

Characterisation of Al-rich microporous micelle-templated silicates. Part II: Spectroscopic and microcalorimetric study of the accessibility of exchanged alkali-cations to carbon dioxide

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Abstract

Two micelle-templated materials with Si/Al ratio = 2.5, exchanged at 43% with Li⁺ ions and at 82% with Na⁺ ions, respectively, have been characterized by means of CO₂ adsorption followed by FT-IR spectroscopy and microcalorimetry, their texture and acidic properties having been studied in a previous paper [B. Bonelli, B. Onida, J.D. Chen, A. Galarneau, F. Di Renzo, F. Fajula, E. Garrone, *Micropor. Mesopor. Mater.* 67 (2004) 95]. CO₂ adsorption shows that no strong basic sites (oxygen anions able to form carbonate-like species) occur at the surface, in contrast to findings with zeolites of comparable composition. CO₂ interacts instead in a linear form with Lewis acidic sites, and reveals that only a part of Na or Li sites are accessible to the probe. The amorphous nature of the walls allows exchangeable alkali-cations to be partially “sunk” among surrounding oxygen anions: the majority of Na⁺ ions are not accessible to CO₂, whereas only about one half of Li⁺ ions are so. A dramatic decrease in the differential heats of adsorption with coverage indicates that interaction with the CO₂ ligand probably implies some extraction of the cations from the amorphous matrix. Na cations only form 1:1 adducts with CO₂, whereas Li cations may form 1:2 species.

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1. Introduction

Synthesis of micelle-templated materials [1,2] involves surfactant molecules differing by the nature of the polar head and the length of the non-polar chain [3]: when the template is a fatty amine (behaving as either cationic or non-ionic surfactants according to its chemical environment [4]), disordered hexagonal mesoporous silicas (HMS) are obtained [5–7]. By introduction of heteroatoms, e.g.

Al [8–13], such materials may behave as acidic catalysts for many reactions [14–16].

Incorporation of large amounts of Al into the framework of micelle-templated silica was attained by Mokaya and Jones, who prepared materials with Si/Al = 6.8 with all Al atoms in tetrahedral co-ordination [17–19]. Recently, MCM-41 materials with Si/Al ratio close to 1 have been obtained, with all Al atoms in tetrahedral co-ordination [20–22]; in particular, Lang and Tuel synthesised [Na]-Al-MCM-41 materials with Si/Al ratio equal to 1.25, preserving long range mesoscopic order and most Al atoms in tetrahedral co-ordination after calcination [22].

In a previous work [23], we reported the preparation of micelle-templated materials with Si/Al = 2.5, together with

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results concerning their textural properties and the strength and stability of acidic sites, as obtained by means of ^{27}Al NMR, XRD, and IR spectroscopy of adsorbed CO and NH_3 .

The present work reports the joint microcalorimetric and IR spectroscopic characterisation of the two Li- and Na-exchanged forms of the same sample, by means of CO_2 as a probe. The original idea was to measure the basic properties of these samples, expected on the basis of a naive comparison with zeolites of similar composition. Carbon dioxide showed the absence of any basicity, and yielded instead information on the strength and the accessibility of cationic acidic sites, complementary to that furnished by CO adsorption [23]. CO_2 interaction in a molecular form with cations, stronger than that of CO (which requires low temperatures to be studied), is readily measured at room temperature: this allowed joint IR spectroscopic and microcalorimetric investigations.

Complementary IR measurements have been carried out concerning CO adsorption at nominal 77 K. Main results have been compared with those concerning Li and Na containing zeolites.

2. Experimental

Li- and Na-exchanged Al-rich microporous micelle-templated silicates (termed as “sample Li” and “sample Na”, respectively) samples were prepared by contacting the parent material, having a ratio $\text{Si}/\text{Al} = 2.5$, synthesised in hydroalcoholic medium in the presence of dodecyl amine, with LiCl and NaCl alcoholic solutions. The final molar ratios, as measured by chemical analysis, were: $\text{Li}/\text{Al} = 0.43$ and $\text{Na}/\text{Al} = 0.82$.

