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Communications to the Editor

Dynamics of Benzene Adsorbed on Ca-LSX Zeolite Studied by Solid-State Two-Dimensional Exchange ^{13}C NMR[†]

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Transport of molecular guest species in confined environments is central to the performance of many permeable materials, including porous catalysts, adsorbents, membranes, and polymers, which are heterogeneous systems characterized by appreciable disorder and complexity. Neutron and X-ray diffraction investigations can provide local structural information for guest configurations that possess sufficiently long range periodic order,[1−3] while complementary structural measurements over much shorter length scales are provided by nuclear magnetic resonance (NMR) techniques.[4−6] Information on local guest species dynamics, however, is often difficult to infer from such studies, although over longer length scales (*ca.* 1 μm) molecular self-diffusion can be measured by means of pulsed-field-gradient NMR methods.[7] Solid-state two-dimensional (2D) exchange NMR strategies pioneered by Spiess and co-workers[8] for studying reorientation geometries and time scales of slow dynamic processes in polymers[9−11] are powerful probes of local environment and dynamics. We report here the first solid-state ^{13}C NMR measurement of analogous transport dynamics of adsorbed hydrocarbon guest molecules on a microporous molecular sieve, specifically, benzene adsorbed on Ca-LSX zeolite.

In recent related studies, 2D exchange ^{129}Xe NMR has been applied to measure slow intercage migration of xenon atoms physically adsorbed on NaA zeolite, relying on high intracage mobility of the xenon atoms to produce narrow isotropic NMR lines.[12,13] Benzene molecules adsorbed on Ca-LSX, however, bind more firmly to Ca^{2+} adsorption sites, causing the measured ^{13}C NMR frequencies to depend on the orientation of the benzene molecules with respect to the external magnetic field $\mathbf{B}_0$. Thus, for a powder C$_6$H$_6$/Ca-LSX sample containing an isotropic bulk distribution of benzene orientations, an inhomogeneously broadened NMR spectrum is obtained. More precisely, benzene molecules spinning rapidly about their 6-fold axes[14] anisotropically average the chemical shift tensors for each molecule, yielding an axially symmetric ^{13}C spectrum.

In a 2D exchange NMR experiment,[15] frequencies in the evolution (t_1) and detection (t_2) periods, which are separated by a mixing time (t_m), are correlated. As a consequence, the observed 2D spectrum may be affected by molecular reorientation (and thus changes in frequencies) during the mixing time or by magnetization transfer via spin diffusion during t_m (which produces changes in frequencies without reorientation). Spin diffusion among nonexchanging benzene molecules adsorbed on Ca-LSX is not appreciable, as established by separate variable temperature experiments (not shown here) that reveal a strong off-diagonal intensity dependence on temperature, consistent with an activated molecular exchange mechanism.[16] Thus, for the C$_6$H$_6$/Ca-LSX system, off-diagonal intensity in a 2D spectrum indicates molecular reorientation during t_m (for typical correlation times 1 ms < τ_c < 1 s), whereas intensity along the diagonal reflects molecules in the same orientation with respect to $\mathbf{B}_0$ both before and after the mixing time t_m. Moreover, exchange between discrete and ordered adsorption sites yields characteristic off-diagonal ridges in the form of an ellipse, from which the angle β between the relative orientations of the adsorbed molecules during t_1 and t_2 can be established directly according to[8]

$$|\tan\beta| = \frac{b}{a} \qquad (1)$$

where *a* and *b* are the minor and major axes, respectively, of the elliptical pattern.

Ca-LSX, (AlO$_2$)$_{96}$(SiO$_2$)$_{96}$Ca$_{48}$, is a faujasite-type zeolite with a silicon-to-aluminum ratio of 1.0 and divalent charge-compensating calcium cations. A bulk loading of two benzene molecules per zeolite supercage was introduced,[17] using benzene ^{13}C enriched to 99% at a single ring site[18] as a compromise between NMR signal enhancement and unwanted effects from ^{13}C−^{13}C dipolar couplings. Two-dimensional exchange ^{13}C NMR spectra were recorded in off-resonance mode using a standard cross-polarization pulse sequence[9] on a Chemagnetics CMX-500 spectrometer operating at 125.4 MHz for ^{13}C and 498.6 MHz for ^{1}H.

Whereas the shape of an off-diagonal 2D spectral pattern allows the geometry of a dynamical molecular event to be

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(18) Benzene 99% ^{13}C enriched at a single ring site was purchased from Isotec, 3858 Benner Road, Miamisburg, OH 45342.

