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PARTIALLY EXCHANGED ZINC A ZEOLITE

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INFRARED AND NEUTRON SCATTERING STUDIES OF ETHENE ADSORBED ONTO PARTIALLY EXCHANGED ZINC A ZEOLITE

by

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ABSTRACT

Infrared and inelastic neutron scattering studies of ethene adsorbed onto ZnNaA zeolite show that the adsorbed molecule occupies a single adsorption site. The C-H stretching modes are not observed in the infrared data but are seen as a broad band in the neutron spectrum. Some low frequency adsorbate-adsorbent modes are assigned.

INTRODUCTION

In vibrational studies of species adsorbed within zeolite frameworks most attention has centered on the changes in the internal mode frequencies of the adsorbate with respect to the free molecule. On adsorption the three rotational and translational modes of the free molecule usually become hindered. These modes, which directly reflect the surface-adsorbate bonding, have not generally been studied because of the difficulties in observing them using optical spectroscopy viz:

- (1) these modes occur below 1000 cm^{-1} and in this region zeolite frameworks are usually extremely absorbing in the infrared.
- (2) many zeolites fluoresce making Raman experiments difficult or impossible.

Neither of these difficulties applies to inelastic neutron scattering (INS) spectroscopy for which there are also no electromagnetic selection rules [1]. In an INS experiment the scattering mechanism involves direct interaction between the incident neutron and the scattering nucleus. Each nucleus has a characteristic incoherent cross section (σ). Since the σ values for the atoms of dehydrated ZnNaA zeolite are very small compared with the very large value ($80 \times 10^{-24} \text{ cm}^2$) for the hydrogen atoms in the adsorbate [1], the zeolite is relatively "invisible" in an INS experiment. The INS spectrum is known to be dominated by those modes which involve large amplitude motion of the hydrogen atoms [1].

We present INS and IR data on C_2H_4 and C_2D_4 adsorbed on a partially exchanged type A zeolite. This represents part of a programme for studying the reactions of small hydrogenous molecules over zeolite catalysts. While we observed C_2H_2 to react very slowly [2] with ZnNaA, C_2H_4 does not seem to do so.

EXPERIMENTAL

The ZnNaA was prepared by ion exchanging NaA (Linde) powder (no binder) for seven days in a 0.1M solution of ZnCl_2 containing the stoichiometrically correct quantity of zinc ions. After washing, the zeolite was analyzed for Zn and Na by atomic absorption. The atomic ratio Zn/Na was determined to be 0.57.

Our IR experiments were carried out on a self-supporting ZnNaA disc in an all-metal cell. Pretreatment (heating to 450°C under a vacuum of 10^{-5} torr) and adsorption, etc., were carried out in-situ. Measurements were made using a Perkin Elmer 510B Infrared Spectrophotometer.

Neutron scattering measurements were made using the beryllium filter spectrometer at AERE Harwell ($100 \rightarrow 800 \text{ cm}^{-1}$) [1] and the filter difference spectrometer ($300 \rightarrow > 4000 \text{ cm}^{-1}$) at Los Alamos National Laboratory [3]. For the Harwell data the transition frequencies have been calculated from the peak maxima using standard correction factors [4]. The Los Alamos data was analyzed as previously described [3]. For the INS experiments the samples were pretreated as for the IR measurements and the samples held in thin-walled aluminium cells. The spectrum of the degassed zeolite was obtained to serve as a background. C_2H_4 was then adsorbed and the spectrum re-run. At Harwell, cover-

ages of 0.95 and 1.75 C_2H_4 (sequentially adsorbed onto the same sample) and of 1.75 C_2D_4 molecules per supercage were studied. The Los Alamos experiment involved an adsorption capacity of 1.03 C_2H_4 molecules per supercage. Adsorption was carried out at ambient temperature and the Harwell measurements were made at 80 K while those at Los Alamos were made at 12 K.