The structural and textural characterisation of the samples, carried out by means of XRD and N_2 adsorption-desorption at 77 K [23], showed that slightly disordered microporous adsorbents were obtained, with a BET surface area of $440 \text{ m}^2 \text{ g}^{-1}$, a micropore diameter of 18 Å and a wall thickness of 13 Å, in line with the observation [18] that, in Al-HMS materials, surface area, pore volume and average pore diameter steadily decrease with increasing amount of Al incorporated into the framework, because of the shrinking of the hexagonal structure during calcination.

^{27}Al MAS-NMR spectra of Na-exchanged sample indicated the presence mostly of tetrahedral Al, stable upon calcination, because of the beneficial presence of exchangeable alkali cations.

For FT-IR measurements, powders were pressed into thin, self-supporting wafers. Spectra were collected, at a resolution of 2 cm^{-1} , in the $7200\text{--}450 \text{ cm}^{-1}$ range on a Perkin Elmer 1720 FT-IR spectrophotometer equipped with a MCT detector. Pre-treatments were carried out using a standard vacuum frame, in a IR cell equipped with KBr windows, allowing spectra to be collected in situ on wafer samples previously out-gassed in the same cell. Wafers were outgassed 1 h at 773 K before adsorption of CO_2 at room temperature.

Microcalorimetric measurements were carried out by means of a Setaram Calvet-type instrument, operated at 303 K. The microcalorimeter was equipped with a volumetric attachment of conventional design for gas dosage and measurement of the corresponding adsorption isotherm. A first adsorption run (yielding the primary isotherm) was followed by prolonged evacuation at room temperature, to remove the reversible fraction of adsorbate, and a second adsorption run (yielding the secondary isotherm) was performed in order to evaluate the reversibility of the adsorption process.

3. Results and discussion

3.1. Composition of the samples

If protons are assumed as the missing charge-balancing species, by exploiting the fact that all chemical elements here present invariably show the same oxidation number and by fixing the coefficient of oxygen equal to two, so to have correspondence with the formulas of mineral aluminosilicates, the following raw formulas are arrived at: $\text{H}_{0.17}\text{Li}_{0.12}\text{Al}_{0.29}\text{Si}_{0.71}\text{O}_2$ and $\text{H}_{0.05}\text{Na}_{0.24}\text{Al}_{0.29}\text{Si}_{0.71}\text{O}_2$. Note that, as with any raw formula, no structural information can be inferred from these expressions, e.g. no information on the type of hydroxyls the charge-compensating protons give rise to. Also note that the two formulas correspond to non-dehydrated samples, and that dehydration can be formally accounted for as loss of water. It results that the overall content of Na is nearly twice that of Li, and that the population of hydroxyls (whatever their nature) is about three times with the Li sample than with the Na sample.

3.2. IR spectra concerning the O–H stretching region of the bare samples and CO adsorption at 77 K

Fig. 1 compares the FT-IR spectra, normalised to unit specific area, of samples Li and Na outgassed at 773 K,

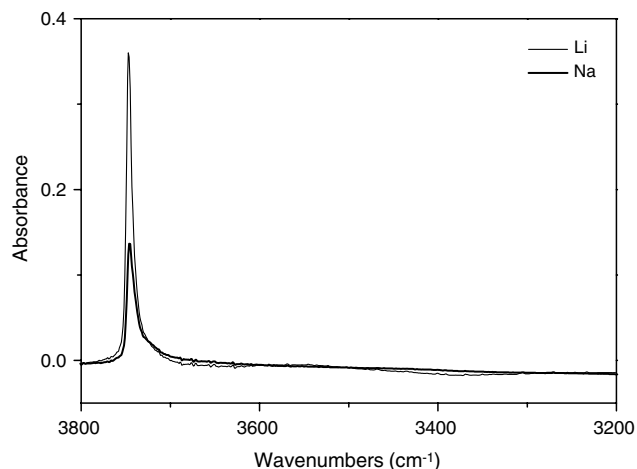


Fig. 1. FT-IR spectra, normalised to unit specific area, of samples Li and Na outgassed at 773 K, in the $3800\text{--}3200 \text{ cm}^{-1}$ range.

in the O–H stretching range: a band is observed at 3746 cm^{-1} , apparently corresponding to free silanols species. This band is about three times more intense with the Li sample than with the Na sample, in accord with the estimated compositions, which indicate a population in OH species about three times larger with sample Li.