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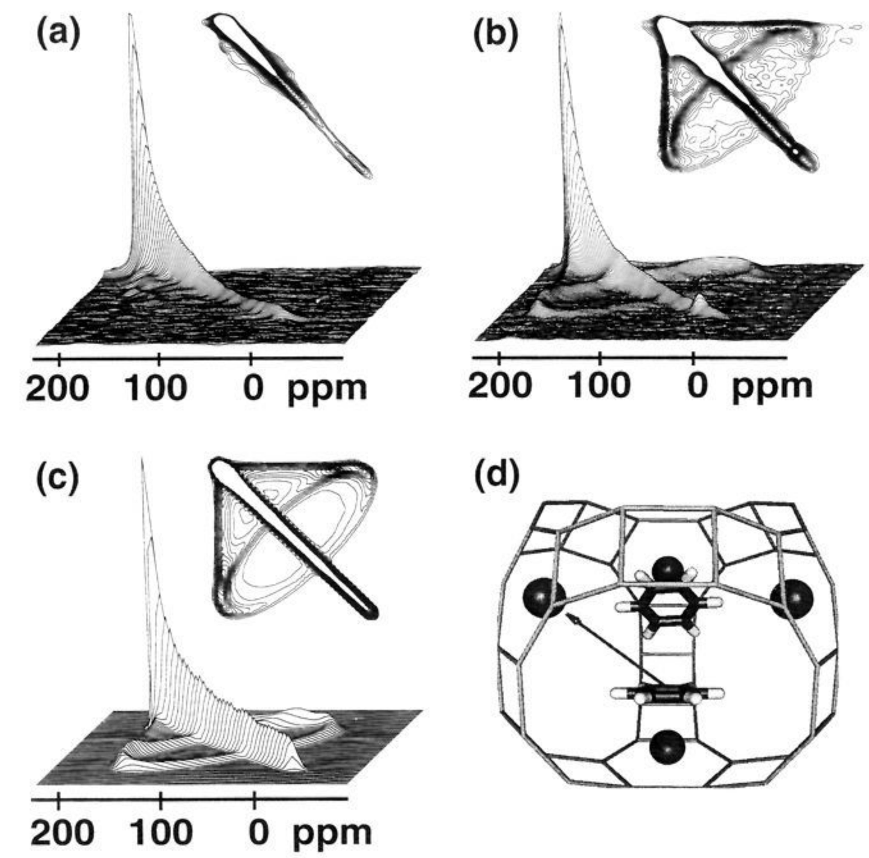

Figure 1. (a−c) Experimental and simulated 2D exchange ^{13}C NMR spectra of benzene adsorbed in the supercages of Ca-LSX zeolite: (a) $T = 298$ K, $t_m = 1$ ms; little or no exchange of benzene molecules occurs among adsorption sites with different orientations on this time scale; (b) $T = 298$ K, $t_m = 300$ ms; the off-diagonal exchange features are consistent with a sizable fraction of benzene molecules reorienting among different well-defined environments $\beta = 109° \pm 3°$ with respect to one another; (c) simulated exchange NMR spectrum for an isotropic distribution of axially symmetric chemical shift tensors that exchange with a correlation time on the order of the mixing time among discrete tetrahedrally-arranged sites ($\beta = 109.5°$). Spectra a and b show reduced upfield intensity compared to spectrum c, because of diminished cross-polarization efficiency far off-resonance. All spectra are referenced to the ^{13}C chemical shift of tetramethylsilane (TMS). (d) Schematic diagram of benzene molecules adsorbed at S_{II} Ca^{2+} cation sites in a Ca-LSX zeolite supercage. Up to four such cation sites may exist in S_{II} positions, which are arranged tetrahedrally in each LSX supercage.

established, relative off-diagonal versus diagonal integrated intensities yield information on the time scale of the motional process. For example, the spectrum of Figure 1a, obtained at $T = 298$ K and with $t_m = 1$ ms, displays only diagonal intensity, reflecting no exchange among different benzene environments during this short mixing period. This is in contrast to the spectrum shown in Figure 1b, acquired at $T = 298$ K and with $t_m = 300$ ms, which reveals a well-resolved elliptical pattern, reminiscent of ellipses observed in similar spectra associated with helical-jump processes in crystalline domains of solid polymers.[9−11] For benzene adsorbed on Ca-LSX zeolite, this indicates molecular exchange during the mixing time t_m between discrete and well-organized benzene environments, whose relative orientations differ by $\beta = 109° \pm 3°$, as determined directly from the axes of the elliptical intensity distribution. This is in good agreement with the simulated spectrum shown in Figure 1c for an isotropic distribution of axially symmetric chemical shift tensors that exchange among discrete sites at the apices of a tetrahedron ($\beta = 109.5°$).

Figure 1d schematically depicts chemical exchange of benzene molecules among Ca^{2+} cations in tetrahedrally arranged S_{II} adsorption sites within a single Ca-LSX supercage. For correlation times much shorter than the mixing time (by a factor of at least 5), a 3:1 off-diagonal-to-diagonal intensity ratio is expected for a jump process among four sites. The off-diagonal-to-diagonal intensity ratio is about two for the spectrum in Figure 1b ($t_m = 300$ ms), demonstrating that at room temperature the correlation time for discrete hopping of benzene molecules is on the order of 100 ms. Experiments with longer mixing times (spectra not shown here) yield intensities approaching a 3:1 ratio, indicating that benzene molecules sample all Ca^{2+} adsorption sites within a supercage on longer time scales.[16]

The LSX supercages are tetrahedrally distributed within the unit cell, so that S_{II} positions in neighboring supercages are at relative orientations of $\beta = 0°$, 70.5°, 109.5°, or 180°. Consequently, for this system, intracage and intercage transport cannot be distinguished on the basis of the reorientation angle, as they will give rise to the same elliptical patterns in 2D exchange NMR spectra. Nevertheless, intracage adsorbate exchange is expected to predominate, because of the higher energy barrier to intercage transport through the 12-ring window separating adjacent supercages.[19]

In complicated heterogeneous systems, the ability to examine and measure highly localized dynamical phenomena is difficult and often obscured by disorder to varying extents. The sensitivity of two-dimensional exchange NMR methods to short-range features of molecular environment opens new avenues for investigating adsorbate structure and mobility in microporous materials. These measurements are analogous to the powerful class of multidimensional exchange NMR experiments used to study slow dynamic processes in polymers and manifest the close molecular-level links between polymeric solids and microporous materials containing included guest species. The new quantitative insights available from 2D exchange ^{13}C NMR characterization of adsorbed species in molecular sieves are expected to produce important tests of developing theories of diffusion and adsorption and provide new inputs to computational descriptions of mass transport in microporous materials.

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