

NOI MATERIALE MEZOPOROASE BAZATE PE SBA-15 MODIFICAT CHIMIC CU 3-AMINOPROPIL-TRI(M)ETOXISILAN

NEW MESOPOROUS MATERIALS BASED ON FUNCTIONALIZED SBA-15 WITH 3-AMINOPROPYL-TRI(M)ETHOXYSILANE

CEZAR COMĂNESCU^{1*}, PETRU PALADE², DENISA FICAI¹, CORNELIA GURAN¹

¹Universitatea "POLITEHNICA" București, Str. Gheorghe Polizu nr. 1, sector 1, cod 011061, București, România

²Institutul Național de Cercetare Dezvoltare pentru Fizica Materialelor (INCDFM), str. Atomiștilor nr. 105, Măgurele, România

Lucrarea de față prezintă sinteza și caracterizarea unor materiale funcționalizate de tip SBA-15, prin sinteza optimizată, conducând la materiale mezoporoase bine organizate, din grupul de simetrie p6mm. Am obținut și caracterizat prin co-condensare SBA-APTMS și SBA-APTES.

S-au investigat rezultatele obținute prin varierea rapoartelor molare inițiale APTMS/TEOS și APTES/TEOS și prin folosirea unor timpi variabili de prehidroliză a TEOS. Izotermele de adsorbție a N₂, FT-IR, NIR și XRD au fost folosite pentru stabilirea particularităților mezostructurale ale materialelor sintetizate (SBA-15, SBA-APTMS x%, SBA-APTES x%, cu x= 2, 4 și 8 % rapoarte molare).

The present paper presents the synthesis and characterization of some new functionalized SBA-15 silica, by an improved synthesis route leading to well-organized mesoporous materials belonging to p6mm symmetry group. In a one-pot co-condensation synthesis we obtained and characterized SBA-APTMS and SBA-APTES samples.

Variation of the initial APTMS/TEOS and APTES/TEOS molar ratios and different TEOS pre-hydrolysis time were investigated. N₂ sorption, FT-IR, NIR and XRD method were employed in determining the mesostructure characteristics of the obtained materials (SBA-15, SBA-APTMS x%, SBA-APTES x%, with x= 2, 4 and 8 % molar percent).

Keywords: SBA-15, pre-hydrolysis, functionalization, APTMS, APTES

1. Introduction

Since the discovery of M41S materials in the late 1980s, synthesis of high surface area, large pore volume and large pore sizes became the main goal of each and every mesoporous material synthesis. The researchers are driven by the multiple applications of mesostructured materials, including catalysis, sensors design, separation procedures and controlled release drug delivery systems. These fields require incorporation of organic moieties into the silica framework by organic-inorganic hybridization and both pore and morphology control. The functionalization of silica framework proved to be an efficient method for obtaining high quality mesoporous materials. Tuning the key factors (incorporation of organic moieties into the silica framework by organic-inorganic hybridization and both pore and morphology control) may potentially lead to materials excellent for various applications [1-3].

The surface functionalization is done by organic-inorganic hybridization and is achieved by two methods: direct co-condensation synthesis and grafting post-synthesis. Post-synthesis raised some problems regarding the pore size reduction, surface pore blocking, active sites distribution and amount of incorporated moiety [4]. Amino-functionalized mesoporous materials for instance provide due to

the contained organic moiety a good starting material for base-catalyzed reactions, drug delivery systems, enzyme immobilization, removing heavy metals from wastewaters and as nanoparticle stabilizers [5].

The traditional method to synthesize these amino-functionalized materials is the post-synthesis method, which involves the reaction between the aminopropyltrialkoxysilane and the silanol groups available at the surface of the silica [6]. The states in which the amino-species were found in the obtained materials were mostly hydrogen-bonded to the support or to each other, and this cannot be very efficient in catalysis for instance. The best way to overcome this is to disperse the amine groups on the silica surface, thus limiting their interaction and the amount of hydrogen bonding involved, and direct co-condensation method provides such a mean.

