CrystEngComm

Accepted Manuscript

ROYAL SOCIETY
OF **CHEMISTRY**

www.rsc.org/crystengcomm

Journal Name

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Investigation on crystallization of zeolite A from hydrogels aged under high pressures

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

This paper investigates the influence of aging of zeolite A hydrogel under high pressures on the synthesis of zeolite A. The effects of the aging pressure, aging time and types of gases are examined. The products are characterized by scanning electronic microscopy, X-ray diffraction, and fourier transform infrared. The results indicate that high pressure aging leads to the increase in the nucleation rate, facilitating the formation of zeolite A with high crystallinity, small particle sizes and narrow particle size distribution. The type of gas also exerts influence on the synthesis of zeolite A, as the hydrogels aged under high pressure in the type of gas which has higher solubility in water can produce zeolite A with smaller particle size. Thus, by adjusting the aging pressure and the type of gas used, the size of the resulting zeolite A can be controlled. The mechanism of the high pressure aging is related to the interaction of the gel with the dissolved gas. Influences of aging of the hydrogels on synthesis of zeolite Y, silicalite-1 and SAPO-34 are also observed.

Keywords: Zeolite synthesis; High pressure aging; Gas; Autocatalytic nucleation mechanism

1. Introduction

Zeolites are microporous aluminosilicalite crystals commonly used as adsorbents, ion-exchangers, and catalysts[1]. They are now found to have potential application in membranes[2], microelectronics devices[3], bio-sensors[4], micro-reactors[5] and fuel cells[6]. Conventionally, zeolites are synthesized by autogeneous hydrothermal crystallization of hydrogels composed of alumina, silica, and alkaline sources[7]. During the synthesis, aging is quite commonly applied to accelerate crystallization, control the crystal size and suppress impurity phases[8]. During aging, a significant change of nuclei distribution in the gel matrix will happen[9-10], resulting in a decrease in the duration of crystallization and the nucleation period[11-12]. The crystal size distribution and average particle size of final products become narrower and smaller, respectively, with the prolongation of the aging time[11-12]. Furthermore, aging is useful or even necessary in the synthesis of zeolite membranes without seeding, as it increases the nucleation density on the support[8]. High aging temperatures and long aging times can facilitate the subsequent crystallization and lead to the formation of a pure phase zeolite membrane[8]. Therefore, in some cases, aging is an important step for the successful zeolite formation. Generally, the aging step is carried out by letting the hydrogels stand at ambient temperature and pressure for a certain time before synthesis at elevated temperatures[13]. This man-made zeolite synthesis process (including the aging step) is, sometimes, different from that occurred in nature, as the raw materials for zeolite synthesis quite commonly undergo ultrahigh pressures for the latter[14-15].

The influence of pressurization during the hydrothermal process and on the obtained zeolite crystals has been examined by several groups. For example, Kulkarni et al.[16] found that high crystalline ZSM-5 can be synthesized in a very short hydrothermal synthesis time under 4-5 MPa. Pan et al.[17] revealed that nanosized silicalite-1 crystals with increased crystallinity can be successfully synthesized in a pressurized capillary microreactor (1 MPa). Zhao et al.[18] found that zeolite ZSM-5 can irreversibly transformed to ZSM-11 by skeletal rearrangement under 4 GPa. Huang et al.[19-21] observed occurrence of pressure-induced amorphization of zeolite X, Y, and A at 2-5 GPa, caused by the distortion of cages which form the zeolitic lattice[22]. These results imply that high pressure not only can induce crystallization of the zeolites during hydrothermal process, but also can lead to structure transformation or amorphization for as-synthesized zeolites. To the best of our knowledge, the effect of pressurization during the aging of the hydrogels on zeolite synthesis has not been examined. From this reason, we investigate the crystallization of zeolite A in the hydrogels aged under different pressures generated by various gas cylinders. The crystallization kinetics were also investiged to compare those in the conventional hydrothermal synthesis. The synthesis process is analyzed and the synthesis mechanism is postulated.

