

IMPROVED SYNTHESIS AND STUDY OF ACIDIC PROPERTIES OF 'PLUGS'-CONTAINING AL-SBA-15 MATERIALS

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A novel 'plugs'-containing Al-SBA-15 material (denoted as PAS) was directly synthesized through simultaneous introducing toluene and aluminum precursor into the reaction mixture of traditional SBA-15. Such material not only featured a unique two-step desorption isotherm as conventional plugged SBA-15 synthesized using excessive siliceous precursor, and higher pore wall thickness than that of other analogous materials, but also possessed weak and medium acidic sites, which implied the PAS would offer unusual advantages such as multifunctionality to process a large variety of feed-stocks in acid-involved reaction (e.g. polymerization of tetrahydrofuran) in industrial point of view. In addition, catalytic activity of the PAS was investigated by the tetrahydrofuran (THF) polymerization reaction in the presence of acetic anhydride and compared with Al-doped MCM-41 prepared via conventional direct hydrothermal synthesis. The PAS exhibited good performance on polymerization of THF. Such result could be related to the large pore size and moderate acidic sites.

Keywords: Mesophases; Synthesis; Acidity; Pore structure.

Functional mesoporous materials as solid-acid catalysts have significant applications in catalytic reaction¹⁻⁷. Modified SBA-15 materials with high surface area, large pore diameter, high hydrothermal stability and moderate acid sites are of great potential acid-catalytic materials^{5,8}. The incorporation of acid sites in mesoporous materials is usually achieved either by direct methods during the synthesis of the mesophase^{8,9} or by postsynthetic methods¹⁰. During materials preparation via postsynthetic methods metal oxides were formed in the mesopore channels or on the external surface, which would reduce surface area, pore volume, and pore diameter, or play a negative role in catalysis^{9,11}. Zukal et al.¹⁰ reported that Al-SBA-15 without any blocking of the mesopores by alumina was prepared via post synthetic method with aluminum chlorhydrol as aluminum precursor.

However, the direct incorporation of aluminum into the amorphous silica walls was valuable path to generate acidic sites during the formation of mesophase^{5,12,13}. Yue et al. reported the direct preparation of Al-SBA-15 and found that Al-SBA-15 possessed relatively higher acid catalytic activity than Al-MCM-41⁸. But the highly acidic synthesis gel required for the formation of ordered SBA-15 may limit the co-condensation of Si and Al precursor. Therefore, it is still challenge to find a one-step route to modified SBA-15 with acidity without increasing the complexity of synthesis.

'Plugs'-containing Al-SBA-15 (PAS) is the porous analogue of SBA-15, it possesses the two-dimensional hexagonal mesoporous structure as SBA-15 and moderately acidic sites, which makes this material promising for a variety of reactions such as alkylation of aromatics, hydrocarbon cracking and tetrahydrofuran polymerizing.

In general, the materials analogous to PAS were synthesized using excessive siliceous and aluminum precursor compared to traditional Al-SBA-15^{5,14-16}. As reported elsewhere¹⁷⁻¹⁹, plugged SBA-15 is put forward as a good candidate for industrial applications involving large molecules. However, the pure siliceous material on itself exhibits lower acid catalytic activity because of the lack of enough acid sites. Therefore, modification of plugged SBA-15 is a key step to increase its catalytic activity. In previous study, this type of material had been made catalytically active by post-synthesis modification methods^{15,20-22}. But this modification method may greatly influence the porous properties of the plugged SBA-15 support^{14,20,22}. Alternatively, an in situ formation of heteroatom-incorporated plugged SBA-15 had been found^{23,24}. Regretfully, it was not economical owing to the use of the excessive siliceous and aluminum precursor. Naturally, it is desirable to direct synthesis of PAS using normal siliceous and calculated aluminum precursor.

Here, we reported an improved synthesis method of PAS. The PAS samples were synthesized using the similar synthesis procedure as that of traditional Al-SBA-15^{5,16} except adding constant amount of toluene in preparation. Furthermore, we reported the simultaneous influence of surface acidity and pore size of PAS and Al-doped MCM-41 on polymerization of tetrahydrofuran (THF).

Polytetrahydrofuran is one of the useful intermediates of fibers (Spandex, etc.). The polymerization of THF is a typical example of acid catalytic reaction²⁵. From the simulation result on a kinetic viewpoint, large mesopore structure and moderate acidic sites are highly desirable to suitable mass-range polytetrahydrofuran²⁵.