RESULTS AND DISCUSSION

The IR spectrum of dehydrated ZnNaA and of C_2H_4 adsorbed on it (overpressure of 5 torr) are shown in Fig. 1. Bands due to internal modes of the adsorbed species are clearly seen at 1326, 1451, and 1602 cm^{-1} . These transitions are readily assigned by comparison with the optical data [5] for gaseous C_2H_4 (Table 1). The change in activity of two of the modes reflects the symmetry change on adsorption. On evacuation for five minutes the intensities of the bands fall by at least a factor of 10. These observations are indicative of relatively weak non-dissociative adsorption at a single site. The band narrowing which takes place on adsorption indicates that the adsorbed molecule is not freely rotating. In view of this it is remarkable that we do not observe any bands due to the C-H stretching modes of adsorbed C_2H_4 (expected ca 3000 cm^{-1}). A similar observation for CdX zeolite, has been reported by Yates and Carter [6] although these modes have been readily observed in a wide range of ion-exchanged zeolites.

The reduced intensity of these modes must be consequence of subtle electronic changes on adsorption, and it is known that to further understand these a good normal coordinate analysis is needed which obviously requires the frequencies of the modes to be known. The non-observation of the C-H modes also casts some doubt on the true nature of the adsorbed species. We have studied C_2H_4 and C_2D_4 on ZnNaA using INS spectroscopy (Figs. 2 and 3). These data are summarized in Table 2

INS Data Below 400 cm^{-1}

Two distinct bands are observed in the INS spectra of both adsorbed C_2H_4 and C_2D_4 in this region, and there is little change on increasing the coverage. Since there are no intramolecular modes below 596 cm^{-1} , these transitions must be hindered rotations and/or trans-

lations of the adsorbed molecule relative to the zeolite. The higher wavenumber transitions occur at 310 (C_2H_4) and 237 (C_2D_4) cm^{-1} and, assuming these to be the same transition, this yields an isotopic ratio of 0.76. It is immediately evident that the only reasonable assignment of the 310 (C_2H_4) and 237 (C_2D_4) cm^{-1} bands is to the hindered rotation (τ_x) about the C = C axis. Using gas phase C_2H_4 geometry, the isotopic shift predicted is 0.72 and hence the C_2D_4 mode is expected at 223 cm^{-1} . This is within the errors of the observation. No other mode has such a large isotopic shift since this is the only mode which involves little or no carbon motion. The corresponding mode occurs at 417 (C_2H_4) and 298 (C_2D_4) cm^{-1} for a silver exchanged A zeolite [7]. Since the adsorbed ethene is not easily removed on evacuation of the AgA sample, it is reasonable to expect a higher frequency in this case. The corresponding mode in Zeise's salt ($[KPtCl_3(C_2H_4)H_2O]$) occurs at 1180 cm^{-1} since the metal-ethene bond in this very stable complex is much stronger than in the zeolite [8].

The lower wavenumber bands at 183 (C_2H_4) and 156 (C_2D_4) yield an isotopic ratio of 0.84. This is in good agreement with that expected (0.86) for the hindered rotation about an axis parallel to the surface but perpendicular to the C = C axis (τ_y). This corresponds to the antisymmetric metal-ethene stretching mode of organometallic complexes. In Zeise's salt τ_y occurs at 490 cm^{-1} , once again reflecting its stronger bonding [8].

INS Data Above 400 cm^{-1}

The INS data obtained on ZnNaA + C_2H_4 using the filter difference spectrometer at Los Alamos are shown in Figs. 3(a) and (b) and summarized in Table 2. Clearly the intense band at 318 cm^{-1} corresponds to τ_x observed at 310 cm^{-1} using the Harwell spectrometer. The overtone of this band is seen at 636 cm^{-1} . Above this value relatively narrow bands occur at 825 and 1023 cm^{-1} with broader features centered at ca 1460 and 3050 cm^{-1} . The broad features clearly contain a number of unresolved features. The 3050 cm^{-1} band must be assigned to the four C-H stretching modes, which were not observed in the IR data. Similarly,

the 1460 cm^{-1} band must contain a number of modes including $\nu(\text{C}=\text{C})$, CH_2 scissoring modes and the CH_2 rock.

