J Mater Sci (2009) 44:3211–3217
DOI 10.1007/s10853-009-3427-6

In situ preparation of self-bonded zeolite MCM-22 bodies by vapor-phase transport method

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Received: 15 December 2008 / Accepted: 18 March 2009 / Published online: 7 April 2009

Abstract Self-bonded bodies of zeolite MCM-22 were prepared by vapor-phase transport method. The resultant materials were characterized by means of X-ray diffraction, scanning electron microscope, mercury porosimetry, and nitrogen porosimetry. Self-bonded MCM-22 bodies were in situ prepared at pH 10.0 with the molar composition of $0.05Na_2O:SiO_2:0.033Al_2O_3$. It was found that the bodies, prepared by aluminosilicate gel, had been transformed into zeolite MCM-22. The MCM-22 bodies of which the mechanical resistance was 126 N/cm avoided binder accession. By adding auxiliary chemical–PEG20000 to the aluminosilicate gel, the pore size distributions of MCM-22 bodies could be adjusted. The average pore radius of MCM-22 bodies reached in the 149.41–653.64 nm range when AC/SiO_2 ratio was 1.5×10^{-4}–9.0×10^{-4}.

Introduction

Because of its high adsorption capacity, molecular selectivity, and hydrothermal stabilization, molecular sieves are the important porous materials that are widely used in a number of industries. These porous materials are becoming more important in the synthesis of bulk and fine chemicals where they offer an environmentally benign alternative to corrosive liquid acids and oxidants [1]. Synthetic zeolites and related molecular sieves are generally produced as powders of relatively loosely bonded zeolite particles. At present, optimal utilization of zeolites particles requires that they can be formed to or incorporated in bodies with shapes and properties adapted to the process requirements [2]. The binder is indispensable in order to produce bodies of optimal dimension and form and having a high mechanical resistance [3]. In such bodies, the fact that the zeolite is diluted with a material that in most instances is inert in the process reduces the effective surface area of the product. Moreover, negative effects, such as blocking of the micropores and active sites by the binder, are pronounced when zeolite particles are prepared by adding an inorganic binder [2, 3]. Hence, methods that allow the preparation of binderless zeolite bodies are highly desired.

Self-bonded ETS-4 and ETS-10 pellets were recently prepared using Ti salts by direct hydrothermal conversion [4]. Kaolin extrudates can also be transformed directly to low-silica pellets, such as zeolite A, zeolite 4A, and zeolite Y, by hydrothermal method [5]. Following this method, pellets of merlionite, chabazite, ZSM-4, and ZSM-5 have been successfully prepared [6–9]. The advantage of the direct synthesis of zeolites pellets is to avoid the necessary formation of bodies from the fine zeolitic crystals using an inorganic binder.

The zeolite MCM-22 (IZA code MWW) was first synthesized in the laboratories of Mobil Oil Corporation. Its structure is built of two systems of independent channels, both accessible by elliptic windows of 10-membered TO_4 rings (T = Si or Al). The first channel system is composed of sinusoidal 10-membered channels; the second, by the stacking of supercavities, whose internal diameter of 7.1 Å is defined by 12-membered rings with a height of 18.2 Å [10]. Its particular structure, as well as the possibility of delamination [11] or pillarization [12], makes this zeolite

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very interesting for a series of catalytic reactions, such as isomerization reactions, conversion of methanol to higher hydrocarbons, isobutenehutene alkylation, etc. [13–16].

However, no report has approached the research self-bonded MCM-22 bodies by vapor-phase transport (VPT) method. Self-bonded MCM-22 bodies were in situ prepared using VPT method in this paper. And, preparation parameters, such as pH, SiO_2/Al_2O_3, Na_2O/SiO_2, and the auxiliary chemical (AC)–polyethylene glycol (PEG20000), were changed to investigate their effects on the crystallization and configuration of zeolite bodies.

