Inelastic neutron scattering study of acetonitrile adsorbed on Raney nickel

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A vibrational study of acetonitrile adsorbed on Raney nickel has been performed using inelastic neutron scattering. The chemisorption is associative and no C–H bond breaking is observed up to 393 K. Acetonitrile is found to be adsorbed parallel to the surface. The vibrational modes of the molecule are not very perturbed, this indicates a weak interaction with the surface. The coverage of the metal surface by acetonitrile is small, which has also been observed in the hydrogenation reaction in the gas phase. The excellent selectivity for the primary amine formation can be explained by this weak chemisorption.

Keywords: Acetonitrile; hydrogenation; Raney nickel; inelastic neutron scattering

1. Introduction

Synthesis of amines from catalytic hydrogenation of nitriles is an important industrial process. It is generally performed in the liquid phase in the presence of metallic catalysts and under high hydrogen pressures. The distribution of the products can be quite complicated since condensation and hydrogenation reactions lead to a mixture of primary, secondary and ternary amines [1].

In order to get information on both the reactants and the products behaviour, we are studying the hydrogenation of acetonitrile on Raney nickel catalysts in the gas phase, under atmospheric pressure. We have found that this metal has a high activity in the temperature range 370–420 K and a high selectivity in ethylamine

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(>90%). The adsorption sites and the relative strengths of adsorption of the different species should be easier to determine under these conditions.

Even for a simple molecule like acetonitrile, however, the type of coordination to a metal surface is disputed. Muetterties and coworkers have derived from electron spectroscopic and diffraction techniques, from isotopic labelling experiments and from thermal desorption spectrometry that the main acetonitrile species adsorbed on different nickel single surfaces was bonded through the nitrogen atom only, i.e. with the C–N bond vector normal to the surface [2]. On the other hand, Sexton and Avery have studied by X-ray photoelectron spectroscopy and by electron energy loss spectroscopy the adsorption of acetonitrile on the Pt(111) surface; they concluded that the molecule was bonded via the π system of the C≡N group, i.e. with the C–N bond vector mainly parallel to the surface [3].

We report here a vibrational study of acetonitrile adsorbed on Raney nickel, by inelastic neutron scattering (INS). This technique is well adapted to observe the vibrational modes of hydrogen or hydrogenated molecules adsorbed on surfaces because of the relatively large incoherent cross-section of the proton. The resolution in INS spectroscopy is comparable to the one obtained in electron energy loss spectroscopy (EELS) but the intensities of the bands have completely different origins. Thus, INS is not bound to selection rules, contrary to EELS, and the vibrational intensities are directly related to nuclei displacements. INS has been previously used to characterize the adsorption of hydrogen or hydrocarbons on Raney nickel [4–6]. In this study, we compare the INS spectra of adsorbed and free (in the solid phase) acetonitrile, in order to determine the adsorption geometry and the perturbation of the molecule.

2. Experimental

2.1. SAMPLES

The Raney nickel used for the INS study is the same as the one used in the hydrogenation reaction. It is prepared using standard procedures [7] by NaOH attack on a Ni–Al alloy doped with small amounts of Fe and Cr [8]. The wet material was evacuated with a cryopump to 10^{-7} Torr up to 530 K. This procedure is known to eliminate all the water and chemisorbed hydrogen (this is checked during the neutron experiment). The thermal treatment produces, however, some sintering of the catalyst, its specific area measured by nitrogen adsorption is reduced from 130 to 70 $m^2\ g^{-1}$. 100 g of the dry catalyst was transferred, under vacuum, into a cylindrical aluminium container connected to a manifold.

Acetonitrile was supplied by Aldrich and was of HPLC grade (99.9 + %). For the INS measurements in the solid phase, 4.5 g were quenched to 77 K in a rectangular aluminium cell, to produce a pure β-phase.

2.2. NEUTRON SPECTROMETER

The neutron spectra were obtained at the ISIS spallation neutron source at the Rutherford Appleton Laboratory, UK, using the spectrometer TFXA [9]. This spectrometer is a time-of-flight instrument with an inverse geometry and a time-focusing analyser, it gives good counting rates and good energy transfer resolution ($\Delta E/E = 2\%$) from 2 meV to 1 eV. The estimated absolute accuracy is ± 10 cm^{-1} for solid CH_3CN and ± 20 cm^{-1} for the adsorbed molecule.

