



Low-temperature methanol dehydration to dimethyl ether over various small-pore zeolites

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ABSTRACT

Eight-membered ring small-pore zeolites Rho and KFI have been synthesized, characterized and tested for dehydration of methanol to dimethyl ether at low-temperature, and compared with other zeolites and three different samples of γ -Al₂O₃. Both the zeolites were mainly crystallized from the synthesis gels with the Si/Al ratio of 5.0 by a conventional hydrothermal method without any agitation. The amount of total solid-acid sites was 1.65 mmol g⁻¹ and 2.53 mmol g⁻¹ for zeolite KFI and Rho, respectively. In addition, zeolites SSZ-13, RUB-13, and ZSM-5 were also employed for the reaction. Reaction conditions were optimized for a low-temperature catalytic dehydration of methanol selectively to dimethyl ether. Methanol dehydration efficiency of various zeolitic frameworks is discussed against the strength of solid-acidity, type of channel structure, specific surface area, and particle size. At temperatures ≤ 200 °C, the overall catalytic efficiency of the small-pore zeolites with appropriate medium-strong acidity and 3-D channels was superior to that of the reference γ -Al₂O₃ materials.

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1. Introduction

Dimethyl ether (DME) is a valuable energy carrier and recently gaining increased interests especially for its environmentally benign properties [1–3]. Since the past few years, direct production of DME from syngas and via dehydration of methanol has been getting a lot of attention. DME has many important industrial and household uses. Furthermore, it is an important intermediate for the production of a variety of chemicals and it is adequate to replace the notorious chlorofluorocarbons. Particularly, it has a good prospect for an ultra-clean next-generation synthetic fuel for diesel engines with zero level SO_x, lower NO_x and smoke emissions. Hence, it can play a significant role to mitigate adverse climate changes [2]. Catalytic dehydration of methanol is one of the main routes for the production of DME [1]. Methanol is obtained from various under-utilized and renewable resources e. g. natural gas, coal, and biomass. Recently, the valorization of methanol is attracting a lot of attention for it is an alternate feedstock for the production of useful chemicals e. g. olefins and DME. Various solid-acid materials namely zeolites and γ -Al₂O₃ are used for the production of DME. In the ever changing geopolitical and economic situations, and in order to lessen dependence on petroleum, the

methanol dehydration process to DME offers an attractive route to a sustainable production of a cleaner synthetic fuel.

Zeolitic materials are important solid-acid catalysts for a variety of heterogeneous catalytic reactions. Particularly, the extent and strength of solid-acid sites on a material are important factors in controlling catalytic dehydration reaction [3]. Since the discovery of methanol conversion to hydrocarbons over ZSM-5 (MFI-type zeolite), a number of studies have been devoted to the search of effective catalytic materials for the valorization of methanol [1–5]. Owing to their appropriate solid-acid properties, several zeolitic materials such as ZSM-5, SAPO-34, SAPO-46, AIPO-4, Linde W, Y, mordenite, ferrierite, beta, and clinoptilolite have been reported to be active for the dehydration of methanol [1,6–12]. Among the zeolites, ZSM-5 is one of the most studied and the best catalyst reported for this reaction. Besides methanol dehydration reaction, ZSM-5 along with SAPO-34 is the most extensively studied zeolitic material for methanol-to-olefins (MTO) reaction [1–3]. Formation of products other than DME and deposition of coke are two serious issues for the dehydration reaction carried out at high temperature. On the other hand, when the reaction is performed at low-temperature, achieving an adequate conversion of methanol and removal of the by-product, water, are two main challenging tasks. For a low-temperature methanol dehydration reaction, materials with strong Lewis acidity e. g. bare γ -Al₂O₃ exhibit poor activity because of the poisoning of active sites by water adsorption [13]. On the other hand, materials having strong Bronsted acidity e. g. protonated ZSM-5 and zeolite Y demonstrate high activity

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but were prone to produce secondary products like hydrocarbons and ultimately cause coke deposition [12,13]. In principal, a better resistance to the deposition of heavy hydrocarbons and an adequate removal of the equimolar water produced in the methanol dehydration reaction are important factors for the optimum performance of a particular catalyst.

