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Dinitrogen and carbon monoxide hydrogen bonding in protonic zeolites: Studies from variable-temperature infrared spectroscopy

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Abstract

Adsorption (at a low temperature) of nitrogen on the protonic zeolite H-Y results in hydrogen bonding of the adsorbed N_2 molecules with the zeolite Si(OH)Al Brønsted-acid groups. This hydrogen-bonding interaction leads to activation, in the infrared, of the fundamental N–N stretching mode, which appears at 2334 cm^{-1}. From infrared spectra taken over a temperature range, the standard enthalpy of formation of the $OH \cdots N_2$ complex was found to be $\Delta H^0 = -15.7(\pm 1)$ kJ mol^{-1}. Similarly, variable-temperature infrared spectroscopy was used to determine the standard enthalpy change involved in formation of H-bonded CO complexes for CO adsorbed on the zeolites H-ZSM-5 and H-FER; the corresponding values of ΔH^0 were found to be $-29.4(\pm 1)$ and $-28.4(\pm 1)$ kJ mol^{-1}, respectively. The whole set of results was analysed in the context of other relevant data available in the literature.

Keywords: Adsorption thermodynamics; Carbon monoxide; Dinitrogen; Hydrogen bonding; IR spectroscopy; Zeolites

1. Introduction

Studies on hydrogen bonding are relevant to a wide range of fields spanning biology, chemistry, physics and materials science alike. Molecular recognition and association [1–4], hydrogen exchange and proton tunnelling [5–9], theoretical chemistry [10–13], crystal engineering [14–18] and catalysis are some examples of such fields. Regarding heterogeneous catalysis, studies on hydrogen bonding in acidic (proton-exchanged) zeolites are relevant to both, acid catalysed chemical processes and characterization of zeolites by infrared (IR) spectroscopy of probe molecules. Catalysis by protonic zeolites encompasses a wide range of industrial (petrochemical) processes, including alkane hydrocracking and skeletal isomerization, alkene and alkyne polymerization, alkylation and dehydro-aromatization, which often involve hydrogen bonding followed by proton transfer [19–23]. On the other hand, carbon monoxide and dinitrogen are very often used as IR probe molecules for zeolite characterization [24–29]; increased knowledge about interaction of these molecules with protonic zeolites should help characterization.

The bathochromic shift, Δν(OH), of the Brønsted-acid Si(OH)Al group in protonic zeolites upon interaction with (adsorbed) probe molecules is often used as a quantitative measurement of Brønsted acidity [24,30,31]. However, besides spectroscopic features, the solid–gas interaction energy involved in hydrogen bonding is another relevant parameter to consider. Variable-temperature IR (VTIR) spectroscopy was recently shown [32,33] to be a very valuable technique for simultaneous studies on the spectroscopic and thermodynamic aspects of weak solid–gas interactions. And, in fact, VTIR was already applied to the study of hydrogen bonding of both, CO and dinitrogen in some protonic zeolites [34–36]. New results for the zeolites H-Y, H-FER and H-ZSM-5 are given here, and the field is reviewed with the double aim of (i) highlighting

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the potential of the method used, and (ii) discussing the full set of available data in a broader context than what can be derived from consideration of each gas–solid system alone.

2. Materials and methods

2.1. Experimental details

Samples of zeolites NH_4-ZSM-5, NH_4-FER and NH_4-Y were obtained from a commercial firm, they had Si:Al ratio of 30:1, 27.5:1 and 5.6:1, respectively. Powder X-ray diffraction showed good crystallinity in all cases and confirmed the expected structure type (MFI, FER and FAU, respectively) [37,38]; no additional diffraction peaks were found. From these parent materials, H-ZSM-5, H-FER and H-Y were obtained by in situ thermal treatment inside and IR cell, as described below. During this thermal treatment NH_4^+ ions decompose and yield the protonic form of the zeolite. Total transformation was checked by the absence of bands from the ammonium ion in the corresponding IR spectra.

