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Specific Sorption Sites for Nitrogen in Zeolites NaLSX and LiLSX

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Abstract. Specific sorption sites for nitrogen, N_2, in NaLSX and LiLSX zeolites were investigated using a DRIFT spectroscopic method. Sorption of molecular hydrogen, H_2, by NaLSX or LiLSX zeolite at 77 K with DRIFT control of perturbation of sorbed molecules allowed to discriminate two or three different types of specific sorption sites in the respective zeolites. Their H—H stretching frequencies are 4077 and 4081 cm^{-1} for NaLSX, and 4061, 4084 and 4129 cm^{-1} for LiLSX. With reference to an independent investigation by methods of both sorption thermodynamics and molecular modeling for N_2 sorption on LiLSX, the first two of the corresponding bands were ascribed to H_2 sorption on lithium cations, Li^+, localized in supercages of the faujasite, FAU, zeolite framework at sites SIII and SIII′, while the latter band most likely belongs to H_2 sorption on Li^+ cations at sites SII, and on hydroxyl groups, OH. Sorption of N_2 by Li^+ cations at sites SIII and SIII′ is the strongest, resulting in a decrease of intensity of the corresponding DRIFT bands that stem from subsequent H_2 sorption. Nitrogen sorption by Li^+ cations at sites SII is much weaker. Sorption of N_2 on Na^+ cations at sites SIII in NaLSX zeolite is also stronger than by Na^+ cations at sites SII.

Keywords: sorption, DRIFT spectroscopy, hydrogen, nitrogen, zeolites NaLSX, LiLSX, cation sites

1. Introduction

Zeolites have been continuously developed as sorbents for industrial air separation processes, e.g., pressure swing adsorption, PSA, and pressure-vacuum swing adsorption, PVSA, for oxygen, O_2, production during the past three decades. CaA zeolite was initially used as a first-generation sorbent in PSA processes for O_2 production in the early 1970s. Since then, further development has led to major improvements in both sorbents and processes. In the early 1980s, NaX and CaX zeolites of high selectivity and capacity were introduced into industrial-scale practice resulting in modern PVSA processes that significantly reduced plant-capital costs. In the 1990s, usage of Li^+-containing zeolites such as LiX, Li, $Me^{2+}X$ and Li, $Me^{3+}X$ (McKee, 1964; Chao, 1989; Coe et al., 1993; Fitch et al., 1995) has contributed significantly to further reduction of capital and energy costs, especially due to increases in specific product and yield for O_2. Very recently,

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silver- and copper-containing LiLSX zeolites were proposed for air separation (Hutson and Yang, 2000a, 2000b).

Despite worldwide industrial applicaiton of O_2 PSA and PVSA processes, little is known from literature on fundamental sorption behavior of both N_2, O_2 and their mixtures on various sorbents. Only recently, sorption thermodynamics of N_2 and O_2 on various zeolite sorbents utilized in the above processes has been fully characterized, particularly by using an isosteric sorption technique (Bülow, 1994; Shen and Bülow, 1998, 1999; Bülow and Shen, 1998a, 1998b; Shen et al., 2000a, 2000b, 2001). Characterization of low-silicon X, LSX, materials, i.e., FAU-type zeolites with a silicon-to-aluminum atomic ratio of 1.0 to about 1.1, and various theoretical aspects of their sorption properties and cation locations have become a subject of scientific research (Coe, 1995; Papai et al., 1995; Yang et al., 1996; Bajusz and Goodwin, 1997; Burton et al., 1997; Plévert et al., 1997, 1998; Rege and Yang, 1997; Bülow and Shen, 1998a, 1998b; Shen and Bülow, 1998; Shen et al., 1999a, 1999b, 2000a, 2000b, 2001; Bulanin et al., 2000; Hutson and Yang, 2000a; Hutson et al., 2000; Jale et al., 2000). Since sorption processes for air separation to produce O_2 are based on specific sorption interaction between N_2 molecules and extra-framework Li^+ cations in the FAU structure, a full characterization of specific sites for N_2 sorption is of considerable interest. This topic has been considered by several groups of researchers during recent years (Coe, 1995; Papai et al., 1995; Burton et al., 1997; Plévert et al., 1997, 1998; Bulanin et al., 2000; Jale et al., 2000; Shen et al., 2001) and papers quoted therein. It has been known for a long time that Li^+ cations are stronger sorption sites than Na^+ cations (Barrer and Stuart, 1959; Aristov and Kiselev, 1967; Aristov et al., 1967; Barrer, 1978), while sorption of N_2 by Na^+ cations at sites SIII is stronger than by those at sites SII (Goursot et al., 1997). On the other hand, a direct spectral study of N_2 or O_2 sorption on zeolites is difficult (Coe, 1995) since intensity of the corresponding IR bands is low, while resolution of the bands of molecules sorbed on different sites is rather poor. However, as demonstrated in Kazansky et al. (1984, 1989, 1997, 1998a, 1998b, 1999a, 1999b), Kazansky (1988, 1991, 1994, 1999), Kustov and Kazansky (1991) and Feuerstein and Lobo (1998a), H_2 offers excellent properties as a probe molecule for IR spectroscopy in the Diffuse Reflectance Infrared Fourier Transform (DRIFT) version. It allows to study zeolites modified with regard to the nature of framework-charge compensating cations, in particular to investigate weak sorbate-sorbent interactions, cf., the reviews (Kazansky, 1991, 1999).

