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Synthesis of ordered mesoporous SBA-3 materials using silica gel as silica source

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ABSTRACT

Nanostructured materials have exceptional and highly attractive properties, including catalyst, adsorbent, separation media and chemo sensor. Technical advances in these fields require the development of ordered porous materials with controllable structures, systematic tailoring pore architecture and the synthesis of mesoporous materials using a more economical silica source. Ordered mesoporous silica SBA-3 material has been synthesized successfully using cetyltrimethylamonium bromide (CTAB) as a structure-directing agent, NaOH and inexpensive silica gel as a silica source without additives. We studied the influence of NaOH concentration on the structure and morphology of mesoporous silica SBA-3. This variation was defined as modulus $L=[\mathrm{NaOH/SiO_2}]$ ratio. The structural order of the samples was found to be greatly affected by L variations. The results suggest that, by controlling the L value (0.70–1), SBA-3 is obtained with appropriate physicochemical characteristics.

1. Introduction

In 1998, Zhao et al. [1] synthesized a new type of mesoporous materials named SBA (Santa Barbara Amorphous), with a uniform two-dimensional hexagonal structure . These materials have been widely used as catalyst, adsorbent and separation media, and have been the host of different applications. An important effort has been made to synthesize, within the mesoporous range, regular and well-defined pore structure materials [2,3]. The most widely spread types of MMM such as MCM-41 and SBA-3 have a hexagonal (honeycomb-like) structure, with amorphous walls and a highly ordered arrangement of channels. These MMMs differ one from another only by synthesis conditions. On the other hand, the main drawback is that the expensive source of silicon alkoxide ($\mathrm{Si(OEt)_4}$ or $\mathrm{Si(OMe)_4}$) prevents any application requiring large amounts of materials. Using water-soluble silicate as a silica source, highly ordered mesoporous silica was prepared [4,5]. Chen et al. [6] studied the synthesis of SBA-3 with secondary silica source, finding an increased ratio of micropore-to-mesopore volume. Liu et al., [7] successfully synthesized mesoporous materials from mixtures of sodium silicate and TEOS, only by adjusting the molar ratio. Many strategies have been implemented in order to obtain highly ordered mesoporous silica, using as a cheaper source of silica and sodium silicate, [8–10]. Jo et al. [11] synthesized mesoporous materials with water glass for largescale preparation , but not on literature studies describing the synthesis of highly ordered mesoporous materials using silica gel as silica source. In this paper, we report our first results of higher regular SBA-3 synthesized by a sol–gel method using silica gel as silica source and NaOH. We studied the variation of L modulus, $L=[\mathrm{NaOH/SiO_2}]$. The samples obtained were characterized by XRD, BET, FTIR and TEM. Our research provides an important approach to synthesize ordered mesoporous materials, which may find applications in catalysis and as hosts to obtain potential semiconductor nanocomposites or as hydrogen storage.

2. Experimental procedure

The mesoporous silicate was synthesized by silica gel and NaOH generating "in situ" sodium silicate solutions. The designed procedure was the following. In the first step, commercial silica gel 60 MERCK was dissolved in NaOH solution at 333 °K forming Na silicate solution; the solution was then cooled at room temperature. We defined modulus L as the ratio of molar concentration of $[\mathrm{NaOH/SiO_2}]$; thus NaOH concentration was varied from $L=0.70$–5. In a typical synthesis of SBA-3, 0.63 g of CTAB was dissolved in the HCl solution with continuous stirring at room temperature. The sodium silicate solution was added by slow drip to acidic solution. The mixture was stirred for 45 min. The molar composition of the final reactant was: Nax: $\mathrm{H_2O}$: HCl: CTAB: $\mathrm{SiO_2}$; $x=0.6-5$: 71.5: 26.5: 0.108: 0.83. After 45 min, a white precipitate was obtained; it was then filtered, washed and dried at 323 °K over night. The

