

# Hydrogen adsorption on magnesium-exchanged zeolites

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By means of variable-temperature FTIR spectroscopy, the standard adsorption enthalpy of hydrogen on the zeolite (Mg,Na)-Y was found to be  $\Delta H^\circ = -17.5 \text{ kJ mol}^{-1}$ , which suggests that magnesium-containing porous materials are good candidates in the search for suitable adsorbents for reversible hydrogen storage.

The search for safe, and cost effective, storage and transport of hydrogen constitutes a forefront issue of current technological development, in view of the potential use of this gas as an energy source in a sustainable (and cleaner) energy scenario. This is so much the case at a time when increasing worldwide demand for energy is placing considerable strain on petroleum supplies. Among the potential solutions<sup>1</sup> being investigated, an attractive possibility is reversible hydrogen adsorption on a microporous solid. Zeolites,<sup>2,3</sup> metal-organic frameworks<sup>4,6</sup> and porous carbons<sup>7,8</sup> are among the adsorbents being investigated. Zeolites were reported to have a maximum hydrogen loading capacity in the range of 3–4.5 wt%.<sup>9,10</sup> This uptake is below the current target (6.5 wt%) for energy density in hydrogen storage systems for the automotive sector.<sup>11</sup> However, adsorbents capable of a reversible uptake of about 4.5 wt% hydrogen are still worthy of study for both stationary and mobile fueling applications.

Besides maximum uptake, the strength of the gas-solid interaction is another important parameter to consider. For an optimum delivery cycle the adsorption enthalpy ( $\Delta H^\circ$ ) should be neither too low (so as to enhance storage) nor too high (to facilitate release); an optimum value of  $\Delta H^\circ = -15 \text{ kJ mol}^{-1}$  has recently been proposed.<sup>12</sup> To our knowledge, reported values of the standard adsorption enthalpy of hydrogen on zeolites go from about  $-5$  to  $-10 \text{ kJ mol}^{-1}$ ; the smaller of these values corresponds to alkali-metal-exchanged ferrierite,<sup>13,14</sup> and the largest to protonic chabazite<sup>3</sup> and the MFI-type zeolite Na-ZSM-5.<sup>15</sup> On the other hand, from adsorption isotherms recorded at 77 and at 87 K, an isosteric heat of adsorption in the range of 7.0–9.5  $\text{kJ mol}^{-1}$  was recently derived<sup>16</sup> for  $\text{H}_2$  adsorption on an aryldicarboxylate-bridged framework incorporating  $\text{Mg}^{2+}$  ions. We report here on hydrogen adsorption on the faujasite-type (Mg,Na)-Y zeolite, which was found to show a significantly higher hydrogen adsorption enthalpy.

The zeolite sample used was prepared from Na-Y (synthesized by standard methods) by repeated ion exchange with a 0.5 M aqueous solution of magnesium nitrate, and checked by powder X-ray diffraction. For infrared (IR) spectroscopic measurements (see below) a thin, self-supported wafer of the zeolite sample was

prepared and outgassed in a dynamic vacuum (residual pressure  $<10^{-4}$  mbar) for 3 h at 700 K, inside the IR cell<sup>17</sup> which allowed *in situ* sample outgassing, gas dosage and variable-temperature IR spectroscopy to be carried out. After recording the background spectrum of the zeolite wafer at liquid nitrogen temperature, the IR cell was dosed with hydrogen and closed. IR spectra were then recorded (at  $3 \text{ cm}^{-1}$  resolution) at several fixed temperatures within the range of 120–150 K, while simultaneously registering the sample temperature and hydrogen equilibrium pressure inside the cell.

Variable-temperature IR spectroscopy was recently shown<sup>18</sup> to be a convenient method for measuring gas-adsorption heats, particularly when a small gas-solid interaction energy is involved; which makes adsorption calorimetry difficult to be performed at the required accuracy level. In essence, the basis of the spectroscopic method is as follows. At any given temperature, the integrated intensity of a characteristic IR absorption band (of the adsorbed molecule) should be proportional to the fractional coverage,  $\theta$ , thus giving information on the activity (in the thermodynamic sense) of the adsorbed species; simultaneously, the equilibrium pressure gives the activity of the gas phase. Hence, the corresponding adsorption equilibrium constant,  $k$ , can be determined, and the variation of  $k$  with temperature leads to the corresponding value of adsorption enthalpy. Integrated IR absorbance,  $A$ , temperature,  $T$ , and hydrogen equilibrium pressure,  $p$ , are interrelated by the Langmuir-type equation:

$$\theta = A/A_M = k(T) p/[1 + k(T)p] \quad (1)$$

where  $A_M$  stands for the integrated absorbance corresponding to full coverage ( $\theta = 1$ ). Combination of eqn. (1) with the well known van't Hoff eqn. (2) gives eqn. (3) below:

$$k(T) = \exp(-\Delta H^\circ/RT)\exp(\Delta S^\circ/R) \quad (2)$$

$$\ln[A/(A_M - A)p] = (-\Delta H^\circ/RT) + (\Delta S^\circ/R) \quad (3)$$

from which  $\Delta H^\circ$  can be derived. Further details on this method can be found elsewhere.<sup>18,19</sup>