Experimental

The aluminosilicate gel bodies were prepared according to the procedure described in the previous reports [17, 18] with some modifications. The detailed procedure was described as follows. The solution A was prepared by dissolving colloidal silica (AR, Qingdao Ocean Chemical Reagents Co., China) in deionized water. The solution B was obtained by dissolving NaOH (AR, Beijing Chemical Reagents Co., China) and sodium aluminate (AR, Beijing Chemical Reagents Co., China). The solution A was poured into the solution B and the sol–gel was dissolved in 200 mL deionized water in a beaker. The contents of the beaker were carefully mixed and nitric acid (AR, Beijing Chemical Reagents Co., China) was slowly added to adjust the pH of the sol–gel. Polyethylene glycol (20,000 g/mol, AR, Beijing Chemical Plant, China) was then added to the mixture as an AC, whose function was to adjust the size of the macropores. Stirring sol–gel to the well-dispersed mixture, the homogeneous sol–gel was aged at 353 K for 24 h. The sol–gel after aging was dried in air at 373 K overnight. The composition of the aluminosilicate gel in terms of oxide molar ratio was $x\mathrm{Na_2O{:}SiO_2{:}}y\mathrm{Al_2O_3{:}}z\mathrm{AC}$ ($0.045 \le x \le 0.08$, $0.0125 \le y \le 0.05$, $0 \le z \le 9.0 \times 10^{-4}$). Then, the dried aluminosilicate gel was mixed and kneaded with deionized water according to mass ratio 1:1.3 (the dried gel:H_2O). The kneading aluminosilicate gel was extruded into pillared bodies on F-26 twin screw extruder. After drying in air at 373 K overnight, the pillared bodies were cut into 2–3 cm columns.

For the in situ preparation process of VPT method, the bodies prepared by amorphous aluminosilicate gel were placed in a raised Teflon holder inside a Teflon-lined autoclave. The configuration of the holder was such that only vapor from the solvent mixture would be able to contact the bodies, as shown in Fig. 1. A mixture liquid of hexamethyleneimine (HMI, ACROS ORGANICS, USA) and deionized water was poured into the bottom of the autoclave to produce vapor molecules. The mass ratio of HMI, deionized water, and the gel was 2:3:1. In situ preparation was carried out in the Teflon-lined autoclave at 423 K for 168 h. The products were recovered, filtered, washed with deionized water, and finally dried at 373 K overnight to obtain the as-synthesized products. Zeolite bodies were obtained by calcining the as-synthesized products for 8 h in air at 813 K.

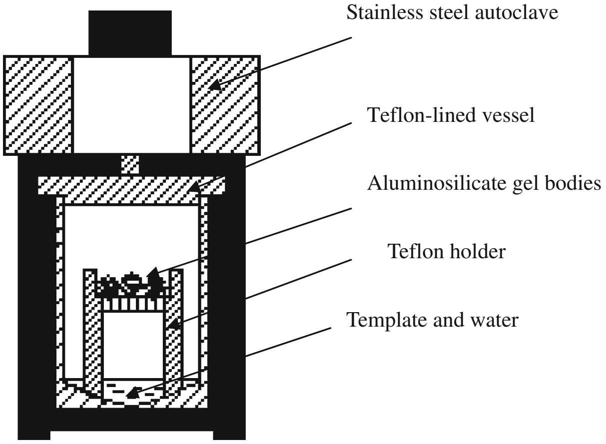

Fig. 1 Schematic illustration of the autoclave used for in situ preparation by VPT method

X-ray diffraction (XRD) patterns were collected on the Bruker D8 ADVANCE powder diffractometer using Ni-filtered Cu Kα radiation source at 40 kV and 20 mA, from 2° to 40° with a scan rate of 1°/min. The relative crystallinity was calculated by comparing the intensities of the peaks appearing $2\theta = 25.9°–26.1°$ in the calcined samples to those found in the fully crystalline reference material. The reference material was prepared from an aluminosilicate gel with molar composition $0.05\mathrm{Na_2O{:}SiO_2{:}}0.033\mathrm{Al_2O_3}$ at pH 10.0. Scanning electron microscope (SEM) images were recorded on a Hitachi S-4700. The gun type was cold cathode and the accelerating voltage was 20 kV. The samples for SEM observation were coated with Au. The mechanical resistance of zeolite bodies was performed using a DL II smart particle intensity detector. N_2 adsorption isotherms were measured in Sorptomatic (Thermo Co., USA) instrument at liquid nitrogen temperature 77 K. Before the adsorption measurement, the calcined samples were degassed at 300 °C and 3.0×10^{-4} Pa for 10 h. The pore sizes were obtained by HK method. Two porosimeter devices, Pascal 140 and Pascal 240(Thermo Co., USA), were used to measure the pore size distribution and the average pore radius of zeolite bodies. Pascal 140 working at moderate pressure from 20 Pa up to 400 kPa allows to characterize macropores. Pascal 240 was used to determine the micropores distribution with pressure varying from 0.1 to 200 MPa. Porosimeters Pascal 140 and Pascal 240 were coupled with a numerical station to acquire and record experimental data. The pore size distributions were obtained by cylindrical model.

