Oxygen and Structural Effects on Silicalite ^{29}Si Spin−Lattice Relaxation Studied by High-Resolution ^{29}Si Solid-State NMR

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Monodisperse silicalite crystals (170 μm × 40 μm × 40 μm) have been synthesized and the ^{29}Si spin−lattice relaxation rates have been measured by high-resolution solid-state NMR. Loading of 5 wt % *p*-xylene into the silicalite channel system reduces the ^{29}Si spin−lattice relaxation time compared to that of empty silicalite. The relaxation time is unaffected when *p*-xylene was replaced by *p*-xylene-d_{10} of the same loading. This indicates that dipole−dipole coupling between protons of guest molecules and silicon atoms does not contribute significantly to the ^{29}Si spin-relaxation time. A novel method employing aromatic endoperoxide is demonstrated for controlled addition of molecular oxygen into silicalite samples. The results showed that interaction with a paramagnetic oxygen molecule is not the only relaxation mechanism for ^{29}Si nuclei, and that zeolite structural changes caused by loaded organic guest molecules also play an important role in determining the ^{29}Si spin−lattice relaxation time.

Introduction

ZSM-5 (MFI topology) is a very important zeolite, widely used as shape-selective catalysts in industry. Figure 1 shows a schematic representation of the void space topology of MFI zeolite in relation to a crystal. ZSM-5 has exceptional size/shape selectivity with respect to the three xylene isomers to selectively produce *p*-xylene upon disproportionation of toluene. Thus, in the past several decades *p*-xylene/MFI complexes were extensively studied, both experimentally and theoretically.[1−7]

^{29}Si solid-state NMR has been widely used to study zeolite structures and probe the interaction between the zeolite host and organic guest molecules,[8,9] especially for *p*-xylene/MFI systems.[6,10,11] The *p*-xylene/MFI complex at room temperature can adopt three known distinct structures depending on the loading: a monoclinic one ($P2_1/n$) corresponding to the empty MFI zeolite,[12] and two orthorhombic structures, one containing two to four *p*-xylene molecules per unit cell ($Pnma$), and a second orthorhombic one containing eight *p*-xylene molecules in a unit cell ($P2_12_12_1$).[4,13,14]

Most high-resolution solid-state NMR studies have concentrated on chemical shift analysis and silicon site connectivity.[8,10,15−18] ^{29}Si spin−lattice relaxation time is another important parameter that can be used to probe the dynamics and interaction in the supermolecule formed by guest molecules adsorbed within the zeolite host. Several studies reported in the mid-1980s on the guest/MFI system[19−21] showed that interaction with paramagnetic oxygen was the dominant mechanism for the ^{29}Si spin−lattice relaxation process in MFI zeolites, whereas the Si/Al ratio, impurities found inside

