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Thermodynamic studies on hydrogen adsorption on the zeolites Na-ZSM-5 and K-ZSM-5

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Abstract

Adsorption of dihydrogen onto the zeolites Na-ZSM-5 and K-ZSM-5 renders the fundamental H–H stretching mode infrared active. The corresponding infrared absorption bands were found at 4101 and 4112 cm^{-1} for H_2/Na-ZSM-5 and H_2/K-ZSM-5, respectively. Thermodynamic characterization of the adsorbed state was carried out by means of variable-temperature infrared spectroscopy; simultaneously measuring integrated band intensity, temperature and equilibrium pressure of the gas phase. For the H_2/Na-ZSM-5 system, the standard adsorption enthalpy and entropy resulted to be $\Delta H^\circ = -10.3$ (±0.5) $\mathrm{kJ\,mol^{-1}}$ and $\Delta S^\circ = -121$ (±10) $\mathrm{J\,mol^{-1}\,K^{-1}}$. For H_2/K-ZSM-5 corresponding values were -9.1 (±0.5) $\mathrm{kJ\,mol^{-1}}$ and -124 (±10) $\mathrm{J\,mol^{-1}\,K^{-1}}$, respectively.

Keywords: Adsorption thermodynamics; Hydrogen; FTIR; Zeolites; ZSM-5

1. Introduction

Zeolite molecular sieves are often used for industrial gas separation processes based on differences in adsorption strength among components of a gas mixture. Thus, pressure swing adsorption (employing zeolites) is commercially used, inter alia, for producing oxygen from air and hydrogen from a variety of feedstocks; such as refinery off-gas and hydrogen-rich gas from steam reforming of hydrocarbons. On the other hand, both zeolites and active carbons can be considered [1–3] as being potential candidates for large-scale hydrogen storage in cryogenically cooled vessels; a subject of current interest in view of the potential use of this gas as a cost-effective energy vector for buildings and transportation.

Regarding hydrogen, it should be clear that precise knowledge of the interaction energy between the gas and the adsorbent would facilitate improvement of the above mentioned applications. However, direct measurement of such an interaction energy by adsorption microcalorimetry is a difficult task to perform. This is so because the low temperature needed for adsorption to take place, and the small amount of heat evolved, demand very stringent requirements on instrument design and sensitivity.

We have recently shown [4,5] that variable-temperature infrared (IR) spectroscopy can advantageously be used for studying adsorption thermodynamics of weakly interacting adsorbent–adsorbate systems, and the method is applied here to hydrogen adsorption on both

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Na-ZSM-5 and K-ZSM-5. Related work on Li-ZSM-5 was reported elsewhere [6].

Interaction of the dihydrogen molecule with the zeolite adsorbing centres renders the fundamental H–H stretching mode IR active. By measuring the integrated intensity of the corresponding IR absorption band over a range of temperature, and the corresponding gas equilibrium pressure, the desired values of adsorption enthalpy and entropy are obtained. These values fully characterise the adsorbed state, as shown below.

2. Experimental details

The Na-ZSM-5 and K-ZSM-5 samples used were prepared from a commercial NH_4-ZSM-5 sample (Si/Al = 25) by ion exchange with the corresponding alkali-metal nitrate solutions. Powder X-ray diffraction showed good crystallinity in both cases, and absence of any diffraction line not assignable to the corresponding MFI structure type. Complete ion exchange was checked by the absence of IR absorption bands corresponding to either the ammonium ion or the Brønsted-acid OH group, which would be formed during thermal activation (see below) of the zeolite samples if total exchange of alkali-metal ions for ammonium did not take place. For IR spectroscopic measurements, thin self-supported wafers of the zeolite samples were prepared and activated (outgassed) in a dynamic vacuum (residual pressure $< 10^{-7}$ bar) for 2 h at 700 K inside an IR cell [7], which allowed in situ high-temperature activation, gas dosage and variable-temperature IR spectroscopy to be carried out. For each sample, after running the blank spectrum of the zeolite wafer at 77 K the cell was dosed with hydrogen, it was then closed and spectra were taken at 2–5 K intervals while simultaneously recording sample temperature and hydrogen equilibrium pressure inside the cell. A platinum resistance thermometer and a capacitance pressure gauge were used for this purpose. The precision of these measurements was of about ±2 K and $\pm 2 \times 10^{-5}$ bar, respectively. In order to check reproducibility, and also for improving accuracy, three independent sets of measurements were taken on each sample. In these independent runs different initial doses of hydrogen were used, so as to cover a larger pressure range. Note that the high thermal conductivity of hydrogen, together with the static nature of measurements, should minimize (possible) temperature gradients inside both the IR cell and the sample wafer. Since no temperature offset effects were found when plotting results from data obtained under widely different hydrogen pressure (in the different runs for each sample), it seems reasonable to assume that temperature gradients (if any) were of little concern. Transmission FTIR spectra were recorded at 3 cm^{-1} resolution by means of a Bruker IFS66 spectrometer.

