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Enhancement of D₂/H₂ Selectivity in Zeolite A through Partial Na-K Exchange: Single Gas and Co-adsorption Studies at 45 – 77 K

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Abstract

We report D_2/H_2 adsorption selectivities under cryogenic temperatures (45 – 77 K) in Na and K-Na exchanged zeolites A (LTA structural code) measured by co-adsorption technique. These values are systematically compared with Ideal Adsorbed Solution Theory (IAST) predictions based on the single gas adsorption isotherms. For NaA zeolite the evolution of the selectivity as a function of total pressure and gas mixture composition at 77 K shows ideal behavior. In contrast, as temperature decreases, D_2/H_2 selectivity rises exponentially and its values can no longer be predicted by IAST. We found that in these conditions the evolution of the selectivity can be described by a simple quantum sieving model based on a spherical particle in a one-dimensional cylindrical pore. Partial substitution of Na by K influences significantly the properties of LTA zeolite in D_2/H_2 adsorption at 77 K. The adsorbed amounts decrease with K content, but the D_2/H_2 selectivity rises attaining the maximum value in $K_{1.6}Na_{10.4}A$, which surpasses that measured in NaA. A detailed study of D_2/H_2 mixture adsorption in zeolite revealed its non-ideal behavior even at 77 K. Upon the decrease of temperature the uptakes of D_2 and H_2 in $K_{1.6}Na_{10.4}A$ decrease and the selectivity rises more steeply than in the case of NaA. Due to this effect at 48 K for 25% D_2 + 75% H_2 mixture the D_2/H_2 selectivity of 23.0 is attained in $K_{1.6}Na_{10.4}A$ ($P = 648$ hPa, loading - 1.9 mmol.g⁻¹) whereas the value of 8.5 is obtained in NaA ($P = 574$ hPa, loading - 10.3 mmol.g⁻¹). The improved D_2/H_2 selectivity in $K_{1.6}Na_{10.4}A$ zeolite is explained by the fact that some α -cages in this material are accessible only to D_2 molecules.

Keywords: quantum sieving, hydrogen isotope separation, co-adsorption, selectivity

1. Introduction

Separation of hydrogen isotopes using adsorption on microporous solids has recently attracted attention as an alternative method to cryogenic distillation^{1,2}. This approach is based on the stronger adsorption of heavier isotopes in the pores whose size is comparable with the de Broglie wavelength of the molecules (1.40 Å for H₂ and 0.99 Å for D₂ at 77 K). This effect (called “quantum sieving”) appears due to quantization of the translational motion of the adsorbed molecules at low temperature (< 100 K)^{3,4}. In these conditions the value of the zero point energy of heavier isotope becomes lower resulting in its stronger interaction with the adsorbent. The selectivity towards heavier isotope was shown to increase with decreasing pore size of the adsorbent³. Given the size of the hydrogen molecule (~ 3 Å), the zeolites with 8 member rings (8MR) having pore openings of ca. 4 Å present a potential interest for the separation of hydrogen isotopes as follows from our recent studies of CHA zeolites which also contain 8MR^{5,6}.

Among the cation-rich zeolites having small pores LTA type materials are one the most attractive type of zeolites due to special structural features. Na-LTA structure can be described as an assemblage of α -cages having the composition Na₁₂Al₁₂Si₁₂O₄₈ in which the cations occupy three different positions⁷ (Fig.1). 8 cations are located in the center of 6-member oxygen rings inside the α -cages (6MR, SI). Other 3 cations occupy six windows consisting of 8 oxygen atoms (8MR, SII) which connect the α -cages between them. In this position one cation is shared between two α -cages and therefore one 8MR aperture contains 1/2 cation. The 12th cation in Na-LTA zeolite is located near 4-member rings (4MR, SIII). Changing the cations located in the pore windows allows to adjust their size and thus to control the access of the molecules to the α -cages. While the sodium form of LTA has the pore openings of ~ 4 Å, a partial exchange with potassium results in appearance of K⁺ in SII and decrease of the effective pore size down to ~ 3 Å. In

contrast, in mixed $4\text{Ca}^{2+} - 4\text{Na}^+$ LTA all eight cations can be localized on SI sites and the windows become cation free with their aperture increasing to $\sim 5 \text{ \AA}$.