2. Experimental Section

2.1 Preparation of zeolite A from the hydrogels aged under high pressures

The hydrogel for zeolite A was prepared according to a modified reported procedure with a molar ratio of $5.85Na_2O$: $2.7SiO_2$: $1Al_2O_3$: $182H_2O$[23]. First, a sodium aluminate solution was prepared by adding 5.06 g of sodium hydroxide (96 wt % NaOH, Sinopharm) and 3.24 g of sodium aluminate (41 wt % Al_2O_3, Sinopharm) into a polypropylene (PP) beaker pre-filled with 88.1 g of deionized water. The obtained solution was stirred for 30 min until it became clear. Afterward, 5.25 g of 40 wt% aqueous colloidal silica (Zhejiang Yuda) was dropwise added to the obtained solution under stirring. The solution was continuously stirred for 30 min at room temperature to obtain the final hydrogel.

The obtained hydrogel was then transferred into a 600 mL stainless steel autoclave (Parr 4848). After sealing, the autoclave was connected to a N_2 cylinder by a pressure regulator to 2, 5, 8, 10 MPa. Afterward, the system was let stand at room temperature for certain times. Finally, a discharge pipe was connected to the valve of the autoclave, and the pressure in the autoclave was slowly released by carefully opening this valve. The autoclave cap was carefully opened and the hydrogel was promptly poured into a PP bottle and sealed it with a cap. Then, it was put into an oven which was preheated to 80 °C for 3 h. Finally, the product was collected by repeatedly washing with deionized water and filtering, and dried at 80 °C for 12 h. For comparison, similar synthesis was also conducted using the hydrogel aged under ambient pressure.

2.2 Characterization

X-ray diffraction (XRD) patterns were recorded by a Bruker D8-Advance powder diffractometer with Ni-filtered Cu Kα radiation source at 40 kV and 40 mA at a scan rate of 5°/min and step size of 0.05°. Crystallinity was calculated by dividing the sum of intensities of the prominent peaks (2θ = 7, 10, 12.5, 21.5, 24, 26, 27, 30, and 34°) of a sample by that of the standard reference prepared following Ref. 24.

The size and morphology of zeolite crystals were investigated by scanning electronic microscopy (SEM, LEO-1530 or Hitachi-S4800). The mean particle size and particle size distribution (PSD) of samples were also determined on Malven Zetasizer 3000 HAS by preparing a suspension with a zeolite concentration of ~ 1 wt%. Based on the PSD data, the average crystal size ($\bar{D}$) and specific number of crystals (N_s, number of crystals per one gram of the crystalline end product) were calculated as follows[25].

$$\bar{D} = \sum N_i \times D_i / \sum N_i$$

$$N_s = \sum N_i / (\pi/6) \times \rho \times \sum N_i \times (D_i)^3$$

Where, N_i is the number frequency of the crystals having the size between D and ΔD, $D_i = D + \Delta D/2$. D is the measured equivalent spherical diameter and ρ is the density of zeolite A, which is 2 g/cm^3.

The Fourier transform infrared (FTIR) spectra were obtained on the Nexus 870 FTIR spectrometer. Before the measurement, the hydrogel was first stirred with a glass rod. Then, one drop of the reaction mixture was dropped on a KBr wafer. After drying with an infrared lamp, the sample was ready for the FTIR measurement in which the spectra were recorded in the wavenumber range of from 1600 to 400 cm^{-1}.

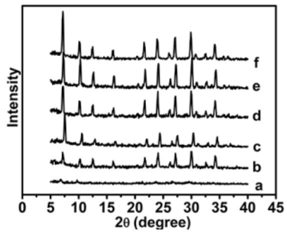

Fig. 1 XRD patterns of the products obtained from hydrogels aged at ambient pressure (a), 2 MPa (b), 5 MPa (c), 8 MPa (d), 10 MPa (e) N_2 atmosphere. The hydrothermal synthesis was conducted at 80 °C for 3 h.

