Probing the Alkyl Ligands on Silylated Mesoporous MCM-41 Using Hyperpolarized \(^{129}\)Xe NMR Spectroscopy

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Variable-temperature hyperpolarized (HP) \(^{129}\)Xe NMR spectroscopy has been employed to characterize surface properties of mesoporous MCM-41 modified by silylation treatment. The characteristic chemical shifts responsible for \(^{129}\)Xe–surface interactions exhibit strong correlations with both the surface coverage and chain length of the grafted alkylsilanes. Consequently, the deshielding medium contribution due to individual alkyl ligand can be deduced based on the group contribution analysis revealing the potential use of HP \(^{129}\)Xe NMR for probing the surface properties of organic-functionalized porous materials.

1. Introduction

Recent developments in custom-tailoring the surface properties of inorganic–organic composite materials by direct synthesis or postsynthesis modification/functiononalization have attracted much attention.\(^1\) In particular, surface grafting of mesoporous silicas\(^2\) with organic moieties that can be attained either by silylation\(^2\)–\(^9\) or by esterification\(^10\) of the surface silanol groups\(^6\)–\(^8\) existing on the channel walls provides opportunities for precise control of pore sizes, surface properties, and stabilities\(^4\)–\(^6\) of the mesoporous materials rendering for advance applications in many areas of science and technology.\(^1,11\) Although intensive studies on modification of MCM-41 and other mesoporous materials by silylation have been made, some problems, such as the nature, distribution, and coverage of the alkyl ligands on the pore walls, still demand a better understanding that the present work aims to provide. Here, we report the first use of hyperpolarized (HP) \(^{129}\)Xe NMR\(^12\) for measuring the shielding constants of pairwise interactions between \(^{129}\)Xe and the alkylsilane constituent groups (\(\text{Si}–\text{CH}_2–, \text{CH}_2–, \text{and CH}_3–\)) grafted on the internal pore walls of siliceous MCM-41.

2. Experimental Section

Preparation and Physical Properties of Silylated MCM-41. A siliceous MCM-41 molecular sieve (pore diameter 2.6 nm, hereafter denoted as SM41) was prepared by the “delayed neutralization” procedure\(^1\) using cetyltrimethylammonium bromide as the structure-directing agent and sodium silicate as the silica source. Silylated MCM-41 samples with different coverages (\(\rho\)) and carbon chain lengths (\(n\)) of alkylsilanes, denoted as \(n\text{CM41}(\rho)\), were obtained by refluxing the parent MCM-41 and desired amount of various alkyl(trichlorosilanes), that is, \(\text{CH}_3(\text{CH}_2)_{n-1}\text{SiCl}_3\) (\(n = 1, 4, 8, \text{and} 12\)), with toluene at 353–373 K for 1–5 h, filtering, and then drying at 373 K for at least 3 h. Table 1 summarizes the physical properties of silylated MCM-41 samples. The total pore volume (\(V\)) and specific surface area (\(S\)) for each sample were determined from \(N_2\) adsorption/desorption measurements (Micromeritics; ASAP 2010) done at 77 K. It is clear that grafting of organic moieties onto the inner surfaces of MCM-41 (see Supporting Information) leads to consistent decreases in both \(V\) and \(S\). The surface coverage, \(\rho\), of alkylsilane ligand for each sample was determined by elemental analysis (Perkin-Elmer; 2400II) according to the following formula:

\[
\rho = \frac{W_{N\text{a}}(nM)}{\{1 - [W/(nM)][nM_C + (2n + 1)M_H]\}S}
\]

where \(W\) is the carbon content in gram per gram sample, \(N_a\) is the Avogadro’s number, and \(M_C\) and \(M_H\) indicate the atomic mass of carbon and proton, respectively.

Variable-Temperature (VT) HP \(^{129}\)Xe NMR Experiments. HP \(^{129}\)Xe gas was fabricated by an optical pumping setup consisting of a 30-W diode laser with a wavelength of 794.8 nm (Coherent; FAP-30), a circular polarizer unit (Coherent; CPU), a mass flow controller (Matheson; 8272-0413), and an optical pumping cell containing about 1 g of Rb metal. The optical pumping station was placed in the fringe field (ca. 200
The temperature was calibrated using the 209 Pb NMR signal of solid samples. The measurements are in excellent agreement with earlier studies. A further decrease in temperature (<210 K) results in a subtle increase in the CS and a gradual increase in the line width (Δω) of 1.09 and 1.31 nm⁻², respectively. The VT spectra obtained with a Xe partial pressure of about 15.2 Torr was facilitated by introducing a gas mixture (97% He, 1% N₂, and 2% natural Xe) into the pumping cell. The pumping process was effective in anchoring the alkylsilanes on the surfaces (see Supporting Information) and consequently alters the local environments that can be detected by the adsorbed Xe atoms. Obviously, the aforementioned surface silylation treatment is effective in anchoring the alkylsilanes on the surfaces (see Supporting Information) and consequently alters the local environments that can be detected by the adsorbed Xe atoms. In this context, the presence of alkylsilanes in modified samples not only introduces an additional (Xe–ligand interactions) contribution to the CS but also creates, to various extents, hindrances to the pathways of Xe or even different pore environments depending on n and ρ of the samples. For example, at the extremes of long alkyl chain length and high surface coverage, as for the case of sample 12CM41(1.31), two broad overlapped peaks at about 103 and 144 ppm were observed at increasing alkyl chain lengths as well as population densities of the alkylsilanes grafted on the inner pore walls of MCM-41.

