

Synthesis of dimethyl ether from methanol in the presence of silica based catalysts

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Introduction

Due to limited oil deposits new alternative raw materials of petroleum industry are studied. Natural gas is one of the most important raw materials for production of synthetic fuels. The Fischer–Tropsch process is an example of successful technology of liquid fuel production starting from natural gas. Dimethyl ether (DME) is another interesting product, that could be produced starting from natural gas (stream reforming of natural gas → synthesis of methanol by reaction of CO and H₂ → synthesis of DME, or alternatively synthesis of DME directly by reaction of CO and H₂). DME may be used as diesel substitute, due to its high cetane number and similar physical properties to diesel fuel, producing lower amounts of NO_x, SO_x and soot. Since dimethyl ether is easily liquefied and has similar properties to propane and butane (main components of LPG), thus it is possible to use it as LPG substitute. Dimethyl ether synthesis from alcohol is acid-catalyzed, exothermic reaction. Catalysts with strong acid sites produce light olefins as a main product and promote coke formation, while catalysts with medium and weak acid sites convert methanol mostly to dimethyl ether. The presented studies reports application of various silica material modified in different ways in the role of the catalysts for DME synthesis.

Materials and Methods

Acid-treated vermiculite, micro-mesoporous Beta zeolite and mesoporous SBA-15 silica doped with alumina species were used as catalysts for the DME synthesis. Acid-activation of vermiculite was done according to the procedure described by Chmielarz et al. [1]. Vermiculite was dispersed in a solution of nitric acid (0.8 M) and stirred at 368 K for 2, 8 or 24 h. Then, the samples were filtered, washed with distilled water, dried and finally calcined. The obtained materials are designated as V2, V8 and V24, respectively. Raw vermiculite (V0) was used as a reference sample.

Beta micro-mesoporous Beta zeolite (HBeta/m) was synthesized by the non-templating method, according to the procedure described by Rutkowska et al. [2]. HBeta zeolite was used as a reference catalyst

SBA-15 was synthesized according to the procedure described in [3]. Then, obtained SBA-15 was functionalized with surface thiol organosilicates by grafting of (3-mercaptopropyl)trimethoxysilane. Subsequently, –SH groups grafted on the silica surface were converted to –SO₃H by oxidation with a solution of H₂O₂. Then, the solid product was filtered, washed with distilled water and ethanol (1:1) and dried. A solution of alumina oligocations was prepared according to the procedure described in [4]. The slurry of modified SBA-15 dispersed in alumina oligocations solution was stirred for 24 h, then the product was separated by filtration, washed with distilled water, dried and finally calcined. The obtained material is referred as SBA-15o. Non-modified SBA-15 was used as a reference catalyst.

The obtained samples were characterized with respect to: textural parameters (BET), structure (XRD, FT-IR, UV-vis-DRS), chemical composition (XRF) and surface acidity (NH₃-TPD) and tested in role of catalysts for DME synthesis from methanol. The experiments were performed in a fixed-bed flow microreactor system equipped with a gas chromatograph.

Results and Discussion

Acid-treatment of vermiculites only slightly activate them in the process of DME synthesis. In this case methanol conversion did not exceed 20% in the studied temperature range (Fig. 1). The best catalytic results in the range of low temperatures were obtained for the zeolite samples. Methanol conversion reached nearly 90% above 460 K for both catalysts with selectivity to DME above 95%. At higher temperature selectivity to DME drastically decreased. This effect is related to the rapid formation of carbon deposits in the micropore system of these materials. On the other hand SBA-15o was found to be active in methanol conversion in the high temperature range. It could be explained by fast transport of reagents through mesoporous system of these materials, which allows significantly reduce the carbon deposit formation (in comparison to zeolite-like materials).

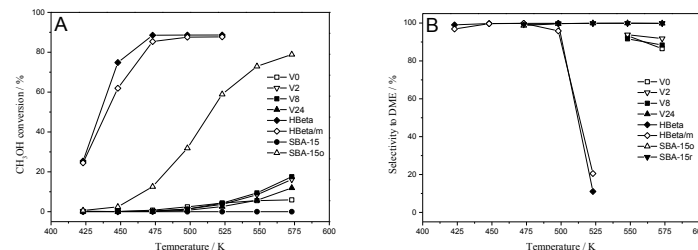


Figure 1. CH₃OH conversion (A) and selectivity to DME (B) obtained for silica catalysts

Significance

Beta zeolites and SBA-15 doped with alumina clusters were found to be active and selective catalysts for DME synthesis. Their catalytic performance depends on surface acidity as well as porous structure.

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