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**D<sub>2</sub>/H<sub>2</sub> separation by quantum sieving in LiNaA zeolites: the role of aperture size and strong guest - cation interactions**

Igor Bezverkhyy<sup>a\*</sup>, Victor Boyer<sup>a</sup>, Clément Cabaud<sup>b</sup>, Jean-Pierre Bellat<sup>a</sup>

<sup>a</sup> Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS-Université de Bourgogne,  
BP 47870, 21078 Dijon Cedex, France

<sup>b</sup> CEA, DAM, VALDUC, 21120 Is-sur-Tille, France

Corresponding author:

email: [igor.bezverkhyy@u-bourgogne.fr](mailto:igor.bezverkhyy@u-bourgogne.fr)

ORCID: 0000-0001-8762-6687

## Abstract

The quantum sieving is a promising approach for the separation of hydrogen isotopes under cryogenic conditions ( $< 100$  K) in microporous solids. To evaluate the role of pore size and guest-cation interaction strength in this process, the adsorption properties of Li-exchanged LTA zeolites ( $\text{Li}_8\text{Na}_4\text{A}$  and  $\text{LiA}$ ) for  $\text{D}_2$  and  $\text{H}_2$  were studied. The single gas adsorption isotherms were measured at different temperatures (40 – 92 K) and the equilibrium  $\text{D}_2/\text{H}_2$  selectivities were determined using a coadsorption manometric technique. The isosteric heat of adsorption ( $Q_{\text{iso}}$ ) as a function of loading was determined from the single gas isotherms. It was found that in the partially exchanged material  $\text{Li}_8\text{Na}_4\text{A}$  the variation of  $Q_{\text{iso}}$  is smaller than in  $\text{NaA}$  zeolite. In contrast, in  $\text{LiA}$  at low loading ( $< 2$  molec/uc) extremely high values were observed (15.0 kJ/mol for  $\text{D}_2$  and 13.8 kJ/mol for  $\text{H}_2$ ) indicating the presence of strongly adsorbing sites. After the filling of these sites the  $Q_{\text{iso}}$  decreases and remains almost constant reflecting weaker interactions between the guest molecules and  $\text{Li}^+$  cations located inside the cages (6MR sites). The  $\text{D}_2/\text{H}_2$  selectivity at 40 K and high loading ( $\sim 11$  mmol/g) increases in the order:  $\text{Li}_8\text{Na}_4\text{A} < \text{LiA} < \text{NaA}$ . This finding shows that the presence of strongly adsorbing sites in  $\text{LiA}$  does not allow to increase  $\text{D}_2/\text{H}_2$  selectivity. The smaller aperture size in  $\text{NaA}$  than in  $\text{LiA}$  (due to a larger size of  $\text{Na}^+$  cations) appears thus to be more important factor for quantum sieving in LTA zeolites than the strong guest-cation interactions.

**Keywords:** quantum sieving, hydrogen isotope separation, coadsorption, LTA zeolite

## Introduction

Cation exchange in zeolites is the most powerful tool for designing the zeolite-based sorbents for a particular gas separation process. In small pore zeolites (LTA, CHA ...) the cations are located in the pore apertures and changing the size of cations allows thus to tune the pore size and to create the molecular sieving effect. In large pore zeolites (FAU, MOR ...) the nature of cation has less influence on the pore size and it is rather the difference in the interaction strength between the zeolite and the guest molecules which governs the selectivity. In this context Li-exchanged zeolites show particular properties in several applications. Thus, Li-containing LSX zeolite (low silica FAU, Si/Al = 1) shows high efficiency in air separation and this material is used on the industrial scale for this application (Yang 2003; Hutson et al. 1999; Koh et al. 2018). A similar LSX zeolite shows high H<sub>2</sub> storage capacity (Li and Yang 2006) and Li-exchanged small pore zeolites (LTA,CHA) demonstrate very promising CO<sub>2</sub>/N<sub>2</sub> selectivity (Cheung and Hedin 2014). All these applications are related to the small size of Li<sup>+</sup> (0.76 Å (Shannon et al. 1976)) due to which Li<sup>+</sup> possesses a strong polarization ability and can induce a large dipole moment on non-polar molecules. A combination of induced dipole moment and short cation-molecule distance (due to small size of Li<sup>+</sup>) result in very strong guest – cation interactions in lithium – exchanged zeolites (Yang 2003).

Along with the pore size, strong guest - cation interactions play an important role in D<sub>2</sub>/H<sub>2</sub> separation based on the quantum sieving effect (Beenakker et al. 1995). Indeed, it has been shown that high D<sub>2</sub>/H<sub>2</sub> selectivity can be achieved in different materials exhibiting strong guest – cation interactions: MOFs containing coordinatively unsaturated cations (Tuefel et al. 2013; FitzGerald et al. 2013; Weinrach et al. 2017; Ha et al. 2022) or Cu- and Ag – exchanged zeolites (Xiong et al. 2020; Zhang et al. 2022). Surprisingly, Li-exchanged zeolites have not been studied in detail for D<sub>2</sub>/H<sub>2</sub> separation with exception of LiX zeolite characterized at 77 K in our previous work (Giraudet et al. 2018).

