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^{13}C NMR from Benzene Sorbed on Zeolites[1]

The high sensitivity to the environment of ^{13}C NMR line shifts from adsorbed molecules provides a means of measuring adsorbent–adsorbate interactions. Several studies have been made with this technique using different adsorbed molecules. On the basis of the observed shifts, relative to those in liquids, suggestions concerning interactions of molecules with active surface sites have been advanced (*1–3*).

Important information on adsorption can also be obtained from analysis of the broadening and the line shape of ^{13}C NMR spectra. Thus Kaplan *et al.* (*4*) showed that the chemical shift anisotropy could be used to characterize molecular rotation and reorientation. The same approach was used by Sefeik *et al.* (*5*) for characterization of the adsorption sites of small-port mordenite. In the present work the broadening of the ^{13}C NMR spectral lines of benzene was used in a study of the interaction of benzene molecules with NaY zeolite.

EXPERIMENTAL

The NaY zeolite contained less than 400 ppm of paramagnetic impurities (iron). Aliquots were pretreated either by calcination in air at 500°C for 24 hr or in a vacuum ($p \simeq 10^{-5}$ Torr) at the same temperature for 4 hr. The sorption of benzene on the samples treated in air was accomplished by adding a known volume of liquid benzene into the tube containing the zeolite. A standard BET system was used for the samples treated in vacuum. The systems were allowed 1 hr to equilibrate before the NMR spectra were determined. ^{13}C NMR spectra were measured at 20 MHz with a varian CFT-20 spectrometer operating under proton decoupled conditions. The pulsewidth was 21 msec with no pulse delay. A concentric sample tube containing D_2O was used for an internal lock. Chemical shifts were measured relative to liquid benzene. The susceptibility correction was not made on the measured shifts. All NMR spectra were recorded at room temperature.

RESULTS AND DISCUSSION

Figure 1 presents the ^{13}C NMR spectra of benzene sorbed in air on NaY zeolite for different coverages. The same picture was obtained when sorption was performed *in vacuo*. Within experimental error, the chemical shift was coincident with that for liquid benzene. Moreover, this parameter did not depend on surface coverage. The linewidth, however, was strongly dependent on coverage (Fig. 2).

The line which had a width of 300 Hz at low coverages became very broad when the sorption approached four molecules of benzene per supercage ($\simeq 10^3$ Hz). At still higher sorption, the linewidth abruptly narrowed again to a value of less than 100 Hz. In this range the spectrum consisted of a narrow line, the integral intensity, I, of

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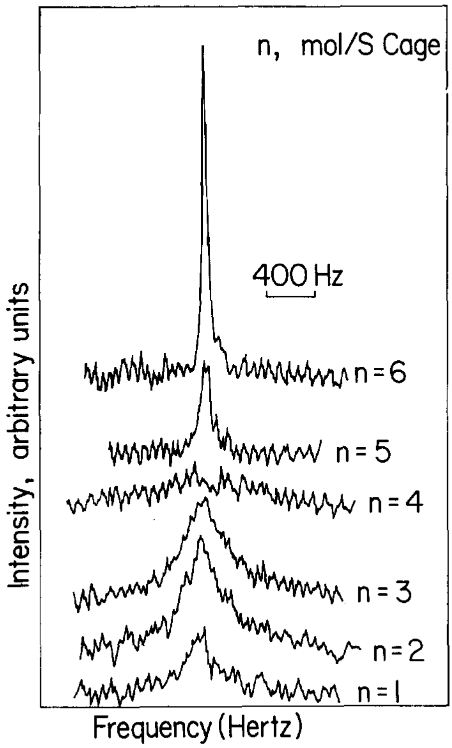

FIG. 1. ^{13}C NMR spectra of benzene sorbed in Na$^+$ zeolite at different coverages; n equals the number of benzene molecules per supercage. The number of accumulations was 4×10^4. Experiments were performed at room temperature and the sorption was in air.

which could be expressed by $I = A(n - 4)$, where A is a constant and n is the number of molecules per supercage.

