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Hexane cracking catalyzed by MSE-type zeolite as a solid acid catalyst

Yoshihiro Kubota*, Satoshi Inagaki, Kazuyoshi Takechi

Division of Materials Science and Chemical Engineering, Graduate School of Engineering, Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501, Japan

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ABSTRACT

MCM-68 (**MSE** topology) with three-dimensional 12–10–10-ring channel system was focused on, expecting the hybrid character of ZSM-5 (**MFI** topology) and beta (***BEA** topology), as a solid acid catalyst for hexane cracking reaction. The proton form of MCM-68 without dealumination having Si/Al ratio around 12 was deactivated rapidly during the reaction due to heavy coke formation, whereas dealuminated MCM-68 exhibited sufficient catalytic activity and durability to coke formation for hexane cracking at the reaction temperatures from 450 to 600 °C. The dealuminated MCM-68 also had higher propylene selectivity of 45–50% in comparison with other zeolite catalysts such as ZSM-5, mordenite and beta at the reaction temperatures of 450 to 600 °C. Both the MCM-68 catalysts before and after dealumination were regenerated after the reaction at 600 °C to exhibit almost the same performance as the initial catalyst. At higher reaction temperature such as 650 °C, the catalyst was deactivated rapidly mainly due to coke formation again. In order to avoid this deactivation, modification of MCM-68 with lanthanum oxide simply by impregnation was performed. The La-modification mainly deactivated the active site on the external surface and was found to be an effective way for avoiding heavy coke formation to maintain catalytic activity and selectivity to propylene.

1. Introduction

Propylene is an important synthetic intermediate for petrochemicals and functional organic materials. Currently, worldwide propylene production comes from steam cracking (ca. 70%), refinery fluid catalytic cracking (FCC) (ca. 28%), and other deliberate processes (ca. 2%) such as propane dehydrogenation and metathesis [1,2]. It is well known that propylene yield in the fluid catalytic cracking (FCC) processes has been enhanced using zeolite Y (**FAU** topology [3]) and ZSM-5 zeolite (**MFI** topology [3]) catalysts by the control of the synthetic parameters, post-synthetic treatment such as steaming, and further modification with alkaline-earth or rare-earth metals. Over the past decade, new types of zeolite materials with large (12-ring; 12-R) or extra-large (>12-R) micropores have been synthesized and tested as FCC catalysts or as their additives [4]. Based on the various results, zeolite frameworks with multi-dimensional 10-R or 12-R micropores would be suitable for propylene production in the FCC process. A promising candidate is the **MSE** topology having a characteristic structure in which a 12-R straight channel intersects with two independent tortuous 10-R channels and has a supercage (18-R × 12-R), which is accessible only through 10-R channels [3]. The "type material" of **MSE** is MCM-68 [5,6], and we focused on this zeolite or its analogues as a candidate for the catalytic cracking of paraffins [4]. The features of the MCM-68 zeolite have attracted attention, because there are only a handful of acidic zeolites that contain three-dimensional channel systems with large pores. Zeolites of this type are potentially useful as shape-selective catalysts for the alkylation of aromatics [7–10], toluene disproportionation [10], and the production of propylene by naphtha cracking [4]. In addition, other applications as hydrocarbon traps [11] have been independently reported. The cracking of *n*-alkane, especially *n*-hexane, is often examined as a model reaction for the FCC catalytic test [12–16]. In this study, we have investigated the catalytic properties of Al-MCM-68 and post-synthetically treated MCM-68 for hexane cracking.

2. Experimental

2.1. Chemicals and materials

The commercially available reagents were used as received without further purification. ZSM-5 (JRC-Z5-90H, Si/Al = 45) and mordenite (JRC-Z-HM90, Si/Al = 45) are Japan Reference Catalysts obtained from Catalysis Society of Japan [17].

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* Corresponding author. Tel.: +81 45 339 3941; fax: +81 45 339 3941.
E-mail address: kubota@ynu.ac.jp (Y. Kubota).

