



Short Communication

Methanol conversion to lower olefins over RHO type zeolite

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ABSTRACT

Eight-membered ring small-pore zeolite of RHO-type topology has been synthesized, characterized and tested for methanol-to-olefin (MTO) reaction. The zeolite was hydrothermally crystallized from the gel with Si/Al ratio of 5.0. It showed a high BET specific surface area ($812 \text{ m}^2 \text{ g}^{-1}$), micropore volume ($0.429 \text{ cm}^3 \text{ g}^{-1}$), and acid amount (2.53 mmol g^{-1}). Scanning electron microscopy observations showed small crystallites of about $1 \mu\text{m}$. The zeolite was active for MTO reaction with 100% methanol conversions at 623–723 K, whereas selectivity to lower olefins changed with time.

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1. Introduction

Lower olefins, namely ethylene and propylene, are the most important building-blocks in petrochemical industry and the chemicals produced in the largest quantities per annum. Currently, lower olefins are mainly derived from naphtha with high input of energy. Environmental legislations, depleting reserves of naphtha and growing global market have been pushing for the development of alternate routes to their production. Recently, methanol obtained from various under-utilized and renewable resources e. g. natural gas, coal and biomass is getting attention as an alternate feedstock for the production of useful chemicals. In the changing geopolitical and economic situations, in order to lessen dependence on naphtha, the MTO process offers an attractive route to the production of lower olefins [1–6].

Zeolitic materials are important solid-acid catalysts in the heterogeneous catalytic reactions. Since the early 1970s discovery of methanol conversion to hydrocarbons over ZSM-5, a number of studies have been devoted to the search for an effective catalyst and for the understanding of MTO process [1–16]. Among various types of catalyst examined for the MTO reaction, ZSM-5 and SAPO-34 are the most extensively studied materials. Pertaining to their structure and acidic properties, eight-membered ring (8-MR) CHA-type materials e. g. SAPO-34 are one of the best catalysts for selective production of lower olefins. On the other hand, ZSM-5 is widely reported as the most stable catalyst [1–6]. From the 8-MR zeolites, a zeolite with RHO topology was selected for the present study. It has a 3-dimensional network of channels and LTA

α -cages. Ball-and-stick model framework structure of RHO topology is shown in Fig. 1. The model structure was generated from the CIF data using program VESTA. The RHO zeolite has a typical composition of $\text{Na}_{6.8}\text{Cs}_{3.0}[\text{Al}_{9.8}\text{Si}_{38.2}\text{O}_{96}]\cdot 29\text{H}_2\text{O}$ and intersecting 8-MR ($3.6 \text{ \AA} \times 3.6 \text{ \AA}$) channels [17,18]. Intensive studies were conducted for the syntheses of methylamines over RHO [18]. To the best of our knowledge, however, there is no report on RHO for the MTO reaction.

2. Experimental

2.1. Preparation of catalyst

The zeolite was hydrothermally synthesized mainly following the reported recipe [17]. At first $\text{Al}(\text{OH})_3$ (Wako) was dissolved in aqueous NaOH (Wako) solution by refluxing at 373 K, and cooled to room temperature. Then an aqueous solution of $\text{CsOH}\cdot\text{H}_2\text{O}$ (Alfa Aesar) was added under stirring. Finally, a homogeneous gel was obtained with addition of colloidal silica AS-40 (Aldrich) under vigorous stirring. The Si/Al ratio of the gel was 5.0 with a batch composition of $1.8\text{Na}_2\text{O}:0.3\text{CsO}:1.0\text{Al}_2\text{O}_3:10\text{SiO}_2:100\text{H}_2\text{O}$. No organic structure directing agent (SDA) was used for this synthesis. The gel was stirred for 2 h and then taken in a polypropylene bottle. Hydrothermal crystallization was carried out for 10 days at 353 K. The product was separated by filtration, washed with water and dried at 353 K. To obtain H-type zeolite, first the counter cations were exchanged for ammonium by mixing 1.0 g of the zeolite with 100 ml aqueous solution of 1 M NH_4NO_3 (Wako) and refluxing at 333 K for 3 h. Ammonium-exchanged zeolite was separated and washed with water followed by two repetitions of the exchange process. The obtained material was dried, and then calcined at 823 K to get H-type zeolite.

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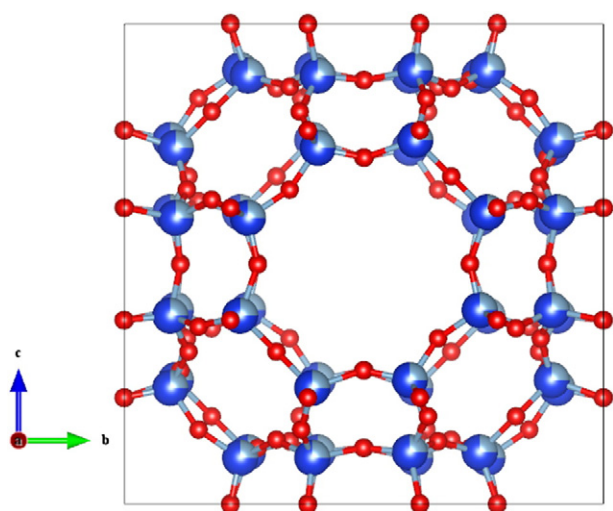


Fig. 1. Ball-and-stick model structure of RHO type zeolite; blue spheres represent position of Si/Al, and red spheres represent oxygen.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultim III diffractometer using Cu K α at 40 kV and 40 mA. Field-emission scanning electron microscopy (SEM) images were taken on a Hitachi S-5200 microscope operated at 2 kV. Chemical compositions were analyzed by a Shimadzu ICPE-9000 spectrometer. For ICP analysis, samples were digested in 4 M KOH (Wako) aqueous solution. N₂ sorption isotherms were measured on Belsorp-minill (BEL Japan), at 77 K. Before N₂ sorption, the sample was outgassed for 6 h at 423 K. BET specific surface area (S_{BET}) and micropore volume were calculated by BET and t -plot methods, respectively. NH₃ temperature programmed desorption (NH₃-TPD) profile was assessed on a Multitrack TPD instrument (BEL Japan). Thermogravimetric analysis (TGA) was carried out on Rigaku Thermo Plus apparatus.

