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Synthesis, characterization and catalytic activity of acid-base bifunctional materials through protection of amino groups

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1. Introduction

Since the discovery of ordered mesoporous M41S [1,2], a variety of ordered mesoporous materials have been synthesized using a surfactant templating method. Surface-modified mesoporous materials with different active sites have been extensively investigated in recent years for catalysis [3–6], separation [7,8], chemical sensing [9], and nanoscience [10,11]. Many monofunctionalized SBA-15 mesoporous silica catalysts have been prepared [12-21], which have unique properties alone or in combination with other functional groups. However, some catalytic reactions need multifunctionality of active sites with cooperative effect, e.g. the combination of acid and base properties [22-26]. Previous work on bifunctional solid-catalyst synthesis mainly focuses on the use of metal centers with acid sites [27-31]. Recently, much effort has been devoted on the combination of organic functional groups, bifunctionalized mesoporous silica nanosphere materials with ureidopropyl group and 3-[2-(2-aminoethylamino)ethylamino]-propyl group [27], amine functional groups and thiols [30,31]. Katz et al. [18,32] reported the synthesis of imprinted amines in bulk silica by using the protection of carbamate groups, which was commonly used as protecting agents for amino groups in synthetic chemistry. Zeidan et al. reported that SBA-15

ABSTRACT

Acid–base bifunctional mesoporous material SO₃H-SBA-15-NH₂ was successfully synthesized under low acidic medium through protection of amino groups. X-ray diffraction (XRD), N₂ adsorption–desorption, transmission electron micrographs (TEM), back titration, ¹³C magic-angle spinning (MAS) NMR and ²⁹Si magic-angle spinning (MAS) NMR were employed to characterize the synthesized materials. The obtained bifunctional material was tested for aldol condensation reaction between acetone and 4-nitrobenzaldehyde. Compared with monofunctional catalysts of SO₃H-SBA-15 and SBA-15-NH₂, the bifunctional sample of SO₃H-SBA-15-NH₂ containing amine and sulfonic acid groups exhibited excellent acid–basic properties, which make it possess high activity for the aldol condensation.

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containing sulfonic acid and thiol exhibited a cooperative effect in a condensation reaction [20]. Dufaud and Davis reported a multifunctional heterogeneous SBA-15 containing primary amine and sulfonic acid [19]. However, the equilibrium between acid and base is likely very important in the catalytic reaction process. Therefore, Zeidan et al. investigated the effect of the balance between acid and base groups by varying the pKa of the acidic groups [33]. Alauzun et al. [34] reported the synthesis of bifunctional mesoporous materials containing two antagonist functions, an acidic group in the framework and a basic one in the channel pores. Our group has reported two acid-base bifunctional mesoporous materials benzyl-APS-S-SBA-15 (APS: (3-trimethoxysilanyl-propyl)-amine) and anthracyl-APS-S-SBA-15 by controlling steric hindrance [35]. Very recently, Thiel et al. described the synthesis of various bifunctional acid-base materials for cooperative catalytic reactions [36].

Among the well-known mesoporous materials, SBA-15 has relatively good hydrothermal stability [37], hexagonal arrays of uniform pores, high special surface area and large pore volume. However, the inherent lack of active sites, such as acid and basic sites of adequate strength, has severely restricted its application in industry. It is still a challenge for its surface functionalization. In this paper, we report a method to synthesize acid–base bifunctional materials under low acidic medium through protection of amino groups. The method is important to prevent interaction between acid and base, and generate an efficient catalyst. The catalytic activity of the materials in aldol condensation reaction between acetone and 4-nitrobenzaldehyde was investigated.

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Scheme 1. Synthesis of NH₂-SBA-15-SO₃H.

2. Experimental

2.1. Chemicals and materials

Pluronic123 ($EO_{20}PO_{70}EO_{20}$) (Aldrich), HCl (A.R), 4-nitrobenzaldehyde (Acros), acetone (A.R), tetraethyorthosilicate (Aldrich), 3-aminopropyltrimethoxysilane (APTMS) (Aldrich), ethanol (A.R), 3-mercaptopropyltrimethoxysilane (MTPMS) (Aldrich), di-tertbutyl dicarbonate (Acros) were commercially available and used as received.