If these silanol species correspond to the H species balancing the charge of Al ions substituting for Si species, an acidic character is expected. The inset of Fig. 2 shows the effect of 0.5 mbar CO on the O–H stretching region of samples Na and Li. Only one curve is reported, the effect being the same. A shift of about 90 cm^{-1} is observed, typical of the interaction of CO with silanols. The conclusion is that either these silanol species are not the expected charge-balancing entities or, for unknown reasons, these charge-balancing species have acidic character not more pronounced than that of usual isolated silanols, as those occurring in Al-free mesoporous systems.

The body of Fig. 2 compares the FT-IR spectra collected after dosing 0.5 mbar CO, at a nominal temperature of 77 K on the two samples in the CO stretching region. Weak bands are observed with sample Li at 2230 and 2205 cm^{-1} , assigned to CO adsorbed on Al^{3+} sites characterized by a different protrusion from the surface [23]. The occurrence of some Al^{3+} ions at the surface is expected with sample Li, as a consequence of dealumination, because of the high Al content of the sample and of the limited exchange reached in this case.

The prominent band at 2186 cm^{-1} is assigned to CO molecules adsorbed on Li^+ ions. With the zeolite Li-ZSM-5 [24], two species of adsorbed CO, referred to as $\text{Li}_\text{A}\text{-CO}$ and $\text{Li}_\text{B}\text{-CO}$, have been observed at 2193 and 2187 cm^{-1} , respectively: the former has been interpreted as due to Li cations fully available to interaction, and exhibiting therefore the full polarising power of the cation; the latter is ascribed to Li^+ ions partially sunk among framework oxygen atoms. The band at 2186 cm^{-1} in Fig. 2 most probably is related to CO molecules adsorbed

on Li^+ ions somewhat buried into the sample walls: no exposed species, similar to $\text{Li}(\text{CO})_\text{A}^+$, are observed at higher wavenumbers, as probably the amorphous nature of the walls does not allow the occurrence of such sites.

With sample Na, only the band of CO adsorbed on Na^+ ions is observed at 2174 cm^{-1} : the absence of bands due to Al^{3+} Lewis sites is related to the higher degree of exchange reached with Na, with consequent stabilization of aluminium species in tetrahedral co-ordination [25,26].

It is worth of note that, although the exchange with Na^+ ions was more extensive, the intensity of the CO band in this case is much lower than with the Li sample. A possible reason for this discrepancy is a stronger interaction with Li cations than with Na cations. Alternatively, the lower intensity could be an evidence that not all Na^+ sites are accessible to CO. To answer this question, room temperature interaction of CO_2 was studied from a quantitative (volumetric and calorimetric) point of view.

3.3. IR data concerning CO_2 adsorption

CO_2 is commonly used as a probe for the basicity of solids as it may form carbonate-like species with suitably basic oxygen atoms, giving rise to characteristic bands in the $1700\text{--}1300\text{ cm}^{-1}$ region [27]. It can also interact with Lewis acidic centres, forming linear molecular species, the C–O antisymmetric stretching mode of which strongly absorbs in the $2400\text{--}2300\text{ cm}^{-1}$ range [28]. CO_2 has four fundamental modes: the symmetric stretch ν_1 , the doubly degenerate bending vibration ν_2 , and the antisymmetric stretch vibration ν_3 . For symmetry reasons, the ν_2 and ν_3 modes are IR active, whereas ν_1 is only Raman active. In the free molecule, these modes appear at 1388.3 (ν_1), 667.3 (ν_2) and 2349.3 (ν_3) cm^{-1} [29].

