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Novel porous organosilica containing amino and β-cyclodextrin groups

Stephanie Degoutin · Maryse Bacquet

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Abstract The elaboration of new hybrid mesoporous silica materials containing β-cyclodextrin groups and amine functions is reported. The synthesis is based on a direct co-condensation between β-CDAPS, a hybrid precursor obtained by reaction between tosyl-β-cyclodextrin and aminopropyltrimethoxysilane previously described, and tetraethyl orthosilicate via a sol–gel pathway templated by three different surfactants: anionic (sodium dodecylsulfate), cationic (cetyltrimethylammonium bromide) or neutral (Triton X-45) ones. The chemical structure and morphology are characterized and analyzed for all the series. Finally, the templating based mechanisms are investigated by comparing these samples with series prepared without template or without cyclodextrin.

Keywords Organosilica · Porous materials · β-cyclodextrin · Templating mechanisms

1 Introduction

Since years, the grafting of organic species onto silica has been studied. The first interest is due to the accessibility of functional groups that could lead to several potential applications such as decontamination [1–4], sorption and release of bioactive molecules [5–7], analytical [8, 9] and optical applications [10]. Since the discovery of mesoporous silicas by Kresge et al. [11], methods using surfactants to control porosity have caused a growing interest [12–14]. A wide variety of surfactants has been studied: cationic [11], anionic [15, 16], neutral [17].

The preparation of functionalized mesoporous materials can be achieved by two different ways: the post-synthesis grafting on mesoporous silica or the one-pot synthesis by co-condensation between a trialkoxyorganosilane and a tetraalkoxysilane. For example, several groups published results on the grafting of cyclodextrins [18–22] or amino groups [23] onto silica materials.

Our work concerns the elaboration by direct synthesis using sol–gel process of new hybrid bifunctional mesoporous materials templated by surfactants. Such materials would be useful for sorption and release of mixture of molecules with high selectivity. The chosen functions are amino groups and β-Cyclodextrin (β-CD). β-CDs are cyclic oligosaccharides composed of 7 glucopyranose units resulting in a torus shape, where the cavity is hydrophobic inside and hydrophilic outside. This cavity allows inclusion interactions with a wide range of guest molecules, especially small aromatic molecules. Different surfactants have to be tested in order to find the optimal incorporation and surface distribution of both reactive functions and porosity.

Several research groups have studied amino or cyclodextrin mesoporous silica. The preparation of cyclodextrin-functionalized mesoporous silica by direct synthesis has been studied by Mercier et al. [24, 25]. and Liu et al. [26–28]. Mercier et al. prepared CD-HMS materials from multifunctional-β-CD (monochlorotriazinyl-β-CD) in presence of dodecylamine and incorporated up to 0.39 mmol/g of β-CD. The materials were constituted of particles with mesopores (diameter ∼4 nm) and macrovoids. They investigated adsorption capacities of CD-HMS materials on aromatic molecules [24] and pesticides [25] and proved the

S. Degoutin · M. Bacquet
Université Lille Nord de France, 59000 Lille, France

S. Degoutin (✉) · M. Bacquet
Unité des Matériaux et Transformations (UMET), CNRS-UMR 8207, Université Lille 1, Bât C6, 59655 Villeneuve d'Ascq Cedex, France
e-mail: stephanie.degoutin@univ-lille1.fr

accessibility of the majority of the binding sites. More recently, Liu et al. reported the synthesis of β-CD-based mesoporous silicas without surfactant [26], with a cationic surfactant [27] and a block copolymer [28]. They prepared first a silane-β-CD derivative and co-condensed it with tetraethyl orthosilicate. A uniform mesoporosity was achieved.

The formation of amino-functionalized templated mesoporous silicas has been analyzed by Tatsumi et al. [2]. They tested two surfactants: anionic (sodium dodecylsulfate) and cationic (cetyltrimethylammonium bromide) ones. The influence of the pH of the mother gel on the morphology of the resulting materials was investigated. The obtained mesoporous silica materials exhibit high specific areas with a uniform pore distribution. To the best of our knowledge, the preparation of mesoporous silicas with both cyclodextrins and free amine functions in the same material has not been published yet.

We now wish to report our results about the synthesis of mesoporous hybrid silicas templated by three types of surfactants, expected to interact differently with the organic functions: β-cyclodextrin and amino groups. In order to control the quantity of reactive functions brought into the reaction mixture, we prepared first a hybrid precursor from condensation between monosubstituted β-cyclodextrin and (3-aminopropyl)trimethoxysilane that is described in a previous paper [29]. Then this hybrid precursor, called β-CDAPS, was co-condensed with tetraethyl orthosilicate in presence of surfactant via a sol–gel process. The proportions of functional sites (amine functions and CD groups) were determined as well as the morphology and the porosity of our materials. By comparison with hybrid materials obtained without surfactant or without cyclodextrins, templating mechanisms will be discussed and suggested for each surfactant.

