INFLUENCE OF NaCl ADDITION ON THE SYNTHESIS OF SBA-15 MESOPOROUS SILICA

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În această lucrare se prezintă rezultatele studiilor noastre efectuate în vederea stabilirii condițiilor optime de sinteză a unor materiale mezoporoase de tip SBA-15. Am investigat influența NaCl adaugată amestecului de reacție (în cantități diferite), rolul temperaturii şi al tratamentului hidrotermal asupra proprietăților materialului siloxanic final. În condiții de lucru bine stabilite au fost obținute cinci materiale mezoporoase (S1-S5), dintre care unul, S4, prezintă proprietăți superioare (aria specifică 527 m^2/g şi volumul de pori 0,5 cm^3/g).

In this paper we present our results obtained on tuning the synthesis parameters for obtaining pure mesoporous silica of SBA-15 type. We have investigated the influence of NaCl added in the reaction mixture (in different quantities) and the role of the synthesis temperature and hydrothermal treatment on the properties of the final siloxanic material. In well established conditions we have obtained five different mesoporous materials (S1-S5) from which S4 has high quality (527 m^2/g specific surface area and 0.5 cm^3/g pore volume).

Keywords: SBA-15, mesoporous silica, BET measurement, specific surface area

1. Introduction

The use of inorganic salts during the synthesis of mesoporous materials with triblock copolymers allows a wider synthesis temperature domain. In reported synthesis of SBA-15 mesoporous materials, the use of commercially available P123 surfactant and a precise temperature control for hydrothermal treatment in the range 100 – 145 ^{0}C are employed for high mesostructure ordering [1]. On the other hand inorganic salts have been used to control the porosity and the morphology of SBA materials, which otherwise doesn't vary much with the synthesis temperature [2]. Other combined synthesis methods have been used for tuning the micropore-mesopore balance in the final siloxanic material, for instance B.L.Newalker managed through microwave-hydrothermal approach to obtain micropore-free SBA-15 [3]. Various metal cations have been investigated and are known to form complexes with the polymeric ethylene oxide oligomers $(EO)_n$: Co^{2+}, Ni^{2+}, Mn^{2+}, Mg^{2+}. The use of salts like K_2SO_4 and triblock

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copolymers of F108 type have even lead to mesoporous single crystals [4], while salts are considered responsible for the improved hydrothermal stability of the MCM-41 materials [5] and the high ordering of the large-pore mesoporous organosilicas [6]. Ionic strength influence has been investigated in detail, through a wide range of alkali halide (NaCl) concentration. The properties of the final siloxanic materials have been investigated by N_2 sorption isotherms using Brunauer–Emmett–Teller (BET) method. Achieving same surface area at completely different NaCl molar concentrations implies that a possible variation of the type $S_{BET}=S_{BET}$ ([NaCl]) is not linear. Denoting the nonionic surfactants of the P123 type by N^0 and tetraethoxysilane by I^0 the pathway to mesoporous silica in the presence of Na^+ cations can be formulated as $(N^0H^+Na^+X^-)I^0$. The electrostatic forces are generated by both hydrogen bonds and complexation of EO groups by the small cation Na^+.

The structure-directing micelles allow polymerization of the inorganic silica source (TEOS in our case) around their surfaces and thus create a shorter or longer-range framework order. The pathway used for the self-assembly is many times matching the ionic surfactant (S^+ or S^-) and the inorganic species (I^+ or I^-), which leads to minimization of the electrostatic energy. This assembly path may lead to lamellar, cubic or hexagonal orderings in the final material. However, relying only on H-bonding in the absence of electrostatic interactions the S^0I^0 or N^0I^0 pathways lead to disordered materials. The ordering of such materials was proved by platinum or carbon replications, by nanocasting strategy [7], and N_2 sorption methods [8], TEM investigations and small angle X-ray diffraction (SAXS).

