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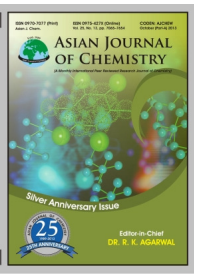

Recycling Mother Liquor to Synthesize Mesoporous SBA-15 Silica

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SBA-15, a type of mesoporous silica, was prepared using recycled mother liquor. The results showed that ethanol accumulation in the mother liquor with continuous recycling damages the ordered structure of SBA-15 silica. The open heating of the mother liquor above 95 ºC for 2 h can effectively remove ethanol, reducing the ethanol content to below 5 %. The P123 (pluronic $EO_{20}PO_{70}EO_{20}$ triblock copolymer) and HCl remain in the mother liquor and can thus be utilized in the next preparation. Such treatment allows the mother liquor to be recycled at least five times. In this way, almost no acid or wastewater is discharged. The structures of the synthesized SBA-15 silicas are as well ordered as those from the fresh liquor except for slightly smaller pores and thicker pore walls. Its environmentally friendly character and cost-effectiveness make this method highly suitable for industrial SBA-15 silica production.

Key Words: Porous materials, Amorphous materials, SBA-15, Mother liquor recycling, Environmentally friendly.

INTRODUCTION

SBA-15, a type of ordered mesoporous silica, has attracted tremendous attention for its many potential applications as an adsorbent[1,2], hydrogen storage material[3,4], drug delivery medium[5-7] and hard template for other nanostructure materials[8-11], especially as a versatile catalyst and a catalyst support[12-15] due to its remarkably high hydrothermal stability, easily controlled pore size and high surface area. We recently determined that the zeolite Y/Al-SBA-15 composite exhibits excellent catalytic performance for hydrocracking heavy oil as a carrier[16] and its good stability after 1500 h of running time indicates its viability for actual applications.

However, the scaled-up applications of SBA-15 silica are severely restricted by two hurdles *viz.*, its high cost and the need to treat the large amount of acid wastewater generated in the production process. Many efforts have been made to synthesize SBA-15 silica in a simple and cost effective manner[17-23], but less concern is given to the latter. Indeed, approximately 55 tons of 1.5 mol/L HCl wastewater, which also contains 800 kg of the P123 (pluronic $EO_{20}PO_{70}EO_{20}$ triblock copolymer), are generated to produce one ton of SBA-15 silica according to the reported reactant ratio[24]. Thus, wastewater treatment must be addressed to ensure environmental friendliness.

Although recycling of the acidic mother liquor is attractive, little research work was done on it[25]. Therein, the mother liquid was recycled only twice and no results of more recycles were given. Obviously, it has less value in actual application. In previous work[26], we have reported that the more recycle of mother liquor is possible in the scale-up production of SBA-15 silica if the mother liquid was treated to remove ethanol before used.

In this paper, we reported a whole research work of recycling mother liquor to synthesize mesoporous SBA-15 silica. It provided the full characterizations to reveal the influence of recycling mother liquor on the structures of SBA-15 silicas, such as the structure order, particle size, porous size, porous wall thickness and hydrothermal stability and discussed in detail to illustrate the reasons of above influence and the self-assembly process for the ordered mesoporous SBA-15 silica in the recycled mother liquor. The influence of recycling of the mother liquor on the hydrothermal stability of the SBA-15 silica is also be studied.

EXPERIMENTAL

Normalized synthesis: As previously reported[24], 5 g of P123 (pluronic $EO_{20}PO_{70}EO_{20}$ triblock copolymer, Sigma-Aldrich Company Ltd. (USA), Mav 5800) was dissolved in 180 mL of 1.5 mol/L HCl. Next, 10.5 g of tetraethylorthosilicate (TEOS, Shanghai Chemical Corp. (China), 98 %) was added and hydrolyzed at 40 ºC for 10 h under vigorous stirring. After crystallization at 100 ºC for 48 h, drying at 100 ºC for 4 h and calcination at 550 ºC in air for 4 h, the sample, denoted as SBA-15-Normal, was obtained.

Synthesis with the mother liquor: All processes were the same as above, except that TEOS was hydrolyzed in the mother liquor, which had been supplemented with 50 % P123 (2.5 g), 10 % HCl (2.7 mL conc. HCl) and the appropriate amount of water before the recycling. SBA-15-1st, SBA-15-3rd and SBA-15-5th samples were prepared using the once, third and fifth recycles of the mother liquors, respectively, which had been openly heated above 95 ºC for 2 h to evaporate ethanol before use. The evaporated ethanol and water were collected in another container after cooling. SBA-15-No-1st, SBA-15-No-2nd and SBA-15-No-3rd samples were prepared directly using the once-, twice- and thrice-recycled mother liquors, respectively, without heating to remove ethanol.