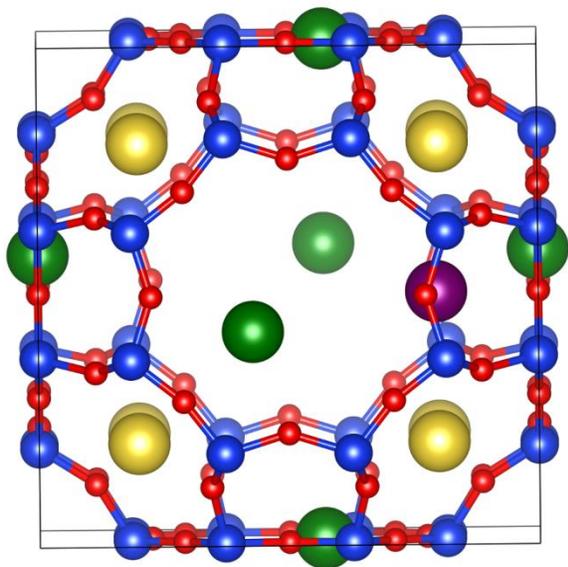


Figure 1 Schematic presentation of cationic positions in the α -cage of LTA zeolite (composition - $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$). Cationic sites: yellow – SI (6MR), green – SII (8MR), violet – SIII (4MR). Framework atoms: blue – Si or Al, red – O.

Due to these special properties and their accessibility on industrial scale, LTA zeolites were studied in hydrogen isotope separation. The main body of this work has been realized however using the chromatography⁸ with only a few studies using co-adsorption measurements, but only at 77 and 87 K⁹⁻¹². Recently it has been shown that for short contact time between H_2 - D_2 mixture and 5A zeolite the co-adsorption equilibrium is not achieved¹³. In light of this result it can be supposed that selectivities previously reported do not probably correspond to the equilibrium state. It would be useful therefore to reevaluate them under well controlled equilibrium conditions.

Given these circumstances, in the first part of the present work we measured the adsorption isotherms of H_2 and D_2 on 4A zeolite at different temperatures and compared the selectivities

predicted by Ideal Adsorbed Solution Theory (IAST) with the values measured by co-adsorption under equilibrium conditions at 45 – 77 K. In the second part the same approach was used to evaluate the effect of Na/K ratio in LTA zeolite on D₂/H₂ adsorption selectivity. Adsorption of single gases on a series of materials with different Na/K ratio showed that the adsorbed amounts of H₂ and D₂ decrease with increasing potassium content as expected. In contrast we have found that the D₂/H₂ selectivity (estimated by IAST) does not vary monotonously with K⁺ amount, the highest value being observed for the zeolite containing 1.6 K⁺ per unit cell. The properties of this material were studied therefore in detail at different temperatures by single gas adsorption and by co-adsorption.

2. Experimental

Materials

Binderless zeolite NaA in powdered form was obtained from Union Carbide (unit cell composition used in the work: Na₁₂Al₁₂Si₁₂O₄₈, M = 1704.6 g/mol). KCl and NaCl were purchased from ROTH.

Preparation of mixed cation K-Na zeolites

Mixed cation KNaA zeolites were prepared by cation exchange using NaA zeolite and solution containing KCl and NaCl in varying proportion. To obtain the cationic composition K_{1.6}Na_{10.4}A studied in detail in the present work, the following procedure was employed. 3.689 g of NaCl and 0.487 g of KCl were dissolved in 335 mL of deionized water and 1.2 g of hydrated NaA zeolite was added to the solution. The suspension was stirred at room temperature (~ 295 K) for 60 h. Then, the solution was decanted and the powder washed three times with 200 mL of water. After

filtration the solid was dried under ambient conditions for 24 h. To obtain other compositions, different amounts of NaCl and KCl were used during exchange (Table S1).

Determination of samples composition

The chemical composition of the used zeolites was determined by energy dispersion spectroscopy (EDS) using a scanning electron microscope JEOL 7600F. The powdered samples were pressed and some pieces of the obtained tablets were deposited on a carbon tape covering the sample support. Use of the pieces of tablet in analysis allowed to obtain a flat surface of the sample, a key parameter for the precise EDS analysis. It should be noticed that the depth of EDS analysis (1-2 μm) is comparable with the size of the crystallites of the used zeolite (Fig.S1) and therefore the obtained composition corresponds to the bulk one. In order to obtain a representative composition of the whole sample, a large area was chosen (500 x 500 μm^2) and different zones (up to 10) were analyzed inside this area. The differences between the analyzed zones were negligible (< 0.1 at. %) which shows that the determined concentrations are the bulk ones. Before each analysis the EDS detector was calibrated using the internal standards of the analyzed elements (Na, K, Al, Si).