In this work we report the improved synthetic route that allows highly dispersed amine-groups on the silica surface, by a co-condensation method, although previous reports suggest that the usage of non-ionic surfactants during such a reaction hinders the silica structure to develop, by negative effect of aminopropyltrialkoxysilane on silica-surfactant micelles [7]. This approach shows that organic moieties can be incorporated into the silica matrix, given that a proper concentration of propy-

* Autor corespondent/Corresponding author,
Tel.: 0040 734722463 e-mail:drums1605@yahoo.com

lamino- precursor and TEOS pre-hydrolysis are provided.

2. Experimental

2.1. Chemicals and synthesis

Surfactant Pluronic P123 (PEO₂₀PPO₇₀PEO₂₀, M_{av}=5800), TEOS (98%), 3-aminopropyl-trimethoxysilane (APTMS), 3-aminopropyl-triethoxysilane (APTES), hydrochloric acid (37%), ethanol (95%), acetone (99%) and KBr (IR grade) were purchased from Sigma-Aldrich and used without further purification.

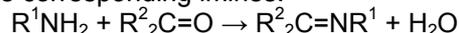
2.2. Synthesis of functionalized SBA- APTMS and -SBA- APTES materials

Aminopropyl-functionalized SBA-15 materials were obtained during a one-pot synthesis, rather than post-synthesis grafting [8]. In a typical synthesis, 2.5 g P123 was dissolved in 79 mL H₂O and 12.6 mL HCl 37% solution under vigorous stirring at 35 °C. TEOS addition is followed a pre-hydrolysis time between 0-1.5 hours [Table 1]. Afterwards APTMS or APTES were added dropwise into the reaction mixture. The molar concentration was (1-x) TEOS: x APTMS (APTES) : 0.017 P123: (5.91+x) HCl : 194 H₂O, ensuring identical reaction conditions for all the samples, regardless of the amount of functionalization compound (APTMS/APTES) added. The functionalization was targeted below 10%, in order to obtain high quality, high surface area materials. We used the following molar ratios: x= 0.02, 0.04 and 0.08 (or in percents 2%, 4% and 8%) for functionalization of SBA-15. The mixture was stirred at 39 °C for 18-24 h and then was transferred into a polypropylene flask, heated to 90 °C and allowed to age for 24 h in static conditions. The products were filtered and air dried at 80 °C in drying oven. We denote the obtained materials as SBA-APTMS-x or SBA-APTES-x.

In order to avoid the destruction of the aminopropyl functionalization, we used instead of standard air calcination at 550 °C (typical in SBA-15 synthesis) the solvent extraction approach. One gram of as-synthesized sample was washed several times with water and ethanol, mixed afterwards with 200 mL C₂H₅OH for 6 h, then the product was filtered and the operation was repeated twice. In the final step the products were dried overnight at 70 °C.

Standard SBA-15 synthesis. For reference, a standard SBA-15 sample was prepared in parallel; the synthesis conditions are rather similar, with the absence of the aminopropyl modifiers and the calcination for 6 h in air at 550 °C, instead of the ethanol solvent extraction described above.

Modification of as-synthesized SBA-APTMS 8% by acetone treatment. Given the successful incorporation of 3-aminopropyl groups into the hexagonal silica framework, the surface of the obtained material becomes active towards base-catalyzed reactions (Knoevenagel, Claisen-Schmidt condensation). Moreover, the primary amine moieties (R-CH₂-CH₂-CH₂-NH₂) could potentially react with aldehydes and ketones to form the corresponding imines.



In an attempt to produce further functionalization of the SBA-15 surfaces, 0.5 g as-synthesized SBA-APTMS-0.08 (containing thus the highest loading of aminopropyl groups in the series) was impregnated with pure acetone, by incipient wetness method. This was repeated until 2 mL acetone were used, to ensure all amine active sites have been reached. Subsequent treatment for 2 h in pure acetone with mixing would ensure reaction of the two moieties (amino from silica and carbonyl group provided by acetone).