Evaluation of hydrothermal stability: The SBA-15-Normal and SBA-15-3rd samples were treated in a tube furnace under a 100 % H_2O stream at 800 ºC for 3, 6, 12 and 24 h.

Characterization: X-Ray diffraction (XRD) patterns were recorded on a Bruker D8 X-ray diffractometer (Germany) with Ni-filtered CuK_α radiation (40 kV, 40 mA).

Nitrogen adsorption-desorption isotherms were measured at 77 K with a Micromeritics Tristar 3000 analyzer. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas using adsorption data in a relative pressure range from 0.05-0.20. The pore size distributions (PSDs) were derived from the adsorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) model. The total pore volume V_t was estimated from the amount adsorbed at a relative pressure P/P_0 of 0.995.

Transmission electron microscopy and scanning electron microscopy images were obtained with a JEOL 2011 microscope operated at 200 kV and a Philip XL30 instrument, respectively.

^{29}Si nuclear magnetic resonance and FT-IR spectra were recorded on Bruker DSX-300 and Nicolet FT-IR Avater 360 instruments, respectively. All samples for IR measurement were pre-treated at 450 ºC in a 1.0×10^4 Pa vacuum for 5 h.

The HCl concentrations of the solutions were determined by titration with 0.2000 mol/L NaOH solution. The ethanol content was measured by gas chromatography using an Agilent 6890 instrument. The P123 content was determined by comparing the mass loss of the calcined mother liquor and the dried sample.

RESULTS AND DISCUSSION

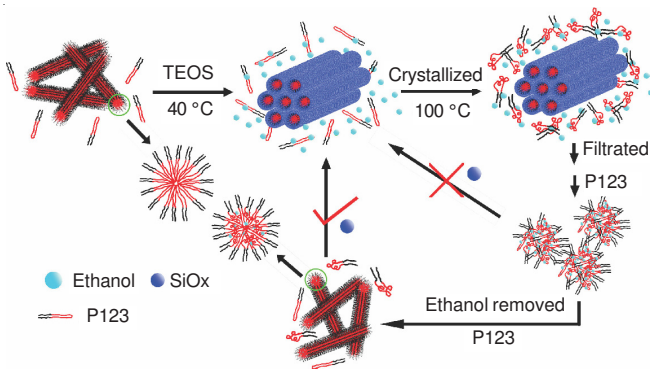
P123, HCl and SiO_2 contents in the two mother liquors: Two mother liquors, denoted as ML-1 and ML-2, were obtained by filtration before and after crystallization when preparing SBA-15-Normal. Table-1 shows that ML-1 contains 0.90 wt % P123, 0.052 wt % SiO_2 and 1.335 mol/L HCl. Relative to the fresh solution with TEOS added, 32.6 % of the P123 surfactant, 3.10 % of the SiO_2 and 93.4 % of the HCl remained in this mother liquor.

ML-2 contains 1.43 wt % P123, 0.035 wt % SiO_2 and 1.314 mol/L HCl, which are equivalent to 51.8, 2.09 and 92.0 % of respective original contents. This result suggests that half of the P123 surfactants have not self-assembled effectively to form the ordered micelles and been aggregated by silica species in the solution. These aggregations are free and removed by ML-2 during filtration (**Scheme-I**). The remaining P123 and HCl can be used as materials in the next preparation; thus, only 50 % of the P123, 10 % of the HCl and the appropriate amount of water were supplied into the mother liquor in each recycle.

TABLE-1
P123, SiO_2, AND HCL CONTENTS OF SOME OF THE MOTHER LIQUORS

Liquor	P123 content (wt %)	SiO_2 content (wt %)	HCl content (mol/L)
Fresh liquor[a]	2.76	0	1.429
ML-1[b]	0.90	0.052	1.335
ML-2[c]	1.43	0.035	1.314

[a]P123 and HCl solution before the hydrolysis of TEOS for preparing SBA-15-Normal. [b]Mother liquor filtrated before crystallization of SBA-15-Normal. [c]Mother liquor filtrated after crystallization of SBA-15-Normal.



