Methanol and Dimethyl Ether from Syngas by Novel Copper-Silicate Structured Core-Shell Type Microsphere Catalysts

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Methanol and dimethyl ether (DME) are two of the most promising environmentally friendly non-petroleum fuel alternatives, with octane and cetane numbers of 100 and 55, respectively [1]. Besides being clean transportation fuels with no particulate matter emissions, they can also be used as fuels in direct methanol and DME fuel cells; they also serve as the starting materials for synthesizing valuable chemicals.

Conventionally, methanol is synthesized from synthesis gas via a catalytic step using $Cu/ZnO/Al_2O_3$ type catalysts, and dehydration of methanol produces DME over a solid acid catalyst. However, advances in catalysis made it possible to produce DME directly from syngas using bifunctional catalysts [2-5]. Direct synthesis of DME from syngas also has significant thermodynamic advantages over the conventional two-step process. This single-step process for DME synthesis requires the development of bi-functional catalysts containing both methanol synthesis and dehydration sites.

In the present study, bi-functional micro-sphere catalysts with a core-shell structure are synthesized following a new micro-capsulation procedure. The core section of these micro-spheres is copper, while the shell section is mainly silicate. In order to increase the dehydration activity of these catalysts, 5-25% silicotungstic acid (STA) was incorporated into the silicate-structured shell section. Basing on the TPR results, these micro-spheres were reduced by hydrogen at 300^{o}C. SEM images showed the formation of spherical micro-spheres with diameters of 100-200 nm. A significant increase in both Lewis and the Bronsted acidities was achieved by increasing the amount of STA impregnated into the silicate layer covering the copper core of these materials. Methanol and DME synthesis tests, performed at 50 bar and 275^{o}C, proved that these bifunctional catalysts were highly promising for the simultaneous synthesis of methanol and DME from syngas. In the experiments conducted at a space-time of 0.7 s.g/cm^3, the conversion of CO increased from 21% to 41%, with an increase in the STA content of the catalyst from zero to 15%. The DME to methanol selectivity ratio also increased from 0.6 to 5.6 with this increase in the STA content due to the higher Bronsted acidity of the catalysts having more STA. It is concluded that core-shell type micro-sphere catalysts prepared in this study showed excellent performance for methanol and DME synthesis from syngas, and the product distribution can be adjusted by changing the STA content of the catalyst.

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