Variable temperature $^{129}\text{Xe}$ NMR studies of xenon adsorbed on mesoporous MCM-41 molecular sieves

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A comprehensive variable temperature $^{129}\text{Xe}$ NMR study of xenon adsorbed on mesoporous MCM-41 molecular sieves with varied pore sizes, morphology and aluminum concentration has been made. The observed $^{129}\text{Xe}$ NMR chemical shifts ($\delta$) of the adsorbed Xe exhibit a strong dependence on Xe loading ($\rho$) and temperature ($T$). At low Xe loading, the $^{129}\text{Xe}$ chemical shifts show a concave upward dependence on Xe density which vary with temperature and pore size of the adsorbent. Whereas at high loading, a nearly linear relation between the observed chemical shifts and effective Xe density was found whose slopes of $\delta$ vs $\rho_{\text{eff}}$ is temperature dependent. Regressional fitting based on a two-site exchange model enable us to fit the observed $\delta(T, \rho)$ data in a least squares sense to second-order polynomial with $\rho$. The temperature variations of the Xe-wall interaction at zero density as well as the Xe-Xe interactions were derived explicitly and compared with the results available for bulk Xe, Xe adsorbed on microporous materials and on polymer surfaces.

1. INTRODUCTION

The structure and dynamic properties of molecules adsorbed in microporous/mesoporous materials have drawn much research attention in recent decades. A number of papers have recently appeared on the application of using probe molecules to characterize the pore structure of the mesoporous adsorbent such as MCM-41 [1, 2]. In this paper, we report results of variable temperature $^{129}\text{Xe}$ NMR of Xe adsorbed in MCM-41 molecular sieves with varied pore size, morphology and Al concentrations. $^{129}\text{Xe}$ NMR [3, 4] is known to be a very sensitive probe of local environment inside porous materials. The subject has been reviewed by several authors [5-8].

There are several reasons for doing variable temperature $^{129}\text{Xe}$ NMR of Xe adsorbed on MCM-41. First, the straight, unconnected channels of controllable pore size make MCM-41 an ideal model adsorbent for both theoretical and experimental investigation of critical phenomena of molecules in a confined space. Second, $^{129}\text{Xe}$ NMR provides an excellent
probe to investigate the morphology and topology of MCM-41 materials which are not well known at the present. Third, at the limit of extreme dilution, the interactions between a Xe atom (adsorbate) and the wall of mesoporous materials (adsorbent) such as MCM-41 are not known and thus demand further investigation. Furthermore, it would be interesting to compare the temperature and density dependence of $^{129}$Xe chemical shifts in the present system with those obtained from bulk fluid or solid Xe [9-11] and that from Xe adsorbed on microporous materials [4, 12-15]. Such observations should provide valuable information on Xe interactions in both macroscopic and microscopic levels.

2. EXPERIMENTAL SECTION

2.1. Preparation and characterization of mesoporous materials

Powdered MCM-41 molecular sieves (Si/Al = 37) with varied pore diameters (1.80, 2.18 and 2.54 nm, denoted by Ma, Mb and Mc, respectively) were synthesized following the conventional procedure using sodium silicate, sodium aluminate and compounds such as cetyltrimethylammonium bromide (C$_{16}$TMAB), myristyltrimethylammonium bromide (C$_{14}$TMAB) and dodecyltrimethylammonium bromide (C$_{12}$TMAB) as the source materials for Si, Al and quaternary ammonium surfactants, respectively [16]. A pure-silica form MCM-41 sample (denoted as SM, pore diameter 2.44 nm) was synthesized with the same procedure but in the absence of sodium aluminate source material. Moreover, an ordered mesoporous MCM-41 with a hollow tubules-within-a-tubule hierarchical structure (Fig. 1) of C$_{16}$MTAB system (sample denoted as TM, Si/Al = 37, pore diameter 2.64 nm) was also synthesized under highly alkaline condition by careful control of the surfactant-water content and lower silica condensation rate [17]. The structure and morphology of all the synthetic MCM-41 molecular sieves were confirmed by powder X-ray diffraction and transmission and scanning electron microscopy. Their pore sizes, surface areas and pore volume were deduced from the N$_2$ adsorption-desorption isotherm data obtained at 77 K (Table 1).