Scheme-I: Schematic illustration of the self-assembly process for the ordered mesoporous SBA-15 silica in the recycled mother liquor

Comparing the two mother liquors, the amount of P123 surfactant in ML-2 is much larger than that in ML-1, indicating that some P123 molecules have been released from the micelles into the solution when the hydrolyzed products are crystallized at 100 ºC, possibly due to micelle shrinkage resulting from the consolidation of the assembled silica species around the micelles under crystallization.

Synthesis of SBA-15 silicas by the mother liquors: As shown in Fig. 1A, SBA-15-Normal exhibits three well resolved peaks at $2\theta = 0.90^\circ$ and 1.5-2.0º, corresponding to the (100), (110) and (200) diffraction peaks, which are characteristic of an ordered 2D hexagonal mesostructure (space group, p6 mm)[24,27]. SBA-15-1st, which was prepared in the first recycle of the mother liquor, also shows three well resolved diffraction peaks; however, the (100) peak shifts slightly (by $2\theta = 0.02^\circ$) toward higher angles. Its intensity is as strong as that of SBA-15-Normal. After the third and fifth recycle, SBA-15-3rd and SBA-15-5th still exhibit diffraction peaks with intensities approximately equal to those of SBA-15-Normal. Their (100) peaks shift toward higher angles by $2\theta = 0.03^\circ$, similarly to SBA-15-1st.

SBA-15-Normal, SBA-15-1st, SBA-15-3rd and SBA-15-5th all exhibit typical type IV curves comprised of H_1-type hysteresis loops with parallel adsorption and desorption, as shown in Fig. 2, which indicate that they possess a cylindrical pore structure with a regular array of SBA-15 silica. These

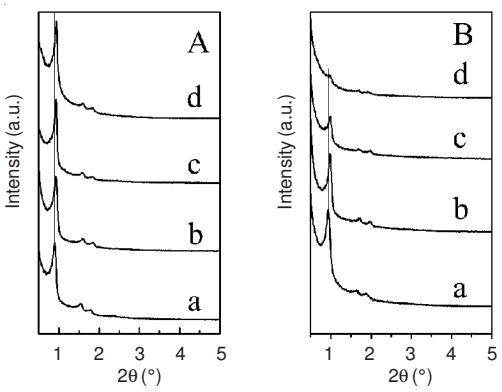


Fig. 1. XRD patterns of the samples prepared from the mother liquors with ethanol removed (A) (SBA-15-Normal (a), SBA-15-1st (b), SBA-15-3rd (c) and SBA-15-5th (d)) and prepared from the mother liquors without ethanol removed (B) (SBA-15-Normal (a), SBA-15-No-1st (b), SBA-15-No-2nd (c) and SBA-15-No-3rd (d))

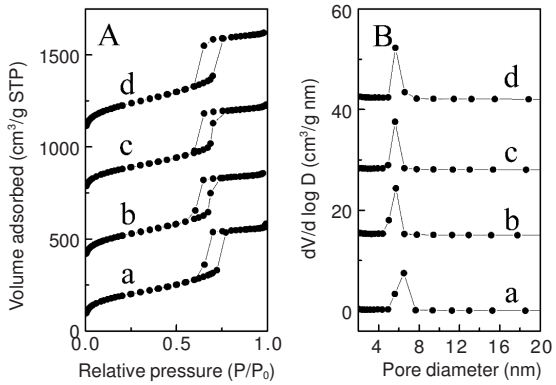


Fig. 2. N_2 sorption isotherms (A) and pore size distribution curves (B) of SBA-15-Normal (a), SBA-15-1st (b), SBA-15-3rd (c) and SBA-15-5th (d)

perfect, regular pores are observed clearly in TEM images (Fig. 3A). The pore sizes for SBA-15-1st, SBA-15-3rd and SBA-15-5th are *ca.* 5.6-5.7 nm with wall thicknesses of 5.3-5.4 nm. They have slightly smaller pores and thicker walls than SBA-15 Normal, which has a pore size of 6.5 nm and wall thickness of 4.83 nm (Table-2). The surface areas of SBA-15-1st, SBA-15-3rd and SBA-15-5th are 711.0, 647.0 and 807.8 m^2/g, respectively, which are comparable with that of SBA-15-Normal (658.4 m^2/g). The yields of all four samples are close to 100 %.