In this paper, a DRIFT study of H_2 sorption by NaLSX and LiLSX zeolites is utilized to detect and to identify specific sorption centers in these zeolites as they were suggested for N_2 by both sorption isosteric measurements and molecular modeling (Jale et al., 2000; Shen et al., 2001). These latter efforts have led to a series of quantified conclusions, some of which are relevant to the DRIFT study in this paper. In general terms, they are summarized as follows: (i) Lithium cations in LiLSX with highest interaction energy for N_2 exhibit a relatively strong and homogeneous sorption energetics, viz., (25–28) kJ/mol in terms of isosteric sorption heat, over a N_2 concentration range that expands to *c.* 2 mol/kg; (ii) there are about four N_2 molecules sorbed on energetically nearly homogeneous sorption sites inside one supercage of LiLSX, which suggests that there are about four energetically nearly equivalent Li^+ cations accessible for N_2 molecules per supercage; (iii) LiLSX shows a specific sorption interaction with N_2, which is significantly stronger than that of O_2 for the same zeolite, i.e., (11–13) kJ/mol for the latter, which is almost non-specific; (iv) the differences in sorption behavior of N_2 and O_2 on LiLSX, which are relevant to air separation, stem from both differences in molecular quadrupole moments (the one for N_2 is by a factor of *c.* 2.3 larger than that for O_2), which are responsible for the electrostatic interaction of N_2 with Li^+ cations on special extra-framework sites, and from cation siting; (v) the interaction between N_2 and the zeolite framework, which is nearly non-specific as well, is specified by energies that change little over a broad concentration region, *c.* (4–8) mol/kg, with a difference of *c.* (3–4) kJ/mol between the isosteric sorption heats for the two gases.

For LiLSX with $Si/Al = 1.0$ in the FAU framework, from a crystallographic point of view, there are 96 Li^+ cations per unit cell. According to Plévert et al. (1997), sites SI′ and SII are fully occupied by 32 Li^+ cations each, and the remaining 32 Li^+ cations are equally distributed between sites SIII and SIII′ in eight supercages, i.e., 16 Li^+ cations at sites SIII and 16 at sites SIII′, for the room-temperature cubic phase of LiLSX that was identified by neutron diffraction at 300 K. Positions SIII and SIII′ are both inside the supercages; they differ slightly in their relative distances from the plane of

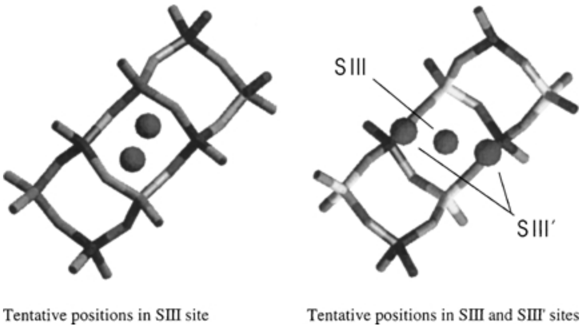

Figure 1. Possible differences in tentative SIII and SIII′ cation positions in a FAU structure.

four-member rings and Al positions in the ring structure: sites SIII are ascribed to (or close to) the center of four-member rings, SIII′ near to the edge of the latter ones in the twelve-member rings, tentative possibilities of which are shown schematically in Fig. 1. The low-temperature orthorhombic phase of LiLSX that was identified by neutron diffraction at 10 K, favors a lower occupancy of the highly coordinated sites SII and a significant increase of the number of cations in the supercage, most of them in a new low-coordinated site SIII′ (Plévert et al., 1997).

