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Distinguishing Surface versus Buried Cation Sites in Aluminosilicate Mesoporous Materials

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Mesoporous MCM-41 materials have received particular attention because of their unique structures with organized porosity and controllable, narrow mesopore size distribution.[1] These purely siliceous materials, however, have relatively low acidity and none of the ion-exchange capacity required for many applications. To increase the number of acidic sites, framework silicons are substituted by heteroatoms. The most common method is via “direct synthesis” where an aluminum-containing precursor is added to the gel prior to hydrothermal synthesis. Materials prepared this way have homogeneous aluminosilicate walls and a moderate acidity similar to that of amorphous silica-alumina. It is not yet completely known why, but much stronger acidity and hydrothermal stability has been reported when aluminum is incorporated into the wall surface of siliceous MCM-41 through a postsynthetic grafting procedure.[2] Intuitively, the answer lies in the different nature and accessibility of the acidic sites, and this can be determined by locating the aluminum within the Al-MCM-41 sample and by determining the nature of the charge-compensating species (protons or cations).

This task is of particular importance, yet it remains a challenging goal as the MCM-41 walls are an amorphous and locally disordered structure even though their channels have a long-range periodicity. Solid-state NMR spectroscopy has proved to be a powerful technique for studying amorphous solids, including MCM-41 materials, where ^{27}Al and ^{29}Si NMR are widely used to find the coordination of the aluminum and silicon atoms. Recently, proton-bearing sites in Al-MCM-41 have been studied with double-resonance NMR spectroscopy.[3]

There have been many studies on the preparation and ion-exchange of Al-MCM-41,[2−4] but surprisingly little has been reported on the locations of the *cations.*[5] The focus of the current work is a novel means of distinguishing cations in the surface regions of the walls from those further inside the walls. It is known that in the case of zeolites and alumino-silicates, NMR spectroscopy (mainly ^{6,7}Li, ^{23}Na, ^{133}Cs, and recently ^{85,87}Rb[6]) is the most informative and straightforward method for examining the cation sites of the framework.[7] In dehydrated zeolites, crystallographically different sites can easily be identified with high-field MAS NMR, whereas in hydrated zeolites NMR usually shows only a single dynamically averaged resonance.

We find, however, that in the NMR of completely hydrated cation-exchanged Al-MCM-41 samples at least two types of cations are readily differentiated:[8] For samples prepared by grafting (Al-MCM-41 g),[9,10] very narrow single isotropic lines in the ^{7}Li and ^{23}Na NMR spectra indicate a high mobility of the corresponding cations (Figure 1). Such mobility can be attributed to their predominant location on the surface of the framework walls in close proximity to surface aluminum species.[11] However, in hydrated samples prepared by direct synthesis (Al-MCM-41d) the spectra consist of a superposition of narrower and broader components (Figure 1). The narrower line can also be attributed to mobile cations located on and in a surface layer, although this line is broader than in the grafted material. The broader line corresponds to the cations with more restricted mobility, most likely located inside the walls. The presence of such cations is not unexpected since, due to the direct synthesis, a considerable part of the aluminum, and therefore the charge balancing cations should be located inside the walls.[3,4c,12] The hindered mobility of these cations results in severe broadening of the NMR lines, even though the samples are fully hydrated. Nevertheless, these cations can be easily exchanged with other alkali metal cations in a zeolite-like fashion,[9] possibly by an ion diffusion process.

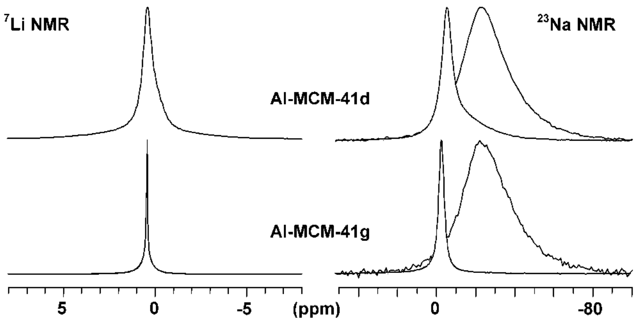

Figure 1. Left: ^{7}Li MAS NMR spectra of hydrated Li-Al-MCM-41 samples prepared by grafting (bottom) and direct synthesis (top). Right: ^{23}Na MAS NMR spectra of Na-Al-MCM-41 samples (narrow, hydrated; broad, dehydrated).