These results suggest that well ordered SBA-15 silicas can be prepared using the ethanol-removed mother liquors, even after five recycles. SBA-15-1st, SBA-15-3rd and SBA-15-5th do not differ strongly in structure but have slightly smaller pores and thicker walls than the silica prepared from the fresh solution. These differences may result from the structure change of P123 molecules at different temperatures. As

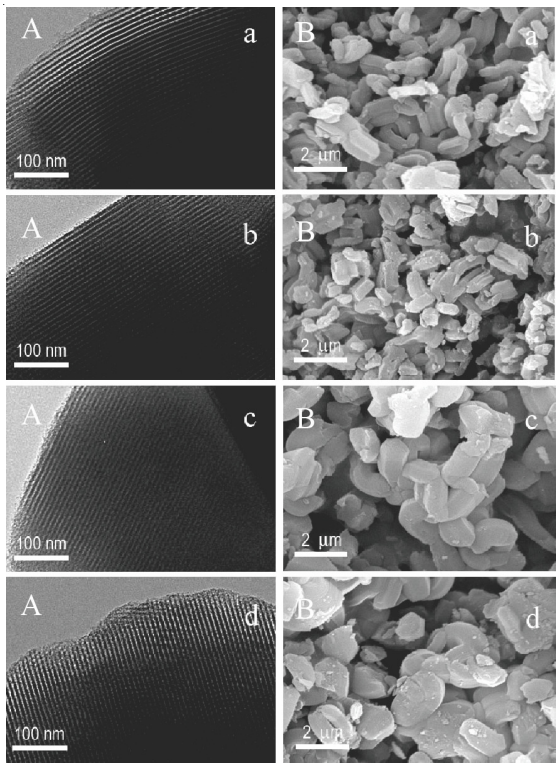


Fig. 3. SEM (A) and TEM (B) images of SBA-15-Normal (a), SBA-15-1st (b), SBA-15-3rd (c) and SBA-15-5th (d)

illustrated in **Scheme-I**, P123 molecules, dissolved below 40 ºC, present as stretched PPO and PEO chains in the fresh solution. When the temperature increases to 100 ºC for crystallization, the solubility of P123 becomes poor and the hydrophobic PPO chains begin to twist, whereas the hydrophilic PEO chains do not. These twisted PPO chains cannot recover their original form well when the temperature decreases to 40 ºC again because of twining. Thus, after the mother liquor is supplied with 50 % fresh P123, the twisted and stretched P123 molecules self-assemble to form smaller micelles than before, which would reduce the pore size of the SBA-15 silica products and increase the pore wall thickness because the same amount of SiO_x is assembling around smaller micelles.

In all of the recycles, 50 % of the P123 in the mother liquors is twisted from the previous preparation and 50 % is newly supplied stretched P123; thus, SBA-15-1st, SBA-15-3rd and SBA-15-5th have the same pore size and wall thickness.

SEM images (Fig. 3B) show that these samples have a rod-like morphology and their particle size gradually increases from 0.5 μm × 2 μm for SBA-15-Normal to 2 μm × 2 μm for SBA-15-5th with increasing recycling of the mother liquor. The cause of this increase may be that some silica species remaining in the mother liquor may act as crystal seeds on which the mesoporous silica can form larger particles.

TABLE-2
STRUCTURAL PARAMETERS AND YIELDS OF MESOPOROUS SBA-15 SILICAS

Sample	S_{BET} (m^2/g)	V_{BJH} (cm^3/g)	d_{100} (nm)	D_{BJH} (nm)	A_0 (nm)	Pore wall thickness (nm)	Yield (%)
SBA-15-Normal	658.4	0.88	9.80	6.50	11.33	4.83	97.6
SBA-15-1st	711.0	0.83	9.60	5.71	11.09	5.38	97.2
SBA-15-3rd	647.0	0.82	9.50	5.63	10.97	5.34	98.0
SBA-15-5th	807.8	0.96	9.50	5.65	10.97	5.32	97.3

Influence of ethanol in the mother liquors: The success of the recycling benefits from the effective ethanol removal from the mother liquor. We studied the effects of using the mother liquors directly without any other treatment (*e.g.*, ethanol removal), as reported[25], but also supplying them with 50 % P123, 10 % HCl and the necessary amount of water in each recycle. Fig. 1B shows that SBA-15-No-1st also exhibits three well resolved (100), (110) and (200) diffraction peaks at 2θ = 0.90º and 1.5-2.0º. Their intensities are comparable with that of SBA-15-Normal. SBA-15-No-2nd exhibits less intense diffraction peaks and the diffraction peaks in SBA-15-No-3rd are almost non-existent. These results clearly indicate that the ordered mesostructure of SBA-15 silica worsens with further recycling of the mother liquor without ethanol removal.