The obtained material was denoted SBA-APTMS 0.08 – Me₂C=O. This functionalized silica material was characterized by XRD, BET, IR and NIR. Below is given a table containing the most important characteristics of the 3-aminopropyl functionalization.

2.3. Sample characterization

N₂ sorption measurements were performed on a Quantachrome Instruments NOVWin 1200e at 77 K (liquid nitrogen temperature). The samples were degassed for 12 h at 100 °C prior to the measurements. The specific surface area were computed by Brunauer-Emmett-Teller (BET) method in the P/P₀ range of 0.05 – 0.3. Pore size distribution was estimated using the Barrett-Joyner-Halenda (BJH) method based on the adsorption branch of the isotherms, while the pore size was calculated from the peak position of the distribution curve. The pore volume was taken in the proximity of the point P/P₀ = 0.99.

Tabelul 1

Syntheses conditions used for obtaining functionalized SBA-15 / Condițiile sintezei materialelor SBA-15 funcționalizate

Synthesized material <i>Material sintetizat</i>	TEOS prehydrolysis time <i>Timp de prehidroliză a TEOS</i> [h]	Mixing time <i>Timp de amestec</i> [h]	Time of hydrothermal treatment <i>Timp de tratament hidrotermal</i> [h][90 °C]
SBA-15-APTMS 2%	0.5	18	24
SBA-15-APTES 2%	0.5	18	24
SBA-15-APTMS 4%	1.5	18	24
SBA-15-APTES 4%	1.5	18	24
SBA-15-APTMS 8%	1.5	18	24
SBA-15-APTES 8%	1.5	24	24

IR measurements were carried out on a Jasco FT-IR 620 Spectrophotometer. IR grade KBr was used to prepare the samples and the witness sample for background removal. The resolution was 4 cm^{-1} , and the domains were $7000\text{--}4000\text{ cm}^{-1}$ (NIR) and $4000\text{--}400\text{ cm}^{-1}$ (IR). The scanning was set to 64 times.

XRD data was collected on a Bruker D8 Advance using the Cu K α line ($\lambda = 0.154\text{ nm}$); the X-ray source is a 2.2 kW Cu anode long fine focus ceramic X-ray tube. The running conditions for the X-Ray tube are 40 kV and 40 mA. The measurements were performed between the range $2\theta = 5.0 - 60^\circ$ with a step size of 0.5° .

3. Results and discussions

3.1. Functionalization of SBA-15 with APTMS / APTES

All obtained materials exhibited a type IV hysteresis loop (I.U.P.A.C. classification), with a pronounced capillary condensation occurring at $P/P_0 = 0.6 - 0.7$. This is particularly valid for mesostructured materials.

3.1.1. TEOS pre-hydrolysis time influence on the mesostructure formation

Using functionalization technique without TEOS prehydrolysis usually results in a lack of structure ordering in the obtained materials. This can be explained by the fact that adding APTMS or APTES in the reaction mixture (rapidly premixed with TEOS) inhibits the mesostructure development. As the percent of 3-aminopropyl-precursor increases, the ordering decreases rapidly. [9]

However, there should be an optimum prehydrolysis time for TEOS, which would allow both development of hexagonal framework and a good incorporation of organic moiety. Thus, when using 30 min to pre-hydrolyze TEOS, the obtained structure exhibited a somewhat lower ordering than for a 90 min hydrolysis time. An increase of this parameter beyond 2 h will lower total pore volume and surface area, although slightly increasing the pore size. The samples show a H1 hysteresis loop in the isotherms, which are typical for narrow pore size distributions (Fig. 1).