Results and discussion

Effect of pH value

The XRD patterns of zeolite bodies were obtained at different pH value from $0.05Na_2O:SiO_2:0.033Al_2O_3$, which was shown in Fig. 2. The figure clearly showed that the products had no MCM-22 crystal phase but amorphous when the pH value was less than 9.64. When the pH value was more than 9.64, the obtained results were better. The peak positions were consistent with the XRD results for MCM-22 crystal structure observed by Lawton et al. [19], and except MCM-22 crystal structure, no other crystalline phases were detected. The relative crystallinity was 91.4%, 100%, 86.7%, and 83.1%, while the pH value was 9.64, 10.0, 10.70, and 12.03, respectively.

The mechanical resistance of zeolite bodies prepared at different pH was tested and the values were shown in Fig. 3. The values of mechanical resistance were 113, 126, 85, and 69 N/cm, while the pH was 9.64, 10.0, 10.70, and 12.03, respectively. From Fig. 3, it could be seen that the value of mechanical resistance was consistent with the relative crystallinity. Silicon source and aluminum source could be dissolved more easily in the suitable pH value system and facilitate the fast creation of more nuclei [20]. In this way, the results of the experiment suggested that suitable pH value for preparation self-bonded MCM-22 bodies was 10.0.

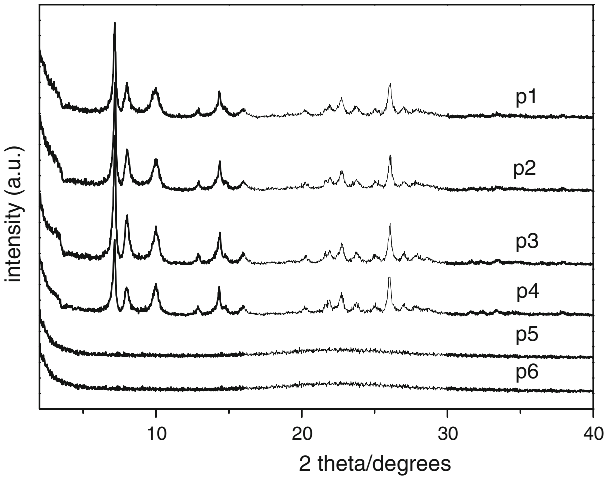

Fig. 2 XRD patterns of zeolite bodies prepared at different pH value (p1, 12.03; p2, 10.70; p3, 10.0; p4, 9.64; p5, 9.28; p6, 8.49)

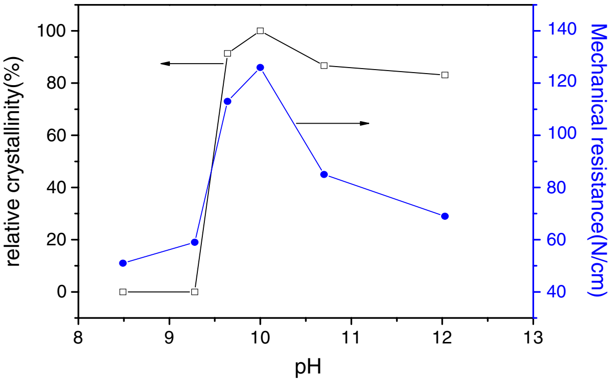

Fig. 3 The mechanical resistance and the relative crystallinity of zeolite bodies prepared at different pH value

Effect of SiO_2/Al_2O_3 ratio

Scanning electron microscope micrographs of zeolite bodies prepared at different SiO_2/Al_2O_3 from $0.05Na_2O:SiO_2$ at pH 10.0 were depicted in Fig. 4. It could be seen that the products had no MCM-22 crystal phase but amorphous at low SiO_2/Al_2O_3 (SiO_2/Al_2O_3 ratio was 20), as shown in Fig. 4am. When SiO_2/Al_2O_3 ratio was 80, there was other crystal phase except MCM-22 in the sample, as shown in Fig. 4bm. From Fig. 4, it could be known that there were some impurities such as amorphous matters or other crystal phase in the samples when SiO_2/Al_2O_3 ratio was too low or too high. When SiO_2/Al_2O_3 ratio was 30 and 50, there were all MCM-22 crystal chips regardless of the surfaces or the interiors of the bodies, as shown in Figs. 4cm, cn, dm, and dn. It could be known that the bodies, prepared by aluminosilicate gel, have been fully transformed into zeolite MCM-22.

