



Catalytic dehydration of methanol to dimethyl ether over micro–mesoporous ZSM-5/MCM-41 composite molecular sieves

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ABSTRACT

A series of micro–mesoporous ZSM-5/MCM-41 composite molecular sieves were prepared by combining a microporous zeolite silica source with nano self-assembly methods, and characterized by SEM, TEM, XRD, N₂ adsorption and desorption, TPD of ammonia, and their catalytic performance for the dehydration of methanol to dimethyl ether (DME) in a fixed bed microreactor at atmospheric pressure. Among these catalysts, the ZSM-5/MCM-41 sample alkali-treated with 1.5 mol/L NaOH solution, in which the relative crystallinity of ZSM-5 and MCM-41 are 54.5% and 30.5%, respectively, gave the best activity ($X_{\text{MeOH}} > 80\%$) with 100% selectivity and a long lifetime in a wide range of temperature from 190 °C to 300 °C. From the characterization and activity data, the formation mechanism of the micro–mesoporous composite molecular sieves was proposed to be a liquid–crystal templating mechanism.

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1. Introduction

In recent years, dimethyl ether (DME) has received global attention as a green alternative fuel for diesel engines because of the increasingly inadequate petroleum supply and stringent environmental regulations [1,2]. Additional uses for DME include the replacement of chlorofluorocarbons as the aerosol propellant in the cosmetic industry [3], as a family cooking gas, and as a hydrogen carrier for fuel cell [4,5]. There are two main ways to produce DME: methanol dehydration over a solid acid catalyst (Eq. (1)) and direct synthesis from synthesis gas over a hybrid catalyst comprising a metal oxide and a solid acid (Eq. (2)) [6–8].



The direct synthesis of DME usually uses a bifunctional catalyst containing a metal oxide to catalyze synthesis gas to methanol and a solid acid for methanol dehydration in a single reactor. However, the optimum catalytic reaction temperatures of the two component reactions are different [9], and it is difficult to operate the process in a way which ensures that the two reactions both have high

activity and selectivity. Kim et al. [3] have tried a mixed catalyst of Cu/ZnO/Al₂O₃ and ZSM-5, but because Cu/ZnO/Al₂O₃ has high activity and selectivity at 270–290 °C while ZSM-5 showed poor selectivity when the reaction temperature is higher than 260 °C, there was a limit on the performance of the integrated reactions and process. Thus, it is important to develop a catalyst for converting methanol to DME that also has good activity and selectivity in a temperature range that fits well with that of Cu/ZnO/Al₂O₃ for converting synthesis gas to methanol.

Methanol dehydration to DME over a solid acid as catalyst in a fixed bed reactor was first reported by Mobil in 1965 [10]. Since then, many methanol dehydration catalysts have been examined, for instance, γ -alumina [11], alumina–silica mixtures [12], crystalline aluminosilicates [13], crystalline zeolites [1], clay [2], and phosphates [14] such as aluminium phosphate. The catalytic mechanisms on solid acids are determined by their properties. It is generally accepted that Brønsted acid and Lewis acid sites are the active sites for the dehydration of methanol to DME [15]. The Brønsted acid site is a strong acid with high catalytic activity. As a result, on a catalyst that contains many Brønsted acid sites, the catalytic reaction of methanol to DME process has many secondary reactions that reduce the catalyst selectivity.

Molecular sieves are widely used in heterogeneous catalysis, but their small microporous channels in which the size of the reacting molecules and the micropore diameter are similar can slow down their reactions [16]. For example, although ZSM-5 is a microporous zeolite that has high activity, it also has some disadvantages like low selectivity and short catalytic lifetime [8]. The reason for

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