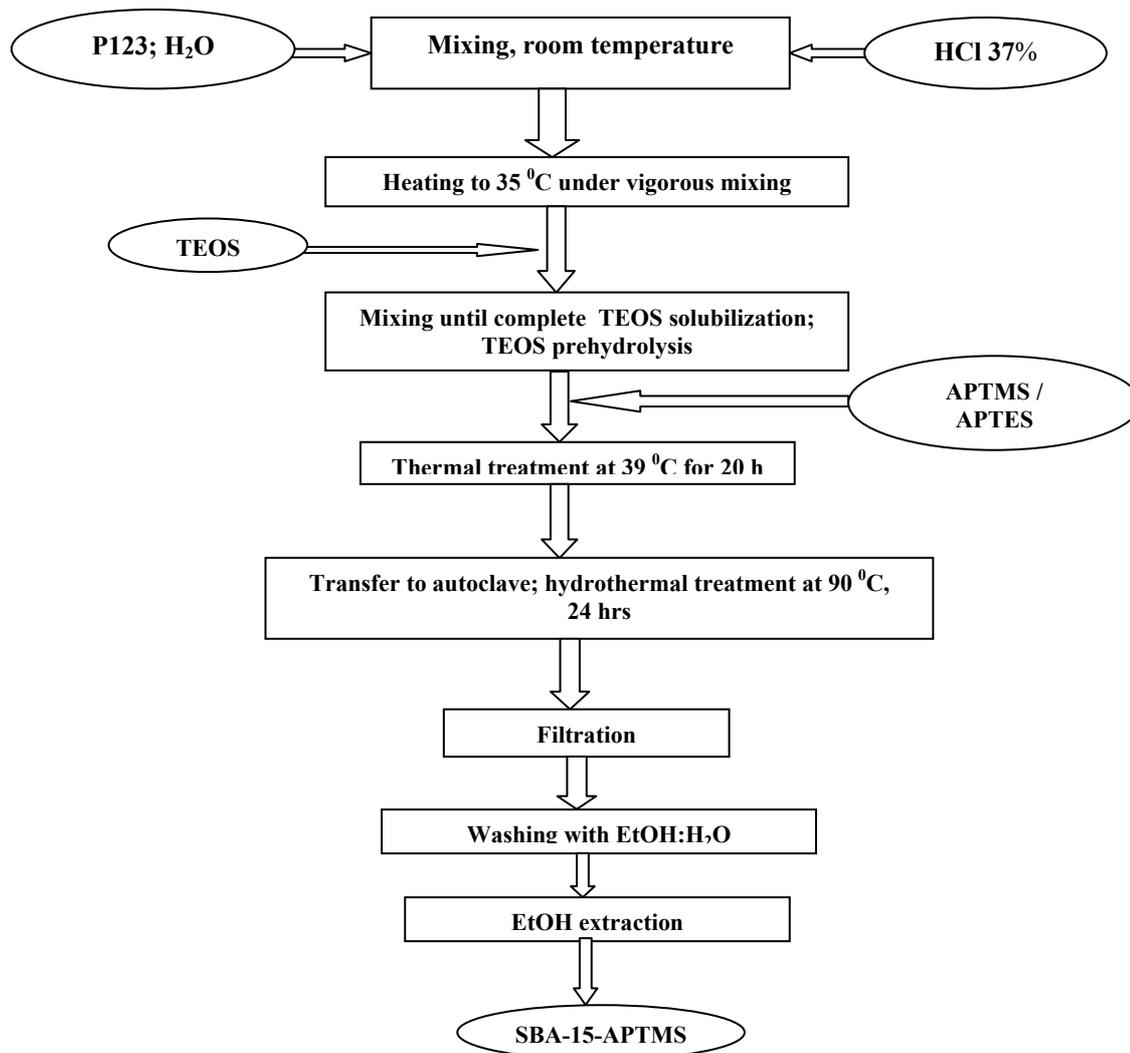


Fig. 1 - Flowchart for SBA-15 functionalization / Schema funcționalizării SBA-15.

We chose the co-condensation method for preparing SBA-APTMS and SBA-APTES samples, primarily because of two reasons: the loading of functional groups is higher than in the case of post-grafting method, and an optimum prehydrolysis time. In the case of the alternative method, namely the post-grafting method, a previously prepared SBA-15 sample would be treated with APTMS/APTES; however, in using this method one must pay attention to the fact that anchoring points for the immobilization of aminopropyl groups are lower and depend on the accessible silanol groups. Thus, grafting procedure never leads to high organic moiety incorporation.

