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Article

Facile solvothermal post-treatment to improve hydrothermal stability of mesoporous SBA-15 zeolite

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ABSTRACT

A simple and effective approach is demonstrated to improve the hydrothermal stability of mesoporous SBA-15 zeolite via a post-synthesis treatment of organic solvents, such as cyclohexane, toluene and *n*-butanol, at 157 or 190 °C for 6–24 h. After hydrothermal treatment at 800 °C for 12 h in 100% steam, the treated SBA-15 retained a well-ordered mesostructure, and retained high surface areas of 192–281 m²/g. SBA-15 zeolite treated by cyclohexane at 190 °C for 24 h showed the highest hydrothermal stability. The stabilization mechanism suggests that the solvothermal treatment has a significant promoting effect on dehydrating Si–OH groups in silica walls to form stable Si(OSi)₄ from Si(OSi)₂(OH)₂ or Si(OSi)₃OH groups. As a result, the wall defects after solvothermal treatment decrease, and the stability of silica is improved remarkably. This promoting effect strongly depends on the solvent properties, treatment temperature, and precursors of SBA-15 zeolite. The treatment by a nonpolar and low boiling point organic solvent displays the highest promoting effect on the calcined SBA-15 zeolite. This approach is simple, has low energy consumption and has potential application in the laboratory and for industry to prepare hydrothermally stable well-ordered mesoporous SBA-15 zeolite.

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1. Introduction

Mesoporous silica, such as SBA-15, has attracted much attention because of their interesting mesostructure and wide application in catalysis as supports [1–5]. The ordered mesopores can improve the diffusion of bulk molecules in channels, catalytic activity, and selectivity. However, many catalytic reactions, such as oxidation, hydrogenation, dehydration, hydration, and Fischer-Tropsch synthesis, are often carried out in the presence of H₂O or even in aqueous solution, and catalysts used in cracking are regenerated in steam at a high temperature. Therefore, high hydrothermal stability is an important feature

of catalytic supports [6–9]. However, mesoporous silica has poor hydrothermal stability. When heated in aqueous solutions or steam for a long duration, the material suffers from the collapse of its ordered mesostructure and a corresponding loss of surface area [10]. Therefore, much research has focused on improving the hydrothermal stability using various approaches, such as removing surface Si–OH groups by silylation [11–14] and F[−] ions [15–17] to form a hydrophobic surface, thickening mesopore walls by adding inorganic salts or using surfactants [18,19], assembling from nanosized zeolite precursors or transferring zeolites to mesoporous materials [20–24], incorporating heteroatoms into the framework [25–28], and

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enhancing the silica condensation of pore walls [29–32].

The silica condensation is an important factor to determine the hydrothermal stability of mesoporous silicas [29–36]. Zhang et al. [29] employed a carbon propping high-temperature treatment at 800 °C to increase the condensation degree. This approach showed superior hydrothermal stability in pure steam at 800 °C for 12 h, but involved a relatively high energy consumption and complicated process. Du et al. [7] successfully synthesized hydrothermally stable mesoporous materials using fluorine-containing surfactants as templates at a high crystallization temperature of 150–220 °C. This success relies on fluorine-containing surfactants having a higher thermal stability than that of the triblock copolymer Pluronic P123, which is used as the backbone to make SBA-15. Thus, the mesopore walls were more condensed at higher crystallization temperatures. However, fluorine-containing surfactants are expensive and environmentally unfriendly, and their application is limited. Pan et al. [31] developed a facile and environmentally friendly approach to increase framework crosslinking using Pluronic P123 as a template. This approach employed a high-temperature hydrothermal crystallization (approximately 200 °C), and the pH was adjusted between 1 and 3 to avoid decomposing the copolymer. The obtained mesoporous aluminosilicates retained an ordered mesostructure after treatment at 800 °C for 5 h in 15% steam with N₂ gas (45 mL/min). However, no results for hydrothermal treatment at 800 °C in 100% steam were given. Therefore, there is potential to further design a simple, highly effective, low energy consumption, and environmentally friendly approach to promote silica condensation and improve the hydrothermal stability of mesoporous SBA-15 zeolite.