To evaluate the potential of Li-containing zeolites in separation of D<sub>2</sub> from H<sub>2</sub>, in the present work we characterized the properties of different Li-exchanged LTA zeolites. To understand the motivation

of our study the structure of Li-exchanged LTA zeolite should first be described. The cation positions in LTA structure containing  $\text{Na}^+$ ,  $\text{Li}^+$  or both cations are rather similar (Fig.S1) (Yanagida et al. 1973, Carey et al. 2014). Eight of 12 cations are located in 6-member ring (6MR) windows (site I) and three cations occupy 8MR windows which connect the  $\alpha$  – cages (site II). The last of 12 cations in NaA zeolite occupies the site III located near 4MR window, but in LiA the position of this cation could not be determined (Carey et al. 2014). In partially exchanged zeolite  $\text{Li}_8\text{Na}_4\text{A}$   $\text{Na}^+$  cations occupy preferentially 8MR windows while  $\text{Li}^+$  are located in 6MR sites as shown by Reed and Breck (1958). Given that  $\text{Li}^+$  cation has a smaller size than  $\text{Na}^+$  (0.76 Å and 1.02 Å respectively (Shannon et al. 1976)), our choice to study Li-exchanged LTA zeolites can appear surprising. Indeed, replacing  $\text{Na}^+$  by  $\text{Li}^+$  in 8MR windows should increase their aperture size, while to enhance the  $\text{D}_2/\text{H}_2$  selectivity in NaA one needs smaller aperture size which should be as close as possible to the size of  $\text{H}_2$  molecules ( $\sim 2.9$  Å). It is important however to note that replacement of  $\text{Na}^+$  by  $\text{Li}^+$  (even partial) results in the decrease of the cell parameter (Reed and Breck 1958). One can thus keep  $\text{Na}^+$  cations in 8MR windows and decrease their aperture size through reducing the cell parameter. Due to smaller size of 8MR windows in such material the  $\text{D}_2/\text{H}_2$  selectivity could be enhanced. To check this hypothesis we prepared two Li-containing LTA zeolites ( $\text{Li}_{8.2}\text{Na}_{3.8}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$  and  $\text{Li}_{11.6}\text{Na}_{0.4}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$ ) and studied in detail their properties at different temperatures both in single gas adsorption and in coadsorption in order to determine the equilibrium  $\text{D}_2/\text{H}_2$  selectivity of these sorbents at cryogenic temperatures (39 – 77 K).

## 2. Experimental

### 2.1 Materials synthesis

Binder-free zeolite NaA in a powdered form was obtained from Union Carbide (unit cell composition used in the work:  $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$ ,  $M = 1704.6 \text{ g/mol}$ ). LiCl was purchased from ROTH.

The Li-exchanged zeolites used in the work were obtained from NaA by cation exchange with LiCl at room temperature ( $\sim 22^\circ\text{C}$ ). Partially exchanged sample ( $\text{Li}_{8.2}\text{Na}_{3.8}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$ ) was obtained through unique exchange step in which 5 g of hydrated NaA were placed in a solution containing 11.2 g of LiCl in 50 mL of water. After stirring for 16 h the solid was filtered, washed with deionized water (250 mL) and dried in ambient air. The almost fully exchanged LiA ( $\text{Li}_{11.6}\text{Na}_{0.4}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$ ) was prepared using the same exchange conditions, but applying eight exchange steps of 8 – 16 h duration with decantation of the solution between the steps.

## *2.2 Materials characterization*

The chemical composition of the zeolites was determined by energy dispersive X-ray spectroscopy (EDX) in scanning electron microscope JEOL 7600F. The samples were pressed and some pieces of the obtained pellets were deposited on a carbon tape covering the sample support. In order to obtain a representative bulk composition of the sample, a large analysis area was chosen ( $500 \times 500 \mu\text{m}^2$ ) and different zones (up to 10) were analyzed inside this area. Before analysis of each sample the EDS detector was calibrated using the internal standards. Li content was calculated from the difference between the amounts of Al and Na.

XRD patterns of the solids were measured in the range of 2-theta  $3^\circ - 50^\circ$  with a diffractometer Bruker D8-A25 Discover equipped with a LynxEye XE detector using Cu  $K\alpha$  radiation. The obtained XRD patterns were treated using FullProf software package. The cell parameters were determined using DICVOL software included in the package.

