Organosilica Mesoporous Materials with Double Functionality: Amino Groups and β-Cyclodextrin Synthesis and Properties

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Abstract Our work concerns the preparation of new organofunctional mesoporous silica gels. The goal of this study is to combine in a unique material –on one hand β-cyclodextrin (β-CD), able to form stable inclusion complexes with many organic molecules, – and on the other hand aminogroups (from aminopropylsilane precursor) which are likely to chelate metallic cations. At the same time the formation of a mesoporous silica network would improve and regulate the access to functional sites. In order to tailor the functionalities content of our materials, a preparation in two steps has been chosen. First, a new silica precursor (β-CDAPS) has been synthesized from a β-CD derivative and (3-aminopropyl) trimethoxysilane (APS). A detailed characterization of the obtained product has helped to determine the structure of β-CDAPS repeating unit and quantify its functionality. Then this hybrid precursor has been co-condensed with tetraethylorthosilicate (TEOS) via a sol-gel process involving the use of surfactants by a S−I+ mechanism. Porous and chemical structures of a series of these functional mesoporous silicas were characterized. Finally, preliminary adsorption tests of aqueous model pollutants, carried out on these hybrid materials, have been discussed.

1 Introduction

Templated mesoporous silica materials have been discovered by Kresge et al. in 1992 [1, 2]. Since then, efforts have been made to produce by direct co-condensation synthesis hybrid materials functionalized by different types of reactive groups,

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including amino groups [3–8] and cyclodextrin moieties [9–15]. However, mesoporous materials then obtained are functionalized by only one kind of functional group. Our purpose is to prepare by the direct co-condensation method new hybrid materials functionalized by both amino groups and β-cyclodextrin moieties. Such materials do not exist in the literature and would be useful for decontamination of mixed polluted effluents, where metallic and organic pollutants occur simultaneously. On the one hand, cyclodextrins (CDs) are cyclic oligosaccharides with a torus shape and are able to form stable inclusion complexes with many organic molecules. On the other hand, amino groups are likely to chelate metallic cations.

A preparation in two steps has been chosen: first a new hybrid silica precursor β-CDAPS, containing β-CD groups and amine functions, has been prepared and characterized. Then, this precursor has been co-condensed with tetraethyl orthosilicate (TEOS) via a sol-gel process involving the use of surfactant. We chose the anionic surfactant sodium dodecylsulfate (SDS). The chemical and structural characterization combined with adsorption tests of *p*-nitrophenol and lead nitrate led to the evaluation of the accessibility and the effectiveness of the binding functions in these hybrid materials.

2 Experimental Section

2.1 Materials and Methods

β-cyclodextrin (β-CD) was supplied by Roquette Frères (France). (3-aminopropyl) trimethoxysilane (97%) (APS), tetraethyl orthosilicate (99.999%) (TEOS) and N,N-dimethylacetamide (99%) (DMAc) were purchased from Aldrich and used without further purification. Sodium dodecylsulfate (>97%) (SDS) was obtained from Fluka. Para-nitrophenol (99%) (p-NP) was supplied by Acros Organics and lead(II) nitrate (99.99%) by Sigma.

ThermoGravimetric Analysis (TGA) was performed on TGAQ50 (TA Instruments) under air up to 800°C. FTIR spectra were obtained on a Spectrum One from Perkin Elmer Instruments. Elemental Analysis was performed by Service Central d'Analyse from CNRS located at Vernaison (France). Conductimetry back-titration of amine functions (after contact with HCL 0.1 N in excess) was performed using a Tacussel conductimetry probe by a 0.1 M NaOH solution. Porosimetry measurements were performed on a SORPTOMATIC 1990 from CE Instruments: specific surface areas were calculated using BET model between $P/P_0 = 0$ and $P/P_0 = 0.4$ and pore size repartitions were determined using BJH model. SEM photos were obtained on an Ultra 55 (Zeiss).

Adsorption capacities were studied -by Atomic Emission Spectroscopy (Vista-Pro ICP-OES from VARIAN) for lead analysis and -by UV Spectrometry (Nicolet Evolution 300 from ThermoElectron Corporation) for *p*-nitrophenol determination.