All the neutron spectra were recorded at 20 K, the cells being placed in a cryostat. The evacuation and loading of the Raney nickel sample was performed out of the cryostat, on an all-metal vacuum line.

3. Results

The INS spectrum of solid acetonitrile is shown in fig. 1 (a). The largest peak at 160 cm^{-1} corresponds to the methyl torsion which has zero-frequency in the gas phase but becomes a libration in the crystal. The peaks at $\sim$ 75 and 120 cm^{-1} are due to the other lattice modes. The internal modes of CH_3CN have been well characterized by infrared and Raman spectroscopies [10–14]. The lowest frequency mode is found at 396 cm^{-1}, it corresponds to a C–C–N bend motion, of E symmetry (ν_8). The C–C stretch, ν_4 (A_1), produces a weak band at 928 cm^{-1}; the CH_3 rock, ν_7 (E), is found at 1056 cm^{-1} and the symmetric and antisymmetric CH_3 deformations, ν_3 (A_1) and ν_6 (E), are observed at 1390 and 1453 cm^{-1}, respectively (see table 1). The C–N stretch, ν_2 (A_1), which is measured in infrared at

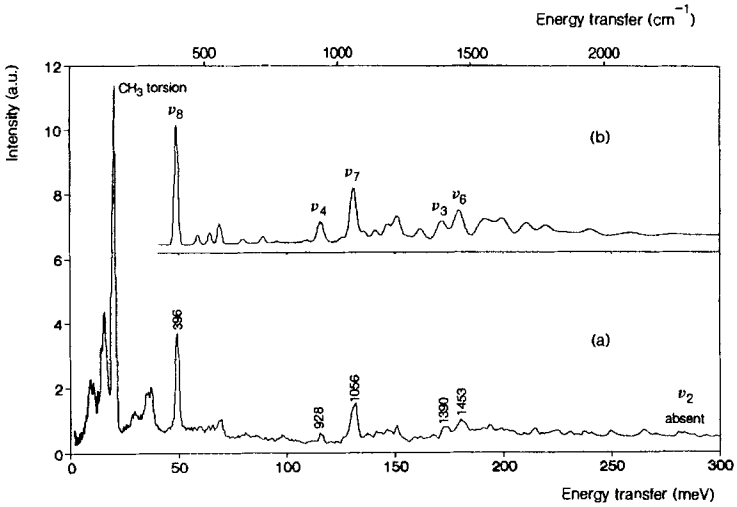

Fig. 1. INS spectra of solid acetonitrile (β-phase) (a) experimental, (b) calculated.

Table 1
Band positions for solid acetonitrile (β-phase) and for acetonitrile adsorbed on Raney nickel at 323 and 393 K

Solid CH_3CN		CH_3CN/Raney nickel			
		323 K		393 K	
75 } 120	lattice modes	100	trans.+ rot.	52 100	τCH3
160	L_{CH_3}	160	L_{CH_3}		
396	ν_8	392	ν_8	385	ν_8
928	ν_4				
1056	ν_7	1047	ν_7	1042	ν_7
1390	ν_3				
		1427	$\nu_3 + \nu_6$	1450	$\nu_3 + \nu_6$
1453	ν_6				

2250 cm^{-1}, is not observed in the INS spectrum. This is due firstly to the fact that the hydrogen atoms hardly move during this vibration. Further, the INS intensities of the fundamentals are reduced for increasing energy transfer because of the effect of the Debye–Waller factor [15]. This is clearly apparent in fig. 1 (a) where ν_8 has a larger intensity than ν_7, even if the CH_3 rock motion implies much more the hydrogen atoms than the C–C–N bend. The Debye–Waller factor is also very effective in the C–H stretching region so that the INS spectrum is fairly flat in that range for this compound. Our INS data are very similar to those recently reported by Gamlen et al. [16], but our force field calculation is different.

To study the adsorption of acetonitrile on Raney nickel, the INS spectrum of the degassed catalyst was first recorded at 20 K (fig. 2 (a)). The peaks which are observed below 400 cm^{-1} are due to phonons of the nickel sample and of the aluminium container. This spectrum is useful to check that hydrogen has been well evacuated from the catalyst since no intensity is found between 800 and 1200 cm^{-1}, where the hydrogen–nickel vibrations are observed [5].