The assignment of the 825 (sharp) and 1024 cm^{-1} bands is more difficult. Although bands are observed in the INS spectrum of Zeise's salt [9] at 840 and 1030 cm^{-1} , in good agreement with the $\text{C}_2\text{H}_4 + \text{ZnNaA}$ data, the data for the complex also contains an intense band at 720 cm^{-1} . No similar band is found for the adsorbed species. An examination of the INS data [9] for $\text{C}_2\text{H}_4 + \text{Ag13X}$ also shows bands at ca 820 and 1000 cm^{-1} with a minimum close to 700 cm^{-1} . Thus the zinc A and silver 13X data are comparable in this respect, and the adsorbed molecule is spectroscopically more similar to gaseous ethene than it is to the strongly bonded form in the complex. Although it is known that the $\nu(\text{C}=\text{C})$ stretching mode is mixed [8] and so comparisons between compounds based on the value of this mode are dubious, it is worth noting that $\nu(\text{C}=\text{C})$ occurs at 1602 cm^{-1} on ZnNaA and at 1623 cm^{-1} in gas phase C_2H_4 . These similar values imply a relatively weak perturbation of the double bond on adsorption.

The INS bands at 720 and 840 cm^{-1} in Zeise's salt were assigned [9] to CH_2 rocking modes (ν_{17} and ν_{23}). In the gas phase these modes (ν_{10} and ν_6 respectively) occur at 826 and 1236 cm^{-1} [5]. It is likely, therefore, that the 825 and 1024 cm^{-1} bands we observe correspond to the CH_2 rock and CH_2 twisting modes which occur at 826 (ν_6) and 1023 (ν_4) cm^{-1} respectively in uncoordinated C_2H_4 [5].

We have not attempted to assign the weak bands in the region $480\text{--}650\text{ cm}^{-1}$ (Figs. 2 and 3(a)). None of the hindered rotations or translations of adsorbed C_2H_4 can occur in this region nor are there any intramolecular C_2H_4 modes. It is possible that we are observing framework vibrations enhanced in intensity by the "riding" motion of the adsorbed species, but this must be regarded as only a tentative explanation.

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TABLE 1

IR Bands (cm^{-1}) and Their Assignments for
 C_2H_4 Adsorbed on ZnNaA Zeolite

<u>Assignment</u>	<u>Activity (gas phase)</u>	<u>Gas Phase [5]</u>	<u>Adsorbed</u>
ν_2 (C = C stretch)	Raman	1623	1602
ν_{12} (CH_2 deformation)	IR	1443	1451
ν_3 (CH_2 deformation)	Raman	1342	1326

TABLE 2

INS Data (cm^{-1}) and Assignments for C_2H_4 Adsorbed
on ZnNaA Zeolite

C_2H_4	C_2D_4	Observed Deuteration Shift	Predicted Deuteration Shift	Assignment
183	156	0.84	0.86	τ_y
310	237	0.76	0.73	τ_x
490				Amplified
566				zeolite modes
636				Overtone of τ_x
825				CH_2 Rock
1024				CH_2 Twist
1460				$\nu(\text{C}=\text{C})$ CH_2 scissoring CH_2 rock etc.
3050				C-H stretching modes

FIGURE CAPTIONS

Figure 1. Infrared spectrum of ZnNaA (a) after heating under vacuum to 450°C and (b) after adsorption of C_2H_4 at an overpressure of 5 torr.

Figure 2. INS data (80K) on ZnNaA obtained at AERE Harwell,
o ZnNaA + C_2H_4 (0.95 molecules per supercage)
x ZnNaA + C_2H_4 (1.75 molecules per supercage)
+ ZnNaA + C_2D_4 (1.75 molecules per supercage)
The data have the spectrum of the degassed zeolite subtracted and the "o" data points have been multiplied by a factor of two.

Figure 3. INS spectrum (12K) of ZnNaA + C_2H_4 (1.03 molecules per supercage) obtained at Los Alamos (1 meV $\sim$ 8.067 cm^{-1}). The spectrum of the degassed zeolite has been subtracted.

x

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ETHYLENE ADSORBED ON DEHYDRATED ZnNa Azeolite

(a) background; (b) (a) + 5 Torr C₂H₄

Fig. 3a.

Fig 3b