In the conventional synthesizing system, the negative charges of the MCM-22 precursors were originated from either the $\equiv Si-O^{-}-Al\equiv$ sites (formed by aluminum atoms inserted into the framework) or the$\equiv Si-O^{-}\cdots HOSi\equiv$defect sites (formed by the reaction between the OH^{-} and silanol groups). If the aluminum content was relatively high ($SiO_2/Al_2O_3 < 15$), the amount of the HMI^{+} required for the formation of stable MCM-22 precursors was not sufficient to match the amount of the $\equiv Si-O^{-}-Al\equiv$ sites, leading to the formation of other phases. When the aluminum content was relatively low ($SiO_2/Al_2O_3 > 50$), the $\equiv Si-O^{-}-Al\equiv$ sites would be totally compensated by HMI^{+}. At the same time, a number of $\equiv Si-O^{-}\cdots HOSi\equiv$ defect sites were produced to compensate the surplus HMI^{+}, which made the MCM-22 precursor unstable and resulted in the formation of other phases [21, 22]. In this way, it could get the same results from the experiment, the suitable SiO_2/Al_2O_3 ratio was in the 30–50 range.

Effect of Na_2O/SiO_2 ratio

To study the effect of Na_2O on the preparation self-bonded zeolite MCM-22 bodies, the Na_2O/SiO_2 ratio was varied from 0.045 to 0.08 while keeping the formulation at $SiO_2:0.033Al_2O_3$ and pH was 10.0. Figure 5 showed XRD