Electrical assembly pathways allow a lower synthesis temperature range (20-65 ^{0}C) [9] and to a long-range order in the framework, which can be desirable for improving catalytic activity (facilitating the access to reactive framework sites) or electronic applications (structural periodicity may be important). SBA-15 materials can be used successfully in biomolecules immobilization and catalysis. Moreover, mesoporous materials have been extensively studied for conception of a new fuel cell, given the scarce fossil fuels available today [10].

2. Experimental

2.1. Materials

The materials used to prepare SBA-15 are TEOS (tetraetoysilane, 98% purity, Sigma-Aldrich), Pluronic P123 (block co-polymer, Sigma-Aldrich, MW ~5800), HCl conc. (36-38%), NaCl (purris), CH_3CH_2OH and distilled H_2O. All reagents were of high purity and were used as received without further purification.

2.2. SBA-15 material synthesis

In this work we focus on synthesis of ordered mesoporous silica by a combined proposed pathway $(N^0H^+Na^+X^-)I^0$. This route enhances the amount of H-bonding, because it uses, in addition to classical H-bonding interaction between neutral surfactants (S^0) and neutral inorganic species (I^0), also the H-bonding created between the complex formed by the metal cation (Na^+) and the polyethylene oxide groups in the nonionic surfactant ($EO_{20}PEO_{70}EO_{20}$) and the neutral inorganic species (I^0). The proposed pathway is a modification of the acid-mediated pathway $N^0(H^+X^-)I^+$, in which we also accounted for the contribution of the metal cation (Na^+). The obtained materials have a hexagonal mesostructure. Using NaCl as a structure modifier lead to a long-range framework ordering, in addition to the mesoporous structure. The synthesis scheme is summarized in Fig. 1.

The nonionic surfactant (P123) is removed either by ethanol extraction (Soxhlet extraction) or by calcination at 550 ^{0}C for 6 hours with a heating ramp of 1 degree per minute. The solvent extracted products are, moreover, free of Na^+ cation and the halide counterion (Cl^-). Hydrogen bonds are formed between the uncomplexed EO units (through the oxygen atom) of the cationic complex (N^0Na^+) and the protons from both hydrolyzed I^0 silica source (TEOS hydrolysis leads to silanol groups)) and the acidic reaction media (HCl). The halide counterion (Cl^- from NaCl and HCl) closes the charge balance at the silica-surfactant interface. However, the anion role is less significant, as using a different Na^+ salt (Na_2SO_4) in corresponding concentration, we obtained similar materials.