Fig. 3 reports FT-IR difference spectra recorded on sample Li outgassed at 773 K, in the ν_3 stretch range: the main

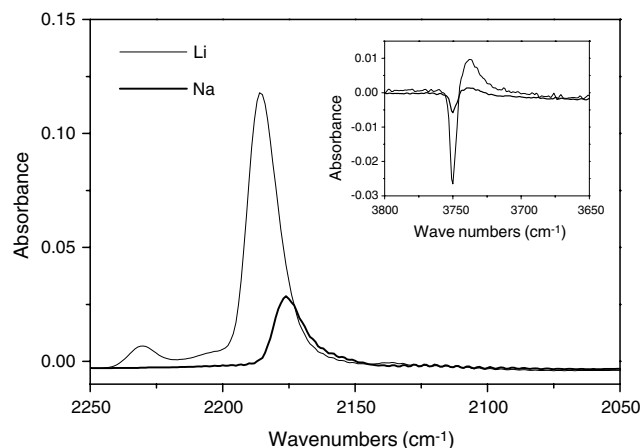


Fig. 2. FT-IR difference spectra collected after dosing about 0.5 mbar CO on samples Li and Na treated at 773 K, in the $2250\text{--}2050\text{ cm}^{-1}$ range. Inset: the O–H stretching region.

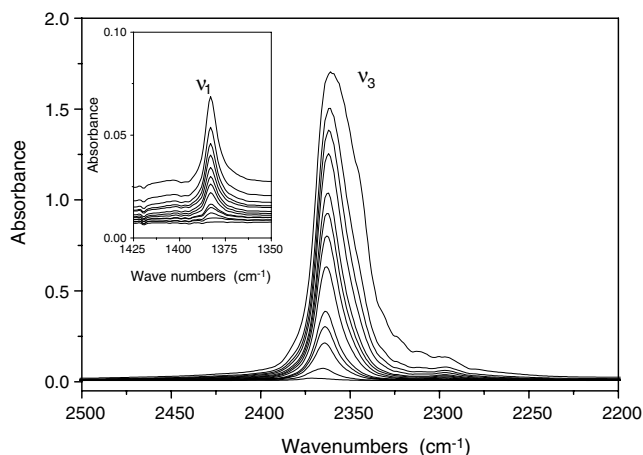


Fig. 3. FT-IR difference spectra concerning the adsorption of CO_2 on sample Li outgassed at 773 K, in the $2500\text{--}2200\text{ cm}^{-1}$ range. Inset to figure: same spectra, in the $1425\text{--}1350\text{ cm}^{-1}$ range. Equilibrium pressures: 7.0×10^{-3} ; 0.07; 0.35; 0.60; 2.40; 4.30; 6.20; 8.90; 17.8; 28.1; 47.5; 125 mbar (from inner to outer spectra).

band at 2365 cm^{-1} , slightly shifting with coverage to lower wavenumbers (2362 cm^{-1}), is assigned to CO_2 molecules adsorbed on Li^+ ions. This band is slightly asymmetric, presumably due to CO_2 interacting with small amount of Al^{3+} species, also observed by means of CO adsorption (Fig. 2). A satellite band at 2300 cm^{-1} , shifting with coverage to 2297 cm^{-1} , is due to $^{13}\text{CO}_2$ molecules adsorbed on Li^+ sites.

At lower wavenumbers, no bands have been detected in the carbonate-like species range, showing that no strong Lewis basicity is available at surface.

The band at 1383 cm^{-1} (Inset to Fig. 3) is due to the ν_1 stretch mode, which is only Raman active in the free molecules, but becomes IR active when CO_2 molecule is linearly co-ordinated to a Lewis site.

The shift with coverage of the 2365 cm^{-1} band to lower wavenumbers is remarkable, because a similar shift is not observed with the Na sample. The relatively small intensity of ν_3 band is surprising, because its molar extinction coefficient is substantial, of the order of 400 km mol^{-1} [30]: this seems to indicate, in line with the CO result reported in Ref. [23], that few Li^+ sites are actually accessible to CO_2 .

It is of interest to compare the FT-IR spectra in Fig. 3 with similar spectra, reported in Fig. 4, concerning the adsorption of CO_2 on a Li-ZSM-5 zeolite ($\text{Si}/\text{Al} = 25$ and $\text{Li}/\text{Al} = 1$, overall composition $\text{Li}_{0.04}\text{Al}_{0.04}\text{Si}_{0.96}\text{O}_2$). In such a system, Li^+ ions are expected to be accessible at the surface and to co-ordinate CO_2 molecules. Fig. 4 shows a main band due to the ν_3 stretch mode of CO_2 adsorbed on Li^+ ions at 2365 cm^{-1} with a minor component at about 2376 cm^{-1} (asterisk) due to adsorption on some extra-framework Al sites. Equilibrium pressures are remarkably low, in the range of 1.3×10^{-3} to 2.6×10^{-2} mbar.

