Mesoporous organosilicas functionalized by alkyl groups: synthesis, structure and adsorption properties

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Abstract. Mesoporous organosilicas were synthesized by sol-gel co-condensation of tetraethoxysilane and appropriate alkoxy silanes in the presence of Pluronic P123 surfactant. Hexyl, dodecyl, and octadecyl alkyl chains have been incorporated into mesopores by such co-condensation. Obtained materials were characterized by X-ray diffraction, FTIR spectroscopy, nitrogen adsorption measurements and thermogravimetry. Two resulted materials have highly ordered SBA-15 structure (p6m symmetry), other two are less ordered. All the materials exhibit well-developed porous structure (surface areas 500 to 830 m²/g, pore volumes 0.65–1.32 cm³/g) and a high content of organic pendant groups introduced during co-condensation. All materials are thermally stable to 180°C, after that thermal decomposition of alkyl pendant groups starts.

1. Introduction

Ordered mesoporous silicas (OMOs) are very attractive materials due to their high surface areas, large pore volumes, large, uniform and adjustable pore sizes, and diverse morphology what makes them potential catalysts and adsorbents [1]. The first successful attempt in this field was done by researchers from Mobil when a family ordered mesoporous aluminosilicates, denoted as M41S materials, was obtained by supramolecular templating approach [2].

The use of cationic surfactants as templates made it possible to obtain materials with the sizes of the pores in the range of 2-7 nm. Sometimes, such pores are too small for catalytic or sorption application. Besides, M41S materials have some unfavorable properties, such as low thermal and hydrothermal stability. Thus, a lot of efforts have been done to broad the accessible size of the pores and improve mechanical properties of OMS materials.

After discovery of M41S materials a broad spectrum of other mesoporous materials has been discovered. The range of surfactants used as the structure directing agents has been gradually spreading from long-chain quaternary ammonium via anionic and neutral to nonionic polyethylene oxide [3]. In 1998 the use of a commercially available block copolymers resulted in obtaining a new family of mesoporous materials called SBA materials. These materials exhibited various types of ordered structure and large sizes of mesopores up to 30 nm [4]. Structure of SBA differs from M41S not only because of the bigger size of the mesopores. Ordered primary mesopores are additionally connected with each other through a network of micropores and smaller mesopores [5]. It is schematically depicted in Fig. 1. SBA materials have also thicker interpore walls, what improves the thermal and hydrothermal properties [6]. The most studied structure from this group is the hexagonally ordered structure with the p6m symmetry called SBA-15.
A very important advantage connected with the sol-gel synthesis of silica materials is the possibility of introduction of the organic groups into the ordered structure during the one-pot synthesis. In this way new organic-inorganic hybrids with desired optical, mechanical and electrical properties can be created, what make such materials attractive in adsorption, catalysis or sensing [7]. Functionalized materials are called ordered mesoporous organosilicas (OMOs) or periodic mesoporous organosilicas (PMOs) depending on the type of moieties incorporated (side-end groups sticking inside the pores in the case of the former or bridging groups incorporated in the mesopores walls in the case of the latter). Such a surface functionalization leads to materials differing in the reactivity, pore accessibility and distribution of organic groups. Particularly, the co-condensation route seems to be very attractive as it affords to control simultaneously the surface and structural properties of the resulting OMOs, even those with high loadings of pendant organic functionalities. These groups can be attached to the internal and external surfaces of mesopores as well as incorporated in the framework as uniformly integrated bridges. Using co-condensation route different types OMO materials have been obtained. They can contain different pendant groups like, for example, alkyl [8], vinyl [9], carboxylic [10], thiol [11] amine [12].

Fig. 1. Scheme of the a) microscopic structure of SBA-15, b) porosity in OMO materials

The main goal of this work is to take advantage of co-condensation method to introduce alkyl chains of different length (hexyl, dodecyl and octadecyl) into the silicate structure and study how structural-adsorption properties change due to incorporation of these chains in the final samples.

2. Experimental

2.1. Reagents

The following compounds were used: tetraethoxysilane: (TEOS, 96%, ABCR), hexyltriethoxysilane (HTES, 95%, ABCR), dodecyltriethoxysilane (DTES, 95%, ABCR), octadecyltriethoxysilane (OTES, 95%, ABCR), poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer Pluronic P123 (P123, BASF), hydrochloric acid (37%, POCH), ethanol (99.8%, POCH). All chemicals were used as received.