## *2.3 Adsorption and coadsorption measurements*

The single gas D<sub>2</sub> or H<sub>2</sub> adsorption isotherms at different temperatures were measured using a Micromeritics ASAP 2020 sorptometer. The samples were degassed at 673 K under secondary vacuum ( $< 10^{-4}$  hPa) for 16 h. The high purity D<sub>2</sub> and H<sub>2</sub> gases were purchased from Air Liquide (France) and were additionally dried using 4A zeolite cartridges from Agilent. The coadsorption measurements were performed using a home-made manometric setup for D<sub>2</sub>/H<sub>2</sub> mixture with the initial composition 25%D<sub>2</sub> - 75%H<sub>2</sub>. The detailed description of the setup and of the measurement procedure is given in our previous work (Bezverkhyy et al. 2020a).

In the present work a modified procedure of coadsorption measurement was used along with that used in our previous works. The difference consists in the manner of introducing the D<sub>2</sub>/H<sub>2</sub> mixture in the measurement cell. In the procedure used in our previous works the gas mixture prepared in the reference cell is introduced into the measurement cell which is already at the measurement temperature and then maintained for 24 h (Bezverkhyy et al. 2020a). This procedure will be designated in the text as a “cold contact” protocol. In the present work for some measurements realized at 38 – 40 K we used another procedure which will be designated as a “room temperature contact” protocol. In this case the D<sub>2</sub>/H<sub>2</sub> mixture was introduced in the measurement cell under ambient temperature ( $\sim 295$  K) and maintained under these conditions for 1 h. Then the cell was placed in the cryostat (at 90 K), cooled down to 38 – 40 K (in  $\sim 16$  h) and maintained for 24 h. This procedure allows to achieve equilibrium more rapidly than a “cold contact” protocol (see discussion in section 3.3).

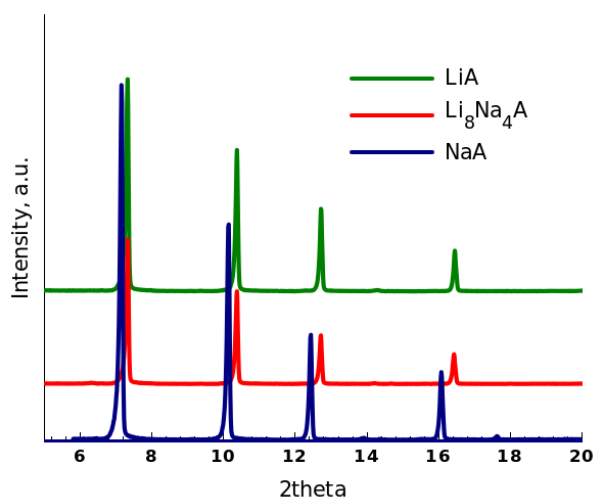
### **3. Results and discussion**

#### *3.1 Sample characterization*

The XRD patterns of NaA and Li-exchanged zeolites confirm preservation of the crystalline structure and a significant decrease of the cell parameter after exchange (Fig.1 and Table 1). It is interesting to note that the cell parameter changes noticeably already after a partial exchange. Indeed, the cell contracts by 0.2487 Å when passing from NaA to Li<sub>8</sub>Na<sub>4</sub>A sample, while the change is only of 0.0329 Å after further replacement of Na<sup>+</sup> by Li<sup>+</sup>.

**Table 1** Composition and cell parameters of the samples used in the work

Sample designation	Composition	Molar weight, g/mol	Cell parameter, Å
NaA	Na <sub>12</sub> Al <sub>12</sub> Si <sub>12</sub> O <sub>48</sub>	1704.64	12.3011
Li <sub>8</sub> Na <sub>4</sub> A	Li <sub>8.2</sub> Na <sub>3.8</sub> Al <sub>12</sub> Si <sub>12</sub> O <sub>48</sub>	1573.03	12.0524
LiA	Li <sub>11.6</sub> Na <sub>0.4</sub> Al <sub>12</sub> Si <sub>12</sub> O <sub>48</sub>	1518.47	12.0195



**Figure 1** XRD patterns of the pristine NaA zeolite and the Li-exchanged materials used in the work.

### 3.2 Single gas adsorption



Comparison of H<sub>2</sub> and D<sub>2</sub> adsorption isotherms in the studied zeolites at 77 K shows two important features (Fig.S2).