Two facts emerge from the comparison. The wavenumber of the ν_3 mode is the same for the two systems, i.e. the

CO_2 molecule basically probes the cation and not its environment: this conclusion is supported by similar evidence concerning CO_2 adsorption on Na cations embedded in different systems, e.g. Na-ZSM-5 [31], Na-Y [32], Na-X [33], and Na-MCM-41 [34]. As to the intensity of the ν_3 mode, with Li-ZSM-5 the band is very intense and the absorption goes out of scale at very low equilibrium pressures (dotted spectrum refers to a CO_2 equilibrium pressure of 2.6×10^{-2} mbar), in contrast with that observed for sample Li, which has a threefold content in Li cations.

Fig. 5 reports FT-IR difference spectra recorded after CO_2 adsorption on sample Na outgassed at 773 K. The main band at 2356 cm^{-1} is assigned to CO_2 molecules adsorbed on Na^+ sites. As observed with sample Li, the ν_3 mode band is slightly asymmetric, probably due to some CO_2 molecules adsorbed on small amount of extra-framework Al sites, and no band due to carbonate species has been detected.

With sample Na, the ν_3 mode falls invariably at 2356 cm^{-1} even at high equilibrium pressures. This suggests that Na^+ ions probably can co-ordinate only one CO_2 molecule, in contrast to the findings for the Na-ZSM-5 system, where the band was seen to shift to lower wavenumbers from the initial value of 2356 cm^{-1} , due to the adsorption of a second CO_2 molecule.

Fig. 6 reports optical isotherms, obtained by plotting integrated intensities of ν_1 and ν_3 modes (in cm^{-1}) as a function of equilibrium pressures (0.07–125 mbar), for sample Li (a) and sample Na (b). This latter case is simpler, and will be discussed first. The integrated intensities of the two modes appear strictly proportional, the ν_1 mode (only Raman active in the free molecule) being about 115 times less intense than the ν_3 mode, in agreement with similar results for Li- and Na-ZSM-5. We assume such proportionality as an evidence that the same species are involved along the adsorption experiment, i.e. that no two-ligand

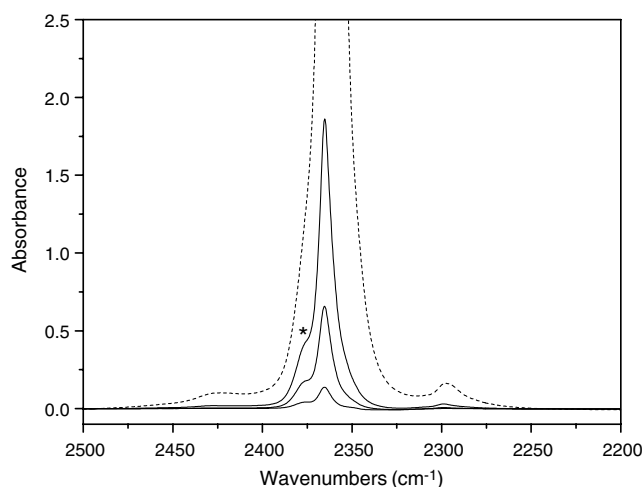


Fig. 4. FT-IR difference spectra concerning the adsorption of CO_2 on Li-ZSM-5 sample outgassed at 725 K, in the $2500\text{--}2200\text{ cm}^{-1}$ range. Equilibrium pressures in the 1.3×10^{-3} – 2.6×10^{-2} mbar range. Dotted spectrum refers to a CO_2 equilibrium pressure of 2.6×10^{-2} mbar (asterisk: see text).