Temperature control

The temperature was maintained using a Gifford – McMahon He cryocooler from Micromeritics both in single gas and in co-adsorption measurements. In addition to the temperature measurement integrated in the cryostat, one more probe (DT-470 silicon diode from Lake Shore Cryotronics) was fixed directly on the external surface of the sample cell using Kapton tape. It was found that the temperature measured on the cell wall is different from the setpoint temperature by 1 - 5 K depending on temperature. In the present work the value measured by the

diode fixed on the cell wall was used as the adsorption temperature. During the measurements the cooled cavity of the cryostat containing the cell was covered and continuously purged with He in order to prevent condensation of ambient air.

Single gas adsorption measurement

The single gas adsorption isotherms were measured using ASAP 2020 apparatus from Micromeritics. The samples were degassed at 673 K for 16 h before the measurements. After degassing, the samples were transferred to the measurement port, additionally evacuated at room temperature for 3 h and then placed in the cryostat at 90 K. Then, the temperature decrease was initiated and after attaining the desired adsorption temperature (3 - 16 h) the measurement was started.

H₂ and D₂ gases were purchased from Air Liquide (France) and were additionally dried using zeolite filled cartridges from Agilent. The same gases were used for the co-adsorption experiments.

Co-adsorption measurements

The co-adsorption measurements were done using the home built setup described in ¹². The co-adsorption technique allows to measure the thermodynamic selectivity:

$$S(D_2/H_2) = \frac{x(D_2) \cdot y(H_2)}{y(D_2) \cdot x(H_2)}$$

where x is the fraction in the adsorbed phase and y is the gas fraction of each gas. The details of the measurement procedure of D₂/H₂ selectivity corrected for the thermodiffusion is described in our previous work ⁵. In the following these corrected selectivity values are used as co-adsorption selectivity.

The equilibrium time of 16 h for 4A zeolite and of 24 h for $K_{1.6}Na_{10.4}A$ was chosen on the basis of the complementary experiments performed with different contact times whose results are presented in Fig.S2. It can be concluded that the equilibrium value of selectivity is reached after 16 h in the case of 4A zeolite. In contrast, for $K_{1.6}Na_{10.4}A$ the equilibrium is attained only after 24 h of the contact between the gaseous mixture and the sorbent. Based on these experiments we chose 16 h for 4A and 24 h for $K_{1.6}Na_{10.4}A$ as the contact time allowing to achieve co-adsorption equilibrium in all performed measurements.

3. Results and discussion

3.1. Adsorption properties of NaA zeolite

3.1.1. Experiments at 77 K

Co-adsorption. The variation of D_2/H_2 selectivity as a function of loading and gas fraction of D_2 is presented in Fig.2. First, we notice that the obtained selectivity values are very close to those reported previously. Thus, in comparable conditions (650 hPa, 50% D_2 + 50% H_2) we obtained D_2/H_2 selectivity of 2.8 while the values of 2.5 – 2.6 were reported in ⁸⁻¹⁰. Another important observation concerns the decrease of D_2/H_2 equilibrium selectivity with loading (Fig.2). This effect was previously observed for hydrogen isotopes in LTA ⁹⁻¹² and FAU ^{12,14} zeolites and it can be correlated with the decrease of the interaction strength with loading. At low loading the adsorption is governed by strong adsorbate – cation interactions while at higher loading weak adsorbate – adsorbate interactions dominate. Strong interactions of D_2 and H_2 with charge compensating cations result in a large difference in their zero point energies and thus in higher selectivity at low loading. The same mechanism was shown to provide the high D_2/H_2 selectivity at low loading in MOF materials containing coordinatively unsaturated cations ¹⁵⁻¹⁷.