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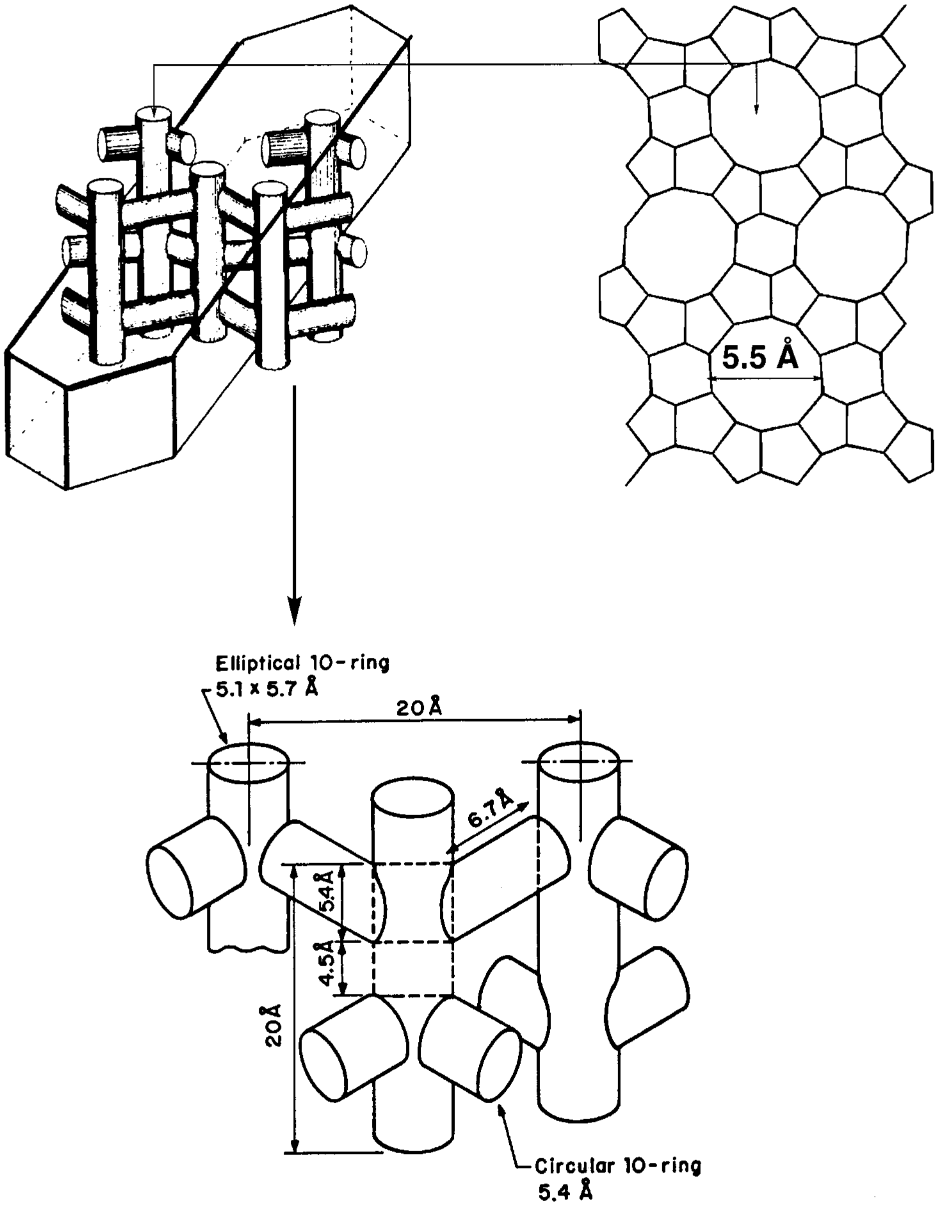

Figure 1. Schematic representation of the MFI zeolite structure.

the zeolite, as well as cations in the zeolite were shown to play only a minor role. Additionally, adsorption of certain organic molecules was capable of displacing oxygen inside the zeolite channel system, elongating the ^{29}Si spin-relaxation time. On the other hand, van de Ven measured a series of MFI zeolites and reported a *reduction* of ^{29}Si spin−lattice relaxation time when the guest molecules were loaded into MFI zeolites.[22] All those studies suffered from poor spectral resolution and, consequently, the mechanistic interpretation of ^{29}Si spin−lattice relaxation still remains unclear.

To better understand the mechanism for ^{29}Si relaxation in the presence of added organic molecules and molecular oxygen, we have synthesized and investigated the ^{29}Si NMR of large silicalite crystals. We find that excellent high-resolution ^{29}Si MAS spectra can be routinely obtained. We chose *p*-xylene as our guest molecule since the ^{29}Si NMR of the *p*-xylene/MFI system has been well characterized in the literature.[10,11,23] We describe a novel method that allows the convenient addition of oxygen to samples without removal of the samples from the spectrometer. This novel method also has the potential of allowing oxygen to be added to samples in a “pulsed” manner and to thereby study the “diffusion” of the oxygen through the silicalite framework by observation of the relaxation of the ^{29}Si nuclei. We measured the ^{29}Si spin−lattice relaxation time for each resolved silica site in both empty silicalite and silicalite loaded with *p*-xylene. We showed that interaction with molecular oxygen is not the only dominant relaxation mechanism, but that structural changes caused by the loading of organic guest molecules can also play a significant role in the ^{29}Si relaxation process.

The effect of oxygen was studied by the added oxygen from the decomposition of endoperoxide **1** inside the rotor. Endoperoxide **1** (Scheme 1) does not persist at

