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Direct synthesis of highly ordered large-pore functionalized mesoporous SBA-15 silica with methylaminopropyl groups and its catalytic reactivity in flavanone synthesis

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Abstract

Functionalized SBA-15 mesoporous silica materials with a *p6mm* symmetry have been synthesized through a simple co-condensation approach of tetraethylorthosilicate (TEOS) and (3-(methylamino)propyl)trimethoxysilane (MAPTMS) using amphiphilic block co-polymers under acidic conditions. The influence of the amount of MAPTMS in the initial synthesis mixture on the mesostructural properties of the resultant materials was studied by varying the molar ratios of MAPTMS to TEOS. X-ray powder diffraction (XRD) and N₂ sortpion results indicated that the ordering of the mesoporous structure was dependent on the amount of MAPTMS added in the initial mixture. Solid-state nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA) and elemental analysis showed that the incorporation of the organic groups in the silica framework increased with the MAPTMS concentration in the synthesis mixture. TEOS pre-hydrolysis prior to the addition of MAPTES had great influence on the crystallographic ordering, pore size, surface area and pore volume of the resultant functionalized mesoporous silica materials. Moreover, the addition of inorganic salt in the initial mixture could greatly enhance the mesostructure ordering and stability of the mesoporous materials. With the aid of NaCl salt, the modified SBA-15 materials with the content of methylaminopropyl groups up to 2.37 mmol/g still possessed well-ordered mesoporous structure and had high specific area of 200 m²g⁻¹ and pore volume of 0.29 cm³/g. The modified SBA-15 showed high catalytic activities and selectivities toward flavanones synthesis through the Claisen–Schmidt condensation of substituted acetophenones and benzaldehyde derivatives and subsequent intramolecular Michael addition in the absence of solvent.

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1. Introduction

Since the discovery of ordered mesoporous silica M41S [1,2], a variety of ordered mesoporous materials such as SBA-15 [3], FSM-16 [4], KIT-1 [5], MSU [6],

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and HMS [7] have been synthesized under a wide range of pHs from highly basic to strongly acidic conditions using cationic, anionic, neutral, nonionic surfactants. Many research efforts have focused on functionalization of organic groups onto the surface of the mesoporous silica materials by the direct incorporation of organic groups through co-condensation of siloxane and organosiloxane precursors or by grafting (post-synthesis reaction) the organic groups onto the surface of the mesoporous silica [8–21] due to their potential applications in the field of catalysis [22–25], separation [26– 29], sensor design [30], and nanoscience [31,32]. The

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co-condensation method is often preferred to the postsynthesis pathway because it minimizes processing steps and produces mesoporous materials with relatively uniform distribution of the organic functionalities [33] and high loadings of organic functionalities without closing the framework mesopores [34].

Mesoporous silica materials functionalized with amino groups have been found to be effective in basecatalyzed reactions [22,34-36] or further post-synthesis functionalization [37,38]. However, most of the related work was on the modification of the small mesopores of MCM-type [19,39,40], and HMS-type [41] materials, which were synthesized under basic or neutral conditions. Well-ordered mesoporous materials with large pores (>4.5 nm) have recently attracted particular interest from the practical point of view. The large pore diameters of the materials facilitate the molecule diffusion and accessibility to catalytic functional sites and improve catalytic reactivity. As to the large mesoporous silica synthesized using amphiphilic block co-polymers under acidic conditions, only poorly ordered materials were obtained by co-condensation of tetraethylorthosilicate (TEOS) and 3-aminopropyltriethoxysilane (APTES) [42–44]. It was proposed that the protonated amine groups would interfere with the self-assembly of the co-polymer pore-directing agent and the silica precursor under the strong acidic condition [42]. Recently, we have successfully synthesized well-ordered aminopropyl-functioanlized SBA-15 with high surface area and large pore size by one-pot synthesis via the prehydrolysis of TEOS prior to the addition of APTES [21]. In the present study, we extend the technique to synthesize SBA-15 functionalized with methylaminopropyl groups. However, as the functional group became even more hydrophobic, the addition of inorganic salts into the synthesis solution was found to be essential in order to obtain materials of well-ordered mesopores and with high loadings of the functional group. Inorganic salts have been used to improve the hydrothermal stability [45,46], control the morphology [47–49], tailor the framework porosity [50,51], and improve the mesostructure ordering [13,52] during the formation of mesoporous materials. Here, we report the one-pot synthesis of highly ordered SBA-15 containing methylaminopropyl groups of as high as 2.37 mmol/g, using triblock co-polymer Pluronic P123 (EO₂₀PO₇₀EO₂₀) as the structure-directing agent under a strong acidic condition with the aid of inorganic salt and pre-hydrolysis of TEOS. The obtained materials were characterized by various physical and chemical techniques. Moreover, the methylaminopropyl-functionalized SBA-15 was also used as a base catalyst in the synthesis of flavanones through the Claisen-Schmidt condensation and subsequent intramolecular Michael addition of substituted acetophenones and benzaldehyde derivatives in the absence of solvent.

