

Direct Measurement of Intercage Hopping in Strongly Adsorbing Guest-Zeolite Systems

D. E. Favre,¹ D. J. Schaefer,¹ S. M. Auerbach,² and B. F. Chmelka^{1,*}

¹Department of Chemical Engineering, University of California, Santa Barbara, California 93106

²Departments of Chemistry and Chemical Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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Solid-state exchange ¹³C NMR has been used to measure directly discrete *intercage* hopping of strongly adsorbed molecules on a nanoporous zeolite. Such intercage motions represent the molecular transport events that are central to macroscopic diffusion of guest molecules through zeolite pore spaces. Apparent activation energies of 73 and 76 kJ/mol have been measured for intra- and intercage hopping, respectively, of benzene molecules on Ca-Y zeolite. Exchange NMR measurements at 338 to 368 K yield benzene self-diffusion coefficients from 10^{-19} – 10^{-18} m²/s, values which are well below the range of diffusivities accessible from other equilibrium techniques. [S0031-9007(98)07933-2]

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The transport of adsorbed molecules inside the cavities of porous solids has often been described as “random walks” constrained by the geometries of the pores [1]. However, identifying and quantifying the elementary motional processes that govern molecular transport and ultimately macroscopic diffusion of guest molecules in heterogeneous porous materials can be extremely difficult. Experimental measurements are challenged by the existence of several distinct pathways for diffusion that must be disentangled. To this end, we have applied solid-state exchange ¹³C nuclear magnetic resonance (NMR) spectroscopy methods to probe directly and uniquely the molecular origins of such transport behaviors for benzene molecules adsorbed on crystalline Ca-Y zeolite. These results represent direct measurements of the molecular hopping events that are responsible for the macroscopic diffusion of strongly adsorbed molecules on a three dimensionally ordered nanoporous host.

While a variety of powerful experimental and computational techniques has been demonstrated for characterizing rapid motions of weakly adsorbed molecules on porous solids [1–3], measurements of molecular reorientation geometries and dynamics of strongly adsorbed species have been more elusive. For example, detailed measurements of mean translational jump lengths and rapid (10^{-12} – 10^{-8} s) molecular reorientations are accessible using incoherent quasielastic neutron scattering (IQNS) techniques [2]. By comparison, solid-state exchange NMR methods [4] provide direct and unambiguous means of monitoring slow (10^{-3} – 10^2 s) molecular reorientation events via changes in orientation-dependent NMR frequencies. Such methods have been applied to the study of geometries and time scales of molecular reorientations in polymers [4]. They have also been used to quantify the hopping of weakly adsorbed ($\Delta H_{\text{ads}} \approx -25$ kJ/mol; Ref. [5]) ¹²⁹Xe atoms among different cavities of Na-A zeolite [6]. In previous work [7], we have used exchange ¹³C NMR to study intracage hopping dynamics of benzene molecules strongly adsorbed ($\Delta H_{\text{ads}} \approx -134$ kJ/mol;

Ref. [8]) on highly ordered Ca-LSX zeolite. Apparent activation energies of 66 ± 6 kJ/mol were observed for benzene jump reorientations, primarily among Ca²⁺ adsorption sites within single supercages; however, intra- and intercage motions could not be distinguished due to the highly symmetric arrangement of the adsorption sites. Recent exchange ²H NMR results for benzene adsorbed on Na-Y have measured an apparent activation energy of 40 ± 2 kJ/mol for benzene site hopping in the limit of full loading (5 molecules/supercage), under conditions where both intra- and intercage processes are expected to occur; the different processes, however, were not distinguished, but characterized together by a one-decade-wide log-normal distribution of correlation times [9]. Here we present direct measurements of intercage hopping by strongly adsorbed molecules in a large-pore zeolite, from which motional correlation times are determined, and very low macroscopic intracrystallite diffusion coefficients are calculated.