In this study, we propose a facile approach to enhance the silica condensation of mesoporous SBA-15 zeolite *via* a post-synthesis treatment of organic solvents at 157 or 190 °C. The obtained SBA-15 zeolites have excellent hydrothermal stability. The effects of solvent, temperature, time, and SBA-15 precursors are investigated to discuss the stabilization mechanism.

2. Experimental

2.1. Chemicals

Triblock copolymer Pluronic P123 (EO₂₀PO₇₀EO₂₀, M_r = 5800; Sigma-Aldrich, St. Louis, MO, USA), aluminum isopropoxide (Lingfeng Chemical Corp., Shanghai, China, analytical grade), tetraethyl orthosilicate (TEOS; Sigma-Aldrich; analytical grade 98%), toluene, cyclohexane, *n*-butanol and hydrochloric acid (Shanghai Chemical Corp., Shanghai, China; analytical grade) were used as received without further purification.

2.2. Synthesis of SBA-15

Mesoporous SBA-15 was synthesized according to a previously published technique [37]. For a typical synthesis procedure, 25.0 g of P123 was dissolved in 750 mL of HCl solution (2 mol/L) at 35 °C, 52.0 g of TEOS was added into the solution and hydrolyzed at 35 °C for 12 h with vigorous stirring. The mixture

was transferred into a Teflon vessel, sealed and heated at 100 °C for 48 h. The resulting SBA-15 was filtrated, washed, dried at 100 °C for 4 h and calcined at 550 °C for 5 h.

2.3. Solvothermal treatment

Calcined SBA-15 zeolite (10.0 g) was mixed with 50 mL of solvent, which was toluene, cyclohexane, *n*-butanol, or water, in a Teflon vessel, sealed and heated without stirring to temperature of 157 or 190 °C for 3, 6, 12, and 24 h. After filtration, the samples were dried at 120 °C for 4 h, and calcined at 550 °C in air for 5 h. They were named S15(*x*)-*T*(*t*), where *x* is T, C, B, or H corresponding to toluene, cyclohexane, *n*-butanol, or water, respectively, *T* is the treatment temperature of 157 or 190 °C, and *t* is the treatment time of 3, 6, 12, or 24 h.

2.4. Evaluation of hydrothermal stability

All samples (0.3 g) were pressed into discs at 1.0 MPa and put into a tube furnace. After they were heated to 800 °C, 100% steam with gas flow (1000 mL/min) was introduced into the furnace, and the duration of hydrothermal treatment was 12 h.

2.5. Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 X-ray diffractometer (Karlsruhe, Germany) with Ni-filtered Cu K_{α} radiation (40 kV, 40 mA). Nitrogen adsorption-desorption isotherms were measured at –196 °C with a Micromeritics Tristar 3000 analyzer. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas using adsorption data in a relative pressure range from 0.05 to 0.2. The pore size distributions were derived from the adsorption branches of the isotherms using the Barrett-Joyner-Halenda model. The total pore volume V_t was estimated from the amount adsorbed at a relative pressure p/p_0 of 0.995. The true density of SBA-15 zeolite was measured by Beijing JWGB Sci. & Tech. Co., Ltd on a BT122T-B pore size analyzer. Before measuring, all samples were degassed at 250 °C for 6 h. ²⁹Si NMR spectra were performed on a Bruker AVANCE AV 400MHz spectrometer at a frequency of 59.621 MHz, a recycling delay of 600 s, a radiation frequency intensity of 62.5 kHz, and a reference sample of [(CH₃)₃SiO]₈Si₈O₁₂. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images were taken using a JEOL 2011 microscope operated at 200 kV and a Philips XL30, respectively. FTIR spectra were recorded on a Nicolet FTIR Avatar 360 at 120 °C. The samples were pressed directly in a mold without adding any other additives, such as KBr, and pre-treated at 450 °C in a 1.0 × 10^{–4} Pa vacuum for 5 h.