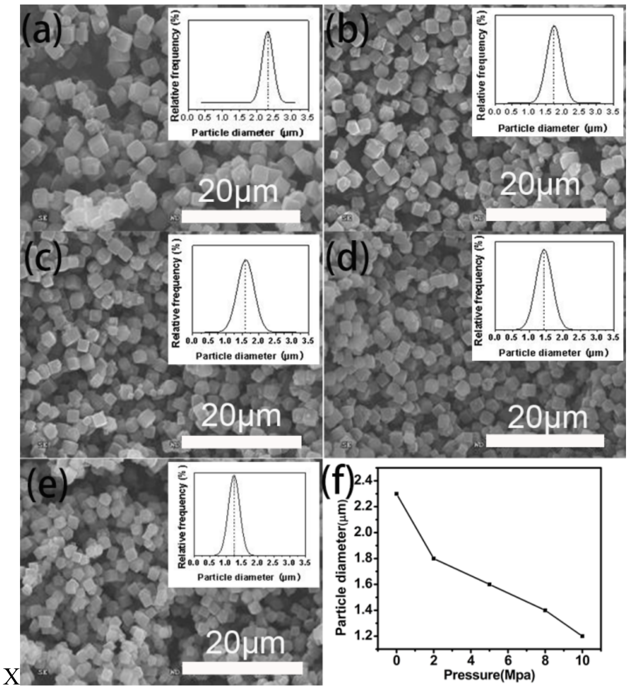

Fig. 2 SEM images and particle size distributions of the products obtained from hydrogels aged at ambient pressure (a), 2 MPa (b), 5 MPa (c), 8 MPa (d), 10 MPa (e) N_2 atmosphere and a plot of the average diameter of zeolite A as a function of the aging pressure(f). The hydrothermal syntheses were conducted at 80 °C for 3 h.

The structure of the hydrogel was investigated by transmission electron microscope (TEM JEL-200CX). The sample was prepared by filtrating the aged hydrogel, dispersing the collected solid in ethanol with ultrasonication treatment, and depositing a droplet of the resultant suspension onto Cu grids coated with a thin holey carbon support film.

3. Results and Discussion

3.1 Effect of the aging pressure

We first chose nitrogen as the gas source for pressurizing the hydrogels during the aging process. A series of pressures from 2 to 10 MPa were applied. After high-pressure aging for 24 h, the hydrogels were hydrothermally treated at 80 °C for 3 h. Fig. 1 shows XRD patterns of the products obtained from the hydrogels aged under ambient and high pressures. All the products prepared from aged hydrogels display XRD diffraction peaks ascribed to zeolite A (Figs. 1b-f), except the one obtained from the hydrogel aged under ambient pressure that is amorphous (Fig. 1a). With the pressure applied during aging increased from ambient pressure to 2, 5, 8 and 10 MPa, the intensities of the XRD peaks

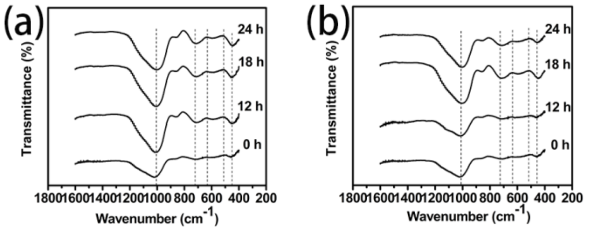

Fig. 3 FTIR spectrum of the hydrogels aged at 10 MPa N_2 atmosphere (a) and ambient pressure (b) for different times.

become stronger, indicating the increase in crystallinity of the products.

Figs. 2a-e show the SEM pictures of the resultant products obtained from the aged hydrogels mentioned above. All the samples exhibit cubic morphology, typical morphology of zeolite A. Insets in Figs. 2a-e exhibit the particle size distributions of the resulting products. Obviously, the pressure applied during aging has strong influence on the particle size distribution. The particle sizes range from 0.7 to 3 µm for product obtained from the hydrogels aged at ambient pressure (inset in Fig. 2a), while they range from 0.7 to 2.3 µm (inset in Fig. 2c) and from 0.7 to 1.7 µm (inset in Fig. 2e) for products obtained from hydrogels aged at 5 and 10 MPa, respectively. In addition, Fig. 2f shows the mean particle sizes of these products as a function of the pressures applied during aging. Apparently, the mean crystal size of zeolite A decreases from 2.2 to 1.2 µm with the increase in the pressure applied. The specific numbers of crystals (*Ns*) of products obtained from the hydrogels aged at 2, 5, 8 and 10 MPa are 4.31, 6.27, 8.34 and 12.6 $\times 10^{10}$, respectively. These results indicate that aging of the hydrogels under high pressures leads to the formation of zeolite A crystals with high crystallinity, small particle sizes, and narrow particle size distribution.