The catalytic activity test implied the PAS would have a great advantage on catalytic reaction involving large molecular (e.g. polymer of THF).

EXPERIMENTAL

Synthesis of PAS and ACM-10

The typical preparation procedure of PAS is described as follows: 3.0 g of P123 (Aldrich) was dissolved in 90 ml of HCl (pH 1.5). Subsequently, 100 mg of toluene was added dropwise into above mixture to get solution A. Then, 6.6 g of TEOS and a certain amount of aluminum isopropoxide (AIP; Aldrich) were added to 5 ml of HCl (pH 1.5) to get solution B. Solution B was stirred under supersonic condition at room temperature for about 15 min, and then it was added to the solution A. The mixture of solutions A and B was stirred at 313 K for 24 h. Then it was transferred into an autoclave to age at 353 K for 24 h. The resultant solid was filtered, washed and dried at 353 K for at least 12 h. The PAS samples were finally obtained after being calcined at 773 K for 6 h. The samples were named as PAS- x where x varies depending on the Si/Al molar ratio in gel used in the synthesis ($x = 10, 15, 20$).

Reference Al-doped MCM-41 with 10 of Si/Al molar ratio in gel (denoted as ACM-10) was synthesized using cetyltrimethylammonium bromide (CTAB) as a structure-directing agent according to ref.¹⁶.

Characterization of Catalysts

X-ray diffraction (XRD) measurements were performed on a Bruker D8 advance diffractometer using $\text{CuK}\alpha$ radiation (40 kV, 40 mA). Transmission electron microscopy (TEM) images were taken using a JEOL JEM-2100 microscope operating at 200 kV. Nitrogen adsorption-desorption isotherms were recorded on a Micromeritics ASAP 2020 instrument using nitrogen as the adsorbate at liquid nitrogen temperature (77 K). ^{27}Al MAS NMR spectra were recorded at 104.3 MHz on a Bruker DRX-400 spectrometer equipped with a magic angle spin probe at room temperature. The total sample acidities were determined via the temperature-programmed desorption (TPD) of ammonia. A sample of 0.1 g (40–60 mesh) was introduced into the quartz sample tube and pretreated in a helium flow at 750 K for 2 h. Several ammonia pulses were flushed through the sample tube till saturation. After saturation, weakly adsorbed ammonia was eliminated by flow of dry helium (flow rate of 50 ml/min) at the same temperature, and then the temperature increased to 700 K with a linear heating rate of 10 K/min under the dry helium. The amount of ammonia evolved from the sample was determined using thermal conductivity detector.

Catalytic Activity Test

In order to investigate the catalytic activity of PAS, polymerization of THF in the presence of acetic anhydride was studied. The typical test procedure was as follows: 0.5 g of selected PAS sample introduced to a flat bottom flask with string bar. Subsequently, a mixture of 10 g of THF and acetic anhydride (10 vol.%) were charged in this flat bottom flask. The flask was sealed and was set in oil bath at 313 K for 6 h. Then the catalyst was separated by filtration, and the polymer was obtained through removing the excessive THF by a rotary evaporator. The resulted polymer was analyzed by the method as reported before²⁶.

RESULTS AND DISCUSSION

The main physicochemical properties of the PAS and ACM-10 samples are summarized in Table I.

It can be seen from Table I that with increasing of Si/Al ratios a slight change occurred for texture structure parameter. Interestingly, such material possesses low mesopore surface area and an extra thicker pore wall compared to reported plugged SBA-15 synthesized using excessive silica precursor¹⁷ or Al-containing plugged SBA-15 synthesized using excessive aluminum precursor¹⁴, which suggested that PAS pores may be separated by thicker silica wall²⁷ and implied higher stability¹⁴.

The structural parameters of PAS materials determined from the XRD patterns (Fig. 1) were reported in Table I. Highly intensive (100) peaks together with two higher-angle peaks of (200) and (210) scatterings can be seen on all samples, indicating these mesoporous materials with a p6mm symmetry²⁸. The 2D hexagonal pore arrays were further confirmed by TEM images (Fig. 2). However, it can be seen from Table I that with the increase of Si/Al ratios a slight change occurred for the length of the unit cell a_0 of PAS samples.