3.1.2. Influence and importance of APTM(E)S / TEOS loading amount on final SBA-APTMS-x

At lower concentration, FT-IR data (discussed below) and N₂ sorption measurements confirm that the material synthesized using APTES proves to be of higher quality than the one synthesized using APTMS. The surface area is considerably higher for the former. That implies that at lower hydrolysis time (30 min), addition of APTES is desirable, as it hydrolyses slower and does allow mesopores to build up, affecting less the formed structure. However the APTMS hydrolyses faster and is involved right from the start in the mesopore formation. At lower concentration of the aminopropyl precursor and lower TEOS prehydrolysis time the APTMS is less desirable; using APTES creates a higher degree of ordering in the silica, which in return afford a higher surface area.

3.2. N₂ sorption results

The N₂ sorption measurements (done at 77 K) are showing the differences that occur in the synthesized materials, by varying the loading of the organic moiety.

SBA-15 has a distinct position, given the thermal treatment at 550 °C, which further refines and strengthens the silica framework; it shows unrestricted monolayer-multilayer adsorption. Most of the functionalized materials have similar H1 hysteresis loops, exhibiting a type IV isotherm (Fig. 2).

The acetone treatment performed on the sample with the highest aminopropyl groups loading showed a considerable improvement over the parent compound. The SBA-APTMS 8% had a $S_{BET} = 685 \text{ m}^2/\text{g}$, following a decreasing trend with the increase in organic moiety content (Fig. 3). The specific surface area decreases from $731 \text{ m}^2/\text{g}$ (SBA-APTMS x=4%) to $685 \text{ m}^2/\text{g}$ (SBA-APTMS x=8%). However, upon (CH₃)₂C=O treatment, the pore size slightly decreases but the pore volume increases with more than 24%, to $1.24 \text{ cm}^3/\text{g}$. Moreover, the specific surface area determined by BET method is the highest obtained amongst the samples presented herein, $839 \text{ m}^2/\text{g}$ (Table 2).

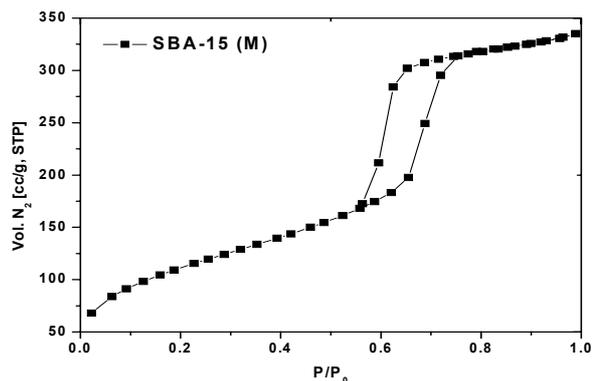


Fig. 2 – N₂ sorption isotherm pattern for SBA-15, a mesoporous siloxanic material / Izoterma de adsorpție N₂ a SBA-15, material siloxanic mezoporos nefuncționalizat.

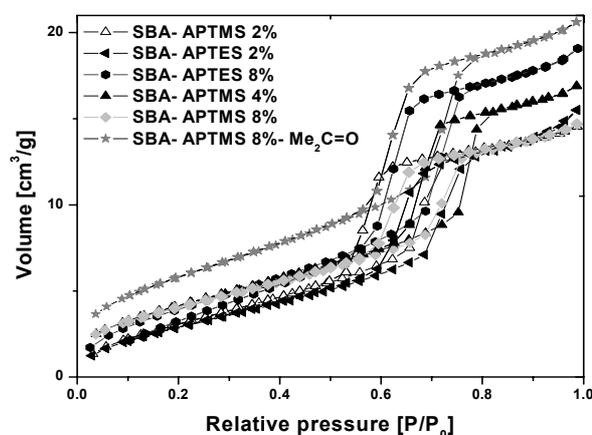


Fig. 3 – N₂ sorption isotherms afforded by functionalized SBA-15 materials / Izoterma de sorpție N₂ a materialelor SBA-15 funcționalizate.