3.2 Effect of the aging time

To investigate the effect of pressure on the formation of zeolite A, we made FTIR spectra of the freshly prepared hydrogel as well as the hydrogels aged under both ambient pressure and 10 MPa, for 12, 18 and 24 h. The results are shown in Fig. 3. The sample without aging exhibits no obvious broad band in the region from 500 - 600 cm^{-1} ascribed to D4R units contained in the zeolite nuclei in the gel matrix[26-28], while samples aged under 10 MPa for 12, 18 and 24 h present relative obvious band in this range (Fig. 3a), indicating the formation of tertiary structural building block contained in 'quasi-crystalline' zeolite phase formed in the gel matrix during aging. Broad bands at 450 cm^{-1} and 720 cm^{-1} ascribed to Si-O-T bending (T=Si or Al)[29- 30] and a band at about 1000 cm^{-1} corresponding either to the stretching vibrations of the Si-O bond in SiO_4 or to the skeleton of bonded SiO_4 tetrahedra can be observed on all samples. However, the band intensities are quite weak for the hydrogel without aging, while they become stronger with prolongation of the aging time for samples aged under 10 MPa, indicating the increase in the polymerization degree of SiO_4 tetrahedra and appearance of the zeolite crystallization seed due to the presence of the sodium-aluminiosilicate cluster[27]. Obvious bands at 450 cm^{-1}, 720 cm^{-1} and 1000 cm^{-1} appear on the sample aged under ambient pressure for 18 h (Fig. 3b). Simultaneously, the band intensities of the samples aged under ambient pressure for 18 and 24 h are weaker than those aged under 10 MPa for 18 and 24 h. It is needed to note that all the above samples exhibit no XRD diffraction peaks, indicating the formation of the nucleus rather than the crystal of zeolite A during the aging period. These results indicate that aging of the hydrogels under high pressures enhances the possibility of the formation of zeolite A nuclei.

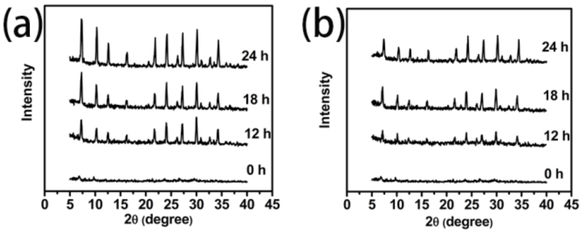

Fig. 4 XRD patterns of the products obtained from hydrogels aged at 10 MPa N_2 atmosphere (a) and ambient pressure (b) for different times. The hydrothermal syntheses were conducted at 80 °C for 6 h.

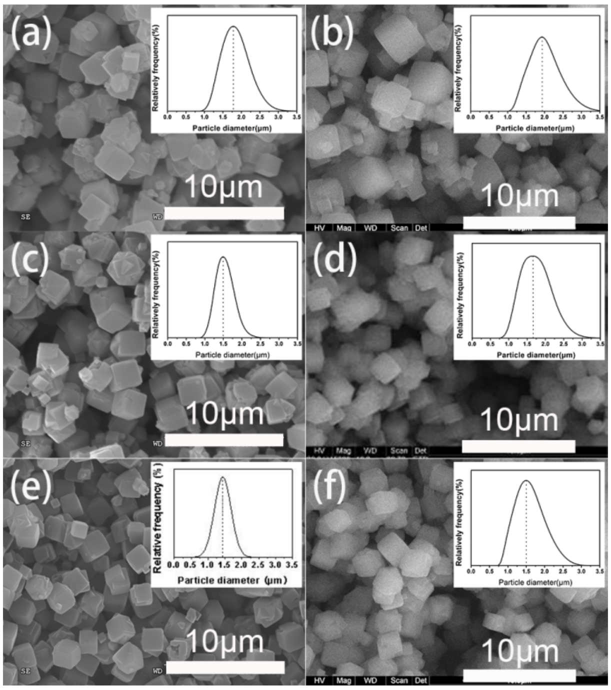

Fig. 5 SEM images and particle size distributions of the products obtained from hydrogels aged at 10 MPa N_2 atmosphere for 12 h (a), 18 h (c), 24 h (e), and aged at ambient pressure for 12 h (b), 18 h (d), 24 h (f). The hydrothermal syntheses were conducted at 80 °C for 6 h.