Figure 3a shows the nitrogen adsorption isotherms of PAS samples with different Si/Al ratios. Although it can be seen that the capillary condensation step is slightly shifted to higher relative pressures with the increased

TABLE I
Structural parameters of PAS samples and ACM-10^a

Parameter ^a	PAS-10	PAS-15	PAS-20	ACM-10
S_{BET} , m ² /g	698	655	769	865
S_{ME} , m ² /g	182	162	223	844 ^b
V_{tot} , ml/g	0.74	0.78	0.80	0.84
V_{mi} , ml/g	0.085	0.076	0.10	–
V_{me} , ml/g	0.66	0.70	0.70	0.84
D , nm	7.4	7.3	7.3	2.8
a_0 , nm	12.0	12.2	12.0	4.7
H_{W} , nm	4.6	4.9	4.7	1.9

^a a_0 , lattice parameter calculated from $a_0 = 2d(100) \times 3^{-1/2}$; S_{BET} , BET specific surface area; S_{ME} , mesopore surface area; V_{tot} , total pore volume; V_{mi} , micropore volume; V_{me} , mesopore volume; D , pore diameter from the adsorption branch by the Barrett–Joyner–Halenda (BJH); H_{W} , pore wall thickness calculated from $H_{\text{W}} = a_0 - D$. ^b t -Plot external surface area.

aluminum content in gel, all PAS samples possessed similar pore size centered about 7.3 nm (Fig. 3b). Contrary to the isotherm of SBA-15 with Type H1 hysteresis loop, all isotherms of PAS samples (Fig. 3a) featured a unique two-step desorption isotherms.

A one-step capillary condensation is observed in all absorption branches, which indicates uniform mesopores, while all samples show a two-step capillary evaporation, which indicates the presence of 'plugs' and/or 'constrictions' in their mesoporous channel^{17,18}. Similar isotherms had

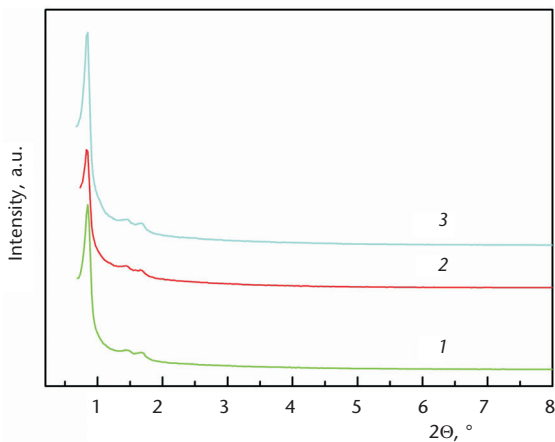


FIG. 1
XRD patterns of PAS samples: PAS-10 (1), PAS-15 (2) and PAS-20 (3)

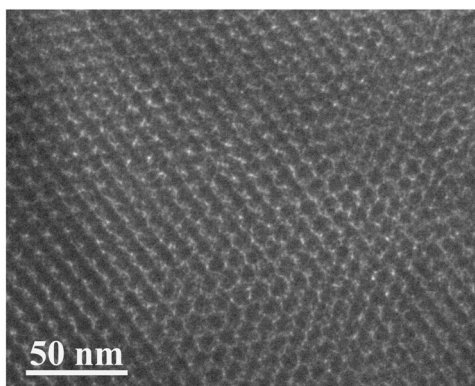


FIG. 2
TEM image of selected sample PAS-15

been reported for conventional plugged SBA-15 prepared with excess of silica source^{14,17}. The slope of isotherms of PAS after the low-pressure adsorption step were low to some extent, corresponding to a lower area of mesopore surface area²⁷, which can be proved by the experimental results in Table I. For the prepared PAS, the 'plugs' formation could be related to solubilization of silica species in the P123 micellar cores. Due to the presence of toluene these solubilized silica species may remain relatively unhydrolyzed or partially hydrolyzed even after 24 h²⁹. These silica sources