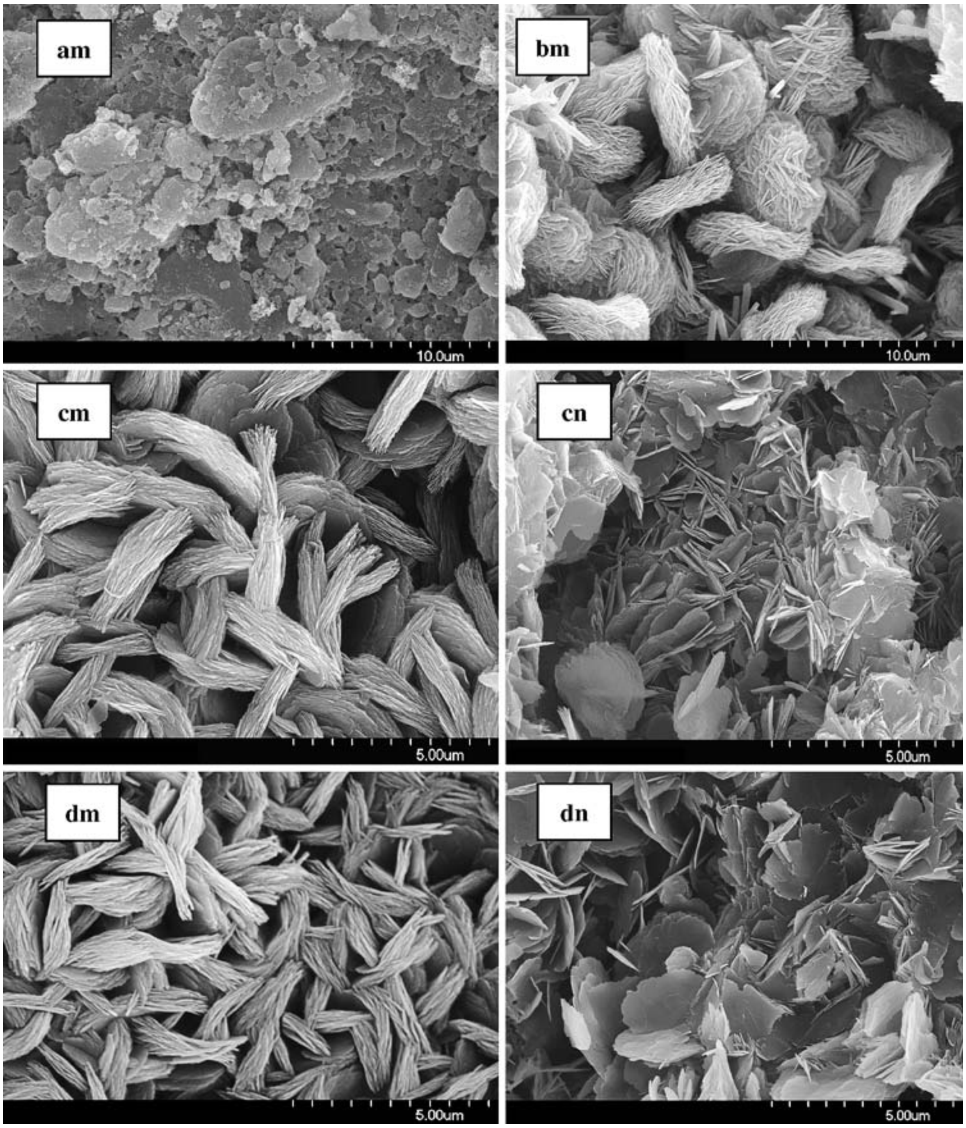

Fig. 4 SEM micrographs of zeolite bodies prepared at different SiO_2/Al_2O_3 ratio (**a** 20; **b** 80; **c** 30; **d** 50; **m** the surface of zeolite bodies; **n** the cross section of zeolite bodies)

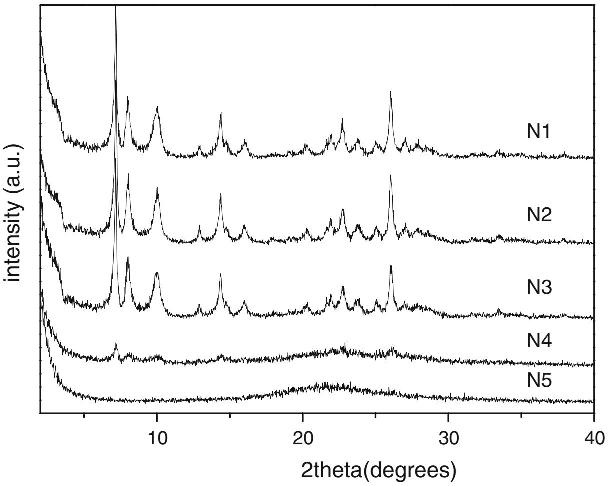

Fig. 5 XRD patterns of zeolite bodies prepared at different Na_2O/SiO_2 ratio (N1, 0.045; N2, 0.05; N3, 0.06; N4, 0.07; N5, 0.08)

patterns of the samples obtained at various Na_2O/SiO_2 ratios. It could be seen that the highly relative crystallinity could be obtained when the Na_2O/SiO_2 ratio was 0.045–0.06. However, when the Na_2O/SiO_2 ratio was 0.08, only amorphous aluminosilicate gel was observed. The relative crystallinity was 86.7%, 100%, and 95.7%, while the preparation conditions were N1, N2, and N3, respectively. The mechanical resistance and the relative crystallinity of zeolite bodies prepared at different Na_2O/SiO_2 ratio were shown in Fig. 6. Figure 6 showed that the mechanical resistance of zeolite bodies was 108, 126, and 123 N/cm, while the Na_2O/SiO_2 ratio was 0.045, 0.05, and 0.06, respectively. From Fig. 6, it could be known that the value of mechanical resistance was enhanced with the relative crystallinity increased. The conclusion was consistent with the result of the effect of pH value. Na^+ cation acted as a charge balancing agent and could enhance nucleation.

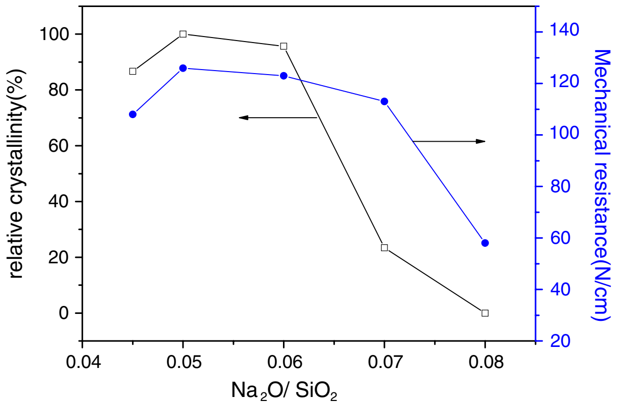

Fig. 6 The mechanical resistance and the relative crystallinity of zeolite bodies prepared at different Na_2O/SiO_2 ratio

Cheng et al. [23] investigated that adding a certain amount of Na^+ cation could stimulate the growth of zeolite crystals. It could obtain high mechanical resistance of MCM-22 bodies when Na_2O/SiO_2 ratio was about 0.05.

