Materials Letters 64 (2010) 545–548

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Characterization and acidic properties of Al-SBA-3 mesoporous material

Oscar A. Anunziata [*], María L. Martínez, Marcos Gomez Costa

Grupo Fisicoquímica de Nuevos Materiales. Centro de Investigación y Tecnología Química. Facultad Córdoba. Universidad Tecnológica Nacional. 5016-Córdoba, Argentina

ARTICLE INFO

Article history:
Received 23 July 2009
Accepted 30 November 2009
Available online 4 December 2009

Keywords:
Al-SBA-3
Mesoporous material
Synthesis
Characterization

ABSTRACT

SBA-3 mesostructured silica containing framework aluminum is reported here. This material was successfully synthesized using sodium aluminate via post synthesis method. The structural properties of this novel material were studied by X-ray diffraction and FTIR. The Al insertion was determined by ^{27}Al-NMR and the acidity was monitored by infrared spectroscopy of Pyridine adsorption/desorption. The ^{27}Al NMR results indicate that Al has been effectively incorporated into the framework of SBA-3 material by post-synthesis method. The bridging hydroxyl (Si_3O–Al–OH) acid sites are observed after the adsorption of basic probe molecules, such as pyridine; this fact strongly supports the presence of Bronsted acid sites. The alumination of Si-SBA-3 produces stronger Brønsted acidity than the conventional mesoporous aluminosilicates.

1. Introduction

In 1998, Zhao et al [1] synthesized a new type of mesoporous material called SBA, with uniform two-dimensional hexagonal structure; this material is characterized by larger pore size up to approximately 25 nm that allows bulky molecules to enter into the pores, among different supports with ordered pore structure [2]. Many investigations have indicated that Al-SBA-15 materials show much higher catalytic activity compared with Al-MCM-41 material [3]. Two methods including direct synthesis and post-synthesis have been developed to incorporate Al into the framework of mesoporous materials. However, the direct synthesis seems infeasible for some materials such as SBA-15 [4], because the majority of aluminum precursors will dissolve in the strong acidic media during the synthesis procedure. Previous works on post-synthesis for alumination of SBA family [4–6], showed that this process is well adopted to the mesoporous material, but not to SBA-3. The nature of acid sites in Al-SBA-3 has been studied using pyridine as probe molecule. In the same way, we studied the effect of the variation of the surfactant and aluminum content and its influence in the structural and acidic properties of Al-SBA-3.

2. Materials and methods

2.1. Synthesis and characterization of Si-SBA-3 and Al-SBA-3

The mesoporous aluminosilicate was synthesized by hydrolysis of tetraethylorthosilicate (TEOS) and sodium-aluminate at room temperature, in an aqueous acidic solution, using cetyltrimethylammonium bromide (CTAB) as surfactant. The designed procedure was the following: the surfactant was mixed with water and HCl; then, 3 g of TEOS were added, stirring to form a mixture with a molar composition of: TEOS:H_2O:HCl:CTAB = 1:130:9.2:0.12 [7]. After 45 min, a white precipitate was obtained, and then it was filtered, washed and dried at room temperature. The material was then, immersed in ethanol reflux for 6 h in order to extract the surfactant and calcined at 550 °C in air for 6 h. The obtained material was denoted as Si-SBA-3. The alumination procedure of SBA-3 was carried out as follows [4,5]: Silica SBA-3 (1 g) was stirred in 50 ml of water, containing dissolved sodium-aluminate, at room temperature for 20 h and pH of 5.6. The synthesis was carried out at this pH, because sodium aluminate is not stable in acid medium ($pH<3$), and it reacts rapidly with protons to generate aqueous Al^{3+} ions. When pH is enough high, deposition of aluminium hydroxide will occur. The mixture was filtered, washed, dried at room temperature overnight and then calcined in air at 550 °C for 5 h. Finally, Al-SBA-3 sample with theoretical Si/Al = 20 was obtained. The calcined Al-SBA-3 mesoporous material was placed in a 1 M NH_4Cl solution and stirred at 80 °C for 40 h. The solid was filtered, washed with deionized water and dried at 80 °C overnight. The solid powder was calcined at 550 °C for 5 h. The materials were characterized by XRD and Py-FTIR. FTIR spectra for acidic properties of the samples were obtained with self-supported wafers in a vacuum cell with CaF_2 windows in a JASCO 5300 Fourier Transform Spectrometer. Prior to the FTIR experiments, the samples were degassed ($p<10^{-3}$ Pa) at 400 °C for 4 h. On the other hand, the fingerprints of the samples were obtained using wafers of SBA in KBr in a vacuum cell with special KBr windows. XRD patterns were recorded in the Philips X'Pert PRO PANalytical diffractometer under Cu Kα radiation ($\lambda = 1.5418$). Solid state NMR spectra were taken on a BRUKER MSL300 spectrometer operating at 78.2 MHz for ^{27}Al. We used a BRUKER MAS 300WB CP1H-BBWH. VTN-BL4 probe with 4 mm o.d. zirconia rotors. Elemental analysis was performed by inductively coupled plasma-atomic emission spectroscopy (VISTA-MPX) operated with high