2.2. Sample pretreatment and xenon adsorption

Sample cells were made with 7 mm i.d. pyrex tubing with a pre-pulled neck at about 23 mm from the bottom. The sample cell was first attached to a vacuum stopcock and an adapter so that it can be conveniently set up for dehydration of the sample on a vacuum apparatus and for the succeeded adsorption of Xe. Sample (ca. 0.1 g) was first placed into the necked pyrex sample cell and then subjected to dehydration. Dehydration was performed on a vacuum manifold by gradual heating (1 °C min$^{-1}$) to 350 °C in vacuum (< 10$^{-3}$ Torr) and maintained at the temperature for over 40 h. Sample weight was carefully monitored during each procedure.

After sample dehydration, a known amount of Xe (natural abundant or 70% $^{129}$Xe-enriched) in a calibrated volume was transferred into MCM-41 by chilling the bottom of the sample cell with liquid N$_2$ then the sample cell was sealed off with a mini-torch. Special cares were taken in minimizing the dead volume of each sample cell during glass sealing. For practical purposes, the amount of Xe adsorbed, p, is expressed as the number of Xe atoms per effective free volume of anhydrous MCM-41 at room temperature. As a result, samples with varied Xe loading ranging form 2-245 amagat (the gas density at 0 °C and 1 atm) were prepared. One should bear in mind that the Xe loading so determined represents only the apparent Xe density (Xe inside the sample cell). This density represents the effective density
Table 1
Characteristics of the MCM-41 samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al</th>
<th>Pore diameter (nm)(^a)</th>
<th>Pore volume (ml/g)(^a)</th>
<th>(\delta_\alpha(\rho = 0)) (ppm)(^b)</th>
<th>(\sigma_1) (ppm/amagat)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM</td>
<td>37</td>
<td>2.64</td>
<td>1.05</td>
<td>56.8</td>
<td>0.485</td>
</tr>
<tr>
<td>Ma</td>
<td>37</td>
<td>2.54</td>
<td>1.15</td>
<td>52.4</td>
<td>0.122</td>
</tr>
<tr>
<td>Mb</td>
<td>37</td>
<td>2.18</td>
<td>0.96</td>
<td>58.0</td>
<td>0.189</td>
</tr>
<tr>
<td>Mc</td>
<td>37</td>
<td>1.80</td>
<td>0.96</td>
<td>73.0</td>
<td>0.271</td>
</tr>
<tr>
<td>SM</td>
<td>∞</td>
<td>2.44</td>
<td>0.82</td>
<td>55.8</td>
<td>0.054</td>
</tr>
</tbody>
</table>

\(^a\)Derived from N\(_2\) adsorption isotherms.  \(^b\)Obtained from Fig. 2.

\((\rho_{\text{eff}},\text{represents Xe inside the pore of MCM-41})\) only when at low enough temperature and below saturation loading at which the amount of gaseous Xe (outside of the pore) is negligibly small. The effective Xe density, which depends on both the amount of adsorbent and the temperature, was calibrated by xenon adsorption isotherms done at specific temperatures. We note that it was calibrated effective density that were actually used during the regresional fitting which were performed on a personal computer using Microlcal Origin developed by Microlcal Software, Inc. None of our samples reached saturation loading and for temperature below ca. 230 K, nearly all of the Xe were adsorbed within the pore of MCM-41.

2.3. Variable temperature \(^{129}\text{Xe}\) NMR experiments

All \(^{129}\text{Xe}\) NMR measurements were performed at 83,012 MHz on a Bruker MSL-300P spectrometer. The automatic temperature regulator is accurate to at least 1 °C, with a precision of about ± 0.1 °C. The accuracy and linearity of the regulator reading with temperature were calibrated by proton chemical shift of either methanol (for T ≤ 300 K) or ethylene glycol (for T ≥ 300 K). We estimate that all temperatures were known to ± 2 °C. For room temperature (298 K) measurements, a designed sample tube was used [18]. The free-induction-decay signals were accumulated typically with a relaxation delay of 0.3 s. The \(^{129}\text{Xe}\) chemical shift was referred to gaseous Xe at zero density [11].