Tabelul 2

Physico-chemical properties of ethanol extracted, aminopropyl functionalized SBA-15 / Proprietăți fizico-chimice ale SBA-15 funcționalizate cu grupări aminopropil, după extracția cu etanol

Sample Proba	PSD [nm]	$S_{BET} [\text{m}^2/\text{g}^{-1}]$	Pore vol. Vol. pori [$\text{cm}^3/\text{g}^{-1}$]
SBA-15	7.06	782	1.382
SBA-APTMS 2%	6.86	371	0.637
SBA-APTMS 4%	6.62	731	1.21
SBA-APTMS 8%	5.95	685	1.02
SBA-APTES 2%	7.9	458	0.901
SBA-APTES 8%	7.26	703	1.277
SBA-APTES 8%-Me ₂ C=O	5.91	839	1.241

3.3. FTIR results

FT-IR was used to verify that the aminopropyl groups were successfully incorporated into the framework, and that the Si-C bond was still intact after the synthesis.

The near infrared (NIR) spectra provided proof that the aminopropyl group was indeed-functionalized on the support. NIR spectra showed that for SBA-APTES 2%, SBA-APTMS 8% and its acetone modification one may identify the bands corresponding to the functionalized groups. The vibration peaks at 4350 cm^{-1} are assigned to the symmetry stretching (ν_{sym}) modes and the combination ($\nu + \delta$) peak of stretching vibration (ν) and bending (δ) modes of the primary amine groups [10]. The peak at $5200\text{--}5300\text{ cm}^{-1}$ range were assigned to the vibration transition of $-\text{CH}_2-$ moieties of the anchored aminopropyl groups.

The diluted samples afforded only small NIR intensity peaks, but in the range supporting the $-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$ functionalization (Fig. 4).

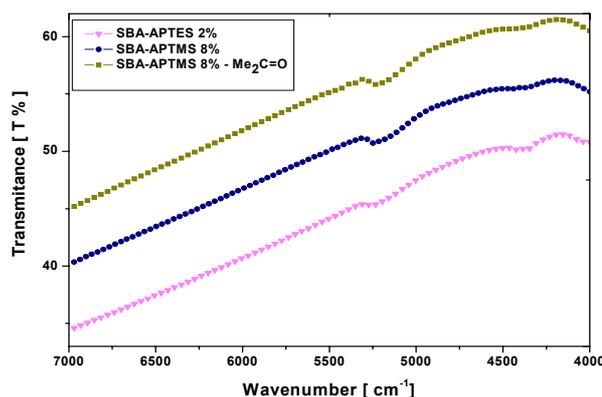


Fig. 4 - NIR data for the series of functionalized SBA-15. Rezultatele infraroșu apropiat pentru o serie de materiale SBA-15 funcționale.