2. Experimental

2.1. Chemicals and synthesis

Surfactant P123 (EO₂₀PO₇₀EO₂₀, $M_{av} = 5800$) and (3-(methylamino)propyl)trimethoxysilane (MAPTMS, 97%) were purchased from Aldrich. TEOS (98%), hydrochloric acid (37%), ethanol (95%), and NaCl (99.5%) were from Acros. All chemicals were used as received.

Methylaminopropyl-functionalized SBA-15 materials were prepared by one-pot synthesis method. In the typical synthesis, Pluronic 123 (4 g) was dissolved in 125 g of 2.0 M HCl solution with stirring at room temperature. After adding TEOS, the resultant solution was hydrolyzed at 40 °C for a period of 0-3 h, and then MAPTMS was slowly added into the solution. The molar composition of the mixture was (1 - x) TEOS: x MAPTMS: 6.1 HCl: 0.017 P123: 165 H₂O, where x varied from 0 to 0.20, or MAPTMS/(TEOS + MAP-TMS = 0–20% The resulting mixture was stirred at 40 °C for 20 h and then transferred into a polypropylene bottle and aged at 90 °C under static condition for 24 h. The solid product was recovered by filtration and dried at room temperature overnight. The resultant samples are denoted as $M0 \sim 20/SBA$ (for example, M10/SBA for x = 0.10). In order to investigate the influence of inorganic salt on the mesostructure of the materials, the desired amount of NaCl was added into the starting aqueous solution, and the resultant samples are denoted as M0 \sim 20/SBA-yNaCl, where y is the molar concentration of NaCl (y = 0.5, 1.0, 1.5 M) in the initial aqueous solution.

The template was removed from the as-synthesized material by solvent extraction process. One gram of the as-synthesized sample was added into 300 ml of 95% ethanol and refluxed for 24 h, followed by filtration, washing several times with water and ethanol, and drying at 50 °C.

2.2. Sample characterization

X-ray powder diffraction (XRD) patterns were obtained on a PANalytical X'Pert Pro diffractometer using CuK α radiation ($\lambda = 1.5418$ Å) at 45 kV and 40 mA. The data were collected from 0.5° to 5° (2 θ) with a resolution of 0.02°.

 N_2 adsorption-desorption isotherms were measured using Micromeritics Tristar 3000 at liquid nitrogen temperature. Before the measurements, the samples were degassed at 100 °C for 12 h. The specific surface areas were evaluated using Brunauer-Emmett-Teller (BET) method in the P/P_0 range of 0.05–0.3. Pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method based on the adsorption branch of the isotherms, and the pore size was reported from the peak position of the distribution curve. The pore volume was taken at the $P/P_0 = 0.990$ point.

Thermogravimetric (TG) analyses were carried out on a Du Pont 951 thermogravimetric analyzer with a heating speed of 10 °C/min under air in a flow of 50 ml/min. N elemental analyses (EA) were performed on a Heraeus CHNS elemental analyzer.

Transmission electron microscopy (TEM) was performed on a Hitachi H-7100 electron microscope, operating at 75 kV. The scanning electron microscopy was carried out on a Hitachi S-800 Electron Microscope.

The ²⁹Si and ¹³C NMR experiments were carried out at frequencies of 79.4 and 75.5 MHz, respectively, on Bruker DSX400WB and DSX300 Solid State NMR spectrometers equipped with a commercial 4 mm MAS-NMR probe. All spectra were measured at room temperature. The magic-angle spinning frequencies were set at 6 kHz for all experiments and the variation was limited to ± 3 Hz using a commercial pneumatic control unit. Chemical shifts were externally referenced to TMS for ²⁹Si and ¹³C. For the ²⁹Si Bloch-decay experiment, the number of scan was set to 3072 and the recycle delay was set to 60 s. ${}^{13}C{}^{1}H$ cross-polarization spectrum was measured with a recycle delay of 5 s and the contact times were 3 ms. During the contact time the ¹H nutation frequency was set equal to 50 kHz, and a linear ramping was applied to the nutation frequencies of ¹³C (27.3–43.0 kHz). Proton decoupling field during the acquisition period was 83 kHz.