3. RESULTS AND DISCUSSION

3.1. Room temperature \(^{129}\text{Xe}\) NMR studies

3.1.1. Characterization of tubular MCM-41

Room temperature \(^{129}\text{Xe}\) NMR spectra of the tubular (TM) and non-tubular (Ma) MCM-41 sample are shown in Fig. 1. Unlike sample Ma (Fig. 1a) whose uniform channel system exhibits only a single resonance, the spectrum of sample TM show two distinct resonance peaks (Fig. 1b). The peak appears at ca. 15 ppm, upfield from the main resonance is assigned to Xe adsorbed in macropores of the tubular MCM-41. The intensity of the macropore peak
Figure 1. Schematic of the tubular MCM-41 (top) and $^{129}$Xe NMR spectra of (a) MCM-41 & (b) tubular MCM-41.

Figure 2. $^{129}$Xe chemical shift vs Xe loading (298 K) for various samples.

Figure 3. Correlation of $\delta_a$ with pore size for (a) MCM-41 and (b) zeolites. The solid lines indicate the fitting results.

Figure 4. Variations of $^{129}$Xe chemical shift with temperature for sample Ma with various apparent Xe density ($\rho$).

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$B_0$</th>
<th>$B_1$</th>
<th>$B_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ma</td>
<td>0.4766</td>
<td>$6.1 \times 10^{-4}$</td>
<td>$-5.92 \times 10^{-6}$</td>
<td>$-21.4922$</td>
<td>0.1806</td>
<td>$-4.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>TM</td>
<td>0.8235</td>
<td>$-29.8 \times 10^{-4}$</td>
<td>$3.96 \times 10^{-6}$</td>
<td>$-12.9020$</td>
<td>0.1074</td>
<td>$-2.9 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Superscript a

Fitted to second-order, that is, $\sigma_{1a}(T) \approx A_0 + A_1T + A_2T^2$ and $\sigma_{2a}(T) \approx B_0 + B_1T + B_2T^2$. 
decreases with decreasing temperature and become invisible for temperature below ca. 220 K indicating the migration of Xe from the macropore to the mesopore while lowering the temperature.

3.1.2. Effects of pore size and Al concentration
The variations of the observed $^{129}$Xe chemical shift with pore size are shown in Fig. 2. At low loading, the chemical shift show a parabolic-like curvature. However, no such behavior was found for pure-silica sample (SM). Although the reasons for the parabolic-like chemical shift dependence is not fully known, it is at least partly due to the presence of Al. MCM-41 is known, thus far, to possess partially crystalline structure closely related to amorphous silica [19]. Cheung [12] ascribed the parabolic-like chemical shift behavior observed in amorphous alumina and silica-alumina at low Xe loading to the presence of a broad distribution of micropores and the inverse dependent with pore size. Ito and Fraissard [3] expressed the room temperature $^{129}$Xe NMR chemical shift of Xe adsorbed in porous adsorbent as $\delta = \delta_0 + \delta_1(p) + \sigma_1 p$, where $\delta_0 = 0$ is the chemical shift reference, $\delta_1(p = 0)$ represents the interaction between a Xe atom and the wall of the adsorbent. The last term represents the contribution arises from binary Xe-Xe interactions which, at moderate loading, is linear with $p$. The observed values of $\delta_0$ and $\sigma_1$ are depicted in Table 1.