2.2. Sample preparation

2.2.1. Synthesis of 3-tert-

butyloxycarbonylaminopropyltrimethoxysilane (NHBoc, I)

I was prepared by mixing 3-aminopropyltrimethoxysilane (APTMS) (0.77 mL, 4.1 mmol) and di-tert-butyl dicarbonate (BOC) (1.005 g, 4.6 mmol) in 30 mL of anhydrous ethanol [38]. The mixture was stirred overnight at room temperature. Subsequently, the additional solvent was removed under vacuum. The residual liquid was distilled to afford 1.2 g of I (3 mmol).

2.2.2. Synthesis of bifunctional materials

1.02 g of $EO_{20}PO_{70}EO_{20}$ (P123) was dissolved in 40 g of distilled water, Then, 5.05 mL of TEOS (prehydrolysis 50 min in pH = 4.0) was injected. The mixture was allowed to stir at 40 °C for 40 min. Subsequently, premixing of 0.6 g I and 0.33 mL 3-mercaptopropyltrimethoxysilane (MTPMS) was added in to the system. The reaction mixture was stirred at 40 °C for 20 h, and then heated to 100 °C for 24 h in oven. The resulting solid was cooled to room temperature, and rinsed with excess H₂O until the slurry reached a neutral pH value. Next, the solid was allowed to dry overnight on a filter. Then the dried solid was extracted with EtOH (400 mL/g) by refluxing for 48 h to remove additional P123. The obtained solid was washed with copious amount of water until a neutral pH value reached. Finally, these solid was dried at 80 °C under vacuum for 12 h, and NHBoc-SBA-15-SH was obtained [20].

The NHBoc-SBA-15-SH was washed and treated with H_2O_2 solution at room temperature for 3 h. Then the diluted sulfuric acid solution was added and the reaction was kept for 30 min, the SH group on NHBoc-SBA-15-SH was totally oxided into SO₃H. The product was washed with copious amount of water until a neutral pH value reached, and then dried overnight to obtain a dry white solid termed NHBoc-SBA-15-SO₃H.

Deprotection amino group was completely achieved by thermal treatment of NHBoc-SBA-15-SO₃H at 185 °C under vacuum for 4 h. The resulting bifunctional mesoporous silica contained both aminopropyl groups and sulfonic acid groups, named NH₂-SBA-15-SO₃H (Scheme 1).

2.3. Characterization

N₂ adsorption-desorption isotherms were obtained on a Micromeritics ASAP 2020 system at liquid N₂ temperature $(-196 \ ^{\circ}C)$. Before measurements, the samples were outgassed at 100 °C for 24 h. The specific surface area was calculated by using the Brunauer-Emmett-Teller (BET) method and the pore size distributions were measured by using Barrett-Joyner-Halenda (BJH) analyze from the adsorption curve of the isotherms. Powder X-ray diffraction patterns (XRD) were collected using a Siemens D5005 (0.2° /min) with Cu K α radiation (40 kV, 30 mA). Transmission electron microscope (TEM) was performed on a Hitachi H-8100 electron microscope, operating at 200 kV. The solid-state ²⁹Si MAS NMR spectra were measured using a Varian infinity-400 spectrometer with a frequency of 59.63 MHz and 7.5 mm zirconia rotors spun at 4 kHz. ¹³C CP/MAS NMR spectra were measured using a Bruker AM-300 spectrometer with a frequency of 75.48 MHz. Elemental analyses (EA) of sulfur and nitrogen were performed on a VarioEL CHN elemental analyzer. A back titration method was used to measure the amount of acid-base centers of the materials according to the modified procedure in literature [35]. 0.1 g of the sample was added to a conical beaker, and then 10 mL 0.01 M HCl (or NaOH) solution was added. The mixture was stirred at room temperature for half an hour; then, the mixture was filtered and rinsed repeatedly for four times with 25 mL of distilled water. The resulting filtrate was titrated with 0.01 M NaOH (or HCl) solution using phenolphthalein as indicator.

2.4. Catalytic experiments

The aldol condensation reaction was performed in a flask under N₂. First, 4-nitrobenzaldehyde (76 mg, 0.5 mmol) was dissolved in acetone (10 mL). Then catalytic reaction was carried out over 0.05 mmol the total amount of amine and/or sulfonic acid functional catalyst at 50 °C for 20 h. Then filtration was used to remove the solid catalyst. After washing with acetone and chloroform, the resulting product was analyzed by ¹H NMR in CDCl₃ [32].

