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 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/functionalization 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 Xe and the alkylsilane constituent groups (Si−CH$_2$−, CH$_2$−, 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[13] using cetyltrimethylammonium bromide as the structure-directing agent and sodium silicate as the silica source. Silylated MCM-41 samples with different coverages (ρ) and carbon chain lengths (n) of alkylsilanes, denoted as nCM41(ρ), were obtained by refluxing the parent MCM-41 and desired amount of various alkyltrichlorosilanes, that is, CH$_3$(CH$_2$)$_{n-1}$SiCl$_3$ (n = 1, 4, 8, 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, ρ, of alkylsilane ligand for each sample was determined by elemental analysis (Perkin-Elmer; 2400II) according to the following formula:

$$\rho = \frac{WN_A/(nM)}{\{1 - [W/(nM)][nM_C + (2n+1)M_H]\}S} \quad (1)$$

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

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

sample	silylating reagent	n	V^a (cm³/g)	S^a (m²/g)	V/S (nm)	K_0^b (×10¹¹ Torr⁻¹ m⁻²)	ΔH_a^b (kJ/mol)	δ_s^b (ppm)	ρ (nm⁻²)
SM41			1.03	1075	0.96	10.2 ± 2.6	16.8 ± 0.6	105.4 ± 0.6	
1CM41(1.33)	CH_3SiCl_3	1	0.89	1001	0.89	6.2 ± 2.4	17.8 ± 1.0	112.2 ± 0.9	1.33
4CM41(0.26)	$CH_3(CH_2)_3SiCl_3$	4	0.90	1047	0.86	10.2 ± 1.6	16.1 ± 0.4	109.4 ± 0.5	0.26
4CM41(1.09)	$CH_3(CH_2)_3SiCl_3$	4	0.67	994	0.67	14.6 ± 5.5	15.3 ± 1.0	120.9 ± 1.2	1.09
8CM41(0.11)	$CH_3(CH_2)_7SiCl_3$	8	0.93	1042	0.89	12.7 ± 1.7	16.0 ± 0.3	107.0 ± 0.4	0.11
8CM41(0.48)	$CH_3(CH_2)_7SiCl_3$	8	0.79	976	0.81	5.4 ± 1.5	17.7 ± 0.7	117.2 ± 0.7	0.48
8CM41(1.15)	$CH_3(CH_2)_7SiCl_3$	8	0.49	813	0.60	6.8 ± 1.3	17.1 ± 0.5	135.8 ± 0.5	1.15
12CM41(1.08)	$CH_3(CH_2)_{11}SiCl_3$	12	0.46	573	0.80	2.7 ± 1.2	19.4 ± 0.8	145.6 ± 0.7	1.08
12CM41(1.31)	$CH_3(CH_2)_{11}SiCl_3$	12	0.11	44	2.50	9.4 ± 4.0	19.8 ± 1.1	155.4 ± 1.1	1.31

a Obtained from N_2 adsorption/desorption measurements (see Supporting Information). *b* Obtained by fitting the temperature-dependent ^{129}Xe CS data to eq 2.

G) of the superconducting magnet. The spin-exchange optical pumping process was facilitated by introducing a gas mixture (97% He, 1% N_2, and 2% natural Xe) into the pumping cell maintaining at constant pressure (4 atm), temperature (423 K), and gas flow rate (ca. 100 scc/min) while subjecting to irradiation of left-circularly polarized light. As a result, an estimated polarization of about 2% for HP ^{129}Xe gas was achieved, corresponding to an achievable signal enhancement factor of about 3500. The optical pumping unit was connected to a home-designed sample tube (via 1/16 in. Teflon tubing) such that the fabricated HP ^{129}Xe gas can be continuously delivered to the NMR sample cell under ambient pressure, equivalent to a Xe partial pressure of about 15.2 Torr. It should be mentioned that He and N_2 in the gas mixture have no significant effect on ^{129}Xe NMR spectra. Prior to each NMR run, about 0.5 g of the sample was first tightly hand-packed into the sample tube (10 mm o.d.) before subjecting to thermal treatment (at 423 K for 12 h) under a vacuum ($<10^{-5}$ Torr) to ensure complete removal of moisture and residual solvent. All HP ^{129}Xe NMR spectra were acquired on a Bruker Avance 300 NMR spectrometer at a Larmor frequency of 83.012 MHz using a single-pulse sequence with a $\pi/2$ pulse of 15 μs and a recycle delay of 5 s. Typically, spectra with excellent sensitivity can be attained by accumulating about 64−128 free-induction-decay signals. VT experiments were conducted in the temperature range of 150−298 K, as limited by our facility. Sample temperature was calibrated using the ^{209}Pb NMR signal of solid $Pb(NO_3)_2$.[14] The ^{129}Xe NMR chemical shift (CS) was referenced to that of xenon gas extrapolated to zero pressure.

