Synthesis and characteristics of SBA-15 with thick pore wall and high hydrothermal stability

Junhong Wanga, Hongguang Gea, Weiren Baoa,∗,†

a School of Chemical and Environment Science, Shaanxi University of Technology, Hanzhong 723000, PR China
b State Key Laboratory Breeding Base of Coal Science and Technology Co-founded by Shanxi Province and Ministry of Science and Technology, Taiyuan University of Technology, Taiyuan 030024, PR China

Abstract
Highly ordered SBA-15 mesoporous molecular sieves with thick pore wall and extremely high hydrothermal stability have been synthesized successfully by a facile procedure which directly added the required amount of PVA powder during preparation. As-synthesized materials were characterized by means of X-ray diffraction, nitrogen adsorption–desorption, scanning electron microscope and transmission electron microscope. Results show that the thickness of pore wall of calcined materials is about 5.3 nm, the pore diameter is about 5.6 nm, and the materials have highly ordered mesoporous structure and excellent thermal and hydrothermal stability. The basic structure and morphology of as-synthesized samples are nearly unchanged on addition of different amounts of PVA powder, but specific surface areas and pore volume change. It can be expected that these mesoporous materials with highly hydrothermal stability will have a potential application prospect in the fields of multi-disciplinary.

1. Introduction
Emphasis has already been placed on the fact that mesoporous materials have superior structure properties, such as large specific surface area, uniformity large pore diameter and thick silica wall, and potential apply in the fields of catalysis, adsorption, separation, drugs delivery and optical devices[1–4]. However, one main reason that these mesoporous materials have not been widely applied in industry is their relatively poor hydrothermal stability.

Among of these mesoporous materials, SBA-15 has thick pore wall and relatively high hydrothermal stability to gain extensively study[5–8] and various strategies have been employed to improve further its hydrothermal stability. These approaches contain the past-treatment with organosilane[9,10], pH adjusting[11], increasing hydrothermal treatment temperature[12,13], removing surface Si–OH groups by silylation and F-ions[14,15], addition of crystal seed precursors[16,17], doping heteroatoms[18,19], and addition of inorganic salts[20,21]. These methods have played an important role in improving hydrothermal stability of mesoporous materials. But some methods were too complex to control their synthesis conditions, some reagents were expensive and some had high energy and time consumption. Therefore, a cheap and convenient method to synthesize highly ordered and hydrothermally stable mesoporous molecular sieves is still a challenge.

This paper describes a facile and cheap method to synthesize SBA-15 mesoporous molecular sieves with thick pore wall and extremely high hydrothermal stability by simple addition of the required amount of PVA powder in the course of synthesizing. The mesoporous materials synthesized by this method have high ordered mesopores structure and their orderliness can still keep after they were boiled for 30 days at 105 ºC water. It can be expected that these SBA-15 mesoporous materials will have a potential application prospect as catalyst carrier and adsorbent under high hydrothermal condition.

2. Experimental section
In a typical procedure, 2.0 g of P123 was dissolved in 60 mL of 2 M HCl and 15 mL of deionized H2O at 35 ºC with stirring. The desired amount of PVA powder was added after the above solution became clear. The solution was stirred about 4 h before 4.30 g of tetraethylorthosilicate (TEOS) was added. Then, the sticky intermixture was stirred continually for 20 h at 35 ºC and aged for another 24 h at 100 ºC under static condition. The solid product was filtered, washed, dried and calcined, gained SBA-15 samples.

The X-ray diffraction (XRD) patterns were acquired on the Netherlands X’Pert PRO power diffractometer using Cu Kα radiation.
The data were collected from 0.04 to 10 (2θ) with a resolution of 0.001° and treated by software Jade 6.5. Scanning electron microscopy (SEM) images were produced by field emission scanning electron microscopy with a Hitachi S4800. Transmission electron microscopy (TEM) images were recorded on a FEI Tecnai G2 f 20s-Twin electron microscope operated at 200 kV. N2 adsorption–desorption isotherms were measured at 77 K was measured on a Micromeritics ASAP 2020 volumetric adsorption analyzer. The samples were degassed at 573 K for 3 h under nitrogen before measurement. Specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method over the partial pressure (P/P0) range 0.037–0.2, where a linear relationship was maintained. Pore size distributions were estimated using the Barrett–Joyner–Halenda (BJH) model through the desorption branch of the isotherm.

3. Results and discussion

In this study, we directly added the required amount of PVA powder as assistant template to synthesize SBA-15. Additional amount of PVA was 4.3, 2.2 and 1.1 g and they were assigned as SBA-15-1, SBA-15-2 and SBA-15-3, respectively.

Fig. 1 shows the low angle XRD patterns of calcined SBA-15 synthesized by addition of different amounts of PVA powder. The observed three well-resolved peaks which are indexed as (100), (110), and (200) reflections associated with two dimensional hexagonal symmetry array of mesoporous structure [5–7], indicating that the orderliness of SBA-15 does not decrease or even increase by the addition of PVA powder. This can also be seen from Fig. 5. This is because PVA acts as a soft template to enhance the level of silica condensation and thus to improve the mesoporous structural orderliness and yield better textural properties [22,23]. In addition, it can be seen that 2θ angle value of three samples is the same suggesting that the lattice spacing of SBA-15 has nothing to do with addition amount of PVA. According to software Jade 6.5, the lattice spacing d(100) of three samples is 10.94 nm (Table 1) and close to the superior limit of conventional SBA-15 in the literatures [7,8].

