



Dimethyl ether to olefins over dealuminated mordenite (MOR) zeolites derived from natural minerals



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ABSTRACT

Recent development in shale gas production ensures the availability of cheap feedstock for petrochemicals. Dimethyl ether (DME) is one of the most promising derivatives from natural gas. In this work, we developed catalysts from low-cost natural minerals for the conversion of DME to olefins as one of the most important feedstocks for the petrochemical industry. The catalytic performance of a series of hierarchical mordenite zeolites derived from natural mineral by nitric acid dealumination was studied in the conversion of dimethyl ether (DME) to light olefin compounds. The degree of dealumination was strongly dependent on the treatment period. The DME conversion and olefins selectivity over these materials were investigated at 350 °C and 1 atm. The nitric acid dealumination has a positive effect on both DME conversion and ethylene to butylene selectivity. The fabrication of hierarchical zeolites from natural minerals will stimulate related studies to produce cost-effective catalysts derived from natural resources.

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1. Introduction

Among the hydrocarbon raw-materials required by the petrochemical industries, olefins, particularly ethylene to butylene, are currently being considered for a wide range of applications (Muraza, 2015). This can be attributed to the key characteristics of these compounds. They can easily be polymerized to generate high grade polymers or oligomers, their relative reactivity permits cheap alkylation as well as conversion to corresponding oxygenates (Buchanan, 2000). Propylene and butylene for example are good candidates for the production of fuel products, with negligible inhibition property to the desired performance of catalytic converters in automobile engines. Olefins are normally produced by petroleum refineries during fluid catalytic cracking (FCC) (Belohlav et al., 2003; Froment, 1981). The thermally mediated process involved initial vaporization of the liquid feedstock into vapor that actively interacts with catalyst (usually zeolite like ZSM-5) to yield an important composition of olefins in addition to the gasoline range

paraffins via a carbenium ion assisted mechanism, involving Brønsted acid sites participation (Buchanan and Adewuyi, 1996; Buchanan, 1991; Buchanan et al., 1996).

There are a number of factors that greatly limit the high selectivity to olefins during the FCC process. Production of large gasoline fraction (up to 50% or more), as well as high selectivity to methane among the gaseous products in preference to olefins and catalyst deactivation due to high temperature have been the troubling reasons. Other identified difficulties include olefins polymerization at the intermediate stages, fluidization of the catalyst system, feed flow stability problems and inability to maintain the desired catalyst properties (Kalota and Rahmim, 2003; Otterstedt et al., 1986; Degnan et al., 2000). An important alternative given emphasis in the research community today is the production of olefins from catalytic conversion of dimethyl ether (DME). The lowest ether can easily be prepared from sustainable biomass feedstock, synthetic gas and/or cheaper methods and have been characterized to be associated with unique handling properties that favor its wide range industrial applications (Lee and Sardesai, 2005; Vishwanathan et al., 2004a; Aboul-Fotouh, 2014). For example, Lee et al. (Lee and Sardesai, 2005) and Vishwanathan et al. (Vishwanathan et al., 2004b) have produced DME from

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methanol to very high selectivity using Cu supported ZnO–Al₂O₃ and Na promoted ZSM-5 catalysts. Similarly, Mench et al. (Mench et al., 2004) and Sorenson et al. (Sorenson, 2001) documented its applications in fuel cells and diesel and gasoline engines.

However, the direct conversion of the DME to olefins is receiving great interest due to the industrial demand of the net products. Different catalysts and operation parameters are so far been evaluated (DME – to – olefins. Focus, 2013; Idemitsu process, 2007). Khadzhiev et al. (Khadzhiev and et al., 2013) showed the activity of La–Zr supported ZSM-5 and alumina to depend on catalyst pre-treatment and operational temperature. The co-support systems favor catalyst stability whereas thermal action on ZSM-5 and air-steam pre-treatment of the overall catalyst enhanced catalyst selectivity to olefins, especially propene, at lower temperatures close to 500 °C. Abasov et al. (Abasov et al., 2013) found the activity over zeolites Y and ZSM-5 to depend on the structure and Brønsted acidity of the zeolitic material, with high selectivity to ethylene production as the main reaction product. ZSM-5 with narrower pores and higher acidity yield a limited selectivity. In a related development, Kolesnikova et al. (Kolesnikova and et al., 2013) found the simultaneous addition of TiO₂ and sulfur to enhanced the formation of moderate acid sites for a H-ZSM-5 system. This factor favors DME conversion, doubled C₂ and C₃ olefins selectivity and significantly decreased paraffins production under mild reaction parameters. The catalyst stability was similarly retained. However, modification with Pd and alumina support yield significant selectivity towards paraffins production even after oxidative post-treatment. Kolesnichenko and co-workers (Kolesnichenko and et al., 2011) showed ethylene to be generated via intermediate ethanol formation from DME isomerization over a Rh modified ZSM-5/Al₂O₃. DME conversion and olefins (ethylene to butylene) selectivity reached 99.5 and 50%, respectively, for the optimal Rh loading of 0.1 wt.%. Gorayainova et al. (Gorayainova and et al., 2011) demonstrated modification with Mg instead of Rh to yield lower DME conversion of 85.6% but with enhanced olefins selectivity of 67.2%. The catalyst was more preferential to ethylene (33.6%) production and exerts stability after repeated application cycles.