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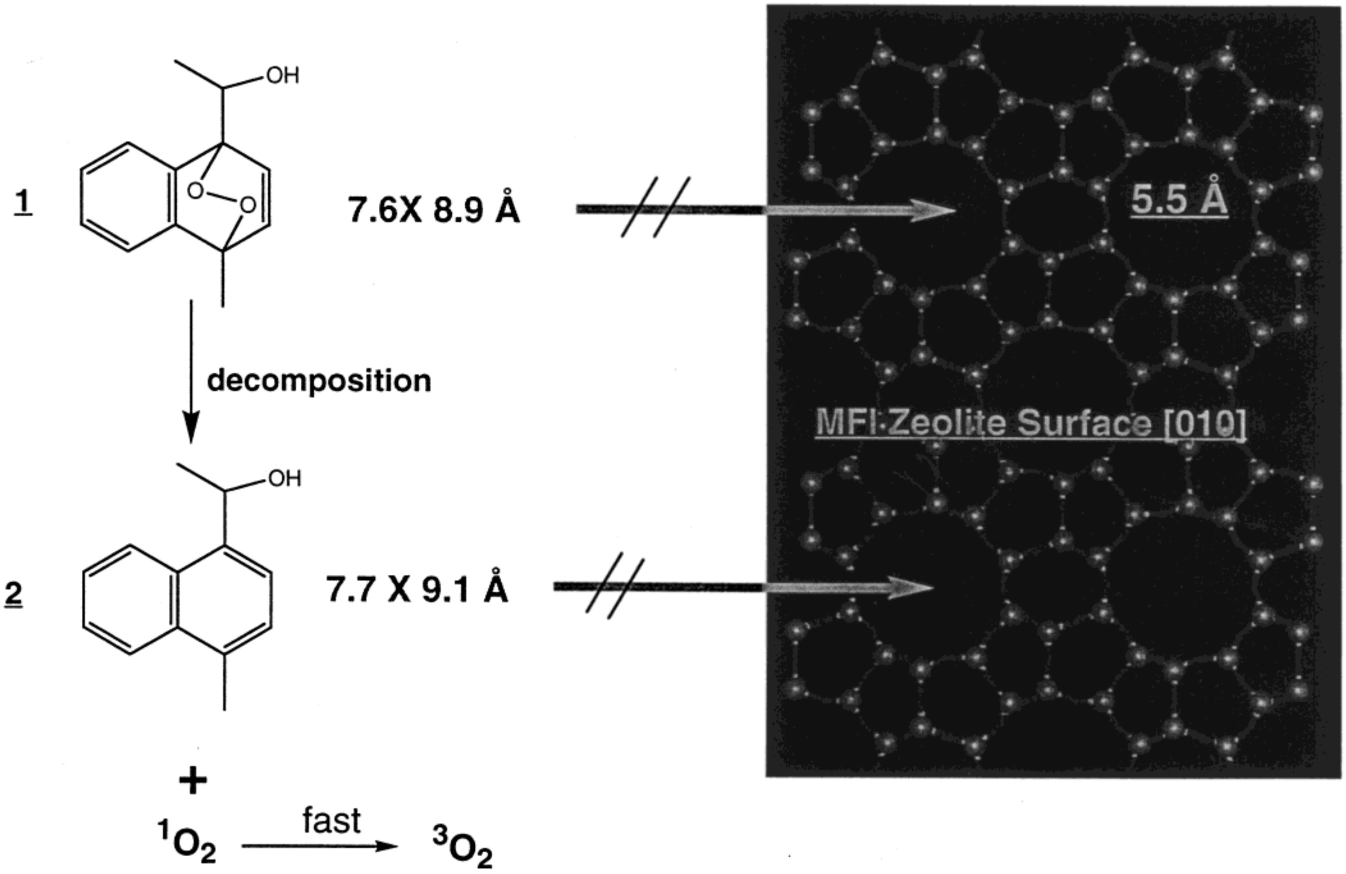
Scheme 1. Decomposition of 1-(1′-Hydroxylethyl)-4-methyl-1,4-epidioxy-1,4-dihydronaphthalene 1



room temperature and it releases singlet oxygen effectively by decomposition (Scheme 1).[24,25] Singlet oxygen has a very short lifetime (microsecond to millisecond) and by the time it diffuses into the zeolite, it decays to normal ground-state oxygen, a triplet paramagnetic molecule.[26] This gives us the ability to generate and add molecular oxygen to the silicalite complex in situ.

