Hyperpolarized $^{129}\text{Xe}$ NMR investigation of multifunctional organic/inorganic hybrid mesoporous silica materials

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Received 4th May 2005, Accepted 16th June 2005
First published as an Advance Article on the web 7th July 2005

An extensive study has been made on a series of multifunctional mesoporous silica materials, prepared by introducing two different organoalkoxysilanes, namely 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (AEPTMS) and 3-cyanopropyltriethoxysilane (CPTES) during the base-catalyzed condensation of tetraethoxysilane (TEOS), using the variable-temperature (VT) hyperpolarized ($^{129}\text{Xe}$) NMR technique. VT $^{129}\text{Xe}$ NMR chemical shift measurements of adsorbed xenon revealed that surface properties as well as functionality of these AEP/CP-functionalized microparticles (MP) could be controlled by varying the AEPTMS:CPTES ratio in the starting solution during synthesis. Additional chemical shift contribution due to Xe-moiety interactions was observed for monofunctional AEP-MP and CP-MP as well as for bifunctional AEP/CP-MP samples. In particular, unlike CP-MP that has a shorter organic backbone on the silica surface, the amino groups in the AEP chain tend to interact with the silanol groups on the silica surface causing backbone bending and hence formation of secondary pores in AEP-MP, as indicated by additional shoulder peak at lower field in the room-temperature $^{129}\text{Xe}$ NMR spectrum. The exchange processes of xenon in different adsorption regions were also verified by 2D ESY X H NMR spectroscopy. It is also found that subsequent removal of functional moieties by calcination treatment tends to result in a more severe surface roughness on the pore walls in bifunctional samples compared to monofunctional ones. The effect of hydrophobicity/hydrophilicity of the organoalkoxysilanes on the formation, pore structure and surface property of these functionalized mesoporous silica materials are also discussed.

Introduction

Organically modified mesoporous silicas prepared by either direct synthesis or post-synthesis modification/functionozation have attracted much attention due to their potential applications as selective catalysts, adsorbents, and sensors. To realize these applications, it is essential to obtain capabilities in custom-tailoring the surface properties and in controlling the particle and pore morphologies of these materials. Recently, we have reported an approach that allows a synergistic control over the pore structure, particle morphology, and surface functionalization by introducing different molar ratios of organoalkoxysilane precursors that could provide different non-covalent interactions with the cationic surfactant template, cetyltrimethylammonium bromide (CTAB), in a base-catalyzed condensation of silicate. For example, a series of bifunctional mesoporous silica materials were prepared by introducing different molar ratios of two organoalkoxysilanes, namely 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (AEPTMS) and 3-cyanopropyltriethoxysilane (CPTES) to a base-catalyzed condensation of tetraethoxysilane (TEOS) in the presence of CTAB. These bifunctional mesoporous organic–inorganic hybrid materials exhibited fine-tuned chemical accessibility in terms of $\text{Cu}^{+}$ adsorption capability. However, an unexpected nonlinear correlation between the $\text{Cu}^{+}$ adsorption capability with the amount of AEP groups in such AEP/CP bifunctional silicas were evident, indicating that the CP functionality, which is relatively more hydrophobic in nature, should also play an active role in the observed decrease in chemical accessibility per AEP group. Thus, a more detailed understanding of the conformation of organic moieties and related guest-host interactions in the confined space demands further investigation.

$^{129}\text{Xe}$ NMR spectroscopy is an unique and powerful tool for probing local environments of xenon adsorbed in various systems, such as porous materials, polymers, biomolecules and liquid crystals. Unlike conventional $^{129}\text{Xe}$ NMR in which the nuclear spin polarization is governed by Boltzmann equilibrium, laser-polarized $^{129}\text{Xe}$ NMR facilitates a metastable polarization transfer from the alkali-metal electronic spin to the $^{129}\text{Xe}$ nucleus by the spin exchange optical pumping method, thus capable of enhancing signal sensitivity by $10^{5}$–$10^{6}$ orders of magnitude at dilute Xe loading. Thus, the hyperpolarized (HP) $^{129}\text{Xe}$ NMR technique is particularly useful for systems with low surface area and/or long spin–lattice relaxation times ($T_1$), and has found widespread applications, for examples, in surfaces, nanocrystals or thin films, porous materials, magnetic resonance imaging and medical imaging, and sensors, etc. In the case of conventional $^{129}\text{Xe}$ NMR, the observed $^{129}\text{Xe}$ chemical shift of Xe adsorbed on porous substrates can be expressed as:

$$\delta = \delta_0 + \delta_s + \sigma_{\text{Xe-Ce}} P_{\text{Xe}}$$

where $\delta_0 = 0$ ppm is the reference chemical shift, $\delta_s$ represents the characteristic chemical shift due to Xe-wall interactions, corresponding to the shift at zero Xe loading, and $\sigma_{\text{Xe-Ce}}$ is the contribution due to Xe-Xe interactions, $P_{\text{Xe}}$ is the concentration of Xe in the environment of the surface adsorption site. The last term, $\sigma_{\text{Xe-Ce}} P_{\text{Xe}}$, is the contribution due to Xe-Xe interactions, $P_{\text{Xe}}$ is the concentration of Xe in the environment of the surface adsorption site. The last term, $\sigma_{\text{Xe-Ce}} P_{\text{Xe}}$, is the contribution due to Xe-Xe interactions.
which normally increases linearly with Xe loading, \( \rho_{Xe} \). Whereas for HP,\(^{129}\)Xe NMR, since the experiments are normally carried out at dilute Xe loading, the chemical shift contribution arising from Xe–Xe interactions can be greatly depressed. More recently, similar technique has been applied to probe the geometry and interconnectivity of pores in organic aerogels\(^{17}\) and the properties of amines and alkyl ligands\(^{18}\) of mesoporous silicas modified with alkylsilanes.

The objective of this work is to investigate the structural and surface properties of the aforementioned organic–inorganic hybrid mesoporous materials using variable-temperature (VT) HP-\(^{129}\)Xe NMR and two-dimensional exchange spectroscopy (2D EXSY) NMR techniques.\(^{20}\) A series of bifunctional mesoporous silicas synthesized by introducing different molar ratios of APTMS and CPTES precursors to a base-catalyzed co-condensation of silicate have been examined along with AEP- and CP-monofunctional silicas. Various information regarding to the conformation, hydrophilicity/hydrophobicity, and functionalities of the AEP/CP groups and their correlations with the structural porosity, surface roughness and related Xe-moiety interactions, which can be inferred from the temperature dependence of \(^{129}\)Xe characteristic chemical shift \((\delta_x)\), has been investigated and compared with the \(^{13}\)C CP-MAS NMR results reported earlier.\(^{5}\)

### Experimental section

#### Materials

Various mono- and bifunctional mesoporous silicas were prepared following the procedures described in an earlier report.\(^{5}\) Accordingly, a series of micrometre-sized particles (MP) of organic–inorganic hybrid materials with varying molar concentrations of organoalkoxysilane precursors ranging from 100% APTMS to 100% CPTES, with the total amount of APTMS + CPTES relative to TESO fixed at 12.8 mol% were obtained. Herein, we denote the monofunctionalized micro-particles as AEP-MP or CP-MP and the bifunctionalized materials as AEP/(CP(x)/y)-MP, where \(x/y\) denotes the relative ratio of APTMS/CPTES in the initial reaction mixture. All samples were template extracted either by acid extraction or by calcination treatments. Further experiments by \(^{13}\)C CP-MAS NMR confirmed that no extra organic groups other than the designated functional groups are present in the AEP/(CP(x)/y)-MP samples, indicating a complete removal of template by the aforementioned treatments.\(^{26}\) Separate experiments by field-emission scanning electron microscopy (FE-SEM) revealed that, in contrast to the pure MCM-41 mesoporous silica synthesized under the same conditions, the AEP/CP-MP samples exhibit spherical shapes, whereas AEP-MP and CP-MP resulted in sphere and rod shapes and sizes, i.e., from spheres with an average diameter of 3 \(\mu\)m to rods with an average size of 1.0 \(\times\) 0.2 \(\mu\)m.\(^{26}\) The average diameters of AEP/CP-MP spheres decreased as the relative ratio \((x/y)\) changed from 5/5 to 1/9. Calcination treatments of the samples were carried out at 823 K under flowing air for 4 h, they are denoted as AEP-MP and AEP/(CP(x)/y)-MP-MPC, respectively.