3. Results and discussion

3.1. Hydrothermal stability

The calcined SBA-15 without solvothermal treatment displayed three resolved diffraction peaks at $2\theta = 0.86^\circ$ and be-

tween 1.5° and 2.0° , corresponding to the (100), (110) and (200) reflections of a 2D hexagonal mesostructure (Fig. 1(a-1)). The sample showed a typical type IV isotherm with a H_1 -type hysteresis loop (Fig. 2(a-1)), a high surface area of $745 \text{ m}^2/\text{g}$, a large pore volume of $1.27 \text{ cm}^3/\text{g}$, uniform pores of 5.83 nm in diameter (Table 1), and a well-ordered hexagonal mesostructure with a fiber-shape morphology (Fig. 3A(a) and Fig. 4A(a)). These results suggest that SBA-15 has a well-ordered mesostructure. When the untreated SBA-15 sample was treated hydrothermally at 800°C for 12 h in 100% steam, no diffraction peaks were shown in the XRD spectrum (Fig. 1(b-1)). There was no H_1 -type hysteresis loop in the N_2 adsorption isotherm (Fig. 2(b-1)). The surface area decreased drastically to $71 \text{ m}^2/\text{g}$ (Table 1), corresponding to a surface area loss of approximately 90% after hydrothermal treatment. The SEM image shows that the original fiber-shape morphology was lost and became glass-like (Fig. 3A(b)). There were no ordered mesopores observed in the TEM image (Fig. 4A(b)). These results suggest that the pore structure of the calcined SBA-15 was broken completely because of the severe hydrothermal treatment of 100% steam at 800°C for 12 h .

When the calcined SBA-15 was treated in cyclohexane at 190°C for 24 h , the XRD pattern showed that all the diffraction

peaks of sample S15(C)-190(24) at $2\theta = 0.86^\circ$ – 2.0° were resolved (Fig. 1(a-2)). The type IV adsorption isotherms showed a H_1 -type hysteresis loop (Fig. 2(a-2)), and the fiber-shape morphology (Fig. 3B(a)) was retained. Well-ordered and slightly larger mesopores than those before cyclohexane treatment were observed clearly in the TEM image (Fig. 4B(a)). These results indicate that the cyclohexane treatment does not damage the mesostructure of SBA-15 zeolite. As shown in Table 1, the surface area of sample S15(C)-190(24) decreased to $355 \text{ m}^2/\text{g}$ from that of the untreated SBA-15 sample at $745 \text{ m}^2/\text{g}$, as well as a decrease in pore volume to 1.03 from $1.27 \text{ cm}^3/\text{g}$. This loss corresponded to a 52% reduction of surface area and 19% reduction of pore volume after cyclohexane treatment. The micropore surface area and pore volume were reduced to 55 from $154 \text{ m}^2/\text{g}$ and 0.13 from $0.27 \text{ cm}^3/\text{g}$, respectively, which were a 64% loss of micropore surface area and a 52% loss of micropore pore volume. The cyclohexane treatment affected the microstructure of SBA-15 more than the mesostructure. Compared with SBA-15, sample S15(C)-190(24) showed a lower lattice constant of 11.47 nm , a larger pore at 7.99 nm in diameter, and a thinner wall thickness of 3.48 nm , suggesting that the walls had shrunk and become denser during cyclohexane treatment. This shrinkage is also reflected by the true

Fig. 1. XRD patterns of SBA-15 (1), S15(C)-190(24) (2), S15(T)-190(24) (3), S15(B)-190(24) (4), S15(C)-157(24) (5) and S15(H)-190(24) (6) before (a) and after (b) treated hydrothermally at 800°C for 12 h in 100% steam.