In Fig. 3, the values of $\delta_0$ is plotted against pore size for the non-tubular MCM-41 samples. The pore size dependence of $\delta_0$ can be described by the empirical relation: $\delta_0 = 129/(d - 0.0203)$, where $d$ is the pore diameter in nm. The empirical relation, $\delta_0 = 49.9/(d - 0.2346)$, derived by Demarquay and Fraissard [20] for Xe adsorbed in microporous zeolites is also shown in Fig. 3 for comparison. It is clear that a sizable discrepancy (ca. 60 ppm in the vertical axis) exists between the two empirical relations arising from Xe adsorbed in mesoporous and microporous adsorbents. The reason for such discrepancy is not fully understood at present. However, a discrepancy of over 30 ppm was observed for a known structure of AlPO$_4$-5 [21]. The discrepancy may be due to the difference in the local environment experienced by the adsorbed Xe. Recent molecular simulation study [22] showed that the partially crystalline structure of MCM-41 [19] possesses a high skeletal density of ca. 2.7 g cm$^{-3}$, which is equivalent to ca. 27 T-sites per nm$^3$ for solid alone and 11-19 T-sites when the pore spaces are also included. The skeletal density of MCM-41 is very close to quartz (2.66 g cm$^{-3}$) and is indeed substantially higher than amorphous silica (2.2 g cm$^{-3}$) and zeolites (typically less than 2 g cm$^{-3}$). Thus, comparing with microporous zeolites, the observed downfield chemical shift in mesoporous MCM-41 is probably not unreasonable.

3.2. Variable temperature $^{129}$Xe NMR studies
Figure 4 shows the temperature variation of $^{129}$Xe chemical shifts of Xe adsorbed in non-tubular MCM-41 sample (Ma) with the apparent Xe loading. Similar results were also found for the tubular MCM-41 sample (TM). In Fig. 5, the observed chemical shift is plotted against the calibrated Xe loading ($p_{cal}$). At a given temperature, the observed chemical shifts at low loading also exhibit a parabolic-like curvature with a broad minimum. Whereas at high loading, a nearly linear dependent chemical shift with Xe loading is observed.

The observed $^{129}$Xe chemical shift can be expressed as a weighted average between two sites in rapid exchange, namely the adsorbed and non-adsorbed (gaseous) xenon. For a
Table 3
Assorted parameters obtained from the data fitting

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta E_{\text{ads}}$ (exp) (kcal/mol)</th>
<th>$\Delta E_{\text{ads}}$ (fit) (kcal/mol)</th>
<th>$\delta_{\text{on}}$ (ppm)</th>
<th>$\delta_2(300 \text{ K})$ (ppm)</th>
<th>$\sigma_{1n}(300 \text{ K})$ (ppm/amagat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ma</td>
<td>2.1 $\pm$ 0.5</td>
<td>2.43 $\pm$ 0.08</td>
<td>106.6 $\pm$ 0.6</td>
<td>59.0 $\pm$ 0.3</td>
<td>0.170 $\pm$ 0.010</td>
</tr>
<tr>
<td>TM</td>
<td>1.9 $\pm$ 0.5</td>
<td>2.39 $\pm$ 0.15</td>
<td>105.6 $\pm$ 1.0</td>
<td>60.0 $\pm$ 0.5</td>
<td>0.285 $\pm$ 0.005</td>
</tr>
</tbody>
</table>

Figure 5. Variations of $^{129}$Xe chemical shift with calibrated effective Xe density ($\rho_{\text{en}}$) at different temperatures.

Figure 6. Plot of $\delta_2$ vs $T$ for samples TM and Ma compared with that of Xe on NaY zeolite and polymer surface. The solid lines indicate the fitting results.

Figure 7. Plot of $\sigma_1(T)$ vs $T$ compared with results obtained from gaseous Xe. Solid lines indicate the fitting results.

Figure 8. Plot of $\sigma_2(T)$ vs $T$ compared with results obtained from gaseous Xe. Solid line indicates the fitting results.
quantitative analysis of the experimental results, we fit the data with a polynomial function to second-order, such that

$$
\delta(\rho, T) = P_a(T)\delta_a(\rho_a, T) + P_g(T)\delta_g(\rho_g, T) = \delta_a(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \ldots \tag{1}
$$

where $P_a$ and $P_g$ are the probabilities of finding the adsorbed and gaseous xenon, respectively; $P_a + P_g = 1$. $\rho_a$ and $\rho_g$ are, respectively, the density of adsorbed and gas density; $\rho = \rho_a + \rho_g$.