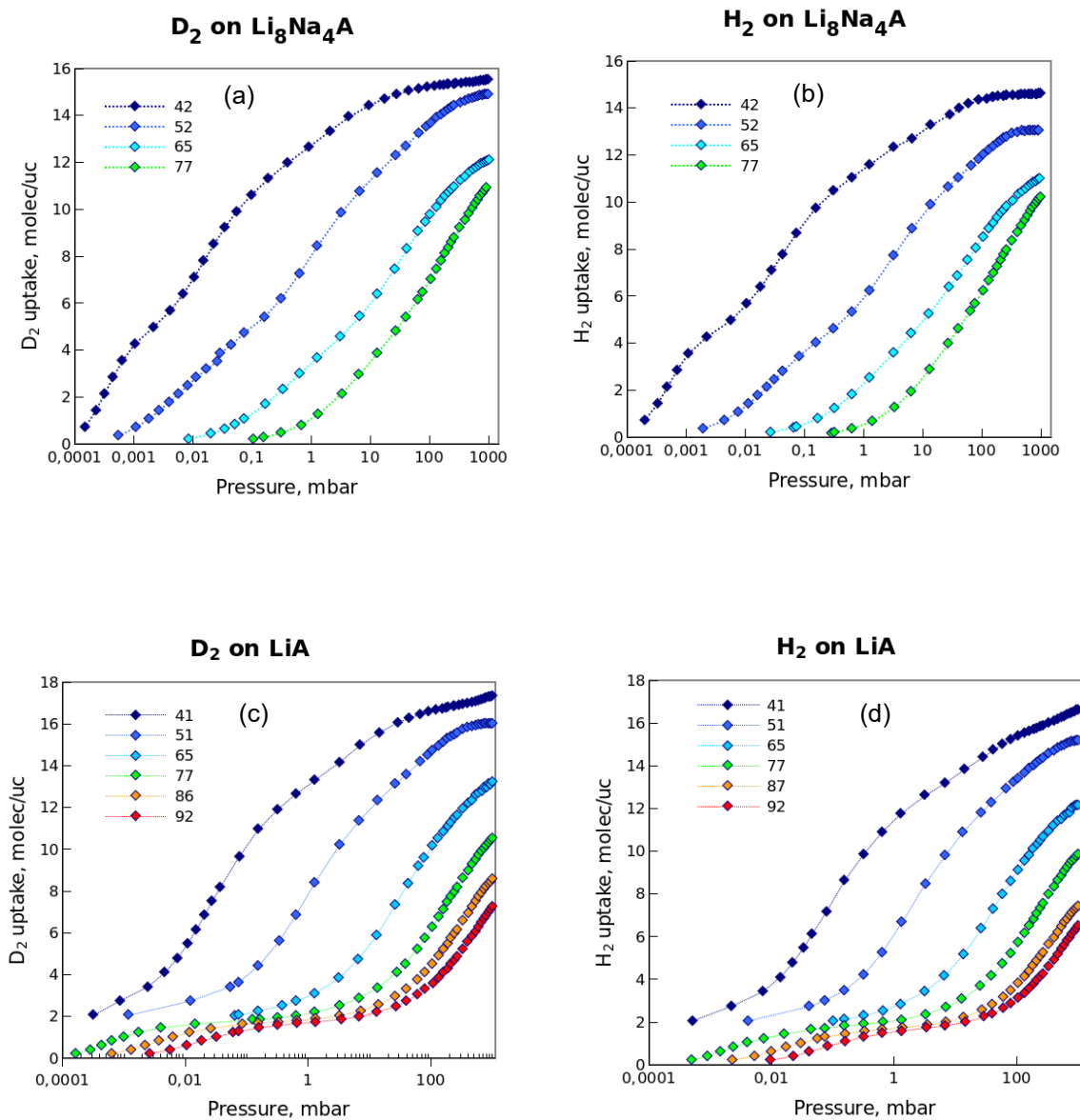
First, NaA zeolite adsorbs more hydrogen and deuterium than lithium-exchanged zeolites. Partially exchanged Li<sub>8</sub>Na<sub>4</sub>A zeolite adsorbs more than the fully exchanged LiA zeolite. When the lattice parameter of the zeolite decreases following the substitution of sodium by lithium, the adsorption capacity of the isotopes decreases because the available volume of the  $\alpha$  cage is smaller. This phenomenon can partly explain the difference in adsorption capacity observed between zeolites, in particular between the lithium – containing zeolites. But it is not sufficient to explain the relatively large difference between the latter and the NaA zeolite. Other parameters might influence the adsorption capacity of these zeolites such as the exact positions of the cations in the  $\alpha$  cage for example.

Another observation concerns the shape of the isotherms at low pressure (Fig.S2). Both for H<sub>2</sub> and D<sub>2</sub> one can distinguish a notable difference in behavior between the LiA zeolite and the two other materials. In LiA the adsorption begins at a much lower pressure ( $\sim 10^{-4}$  mbar) and the isotherm presents a plateau between 0.01 and 1 mbar. This type of behavior has already been observed on other adsorbents such as MgX zeolite [14]. It is characteristic of a strong interaction between charge compensating cations and the adsorbed molecules. Since this phenomenon is not observed in LiNaA (which contains Li<sup>+</sup> only in sites I), one can conclude that it is Li<sup>+</sup> cations located in site II (8MR windows) and possibly in site III (4MR) which are at the origin of this effect.