The data are summarized in Fig. 2. The data suggested that at high coverage, the benzene in the zeolites formed two phases. One of these was characterized by a high mobility of the molecules and gave rise to a narrow line in the spectrum. The other corresponded to molecules having low mobility with corresponding large broadening of the line (too large to be detected in the NMR spectrum).

The data for proton relaxation of benzene sorbed in zeolites (*6*) is helpful in interpreting the nature of these phases. The longitudinal relaxation times found at a coverage of less than four molecules per supercage suggested that the motion of the benzene molecules should be described by a correlation time τ_c. Values of τ_c could be attributed to the mean lifetimes of the complexes formed as benzene molecules became localized due to the interaction between these molecules and Na$^+$ located in the supercages. Accordingly (*6*), our ^{13}C data may be treated with a value τ_c derived from Eyring's equation:

$$\tau_c = (h/kT)(f_1/f_1\ddagger)\exp(E_c/RT), \quad (1)$$

where f_1 is the partition function of the molecules coordinated to Na$^+$ and $f_1\ddagger$ is the partition function corresponding to the molecule in the activated complex (during its jump from one Na$^+$ ion to another). Alternatively, we may write:

$$\text{Hopping rate} = C_a\nu_c = k\theta(1 - \theta), \quad (2)$$

where $\nu_c = 1/\tau_c$ and $C_a = n_s\theta$; n_s is the number of sites available for adsorption, i.e., the four Na$^+$ per supercage. Thus, $\tau_c \propto 1/(1 - \theta)$; the probability that a given adsorbed molecule will hop in time τ_c is proportional to $(1 - \theta)$. Comparing Eqs. (2) and (1), it is seen that the ratio $f_1\ddagger/f_1$ is proportional to the fraction of unoccupied centers $(1 - \theta)$. Taking into account that the number of Na$^+$ ions in the supercage of a Y-type zeolite which is available for adsorption of benzene is equal to 4, it is clear that to this point an increase in the fraction occupied must lead to larger

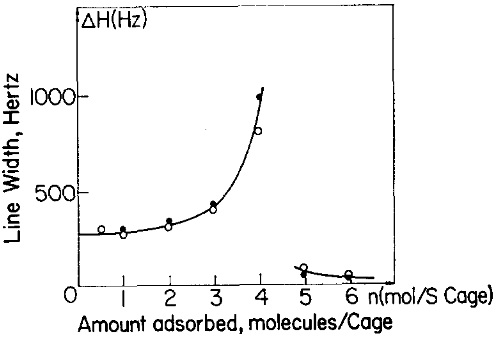

FIG. 2. Dependence of the linewidth of ^{13}C NMR spectra for benzene sorbed in zeolite as a function of coverage. Open circles represent sorption *in vacuo* and closed circles sorption in air.

values of τ_c and hence to the broadening of the NMR line.

The maximum in the broadening was observed at a coverage of four molecules per supercage (Fig. 2), since in this situation all the Na^+ ions are occupied by benzene molecules and the correlation time has taken on its highest value. At still higher coverages more benzene is sorbed, and these molecules now cannot become coordinated with the already occupied Na^+. Hence, these molecules are free and form a highly mobile phase which provides a narrow line in the NMR spectrum. The diffusion of these molecules between adjacent supercages of the zeolite is not restricted by interaction with the Na^+ ions, as would be the case at lower coverages. Of course in zeolites an exchange also exists between coordinated and "free" molecules, but the rate of this process is small compared with the diffusion rate of the free molecules and is not sufficient to affect the spectrum. This explanation of the results is in agreement with data on the differential heat of benzene adsorption in zeolites. It is known that the heat of adsorption is almost constant for an amount of benzene up to four molecules per cage and rapidly decrease at higher sorptions (*7*). This fact also was explained by the preferential adsorption of benzene molecules on Na^+ ions.

Thus, the data show that at coverage higher than four molecules per cage, the NMR spectrum of benzene adsorbed on zeolite corresponds to the "free" molecules and does not yield any information about the adsorbent–absorbate interaction.

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