Feuerstein and Lobo (1998a) narrowed the temperature region into (220–230) K for the LiLSX-space-groups' transition, cubic *Fd3* ↔ orthorhombic *Fddd*. However, they did not find Li^+ cations at sites SIII′ from either ^6Li and ^7Li MAS NMR or neutron diffraction experiments (the latter were performed at 10 and 296 K). They rather witnessed a high mobility of the site-SIII Li^+ cations at temperatures, >233 K, which increases with temperature (Feuerstein and Lobo, 1998a, 1999).

In grand canonical *Monte Carlo* simulations by MSI Cerius^2 (Jale et al., 2000), both of the two sets of the above structure data (Plévert et al., 1997; Feuerstein and Lobo, 1998a) and cation locations described therein were taken into account for N_2 sorption on LiLSX. The MSI Cerius^2 cation locator module was also used to predict Li^+ cation positions (Jale et al., 2000). Findings of the latter study relevant to the current work, are summarized as follows: (i) The interaction energies between N_2 molecules and Li^+ cations at sites SIII and SIII′ are similar; (ii) Li^+ cations that occupy sites SII are not involved in the sorption process for N_2 at given conditions, due to their screening by lattice oxygen atoms (positions shifted towards SII′); (iii) four Li^+ cations per LiLSX supercage represent the accessible specific sorption sites; (iv) as follows from sorption thermodynamic results (Jale et al., 2000; Shen et al., 2001) each of these four Li^+ cations contribute to N_2 sorption, and they exhibit a nearly equivalent interaction energy; (v) hence, these sorption centers are the Li^+ cations at sites SIII and, possibly, SIII′; (vi) the consistency in both strength and quantity of sorption sites between sorption-isosteric data and those from molecular simulation caused a remarkable agreement between sorption isotherms determined by the two techniques over a wide temperature range up to ambient temperature, which had been confirmed, in addition, by independent microbalance experiments (Jale et al., 2000; Shen et al., 2001); (vii) simulated distributions of N_2 molecules within zeolite supercages show a strong segregation with regard to their localization at low-energy sites (strong electrostatic interaction), which is close to cations at positions SIII or SIII′.

To check those conclusions on the distribution of Na^+ and Li^+ cation-sorption sites, in this paper we used as test the low-temperature sorption of H_2 with DRIFT control of H_2 perturbation. Hydrogen sorption was carried out on Na^+ and Li^+ cationic forms of LSX zeolite evacuated at elevated temperature, or after presorption of N_2 at low temperature. Since the strongest sorption sites sorb preferentially N_2, subsequent H_2 sorption takes place on the weaker sites that remain unblocked by N_2 presorbed. Unfortunately, sorption isosteric data and molecular simulation results for N_2 on NaLSX zeolite cannot be communicated at the time being.

2. Experimental

2.1. NaLSX and LiLSX Zeolites

Zeolite NaLSX and its derivative LiLSX both with a FAU-framework silicon-to-aluminum atomic ratio, $Si/Al = 1.01$, were prepared and cation-exchanged following procedures given in Ojo et al. (1996) and Fitch et al. (1995), respectively. Cation exchange, Na^+ by Li^+, was performed by aqueous solutions of LiCl. Its extent was close to 100%, cf., Table 1.

Therein, the chemical composition of LiLSX zeolite is shown as obtained by Inductively Coupled Plasma Atomic Emission Spectroscopy, ICPAES. The NaLSX and LiLSX crystals were agglomerated into binderless particles with an average size of *c*. 1.5 mm. The NaLSX and LiLSX materials for this investigation were identical with those used in Kazansky et al. (1999b)

Table 1. Chemical composition of LiLSX zeolite crystals measured by ICPAES.

	Composition, wt.%
Compound	LiLSX
Loss of ignition	30.23
Al_2O_3	27.31
SiO_2	32.85
Na_2O	<0.1
K_2O	<0.1
CaO	–
Li_2O	7.88
Total	98.47

and Jale et al. (2000) as well as Shen et al. (2001), respectively.

2.2. DRIFT Spectroscopy

Before spectroscopic measurements were carried out, the agglomerated zeolite samples were evacuated at 673 K for 2 hours. The rate of temperature increase was equal to 3.5 K/min. Sorption of H_2 on samples pretreated in vacuo, took place at 77 K and different equilibrium pressures.