Fig. 2. N_2 sorption isotherms of SBA-15 (1), S15(C)-190(24) (2), S15(T)-190(24) (3), S15(B)-190(24) (4), S15(C)-157(24) (5) and S15(H)-190(24) (6) before (a) and after (b) treated hydrothermally at 800°C for 12 h in 100% steam.

Table 1

Structure parameters of the mesoporous SBA-15 zeolite before and after hydrothermal treated at 800 °C for 12 h in 100% steam.

Treatment	Sample	A_{BET} (m^2/g)	A_{micro} (m^2/g)	V_{BJH} (cm^3/g)	V_{mic} (cm^3/g)	D_{BJH} (nm)	2θ (°)	A_0 (nm)	d_{wall} (nm)	ρ (g/cm^3)
Before treatment	SBA-15	745	154	1.27	0.27	5.83	0.86	11.86	6.03	1.88
	S15(C)-190(24)	355	55	1.03	0.13	7.99	0.89	11.47	3.48	2.70
	S15(T)-190(24)	477	61	0.96	0.18	6.74	0.86	11.86	5.12	2.92
	S15(B)-190(24)	477	76	1.00	0.19	6.82	0.89	11.47	4.65	2.92
	S15(C)-157(24)	546	43	1.02	0.20	7.35	0.88	11.60	4.25	2.81
	S15(H)-190(24)	255	41	0.72	0.10	7.13	0.86	11.86	4.73	—
After treatment	SBA-15	71	2	0.26	0.02	2.45	—	—	—	—
	S15(C)-190(24)	281	51	0.54	0.10	5.72	1.00	10.20	5.48	—
	S15(T)-190(24)	239	39	0.48	0.09	5.65	1.02	10.00	4.45	—
	S15(B)-190(24)	192	16	0.43	0.07	5.89	0.99	10.31	4.42	—
	S15(C)-157(24)	256	26	0.52	0.09	5.33	1.01	10.11	4.78	—
	S15(H)-190(24)	54	1	0.20	0.02	2.43	—	—	—	—

 ρ : the true density of sample.

densities shown in Table 1. Sample S15(C)-190(24) showed a true density of 2.70 g/cm³, which was larger than that of SBA-15 (1.88 g/cm³). The larger pore sizes of SBA-15 after cyclohexane treatment is beneficial for the diffusion of bulk reactants when used in catalysis, and may be an additional benefit of cyclohexane treatment.

The diffraction peaks were retained when S15(C)-190(24) sample was treated hydrothermally at 800 °C for 12 h in 100% steam (Fig. 1(b-2)), and a clear H₁-type hysteresis loop was shown in Fig. 2(b-2). The fiber-shape morphology was main-

tained the same as that before hydrothermal treatment, and the bundles were still close together (Fig. 3B(b)). The ordered mesostructure was observed clearly in Fig. 4B(b), whereas a few irregular large-sized pores appeared on the walls, which may be a result of the steam. These results suggest that the cyclohexane treatment of SBA-15 is a promoting effect on improving hydrothermal stability. Moreover, cyclohexane can be recycled and was used three times without any purification. The obtained samples displayed the same properties of mesostructure and high hydrothermal stability as those made using fresh cyclohexane. Furthermore, the solvent of cyclohexane can be recovered and purified easily using distillation.

3.2. Effects of solvents and temperature

Both samples of S15(T)-190(24) and S15(B)-190(24) presented well-ordered mesostructure as shown in Fig. 1(a-3) and (a-4) and Fig. 2(a-3) and (a-4), and surface areas of 477 m²/g (Table 1). The surface areas were larger than that of S15(C)-190(24), which was 355 m²/g, suggesting that cyclohexane treatment affected the structure of silica more than toluene or butanol treatments under the same conditions. When treated hydrothermally at 800 °C for 12 h in 100% steam, S15(T)-190(24) and S15(B)-190(24) samples also retained ordered mesostructures as confirmed in Fig. 1(b-3) and

Fig. 3. SEM images of SBA-15 (A) and S15(C)-190(24) (B) before (a) and after (b) treated hydrothermally at 800 °C for 12 h in 100% steam.