---

[*] Corresponding author. Tel.: +54 351 4690585.
E-mail address: oanunziata@scdt.frc.utn.edu.ar (O.A. Anunziata).

0167-577X/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2009.11.072

frequency emission power of 1.5 kW and plasma airflow of 12.0 L/min. The surface area was determined by the BET method using a MICROMERITICS Chemisorb 2720 apparatus, equipped with a TCD detector.

3. Results and discussion

3.1. ICP and BET

The results of ICP elemental analysis, which was employed to determine the composition of Al-SBA-3 sample, indicated the amounts of metal (Al) in the final Al-SBA-3 product are in close agreement with theoretical value, Si/Al = 19.8. The BET specific surface area decreases with the Al content, from 1024 (pristine SBA-3) to 770 m^2/g for Al-SBA-3, due to the occupation of guest species on the surface of the pores as well as the in equable contribution of the additional mass Al_2O_3 in the sample.

3.2. X-ray diffraction patterns and solid state NMR spectra

The X-ray diffraction patterns of as made Si-SBA-3 and Al-SBA-3 material are shown in Fig. 1A. The presence of three Bragg angles can be distinguished in hexagonal lattice symmetry, typical of SBA-3 structure. Moreover, XRD patterns indicate that the hexagonally ordered structure of SBA-3 was persistent after the modification procedure. A prominent peak, hkl = [100] as well as weaker peaks of [110] and [200] were observed in Al–SBA-3, which allowed us to corroborate, that the obtained mesoporous sample has a highly ordered pore system with a high porosity [8]. Fig. 1B shows the ^{27}Al solid-state MAS-NMR spectra of the Al-SBA-3 sample. The spectra exhibit two peaks with shifts of 50 ± 2 and 0.7 ± 2 ppm. The signal at 50 ± 2 ppm is assigned to tetrahedral coordinated framework aluminium (Td-Al). The signal at 0.7 ± 2 ppm is assigned to octahedral coordinated (Oh–Al) non-framework aluminium [9]. As it can be observed, aluminium was incorporated mainly with tetrahedral coordination in the framework of SBA-3 prepared by the present post-synthesis procedure.

3.3. FTIR spectroscopy

FTIR results show that there is an abundance of silanol groups present in the siliceous SBA-3 material, which give rise two hydroxyl stretching bands, a sharp band at 3740 cm^{-1} due to isolated terminal silanol (Si–OH) groups and another broad band at 3400 cm^{-1} attributed to hydrogen-bonding silanol groups.

