

# SITE-HOPPING DYNAMICS OF BENZENE ADSORBED ON CALCIUM-EXCHANGED FAUJASITE-TYPE ZEOLITES

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## ABSTRACT

Molecular hopping motions of benzene adsorbed on calcium-exchanged faujasite-type zeolites have been characterized by solid-state <sup>13</sup>C NMR. Predominantly intracage hopping dynamics were measured for benzene adsorbed on Ca-LSX zeolite (Si/Al = 1.0). More complicated dynamics including both intracage and intercage hopping were probed for benzene adsorbed on Ca-Y zeolite (Si/Al = 2.0). Distinguishing between intra- and intercage guest hopping events is important, because only intercage hopping events give rise to guest molecule diffusion within a given crystallite. Intra- and intercage molecular processes are intimately connected with the local structure and composition of the zeolite host matrix. The local (~10<sup>-9</sup> m) hopping motions of molecules among adsorption sites play a primary role in accounting for the macroscopic transport properties of these materials.

## INTRODUCTION

Understanding the molecular origins of macroscopic adsorption, diffusion, and reaction properties of guest molecules adsorbed inside zeolite cavities and channels is important for establishing and controlling key materials and process parameters for a wide range of applications in separations and catalysis. Because intracrystallite diffusion arises from a series of nanoscale hopping events between adsorption sites in different supercage cavities, it is important to distinguish between intra- and intercage processes. Hopping among different adsorption sites within a single supercage does not lead to macroscopic benzene transport. We have recently used static two-dimensional (2D) exchange and one-dimensional (1D) exchange-induced sidebands (EIS) <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy experiments to probe directly the geometry and time scale associated with slow reorientation dynamics of benzene molecules adsorbed on Ca-LSX zeolite [1]. Detailed, quantitative insights were obtained on intracage benzene jump motions among Ca<sup>2+</sup> SII cation adsorption sites. However, due to the high symmetry of this host/guest system, intra- and intercage hopping could not be distinguished. Here, we demonstrate that several site-hopping processes can be distinguished for benzene adsorbed on zeolite Ca-Y (Si/Al = 2.0).

The motions of benzene adsorbed on faujasite-type zeolites have been studied by a variety of solid-state NMR techniques. Rapid rotation of benzene molecules about the six-fold

axes normal to their aromatic planes has been established using  $^1\text{H}$  and  $^2\text{H}$  NMR lineshapes [2-4]. Evidence for benzene adsorption at SII cation sites is provided by the mobilities of a series of related adsorbates (cyclohexane, cyclohexene, cyclohexadiene, benzene, and toluene), as inferred from proton NMR  $T_1$  and  $T_2$  relaxation times at temperatures from about 153 to 373 K [5]. The observations are consistent with neutron diffraction measurements at 4 K, which showed benzene molecules to be adsorbed at the SII cations [6]. Modeling of the second moments of  $^1\text{H}$  NMR lineshapes has furthermore permitted the mean distance between an adsorbed benzene molecule and an SII cation to be determined [2,4]. The geometry and dynamics associated with rapid reorientation of adsorbed benzene molecules can be characterized by modeling  $^1\text{H}$  and  $^2\text{H}$  NMR lineshape and relaxation data [3-5]. For slower motions, the  $^{13}\text{C}$  exchange NMR techniques used here permit direct and unambiguous characterization of the number and geometry of adsorption sites, as well as the molecular reorientation dynamics among them. Finally, for molecular displacements over several microns, translational self-diffusion coefficients for adsorbed benzene can be measured directly using  $^1\text{H}$  pulsed-field-gradient or static-field-gradient NMR techniques [5,7-9].

## EXPERIMENTAL

Samples of Ca-LSX and Ca-Y zeolites were dehydrated in glass ampoules under vacuum, loaded with benzene  $^{13}\text{C}$ -enriched to 99% at a single ring site, and flame-sealed. All  $^{13}\text{C}$  NMR spectra were acquired on a Chemagnetics spectrometer operating at frequencies of 180.1 and 45.3 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively. The  $^{13}\text{C}$   $\pi/2$ -pulse length varied between 4.3 and 5.0  $\mu\text{s}$ .