Fig. 4. TEM images of SBA-15 (A) and S15(C)-190(24) (B) before (a) and after (b) treated hydrothermally at 800 °C for 12 h in 100% steam.

(b-4) and Fig. 2(b-3) and (b-4), but displayed lower surface areas of 239 and 192 m²/g, respectively, than sample S15(C)-190(24), which was 281 m²/g. These results suggest that the cyclohexane treatment has the largest effect on promoting the hydrothermal stability of SBA-15. Sample S15(C)-157(24) showed an improved hydrothermal stability after treatment at 800 °C for 12 h in 100% steam. The well-ordered mesostructure was retained (Fig. 1(b-5) and Fig. 2(b-5)), and a high surface area of 256 m²/g was recorded; however, the surface area was slightly smaller than that of sample S15(C)-190(24) (Table 1). This result suggests that the treatment temperature was important in promoting the hydrothermal stability of zeolite.

H₂O was chosen as a treatment solvent and sample S15(H)-190(24) displayed only a small diffraction peak of the (100) reflection at $2\theta = 0.86^\circ$. There were no peaks of the (110) and (200) reflections, which would be observed at $2\theta = 1.5^\circ$ – 2.0° (Fig. 1(a-6)). The H₁-type hysteresis loop became smaller than those of the other solvothermal treatment samples (Fig. 2(a-6)). These results indicate that most of the ordered mesostructure had lost during H₂O treatment. Moreover, after the sample was treated hydrothermally at 800 °C for 12 h in 100% steam, the diffraction peak and hysteresis loop were no longer present as shown in Fig. 1(b-6) and Fig. 2(b-6), respectively. The surface area decreased to 54 m²/g. These results suggest that the hydrothermal stability of S15(H)-190(24) sample is not improved by H₂O treatment.

3.3. Effect of duration

The calcined SBA-15 was treated in toluene at 190 °C for 3, 6, 12, and 24 h, and the XRD patterns and N₂ sorption isotherms confirm that all the samples retained a well-ordered mesostructure (figures not shown). However, their BET surface areas were lower than the untreated SBA-15, and the area decreased with the increase of time until 6 h, then kept around 480 m²/g, as shown in Fig. 5(1). This result suggests that the structure change in SBA-15 caused by toluene treatment mainly happens within the first 6 h. As the samples were hydro-

Fig. 5. BET surface areas of SBA-15 samples treated with toluene at 190 °C against the time before (1) and after (2) treated hydrothermally at 800 °C for 12 h in 100% steam.

thermally treated at 800 °C for 12 h in 100% steam, the surface area increased with the increase of time at first, then maintained at approximately 240 m²/g after 6 h (Fig. 5(2)). Obviously, the toluene treatment in the first 6 h played a more important role in improving the hydrothermal stability. The results indicate that the improved hydrothermal stability results from the effect of toluene treatment on the structure of silica. Because the improved effect is most obvious in the first 6 h, the treatment time can be shortened, saving energy and increasing the efficiency of this approach.

