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Synthesis of ITQ-2 Zeolites and Catalytic Performance in *n*-Dodecane Cracking

Jiangge Hao [1], Ying Wang [1], Guozhu Liu [1], Jingwen Zhang [1], Guozhu Li *[,1], Xuesong Ma [2]

[1] Key Laboratory of Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
[2] Science and Technology on Scramjet Laboratory, Beijing 100074, China

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ABSTRACT

ITQ-2 zeolites were prepared by sequential alkali-swelling and ultrasonic-delamination of precursor MCM-22 and characterized by X-ray powder diffraction, scanning electron microscopy, nitrogen adsorption–desorption, ammonia temperature-programmed desorption and *in-situ* Fourier-transform infrared spectroscopy. The delamination induced a change in the morphology of ITQ-2 zeolites from aggregated thin platelets to scattered platelets, together with a significant increase in external specific surface area, which reached a plateau at the ultrasonic treatment time of 3 h. The catalytic cracking of *n*-dodecane over ITQ-2 zeolites was evaluated with ITQ-2 coated on the inside wall of a tubular reactor at 550 °C and 4 MPa. The sample obtained by ultrasonic treatment of 3 h (ITQ-2-3) gave the highest initial conversion of *n*-dodecane, whereas those of 5 h and 1 h gave the conversion even lower than MCM-22, which was in agreement with the trend of the ratio of strong Lewis acid to the total acid amount. Although the amount of cokes deposited on ITQ-2-3 was larger than that on MCM-22, the former deactivated slowly, suggesting that a large external specific surface area benefits the stability of zeolite coatings.

1. Introduction

There has been a growing interest during the last years in the catalytic cracking of hydrocarbon fuels due to the potential to enhance engine performance over the entire spectrum of flight regimes. For hypersonic flight, hydrocarbon fuels can serve as not only source of heat through combustion, but also coolant through the cracking reaction to remove waste heat from aircraft systems [1–3]. Huang *et al.* [4] studied the catalytic cracking of flight fuels JP-7 and JP-8+100 in a zeolite-coated tubular reactor and found that hydrocarbon fuels could offer sufficient cooling capacity (heat sink) for supersonic aircrafts. Sobel and Spadaccini [5] performed a series of catalytic cracking tests over SAPO-34 and Y zeolite coatings at the conditions simulative of high-speed flight (650 °C and 2.4 MPa) and concluded that the catalyst-coated surface was effective and essential to the practical aircraft application of hydrocarbon fuels. Fan *et al.* [6] studied the catalytic cracking of China no. 3 aviation kerosene over wall-coated HZSM-5 zeolite at conditions similar to the practical scramjet applications (777 °C and 7.0 MPa). Liu *et al.* [7,8] investigated the effects of the Si/Al ratio, crystal size (nano- and microscale) of ZSM-5 zeolite coated on the wall of a tubular reactor on the catalytic cracking of *n*-dodecane at 550 °C and 4 MPa. The authors found that this wall-coated catalyst could significantly reduce pressure drop and thermal resistance, and the conversion and product distribution were dependent upon the acidity of ZSM-5 and diffusivity of reactants and products. The ZSM-5 zeolite with a high Si/Al ratio which possessed the relatively large amount of Lewis acid sites and small amount of Brønsted acid sites, and the nanoscale zeolite exhibited the higher catalytic cracking activity and stability. However, the sole presence of micropores in the zeolite inhibited facile mass transfer of bulky molecules to and from the active sites, limiting the catalytic performance.

Layered ITQ-2 zeolite combining the benefits of the large accessible external specific surface and the strong intrinsic acidity has been received growing attention in recent years due to their potential as catalysts in converting bulky molecules. Corma *et al.* [9–11] synthesized first time ITQ-2 zeolites by swelling of precursor MCM-22 with hexadecyltrimethylammonium bromide and tetrapropylammonium hydroxide followed by exfoliation of the resultant swollen sample at ultrasound conditions. The authors found this new layered material exhibited higher liquid product selectivity in cracking small molecule reactants such as *n*-decane and better catalytic activity in cracking larger molecule reactants such as 1,3-diisopropylbenzene (DIPB) and vacuum gasoil than MWW-type zeolites. Other reactions catalyzed by ITQ-2 zeolites that have been reported include alkylation of biphenyl with propylene [12], isomerisation of *m*-xylene [13], hydroxyalkylation of 2-methoxynaphthalene and naphthalene with paraformaldehyde [14], and MTO reaction (methanol to olefins) [15]. Additionally, supported NiMo/ITQ-2 and Pt/ITQ-2 [16], Ga/ITQ-2 [17] and heteroatom B-ITQ-2 [18] were prepared and employed as catalysts for the mild hydrocracking (MHC) of vacuum gasoil and aromatic hydrogenation [16], and dehydrogenation of propane to propylene [17].

