Synthesis of dithiocarbamate-functionalized mesoporous silica-based materials: interest of one-step grafting

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The classical approach to prepare dithiocarbamate-functionalized silica involves a two-step procedure based on the reaction of carbon disulfide with a pre-formed amine modified silica sample. A novel approach is proposed here, involving the direct grafting of silica surfaces with the aid of a siloxydithiocarbamate precursor. Functionalization has been applied to three silica samples (a non-ordered silica gel and two ordered mesoporous solids with distinct pore size) to evidence possible effects of mesostructural order and/or pore size of the materials. The performance of the one-step method has been compared to the two-step one and qualitatively discussed in terms of derivatization efficiency regarding the integrity of dithiocarbamate organo-functional groups. Thanks to complementary physico-chemical techniques (N_2 adsorption/desorption, solid-state NMR, XPS, XRD), the interest of direct grafting has been clearly demonstrated as it allows to access in one step dithiocarbamate-functionalized silicas free of residual amine groups. Moreover, the use of a base in the two-step procedure is likely to induce some degradation of the silica materials. The advantageous features of the direct grafting process were also discussed with respect to Hg(II) adsorption to these materials.

1. Introduction

Silica-based organic–inorganic mesoporous hybrid materials have been the focus of many studies over the last few years as they combine in a single solid the attractive characteristics of an inorganic porous framework (*i.e.* high specific surface area, great porosity, good mechanical stability) and the chemical reactivity of the organic moieties.[1–4] The judicious choice of the organo-functional group gives the unique opportunity to tune the properties of the final material with respect to the target application (catalysis,[5,6] separation sciences,[7–9] electrochemistry,[9–13] optics[14,15]...).

Preparation of functionalized silica *via* covalent attachment of organic moieties to the inorganic matrix can be achieved by two ways: (1) in one step by co-condensation of tetraalkoxysilane with one or several organoalkoxysilane precursors according to the sol–gel process,[1–4,16–19] or (2), by covalent grafting of an organoalkoxysilane reagent onto a preformed silica support (post-grafting).[4,5,19–21] Despite the large number of commercially available silylated compounds, the scope of functional groups that can be directly incorporated into the silica-based materials has still to be expanded. A mean of overcoming this restriction consists in using commonly available grafted silicas (bearing, *e.g.*, –Cl, –CN or $-NH_2$ groups[22–27]) as intermediates for further derivatization to get more sophisticated organic functions.

Such an indirect route is the only one reported to date to get dithiocarbamate-functionalized silicas.[28–31] These materials have been indeed prepared according to a two-step procedure involving (1) the access to an amino-modified silica (easily obtained by post-grafting or direct synthesis[25–27,32]) and (2) its subsequent reaction with carbon disulfide CS_2 in order to ensure conversion of the amine groups into dithiocarbamate moieties. Depending on the authors, this second step can be performed with or without adding a base in the medium. Already in the 1970s, Leyden *et al.* obtained a series of dithiocarbamate-functionalized silica gels by reaction of amino-silicas with CS_2 in the presence of tetramethylammonium hydroxide, which were then applied to preconcentration of metal ions.[28,29,33] Venkatesan *et al.* have applied a similar procedure using first non-ordered K60 silica gel and next extending this functionalization route to mesostructured materials *via* the reaction of CS_2 on aminopropyl-grafted MCM41 using sodium hydroxide.[34,35] In contrast, Mahmoud *et al.* did not employ any base when performing the same kind of reaction with silica gel grafted with linear mono- and poly-amines (bearing one to four amine groups), the materials being again applied to uptake of metal species.[30,36] Note that this classical two-step procedure has been also applied to many other solids such as resins,[37,38] starch derivatives,[39] polymer/organosmectite[40] composites or carbon nanoparticles.[41]

Despite their long-standing interest and widely uses, few works are devoted to rigorous characterization of the so-obtained

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materials[36] as they are often just briefly characterized (commonly by elemental analysis and/or spectroscopic techniques)[42] to check the presence of dithiocarbamate groups. Therefore, even if these techniques are likely to provide evidence for conversion of amine groups into dithiocarbamate moieties, no clear data have been reported dealing with the degree of functionalization. The only available information relies on dithiocarbamate resins prepared this way for which the obvious presence of unreacted amines (up to 75%) in the final solid upon reaction with carbon disulfide has been pointed out.[38,43] To our knowledge, nothing similar has been clearly described concerning silica and this might be of great importance to fill this gap given the poor stability of silica in alkaline medium.[44] The presence of residual amine groups in the final material could also be a factor restricting its reactivity, especially as amine-grafted silica has been proven to be poorly stable in aqueous medium.[45] Incomplete transformation of amine-grafted silica into its dithiocarbamate form can be affected by the conditions applied to perform the derivatization reaction (presence of base or not) or by a lack of accessibility for the CS_2 reactant to the amine groups located in the porous structure.

In a recent work, we reported a novel efficient synthesis of siloxydithiocarbamate derivatives likely to be used for direct grafting.[46] In the present study we have thus compared the effectiveness of the two functionalization processes: the direct grafting using the synthetic siloxydithiocarbamate reagent and the secondary derivatization approach involving the chemically-applied reaction of CS_2 over amine-grafted silica. Three silica samples have been used, an amorphous silica gel (K60) and two ordered mesoporous silicas (SBA15 and MCM41-type) exhibiting different pore sizes in order to investigate the effect of the materials characteristics on the properties of final materials. Several characterization techniques (nitrogen adsorption–desorption, infrared analysis, solid-state nuclear magnetic resonance, X-ray photoelectron spectroscopy, X-ray diffraction) have been used to evidence the differences between the two functionalization approaches and, in final, to point out the interest of the direct one. The reactivity of all materials towards Hg(II), chosen as a model analyte, has been also investigated to further compare the efficiency of the adsorbents.

2. Experimental

2.1 Chemicals, reagents and solutions

Analytical grade chemicals purchased from the following suppliers were used for solid sample preparation: tetraethoxysilane (TEOS, 98%, Aldrich), cetyltrimethylammonium bromide (CTAB, 98%, Fluka), Pluronic P123 (BASF), ammonia (14.6 mol dm^{-3}, Riedel-de Haën), ethanol (99.8%, Riedel-de Haën), chlorhydric acid (12.1 mol dm^{-3}, Riedel-de Haën).