Poisoning of H_2 sorption by presorption of N_2 was performed in two different ways. As to a first, to perform it in a more selective manner, N_2 was sorbed at various equilibrium pressures at temperature, 180 K. Then H_2 was added at a pressure, 100 torr; the optical cell was cooled down to 77 K; and DRIFT spectra were recorded at this temperature. As to a second, dehydrated zeolites were exposed to $(N_2 + H_2)$ mixtures of various compositions also at a temperature, 180 K, in a glass circulation system. This temperature and gas circulation was used to accelerate sorption equilibration processes for N_2 inside zeolite crystallites. The pressure of H_2 was always kept equal to 100 torr, while the pressure of N_2 was varied from 1 to 30 torr. After such pretreatment, DRIFT measurements were also performed at 77 K using a Nicolet “Impact 410” spectrophotometer equipped with a custom-made diffuse reflectance attachment (Kazansky, 1991, 1999). DRIFT spectra were transformed into Kubelka-Munk units by a standard program assuming that the reflection ability of sorbent samples at 5000 cm^{-1} was equal to 0.9. This is close to a value reported in literature for a number of white oxides.

3. Results and Discussion

3.1. Nitrogen Sorption by NaLSX and LiLSX Zeolites

DRIFT spectra of N_2 sorbed by NaLSX and LiLSX at low temperature are shown in Fig. 2(a) and (b), respectively. In both cases, the spectra correspond to single bands with *maxima* at 2335 and 2341 cm^{-1}, respectively. The appearance of these bands indicates polarization of N_2 molecules, which results from their sorption on Na^+ or Li^+ cations, and causes the IR-activity of N≡N stretching vibrations.

The larger shift of the N≡N stretching vibrations for N_2 sorbed by LiLSX zeolite from the stretching frequency of the free N_2 molecule (2331 cm^{-1} as detected by Raman spectroscopy) indicates a stronger perturbation of molecules sorbed by Li^+ rather than by Na^+ cations. However, neither of these DRIFT lines is resolved due to a variation in strength of sorption interaction of N_2 with different sorption sites.

In addition to the stretching band in the spectrum of Fig. 2(b) for the LiLSX zeolite, where the band of N≡N stretching vibrations is narrower, two low-intense satellites at 2328 and 2355 cm^{-1} are also clearly visible. Similar to sorbed H_2 molecules, the separation of these bands from the main stretching band that amounts to about ±14 cm^{-1}, corresponds to the frequency of N_2 oscillations relative to the sorption sites.

Single-band *maxima* shown in Fig. 2(a) and (b) for N_2 in NaLSX and LiLSX coincide with those at high

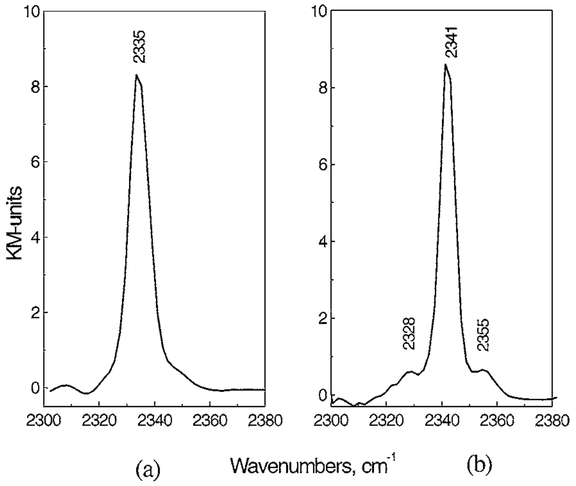

Figure 2. DRIFT spectra of N_2 sorbed by zeolites NaLSX (a) and LiLSX (b) at 180 K and at equilibrium pressure of 30 torr. The spectra were recorded at 77 K.

sorption phase concentration described by Bulanin et al. (2000), which were found as a result of a low-temperature FTIR spectroscopic study of N_2 and other gases on similar zeolite materials. Therein, the behavior of FTIR spectra had been further detailed with regard to concentration and temperature, however, no final conclusion, particularly with regard to the LiLSX case, was drawn regarding possible N_2 population at SIII and SIII′ positions.

A N≡N stretching vibration for N_2 sorbed by a Li, KLSX zeolite (70% Li^+) with the bond maximum at 2342 cm^{-1} and measured by DRIFT spectroscopy, was first described by Coe (1995).