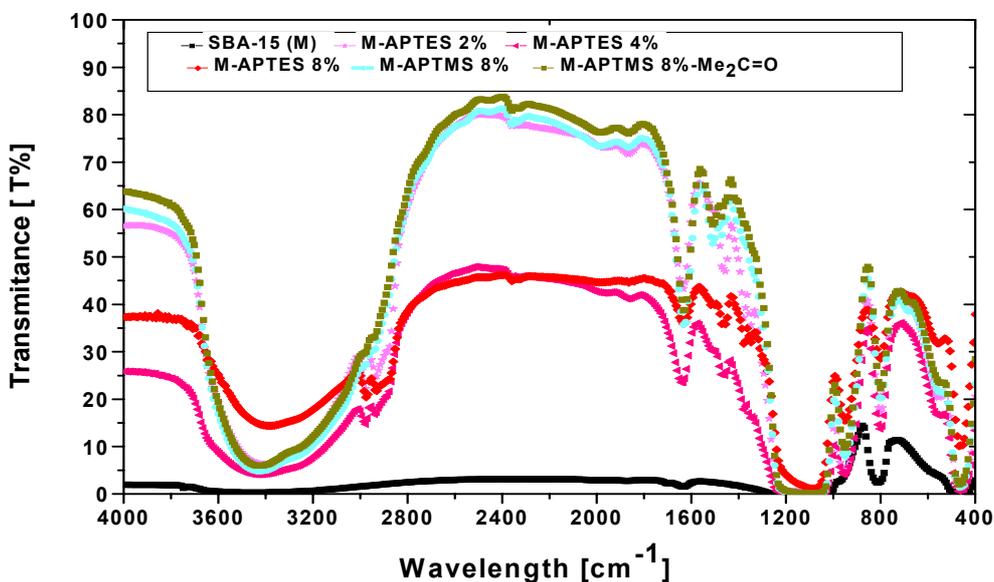


Fig. 5 - FT-IR results on studied samples (SBA-15, SBA-APTES 2, 4 and 8%, SBA-APTMS 8% and SBA-APTMS 8% - $\text{Me}_2\text{C}=\text{O}$). Rezultatele FT-IR ale probelor studiate (SBA-15, SBA-APTES 2, 4 and 8%, SBA-APTMS 8% și SBA-APTMS 8% - $\text{Me}_2\text{C}=\text{O}$).

FT-IR measurement carried out in the $4000 - 400\text{ cm}^{-1}$ showed the presence of the incorporated aminopropyl moieties (Fig. 5). The band corresponding to the asymmetric mode of the N-H vibration is contained into the broad peak at 1630 cm^{-1} . The bands at 1490 and 1470 cm^{-1} are attributed to the bending vibration of the C-H in the propyl group of APTMS / APTES. These are more refined in the case of APTMS, where they can be distinguished as two separate peaks. The bands between 2800 and 3000 cm^{-1} come from stretching of C-H in the propyl as well as the bridging ethylene groups. The incorporation of the amine moiety is further sustained by the C-H vibration of the ethylene groups.

At 2939 and 2978 cm^{-1} we identify the C-H bands (which increase in intensity as the concen-

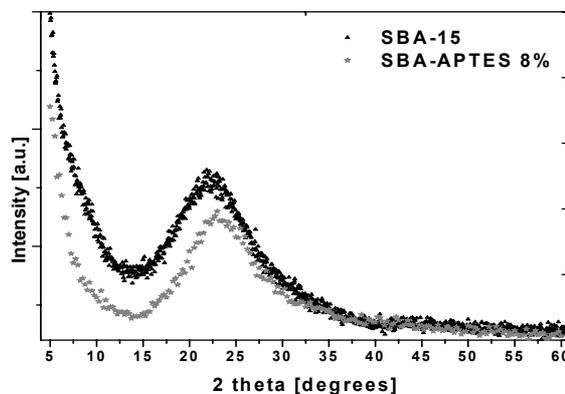


Fig. 6 - XRD spectra for two as-synthesized materials (SBA-15 and SBA-APTES 8%) / Spectrele XRD pentru două dintre materialele sintetizate (SBA-15 și SBA-APTES 8%) .

tration of aminopropyl increases from 2% to 8%, the organic moiety loading on the mesoporous silica increasing accordingly). These C-H bands belong to sp^3 hybridized C, which could also be attributed to some traces of surfactant after ethanol extraction. The 943 cm^{-1} can be assigned to C-O bond, and bending vibrations.

3.4. XRD data

The cristalinity of the SBA-APTES 8% sample is lower than that of pure SBA-15; by functionalization the materials becomes less ordered, and more amorphous (Fig. 6).

4. Conclusion

Seven (7) functionalized samples have been prepared starting from a modified SBA-15 synthesis route. APTMS and respectively APTMS have been used to introduce the 3-aminopropyl organic functions into the silica framework, by the co-condensation technique (SBA-APTMS 2,4,8 %; SBA-APTES 2,4,8 %); one sample was prepared by a post-grafting method (SBA-APTMS8%- $\text{Me}_2\text{C}=\text{O}$). The TEOS pre-hydrolysis proves to be vital for mesopore evolution and framework strengthening, while addition of organo-modified tri(m)ethoxysilane before a certain critical time (around 1 h) leads to poorer quality samples. The aminopropyl groups hinder somewhat the hexagonal silica organization. The co-condensation method proves each time superior results, higher surface areas and more ordered materials, as they allow for easy incorporation of organic moieties, while only a limited number of silanol groups are available post-synthesis for this purpose.