Fig. 1 shows variable-temperature FTIR spectra, in the H–H stretching region, of hydrogen adsorbed on the zeolite sample under study. A single H–H stretching band is seen, centred at  $4056 \text{ cm}^{-1}$ . This band corresponds to the dihydrogen molecule polarized by  $\text{Mg}^{2+}$  ions. Polarization renders IR-active the fundamental H–H stretching mode, which is only Raman-active (at  $4163 \text{ cm}^{-1}$ ) for the free  $\text{H}_2$  molecule. Additional (much weaker) bands were also seen at 4117 and  $4124 \text{ cm}^{-1}$  (not shown), and assigned to hydrogen interacting with  $\text{Na}^+$  ions.<sup>20</sup> These latter bands come from an incomplete ion exchange of  $\text{Mg}^{2+}$  for  $\text{Na}^+$ ,

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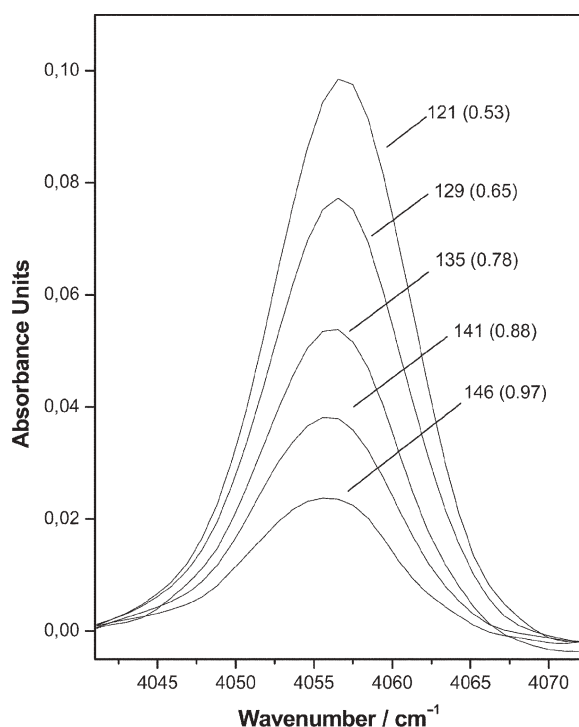


Fig. 1 Variable-temperature FTIR spectra (zeolite blank subtracted) of hydrogen adsorbed on (Mg,Na)-Y. Temperature, in K, and pressure (mbar, in brackets) are as shown.

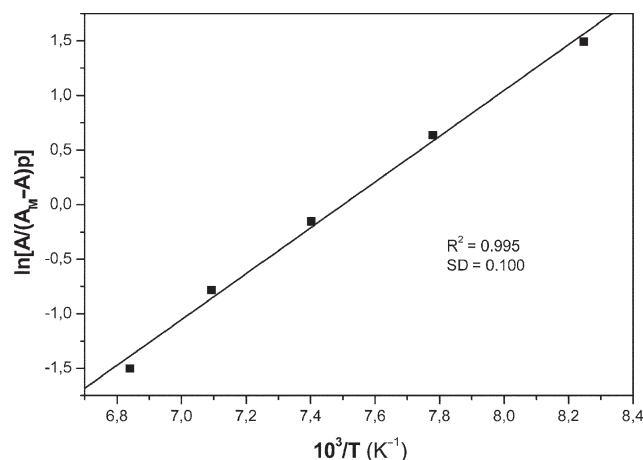


Fig. 2 Plot of the left-hand side of eqn. (3) against reciprocal temperature for the spectra shown in Fig. 1.  $R$ , linear regression coefficient; and  $SD$ , standard deviation.

but they are of no concern here. Fig. 2 shows the plot of the left-hand side of eqn. (3) versus the reciprocal temperature for the IR spectra depicted in Fig. 1. From the linear plot in Fig. 2, the standard adsorption enthalpy of hydrogen was determined to be  $\Delta H^\circ = -17.5 (\pm 1) \text{ kJ mol}^{-1}$ . This value is considerably higher than those previously reported<sup>13–15</sup> for hydrogen adsorption on alkali-metal-exchanged zeolites; it is about  $20\times$  higher than the liquefaction enthalpy of hydrogen, which is  $0.9 \text{ kJ mol}^{-1}$  (at 20.45 K). Previous theoretical calculations<sup>21</sup> showed that the  $\text{H}_2$  interaction with alkali-metal cations is dominated by the

polarization contribution. Hence, the high  $\Delta H^\circ$  value found for  $\text{H}_2$  on (Mg,Na)-Y should be attributed to the high polarizing power of the  $\text{Mg}^{2+}$  ion. A value of the adsorption enthalpy as high as  $-17.5 \text{ kJ mol}^{-1}$  should facilitate hydrogen storage in cryogenically cooled vessels, and suggests that a further search for porous materials containing magnesium can be highly fruitful. In particular, attention is drawn to magnesium-containing metal-organic frameworks; this is because these materials offer good chances for tailored design of pore structures,<sup>22</sup> and hydrogen uptake in some of them was recently reported<sup>23</sup> to be as high as 7.5 wt%.

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