Chemicals for functionalization of the silica samples were used without further purification: APTES (3-aminopropyltriethoxysilane, 99%, Aldrich), carbon disulfide (purum, Fluka), propan-2-ol (99.8%, Carlo Erba), tetraethylammonium hydroxide (Et_4NOH, 1.5 mol dm^{-3} in methanol, Sigma-Aldrich) and dry toluene (Prolabo).

For mercury(II) adsorption experiments, all the solutions were prepared with high-purity water (18 MΩ cm) obtained from a Millipore MilliQ water purification system. Mercury (II) solutions were obtained from its nitrate salt $Hg(NO_3)_2$ (min. 99%, Merck)—**CAUTION**, mercury is highly toxic!—and their concentration were checked using a Hg(II) certified standard solution (1000 mg dm^{-3} in 1.40 mol dm^{-3} nitric acid, TITRINORM, Prolabo). Buffer solutions were prepared from sodium acetate (99.5%, Riedel-de Haën) and pH was adjusted with nitric acid (14.4 mol dm^{-3}, Merck). The electrolyte medium used for the electrochemical detection of Hg(II) was prepared from NaCl (99%, Prolabo), ethylenediaminetetraacetate (EDTA, disodium form, 99%, Prolabo) and perchloric acid (9.14 mol dm^{-3}, Riedel-de Haën).

2.2 Silica samples

Three types of mesoporous silica have been used in this study: a commercially available silica gel (K60) and two synthetic ordered mesoporous silica samples with hexagonal mesostructures (MCM41 and SBA15).

Silica gel was the chromatographic grade Kieselgel 60 (K60), as purchased from Merck.

MCM41 was synthesized according to an adapted procedure from that reported by Schumacher *et al.*[47] 0.9 g of CTAB was slowly added to a mixture of 50 cm^3 of distilled water and 50 cm^3 of ethanol at room temperature under constant stirring for 1 min. After complete dissolution, 13.6 cm^3 of aqueous ammonia were quickly added to the solution, which was further stirred for 10 min (pH is about 11.5) before adding 3.64 cm^3 of TEOS and keeping stirring for 6 more hours at room temperature. The solution was then introduced in a round-bottom flask and left 24 h at 70 °C. The solid was recovered by filtration on Büchner, washed with distilled water and dried at 70 °C overnight. The template (CTAB) was removed by calcination, which was carried out by slowly increasing temperature from room temperature to 550 °C in 4 h and heating at 550 °C for 6 h.

The synthesis of SBA15 was adapted from the procedure reported by Zhao *et al.*[48] In a polypropylene flask, 4 g of the amphiphilic triblock copolymer Pluronic P123 were dissolved in 126.8 cm^3 of distilled water containing 1.6 mol dm^{-3} HCl. The mixture was then heated at 40 °C under vigorous stirring until complete dissolution of the surfactant P123. Afterwards, 9.1 cm^3 of TEOS were quickly added to the solution and the mixture was left to stir at 40 °C for 24 h. Agitation was stopped and the solution in a closed flask was left undisturbed in an oven at 100 °C for 24 h. The resulting white solid was filtered on Büchner, successively washed with distilled water and ethanol and dried in an oven at 90 °C overnight. The template was removed by calcination (slow linear increase in temperature in 4 h to 500 °C and heating at 500 °C for 6 h).

2.3. Functionalization of silica samples

K60, SBA15 and MCM41 silica samples have been functionalized with amine and dithiocarbamate moieties. Dithiocarbamation has been performed according to various procedures. Prior to functionalization, silica samples were dried at 130 °C overnight to remove adsorbed water molecules onto the material surface to avoid uncontrolled polycondensation of silylated derivatives.

2.3.1. Synthesis of amine- and dithiocarbamate-modified silicas: one-step functionalization. Direct grafting of amine and dithiocarbamate moieties onto the silica surface was performed in dry toluene under a nitrogen atmosphere using 3-aminopropyltriethoxysilane or *N*-[3-(triethoxysilyl)propyl]-carbamodithioic acid sodium salt, whose synthesis has been reported in one of our recent previous paper.[46] Typically, 1 g of silica was suspended in 50 cm^3 of dry toluene and stirred a few minutes at room temperature before slow addition of the silylated precursor. The suspension was then refluxed for 2 hours,[20] left to cool to room temperature and filtered. The resulting solid was washed several times with toluene and dried at 100 °C in an oven for 2 hours. The as-functionalized silica samples were then stored in a dessicator under vacuum. Amine- and dithiocarbamate-grafted silicas are, respectively, denoted "silica-NH_2" and "silica-dtc" hereafter ("silica" being either K60, MCM41 or SBA15).

2.3.2. Synthesis of dithiocarbamate-modified silicas: two-step procedure. For comparison purposes, dithiocarbamate-modified silicas were also prepared according to the two-step procedure reported in the literature, which consists in the reaction of CS_2 with aminopropyl-grafted silicas. Depending on the authors, this reaction is carried out with or without the use of a base added in the medium. These two routes have been followed in this work.

Synthesis without a base. 1 g of aminopropyl-silica was suspended in 50 cm^3 of dry toluene and CS_2 (3 mmol per gram of silica) was added. The reaction mixture was refluxed for 2 h. After cooling to room temperature, the suspension was filtered. The silica was rinsed with toluene and dried in an oven at 100 °C for 2 h. These samples are denoted "silica-NH_2+CS_2" (silica = K60, MCM41 or SBA15).

Synthesis in basic medium. 1 g of aminopropyl-silica was suspended in 50 cm^3 of toluene and 10 cm^3 of propan-2-ol. CS_2 (3 mmol per gram of silica) and Et_4NOH (3 mmol per gram of silica) were then added to the solution and the mixture was refluxed for 2 h, left to cool to room temperature, and filtered. The resulting solid was washed several times with propan-2-ol (to remove as much as possible residual Et_4NOH) and toluene before drying at 100 °C for 2 h. These samples are denoted "silica-NH_2+CS_2/OH" (silica = K60, MCM41 or SBA15).