2 Experimental

2.1 Chemicals

β-cyclodextrin (β-CD) was supplied by Roquette Frères (France). (3-aminopropyl)trimethoxysilane (97 %) (APS), tetraethyl orthosilicate (99.999 %) (TEOS) and cetyltrimethylammonium bromide (CTAB) were purchased from Aldrich and used without further purification. Sodium dodecylsulfate (>97 %) (SDS) and Triton X-45 (4-(1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol) were obtained from Fluka.

2.2 Synthesis of hybrid silica materials

The synthesis was adapted from literature [2]. The surfactant was dissolved or dispersed in water–ethanol (molar ratio 9:1) with a homogenizer, 6,500 rpm (Ultra-Turrax, IKA) at 303 K. Then silane precursors [TEOS (T), β-CDAPS (b), APS (A)] dispersed in a water–ethanol mixture were added in varying proportions. For each sample the molar proportion of surfactant was chosen equal to 10 % of molar proportion of the precursors. The mother gel molar composition was 0.5 TEOS: x β-CDAPS: (0.5 + x)/10 surfactant: 180 H_2O: 20 EtOH. The resulting mixture was stirred 1 h at room temperature and kept statically for 2 days at 373 K. The precipitate obtained was filtered without any washing. Surfactant elimination was performed using Soxhlet extraction over ethanol and water for 2 days each. The obtained product was dried under vacuum at 333 K for 1 day. For each surfactant, samples with two different molar proportions of β-CDAPS were prepared. The hybrid silica materials were designated TbSX (S = SDS), TbCX (C = CTAB), TbTX (T = Triton X-45) or TA(surfactant's first letter), where X = 1 and 2 corresponds to x = 0.25 and 0.1 respectively. Another series of materials has been synthesized in the same conditions, but without surfactant (samples designated Tb1, Tb2 and TA). Molar compositions of initial batches of all the samples are gathered in Table 1.

2.3 Characterizations

ThermoGravimetric Analyses were performed on TGAQ50 (TA Instruments) under air up to 800 °C. FTIR spectra of sample KBr pellets 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 titration of the amine functions in organosilica particles was performed by back-titration of unreacted HCl. Typically, 100 mg of sample were immersed under stirring at room temperature in a

Table 1 Batch molar compositions of hybrid samples in H_2O:EtOH 180:20, where T = TEOS, b = β-CDAPS, A = APS, S = SDS, C = CTAB and T = Triton X-45

Sample	TbS1	TbS2	TbC1	TbC2	TbT1	TbT2	Tb1	Tb2	TAS	TAC	TAT	TA
TEOS	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
β-CDAPS	0.25	0.1	0.25	0.1	0.25	0.1	0.25	0.1	–	–	–	–
APS	–	–	–	–	–	–	–	–	0.5	0.5	0.5	0.5
Surfactant	0.075	0.06	0.075	0.06	0.075	0.06	–	–	0.1	0.1	0.1	–

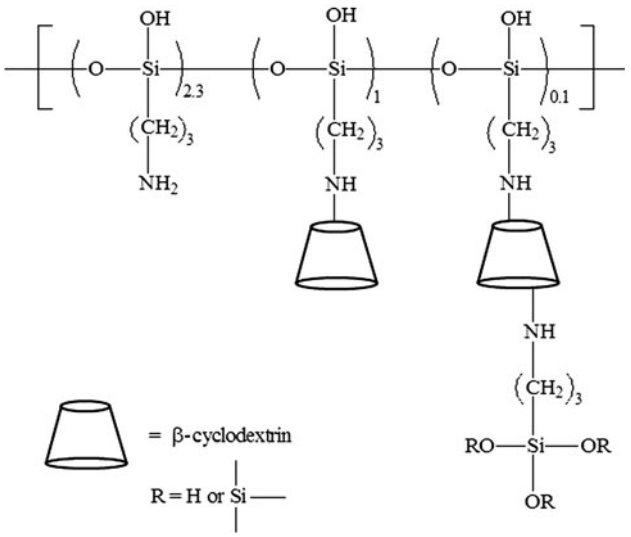

Fig. 1 Simplified representation of the composition of β-CDAPS

solution containing 20 mL of distilled water and 10 mL of HCl 0.1 N. Unreacted HCl was then titrated by NaOH 0.1 N. Porosimetry measurements were carried out on dried samples (333 K, 24 h under vacuum with a pressure of 10^{-6} mmHg) on a SORPTOMATIC 1990 from CE Instruments: specific surface areas were calculated using BET model and pore size repartitions were determined using BJH model. SEM photos were obtained on a Ultra 55 (Zeiss) microscope at the IEMN (UMR CNRS 8520, Lille, France). Solid-state NMR spectra were obtained on Brüker Advance at 100 MHz for CP-MAS ^{29}Si NMR and at 400 MHz for ^{13}C NMR.