The presence of aluminum in SBA-3 silica greatly reduces the intensities of the hydroxyl stretching bands associated with silanol groups. This suggests that the silanol groups are consumed upon aluminum incorporation. The framework vibration region of the FTIR spectra for the Si-SBA-3 and Al-SBA-3 materials is shown in Fig. 1C. A signal at around 969 cm^{-1}, which is assigned to asymmetric stretching of Si–O bond neighboring surface silanol groups [3], was emerged on the spectra of the pristine SBA-3 sample. However, this band is absent with the modification of SBA-3 with the post-alumination procedure, which indicated that the surface silanol groups around 969 cm^{-1} interacted with the Al species and contributed to form the Si–O–Al in the process of modification. All materials give bands at around 1085 cm^{-1} (T–O asymmetric stretching) and 800 cm^{-1} (T–O symmetric stretching) due to the intrinsic vibration of TO_4 tetrahedral (T = Si, Al) [3]. The spectra of the Al-SBA-3 materials show additional features in the vicinity of the 1085 and 800 cm^{-1} stretching bands, which absorption frequency shifts downward, with aluminum incorporation. These features can be assigned to Al–O–Si bending vibrations, indicating incorporation of aluminum into the SBA-3 silica matrix [9]. Fig. 2A and B show the infrared spectra of the pyridine adsorbed on the Si-SBA-3 and Al-containing SBA-3 samples subjected to evacuation at 25, 100, 200, 300 and 400 °C and 10^{-3} Pa (the amount of Bronsted and Lewis sites as mmol Py/g was shown in Table 1). Different signals can be observed in the region between 1700–1400 cm^{-1}. According to the literature data [6,10] after evacuation at room temperature, the bands at 1597 and 1444 cm^{-1} are assigned to hydrogen-bonded pyridine (PyH^+). The bands at 1454 and 1624 cm^{-1} are due to strong pyridine bound to Lewis sites; the band at 1579 cm^{-1} is due to weak Lewis-bound pyridine and the bands at 1547 and 1641 cm^{-1} to pyridinium ion ring vibration due to pyridine bound to Brønsted acid sites (PyH^+). A band at 1491 cm^{-1} was assigned to pyridine associated with both, Brønsted and Lewis sites. Two new signals (1547 and 1641 cm^{-1}) appear in the Al-SBA-3 spectra in comparison with the Si-SBA-3

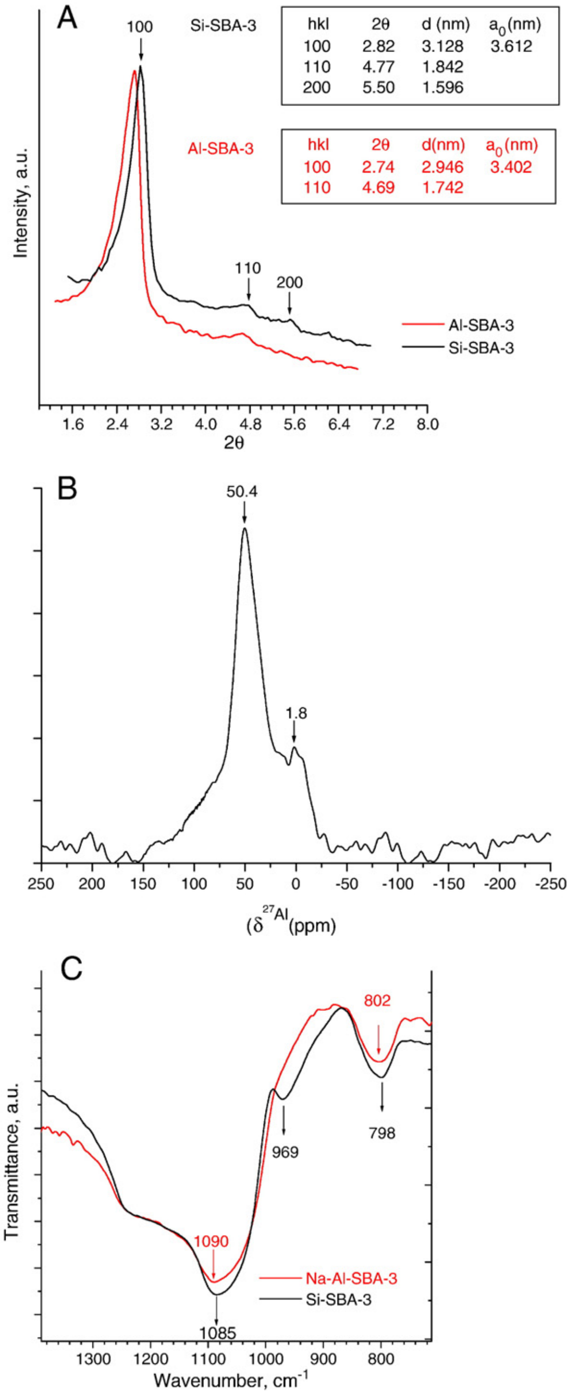

Fig. 1. X-ray diffraction patterns of Na–Al-SBA-3 and SBA-3 (A), ^{27}Al-MAS-NMR spectra (B) and FTIR of Si-SBA-3 and Al-SBA-3 (C).