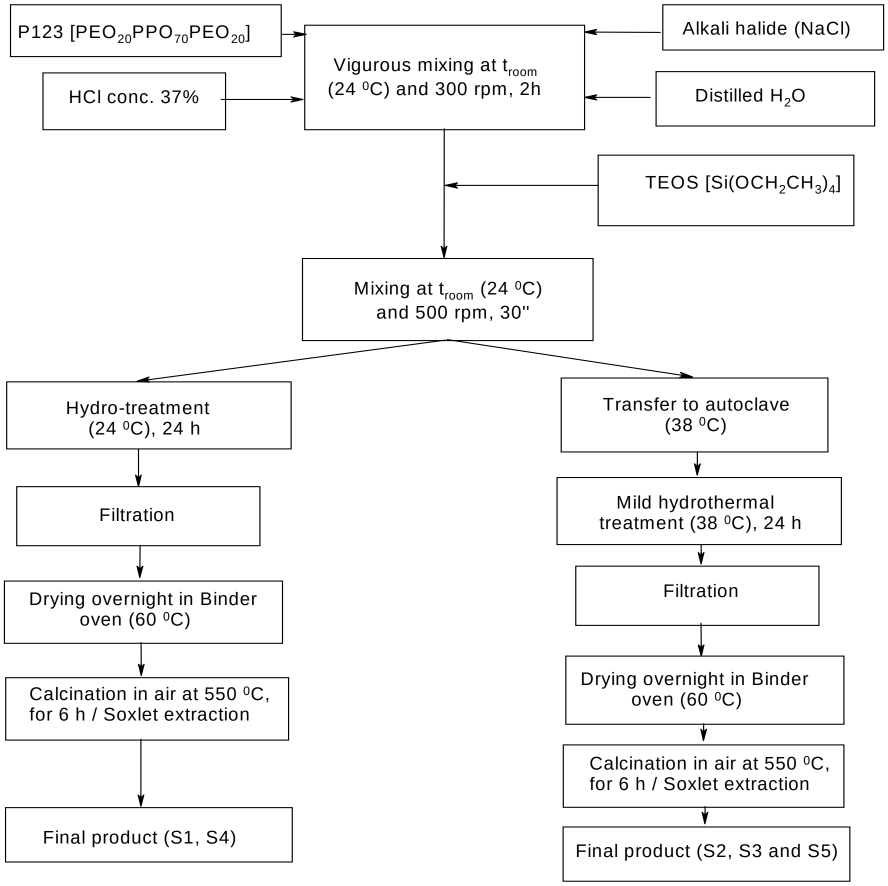

Fig.1. Synthesis scheme for samples S1-S5

2.3. Analysis

N_2 sorption measurements were performed at 77 K on a Quantachrome NovaWin 1200e analyser. The samples were degassed overnight at 80 ^{0}C and high vacuum (10^{-4} bar) prior to the measurement. The PSD (pore size distribution) was computed using the DFT model and using the data collected from adsorption branch of the isotherm.

Small angle X-ray powder diffraction was performed on a Bruker D8 Advance between 0.7 and 3 degrees (2 theta) with increment 0.005 and a scanspeed of 1. SAXS diffraction was carried out in order to detect the peaks associated with the characteristic diffraction planes, which is the case for OMS (ordered meseoporous silica) or OMC (ordered mesoporous carbon).

Transmission electron microscope Tecnai 12 (FEI) is a new generation microscope operated at 40 kV (possible values range from 20 to 120 kV), maximum magnification (120X – 300 000X). The TEM images were recorded in the range 5-100 nm and show the ordered structuring of the siloxanic materials synthesized herein.

3. Results and discussions

We obtained different degrees of ordering in the final materials over various metal salt concentration domains (confirmed by SAXS and N_2 sorption patterns). Small angle X-ray diffractions are shown in Fig. 2 and the N_2 adsorption-desorption isotherms for all the synthesized samples (S1-S5) are depicted in Fig. 3. These have been obtained by using Pluronic P123 as nonionic surfactant and Na^+ as structure modifier (Fig. 1). The hysteresis loop shows the filling and the emptying of the framework empty space. For the 1D hexagonal structure, as obtained by using small NaCl concentrations and room temperature, we obtained a small hystheresis. However, slight increase of the reaction temperature leads to a significant larger hysteresis loop.

The experimental conditions used for synthesizing the NaCl-aided SBA-15 are illustrated in Table 1. The pore size distribution using the adsorption branch of the recorded N_2 sorption isotherm are presented in Fig. 4. Samples obtained at temperatures (24 and 38 ^{0}C) lower than the regular synthesis temperature (100-145 ^{0}C) present a relatively broad PSD, centered at low pore size values. Sample S1, the reference sample (no salt used, r=0) has the peak of PSD at 3.05 nm, while the others are as follows: S2 has 2 peaks at 4.1 nm and 4.46 nm; S3 has it's pores centered at 5.31, S4 at 4.09 and S5 peaks at 5.83 nm. These variations show a clear dependence of the final material properties on the synthesis conditions employed.

Table 1

Experimental conditions for samples S1-S5 synthesis

Sample No.	*$[NaCl]_i$ (M)*	*Thermal pre-treatment Temperature (^{0}C)*	*Thermal pre-treatment time (h)*	*Hydrothermal treatment temperature (^{0}C)*	*Hydrothermal treatment time (h)*
S1	*0*	*24*	*24*	□	□
S2	*1.2*	□	□	*38*	*24*
S3	*2.4*	□	□	*38*	*24*
S4	*1.2*	*24*	*24*	□	□
S5	*2.4*	□	□	*38*	*24*

The BET surface area is computed in the region of relative pressure (P/P_0) between 0.05 and 0.35, the portion of the graph where the isotherm plot is closely linear. The correlation coefficient was 0.99 or better for all the fits, proving the estimation of S_{BET} to be fairly precise. The BET specific surface area, pore diameter and pore volume strongly depend on the synthesis time and temperature. Based on the BET surface area and PSD results sample S4 was selected for further investigation regarding possible catalytic activity (Table 2).