2.3. Catalytic reactions

Before the reaction, the functionalized SBA-15 materials were treated with methanol solution of tetramethylammonium hydroxide (TMAOH) to remove the residue Cl⁻ ions and to neutralize the protonated amine groups. 1 g of the ethanol-extracted sample was suspended in 50 ml of 0.2 M methanol solution of TMAOH at room temperature for 20 min. The solid was recovered by filtration, washed with methanol, and finally dried at 120 °C for one day. All the catalytic reactions were carried out in a sealed flask with a magnetic stirrer immersed in a thermostat bath. In a typical experiment, 15 mmol of benzaldehyde derivative A and 10 mmol of substituted 2'-hydroxyacetophenone **B** in the absence of solvent were mixed and heated to 140 °C of the reaction temperature, and then 0.15 g of the dried catalyst was rapidly added into the reactor. After the reaction, the catalyst was separated by filtration. The products were analyzed using a Chrompak CP 9000 gas chromatograph (GC) equipped with $30 \text{ m} \times 0.32 \text{ mm}$ RTX-50 capillary column and FID detector. Individual reaction product was identified by GC-Mass spectrometry (HP6890 mass spectrometer connected with a 30×0.25 mm RTX-50 capillary column). After the reaction, the catalyst was filtered and washed with CH₂Cl₂.

Then the solid was refluxed in fresh CH_2Cl_2 for 3 h, followed by filtration and washing again with CH_2Cl_2 . The organic materials were recovered after evaporating the solvent from the filtrate mixture. It accounted for more than 95% of the starting reactants.

3. Results and discussion

3.1. Functionalization of SBA-15 with MAPTMS

3.1.1. Influence of pre-hydolysis of TEOS

The pre-hydrolysis of TEOS prior to the addition of MAPTMS was found to have great influence on the structure, physical properties and stability of the methylaminopropyl-functionalized SBA-15 materials, synthesized using P123 as pore-directing agent under acidic condition. Fig. 1 shows the XRD patterns of the as-synthesized and ethanol-extracted M10/SBA with different pre-hydrolysis periods. It can be seen that the sample synthesized without TEOS pre-hydrolysis is Xray amorphous. When the TEOS pre-hydrolysis time is 1 h or 2 h, one intense peak indexed to (100) diffraction and higher order weak (110) and (200) diffractions appear for the as-synthesized samples, suggesting a highly ordered, hexagonally arranged pore structure, characteristic of SBA-15 [3]. The intensity of the diffraction peaks increases with the pre-hydrolysis time, indicating more ordered mesoporous structure was formed. However, as the TEOS pre-hydrolysis time further prolongs to 3 h, the intensity of the (100) diffraction greatly decreases and the (110) and (200) diffractions are almost unresolved. After ethanol extraction, the samples with the pre-hydrolysis time of 2 h and 3 h have their XRD patterns retained, while the sample of 1 h pre-hydrolysis time shows only one broad (100) reflection peak. These results indicate that pre-hydrolysis time of 1 h is not



Fig. 1. XRD patterns of (a) as-synthesized and (b) ethanol-extracted M10/SBA materials with different TEOS pre-hydrolysis periods.

enough to obtain functionalized SBA-15 of high stability, probably due to the incomplete condensation of the silanol groups. However, longer pre-hydrolysis time up to 3 h would also hinder the formation of ordered mesoporous SBA-15 structure. This may be due to that the surfactant-silica assembly formed in the long TEOS pre-hydrolysis period, such as 3 h, is too compact to allow MAPTMS to diffuse freely into the soft area and condensate on silica framework. The MAPTMS might then concentrate near the pore mouth and partially block the pores. Indeed, Table 1 shows that the extracted functionalized material synthesized with 2 h TEOS pre-hydrolysis gives the greatest surface area, pore size and pore volume. Moreover, elemental analyses indicate that the amount of amine groups incorporated in the silica framework, $\approx 1.4 \text{ mmol/g}$, is independent of the pre-hydrolysis period of 0–3 h.

It was also noticeable that no precipitate was observed in the mixture of TEOS and MAPTMS (9:1) at 40 °C under acid condition if TEOS was not pre-hydrolyzed. In subsequent aging period at 90 °C, only transparent gel was formed. When the TEOS/MAPTMS molar ratio was increased to 8.5:1.5, the precipitate was not formed even in the aging period at 90 °C. These are different from those reported in the synthesis of mesoporous amine-functionalized silica under neutral and basic conditions [19,41,53]. That can be explained by the following reasons. On one hand, the protonated methylaminopropyl groups may interfere the self-assembly of the co-polymer surfactant and the silica precursors. On the other hand, the protonated amine groups probably interact with the ethoxy groups of TEOS strongly through hydrogen bond so that the hydrolysis and condensation of ethoxysilane are inhibited. Therefore, by pre-hydrolysis of TEOS in the presence of P123 and acid, the surfactant micelles can assemble with TEOS without the perturbation from amine groups.