Zeolite Ca-Y contains a network of supercage cavities arranged on a diamond lattice and connected by ~ 7.4 -Å-diameter window apertures [10]. The crystalline aluminosilicate structure contains charge-compensating Ca²⁺ cations, the number and siting of which depend on the silicon-to-aluminum ratio (Si/Al) of the anionic framework. The extra-framework cations occupy distinct positions associated with Al sites inside the dehydrated zeolite cavities and represent energetically preferred sites for adsorption of molecular guest species. Each supercage of Ca-Y zeolite (Si/Al = 2.0) is expected to have on average two of the four so-called *S*_{II} sites occupied by Ca²⁺ cations [11]. Benzene adsorption occurs preferentially on the *S*_{II} cations, and a second, less favorable adsorption site exists at the center of the windows (*W*) connecting two adjacent supercages [11,12]. The four *S*_{II} sites within each supercage are arranged tetrahedrally; inverting the tetrahedron gives the arrangement of the four windows connecting adjacent supercages, two of which are shown in Fig. 1.

Benzene molecules adsorbed on Ca-Y zeolite rotate rapidly about their sixfold axes, rendering the orientation dependence of ^{13}C NMR frequencies axially symmetric [7]. Changes in the orientations of such adsorbed guest molecules are manifested by frequency changes that are measurable over 10^{-3} – 10^2 s time scales using exchange NMR techniques [4]. In particular, for dynamic processes in this slow regime, static 2D exchange NMR allows molecular reorientation geometries to be determined precisely. For example, static 2D exchange ^{13}C NMR spectra (not shown here [13]) of benzene on Ca-Y zeolite acquired over a range of temperatures (258–348 K) establish that the benzene molecules reorient among discrete adsorption sites through mean angles of 71° or $109^\circ \pm 3^\circ$ [14]. The reorientation of benzene molecules between two S_{II} cations in the same Ca-Y supercage is essentially equivalent to hopping between two vertices of a tetrahedron, a process that is consistent with the reorientation angle geometry observed in the static 2D exchange spectra. However, hopping to or from window sites is also consistent with the observed 71° or 109° reorientation angles, so that four potential elementary hopping processes must be considered (Fig. 1): $S_{\text{II}}-S_{\text{II}}$, $S_{\text{II}}-W$, $W-S_{\text{II}}$, and $W-W$ jumps.

Whereas the time scale of slow molecular jump motions can be measured from a series of static 2D exchange spectra, in practice substantially higher sensitivity and precision are achieved under conditions of magic-angle spinning using exchange-induced sidebands (EIS) ^{13}C NMR [7,15]. The EIS technique requires slow spinning of the sample at an angle inclined 54.74° with respect to the static magnetic field, which incompletely averages the chemical shift anisotropy. This yields a spectrum with a centerband peak at the position of the isotropic ^{13}C chemical shift and a manifold of spinning sidebands that are separated

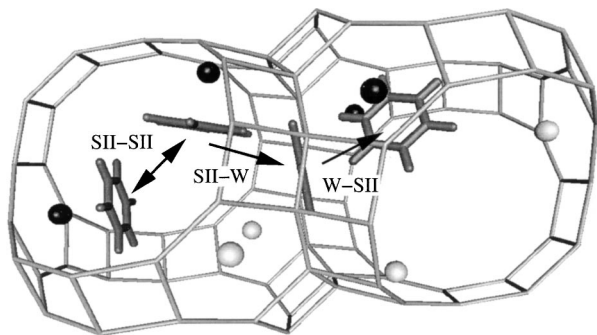


FIG. 1. Schematic diagram of two Ca-Y zeolite supercages, which contain an average of two S_{II} Ca^{2+} cations each (dark spheres) that serve as primary adsorption sites for benzene molecules, as indicated. Actual cation positions among the four possible S_{II} sites in each cage (unpopulated sites are indicated by the white spheres) are generally uncorrelated among different supercages [11]. Three elementary hopping processes are indicated: hopping from one S_{II} cation adsorption site to another S_{II} cation site within the same supercage ($S_{\text{II}}-S_{\text{II}}$), from an S_{II} site to a window site separating adjacent supercages ($S_{\text{II}}-W$), and from a window site to an S_{II} site ($W-S_{\text{II}}$).

from each other by the sample spinning frequency. In the EIS pulse sequence [16], these sidebands are suppressed by applying the so-called total-suppression-of-spinning-sidebands sequence [17]. This is followed by a variable mixing time, during which exchange processes may occur that cause suppressed sidebands to reappear. Importantly, the intensities of the reintroduced sidebands depend on the kinetics and number of sites participating in the exchange processes, as discussed below. Correlation times for such exchange processes are subsequently obtained by fitting kinetic expressions to the ratio of the intensities of all sideband peaks to the total spectral intensity, $R^{\text{EIS}}(t_m)$, as a function of the mixing time [15]. In conjunction with the static 2D exchange data, which provide direct and unambiguous evidence for jump-type reorientation motions and their geometries, the resulting EIS-measured correlation times can be assigned to specific molecular processes with high degrees of confidence [7,15].