The geometry of slow ( $10^{-3}$ - $10^2$  s) molecular reorientation for adsorbed benzene has been measured using static 2D exchange  $^{13}\text{C}$  NMR [10,11], which monitors changes in orientation-dependent NMR frequencies by correlating frequencies during the evolution ( $t_1$ ) and detection ( $t_2$ ) times, which bracket a mixing time  $t_m$ ; see Figure 1(a). Static 2D exchange spectra were acquired in an off-resonance mode. Normally 128 complex points with a dwell time of 15  $\mu\text{s}$  were acquired in the detection period; 40 points with a 30  $\mu\text{s}$  dwell time were measured in the evolution period. A typical delay time of 65  $\mu\text{s}$  was used between the two pulses of the Hahn-echo sequence in the detection time. The data array was zero-filled to dimensions ( $\omega_1 \times \omega_2$ ) = 256 x 512 prior to Fourier transformation. The final spectrum, with a spectral width of  $2\pi \times 16.7$  kHz in both dimensions, was obtained by cutting the 2D array to dimensions 128 x 128 and discarding the 7/8 of the 2D Fourier transform containing either baseline in  $\omega_2$  or the completely equivalent spectrum in the  $\omega_1$  dimension. Static 2D exchange  $^{13}\text{C}$  NMR spectra were measured for an average loading of about 0.5 benzene molecules per Ca-Y supercage; static 2D spectra of samples containing 2 benzene molecules per Ca-LSX supercage are shown elsewhere [1,12].

The time scales of slow molecular reorientation were quantified using the closely related EIS  $^{13}\text{C}$  NMR technique [13,14]. The EIS experiment is conducted under conditions of magic-

angle spinning (MAS) using 7.5-mm diameter zirconia rotors and a relatively slow spinning speed ( $\nu_R = 2200$  Hz). As shown in Figure 1(b), a Total Suppression of Sidebands (TOSS) sequence [15] was used in place of the evolution ( $t_1$ ) time. The TOSS timings were  $\tau_1/T_R = 0.1888$ ,  $\tau_2/T_R = 0.2301$ ,  $\tau_3/T_R = 0.8112$ ,  $\tau_4/T_R = 0.17699$ , and  $\tau_5/T_R = 2.0$  [16], where  $T_R$  is the rotor period of  $454.55 \mu\text{s}$  and  $\tau_i$  represents the time interval between the  $i^{\text{th}}$  pulse and the end of the cross-polarization time.

Whereas slow molecular jump reorientations may be quantified using exchange NMR experiments, to quantify faster motions it is necessary to analyze the distortion and averaging effects [17] that these more rapid reorientations have on static  $^{13}\text{C}$  NMR spectra acquired using the Hahn-echo sequence shown in Figure 1(c). For the echo spectra, it is possible to separate the slow and fast molecular reorientation motions and quantify their respective contributions to the spectra. An echo delay of  $143 \mu\text{s}$  was used.

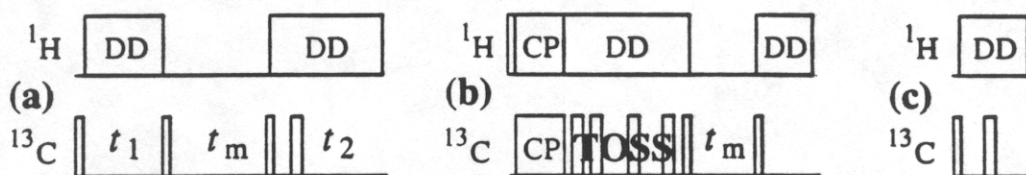


Figure 1. Schematic diagrams of (a) static 2D exchange, (b) EIS, and (c) Hahn-echo  $^{13}\text{C}$  NMR pulse sequences. High-power dipolar decoupling (DD) was applied during the evolution and detection periods, and cross-polarization (CP) with a contact time of 1.5 ms was used in the EIS experiment (b) to transfer magnetization from  $^1\text{H}$  to  $^{13}\text{C}$ .

## RESULTS AND DISCUSSION

For benzene adsorbed on zeolites Ca-LSX and Ca-Y, an energetically preferred adsorption site exists above each  $\text{Ca}^{2+}$  SII cation in the supercage cavities; four such sites exist in Ca-LSX [18] and are shown schematically in Figure 2.

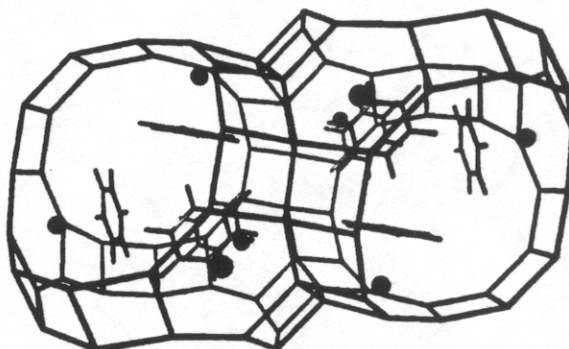


Figure 2. Schematic diagram of benzene molecules adsorbed at the four SII cation sites in each of two adjacent Ca-LSX supercages.