3.2. *Hydrogen Sorption by NaLSX and LiLSX Zeolites*

Figure 3(a) depicts DRIFT spectra of H_2 molecules sorbed by NaLSX zeolite at 77 K at a series of equilibrium pressures of H_2. At a pressure, 100 torr, the maximum of the H—H stretching vibrations from H_2 perturbed by interaction with Na^+ cations is observed at 4081 cm^{-1}. The much weaker band at 4220 cm^{-1} should be attributed to the high-frequency satellite that originates from oscillations of H_2 molecules relative to sorption sites. The low-frequency satellite of sorbed H_2 is invisible due to its much lower intensity. Indeed, at 77 K the first vibrational level of H_2 oscillations relative to Na^+ cations is unpopulated, due to a high frequency of these oscillations. Therefore, only the band at 4220 cm^{-1} is visible, which corresponds to the combination of the H—H stretching vibration with the 0 → 1 vibrational transition due to oscillations of sorbed molecules relative to Na^+ cations.

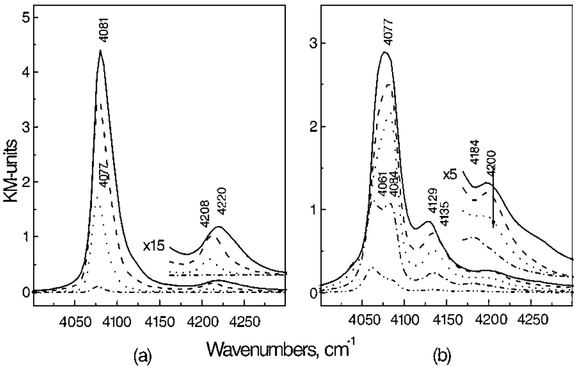

Figure 3. DRIFT spectra of molecular H_2 sorbed at 77 K by NaLSX (a) and LiLSX (b) zeolites at pressures of 100 (—), 10 (---), 1 (...), 0.1 (-.-.-), 0.05 (-..-..) torr.

At lower pressures, the maximum of the absorption band at 4081 cm^{-1} is shifted towards 4077 cm^{-1}, while that of the satellite is shifted towards 4208 cm^{-1}. This proves H_2 sorption on at least two different sites. Interaction of H_2 with the weaker sites at higher pressure results in the stretching frequency of 4081 cm^{-1}, and the frequency of the satellite of 4220 cm^{-1}. Sorption on the stronger sites at the lower pressure corresponds to the H—H stretching frequency of 4077 cm^{-1} and the satellite frequency of 4208 cm^{-1}.

The spectrum of H_2 sorbed by LiLSX, cf., Fig. 3(b), is more complex if compared to that of NaLSX, cf., Fig. 3(a). At a pressure, 100 torr, the most intense band has a relatively flat *maximum* at 4077 cm^{-1}. Below a pressure of *c.* 1 torr, it splits into two bands with their *maxima* at 4061 and 4084 cm^{-1}. The position of the high-frequency satellite of this band at 4200 cm^{-1} also depends on H_2 pressure. This again indicates the existence of two different sites for H_2 sorption.

The position of the high-frequency band at 4129 cm^{-1} fits the frequency range of H_2 sorption by surface-hydroxyl groups, OH^- (Kazansky et al., 1989; Kazansky, 1991, 1994). Indeed, the amount of OH^- groups in the LiLSX zeolite under investigation is about five times higher than that in the parent NaLSX material, cf, Fig. 4. However, the overall concentration

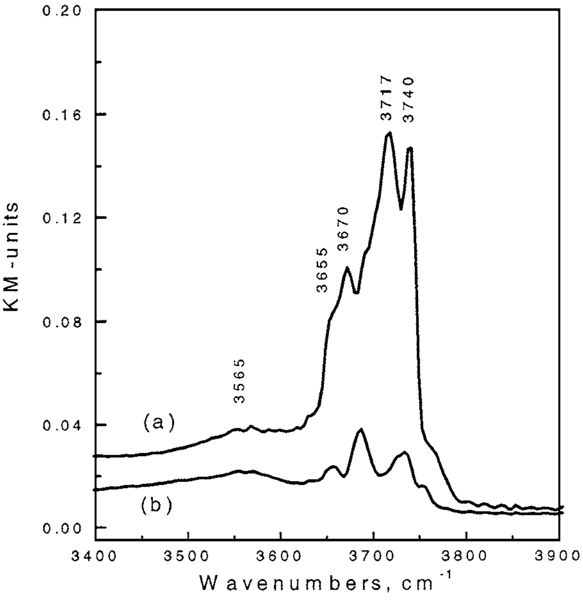

Figure 4. DRIFT spectra of OH^- groups in LiLSX (a) and NaLSX (b) zeolites.

Table 2. Wavenumbers and their assignments.