3.4. ²⁹Si NMR spectra

As shown in Fig. 6, all the samples displayed three peaks centered at $\delta = -90$, -100 , and -110 , which were attributed to silicon atoms with two siloxane bands and two silanol groups $[(\text{SiO})_2\text{Si}(\text{OH})_2(\text{Q}_2)]$, three siloxane bonds and one silanol group $[(\text{SiO})_3\text{SiOH}(\text{Q}_3)]$, and four siloxane bonds, $(\text{SiO})_4\text{Si}(\text{Q}_4)$, respectively [38]. The $Q_4/(Q_3+Q_2)$ ratios were 0.34, 0.56, 0.50, and 0.54, corresponding to untreated SBA-15, S15(C)-190(24), S15(T)-190(24), and S15(C)-157(24), respectively. The ratio increased after SBA-15 was treated with cyclohexane or toluene, suggesting that solvothermal treatment can promote the crosslinking of amorphous walls to form $\text{Si}(\text{OSi})_4$ from $\text{Si}(\text{OSi})_2(\text{OH})_2$ or $\text{Si}(\text{OSi})_3\text{OH}$, and increase the silica condensation degree of the walls. The $Q_4/(Q_3+Q_2)$ ratios correlated with the surface areas of samples treated hydrothermally at 800 °C for 24 h in 100% steam. This result suggests that the crosslinking of amorphous walls by solvothermal treatment is important in improving the hydrothermal stability of SBA-15. The $Q_4/(Q_3+Q_2)$ ratio of S15(B)-190(24) sample was 0.36, which was slightly higher than that of SBA-15, but much lower than those of S15(T)-190(24) and S15(C)-190(24). This result suggests that *n*-butanol treatment has a lower promoting effect on the crosslinking of walls than those of toluene and cyclohexane treatments. However, sample S15(H)-190(24) showed the highest $Q_4/(Q_3+Q_2)$ ratio (0.6) and the highest crosslinking but the worst hydrothermal stability. This contradiction is discussed below.

Fig. 6. ²⁹Si NMR spectra of SBA-15 (1), S15(C)-190(24) (2), S15(T)-190(24) (3), S15(B)-190(24) (4), S15(C)-157(24) (5) and S15(H)-190(24) (6).

3.5. IR spectra

In Fig. 7, all the samples show an intense hydroxyl band at 3740 cm^{-1} , which results from the vibration of free Si–OH groups on the walls of SBA-15. Compared with SBA-15, the spectra of S15(C)-190(24), S15(T)-190(24), S15(B)-190(24), S15(C)-157(24), and S15(H)-190(24) displayed weaker hydroxyl band intensity, indicating a hydroxyl group loss of 59.9%, 37.5%, 54.9%, 58.1%, and 62.3%, respectively. This decrease may result from two possibilities, the dehydration of Si–OH groups to form Si–O–Si bands, or the reaction of Si–OH groups with other active reactants, such as alcohols and acids. The S15(T)-190(24), S15(C)-157(24), and S15(C)-190(24) samples only used nonpolar and inert solvents of toluene and cyclohexane. Therefore, the only reason for the decrease in hydroxyl groups in these samples is dehydration between Si–OH groups and crosslinking, which is in agreement with the ^{29}Si NMR results. The IR spectra of samples that were not calcined after solvothermal treatment showed that the S15(B)-190(24) sample displayed C–H vibration bands at $2850\text{--}3250\text{ cm}^{-1}$ (figure not shown). However, no C–H bands appeared in the spectra of S15(T)-190(24) and S15(C)-190(24) samples. This result suggests that some Si–OH groups on the walls reacted to form Si–O–C₄H₉ during *n*-butanol treatment at high temperature. The formation of Si–O–C₄H₉ bands decreases dehydration between Si–OH groups to form Si–O–Si bands. Therefore, S15(B)-190(24) has a low ratio of $Q_4/(Q_3+Q_2)$ but a weak intensity of hydroxyl bands.

3.6. Effect of the SBA-15 precursors and solvent amount

Three precursors to solvothermal treated SBA-15 were calcined, as-made (not calcined) and washed (P123 surfactants were removed by washing with ethanol and not calcined) SBA-15 samples. They were treated in toluene at $190\text{ }^{\circ}\text{C}$ for 12 h, and hydrothermally at $800\text{ }^{\circ}\text{C}$ for 12 h in 100% steam. S15(T)-190(12) sample displayed a high surface area of $242\text{ m}^2/\text{g}$. However, S15(T)-A-190(12) sample, which was from the as-made SBA-15, recorded a $148\text{ m}^2/\text{g}$ surface area. S15(T)-B-190(12) sample, which was from the washed SBA-15,

only recorded a $45\text{ m}^2/\text{g}$ surface area, which was as low as that of SBA-15 without toluene treatment. The toluene treatment displayed the highest stability promoting effect on the precursor of calcined SBA-15. The differences were because the structure change of three precursors was not the same at the introduction of liquid at high pressure. A detailed explanation is given below.