Benzene molecules adsorb on the SII cations with their aromatic planes essentially parallel to the six-rings that form part of the  $\beta$ -cage structures. The four SII sites in one supercage are arranged tetrahedrally; inverting this tetrahedron yields the orientations of the four windows connecting adjacent supercages. The supercages are arranged on a diamond lattice, so all windows and SII sites are at relative angles of  $0^\circ$ ,  $70.5^\circ$ ,  $109.5^\circ$ , or  $180^\circ$  to each another. At higher concentrations of benzene than used here, neutron diffraction investigations of Na-Y containing 2.6 molecules/supercage have revealed a second adsorption site at the centers of the 12-ring windows (W) adjoining adjacent supercages [6].

The reorientation geometry for benzene hopping among adsorption sites in Ca-Y zeolite is obtained from 2D exchange  $^{13}\text{C}$  NMR spectra, shown in Figure 3. The contour plot in Figure 3(a) shows a diagonal-only spectrum, indicating that at 258 K the  $^{13}\text{C}$  NMR frequencies are the same in the evolution and detection periods (*i.e.*,  $\omega_1 = \omega_2$ ) for a mixing time of  $t_m = 1000$  ms. Thus, the benzene molecules do not hop among adsorption sites on this time-scale. In contrast, Figure 3(b) acquired at 348 K with  $t_m = 320$  ms, shows substantial off-diagonal intensity, the shape of which indicates that molecules reorient through angles of approximately  $71^\circ$  or  $109^\circ$  [11] (although the sensitivity and resolution are insufficient to determine the reorientation angle distribution in detail.) At a higher loading of 2 molecules per Ca-LSX supercage, benzene molecules have been shown to exchange among the four equivalent SII  $\text{Ca}^{2+}$  cation sites within the LSX supercages [1,12]. The dynamic exchange processes for benzene adsorbed on Ca-LSX occur via discrete  $71^\circ$  or  $109^\circ \pm 3^\circ$  molecular jumps, with an angular distribution of  $10^\circ \pm 5^\circ$ , as quantified using 2D exchange  $^{13}\text{C}$  NMR spectra and stimulated echoes associated with the 2D NMR time-domain signals [1,12].

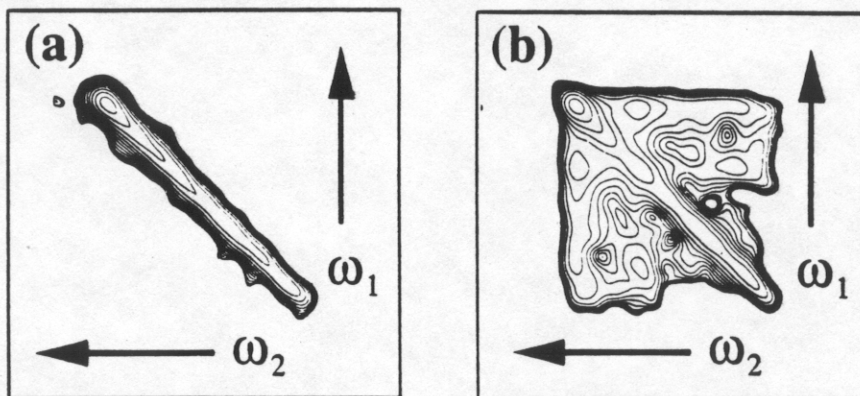


Figure 3. Contour plots of static 2D exchange  $^{13}\text{C}$  NMR spectra of a sample containing a bulk average of 0.5 molecules of adsorbed benzene per Ca-Y supercage. (a) A diagonal-only spectrum acquired at 258 K indicates that molecules do not hop among adsorption sites on the time scale of  $t_m = 1000$  ms. (b) The shape of the off-diagonal intensity in the spectrum acquired at 348 K with  $t_m = 320$  ms indicates that molecules reorient through approximately tetrahedral jump angles.