Experimental Section

Silicalite crystals were synthesized as described in the literature with minor modifications.[27] The starting materials were Aerosil-200 (fused silicon dioxide, 99.8%−100%, Degussa Corporation), ammonium fluoride (Aldrich Chemical Co., 98%), tetrapropylammonium bromide (Aldrich Chemical Co., 98%) and deionized water. Instead of using Aerosil directly in the synthesis, a thin gel was first made from Aerosil and deionized water. Subsequently, most of the water was gently evaporated at 80 °C, and the resulting material was heated at 500 °C overnight. The baked Aerosil was then thoroughly ground to make a precursor silicon source for the synthesis. This "precursor" method afforded much cleaner and more uniform crystals compared to those using Aerosil directly. The synthesis was carried out in 250-mL Teflon beakers which were placed into stainless steel autoclaves. The reaction was conducted for 3 days at 170 °C. Subsequently, the crystals were washed, dried, and calcined at 500 °C for 12 h. The calcined crystals (nearly 100% crystallinity) were sieved to remove crystal aggregates and smaller crystals. The crystals were inspected with a scanning electron microscope (SEM, Hitachi S-510) and its ^{29}Si solid-state NMR was recorded. Synthesis of the racemic endoperoxide **1** was prepared as previously described.[25]

The loading of *p*-xylene into the silicalite was accomplished as follows. A total of 300 mg of freshly calcined silicalite was mixed with 15 mg of *p*-xylene in 0.5 mL of isooctane. The resulting *p*-xylene/silicalite supramoleculular system contains about four *p*-xylene molecules per unit cell. After stirring overnight, the solvent was gently removed under argon gas and dried under high vacuum (10^{-5} Torr) overnight. The sample was then sealed on a vacuum line and heated at 80 °C for 12 h to ensure homogeneous distribution of guest molecules inside the silicalite crystals.[28]

For the experiments producing oxygen through endoperoxide decomposition, about 15 wt % **1**, was loaded onto silicalite or *p*-xylene/silicalite in a similar way to that of loading *p*-xylene, except that methylene chloride (dried over CaH_2) was used as the solvent. The sample was quickly sealed in a NMR rotor and transferred to the NMR probe. Similarly loaded control samples containing endoperoxide were analyzed for $^1O_2$ emission at 1268 nm, before and after NMR measurements for both empty silicalite and *p*-xylene/silicalite complex. From the control samples, the intensity of emission of singlet oxygen was reduced by ~80% during the span of the NMR experiment.

^{29}Si MAS NMR spectra were obtained at 59.62 MHz with a Bruker DRX-300 widebore spectrometer. The magic angle was set up using ^{79}Br resonance of KBr and samples were spun at 5 kHz unless otherwise noted.

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(28) The integral from ^{2}H NMR spectra of *p*-xylene-d_{10} as a function of loading, increased linearly up to 8 wt % loading. Additionally, the intensity of the proton signals from the solid-state NMR of *p*-xylene were also linearly dependent on the loading of *p*-xylene from 0.2 to 10 wt %. The non-*p*-xylene peaks can be safely ascribed to Si−OH groups and to hydrogen-bonded Si−OH groups by comparing them with known values from the literature. (For example, see: Bronnimann, C. E.; Zeigler, R. C.; Maciel, G. E. *J. Am. Chem. Soc.*, **1988**, *110*, 2023−2026.) No detectable signals from isooctane were observed from spectra taken after the loading protocol.