#### HP-\(^{129}\)Xe NMR studies

All samples were compressed by pressure of 100 MPa for 10 min, crashed into small pellets, and then dehydrated under vacuum at 423 K for 12 h prior to the HP \(^{129}\)Xe NMR experiments. The above post-synthesis treatment procedure effectively eliminate the effect arising from fast exchange between Xe adsorbed in the intra- and inter-particle voids while avoid jeopardizing the textural structures of the samples.\(^{21}\) Detailed descriptions of the continuous-flow optical pumping apparatus for fabricating the HP-\(^{129}\)Xe gas can be found elsewhere.\(^{19}\) Briefly, the spin-exchange optical pumping process was facilitated by introducing a gas mixture of 97% He, 1% N\(_2\), and 2% Xe (natural abundance) into the pumping cell (containing 1 g Rb metal and placed under a magnetic field of \(ca.\) 200 G) maintained at 4 atm and 423 K, while subjecting to irradiation of left-circularly polarized light (wavelength 794.8 nm) generated by a diode laser (Coherent; FAP-30). The resulting gas mixture containing HP-\(^{129}\)Xe (polarization \(ca.\) 2.4%) was introduced into a home-built NMR tube \((\text{tube} \; \text{via} \; 1/16 \; \text{inch Teflon tubing and continuously flew through the sample at } ca.\; 100 \; \text{sec} \; \text{min}^{-1} \; \text{at 1 atm}}\), the gas mixture was eventually vent to the atmosphere. As such, this corresponds to an equilibrium Xe partial pressure of \(ca.\; 15.2 \; \text{Torr}\). It has been found that the presence of He and N\(_2\) buffer gases has no significant effect on the resultant HP-\(^{129}\)Xe NMR spectrum.\(^{12}\) Separate experimental tests using the batch setup confirmed that the achievable signal enhancement factor was \(ca.\; 3500\).

All HP-\(^{129}\)Xe NMR spectra were acquired on a Bruker Avance 300 NMR spectrometer at Larmor frequency of 83.012 MHz using a single-pulse sequence with a \(\pi/2\) pulse (15 \(\mu\)s) and a recycle delay of 5 s. Typically, 64–256 free induction decay (FID) signals were accumulated for each spectrum. VT experiments were carried out in the temperature range 160–298 K. The actual sample temperature was calibrated using the \(^{207}\)Pb NMR signal of solid Pb(NO\(_3\))\(_2\).\(^{22}\) The \(^{129}\)Xe NMR chemical shift was referenced to extremely diluted xenon gas (as 0 ppm). To verify the origins of the observed \(^{129}\)Xe resonances, additional experiments were also carried out by 2D EXSY \(^{129}\)Xe NMR technique\(^{20}\) at room temperature (298 K) using a 90–\(t_1\)–90–\(t_2\)–90–\(t_2\) pulse sequence. The 2D NMR spectrum was acquired with a spectral width of 12.5 KHz and 512 and 2048 points were acquired for the \(t_1\) and \(t_2\) dimensions, respectively, while changing the mixing time \((t_m)\) from 1 to 25 ms.

### Results and discussion

#### VT HP-\(^{129}\)Xe NMR

Figs. 1 and 2 display the VT HP-\(^{129}\)Xe NMR spectra of various functionalized materials before and after the calcination, respectively. In general, most spectra exhibit two main resonances, the sharp peak at \(ca.\; 0\; \text{ppm}\) can be unambiguously assigned to free gaseous Xe whereas the peak with higher chemical shift (or lower field) is attributed to Xe adsorbed in the mesopores. The observed chemical shift should be a weighted average of the fast exchange between Xe residing in different adsorption regions in the mesopores (see below). An expected increase in \(^{129}\)Xe chemical shift of the adsorbed Xe with decreasing temperature was observed for each sample, as depicted in Fig. 3. In view of the very low Xe loading (15.2 Torr) in the continuous-flow HP-\(^{129}\)Xe NMR experiments, it is anticipated that only a dilute adsorption layer with a very weak contribution of Xe–Xe interactions to the observed chemical shift. As the temperature decreases, the adsorbed Xe should spend a longer time residing on the pore surface and thus causing the \(^{129}\)Xe NMR resonance to shift downward. For \(T < 200\; \text{K}\), a sharp increase in chemical shift is evident, which may be attributed to the condensation of xenon. Only below such low temperature does the chemical shift contribution due to Xe–Xe interactions become significant. Eventually, the \(^{129}\)Xe chemical shift is expected to approach that of bulk liquid Xe (ca. 255 ppm) and solid Xe (ca. 305 ppm).