2.2 Synthesis of Hybrid Precursor β-CDAPS Containing Amino Groups and β-CD Moieties

First, Tosyl- -cyclodextrin (β-CDOTs) was synthesized according to reference [16]. RMN ^{1}H spectroscopy and Elemental analysis revealed that 91% molar of monotosyl-βCD and 9% molar of ditosyl-βCD were obtained. β-CDOTs contained about 6% w/w of water, determined by the Karl Fischer method.

Then, in a tricol, heated at 303 K under nitrogen, 5 g (0.004 mole) of β-CDOTs were dissolved in 125 mL of DMAc (kept previously on molecular sieves) until the solution cleared. 7 mL (0.04 mole) of (3-aminopropyl)trimethoxysilane (APS) were added dropwise. The solution was vigorously stirred for 1 hour and then precipitated in 1.4 L of acetone (distilled twice, on molecular sieves). The white precipitate was kept under stirring for 2 hours and filtered. The product obtained (β-CDAPS) was dried 2 days at 353 K under vacuum and crushed to form homogeneous yellow powder. The reaction scheme expected is presented on Fig. 1. Si, N, C, N, H contents were determined by TGA, amine titration and elemental analysis.

2.3 Synthesis of Hybrid Silica Materials Using an Anionic Surfactant

The synthesis was adapted from reference **[6]**. Sodium dodecylsulfate (SDS) was dissolved in water-ethanol (molar ratio 9:1) with a homogenizer (Ultra-Turrax T25) at 293 K. Then the precursor β-CDAPS (dispersed in a water-ethanol mixture) and tetraethyl orthosilicate (TEOS) were added in varying proportions. The resulting mixture was stirred 1 h at 293 K and kept statically for 2 days at 373 K. The precipitate obtained was filtered. Surfactant elimination was performed using Soxhlet extraction over ethanol and water (2×400 ml for each solvent) and for 2 days each. The obtained product was dried under vacuum at 333 K for 1 day. The initial molar

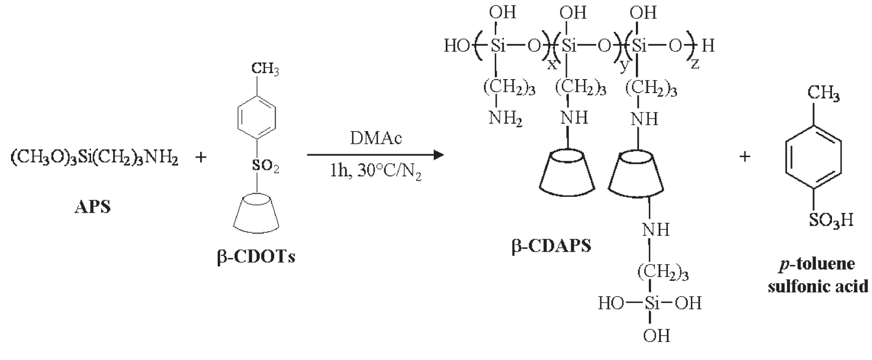

Fig. 1 Synthesis scheme of β-CDAPS

composition was 0.5 TEOS: x β-CDAPS: 0.1 SDS: 180 H_2O: 20 EtOH where x is equal to 0.5, 0.25 or 0.1. The obtained hybrid silica materials were designated TbSn, where n = 1, 2 and 3 corresponds to x = 0.5, 0.25 and 0.1 respectively.

2.4 Synthesis of Hybrid Silica Materials Without Surfactant

The synthesis was the same as the one presented above but without the use of surfactant. TEOS was added to a β-CDAPS solution (in a water-ethanol mixture with molar ratio 9:1) in varying proportions. The resulting mixture was stirred 1h at ambient temperature and then kept statically for 2 days at 373 K. The precipitate obtained was filtered and the powder dried under vacuum at 333 K. The initial molar composition was 0.5 TEOS: x β-CDAPS: 180 H_2O: 20 EtOH where x is equal to 0.5, 0.25 or 0.1. The obtained hybrid silica materials were designated Tbn, where n = 1, 2 and 3 corresponds to x = 0.5, 0.25 and 0.1 respectively.