The N₂ sorption isotherms of the extracted M10/SBA materials synthesized with different TEOS pre-hydrolysis periods are illustrated in Fig. 2. The sample without TEOS pre-hydrolysis displays the characteristic type I isotherm of the IUPAC classification with very low N₂ adsorption volume and no apparent hysteresis loop. All the samples with the pre-hydrolysis time of 1–3 h exhibit type IV isotherms with clear H1 type hysteresis at

Table 1

Physical properties and N contents of the extracted M10/SBA-15 with different pre-hydrolysis periods

Pre-hydrolysis period (h)	d_{100} spacing (Å)	Pore diameter (Å)	$S_{\rm BET}$ (m ² /g)	Pore volume (cm ³ /g)	N content by EA (mmol/g)
0	_	_	364	0.21	1.43
1	89.5	59.0	403	0.41	1.37
2	90.8	64.4	528	0.59	1.41
3	87.1	61.4	236	0.33	1.44



Fig. 2. Nitrogen sorption isotherms and BJH pore size distribution plots (inset) of the extracted M10/SBA-15 with different TEOS prehydrolysis periods. (\blacksquare) 0 h, (\Box) 1 h, (\bigoplus) 2 h, and (\preccurlyeq) 3 h.

high relative pressure, similar to that of pure siliceous SBA-15. However, the sample with the 2 h pre-hydrolysis time shows a steep increase in adsorption at $P/P_0 = 0.6-0.7$, while the other two display gradual increases at $P/P_0 = 0.4-0.7$, indicating that the former possesses larger mesopores and narrower BJH pore-size distribution than the other two samples, as shown in the inset of Fig. 2. Since 2 h TEOS pre-hydrolysis led to the sample with the greatest surface area, pore size and pore volume, the materials studied hereafter were prepared under this condition.

3.1.2. Functionalized SBA-15 with different amounts of MAPTMS synthesized without inorganic salt

The XRD patterns of the as-synthesized and the extracted SBA-15 materials with different MAPTMS concentrations in the starting mixture are shown in Fig. 3.



Fig. 3. XRD patterns of (a) as-synthesized and (b) ethanol-extracted SBA-15 materials with different MAPTMS contents in the initial mixture.

All the as-synthesized MAPTMS-functionalized SBA-15 materials contain well-ordered hexagonal arrays of onedimensional channel structure (Fig. 3(a)). However, the (100) peak intensity decreases and the higher order (110) and (200) diffractions become ill-resolved when the MAPTMS molar contents in the synthesis gel is greater than 15%, demonstrating that the ordering of the mesostructure decreases with the MAPTMS content. The phenomenon was explained by that the organic groups would perturb the self-assembly of surfactant micelles and the silica precursors. After ethanol extraction, the samples with 5% and 10% MAPTMS were found to still have the intense (100) peak and two well-resolved (110) and (200) peaks retained (Fig. 3(b)), while the intensity of the (100) peak decreases drastically and the higher order diffraction peaks disappear completely as the MAPTMS contents further increase. The results imply that the ordered hexagonal arrays of one-dimensional channels in the samples synthesized with high MAPTMS concentrations could not stand the ethanol extraction process.

The TG and DTG profiles of the as-synthesized and ethanol extracted samples of SBA-15 with 10% MAP-TMS in the synthesis mixture are compared with the TG profile of as-synthesized pure siliceous SBA-15, as shown in Fig. 4. The as-synthesized M10/SBA has 2% weight loss at temperature lower than 100 °C, attributed to the loss of small amount of adsorbed water. Immediately followed is a large weight loss of $\approx 34\%$ in the temperature range of 160-500 °C. The corresponding DTG profile resolves this weight loss into two peaks at 254 and 317 °C. The former is assigned to the thermal removal of P123 surfactant and the latter is attributed to the decomposition of organic functional groups. After extraction, only a weight loss of $\approx 10\%$ is retained at $230 \sim 500$ °C and it is attributed to the decomposition of methylaminopropyl groups incorporated in SBA-15.



Fig. 4. TGA and DTG profiles of the as-synthesized pure siliceous SBA-15 (dash dot dot), the as-synthesized (dash), and the extracted (solid) functionalized SBA-15 with 10% MAPTMS in the initial mixture.

In other words, most of the P123 surfactant has been removed from the as-synthesized sample through ethanol extraction. The higher decomposition temperature of the P123 surfactant in the as-synthesized M10/SBA, in comparison to that of pure siliceous SBA-15, implies that the amine groups have stronger interaction with the surfactant than the silanol groups. Besides, the 1– 3% weight losses above 500 °C are likely due to the dehydroxylation of the silicate networks [54] or the elimination of residual ethoxy groups from the incomplete hydrolysis of TEOS [42].