2.4 Analytical procedures applied for Hg(II) sorption

Hg(II) uptake was investigated from batch experiments. An accurate amount of silica was quickly suspended in a 200 cm^3 of 0.10 mol dm^{-3} acetic buffer (pH 5) solution containing 1.0×10^{-4} mol dm^{-3} $Hg(NO_3)_2$, so that the Hg(II)-to-organic moieties ratio was adjusted to 1. The slurry was mechanically stirred using a shaking table at room temperature for 14 h (a time necessary to get steady-state, as checked by kinetic experiments). At this point, the solid particles were filtered off and the Hg(II) ion concentration remaining in solution was measured by anodic stripping differential pulse voltammetry on a rotating gold electrode,[49] using a μ-Autolab potentiostat associated to the GPES electrochemical analysis system (Eco Chimie). The amount of adsorbed Hg(II) on the solid phases was calculated by difference with respect to the Hg(II) starting concentration in solution.

The speed of Hg(II) binding to the adsorbents was characterized by analyzing the extent of uptake as a function of time. This was achieved from suspensions containing dithiocarbamate-functionalized silica particles and Hg(II) from which aliquot of the well-mixed slurry were sampled at various time intervals, immediately filtered using a plastic syringe mounted on a filter holder containing a 0.45 μm membrane filter, and solution-phase Hg(II) concentrations were determined by the same method as above.[49] Again, the amount of adsorbed species on the solid phases was calculated by difference with respect to the Hg(II) starting solution concentration.

All electrochemical measurements have been performed in a conventional single-compartment cell assembled with a rotating disk gold electrode, an Ag/AgCl reference electrode (Metrohm, no 6.0733.100) and a Pt wire auxiliary electrode. The electrolyte medium was made of 1.2×10^{-3} mol dm^{-3} EDTA, 7.2×10^{-3} mol dm^{-3} NaCl and 2.8×10^{-4} mol dm^{-3} $HClO_4$. Stripping voltammograms were recorded after 30 s electrolysis at +0.3 V, by scanning potentials in the different pulse mode up to +0.8 V. Analysis was performed after appropriate dilution of the sample to fall into the linear range of the technique (0.1–1 μm).

2.5 Instrumentation

All samples have been characterized by elemental analysis to determine the amount of grafted organo-functional groups in the materials. This was made using a Thermofinnigan FlashEA 1112 analyzer at the Service d'Analyse Elementaire of the Université H. Poincaré, Nancy. Specific surface areas and pore volumes were calculated by the BET (Brunauer-Emmett-Teller) method from nitrogen adsorption-desorption isotherms recorded at 77 K in the relative pressure range from about 10^{-5} to 0.99 on a Coulter SA 3100 analyzer. Prior to measurements, silica samples were outgassed at 60 °C overnight. The IR spectra were recorded on a Bruker Equinox IFS 55 Raman-IR spectrometer (KBr pellets). Grafted organic moieties were characterized by solid state ^1H–^{13}C cross-polarization magic angle spinning (CPMAS) nuclear magnetic resonance performed at room temperature on a Bruker Avance II (B_0 = 7.1 T) operating at 75.47 MHz. Spectra were recorded at a spinning frequency of 4 kHz, a ^1H $\pi/2$ pulse duration of 4 μs, a contact time of 2 ms and a recycle delay of 10 s. The structural order of mesoporous materials was evaluated by powder X-ray diffraction (XRD). Diffraction patterns were recorded at room temperature on a powder PANanalytical X'PERT PRO diffractometer, equipped with a Cu anode (λ(Mo-Kα) = 1.5418 Å, $0.5 < 2\theta < 10°$, 0.02 s^{-1}). X-Ray photoelectron spectroscopy (XPS) analyses were carried out on a KratosAxis Ultra spectrometer (Kratos Analytical, UK) with a hemispherical energy analyzer using a monochromatic Al-Kα source (1486.6 eV). Spectra were analyzed using the Vision 2.2.0 software from Kratos.

3. Results and discussion

3.1 General considerations: porosity measurements and elemental analysis

All materials obtained by direct grafting of silica samples (K60, SBA15 and MCM41) with either APTES or *N*-[3-(triethoxysilyl)propyl]carbamodithioic acid sodium salt, as well as amine-functionalized silicas subsequently derivatized with CS_2 (alone or in the presence of base) have been characterized by nitrogen adsorption-desorption measurements and elemental analyses (Table 1).

For the materials obtained by the one-step functionalization method, both specific surface areas and pore volumes were found to decrease upon grafting as a consequence of the space occupied by organic groups. This effect was however more marked when grafting the dithiocarbamate precursor in comparison to the amine one, in spite of the slightly lower amounts of grafted ligands (about 15% less dithiocarbamate than amine groups). This can be ascribed to the fact that the dithiocarbamate function is bulkier than the amine one and occupies then more space into the material. Such porosity loss was also function of the degree of organization in the material and the (average) pore size of the starting silica sample (about 7 nm for K60 and SBA15, and 3 nm for MCM41). As already observed for other grafting agents,[32,50] comparing K60 and SBA15 materials indicates that the decrease in pore volume upon grafting was hardly lower after functionalization in SBA15 due to the regular morphology of the mesopore channels (in comparison to pore clogging effects in non ordered silica gels). On the other hand, the porosity losses were more important when grafting silica samples of smaller pore size (compare data obtained for MCM41 and SBA15 in Table 1). The amount of grafted ligands was also found to increase with the specific surface area of the starting material following the order: K60 < SBA15 < MCM41. Comparison of MCM41 and K60 silica displaying both similar volume pore ($\sim$0.8 $cm^3\ g^{-1}$) but different surface areas (more than twice higher for MCM41) gives evidence for interest of high surface specific area materials, as the organic content in MCM41 is up to 18% larger (aminopropyl-grafted). This is probably due to the enhanced accessibility to a higher number of surface silanol groups that promote the grafting efficiency.