Effect of PEG20000

For zeolite bodies, it was observed that the pore size distributions of zeolite bodies were catalytic properties influencing the access to reactants [24]. Therefore, zeolite bodies might be a highly favorable catalyst for some reactions if the pore size distributions of zeolite bodies could be adjusted. In order to adjust the pore size distributions of zeolite bodies, the PEG20000 was added to the aluminosilicate gel and the influence of adding AC on the preparation self-bonded MCM-22 bodies was researched. The SEM micrographs and XRD patterns of zeolite bodies prepared at different AC/SiO_2 from $0.05Na_2O:SiO_2:0.033Al_2O_3$ at pH = 10 were shown in Figs. 7 and 8, respectively.

When zeolite bodies were prepared by adding AC, there were all MCM-22 crystal chips regardless of the surfaces or the interiors of the bodies, as shown in Fig. 7. From Fig. 8, it could be seen that the XRD patterns of the zeolite bodies prepared by adding AC agreed well with the XRD results for MCM-22 crystal structure observed by Lawton et al. [19]. The conclusion was consistent with the results of the SEM. It showed that the bodies, prepared by adding AC, had been transformed into MCM-22 bodies. By further observation (Fig. 7en, fn), it could be known that the MCM-22 crystal chips are made up of the channels of different size in the interiors of MCM-22 bodies. Pore size distributions of MCM-22 bodies prepared at different AC/SiO_2 were plotted on Fig. 9. When AC/SiO_2 ratio was 1.5×10^{-4} and 3.0×10^{-4}, the main radius distribution of MCM-22 bodies was in the 10–200 nm range. The radius of 400–1,000 nm became the dominant class in the pore size distribution when AC/SiO_2 ratio was 9.0×10^{-4}. The average pore radius of zeolite bodies was 149.41, 180.79, 478.07, and 653.64 nm, while AC/SiO_2 ratio was 1.5×10^{-4}, 3.0×10^{-4}, 4.5×10^{-4} and 9.0×10^{-4},