3. Results and discussion

3.1. Characterization of the prepared samples

Fig. 1 shows the XRD patterns of SH-SBA-15-NHBoc, SO₃H-SBA-15-NHBoc and SO₃H-SBA-15-NH₂. All samples showed a prominent peak at $2\theta = 0.8^{\circ}$. However, the intensity of the diffraction patterns of SO₃H-SBA-15-NH₂ was much larger than that of SH-SBA-15-NHBoc. The decrease in the intensity of the (1 1 0) and (2 0 0) peaks for SH-SBA-15-NHBoc and SO₃H-SBA-15-NHBoc was observed, which indicates that a decreased pore structural ordering due to the multi-step synthesis procedures.

The TEM images of sample SO_3H -SBA-15-NH₂ are shown in Fig. 2. Parallel straight pores and hexagonally arrayed pores were clearly observed, which can be ascribed to the (1 1 0) and (1 0 0) directions of p6 mm phase, respectively. TEM images provide evidence for that the structural ordering of SO_3H -SBA-15-NH₂ remains intact after the organic modifications. These results, together with the XRD patterns, confirmed the formation of the highly ordered mesostructure.

The N₂ adsorption–desorption isotherms and pore size distributions of SH-SBA-15-NHBoc, SO₃H-SBA-15-NHBoc and SO₃H-SBA-15-NH₂ are shown in Fig. 3. It can be seen that the samples displayed a type IV isotherm with H1 hysteresis and a sharp increase in volume adsorbed at $P/P_0 \approx 0.72$, indicating that the ordered mesoporous structure of SBA-15 was well remained. The structural properties of the different mesoporous materials are listed in Table 1. It can be found that the specific surface area gradually decreases from SO₃H-SBA-15-NH₂ to SO₃H-SBA-15-NHBoc and SH-SBA-15-NHBoc. The pore diameter increases from 7.6 nm for SH-SBA-15-NHBoc to 8.3 nm for SO₃H-SBA-15-NH₂.

The incorporation of carbamate groups in the mesoporous materials and transformation of carbamate groups to the corresponding primary amine were confirmed by solid-state ¹³C



Fig. 1. XRD patterns of the synthesized samples: (a) SH-SBA-15-NHBoc, (b) SO_3H -SBA-15-NHBoc, and (c) SO_3H -SBA-15-NH₂.

MAS NMR (Fig. 4). The ¹³C CP/MAS NMR spectrum of SO₃H-SBA-NHBoc (Fig. 4a) demonstrates that the carbamate group remains intact as shown by the signals at 25.95 ppm (CH₃ resonances of tert-butyl), 158.00 ppm (carbonyl resonances) and additional signals attributed to the propyl spacer [39]. The resonances associated with the carbamate protecting group (25.95 and 158.00 ppm) disappeared after thermal treatment under N₂ flow, indicating that the carbamate deprotection can be successfully achieved by thermal treatment.

Solid-state ²⁹Si MAS NMR spectroscopy has been proven to be the most useful technique for providing chemical information regarding the condensation of organosiloxane. As shown in Fig. 5, the peaks with chemical shift at -106.9, and -111.9 ppm were attributed to the Q³ and Q⁴ bands of Si(OH)(OSi)₃, and Si(OSi)₄ silicate species, respectively. In addition, the



Fig. 2. TEM images of sample SO₃H-SBA-15-NH₂: (a) in direction perpendicular to pore axis and (b) in direction of pore axis.



Fig. 3. N2 adsorption isotherm and pore size distributions of samples: (a) SH-SBA-15-NHBoc, (b) SO3H-SBA-15-NHBoc, and (c) SO3H-SBA-15-NH2.



Fig. 4. Solid-state ¹³C MAS NMR of samples: (a) SO₃H-SBA-15-NHBoc and (b) SO₃H-SBA-15-NH₂.



Fig. 5. Solid-state ²⁹Si MAS NMR of samples SO₃H-SBA-15-NH₂.

Table 1	
Pore structural properties	of functionalized samples.

Samples	BET surface	Pore size ^a	Pore vol.
	area (m ² g ⁻¹)	(nm)	(cm ³ g ⁻¹)
SH-SBA-15-NHBoc	264.7	7.6	0.48
SO ₃ H-SBA-15-NHBoc	385.0	8.1	0.59
SO ₃ H-SBA-15-NH ₂	433.0	8.3	0.62

^a Calculated by using the BJH model on the adsorption branch of the isotherms.

resonance peaks from -50 to -70 ppm can be attributed to T^m ($T^m = RSi(OSi)_3(OH)_3$, m = 1-3), confirming that the silane organic moieties are incorporated as a part of the silica wall structure and a significant fraction of the surfactant is still present even after the surfactant extraction as well as multi step synthesis procedures [40,41].

