The synthesis of mesoporous aluminosilicate using microcline for adsorption of mercury(II)

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Received 25 April 2007; accepted 30 June 2007
Available online 20 August 2007

Abstract

An economical mesoporous aluminosilicate was synthesized with microcline as starting material and the precursor 13X zeolite as seed for crystal structure on mesoporous walls. In this method, a mixture of microcline and Na\textsubscript{2}CO\textsubscript{3} with a molar ratio of 1:1.05 was first calcined at 1093 K for 2.5 h. The calcined materials were mixed with 35 ml C\textsubscript{16}TMABr aqueous solution (containing 8.2 g C\textsubscript{16}TMABr) and the precursors of 13X zeolite, resulting in mesoporous aluminosilicate after crystallization of the solution at 378 K for 48 h and calcination of the powder at 823 K for 5 h. The as-synthesized sample has a uniform pore diameter distribution centered at 3.7 nm. The as-synthesized sample had BET surface area of 725 m\textsuperscript{2}/g and BJH mean pore diameter of 3.7 nm. The FT-IR results revealed that the building units of 13X zeolite were inserted into the pore walls of the as-synthesized sample. The adsorption ratio of mercury(II) onto the as-synthesized adsorbent was about 95%. The adsorption process was found to be spontaneous and can be explained by particle diffusion and chemical ion-exchange mechanisms. The equilibrium concentration of mercury(II) using the as-synthesized sample as the adsorbent was under 1 µg/L, making the concentration of mercury meet the limit for drinking water in China as recommended by the World Health Organization.

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Keywords: Mesoporous; Microcline; Mercury(II) adsorption; Adsorption mechanism; Aluminosilicate

1. Introduction

The presence of mercury in the environment is a serious global social and environmental problem. Many industrial facilities, such as metal plating, mining operations, fertilizer industry, tanneries, and textile industries, discharge heavy metals, including mercury, via their waste effluents. A very low concentration of mercury in water can cause severe physiological and health effects. Conventional methods for the removal of mercury ions from waste streams include carbon adsorption [1], ion exchange [2,3], chemical precipitation [4], membrane filtration [5], coprecipitation/adsorption [6], and photoreduction [7,8]. But most of these methods require either high energy or large quantities of chemicals. Conventional precipitation methods do not always provide a satisfactory removal rate to meet pollution control limits; synthetic ion-exchange resins are often expensive [9–11], and adsorbents have low mechanical strength, weak hydrothermal stability, or a weak chemical union with the metals. These factors have led the scientific community to develop new techniques and adsorbents to remove mercury from the environment.

Porous silica is a class of materials that have been considered hopeful adsorbents for mercury removal. Mesoporous silica materials were first synthesized in 1992 [12]. The so-called M41S materials are prepared with micelles of quaternary ammonium detergents as the template. M41S materials have relatively large and uniform pore size (20–500 Å), large surface areas (up to 1000 m\textsuperscript{2}/g), highly ordered pore structures, and very narrow pore-size distributions. These interesting properties make porous silica an attractive candidate for appli-
cations in separation technologies, heterogeneous catalysis, and biomedicine [13–15]. But porous silica has poor hydrothermal stability [16], which hinders it from being widely utilized. Several successful methods for improving its hydrothermal stability are already used, such as increasing thickness of the porous walls, incorporating primary and secondary building units of zeolite into the porous walls, and increasing the degree of silica condensation [17–21]. Among all the methods mentioned above, mesoporous materials with their porous walls containing zeolite-building units are the most attractive. Some work has been done concerning the assembly of mesoporous materials with preformed nanosized zeolite precursors. This has improved the hydrothermal stability of the mesoporous materials considerably [19–21].

Most mesoporous aluminosilicate molecular sieves are synthesized with pure chemicals, tetraethoxysilane, aluminum isopropoxide, sodium aluminate, and other aluminosilicates as Si and Al sources. Very limited mesoporous aluminosilicates were synthesized from natural ores. Recently, metakaolin was used and Al sources. Very limited mesoporous aluminosilicates were synthesized from natural ores. Recently, metakaolin was used as an aluminum source in the synthesis of Al-MCM-41 [22]; NaY and kaolin were used as starting materials to synthesize kaolin/NaY/MCM-41 composites that exhibit good hydrothermal stability [23]; and fly ash was used to synthesize MCM-41 [24,25]. Microcline, an ore, is rich in silicon and aluminum, is very cheap, and can easily be obtained. The silicon and alumina in microcline are mixed uniformly on the atomic scale. Obviously, using microcline as the starting material to synthesize mesoporous aluminosilicates is of great importance. Microcline is often used to prepare potassium carbonate [26] and to synthesize 13X zeolite [27]. However, studies of synthesizing mesoporous molecular sieves containing Al and Si oxides using microcline as starting material are scarce.

