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ADSORPTION SITES IN ZEOLITES A AND X PROBED BY COMPETITIVE ADSORPTION OF \( \text{H}_2 \) WITH \( \text{N}_2 \) OR \( \text{O}_2 \): IMPLICATIONS FOR \( \text{N}_2/\text{O}_2 \) SEPARATION

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ABSTRACT

We determine details of the adsorption of \( \text{O}_2 \) or \( \text{N}_2 \) in \( \text{Na}^+ \) and \( \text{Li}^+ \) exchanged zeolites by way of their effect on coadsorbed \( \text{H}_2 \) molecules using inelastic neutron scattering (INS) techniques. Adsorption site occupancies are deduced with the aid of MC simulations. The expected stronger binding of \( \text{N}_2 \) (compared with \( \text{O}_2 \)) in \( \text{LiX} \) is evident in coadsorption spectra of \( \text{N}_2 \) or \( \text{O}_2 \) with \( \text{H}_2 \).

INTRODUCTION

We have previously demonstrated [1-3] the significant potential of using INS studies of adsorbed \( \text{H}_2 \) as a local probe of adsorption sites in zeolites. The reasons for this are the small size of the hydrogen molecule and its considerable mobility within the cavities and channels of these structures, the nature of the interaction of neutrons with hydrogen, and the high sensitivity of the rotational tunnel splitting of the
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librational ground state (ortho-para transition for free H₂) of the adsorbed H₂ to the barrier height. This transition is not directly observable by optical techniques because it requires a change in the total nuclear spin of the molecule. In the present case the barrier to rotation is provided by the interaction between the H₂ molecule and the cations and framework atoms. These hindered rotations of the H₂ molecule have large amplitudes which in conjunction with the more than one order of magnitude higher neutron scattering cross-section of H compared with that of any other element gives rise to very strong INS intensities. Related studies [4-7] have also been carried out by IR spectroscopy of the H-H stretching band which becomes IR-active in the electrostatic field in the zeolite. v(HH) experiences small shifts ( < 100 cm⁻¹) upon adsorption of the H₂ molecule which has also be associated [6,7] with adsorption at particular sites in a variety of zeolites.

We now apply this technique to the study of competitive adsorption of H₂ with either N₂ or O₂ in Na- and Li-exchanged zeolites A and X in order to gain information relevant to adsorption and separation of these molecules. Li plays a unique role in modern zeolite absorbents including its use (in the form of Li-X) in the commercial production of oxygen by separation (N₂/O₂). Because of the larger quadrupole moment of oxygen or nitrogen one would expect those to absorb more strongly than hydrogen and thus displace H₂ from its most favored adsorption sites. O₂ and N₂ are, however, essentially “invisible” to neutrons in the presence of hydrogen molecules because of the large difference in neutron scattering cross-section. Our experiments therefore record the effect on the H₂ molecules of the co-adsorption of O₂ or N₂.

**EXPERIMENTAL SECTION**

For the INS measurements the zeolite samples were dehydrated by standard procedures, and placed into a sealed Al sample holder with in-situ access for gas adsorption. Adsorption of H₂ and/or O₂ or N₂ to the desired loading level (# of
molecules per supercage) was carried out in-situ from an external gashandling system with the cell at a temperature of about 150K.

The inelastic neutron scattering spectra were collected at 15K on the QENS spectrometer [8] at the Intense Pulsed Neutron Source of Argonne National Laboratory. Standard data reduction programs were used for normalization of the data and conversion to a linear energy scale.

Molecular Dynamics simulations were carried out with the use of Cerius2 software (Molecular Simulations Inc.). Our calculations [3] of the rotational states of adsorbed H₂ in a MC random walk will be reported in a future publication.

RESULTS AND DISCUSSION

Shown in Fig. 1 are the INS spectra for two molecules H₂ per supercage in fully exchanged in NaX and in LiX. Since in principle both rotational and translational modes may be observed we have also collected INS spectra for HD in these zeolites to utilize the different isotope effects for the two types of excitations to aid in the assignment of the lines. For NaX we conclude that the peak at 18 cm⁻¹ is a rotational transition (which corresponds to a two-fold barrier V₂ to rotation of 1.9 kcal/mol) while the broader band at 47 cm⁻¹ is the center-of-mass (CM) translational mode. This may be compared with our result [3] (not shown) for one H₂ in Na-A for which we find a broad rotational band at approximately 27 cm⁻¹. We interpret the latter observation on the basis of MC simulation studies which show the location of the adsorbed H₂ molecule to be most of the time at or around the NaIII cation. Analysis of the barrier to rotation experienced by the H₂ molecule at each location along the MC random walk yields a distribution of rotational barrier heights and associated transition frequencies with a peak close to that derived from experiment (mean value of V₂ = 1.5 kcal/mol). Since the most likely adsorption site for H₂ in NaX should also be a type III cation we therefore find that H₂ in NaX interacts more strongly with the same type of cation as in NaA.
Figure 1. Inelastic neutron scattering spectra (T = 15K) of (top) two H₂ per supercage in NaX and (bottom) 2 H₂ per supercage in LiX.