It is remarkable yet explainable that the dramatic difference observed in the spectra of the hydrated samples is somewhat diminished when the samples are dehydrated. For Na-exchanged samples, the ^{23}Na NMR MAS spectra have the form of similar broad lines, asymmetric due to second-order quadrupolar interactions (Figure 1). Such spectra typify quadrupolar nuclei in a disordered environment with distributions in both quadrupolar coupling parameters and isotropic chemical shifts.[13] We can conclude that the oxygen environment of sodium cations in dehydrated samples, whether prepared by direct synthesis or by grafting, is similar to that in silicate glasses. A similar conclusion follows from analysis of the ^{7}Li NMR spectra of dehydrated Li-Al-MCM-41 samples, with one significant exception. Because of the smaller quadrupolar moment of the ^{7}Li nuclei, ^{7}Li NMR spectra usually have better resolution than ^{23}Na NMR. ^{7}Li NMR spectra of dehydrated samples prepared by the two methods are, at first glance, similar; but closer inspection reveals differences (Figure 2). For the grafted sample the line is symmetric (maximum −0.70 ppm), whereas for the sample prepared by direct synthesis the line is asymmetric toward

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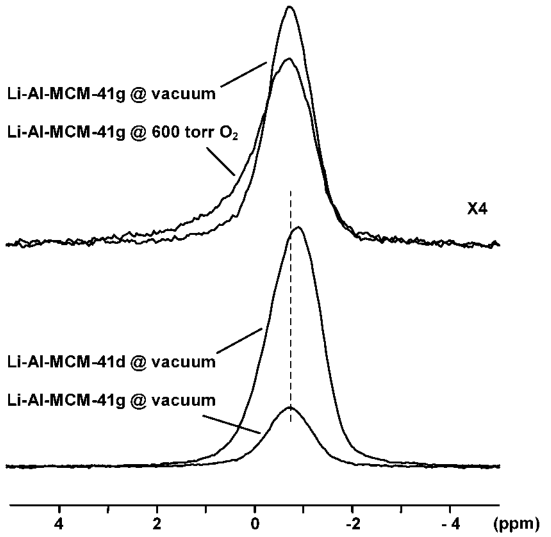

Figure 2. ^{7}Li MAS NMR spectra of dehydrated Li-Al-MCM-41 samples. The relative intensities of the spectra have been preserved.

larger shifts (maximum −0.85 ppm). This type of asymmetry in ^{7}Li MAS spectra is most likely caused by a distribution of the isotropic chemical shift. Recently it was shown that in lithium silicates ^{6,7}Li NMR chemical shifts correlated with the oxygen coordination number,[13b,14] with the smallest shifts for LiO$_6$ sites, increasing gradually through LiO$_5$ and LiO$_4$ to LiO$_3$. The fact that in dehydrated Li-Al-MCM-41d the line is asymmetric toward larger shifts indicates a distribution of the oxygen coordination density from the highest, as would be thought for Li cations located inside the aluminosilicate wall, to the lowest, likely on the very surface of the walls. These Li species with low coordination are the only ones found in the spectrum of dehydrated Li-Al-MCM-41g (Figure 2). In both cases the lines are significantly broader as compared to crystalline Li-compounds, e.g. dehydrated Li-zeolites, indicating the disordered characteristics of amorphous materials. This kind of site distribution has also been detected in the ^{7}Li SATRAS NMR spectra of both samples.[15]

It is also possible to discriminate lithium cations located on the surface and in the bulk of the material with the use of molecular oxygen as a paramagnetic shift agent. For example, in zeolite Li-X the adsorption of O$_2$ causes noticeable broadening and downfield shifts in ^{7}Li MAS spectra of only those lithium cations that are accessible to oxygen.[16] There were no appreciable changes in the ^{7}Li NMR spectra of Li-Al-MCM-41d after oxygen adsorption. The spectra of Li-Al-MCM-41g, however, show noticeable broadening, indicating the accessibility of some of the Li cations to oxygen and, therefore, the surface location of these cations (Figure 2).