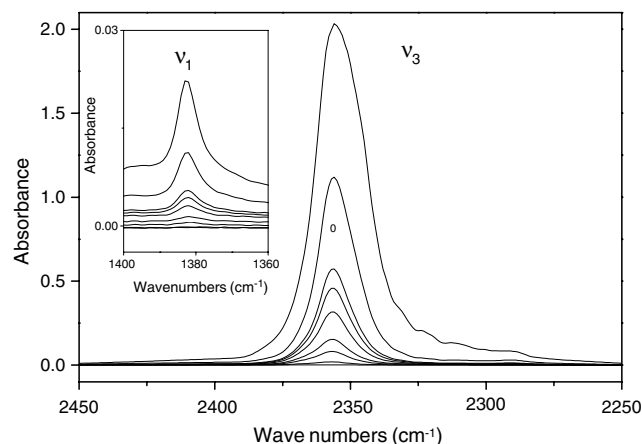


Fig. 5. FT-IR difference spectra concerning the adsorption of CO_2 on sample Na outgassed at 773 K, in the $2450\text{--}2250\text{ cm}^{-1}$ range. Inset to figure: same spectra, in the $1400\text{--}1360\text{ cm}^{-1}$ range. Equilibrium pressures: 9.0×10^{-3} ; 0.10; 0.50; 1.0; 3.0; 5.0; 7.0; 15.0; 25.0; 120 mbar (from inner to outer spectra).

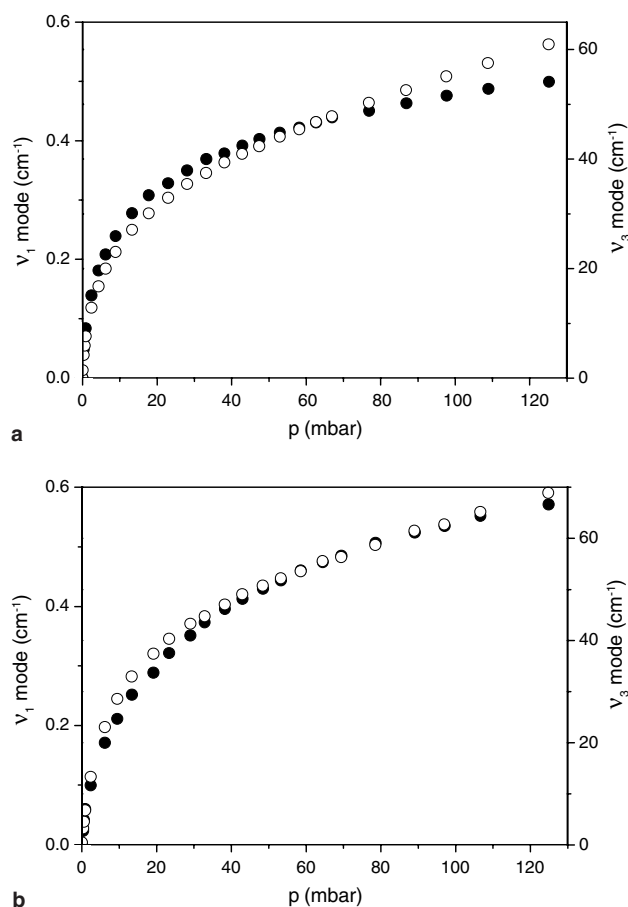


Fig. 6. Optical isotherms concerning the adsorption of CO₂ measured on samples Li (a) and Na (b) outgassed at 773 K: full symbols refer to the v_1 mode, empty symbols to the v_3 mode. Equilibrium pressures in the 7.0×10^{-3} –125 mbar range.

species are formed with sample Na, in line with the constancy of the related wavenumbers.

The situation is different with sample Li, where only a rough proportionality is seen between the two modes, with deviations at high pressures. This is probably an evidence that to some extent two-ligand adducts are formed in this case, along with one-ligand species, as also suggested by the shift in wavenumber of the related bands.

3.4. Volumetric and microcalorimetric results

Fig. 7a reports volumetric isotherms (adsorbed amounts n_a , $\mu\text{mol g}^{-1}$, vs equilibrium pressures, mbar) measured on sample Li outgassed at 773 K: full symbols refer to primary adsorption run, empty symbols to the secondary run, performed after prolonged evacuation at room temperature. Differences between the two runs lie within the experimental error: CO₂ adsorption is a reversible phenomenon at 303 K.