The solvent amount was important in improving hydrothermal stability. S15(T)-C-190(12) sample, obtained by treating 10.0 g of the calcined SBA-15 with 5 mL of toluene instead of 50 mL at $190\text{ }^{\circ}\text{C}$ for 12 h, displayed a lower hydrothermal stability than S15(T)-190(12). After hydrothermal treatment at $800\text{ }^{\circ}\text{C}$ for 12 h in 100% steam, the sample only retained a $187\text{ m}^2/\text{g}$ surface area, which was lower than that of S15(T)-190(12) ($242\text{ m}^2/\text{g}$). Ten grams of SBA-15 sample has 12.7 cm^3 of pore volume, and all the pores cannot be filled by 5 mL of toluene liquid, but it can be filled by toluene gas. Thus, the liquid at a high pressure has a higher promoting effect than gas, even when both pressures are the same.

3.7. Discussion

During the solvothermal treatment of SBA-15, high temperature, high pressure, and solvent type are important factors to improve hydrothermal stability. In a closed vessel, the organic solvent can auto-generate a high pressure at a high temperature, such as 0.64 MPa for toluene at $190\text{ }^{\circ}\text{C}$, and 1.13 MPa and 0.83 MPa for cyclohexane at $190\text{ }^{\circ}\text{C}$ and $157\text{ }^{\circ}\text{C}$, respectively [39]. The introduced liquid at a high pressure exerts a strong pressure on the pore walls of SBA-15, and forces nearby Si–OH groups close together. Thus, the hydroxyl groups, which were originally unable to dehydrate because of the separating distance, have opportunities to form stable Si–O–Si bonds at high temperatures. Thus, the silica walls are crosslinked better, and the defects decrease, as shown in Scheme 1. As a result, the hydrothermal stability of SBA-15 improves remarkably.

Among the solvents tested, the auto-generated pressure of cyclohexane at $190\text{ }^{\circ}\text{C}$ is the highest, and thus the walls of SBA-15 would be subject to the highest pressure and increase the dehydration of Si–OH groups. Therefore, S15(C)-190(24) displays the highest hydrothermal stability, compared with that of S15(C)-157(24) and S15(T)-190(24).

During *n*-butanol treatment, the solvent can react with some Si–OH groups to form Si–O–C₄H₉ groups. This formation is detrimental to the dehydration of Si–OH groups, resulting in poor crosslinking. Though the surface becomes hydrophobic owing to the formation of Si–O–C₄H₉ groups, Si–O–C₄H₉ groups are not stable and may revert to Si–OH groups when the sample is calcined in air or hydrothermally treated at $800\text{ }^{\circ}\text{C}$. Therefore, the *n*-butanol treatment shows less stabilization on SBA-15 than that of toluene or cyclohexane treatments. S15(H)-190(24) sample shows increased crosslinking but does not improve hydrothermal stability because the crosslinking collapses the ordered mesostructure.

Three precursors of SBA-15 were evaluated using toluene treatment. For the calcined SBA-15, the calcining process removing P123 surfactants before solvent treatment may have an

Fig. 7. IR spectra of SBA-15 (1), S15(C)-190(24) (2), S15(T)-190(24) (3), S15(B)-190(24) (4), S15(C)-157(24) (5) and S15(H)-190(24) (6).

