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Carbon monoxide, dinitrogen and carbon dioxide adsorption on zeolite H-Beta: IR spectroscopic and thermodynamic studies

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ABSTRACT

Variable temperature IR spectroscopy (VTIR) was used to investigate the adsorption thermodynamics of carbon monoxide, dinitrogen and carbon dioxide on the protonic zeolite H-Beta. Interaction of the adsorbed gases with the zeolite Brønsted acid sites was found to involve an enthalpy change of −27, −19 and −33 kJ mol^{-1} for CO, N_2 and CO_2, respectively; the corresponding entropy change was −150, −140 and −146 J mol^{-1} K^{-1}. The adsorbed gases showed also a weak interaction with silanols, which involves a ΔH^0 value in the approximate range of −7 to −10 kJ mol^{-1}. These results were discussed in the context of gas separation and carbon capture and sequestration (CCS) using zeolites.

1. Introduction

Separation of gas mixtures by selective adsorption on porous solids is of interest to many present day technological processes. Among them, separation of methane from CO_2 in natural gas, H_2 from CO and CO_2 in syngas production or CO_2 from air in submarines and spacecraft are but a few examples. Looking ahead, current concern about the increasing level of carbon dioxide in the atmosphere is propelling research on reversible CO_2 adsorbents capable of separating carbon dioxide from flue gases (mainly N_2) of coal fired power stations; a process directly involved in carbon capture and storage (or sequestration), CCS [1–5]. Current technology for CCS related to energy production uses mainly alkanolamine solutions [6–9], but, besides being energy-intensive and expensive [10–12], that technology can pose environmental hazards derived from accidental spills and from waste processing [13,14]; hence the convenience to search for cheaper and safer CO_2 adsorbents. Among them, porous solids constitute a main line of research [15,16].

For gas separation using porous adsorbents, the gas–solid interaction energy is of the utmost importance, since the difference in that energy can be a main factor ruling the separation process. Main types of porous materials currently under active research (regarding mainly CO_2 separation) are porous carbons [17–20], zeolites [21–26] and metal-organic frameworks [27–31]. Zeolites have the advantage of combining low cost, relatively high stability and ease ion exchange [32]; which facilitates tuning of gas–solid interaction energy, since exchangeable cations constitute the main gas adsorbing centers in zeolites.

We report on variable temperature IR (VTIR) studies of the interaction of CO, N_2 and CO_2 with the protonic zeolite H-Beta. The VTIR method has the advantage (over more classical IR spectroscopy) of being able to give not only the IR spectroscopic signature of gas adsorption complexes, but also the corresponding values of standard adsorption enthalpy and entropy that rule the thermodynamics of the adsorption process [33,34]. The results obtained are discussed in the broader context of reported data for adsorption of the same gases on other protonic [35–39] and also on cation exchanged [40–43] zeolites. For the sake of completion we report also on the thermodynamics of interaction of the adsorbed gases with free silanols of the zeolite; a subject which, to our knowledge, was not dealt within previous studies.

2. Materials and methods

A sample of the beta zeolite in the ammonium form (NH_4-Beta) having a nominal Si:Al ratio of 20:1 was obtained from Tosoh (Japan) and checked by powder X-ray diffraction, as shown in Fig. 1;

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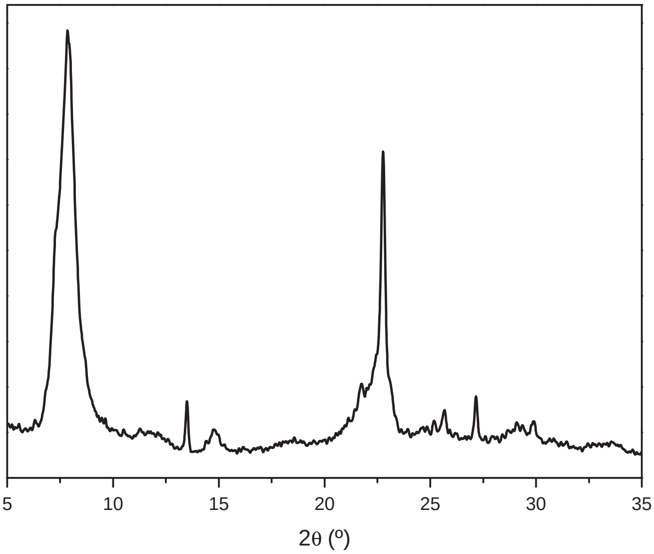

Fig. 1. X-ray diffractogram (CuKα radiation) of the H-Beta sample.

all diffraction lines can be assigned to the expected structure type [44]. BET surface area was 500 $m^2 g^{-1}$, and the pore diameter was in the range of 0.5–0.7 nm. From that parent material, H-Beta was prepared by thermal treatment inside an IR cell as described below; total conversion of NH_4-Beta into H-Beta was checked by the absence (in the corresponding IR spectrum) of any IR absorption bands corresponding to the ammonium ion. For IR spectroscopy, a thin self-supported wafer of the zeolite sample was prepared and heated at 700 K for 3 h under a dynamic vacuum (residual pressure $< 10^{-4}$ mbar) inside a home made IR cell [45] which allowed on-line thermal treatment of the zeolite wafer, gas dosage and variable temperature IR spectroscopy to be carried out. After thermal treatment the cell was dosed with 0.1 mbar of helium, to improve thermal contact between the cell body and the sample wafer. After recording the sample background spectrum the cell was dosed with the gas under study (CO, N_2 or CO_2) and closed and IR spectra were recorded within a relatively large temperature range (see below), while simultaneously registering temperature and gas equilibrium pressure inside the cell. A platinum resistance thermometer (Tinsley) placed close to the sample wafer and a capacitance pressure gauge (MKS, Baratron) were used for that purpose. Precision of measurements was better than $\pm 10^{-2}$ mbar for pressure and ±2 K for temperature. Pressure correction (for helium inside the cell) was determined from a calibration plot as described elsewhere [46]. Transmission FT-IR spectra were recorded, at 3 cm^{-1} resolution, on a Bruker IFS66 spectrometer; 64 scans were accumulated for each spectrum.