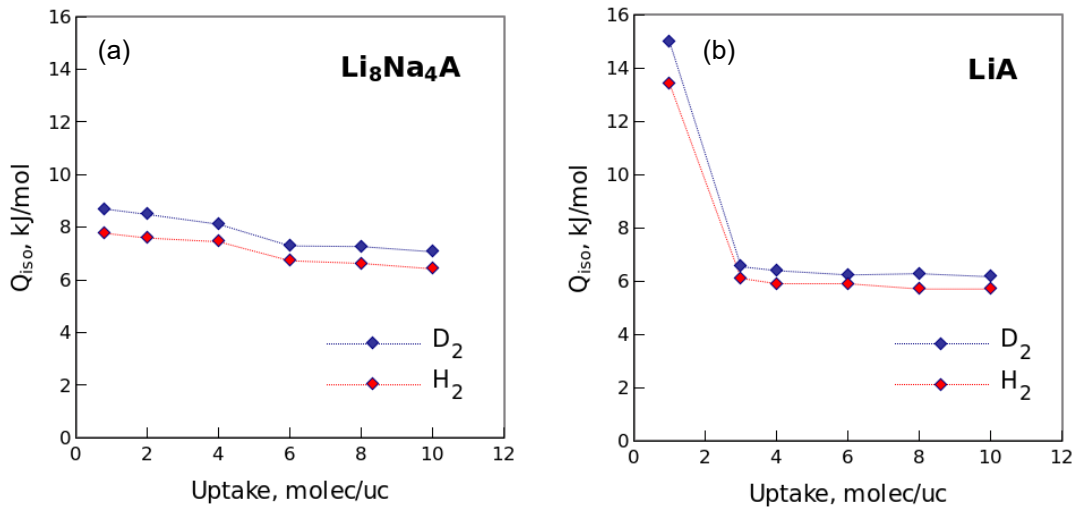
The H<sub>2</sub> and D<sub>2</sub> adsorption isotherms measured at different temperatures for Li<sub>8</sub>Na<sub>4</sub>A and LiA are presented in Fig.2. This data allows to calculate the isosteric heat of adsorption as a function of loading (Fig.3 and Table 2).

For Li<sub>8</sub>Na<sub>4</sub>A material the isotherms were measured in the range 40 – 77 K which allows to calculate the isosteric heat for loadings from 1 to 10 molec/uc. In contrast, for LiA the additional adsorption isotherms were also measured at 86 and 92 K. The necessity of these measurements is due to the

presence of very strong guest-cation interactions in this material. Because of this phenomenon, below 77 K the equilibrium pressures for loadings smaller than 2 molec/uc are too low to be measured in our setup. At 86 and 92 K the corresponding pressures become measurable and the isosteric heat for loadings below 2 molec/uc can be determined with confidence (Fig. 2c and 2d).



**Figure 2** D<sub>2</sub> and H<sub>2</sub> adsorption isotherms on LiA (a), (b) and on Li<sub>8</sub>Na<sub>4</sub>A (c), (d) zeolites at different temperatures.



**Figure 3** Variation of the isosteric heat of adsorption for D<sub>2</sub> and H<sub>2</sub> in Li<sub>8</sub>Na<sub>4</sub>A (a) and LiA (b) zeolites.

**Table 2** Isosteric heat of adsorption for NaA, Li<sub>8</sub>Na<sub>4</sub>A and LiA zeolites studied in the work

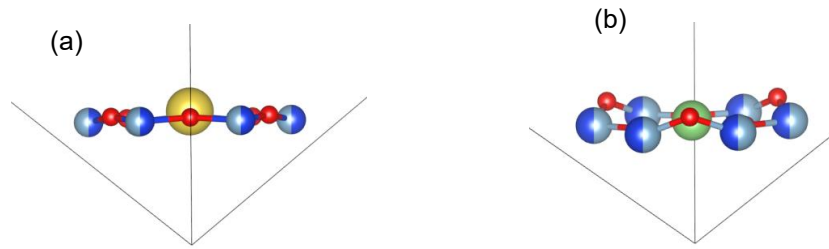
Zeolite	$Q_{iso}(H_2)$ at 1 molec/uc kJ/mol	$Q_{iso}(H_2)$ at 10 molec/uc kJ/mol	$Q_{iso}(D_2)$ at 1 molec/uc kJ/mol	$Q_{iso}(D_2)$ at 10 molec/uc kJ/mol
NaA	9.3	6.0	11.1	7.1
Li <sub>8</sub> Na <sub>4</sub> A	7.7	6.4	8.4	7.1
LiA	13.4	5.7	15.0	6.2

For Li<sub>8</sub>Na<sub>4</sub>A (Fig.3a) the evolution of the isosteric heat of adsorption of H<sub>2</sub> and D<sub>2</sub> with loading follows a trend typical for cationic zeolites (Llewellyn and Maurin 2005) and similar to that observed in NaA in our previous work (Bezverkhyy et al. 2020b). The value of  $Q_{iso}$  is high at the low loading due to the interactions of hydrogen or deuterium molecules with cations and then it smoothly decreases with loading. This decrease reflects the increasing contribution into  $Q_{iso}$  of weak intermolecular interactions. In contrast, for LiA the value of  $Q_{iso}$  changes with loading in a peculiar manner: a very high value is observed at 1 molec/uc which decreases sharply at 3 molec/uc and then

remains almost constant (Table 2 and Fig.3b). The value of  $Q_{\text{iso}}$  at 2 molec/uc cannot be determined with confidence since at this loading a plateau is observed (Fig. 2c and 2d) and therefore the value of the equilibrium pressure corresponding to 2 molec/uc is poorly defined.