Zeolite	Wavenumbers of H–H stretching vibrations, cm^{-1}	Wavenumbers of high-frequency satellites, cm^{-1}	Wavenumbers of sorbed H_2 vibrations relative to sorption sites, cm^{-1}	Assignments of wavenumbers to sorption sites
NaLSX	4077	4208	131	Na^+ at SIII sites
	4081	4220	139	Na^+ at SII sites
LiLSX	4061	4184	123	Li^+ at SIII sites
	4084	4200	116	Li^+ at SIII′ sites
	4129	–	–	OH^- groups and
	4135	–	–	Li^+ at SII sites

of OH^- groups is too low to explain the intensity of the band, 4129 cm^{-1}, of sorbed H_2, cf., Fig. 3(b). In addition, at lower H_2 pressures, the maximum of this band shifts towards 4135 cm^{-1} demonstrating, thus, a complex nature of the band. Therefore, the band at 4129 cm^{-1} represents most likely a superposition of H_2 sorption by OH^- groups and Li^+ cations, which very weakly perturb sorbed H_2.

A comparison of the spectra presented in Fig. 3(a) and (b) indicates a stronger H_2 sorption by LiLSX compared to that by NaLSX. Indeed, for the latter zeolite the intensity of the band from sorbed H_2 at a pressure, 0.1 torr, is very low. In contrast, the DRIFT spectrum of H_2 sorbed by LiLSX zeolite disappears only at a pressure, 0.01 torr. In agreement with the stronger perturbation, sorption of H_2 that corresponds to the band at 4061 cm^{-1}, is also the strongest.

Table 2 presents a summary of wavenumbers for the bands that result from H_2 sorption by NaLSX and LiLSX zeolites and their possible assignments. The identification of additional accessible sorption sites in LiLSX as compared to those described in prior art (Feuerstein and Lobo, 1998a, 1998b; Feuerstein et al., 2000) could, inter alia, be due to the high resolution of DRIFT experiments with respect to sorption phase concentration (in literature work referred to, experiments were performed at high concentrations for O_2 and N_2, which correspond to gas pressures of about 600 and 760 torr, respectively.)

3.3. *Co-sorption of N_2 and H_2 by NaLSX and LiLSX Zeolites*

Figure 5 depicts the spectra of H_2 sorbed by NaLSX zeolite after preliminary sorption of N_2 at various equilibrium pressures at 180 K (Fig. 5(a)), and after presorption of $(N_2 + H_2)$ mixtures of various compositions (Fig. 5(b)). In both cases, the evolution of the spectra is similar to each other. Increasing equilibrium pressure of N_2 as well as sorption by this zeolite of $(N_2 + H_2)$ mixtures with higher N_2/H_2 concentration ratios result in poisoning of sorption sites for H_2.

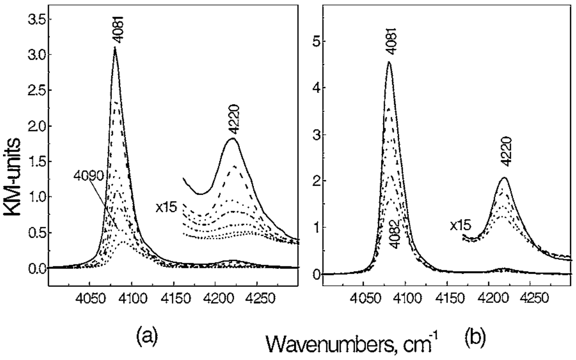

Figure 5. DRIFT spectra of H_2 sorbed by NaLSX zeolite at 77 K: (a) After presorption of N_2 at 180 K at different equilibrium pressures of 0, 2, 4, 6, 10, 15 and 20 torr, from top to bottom; (b) Sorption of H_2 from $(N_2 + H_2)$ mixtures with N_2/H_2 concentration ratios that amount to 0, 0.02, 0.05, 0.1 and 0.2, from top to bottom.

A comparison of Fig. 3(a) and 5(a) also indicates that poisoning of H_2 sorption sites by N_2 results in a gradual shift of the band at 4081 cm^{-1} towards 4090 cm^{-1}. In addition, the high-frequency satellite of this band becomes broader and more asymmetric. Both these effects should be due to selective sorption of N_2 by the stronger sorption sites, which eliminates the H—H stretching band at 4081 cm^{-1} and the satellite band at 4220 cm^{-1}.