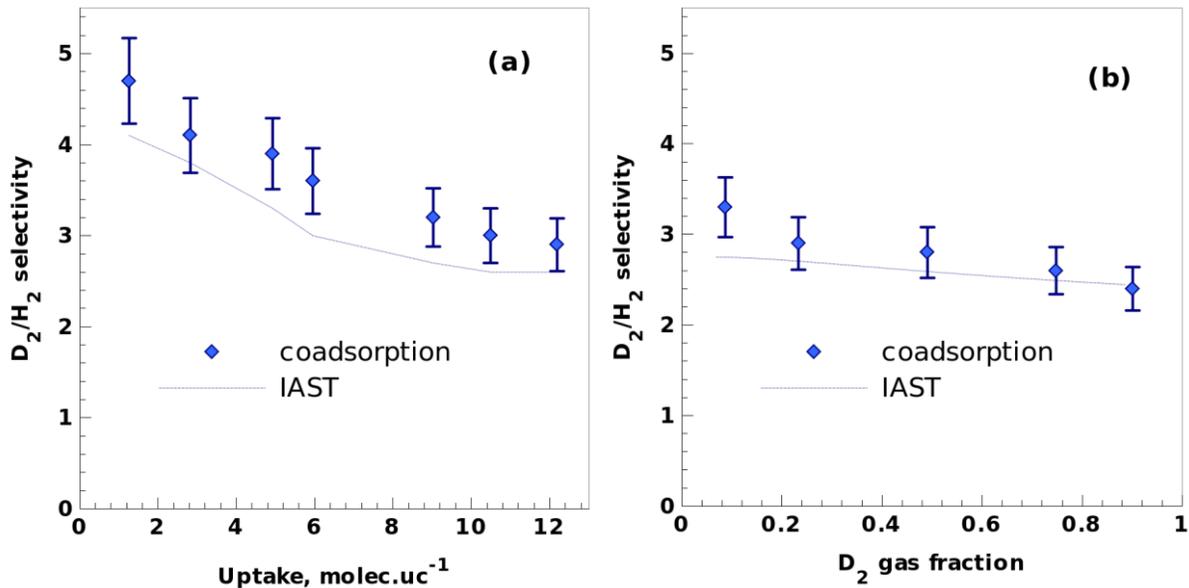


Figure 2 D_2/H_2 co-adsorption selectivity for NaA zeolite measured at 77 K as a function of total loading for 25 D_2 /75 H_2 mixture (a) and as a function of D_2 gas fraction under 660 hPa (b).

Even if IAST gives only the equilibrium selectivity (the diffusion effects are not taken into account), comparison between co-adsorption and IAST is important from a practical point of view when studying mixture adsorption. In the case of D_2 and H_2 co-adsorption on NaA zeolite the measured selectivities decrease with loading as well as with D_2 fraction in gas phase (Fig.2) and the obtained values agree fairly well with those calculated by IAST (see SI for details of IAST calculations). Despite a small deviation, it can be concluded that the adsorption of D_2/H_2 mixture in 4A zeolite at 77 K follows the ideal behavior which is in agreement with the previous study¹³.

3.1.2. Experiments at 48 - 77 K

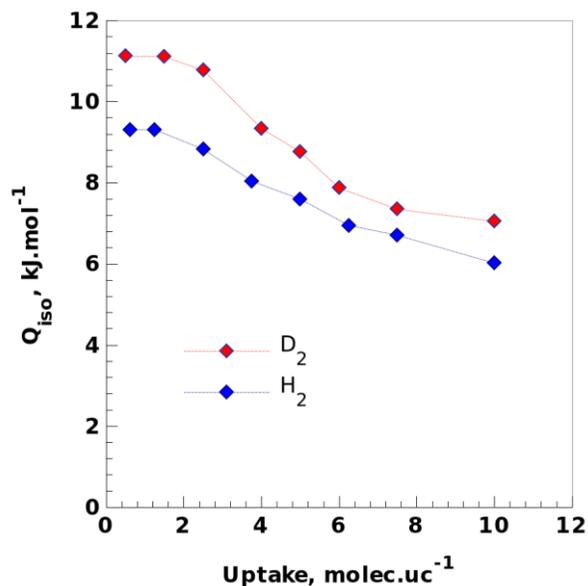


Figure 3 Isosteric heat of adsorption for D₂ and H₂ in NaA zeolite as a function of uptake.