 N_2 sorption isotherms of the functionalized SBA-15 with different MAPTMS contents are shown in Fig. 5. The samples prepared with 5% and 10% MAPTMS exhibit type IV isotherms with H1 hysteresis loops, while the sample with 15% MAPTMS only shows a very small hysteresis loop of H2 type. When the MAPTMS was increased to 20%, no hysteresis loop was observed. Fig. 5(b) shows that the M5/SBA and M10/SBA materials synthesized with lower MAPTMS contents have narrow pore size distributions with the diameters in



Fig. 5. The (a) nitrogen sorption isotherms and (b) BJH pore size distribution plots of the extracted SBA-NH₂ materials with different MAPTMS concentrations in the initial mixture. (\blacksquare) 5%, (\Box) 10%, (\bullet) 15%, and (\bigcirc) 20%.

52-70 Å, while that of higher MAPTMS content has either a broad pore size distribution in the smaller pore range (M15/SBA) or contains negligible pore volume (M20/SBA). Table 2 shows that the BJH pore diameter, BET surface area, and pore volume of the extracted functionalized SBA-15 decrease with the increase in amine content. In contrast, the wall thickness increases from 29.9 to 40.5 Å when 10% MAPTMS groups were incorporated and further increases to 65.9 Å as the MAPTMS raises to 15%. These results are attributed to the occupation of large organic molecules on the surface of the pores as well as the perturbation of methylaminopropyl groups during the silicate condensation process. Table 2 also shows that the d_{100} spacing of the extracted materials shrinks in \approx 3 Å when MAPTMS contents are in 5-10%, but that decreases drastically as the MAPTMS content further increase to 15%, indicating that the presence of MAPTMS did affect the selfassembly process.

3.1.3. Influence of inorganic salt

XRD patterns of the as-synthesized and the ethanolextracted materials containing 15 and 20 mol% MAP-TMS with the addition of various amounts of NaCl salt in the synthesis mixture are shown in Fig. 6. All the samples exhibit one (100) intense peak and two weak (110)and (200) peaks. These results are different from those in Fig. 3, where the materials synthesized with 15 and 20 mol% MAPTMS lost the crystallographic ordering after ethanol-extraction, indicating that the addition of NaCl to the synthesis mixture greatly improve the stability of the functionalized silica framework. Moreover, the d-spacings of the (100) diffraction peak was found to increase from 82 Å for M15/SBA to 91 Å for M15/ SBA-NaCl. Similar salt effect was also observed in the synthesis of periodic mesoporous organosilicas [13,52]. It was proposed that the addition of the salt electrolyte might influence the hydrolysis and condensation kinetics of the silica precursors [55]. Moreover, the salting-out effect of the inorganic electrolyte may stabilize the

Table 2

Physicochemical properties of the extracted functionalized materials synthesized with various concentrations of MAPTMS and NaCl in the initial mixtures

Sample	d ₁₀₀ spacing (Å)	Pore diameter (Å)	$S_{\rm BET}$ (m ² /g)	Pore volume (cm ³ /g)	Wall thickness (Å)
M0/SBA	93.2	77.8	769	1.04	29.9
M5/SBA	89.3	67.0	602	0.71	36.1
M10/SBA	90.8	64.4	528	0.59	40.5
M15/SBA	81.7	28.8	280	0.23	65.9
M20/SBA	_	-	55	0.06	_
M15/SBA-0.5NaCl	91.6	58.5	303	0.35	47.3
M15/SBA-1.0NaCl	90.1	62.0	349	0.47	42.8
M15/SBA-1.5NaCl	90.8	66.5	384	0.50	37.9
M20/SBA-1.5NaCl	91.6	60.3	200	0.29	45.5



Fig. 6. XRD patterns of (A) as-synthesized and (B) ethanol-extracted SBA-15 materials with different MAPTMS and NaCl concentrations in the synthesis mixture: (a) M15/SBA-1.5NaCl, (b) M15/SBA-1.0NaCl, (c) M15/SBA-0.5NaCl, and (d) M20/SBA-1.5NaCl.

micelle structure and facilitate the formation of wellordered mesoporous silica.

