Non-hydrothermal synthesis and characterization of MCM-41 mesoporous materials from iron ore tailing

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Abstract

This study reported a facile synthetic method for MCM-41 mesoporous material at room temperature using iron ore tailing and cetyltrimethylammonium bromide (CTAB) as a silicon source and a structure-directing agent, respectively. The obtained product was systematically characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and nitrogen absorption–desorption measurement. It was confirmed that the as-synthesized material exhibited a well-ordered mesostructure with high surface area of ca. 634 m\textsuperscript{2}/g, large pore volume of 0.61 cm\textsuperscript{3}/g, and average pore diameter of 3.8 nm. The removal efficiency towards model pollutant methylene blue (MB) was performed through produced MCM-41 and 111 mg/g of MB could be eliminated under an optimal condition. Therefore, the material could be potentially used as a low-cost and efficient adsorbent candidate to treat organic contaminants in wastewater or other fields.

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1. Introduction

Since the first new family of ordered mesoporous materials sieve with regular and constant pore diameter from 2 to 10 nm, named M41S, was constructed by the scientists of the Mobil Corporation Strategic Research Center [1–3], numerous research have been concentrated on MCM-41 due to the high specific surface area (up to 1000 m\textsuperscript{2}/g or higher), narrow pore size distribution and high specific pore volume. Mesoporous MCM-41 has been proven very useful as a catalyst/support, an adsorbent, and a nano-reactor for various materials synthesis for its excellent properties [4–7].

Commonly, mesoporous MCM-41 molecular sieves are synthesized by the hydrothermal method in strong base media [8,9], Compared with traditional hydrothermal synthesis route, the benefits of using room-temperature route are (1) short reaction time, (2) saving cost and power, (3) good reproducibility and (4) use of inexpensive autoclaves [10]. The traditional silica sources utilized for the synthesis of mesoporous silica, include sodium silicate, fumed silica, water glass, and tetraethyl orthosilicate (TEOS) [10–13]. However, the major drawback of these precursors is high starting costs of the raw material, which results in high production costs. Furthermore, the high toxicities of these preferred silica precursors and the structure directing agents used during synthesis require careful attention and handling facility [14]. Consequently, it can be an important contribution in the industrial scale production of mesoporous materials to use a cheaper and environmental friendly silica source instead of an expensive reagent in the synthesis of MCM-41. Recently, much attention has been paid to a new process forming mesoporous silica. Misran et al. [15] reported a novel route in the synthesis of MCM-41 mesoporous materials by coal fly ash with the hydrothermal method, using cetyltrimethylammonium bromide (CTAB) as a structure directing agent. Moreover, the application of layered silicate minerals such as bentonite, sepiolite have been reported [14,16,17].

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Among these alternatives, iron ore tailing could be a favorable candidate for the synthesis of novel material. Iron ore tailing is one of the fast accumulated wastes throughout the world with the increasing demand for iron, steel and construction materials [18–22]. In general, iron ore tailing is comprised of quartz, hematite, alumina, and small amount of transition metal oxides. Owing to the high contents of useful SiO$_2$, Fe$_2$O$_3$, and Al$_2$O$_3$ in iron ore tailing, it makes perfect economic outlook to recover these minerals for industrial applications. In this situation, it is a very useful research to covert iron ore tailing into mesoporous materials such as MCM-41.

In this paper, we report an attempt to synthesize MCM-41 at room temperature using silica source from iron ore tailing without a hydrothermal treatment. In this process, the pH value and the initial concentration of structure directing agent/silica ration are controlled.

2. Experimental

2.1. Materials

The iron ore tailing used in this study was collected from the tailing ponds of iron ore industries (Maanshan, China), and dried in the air at 373 K. Hydrochloric acid (HCl) was used for digestion of iron ore tailing, while sodium hydroxide (NaOH) was used for leaching out of SiO$_2$. The structure-directing agent was CTAB. Ammonia solution (NH$_3$·H$_2$O), ethanol and deionized water were used for synthesis of MCM-41 mesoporous materials. MB was used as received for adsorption experiments without purification.

