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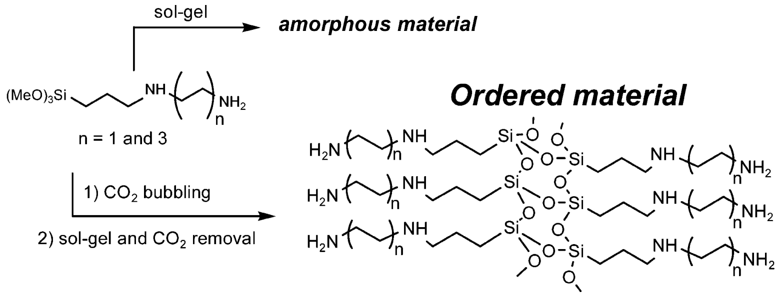

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CO_2 as a Supramolecular Assembly Agent: A Route for Lamellar Materials with a High Content of Amine Groups

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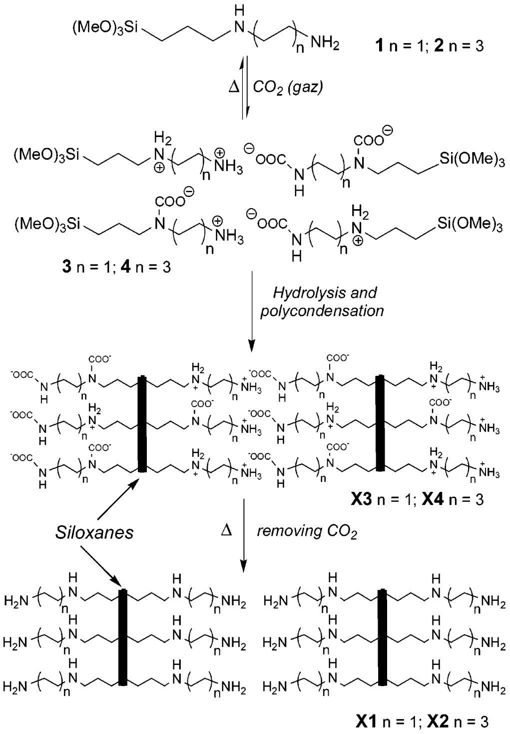
Ordered amine-functionalized silicas[1−9] have received considerable attention in recent years due to their numerous potential applications in catalysis, adsorption, separations, and biomolecules immobilization. These functionalized hybrid materials were prepared mainly according to two methods. The first consists of grafting an aminoalkyltrialkoxysilane onto the pore surface of ordered mesoporous silica.[3,6,8,9] The second approach is a direct synthesis method, which involves the co-condensation of an aminoalkyltrialkoxysilane with tetraethyl orthosilicate (TEOS) in the presence of a structure-directing agent.[1,2,4,5,7,9] However, both methods have their own limitations, that is, irregular repartition of amino groups by grafting and low content of organic groups when the direct synthesis method is used.

Here, we report an original and easy method to synthesize highly amine-functionalized silica with lamellar structure under neutral conditions. Interestingly, the amino centers of these materials are fully accessible, as shown by adsorption of transition metal and lanthanide salts.

First, we used CO_2 gas as the supramolecular assembly agent.[10] Indeed, CO_2 reacts with primary and secondary amine to give ammonium carbamate salts.[11,12] We used the reversibility of this reaction to prepare ordered and highly amine-functionalized silica. We show that the *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane **1** and *N*-(6-aminohexyl)-3-aminopropyltrimethoxysilane **2** react with CO_2 to afford a supramolecular network of silylated ammonium carbamate salts (Scheme 1), the hydrolytic polycondensation of which gives rise to structured hybrid materials. Subsequent loss of CO_2 is readily achieved upon heating, thus generating hybrid materials in which the structure is maintained (well-defined lamellar structure from **2**) and contains free amino groups.

