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One-pot synthesis of high silica MCM-22 zeolites and their performances in catalytic cracking of 1-butene to propene

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ABSTRACT

MCM-22 zeolites with high SiO_2/Al_2O_3 (Si/Al_2) ratios were synthesized by a one-pot procedure with the assisting of boron. Based on this boron-containing method, the Si/Al_2 ratios of the MCM-22 zeolites could be greatly extended from 30 to 600 in control by tuning the Si/Al_2 ratios of the starting gels. ICP-AES and ^{11}B MAS NMR results demonstrated that a small part of the boron still existed in the framework of the MCM-22 after calcination and ammonium exchange. However, the residual boron species had little influence on the physicochemical properties of the MCM-22 samples evidenced by XRD, BET, TG–DTA, NH_3–TPD, and Py-IR determinations. The reaction of catalytic cracking of 1-butene to propene was carried out to study the performances of the high silica MCM-22 catalysts. Increasing of the Si/Al_2 ratios in the MCM-22 zeolites suppressed the formation of byproducts such as propane and aromatics effectively, and the optimal selectivity towards propene was obtained on the sample with a Si/Al_2 ratio of 158.

1. Introduction

MCM-22, a kind of layered zeolite invented by Mobil in 1990 [1], belongs to MWW type and possesses two independent pore systems. One consists of two-dimensional sinusoidal channels composed of slightly elliptical 10-membered rings (MR), and the other is characteristic of 12-MR supercages accessible by 10-MR windows [2]. Due to its unique structure and physicochemical properties, MCM-22 has been widely used in many hydrocarbon catalytic transforming processes such as isomerization [3], alkylation [4], aromatization [5] and cracking [6,7]. Recently, MCM-22 has been found to be a rather active and selective catalyst in the process of catalytic cracking of C_4+ alkenes to propene, with which the C_4+ streams from petrochemicals can be upgraded and the production of propene can be enhanced [7–9].

Conventionally, MCM-22 zeolites were synthesized under hydrothermal conditions using hexamethyleneimine (HMI) as an organic structure directing agent (OSDA) [10–12]. Most of the research works have revealed that suitable SiO_2/Al_2O_3 (Si/Al_2) ratios for the formation of MCM-22 zeolites are ranging from 15 to 80, preferably 20 to 50 [10–14]. Thus, MCM-22 catalysts with such Si/Al_2 ratios might be unsuitable in some applications, especially in reactions which need only mild acidity, for instance, the catalytic cracking of the C_4+ alkenes to propene [15,16] and the isomerization of the *n*-alkenes to their branched isomers [3].

During the past several years, much effort had been dedicated to enlarge the Si/Al_2 ratios of the MCM-22 zeolites, of which post-treatments to low silica MCM-22 were widely applied including hydrothermal treating [17], organic or inorganic acid leaching [18,19] and silanizing with $SiCl_4$ [20]. Previously, the Si/Al_2 ratios of MCM-22 were effectively enhanced to 133 by post-treatment using ammonium hexafluorosilicate in our earlier work [15]. However, this method encountered a dilemma that the zeolite structure may be partially destroyed upon higher Si/Al_2 ratios of the products. Different from the procedures mentioned above, Bao et al. succeeded in synthesizing MCM-22 zeolites with high Si/Al_2 ratios (high silica MCM-22, $Si/Al_2 = 24–1000$) via a complicated three-step strategy: first, preparation of ERB-1 (MWW borosilicate); then, removal of the boron species by calcination and HNO_3 reflux; and finally, alumination of the deboronated ERB-1 with further hydrothermal treatment [21].

On their studying of the intercalating properties of ERB-1, Millini et al. have suggested a boron-containing approach to obtain high silica MWW zeolites using piperidine as an OSDA [22]. Inspired by their work, a one-pot procedure for the synthesis of high silica MCM-22 has been developed by our group, which utilized the assisting action of boron and HMI. In this paper, this one-pot synthesis method is described in detail. The existing states of boron in the zeolites as well as the deboronation process, and their influence on the physicochemical properties of the MCM-22 samples,

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were studied. Also, the performances of the high silica MCM-22 catalysts for catalytic cracking of 1-butene were investigated.

2. Experimental

2.1. Synthesis of the MCM-22 zeolites

The one-pot procedure (hereafter referred to as the boron-containing method to distinguish it from the conventional boron free method) for the synthesis of high silica MCM-22 zeolites is as follows: first, silica sol (25.6 wt% SiO_2, 0.06 wt% Al_2O_3, Qingdao Haiyang Chemical Co. Ltd.), $Al(NO_3)_3 \cdot 9H_2O$ (99.0 %, Shanghai Zhenxin Reagent Factory), sodium hydroxide (96.0%, Shenyang Chemical Reagent Factory), and H_3BO_3 (99.5%, Shenyang Chemical Reagent Factory), together with HMI (95.0%, Sheyang Chemical Factory) were well mixed and stirred vigorously for half an hour at room temperature to give a gel with molar composition of $1.0SiO_2$:(1/*r*)Al_2O_3:$0.1Na_2O$:$0.5B_2O_3$:1.0HMI:$40.0H_2O$ (*r* represents the Si/Al_2 ratio). Then, the gel was transferred into a stainless-steel autoclave, heated to 448 K and held at this temperature for 168 h while being rotated at 60 rpm. After completion of the crystallization, the autoclave was cooled by tap water and the solid product was obtained by filtrating, washing and drying. The samples synthesized were designated as BMCM-22-*r*, e.g., BMCM-22-150.