Two series of dithiocarbamate-functionalized materials have been also obtained according to a two-step functionalization process involving the action of CS_2 on aminopropyl-grafted silica samples in the absence or presence of a base. As shown in Table 1, whatever the pristine material, both specific surface areas and pore volumes of the samples prepared without base are closer to those of the one-step aminopropyl-grafted materials than to those of the one-step grafted dithiocarbamate silicas. This suggests that incomplete conversion of amine groups into dithiocarbamate moieties may have occurred, since the resulting porosity of silica-$NH_2 + CS_2$ materials would have been expected to be lower than those measured for silica-NH_2 solids owing to higher steric hindrance of the dithiocarbamate moiety compared to the amine group. When functionalization was performed under alkaline conditions, dramatic decrease of both the specific surface area and pore volume is noticed as it reaches 57% for K60 and up to 77% for MCM41 compared to the pristine materials. Besides, these values are even much lower than those observed for one-step functionalized silicas (Table 1). This is obviously due to higher conversion yields of the amine groups into dithiocarbamate moieties but this cannot reasonably be the sole effect responsible for such a decrease as pore volumes of silica-$NH_2 + CS_2/OH$ materials were significantly lower than those of the silica-dtc obtained from direct grafting. A complementary explanation might be the collapse of the material framework due to the poor chemical stability of silica in basic medium.[44] However XRD and nitrogen adsorption-desorption data do not show any disorder

Table 1 Physico-chemical characteristics of silica samples, either unmodified, or grafted in one step with amine ($-NH_2$) or dithiocarbamate (–dtc) groups, or obtained from derivatization of amine-grafted silica samples with carbon disulfide in the absence ($-NH_2 + CS_2$) or presence of base ($-NH_2 + CS_2/OH$)

	Nitrogen adsorption–desorption		Elemental analysis			
Sample	BET surface area/$m^2\ g^{-1}$	Total pore volume/$cm^3\ g^{-1}$	N (%)	S (%)	Amount of N-bearing ligands/mmol g^{-1}[a]	S/N ratio
K60	457	0.81	0.0	0.00	0.00	—
K60-dtc	258	0.38	1.63	4.18	1.16	1.12
K60-NH_2	323	0.49	1.80	0.00	1.28	—
K60-$NH_2 + CS_2$	339	0.46	1.77	1.27	1.26	0.31
K60-$NH_2 + CS_2/OH$	197	0.29	2.40	2.76	(1.71)[b]	(0.50)[c]
SBA15	703	0.98	0.00	0.00	0.00	—
SBA15-dtc	314	0.57	1.75	4.61	1.25	1.15
SBA15-NH_2	412	0.72	1.83	0.00	1.31	—
SBA15-$NH_2 + CS_2$	450	0.69	1.79	1.32	1.28	0.32
SBA15-$NH_2 + CS_2/OH$	232	0.39	2.87	4.69	(2.05)[b]	(0.71)[c]
MCM41	1033	0.78	0.00	0.00	0.00	—
MCM41-dtc	388	0.27	1.71	4.67	1.22	1.19
MCM41-NH_2	739	0.40	2.10	0.00	1.50	—
MCM41-$NH_2 + CS_2$	796	0.41	2.08	1.41	1.49	0.30
MCM41-$NH_2 + CS_2/OH$	237	0.16	2.93	4.23	(2.09)[b]	(0.63)[c]

[a] Expressed per gram of grafted material; determined from nitrogen elemental analysis. [b] Overestimated due to the remaining tetraethylammonium moieties into the materials. [c] Underestimated due to the remaining tetraethylammonium moieties into the materials. S contents measured from elemental analyses are largely underestimated; see text at the end of section 3.2.1. for explanation.

(or loss of order). This decrease is most probably due to the base left in the material upon functionalization (despite having washed silica several times with propan-2-ol in which $(Et)_4NOH$ is highly soluble) filling in the pores of the materials. This hypothesis, consistent with the possible interaction of ammonium reagents with silanolate groups, is supported by nitrogen elemental analysis (Table 1) whose values appears to be abnormally high (and then unusable) and ^{13}C solid state NMR (see hereafter).[51]

3.2. Spectroscopic evidences of incomplete conversion of amino-bearing silica into dithiocarbamate moieties: interest of the one-step grafting process

The above results suggest that residual amine groups could exist when attempting to functionalize silica materials according to a two-step derivatization pathway (silica-$NH_2 + CS_2$). Several spectroscopic techniques have been used to analyze this question, including IR, solid state NMR and XPS. Even IR was likely to point out the presence of aminopropyl groups (δNH_2 range: 1590–1650 cm^{-1})[52–55] or dithiocarbamate moieties (δNCS_2 range: 1450–1500 cm^{-1}).[30,42,56,57] This technique was however not usable to distinguish these groups when present in mixture due to signal overlap, in addition to strong vibrational bands of the silica framework.[30,34] On the other hand, such distinction can be performed on the basis of ^1H–^{13}C CPMAS NMR and XPS (N 1s signal).

3.2.1. Solid state ^1H–^{13}C CPMAS NMR.

Fig. 1 depicts the ^{13}C CPMAS NMR spectra run on the one-step amino- and dithiocarbamate-functionalized K60 and SBA15 samples. Assignment of resonances was performed by using ACDlab/Chemsketch 10.0 software. The three resonances at *ca.* 10, 22 and 45 ppm are characteristic of the γ-, β-, α-C of the propyl-NH_2 or propyl-dtc moieties. Furthermore two thinner resonances at *ca.* 18 and 59 ppm corresponding to non-hydrolyzed ethoxy groups[27,58,59] are observed. It is also possible to distinguish the dithiocarbamate-grafted samples as they exhibit a characteristic signal at 180 ppm, assigned to the carbon of the $NHCS_2$ moiety (Fig. 1 A1 and B1, spectrum 'b'). Because this carbon is not protonated, the corresponding intensity is underestimated by the CPMAS experiment. Nevertheless, this signal indicates the presence of dithiocarbamate functions but it is not likely to provide any information on amine moieties eventually contained in the material. Focusing our attention on a restricted spectral window (Fig. 1 A2 and B2), it can be clearly seen that the α–C resonance of the aminopropyl group appears at 43 ppm whereas it is shifted at 47 ppm in the case of dithiocarbamate (some distinction can be also made on the basis of the β-C resonance but this is less marked, especially for SBA15 materials). This 4 ppm shift allows identifying the chemical structure of the organic ligands bound to the silica and could thus be useful to detect the presence of both amine and dithiocarbamate groups in mixture. For this reason, this technique appears to be particularly relevant to determine the nature of the organic moieties in the materials synthesized according to the two-step procedure and to provide information on the extent of amine conversion upon reaction with CS_2.

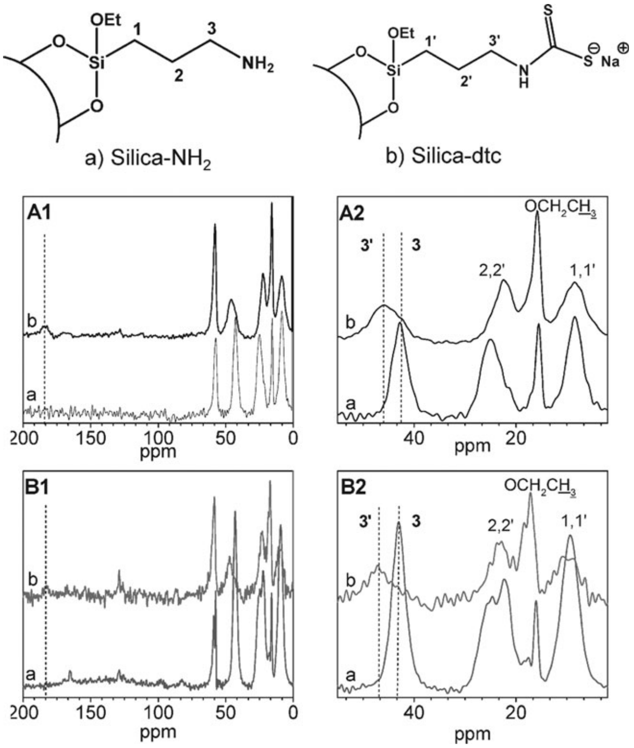

Fig. 1 Solid state ^1H–^{13}C CPMAS NMR spectra of the one-step functionalized K60 (A1 and A2) and SBA15 (B1 and B2) silicas grafted by aminopropyl groups (a) and siloxydithiocarbamate precursor (b). A2 and B2 are expanded views the 0 to 50 ppm region of the A1 and B1 spectra, respectively. On the top are depicted schematic structures of the corresponding functionalized silicas. Carbons from the propyl chain have been numbered to be clearly identified in the discussion.

This is illustrated in Fig. 2, showing the narrow spectra obtained (α-C resonance) obtained for K60-$NH_2 + CS_2$, SBA15-$NH_2 + CS_2$, K60-$NH_2 + CS_2$/OH and SBA15-$NH_2 + CS_2$/OH, and comparing them to the corresponding materials prepared by direct grafting of APTES or *N*-[3-(triethoxysilyl)-propyl]carbamodithioic acid sodium salt. When carried out in the absence of a base (spectrum 'c'), dithiocarbamation leads to materials characterized by two signals at 43 and 47 ppm, indicating unambiguously the presence of both amine and dithiocarbamate functions, as further confirmed by comparison to the signals assigned, respectively, to carbon α of the amino (spectrum 'a') and dithiocarbamate groups (spectrum 'b'). The concomitant presence of both these functions in the materials thus gives evidence for the incomplete conversion of the amine groups into dithiocarbamate moieties.

Increasing the amount of carbon disulfide employed, as done with the SBA15 sample (Fig. 2 B, spectrum 'c'), leads to an increase of the intensity of the signal at 47 ppm (characteristic of propyldithiocarbamate) compared to the one at 43 ppm (aminopropyl). This indicates that the increase of carbon disulfide enables to improve the amine/dtc conversion degree, which remains however incomplete. Even better results can be obtained in basic medium (spectrum 'd'), where the dithiocarbamate moiety signal at 47 ppm appears to be the major one. The use of alkaline conditions seems

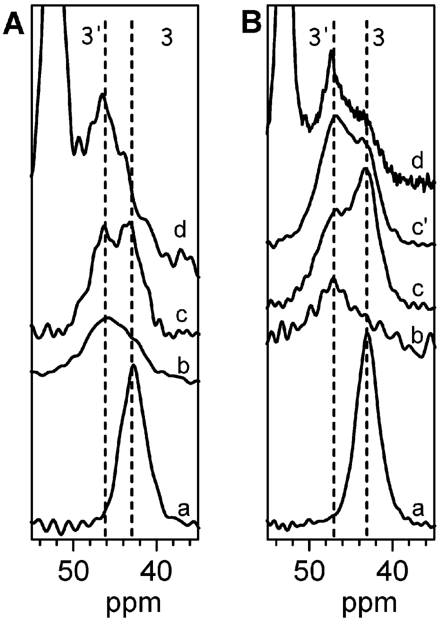

Fig. 2 Solid state ^1H–^{13}C CPMAS NMR spectra of the one-step functionalized K60 (A) and SBA15 (B) silicas grafted by aminopropyl groups (a) and the siloxydithiocarbamate precursor (b) and the dithiocarbamate-modified solids prepared according to the two-step procedure without a base using 1.5 eq. (c) or 15 eq. (c′) of CS_2, and with tetraethylammonium hydroxide (d).

therefore to enhance the conversion of the amine-grafted silica into dithiocarbamate-functionalized material, in agreement to what is known for the preparation of solution-phase dithiocarbamate derivatives from primary amines.[60–62] The intense peak appearing additionally at 52 ppm using this preparation pathway is ascribed to the ethyl groups from the base (Et_4NOH), indicating that some of this compound remains in the final material (despite having rinsed it extensively upon functionalization), as already suggested above from porosity measurements and elemental analysis.

Furthermore, it is noteworthy that amine conversion is incomplete in both non-ordered K60 and mesostructured SBA15 materials. At first sight, these results could be a little bit surprising as the regular mesopore structure in SBA15 is proven to ensure better accessibility of the species towards active sites compared to K60 whose porosity is not well structured.[50,63,64] However, contrary to the co-condensation method, post-synthesis grafting is known to lead to irregular distribution of functional groups (*i.e.*, higher content of organic functions at the mesopore entrance[65–67]), so that the derivatization reaction conversion could be limited by steric constraints, confirming the two-step procedure is less interesting than one-step functionalization. The existence of some microporosity (10%) in SBA15, which was found to disappear upon APTES grafting, may also contribute to explain some restricted accessibility to amine groups but this is expected to play a minor role as similar restriction was observed with the MCM41 sample which did not contained microporosity.

