Electronic Supplementary Information

Selective formation of propylene by hexane cracking over MCM-68 zeolite catalyst

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Figure S1 XRD patterns of (a) MCM-68(13), (b) dealuminated MCM-68(51), (c) ZSM-5(45) (d) mordenite(45) and (e) dealuminated beta(41).

Figure S2 Typical SEM images of (a) MCM-68(13) and (b) dealuminated MCM-68(51).

Figure S3 Ammonia temperature-programmed desorption (NH_3-TPD) profiles of (a) MCM-68(13), (b) dealuminated MCM-68(51), (c) ZSM-5(45), (d) mordenite(45) and (e) dealuminated beta(41).

Experimental

Preparation of zeolite catalysts

MCM-68 zeolite (**MSE**) was synthesized according to our previous papers.[12–14] The calcined MCM-68 was treated with aqueous NH_4NO_3 solution (zeolite: NH_4NO_3: H_2O = 4.5 g: 9.0 g: 225 g) at 80 ºC for 24 h twice to obtain NH_4^+-form MCM-68. The NH_4^+/MCM-68 was calcined at 550 ºC for 6 h again and then the obtained H^+/MCM-68 (Si/Al = 13) was used as a catalyst in the cracking of hexane.

The dealumination of the calcined MCM-68 (Si/Al = 13) was carried out by treating with 0.5*N* HNO_3 solution (30 mL/g-sample) in a 200-mL round-bottom flask at 80 ºC for 2 h. The dealuminated MCM-68 (Si/Al = 51) was employed in the catalytic reaction.

ZSM-5 (**MFI**, JRC-Z5-90H, Si/Al = 45) and mordenite (**MOR**, JRC-Z-HM90, Si/Al = 45) were employed in the cracking of hexane without any pretreatment. Dealuminated zeolite beta (***BEA**, Si/Al = 41) was prepared by the HNO_3 treatment of parent zeolite beta (HSZ-940 HOA, Tosoh, Si/Al = 19) and then was employed in the catalytic reaction.

Characterization

All of the zeolite catalysts were checked concerning their crystallinity and phase purity by X-ray powder diffraction (XRD) on an MX-Labo (Mac Science) using CuKα radiation at 40 kV and 20 mA. The contents of Al in zeolites were measured by using inductively coupled plasma spectrometer (ICP, ICP-8000E, Shimadzu). 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 ºC prior to the measurement. The TPD data were collected at a ramping rate of 10 ºC min^{-1}. The number of acid sites was determined from the area of *h*-peak in their profiles. The coke contents on the used catalysts were determined by thermogravimetry (TG, DTG-60H, Shimadzu). The weight loss from 400 to 800 ºC in the used catalyst was defined as the amount of coke formed during the catalytic reaction. The morphologies of zeolite catalysts were observed by scanning electron microscope (SEM) on an S-5200 (Hitachi).

Reaction procedure

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 ºC for 1 h in a stream of air. The reaction was performed at 450, 500, 550 and 600 ºC for each 70 min. After reducing the temperature to 450 ºC 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 ºC, the feed was switched over to a helium stream, the reaction temperature was increased to 500 ºC, and then the feed was switched over to a helium stream containing hexane again. The reactions at 550 and 600 ºC also were simultaneously performed as the same procedure as shown above. After the reaction at 600ºC, the system was cooled down to room tempearture 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 (Shimadzu) with a flame-ionization detector. The conversion of hexane and the selectivity to each product are calculated on the carbon-basis of the initial amount of hexane.

