

Carbon-13 CP MAS NMR Study on Structures of Octadecyl Chains Influenced by Co-Presence of 3-Aminopropyl Chains on SBA-15

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Functionalized SBA-15 samples by octadecyltrimethoxysilane (OTC) were studied by ¹³C magic angle spinning (MAS) cross polarization (CP) nuclear magnetic resonance (NMR) spectroscopy. In the SBA-15 sample fully functionalized by 3-aminopropyltrimethoxysilane (APS) and OTC in 1:1 molar ratio, octadecyl chains were observed to have, on average, more *trans* conformation than those in the SBA-15 samples fully modified by OTC only. Our results confirm that long chain molecules tend to organize themselves better in the co-presence of short chain molecules on the surface of mesoporous materials by packing of the different length chains in an interdigitized fashion even when the short chains are long enough to have three carbons and a functional group at the ends. In addition, our results indicate that solid-state ¹³C CP MAS NMR spectroscopy is a simple and non-destructive method to probe the molecular structures of the domains composed of long alkyl chains.

Key Words : Solid-state NMR spectroscopy, SBA-15, 3-Aminopropyltrimethoxysilane, Octadecyltrimethoxysilane. Functionalized mesoporous materials

Introduction

SBA-15 is a highly ordered mesoporous silica material in a two-dimensional hexagonal (space group *p6mm*) structure and typically produced in acidic media with a block copolymer.¹ The pore size (up to ~30 nm) and the thickness of the silica wall can be tunable with variable block copolymers and SBA-15 structures have thicker silica wall than MCM-41 structures.¹ Surface functionalized mesoporous silicate materials has been regarded to have the great potential for applications in environmental and industrial processes such as adsorption, separation, and catalysis.²⁻⁴ Not only the functional groups but also molecular structures of the surface bound species of the functionalized mesoporous materials play an important role in efficient utilization of the materials. Due to the chemical shifts sensitive to conformations as well as configurations and the NMR signal related with molecular dynamics, solid-state NMR spectroscopy has been employed as one of the main analytical methods to probe the molecular structures and dynamics of the surface bound^{3,5} and intercalated organic species.^{6,7} Especially, the structures and dynamics of long alkyl chains have been studied intensively by solid-state NMR spectroscopy.⁵⁻⁸ In this work, ¹³C CP MAS NMR is demonstrated as a simple and quick method to check the molecular structure of long alkyl chains bound on the surface. The SBA-15 samples, fully functionalized with OTC only, APS only, and OTC and APS together in 1:1 molar ratio, are compared.

Experimental

SBA-15 was synthesized as reported previously,⁹ with

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triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (EO₂₀-PO₇₀-EO₂₀, P123; Aldrich, U.S.A.) copolymer as a structure directing agent and tetraethyl orthosilicate (TEOS; Aldrich, U.S.A.) as a silica source. In a typical synthesis, 4 g (0.69 mmol) of P123 was dissolved in 30 g of water and 120 g of 2 M HCl solution and then stirred at 35 °C for an hour. Then, 8.5 g (40.8 mmol) of TEOS was added dropwise into the homogeneous solution with stirring at 35 °C for 20 h. The obtained gel was aged at 100 °C without stirring for 24 h. The solid white product was filtered, washed with distilled water and air-dried at room temperature. The dried SBA-15 sample was heated in a tube furnace under air by slowly increasing temperature at 1 °C/min from room temperature to 550 °C and then calcined at the temperature for 6 hours. Then the furnace was turned off to cool naturally under air or dry nitrogen atmosphere. The small angle X-ray Diffraction (XRD) pattern for the calcined SBA-15 was consistent with the XRD patterns in reference 1, indicating our calcined SBA-15 is in *p6mm* hexagonal symmetry. However, our diffraction peaks appear at slightly smaller 2θ values corresponding to larger unit cell parameters and the intense (100) peak reflects a *d* spacing of ~10.2 nm.

Prior to functionalization reactions with OTC and/or APS, SBA-15 materials were refluxed in toluene for 24 hours to increase the hydroxyl group density¹⁰ on the surface of SBA-15. Appropriate amount of APS and/or OTC was injected to 2 mL of absolute toluene under dry nitrogen gas flow. The refluxed and filtered SBA-15 (200 mg) was slowly added to the toluene solution for 10 min with vigorous stirring. Then the mixture was refluxed at 100 °C with stirring for 24 hours. The solid white product was filtered and washed with absolute toluene and dichloromethane.

All solid-state NMR spectra were acquired on a DSX-400

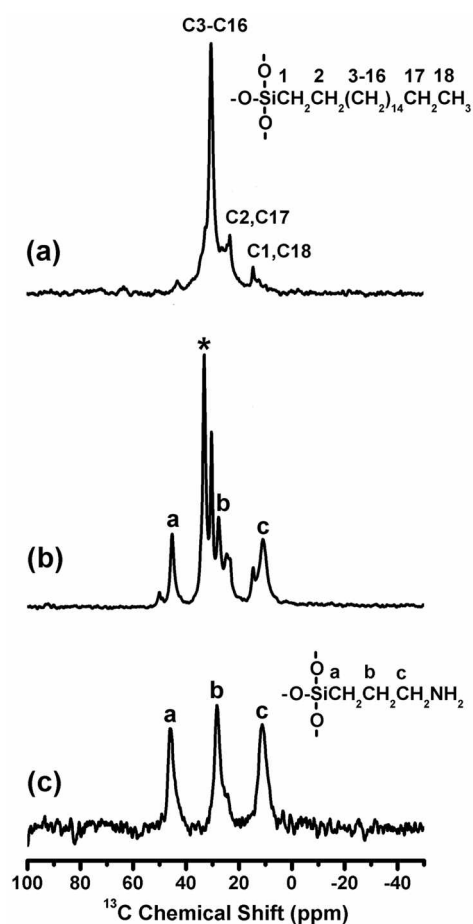


Figure 1. Representative ^{13}C CP MAS NMR spectra of SBA-15 functionalized with OTC only (a), OTC and APS in 1:1 molar ratio (b), and APS only (c). The peak at 30 ppm in (a) and (b) is assigned to the C3-C16 in *trans-gauche* mixture conformation while the additional peak at 33 ppm in (b) (marked by \star) is assigned to the C3-C16 in all *trans* conformation. The peaks not marked in (b) exactly match with the peaks in (a). Refer to the main text for additional information on the peak assignments.