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material was then immersed in ethanol reflux for 6 h in order to extract the surfactant and calcined at 823 K in air for 6 h. The material obtained was denoted as SBA-3 (L), with L=0.70–5. Textural properties of samples were determined from nitrogen physisorption analysis. Measurements of N_2 (99.999%) adsorption–desorption isotherms at 77 K were carried out using a volumetric adsorption apparatus (ASAP 2020 instrument). The X-ray diffraction (XRD) patterns were recorded in the 2θ range from 1.6 to 7° (2θ) with a Philips X'Pert PRO PANalytical diffractometer. The samples were examined with a JASCO 5300 Fourier transform infrared spectrometer (FTIR). The transmission electron microscopy (TEM) micrographs were taken on a TEM JEOL EX2-1200 transmission microscope operated at 120 kV.

3. Results and discussion

The X-ray diffraction patterns of SBA-3(x) materials are shown in Fig. 1A and B. The samples studied exhibit the reflection peaks in the low angle region, characteristic of mesostructures (Fig. 1A). The presence of three Bragg angles can be distinguished in hexagonal lattice symmetry, typical of SBA-3 structure. Table 1 shows the synthesis conditions, diffraction peak corresponding [h k l] Miller index=[100] and the a_0 parameter. No significant change was observed in the lattice parameters of these materials when L modulus increases up to 1. Fig. 1A shows the materials with different L values: when L modulus decreases to 0.70, the diffraction peak [100] is shifted to lower angles and increases its intensity, showing that a more ordered mesostructure could be obtained.

Fig. 1B shows materials synthesized by increasing NaOH molarity (higher L modulus). It was observed that when L reaches values above 1, no formation of mesoporous structure could be seen. When mole number L ratio is less than 1, the synthesized mesophases such as SBA-3 (0.70) and SBA-3 (0.75) show an XRD pattern consisting of (100) and (200) diffraction for the hexagonal array of typical SBA-3 materials. As L ratio is increased to 1, three broad XRD peaks are centered at $2\theta=3.0°$ (strong), 4.2° (very weak), and 4.8° (weak), respectively; for $L>1$, XRD patterns show disordered mesophases. Thus, as L increases, the structure of the synthesized mesoporous silica transforms from a hexagonal packing of one-dimensional channels to a disordered network forming completely amorphous silica materials with no XRD signals.

Fig. 2 shows images of the morphology and ordered mesostructure of SBA-3 (0.75) obtained by SEM and TEM, respectively. It is clear that SBA-3 has regular spherical morphology (see Fig. 2A) with a diameter ranging from 0.8 to 1.3 μm. The TEM images of the sample (Fig. 2B and C) confirm that SBA-3 has a uniformly ordered pore structure with a linear channel array of mesopores, a typical feature of SBA-3 materials with a 2D hexagonal structure. The pore size of the sample is estimated to be around 2 nm from the TEM micrograph, in good agreement with results of N_2 adsorption isotherms (not shown).

Considering Na^+ effect for a cationic surfactant solution containing spherical micelles, an increase in Na^+ concentration causes electrostatic repulsion to constituent ions in the headgroup region. Initially, the screening effect leads to a change from the spherical micelles to elongated one-dimensional micelles. When salt concentration is exceedingly high, the resultant mesophase is further disordered.

The IR lattice vibration spectra in 600–1200 cm^{-1} of calcined samples show the bands resulting from a typical siliceous material, with a main band at 1080 cm^{-1} together with a shoulder at 1227 cm^{-1}, due to asymmetric Si–O–Si stretching modes. There is also a weaker band at 800 cm^{-1}, due to Si–O–Si symmetric

Table 1
Synthesis conditions and physicochemical properties of different SBA-3 materials.