Unlike calcined samples whose \(^{129}\)Xe NMR spectra of the adsorbed Xe all exhibited a symmetrical narrow peak through-out the temperature examined (Fig. 2), broader and somewhat asymmetric lines were observed for most of the functionalized AEP/CP-MP samples. For example, two overlapped peaks at \(512\) and \(2048\) points were acquired for the \(t_1\) and \(t_2\) dimensions, respectively, while changing the mixing time \((t_m)\) from 1 to 25 ms.
MCM-41 mesoporous silica at high surface coverage (1.31 nm$^2$/C$_2$)$^{19}$ In this context, the AEP groups existing on the mesoporous silica surfaces might form an ‘organic phase’ in which the diffusional motion of Xe would be hindered provided that the surface coverage of the organic groups was high enough. The effect of such ‘organic phase’ would be two-fold. First, it might block Xe from accessing to the bare silica surface. Second, it might interact with Xe to result in an additional contribution to the $^{129}$Xe chemical shift. Thus, we attribute a priori the shoulder peak at 98 ppm to Xe residing in the surface ‘organic phase’ and the main peak at ca. 87 ppm to ‘mobile’ Xe in mesopores. Upon decreasing temperature, the latter Xe tends to spend longer time on the pore surfaces grafted with AEP groups, hence, resulting the resonance to move toward down-field (higher chemical shift) and eventually the two lines merge to reveal a singlet at low temperature.

Similarly, the increase in $^{129}$Xe chemical shift (Fig. 3) and slight linewidth broadening observed for bifunctional samples (Fig. 1) compared to the calcined samples (Fig. 2) may also be attributed to the presence of organic groups on the surface of mesoporous silicas, which tends to slow down the exchange of Xe between different local environments.

The interconnectivity between different Xe adsorption regions in the mesopores of AEP-MP was further examined by 2D EXSY NMR spectroscopy (Fig. 4a-c). Accordingly, the exchange between regions with different chemical shifts was revealed by the cross-peaks between the signals of the exchanging sites. Fig. 4a-c showed the 2D spectra of an AEP-MP sample using an exchange time ($t_m$) of 1, 5 and 25 ms, respectively. The observed three diagonal peaks at ca. 0, 87, and 98 ppm in the vertical (F2) axis were assigned (vide supra) to gaseous Xe, ‘mobile’ Xe adsorbed in the mesopores, and Xe residing in the ‘organic phase’, respectively. In addition, the off-diagonal peaks intensified with increasing exchange times set in the experimental pulse sequence. For example, traces of cross peaks appeared at $t_m = 1$ ms (Fig. 4a) indicating that the exchange between the ‘mobile’ (87 ppm) and gaseous (0 ppm) Xe occurred even on a time scale less than a fraction of 1 ms. As $t_m$ is increased to 5 ms, wherein such exchange became more pronounced, the exchange between ‘mobile’ Xe adsorbed in the mesopores and Xe in the ‘organic phase’ (98 ppm) began to take place (Fig. 4b). Eventually, the exchange between the ‘organic phase’ and the gaseous Xe’s was also evident with $t_m = 25$ ms (Fig. 4c), indicating that the exchange between Xe species in different adsorption regions and the gas phase appeared to be completed. Consequently, it can be concluded that the exchange rates between different environments follow the following trend: $k_{gm} > k_{mo} > k_{go}$, where $k_{mo}$ denotes the exchange rate between ‘mobile’ Xe in the mesopores and Xe residing in the ‘organic phase’ and $k_{gm}$ and $k_{go}$ denote exchange rates between gaseous-‘mobile’ Xe and gaseous-‘organic phase’ Xe, respectively, as illustrated in Fig. 5. It is envisaged

![Fig. 1 VT HP-$^{129}$Xe NMR spectra of various functionalized AEP/CP(x/y)-MP mesoporous silicas.](image-url)
that the slower rate observed for $k_{go}$ may manifest itself via the other two exchange processes. Accordingly, the dynamic phenomena obtained from the $^{129}$Xe 2D EXSY experiments provide strong supports to the aforementioned peak assignments for the room-temperature $^{129}$Xe NMR spectrum observed for AEP–MP.

