

## Effect of Molecular Oxygen on the Variable-Temperature $^{29}\text{Si}$ MAS NMR Spectra of Zeolite–Sorbate Complexes

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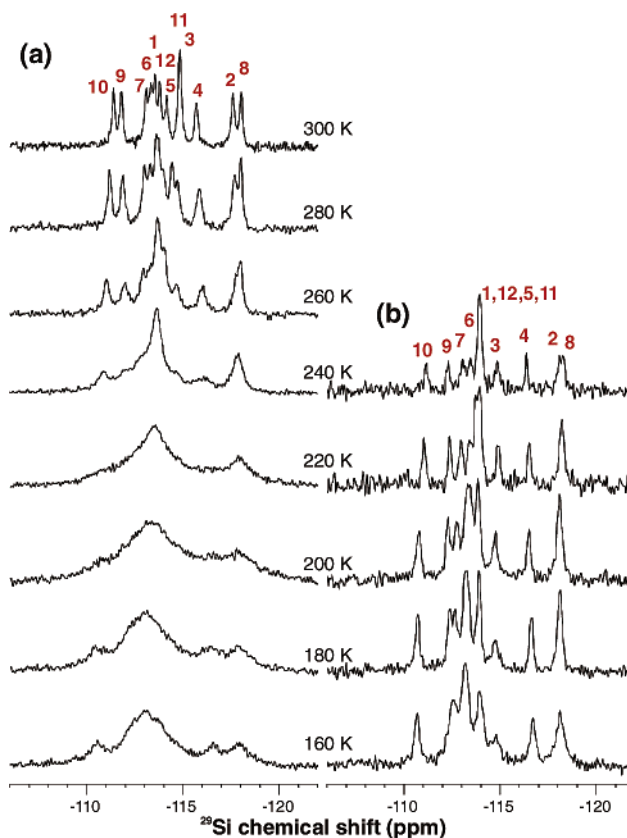
Understanding the interactions between guest species and host zeolite frameworks, which are central to the synthesis and applications of zeolites, requires detailed structural information for these complexes. For most zeolites, structure determination by X-ray diffraction is limited due to their microcrystalline nature and the weak contribution, relative to the framework, of the guest species to the X-ray scattering intensity. Solid-state NMR spectroscopy offers an alternative and complementary method for structure determination of zeolite host–guest complexes.

We have developed an approach to determine the locations of sorbate molecules in highly siliceous zeolite frameworks from solid-state  $^{29}\text{Si}\{^1\text{H}\}$  CP MAS NMR data.<sup>1</sup> This approach requires  $^{29}\text{Si}$  MAS NMR spectra in which most of the resonances arising from the inequivalent Si atoms in the structure are resolved. The peaks are first assigned by performing and analyzing a two-dimensional  $^{29}\text{Si}$  INADEQUATE correlation experiment.<sup>2</sup> The relative rates of  $^{29}\text{Si}\{^1\text{H}\}$  cross polarization measured between the  $^1\text{H}$  nuclei of the sorbate molecule, and those Si atoms whose resonances are resolved in the  $^{29}\text{Si}$  spectrum are then used to determine the location of the sorbate molecule.

Since motions of the sorbate molecules are reduced as the temperature is lowered, it is desirable to collect  $^{29}\text{Si}\{^1\text{H}\}$  CP MAS NMR data at as low a temperature as is reasonably possible. However, for many of the systems we have studied, although the spectra are highly resolved at room temperature, the peaks broaden substantially as the temperature is lowered such that the resolution of the individual  $^{29}\text{Si}$  peaks is lost. This effect is shown in Figure 1a which presents a series of  $^{29}\text{Si}$  MAS NMR spectra<sup>3</sup> of the *p*-dibromobenzene/ZSM-5 complex (pDBB/ZSM5) with a loading of 4 molecules per unit cell (molecules/u.c.).<sup>4</sup> This loss of resolution in the  $^{29}\text{Si}$  spectrum is a significant limitation to application of the solid-state NMR structure determination technique at low temperatures.

This line broadening does not arise from  $^1\text{H}/^{29}\text{Si}$  dipolar interactions as high power  $^1\text{H}$  decoupling does not improve the resolution of the  $^{29}\text{Si}$  spectra at any of the temperatures presented in Figure 1a. Furthermore, the same behavior in the line broadening is observed for the low-loaded *p*-xylene- $d_{10}$ /ZSM-5 complex in which there are no protons.