For IR spectroscopy, thin self-supported wafers of the zeolite samples were prepared and activated (outgassed) in a dynamic vacuum (residual pressure smaller than 10^{-4} mbar) for 3 h at 700 K inside a home made IR cell [39] which allowed in situ sample activation, gas dosage and variable-temperature IR spectroscopy to be carried out. For better thermal contact between the zeolite wafer and the cooled cell, 0.2 mbar of helium was admitted into the sample compartment before recording the background spectrum at liquid-nitrogen temperature. The cell was then dosed with either N_2 or CO and closed, and IR spectra were recorded at several temperature values upon gradual warming up of the IR cell. Simultaneously, temperature and equilibrium pressure inside the cell were registered. A platinum resistance thermometer (Tinsley) and a capacitance pressure gauge (MKS, Baratron) were used for that purpose. Pressure correction (for helium) was determined from a calibration plot, as described elsewhere [35]. Transmission FT-IR spectra were recorded, at 3 cm^{-1} resolution, using a Bruker IFS66 spectrometer.

2.2. Determination of gas adsorption enthalpy and entropy

For both, carbon monoxide and dinitrogen, interaction with protonic zeolites results in hydrogen bonding because of localized adsorption of the gas molecules on the Brønsted-acid (bridging) Si(OH)Al group of the zeolite. Such a process results in progressive erosion of the characteristic O–H stretching band: which is red-shifted when forming the corresponding OH···CO or $OH\cdots N_2$ hydrogen-bonded complex [24,40–42]. Simultaneously, the characteristic IR absorption band of the hydrogen-bonded molecule (CO or N_2) builds up. A set of variable-temperature IR spectra obtained while simultaneously recording IR absorbance, temperature and gas equilibrium pressure can be used to derive the standard enthalpy, ΔH^0, and entropy, ΔS^0, of the hydrogen bonding process. The method, termed VTIR, was explained in detail elsewhere [32]. However, in order to facilitate understanding of the results reported here, a brief account is given below.

Let Eq. (1) represent the adsorption equilibrium of a molecule, M, on the adsorption site, ZOH, representing a zeolite Brønsted-acid centre:

$$\text{ZOH}_{(s)} + \text{M}_{(g)} \rightleftarrows \text{ZOH–M}_{(ads)}. \qquad (1)$$

For any give temperature, T, the integrated intensity, A, of a characteristic IR band (from either the adsorbent or the adsorbed molecule) should be proportional to surface coverage, θ. Therefore, this IR absorption band gives information on the activity (in a thermodynamic sense) of the adsorbed species and the empty sites $(1-\theta)$. At the same time, the equilibrium pressure, p, monitors the activity of the gas phase. Hence, the equilibrium constant, k, for the adsorption process (at that temperature) can be determined. Assuming Langmuir-type adsorption, k is given by Eq. (2) below:

$$\theta = k(T)p/[1 + k(T)p]. \qquad (2)$$

The variation of k with temperature is related to standard adsorption enthalpy and entropy through the van't Hoff equation:

$$k(T) = \exp(-\Delta H^0/RT)\exp(\Delta S^0/R). \qquad (3)$$

Combination of Eqs. (2) and (3) leads to Eq. (4) below:

$$\ln\{\theta/[(1-\theta)p]\} = (-\Delta H^0/RT) + (\Delta S^0/R). \qquad (4)$$

Eq. (4) can also be written as:

$$\ln\{A/[(A_M - A)p]\} = (-\Delta H^0/RT) + (\Delta S^0/R) \qquad (5)$$

where A stands for the actual IR absorbance being measured and A_M is the maximum absorbance (corresponding to $\theta = 1$). By determining θ (or relative absorbance) as a function of T and p over a relatively large temperature range, Eqs. (4) or (5) give direct access to the thermodynamic quantities ΔH^0 and ΔS^0 which characterize the process under study.

3. Results and discussion

3.1. Carbon monoxide adsorption on H-ZSM-5

As shown in Fig. 1 (inset) the blank spectrum of the zeolite H-ZSM-5 (Si:Al = 30:1) displays in the O–H stretching region the characteristic IR absorption bands at 3746 and 3618 cm^{-1} arising, respectively, from silanols and from bridged Si(OH)Al hydroxy groups that constitute the zeolite Brønsted-acid sites [24,43,44]. Upon interaction of the zeolite with adsorbed CO (in the low-pressure range studied) the band due to silanols was not significantly altered, but that corresponding to Brønsted-acid sites decreased till an extent which was a function of temperature. Simultaneously, a new (broader) band, from hydrogen bonded OH···CO species appeared at 3315 cm^{-1}, as shown in the