At different temperatures, ^{13}C EIS spectra reveal that benzene molecules adsorbed on Ca-Y zeolite display significantly different motional behaviors. These data are compiled in Fig. 2, which shows sideband-to-total intensity ratios $R^{\text{EIS}}(t_m)$ for two series of EIS spectra acquired at $T = 298$ and 368 K, for a sample containing 0.5 molecules of adsorbed benzene per Ca-Y supercage. For discrete exchange processes occurring among equivalent sites with a single reorientation geometry, EIS sideband intensities increase monoexponentially according to $R^{\text{EIS}}(t_m) = R_{\text{fe}}(1 - e^{-t_m/\tau})$, where t_m is the experimentally known mixing time, τ is the correlation time, and R_{fe} is the full-exchange (fe) limit of $R^{\text{EIS}}(t_m \rightarrow \infty)$ [15]. A monoexponential fit to $R^{\text{EIS}}(t_m)$ measured at 298 K yields a correlation time of $\tau = 0.81 \pm 0.08$ s ($= \tau_2$; see below) and $R_{\text{fe}} = 0.36 \pm 0.03$. The value of R_{fe} depends on the chemical shift tensor, sample spinning frequency, reorientation angle(s), and the number of exchanging sites [15], the latter of which is the only unknown. Thus, the number of nondegenerate [14] exchanging sites can be extracted

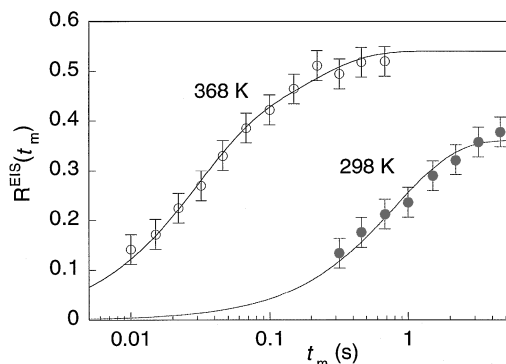


FIG. 2. Semilog plot of sideband-to-total intensity ratios, $R^{\text{EIS}}(t_m)$, measured from EIS ^{13}C NMR spectra at 298 K (filled circles) and 368 K (open circles). The solid lines are monoexponential (298 K) or biexponential (368 K) fits to the respective data. Data cannot be acquired for longer mixing times due to spin-lattice (T_1) relaxation. Experimental details are described elsewhere [7].

unambiguously from the EIS analysis. At 298 K (and below) [13], $R_{fe} = 0.36$ reflects the exchange between two sites that differ in orientations by an angle of 109° [15]; the associated correlation time at 298 K will consequently be designated τ_2 . Compared with the two-site geometry, exchange among all four vertices of a tetrahedron yields a value of R_{fe} that is a factor of 1.5 times larger [15], i.e., $R_{fe} = 0.54$. Intracage exchange between adjacent S_{II} adsorption sites in Ca-Y yields the two-site geometry observed at 298 K, where the intracage S_{II} — S_{II} rate coefficient is given by $k_2 = 1/(2\tau_2)$.

At $T = 368$ K, benzene dynamics are measured that correspond to the exchange of benzene molecules between different Ca-Y supercages. Such intercage motions arise primarily from benzene hopping from an S_{II} site via a window to another S_{II} site in an adjacent supercage cavity (S_{II} — W — S_{II}). A key observation is that intracage and intercage hopping processes are characterized by different kinetics and different numbers of participating sites [18]. Although both processes involve benzene reorientation through a tetrahedral angle, the intracage process involves exchange between, on average, two equivalent S_{II} sites, while the intercage process effectively samples all four vertices of a tetrahedron. Consequently, the mixing-time dependence of the $R^{EIS}(t_m)$ ratios at 368 K can be modeled using a four-site exchange matrix given by