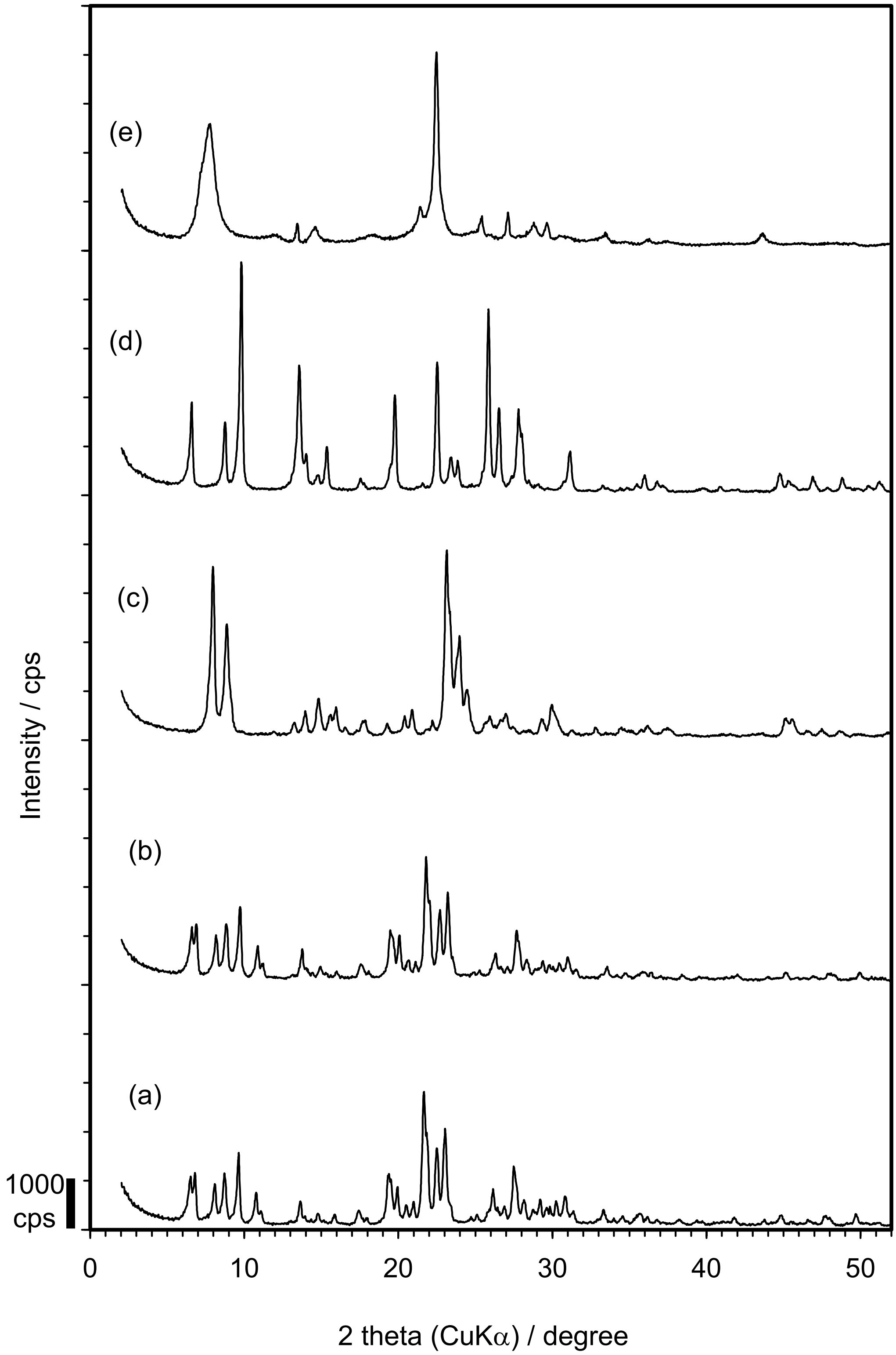
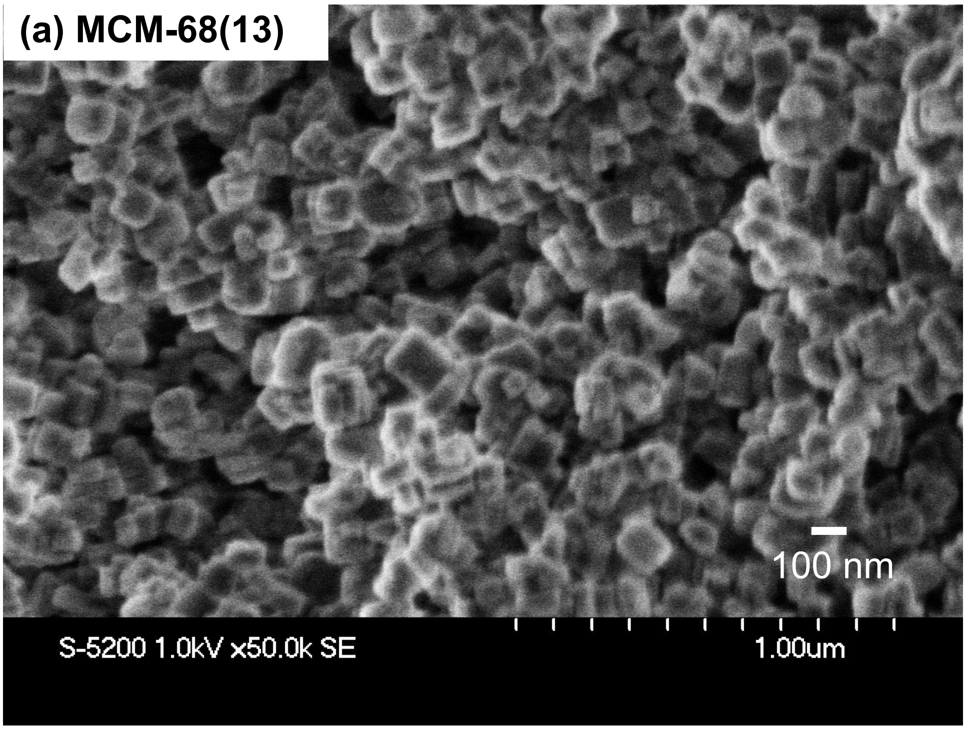