3 Results and discussion

Hybrid silica materials were prepared via a sol–gel pathway from two silica precursors. The silica precursor β-CDAPS is a partially reticulated oligomer constituted of three randomly different units containing primary amino groups and free cyclodextrin cavities as depicted in Fig. 1. The average molecular weight of the repeating group composing β-CDAPS is found equal to 1,712 g mole^{-1}. This precursor was co-condensed with TEOS according to Fig. 2, in a water/ethanol medium at weak basic pH (induced by amino groups).

Surfactants are used in this pathway to induce formation of pores by interacting with silica precursors. In our precursors, two kinds of functional groups are present: amino groups and β-CD moieties. So we have chosen three surfactants that would induce different pore formation mechanisms: an anionic template (SDS), a cationic one (CTAB) with an alkyl chain relatively close to SDS, and a neutral surfactant (Triton X-45) which is a nonionic polyethylene oxide chain containing an aromatic part. In order to identify the mechanisms and study the interactions silica precursor/surfactant, we prepared hybrid materials without template or without β-CD.

Amino groups may be protonated given that the pH of the synthesis is about 9 and the pK_a of an aminopropyl chain is 10.6. Moreover, silanols may be found on their anionic form (the pK_a of silanols is around 7). Finally, several interactions have to be considered, as described in Fig. 3.

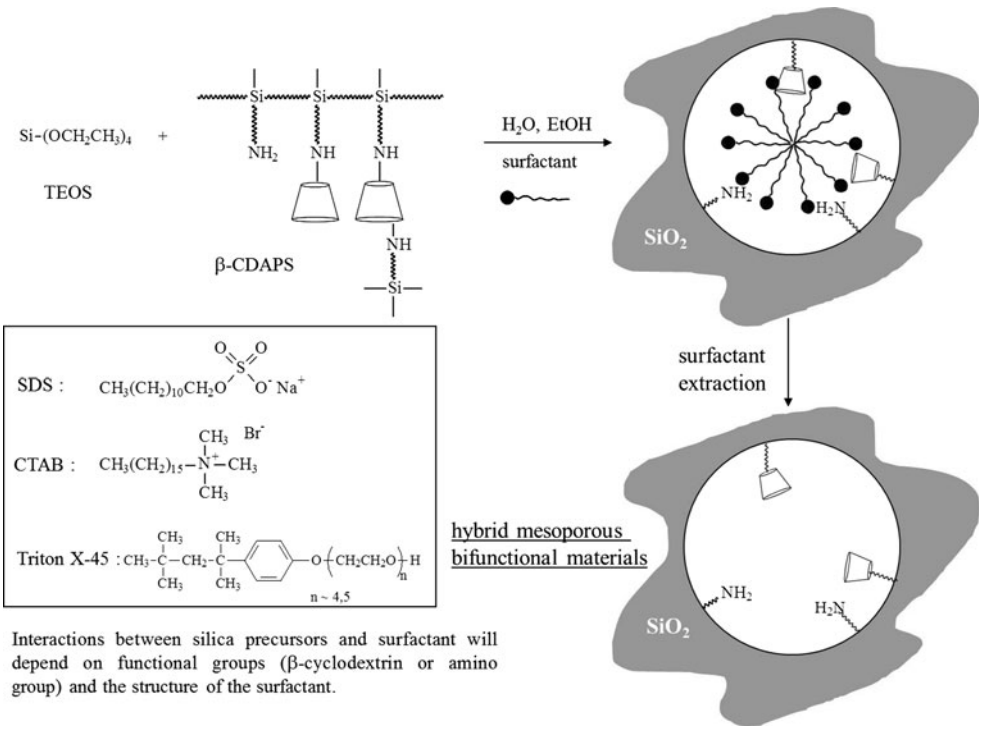

Fig. 2 Preparation of templated hybrid mesoporous bifunctional materials from TEOS and β-CDAPS

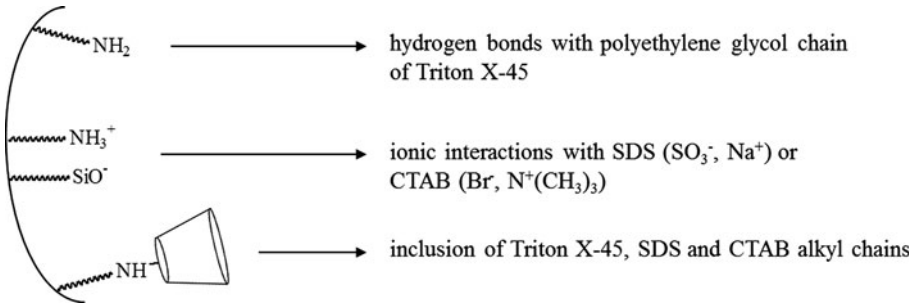

Fig. 3 Possible interactions between functional groups and surfactants

Table 2 Elemental composition, functional groups, specific area (A_{spe}) and pore radius (r_p) of hybrid materials and the hybrid precursor β-CDAPS (*r_p max as shown on Fig. 8b), sd = standard deviation