After this background run, the Raney nickel was taken out of the cryostat and acetonitrile was adsorbed at room temperature. The catalyst was heated at 323 K and a pressure of 95 mbar was measured in the cell at this temperature. The sample was placed back in the cryostat and the INS spectrum, obtained at 20 K, is shown in fig. 2 (b). The amount of acetonitrile adsorbed on Raney nickel can be estimated from the relative intensities of figs. 1 and 2, it corresponds to $\sim$ 4.5 mg/g. After subtraction of the bare catalyst, the spectra shown in fig. 3a and 3b are obtained. It appears from fig. 3a that there is some physisorbed acetonitrile on the sample since a peak due to the methyl torsion is observed at the same frequency as in the solid: 160 cm^{-1}. The large band centered at 100 cm^{-1} is due mainly to hindered transla-

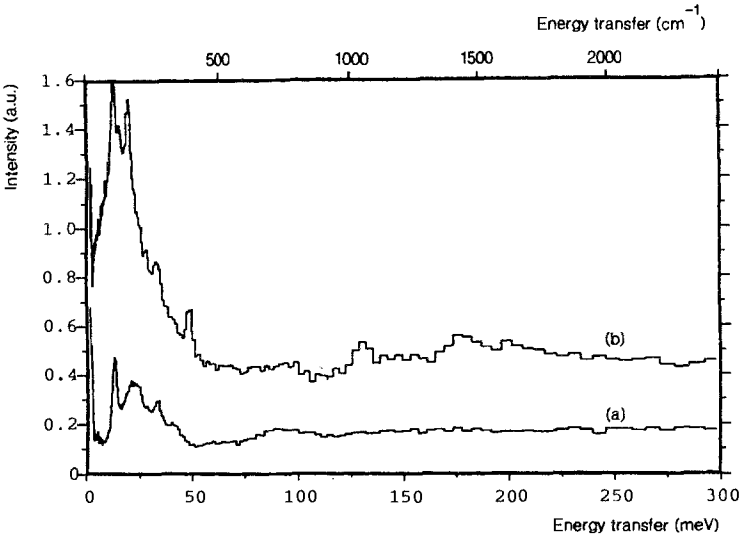

Fig. 2. (a) INS spectrum of bare Raney nickel, (b) INS spectrum of acetonitrile adsorbed at 323 K on Raney nickel.

tions and rotations of the molecule with respect to the surface. The C–C–N bend is observed at 392 cm^{-1}, the CH_3 rock at 1047 cm^{-1} and the CH_3 deformations produce a band at 1427 cm^{-1} (table 1).

The sample was then warmed at 393 K and the INS spectra, recorded at 20 K, are shown in figs. 3c and 3d. It is clear that this treatment has allowed acetonitrile to diffuse throughout the sample since there is no more physisorbed CH_3CN. The intensity at low-frequency has increased and a band at 52 cm^{-1} can now be observed. The C–C–N bend is hardly visible at 385 cm^{-1} but the CH_3 rock and deformations are still visible.

4. Discussion

It is now a common practice to simulate INS spectra starting with the Wilson GF matrix method to compute the frequencies and intensities of the fundamentals and adding multiphonon processes involving the internal modes with the lattice modes [15,17]. We have performed such a calculation for solid acetonitrile using the vibrational assignment derived from optical spectroscopies. Since the mean-square amplitude due to the lattice modes is large for this crystal ($\langle u^2 \rangle = 0.02$ Å^2), we have considered multiphonon lattice modes up to the tenth term. The INS spectrum of the internal mode region, calculated with the force field given in table 2, is shown in fig. 1 (b). The agreement with the experimental spectrum is satisfactory and confirms the previous assignments. The force field used for the simulation is, however, different from the force field derived in the recent INS study of Gamlen et al. [16]. The interaction force constants are too large in ref. [16] compared to

