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Synthesis and characterization of ordered mesoporous silica

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Ordered mesoporous silica SBA-15 materials were synthesized by using Pluronic P123 (non-ionic triblock copolymer, $EO_{20}PO_{70}EO_{20}$) as a template, under acidic condition. These materials were characterized by nitrogen adsorption-desorption measurements, scanning electron microscopy (SEM), X-ray diffraction (XRD) and thermo-gravimetric analysis (TGA). It was found that structural properties can be adjusted by the different temperatures and times in the reaction solutions. Obtained samples have high specific surface area (>600 m^2g^{-1}) and developed mesoporous structure. Also, our measurements have shown that these materials have a certain amount of micropores.

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Keywords: Mesoporous silica, Specific surface, Microporosity

1. Introduction

Since the mesoporous siliceous materials were synthesized [1, 2] there has been an increasing interest in the tailoring of these materials for potential applications in separation and adsorption processes, catalysis etc. One of the most studied mesoporous material is SBA-15, which can be synthesized in large quantities from TEOS in the presence of amphiphilic poly (alkylene oxide)-type triblock copolymers [3, 4]. This material has a highly ordered mesoporous hexagonal structure with mesopore diameters varying from 5 to 30 nm [5, 6]. The pore size and the thickness of the silica walls can be adjusted by varying the heating temperature and time in the reaction solution. Careful investigation of structure of SBA-15 showed that material has certain amount of micropores which connect neighboring mesopores [7].

In order to estimate the influence of parameters of synthesis on structure of materials, in this paper we synthesized SBA-15 at two different temperatures and times in the reaction solutions. Samples were characterized by nitrogen adsorption experiments, XRD, SEM and TGA analysis.

2. Experimental

2.1 Synthesis of SBA-15 samples

SBA-15 samples were synthesized according to standard procedures, using Pluronic P123 (non-ionic triblock copolymer, $EO_{20}PO_{70}O_{20}$, BASF) as a surfactant and tetraethoxysilane (TEOS, 98%) as a sours of silica. A 4.0 g sample of Pluronic P123 was dissolved in 30 g of distilled water and 120 g of 2 M HCl solution with stirring for 1.5 h at 35 ºC. The 8.50 g of TEOS was added drop wise into that solution with vigorous stirring at same temperature for 1.5 h. Since the structure and surface properties of samples depend on time and temperature of aging [1] we changed these two parameters. According to the method proposed by Zhao et al. [1] (sample SBA-15/80), the mixture was stirring for 20 h at 35 ºC, and aged for 48 h at 80 ºC. According to patent [8] (sample SBA-15/100), mixture was stirring for 22 h at 35 ºC and aged for 24 h at 100 ºC.

The final products derived in both methods, were filtered, washed with 600 ml of distilled water and dried at room temperature. Calcinations was carried out in flowing air by slowly increasing temperature from room temperature to 500 ºC in 8 h, and heating for 6 h at 500 °C to decompose the tribloc copolymer.

2.2 Characterization of SBA-15 samples

Adsorption and desorption isotherms of N_2 were measured on SBA-15 samples at -196°C using the gravimetric McBain method. From the isotherms the specific surface area, S_{BET}, pore size distribution, mesopore including external surface area, S_{meso}, micropore volume, V_{mic}, for the samples were calculated. Pore size distribution was estimated by applying BJH method [9] to the desorption branch of isotherms and mesopore surface and micropore volume were estimated using the high resolution α_s plot method [10-12]. Micropore surface, S_{mic}, was calculated by subtracting S_{meso} from S_{BET}.

Scanning electron microscopy (SEM) analyses were carried out on SBA-15 samples using a JEOL 6300F microscope.

Silica samples were characterized by recording their powder X-ray diffraction (XRD) patterns on a Siemens D500 X-ray diffractometer using Cu Kα radiation with a Ni filter. The 2θ angular regions between 5 and 80º were explored at a scan rate of 1 º/s with the angular resolution of 0.02º for all XRD tests.

TGA measurements have been performed on the SETARAM SET- SY Evolution-1750 instrument. Samples were heated from 30ºC to 1500ºC at the heating rate of 10ºC min^{-1} in air atmosphere.

3. Results and discussion

3.1 Adsorption isotherms – BET experiments

Nitrogen adsorption and desorption isotherms as the of N_2 adsorbed and desorbed on the silica materials, SBA-15/80 and SBA-15/100, as a function of relative pressure at –196 °C are shown in Fig. 1. According to the IUPAC classification [13], for the both samples, the isotherms are of type-IV and with a hysteresis loop which is associated with mesoporous materials. The specific surface areas calculated by the BET equation, S_{BET}, are listed in Table 1.