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2.2. Synthesis of MCM-68

MCM-68 zeolite was synthesized as follows: colloidal silica (Ludox HS-40, DuPont, 40 wt% SiO_2, 6.01 g, 100.0 mmol), de-ionized water (40 mL) and $Al(OH)_3$ (Pfaltz & Bauer, 0.78 mg, 10.0 mmol) were mixed in a 180-mL Teflon beaker, and stirred for 10 min. Aqueous KOH solution (5.93 mmol g^{-1}, 6.32 g, 37.5 mmol) was added to the solution, and stirred for further 30 min. Then, *N*,*N*,*N*′,*N*′-tetraethyl-*exo*,*exo*-bicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium diiodide, $TEBOP^{2+}(I^-)_2$, (10.0 mmol) was added as a structure-directing agent (SDA), and the mixture was stirred for another 4 h. The resulting mixture with a molar composition: $1.0SiO_2–0.1TEBOP^{2+}(I^-)_2–0.375KOH–0.1Al(OH)_3–30H_2O$ was taken into a 125-mL Teflon-lined autoclave, and kept statically at 160 °C for 16 days in a convection oven. After cooling the autoclave to room temperature, the obtained solid was separated by centrifuging, washed several times with de-ionized water, and dried overnight. The as-synthesized MCM-68 zeolite was obtained as white powder (6.04 g).

To remove the organic SDA occluded in the pore, the as-synthesized MCM-68 was kept in a muffle furnace, and heated stepwise as follows: the temperature was raised from room temperature to 650 °C under 1 °C min^{-1} of the ramping rate, and maintained at the same temperature for 10 h. Finally, the sample was cooled to room temperature to give a calcined sample as white powder (Si/Al = ca. 12).

2.3. Ion-exchange of calcined MCM-68

Ion exchange from the calcined sample to its NH_4^+ form was carried out using NH_4NO_3 solution as follows: NH_4NO_3 (4.0 g) and the calcined sample (2.0 g) were suspended in H_2O (100 mL) in a 250-mL polypropylene bottle. The bottle was capped tightly and allowed to stand at 80 °C for 24 h with occasional purge of pressure and careful shaking. After cooling down, the sample was separated by filtration, and washed with de-ionized water. This process was repeated twice. The sample was filtered, washed thoroughly with water, and dried overnight at room temperature. Then, the resulting zeolite was again calcined in a muffle furnace. The temperature was raised from room temperature to 550 °C over a period of 4 h, and kept at the same temperature for 6 h to give MCM-68 in H^+ form (Si/Al = ca. 12).

2.4. Dealumination by acid-treatment

The dealumination of the sample obtained in the section 2.2 was carried out by treating with 0.5, 2.0, 4.0, or 6.0 mol L^{-1} HNO_3 solution (30 mL (g-sample)$^{-1}$) under the reflux conditions in a 200-mL round-bottom flask immersed in an oil bath (130 °C) for 2-24 h. After filtration, thorough washing with water, and drying at 80 °C, the dealuminated MCM-68 was obtained. For example, the treatment with 0.5 mol L^{-1} HNO_3 solution for 2 h gave MCM-68 with Si/Al ratio 51.

Beta zeolite was dealuminated by analogous procedures as follows. Beta (Si/Al = 19, Tosoh HSZ-940HOA, 21.0 g) was treated with 0.5 mol L^{-1} HNO_3 solution (600 mL) at 60 °C for 2 h to afford dealuminated zeolite beta (Si/Al = 41), which is denoted by beta(41).

2.5. Modification with La

The lanthanum oxide was loaded on dealuminated MCM-68 by impregnation using a solution of $La(NO_3)_3$ in ethanol. The ratio of weight of La to the weight of support was 0.01 (1 wt%)–0.20 (20 wt%). As a typical example, 0.8 g of MCM-68(50) was suspended in a solution of $La(NO_3)_3·6H_2O$ (0.25 g) in ethanol (40 mL), and this mixture was stirred for 1 min. The whole mixture was evaporated using a rotary evaporator and the residue was calcined in air at 500 or 600 °C.