The elemental analysis results of the extracted functionalized SBA-15 with different MAPTMS concentrations in the synthesis mixture are shown in Table 3. About 90% of the organic moieties from MAPTMS are effectively incorporated in the SBA-15 framework. That value however implies that MAPTMS is more difficult than TEOS to condensate into the silica framework. For the materials synthesized without NaCl, the amino contents analyzed by TG are slightly higher than those by EA. This may be due to that the condensation of silanol groups proceeds in similar temperature range as that for the decomposition of organic groups. In the case of materials synthesized with NaCl, the amino contents analyzed by TG are very close to those by EA. It implies that the silicate condensation is more complete when NaCl is present during the synthesis procedure. As a result, less interference from the condensation of

Table 3

Ν	conte	ents o	f the	extrac	ted fu	nction	nalize	d SB	A-15	5 sy	ynthesi	ized	with
va	rious	conce	ntrati	ions of	MAF	PTMS	and	NaCl	in t	he	initial	mix	tures

Sample	N content by EA (mmol/g)	N content by TG (mmol/g)	Theor. content (mmol/g)	Incorp. ratio based on EA (%)
M0/SBA	0	_	_	_
M5/SBA	0.69	0.87	0.79	87
M10/SBA	1.41	1.47	1.51	93
M15/SBA	1.97	2.07	2.15	92
M20/SBA	2.30	2.54	2.75	84
M15/SBA-0.5NaCl	1.95	1.95	2.15	91
M15/SBA-1.0NaCl	1.94	1.93	2.15	90
M15/SBA-1.5NaCl	1.95	1.93	2.15	91
M20/SBA-1.5NaCl	2.37	2.35	2.75	86

silanol groups is contributed to the weight loss where the decomposition of organic groups occurs. Table 3 also shows that the addition of inorganic salt does not have significant influence on the amount of the amine groups incorporated in the mesoporous materials.

The mesostructural ordering of the extracted samples was confirmed by the TEM images. The extracted M10/SBA displays clear one-dimensional channels (Fig. 7(a)), while the M15/SBA gives only an ill-defined image (Fig. 7(b)). On the other hand, the ordering of pore structures was greatly improved when NaCl was added in the synthesis mixture. Fig. 7(c) and (d) shows both the extracted M15/SBA-1.5NaCl and M20/SBA-1.5NaCl materials have clear one-dimensional channel pores.

The morphology of the functionalized materials was found to vary with the addition of NaCl in the starting solution. The SEM micrographs in Fig. 8(a) and (b) reveal that the extracted MAPTMS-functionalized SBA-15 materials consists of short rod-shaped particles of ≈ 600 nm in length and 300 nm in diameter. For the material synthesized with NaCl, the rod-shaped particles seem to lengthen to fiber-like materials with the length as long as several decade micrometers. Moreover, the fibers of \approx 350 nm in diameter are aggregated to form bundles of \approx 2.5 µm in diameter (Fig. 8(c)).

The N₂ sorption isotherms of the extracted materials with 15% and 20% MAPTMS synthesized with various amounts of NaCl in the initial mixture display the characteristic type IV isotherms with clear H1 type hysteresis at high relative pressure (Fig. 9(a)), in contrast to the type I isotherms observed on the materials synthesized without NaCl. The BJH pore size distributions shown in Fig. 9(b) indicate that the materials synthesized with NaCl have narrow pore size distributions with the diameter ranged in 51–75 Å. Table 2 shows that the pore size, BET surface area, and pore volume of the functionalized materials increase with NaCl concentration. Even when the N content is up to 2.37 mmol $g^{-1}(17.2 \text{ mol}\%)$ MAPTMS), the material synthesized with NaCl still retains pore size of 60.3 Å, surface area of $200 \text{ m}^2/\text{g}$ and pore volume of $0.29 \text{ cm}^3/\text{g}$.

The successful incorporation of MAPTMS in functionalized SBA-15 mesoporous materials is confirmed



Fig. 7. TEM images of the solvent-extracted functionalized SBA-15 synthesized with (a) 10% MAPTMS, (b) 15% MAPTMS, (c) 15% MAPTMS and with NaCl, and (d) 20% MAPTMS and with NaCl.



Fig. 8. SEM images of the ethanol-extracted functionalized SBA-15 synthesized with (a) 10% MAPTMS, (b) 15% MAPTMS, and (c) 15% MAPTMS and with NaCl.