The high  $Q_{\text{iso}}$  value observed at low loading ( $< 2$  molec/uc) can be attributed to the adsorption sites associated with  $\text{Li}^+$  cations located in 4MR windows since they are present only in the fully exchanged LiA. The high interaction strength is due to a small size and good accessibility of  $\text{Li}^+$  placed in this position. It should be noted however that in a fully Li-exchanged LTA zeolite only one 4MR window (out of 12) contains  $\text{Li}^+$  cation. In our LiA sample this number should be even lower if the residual  $\text{Na}^+$  cation (0.4 per unit cell, Table 1) occupies the same site. Therefore, the number of  $\text{Li}^+$  cations in 4MR site is smaller than the number of strongly adsorbed  $\text{D}_2$  or  $\text{H}_2$  molecules ( $\sim 2$  molec/uc). This difference indicates that the structure of the strongly adsorbing sites could be more complex than just a single  $\text{Li}^+$  cation located in the 4MR window. We suggest that these sites could consist of two cations ( $\text{Li}^+$  or  $\text{Na}^+$ ) located in adjacent 4MR and 8MR windows.

The weak variation of  $Q_{\text{iso}}$  in LiA zeolite for loadings higher than 2 molec/uc is rather unusual for cation rich zeolites (Llewellyn and Maurin 2005). It suggests that the  $\text{Li}^+$  cations present in 6MR windows (inside the cages) interact with  $\text{H}_2$  and  $\text{D}_2$  molecules much less strongly than  $\text{Na}^+$  occupying the same positions (Bezverkhyy et al. 2020b). We suggest that this effect is due to a smaller size of  $\text{Li}^+$  cations (0.76 for  $\text{Li}^+$  and 1.02 Å for  $\text{Na}^+$ ) which results into different positions of lithium and sodium cations in 6MR sites. Indeed, it follows from the structural data that  $\text{Na}^+$  cations are exposed into the  $\alpha$  cage while  $\text{Li}^+$  cations are located inside the window plane (Fig.4) (Reed and Breck 1958; Pluth and Smith 1980). Such a position of  $\text{Li}^+$  cations results in their strong shielding by the oxygen atoms which prevents the adsorbate molecules from approaching these cations and decreases the interaction strength.



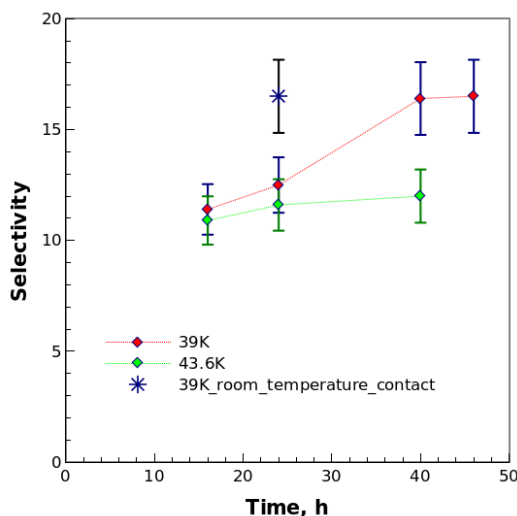
**Figure 4** Position of a cation in the 6MR windows of the LTA structure (site I): Na<sup>+</sup> (yellow) in NaA (a) and Li<sup>+</sup> (green) in Li<sub>8</sub>Na<sub>4</sub>A (b).

It is interesting to note that extremely high isosteric adsorption heats found in LiA zeolite should result in a low mobility of D<sub>2</sub> and H<sub>2</sub> molecules adsorbed at the corresponding sites at the lowest used temperature (~ 40 K). The following equation allows to estimate the residence time  $\tau$  of the adsorbed molecules (de Boer 1953):

$$\tau = \tau_0 e^{Q/RT}$$

where  $\tau_0 = 10^{-13}$  s,  $Q$  is the heat of adsorption,  $T$  is the temperature and  $R$  is the universal gas constant. If the value of 15 kJ/mol (observed for D<sub>2</sub>) is used in this equation, one can obtain that at 40 K the residence time of the molecules is equal to 1077.4 h. Comparison of this value with the time scale of the isotherm measurements (~ 20 h) shows that these adsorption sites are essentially blocked by the adsorbed D<sub>2</sub> molecules. For H<sub>2</sub> molecules ( $Q_{\text{iso}} = 13.4$  kJ/mol) the residence time is much lower (8.8 h), but it is nevertheless comparable with the time scale of the measurements. This estimation of the residence times of the adsorbed molecules indicates that in LiA at temperatures lower than 40 K the strongly adsorbing sites are blocked and the majority of the adsorbed molecules interact weakly with Li<sup>+</sup> cations located in 6MR windows and shielded by the oxygen atoms.