Among zeolitic frameworks, eight-membered ring (8-MR), small-pore zeolites with appropriate solid-acid properties are potential candidates for the conversion of methanol to various chemicals. In addition to KFI and Rho, two other small-pore zeolites SSZ-13 (a CHA-type analog of SAPO-34) and RUB-13 were also examined for the dehydration reaction. These zeolites have a 3-dimensional (3-D) porous structure consisting of intersecting 8-MR channels except for the zeolite RUB-13 that has a 2-dimensional (2-D) network. SSZ-13 and RUB-13 have been reported for the related MTO reaction by Zhu et al. [14], and Yokoi et al. [15], respectively. Previously, we have presented a study on MTO reaction over Rho zeolite [16]. Detailed investigations on low-temperature methanol reaction over zeolites and comparison with γ -Al₂O₃ will provide a better understanding of the catalytic dehydration process towards development of practicable catalyst material.

The main zeolites under investigations, KFI and Rho both have comparable framework densities and a 3-D network of channels (Table S1) [17]. Thus, a comparison of the methanol dehydration process over these zeolite candidates with similar physicochemical and structural properties would be interesting. Rho zeolite has a typical composition of Na_{6.8}Cs_{3.0}[Al_{9.8}Si_{38.2}O₉₆].29H₂O and intersecting 8-MR (3.6 Å × 3.6 Å) channels [17]. Intensive studies were conducted on the RHO-type framework of zeolites for the synthesis of methylamines [18]. Besides our previous study [16], recently Ji et al. investigated on steam-dealuminated RHO-type zeolite for the MTO reaction [19]. Herein, we have extended the use of the zeolite Rho to this important methanol dehydration reaction. KFI zeolite has a typical composition of K₁₈Sr[Al₂₀Si₇₆O₁₉₂].72H₂O (18-crown-6) and intersecting 8-MR (3.9 Å × 3.9 Å) channels [17]. KFI-type zeolite has been reported for sorption and catalytic reactions including MTO, but no detailed study exists on its catalytic use for the production of DME [19]. In addition to Rho and KFI, two other 8-MR zeolites, SSZ-13 and RUB-13 were also employed for the dehydration reaction. Here in, we are reporting an extensive study on low-temperature methanol dehydration over various small-pore zeolites and validating their catalytic efficiency against ZSM-5 and three different samples of γ -Al₂O₃.

2. Experimental

2.1. Preparation of catalysts

The zeolite materials were synthesized under hydrothermal conditions by following the reported recipes [17]. X-ray diffraction (XRD), scanning electron microscopy (SEM), and other instrumental analyses were performed to evaluate phase-purity of the obtained topologies and crystalline morphologies. A detailed elucidation of their other physicochemical properties was important in determining their potential use for this methanol dehydration reaction. For a typical synthesis of Rho zeolite without using a structure directing agent (SDA), first of all, Al(OH)₃ (Wako, Japan) was dissolved in an aqueous solution of NaOH (Wako, Japan) by refluxing at 100 °C. The obtained clear solution was taken in a Teflon beaker and cooled to room temperature (RT). Then an aqueous solution of CsOH·H₂O (Alfa Aesar, US) was added under stirring. Finally, a homogeneous synthesis gel was obtained with a slow addition of colloidal silica AS-40 (40% SiO₂, Aldrich, Japan) under vigorous stirring. The Si/Al ratio of the gel was 5.0 with a batch composition of 1.8Na₂O:0.3CsO:1.0Al₂O₃:10SiO₂:100H₂O. Thus obtained gel was

homogenized for 2 h by stirring and then taken in a polypropylene bottle. Hydrothermal crystallization in a pre-heated oven was carried out for 10 days at 80 °C without any agitation. Besides this gel with Si/Al ratio of 5.0, other synthesis gels with Si/Al ratios of 10 and 20 were also prepared and put for crystallization of RHO-type zeolite. At the end of the crystallization process, the solid product was separated by vacuum filtration, washed with water and dried at 70 °C.