The probability of finding a Xe atom at the wall is given by [23]: $P_a = \rho_a/\rho = \tau_a/(\tau_a + \tau_b)$; $P_g = \rho_g/\rho = 1 - P_a$, where $\tau_a$ is the average time xenon spent on the wall, and $\tau_b$ us the reciprocal of the xenon collision rate with the surface. The average xenon sticking time on the wall is given by $\tau_a = \tau_0 \exp(\Delta E_{ads}/RT)$, where $\tau_0$ is the preexponential factor and $\Delta E_{ads}$ is the energy of adsorption (Table 3), and $R$ is the gas constant. For practical purposes, we express the adsorbed and gaseous chemical shift contributions as second-order polynomial:

$$
\delta_a(\rho_a, T) \approx \delta_{0a} + \sigma_{1a}(T)\rho_a + \sigma_{2a}(T)\rho_a^2; \quad \delta_g(\rho_g, T) \approx \delta_{0g} + \sigma_{1g}(T)\rho_g + \sigma_{2g}(T)\rho_g^2 \tag{2}
$$

The term $\delta_g(\rho_g, T)$ can be expressed explicitly according to the relation given by Jameson and co-workers [11], where $\delta_{0g} = 0$ is the chemical shift reference. Thus, we have

$$
\delta_a(T) = P_a(T)\delta_{oa} \tag{3}
$$

$$
\sigma_1(T) = P_a^2(T)\sigma_{1a}(T) + P_g^2(T)\sigma_{1g}(T) \tag{4}
$$

$$
\sigma_2(T) = P_a^3(T)\sigma_{2a}(T) + P_g^3(T)\sigma_{2g}(T) \tag{5}
$$

The results obtained from the data fitting are shown in Figs. 6-8 and the related parameters are summarized in Tables 2 and 3. We find that, at low temperature, $\delta_a(T < 150 \text{ K})$ appears to reach a limiting value of $\delta_{oa} = 106$ ppm, much higher than the values found for Xe adsorbed on NaY zeolite (86 and 58 ppm at 144 and 298 K, respectively) [12, 18] or on the surface of poly(acrylic acid) polymer (95 ppm) [22]. As shown in Fig. 7, the second virial coefficient of the adsorbed Xe, $\sigma_1(T)$, is seemingly smaller than $\sigma_{1g}(T)$ of the gaseous Xe and seems to vary with the morphology of the adsorbent. As shown in Table 3, $\sigma_{1a}(300 \text{ K}) = 0.170$ and $0.285$ ppm/amu&gat for Ma and TM, respectively, small compare to $\sigma_{1g}(300 \text{ K}) = 0.548$ ppm/amu&gat [11]. Similarly, the fitting results obtained for the third virial coefficient, $\sigma_2(T)$, can also be compared with $\sigma_{2g}(T)$ of the gaseous Xe [11] as shown in Fig. 8. Finally, the fact that the fitted $\Delta E_{ads}$ values are in good agreement with the experimental values (Table 3), indicating that our model gives reasonable and meaningful quantitative description of the system.

4. CONCLUSIONS

In this work, we show that room temperature $^{129}$Xe NMR of the adsorbed Xe is capable of providing structural characteristics of the mesoporous MCM-41 molecular sieves. Regressional fitting of the variable temperature $^{129}$Xe chemical shift data, on the other hand, is capable of providing detailed Xe interactions in the mesoporous adsorbents. Our results
indicate that the Xe interactions in mesoporous solids deviate from not only bulk Xe, but also from Xe adsorbed on microporous adsorbents or polymer surfaces. The detailed dynamics of the adsorbed Xe could also be deduced from the temperature dependence of $\tau_{eq}$ and $\tau_{as}$; this issue shall be discussed elsewhere. More experimental and theoretical studies are under way to investigate the detailed molecular phenomena when they are confined in restricted volume.

REFERENCES