Similar DRIFT spectra of H_2 sorbed by LiLSX zeolite after preliminary N_2 sorption or pretreatment with $(N_2 + H_2)$ mixtures of various compositions are shown in Fig. 6(a) and (b). In both cases, inhibition of H_2 sorption by that of N_2 is less selective. It does not result,

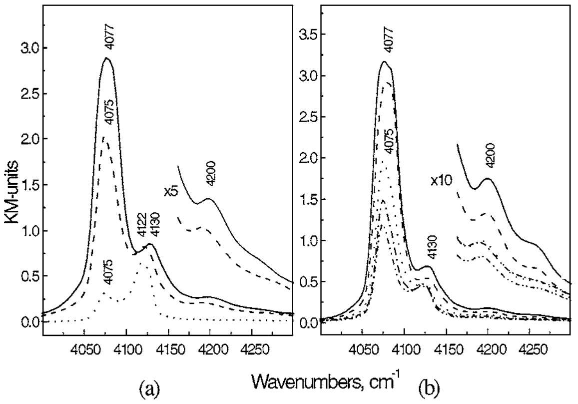

Figure 6. DRIFT spectra of H_2 sorbed by LiLSX zeolite at 77 K: (a) After presorption of N_2 at 180 K at different equilibrium pressures of 0 (—), 4 (---) and 20 (....) torr; (b) Sorption of H_2 from ($N_2 + H_2$) mixtures with N_2/H_2 concentration ratios that amount to 0, 0.01, 0.075, 0.15 and 0.30, from top to bottom.

practically, in a shift of the H—H stretching band to lower frequencies.

Another remarkable feature of the spectra refers to a much smaller influence of N_2 sorption on the intensity of the bands at 4129 and 4120 cm^{-1}. In accordance with the above assignment, this is consistent with weaker sorption of N_2 by OH^- groups or Li^+ cations that weakly perturb sorbed H_2. Lithium cations in sites SII that are not involved in sorption interaction with N_2, could be responsible for this behavior.

The following general conclusions can be drawn from the DRIFT spectra. High-frequency shifts of N≡N stretching vibrations of sorbed N_2 or low-frequency shifts of H—H stretching vibrations of sorbed H_2 relative to frequencies of those vibrations of the free molecules are connected with the interaction of N_2 or H_2 with specific sorption sites. Cations Na^+ and Li^+ that compensate the negative charges of $(AlO_4)^-$-tetrahedra in the FAU framework of zeolites NaLSX and LiLSX, respectively, represent such sites. Regarding the NaLSX case, reference can only be made to studies by single crystal X-ray diffraction on hydrated and dehydrated NaLSX crystals with a Si/Al ratio of 1.06 (Porcher et al., 1999). Studies on NaX zeolites were performed by single crystal X-ray diffraction (Olson, 1995) and ^{23}Na MAS and Multiple Quantum MAS NMR spectroscopy (Lim and Grey, 2000) on dehydrated crystals with Si/Al ratios of 1.18 and 1.25, respectively. The results indicate that Na^+ cations occupy almost all available sites SII (31.0 cations per unit cell (97% occupation of sites SII) (Olson, 1995) or 32 cations (Lim and Grey, 2000), and a major part of sites SIII (29.8 cations per unit cell (62% occupation of sites SIII) (Olson, 1995) or 23 cations (Lim and Grey, 2000)). For NaLSX or LiLSX zeolites with Si/Al $\cong$ 1.0, one can expect a higher occupancy of the SIII sites, as discussed above. For NaLSX in particular, two types of SIII sites with almost equal occupancy by Na^+ cations were identified (Porcher et al., 1999).

In summary, all of the available sites SII and SIII are assumed to be occupied by Na^+ or Li^+ cations. Therefore, in LSX zeolites only two main types of sites that contain Na^+ or Li^+ cations should be expected for N_2 or H_2 sorption.

DRIFT spectra of sorbed N_2, i.e, without H_2 as probe molecule, do not allow for a discrimination of these sorption sites due to the weak perturbation of sorbed N_2 molecules. However, DRIFT spectra of the probe molecule H_2 in accordance with the methodology utilized in this paper, allows for it. The low-frequency shift of the H—H stretching band and the change in shape of the high-frequency satellite of sorbed H_2 at low H_2 pressure support the conclusion on the existence of two different types of sorption sites in NaLSX zeolite, viz., Na^+ cations in positions SII and SIII. For the LiLSX zeolite, this conclusion is even more definite due to the better resolution of the H—H stretching bands (cf., Fig. 3(a) and (b) and Fig. 6, and Table 2).