All NMR spectra have been recorded using the cross polarization technique for reason of enhancing the carbon sensitivity. Since this technique does not give quantitative information, the amount of unreacted amine groups remaining in the material cannot be precisely determined (though allowing to identifying the different species). To this end, we have attempted to perform ^{13}C MAS NMR experiments but the signals were unfortunately barely detectable, even after running overnight, probably due to the too low surface coverage of silica. Accurate quantification of the conversion degree can be in principle determined from elemental analysis of N and S, for which S/N molar ratio of 2 is expected for dithiocarbamate groups. This is indeed what is obtained for the starting precursor *N*-[3-(triethoxysilyl)propyl]-carbamodithioic acid sodium salt (% N = 4.61; % S = 21.28; S/N ratio = 2.0) as raw material, but when diluting this sample with silica gel (by simple mixing as dry powders), the S elemental analysis was largely under-estimated (though N content staying correct), leading to losses in S/N molar ratio by 50–75%. This unexplained under-evaluation of S, which was especially observed when silica was used as diluting matrix (*i.e.*, only 20–25% losses in S/N molar ratio when mixing the precursor with poly(vinyl alcohol)), was also observed using other dithiocarbamate derivatives (*e.g.*, sodium diethyldithiocarbamate). This thus prevents the use of elemental analysis of S content to quantify the conversion degree of the functionalized silicas studied here as even the dithiocarbamate-functionalized materials obtained from the direct route gave rise to measured S/N molar ratios much lower than 2 (around 1, see Table 1). Anyway, in spite of this under-estimation, the incomplete conversion of amine groups in the two-step procedure as well as the effect of the base catalyst were qualitatively confirmed as apparent S/N molar ratios of about 0.3 were estimated for silica-$NH_2 + CS_2$ materials and in the range 0.5–0.7 for silica-$NH_2 + CS_2/OH$ (Table 1).

3.2.2. X-Ray photoelectron spectroscopy. XPS was also employed to characterize the chemical state of the organo-functional groups. The wide spectra point out the elements likely to be present in these materials (Si, O, C, N, S). The narrow spectra corresponding to the S 2p core level obtained for the dithiocarbamate-functionalized silica exhibit a single signal located at binding energies of 161.5 eV (S $2p_{3/2}$) and 162.5 eV (S $2p_{1/2}$), which correspond to the reduced form of sulfur S(−II) as expected for the dithiocarbamate function.[68,69] This S 2p signal can be also useful to check the chemical integrity of this group, for example, upon oxidation (that may occur after prolonged storage in air atmosphere or after heat treatment in the presence of oxygen), additional peaks appear at higher binding energies (*e.g.*, S(+VI) at 168.0 eV for S $2p_{3/2}$ and 169.0 eV for S $2p_{1/2}$).

For the purpose of the present work, the most interesting region of XPS spectra is that corresponding to the N 1s signal (Fig. 3). Indeed, one knows that aminopropyl-grafted silica samples are characterized by two distinct signals located at binding energies of 399.5 and 401.5 eV, corresponding, respectively, to the 'free' amine groups and to protonated ammonium moieties originating from the reaction of aminopropyl functions with surface silanol groups.[45,70–72] The extent of protonation is usually at about 30% relative

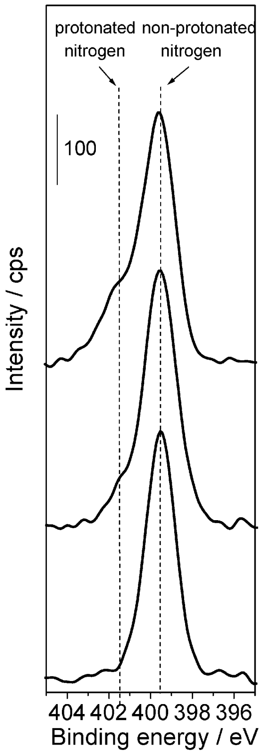

Fig. 3 XPS spectra (N 1s region) of MCM41 silica samples either one-step modified by grafting aminopropyl groups (A) or dithiocarbamate-modified according to the two-step procedure using CS_2 without a base (B) and one-step modified by direct grafting of the siloxydithiocarbamate precursor (C). The dotted lines at 399.5 eV and 401.5 eV stand for the position of the two component peaks corresponding, respectively, to unprotonated and protonated forms of nitrogen.

to the total amount of amine groups in the material, as illustrated on part A in Fig. 3 for the MCM41-NH_2 sample.

When MCM41 was grafted with the siloxydithiocarbamate, the N 1s signal was essentially characterized by a single peak located at a binding energy of 399.5 eV (see part C in Fig. 3), which can be assigned to the non-protonated nitrogen atom of the dithiocarbamate function ($-NHCS_2^-$). The unshared lone pair of nitrogen is there involved in a delocalised system diminishing thus the basicity of the nitrogen atom compared to that of aminopropyl group and limiting therefore its acid–base reaction with silanol groups.

On the other hand, spectrum run on dithiocarbamate-functionalized MCM41 prepared by the two-step derivatization approach clearly shows the two components previously observed corresponding to unprotonated nitrogen ($-NH_2$ or $-NHCS_2^-$) at 399.5 eV and to protonated ammonium moieties at 401.5 eV (see part B in Fig. 3). Their ratio, protonated NH/free NH = 17/83, confirms the presence of residual amine groups in this material, yet in smaller amount than in aminopropyl-grafted MCM41 (protonated NH/free NH = 28/72), in agreement with NMR data. The ratio between protonated NH in silica-NH_2 and silica-$NH_2 + CS_2$ materials could be used to quantify the conversion degree (estimated between 40 and 50% for all samples studied here), but this has to be taken with great care as XPS data are only characteristics of the outermost surface of the solids. Note that one can also notice a very small signal at 401.5 eV (at the noise level) in the MCM41-dtc material, which could arise from some degradation of dithiocarbamate moieties into amine groups (*i.e.*, by CS_2 loss[28,73]), but this phenomenon is assumed to be negligible (NH protonated/NH free < 3%). The sample MCM41-$NH_2 + CS_2$/OH containing residual tetraethylammonium cations, interfering with the signal located at 401.5 eV, was not studied.