3. Results and Discussion

Figure 1a−c illustrates the typical VT-HP ^{129}Xe 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 in addition to the gas peak near 0 ppm. We attribute the low-field peak to Xe adsorbed in the mesopores of SM41. For $T >$ 210 K, a decrease in the sample temperature leads to a gradual increase in the CS (Figure 1d) and decrease in the line width ($\Delta\omega$; 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 $\Delta\omega$ that can be ascribed to the condensation effect. The above observations are in excellent agreement with earlier studies.[15]

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 $\Delta\omega$. Moreover, a consistent increase was also observed for the CS and $\Delta\omega$ with
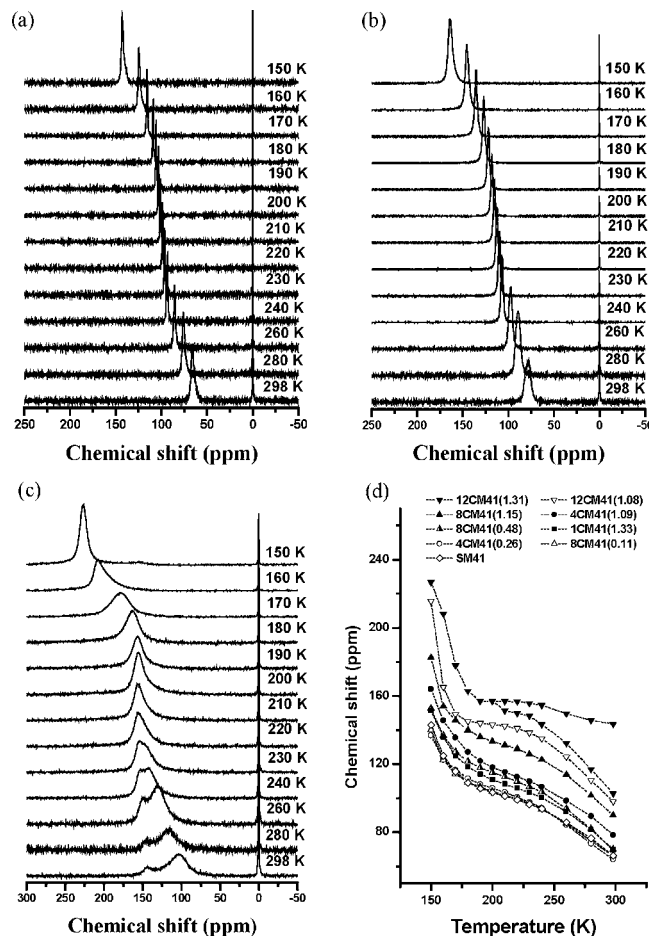

Figure 1. VT-HP ^{129}Xe NMR spectra of (a) SM41, (b) 4CM41(1.09), and (c) 12CM41(1.31). All spectra were obtained with a Xe partial pressure of about 15.2 Torr. (d) Variations of the ^{129}Xe CS with temperature for Xe adsorbed in parent and various silylated samples.

increasing alkyl chain lengths as well as population densities of the alkylsilanes grafted on the inner pore walls of MCM-41. 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
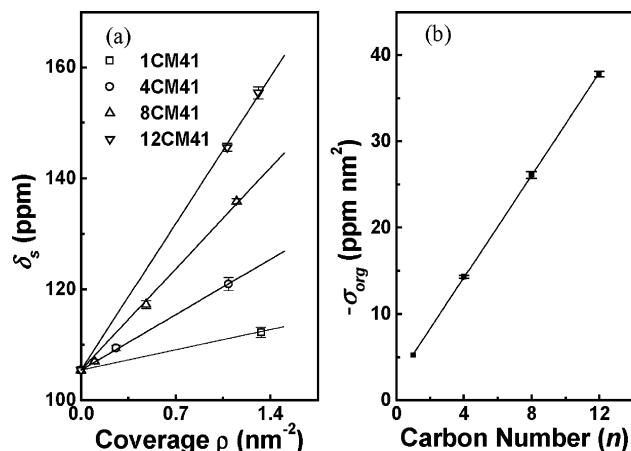
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Figure 2. (a) Variations of δ_s with surface alkylsilane coverage. (b) Plot of shielding $-\sigma_{org}$ against carbon number of grafted alkylsilanes.

room temperature (298 K; see Figure 1c), revealing the existence of two different environments. While both resonance peaks should arise from Xe atoms adsorbed in mesopores, we attribute the high-field peak at 103 ppm to more "mobile" Xe in fast exchange between the central space in the pores and the alkyl−ligand grafted surface, as the single peak observed for silylated samples with shorter alkyl chain lengths ($n \leq 8$), whereas the weaker peak at 144 ppm is most likely due to Xe "entangled" in smaller voids surrounded by the alkylsilanes. That the latter low-field peak appears to be less mobile (more inert to temperature variation) and the two peaks gradually merge with decreasing temperature especially below the reflection point ($T \sim 210$ K) at which condensation of Xe near the pore surfaces occurs provides additional support to the above assignments.