It is possible that this line broadening may be “inhomogeneous”, a reflection of disorder in the sorbate/zeolite complex that may arise from reduced guest molecule motions at lower temperatures. It is known that the ZSM-5 framework is somewhat flexible and interacts quite strongly with the sorbate molecules. Subtle differences in the local geometry of the Si atoms throughout the structure could give rise to distributions of  $^{29}\text{Si}$  chemical shifts and spectra with broader peaks and lower resolution. Fully loaded ZSM-5 complexes with *p*-xylene and *p*-dichlorobenzene (8 molecules/u.c.), in which there should not be any site vacancies, give spectra with sharp peaks at low temperature which seems to be consistent with this proposal. However, the slight increase in resolution in the spectra presented in Figure 1a at temperatures below 200 K is not consistent with



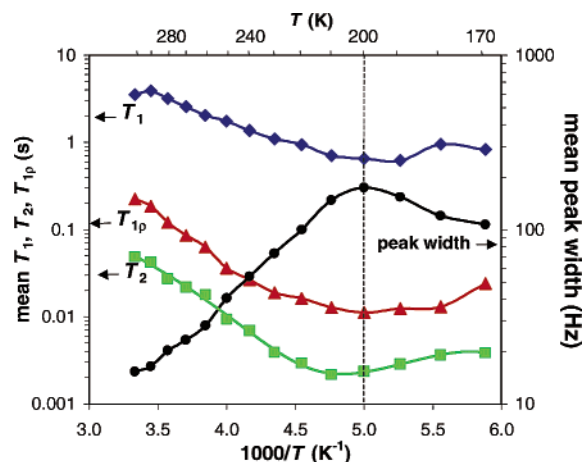
**Figure 1.** Variable-temperature  $^{29}\text{Si}$  MAS NMR spectra of the pDBB/ZSM-5 complex with a loading of 4.0 molecules/u.c. (a) Sample packed in air and spun with air as the drive gas (32 scans with  $90^\circ$  pulses and recycle delays of 5–10 s, no  $^1\text{H}$  decoupling applied, see text). (b) Sample purged with  $\text{N}_2$  gas for 24 h and spun with  $\text{N}_2$  as the drive gas (16 scans with  $45^\circ$  pulses and recycle delays between 60 and 120 s,  $^1\text{H}$  decoupling applied). Peaks were assigned from a two-dimensional  $^{29}\text{Si}$  INADEQUATE spectrum.

the line broadening arising from increased distributions in chemical shifts brought about by structural disorder.

The true nature of the line broadening is revealed by measurement of the  $^{29}\text{Si}$  relaxation times. If the  $T_2$  relaxation time is short enough (such that  $T_2 \approx T_2^*$ ), the resolution in a spectrum becomes limited by  $T_2$ :

$$\text{Peak width at half-height (in Hz)} = 1/(\pi T_2) \quad (1)$$

$^{29}\text{Si}$   $T_1$ ,  $T_2$ , and  $T_{1\rho}$  relaxation times were measured over a range of temperatures, and the mean  $^{29}\text{Si}$  relaxation times are plotted versus temperature in Figure 2. There is a minimum in all of the relaxation times at about 200 K which corresponds to the maximum in the peak width, indicating that the line broadening is a relaxation effect. The minimum mean  $T_2$  value of about 2 ms corresponds to a mean peak width of about 160 Hz according to eq 1, consistent with the measured maximum mean peak width.

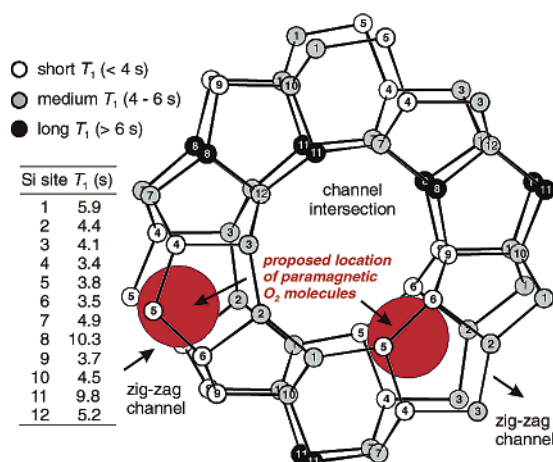


**Figure 2.** Temperature dependence of the  $^{29}\text{Si}$  mean peak widths at half-height (black circles) and  $^{29}\text{Si}$  mean  $T_1$  (blue diamonds),  $T_{1p}$  (red triangles), and  $T_2$  (green squares) relaxation times plotted as  $\log T_x$  vs  $1/T$  for the pDBB/ZSM-5 complex with a loading of 4 molecules/u.c.

Since the resolution of the  $^{29}\text{Si}$  MAS NMR spectra appears to be a function of the  $^{29}\text{Si}$   $T_2$  relaxation times, it is important to identify the source of the  $^{29}\text{Si}$  relaxation. For zeolites, the major relaxation source is often paramagnetic molecular oxygen which fills the empty space in the channels of the zeolite.<sup>5</sup> To confirm this is the present case,  $^{29}\text{Si}$  MAS NMR spectra were collected on the pDBB/ZSM-5 sample after placing the sample in a flow of  $\text{N}_2$  gas for 24 h. The low-temperature MAS was performed using  $\text{N}_2$  rather than air for the drive gas to prevent  $\text{O}_2$  from re-entering the sample. In Figure 1b, the series of  $^{29}\text{Si}$  spectra of the oxygen-reduced sample are compared to those of the same sample packed in air. The difference in the resolution between these spectra is very striking, clearly indicating that the paramagnetic molecular oxygen is responsible for the line broadening.