3. Results and discussion

IR spectra of dihydrogen adsorbed (at 77 K) on alkali-metal-exchanged faujasites, mordenite, and A-type zeolites were reported by several authors [8–13]; mainly with a view of using dihydrogen as a probe molecule for IR spectroscopic studies of zeolites and related materials. These spectra show a main IR absorption band in the 4070–4100 cm^{-1} range which corresponds to the fundamental H–H stretching mode of adsorbed dihydrogen. Perturbation of the molecule (mainly) by the cationic adsorption centre renders this vibrational mode IR active and causes a bathochromic shift from the gas phase value of 4163 cm^{-1} corresponding to the free molecule (Raman active H–H stretching vibration). Earlier studies [8,14] suggested that the H_2 molecule is adsorbed on alkali-metal cations of zeolites forming T-shaped adsorption complexes. However, more recent work [10,12,15] has shown that the adsorbed molecule can also interact with neighbouring anions of the zeolite framework. Hence, the adsorption centre should be taken to represent both the extra-framework alkali-metal cation and the nearby oxygens [16].

Fig. 1 shows some selected variable-temperature IR spectra, in the H–H stretching region, of hydrogen adsorbed on Na-ZSM-5; the H–H stretching band is seen at 4101 cm^{-1}. For hydrogen adsorbed on K-ZSM-5, corresponding spectra are depicted in Fig. 2; which shows the H–H stretching band at 4112 cm^{-1}. For the

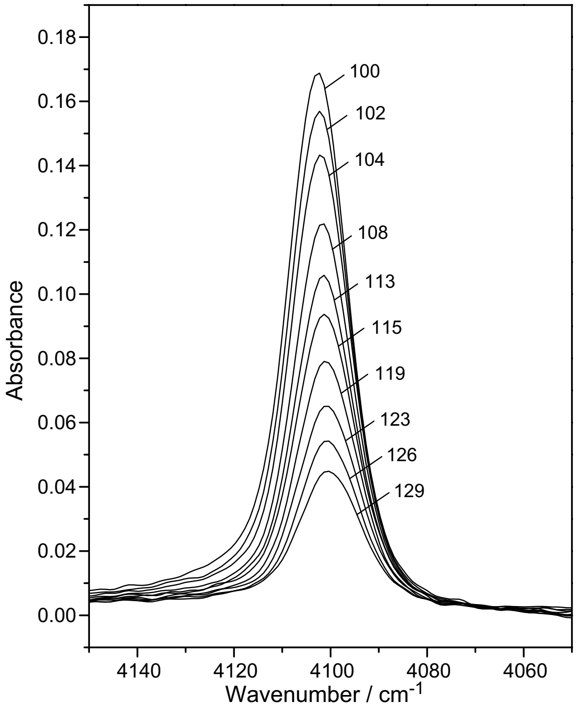

Fig. 1. Selected difference IR spectra (zeolite blank subtracted) in the H–H stretching region corresponding to the large hydrogen dose on Na-ZSM-5 (Table 1). Numbers denote temperature in K.