In the VT HP-$^{129}$Xe NMR experiments, the concentration of Xe in the gas mixture flowing through the sample placed in the detection (NMR coil) region was extremely low (ca. 2%, equivalent to a Xe partial pressure of 15.2 Torr) and thus could be fitted adequately to the dilute adsorption (Henry’s Law) regime. Therefore, the temperature dependence of the observed $^{129}$Xe chemical shift, particularly for $T > 200$ K, could be approximated by the following equation derived based on the fast-exchange model:\(^{23}\)

$$\delta = \delta_s \left[ 1 + \frac{V}{S K_0 R T^{1/2} \exp(\Delta H_a / RT)} \right]^{-1}$$  \hspace{1cm} (2)

where $\delta_s$ is the characteristic chemical shift, representing the shift arising from Xe–surface interactions, $V$ and $S$ represent the free volume and specific surface area of the mesoporous materials, respectively, $R$ is the universal gas constant, $K_0$ is the pre-exponent of Henry’s constant, and $\Delta H_a$ is the adsorption enthalpy. Values of $V$ and $S$ can be derived from $\text{N}_2$.

Fig. 2 VT HP-$^{129}$Xe NMR spectra of various calcined AEP/CP(x/y)-MPC mesoporous silicas.

Fig. 3 Variations of HP-$^{129}$Xe NMR chemical shift with temperature observed for various samples.
adsorption/desorption data measured at 77 K and the other parameters \( \delta_s, K_0 \) and \( \Delta H_s \) can be determined by least-square fittings of the observed VT HP-\(^{129}\)Xe NMR chemical shift results to eqn. (2), as summarized in Table 1. Since the chemical shift contribution arising from Xe-Xe interactions becomes more significant at low temperature, only those experimental results obtained at \( T > 200 \) K were used during data fittings.\(^{19,21,24}\) All observed \( \Delta H_s \) values fall in the range of 9–17 kJ mol\(^{-1}\), as expected for physical adsorption of Xe.

**Analysis of characteristic chemical shifts (\( \delta_s \))**

Since the characteristic chemical shift, \( \delta_s \), reflects interactions between Xe and the surface of the substrate. In this context, for the functionalized porous materials, the values of \( \delta_s \) should arise from Xe interacting with the bare surface of the mesoporous silica as well as with the soft organic moieties. Therefore, it would be helpful to compare the \( \delta_s \) contribution due to Xe-moieties interactions observed for various bifunctional mesoporous MCM-41 samples investigated herein. Since the \( \delta_s \) values observed for CP-MPC and AEP-MPC samples after removal of organic ligands by calcination were 104.9 and 106.0 ppm, respectively (Table 1), which are nearly identical (within experimental error; \( ca. \pm 1 \) ppm) to that of 105.4 ppm found previously for a bulk siliceous MCM-41 material (pore diameter \( ca. 2.54 \) nm)\(^{19,25}\) synthesized using the conventional procedure.\(^{25}\) Foreseeably, the surface properties of these materials, as detected by the adsorbed Xe, should be practically the same. On the other hand, an averaged \( \delta_s \) an increase of \( ca. 7–9 \) ppm, was observed (Fig. 6) for the calcined samples originally prepared with various AEP/CP/PC (or X/Y) ratios compared to the calcined AEP-MPC or CP-MPC samples, indicating a more severe surface roughness\(^{26}\) in the bifunctional than monofunctional mesoporous silica materials after calcinations.

