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

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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 aluminosilicalte crystals commonly used as adsorbents, ion-exchangers, and catalysts. They are now found to have potential application in membranes, microelectronics devices, bio-sensors, micro-reactors and fuel cells. Conventionally, zeolites are synthesized by autogeneous hydrothermal crystallization of hydrogels composed of alumina, silica, and alkaline sources. During the synthesis, aging is quite commonly applied to accelerate crystallization, control the crystal size and suppress impurity phases. During aging, a significant change of nuclei distribution in the gel matrix will happen, resulting in a decrease in the duration of crystallization and the nucleation period. The crystal size distribution and average particle size of final products become narrower and smaller, respectively, with the prolongation of the aging time. Furthermore, aging is useful or even necessary in the synthesis of zeolite membranes without seeding, as it increases the nucleation density on the support. High aging temperatures and long aging times can facilitate the subsequent crystallization and lead to the formation of a pure phase zeolite membrane. 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. 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.
reported procedure with a molar ratio of 5.85Na₂O: 2.7SiO₂: 1Al₂O₃: 182H₂O. 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 % Al₂O₃, 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 N₂ 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-35S4800). The mean particle size and particle size distribution (PSD) of samples were also determined on Malven Zetasizer S4800. The mean particle size and particle size distribution of ~ 1 wt%. Based on the PSD data, the average crystal size (D) and specific number of crystals (Ns, number of crystals per one gram of the crystalline end product) were calculated as follows:

\[
D = \frac{\sum N_i \times D_i}{\sum N_i},
\]

\[
N_s = \frac{\sum N_i \times (\frac{\pi}{6}) \times \rho \times \sum N_i \times (D_i)^3}{\sum N_i \times (D_i)^3}.
\]

Where, Nᵢ is the number frequency of the crystals having the size between D and ΔD, Dᵢ = D + ΔD/2. D is the measured equivalent spherical diameter and ρ is the density of zeolite A, which is 2 g/cm³.

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.

The structure of the hydrogel was investigated by transmission electron microscope (TEM JEL-200CX). The sample was prepared by filtering 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. The hydrothermal syntheses were conducted at 80 °C for 3 h.
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 ($N_s$) of products obtained from the hydrogels aged at 2, 5, 8 and 10 MPa are 4.31, 6.27, 8.34 and 12.6 ×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\textsuperscript{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)\textsuperscript{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-aluminosilicate cluster\textsuperscript{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 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 $N_s$ of 4.35, 5.12 and 8.34
in the gel matrixes. The nucleation rate and crystallization rate of 30
considerable difference in the number and distribution of nuclei
hydrogel aged at 10 MPa. These phenomena indicate
ambient pressure to 1.2
25 (Table 1). This is ascribed to the effect of high pressure aging.

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

<table>
<thead>
<tr>
<th>Samples</th>
<th>Nucleation rate (h⁻¹)</th>
<th>Crystallization rate (X% · h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite A obtained from</td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydrogel aged under 10 MPa</td>
<td>1.8</td>
<td>87</td>
</tr>
<tr>
<td>Zeolite A obtained from</td>
<td>1</td>
<td>73</td>
</tr>
<tr>
<td>hydrogel aged under ambient</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pressure</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*X denotes as the crystallinity of the sample.

3.4 Effect of the type of gas

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. 8 shows the XRD patterns of the resultant products.

Amorphous product is obtained from the hydrogel aged in CO₂
(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
CO₂. Zeolite A is synthesized from the hydrogels aged in He, H₂
and O₂ (Fig. 7 b-d), which exhibits cubic crystals, with an
average sizes of 1.7, 1.2 and 0.9 μm, with Xs of 4.39, 14.9,
33.6×10¹⁰, 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, H₂, and O₂ in water,
which are 0.6 mL/L, 18.2 mL/L and 31 mL/L, respectively, at
ambient temperature and pressure. 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< H₂< O₂). 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. 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

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.

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 matrices. 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.
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 N₂ atmosphere.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystal sizes (µm)</th>
<th>XRD crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High pressure aging</td>
<td>Conventional aging</td>
</tr>
<tr>
<td>Silicalite-1</td>
<td>34</td>
<td>52</td>
</tr>
<tr>
<td>SAPO-34</td>
<td>10</td>
<td>18</td>
</tr>
<tr>
<td>Zeolite Y</td>
<td>0.7</td>
<td>1.1</td>
</tr>
<tr>
<td>AlPO4-5</td>
<td>26</td>
<td>37</td>
</tr>
</tbody>
</table>

In order to verify the above proposed mechanism, we observed the gels without aging and those aged under ambient pressure and at 10 MPa N₂ 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 N₂ atmosphere (Fig. 9 b and c). The number of bright spots in the gels aged at 10 MPa N₂ 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. 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 AlPO₄-5 (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 N₂ 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 

Fig. 9 TEM images of products obtained from hydrogels without aging (a), aged under ambient pressure (b) and at 10 MPa N₂ atmosphere (c) for 24 h.
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 silica-lite-1, and aluminophosphate molecular sieves, such as SAPO-34 and AlPO4-5.

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Notes and references

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