The time-scale(s) of molecular reorientation and the number of sites participating in the exchange processes can be obtained from a series of static 2D exchange spectra, though acquisition of such a series of spectra can be quite time-consuming. This information can be obtained more rapidly via the acquisition of a series of 1D EIS  $^{13}\text{C}$  NMR spectra [1,14]. As shown in Figure 4(a), in the absence of NMR frequency changes during the mixing time, a centerband-only  $^{13}\text{C}$  EIS spectrum is obtained. The centerband-only EIS spectrum is analogous to the diagonal-only 2D exchange spectrum in Figure 3(a). Frequency changes, such as those due to molecular reorientation or magnetization transfer via spin diffusion [1], result in the appearance of spinning sidebands in the EIS spectrum, as shown in Figure 4(b). Reorientation time scales are obtained by fitting kinetic expressions to the ratio of sideband-to-total intensity  $R^{EIS}(t_m)$  in the EIS spectra as a function of the mixing time  $t_m$ , while the number of sites is given by this ratio in the limit of long mixing time or full exchange (fe),  $R_{fe}$ .

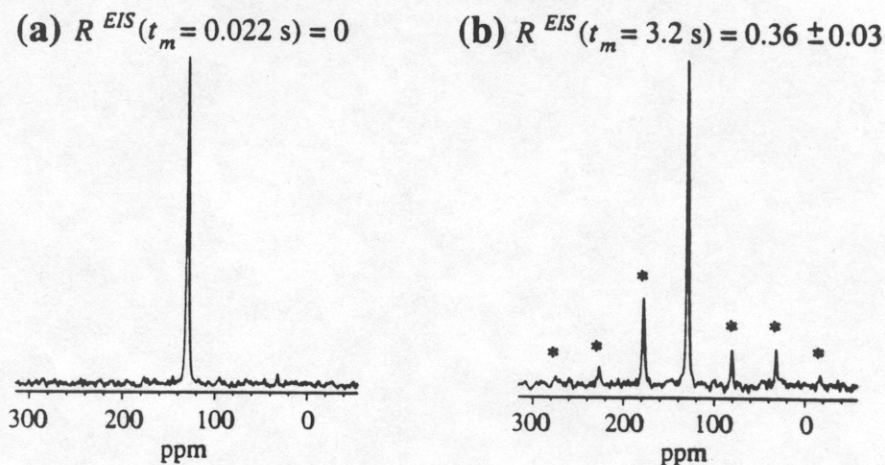


Figure 4. EIS  $^{13}\text{C}$  NMR spectra of a sample (same as in Fig. 3) containing a bulk average 0.5 molecules of adsorbed benzene per Ca-Y supercage acquired at 298 K. (a) A center-band-only spectrum obtained using a short mixing time,  $t_m = 0.022$  s, reflects the absence of NMR frequency changes (and thus the absence of molecular hopping) during the mixing time. (b) Spinning sidebands, denoted by \*, reappear in the EIS spectrum acquired with longer mixing time,  $t_m = 3.2$  s.

The EIS  $^{13}\text{C}$  NMR sideband-to-total intensity ratios  $R^{EIS}(t_m)$  for benzene adsorbed on Ca-LSX (0.5, 1 and 2 molecules/supercage), acquired in the temperature range of 218-338 K, display mono-exponential behavior within experimental resolution [1]. All EIS ratios  $R^{EIS}(t_m)$  for this system approach a full-exchange limit of about  $R_{fe} = 0.53 \pm 0.03$ , reflecting a four-site exchange geometry [14]. The long-time limit  $R_{fe}$  contains a stoichiometry factor  $(N-1)/N$  that reflects the number of exchange sites  $N$  [14]. The EIS spectra corroborate static 2D exchange spectra acquired with long mixing times, which confirm molecular reorientation among the four

equivalent SII sites of Ca-LSX (Si/Al = 1.0) [1,12]. Low temperature (< 338 K) EIS spectra for benzene adsorbed on Ca-Y zeolite also display mono-exponential behavior, but approach a different limit,  $R_{fe} = 0.36 \pm 0.03$  [19]. The limit  $R_{fe} = 0.36$  is consistent with a two-site exchange process involving benzene molecules adsorbed on Ca-Y zeolite (Si/Al = 2.0), which is expected to have an average of two SII  $\text{Ca}^{2+}$  cation adsorption sites per supercage.