This paper reports an economical way to synthesize mesoporous molecular sieve from microcline powder as starting material, the precursors of microporous 13X zeolite as seeds for crystal structure on mesopore walls, by integrating the synthesis process of MCM-41 and 13X zeolite, with C16TMABr as structure-directing agent. To test their sorption properties, the as-synthesized mesoporous aluminosilicate was used in further regeneration of aqueous solution contaminated by low mercury(II) content (20 µg/L), and the results were compared with those for pure Si-MCM-41 and 13X zeolite.

2. Experimental

2.1. Chemicals and materials

Microcline powder used in this work was collected from Song County in mid-China with an average molar mass 68 g/mol. The chemical composition of microcline is listed in Table 1. The main components of microcline are silica (65.00 wt%) and alumina (16.38 wt%), with a small amount of other elements including Fe, Ca, Na, and K. Other chemicals used in the synthesis process, including Na2CO3, C16TMABr, Na2SiO3·9H2O, NaOH, Al(OH)3, hydrochloric acid, and silica, were supplied by Beijing Chemical Reagents Company (China).

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>FeO</th>
<th>Na2O</th>
<th>K2O</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>HN-1</td>
<td>65.00</td>
<td>16.38</td>
<td>0.66</td>
<td>0.48</td>
<td>0.86</td>
<td>0.89</td>
<td>13.83</td>
</tr>
</tbody>
</table>

2.2. Synthesis

2.2.1. Preparation of Si and Al sources

Microcline powder was milled to such a grain size that more than 95% of particles were under 77 µm. Based on our group’s previous study on microcline [26,27], the proper molar ratio of microcline powder and Na2CO3 was 1:1.05, the calcination temperature was about 1093 K, and the calcination time was 2.5 h for high solubility (90%). Then the microcline compound was dissolved in 0.01 mol/L NaOH aqueous solution and aged in the static state for 24 h at 293 K.

2.2.2. Preparation of precursors of 13X zeolite

The precursors of 13X zeolite were prepared as previously reported in the synthesis of 13X zeolite [28]. The main process is as follows: the chemicals Na2SiO3·9H2O, NaOH, and Al(OH)3 with molar ratio of Na2O:Al2O3:SiO2:H2O equal to 10:1:8:300, were mixed in distilled water in the boiling state and stirred for 1 h. After that, aged at 293 K in a static state for 24 h to form the precursors of 13X zeolite.

2.2.3. Synthesis of mesoporous adsorbent

In the experiment in synthesizing mesoporous adsorbents, the molar ratio of (SiO2+Al2O3):Na2O:C16TMABr:H2O was equal to 1:0.2:0.15:25.5, and the molar ratio of SiO2:Al2O3 was equal to 40:1. Exactly as follows, 35 ml C16TMABr aqueous solution containing 8.2 g C16TMABr was mixed with the calcined microcline solution, the precursors of zeolite 13X, and silica (8.06 g, as a supplement for changing the Si and Al molar ratio). The pH value of the mixture solution was adjusted to 10.5 with hydrochloric acid, resulting in a gel, after 1 h continuous stirring. The gel was transferred into a 70-mL Teflon-lined stainless autoclave and crystallized at 378 K for 48 h. After crystallization, the autoclave was cooled to 293 K naturally, and the solid product was filtered out and dried at 378 K for more than 10 h. At last, the powder was calcined in air at 823 K for 5 h to remove the surfactant, using a ramping rate of 2 K/min.

2.3. Characterization

X-ray powder diffraction analysis (Siemens D5005) using CuKα (λ = 1.54 Å) radiation was performed to identify the product phase and to calculate the repeat distance on the (100) plane. The surface area and pore size of the sample were measured by nitrogen isotherms at 77.4 K using a Micromeritics ASAP2405 system. The sample was degassed for 10 h at 573 K before the measurements. The pore-size distribution for a mesoporous sieve was calculated using the Barrett–Joyner–Halenda (BJH) model. The infrared (IR) spectrum of the sample was recorded on a Perkin–Elmer FT-IR spectrometer (PE983G) with a resolution of 1 cm−1. The solid state
MAS NMR spectrum was recorded on a VARIAN UNITY IN-OVA 300M spectrometer at 78.155 MHz, using 0.3-µs pulse length, 1-s recycle delays, and a spinning rate of 7 kHz. The accumulation rate was 6500 scans with a repetition time of 0.02 s. Chemical shifts were quoted in ppm from Al(H2O)33+. Transmission electron microscopy (TEM) images were taken on an H-8100 transmission electron microscope operated at 200 kV.