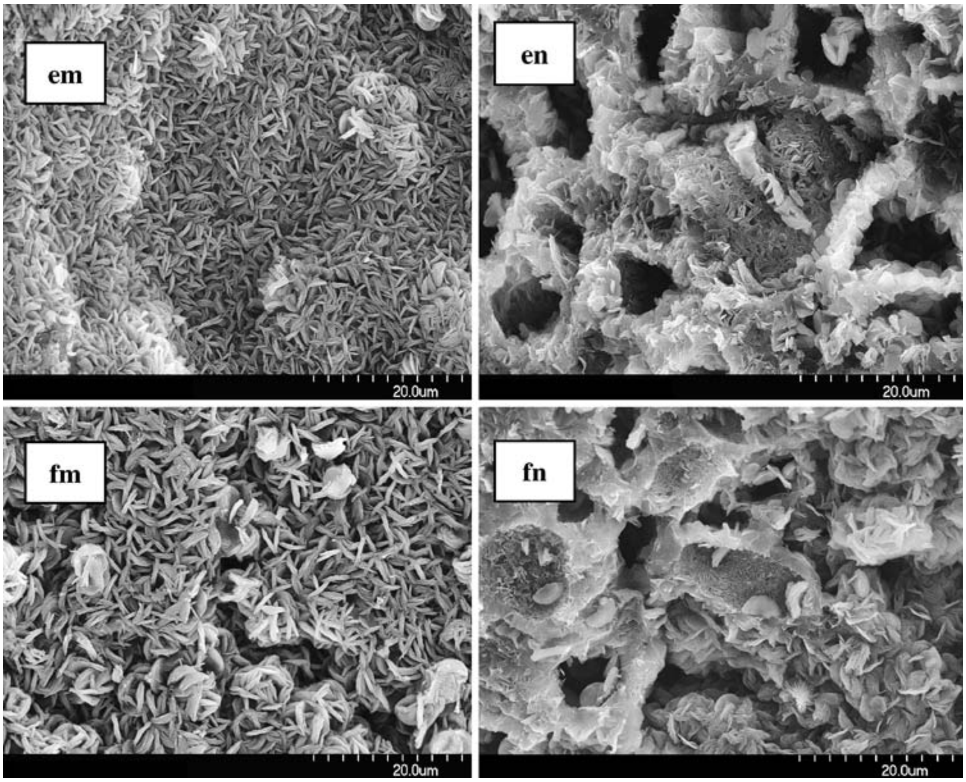

Fig. 7 SEM micrographs of zeolite bodies prepared at different AC/SiO_2 ratio (**e** 1.5×10^{-4}; **f** 9×10^{-4}; **m** the surface of zeolite bodies; **n** the cross section of zeolite bodies)

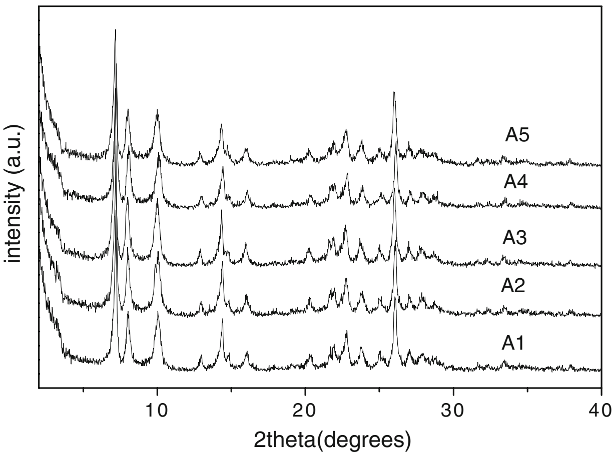

Fig. 8 XRD patterns of zeolite bodies prepared at different AC/SiO_2 ratio (A1, 1.5×10^{-4}; A2, 3.0×10^{-4}; A3, 4.5×10^{-4}; A4, 6.0×10^{-4}; A5, 9.0×10^{-4})

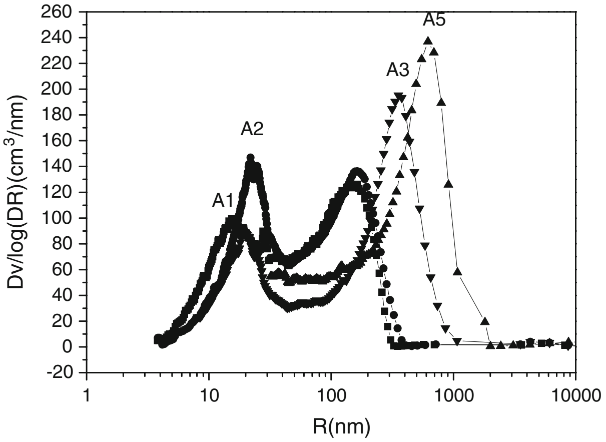

Fig. 9 Pore size distributions of zeolite bodies prepared at different AC/SiO_2 ratio (A1, 1.5×10^{-4}; A2, 3.0×10^{-4}; A3, 4.5×10^{-4}; A5, 9.0×10^{-4})

respectively. It was found that the radius distribution of MCM-22 bodies was transferred to high value with the increase of AC/SiO_2 ratio. With the results of the experiment, it indicated that the pore size distributions of MCM-22 bodies could be adjusted by adding AC.

Figure 10 showed the Hg intrusion–extrusion curves of zeolite bodies was prepared at AC/$SiO_2 = 3.0 \times 10^{-4}$. Because a part of Hg was left in the sample after the first run, the intrusion volume of Hg in the second run was less than in the first run. There was a loop in the Hg intrusion–extrusion curve N, as shown in Fig. 10. It suggested the sample was not broken after the first run and the porous structure of the sample was stable. The nitrogen adsorption and desorption isotherms were measured for zeolite bodies prepared at AC/$SiO_2 = 3.0 \times 10^{-4}$ (Fig. 11). The nitrogen adsorption and desorption isotherms of the sample (Fig. 11a) exhibited the type IV behavior with a hysteresis loop, indicating that the cage-like pore structure existed in the sample. The cage-like pore structure was characteristic of zeolite MCM-22. The HK pore diameter distributions of the sample (Fig. 11b) exhibited the pore size distributions in the micropore and mesopore range. Figures 9 and 11b showed the pore size distributions of zeolite bodies from micropore to macropore range. According to Pérez-Ramírez et al. [25, 26], the zeolite bodies in this article were hierarchical zeolites.