Fig. 4 shows XRD patterns of the products synthesized from hydrogels without aging, aged under ambient pressure and 10 MPa N_2 atmosphere for 12, 18 and 24 h. All the hydrothermal syntheses were carried out at 80 °C for 6 h. Very weak XRD diffraction peaks are observed on the products obtained from the hydrogel without aging, suggesting the formation of mainly amorphous product under this condition. Obvious XRD diffraction peaks appear on samples obtained from the hydrogels aged under 10 MPa, with increased peak intensities as prolongation of the aging time. The XRD peak intensities of the sample aged under ambient pressure are weaker than those aged under 10 MPa. SEM pictures of these samples (Fig. 5) reveal that the crystalline end products obtained from the hydrogels aged under 10 MPa exhibit more well-defined cubic habit, of which the mean particle sizes obtained from the hydrogels aged for 12, 18, 24 h are 1.8, 1.5, 1.4 µm, with *Ns* of 4.35, 5.12 and 8.34

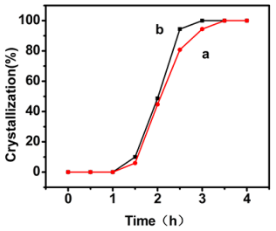

Fig. 6 Crystallization curves of the hydrogels aged under ambient pressure (a) and 10 MPa (b).

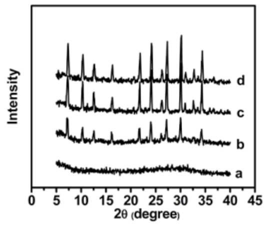

Fig. 7 XRD patterns of the products obtained from hydrogels aged at 10 MPa in carbon dioxide (a), helium (b), hydrogen(c), oxygen (d) atmospheres. The hydrothermal syntheses were conducted at 80 °C for 3 h.

Table 1 The rates of nucleation and crystallization of zeolite A at 80 °C from hydrogels aged under ambient pressure and 10 Mpa.

Samples	Nucleation rate (h^{-1})	Crystallization rate (X% • h^{-1}) *
Zeolite A obtained from hydrogel aged under 10 MPa	1.8	87
Zeolite A obtained from hydrogel aged under ambient pressure	1	73

*X denotes as the crystallinity of the sample.

$\times10^{10}$, respectively. For comparison, the mean particle sizes of the products obtained from the hydrogels aged at ambient pressure for 12, 18, 24 h are 1.9, 1.7, 1.5 μm, with *Ns* of 3.38, 4.38, 6.56 $\times10^{10}$, respectively. The results indicate that both high pressure aging and long aging time can increase the number of nuclei in the gel matrix and promote formation of zeolite A crystals with a narrower particle size distribution.

3.3 Crystallization Kinetics

Fig. 6 shows the crystallization curves of the hydrogels aged at ambient pressure and 10 MPa for 24 h. Clearly, the crystallization of the hydrogels aged at ambient pressure takes about 3.5 h, while the crystallization from hydrogels aged for the same time at 10 MPa is finished in 3 h. And the average particle size decreases from 2.3 μm for the product obtained from the hydrogel aged at ambient pressure to 1.2 μm for the product obtained from the hydrogel aged at 10 MPa. These phenomena indicate considerable difference in the number and distribution of nuclei in the gel matrixes. The nucleation rate and crystallization rate of the hydrogel aged under 10 MPa are a little bit higher than those of the hydrogel aged under ambient pressure, as calculated from the crystallization curves following the method mentioned in Ref. 25 (Table 1). This is ascribed to the effect of high pressure aging.

3.4 Effect of the type of gas

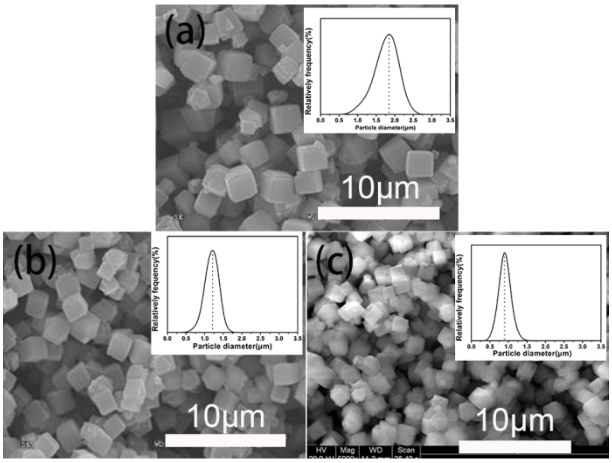

Fig. 8 SEM images and particle size distributions of the products obtained from hydrogels aged at 10 MPa in helium (a), hydrogen (b), oxygen (c) atmospheres. The hydrothermal syntheses were conducted at 80 °C for 3 h.