2.4. Adsorption experiments

In a typical sorption process, 0.2 g adsorbent was suspended in 20 ml aqueous solution with mercury(II) concentration of 20 µg/L, and the adsorption of mercury(II) in aqueous solution onto the mesoporous adsorbent was processed between pH 2 and 6. The mixture solution in a tube was set in a water oscillator, keeping the temperature at 293 K for 10 to 60 min, and the oscillation frequency at 135 rpm. Potassium bichromate was used in the preparation of an aqueous solution contaminated by mercury ions to avoid mercury ions being oxidized, and the molar ratio of K2Cr2O7 and Hg2Cl2 was equal to 1.36:1. The concentration of mercury ions to avoid mercury ions being oxidized, and the molar ratio of K2Cr2O7 and Hg2Cl2 was equal to 1.36:1. The concentration of mercury in aqueous solution was determined by the equation

\[ \theta = \frac{C_0 - C_e}{C_0} \times 100\% , \]

where \( C_0 \) and \( C_e \) are the initial and the equilibrium concentrations of mercury(II) in the aqueous solution.

3. Results and discussion

3.1. Calcination of microcline

To break down the aluminosilicate in the framework, the microcline powder needs to be calcined at a high temperature. Based on our previous work [26,27,29], the temperature for baking of the microcline was usually between 923 and 1153 K, and the additive can be CaCO3, Na2CO3, or K2CO3. Upon consideration of the solubility of CaSiO3, Na2SiO3, and K2SiO3 formed after calcination and the cost of synthesizing molecular sieves, Na2CO3 was chosen as the additive. The composition of the calcined microcline powder is shown in Table 2. The main components of calcined microcline are silica, alumina, and sodium monoxide. The following main reaction occurred during the calcination process deduced from the XRD patterns (not shown) in the equation

\[
\text{KAlSi}_3\text{O}_8 \text{ (microcline) + } 3\text{Na}_2\text{CO}_3 \rightarrow 3\text{Na}_2\text{SiO}_3 + \frac{1}{3}\text{K}_3\text{Al}_3\text{O}_6 + 3\text{CO}_2↑ . \]

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>FeO</th>
<th>CaO</th>
<th>Na2O</th>
<th>K2O</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>HN-2</td>
<td>38.72</td>
<td>9.76</td>
<td>0.39</td>
<td>0.29</td>
<td>0.51</td>
<td>41.88</td>
<td>8.24</td>
<td>99.78</td>
</tr>
</tbody>
</table>

The Na2SiO3 and K3Al3O6 formed during the calcination process may be used as Si and Al sources for synthesizing the molecular sieve.

3.2. X-ray diffraction

The as-synthesized sample is denoted as SAR-3. Fig. 1 shows the XRD pattern of sample SAR-3. The typical long-range ordered hexagonal mesoporous phase can be verified by the observation of three distinct diffraction peaks indexed as (100), (110), and (200) in the low 2θ region of 1.5°–7°. The interplanar distance \( d_{100} \) and the hexagonal unit cell parameter \( a_0 = 2d_{100}/\sqrt{3} \) of sample SAR-3 were 4.39 and 5.07 nm, respectively. The high-angle XRD pattern did not show any diffraction peak (not shown), suggesting that the building units of 13X zeolite were well dispersed in the pore-wall.

3.3. Nitrogen adsorption–desorption isotherms

Fig. 2 shows N2 adsorption–desorption isotherms of the synthesized sample SAR-3. The sample gave a type IV standard isotherm with a deep inflection between relative pressure \( P/P_0 = 0.3 \) and 0.4, characteristics of capillary condensation, indicating the uniformity of the mesopore-size distribution [20]. The slope at a low relative pressure, under 0.3, suggested that there also existed a microporous structure in sample SAR-3. The BET surface area of sample SAR-3 was 725 m2/g, and the BJH mean pore diameter was 3.7 nm. The pore wall thickness was 1.37 nm, calculated by the formula

\[ T = a_0 - d_{\text{BJH}} . \]

where \( a_0 \) is the hexagonal unit cell parameter, determined by XRD, and \( d_{\text{BJH}} \) is the BJH mean pore diameter, given by N2 adsorption.