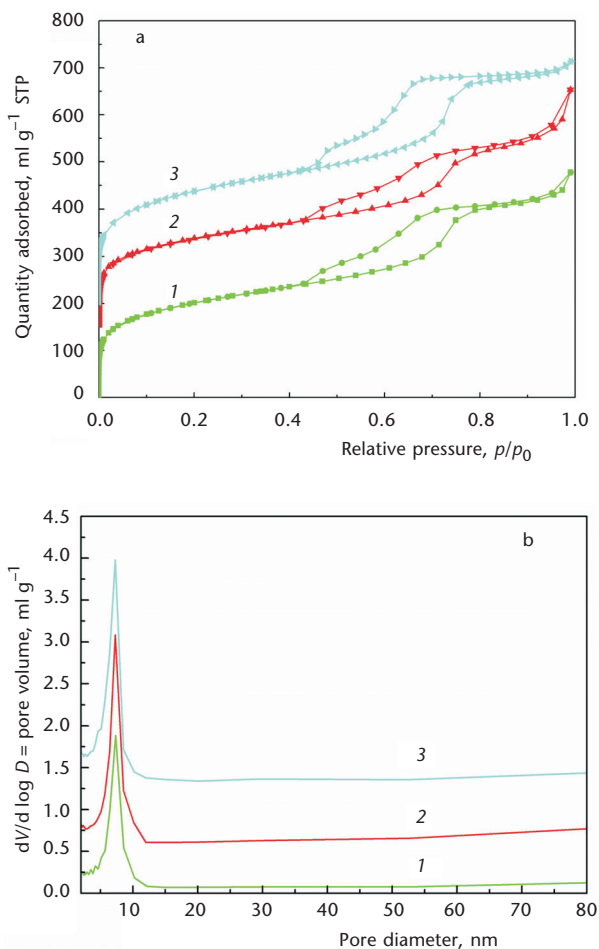


FIG. 3
N₂ sorption isotherms (a) and distribution of pore diameter (b) of PAS samples: PAS-10 (1), PAS-15 (2) and PAS-20 (3)

may cross-link and convert to amorphous silica 'plugs' during calcination, resulting constrictions inside the mesopore channel³⁰.

As seen in Fig. 3b, all PAS samples possess the similar pore size to conventional pure silica plugged SBA-15¹⁷ despite the effect of Al incorporation. It is well known^{29,31}, introducing organic solvents can enlarge the pore-size in surfactant-templated synthesis procedure, so in this work, the maintained pore size could be owing to the toluene introduced.

In comparison with Al-containing plugged SBA-15 reported before¹⁴, the PAS not only maintained large pore size, high specific surface area and moderate acidity, but also possessed higher pore wall thickness, which implied the PAS would offer unusual advantages such as multifunctionality to process a large variety of feed-stocks in acid-involved reaction (e.g. polymerization of tetrahydrofuran) in industrial point of view.

The ²⁷Al MAS NMR spectrum of the selected PAS sample was displayed in Fig. 4. The spectrum showed one sharp peak centered around 50 ppm. This peak was attributed to aluminum atoms in tetrahedral coordination corresponding to framework aluminum species. Furthermore, the spectrum showed another broad peak centered around 0 ppm, which can be assigned to octahedral coordination corresponding to extra-framework aluminum species⁹. However, the PAS exhibited more intensity peak with tetrahedrally coordinated aluminum species than that of Al-containing plugged SBA-15 synthesized using excessive aluminum precursor¹⁴. In general, the tetrahedral aluminum sites and their distribution are very important in catalysis for enhanced activity and stability^{6,32,33}. The described result indicates that

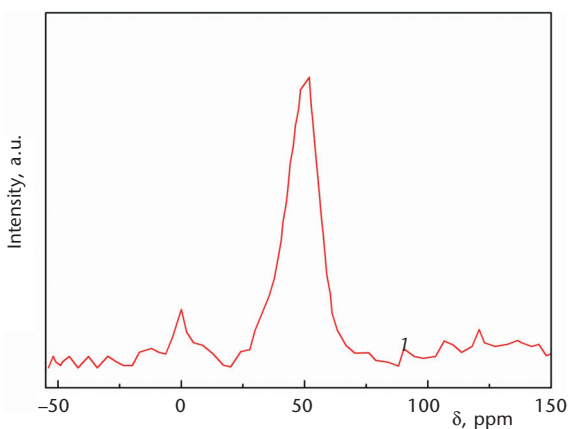


FIG. 4
²⁷Al MAS NMR spectrum of selected PAS sample

the synthetic method was preferred for the preparation of PAS with aluminum predominantly in tetrahedral coordination.