Fig. 9. The (a) nitrogen sorption isotherms and (b) BJH pore size distribution plots of the extracted functionalized SBA-15 materials with different NaCl concentrations in the initial mixture. (\blacksquare) M15/SBA-0.5NaCl, (\Box) M15/SBA-1.0NaCl, (\bullet) M15/SBA-1.5NaCl, and (\star) M20/SBA-1.5NaCl.

by NMR spectroscopy. The ²⁹Si MAS NMR spectra of the functionalized SBA-15 materials in Fig. 10 show three distinct resonance peaks in up-field corresponding

Fig. 10. (a) 29 Si MAS NMR spectra of the functionalized SBA-15 with different MAPTMS loadings and (b) 13 C {1H} CPMAS NMR spectrum of the extracted M15/SBA-15.

to Q^n $(Q^n = \text{Si}(\text{OSi})_n(\text{OH})_{4-n}$, n = 2-4; Q^4 at $\delta = -111$ ppm, Q^3 at $\delta = -101$ ppm, and Q^2 at $\delta = -92$ ppm) and two more peaks in down-field assigned

 T^{m} $(T^{m} = RSi(OSi)_{m}(OH)_{3-m}, m = 1-3; T^{3}$ at to $\delta = -67$ ppm and T^2 at $\delta = -57$ ppm) [18,55]. The appearance of T^m peaks confirms that the organic silane is incorporated as a part of the silica wall structure. The relative integrated intensities of the T^m and Q^n signals (T^m/Q^n) were found to increase with the MAPTMS content in the initial mixture. That implies that the amount of organic moieties functionalized on the silica wall increases with the amount of MAPTMS added in the initial mixture, which is in agreement with the results of elemental and thermogravimetric analysis. After extraction, the decrease of the relative $(Q^2 + Q^3)/Q^4$ intensities may be due to the further dehydroxylation and condensation of partial silanols in the silicate networks during the ethanol extraction. This may be the reason of the slight shrinkage of the cell dimension after ethanol extraction. The M15/SBA material synthesized with various amounts of NaCl shows similar ²⁹Si MAS NMR spectra with three Q^n resonance peaks in up-field and two T^m peaks in down-field (not shown), indicating that the addition of NaCl does not affect the amount of organo-silane moieties incorporated in the silica framework, in consistence with the results of EA and TGA. Moreover, the relative $(Q^2 + Q^3)/Q^4$ intensities were lower than those of the samples synthesized without NaCl. For instance, the $(Q^2 + Q^3)/Q^4$ intensity ratio was 0.57 for as-synthesized M15/SBA-1.5NaCl, while that for as-synthesized M15/SBA was 0.69. These results confirm that the silicate condensation was more complete when NaCl was present in the synthesis mixture.

The ¹³C CP-MAS NMR spectrum (Fig. 10(b)) of the ethanol extracted sample with 10% methylaminopropyl groups clearly displays four peaks at 10, 20, 52, and 34 ppm, corresponding to the C atoms on the Si–CH₂–CH₂–OH₂–NH–CH₃ group in sequence from left to right, respectively. It further confirms that the SBA-15 materials are indeed functionalized with methylaminopropyl groups and the organic moieties are not decomposed during the preparation procedure. In addition, no resonance peaks corresponding to the surfactant P123 are observed in the range of 67–77 ppm, indicating that the surfactant was completely removed during the extraction [21,56], which is in agreement with the result of TG analysis.

3.2. Catalysis reactions

Members of the flavanoid family have attracted much attention due to numerous various pharmacological activities [57]. Traditionally, flavanones were synthesized via the Claisen–Schmidt condensation between benzaldehydes and 2'-hydroxyacetopheone [58,59] and the subsequent isomerization of the 2'-hydroxychalcone intermediates in basic or acidic media under homogeneous conditions. In the past decade, various solid catalysts have been applied to flavanones synthesis, such as magnesium oxide [60], alumina [61], barium hydroxides [62,63], hydrotalcites [64–66], and natural phosphates modified with NaNO₃ or KF [67,68]. However, most of them require the use of expensive toxic solvents to facilitate the heat and mass transfer in the liquid phase reaction systems [60]. As a clean route for organic synthesis, the ultimate goal of many heterogeneous catalytic processes is to eliminate the use of solvents. Recently, amino-modified silicas were found to be effective base catalysts for Knoevenagel condensations, Michael additions and the nitroaldol reactions [34-36]. As large-pore amine-functionalized SBA-15 catalysts, it is expected that they might be efficient base catalysts for the synthesis of flavanones under solvent-free condition. Here the extracted M15/SBA (designated as Cal-1) and M15/ SBA-1.5NaCl (designated as Cal-2) were used to test the Claisen-Schmidt condensation of substituted acetophenones and benzaldehyde derivatives and subsequent intramolecular Michael addition in the absence of solvent.

The XRD pattern of Cal-2 treated with 0.2 M methanol solution of TMAOH is shown in Fig. 11, which demonstrates that the material still retains the well-ordered mesostructure. The physical properties, texture and N content of the treated materials were also found to be almost unchanged.