Experimentally, CO_2 was bubbled through pure precursors **1** and **2** at room temperature. The reaction was exothermic, and CO_2 bubbling was maintained until the temperature of the mixture returns to room temperature (about 20 °C), affording very viscous and translucent physical gels **3** and **4** (see Supporting Information). The mass increase in both cases approaches a molar uptake of CO_2 per mole of precursor **1** or **2**. To measure exactly the uptake of CO_2, loss of CO_2 was achieved by treating the gels **3** and **4** with a mixture of $EtOH/H_2O$ at room temperature. The volume of CO_2 released was stored in a gas buret and measured very accurately, confirming that 1 equiv of CO_2 combines with 1 equiv of the precursors **1** or **2**. This result corresponds to the theoretical value for CO_2 sequestration involving both primary and secondary amino groups. Gels **3** and **4** were characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopies. New resonances observed in the ^{13}C NMR spectra of **3** and **4**, respectively, at 163.8 and 163.6 ppm are mostly prominent and attributable to a carbamate carbonyl groups. Those at 52.1 and 49.2 ppm for **3** and **4**, respectively, were assigned to the methylene groups attached to the carbamate nitrogen atom, in addition to the other sp^3 carbon atoms. The overall data suggest the formation of a supramolecular network of silylated ammonium carbamate salts, as proposed in Scheme 1.

Scheme 1



As carbamates are not stable in water, the hydrolytic polycondensation of the network of silylated carbamates was performed at 30 °C in a 1 M pentane solution in the presence of the stoichiometric amount of water at pH 1.5. This heterogeneous mixture was stirred vigorously to afford a precipitate after about 24 h. It was aged 48 h at 30 °C, then filtered, and washed successively with acetone, ethanol, and ether (3 × 25 mL). After drying carefully for 30 min at 10^{-1} mbar without heating, the white powders **X3** and **X4** were collected in high yield.

It is very important to note that no solid was obtained by hydrolysis and polycondensation under the same experimental conditions starting from **1** or **2** instead of **3** or **4**.

The nitrogen adsorption measurements indicate that all materials **X1** to **X4** are nonporous solids ($S_{BET} < 10\ m^2\ g^{-1}$).

The solid-state ^{13}C CPMAS NMR spectra of **X3** and **X4** (see Supporting Information) revealed that the ammonium carbamate salts remained intact during the sol−gel process. That is chiefly indicated by the resonances at 164.3 and 165.0 ppm, respectively, for **X3** and **X4**, which were attributed to the carbamate carbonyl carbon in addition to the other sp^3 carbon atoms.

The ^{29}Si MAS NMR spectra (see Supporting Information) indicated that the materials **X3** and **X4** are very well condensed.

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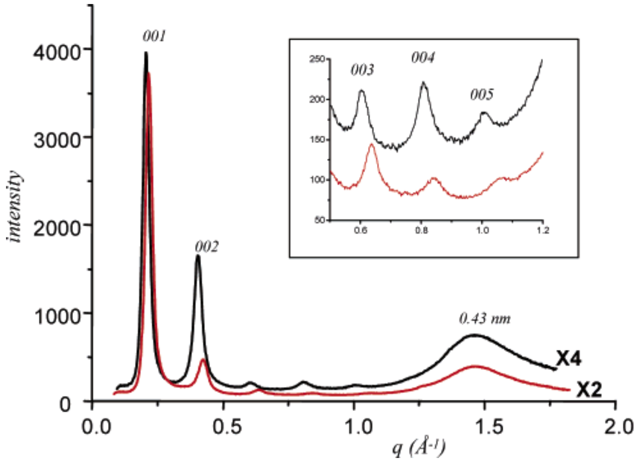

Figure 1. X-ray diffraction patterns of **X4** (black) and **X2** (red). The inset shows the amplified higher order (×5).

Indeed, the spectrum of **X4** exhibited only a signal at −68.2 ppm assigned to the T^3 substructure, while that of **X3** displayed a major resonance at −66.0 ppm (T^3) in addition to a very weak one (5%) at −58.5 ppm assigned to the T^2 substructure.

The X-ray powder diffraction pattern (XRD) of **X4** exhibits low-angle diffraction peaks (Figure 1). The first intense peak at $q = 0.20$ Å^{-1} indicates that the interlayer distance is 3.15 nm. The peaks observed at higher angles corresponding to 1.54, 1.03, 0.78, and 0.62 nm are attributed to second-, third-, fourth-, and fifth-order diffractions, indicating a material with well-ordered layered structure. The broad peak at 0.43 nm can be attributed to alkylene chain packing within the layers.[13] The X-ray powder diffraction pattern of **X3** (see Supporting Information) shows that long-range order is less well defined than for **X4**; the peak at $q = 0.38$ Å^{-1} corresponding to a distance of 1.60 nm is broader with lower intensity than the first peak observed for **X4**. At higher angles, for **X3**, only the first order is observed at 0.90 nm in addition to the broad peak at 0.42 nm. It is worth noting that the XRD patterns of the precursors **1** and **2** exhibit a broad peak centered at 0.54 nm for **1** and 0.53 nm for **2** attributed to the interchain distances. The XRD patterns of the networks of ammonium carbamate salts **3** and **4** display also a broad peak characteristic for the interchain distances. A further peak at 2.10 nm is observed in the XRD pattern for **3**.