2.3. Catalytic activity test

For the MTO process, gas-phase methanol conversion was carried out in a fixed-bed reactor. Typically, 0.1 g of H-type zeolite catalyst sandwiched between quartz wool and packed in a quartz reactor was placed in a furnace. The catalyst was calcined at 773 K for 1 h,

and then the reactor was cooled to the desired temperature for MTO reaction. The reactor was equipped with an online Shimadzu GC-14B gas chromatograph (GC) where hydrocarbons were separated in a HP-PLOT Q column and analyzed by a flame ionization detector (FID). For a typical reaction, 5 kPa of gas phase methanol (99.8%, Wako) diluted with He was steadily passed over the catalyst at temperatures ranging from 623 to 723 K under atmospheric pressure. Weight/flow (W/F) and weight hourly space velocity (WHSV) were kept at 34 g h mol⁻¹ and 1.0 h⁻¹ respectively. First analysis of the products was performed 10 min after the start of the reaction. Later on, reaction products were analyzed every 30 min. Methanol conversion was defined as the amount consumed divided by the amount fed to the reactor. Selectivity was calculated on the carbon mass basis of the effluent from the reactor, and the values are expressed as carbon percent.

3. Results and discussion

3.1. Physicochemical properties

XRD pattern of as-made RHO showed a phase-pure RHO-type zeolite (Fig. 2) [17]. As shown in the inset of Fig. 2, SEM image further confirmed the crystalline nature of the product and revealed a typical sphere-like morphology of the zeolite. Average size of the RHO crystallites (1 μm) was comparable with that of the SAPO-34 [10]. The counter cations were removed by ammonium-exchange and the Si/Al ratio of H-RHO (3.5) was lower than the synthesis gel (5.0) as estimated by ICP. N₂ sorption isotherms were typical of the microporous materials (Fig. 3). H-RHO demonstrated a high S_{BET} (812 m² g⁻¹) and micropore volume (0.429 cm³ g⁻¹) in comparison with other zeolitic materials widely employed for the MTO process [10,15]. NH₃-TPD profile showed two prominent 'l' and 'h' peaks around 480 K and 800 K, respectively (Fig. 4). Total concentration of acid sites (2.53 mmol g⁻¹) was smaller than the predicted from Si/Al ratio of 3.5. Importantly, H-RHO was synthesized in the absence of any organic SDA that is usually the most costly reagent for the syntheses of zeolitic materials. In addition to economic advantage, organic SDA-free syntheses put no load to environment. Imitating natural settings for the formation of zeolites, organic SDA-free syntheses of zeolites are getting much attention in making them environmentally benign [4,5].

3.2. Methanol-to-olefin (MTO) reaction

For MTO reaction, the RHO zeolite showed 100% initial (10 min) conversion of methanol, at reaction temperatures ranging from 623 K

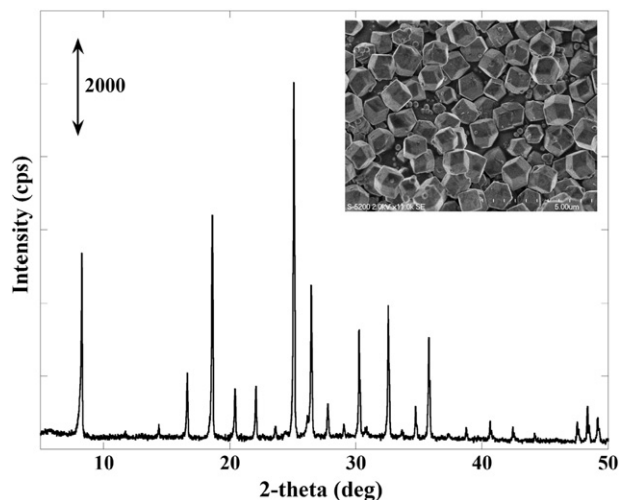


Fig. 2. Powder XRD pattern and SEM image (inset) of as-made RHO-type zeolite.

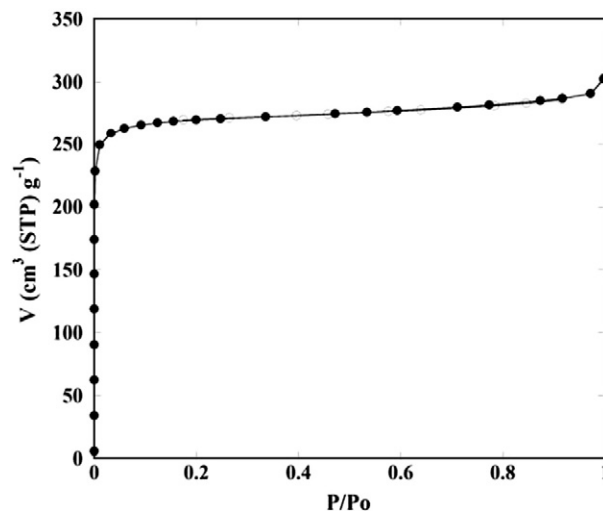


Fig. 3. N₂ sorption isotherms for the H-RHO zeolite recorded at 77 K.

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