For the synthesis of KFI zeolite, at first Al(OH)₃ was dissolved in an aqueous solution of KOH (Wako, Japan) under reflux at 100 °C. After cooling down the solution to RT, the obtained clear solution was poured into a Teflon beaker and mixed with an aqueous solution of SrCl₂·6H₂O (Aldrich, Japan), and 18-crown-6 (Wako, Japan) under stirring. The colloidal silica AS-40 was slowly added to the reaction mixture under vigorous stirring to achieve a homogeneous synthesis-gel. The Si/Al ratio of the synthesis gel was kept at 5.0 with a batch composition of 2.3K₂O:0.1SrO:1.0Al₂O₃:10SiO₂:220H₂O:1.0(18-crown-6). The obtained synthesis gel was further stirred for 0.5 h and then taken in a Teflon vessel and enclosed in a steel bomb. Hydrothermal crystallization under static conditions was carried out for 120 h at 150 °C in a pre-heated oven. The product obtained at the end of the crystallization reaction was separated by vacuum filtration, washed with water and dried at 70 °C. The organic SDA (18-crown-6) in the KFI zeolite was removed by calcination of the as-obtained product at 550 °C. Detailed synthesis and characterizations of SSZ-13 and RUB-13 are found in the reported studies [14,15].

To obtain proton-type solid-acid zeolite catalyst for the methanol dehydration reaction, at first, the counter cations in the zeolite were exchanged with ammonium ions by repeated interactions with aqueous phase NH₄Cl (Wako, Japan). For a typical cation-exchange reaction, 1.0 g of the as-prepared zeolite powder was added into 100 ml aqueous solution of 1 M NH₄Cl and refluxed at 60 °C to 80 °C for 3 h. The NH₄Cl treated zeolite was separated by filtration, washed with water, and followed by two more repetitions of the ion-exchange process. Finally, the ammonium-type zeolite material was dried and then calcined at 550 °C to get H-type zeolites. The inductively coupled plasma (ICP) analyses of the digested sample showed a complete removal of the counter cations by repeated treatments with NH₄Cl solutions.

The catalytic methanol dehydration efficiency of the zeolite materials was compared with three different samples of the industrial catalyst, γ -Al₂O₃. In addition to a commercial γ -Al₂O₃ (Nippon Aerosil, Japan), and a reference γ -Al₂O₃ JRC-ALO-6 obtained from the Catalysis Society of Japan, yet another sample of γ -Al₂O₃ was prepared in our laboratory from a stepwise calcination of boehmite (Wako, Japan) precursor. An appropriate amount of boehmite was taken in a ceramic crucible and calcined at 600 °C for 2 h. At the end of the reaction, the crucible was quenched in air. The obtained product was homogenized by grinding and then re-calcined in a ceramic crucible at 700 °C for 14 h and quenched in air. Thus obtained final product was ground well and used for characterization and in catalytic methanol dehydration testing.

2.2. Characterization

Powder XRD patterns were recorded on Rigaku UltimaIII diffractometer using Cu K α at 40 kV and 40 mA. The XRD patterns were recorded in the 2-theta range of 5° to 50° for the zeolites and 20° to 80° for the γ -Al₂O₃ samples at a scanning speed of 0.01° min⁻¹. Field-emission SEM images were taken on Hitachi S-5200 microscope operated at 2 kV. The chemical composition of the digested zeolites was examined by ICP analysis, using Shimadzu ICPE-9000 spectrometer. For the ICP analysis, at first, the solid zeolite samples were digested in 4 M KOH (Wako, Japan) aqueous solution to prepare a clear solution. N₂ adsorption-desorption isotherms

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