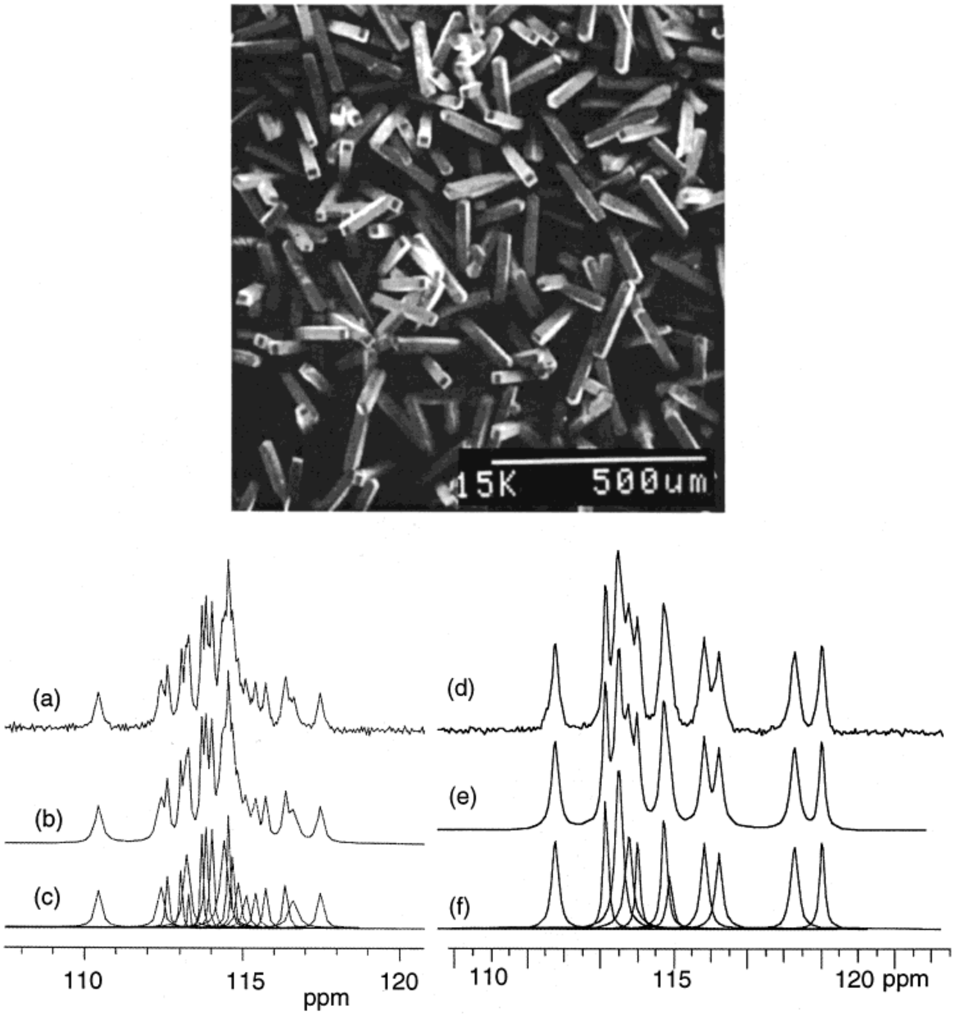

Figure 2. Synthetic silicalite crystals (SEM photo) and ^{29}Si MAS NMR of empty silicalite (a−c) and silicalite loaded with four *p*-xylene per unit cell: (a) and (d) experimental spectra; (b) and (e) simulated spectra; (c) and (f) simulated peaks.

Spin−lattice relaxation times were measured using an inversion−recovery pulse sequence using a recycle delay of 20 s and 100−400 acquisitions were obtained. The spin-relaxation time was obtained by least-square fitting of the intensities of each peak using Bruker XWINNMR software package (Bruker Instruments, Inc.). Although the fitting gave an uncertainty of less than 1%, we estimate the actual uncertainty of the T_1 to be 10% due to the relatively short recycle delay and uncertainty of the oxygen concentration.

Results and Discussion

Silicalite Characterization. Figure 2 shows the SEM image and the ^{29}Si MAS NMR spectra and their simulations based on the literature for both empty silicalite and silicalite loaded with *p*-xylene.[16,18,29] The SEM image is typical for silicalite grown from a weakly basic medium. For empty silicalite, 19 peaks out of the 24 theoretical peaks can be distinguished. For *p*-xylene/silicalite complex, 11 sharp peaks out of the theoretical 12 individual silicon sites are clearly separated, with one of them having doubled intensities.

Spin−Lattice Relaxation Measurement. *Effect of Adsorbed p-Xylene Molecule.* Having established that our silicalite crystals yield high-resolution spectra, we measured the ^{29}Si spin−lattice relaxation time for both empty silicalite and silicalite loaded with *p*-xylene molecules. Figure 3 shows the spectra of spin−lattice measurement. Clearly, different peaks (corresponding to different silicon sites in the unit cell) have different recovery times.

To understand the effect of dipolar−dipolar coupling between guest protons and silicon atoms on the ^{29}Si spin-relaxation time, we also measured the ^{29}Si spin−lattice relaxation time for silicalite containing *p*-xylene-d_{10} at the same loading. One would expect that the ^{29}Si spin-relaxation would be different for *p*-xylene/silicalite and *p*-xylene-d_{10}/silicalite if the dipolar−dipolar coupling is the major relaxation mechanism. In fact, the T_1 spectra of *p*-xylene-d_{10}/silicalite are essentially the same as those for the *p*-xylene/silicalite supramolecular system (spectra not shown). Figure 4 plots the T_1 values for all of the above measurements. We concluded that (a) in general, silicalite loaded with *p*-xylene has a shorter T_1 compared with that of empty silicalite, and (b) isotope substitution of the guest molecule *p*-xylene does not affect the T_1 significantly, indicating that dipolar−dipolar coupling between protons in the guest molecule and lattice silicons do not contribute significantly to the ^{29}Si T_1 relaxation.

