons on cobalt metal particles. However, effect of surface properties on catalyst activity and hydrocarbons yield is not fully understood.

In our work we have studied a number of cobalt-alumina and cobalt-silica-alumina catalysts prepared by wet impregnation technique. Average pore diameter of supports varied from 6 to 100 nm. All the catalysts were activated uniformly in hydrogen at 450°C for 1 hour and the tested in FT synthesis in atmospheric fixed-bed reactor. Non-linear dependence of cobalt crystallite size on average pore diameter of support have been found. For large pore aluminas with pore diameter 40 nm and more, cobalt crystallite size in activated Co-alumina catalysts reaches 14 nm and almost independent on pore diameter.

Catalytic tests demonstrated that large-pore, low surface area supports are preferable in terms of activity. Calculated turnover rates reach $2.6\text{--}3.7 \times 10^{-3} \text{ c}^{-1}$ at 190°C for these catalysts. On the contrary, catalysts based on narrow-pore silica-aluminas display smaller turnover rate of about $0.4\text{--}0.8 \times 10^{-3} \text{ c}^{-1}$. Thus, specific activity of small cobalt crystallites, 6 nm or less, was found to be lower than that of large particles. Molar selectivity to C₅₊ hydrocarbons reaches maximal values of 88-90% for supports with 7-12 nm average pore diameter. These samples provide lowest CH₄ selectivity, 5-7 molar%.