2.2. Extraction of Si solution from iron ore tailing

Iron ore tailing was weighted (100 g), and mixed with 214 mL of HCl (30 wt%) in an oil bath at 373 K for 1.5 h under stirring (200 rpm), aiming at extraction of iron species as much as possible. The leaching rate of iron was up to 95%. The cooled solution was separated from the mixture by filtration. The clear filtrate containing FeCl$_3$ along with washing was stored for other purposes. The content of SiO$_2$ in the acid insoluble residue was close to 80% that it can be used as Si source for the synthesis of MCM-41.

The above acid insoluble residue was firstly dried and then heated in a muffle furnace at 1200 K for several hours so as to get a better dissolution of SiO$_2$. After cooling down, 10 g material mentioned above was mixed with 22 g NaOH. Deionized water was then added to make a solid to liquid volume ratio of 1:2. The aqueous solution was boiled at 373 K for 6 h under stirring, and then the silica was changed to a sodium silicate solution. The resulting suspension was filtered with water several times to remove impurities. The leaching rate of SiO$_2$ was approximately 40% and the colorless, transparent solution was used to synthesize mesoporous silica [23].

2.3. Preparation of MCM-41

1.2 g CTAB was dissolved in 15 g deionized water and stirred for 20 min at room temperature. Then, 80 mL sodium silicate from acid insoluble residue was slowly added to the CTAB solution and stirred for 2 h. After that, the pH value was adjusted to 10.0 by adding ammonia solution. The final molar composition of the gel was CTAB/SiO$_2$/H$_2$O = 0.13:1:220. The mixture was stirred for 30 min, and then the gel was put in an oven at 373 K for 48 h. The resultant solid was filtered, washed repeatedly with deionized water, air-dried overnight at 373 K, and finally calcined at 823 K for 1 h to supply a powder, known as MCM-41.

2.4. Removal of selected organic pollutant

MB (C$_{16}$H$_{18}$ClN$_3$S), a kind of aromatic heterocyclic compound commonly used in the textile industry, was selected as a model pollutant. Then desired amount of as-obtained MCM-41 was added to a 100 mL of 20 mg/L MB stock solution before pH value of the mixture was adjusted to around 7. The adsorption reactions were performed in 250 mL conical flask by shaking at 298 K. The samples were taken every 10 min and centrifuged at 10,000 rpm for 20 min. The supernatant solutions were measured using UV–vis spectroscopy (China, Model T6) on a wavelength of 664 nm.

2.5. Characterization

The crystal structures of the samples were identified by using an X-ray powder diffraction (XRD) with Cu K$_\alpha$ irradiation ($\lambda=0.15406$ nm) and the accelerating voltage and current used were 40 kV and 100 mA at room temperature. A scan angle of $2\theta=1.5–10^\circ$ was used to identify mesoporous material MCM-41, whereas, $2\theta=10–70^\circ$ was used for identifying phases present in the iron ore tailing and acid insoluble residue powder.

FTIR spectra were performed on a PerkinElmer 100 spectrophotometer in the range of 450–4000 cm$^{-1}$, taking dried KBr as background peaks. The samples with KBr powder were pressed into tablets for testing.

The N$_2$ adsorption–desorption isotherms of MCM-41 were measured at 77 K after the samples had been outgassed at 573 K for 60 min. The specific surface area was calculated from the nitrogen adsorption isotherms within the relative pressure range of 0.04–0.10 by the BET method. The total pore volume was obtained from the maximum amount of nitrogen gas adsorbed at partial pressure ($P/P_0=0.985$).

The surface particle morphologies were observed through a scanning electron microscope (CAMBRIDGE S-360). In the SEM analysis, the samples were coated with a thin layer of gold and mounted on a copper stub using a double-stick tape.

Transmission electron microscopy (TEM) experiments were performed by using an instrument (JEOL JEM-2010F) with an accelerating voltage of 200 kV. The samples for electron microscopy were prepared by dispersing in ethanol. A drop of homogeneous dispersed solution was loaded onto a
carbon-coated copper grid and allowed to dry prior for analysis.