2.2. Syntheses of the samples

Syntheses of all mesoporous silicas were performed in the presence of P123 triblock copolymer by co-condensation of TEOS and one of the alkyl-functionalized monomers (HTES, DTES or OTES) to introduce the desired surface functional groups. All materials were synthesized by one-pot route using the similar synthesis procedure reported elsewhere [7]. In a model synthesis, 2g of P123 was dissolved in 60 ml of 2M HCl and 10 ml of deionized water under vigorous stirring at 40°C. After 6 h of stirring a specified volume of TEOS was added dropwise to this solution under vigorous mixing, and then the proper co-monomer was pipetted after 15 minutes. The resulting mixture was stirred for 24 h and aged at 100°C for 48 h. The white solids were thoroughly washed with deionized water, filtered and dried at 70°C. The template was removed by triple extraction with the acidic ethanol (95%) at 70°C. The
numeration of the samples was as follows: A1 - pure silica sample (initial amount of TEOS: 20mmol), A2 - sample synthesized in the system TEOS/HTES (molar ratio 19mmol:1mmol), A3 - TEOS/DTES (19:1), A4 - TEOS/OTES (19:1).

2.3. Measurements

Powder X-ray diffraction (XRD) patterns were recorded using a Seifert RTG DRON-3 diffractometer (CuKα radiation) with 0.02° step size and 10 s step time over a range 0.5°<2θ<5.0° at room temperature.

Nitrogen adsorption isotherms were measured at -196°C using an ASAP 2405N sorptometer after degassing at 105°C. The BET surface area (S_{BET}) was evaluated in the range of 0.05-0.25 p/p_o [13]. The total pore volume (V_p) was calculated by converting the amount adsorbed at a p/p_o=0.99 to the volume of liquid adsorbate. The average pore size (d) was estimated using the BJH method [14].

The FTIR spectra were recorded at room temperature by means of a 1725X Perkin-Elmer spectrometer over the 4000-400 cm⁻¹ range at the resolution of 4 cm⁻¹ and maximum source aperture.

Thermogravimetric analysis was carried out under air atmosphere using a Setsys 16/18 Setaram thermogravimetric analyzer. The weight change (TG) patterns were recorded over a temperature range from 30 to 900°C. The instrument was equipped with a ceramic Al₂O₃ pan. The heating rate was 5°C/min, and the air flow rate was 1dm³/h.

3. Results and discussion

3.1. X-ray diffractometry

Figure 2 presents the XRD patterns for the samples A1-A4. Under the conditions investigated, mesostructured materials with different degree of order were obtained. Three well-resolved peaks are observed in the range of 2θ ≈ 0.8-2° in the case of samples A1 and A4. The peaks can be indexed according to two-dimensional hexagonal p6m symmetry, indicating a well-defined SBA-15 mesostructure: one sharp reflection at 2θ ≈ 0.8 (A1) and 1.0 (A4) indexed as (100) and two minor but distinct reflections at 2θ ≈ 1.5 and 2θ ≈ 1.7, indexed as (110) and (200), respectively. Samples A2 and A3 have a disordered structure which is confirmed by the lack of diffraction peaks on corresponding XRD pattern, apart from one low-intensity signal at 2θ ≈ 1.0.

![Fig. 2. XRD patterns of the samples A1-A4](image)

As the only difference in the synthesis’ procedure was the type of network-functionalizing monomer used (see Table 1), the only factor potentially affecting the final structure is the presence of a certain type of alkyl chains. The presence of hexyl and dodecyl groups leads to almost disordered materials, even at so low concentration of HTES and DTES added. However, in the case of octadecyl-functionalized sample A4 the final structure has high ordering. Apparently, interactions of the bulkier and more hydrophobic octadecyl groups with the micellar poly(oxyethylene) groups may be less disruptive to micelle structure.
3.2. Nitrogen adsorption/desorption measurements

Nitrogen adsorption/desorption isotherms of the materials studied are shown in Fig. 3. All samples exhibit type IV isotherms. Isotherms of the all samples have a sharp capillary condensation step, reflecting capillary condensation of adsorbate in the uniform mesopores channels, and evaporation step related to the evacuation of adsorbate from the pores. Thus, it can be concluded that a framework of materials has a rather uniform array of mesopores with the same diameter. Samples A2 and A3 have a less sharp capillary condensation step, what testifies to deterioration of the structure’s ordering.