Pure siliceous SBA-15 with the same pre-treatment was first tested for the condensation of benzaldehyde and 2'-hydroxyacetophenone and gave negligible conversion (<3%). The reaction results of the Cal-1 and Cal-2 catalysts at 140 °C for 10 h are shown in Table 4. Both catalysts display good conversions of acetophenones **B** and very high selectivities to flavanones **D**. These values, to the best of our knowledge, are the highest selectivities to the corresponding flavanones reported up to date for the Claisen–Schmidt condensations over various catalysts with or without solvent. For the same reaction, the Cal-2 catalyst, which was synthesized with



Fig. 11. XRD pattern of the extracted M15/SBA-15-NaCl after treated with TMAOH.

Table 4

$R \xrightarrow{H} 0 \xrightarrow{H} 0 \xrightarrow{R'} R' \xrightarrow{R'} 0 \xrightarrow{O} 0 \xrightarrow{O} 0 \xrightarrow{H} 0 \xrightarrow{R'} R' \xrightarrow{R'} 0 \xrightarrow{O} 0 \xrightarrow{R'} $							
	Δ	\ I	В	С	D		
Entry	Catalyst	R	R ′	Conv. of B (%)	Sel. to C (%)	Sel. to D (%)	
1	Cal-1	Н	Н	41	30	70	
2	Cal-1	CH ₃ O	Н	45	38	62	
3	Cal-1	Cl	Н	23	26	74	
4	Cal-2	Н	Н	52	31	69	
5	Cal-2	CH ₃ O	Н	72	39	61	
6	Cal-2	Cl	Н	40	25	75	
7	Cal-2	NO_2	Н	35	13	87	
8	Cal-2	Н	CH ₃ O	50	14	86	
9	Spent Cal-2	Н	Н	45	25	75	

Reactions of substituted benzaldehyde A (15 mmol) and substituted 2'-hydroxyacetophenone B (10 mmol) in the absence of solvent over M15/SBA (Cal-1) or M15/SBA-1.5NaCl (Cal-2) catalysts (0.15 g) at 140 $^{\circ}$ C for 10 h

NaCl, shows much higher conversions than Cat-1, although they contain very similar amount of amine groups. This may be due to that well-ordered mesopores of the former more effectively facilitate the diffusion of the reactant and product molecules in liquid phase reactions. The almost same selectivities to flavanones over both Cal-1 and Cal-2 catalysts are due to that the values are the equilibrium distribution between 2'-hydroxy-chalcone and flavanone, confirmed by a separate experiment. In all the reactions, no by-products other than chalcones and flavanones were observed in the reaction products, indicating that Cannizzaro reaction of aldehyde or condensation of ketone did not take place under the reaction conditions.

The substituting groups in the aromatic rings have great influence on the conversion and selectivity. The electron-donating group at the *para*-position of benzaldehyde increases the conversion of the reactants, but decreases the selectivity to flavanones, while the electron-withdrawing groups decrease the conversion but increases the selectivity to flavanones. On the contrary, the electron-donating CH₃O-substituent in 2'-hydroxyacetophenone increases not only the conversion of the reactants, but also the selectivity to flavanone. The steric effect of substituting groups such as NO₂-, Cl-, and CH₃O- were reported to decrease the catalytic activities over other solid catalysts like barium hydroxide, zeolites and hydrotalcites [62-66]. However, that seems to be negligible in our system due to large pore size in the catalysts.

The used catalyst Cat-2, after treated with CH_2Cl_2 in a Soxhlet apparatus for 3 h and then dried at 100 °C overnight, showed 45% conversion of acetophenone and 75% selectivity to flavanone (Table 4) for the reaction between benzaldehyde and 2'-hydroxyacetophenone, indicating that most of the active sites could be regenerated by a simple solvent treatment.

4. Conclusions

Well-ordered methylaminopropyl functionalized SBA-15 with the content of organic moiety up to 2.37 mmol/g was synthesized by co-condensation of TEOS and MAPTMS using P123 as pore-directing agent under acid condition. Pre-hydrolysis of TEOS before the addition of MAPTMS has great effect on the formation of mesoporous structures of the functionalized SBA-15 materials. The long-range ordering of mesoporous structure of the modified materials decreased with the increase of MAPTMS concentration in the initial mixture. The addition of NaCl salt in the starting solution could improve the ordering of mesostructure and the stability of the functionalized materials. When used as solid base catalysts in liquid phase, the MAP-TMS functionalized SBA-15 showed good conversion of the reactants and very high selectivity to flavanones for the Claisen-Schmidt condensation of substituted acetophenones and benzaldehyde derivatives and subsequent intramolecular Michael addition in the absence of solvent. The well-ordered mesopores effectively facilitated the diffusion of the reactant and product molecules in liquid phase reactions.

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