Sample	Elemental composition (%)			Functional groups (mmol/g)			Textural analyses	
sd	Si[a] ±0.1	C ±0.2	N ±0.1	Amine total[b] ±0.10	Amine[c] ±0.10	β-CD[d]	A_{spe} (m^2/g)	r_p* (nm)
TbS1	30.7	24.4	3.9	2.81	0.76	0.39	291	1.87
TbS2	35.5	13.3	2.8	1.99	0.70	0.21	217	1.90
TbC1	28.3	26.5	4.7	3.33	1.58	0.43	391	3.89
TbC2	27.2	20.7	3.1	2.21	1.61	0.33	260	2.38
TbT1	29.3	23.8	4.0	2.87	1.97	0.38	304	6.13
TbT2	23.3	24.5	3.4	2.42	0.56	0.39	210	3.63
Tb1	28.0	21.6	4.3	3.08	3.29	0.35	179	6.45
Tb2	28.8	20.9	3.5	2.52	1.78	0.34	131	6.26
TAS	35.5	12.4	4.2	2.99	1.69	–	75	Broad
TAC	34.3	15.5	5.7	4.10	3.89	–	151	Broad
TAT	33.4	15.3	5.4	3.80	3.89	–	67	14.44
TA	35.2	12.8	4.7	3.34	2.79	–	46	25.70
β-CDAPS	5.8	41.8	2.9	2.13	2.13	0.63	–	–

[a] Average value from TGA residue and elemental analysis

[b] From elemental analysis

[c] From titration ("accessible" amine)

[d] Estimation from %C/%N ratio from elemental analysis

3.1 Structure of hybrid silica materials

The chemical and structural data about all the materials synthesized are gathered in Table 2. In every hybrid silica material, the incorporation of precursor β-CDAPS is highlighted by the detection of carbon and nitrogen from amino groups. Moreover, in final materials carbon proportion is smaller and silicon content is greater than in the initial hybrid precursor, due to TEOS incorporation. %N in hybrid materials are also greater in hybrid materials than in β-CDAPS, which may be due to a partial hydrolysis of NH-β-CD bonds leading to a lower proportion of CD moities than expected. Therefore, the proportion of β-CD groups in hybrid materials is estimated by comparing the ratio %N/%C in the hybrid material and the same ratio in β-CDAPS, assuming that ethyl groups of TEOS are totally hydrolyzed during synthesis process.

Samples TA, TAS, TAC and TAT were prepared without β-CDAPS to investigate the interaction only between amino groups and the surfactant. As we can see on Table 2, in those materials the proportions of total amino groups and amino groups accessible by titration are very close, except for the sample TAS prepared using the anionic surfactant. The specific areas obtained are relatively low, compared to usual mesoporous silicas described in literature. Fig. 4 shows pore size distributions. For TA and TAS, distributions are broad (no templating mechanism). For TAT and TAC, pore distributions are less broad and suggest weak interactions with the template. The broad distributions may be explained by the large number of amino groups at the surface, increasing pore radius.

For the other samples prepared with β-CDAPS, characterizations with different techniques were undertaken in order to prove the presence of each function (amine and