Fig. 3. Nitrogen adsorption/desorption isotherms of the samples A1-A4. Inlets show pore size distributions calculated from adsorption branch of the isotherm by the BJH method

The parameters of the porous structure are summarized in Table 1. All materials exhibit high values of surface area (S_{BET}) ranging from 500 to 830 m²/g. Pure silica sample A1 and sample A4 containing longer alkyl chains inside the primary mesopores have significantly smaller values of S_{BET}. Pore volumes (V_p) also differ among the samples investigated. Relatively high pore volume of the pure-silica sample A1 (1.32 cm³/g) is a result of the lack of alkyl chains in the structure. Addition of small amount of co-monomer (HTES, DTES or OTES – see Table 1) diminishes considerably pore volumes of resulted materials. The rest of the samples have pore volumes in the range 0.65-0.89 cm³/g. The average pore sizes (d) are in the range of 4.6-6.9 nm. Addition of OTES (sample A4) does not change the size of the pore in comparison with the pure-silica sample A1; the pore size distributions (Fig. 3) of these two samples are also very similar and show the presence of small amount of micropores in the structure. In the case of sample A3 the pore size distribution is similar to those of samples A1 and A4, however, there is no sharp peak indicating the dominance of one size of pores in the structure. Sample A2 has a totally different pore size distribution that the rest of the samples–thus the formed structure is different, what is also reflected in the XRD pattern (Fig. 2).

To summarize, it can be said that by small amount of added co-monomer it is possible to strongly influence structure-adsorption characteristics of the final samples. Thus, alkyl groups introduced by co-condensation can be used as a temporary structure-forming agent and after tailoring the desired properties can be removed, for example by calcination.

| sample | Initial molar ratio of monomers, [mmol] | alkyl chain | surface area S_{BET}, [m²/g] | pore volume V_p, [cm³] | average pore size d, [nm] |
|--------|--------------------------------------|------------|----------------------------|------------------------|--------------------------|
| A1     | TEOS 20                              | ---        | 785                       | 1.32                   | 6.7                      |
| A2     | TEOS:HTES 19 : 1                     | C_6H_{13}  | 828                       | 0.65                   | 4.6                      |
| A3     | TEOS:DTES 19 : 1                     | C_{12}H_{25}| 498                       | 0.78                   | 5.7                      |
| A4     | TEOS:OTES 19 : 1                     | C_{18}H_{37}| 514                       | 0.89                   | 6.9                      |
3.3. FTIR spectroscopy

FT-IR/PAS spectra of samples A1-A4 are shown in Fig. 4. A characteristic property of spectra of all materials is the presence of the most intensive and wide absorption band in the region of 1000-1150 cm\(^{-1}\) which has a high-frequency shoulder at 1150-1250 cm\(^{-1}\). The occurrence of this absorption band is definitely attributed to stretching modes of the siloxane framework, \(\nu^{\text{as}}(\equiv\text{Si-O-Si})\). Bands located at \(~450\) cm\(^{-1}\) and \(~800\) cm\(^{-1}\) can be assigned to bending modes of siloxane fragments, \(\delta(\equiv\text{Si-O-Si})\) and out-of-plane bending modes of OH as well as O–Si–OH fragments, respectively [8, 9]. The presence of the -CH\(_2\)- link in the alkyl chain of the monomers (HTES, DTES, OTES) and in the poly(oxyethylene) and poly(oxypropylene) blocks of the template (Pluronic P123) is confirmed by a group of absorption bands in the region of 2860-3030 cm\(^{-1}\), what can be attributed to stretching modes of CH\(_2\) groups, \(\nu^{\text{as}}(\text{CH}_2)\), and possibly CH\(_3\) groups, \(\nu^{\text{as}}(\text{CH}_3)\) (fragments of residual ethoxy groups). It is also confirmed by bands in the region of \(~1410\) cm\(^{-1}\), which can be assigned to bending modes of the CH\(_2\) group, \(\delta(\text{CH}_2)\). It should be noted here that these vibrations come not only from the alkyl chains but also from unextracted template which is present in the final samples (\(~3-5\%)\).

Fig. 4. FTIR spectra of the samples A1-A4

In spectra of all samples a wide band down to 3000 cm\(^{-1}\) is observed with the maximum close to 3450 cm\(^{-1}\). This band arises from the stretching mode, \(\nu(\text{OH})\), of the physically adsorbed water. Low-intensity absorption band at \(~1635\) cm\(^{-1}\) in the IR spectra of all samples corresponds to bending vibrations of water, \(\delta(\text{H}_2\text{O})\).

3.4. Thermogravimetry

The introduction of organic groups into mesostructure was monitored by thermogravimetry. TG patterns of the samples A1-A4 and the corresponding differential TG (DTG) patterns are displayed in Fig. 5. In the range of the temperatures from 30 to 150°C thermodesorption of physisorbed water and ethanol takes place. Two separate peaks on the DTG profiles of all the samples suggest that above-mentioned desorption process takes place in two different types of pores.