Quantification of the functional group loaded in SBA-15 samples was performed for the bifunctional materials using elemental analysis (CHNS). The results of CHNS elemental analysis indicate that there is 0.249 mmol/g of sulfoacid and 0.233 mmol/g of NH₂ for SO₃H-SBA-15-NH₂.





Entry	Catalyst	Conv. (%) ^a	Isolated yield (%)	ated yield (%)	
			A	В	
1	SBA-15	0	0	0	
2	SBA-15-SO ₃ H	6.5	6	0.5	
3	SBA-15-NH ₂	42.8	33.7	9.1	
4	SO ₃ H-SBA-15-NHBoc	24.3	18.2	6.1	
5	SBA-15-A/SBA-15-B ^b	47.2	43	4.2	
6	SO ₃ H-SBA-15-NH ₂	75.2	69.4	5.8	

^a Total conversion. Yields determined through ¹H NMR spectroscopic analysis with THF as the internal standard.

^b 1:1 Mixture of sulfonic acid-functionalized SBA-15 (SBA-15-A) and amine-functionalized SBA-15 (SBA-15-B).

To further confirm the elemental analysis, back titration was performed for the materials. It was found that the SO_3H -SBA-15-NHBoc sample gave a loading of 0.2734 mmol/g of sulfoacid and 0.08309 mmol/g of NH₂. In addition, the sample of carbamate deprotection gave a loading of 0.2457 mmol/g of NH₂. The results are in good agreement with the elemental analysis results.

3.2. Catalytic properties

The materials were used in the aldol condensation between acetone and 4-nitrobenzaldehyde. The numerical results of this reaction over the catalysts are summarized in Table 2. The aldol condensation of 4-nitrobenzaldehyde with acetone was reported to be catalyzed by acid, base and bifunctionalized acid/base catalysts. The reaction results showed that there was almost no conversion for pure silica SBA-15 (Table 2, entry 1). Meanwhile, sulfonic acid functionalized SBA-15 showed relatively low conversion of 6.5% (Table 2, entry 2). The conversion for amine functionalized SBA-15 was 42.8% (Table 2, entry 3). The use of bifunctionalized material through protection amino group gave the conversion of 24.3% (Table 2, entry 4), which indicates that there is weak basicity in the material. However, the bifunctionalized deprotected sample of SO₃H-SBA-15-NH₂ showed the significant conversion of 75.2% (Table 2, entry 6), which was higher than the monofunctional catalysts of SO₃H-SBA-15 and SBA-15-NH₂. Moreover, a physical mixture of acid-functionalized SBA-15 and amine functionalized SBA-15 (Table 1, entry 5) showed an intermediate level of conversion that was lower than the bifunctionalized acid-base catalyst. In addition, a slightly increased catalytic activity for SO₃H-SBA-15-NHBoc sample is noted in Table 2, entry 4 with compared with SBA-15-SO₃H (entry 2), suggesting that a very small amount of amine groups may be not protected with BOC. These results indicated that the acid-base cooperation effect should be involved in the catalytic reaction. In addition, the efficient acid/base active sites might increase due to protection of amino groups from the interaction between acid and base.

We also expect that this bifunctional material can serve as an efficient catalyst for other reactions. Further work is still required to make detailed understanding of the behavior of the coexisting acidic and basic sites in a single material.

4. Conclusions

In this study, a method for successfully synthesizing acid-base bifunctional material through protection of amino group is described. XRD and TEM data provide evidence that the functionalized materials keep a 2D-hexagonal mesoporous framework. Back titration, ¹³C MAS NMR and ²⁹Si MAS NMR confirm that the amine and sulfonic acid are successfully incorporated into the mesoporous SBA-15. Compared with SBA-15-SO₃H and SBA-15-NH₂, bifunctional material SO₃H-SBA-15-NH₂ displays higher catalytic performance, and shows excellent conversion for the aldol condensation reaction. These results indicate that the acidbase cooperation effect should be involved in the catalytic reaction and efficient acid/base active sites might increase during the protection of amino group for prevention of the interaction between acid and base in the bifunctional material.

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