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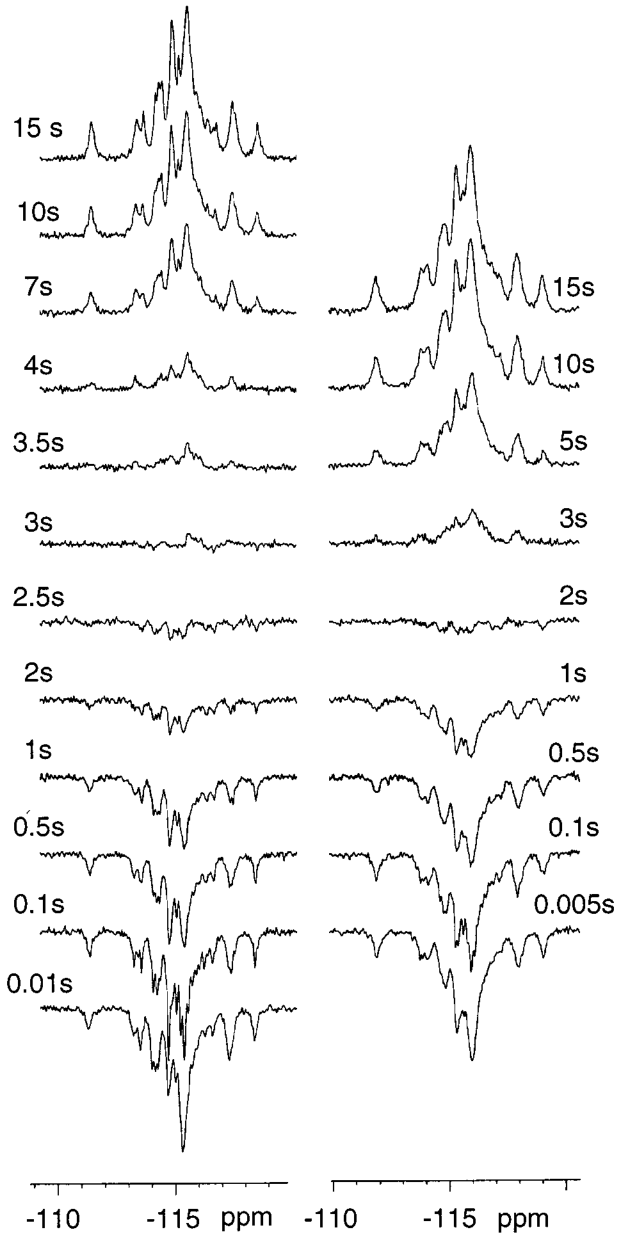

Figure 3. ^{29}Si T_1 spectra of empty silicalite (left) and *p*-xylene/silicalite complex (right). Numbers in the spectra indicate the time delay between the two pulses during the T_1 measurement.

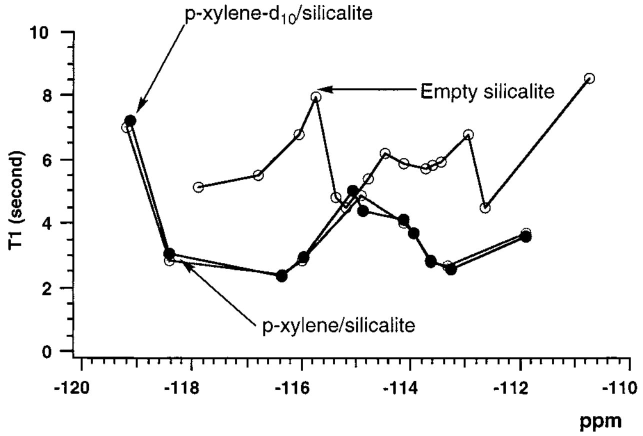

Figure 4. Effect of loaded organic molecules on the ^{29}Si spin–lattice relaxation time.

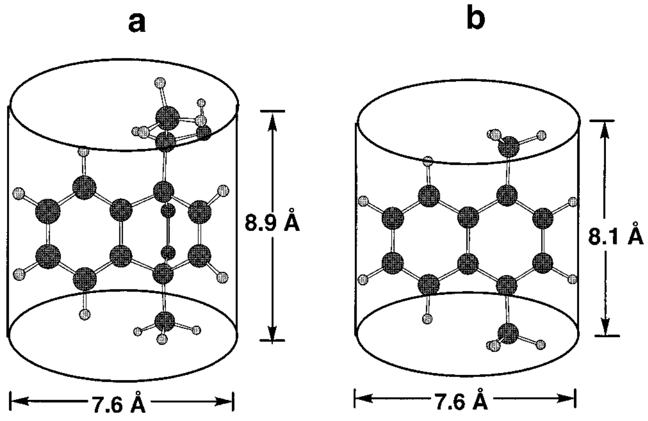

Figure 5. Size of endoperoxide **1** (a) and 1,4-dimethyl naphthalene as the control (b) (see text for details).