$$\begin{bmatrix} -k_2 - 2k_4 & k_2 & k_4 & k_4 \\ k_2 & -k_2 - 2k_4 & k_4 & k_4 \\ k_4 & k_4 & -k_2 - 2k_4 & k_2 \\ k_4 & k_4 & k_2 & -k_2 - 2k_4 \end{bmatrix}, \quad (1)$$

where k_2 is the rate coefficient for intracage S_{II} — S_{II} exchange, and k_4 is the effective rate coefficient for an intercage S_{II} — W — S_{II} benzene hopping process. Solving the accompanying kinetic equations for stationary Markov processes [4] leads to the relation,

$$R^{EIS}(t_m) = \frac{R_{fe}}{3} (3 - 2e^{-2(k_2+k_4)t_m} - e^{-4k_4t_m}), \quad (2a)$$

$$= \frac{0.54}{3} (3 - 2e^{-t_m/\tau_{2,4}} - e^{-t_m/\tau_4}), \quad (2b)$$

where the average supercage residence time is identical to the correlation time $\tau_4 = 1/(4k_4)$, the rate coefficient for intracage S_{II} — S_{II} exchange is $k_2 = 1/(2\tau_{2,4}) - 1/(4\tau_4)$, and the known [7,15] full-exchange four-site limit $R_{fe} = 0.54$ has been imposed to constrain the biexponential fit. Fitting the $R^{EIS}(t_m)$ ratios measured at 368 K in Fig. 2 to Eq. (2b) yields $\tau_{2,4} = 0.027 \pm 0.005$ s [whereas $\tau_2 = 1/(2k_2) = 0.029$ s] and $\tau_4 = 0.18 \pm 0.04$ s. For the low benzene loadings used here and the preference of benzene for S_{II} cation sites [11,12,19], adsorption at the window sites is short lived relative to the time scales of the EIS measurements. We have established the role of the window sites in the intercage benzene transport process by measuring the additional kinetic barrier they introduce, as reflected by τ_4 .

Figure 3 shows an Arrhenius plot of the reciprocal supercage residence time $1/\tau_4$ (open circles) and intracage exchange rate coefficient k_2 (filled circles) compiled from mono- and biexponential fits to ^{13}C EIS results $R^{EIS}(t_m)$ measured over the temperature range 258 to 368 K. The solid line through the open circles in Fig. 3 is an Arrhenius fit to the reciprocal average supercage residence time, $\ln(1/\tau_4)$, which yields a prefactor of $k_0 = 4 \times 10^{11} \text{ s}^{-1}$ (± 1 decade) and an apparent activation energy of $E_a = 76 \pm 8$ kJ/mol. The prefactor k_0 is reasonable for an effective intercage S_{II} — S_{II} hop via a window site [19], and the activation energy is, as expected, greater than for the faster predominantly intracage dynamics measured for benzene adsorbed on Ca-LSX zeolite ($E_a = 66$ kJ/mol) [7].

Using the correlation times $\tau_{2,4}$ and τ_4 and Eq. (2), the intracage S_{II} — S_{II} exchange rate coefficient k_2 has been calculated and is shown in Fig. 3 (filled circles). The Arrhenius plot for k_2 shows two distinct regions that correspond to contributions from two different processes, a temperature-independent one below 298 K and a thermally activated process above 318 K. The temperature-independent exchange is due to magnetization transfer via spin diffusion [20] among ^{13}C nuclei in benzene molecules that may or may not hop among different adsorption sites. Previous measurements [7] have shown that spin diffusion and hopping among adsorption sites are independent processes, so that the measured exchange rate coefficient k_2 is the sum of separate contributions from molecular hopping, $k_0 \exp(-E_a/RT)$, and spin diffusion, k_{SD} . The solid line through the filled circles in Fig. 3 is a fit to $\ln(k_2) = \ln[k_0 \exp(-E_a/RT) + k_{SD}]$, which yields $k_0 = 4 \times 10^{11} \text{ s}^{-1}$ (± 1 decade), $E_a = 73 \pm 7$ kJ/mol,