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* Corresponding author.
E-mail address: gzli@tju.edu.cn (G. Li).

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In this paper, ITQ-2 zeolite was synthesized from MCM-22 precursors by the sequential swelling and delamination and characterized by X-ray powder diffraction, nitrogen adsorption–desorption measurements, scanning electron microscopy, ammonia temperature-programmed desorption and *in-situ* Fourier-transform infrared spectroscopy. The catalytic cracking of *n*-dodecane used as a model reaction to evaluate the catalytic performance of ITQ-2 zeolites was carried out in a tubular reactor with inside wall coatings at 550 °C and 4 MPa. The effects of the microstructure of ITQ-2 zeolites on the catalytic activity and coking were investigated.

2. Experimental

2.1. Materials

Hexamethyleneimine (HMI, 99%) was purchased from Tokyo Kasei Co. (Tokyo, Japan). Cetyltrimethylammonium bromide (CTAB, 99%) was purchased from Guangfu Chemical Reagent Co. (Tianjin, China). Tetrapropylammonium hydroxide solution (TPAOH, 25%, by mass) was purchased from J&K Scientific Co. (Shanghai, China). Sodium aluminate and sodium hydroxide were purchased from Jiangpu Chemical Reagent Plant (Shanghai, China). *n*-Dodecane (99.5%) was purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Ludox (AS-40, 40% SiO_2) was purchased from Sigma-Aldrich Co. (Shanghai, China).

2.2. Catalyst preparation

2.2.1. Synthesis of precursor MCM-22

Precursor MCM-22 (MCM-22(P)) was prepared according to the procedure described in the literature [19]. HMI, sodium aluminates and sodium hydroxide were dissolved in deionized water and then Ludox (AS-40, 40% SiO_2) was added. The mixture (about 150 ml) with molar composition of 4 $A1_2O_3$:15 NaOH:19 HMI:1500 H_2O:100 SiO_2 was stirred for 1 h at room temperature and was transferred into a 200 ml Teflon-lined steel autoclave. The hydrothermal crystallization was carried out at 427 K and autogenous pressure for 11 d. Finally, the products were recovered by centrifugation, washed with deionized water repeatedly and dried in air at 353 K overnight.

2.2.2. Synthesis of ITQ-2

MCM-22(P) (1 g) was suspended in deionized water (4 g) and then CTAB solution (33%, by mass, 8.4 g) and TPAOH solution (2.75 g) were added. The mixture obtained thus was refluxed for 20 h at 353 K. After cooling to room temperature, the mixture was treated in an ultrasonic bath (50 W, 40 kHz) for 1 h. Afterwards, a few drops of concentrated hydrochloric acid (6 $\mathrm{mol \cdot L^{-1}}$) were added until the pH of the slurry was slightly below 2. Finally, the products were recovered by centrifugation, washed with deionized water repeatedly and dried at 333 K overnight. The resultant powders were calcined at 813 K (heating rate of 1 $\mathrm{K \cdot min^{-1}}$) for 8 h, yielding ITQ-2. The ITQ-2 samples synthesized by ultrasonic treatment of 1 h, 3 h and 5 h are assigned as ITQ-2-1, ITQ-2-3 and ITQ-2-5, respectively. For comparison, one portion of MCM-22(P) was calcined in air at 853 K for 4 h, giving MCM-22.