### 3.3 Coadsorption measurements



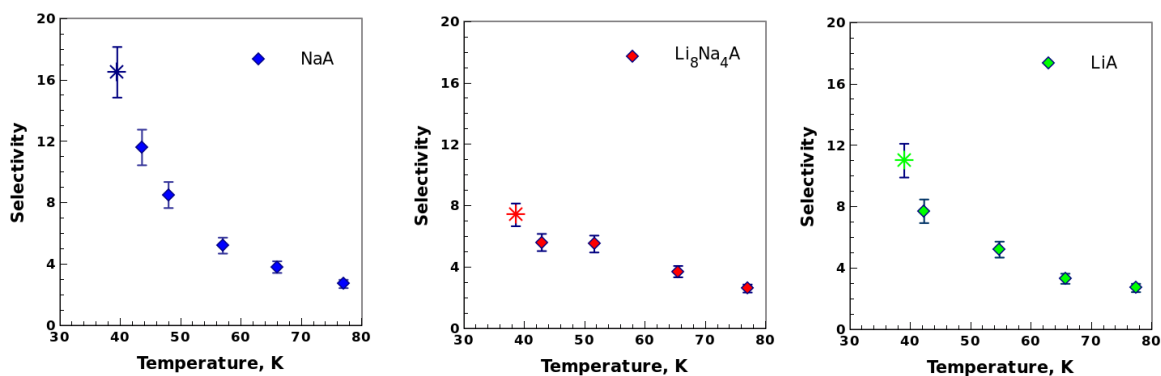
**Figure 5** Variation of  $D_2/H_2$  selectivity in NaA zeolite as a function of equilibration time at different temperatures obtained using different measurement protocols: “cold contact” (diamonds) and “room temperature contact” (asterisk). Initial mixture composition - 25%  $D_2$  – 75%  $H_2$ , initial mixture pressure - 900 mbar.

The first stage of the coadsorption study was dedicated to the determination of the conditions allowing to achieve the coadsorption equilibrium. In our previous work dealing with LTA zeolites (Bezverkhy et al. 2020b) the contact time between the mixture and NaA zeolite was 16 h, but the lowest used temperature was 45 K. Since in the present work we explored lower temperatures (down to 39 K), we checked first if this equilibration time is sufficient to achieve the thermodynamic equilibrium at this temperature. As it follows from Fig.5 at 43.6 K the selectivity remains constant after 24 h within the experimental error (24 h - 11.6 and 40 h - 12.0) therefore we chose the duration of 24 h for all measurements under “cold contact” protocol for  $T > 43$  K. In contrast, at 39 K this duration is clearly insufficient to achieve equilibrium which is obtained only after 40 h of contact.

The observed increase of  $D_2/H_2$  selectivity with the equilibration time is related to a particular arrangement of our setup. The gas mixture is introduced by the top of the sample cell (length ~ 26 cm, internal diameter – 0.95 cm) which contains the degassed zeolite in its bottom part under vacuum and at the measurement temperature. Diffusion coefficient of  $H_2$  in the gas phase is higher than that

of  $D_2$  because of its lower molecular weight (Cussler 2009). Due to a faster  $H_2$  diffusion the gas mixture contacting the zeolite surface after introduction contains more  $H_2$  than the initial mixture. Consequently, the adsorbed phase formed at this moment is richer in  $H_2$  than it should be under equilibrium. During the equilibration stage  $D_2$  molecules from the gas phase replace the excessive  $H_2$  molecules adsorbed in the micropores. As a result, the fraction of  $D_2$  in the adsorbed phase increases and the selectivity rises with time. The slowness of this exchange process (especially at the lowest temperature) is the cause of the long time needed to achieve the equilibrium in our coadsorption measurements.

In order to avoid the initial enrichment of the adsorbed phase with  $H_2$ , we devised the “room temperature contact” protocol described in detail in the Experimental part. As follows from Fig.5, at 39 K this protocol allows to obtain the equilibrium  $D_2/H_2$  selectivity in NaA already after 24 h while a longer contact time is needed under the “cold contact” protocol. The fact that the same value of selectivity is obtained using two different measurement protocols suggests that the true equilibrium state is achieved in our coadsorption experiments. The similar results are obtained for two other zeolites used in our work (see Table S1). We conclude thus that below 40 K the “room temperature contact” protocol guarantees achieving the equilibrium state and therefore we used it instead of the “cold contact” protocol. To indicate this difference the corresponding points are designated by an asterisk in the plots presenting the selectivity as a function of temperature (Fig.6).