Fig. 4 shows that the ethanol content in these mother liquors gradually increases linearly with increasing recycle number. In the fresh mother liquor (without recycle), 4.85 % ethanol was detected due to the hydrolysis of TEOS. After the first recycle, the ethanol content increases to 9.12 wt %. This solution produces SBA-15-No-1st with good quality, maintaining the ordered mesostructure of SBA-15-Normal. However, as the ethanol content increases to 16.24 and 20.12 % in the twice- and thrice-recycled mother liquors, respectively, SBA-15 with little to no mesostructure ordering are produced. These results suggest that the influence of ethanol on the mesostructure ordering depends on its content. When the ethanol content is below 10 %, little influence was observed. As the ethanol content increases further, it eventually affects the self-assembly of the block copolymer, *e.g.*, increasing the critical micelle temperature (CMT) and decreasing the aggregation number of the block copolymer in the micelle[23,28,29], because ethanol is a better solvent for the PPO chains than the PEO chains of the P123[30]. Thus, it distributes more easily in the PPO core than in the PEO corona of P123 micelles, decreasing the hydrophobicity of the PPO core of the micelles. This phenomenon may be the cause of the less ordered mesoporous structures of SBA-15-No-2nd and SBA-15-No-3rd.

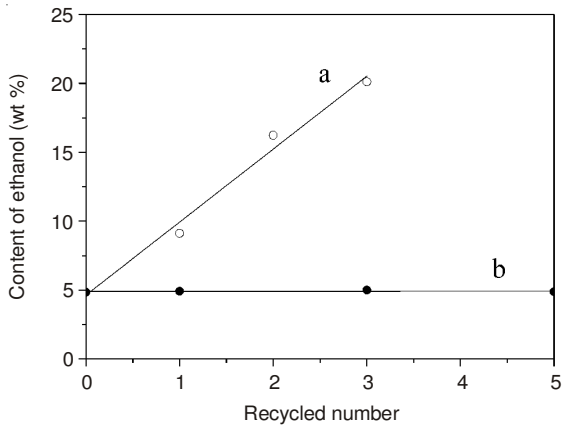


Fig. 4. Ethanol content as a function of the recycle number of the mother liquor (a) without ethanol removal and (b) after openly heating above 95 ºC for 2 h to remove ethanol

Therefore, it is important to remove ethanol when recycling the mother liquor. It was removed by evaporation. The boiling point of an aqueous solution of ethanol is determined by the ethanol content. With decreasing ethanol content, the boiling point increases. When the temperature exceeds 95 ºC under atmospheric pressure, the ethanol content in solution generally remains below 5 %. In this work, the mother liquors were openly heated above 95 ºC for 2 h to evaporate ethanol before use. Fig. 4 shows that their ethanol contents were approximately 5 wt % regardless of recycle number. The ethanol contents were low enough for the preparation of SBA-15 silica, such as SBA-15-No-1st. Therefore, the heating method effectively removes ethanol, as expected, guaranteeing the successful recycling of the mother liquors to prepare well ordered SBA-15 silica.

This heating step can be carried out at the beginning of the crystallization process: after TEOS hydrolysis, the reactor is heated openly until the reactant temperature is above 95 ºC for 2 h and then closed to crystallize at 100 ºC for another 46 h. The mother liquor separated from this process can be directly recycled for the next preparation because the ethanol content is approximately 5 wt %. Therefore, the treatment of the mother liquor would not require extra time or energy.

Hydrothermal stability of SBA-15-3rd: The influence of recycling the mother liquor on the hydrothermal stability of SBA-15 silica deserves attention because its stability determines its possible applications. Fig. 5 shows that the surface areas of SBA-15-Normal and SBA-15-3rd decrease rapidly with increasing time during hydrothermal treatment in a 100 % H_2O stream at 800 ºC. However, the surface area of SBA-15-3rd decreased much more slowly than that of SBA-15-Normal despite having a similar initial surface area. Therefore, SBA-15-3rd, which is prepared from the mother liquor, has a slightly higher hydrothermal stability than SBA-15-Normal, which is prepared from the fresh solution.