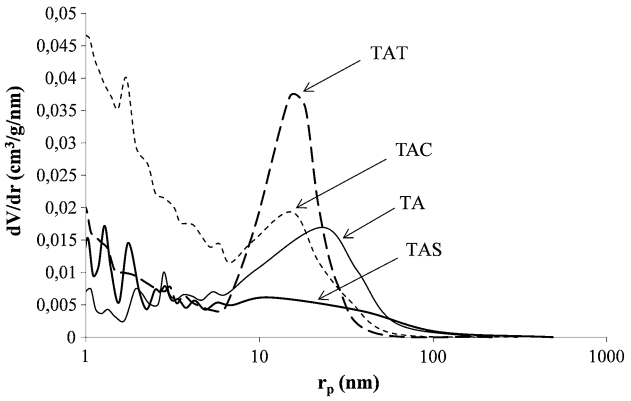

Fig. 4 Pore size distributions of hybrid samples without β-cyclodextrins

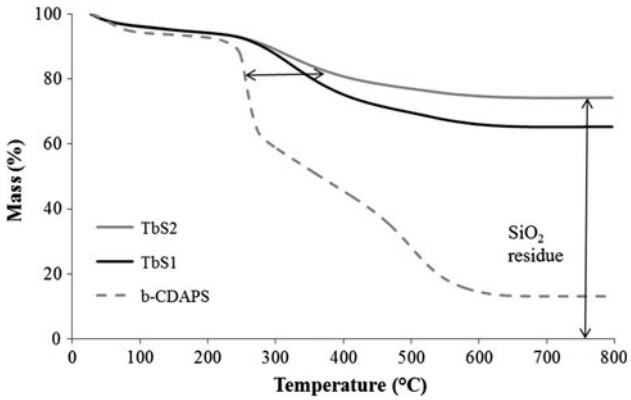

Fig. 5 TGA graphs of hybrid precursor β-CDAPS and TbSX

β-CD) and silica structure. The general aspect of TGA graphs (Fig. 5, example with SDS) highlights better thermal properties of the hybrid materials than the hybrid precursor due to silica network. The residue (based on SiO_2), obtained at high temperature, is characteristic of a silica network and allows the determination of silicium content in the materials given in Table 2. The organic–inorganic structure was also confirmed by solid state ^{29}Si and ^{13}C NMR. The overlay of NMR spectra of TAS (without β-CD) and TbS1 (with β-CD) is shown on Fig. 6.

On ^{13}C NMR spectra, both of them show peaks at 41, 20 and 9 ppm corresponding to CH_2 groups (aminopropyl chain) and a weak peak at 29 ppm, due to residual SDS. Elemental analysis of sulfur (not presented here) proved the elimination of at least 93 % of residual SDS. An additional peak at 71 ppm is detected in the hybrid sample TbS1, and may be allocated to non anomeric carbons from β-CD moities. The silica structure is confirmed by ^{29}Si NMR spectra. The linkages $CH_2Si(O)_3$ and $(SiO)_4$ are respectively detected around -60 ppm and [−90, −100 ppm].

By FTIR spectroscopy, the presence of both silica structure and organic parts are also confirmed. For example, series of materials obtained with CTAB, reported on Fig. 7, reveal CH bounds at 2,935 cm^{-1} (ν_{CH}, w) and 1,470–1,340 cm^{-1} (δ_{CH}, w). C–O-C bounds are detected at 945 cm^{-1} (w) and stacked with Si–O-Si bounds around 1,000 cm^{-1} (br, s). Primary amino groups at 1,555 cm^{-1} (δ_{NH2}, w) and N–H bounds at 684 cm^{-1} (δ_{NH}, w). δ_{NH2} band is stronger in TAC than in TbC2, due to a greater proportion of primary amino groups.

In addition to this chemical determination, the texture of our inorganic–organic materials has been studied by SEM and pore size distributions. Some juxtaposed results are gathered in Fig. 8. SEM photos (Fig. 8a) give information about the shape of the particles. We observed quasi-spherical particles (between 50 and 300 nm) more or less aggregated. Between these particles, voids are present at a macroscopic scale (200–500 nm) due to the extraction and drying steps of the process. The repartition of pore sizes less than 300 nm is given on Fig. 8b for the same samples. A narrow distribution and well defined pore radii in the mesopore range, between 1 and 10 nm, are observed. The r_{pmax} (Table 2) depends on the structure of the template, the smallest pore radius for SDS and the greatest one for Triton. Except for SDS templated materials, the r_p increases with β-CD content. Due to the bulky hybrid β-CDAPS precursor, no periodic organization of the pores is expected.

3.2 Structuring mechanisms for templated hybrid materials containing amino and β-CD groups

In this section we will discuss the results presented above, in order to suggest mechanisms leading to the formation of our hybrid mesoporous materials. We assume silanols are hindered by aminopropyl chains and cyclodextrins and may not interact with surfactant molecules.

3.2.1 Samples prepared in presence of SDS

In our synthesis conditions, SDS concentration was greater than its critical micellar concentration (CMC, 8.4 mM in pure water at 298 [30]). 10 % ethanol in water was used and played the role of co-surfactant (CMC superior than in pure water). Then, the surfactant should form micelles in solution and silanes would associate together around these micelles. Pore size obtained for these materials (1.9 nm) is slightly greater than micelle radius at CMC in pure water (around 1.4 nm [30]).

We can expect two main different interactions: electrostatic interactions between SO_3^- headgroups from SDS and NH_3^+ groups from aminopropyl chains ($S–I^+$ mechanism, S^-: anionic surfactant and I^+: protonated amino groups on inorganic species) or an inclusion of SDS alkyl chain into β-CD cavity. The influence of anionic surfactant (SDS) was studied by comparing templated materials (TbSX) with hybrid materials obtained without surfactant