The dotted horizontal line in Fig. 7a corresponds to an estimated overall stoichiometry Li:CO₂ = 1:1, and shows that such a ratio is far from being reached even at highest

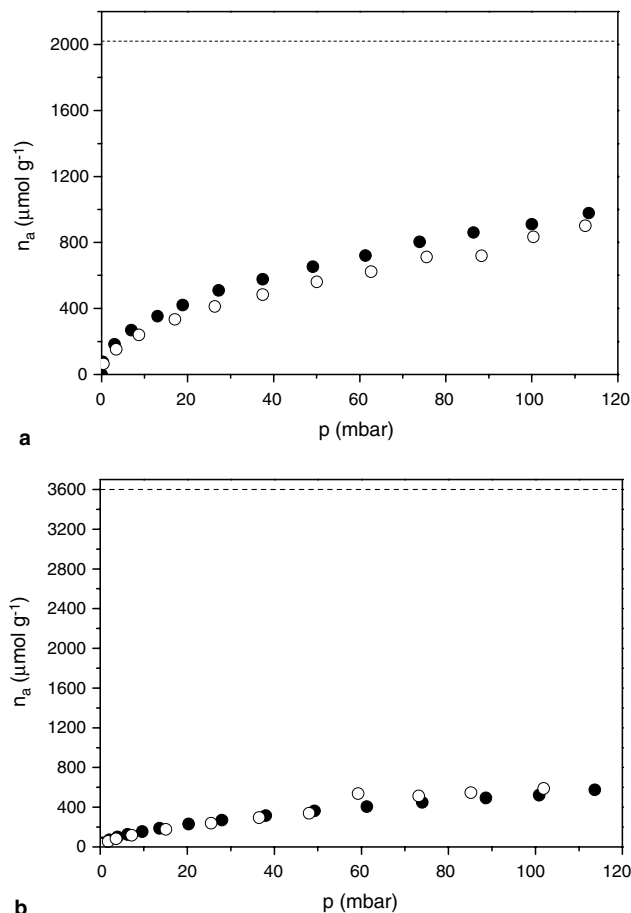


Fig. 7. Volumetric isotherms (adsorbed amounts, n_a ($\mu\text{mol g}^{-1}$), vs equilibrium pressures, mbar) concerning the adsorption of CO₂ measured on samples Li (a) and Na (b) outgassed at 773 K: full symbols refer to primary adsorption run, empty symbols to secondary run. The dotted horizontal lines correspond to an estimated overall stoichiometry M:CO₂ = 1:1 (M = Li or Na).

equilibrium pressures: on the average, only ca. one half of Li⁺ ions is actually accessible to the probe molecule.

Similar volumetric isotherms have been obtained with sample Na outgassed at 773 K (Fig. 7b): in this case, only the 15% of nominal sites seem to be accessible to the probe. This finding is in good agreement with that reported by Lang and Tuel, that in a [Na]Al-MCM-41 material with Si/Al ratio = 1.25 more than 25% of Na cations are not located at the surface [22].

Fig. 8 reports the differential heats of adsorption, q_{diff} (kJ mol^{-1}) versus adsorbed amounts, n_a ($\mu\text{mol g}^{-1}$), on samples Li (empty symbols) and Na (full symbols). With sample Li, an initial value of about 38 kJ mol^{-1} is measured, markedly decreasing with coverage down to about 10 kJ mol^{-1} , even smaller than the condensation enthalpy of CO₂ (25.35 kJ mol^{-1}). The same behaviour is seen with sample Na: the initial heat of adsorption is about 33 kJ mol^{-1} and decreases similarly with coverage. Taking into account that the wavenumbers of CO₂ interacting with Na cations in sample Na are fairly constant with coverage,