For comparison, the synthesis of boron free samples was conducted according to the conventional method using the same raw materials of silicon, aluminum, alkaline and HMI mentioned above. The final gel had a molar ratio of $0.1Na_2O$: $1.0SiO_2$: (1/*r*)Al_2O_3: 0.35HMI: $40H_2O$, and was crystallized at 443 K for 48 h. Similar to the boron-containing samples, the samples of this series were designated as MCM-22-*r*.

2.2. Preparation of the catalysts

The as-synthesized samples were calcined at 823 K for 3 h in air for burning off the OSDA. Then the as-calcined zeolites were ion exchanged triply with 0.8 mol/L of an NH_4NO_3 solution, dried and calcined at 823 K for 2 h to give the H-form zeolites. Finally, the H-form zeolites were pelletized, crushed and sieved to 20–40 mesh particles before employing in the catalytic cracking of 1-butene.

2.3. Characterization of the zeolites

X-ray diffraction (XRD) patterns of the samples were recorded on an X Pert Pro X-ray diffractometer using Cu Kα radiation and operating at 40 kV and 40 mA. Scanning electron microscopy (SEM) images were recorded on a Quanta 200F scanning electron microscopy (FEI Company) at 30 kV.

Chemical compositions of the zeolites were analyzed on an inductively coupled plasma atomic emission spectrometer (ICP-AES, TJA, IRIS Advantage). Prior to the measurements, the samples were dissolved in a mixed solution of HF (1.0 mol/L) and HCl (0.5 mol/L) at room temperature in sealed plastic bottles to avoid volatilization of the SiF_4 and BF_3.

Nitrogen adsorption measurements were carried out at 77 K with a Micrometrics ASAP 2010 equipment. The samples were degassed at 573 K and 10^{-3} Pa for 4 h prior to the adsorption measurements. The specific surface areas and micropore volumes were obtained by the BET and the *t*-plot methods, respectively.

^{11}B magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were collected on an Infinityplus-400 spectrometer at 128.3 MHz using a 4 mm ZrO_2 rotor with a spinning rate of 10 kHz. The spectra were recorded for 200 scans each sample with a $\pi/4$ flip angle and 2 s pulse delay, and the chemical shifts being referenced to H_3BO_3.

Thermo-gravimetric and differential thermal analyses (TG–DTA) of the as-synthesized MCM-22 samples were performed on a Perkin-Elmer Diamond TGS-2 and DTA1700 apparatus. The experiments were carried out in the temperature range of 293–1323 K, with a heating rate of 10 K/min in flowing air (100 ml/min).

Acidity of the H-form MCM-22 samples was determined by the temperature programmed desorption of ammonia (NH_3–TPD) and pyridine adsorption infrared spectra (Py-IR) techniques. The measurements were carried out using the same procedures as in reference [7].

2.4. Catalytic evaluation

Catalytic cracking of 1-butene over the catalysts were carried out in a continuous-flow stainless-steel fixed-bed reactor with an inner diameter of 7 mm. Before a catalytic evaluation, the catalyst was pretreated at 773 K for 1 h at a constant flow of N_2 (20 ml/min). Then, 1-butene (>99.5 wt%, Qilu Petrochemical Co. Ltd.) was introduced at the desired temperature. The products were analyzed on-line by a Varian 3800 GC equipped with a FID and a 100 m PONA column. All isomerized butenes in the products were considered as the unconverted feed stocks. The conversion of the butenes (*X*) and the selectivity (*S*) of a particular product C_xH_y were calculated as follows:

$X = (C_4H_8\%$ in the feed $-$ $C_4H_8\%$ in the products$)/(C_4H_8\%$ in the feed$)$,

$S\,(C_xH_y) = (C_xH_y\%$ in the products$)/(\sum C_iH_j\%$ in the products$)$,

where all the percentages were in weight percent.

3. Results and discussion

3.1. Synthesis of high silica MCM-22 zeolites

A series of high silica MCM-22 samples with various Si/Al_2 ratios (30–600) were synthesized by the boron-containing method. XRD patterns of the as-synthesized and the as-calcined BMCM-22-*r* zeolites were exhibited in Fig. 1. As shown in Fig. 1A, all the as-synthesized samples showed both sharp and broad peaks which matched well with those of the layered precursors of MCM-22 (also designated as MCM-22(P)) [23–25]. Also, XRD patterns of the corresponding as-calcined samples (Fig. 1B) exhibited exact diffraction peaks of the MCM-22 (PDF Card number: 49-0627). After calcination, one noticeable phenomenon was that the 00*l* peaks shifted to higher 2θ degrees with reduced intensities, which was regarded as indications for the process of 2D layered MCM-22 precursors transforming to 3D microporous structures [22,24]. In addition, the XRD peaks of the as-synthesized and the corresponding as-calcined samples became sharper and the intensities increased gradually with increasing of the Si/Al_2 ratios, especially for the 00*l* peaks (e.g. 001, 002 and 004). As the XRD peaks are correlated with the ordering of the structure, this phenomenon undoubtedly suggests a more ordered crystal structure for the samples with higher Si/Al_2 ratios, especially along the *c*-dimension.

The SEM images of several as-synthesized samples were given in Fig. 2. It can be seen that the crystals of the MCM-22 zeolites mainly existed in typical disk-like shape. From literature [26], we know that the *c*-axis of MCM-22 is perpendicular to the plate surface. From Fig. 2, one noticeable phenomenon was observed that the thickness of the plates, viz. the *c*-dimension of the MCM-22 zeolite, increases obviously with the increasing of the Si/Al_2 ratios, which is quite consistent with the XRD results discussed above.