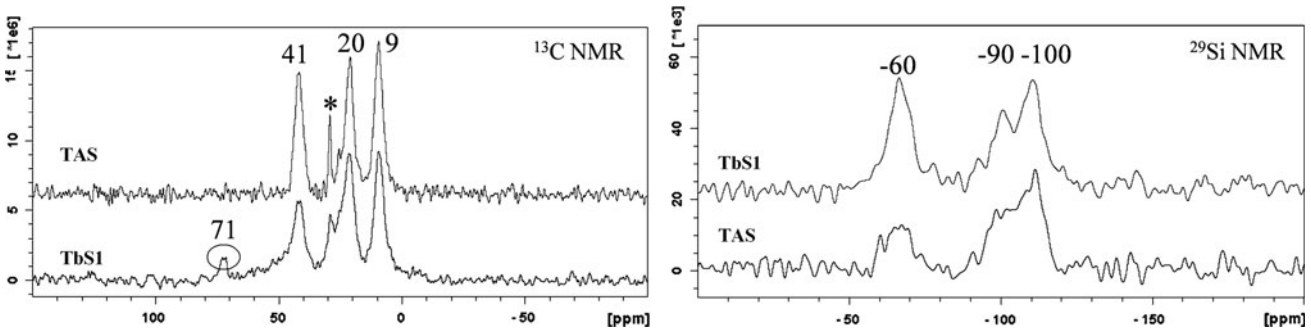

Fig. 6 Solid state CP-MAS ^{13}C and ^{29}Si NMR spectra of TAS and TbS1

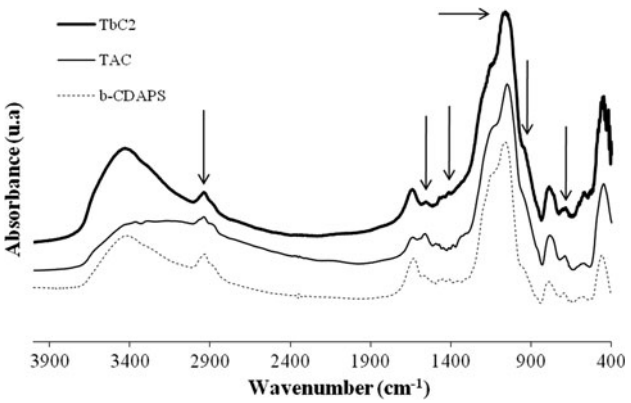

Fig. 7 FTIR spectra of TbC2, TAC and β-CDAPS

(TbX). Without the use of surfactant, accessible amine amount is similar to total amine one. With SDS, elemental composition depends on the proportion of β-CDAPS and SDS in the starting mixture. The anionic surfactant seems to allow a better incorporation of the hybrid precursor during the formation of the structure (%C is important and higher in TbSX). Unexpectedly, amine groups are more accessible when no surfactant is used. The quantity of amino groups interacting with the micelles is limited by the aggregation number of SDS, therefore the excess of amine may be trapped into silica network. Moreover, in all cases steric hindrance due to cyclodextrin moieties may also decrease the accessibility of amine groups.

Materials prepared without SDS present lower specific areas than those prepared with template. For TbSX materials, pore size of 1.9 nm is smaller than pore size obtained without β-CD (TAS). By comparing samples TbS1 and TbS2, it can be noted that pore sizes and accessible amino groups are very close, although total amino groups contents are different in those two materials. This difference may be explained by the number of amino groups (accessible) involved in electrostatic interactions with SDS. This number would be fixed by the number of SDS chains in the spherical micelle and then a limit of accessible amino groups has been reached. In each case the quantity of β-CDAPS is greater than the quantity of SDS in the initial mixture, so the excess of amino groups compared to SDS molecules should be entrapped into silica network. As regards β-CD, it is known to form stable inclusion complexes with SDS but given that the micellar system with the alkyl chain inside the micelle is formed before the addition of β-CDAPS, no interaction should be observed between β-CD and SDS in our samples as described in literature [31].

So the anionic mechanism presented in Fig. 9 seems to be the most appropriate in our case. This mechanism may be noted S–I^+, where S^- corresponds to the surfactant and I^+ to protonated aminopropyl group bounded to the inorganic structure. We assume silanols interact with sodium counter ion.

3.2.2 *Samples prepared in presence of CTAB*

As for SDS, in our synthesis conditions, CTAB concentration was greater than its critical micellar concentration (CMC, 0.9 mM [32]). The surfactant should then form micelles in solution and silane molecules would associate together around these micelles. Pore sizes obtained for these materials are also slightly greater than micelle radius at CMC (around 2–2.5 nm [33]).

With this cationic surfactant we can expect three different mechanisms: electrostatic interactions between $N^+(CH_3)_3$ of CTAB and SiO^-, electrostatic interactions between protonated aminopropyl groups and CTAB involving bromide counter ion or an inclusion of CTAB alkyl chain into β-CD cavity.