Table 2

Characteristics of the obtained siloxanic materials (Samples S1-S5)

Compound	*S_{BET} (m^2/g)*	*$V_{total, pores}$ (cm^3/g)*	*Mean pore diameter (nm)*
S1	*265.52*	*0.182*	*2.744*
S2	*305.82*	*0.273*	*3.569*
S3	*197.62*	*0.218*	*4.408*
S4	*527.51*	*0.501*	*3.797*
S5	*163.92*	*0.298*	*7.286*

The different hysteresis loops arise from different physical mechanisms. Low pressure hystheresis is due to swelling of the adsorbent. The first part of the isotherm is characterized by the fact that the adsorption amount increases rapidly. Such a process occurs in pores with a molecular size, indicating the presence of micropores (less than 2 nm in diameter). N_2 molecules (diameter of 0.364 nm) could fill these pores at low and very-low pressure. Second part of the isotherm (relative pressure $P/P_0 = 0.01 - 0.35$) showed a surface adsorption process (monolayer formation), in which the N_2 adsorption amount increased slowly. After this point, in the third, high partial pressure zone, the isotherm is characterized by a hysteresis loop, due to the capillarity in mesopores. Comparing to a theoretical model, one may conclude that the prepared materials show manifold surface characteristics, consisting of a mixture of pore structures (micropore, mesopore and macropore surface); as adsorption sites on different surfaces have different surface energies, this leads to an isotherm with multi-model characteristics.

From the analyses of the adsorption isotherm by means of BET method, one may obtain the specific surface area, which was found to be the highest for sample S4 (527 m^2/g) (Table 2), a result consistent with the high ordering proven by SAXS measurements (Fig. 2) and TEM pattern (Fig. 5). The SAXS pattern shows the d100 plane. Sample S4 shows the highest ordering and the corresponding peak is the highest of the samples analyzed (Fig. 2).

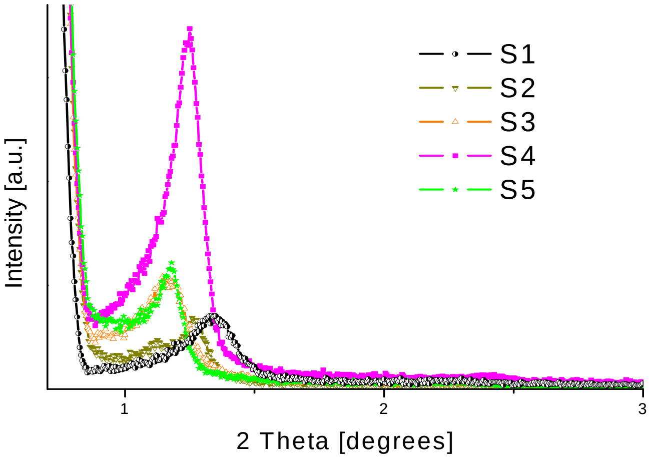

Fig. 2. SAXS for samples S1-S5

Sample S1 presents a large domain of P/P_0 where linearity can be applied, therefore this is a proof of a highly microporous material. The micropore analysis of the isotherm only peaks at about 3 nm, at the very beginning of the mesoporous domain (S1).

Except for the reference sample (S1), all samples present a type IV isotherm (IUPAC), with the hysteresis loop of type H2 (S2-S5). Sample S4 presents a higher specific surface area and is a perfect example for H2 hysteresis. S3 presents a beginning of the hysteresis loop, but is quite narrow (Fig. 3).