Besides in nitrogen atmosphere, we also aged the hydrogels in carbon dioxide, helium, hydrogen, and oxygen atmospheres under 10 MPa for 24 h. The syntheses were conducted at 80 °C for 3 h. Fig. 7 shows the XRD patterns of the resultant products. Amorphous product is obtained from the hydrogel aged in CO_2 (Fig. 7a), resulting from the formation of the carbonic salt which lowers the pH value of the hydrogels (The pH value of the hydrogel lowers from 14 before aging in carbon dioxide atmosphere to 11 after aging in carbon dioxide atmosphere), and the decrease in the concentrations of active silicate, aluminate and aluminosilicate in the liquid phase because of the reaction with CO_2. Zeolite A is synthesized from the hydrogels aged in He, H_2 and O_2 (Fig. 7 b-d), which exhibits cubic crystals, with an average sizes of 1.7, 1.2 and 0.9 μm, with *Ns* of 4.39, 14.9, 33.6$\times10^{10}$, respectively, as shown from SEM pictures of the products (Fig. 8). The decreasing trend in the particle size is similar to the increasing solubility of He, H_2, and O_2 in water, which are 0.6 mL/L, 18.2 mL/L and 31 mL/L, respectively, at ambient temperature and pressure[31]. Since the solubility of a gas obeys the Henry's Law at a fixed temperature, the solubility should increase with the pressure. The high solubility of a gas in the hydrogels can split those big amorphous gels into small gels, leading to fast release of the nuclei in the gel matrix. On the other hand, the decrease in the particle size is related to the increase in polarizability of gases (He< H_2< O_2). Van der Waals' interaction and slight electrostatic interactions of polarized gas molecules with negative charged aluminosilicate framework may exist. Consequently, the chemical composition in the hydrogel may change, which possibly promote the increase in the number of the nuclei[32]. Therefore, the hydrogel aged in the type of gas with a higher solubility in water and a higher polarizability turns to produce zeolite A with smaller particle size. Of course, this gas should not react with any component in the hydrogels. This conclusion can also be used to partly explain why aging of the hydrogels under higher pressures leads to formation of zeolite A crystals with smaller particle sizes than aging under lower pressures. In addition, these results suggest that pressure has not a direct influence on the particle size and PSD of the end product, but has an indirect one, through the amounts of dissolved gases.

Table 2 The crystallinities and mean particle sizes of the resultant products from hydrogels aged under ambient pressure and 10 MPa N_2 atmosphere.

Samples	Crystal sizes (µm)		XRD crystallinity (%)	
	High pressure aging	Conventional aging	High pressure aging	Conventional aging
Silicalite-1	34	52	101	75
SAPO-34	10	18	103	77
Zeolite Y	0.7	1.1	99	61
AlPO4-5	26	37	100	59

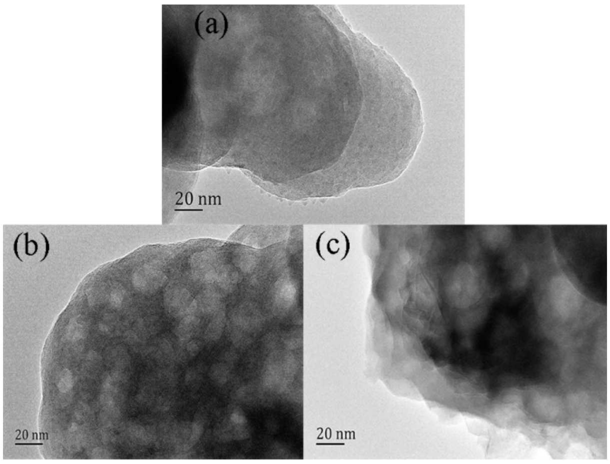

Fig. 9 TEM images of products obtained from hydrogels without aging (a), aged under ambient pressure (b) and at 10 MPa N_2 atmosphere (c) for 24 h.