By comparing samples TbC1 and TbC2, we can see that those materials possess very close accessible amine contents whereas their total amine content is different. This fact may be explained by electrostatic interactions with Br^- as counter ion between CTAB head groups and protonated aminopropyl groups, leading to an almost constant number of accessible amino groups at the surface of the pores. The material obtained without β-CD (TAC on Fig. 4) presents a broad mesoporosity and all amino groups are accessible. In the literature, in opposition to SDS, it has

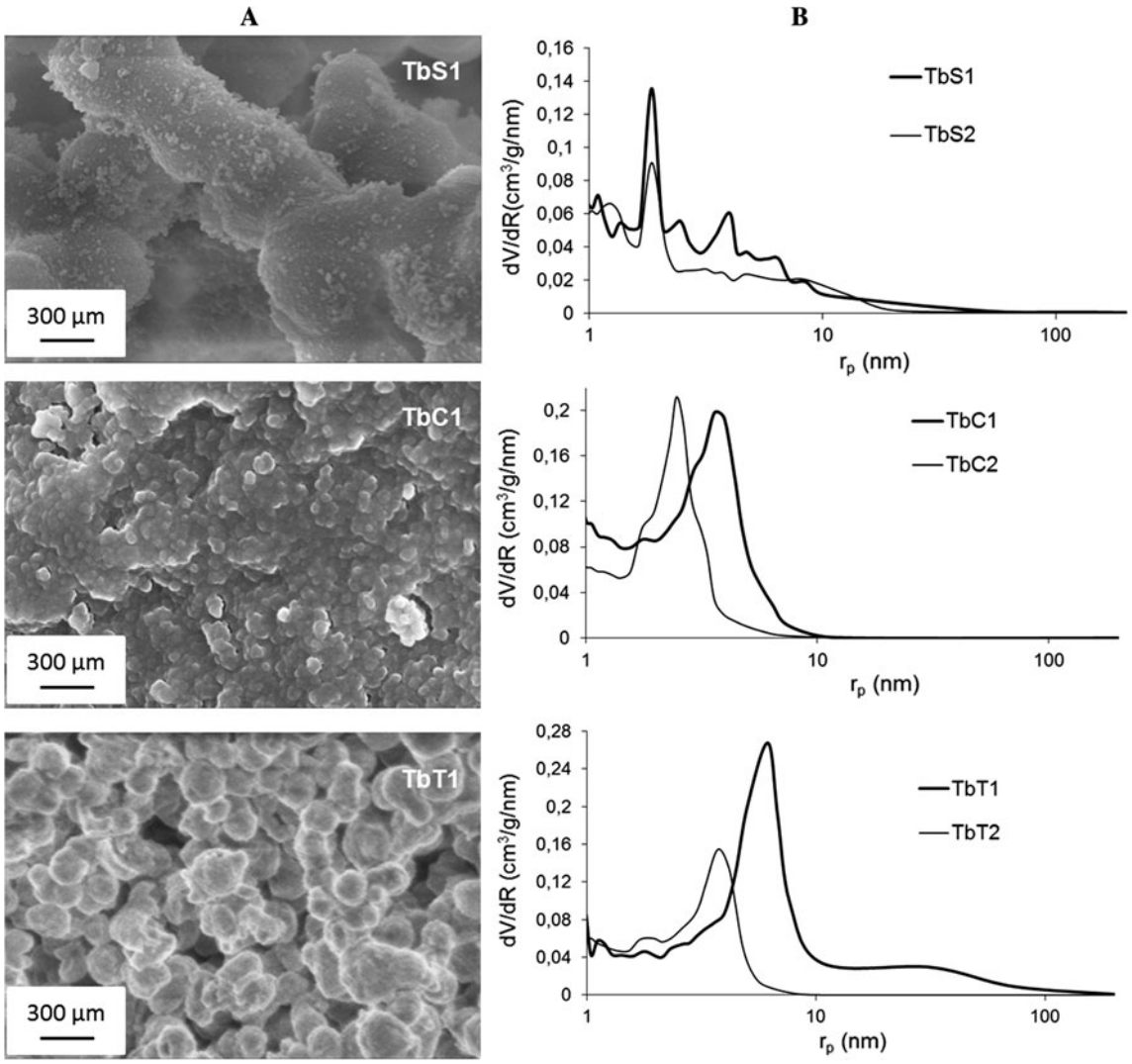

Fig. 8 Textural analysis of the three series of hybrid samples: SEM photos (**a**) and pore size distributions (**b**)

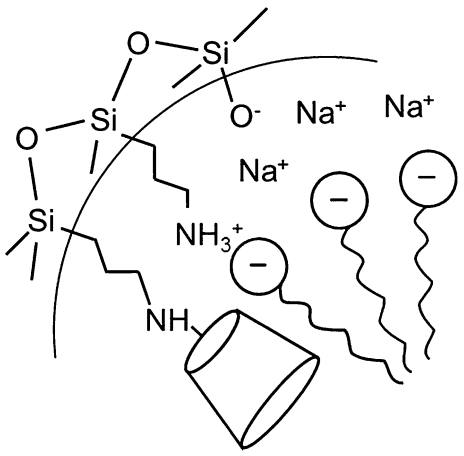

Fig. 9 Anionic formation mechanism $S–I^+$ of hybrid mesoporous materials suggested in presence of SDS

been demonstrated that β-CD disturbs micelles structure through the inclusion with CTAB micelles when the CTAB is in excess [34]. In our conditions, the proportion of β-CD is higher than the proportion of CTAB; so we can expect that the mechanism by inclusion should affect the micellar structure. Nevertheless, the pore distribution in presence of β-CD (TbCX on Fig. 8b) is narrower than without β-CD (TAC on Fig. 4). At the same time, accessible amino groups in TbCX are twice greater than in TbSX (Table 2). These observations suggest that the mechanism involving CTAB is more complicated than the one with SDS: electrostatic interactions between CTAB and protonated amino groups with Br^- as counter ion ($S^+X^-I^+$ mechanism) and an inclusion phenomenon of CTAB into β-CD cavity occur simultaneously (Fig. 10). This double mechanism leads to slightly greater pores, compared to SDS templated materials, and more accessible amine groups.