2.5 Adsorption Tests

Batch tests in aqueous solutions at pH 5 were performed on hybrid silica particles. For Pb^{2+}, 30 mg of support were added to 10mL of an aqueous solution of $Pb(NO_3)_2$ at 100 ppm and stirred for 20 h. For p-NP, 20 mg of support were added to 10 mL of an aqueous solution of p-NP at 20 ppm and stirred for 4 h. Then the solutions were filtered and the supernatants were titrated.

3 Results and Discussion

3.1 Characterization of β-CDAPS Precursor

Native -cyclodextrin is not reactive enough to be condensed directly with APS, so a modified cyclodextrin is needed. Monotosyl-β-cyclodextrin is the most used to prepare mono-functionalized cyclodextrins.

The soft experimental conditions in the synthesis of β-CDAPS were optimized using experimental design. The hybrid precursor β-CDAPS has been characterized in order to determine its structure. FTIR spectra show the presence of amino groups ($1564\,cm^{-1}$) on one hand and siloxane structure ($1100–1000\,cm^{-1}$) on the other hand, confirmed by TGA measurements. This TGA gave a Si ratio of 5.80 ± 0.04%., confirmed by elemental analysis. N content was determined by elemental analysis at 2.98 ± 0.02%, which corresponds to 2.13 ± 0.04 mmol/g of amine functions, also deduced from amine titration.

A quantitative estimation of the β-CDAPS structure was undertaken, taking into account the chemical elements determination (Si, N, C, H) and the presence of primary and secondary amine, cyclodextrin moieties, and Si-O-Si bonds revealed by FTIR spectra.

So a model, consisted of three types of units with x, y, z as molar ratios for each one, was assumed (Fig. 1): y is fixed at 1, z at 0.1 (considering the amount of ditosyl β-CD) and x can vary. From this model, we calculated theoretical values of Si, C, N, H contents for different values of x and compared it with experimental contents. Finally, the best accordance led to a structure of the hybrid precursor β-CDAPS, close to 2.3 aminopropyl groups (x=2,3 in Fig. 1) for 1 β-CD group.

3.2 Characterization of Hybrid Silica Materials

Hybrid silica materials were prepared *via* a sol-gel pathway at pH 9. The influence of anionic surfactant (SDS) was studied by comparing templated materials (TbSn series) with hybrid materials obtained without surfactant (Tbn series). Two mechanisms of mesostructure formation can be considered as represented on Fig. 2. The pka of aminopropyl chain is about 10.6: in the reaction mixture propylamines are partially protonated. Electrostatic interactions between dodecylsulfate anion and NH_3^+ and sodium cation neutralization may then occur, resulting in the condensation of the silica structure around surfactant micelles and aminopropyl groups at the surface of the pores. The other mechanism is SDS chains complexation by β-CD cavity, which would result in β-CD groups located at the surface of the pores and aminopropyl less accessible, due to steric hindrance caused by β-CD bulky groups. A complete characterization of the products and adsorption capacities will help understanding the formation mechanism of mesoporous hybrid silica.

TGA curves of TbSn and SDS are presented on Fig. 3. The lack of deflection in TGA curves of TbSn at 200°C proved the absence of SDS in thses materials (confirmed by elemental analysis which gives a S content lower than 0.3%).The appearances of TbSn thermograms show the formation of the crosslinked silica structure: indeed, the higher the initial TEOS content, the larger the shift and SiO_2

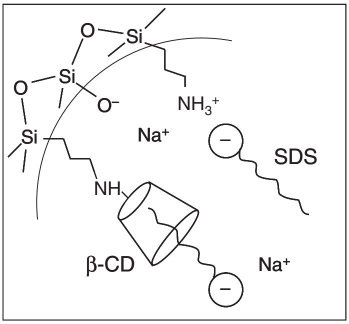

Fig. 2 Schematic representation of the two mechanisms of mesostructure formation expected: electrostatic interaction between SDS dodecylsulfate anion and protonated propylamine and SDS chain complexation by β-CD cavity