The available literature illustrated the catalyst activity, stability and products selectivity during olefins production from DME to depend on the zeolite pore structure and acidity, reaction mechanism, nature and concentration of catalyst modifier and reaction parameters like temperature and space velocity. In the current study, we have evaluated the activity of hierarchical mordenite (MOR) zeolites prepared by dealumination of a parent zeolitic minerals. The success of the hierarchical zeolite production from natural minerals will open plethora opportunities to fabricate cost-effective catalysts from abundant resources.

2. Experimental

2.1. Material and Early Catalyst Characterization

The parent mordenite (MOR) zeolite, named A, was collected from Klaten, Indonesia, as small crushed stones with diameter from 3 to 5 mm. Prior to any type of modifications, the small particles were crushed into fine powder and then characterized by using X-ray diffraction (XRD) and X-ray fluorescence (XRF) to clarify the existing phases and to quantify the elemental composition.

2.2. Catalyst modification

After stating the elemental composition and crystalline phase of the parent sample (zeolite A), the sample was calcined under air flow at 550 °C for 12 h to remove any impurities present. Then, the sample was ion-exchanged using 2 M of NH₄NO₃, 1 g of the sample

in 20 ml of 2 M NH₄NO₃, at 90 °C for 2 h and calcined again under the same conditions as early. Over the ion-exchanged samples, we carried out the acid treatment using 3 M of HNO₃ for 3 (the sample named B) and 6 h (the sample named C) at 90 °C under vigorous stirring, 400 rpm. For each 1 g of the sample, we used 20 ml of dealuminant agent. The dealuminated samples were again ion-exchanged to ensure the samples are in the protonated form. Finally, the samples allowed to dry in air over night and calcined at 550 °C for 12 h.

2.3. Catalyst characterization

The parent and modified samples were characterized to observe the effect of dealumination on the sample crystallinity, elemental compositions, texture properties and morphology. An XRD diffractometer, MiniFlex (Rigaku), was used to examine the effect of dealumination on the sample crystallinity. The X-ray diffraction patterns were recorded over 2θ ranged from 5° to 50° with a speed of 2 and step size of 0.02°. The effect of dealumination on the elemental composition was measured using XRF. The textural properties and morphologies were characterized using scanning electronic microscope (SEM) and nitrogen adsorption–desorption isotherm by Brunauer–Emmett–Teller (BET) method. The N₂ adsorption–desorption isotherm was recorded over a relative pressure (P/P_0) ranged from 0.0 to 0.99. Prior to the analysis condition at –196 °C, the samples were degassed at 350 °C for 10 h.

2.4. Catalytic studies

Catalytic reactions for olefins production from DME were carried out for both the parent and dealuminated MOR systems at 350 °C and atmospheric pressure. The reaction set-up was based on fixed-bed continuous flow, in which 50 mg of the catalyst was loaded to the quartz glass reactor of 4 mm (ID), between quartz wools. The respective helium and DME flow rates were 19 and 1.3 mmol/h. The catalyst weight to DME flow rate ratio (i.e., contact time) was maintained at 0.039 kg h/mol. Reaction products from the exit were generally analyzed with the aid of a gas chromatograph fitted to flame ionization detectors (GC-FID, Shimadzu; GC-14B) and a J and W scientific column (Alumina PLOT).

3. Results and discussion

3.1. Characterization of parent zeolite

The early characterization of the as received sample showed that the material contains three crystalline phases (mordenite, clinoptilolite, and heulandite) but mordenite was the most dominant phase. The comparison of the phases was based on the Reference Intensity Ratio (RIR) provided in the PDXL program from Rigaku. Fig. 1 shows the XRD patterns of the parent material (sample A).

3.2. Dealumination

The effect of HNO₃ (3 M) treatment (i.e., dealumination) of the parent MOR catalyst on the removal of aluminum contents, crystallinity and morphology are presented in Table 1 and Fig. 2 and 3, respectively. The result showed that an increase in the treatment time from 3 to 6 h increases the silica content and lowers the alumina concentration from 81.56 to 82.63 wt.% and 9.22 to 8.88 wt %, respectively. For the parent MOR, the Si/Al was 5.53 but increased to 8.85 and 9.31 after the 3 and 6 h of treatments, respectively.

The overall increase in the Si/Al ratio has a substantial effect on the catalyst acidity and consequently on its activity in the acid-

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