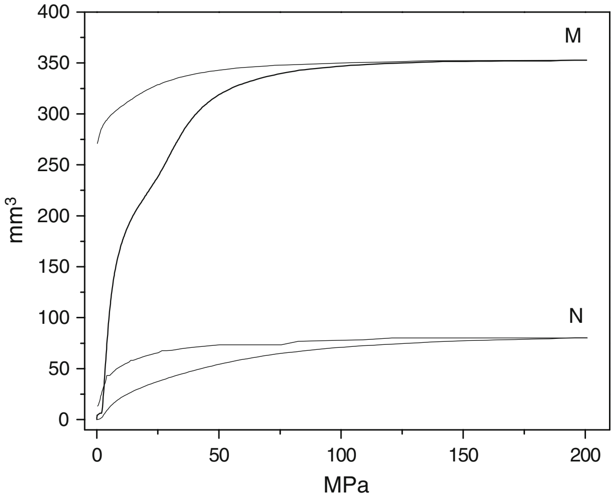

Fig. 10 Hg intrusion–extrusion curves of zeolite bodies prepared at AC/$SiO_2 = 3.0 \times$ 10–4 (**m** the first run the sample; **n** the second run the same sample)

Conclusions

The style of zeolite bodies were produced by zeolite powders and binder. The binder is indispensable in order to produce bodies of optimal dimension and form and having a high mechanical resistance. In this paper, self-bonded MCM-22 bodies were in situ prepared with the molar composition of $0.05Na_2O:SiO_2:30Al_2O_3$ at pH 10.0 by VPT method. There were all MCM-22 crystal chips regardless of the surfaces or the interiors of the bodies and the mechanical resistance of MCM-22 bodies was 126 N/cm. The advantage of the self-bonded MCM-22 bodies was to avoid the necessary formation of bodies from the fine MCM-22 crystals using an inorganic binder.

By adding PEG20000 to the aluminosilicate gel, the pore size distributions of MCM-22 bodies could be adjusted. It was found that the radius distribution of MCM-22 bodies was transferred to high value with the increase of AC/SiO_2 ratio. The average pore radius of zeolite bodies was 149.41, 180.79, 478.07, and 653.64 nm, while AC/SiO_2 ratio was 1.5×10^{-4}, 3.0×10^{-4}, 4.5×10^{-4}, and 9.0×10^{-4}, respectively.

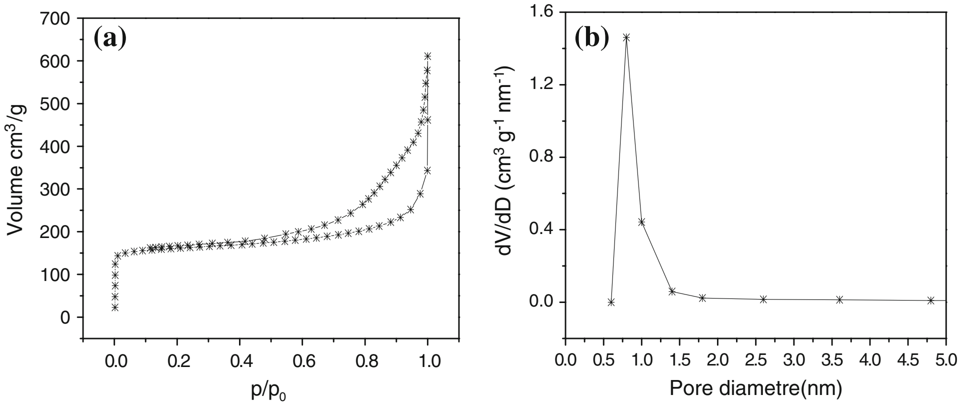

Fig. 11 N_2 adsorption and desorption of zeolite bodies prepared at AC/SiO$_2$ = 3.0 × 10^{-4} (**a** N_2 adsorption and desorption isotherms; **b** HK pore size distributions)

Acknowledgement The authors gratefully acknowledge the financial assistance from the National Natural Science Foundation of China (Nos. 20676011 and 20625621).

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