Figure S1

XRD patterns of (a) MCM-68(13), (b) dealuminated MCM-68(51), (c) ZSM-5(45) (d) mordenite(45) and (e) dealuminated beta(41).



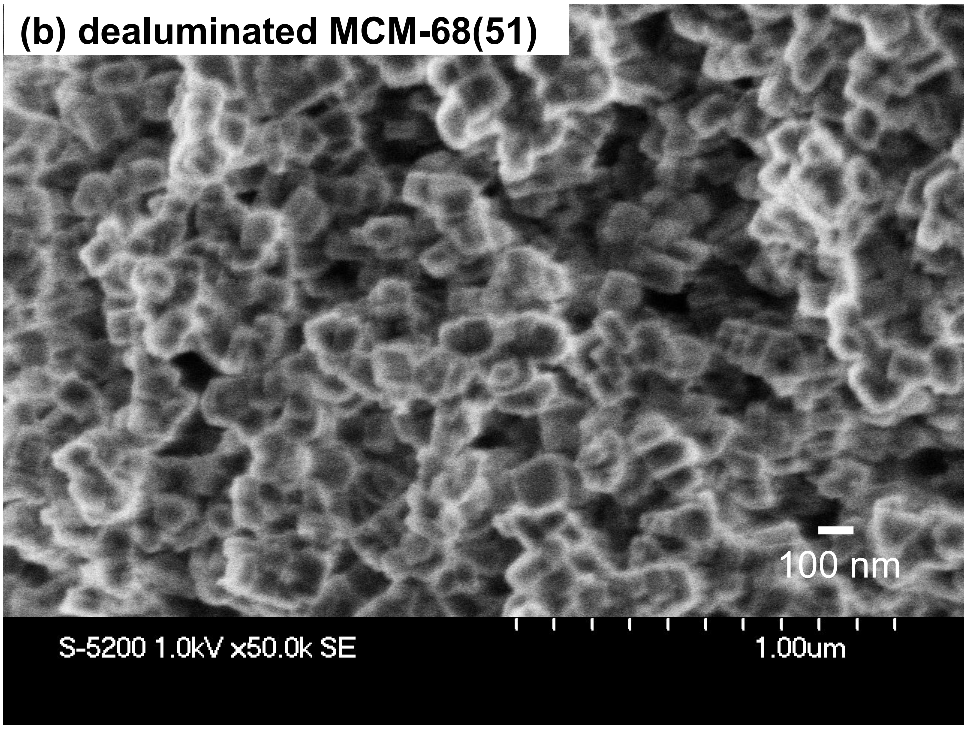


Figure S2

Typical SEM images of (a) MCM-68(13) and (b) dealuminated MCM-68(51).