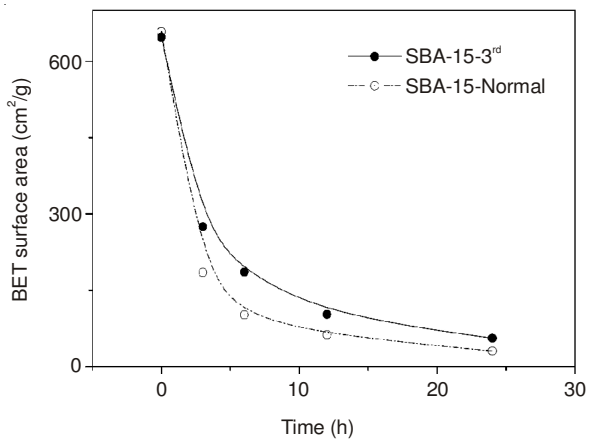


Fig. 5. BET surface areas of SBA-15-Normal and SBA-15-3rd samples as a function of the hydrothermal treatment time under a 100 % H_2O stream at 800 ºC

In the ^{29}Si MAS NMR spectra (Fig. 6), SBA-15-Normal, SBA-15-1st, SBA-15-3rd and SBA-15-5th show two peaks centered at 101 and 110 ppm, which are attributed to silicon atoms with three siloxane bonds and one silanol group, $(SiO)_3$*$SiOH(Q_3)$ and four siloxane bonds, $(SiO)_4$*$Si(Q_4)$, respectively[31]. The Q_4/Q_3 ratios are 4.61, 4.37, 4.50 and 4.42 for SBA-15-Normal, SBA-15-1st, SBA-15-3rd and SBA-15-5th, respectively. These values are quite close, which suggests that the samples prepared from the mother liquors consolidate

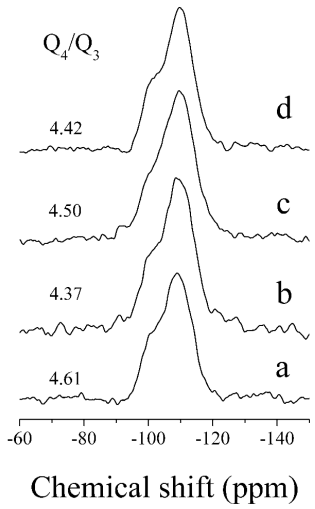


Fig. 6. Solid-state ^{29}Si MAS NMR of SBA-15-Normal (a), SBA-15-1st (b), SBA-15-3rd (c) and SBA-15-5th (d)

as well as SBA-15-Normal. This finding is reasonable because the consolidation between self-assembled silica species in hydrothermal crystallization is mainly determined by the crystallization temperature and acid concentration[32]. In this work, these factors were equal for all preparations.

The four samples exhibit a hydroxyl peak at 3738 cm^{-1} with the same intensity and half-peak width. The hydroxyl peak is comprised of the unconsolidated Si-OH and the framework defects of SBA-15 silica[33], so their constant intensity implies that they consolidate as well in the mother liquor as in fresh solution, which further supports the ^{29}Si MAS NMR analysis.

The hydrothermal stability of SBA-15 silica relies on the density and thickness of the pore wall. SBA-15-1st, SBA-15-3rd and SBA-15-5th consolidate as well as SBA-15-Normal does but have thicker pore walls, giving SBA-15-3rd a slightly higher hydrothermal stability than SBA-15-Normal.

From the above results, it can be concluded that SBA-15 mesoporous materials with good self-assembly and consolidation can be prepared using mother liquors that have been openly heated above 95 ºC for 2 h to evaporate ethanol before recycling. These recycling products have a slightly smaller pores, thicker pore walls and higher hydrothermal stability than the silica prepared from fresh solution. The mother liquor can be recycled at least five times. Based on the high quality of SBA-15-5th, further recycling of the mother liquor is likely possible.

Conclusion

Well ordered SBA-15 mesoporous silicas were prepared using recycled mother liquors. The recycling products have slightly smaller pores, thicker pore walls and higher hydrothermal stability than that prepared in fresh solution. The mother liquor can be recycled at least five times after heating above 95 ºC for 2 h to evaporate ethanol. Such open heating is effective in removing ethanol and is important for successfully recycling the mother liquor. In each recycle, only 50 % P123, 10 % HCl and water as needed must be added into the mother liquor, saving the material cost of SBA-15 silica. This method significantly reduces the discharge of acid, surfactant and water waste. Therefore, it has great advantages for the industrial production of SBA-15 silica in terms of environmental protection and cost control.

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