It is also evident that the \( \delta_s \) values observed for bifunctionalized AEP/CP-MP materials, which seem to scatter in the 118–122 ppm range, are significantly higher than the calcined samples (Fig. 6 and Table 1). Xenon–organic-moiety interactions should be responsible for the observed differences. Accordingly, characteristic chemical shift contribution due to Xe-moiety interactions, \( \delta_{s,moiety} \), can be derived by the simple relation:

\[
\delta_{s,moiety} = \delta_{s,fun} - \delta_{s,calc}
\]

where \( \delta_{s,fun} \) and \( \delta_{s,calc} \) represent the \( \delta_s \) values obtained from the functionalized AEP/CP-MP and calcined AEP/CP-MPC samples, respectively. However, since Xe-moiety interactions and hence \( \delta_{s,moiety} \) should be strongly related to the arrangements, functionality, chain length and coverage (\( \rho \)) of the organic moieties, it is preferable to infer the Xe–moiety interactions in terms of deshielding medium contribution (\( -\sigma_{m,moiety} \)), which can be derived by:\(^{19,26}\)

\[
-\sigma_{m,moiety} = \frac{\delta_{s,moiety}}{\rho}
\]

Accordingly, the values of \( -\sigma_{m,moiety} \) derived from eqn. (4) are also depicted in Table 1. It is intriguing that the \( -\sigma_{m,moiety} \) values obtained from the monofunctional and bifunctional materials fall into two distinct regions, the former observed for CP-MP and AEP-MP samples are higher than 17.7 ppm nm\(^{-2}\) whereas the latter from series of AEP/CP-MP samples are lower than 11.2 ppm nm\(^{-2}\) (Table 1). This could be attributed to the more inhomogeneous distribution of organic moieties in the bifunctional materials compared to the monofunctional ones, as could also be inferred from the discrepancies in the observed values of \( \delta_{s,calc} \) and consequently the values of \( \delta_{s,moiety} \) listed in Table 1. Unfortunately, further justification of the variation of \( -\sigma_{m,moiety} \) with AEP/CP/PC (or X/Y) ratios could not be made directly based on the results obtained from the present study.

Alternatively, complementary information may be inferred from a similar system. In a previous study,\(^{19}\) we employed the similar VT HP-\(^{129}\)Xe NMR technique to probe the surface properties of mesoporous MCM-41 silica grafted with various alkylsilanes by post-synthesis silylation treatment. It was found that the characteristic chemical shifts responsible for Xe-surface interactions exhibited strong correlations with both the surface coverage and carbon chain length (\( nc \)) of the grafted alkylsilanes. Consequently, the deshielding medium contribution due to the individual alkyl ligand could be deduced based on the group contribution analysis by the following empirical relationship:\(^{19}\)

\[
-\sigma_{m,moiety} = 2.96nc + 2.35
\]

Regardless of the differences in the chemical nature of organic ligands on the pore surface of the mesoporous silica between the two sample systems, if one take \( nc = 5 \) for CPTES, an estimated \( -\sigma_{m,moiety} \) value of \( ca. 17.2 \) ppm nm\(^{-2}\) is derived for CP-MP using eqn. (5), comparable to the value 17.7 ppm nm\(^{-2}\)
By the same token, if one takes into account the shift of the Xe–C and Xe–N moieties are practically the same as in the aforementioned alkyl-grafted MCM-41 samples. The reason for such geometric constraints. Conversely, such a bent backbone arrangement was likely to increase the atomic density of the organic phase causing Xe to be ‘entangled’ in the organic phase and thus gave rise to a shoulder peak at 98 ppm. In contrast, the CP and the alkyl moieties existing in the CP-MP and the aforementioned alkyl-grafted MCM-41 samples do not have any basic amino groups that can interact with the surface silanols. In fact, conformations with flexible organic chains experienced by the adsorbed Xe were attributed to the obtained –σ moiety. Although this hypothesis is based on a simplified model, it is in good agreement with our previous findings using 13C CP-MAS NMR, which revealed that the CP backbone in CP-MP is more mobile than that of AEP in AEP-MP.5 Derived from the fitting the temperature dependent chemical shift data (T > 200 K) to eqn. (2). 8 Derived from eqn. (3). 9 Taken from ref. 5, data were derived from 29Si MAS NMR results.