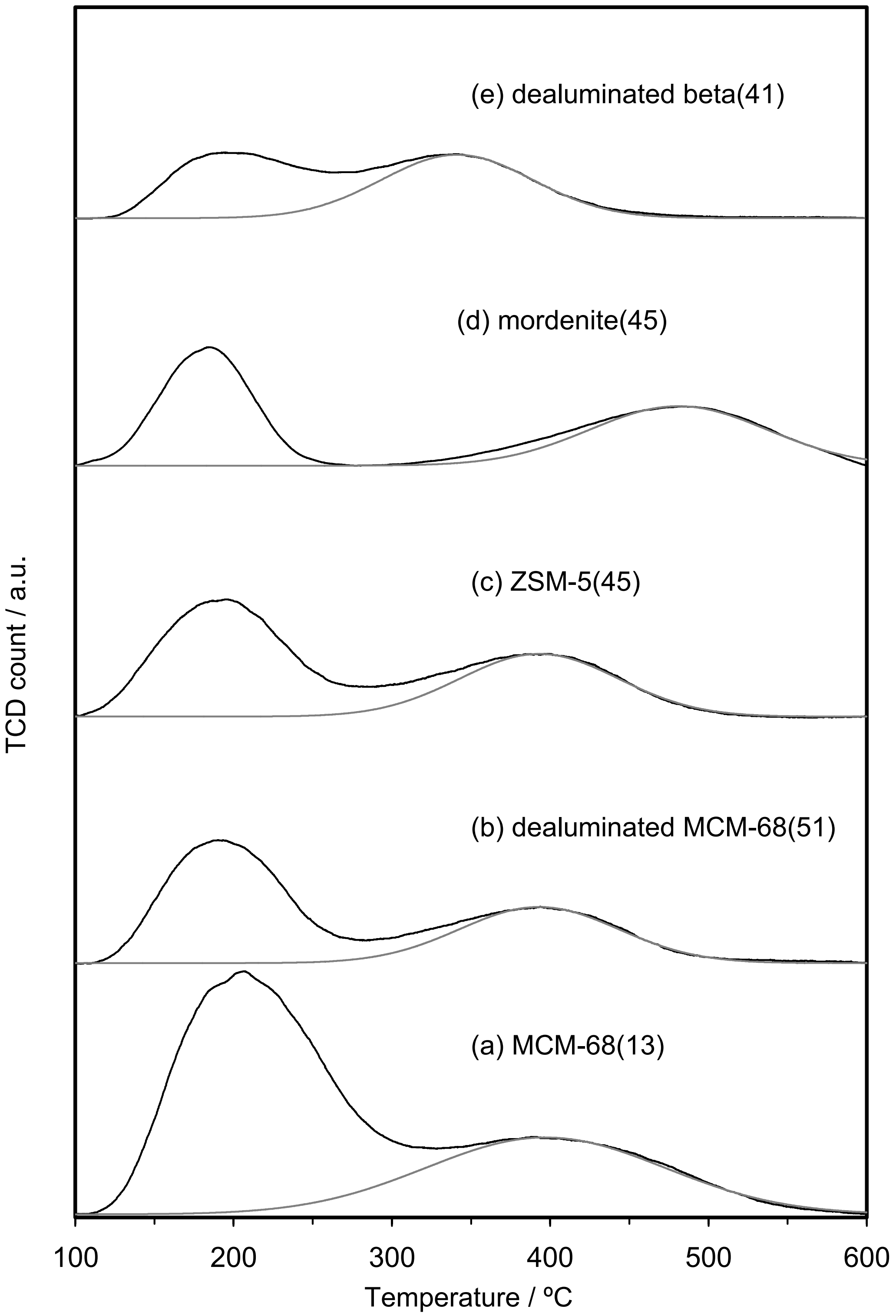


Figure S3
Ammonia temperature-programmed desorption (NH_3-TPD) profiles of (a) MCM-68(13), (b) dealuminated MCM-68(51), (c) ZSM-5(45), (d) mordenite(45) and (e) dealuminated beta(41).