The nature of H_2 low-temperature-sorption sites in FAU zeolites had been discussed previously in Bordiga et al. (1994) and Kazansky (1994, 1999). It was concluded that these sites represent acid-base pairs. The latter were thought to comprise both alkaline cations and adjacent basic framework oxygen atoms, while the influence on the frequency of H—H stretching vibrations of sorbed H_2 of the basic oxygen is even stronger than that of the alkaline cations. It was also concluded that H_2 sorption by sites SIII resulted in larger low-frequency shifts of the H—H stretching vibrations than was sorption by sites SII (Kazansky, 1999).

For NaLSX zeolite, the latter conclusion agrees well with results of the current investigation. A comparison of Fig. 3(a) and (b) indicates that positions for the *maxima* of stretching bands for H_2 sorbed on Na^+ or Li^+ cations in LSX zeolites, differ by a few cm^{-1} only, indicating, thus, a weak dependence of the H—H stretching frequencies on the nature of alkaline cations. In contrast, the different coordination of alkaline cations at sites SII and SIII by the adjacent basic framework oxygen atoms results in a considerably stronger difference in positions of the stretching bands and satellites for H_2 sorbed by NaLSX and LiLSX zeolites at high and low pressures.

In NaLSX zeolite, inhibition of H_2 sorption by preliminary N_2 sorption or sorption of $(N_2 + H_2)$ mixtures indicates disappearance of the sites of stronger H_2 perturbation, i.e., of sites SIII. This results in a narrowing of the corresponding DRIFT band and in shifting of the H—H stretching band from 4081 to 4095 cm^{-1}, cf., Fig. 5(a). Thus, in agreement with results of quantum chemical calculation (Papai et al., 1995), at low pressure, N_2 sorbs preferentially on Na^+ cations at sites SIII, while sites SII remain available for sorption of H_2. Additional supporting information could be derived from experimental data communicated elsewhere (Vaščenko and Serpinsky, 1975; Feuerstein and Lobo, 1998a).

In LiLSX zeolite, low-temperature H_2 sorption revealed three different sorption sites, which—in accordance with the results of Jale et al. (2000) and Shen et al. (2001)—can be assigned as follows: Sorption sites that are not blocked by N_2 sorption with an H—H stretching frequency that equals to (4122–4130) cm^{-1}, most likely belong to Li^+ cations in SII positions. These positions are assigned to the six-member ring planes of the FAU framework, where Li^+ cations—due to their small size—are less accessible to sorbing species. For O_2 sorption, this was directly demonstrated by ^{6}Li MAS NMR experiments with paramagnetic O_2 as a chemical shift agent, which indicated that Li^+ cations at SII sites embedded in the six-ring windows of the structure, are less sensitive in comparison with those at sites SIII (Plévert et al., 1998; Feuerstein and Lobo, 1998b (^{7}Li MAS NMR); Feuerstein et al., 2000). Then, similar to NaLSX zeolite, the sorption centers with stronger N_2 sorption interaction should be attributed to the Li^+ cations at sites SIII, irrespective of their fine-tuned siting topology. This conclusion is strongly supported by sorption thermodynamic and molecular modeling data (Jale et al., 2000; Shen et al., 2001), which were collected at temperatures both below and above the phase-transition range for LiLSX. DRIFT spectroscopic experiments with H_2 sorption allowed for an additional insight. They revealed two different stretching H—H frequencies for these sites, viz., with 4061 and 4084 cm^{-1}. These frequencies belong most probably to interactions with Li^+ cations that are localized at positions SIII and SIII′ in the zeolite framework. This particular observation could be an experimental proof of evidence for the existence of Li^+-SIII′ sorption sites in LSX zeolite sorbents, in the region of cryogenic temperatures. It remains certainly of interest to prove the occurrence of the physical-sorption complex, (quadrupolar N_2 molecule–Li^+-SIII′ site), with an interaction energy in a probable range of *c.* (25–30) kJ/mol as derived tentatively from more general sorption-thermodynamic data (Bülow and Shen, 1998a, 1998b; Shen et al., 2001), at ambient temperature, and possibly at conditions of O_2 PVSA processes.

4. Conclusions

DRIFT spectroscopy with hydrogen as probe molecule at cryogenic temperature is a powerful tool to identify and characterize sorption centers in zeolites, particularly those with relatively weak physical-sorption interaction. The method becomes especially useful if its ability to gather microphysical insight into sorption properties of zeolites is combined with experimental results of sorption-thermodynamic methods and molecular simulation data collected on identical sorbate-sorbent systems. The success of this approach is demonstrated for the cases of sorption of nitrogen and nitrogen-hydrogen mixtures of various compositions by NaLSX and LiLSX zeolites, for which specific sorption sites were identified, and their assignment to particular intracrystalline positions was proposed.

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