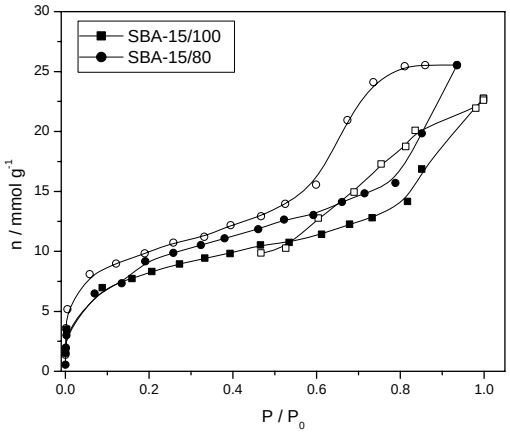

Fig. 1. Nitrogen adsorption and desorption isotherms, as the amount of N_2 adsorbed and desorbed as a function of the relative pressure for the silica materials. Solid symbol – adsorption, open symbol – desorption.

Table 1. Porous properties of the SBA-15/80 and SBA-15/100 silica sample.

Sample	S_{BET} / m^2 g^{-1}	r_{peak} / nm	S_{meso} / m^2 g^{-1}	S_{mic} / m^2 g^{-1}	V_{mic} / cm^3 g^{-1}
SBA-15/80	710	2.9	481	229	0.11
SBA-15/100	641	2.4	367	274	0.13

In Fig. 2 the pore size distribution of the silica materials, SBA-15/80 and SBA-15/100, is shown. For the materials SBA-15/80, the pore radius varies between 1.4 and 6 nm while, in the case of SBA-15/100, pore radius varies between 1.9 and 25 nm which means that synthesis procedure proposed by ref. [1] gives samples with narrow pore size distribution.

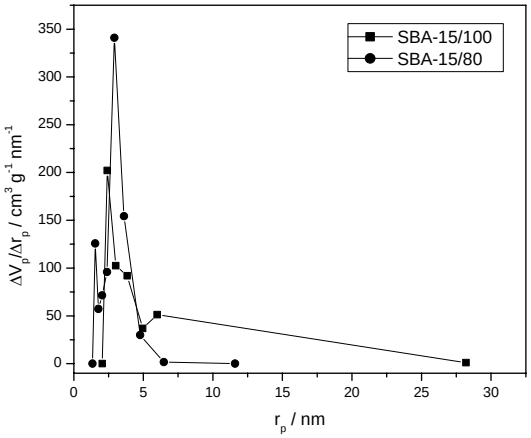

Fig. 2. Pore size distribution (PSD) of the silica materials SBA-15/80 and SBA-15/100.

The α_s plot, obtained on the basis of the standard nitrogen adsorption isotherm, is shown in Fig. 3. The initial parts of α_s plots for silica samples were nonlinear which suggest the presence of microporosity. The straight line in the medium α_s region gives the mesoporous surface areas, which include the contribution of the external surface, S_{meso}, determined by its slope, and the micropore volume, V_{mic}, is given by the intercept. The calculated porosity parameters (S_{meso}, S_{mic}, V_{mic}) are given in Table I. According to our results, synthesis proposed in ref. [1], gives sample with higher S_{BET}, mesoporosity and narrower pore size distribution. Analysis of experimental data confirms the presence of micropores in samples, and ratio of micro and mesopores is larger in sample synthesized according to patent. The micropore volumes obtained by α_s method are 0.11 and 0.13 cm^3 g^{-1} for SBA-15/80 and SBA-15/100, respectively, which is in agreement with literature data [6].

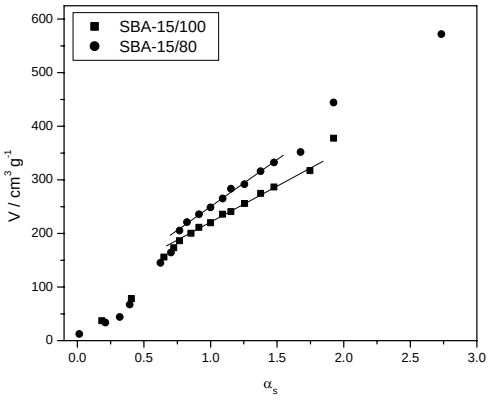

Fig. 3. α_s – plots of the nitrogen adsorption isotherm of the silica materials SBA-15/80 and SBA-15/100.

3.2 SEM analysis

Fig. 4 shows the SEM images of calcinated SBA-15 samples. The larger magnification images reveal that both SBA-15 samples consist of many peanut-like domains with relatively uniform sizes (about 1μm) which are aggregated into wheat-like structures. Similar structures were reported in earlier papers [1].