3.5 Mechanism

The above results indicate that zeolite A with a small particle size, a narrow particle size distribution, a large number of crystals and high crystallinity can be prepared from hydrogels aged under high pressures in various gas atmospheres. It is known that the particle size and the crystal size distribution in the crystalline product depend exclusively on the number and distribution of nuclei in the gel matrix, not on the modification of original hydrogel or by the change of crystallization conditions[32-34]. Hence, aging under high pressures can increase the release rate of the nuclei from the gel matrix and change the chemical conditions under which hydrogel is prepared. Thus the mechanism behind these results may be related to the interaction of the gel with the gas which is dissolved in, which leads to formation of increased number of nuclei in the hydrogel matrix aged under high pressures. On one hand, the interaction of the gel with the gas during the high pressure aging can change the chemical conditions of the original hydrogel, thus increasing the number and distribution of nuclei in the gel matrix. On the other hand, big amorphous gels formed in the original hydrogels are splitted into small gels because of the high pressure and dissolution of the gas. Thus all the gels are to be dissolved at almost the same time because of their small and similar sizes, resulting in more uniform-sized end products after crystallization. This mechanism can clearly explain the great difference in the particle size and *Ns* of the product obtained from hydrogels aged in He from those aged in N_2 and O_2. As there are no interactions between the hydrogels and He, the dissolution of He in the hydrogel plays the main role in the crystallization of zeolite A. Therefore, the hydrogel aged in He produces large-sized zeolite crystals.

In order to verify the above proposed mechanism, we observed the gels without aging and those aged under ambient pressure and at 10 MPa N_2 atmosphere by TEM. The TEM pictures shown in Fig. 9 exhibit that the gel is composed of bright spots and dark area. There is few bright spots in the gel without aging (Fig. 9 a), and more bright spots in the gels aged under ambient pressure and at 10 MPa N_2 atmosphere (Fig. 9 b and c). The number of bright spots in the gels aged at 10 MPa N_2 atmosphere is more than that aged under ambient pressure. The bright spots are believed to be crystallites forms of negative nuclei starting to form at the beginning of the crystal growth which collapse in the vacuum of the TEM, and the dark areas can be attributed to the homogeneous aluminosilicate species[35-36]. Therefore, the increased bright spots indicate the increasing number of nuclei, This indicates that the number of nuclei in the gel aged under high pressures is more than that aged at ambient pressure or without aging, verifying that high pressure aging can increases the number of nuclei in the gel matrix. In addition, we also applied this method on synthesis of zeolite Y, silicalite-1, SAPO-34 and $AlPO_4$-5 (Supporting information). Table 2 lists the experimental conditions and the crystallinities and mean particle sizes of the resultant products. Obviously, aging of the hydrogels under high pressure promote the formation of zeolites with high crystallinity and small particle size. On the other hand, this aging process can accelerate transformation of some metastable zeolites. For example, SAPO-5 is produced from the hydrogel aged under ambient pressure for 24 h, while SAPO-34 is obtained from the same hydrogel aged under 10 MPa N_2 atmosphere for 24 h, after hydrothermal synthesis at 200 °C for 48 h (Figs. S7, S8). Transformation of zeolite X to zeolite P is also observed after the same aging process (Fig. S9).

4. Conclusions

Aging of the hydrogels under high pressures on synthesis of zeolite A was examined. The results indicate that this process results in the formation of zeolite A with high crystallinity, small particle sizes and narrow particle size distribution. The applied pressure is crucial and the solubility and polarizability of the gas play an important role in the formation of the resultant zeolites. The hydrogel aged under high pressure in the type of gas which has higher solubility in water can produce zeolite A with smaller particle size. This effect is ascribed to the interaction of the gel with the dissolved gas, which possibly increases the number and distribution of nuclei in the gel matrix by changing the chemical composition of the original hydrogel, and splits big amorphous gels in the original hydrogels into small ones. Aging of the hydrogel under high pressures not only exerts influence on synthesis of zeolite A, but also have effect on aluminosilicate zeolites, such as zeolite Y and silicalite-1, and aluminophosphate molecular sieves, such as SAPO-34 and $AlPO_4$-5.

Acknowledgments

We are grateful for financial support from the National Natural Science Foundation of China (21076107), Priority Academic Program Development of Jiangsu Higher Education Institutions, and the Research and Innovation Program for College Postgraduates of Jiangsu Province (CXZZ12_0435).

Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental details, XRD patterns and SEM pictures]. See DOI: 10.1039/b000000x/

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