3.3. Effect on mesostructural order

Although performing CS_2 reaction in a basic medium is a good mean of ensuring high conversion of amine into dithiocarbamate, one can wonder about the consequence of such basic conditions on the mesostructure of the ordered materials giving the well-known poor chemical stability of silica at high pH values (at least in aqueous media).[44] This was checked by XRD measurements carried out on the MCM41 silica series, as performed after the various functionalization processes (Fig. 4).

In all cases, the XRD pattern is typical of a hexagonal MCM41-type mesoporous material, with one main reflection appearing at low 2θ value of 2.3° and two peaks of weaker intensity at higher angle values (4.0° and 4.7°), corresponding, respectively, to diffraction plans indexed as 100, 110 and 200 characteristic of a hexagonal structure.[74,75] Similarities between the patterns from the pristine silica (a) and both the one-step amine- (b) and dithiocarbamate- (c) functionalized samples give evidence that the one-step grafting route does not affect the regular structure of the material. In contrast, the obvious decrease of the pattern intensity from the dithiocarbamate modified silica under alkaline conditions

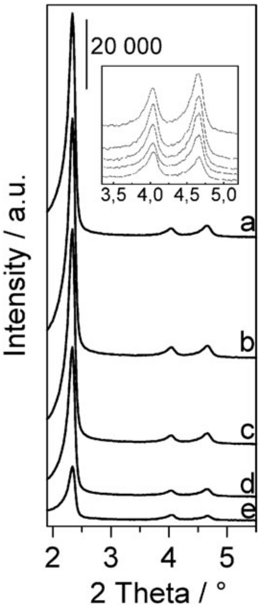

Fig. 4 Power X-ray diffraction patterns for the MCM41 silica samples: pristine MCM41 (a), one-step modified MCM41 by grafting aminopropyl groups (b) or the siloxydithiocarbamate precursor (c), and dithiocarbamate-modified samples prepared according to the two-step procedure using carbon disulfide: without a base (d) or with tetraethylammonium hydroxide (e). The inset is a zoom on the higher angle value peaks.

(e) might be assigned to a partial loss of the mesostructural order in this material. The modification of silica according to the same procedure but free of base does not lead to such a dramatic pattern decrease (d), suggesting that the basic medium might be responsible for partial structure collapse. However, care must be taken considering these results as the three typical diffraction peaks are still clearly discriminated and that intensity decrease could be also due to contrast matching (maybe enhanced by the presence of residual tetraethylammonium groups in the material). This indicates that the mesostructure, even partially damaged is preserved upon functionalization, as also checked for the SBA15 series.

3.4 Reactivity: Hg(II) uptake

Dithiocarbamate materials have been extensively studied for metal uptake as they display good binding properties towards a large range of metal ions, specially Hg(II).[30,35–37,56] These complexing properties have been exploited in this work as an analytical tool to investigate the binding ability towards Hg(II) of the materials prepared according to the direct grafting and the two-step procedure. To this end, all samples prepared have been equilibrated with Hg(II) solution at solid-to-solution ratio adjusted to get an amount of organo-functional groups equal to the amount of Hg(II) in solution. Hg(II) uptake yields for each solid are depicted in Fig. 5.

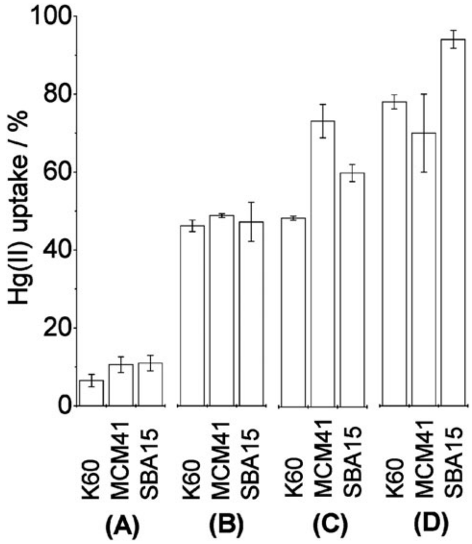

Fig. 5 Effect of the adsorbent type on the yield of Hg(II) uptake after 14 h using amine- and dithiocarbamate-modified mesoporous silicas: one-step aminopropyl-grafted (A), two-step dithiocarbamate-functionalized without (B) or with a base (C) and one-step grafted by the siloxydithiocarbamate precursor (D). Experimental conditions: extraction from a 200 cm^3 starting solution containing 1.0×10^{-4} mol dm^{-3} $Hg(NO_3)_2$ in 0.10 mol dm^{-3} acetate buffer (pH 5) to which the following amounts of adsorbent have been added: (A) 15.6 mg K60-NH_2, 13.3 mg, MCM41-NH_2, or 13.9 mg SBA15-NH_2; (B) and (C) 15.9 mg K60-NH_2+CS_2 (or K60-NH_2+CS_2/OH), 13.5 mg MCM41-NH_2+CS_2 (or MCM41-NH_2+CS_2/OH), or 13.9 mg SBA15-NH_2+CS_2 (or SBA15-NH_2+CS_2/OH); (D) 17.5 mg K60-dtc, 16.4 mg MCM41-dtc, or 16.0 mg SBA15-dtc, so that the amount of organic ligands in the medium was equal to that of Hg(II) at 2.0×10^{-5} mol.

The results clearly indicate that highest sorption yields have been obtained with one-step dithiocarbamate-functionalized material series. Indeed, the materials of the silica-dtc series were likely to extract 75–95% Hg(II) from a rather concentrated (1.0×10^{-4} mol dm^{-3}) solution after 14 h equilibration (see part D in Fig. 5). These uptake values are roughly ten times higher than those achieved with APTES-grafted materials (see part A in Fig. 5) due to the lower affinity of amine groups towards Hg(II) in comparison to the efficient binding of these species by dithiocarbamate moieties.