An ion-exchange/calcination procedure was applied for the preparation of H-form MCM-22 and ITQ-2 from Na-form MCM-22 and ITQ-2. The zeolite (1 g) was added to NH_4NO_3 solution (1 $\mathrm{mol \cdot L^{-1}}$, 15 m*L*) and then the mixture was stirred at 353 K for 6 h. This procedure was repeated twice. The solid phase was separated by filtration, dried at 353 K and calcined at 813 K for 6 h in air.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were measured on a Bruker AXS D8-Focus diffractometer using Cu-K_α radiation ($\lambda = 0.15406$ nm). The data was collected in the 2θ range from 1.5° to 32° with a step size of 0.02° and a step time of 6 s. N_2 adsorption–desorption measurements were carried out at 77 K using a CHEMBET-3000 instrument (Quantachrome, Boynton FL, USA). Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4800 electron microscope (Hitachi Co., Japan). Ammonia temperature-programmed desorption (NH_3-TPD) measurements were carried out on a Micromeritics 2910 (TPD/TPR) (Micromeritics Instrument Co., USA). *In-situ* Fourier transform infrared spectra with pyridine (Py-FTIR) and 2, 6-ditertbutylpyridine (DTBPy-FTIR) as probe molecules were examined on a VERTE70 FTIR spectrometer (Bruker Co., USA) with a resolution of 4 $\mathrm{cm^{-1}}$. The powder samples were pressed to self-supported wafers of ca. 10 $\mathrm{mg \cdot cm^{-2}}$ and were pretreated at 400 °C and vacuum of 10^{-3} Pa for 1 h and then cooled to room temperature. Adsorption of pyridine (or DTBPy) proceeded at 60 °C for 30 min. The excess of pyridine was removed in vacuum by outgassing for 0.5 h at 150 °C and 300 °C, respectively. After each heating period, the temperature was reduced to room temperature and an IR spectrum was recorded.

2.4. Catalytic test

The catalytic cracking of *n*-dodecane was carried out in a tubular reactor wall-coated with zeolites. The reactor was 304 stainless-steel tubes with 300 mm in length, 3 mm in outside diameter and 0.5 mm in wall thickness. A washcoating method was used for the preparation of the zeolite coatings on the inner surface of the reactor [3,7,8] and the solid (the mass fraction of zeolite to inert binder is 1/2) loading amount was (2.23 ± 0.11) $\mathrm{mg \cdot cm^{-2}}$. The tubular reactor was heated by direct current power, and its wall temperature was measured by K-type thermocouples and kept at 550 °C. The reactor pressure was maintained at 4 MPa by a backpressure valve. The feed rate of *n*-dodecane was 10 $\mathrm{ml \cdot min^{-1}}$. The reaction products were cooled first by a condenser and then flowed into a gas–liquid separator. The liquid products collected were analyzed by a HP4890 gas chromatograph (Agilent Technologies, USA) with a flame ionization detector (FID) and a PONA column (50 m × 0.53 mm).

3. Results and Discussion

3.1. Textural properties

3.1.1. XRD

Fig. 1 shows the XRD patterns of MCM-22(P), MCM-22, the swollen sample and ITQ-2 series. The positions and relative intensities of all the diffraction peaks for MCM-22 are in good agreement with those reported in the literature [20,21]. The swollen sample shows a strong peak at $2\theta = 1.6°$, indicating an increase in layer spacing. For ITQ-2 samples, however, this peak at $2\theta = 1.6°$ disappears, together with the disappearance of the (001) and (002) peaks at $2\theta = 3°$–$7°$ and broadening of (100), (220) and (310) peaks at $2\theta = 7°$–$32°$, suggesting the occurrence of delamination, thereby inducing the significant reduction in the long-range order of the structure.

3.1.2. SEM

Fig. 2 shows the SEM images of MCM-22 and ITQ-2 zeolites. A drastic change in the morphology of ITQ-2 samples is observed in Fig. 2. The MCM-22 zeolite is aggregated of thin, randomly connected platelets, whereas the ITQ-2 samples appear to be thin scattered platelets. Among the three ITQ-2 samples, ITQ-2-3 possesses the highest dispersity, suggesting a relatively sufficient exfoliation. But after a severe ultrasonic treatment of 5 h, the surface of particles becomes rough and some amorphous particles are found in the sample (ITQ-2-5). It may be ascribed to the deposition of SiO_2 formed by silicon dissolved from the zeolite framework during ultrasonic treatment at the alkaline conditions.