Specific surface areas as high as $840\text{ m}^2/\text{g}$ have been obtained and high pore volumes, exceeding $1\text{ cm}^3/\text{g}$ ($1.38\text{ cm}^3/\text{g}$), in the case of acetone treated SBA-APTMS 8%. Moreover, for the relatively small APTMS and APTES concentration increments, the N_2 sorption measurements showed a quite narrow pore size distribution and an easy way of fine-tuning the pore size of the obtained materials. This insight could provide the materials used in several applications where surface areas and pore sizes are of outmost importance, such as energy carriers and fuel cells while the aminopropyl moieties can be successfully incorporated in new formulation of drugs used in drug release systems.

Acknowledgements

Support of the Romanian Ministry of Education and Research through the project PNCDI-2 No. 72-196 / 2008 "New complex hydrides for hydrogen storage in hydride tank suitable for vehicular applications" – STOCHICO is strongly acknowledged. C. Comănescu acknowledges the financial support of the POSDRU - ID5159 doctoral fellowship.

REFERENCES

1. Y. Xia, Z. Yang, and R. Mokaya, Simultaneous Control of Morphology and Porosity in Nanoporous Carbon: Graphitic Carbon Nanorods and Nanotubes with Tunable Pore Size, *Chem. Mater.*, 2006, **18**, 140.
2. N. M. Sulca, A. Lungu, G. Voicu, S. A. Garea, and H. Iovu, Advanced Characterization of Polyhedral Oligomeric Silsesquioxanes Used for Nanocomposites Synthesis, *Rev. Mat. Plast.*, 2009, **46**(2), 124.
3. E. Crăciun, A. Ioncea, I. Jitaru, M. Ghiurea, and O. Oprea, Organo-inorganic nanostructures coating materials, *Romanian Journal of Materials*, 2011, **41**(1), 64.
4. L. Mercier, and T.J. Pinnavaia, Direct Synthesis of Hybrid Organic-Inorganic Nanoporous Silica by a Neutral Amine Assembly Route: Structure-Function Control by Stoichiometric Incorporation of Organosiloxane Molecules, *Chem. Mater.*, 2000, **12**, 188.
5. S.H. Tolbert, A. Firouzi, G.D. Stucky, and B.F. Chmelka, Magnetic Field Alignment of Ordered Silicate-Surfactant Composites and Mesoporous Silica, *Science*, 1997, **278**, 264.
6. J.C. Hicks, C.W. Jones, Controlling the Density of Amine Sites on Silica Surfaces Using Benzyl Spacers, *Langmuir*, 2006, **22**, 2676.
7. X. Wang, J. Shah, S.-S. Kim, and T.J. Pinnavaia, A versatile pathway for the direct assembly of organo-functional mesostructures from sodium silicate, *Chem. Commun.*, 2004, 572.
8. F. Berube, F. Kleitz, and S. Kaliaguine, A Comprehensive Study of Titanium-Substituted SBA-15 Mesoporous Materials Prepared by Direct Synthesis, *J.Phys. Chem. C*, 2008, **112**, 14403.
9. X. Wang, K.S.K.Lin, J.C.C.Chan, and S. Cheng, Direct Synthesis and Catalytic Applications of Ordered Large Pore Aminopropyl-Functionalized SBA-15 Mesoporous Materials, *J.Phys.Chem. B*, 2005, **109**, 1763.
10. J. Mijovic, and S. Andjeli, A Study of Reaction Kinetics by Near-Infrared Spectroscopy.1. Comprehensive Analysis of a Model Epoxy/Amine System, *Macromolecules*, 1995, **28**, 2787.