Fig. 3a shows the pore size distribution of SAR-3 in mesoporous area. The result suggested a narrow mesopore-size distribution ranging from 2.5 to 3.4 nm. The micropore-size distribution also found microporous structure in sample SAR-3, for the reason of measurement system, only gave some points (Fig. 3b).

3.4. FT-IR spectroscopy

Fig. 4 shows the FT-IR spectrum of sample SAR-3. On the curve, the vibrational bands at 1097, 802, and 460 cm⁻¹ are attributed to the characteristic silica framework in MCM-41 [30]. Sample SAR-3 exhibits absorption bands around 2923 and 2852 cm⁻¹, assigned to the C–H vibrations of surfactant molecules, because the surfactant molecules were not removed thoroughly when the samples were calcined in an insufficient-oxygen environment. The absorption band around 1443 cm⁻¹ is
attributed to Lewis acid site [31]. The band around 1741 cm$^{-1}$ is attributed to the characteristic of water molecules inside the framework, and the bands around 3300 and 3628 cm$^{-1}$ correspond to OH$^-$ groups from water molecules [32]. This is because the samples absorb some water when they are exposed to the air, and this means that the surface of SAR-3 is hydrophilic. The shoulder vibrational band around 551 cm$^{-1}$ is similar to that of zeolite 13X [33,34], assigned as characteristic of 5-ring and 6-ring T–O–T (T can be Si or Al) in the pore walls.

3.5. $^{27}$Al MAS-NMR

The extent to which aluminum is incorporated into the framework is an important characteristic affecting the surface acidity and reactivity of mesoporous sieves. It is generally agreed that tetrahedrally coordinated aluminum can be identified with framework aluminum, while octahedrally coordinated aluminum may also be present within the pores. Fig. 5 shows the $^{27}$Al MAS NMR spectrum of sample SAR-3. The spectrum of SAR-3 shows only one peak at 57 ppm, which is ascribed to tetracoordinated aluminum [35–38]. This indicated that all the aluminum was incorporated into the silica matrix of SAR-3, and the dealumination phenomenon did not occur for SAR-3 during its calcination process. The amount of octa-coordinated aluminum evaluated by deconvolution of the spectrum was 99.9%.
The formation of framework aluminum by the isomorphic substitution of the silica–alumina phase can create Brønsted acidity [39,40], which is useful in catalysis and adsorption.

3.6. TEM images and chemical composition

Fig. 6 is the TEM images of SAR-3. The image in Fig. 6a reveals hexagonal ordered pore arrangements in the (001) direction, which give a mesopore diameter of about 2 nm in the perpendicular (001) direction. The image in Fig. 6b displays the pores parallel to each other in the (100) or (010) directions.

Table 3 lists the chemical compositions of SAR-3, pure MCM-41, and 13X zeolite. The main components of SAR-3 are silica (72.57 wt%) and alumina (9.16 wt%). The main component of pure MCM-41 synthesized with water glass is silica (95.01 wt%). The main components of 13X zeolite synthesized with microcline from Song County in mid-China are silica (36.15 wt%) and alumina (21.96 wt%).

3.7. Sorption property

3.7.1. Effect of pH

The rates of mercury(II) adsorption onto SAR-3 changed with different pH values, as shown in Fig. 7. The adsorption rates were found to be higher with increased the pH value. This may be explained by the adsorption surface becoming less positive as the pH value increases, and therefore the electrostatic attraction between mercury(II) ions and SAR-3 surface being likely to be increased. The optimum pH value at which the maximum adsorption rate could be achieved was 5.5. For all subsequent experiments, this optimum pH value was used.

3.7.2. Effect of contact time

The adsorption rates as a function of time (Fig. 8) were used to determine an optimum contact time for the adsorption of mercury(II) ions onto SAR-3. As can be seen from the figure, there is a rapid uptake within 20 min and adsorption equilibrium is attained within 30 min.