The INS spectrum of H₂ adsorbed in LiX (Fig. 1) on the other hand shows two prominent peaks that may be attributed to rotational transitions, at 14.5 and 38 cm⁻¹, which suggests that two different sites are occupied in this case. Coadsorption studies of N₂ with H₂ reveal (Fig. 2) that when more than seven N₂ molecules are added to the two H₂ molecules to occupy all the cation sites accessible [9] through the supercage by the larger molecules, the INS intensity for H₂ in NaX becomes distributed over a very wide energy range, while in LiX it is concentrated in the peak near 15 cm⁻¹. Since cross-polarization Li NMR studies of H₂ in LiX [10] provide evidence that the H₂ molecule can enter the sodalite cage and interact directly with Li in the I' site, we tentatively conclude that the peak at 15 cm⁻¹ is indicative of H₂ at the site in the sodalite cage, and that the INS spectrum shows that more H₂ can be forced into such sites when the supercage is being filled with N₂ molecules. This appears not to be possible, according to the INS spectra, in NaX under the conditions used in this
experiment because of the larger size of the Na\(^+\) cation. The second peak at 38 cm\(^{-1}\) for H\(_2\) in LiX should then be assigned to H\(_2\) adsorbed at a type III cation site.

In order to investigate the possible use of H\(_2\) as a "spectator" probe of other processes in the zeolite we compare the INS spectra of 2 H\(_2\) coadsorbed with either N\(_2\) or O\(_2\) (Fig. 2). No difference is evident between coadsorption of four N\(_2\) or O\(_2\) molecules with H\(_2\), but when the coverage is raised to 10 molecules the two INS spectra differ substantially. While coadsorption of N\(_2\) preserves a fairly well-defined spectrum for H\(_2\), the same is not true for O\(_2\) added to H\(_2\). Instead the INS spectrum for H\(_2\) in the presence of 10 molecules of O\(_2\) shows only a series of very weak features.

Figure 2. Inelastic neutron scattering spectra (T = 15K) of two H\(_2\) molecules per supercage in LiX co-adsorbed with N\(_2\) (left) and O\(_2\) (right).
The INS spectrum (not shown) for one molecule H$_2$ per supercage in fully exchanged Li-A, shows a sharp peak at 7 cm$^{-1}$ and a broad band at approximately 68 cm$^{-1}$. The sharp peak at 7 cm$^{-1}$ in Li-A is indicative of a much higher barrier for the adsorbed H$_2$ than found in Na-A and must therefore correspond to a location that has no counterpart in Na-A. Indeed, our MD simulations show that it is possible for two Li$^+$ ions to be in the same 8-ring window. If H$_2$ were in fact adsorb between two such Li$^+$ ions it may well experience a strong barrier to rotation. In fact, the intensity of the line at 7 cm$^{-1}$ was found not to increase with coverage beyond 1 H$_2$/supercage which indicates there the number of such sites is rather small as expected.

The results of our coadsorption experiments described above contain important information for the understanding of the well-known N$_2$/O$_2$ separation efficiency in LiX. It is commonly assumed that type III cations are critical to separation as these bind diatomic molecules more strongly than the less-exposed cations. This is in fact clearly demonstrated by our MC and rotational studies of H$_2$ in NaA. LiA has few (if any) cations in this site which may explain why it is less useful for separation. Moreover, some of the 8-ring windows may be blocked by the presence of two cations. The coadsorption INS spectra in LiX of H$_2$ with high coverage of O$_2$ are more difficult to rationalize. MD simulations [11] for N$_2$ and O$_2$ in CaLSX do however show that N$_2$ molecules will cluster around the cation in well defined potential minima while O$_2$ binds less strongly and thus can be located in a large number of locations inside the supercage. The H$_2$ INS spectrum in the presence of a large number of O$_2$ molecules appears to provide a picture of this distribution. Simulation studies of the coadsorption of H$_2$ with N$_2$ or O$_2$ are in progress to provide a more detailed explanation of these observations.

CONCLUSION

We have demonstrated that INS spectroscopy of adsorbed H$_2$ is a highly sensitive probe of adsorption sites in zeolites especially when combined with
simulations. Moreover, the use of coadsorption of H\textsubscript{2} with other molecules can provide important information on a variety of processes in zeolites of interest.

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REFERENCES