Scheme 1. Stabilization mechanism of the solvothermal treatment on SBA-15.

effect on the crosslinking of silica and the formation of integrated stabilized walls over a large region (Route A in Scheme 1). The stabilized walls can withstand the introduction of a solvent at high pressure and retain the ordered structure. Thus, the dehydration of free Si-OH groups, caused by the solvothermal treatment, has a significant role on stabilizing the calcined SBA-15 and improving hydrothermal stability. However, for washed SBA-15, no further crosslinking can take place as the P123 surfactants were removed. The walls may only be crosslinked in scattered small regions, which can be distorted by the introduction of solvents at a high pressure during the solvothermal treatment and cause disorder in the walls (Route B in Scheme 1). The disordered walls are not stable and collapse in the harsh hydrothermal treatment. Thus, the solvothermal treatment shows no stabilization effect on the washed SBA-15. Though the as-made SBA-15 has the same crosslinking of walls as the washed SBA-15, its walls are supported by P123 molecules. This supporting effect strengthens the walls of as-made SBA-15, and they do not distort as much as that of the washed SBA-15 after the introduction of a solvent at a high pressure. Therefore, the toluene treatment displays a better stabilization effect on the as-made SBA-15 than on the washed SBA-15, but worse one than on the calcined SBA-15.

Because the pores of SBA-15 are only filled by toluene in the gas phase at a high pressure, and not by toluene liquid, the gas can penetrate easily through the pores of the walls and into the bulk of SBA-15, resulting in a decrease of pressure difference between the inner and outer walls. As a result, the pressure forcing Si-OH groups close together is reduced, and the promoting effect of solvothermal treatment is also reduced.

4. Conclusions

Solvothermal treatment displays encouraging results for improving the hydrothermal stability of SBA-15 zeolite. SBA-15 treated by cyclohexane at 190 °C for 24 h can maintain the ordered mesostructure well, and retain a high surface area of 281 m²/g after it was treated hydrothermally at 800 °C for 12 h in 100% steam. The promoting effect of solvothermal treatment is closely related to the temperature, solvent properties, and

precursors of SBA-15 zeolite. This approach only requires a low-handling temperature and inexpensive solvents, which can be recovered and purified easily by distillation. Therefore, this approach is low cost, low energy consumption and has potential application to prepare hydrothermally stable and ordered mesoporous silica in the laboratory and for industry.

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Graphical Abstract

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Facile solvothermal post-treatment to improve hydrothermal stability of mesoporous SBA-15 zeolite

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A simple approach was proposed to improve the hydrothermal stability of SBA-15 via solvothermal treatment by forcing Si–OH groups in the walls close together, dehydrate, crosslink, and promote the silica condensation degree.

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改善SBA-15介孔材料水热稳定性的简单溶剂热后处理方法

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摘要: 提出了一种有效改善SBA-15介孔材料水热稳定性的简单溶剂热后处理方法。SBA-15材料经环己烷、甲苯和正丁醇等有机溶剂在157和190℃密闭容器中分别处理6–24 h后, 可呈现很好的水热稳定性。它们在800℃经100%水蒸气处理12 h, 依然能保持很好的有序介孔结构, 比表面积可高达192–281 m²/g。其中, 经环己烷190℃溶剂热处理24 h的样品表现出最优的水热稳定性。溶剂热处理能显著提升材料孔壁中类似Si(OSi)₂(OH)₂和Si(OSi)₃OH结构的Si–OH基团脱水, 形成稳定的Si(OSi)₄结构, 从而有效减少了SBA-15材料孔壁的缺陷。由此, 介孔材料的水热稳定性得到明显改善。溶剂热处理对SBA-15材料水热稳定性的这种提升作用与所用溶剂性质、处理温度以及SBA-15前驱体的类型密切相关。其中, 以低沸点的非极性溶剂处理焙烧后的SBA-15材料表现出最好的稳定化效果。该方法具有简单、低能耗的特点, 其在制备高水热稳定的有序硅基介孔材料上有很好的潜在应用价值。

关键词: 介孔材料; SBA-15分子筛; 水热稳定性; 溶剂热处理; 脱水

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