3. Results and discussion

3.1. Properties of iron ore tailing and acid insoluble residue

The particle size has a great impact on the extraction of Si from iron ore tailing. The smaller particles exhibit higher reactivity due to higher specific surface area. In the present study, the mean particle size of iron ore tailing is about 2.76 μm. The chemical compositions of iron ore tailing are shown in Table 1. Iron ore tailing primarily constitute of silica and iron oxide with small amounts of alumina, calcium oxide, magnesium oxide and titanium dioxide, while acid insoluble residue are mainly comprised of silica and alumina. The XRD patterns of iron ore tailing and acid insoluble residue are shown in Fig. 1. The XRD signatures of these powders reveal that the main crystalline phases found in the iron ore tailing are quartz, hematite and kaolinite. The almost disappearance of hematite phase shows that iron oxide in its natural crystalline form has reacted with HCl forming FeCl₃ after the acid leaching process. Therefore, the acid insoluble residue, which is comprised of lots of silica as a cheap and green silica source, can be used to produce mesoporous silica MCM-41.

3.2. Characterizations of MCM-41 samples

Hexagonal (MCM-41) mesoporous silica is an example of highly periodic silica phases and it is normally reflected by the highly distinct XRD signatures at low-angle range. Fig. 2 shows the XRD pattern of calcined MCM-41 sample at 2θ angles from 1.5° to 10°. The XRD signatures exhibit a characteristic intense (100) peak and two obvious (110) and (200) reflections at 2θ = 2.3°, 3.9°, 4.4°, respectively. The strong peak (100) directly indicates the presence of MCM-41 structure, and the two weak peaks (110) and (200) can be indexed to the P6mm space group, indicating a hexagonal mesostructure material with a high degree of long range ordering of the structure. The d₁₀₀ is calculated by the Braggs law 2d sin θ = nλ and its value is 3.86 nm. The hexagonal unit cell parameter (the center-to-center pore distance) a₀ is 4.39 nm according to the equation a₀ = 2d₁₀₀/√3. So the value of the pore wall thickness for MCM-41 is about 0.6 nm. In general, the XRD signatures of MCM-41 materials are in agreement with earlier reports [1,24–26].

In addition to X-ray diffraction examination, the formation of the mesoporous structure is also confirmed by sorption tests of the synthesized samples. Fig. 3 shows the N₂ adsorption–desorption isotherms of MCM-41 synthesized from iron ore tailing. The isotherm with a hysteresis for the MCM-41 shows a typical type IV according to the IUPAC classification, which is a typical feature for mesoporous materials [27,28]. The isotherm exhibits three defined stages, with the inflection points at P/P₀ = 0.25 and P/P₀ = 0.4. The first stage is due to monolayer and multilayer adsorption of nitrogen to the walls of the mesopores at low relative pressures (P/P₀ < 0.25). The second stage is characterized by a sharp increase in adsorption (0.25 < P/P₀ < 0.4). As the relative pressure increases, the isotherms show that adsorption amount increases abruptly because of the capillary condensation within the uniform mesopores. The third stage in the adsorption isotherm gradually increases at high P/P₀ (ca. 0.4–1.0) values due to multilayer adsorption on the external surface of the particles. The isotherms of mesoporous materials with high pressure can be attributed to the condensation of nitrogen within voids formed by crystal aggregates.

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron ore tailing (wt%)</td>
<td>50.88</td>
<td>13.62</td>
<td>25.18</td>
<td>0.59</td>
<td>3.26</td>
<td>0.28</td>
</tr>
<tr>
<td>Iron ore tailing (mol/100 g)</td>
<td>0.848</td>
<td>0.134</td>
<td>0.157</td>
<td>0.015</td>
<td>0.058</td>
<td>0.004</td>
</tr>
<tr>
<td>Acid insoluble residue (wt%)</td>
<td>77.10</td>
<td>13.84</td>
<td>1.15</td>
<td>0.49</td>
<td>0.62</td>
<td>0.37</td>
</tr>
<tr>
<td>Acid insoluble residue (mol/100 g)</td>
<td>1.295</td>
<td>0.136</td>
<td>0.007</td>
<td>0.012</td>
<td>0.011</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Fig. 1. X-ray diffraction pattern of iron ore tailing and acid insoluble residue. (Key: (K) kaolinite, (Q) quartz, and (H) hematite).