Sample	L Modulus[a] [$NaOH/SiO_2$]	d_{100} (Å)	a_0 (nm)	S_{BET} (m^2/g)	Porous volume (cm^3/g)	Pore diameter (nm)
SBA-3 (0.70)	0.70	31.00	3.55	933	0.47	1.8
SBA-3 (0.75)	0.75	31.13	3.58	940	0.47	1.7
SBA-3 (1)	1.00	31.30	3.62	945	0.48	1.7
SBA-3 (2)	2.00	–	–	–	–	–
SBA-3 (3)	3.00	–	–	–	–	–

[a] Molar Ratio.

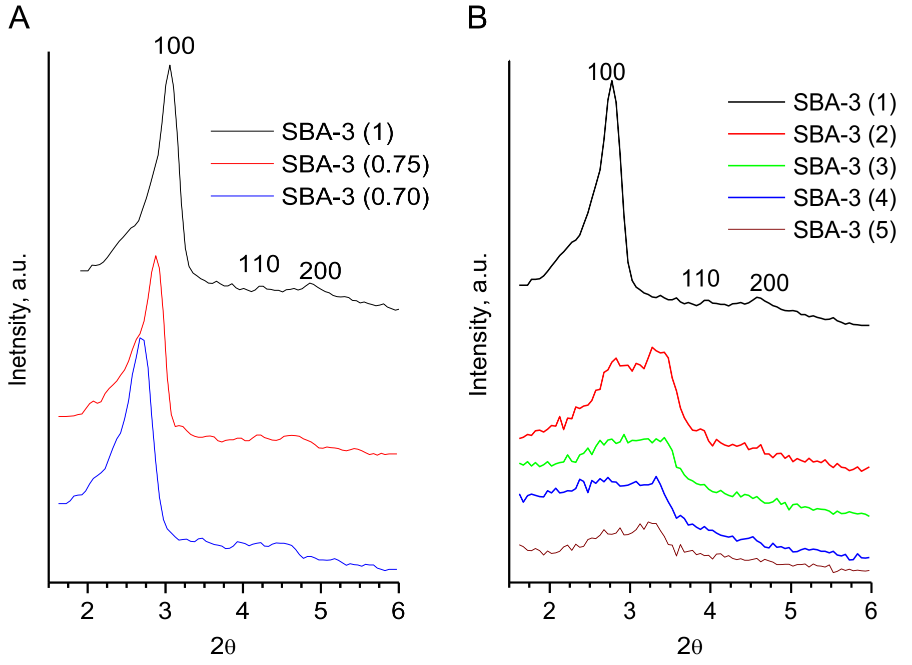

Fig. 1. XRD of mesoporous materials obtained by varying L from 0.70 to 5.