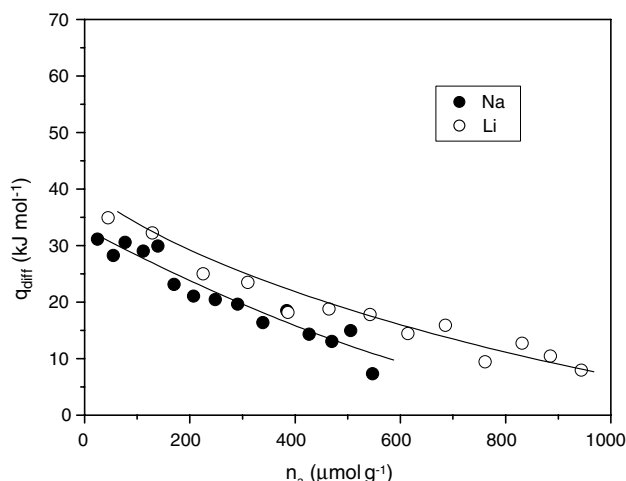


Fig. 8. Differential heats of adsorption q_{diff} (kJ mol^{-1}) versus adsorbed amounts n_a ($\mu\text{mol g}^{-1}$) concerning the adsorption of CO_2 obtained during the first adsorption run on sample Li (empty symbols) and Na (full symbols) outgassed at 773 K.

i.e. the adducts appear all similar to each other, irrespective of the coverage itself, the strong decrease in adsorption enthalpy cannot be ascribed to heterogeneity between Na^+ - CO_2 species. This decrease has therefore probably to be ascribed to conformational changes at the surface, by which the Na cation is brought to protrude in order to be available for interaction, caused by the interaction itself. Rearrangements at the surface are possible due to plastic nature of the Si–O–Si bond [35], but surely of endothermic nature, and decrease the overall exothermic effect. Such phenomena have been already observed by Bolis et al. with respect to the adsorption of CO on doped aluminas [36], and by some of us when studying the adsorption of CO and H_2 on Li-ZSM-5 [24,37]. It is worth to note that with the zeolite Na-ZSM-5, the heat of adsorption of CO_2 on Na^+ ions is definitely higher (49 kJ mol^{-1}), probably due to extra-framework cations which are more accessible to the probe. This is probably the reason why Na cations in the zeolite are able to form two-ligand adducts with CO_2 , in contrast to the present case.

With sample Li, a similar rearrangement phenomenon is likely to occur, and causes the decrease in adsorption enthalpy. The difference between heats of adsorption on Li^+ and Na^+ cations is nearly constant all along the coverage: though limited, such difference is, however, large enough to allow formation of two-ligand adducts with Li and not with Na cations.

4. Conclusions

CO_2 adsorption, followed by means of FT-IR and microcalorimetric measurements, showed that no strong basic sites (oxygen species able to co-ordinate carbon dioxide forming carbonate-like species), occur at the surface of both the sample Li and Na. In agreement with previous

work [23], Lewis acidic sites resulted to be mainly due to the presence of exchangeable alkali-cations, as only small amounts of extra-framework Al^{3+} ions have been detected. This behaviour has been ascribed to a stabilising effect of tetrahedral Al due to the presence of alkali-cation, as confirmed by ^{27}Al -NMR spectra [23].

Li^+ or Na^+ ions result to be less accessible to CO_2 , with respect to the same cation species embedded in different matrices, like ZSM-5 zeolite. This fact has three main consequences: (i) differential heats of adsorption are smaller than those measured for ZSM-5 zeolites; (ii) the CO_2 adsorbed amounts are smaller than those expected on the basis of chemical composition of the materials; (iii) formation of two-ligand adducts does not occur with sample Na, in contrast to the results found for the Na-ZSM-5 system, where extra-framework cations are more unsaturated. Two-ligand adducts are instead probably formed with sample Li; (iv) a strong decrease in the differential heat of adsorption is observed, ascribed to the rearrangement of the surface upon adsorption.

The amorphous nature of the surface is thought to be responsible to the weaker acidic/basic properties of this materials and to the smaller accessibility to probe molecules of exchangeable cations.

The concentration of cations available at the surface with respect to the content of tetrahedral Si or Al atoms is about 5% for sample Li and 3.6% for sample Na. The two figures are not far away from each other, in particular when taking into account that the Li sample probably forms two-ligand adducts: this seems to indicate a structural feature, that whatever the cation and the extent of exchange, the percentage of surface cations is within this relatively narrow range.

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