Chemical analysis shows that the ion exchange capacity of the Al-MCM-41d materials is about 3−4 times higher than that of the grafted samples. This is reflected in the integral intensities of the ^{7}Li NMR spectra (Figure 2).[17] It now becomes clear that just a small fraction of the cations in Al-MCM-41d samples is located at the surface of the walls. But only these particular surface sites should be catalytically active in the proton form of Al-MCM-41 (Brønsted acid sites), for only these are accessible for interaction with organic substrates. In Al-MCM-41g samples, however, most of the active sites are exposed to the surface. To increase the concentration of such sites would improve the catalytic and adsorption properties of MCM-41 materials considerably.

In conclusion, our preliminary NMR studies have revealed that the Li$^+$ and Na$^+$ cations in ion-exchanged Al-MCM-41 obtained through surface grafting of aluminum are located in the surface region of the pore walls, whereas in the directly synthesized Al-MCM-41 a significant number of the cations have migrated inside the pore walls. With this, one can see the great potential of multinuclear solid-state NMR spectroscopy for studying the fine structural details of aluminosilicate mesoporous materials.

Supporting Information Available: XRD patterns, N$_2$ sorption isotherm and pore size distribution curves, and ^{27}Al MAS NMR spectra of ion-exchanged Al-MCM-41 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) ^{7}Li MAS NMR and ^{23}Na MAS NMR spectra were measured on a Bruker DSX-400 spectrometer (magnetic field of 9.4 T) operating at 155.5 and 105.8 MHz, respectively. ^{7}Li and ^{23}Na NMR spectra were referenced to 1 M aqueous LiCl or NaCl. In both cases a simple one-pulse sequence was used, with very short radio frequency pulses ($\pi/6-\pi/12$) and long recycle delays of several seconds to ensure complete relaxation. Samples were either (a) dehydrated at 450 °C for 12 h under dynamic vacuum in 5 mm NMR tubes and then flame-sealed under vacuum or in controlled oxygen or nitrogen atmosphere or (b) hydrated over saturated water solution of KNO$_3$ for 2 days. Spectra were recorded using a Bruker 7 mm MAS probe (MAS at 3.5 kHz) for sealed samples, or a Bruker 4 mm MAS probe (MAS at 10 kHz) for hydrated samples.

(9) For the direct synthesis,[3b] aluminum isopropoxide (Al(O^{i}Pr)$_3$, Aldrich), cetyltrimethylammonium bromide (CTABr, Aldrich), tetraethoxysilane (TEOS, Fluka), and tetramethylammonium hydroxide (TMAOH, Aldrich) were used. The gel molar composition was 1.0 Al(O^{i}Pr)$_3$:1255 H$_2$O:4.32 NaOH:2.13 CTABr:1.0 TEOS:xHBr, pH 11. The starting MCM-41 for the grafting synthesis was synthesized according to ref 10. The Al-grafted MCM-41 was prepared by impregnating 1.0 g of the calcined silica MCM-41 in 50 mL of 0.4 M aluminum chloride solution at 80 °C for 2 h.[2b] Li$^+$ and Na$^+$ forms of Al-MCM-41 were obtained by ion exchange at room temperature. Sample quality was confirmed by X-ray powder diffraction (XRD), nitrogen porosimetry, and ^{27}Al MAS NMR spectroscopy (see Supporting Information).

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(15) Analysis of ^{7}Li SATRAS NMR spectra of both samples gives quadrupolar coupling constants of 0.15−0.20 MHz, which is typical for ^{7}Li in oxide compounds, e.g. in dehydrated LiA and LiX zeolites or in silicates.

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(17) Quantitation of spectra of quadrupolar nuclei is not straightforward.

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