By contrast, dithiocarbamate-functionalized materials synthesized using carbon disulfide reaction were characterized by sorption yields significantly lower than silica-dtc: 40–50% for silica-NH_2+CS_2 and 50–70% for silica-NH_2+CS_2/OH (see Fig. 5(B) and (C)). The binding ability of these materials is therefore an intermediate between the amine and dithiocarbamate one-step functionalized silicas consistent with the concomitant presence of amine and dithiocarbamate groups into the materials. The lower binding ability of these silicas compared to that observed for dithiocarbamate one-step functionalized materials is attributed to the poor affinity of the residual amine groups into the solids towards Hg(II) species. In that series, the better Hg(II) uptake observed with silica derivatized in the presence of a base is consistent with the results from previous analyses indicating enhanced conversion of amine groups into dithiocarbamate moieties under alkaline conditions. These results clearly demonstrate the crucial interest of limiting the amount of unreacted amine groups in dithiocarbamate materials for further applications in solid/liquid extraction and confirm thus the advantage of the one-step grafting procedure to access dithiocarbamate-functionalized silicas.

Considering further the behaviour of the materials grafted with siloxydithiocarbamate (one-step procedure) reveals that the highest Hg(II) uptake is reached with SBA15 materials as nearly 94% of the ligands grafted on this material are accessible to Hg(II) binding on the basis of the stoichiometric Hg(II)/dithiocarbamate moiety ratio; by comparison, K60 and MCM41 exhibit lower capacity of, respectively, 78% and 70% (see part D in Fig. 5). Comparison of SBA15 and K60 materials, both displaying approximately the same pore size (~7 nm), demonstrates the interest of the regular structure of the SBA15 silica leading to a better accessibility of the metal species to the grafted sites. In the case of non-ordered K60, this accessibility might be restricted due to the sinuous (irregular) porosity which could lead to pore blocking, as previously reported for Hg(II) binding to thiol-functionalized silica-based materials.[62,63] Although displaying the same hexagonal mesopore organisation as SBA15, the MCM41-based materials extracted a lower amount of Hg(II), which can be attributed to the smaller pore size of these solids (about twice lower: ~3 nm) and lower volume pore upon functionalization (0.27 cm^3 g^{-1} *vs.* 0.57 cm^3 g^{-1} for SBA15). Nevertheless, it is worth noting that MCM41-dtc displays Hg(II) binding capacity of the same order of magnitude as that of K60, confirming again the good accessibility to ligands immobilized in mesostructured materials compared to the non-ordered ones.

Further investigation on the speed of the uptake process was performed by monitoring the amount of immobilized Hg(II) as

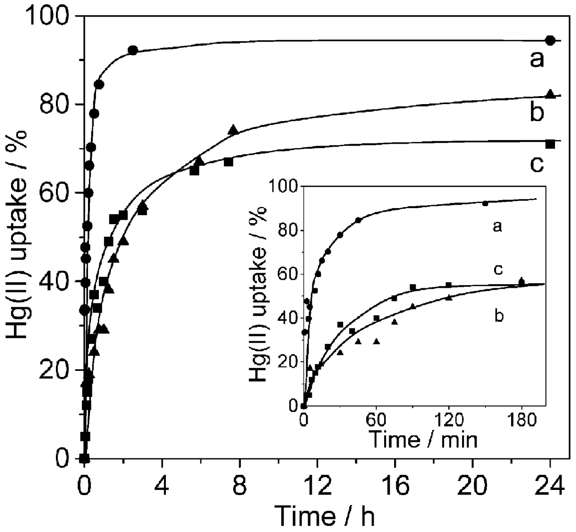

Fig. 6 Hg(II) adsorption as a function of time for one-step dithiocarbamate-functionalized silica samples: SBA15-dtc (a), K60-dtc (b) and MCM41-dtc (c). Experimental conditions: 200 cm^3 of starting solution containing 1.0×10^{-4} mol dm^{-3} $Hg(NO_3)_2$ in 0.10 mol dm^{-3} acetate buffer (pH 5) to which selected amounts of adsorbent were added to keep constant the dtc/Hg(II) ratio at unity (2.0×10^{-5} mol of each): 16.0 mg SBA15-dtc (a), 17.5 mg K60-dtc (b), or 16.4 mg MCM41-dtc (c). The inset is a zoom on the first minutes of the experiments.

a function of time for silica-dtc series (Fig. 6). The uptake process was very fast when using the SBA15-dtc adsorbent (nearly 92% of Hg(II) was extracted after 3 hours, before reaching a plateau), which is much faster than Hg(II) binding to the non-ordered K60-dtc material (compare curves (a) and (b) in Fig. 6) in spite of rather similar pore sizes. This is consistent with previous reports dealing with Hg(II) binding to thiol-functionalized silica materials.[50,63] Such advantage belonging to the mesostructural order was also exhibited by MCM41-dtc for which binding kinetics were slightly faster than K60-dtc at the beginning of the experiment in spite of a pore size twice smaller for MCM41 than for the non-ordered K60 material.

4. Conclusion

Non-ordered and mesostructured dithiocarbamate functionalized silicas have been prepared according to both (1) the typical two-step procedure described in the literature, based on the reaction of aminosilica with carbon disulfide and (2) a new approach consisting in the direct grafting of a siloxydithiocarbamate onto the silica surface. Characterizing these materials using various and complementary techniques has allowed comparing these two functionalization routes by pointing out limitations of the commonly used pathway and by highlighting the interest of the one-step method, as a result of incomplete conversion of amine moieties into dithiocarbamate functions by the two-step method. Although performing this reaction with a base improves the conversion yield, some unreacted amine moieties are still left in the final materials and these basic conditions could lead to partial structural degradation in the case of mesostructured materials when used in aqueous medium. In contrast, the one-step grafting method allows accessing directly to dithiocarbamate-functionalized silica materials, free of unreacted amine, without any damage to the silica framework. This is especially important with respect to practical application of these adsorbents, as illustrated here *via* Hg(II) uptake. This has indeed revealed that direct grafting of siloxydithiocarbamate gives rise to a material displaying more efficient binding of Hg(II) compared to those prepared in two steps whose complexing properties are lowered by the existence of remaining amine groups having little affinity for these species.

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