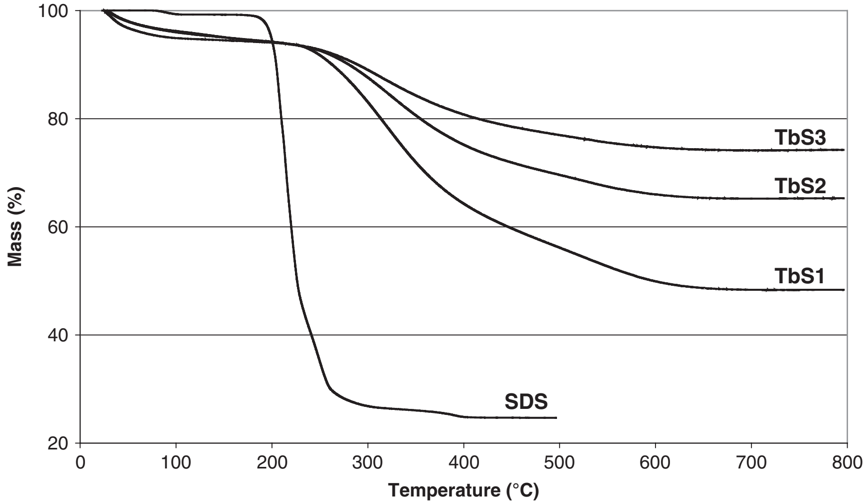

Fig. 3 TGA curves under air of SDS and TbSn materials

residue at 800°C in the TGA curve. Moreover, the anionic surfactant seems to allow a good incorporation of the hybrid precursor during the formation of the mesostructure and may play a role of compatibilizer between TEOS and β-CDAPS. The evolution of the quantity of β-CDAPS incorporated in the final product was as expected.

The presence of organic groups (attributed to β-CD moieties and amino groups) was shown from %C and %N determined by elemental analysis. These values for the different materials are gathered in Table 1.

The morphology of the hybrid silica materials was studied by SEM. Figure 4 shows photos obtained for samples TbS2 and Tb2. The structure of Tb2 is denser and is constituted of particles of 80 nm diameter whereas TbS2 presents a less compact texture with particles of 300 nm diameter.

Pore size distributions of TbSn samples are shown on Fig. 5. This series of hybrid materials present mesopores with a major family of pores with radius at about 2 nm. By comparison with radii of materials synthesized without surfactant (*Tbn, rp between 6 nm and 16 nm*) in Table 1, we proved the benefit of using SDS to obtain smaller pores with a narrower distribution.

3.3 Study of Adsorption Capacities

Results of adsorption capacities tests are gathered in Table 1. Samples prepared in the presence of SDS present good efficiency towards Pb^{2+} cations and *p*-nitrophenol. By comparing two samples with equivalent numbers of accessible amines (e.g TbS1 and Tb3), we can see that these samples adsorb the same quantities of Pb^{2+} cations.

Table 1 Proportions of total amino groups and β-CD (determined by elemental analysis), accessible amines (titration by conductimetry), specific surface areas, pore radii and adsorption capacities of lead cation and *p*-nitrophenol for the different samples

Initial molar composition				Physicochemical characterization					Adsorption results	
Sample	TEOS	β-CDAPS	SDS	S_{spe} (m^2/g)	r_p (nm)	Total amines (mmol/g)	Accessible amines (mmol/g)	β-CD (mmol/g)	Pb^{2+} (μmol/g)	p-NP (μmol/g)
Tb1	0.5	0.5	–	334	15 to 25	–	4.4	–	203	24
Tb2	0.5	0.25	–	179	6.4	3.1	3.3	0.35	102	10
Tb3	0.5	0.1	–	131	6.3	2.5	1.8	0.34	88	10
TbS1	0.5	0.5	0.1	257	2.0	3.3	1.8	0.63	87	61
TbS2	0.5	0.25	0.075	291	1.9	2.8	0.8	0.39	35	19
TbS3	0.5	0.1	0.06	217	1.9	2.0	0.7	0.21	26	10