Fig. 2. X-ray diffraction patterns of MCM-41 samples.
The BET equation is applied to the monolayer region on the isotherm to estimate the surface area and the average pore diameter is calculated by gas desorption measurements. The BET surface area, specific pore volume and average pore diameter of MCM-41 from iron ore tailing are 634 m$^2$/g, 0.61 cm$^3$/g and 3.85 nm, respectively. The values of structure parameters (surface areas and pore diameters) are in good agreement with values of generally synthesized materials, although lower than those of MCM-41 prepared from pure silica source of TEOS in literatures [10,29,30]. This result indicates that mesoporous materials prepared from TEOS would be more reactive and have higher amount of silicate anions. The present higher amount of silicate anions could condense and hydrolyze, resulting in higher surface area[31].

Fig. 4 shows the FTIR spectrum of the MCM-41 from iron ore tailing over the range of 450–4000 cm$^{-1}$. In the spectrum, there are no peaks at ca. 2921 cm$^{-1}$ and ca. 2851 cm$^{-1}$ corresponding to $n$-C–H and $d$-C–H vibrations of surfactant molecules, indicating that all organic materials are removed during calcination[32].

The broad band at ca. 3446 cm$^{-1}$ may be attributed to surface silanols and the adsorbed water molecules, while some bands at ca. 1636 cm$^{-1}$ are caused by deformation vibrations of the adsorbed water molecules [33–35]. The characteristic absorption bands at ca. 1239 cm$^{-1}$ and ca. 795 cm$^{-1}$ correspond to asymmetric and symmetric stretching vibrations of surface Si–O–Si bridges, respectively. Generally, for calcined MCM-41, the strong band at ca. 1088 cm$^{-1}$ is assigned to internal and external asymmetric Si–O stretching vibrations. The bands at ca. 966 cm$^{-1}$ and ca. 460 cm$^{-1}$ are due to the stretching and bending vibration of surface Si–O-groups, respectively. All these bands are typical of mesophase silica.

SEM images of surfactant-free MCM-41 sample are shown in Fig. 5. It is observed that the particles with aggregates of crystalline compounds in Fig. 5a have a uniform spherical morphology with a mean size of about 1–2 μm. Fig. 5b shows that these particles are formed through the aggregation of very fine, homogeneous grains approximately 200 nm in size.

The internal morphology is observed by transmission electron microscope (TEM) in Fig. 6. As shown in Fig. 6a, the MCM-41 silica has a spherical morphology and agglomeration, which accords well with the conclusion of Fig. 5. From Fig. 6b, we can notice that the obtained MCM-41 shows quite well ordered hexagonal arrays of mesopores, which may suggest the presence of porous structures. The distance between the mesopores about 3 nm is in good agreement with the value determined from XRD and N$\text{\textsubscript{2}}$-adsorption measurements values (ca. 3.8 nm), which confirms that the materials indeed possess a uniform pore system.

3.3. Application in wastewater treatment

It has been shown that mesopores materials with high specific surface areas and ideal pore size distributions usually possess desirable adsorption properties for the removal of pollutants from water [6]. Herein, we used the as-prepared samples to investigate its application in water treatment. As shown in Fig. 7, the whole adsorption process can be divided into two stages. In the first stage, MB is significantly adsorbed within 10 min, and in the following stage up to 60 min, MB molecules are gradually adsorbed. With the increase of MCM-41 addition, the removal capacity gradually increased. The final efficiency of MB removal was up to 97% within 60 min without any other additives at room temperature. The maximum adsorption capacity of MCM-41 is calculated to be 111 mg/g. The favorable performance can be attributed to the porous structure and high surface area of the as-prepared sample. From the above discussion, the as-prepared sample will be an excellent candidate to be applied in the water treatment.

4. Conclusion

In summary, mesoporous silica material MCM-41 has been successfully synthesized using the iron ore tailings as the silica source at room temperature. The characterization of powder
X-ray diffraction of the mesoporous silica is comparable to that derived from using pure silica source. It was shown that the as-prepared samples possessed large pore size, pore volume, and BET surface area. Meanwhile, the electron microscopy results of MCM-41 material indicated that the long-range order structure was achieved and the regular mesoporous hexagonal structure of typical MCM-41 was retained after calcination. The as-prepared MCM-41 materials with mesoporous structures exhibit excellent adsorption capacities toward MB molecules in aqueous solution. Iron ore tailing can be a potential candidate used as a heap source of silica in the production of mesoporous MCM-41 materials.

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References