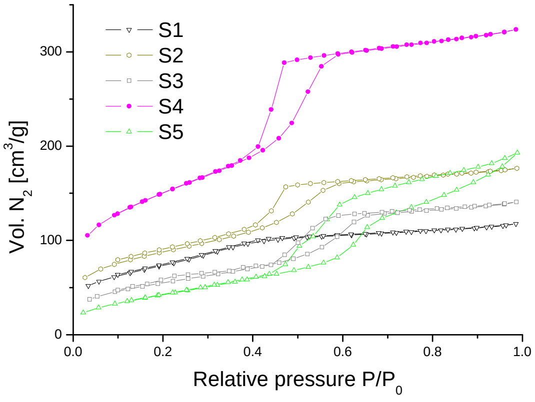

Fig. 3. The N_2 adsorption-desorption isotherm plots for calcined mesoporous silica (S1-S5)

Sample S5 shows a broader hysteresis loop as compared to S3, while samples S2 and S4 show both a H2 hysteresis loop with S4 being more pronounced in intensity and shape. Judging by its shape and dimension, we can predict S5 to have the broadest pore distribution of the samples, as will be confirmed by PSDs (Fig. 4).

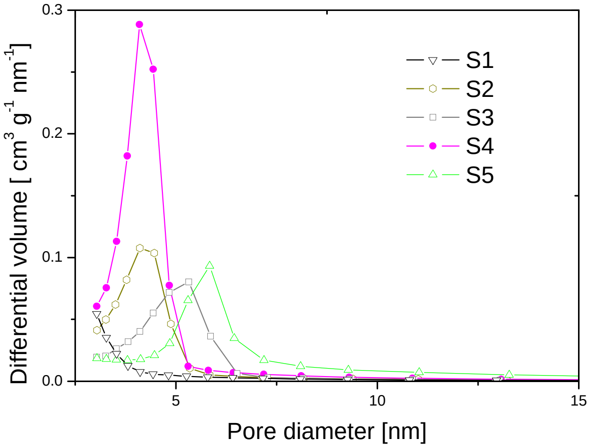

Fig.4. PSD (Pore size distribution) patterns calculated by the BJH method on adsorption branch.

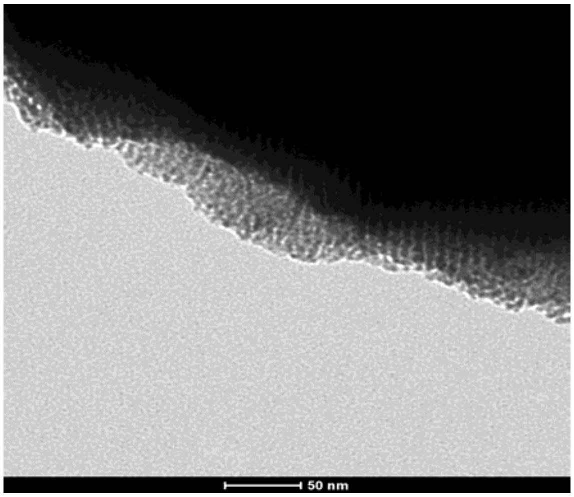

Fig. 5. TEM images of sample S4, recorded at 50 nm scale.

Type IV isotherms are interesting by their hysteresis loop, associated with capillary condensation occurring in mesopores, the limiting uptake being over a range of high P/P_0. This type of isotherm is characteristic to many mesoporous industrial adsorbents.

The planes of the OMS can be observed from the pattern shown by TEM images of sample S4 (characteristic image in Fig. 5). At a 50 nm scale the transmission microscope reveals the parallel orientation of the silica planes (the microscope is oriented perpendicular to the axis of the mesopores).

4. Conclusion

A reproducible synthesis of high surface area (527 m^2/g) SBA-15 materials using tetraethyl ortosilicate (TEOS) as silica source is presented in the present paper. This was achieved by controlling the micelle environment with the addition of alkali halide salt (NaCl). This mesoporous silica will be further investigated through its carbon replica, and the findings will be published in a forthcoming paper.

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