3.7.3. Effect of different adsorbents

The adsorption experiments were carried out at pH 5.5, adsorption time 30 min, and temperature 293 K using SAR-3, Si-MCM-41 [41], and 13X zeolite [28]. The adsorption rates are given in Table 4, and for comparison, the structure properties of SAR-3, Si-MCM-41, and 13X zeolite are also included in Table 4. The rates of mercury(II) adsorption onto SAR-3, Si-MCM-41, and 13X zeolite were 95, 79, and 71%, respectively. The sorption rate of SAR-3 was increased 16% compared with that of Si-MCM-41, and 24% compared with that of 13X zeolite. The equilibrium concentration of mercury(II) with SAR-3 as the adsorbent was 0.9 µg/L, smaller than the mercury limit (1 µg/L) for drinking water in China recommended by the World Health Organization, while that with Si-MCM-41 as the adsorbent was 4.25 µg/L, and that with 13X zeolite as the adsorbent was 5.7 µg/L. The low equilibrium concentration of mercury(II) with SAR-3 as the adsorbent may be the reason that the building units of 13X zeolite in the pore wall strengthened the acidity.
adsorption constant, $J \text{ mol}^{-1}$, and $E$ is the magnitude of the sorption potential [42]. In order to understand the adsorption mechanisms, the D–R isotherm describes adsorption on a single type of uniform pores. In this respect the D–R isotherm is an analogue of the Langmuir type but it is more general, because it does not assume a homogeneous surface or constant sorption potential [42]. In order to understand the adsorption type, a D–R isotherm was obtained. The D–R isotherm is given by the following equation:

$$Q = Q_m \exp(-k \varepsilon^2).$$

The linearized form of the equation is given as

$$\ln Q = \ln Q_m - k \varepsilon^2,$$

where $\varepsilon$ (Polanyi potential) is $[RT \ln(1 + (1/C_e))]$ ($R$ is the gas constant, J mol$^{-1}$ K$^{-1}$; $T$ is the absolute temperature, K; and $C_e$ is the equilibrium concentration of metal ions, mmol L$^{-1}$), $Q$ is the amount of solute adsorbed per unit weight of adsorbent (mol g$^{-1}$), $k$ is a constant related to the adsorption energy (mol$^2$ kJ$^{-2}$), and $Q_m$ is the adsorption capacity (mol g$^{-1}$).

The values of $Q_m$ and $k$ were calculated from the intercept and slope of $\ln Q$ versus $\varepsilon^2$ plot, and $k$ has two values ($-0.0109$ and $-0.0027$) in the present work. The mean free energy of adsorption ($E$) was calculated from the $k$ values using the equation

$$E = (-2k)^{-0.5}.$$

The magnitude of $E$ is useful for estimating the type of adsorption process. If $E$ is between 8 and 16 kJ/mol, the adsorption process occurs by chemical ion exchange, and if $E$ is less than 8 kJ/mol, the adsorption is physical in nature. From Eq. (6), the numerical values of $E$ were calculated as 6.67 and 13.57 kJ/mol for adsorption times of 0–20 and 20–30 min, respectively, indicating that the first adsorption period involves a particle diffusion mechanism, and the second period involves a chemical ion-exchange mechanism.

### 4. Conclusions

The mesoporous adsorbent, inlaid with zeolite 13X building blocks in its pore walls, was hydrothermally synthesized with microcline as aluminum and silicon source and precursors of microporous 13X zeolite as seeds for crystal structure on mesopore walls by integrating the synthesis processes of MCM-41 and 13X zeolite. The BET surface area of the as-synthesized sample was 725 m$^2$/g and the pore volume was 0.67 cm$^3$/g. The BJH mean pore diameter of the adsorbent was 3.7 nm, the mean pore-wall thickness was 1.37 nm, and the adsorbent has a narrow pore size distribution ranging from 2.5 to 3.4 nm. The adsorption rate of mercury(II) onto the as-synthesized sample was 95%, increased 16% over that of mercury(II) onto Si-MCM-41 and 24% over that of mercury(II) onto 13X zeolite. The adsorption process was found to be spontaneous and can be explained by particle diffusion and chemical ion-exchange mechanisms. The equilibrium concentration of mercury(II) in the aqueous solution using the as-synthesized sample as the adsorbent was 0.9 µg/L, under the mercury limit (1 µg/L) for drinking water in China recommended by the World Health Organization.

### Acknowledgments

The work was funded by the National Laboratory of Mineral Materials, China University of Geosciences, Beijing, People’s Republic of China (Grant 06006), and the Beijing Synchrotron Radiation Laboratory, Institute of High Energy Physics, Chinese Academy of Science.

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