At a low bulk loading of 0.5 molecule of adsorbed benzene per Ca-Y supercage, and given the energetic preference for adsorption at SII sites, intercage hopping at low temperatures is primarily due to a serial SII-W-SII hopping process [19]. However, as the loading increases, adsorption at window sites and window-to-window (W-W) hops are expected to become more important. This can be seen by comparing Hahn-echo  $^{13}\text{C}$  NMR spectra for samples containing an average of 0.5 or 1 molecule of adsorbed benzene per Ca-Y supercage. The spectrum in Figure 5(a) acquired at 258 K (bulk average of 0.5 molecules/supercage) indicates that adsorbed benzene molecules spin rapidly about their six-fold axes, rendering axially symmetric the averaged orientation dependence of the  $^{13}\text{C}$  NMR frequency. Even at low loadings, a fraction of the adsorbed benzene molecules experience additional rapid (<  $10^{-4}$  s) mobility among tetrahedrally arranged adsorption sites, which causes further motional averaging and yields a narrow isotropic peak in the spectrum. At 258 K, such rapid motions are not observed for a loading of 0.5 molecules/supercage, consistent with the diagonal-only static 2D  $^{13}\text{C}$  NMR spectrum acquired at this temperature (Fig. 3(a)). However, at 348 K, a small narrow isotropic peak does account for 5-10 % of the overall intensity of the static spectrum. The relatively low intensity of this narrow peak indicates that the SII  $\text{Ca}^{2+}$  cations are the dominant adsorption sites at the low guest loading of 0.5 molecule per supercage.

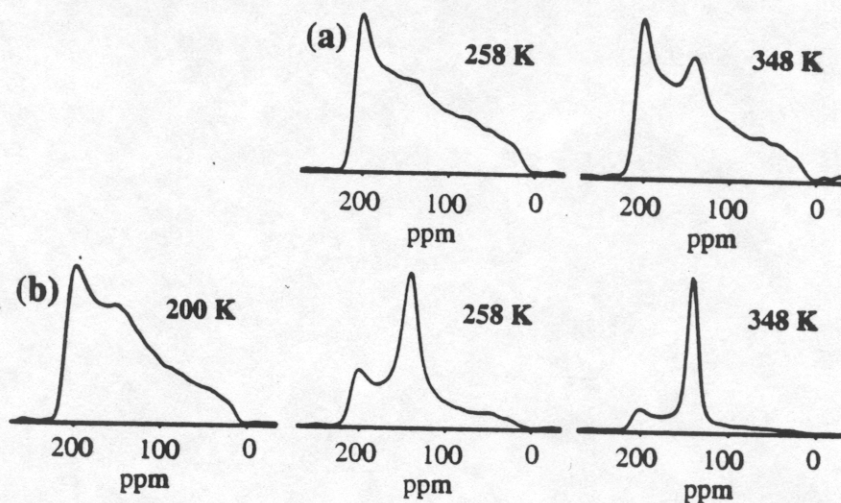


Figure 5. Hahn-echo  $^{13}\text{C}$  NMR spectra for samples containing (a) an average of 0.5 molecule of adsorbed benzene per Ca-Y supercage acquired at 258 and 348 K, and (b) 1 molecule of adsorbed benzene per Ca-Y supercage acquired at 200, 258, and 348 K.

For a bulk concentration of 1 molecule of adsorbed benzene per Ca-Y supercage, the contribution of the narrow isotropic peak is substantially higher, accounting for 40-45 % of the overall spectrum intensity at 258 K, and dominating the spectrum at 348 K, as shown in Figure 5(b). While the SII cations are the dominant adsorption sites at a loading of 0.5 molecules/supercage, other sites (such as the 12-ring windows) can thus be concluded to play an increased role in benzene site-hopping dynamics as the loading is increased. This is consistent with other studies of the concentration dependence of benzene site occupation and dynamics in faujasite systems [6,20-22].

## CONCLUSIONS

A combination of  $^{13}\text{C}$  exchange and Hahn-echo NMR experiments have been used to separate different dynamic hopping processes of adsorbed benzene occurring with different time scales. Reorientation angles were quantified using static 2D exchange NMR. Slow hops undergone by benzene molecules between SII cations within the same supercage and slightly slower intercage hops primarily due to a serial SII-W-SII process were quantified using EIS. More rapid reorientation motions, reflecting the influence of adsorption sites other than SII sites, were observed using Hahn-echo measurements. These measurements permit the influences of local zeolite composition and structure on the adsorption and mobilities of guest species to be studied directly at a molecular level. The exchange NMR measurements probe molecular transport on short ( $\sim 10^{-9}$  m) length scales and are complementary to pulsed-field-gradient NMR measurements, which probe diffusion over longer distances ( $> 10^{-6}$  m). The ultimate objective of this and ongoing studies is the quantitative connection between molecular adsorption and dynamic processes and the macroscopic diffusion properties of heterogeneous hydrocarbon/zeolite systems.

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