Fig. 5. TG profiles of the samples A1-A4 (left panel) and the corresponding DTG profiles (right panel)

In the case of the well-ordered samples A1 and A4 (see Fig. 2.) the separation of DTG peaks is sharper in comparison to the samples A2 and A3 and indirectly testifies to the presence of two types of
pores: primary mesopores and interconnecting micropores and smaller mesopores in the final structures A1 and A4 (see Fig. 1.). Thus, thermodesorptio of water and ethanol takes place first from the mesopores, and after from the micropores. In the range from 180 to 500°C template removal and decomposition of incorporated organic groups take place. These two processes usually occur simultaneously, however, in the case of the sample A4 with octadecyl chains incorporated in the mesopores, two well separated peaks can be seen on corresponding DTG profile. The region above 500°C reflects the condensation of silanol groups and decomposition of some residual organic groups.

Assuming that the same amount of the unextracted template is present in all samples (~3-5%, as in the pure-silica sample A1) it is possible to estimate the amount of introduced organic functionalities present in the final samples. The amounts of hexyl, dodecyl and octadecyl groups represent around 65-90% of the values estimated on the basis of the initial molar composition of synthesis mixture, indicating quite a good incorporation efficiency.

4. Conclusions

Mesoporous organosilicas functionalized with hexyl, dodecyl and octadecyl groups were synthesized by co-condensation of appropriate monomers. Majority of initially introduced groups was successfully introduced into the mesostructure and is present in final samples as indicated by FTIR spectroscopy and thermogravimetry. The type of co-monomer added during the synthesis to introduce alkyl groups has a tremendous impact on the ordering of the final structure and all structure-adsorption characteristics such as specific surface area, pore volume, pore sizes and pore size distribution. This creates a possibility of tailoring the final properties of mesoporous silica materials only by varying of the type of the monomers used in the synthesis.

References
[1] E. B. Celer, M. Jaroniec, J. Am. Chem. Soc. 128, 14408-14414 (2006)
[2] C. T. Kresge et al., Nature 359(6397), 710-712 (1992).
J. S. Beck et al., J. Am. Chem. Soc. 114(27), 10834-10843 (1992).
[3] Yu et al. in: “Nanoporous Materials: Science and Engineering” edited by G. Q. Lu and X. S. Zhao (Imperial College Press, London, 2004), pp. 14-48.
[4] D. Y. Zhao et al., Science 279(5350), 548-552 (1998).
D. Y. Zhao et al., J. Am. Chem. Soc. 1209(24), 6024-6036 (1998).
C. G. Goltner et al., Angew. Chem. Int. Ed. 37(5), 613-616 (1998).
[5] R. Ryoo et al., J. Phys. Chem. B 104(48), 11465-11471 (2000).
[6] F. Zhang et al., J. Phys. Chem. B 109(18) 8723-8732 (2005).
[7] R. M. Grudzien, B. E. Grabicka, M. Jaroniec, Adsorption 12(5-6), 293-308 (2006).
[8] Kruk, M., T. Asefa, N. Coombs, M. Jaroniec, A.G. Ozin, J. Mater. Chem. 12, 3452 (2002)
[9] Wang, X., K.S.K. Lin, J.C.C. Chan, and S. Cheng, J. Phys. B, 109, 1763 (2005)
Kao, H.M., J.-D. Wu, Ch.-Ch. Cheng, A.S.T. Chiang, Micropor. Mesopor. Mater., 88, 319 (2006)
Wei, Q., et al., Materials Letters 61, 1469–1473 (2007)
[10] Yang, Ch.-M., Y. Wang, B. Zibrowius, F. Schuth, Phys. Chem. Chem. Phys., 6, 2461 (2004)
Fiorilli, S., B. Ondia, B. Bonelli, and E. Garrone, J. Phys. Chem.B, 109, 16725 (2005)
[11] Hodgkins, R.P., A.E. Garcia-Bennett, P.A. Wright, Micropor. Mesopor. Mater. 79, 241-252 (2005)
Wang, X., K.S.K. Lin, J.C.C. Chan, and S. Cheng, J. Phys. B, 109, 1763 (2005)
[12] Zhang F., Y. Yan, H. Yang, Y. Meng, Ch. Yu, B. Tu, D. Zhao, J. Phys. Chem. B 109, 8273 (2005)
Maria Chong A. S., X. S. Zhao, J. Phys. Chem. B 107, 12650-12657 (2003)
[13] Brunauer, J. S., P. H. Emmet, E. Teller, J. Am. Chem. Soc. 60, 309 (1938)
[14] Barrett, E. P., L. G. Joyner, P. Halenda, J. Am. Chem. Soc. 73, 373 (1951)