Thus, in both cases, the long chains are in close proximity before the hydrolytic polycondensation. During the sol−gel process in pentane, the supramolecular network of ammonium carbamate **4** assembles in a very well defined lamellar nanostructure, while a less pronounced self-assembly results from the hydrolytic polycondensation of **3**. As the only difference between the supramolecular networks **3** and **4** is the length of the chains, the better structuration for the material **X4** in comparison to that of **X3** shows the importance of the weak van der Waals interactions between the long chains in the process of self-assembly. These results are in agreement with long-range order formed during the hydrolytic polycondensation in hydrophilic conditions of bridged organosilica with long alkylene chains [$(MeO)_3Si(CH_2)_nSi(OMe)_3$ with $n = 12$, 18, and 30], thanks to hydrophobic van der Waals interactions.[14]

To remove CO_2 and recover the amino groups, the materials **X3** and **X4** were heated at 80 °C under vacuum for 12 h, giving rise, respectively, to the materials **X1** and **X2**. Their solid-state ^{13}C CPMAS NMR spectra revealed, in both cases, the absence of a peak attributed to the carbamate carbonyl carbon, indicating that the removal of CO_2 was complete (see Supporting Information). It is worth noting that the peaks corresponding to the sp^3 carbon atoms of the alkyl chains are notably sharper than those observed in the corresponding materials **X3** and **X4**, in agreement with a higher mobility of the chains. In addition, the degrees of polycondensation were not affected by the decarboxylation, while the ^{29}Si MAS NMR spectra of **X1** and **X2** are very similar to these of **X3** and **X4**.

Interestingly, the X-ray powder diffraction patterns of **X1** and **X2** showed that the structure of the materials was maintained after removal of CO_2. The XRD pattern of **X2** (Figure 1) exhibits an intense peak at 2.90 nm followed by peaks at higher angles (1.48, 0.99, 0.75, and 0.59 nm) attributed, respectively, to second, third, fourth, and fifth order, which corresponds to a well-ordered layered structure. It is worth noting that these five peaks were very slightly shifted in comparison to those of the material **X4**. This shift can be explained by the narrowing of the layers.[12] The XRD pattern of **X1** (see Supporting Information) exhibits only a peak at 1.64 nm in addition to the broad peak at 0.45 nm, indicating a low order of regularity for **X1**.

The accessibility of the amine functional groups in **X1** and **X2** was investigated by testing their ability to complex transition metal or lanthanide salts. The solids **X1** and **X2** were treated with an ethanolic solution of $CuCl_2$, $Eu(NO_3)_3$, or $Gd(NO_3)_3$ under reflux for 12 h. The resulting solids, termed **MX1** and **MX2**, were copiously washed with EtOH to eliminate the noncomplexed salts. The filtrate containing the excess of salts was titrated by complexometry measurements for lanthanide salts and by conductimetry for Cu^{II}. The ratio of metal cations per diamine moieties in **MX1** was found to be exactly 1/1 for Cu^{II} and Eu^{III} and in **MX2**, 1/1 in the case of Cu^{II}, and 1/2 in the case of Eu^{III} and Gd^{III}. Results of elemental analyses of Cu^{II}, Eu^{III}, Gd^{III}, Cl, and N gave rise to exactly the same ratio M^{n+}/diamine as that found by titration. The Cu^{II} and Eu^{III} loading capacities for **X1** and **X2** are very high (6.5 mmol/gram of **X1** and 4.8 and 2.4 mmol/gram of **X2**).

In summary, we have described a new method for the formation of ordered and highly amine-functionalized silica by using the reversible covalent binding of CO_2 to amines. The fast and high accessibility of the amino groups makes these organosilicas promising materials for CO_2 uptake and storage, environmental remediation, heterogeneous catalysts, and biomolecules immobilization.

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Supporting Information Available: ^{13}C solid NMR spectra of **X1**−**X4**, ^{29}Si solid NMR spectrum of **X3**, and XRD patterns of **X1** and **X3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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