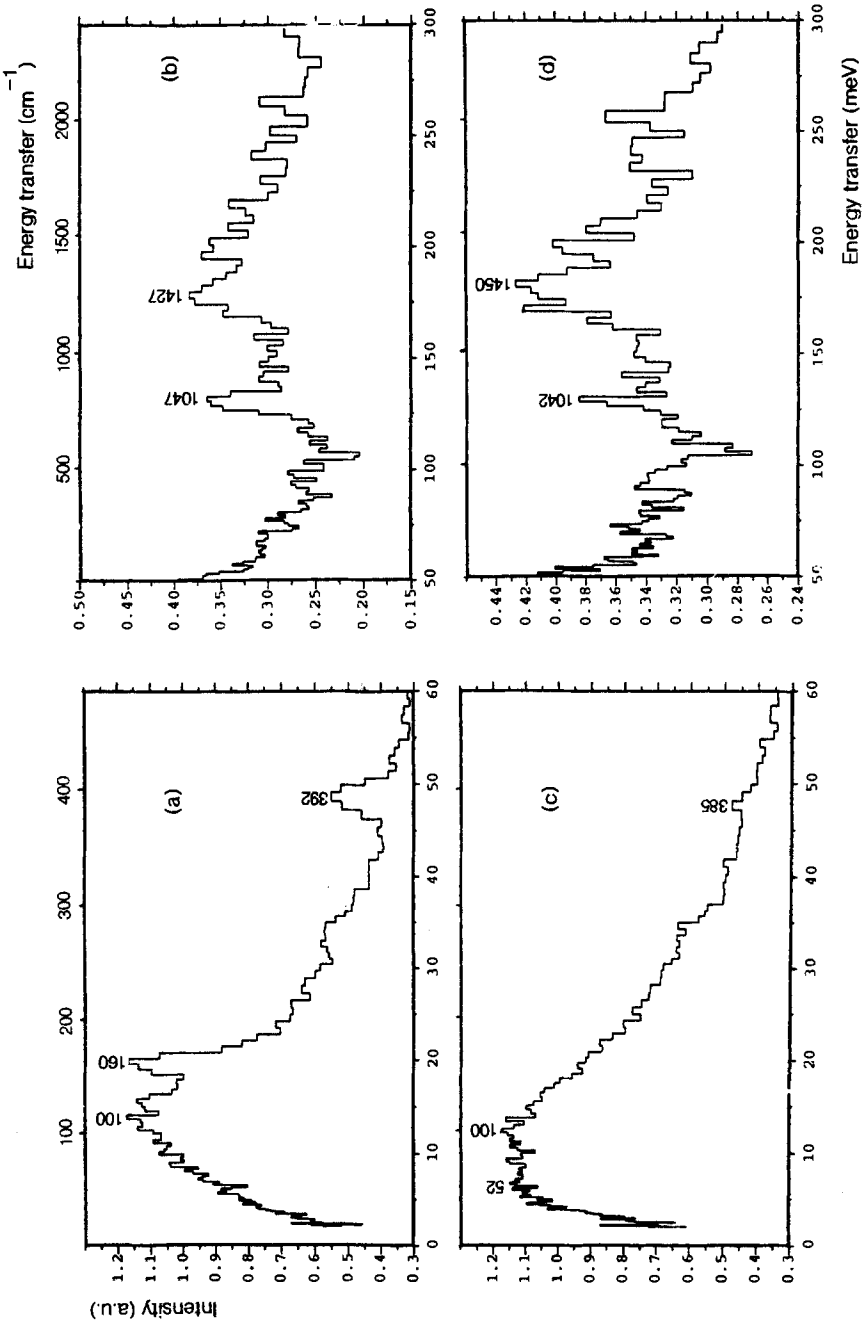

Fig. 3. INS spectra of acetonitrile on Raney nickel: (a) and (b) after adsorption at 323 K, (c) and (d) after adsorption at 393 K (the signal of the bare catalyst has been subtracted).

Table 2
Force field for acetonitrile (solid). The valence force constants are in mdyn $Å^{-1}$, the deformations in mdyn Å rad^{-2} and the bond–angle interactions in mdyn rad^{-1}

Force constant	Value	Force constant	Value
CN stretch	15.327	CCN bend	0.394
CC stretch	6.993	CN stretch/CC stretch	−0.669
CH stretch	4.807	CCH def./CCH def.	−0.044
CCH def.	0.558	CH stretch/CH stretch	0.058
HCH def.	0.529	CCN bend/CCH def.	−0.100

the diagonal constants and this demonstrates the difficulty in obtaining an experimental force field, even using the additional information contained in the INS intensities.