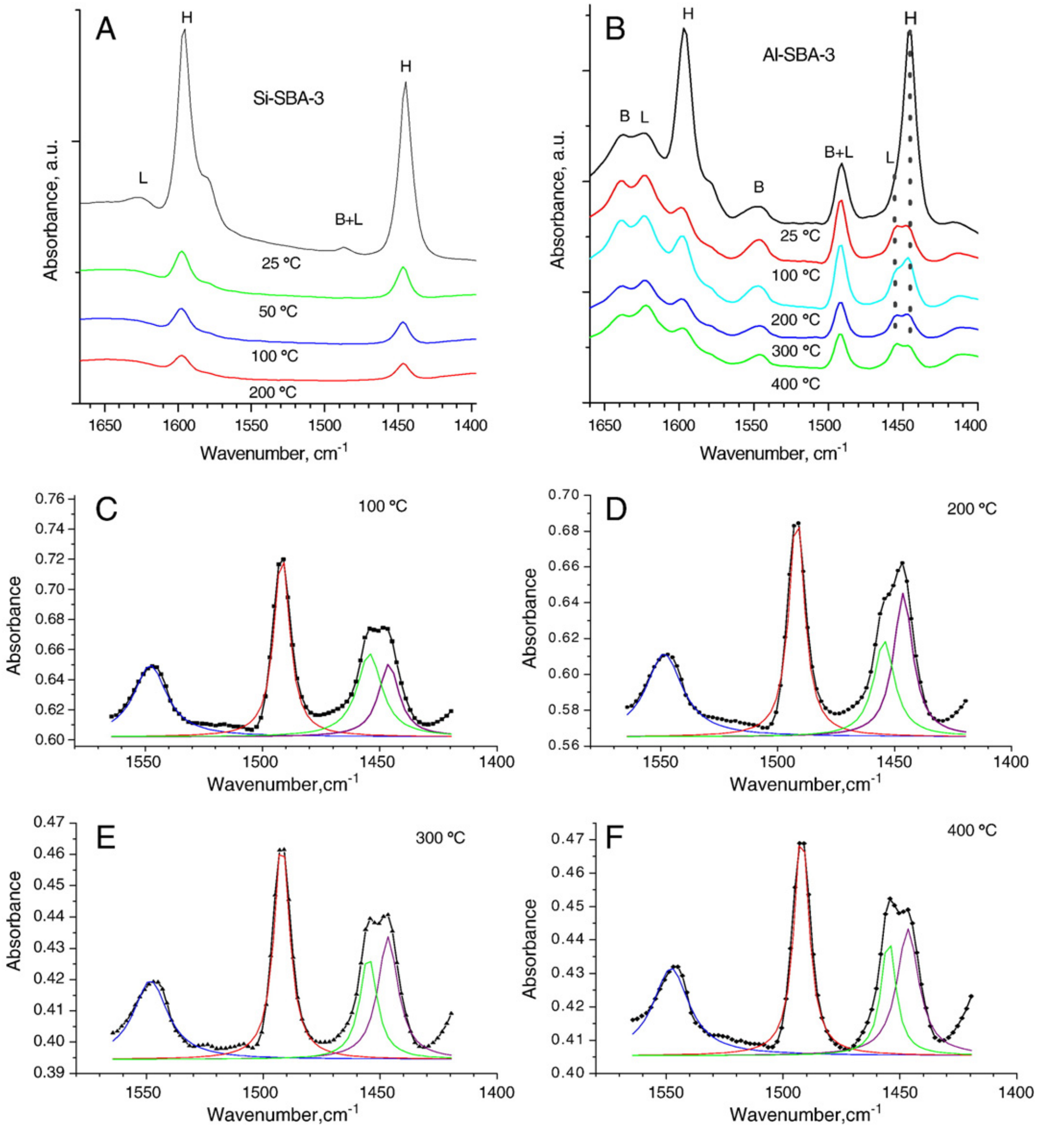

Fig. 2. FTIR of Py desorbed on Si-SBA-3 (A) and Al-SBA-3 (B) at different temperatures; and desorption of Py of Brønsted and Lewis acid sites as function of temperature. Deconvoluted and original FT-IR spectra of pyridine desorbed on Al-SBA-3 (C).