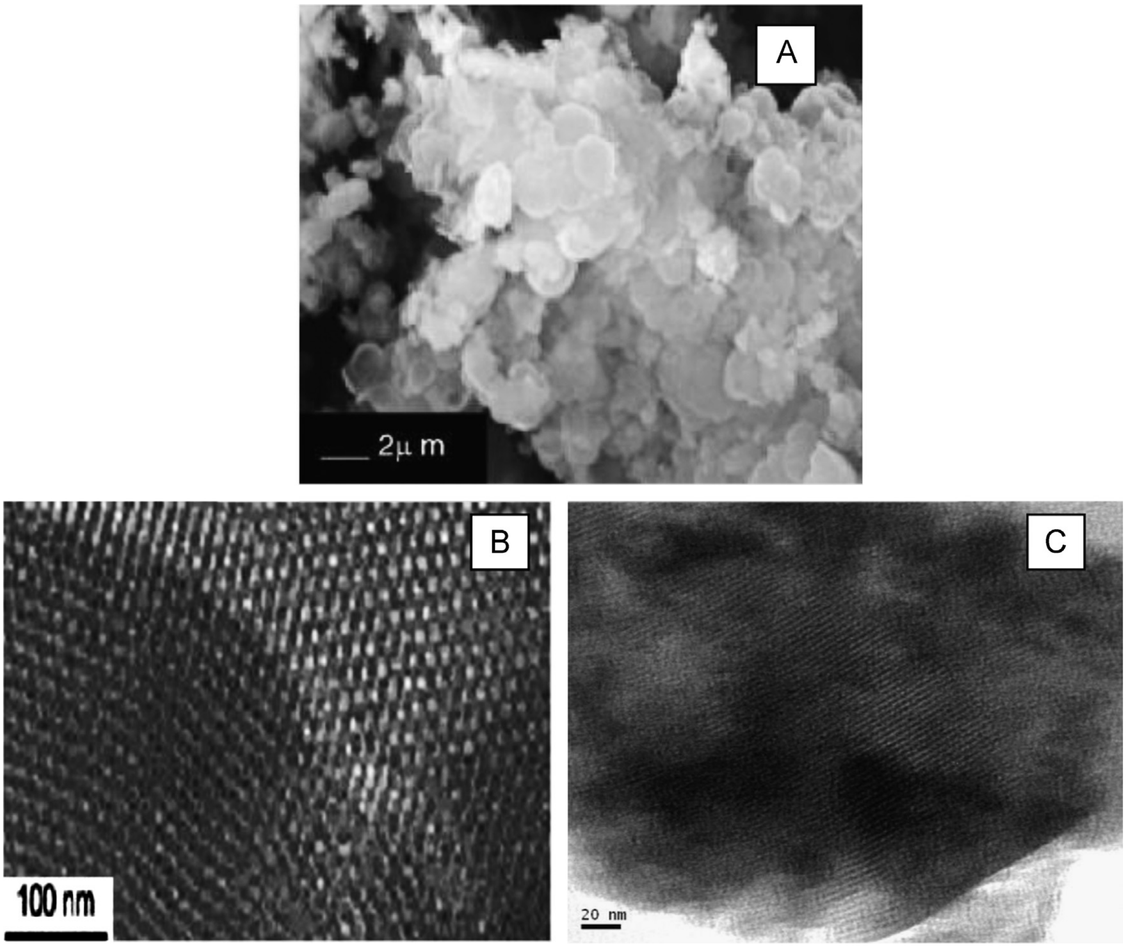

Fig. 2. SEM (A) and TEM (B and C) micrographs of SBA-3 (L=0.75).

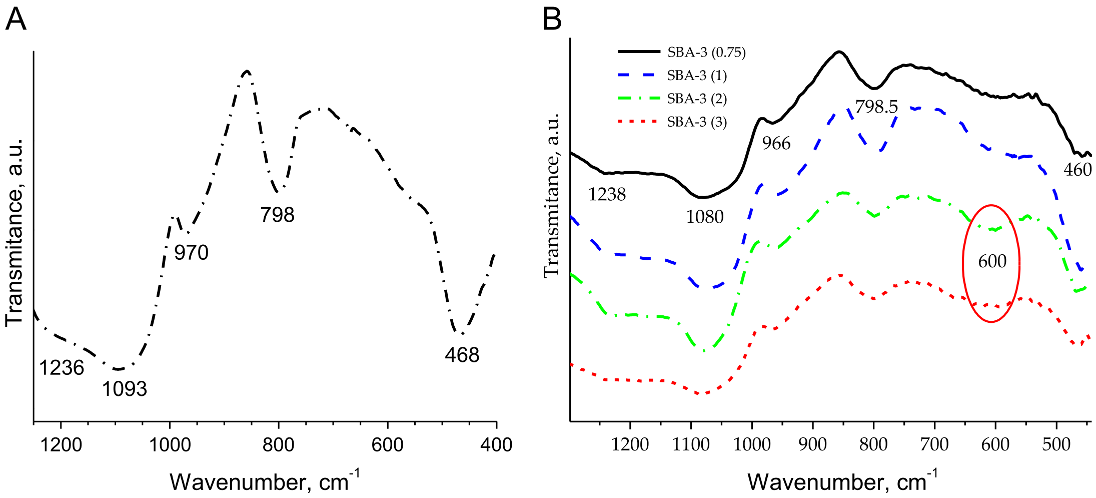

Fig. 3. FTIR of silica gel (A) and SBA-3 synthesized by different NaOH/SiO$_2$ molar ratios.

stretching modes and a strong band at 450 cm^{-1}, due to rocking Si–O–Si (Fig. 3).