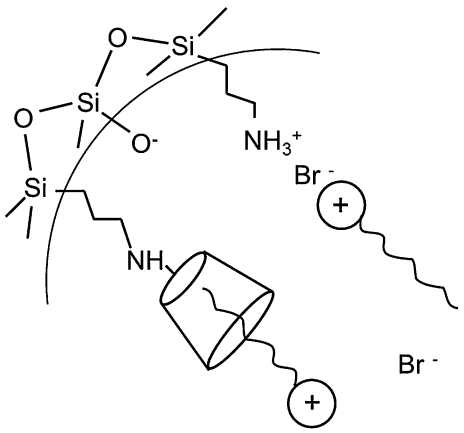

Fig. 10 Cationic formation mechanism $S^+X^-I^+$ and inclusion phenomenon of hybrid mesoporous materials suggested in presence of CTAB

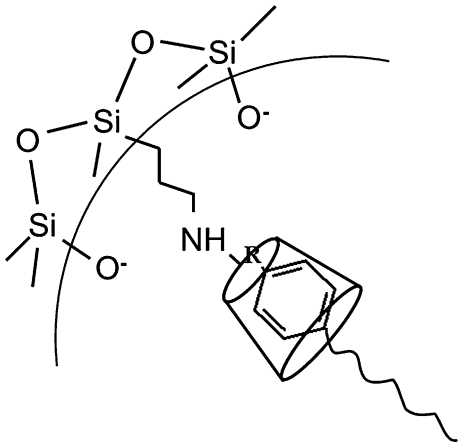

Fig. 11 Inclusion mechanism of Triton X-45 into β-CD cavity proposed for the formation of hybrid mesoporous materials

3.2.3 Samples prepared in presence of Triton X-45

As for SDS and CTAB, in our synthesis conditions, Triton X-45 concentration was greater than its critical micellar concentration (CMC given by supplier Dow, 0.13 mM), especially in a water/ethanol mixture. The surfactant should then form micelles in solution and silane molecules would associate together around these micelles. Two mechanisms can be considered: neutral interactions by hydrogen linkages between polyethylene oxide chains and aminopropyl groups (N^0I^0 mechanism) and an inclusion mechanism of Triton X-45 into β-CD cavity because of the strong affinity of the surfactant towards the hydrophobic cavity of cyclodextrin. It has been demonstrated in the literature that the phenyl part of Triton X-45 can be included into β-CD cavity by forming a 1:1 complex [29].

Triton X-45 plays a role as neutral template. Its presence induces a decrease of pore size, when we compare pore size obtained in TAT and TbTX series with TA (without template and β-CD). Moreover, samples TbT2 and TbT1 possess smaller pore size compared to TAT. Nevertheless, it is difficult to correlate β-CD and amine contents and the final structure. But we can notice that without β-CD in the hybrid material, all amino groups are accessible, whereas the presence of β-CD in the initial mixture leads to a lack of amino groups accessibility. This could be explained by the inclusion of Triton X-45 into β-CD cavity which modifies micellar organization.

As depicted on Fig. 11, we propose a predominant mechanism of inclusion of Triton X-45 into β-CD cavity.

4 Conclusions

Novel templated mesoporous organosilica containing both cyclodextrin and free amino groups were prepared and characterized. Three surfactants were chosen. Each of them has a different impact on the pore size and the repartition of the chemical groups. Except for the materials using SDS as anionic template, for which major mechanism is of electrostatic type, a more complex interaction mechanism, involving cyclodextrin also, is observed with cationic and non ionic surfactants. In the three cases, the use of the surfactant gives materials with smaller pores. Nevertheless, when the micelle mechanism is disturbed by β-CD, the greater are the pores. Besides, monitoring the chemical functionalities of these mesoporous organosilica is less obvious. In particular, β-CD amount in the final materials remains relatively low regardless of initial molar ratio of the β-CD precursor. Finally we have at one's disposal 3 series of mesoporous organosilicas with 3 pore sizes, depending on the type of surfactant.

So further investigations are actually undertaken, in our team, first to increase β-CD content in the precursor and second to determine the influence of functionalities contents and pore size on potential applications in decontamination or in release of molecules specifically adsorbed on these hybrid particles.

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