Table 1 Physical properties and NMR parameters of various samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>V/cm³ g⁻¹</th>
<th>S/m² g⁻¹</th>
<th>δXe/ppm</th>
<th>10⁻¹²Kₒ Torr⁻¹ m⁻²</th>
<th>ΔHₓkJ mol⁻¹</th>
<th>δₓ molény ppm⁻¹</th>
<th>ρ/nm⁻²</th>
<th>σₓ molény ppm·nm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP-MP</td>
<td>0.68</td>
<td>1012</td>
<td>118.2 ± 1.2</td>
<td>1.4 ± 0.9</td>
<td>16.2 ± 1.7</td>
<td>13.3</td>
<td>0.75</td>
<td>-17.7</td>
</tr>
<tr>
<td>AEP/CP(1/9)-MP</td>
<td>0.51</td>
<td>967</td>
<td>118.4 ± 0.5</td>
<td>1.2 ± 0.4</td>
<td>17.1 ± 0.9</td>
<td>6.4</td>
<td>1.02</td>
<td>-6.3</td>
</tr>
<tr>
<td>AEP/CP(2/8)-MP</td>
<td>0.43</td>
<td>801</td>
<td>121.7 ± 0.9</td>
<td>5.8 ± 0.4</td>
<td>12.8 ± 0.6</td>
<td>7.7</td>
<td>1.05</td>
<td>-7.3</td>
</tr>
<tr>
<td>AEP/CP(3/7)-MP</td>
<td>0.56</td>
<td>981</td>
<td>121.3 ± 0.5</td>
<td>6.1 ± 1.0</td>
<td>12.7 ± 0.3</td>
<td>8.2</td>
<td>0.73</td>
<td>-11.2</td>
</tr>
<tr>
<td>AEP/CP(5/5)-MP</td>
<td>0.38</td>
<td>722</td>
<td>118.6 ± 0.6</td>
<td>7.6 ± 0.8</td>
<td>11.7 ± 0.1</td>
<td>6.0</td>
<td>0.92</td>
<td>-6.5</td>
</tr>
<tr>
<td>AEP-MP</td>
<td>0.57</td>
<td>806</td>
<td>119.2 ± 1.1</td>
<td>2.6 ± 1.2</td>
<td>14.6 ± 1.2</td>
<td>13.2</td>
<td>0.56</td>
<td>-23.6</td>
</tr>
<tr>
<td>CP-MPC</td>
<td>0.70</td>
<td>1149</td>
<td>104.9 ± 1.0</td>
<td>3.9 ± 1.1</td>
<td>12.9 ± 0.8</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>AEP/CP(1/9)-MPC</td>
<td>0.50</td>
<td>958</td>
<td>112.0 ± 1.3</td>
<td>4.2 ± 1.1</td>
<td>10.5 ± 0.6</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>AEP/CP(2/8)-MPC</td>
<td>0.50</td>
<td>951</td>
<td>114.0 ± 1.4</td>
<td>4.5 ± 1.2</td>
<td>8.6 ± 0.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>AEP/CP(3/7)-MPC</td>
<td>0.54</td>
<td>1027</td>
<td>113.1 ± 0.8</td>
<td>7.5 ± 1.7</td>
<td>9.2 ± 0.3</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>AEP/CP(5/5)-MPC</td>
<td>0.58</td>
<td>982</td>
<td>112.6 ± 0.5</td>
<td>5.5 ± 1.4</td>
<td>8.5 ± 0.4</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>AEP-MPC</td>
<td>0.66</td>
<td>1019</td>
<td>106.0 ± 1.9</td>
<td>3.9 ± 2.4</td>
<td>13.1 ± 1.6</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*a* Taken from ref. 5, data were obtained from N₂ adsorption/desorption experiments at 77 K. 