The TPD profile of pure silica SBA-15 material (1 in Fig. 5) shows a lower broad peak, indicating that SBA-15 material has very weak acid sites. While the TPD profiles of PAS samples (2–4 in Fig. 5) show two peaks at about 450 K (or 473 K) and 603 K, although another PAS sample (5 in Fig. 5) exhibit low peak at about 443 K. These results indicate that the present peak at about 473 K may correspond to desorption of NH_3 from the weak acid sites and the peak at about 603 K may correspond to desorption of NH_3 from the medium acid sites¹⁶. These moderate acid sites are very helpful to catalyze polymerization and alkylation reactions involving large molecules²⁵. However, the total peak area in the TPD profile of PAS-10 is lower than that of ACM-10, indicating that ACM-10 material has more medium acidic sites than that of PAS-10 with the same Si/Al ratio.

TABLE II
Catalytic activity of PAS and ACM-10 samples

Parameter	PAS-10	PAS-15	PAS-20	ACM-10
Yield, %	42.8	47.2	31.1	16.1
Mn^a	1769.0	1700.2	1710.1	1143.3

^a Number-average molecular weight.

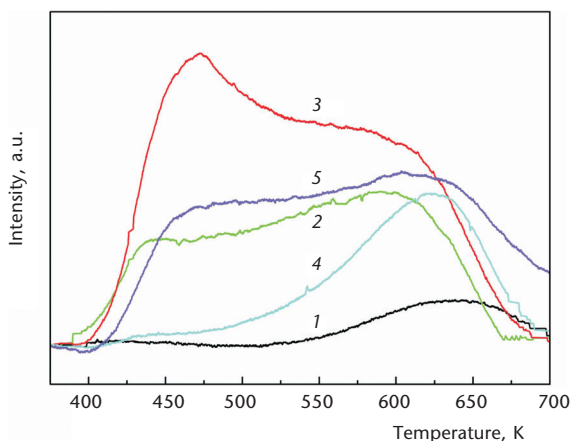


FIG. 5
 NH_3 -TPD profiles of SBA-15, PAS and ACM-10 samples: SBA-15 (1), PAS-10 (2), PAS-15 (3), PAS-20 (4) and ACM-10 (5)

In order to investigate the catalytic activity of PAS and ACM-10, we carried out the bulk polymerization of THF. The results are listed in Table II. Both synthetic conditions and analytic method of polymer were similar to those in our previous work²⁶.

As seen in Table II, the prepared polymer had similar molecular weight using PAS catalysts. Although the molecular weights of polymer were comparable, it is interesting that PAS-10 catalysts exhibited 37.87% increase in yield compared with PAS-20. The similar results were also shown compared PAS-20 with PAS-15. Such result indicated that catalytic performance was related to the Si/Al molar ratio. It is well known that Al atom incorporated into material frameworks could lead to the formation of acid sites. That is to say, the catalytic activity in THF polymerization reaction is related to surface acid sites, which was consistent to reported work²⁵.

A comparison of PAS-10 with ACM-10 catalyst indicated that the PAS had higher catalytic activity than ACM-10 despite its slightly low acidic site content detected by ammonia TPD (2 and 5 in Fig. 5). The reason could be related to large pore size and unique pore structure of the PAS, since large pore size may be useful to synthesize high number-average molecular weight (M_n)²⁵. Such fact also indicated that besides the acidity of catalyst the pore diameter had a great influence on the catalytic performance in the polymerization of THF. The larger pore size is helpful to polymer diffusing and desorption²⁵.

The introduced aluminum not only incorporates into silica framework, which leads to moderate acidic sites, but also may increase pore wall thickness of the PAS. The formation mechanism of relatively thicker wall in this system is still unidentified and future study is desirable.

CONCLUSIONS

The PAS material was directly synthesized by addition of toluene and aluminum precursor into synthesis system of surfactant-templated SBA-15. XRD and nitrogen adsorption studies confirm that the PAS possesses particular mesostructure with partial plugs in the pore channel and higher pore wall thickness than that of other reported plugged SBA-15. ²⁷Al MAS NMR and TPD studies also confirm aluminum incorporation with predominantly tetrahedral coordination and moderate acidity.

Compared to ACM-10 PAS showed good performance on polymerization of THF. More, the valuable fact is that both the surface acidity and pore size simultaneously influence the polymerization of THF. Obviously, the PAS with increased pore wall thickness and moderate acidic sites would offer unusual

advantages such as improved hydrothermal stability and multifunctionality to process a large variety of feed-stocks in acid-involved reaction in industrial point of view.

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