3. Results and discussion

3.1. Carbon monoxide adsorption

The blank IR spectrum of H-Beta (Fig. 2, bold spectrum) shows distinctive IR absorption bands at 3737 and at 3615 cm^{-1}. Following previous reports [47,48], the strong band at 3737 cm^{-1} is assigned to isolated silanol groups (being the tail on the low wavenumber side due to H-bonded silanols) and the weaker band at 3615 cm^{-1} is assigned to Brønsted acid hydroxyl groups (Al–O(H)Si groups). The rather broad nature of this band is in agreement with the presence of two kinds of framework aluminum atoms, and corresponding Brønsted acid Al–O(H)Si groups, as shown by ^{27}Al and ^{1}H MAS NMR spectroscopy [49].

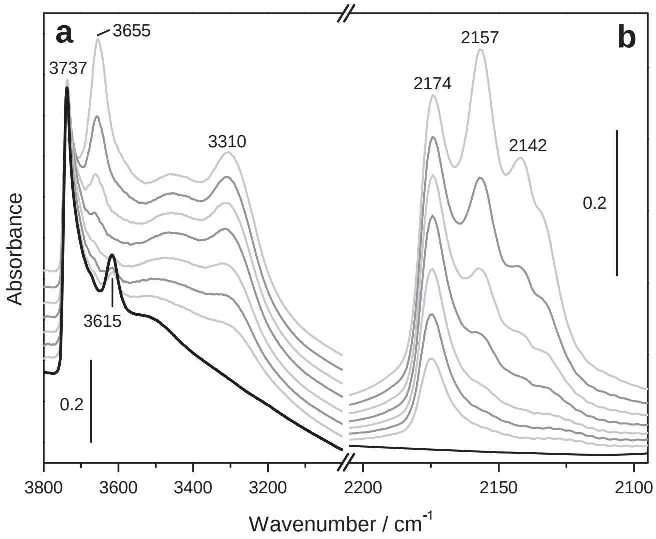

Fig. 2. Representative variable temperature IR spectra of CO adsorbed on H-Beta: (a) O–H stretching region, and (b) C–O stretching region. Blank zeolite spectrum shown in black. From top to bottom, temperature goes from 142 to 203 K, and equilibrium pressure from 4.69 to 10.59 mbar.

Fig. 2 (gray spectra) shows some representative variable temperature IR spectra of CO adsorbed on H-Beta. After CO adsorption, the band at 3615 cm^{-1} loses intensity to an extent that is a function of temperature and equilibrium pressure; and, till a smaller extent, the same does the silanol band at 3737 cm^{-1}. Simultaneously, new IR absorption bands build up at 3310 and at 3655 cm^{-1}. These spectroscopic changes are well known [48–52] to arise from H-bonding of the CO molecule (through the C atom) with the corresponding hydroxyl groups of the zeolite (see Fig. 2); being the effect less pronounced in the case of silanols because of their weaker interaction with CO, as compared to the interaction between CO and Brønsted acid sites. In the C–O stretching region a complex IR absorption band appears, showing peaks at 2174, 2157 and 2142 cm^{-1} (Fig. 2b). Following literature reports [50–53] on CO adsorption on other zeolites, the bands at 2174 and 2157 cm^{-1} are assigned to CO interacting (through the C end) with Brønsted acid OH groups and with silanols, respectively, while the band at 2142 cm^{-1} corresponds to free (liquid-like) CO; note that this band only appears at the lowest temperature.

A series of IR spectra recorded over a relatively large temperature range, while simultaneously recording temperature and equilibrium pressure of a reversibly adsorbed (physisorbed) gas, can be used to determine standard adsorption enthalpy, ΔH^0, and entropy, ΔS^0, through the van't Hoff equation:

$$K(\mathrm{T}) = \exp(-\Delta \mathrm{H}^0/\mathrm{RT})\exp(\Delta \mathrm{S}^0/\mathrm{R}) \tag{1}$$

On the other hand, the integrated absorbance, A, of a characteristic IR absorption band of either the solid adsorbent or the adsorbed gas can be related to the surface coverage, θ, through the Langmuir-type equation:

$$\theta = (A/A_M) = K(\mathrm{T})p/[1 + K(\mathrm{T})p] \tag{2}$$

where p is the equilibrium pressure and A_M stands for the integrated IR absorbance corresponding to full coverage ($\theta = 1$). Combination of Eqs. (1) and (2) leads to Eq. (3) below:

$$\ln[A/(A_M - A)p] = (-\Delta \mathrm{H}^0/\mathrm{RT}) + (\Delta \mathrm{S}^0/\mathrm{R}) \tag{3}$$

which can also be written as: