

OXYGENATES *via* SYNTHESIS GAS

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EXECUTIVE SUMMARY

Methanol synthesis from H_2/CO has been carried out at 7.6 MPa over zirconia-supported copper catalysts. Catalysts with nominal compositions of 10/90 mol% and 30/70 mol% Cu/ZrO₂ were used in this study. Additionally, a 3 mol% cesium-doped 10/90 catalyst was prepared to study the effect of doping with heavy alkali, and this promoter greatly increased the methanol productivity. The effects of CO₂ addition, water injection, reaction temperature, and H_2/CO ratio have been investigated. Both CO₂ addition to the synthesis gas and cesium doping of the catalyst promoted methanol synthesis, while inhibiting the synthesis of dimethyl ether. Injection of water, however, was found to slightly suppress methanol and dimethyl ether formation while being converted to CO₂ via the water gas shift reaction over these catalysts. There was no clear correlation between copper surface area and catalyst activity. Surface analysis of the tested samples revealed that copper tended to migrate and enrich the catalyst surface.

The concept of employing a double-bed reactor with a pronounced temperature gradient to enhance higher alcohol synthesis was explored, and it was found that utilization of a Cs-promoted Cu/ZnO/Cr₂O₃ catalyst as a first lower temperature bed and a Cs-promoted ZnO/Cr₂O₃ catalyst as a second high-temperature bed significantly promoted the productivity of 2-methyl-1-propanol (isobutanol) from H_2/CO synthesis gas mixtures. While the conversion of CO to C₂₊ oxygenates over the double-bed configuration was comparable to that observed over the single Cu-based catalyst, major changes in the product distribution occurred by the coupling to the zinc chromite catalyst; that is, the productivity of the C₁-C₃ alcohols decreased dramatically, and 2-methyl branched alcohols were selectively formed. The desirable methanol/2-methyl oxygenate molar ratios close to 1 were obtained in the present double-bed system that provides the feedstock for the synthesis of high octane and high cetane ethers, where the isobutanol productivity was as high as 139 g/kg cat/hr.

Higher alcohol synthesis has been investigated over a Cs/Cu/ZnO/Cr₂O₃ catalyst at temperatures higher (up to 703K) than those previously utilized, and no sintering of the catalyst was observed during the short-term testing. However, the higher reaction temperatures led to lower CO conversion levels and lower yield of alcohols, especially of methanol, because of equilibrium limitations. With the double catalyst bed configuration, the effect of pressure in the range of 7.6-12.4 MPa on catalyst activity and selectivity was studied. The upper bed was composed of the copper-based catalyst at 598K, and the lower bed consisted of a copper-free Cs-ZnO/Cr₂O₃ catalyst at a high temperature of 678K. High pressure was found to increase CO conversion to oxygenated products, although the increase in isobutanol productivity did not keep pace with that of methanol. It was also shown that the Cs/Cu/ZnO/Cr₂O₃ catalyst could be utilized to advantage as the second-bed catalyst at 613-643K instead of the previously used copper-free Cs-ZnO/Cr₂O₃ catalyst at higher temperature. With double Cs/Cu/ZnO/Cr₂O₃ catalysts, high space time yields of up to 202 g/kg cat/hr, with high selectivity to isobutanol, were achieved.

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