spectrometer (Bruker Biospin GmbH, Germany) with a magnetic field strength of 9.4 T and 4 mm rotors at room temperature. ^{13}C CP MAS spectra were acquired with 3 s pulse sequence repetition delay, 5 μs proton pulse length (90° flip), 2 ms contact time, a spectral width of 100 kHz, and a spinning rate of 6 kHz. All chemical shifts in ppm were referenced to external tetramethylsilane.

Results and Discussion

Representative ^{13}C CP MAS NMR spectra of the SBA-15 samples functionalized with OTC only, OTC and APS in 1:1 molar ratio, and APS only in a saturation coverage are shown in Figure 1a, 1b, and 1c, respectively. The peaks in Figures 1a and 1c were assigned as denoted, by comparison to the spectra simulated with the ChemDraw program and consistent with the previous reports.^{5,11} It can be easily recognized that the peaks of 3-aminopropyl chains attached on SBA-15 did not change their chemical shifts even in the co-presence of octadecyl chains on the surface of SBA-15.

On the other hand, a new peak from the internal carbons (C3-C16) of octadecyl chains appears at 33 ppm in the co-presence of 3-aminopropyl chains on the surface of SBA-15 in addition to the peak at 30 ppm for the C3-C16 in the absence of 3-aminopropyl chains.

It is quite well-known that ^{13}C chemical shifts of the methylene carbons located in the middle of a long alkyl chain are very sensitive to their conformation.⁵⁻⁷ The methylene carbons in all *trans* conformation have a chemical shift between 34.2 and 32.8 ppm according to their molecular packing and motional state while the chemical shift of those in *trans-gauche* mixture conformation is upfield shifted.^{3,5,7} The more *gauche* conformation is present, the more chemical shift is upfield shifted. The maximum shift of methylene carbons due to conformation difference was reported as ~ 5 ppm.¹² Hence, the chemical shift of the C3-C16 peak, at 30 ppm, for octadecyl chains on the SBA-15 surface functionalized only with OTC indicates that the carbons are in *trans-gauche* mixture conformation. The additional peak at 33 ppm in Figure 1b suggests a new functionalized surface domain in which the C3-C16 carbons are in an all *trans* conformation. Hence, by co-condensation with APS the new domain was produced in addition to the domain functionalized with octadecyl only chains with the C3-C16 in *trans-gauche* mixture conformation as observed in the SBA-15 sample functionalized OTC only. Our results indicate that OTC was not homogeneously co-condensed with APS on the surface of SBA-15 and APS co-condensed with OTC induced all *trans* conformation for the C3-C16 of the octadecyl chains next to 3-aminopropyl groups. As a result, the population of *trans* conformation of the octadecyl chains was, on average, increased in the presence of 3-aminopropyl groups on the surface of SBA-15. Previously it was reported that the mixture of molecules with a linear propyl chain capped with a non-carbon functional group (a long chain molecule) and a methyl carbon only (a short chain molecule) for surface modification produces denser surface functionalization and better hydrothermal stability than either molecules only.^{10,13} Our results imply that even when the short chain is longer than a methyl group, the mixture of surface functionalization molecules with a long chain and a short chain produces better ordered long chain molecules on the surface. However, more than a single peak for the C3-C16 of the octadecyl chains show that the surface functionalization with the mixture of OTC and APS were done *inhomogeneously* and resulted in two different surface domains or phases: the one functionalized with OTC only and the other functionalized with 3-aminopropyl and octadecyl groups together on the SBA-15 surface. Outer surface of SBA-15 is also functionalized during our functionalization process, however, the contribution of NMR signal from the functionalized outer surface is negligible compared to that from the functionalized inner surface. Therefore, the detection of all *trans* conformation suggests the pore size of the SBA-15 is large enough to hold this extended octadecyl chains. Although the better ordering manifested as all *trans* conformation can be explained by interdigitation of short

chain molecules and long chain molecules on the silica surface, the explanation does not have enough supporting data and the mechanism for the better ordering is not clear at this moment. In general, ^{13}C CP MAS spectra can be acquired in much shorter time than ^{13}C MAS spectra without CP. However, peak intensities of ^{13}C CP MAS spectra tend to intensify less mobile carbons with more protons nearby and consequently are not linearly proportional to the number of carbons related with each peak.

Conclusion

Our results demonstrate that ^{13}C CP MAS NMR spectroscopy can provide a lot of information on molecular structures even with a simple experiment, especially on the conformation of alkyl chains and surface functionalization domains. Systematic studies will be pursued in the near future to search the optimum condition for homogeneous functionalization of mesoporous materials and the relationship between the structures and dynamics of the octadecyl chains and the molar ratios of APS and OTC in the co-condensation. How the better ordering of the long alkyl chains is produced in the presence of short chain molecules will be probed. In addition, ^{13}C CP MAS and ^{13}C MAS without CP NMR data will be compared to develop a method to get quantitative information from ^{13}C CP MAS NMR spectra.

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