spectra, suggesting that Brønsted acid sites have been generated in the aluminosilicate sample. Klimova et al. [6], have studied the acid properties of Al-SBA-15 (Si/Al = 20). They have obtained a sample with 0.61 mmol Py/gr, whereas in this work we have obtained a much higher amount of Py retained at the same conditions, indicating the stronger acidity of the synthesized Al-SBA-3 in comparison with others Al-SBA conventionally prepared [10,11].

4. Conclusions

This is our first report on the preparation of Al-containing SBA-3 mesostructured material. This method allows the preparation of Al-SBA-3 materials without significant changes in the original pore structure and the long-range periodicity order of the parent SBA-3 sample, the incorporation of heteroatoms in tetrahedral framework positions of SBA-3 structure, by trivalent element as Al, produces a considerable Brønsted acidity. Extra-framework species, obtained by removal of Al from framework positions during thermal treatment, generate Lewis sites with different strength. These studies have shown that the Al-SBA-3 material contains Brønsted and Lewis acid sites with medium acidity, which makes them appropriate to be used as acid catalysts, catalytic supports and adsorbents. Our results indicate that the incorporation of aluminum into the Si-SBA-3 material by post-synthesis is a useful tool to adjust the acidic properties of mesoporous molecular sieves, to achieve materials with stronger acidity properties than the conventional mesoporous aluminosilicate. We have news result of the effect of Al content on the structural regularity by NMR-MAS, HRTEM and SEM to corroborate the insertion of Td-Al.

Table 1
Quantification of Bronsted and Lewis sites in Al-SBA-3.

Desorption temperature	Bronsted sites (mmol Py/g)	Lewis sites (mmol Py/g)	Bronsted/Lewis ratio
25 °C	0.243	0.116	2.089
100 °C	0.137	0.083	1.644
200 °C	0.126	0.068	1.848
300 °C	0.076	0.034	2.209
400 °C	0.070	0.031	2.237

Acknowledgments

O.A.A. and M.B.G.C Conicet Researchers. M.L.M. Conicet Fellowship. The authors are grateful to CONICET Argentina. PIP No 6394 (2005–

2009); FONCYT PICT No 14-14485 (2005–2009) and Ministerio de CyT Cordoba Argentina 2007–2010.

References

[1] Zhao D, Feng J, Huo Q, Melosh N, Fredrckson G, Chmelka B, Stucky G. Science 1998;279:548–52.
[2] Mesa M, Sierra L, Guth J. Micropor Mesopor Mater 2008;112:338–50.
[3] Anunziata O, Beltramone A, Martínez M, López-Belon L. J Colloid Sci 2007;315:184–90.
[4] Hu W, Luo Q, Su Y, Chen L, Yue Y, Ye C, Deng F. Micropor Mesopor Mater 2006;92:22–30.
[5] Luan Z, Hartmann M, Zhao D, Zhou W, Kevan L. Chem Mater 1999;11:1621–7.
[6] Klimova T, Reyes J, Gutierrez O, Lizama L. Appl Catal A: Gen 2008;335:159–71.
[7] Huo Q, Margolese D, Cielsa U, Demuth D, Feng P, Gier T, Sieger P, Firouzi A, Chmelka B, Schüth F, Stucky G. Chem Mater 1994;6:1176–91.
[8] Chen F, Xu X, Shen S, Kawi S, Hidajat K. Micropor Mesopor Mater 2004;75:231–5.
[9] Anunziata O, Beltramone A, Cussa J. Catal Today 2008;133–135:891–6.
[10] Gómez-Cazalilla M, Mérida-Robles J, Gurbani A, Rodríguez-Castellón E, Jiménez-López A. J Solid State Chem 2007;180:1130–40.
[11] Klimova T, Lizama, Amescua L, Roquero P, Terrés E, Navarrete J, Domínguez J. Catal Today 2003;98:141–50.