**Figure 6**  $D_2/H_2$  selectivity as a function of temperature for the zeolites studied in the work. Points designated by diamonds are obtained using the “cold contact” protocol after 24 h of contact. The points designated by an asterisk are obtained by using “room temperature contact”. Initial mixture composition: 25%  $D_2$  – 75%  $H_2$ , initial pressure - 900 mbar.

Analysis of the data presented in Fig.6 shows that partial exchange of  $Na^+$  with  $Li^+$  in  $Li_8Na_4A$  does not allow to enhance the  $D_2/H_2$  selectivity of LTA zeolite. In this material  $Li^+$  cations occupy 6MR windows and  $Na^+$  are located in 8MR sites connecting the cages (Reed and Breck 1958). Due to decrease of the cell parameter the size of 8MR windows in  $Li_8Na_4A$  should be smaller than in NaA. However, despite this smaller window size the selectivity of  $Li_8Na_4A$  is the lowest of the studied solids. This effect suggests that the window size is not the unique parameter determining the selectivity. Another important property is the strength of guest – cation interactions (Xiong et al. 2020; Zhang et al. 2022), which is not sufficient in  $Li_8Na_4A$  as confirmed by small values of the isosteric heat (see Fig.3). The weak adsorbate – cation interactions in this material result thus in the decrease of selectivity in  $Li_8Na_4A$  in comparison with NaA despite the smaller size of 8MR windows in the Li-containing material.

The importance of the interaction strength is confirmed by the increase of selectivity in LiA material. In this zeolite the size of 8MR windows is larger than in NaA and  $LiNaA$  since these windows are occupied by small  $Li^+$  cations. However, the presence of extremely strong adsorption sites accommodating  $\sim 2$  molec/uc allows apparently to compensate this difference and increase the selectivity at 39 K from 7.4 to 11. The selectivity of LiA remains however lower than that of NaA



(16.5). The fact that NaA demonstrates the highest selectivity among the studied LTA zeolites can be explained by the optimal balance of the two key properties. On the one hand, NaA possesses the pores of small size ( $\sim 3.8 \text{ \AA}$ ) due to the presence of  $\text{Na}^+$  cations in 8MR windows. On the other hand, NaA contains a high concentration of exposed  $\text{Na}^+$  cations which can efficiently interact with the guest molecules.

Comparison of Li-exchanged zeolites with NaA shows the important role of both parameters, aperture size and interaction strength, to achieve a high  $\text{D}_2/\text{H}_2$  selectivity. Indeed, the decrease of the size of 8MR windows in  $\text{Li}_8\text{Na}_4\text{A}$  does not allow to enhance the selectivity because of a low interaction strength between the adsorbed molecules and  $\text{Li}^+$  cations located in 6MR sites. In LiA zeolite the  $\text{Na}^+$  cations located in 8MR and 4MR sites are replaced by  $\text{Li}^+$  which results in appearance of very strong guest – cation interactions. However, the  $\text{D}_2/\text{H}_2$  selectivity remains lower than in NaA because of a larger size of 8MR windows occupied by  $\text{Li}^+$ . Our study shows thus that in zeolites a combination of a large number of cations strongly interacting with the guest molecules with a small size of the aperture is necessary for obtaining high selectivity.

## Conclusions

In this work the adsorption properties of Li-exchanged NaA zeolites were studied for  $\text{D}_2/\text{H}_2$  separation using the single gas and coadsorption measurements at 38 – 77 K. It is shown that despite a smaller size of  $\text{Li}^+$  cations, the isosteric heat of  $\text{H}_2$  and  $\text{D}_2$  adsorption decreases after substitution of  $\text{Na}^+$  cations located in 6MR windows ( $\text{Li}_8\text{Na}_4\text{A}$  zeolite). This decrease is explained by a shielding of  $\text{Li}^+$  cations located in 6MR windows by oxygen atoms. In contrast, the fully-exchanged material (LiA) contains the adsorption sites with very high isosteric heat of adsorption (15 kJ/mol for  $\text{D}_2$ ) which can be associated with  $\text{Li}^+$  cations located in 8MR and/or 4MR windows. The adsorption capacity of these sites is however low ( $< 2 \text{ molec/uc}$ ) and the adsorption at high loading is dominated by the weak sites related to  $\text{Li}^+$  located in 6MR windows. Despite the presence of strong adsorption sites in LiA, the

D<sub>2</sub>/H<sub>2</sub> selectivity at 39 K measured by the coadsorption technique varies in the order: NaA > LiA > LiNaA. This result shows that the *high content* of cations which interact efficiently with the guest molecules is a key factor for D<sub>2</sub>/H<sub>2</sub> separation in zeolites. Another finding of our study concerns the methodological aspect of D<sub>2</sub>/H<sub>2</sub> coadsorption measurements below 40 K. We found that the kinetics of attaining the equilibrium is very sluggish in these conditions and we devised a novel measurement protocol which allows to circumvent this obstacle.

### Supplementary Information

The online version contains supplementary material available at ...

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### Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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