2.6. Characterization

The crystallinity and phase purity of the zeolite catalysts were examined by powder X-ray diffraction (XRD) on an Ultima-IV (Rigaku) using Cu*K*α radiation at 40 kV and 20 mA. The Si/Al molar ratio in the bulk were measured by means of inductively coupled plasma, atomic emission spectrometer (ICP-AES, ICPE-9000, Shimadzu). The amount of coke formed during the reaction was estimated by thermal analysis (TGA) of recovered catalysts using a Shimadzu DTG-60H thermogravimetric analyzer. The weight loss from 400 to 800 °C in the used catalyst was defined as the amount of coke formed during the catalytic reaction. Nitrogen adsorption and desorption isotherms at −196 °C were measured for the samples pre-treated at 400 °C for 2–6 h on a Belsorp MAX or a Quantachrome Autosorb-1 gas adsorption instrument. The specific surface area (S_{BET}) and micropore volume (V_{micro}) were calculated using the BET method and the *t*-plot method, respectively. The number of acid sites was measured by using the temperature-programmed desorption (TPD) of ammonia on a BELCAT-B (Japan Bel Inc.). The catalyst employed was preheated at 500 °C prior to the measurement. The TPD data were collected at a ramping rate of 10 °C min^{-1}. The number of acid sites was determined from the area of *h*-peak [18] in their profiles. The cracking of cumene or 1,3,5-triisopropylbenzene (TIPB) was performed at 300 or 400 °C under atmospheric pressure in a pulse-type quartz-tube microreactor (see Fig. S1) under a stream of helium (30 cm^3 (NTP) min^{-1}). The catalyst amount, dose amounts of cumene and TIPB are 20 mg, 0.8 μL, and 0.6 μL, respectively. FE-SEM images were recorded on a Hitachi S5200 or a JEOL JSM-7001F microscope.

2.7. Catalytic reaction

An appropriate amount of each zeolite catalyst was pelletized without any binder, roughly crushed and then sieved to obtain catalyst pellets with 500–600 μm in size. The cracking of hexane was performed under atmospheric pressure in a down-flow quartz-tube microreactor with 8 mm of inner diameter. Prior to running the reaction, 100 mg of catalyst pellets were packed in a fixed-bed of the reactor, and preheated at 650 °C for 1 h in a stream of air. The reaction was performed at 450, 500, 550, and 600 °C for each 70 min. After reducing the temperature to 450 °C in a stream of helium, the feed was switched over to a helium stream containing an appropriate amount of hexane and 5.0 vol% of methane as a reactant and internal standard, respectively (W/F = 12.1 g-cat h (mol-hexane)$^{-1}$). After 70 min of the reaction at 450 °C, the feed was switched over to a helium stream, the reaction temperature was increased to 500 °C, and then the feed was switched over to a helium stream containing hexane again. The reactions at 550 and 600 °C also were simultaneously performed as the same procedure as shown above.

The regeneration experiment was carried out using the same apparatus. The feed was switched over to an air stream after the reaction at 600 °C, and then the used catalyst was heated at 650 °C for 60 min. After reducing the temperature to 450 °C in a stream of helium, the reaction was carried out by the same procedure as described above.

The reaction at 650 °C was separately performed for 280 min in a stream of helium. The feed was switched over to a helium stream containing an appropriate amount of hexane (W/F = 19.6 g-cat h (mol-hexane)$^{-1}$). After the reaction at 650 °C, the system was cooled down to room temperature in a helium stream and then the used catalyst was recovered. The reactants and products were separated by using a capillary column with HP-PLOT Q (i.d., 0.53 mm; length 30 m; Agilent Technology) and analyzed by using GC-14B