### TABLE 1: Physical Properties and NMR Parameters of the Parent and Silylated MCM-41 Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Silanizing reagent</th>
<th>n</th>
<th>V° (cm³/g)</th>
<th>S° (m²/g)</th>
<th>V/S (nm)</th>
<th>Kc (×10⁻¹¹ Torr⁻¹ m⁻²)</th>
<th>ΔHc (kJ/mol)</th>
<th>Δω (ppm)</th>
<th>ρ (nm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM41</td>
<td>0.11</td>
<td>1</td>
<td>1.03</td>
<td>1075</td>
<td>0.96</td>
<td>10.2 ± 2.6</td>
<td>16.8 ± 0.6</td>
<td>105.4 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>1CM41(1.33)</td>
<td>CH₃SiCl₃</td>
<td>4</td>
<td>0.89</td>
<td>1001</td>
<td>0.89</td>
<td>6.2 ± 2.4</td>
<td>17.8 ± 1.0</td>
<td>112.2 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>4CM41(1.09)</td>
<td>CH₃(CH₂)₄SiCl₂</td>
<td>4</td>
<td>0.90</td>
<td>1047</td>
<td>0.86</td>
<td>10.2 ± 1.6</td>
<td>16.1 ± 0.4</td>
<td>109.4 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>8CM41(1.11)</td>
<td>CH₃(CH₂)₈SiCl₄</td>
<td>4</td>
<td>0.67</td>
<td>994</td>
<td>0.67</td>
<td>14.6 ± 5.5</td>
<td>15.3 ± 1.0</td>
<td>120.9 ± 1.2</td>
<td></td>
</tr>
<tr>
<td>8CM41(1.04)</td>
<td>CH₃(CH₂)₈SiCl₄</td>
<td>8</td>
<td>0.93</td>
<td>1042</td>
<td>0.89</td>
<td>12.7 ± 1.7</td>
<td>16.0 ± 0.3</td>
<td>107.0 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>12CM41(1.08)</td>
<td>CH₃(CH₂)₁₂SiCl₈</td>
<td>12</td>
<td>0.46</td>
<td>573</td>
<td>0.80</td>
<td>2.7 ± 1.2</td>
<td>19.4 ± 0.8</td>
<td>145.6 ± 0.7</td>
<td></td>
</tr>
<tr>
<td>12CM41(1.31)</td>
<td>CH₃(CH₂)₁₂SiCl₈</td>
<td>12</td>
<td>0.11</td>
<td>44</td>
<td>2.50</td>
<td>9.4 ± 4.0</td>
<td>19.8 ± 1.1</td>
<td>155.4 ± 1.1</td>
<td></td>
</tr>
</tbody>
</table>

a Obtained from N₂ adsorption/desorption measurements (see Supporting Information). b Obtained by fitting the temperature-dependent ¹²⁹Xe CS data to eq 2.

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3. Results and Discussion

Figure 1a–c illustrates the typical VT-HP ¹²⁹Xe NMR spectra for parent (SM41) and silylated MCM-41 samples, namely, 4CM41(1.09) and 12CM41(1.31), modified using butyltrichlorosilane and dodecyltrichlorosilane and possessing ρ values of 1.09 and 1.31 nm⁻², respectively. The VT spectra obtained from SM41 show a single, symmetric resonance at a higher CS (Figure 1d) and decrease in the line width (Δω; Figure 1a) because of an increase in Xe adsorption. However, a further decrease in temperature (T < 210 K) results in a subtle increase in the CS and a gradual increase in Δω that can be ascribed to the condensation effect. The above observations are in excellent agreement with earlier studies.