Effect of Oxygen in the Presence of p-Xylene. We employ a novel and convenient method to investigate this effect. Endoperoxide **1** (Scheme 1) was used to generate and add molecular oxygen into the silicalite complex. From computational analysis of the molecular cross section of endoperoxide **1** and comparison to the size/shape characteristics of the pores (~5.4–5.6 Å diameter) on the external surface of a MFI crystal (Figure 5a), it is clear that neither the endoperoxide nor its decomposition product **2** (see Scheme 1) is able to access the internal surface. Therefore, neither **1** nor **2** is expected to affect the structure of silicalite or the resulting NMR spectra.

We measured the spin-relaxation time of silicalite loaded with only endoperoxide and silicalite loaded with both *p*-xylene and endoperoxide to compare the oxygen effect on those systems. As a control, we also measured the T_1 of silicalite loaded with 1,4-dimethyl naphthalene (Figure 5b), a commercially available compound with a similar structure and molecular dimension to that of decomposition product **2**. Figure 6 shows the T_1 points of the silicalite loaded with endoperoxide, *p*-xylene/silicalite loaded with endoperoxide, and the T_1 for their corresponding "empty" samples.

From Figure 6, we can clearly see that loading with endoperoxide enhances the spin–lattice relaxation for the empty silicalite, but it does not change the spin–lattice relaxation time for the *p*-xylene/silicalite complex within experimental uncertainty. The T_1 values of the control experiment (silicalite loaded with 1,4-dimethyl naphthalene) show an identical spin–lattice relaxation time with that of empty silicalite, indicating that large molecules adsorbed on the external surface do not change the structure and the spin–lattice relaxation time of silicalite.

The results from high-resolution ^{29}Si NMR measurements of synthetic silicalite loaded with *p*-xylene (5% w/w loading) clearly show that the ^{29}Si spin-relaxation time is faster compared to empty silicalite. Different silicon sites apparently have different spin–lattice relaxation times in both systems, although there appears to be a lack of correlation between the mean tetrahedral angle and the chemical shift of various silicon sites.[18] It is interesting to note that for the silicon site with the largest mean tetrahedral angle (hence the largest absolute chemical shift value), the spin–lattice

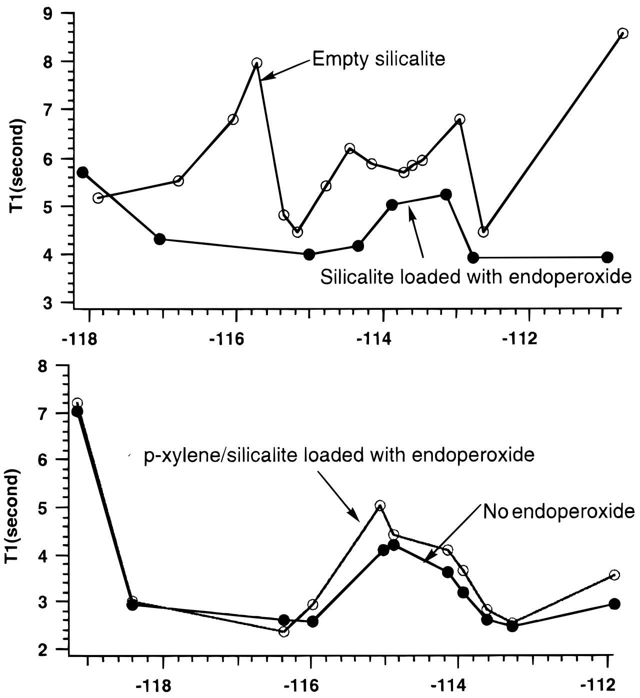

Figure 6. Effect of oxygen on the ^{29}Si spin−lattice relaxation time: (top) silicalite and (bottom) *p*-xylene/silicalite system.