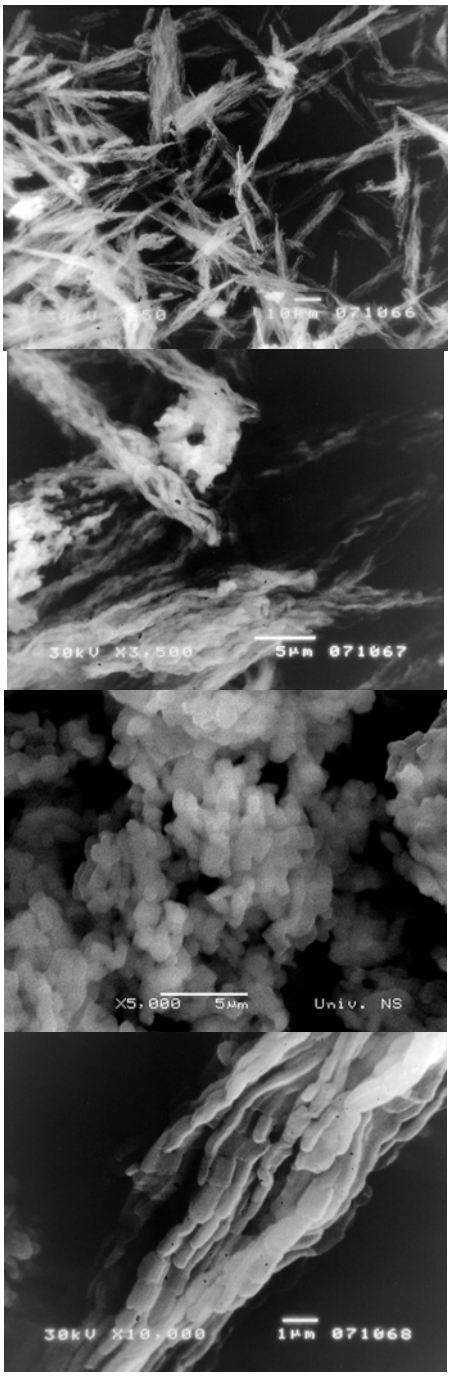

Fig. 4. Scanning electron microscopy (SEM) images of silica material: (a) and (b) SBA-15/80 and (c) and (d) SBA-15/100.

3.3 XRD analysis

The XRD pattern of SBA-15/80 is shown in Fig. 5. SBA-15/80 exhibits a single very broad peak at about 23°, which is the characteristic of amorphous silica. XRD pattern of SBA-15/100 sample was not given because of similarity.

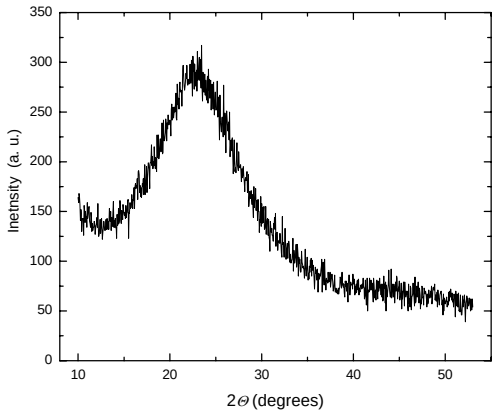

Fig. 5. X-ray diffraction (XRD) pattern of silica material SBA-15/80.

3.4 TGA/DTA analysis

The TGA measurements synthesized SBA-15/80 sample was carried out in air, and the thermal degradation behaviour is displayed in Fig. 6. Silica sample exhibits three weight loss steps in the TGA curve with a total weight loss of about 55 wt.%. The weight loss near 100°C is assigned to water desorption, whereas the weight losses at 212°C and 450°C are assigned to desorption and decomposition of the surfactant. Above 600°C all of the organic surfactant has been removed and synthesized inorganic material shows good thermal stability.

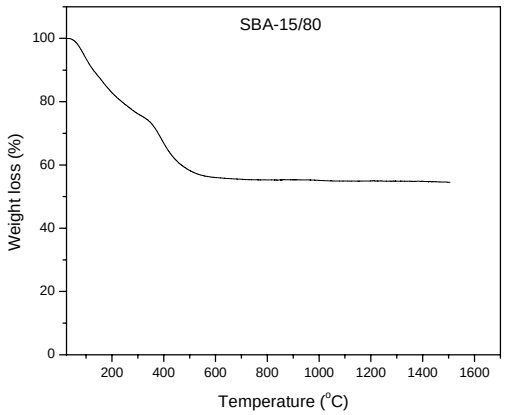

Fig. 6. TGA curve for SBA15/80 sample.

4. Conclusions

Mesoporous silica SBA-15 materials were successfully synthesized under acidic conditions. Characterization showed that materials have large specific surface, developed mesoporosity and microporosity. Structure properties of ordered mesoporous silica SBA-15 are function of different temperatures and times in the reaction solutions. Also, investigations in this paper confirm the presence of micropores in silica samples.

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