In the case of acetonitrile adsorbed on Raney nickel, the problem is even more difficult because (i) the adsorption geometry is not known, and (ii) the vibrations of CH_3CN relative to the surface produce a broad distribution with a limited number of peak maxima. Several informations can nevertheless be obtained from the INS spectra. First of all, the vibrations of atomic hydrogen are not observed in the range 800–1200 cm^{-1}. This means that acetonitrile chemisorption on Raney nickel is associative and that C–H bond breaking is negligible up to 393 K, in agreement with the work performed on Ni single crystals [2]. This is different from the results obtained for benzene [4] where it was found that 15% of the molecules were totally dehydrogenated after adsorption on Raney nickel at room temperature.

The type of coordination of acetonitrile with the nickel surface can also be determined from the INS spectra. If the molecule was bonded to the surface only through the nitrogen atom, a peak due to the methyl torsion should be clearly observed, as in the solid (fig. 1). On the contrary, a broad distribution is observed at low frequencies after thermal treatment at 393 K. The methyl torsion is assigned to the broad band centered at 52 cm^{-1} in fig. 3c since this band has gained in intensity after the disappearance of physisorbed acetonitrile (fig. 3a). We conclude that the torsional potential is greatly modified by interactions with nickel atoms and that therefore the molecule is adsorbed parallel to the surface. This conclusion was also reached by Sexton and Avery [3] using as main argument the decrease of the ν(CN) stretching mode which was placed at 1615 cm^{-1} on Pt(111) and at 1680 cm^{-1} on Ni(111). They proposed that the CN triple bond rehybridized to a double bond with both the C and N atoms attached to the surface. We have performed a normal coordinate analysis of CH_3CN adsorbed either parallel or perpendicular to a Ni(111) surface. We find that ν_2 can be shifted from 2250 to 1680 cm^{-1} by decreasing the CN stretching force constant to 9 mdyn $Å^{-1}$, which is close to the value corresponding to a double bond (the CC force constant has also to be decreased and the value corresponds to a single bond). Unfortunately, the INS intensity of ν_2 is too small, even if it gains in intensity due to coupling when the frequency is low-

ered, so that the degree of hybridization cannot be specified. However, for a strongly perturbed acetonitrile, the CCN bond will no longer be linear and a lifting of degeneracy is expected for the E modes. The normal coordinate analysis which we have performed indicates that new vibrations should appear between 400 and 1400 cm^{-1}. The peak observed at 520 cm^{-1} in the EELS spectra [2] could thus be assigned to the CCN bend of a nonlinear molecule. On Raney nickel, no new bands are detected and the INS results are in favour of a weakly perturbed molecule. This is in agreement with the fact that the saturation of the surface is not reached at room temperature. Considering an average value of 1.5×10^{19} surface nickel atoms per square meter and noting that 0.45 g of CH_3CN has been adsorbed by 100 g of catalyst (with a specific area of 70 $m^2\ g^{-1}$), an approximate surface coverage of 0.26 is obtained at 323 K, if one makes the hypothesis that one acetonitrile molecule occupies four nickel atoms.

5. Conclusion

The adsorption of acetonitrile on Raney nickel has been studied by inelastic neutron scattering at 323 and 393 K. The chemisorption is associative and C–H bond breaking is negligible up to 393 K. The INS results indicate that the molecule is adsorbed parallel to the surface and probably linear. The internal vibrational modes of the molecule are weakly perturbed so that the interaction with the nickel surface, which occurs via the π system of the C≡N group, must be small. The surface is not saturated at 323 K, an approximate surface coverage of 0.26 being derived from the INS measurements.

One can try to deduce some implications of these observations for the hydrogenation reaction of acetonitrile in the gas phase. The first point is that, compared to the hydrogenation of an ethylenic hydrocarbon, the rate is three orders of magnitude lower, in spite of the fact that both molecules are π-adsorbed. But whereas the order of the reaction is zero with respect to the hydrocarbon, it is positive (0.6) with respect to the nitrile. This means that in the competitive adsorption with hydrogen, the coverage of the metal surface by the nitrile remains weak. A consequence of this weak chemisorption is also the excellent selectivity for the primary amine formation, by a limitation of secondary reactions in the adsorbed phase between an intermediary imine and the amine [18].

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