N2 adsorption–desorption isotherms tested were done to further research the changes of mesoporous structure of calcined materials (Fig. 2). The corresponding textural property parameters are given in Table 1. As shown in Fig. 2, all isotherms of samples are type IV with a H1-type loop (Fig. 2a) and the narrow pore size distribution (Fig. 2b) originated from a capillary condensation

![Fig. 1. XRD patterns of SBA-15 synthesized by addition of different amounts of PVA powder and calcined for 6 h at 550 °C in air.](image1)

![Fig. 2. N2 adsorption–desorption isotherms (a) and pore size distribution curves (b) of calcined SBA-15 samples.](image2)

![Fig. 3. Comparison of XRD pattern of SBA-15-3 boiled for 20 days and 30 days and SBA-15 synthesized by a conventional method boiled for 72 h at 105 °C water.](image3)

<table>
<thead>
<tr>
<th>Sample</th>
<th>d(100) (nm)</th>
<th>a00 (nm)</th>
<th>SBET (m² g⁻¹)</th>
<th>Dpore (nm)</th>
<th>Vt (mL g⁻¹)</th>
<th>Vs (mL g⁻¹)</th>
<th>Dv (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-1</td>
<td>9.47</td>
<td>10.94</td>
<td>646</td>
<td>5.63</td>
<td>0.796</td>
<td>0.073</td>
<td>5.26</td>
</tr>
<tr>
<td>SBA-15-2</td>
<td>9.47</td>
<td>10.94</td>
<td>514</td>
<td>5.66</td>
<td>0.735</td>
<td>0.031</td>
<td>5.28</td>
</tr>
<tr>
<td>SBA-15-3</td>
<td>9.47</td>
<td>10.94</td>
<td>687</td>
<td>5.63</td>
<td>0.896</td>
<td>0.076</td>
<td>5.31</td>
</tr>
</tbody>
</table>

*a d00 interplanar spacing for calcined sample.
*b a0 = 2d00/√3.
*c Pore wall thickness, Dm = a0 − Dpore; Vt = total pore volume; Vs = micropore volume.

Table 1: Textural properties of calcined SBA-15 samples synthesized by addition of different amounts of PVA powder. SBET, specific surface area; Dpore, pore diameter.
taking place in the mesoporous with different pore sizes, the
typical characteristic of ordered mesoporous materials with large
and uniform mesopores. From Table 1, it can be seen that (100)
interplanar spacing and pore diameter of the samples are nearly
unchanged, but specific surface areas and pore volume are
different as adding different amounts of PVA powder. Thickness
of pore wall of three samples is almost the same or so 5.3 nm
(Table 1 and Fig. 2b), which is conducive to aggrandizing thermal
and hydrothermal stability of mesoporous SBA-15 (Fig. 3) and will
have a potential application prospect.

Fig. 4 shows the SEM images of calcined SBA-15 synthesized by
adding different amounts of PVA powder. (a) SBA-15-1; (b) SBA-15-2; (c) SBA-15-3.

boiled for 72 h at 105 °C water. It can be seen that (100) and (300)
peaks of SBA-15-3 still remain well, only decrease these peak
intensity, and that the peaks of SBA-15 completely disappear
indicating that SBA-15 samples synthesized by addition of PVA
powder have much higher hydrothermal stability than that of SBA-
15 synthesized by traditional method. In addition, we also tested
the thermal stability of these samples. Results shown that their
(100) peaks still exist but intensity weak when the samples
calcined for 2 h at 900 °C indicating that SBA-15 samples synthe-
sized by both methods have almost the same high thermal
stability.

Fig. 5 shows the TEM images of calcined SBA-15-3 synthesized by
addition of PVA powder. (a) In the direction of the pore axis and (b) in the direction perpendicular to the
pore axis.

The mesostructure of calcined material SBA-15-3 was also
investigated with TEM. As shown in Fig. 5, the material synthesized

Fig. 4. SEM image of calcined SBA-15 synthesized by adding different amounts of
PVA powder. (a) SBA-15-1; (b) SBA-15-2; (c) SBA-15-3.

Fig. 5. TEM images of calcined SBA-15-3 synthesized by addition of PVA powder.
(a) In the direction of the pore axis and (b) in the direction perpendicular to the pore axis.
by addition of PVA powder exhibits a highly ordered hexagonal crystal structure composed of two-dimensional channels with uniform pore size and wall thickness record along (100) and (110) directions, respectively, in accordance with the results of XRD. In addition, the sample shows a thick pore wall (Fig. 5b dark line), this may be a reason that the samples synthesized by addition of PVA powder have a high thermal and hydrothermal stability. According to the pore diameter data from N$_2$-adsorption/desorption isotherms and else literature [24], the thickness of pore wall calcined material is almost consistent with the result of Table 1.

4. Conclusion

In summary, we have introduced a facile strategy to synthesize SBA-15 silica with a highly ordered mesoporous structure, almost constant 5.6 nm pore diameter and 5.3 nm pore wall thickness by direct addition of the required amount of PVA powder in the process of mesoporous materials preparation. These SBA-15 mesoporous materials have an especial high hydrothermal stability so that they will have a broad potential applicability in the fields of chemistry, petrochemistry, fine chemical industry and material manufacturing industry and so on.

Acknowledgment

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References