relaxation time for empty silicalite is the smallest (−118 ppm, $T_1 = 5.15$ s), but the same silicon site in the *p*-xylene/silicalite complex has the longest spin−lattice relaxation time (−119 ppm, $T_1 = 7$ s). It seems that this site is more likely located in the intersections of silicalite where it is more open to the channel system. In the empty silicalite, this site has more contact time with paramagnetic molecular oxygen in the air so that it has a faster spin−lattice relaxation time. When *p*-xylene is adsorbed inside the silicalite channel system, it experiences more shielding to this silicon site, since *p*-xylene tends to stay in the intersections.[23] Consequently, the oxygen has less contact with the silicon site, making the spin−lattice relaxation time longer for this site compared to other silicon sites. Using *p*-xylene as the guest molecule, we confirmed that adsorbed guest molecules can partially block or at least retard the diffusion of oxygen inside the silicalite crystal, making it less accessible to the silicon sites.

Experiments on silicalite loading with endoperoxide **1** are also consistent with this result. Comparing the spin−lattice relaxation time of empty silicalite and silicalite loaded with endoperoxide, we found that the spin−lattice relaxation is enhanced when endoperoxide is added. Since neither endoperoxide **1** nor its decomposition product can diffuse inside the silicalite framework, the net effect is that supplemental oxygen is added into the sealed rotors (the rotors were filled with air at the beginning of all the experiments). At this point, oxygen is added continuously and its effect is an overall one during the entire experiment. We realize that this is not a quantitative way of adding oxygen, but it is a simple way to study the effect of oxygen at its initial stage, and the effect is obvious. For a similar experiment with *p*-xylene/silicalite, however, we found that the spin−lattice relaxation time is virtually unaffected within experimental error.

Now we need to ask the question, why is the spin−lattice relaxation time of ^{29}Si nuclei in the *p*-xylene/silicalite complex smaller than that of empty silicalite? If the spin−lattice relaxation time is purely due to the interaction with oxygen, regardless of its source, one would expect the *p*-xylene/silicalite system to possess a longer spin−lattice relaxation time, since the silicon sites are less accessible to the oxygen. Lefebvre reported that ^{1}H−^{29}Si cross-polarization gave a strong signal at about 5% loading.[30] Strong polarization transfer also means strong dipolar−dipolar couplings between the two nuclei. The result of *p*-xylene-d_{10}/silicalite seems to give a negative answer to that question (Figure 4).

It is interesting to note that in the literature report, adsorption of linear molecules such as hexane inside the MFI channel system increases the spin−lattice relaxation time of ^{29}Si nuclei, while adsorption of aromatic molecules such as benzene decreases the spin−lattice relaxation time.[16,18] Our results of involving *p*-xylene/silicalite also show this trend. While the effect of oxygen on the ^{29}Si spin−lattice relaxation is most likely due to its accessibility to the silicon nuclei, the effect of the adsorbed guest molecules can be rather complicated. The local structural changes of zeolite brought on by included guest molecules seem to provide another relaxation mechanism yet to be understood. This is further complicated by the fact that different molecules have different degrees of interactions with the zeolite lattice. For example, while adsorption of *p*-xylene gives the classical loading dependence of MFI zeolite lattice, the same loading of other molecules such as benzene does not give the same structural change. These are possibly due to the subtle changes in the molecule's shape and size. Hence, the effect of adsorbed molecules on the ^{29}Si spin−lattice relaxation cannot be fully explained and further investigations are required for these results to be understood.

Conclusions

With the synthesis of large silicalite crystals, very high resolution ^{29}Si MAS NMR can be obtained routinely on commercial instrumentation. High-resolution ^{29}Si spin−lattice relaxation measurements employing a novel method to generate oxygen in situ confirmed that oxygen is the major relaxation agent of ^{29}Si in zeolites and that different silicon sites have different relaxation times. The distribution of the T_1 values is probably due to the different oxygen accessibility as it diffuses through the framework. Absorption of four *p*-xylene molecules per MFI unit cell changes the symmetry of the MFI zeolite and reduces the spin−lattice relaxation time. Changing the guest molecule from normal *p*-xylene to *p*-xylene-d_{10} does not affect the ^{29}Si T_1 values, excluding dipole−dipole coupling between protons in guest molecules and silicon atoms as the factor in the ^{29}Si spin-relaxation acceleration. Further studies are needed and are in progress to understand the effect of the adsorbed organic guest molecules. Also further refinement of the endoperoxide method will be pursued to invent systems capable of detecting the diffusion of oxygen throughout the MFI framework.

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