**Formation mechanism and surface properties**

Assuming that the calcination treatment was sufficient in removing all organic moieties without jeopardizing the structure of the mesoporous silica, the aforementioned surface roughness observed for the calcined AEP/CP-MP samples (Fig. 6) should be strongly related to the synthesis conditions. These functionalized mesoporous silicas were prepared via a co-condensation reaction of TEOS with organoalkoxysilanes in a diluted aqueous solution of cetyltrimethylammonium bromide (CTAB). Based on the conventional surfactant-templated mechanism proposed for the formation of mesoporous MCM-41 materials under similar conditions, the oligomeric silicate polyanions acting as multidentate ligands should interact with cationic surfactant head groups to form surfactant/silica bilayers of lamellar phase. Subsequent condensation of these silicate clusters would lead to a reduction of negative charges at the interface. As a result, the different charge-density matching between the surfactant and the silicate provoked the formation of a hexagonal surfactant–silicate composite which yielded the mesoporous structure after removal of surfactant template. However, for the multifunctional materials studied obtained from this study. This is, of course, based on an oversimplified assumption that similar Xe-moieties were adsorbed in the two different mesoporous materials, namely alkylsilane-grafted MCM-41 and CP-MP that have CH₃ and CH₂ as end groups, respectively, i.e., the intrinsic chemical shift of the Xe–C and Xe–N moieties are practically the same because of the same atomic number of the organic backbone. By the same token, if one takes nₓ = 10 for AEP/CP'(x)/MPC, an estimated —σₓ molény value of ca. 32.0 ppm nm⁻² for the AEP moiety in AEP-MP could be obtained. However, a significantly smaller value of 23.6 ppm nm⁻² was observed, which could be fitted to a value of nₓ = 7 by using eqn. (5). Furthermore, it is noteworthy that the presence of two broad, overlapping ¹²⁹Xe resonances in the spectra of AEP-MP around room temperature (Fig. 1a) clearly suggested the existence of a strong Xe-AEP interaction considering its medium coverage (0.56 nm⁻²) and backbone length. In this context, the observation mentioned above could be explained by a “prone” or “bent” conformation of the AEP moiety on the mesopore surfaces as depicted in Fig. 7. As we reported in a previous study, the basic amino groups of the AEP functionality indeed could strongly interacted (hydrogen-bonded) with the silanol groups on the surface of the mesoporous silica. Consequently, the AEP group will be less flexible and hence result in a decrease in interactions between Xe and each constitutional atom due to such geometric constraints. Conversely, such a bent backbone arrangement was likely to increase the atomic density of the organic phase causing Xe to be ‘entangled’ in the organic phase and thus gave rise to a shoulder peak at 98 ppm. In contrast, the CP and the alkyl moieties existing in the CP-MP and the aforementioned alkyl-grafted MCM-41 samples do not have any basic amino groups that can interact with the surface silanols. In fact, conformations with flexible organic chains experienced by the adsorbed Xe were attributed to the obtained —σₓ molény. Although this hypothesis is based on a simplified model, it is in good agreement with our previous findings using ¹³C CP-MAS NMR, which revealed that the CP backbone in CP-MP is more mobile than that of AEP in AEP-MP. 

**Fig. 6** The characteristic chemical shifts (δXe) observed for various functionalized AEP/CP'(xy)/MP (closed symbol) and calcined AEP/CP'(xy)/MPC (open symbol) materials against the percentage of AEPTMS in terms of total organoalkoxysilanes.

**Fig. 7** Schematic illustrations of possible AEP backbone arrangements on the silica surfaces of AEP-MP material.

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herein, the presence of additional organic groups (AEP and/or CP) that are covalently bonded to the silicate surface would foreseeably alter the interfacial property of the surfactant-silicate assemblies. More specifically, the presence of the hydrophobic CP groups are likely to penetrate into the surfactant phase during formation of the surfactant-silicate interface in a way analogous to MCM-41 formation thus leading to a similar silicate ordering and hence a more uniform (smoother) silica surface, as evidenced by the similar δ values observed for CP-MPC (104.9 ppm) and Si-MCM-41 (105.4 ppm). On the other hand, the more hydrophilic AEP moieties tend to occupy the space between the surfactant and the silicate forming a surfactant-AEP/silicate interface. Although only a slightly higher δ value was observed for AEP-MPC (106 ppm) compared to CP-MPC and Si-MCM-41, indicating a slightly rougher silica surface. It is noteworthy that the interactions between the amino groups on the AEP chains and the neighboring silanol groups indeed play an important role in curling the surfactant micelles, whereas the hydrophilic CP moieties would lead to a non-uniform surfactant/silicate interface. For example, the more hydrophilic CP moieties would tend to closely associate themselves with the surfactant micelles, whereas the hydrophobic and spatially demanding AEP-bonded silicas would likely be slightly further away from the micellar interface in order to accommodate a less favorable charge-density matching. Such an effect could perhaps provide an explanation to the more sev...