In the case of silylated samples, introduction of organic ligands onto the pore walls of the mesoporous silica leads to the expected increase in both the CS and Δω. Moreover, a consistent increase was also observed for the CS and Δω with increasing alkyl chain lengths as well as population densities of the alkylsilanes grafted on the inner pore walls of MCM-41.
210 K were used during data fittings. All observed overall sample weight, that is, the weight of the MCM-41 silica were derived from N$_2$ adsorption isotherms at 77 K, and the VT-HP 129 Xe CS results to eq 2. Because the CS contribution decreasing temperature especially below the reflection point (temperature variation) and the two peaks gradually merge in smaller voids surrounded by the alkylsilanes. That the latter weaker peak at 144 ppm is most likely due to Xe “entangled” samples with shorter alkyl chain lengths (ligand grafted surface, as the single peak observed for silylated 41 materials, prepared by silylation treatment using various aminosilane-functionalized MCM-41 samples also showed the same linear dependence of $\delta_i$ with $\rho$.

Presumably, $\delta_i$ should be the sum of two contributions, namely, $\delta_{\text{MCM}}$ and $\delta_{\text{org}}$, arising from Xe–silica wall and Xe–moeity interactions, respectively. Because $\delta_{\text{MCM}}$ can be directly obtained from the SM41 sample (105.4 ppm), the explicit dependence of $\delta_{\text{org}}$ on $\rho$ can then be expressed as

$$\delta_{\text{org}} = -\sigma_{\text{org}} \rho \tag{3}$$

where $-\sigma_{\text{org}}$ represents intrinsic shielding due to intermolecular van der Waals Xe–alkyl ligand interactions. Moreover, the $-\sigma_{\text{org}}$’s so determined are found to show a strong correlation with $n$ (Figure 2b). The linear dependence of $-\sigma_{\text{org}}$ on $n$ can be interpreted on the basis of a group contribution analysis proposed earlier for Xe dissolved in linear solvents. Accordingly, $-\sigma_{\text{org}}$ can be expressed by pairwise additive intermolecular Xe–ligand shielding functions:

$$\sigma_{\text{org}} = \sum_i \sigma_i = (\sigma_{\text{CH}_3} - \sigma_{\text{CH}_2}) + n\sigma_{\text{CH}_2} \tag{4}$$

where $-\sigma_{\text{CH}_3}$ and $-\sigma_{\text{CH}_2}$ are the deshielding medium contributions due to methyl and methylene groups, respectively. Thus, an explicit value of $-\sigma_{\text{CH}_3}$ and $-\sigma_{\text{CH}_2}$ can be extracted as 5.31 and 2.96 ppm nm$^2$, respectively. Consequently, $\delta_i$ can be expressed by a simple empirical relation in terms of $n$ and $\rho$:

$$\delta_i = 105.4 + \rho(2.35 + 2.96n) \tag{5}$$

However, it is noted that the $\sigma_{\text{CH}/\sigma_{\text{CH}_2}}$ ratio of 1.79 obtained in this study deviates from 1.2 to 1.26 found for Xe dissolved in linear solvents. The discrepancy is likely due to additional contributions arising from (i) deshielding of the Si–CH$_2$ end groups that were covalently bonded with the silica framework and/or (ii) the bulk magnetic susceptibility effect. Unfortunately, these cannot be obtained directly in this study. Alternatively, if one takes the theoretical finding of $\sigma_{\text{CH}/\sigma_{\text{CH}_2}}$ = 1.216 into account and by taking

$$\sigma_{\text{org}} = \sum_i \sigma_i = (\sigma_{\text{CH}_3} - \sigma_{\text{CH}_2}) + (\sigma_{\text{Si–CH}_3} - \sigma_{\text{CH}_2}) + n\sigma_{\text{CH}_2} \tag{6}$$

the shielding constants arise from interactions between Xe and each individual alkylsilane constituent group can, thus, be respectively determined as $-\sigma_{\text{Si–CH}_2} = 4.72$, $-\sigma_{\text{CH}_3} = 3.55$, and $-\sigma_{\text{CH}_2} = 2.96$ ppm nm$^2$.

4. Conclusions

The potential use of VT-HP $^{129}$Xe NMR for probing the surface properties of organic-functionalized mesoporous MCM-41 materials, prepared by silylation treatment using various alkylsilanes with different carbon chain lengths and coverages,
has been demonstrated. Unlike the conventional method, HP $^{129}\text{Xe}$ NMR renders highly sensitive detection of Xe local environments even at very dilute loading and, thus, should facilitate future syntheses and applications of novel nanostructured materials with engineered properties.

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Supporting Information Available: Assorted solid-state $^{13}\text{C}$ CP and $^{29}\text{Si}$ MAS NMR spectra, X-ray diffraction patterns, and $\text{N}_2$ adsorption/desorption isotherms observed for the parent and silylated MCM-41 materials. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