It is possible to extract the physical parameters related to the adsorption properties of materials from the temperature dependence of the ^{129}Xe CS, as shown in Figure 1d. In the present case, the observed CS of Xe adsorbed in silylated MCM-41 is indicative of physical adsorption of Xe in cylindrical pores of surface-modified MCM-41. In the fast-exchange approximation and dilute adsorption (Henry's Law) limit, the temperature dependence of the observed CS (δ) can be expressed as[16]

$$\delta = \delta_s/\{1 + V/[SK_0T^{1/2}\exp(\Delta H_a/RT)]\} \tag{2}$$

where V and S represent the free volume and specific surface area of the mesoporous materials, respectively. K_0 is the pre-exponent of Henry's constant, R is the universal gas constant, ΔH_a is the heat of adsorption, and δ_s is the characteristic CS reflecting the xenon−surface interactions. Values of V and S were derived from N$_2$ adsorption isotherms at 77 K, and K_0, ΔH_a, and δ_s were then determined by least-squares fittings of the VT-HP ^{129}Xe CS results to eq 2. Because the CS contribution from Xe−Xe interactions becomes more significant at low temperature, only those experimental results obtained at $T > 210$ K were used during data fittings.[15b] All observed ΔH_a values fall in the range of 15−20 kJ/mol, as expected for physical adsorption of Xe.

More importantly, for samples grafted with the same alkylsilane, the observed δ_s's are found to depend linearly on ρ (Figure 2a). At first glance, one might speculate that the observed increase in δ_s with increasing alkylsilane coverage (ρ) is merely due to the effective reduction of pore size rather than Xe−alkyl ligand interactions. However, it should be pointed out that the pore volume V is calculated on the basis of the overall sample weight, that is, the weight of the MCM-41 silica

and grafted silylating reagents. As such, the average pore size of each sample may be estimated on the basis of the ratio $\eta V/S$, where η is the geometry factor varying with the pore geometry.[16,17] As shown in Table 1, the V/S ratios obtained from various samples scatter in the range from 0.60 to 0.96 nm except for the 12CM41(1.31) sample whose value obviously deviates from others possibly due to the change in the geometry factor η caused by the crowded dodecyl groups on the pore surfaces. The fact that no obvious correlation between δ_s and V/S was found among the various samples examined supports the concept that the observed δ_s variation is indeed due to differences in their surface properties. Our recent studies on a series of amino-silane-functionalized MCM-41 samples also showed the same linear dependence of δ_s with ρ.

Presumably, δ_s should be the sum of two contributions, namely, δ_{MCM} and δ_{org}, arising from Xe−silica wall and Xe−moiety interactions, respectively. Because δ_{MCM} can be directly obtained from the SM41 sample (105.4 ppm), the explicit dependence of δ_{org} on ρ can then be expressed as

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

where $-\sigma_{org}$ represents intrinsic shielding due to intermolecular van der Waals Xe−alkyl ligand interactions. Moreover, the $-\sigma_{org}$'s so determined are found to show a strong correlation with n (Figure 2b). The linear dependence of $-\sigma_{org}$ on n can be interpreted on the basis of a group contribution analysis proposed earlier for Xe dissolved in linear solvents.[18] Accordingly, $-\sigma_{org}$ can be expressed by pairwise additive intermolecular Xe−ligand shielding functions:

$$\sigma_{org} = \sum_i \sigma_i = (\sigma_{CH_3} - \sigma_{CH_2}) + n\sigma_{CH_2} \tag{4}$$

where $-\sigma_{CH_3}$ and $-\sigma_{CH_2}$ are the deshielding medium contributions due to methyl and methylene groups, respectively. Thus, an explicit value of $-\sigma_{CH_3}$ and $-\sigma_{CH_2}$ can be extracted as 5.31 and 2.96 ppm nm^2, respectively. Consequently, δ_s can be expressed by a simple empirical relation in terms of n and ρ:

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

However, it is noted that the $\sigma_{CH_3}/\sigma_{CH_2}$ ratio of 1.79 obtained in this study deviates from 1.2 to 1.26 found for Xe dissolved in linear solvents.[18] 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[18] of $\sigma_{CH_3}/\sigma_{CH_2} = 1.216$ into account and by taking

$$\sigma_{org} = \sum_i \sigma_i = (\sigma_{CH_3} - \sigma_{CH_2}) + (\sigma_{Si-CH_2} - \sigma_{CH_2}) + n\sigma_{CH_2} \tag{6}$$

the shielding constants arise from interactions between Xe and each individual alkylsilane constituent group can, thus, be respectively determined as $-\sigma_{Si-CH_2} = 4.72$, $-\sigma_{CH_3} = 3.55$, and $-\sigma_{CH_2} = 2.96$ 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]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.

Supporting Information Available: Assorted solid-state ^{13}C CP and ^{29}Si MAS NMR spectra, X-ray diffraction patterns, and 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.

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