The individual  $^{29}\text{Si}$  nuclei have quite different relaxation times, suggesting that the oxygen molecules are localized relatively specifically in the zeolite channel system. For example, the  $T_1$  relaxation times, measured for the 12  $^{29}\text{Si}$  peaks in the fully resolved  $^{29}\text{Si}$  MAS NMR spectrum of the pDBB/ZSM-5 complex with a loading of 3.5 molecules/u.c. at 300 K, range from 3 to 10 s. In Figure 3, the different Si atoms of the ZSM-5 framework are coded according to their  $T_1$  relaxation times. The shortest  $T_1$  values belong to Si4, Si5, Si6, and Si9 which are part of the “zigzag” channel, while the longest belong to Si8 and Si11 which are in the channel intersection. These different relaxation times suggest that the oxygen molecules are localized mainly in the zigzag channels. This in turn suggests that the pDBB molecules are located in the channel intersection, blocking Si8 and Si11 from the  $\text{O}_2$  molecules. This pDBB location has been confirmed by analyzing  $^{29}\text{Si}\{^1\text{H}\}$  CP MAS NMR data and is consistent with the XRD structure of the similar *p*-dichlorobenzene/ZSM-5 complex.<sup>6</sup> This analysis of the  $^{29}\text{Si}$   $T_1$  relaxation times, which identifies the regions of the zeolite where the oxygen molecules are excluded, provides a simple method for roughly determining the location of the sorbate molecules.

The  $^{29}\text{Si}$  relaxation arises from fluctuations in the weak electron–nuclear couplings between the unpaired electron in the  $\text{O}_2$  molecules and the  $^{29}\text{Si}$  nuclei, most likely through a pseudocontact (through space) mechanism. The temperature dependence arises from changes in the rate of  $\text{O}_2$  molecular motions. Perhaps it could be “in place” motion or diffusion, or it could be a complex mixture of motions as the  $\log T_x$  vs  $1/T$  curves do not seem to fit with a simple mechanism, especially because of the fact that there is a minimum in the  $T_2$  curve. It is important to note that “empty” ZSM-5 does not exhibit this line broadening behavior over this temperature



**Figure 3.** ZSM-5 framework with Si sites coded according to  $^{29}\text{Si}$   $T_1$  relaxation times for the pDBB/ZSM-5 complex with 3.5 molecules/u.c. at 300 K. On the basis of these data, the paramagnetic oxygen molecules are proposed to be localized mainly in the zigzag channels and the sorbate molecules in the channel intersection. The spheres represent those regions in the zeolite where the oxygen molecules are proposed to be localized.

range, suggesting that the sorbate molecules have a significant influence on the  $\text{O}_2$  motions, including limiting diffusion.

It is important to be aware of the fact that, over the course of a long experiment in which  $\text{N}_2$  is used as the bearing and drive gases for MAS, it may be possible for  $\text{O}_2$  in the pores of zeolites to be displaced, potentially leading to dramatic changes in the spectrum and relaxation times during the experiment. In the presence of paramagnetic  $\text{O}_2$ , the  $^1\text{H}$   $T_{1p}$  relaxation time can be very short at low temperatures, leading to inefficient  $^{29}\text{Si}\{^1\text{H}\}$  cross polarization. By reducing the  $\text{O}_2$ , the  $^1\text{H}$   $T_{1p}$  times become longer, giving rise to more efficient  $^{29}\text{Si}\{^1\text{H}\}$  cross polarization.

Although it is important to keep in mind that there may be other reasons for line broadening, it may be possible to distinguish between “homogeneous” and “inhomogeneous” broadening by checking whether the line widths are directly related to  $T_2$  according to eq 1. If the line broadening is “inhomogeneous”, then the  $^{29}\text{Si}$  spectra may detect disorder in the zeolite–sorbate complex. If the line broadening is “homogeneous”, then purging with  $\text{N}_2$  may lead to increased spectral resolution.

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## References

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- (3) Solid-state NMR experiments were performed using a Bruker AVANCE DSX-400 NMR spectrometer and a Bruker CP MAS NMR probe modified with a standard speed 7 mm Kel-F MAS stator from Doty Scientific. Low-temperature MAS experiments were performed using cooled  $\text{N}_2$  as the bearing gas and either  $\text{N}_2$  or air as the drive gas.
- (4) The pDBB molecules were loaded into a sample of ZSM-5 by carefully weighing and mixing the appropriate amounts in a pre-scored glass ampule which was subsequently evacuated on a vacuum line, flame-sealed, and placed in an oven at 100 °C for 12 h to equilibrate.
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