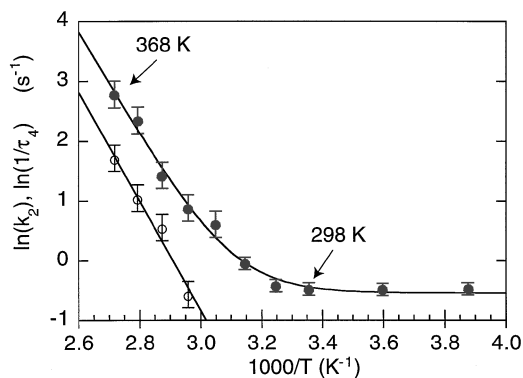


FIG. 3. Arrhenius plots of the intracage exchange rate coefficient k_2 (filled circles) and reciprocal supercage residence time $1/\tau_4$ (open circles) for benzene jump reorientation motions on Ca-Y zeolite. Two processes can be clearly identified as contributing to k_2 : temperature-independent spin diffusion which dominates below 298 K, and hopping of benzene molecules between Ca^{2+} S_{II} cations sites, an activated process which dominates above 318 K. The filled circles are fit with $\ln(k_2) = \ln[k_0 \exp(-E_a/RT) + k_{SD}]$. A single straight line is obtained for the $\ln(1/\tau_4)$ data, reflecting motion between different supercages; the open circles are fit with $\ln(1/\tau_4) = \ln[k_0 \exp(-E_a/RT)]$.

and $k_{SD} = 0.58 \pm 0.07 \text{ s}^{-1}$. The prefactor k_0 is reasonable for an attempt frequency for an elementary hopping process. Comparing k_2 and k_4 [Eq. (2a)] over the temperature range 338–368 K reveals that intracage benzene hopping dynamics are about 13 times faster than intercage benzene jump reorientations. These results are consistent with activation energies that we have separately calculated for the intercage and intracage benzene hopping processes in Ca-Y using a host-guest potential energy surface developed for cation-containing faujasite structures [19]. Jump activation energies of $E_a(S_{II}-W) = 78 \text{ kJ/mol}$ and $E_a(S_{II}-S_{II}) = 72 \text{ kJ/mol}$ are obtained for the minimum energy paths, in good agreement with the experimentally measured values above.

Self-diffusion coefficients D for low loadings of benzene adsorbed on Ca-Y zeolite can be calculated using the equation $D = a^2/(6\tau_4)$ [21], where a is a kinetic intercage hopping length. This length is slightly larger than the 10.76 Å crystallographic distance between the centers of adjacent supercages [12] and increases slightly as window sites become more populated at higher temperatures or loadings [21]. Using $a = 11 \text{ Å}$ and taking the values of τ_4 from Fig. 3, benzene self-diffusion coefficients of $D = (1.1 \pm 0.4) \times 10^{-19} \text{ m}^2/\text{s}$, $(3.4 \pm 1) \times 10^{-19} \text{ m}^2/\text{s}$, $(5.6 \pm 2) \times 10^{-19} \text{ m}^2/\text{s}$, and $(1.1 \pm 0.4) \times 10^{-18} \text{ m}^2/\text{s}$ are obtained at temperatures of 338, 348, 358, and 368 K, respectively.

The very low self-diffusion coefficients reported here are difficult to measure using other experimental methods. They are several orders of magnitude below the ranges of diffusivities currently accessible by other equilibrium techniques, such as IQNS [2] and pulsed- (PFG) or static-field gradient NMR methods [1,22]. Diffusivities on the order of 10^{-12} – $10^{-9} \text{ m}^2/\text{s}$ have been reported at 458 K for benzene adsorbed on Na-X zeolite, using a variety of equilibrium and nonequilibrium methods, including IQNS, PFG NMR, zero length column (ZLC), piezometric, and gravimetric measurements [23]. Experimental diffusivities of about $2 \times 10^{-12} \text{ m}^2/\text{s}$ for benzene on Ca-X zeolite have been reported using the tracer ZLC (TZLC) technique [24] over the temperature range of 468–528 K. The TZLC findings, however, do not agree with separate PFG NMR results [25], exchange NMR measurements presented here and in Ref. [7], or modeling predictions [26]. In this respect, the exchange NMR measurements present a significant advantage, namely, direct access to molecular reorientation geometries and dynamics underlying slow site-hopping processes.

Exchange NMR has been applied to measure the molecular transport events that govern diffusion of strongly adsorbed molecules on an ordered nanoporous solid. The connection between molecular motions and intracrystallite diffusion in these systems offers improved prospects for predicting guest transport behaviors from adsorbent composition and structure. This has important implications for understanding the progress of reactions at heterogeneous solid surfaces.

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*Author to whom correspondence should be addressed.

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