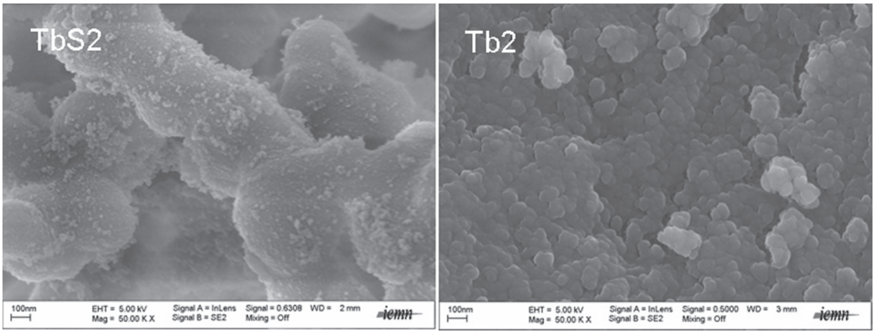

Fig. 4 SEM photos of hybrid materials prepared with SDS (TbS2) and without SDS (Tb2)

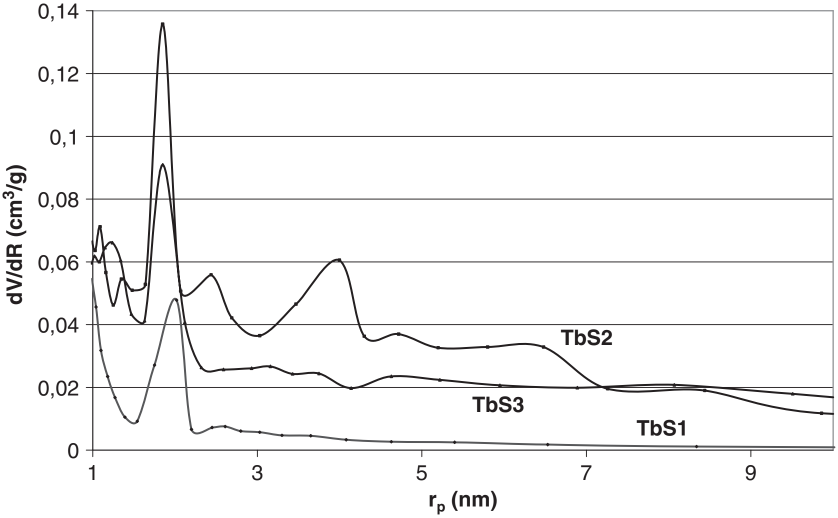

Fig. 5 Pore size distributions of hybrid materials prepared in presence of SDS (TbS1, TbS2 and TbS3)

On the other hand, the adsorption of *p*-nitrophenol is better for samples prepared in the presence of SDS. Indeed, for the same quantity of βCD, TbS2 is more efficient for p-NP adsorption than Tb2.

3.4 Determination of Anionic-Templated Formation Mechanism

In our synthesis conditions, the concentration of SDS during the preparation of sample TbS1 was lower than its Critical Micellar Concentration: this material will be excluded of the following discussion.

When the hybrid materials are synthesized in the presence of SDS, they possess lower pore sizes, due to the formation of SDS micelles. In these materials, a greater amount of β-CD groups has been incorporated (not necessarily all accessible) than in materials without template. However, the amount of accessible amino groups is lower and very similar for TbS2 and TbS3, although total amines are different. A plateau seems to be reached at around 0.8 mmol/g of accessible amino groups.

This may be explained as follows: the SDS interacts with the maximum of partially protonated aminopropyl groups, by electrostatic interactions between dodecylsulfate anion and NH_3^+ and sodium cation neutralization. The remaining amino groups are entrapped into the silica network. The amount of β-CD moieties incorporated depend on the initial molar ratio of β-CDAPS, and not of the presence or not of SDS. β-CD groups may not interact with SDS. We can say, that for these hybrid materials, the templated mechanism is a S^-I^+ one (S^- for anionic surfactant, I^+ for cationic aminosilica species).

4 Conclusion

Hybrid mesoporous materials have been prepared using the anionic-templating route by electrostatic interactions between SDS and aminopropyl groups. They possess accessible amino groups (up to 0.8 mmol/g) and β-CD moieties (up to 0.39 mmol/g). Preliminary adsorption tests showed that these materials are promising for environmental purposes.

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