The FTIR spectra shown in Fig. 3 compare silica gel and four SBA-3 samples, L=0.75, 1, 2.0 and 3.00. As other spectral regions do not show notable differences, we focus on the spectral region between 400 and 700 cm^{-1}, where two peaks may be assigned to the framework vibrations: one band around 460 cm^{-1} and another at 580–600 cm^{-1}. The intense 460 cm^{-1} peak may be assigned to the Si–O bending vibrations. The weak peak at 580–600 cm^{-1} is located in about the same position as the peaks which can be assigned to the stretching mode of a double-ring unit in ordered, or at least locally ordered silicates. This band was assigned by Halasz et al. [12] as an asymmetric bending: δ_{as} (Na) O–Si–O(Na). When L is increased in the synthesis, the peak at 580–600 cm^{-1} shows a shift to higher frequency, about 20 cm^{-1}. These results show that with $L > 1$, materials have a lower local ordering of their structure. Therefore, when L increases, the amount of sodium present in the synthesis also increases, preventing the formation of mesostructure. In addition, on the basis of the analysis of FTIR, the appearance of species as (Na)O–Si–O(Na) may hinder the interaction between CTAB and silicon during the nucleation process in the SBA-3 synthesis. To destabilize an aqueous silica sol, it is necessary to reduce the degree of hydration. At higher Na concentration ($L > 1$), it would produce ion exchange between $\equiv$Si–OH and Na+. The unhydrolyzed Na acts as counter-ion; since the silanol groups are the adsorption sites for water, the removal of Si–OH by ion exchange reduces the amount of hydration and lessens the stability of colloid, coagulating immediately. In this way, the directionator agent (CTAB) cannot interact with silica during hydrolysis and condensation reactions, obtaining non mesostructured materials (samples with $L > 1$). Considering the conditions that the reaction system before precipitating required siliceous prepolymers for the synthesis of organized mesoporous silica, if prepolymers ($L < 1$) are formed, the surfactant ions bind and precipitate as mesomorphic surfactant ion-polymerized silica complex. When L»1, the prepolymers are not formed and precipitated as structurally disordered material. Thermogravimetry (TG), of the as-synthesized mesoporous SBA-3 samples (not showed), indicated the total mass loss was in the range of 4–38 mass% (as L varied from 5 to 0.70). There are two thermal transitions, below 100 °C and around 300 °C. The thermal transitions below 100 °C correspond to the loss of imbibed water; around 300 °C the surfactant elimination. The progresses in the thermal analysis observed for the samples indicated that, the mass loss of surfactant (300 °C), is higher for samples with L=0.70–1 (38–36%). From the samples with L»1 is significantly lower or absent (4–0% for L=2–5). This implies that the surfactant in the silicate surfactant co-assembly is needed to make ordered SBA-3 nanostructured material, in agreement with XRD and IR studies.

4. Conclusions

We have shown that a promising, simple and low-cost method was developed to synthesize mesoporous silica SBA-3 by using inexpensive silica gel, as a silica source under acidic condition. According to XRD, BET, SEM and TEM studies, SBA-3 mesoporous materials can be synthesized with uniformly ordered pore structure, controlling $NaOH/SiO_2$ ratio, defined as modulus L between 0.70 and 1. It should be noted that mesoporous SBA-3 material exhibits high specific surface area (950 m^2/g). These are the first steps in the synthesis of SBA-3 by using an “in situ” prepared solution of sodium silicate. This method may be useful in the design and preparation of mesoporous silica type SBA-3, and other mesoporous materials, opening up new possibilities for applications requiring large quantities of material.

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