Single gases. The adsorption isotherms of H₂ and D₂ measured at different temperatures are presented in Fig.S3. As expected, the uptakes increase strongly with decreasing temperature and adsorbed amount of D₂ is always higher than that of H₂. Using the adsorption isotherms at different temperatures the values of the isosteric enthalpy of adsorption were calculated for H₂ and D₂ (Fig.3). It appears that hydrogen isotopes are rather strongly adsorbed at low loading with enthalpies of ~ 10 kJ/mol due to interactions with sodium cations. The enthalpy values and the amounts adsorbed are in good agreement with the data of Stéphanie-Victoire et al.¹⁸ obtained by thermogravimetry. The observed decrease of the heat of adsorption with loading is due to the decrease of adsorbent – adsorbate interactions which is not compensated by the increase of adsorbate – adsorbate interactions. This effect is systematically observed in cationic zeolites for different adsorbed species¹⁹. The decrease of the isosteric heat of adsorption can thus be

correlated with the decline of D_2/H_2 selectivity with loading in NaA zeolite at 77 K as mentioned above.

Co-adsorption. Figure 4 presents the variation of the selectivity (both experimental and calculated by IAST) as a function of temperature (the corresponding adsorbed amounts are given in Table S2). Two important observations can be made. First, the selectivity increases exponentially with lowering temperature as predicted by quantum sieving models⁴. Second, the agreement with the IAST observed at 77 K, no longer exists at low temperatures. We discuss these two points in detail below.

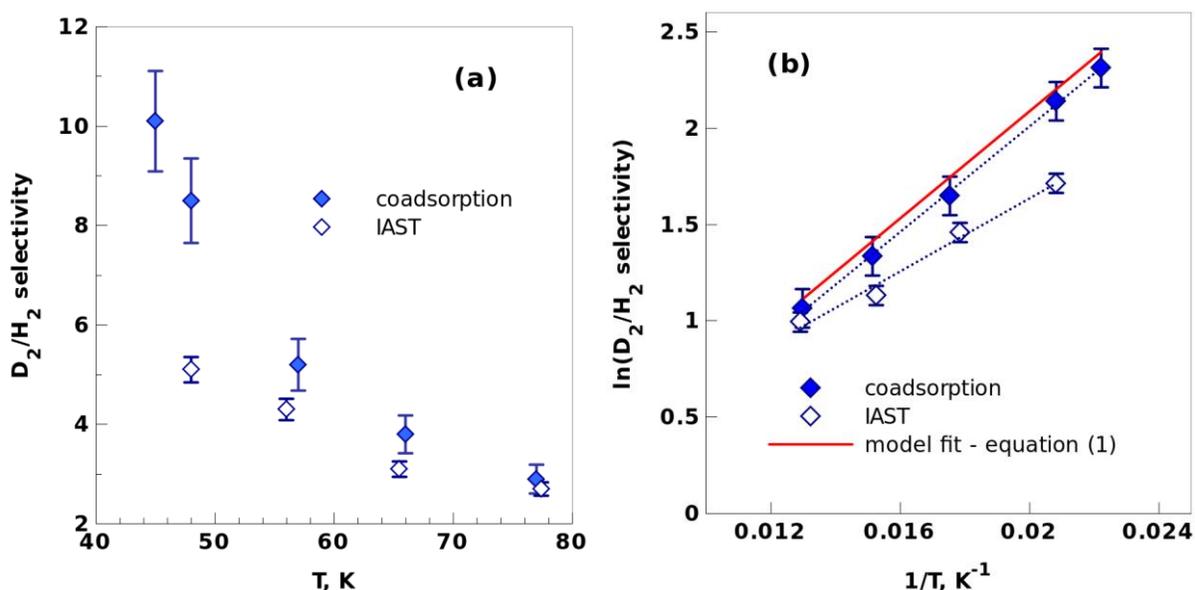


Figure 4 D_2/H_2 selectivity in NaA as a function of temperature (a) and logarithm of selectivity as a function of $1/T$ (b) (initial mixture composition - $25D_2/75H_2$). Blue dotted lines – linear regression, red full line – fit based on equation (1).

The most general description of the quantum sieving phenomenon in a one-dimensional pore suggests an exponential dependence of the selectivity extrapolated at zero pressure (S_0) on the inverse temperature⁴. It is worth noting that despite the fact that in our study the selectivities were measured at high loading (see Table S2), the exponential dependence holds (Fig.4b). Using

the model of quantum sieving based on a particle in a potential well proposed by Beenakker et al.³, the following equation can be obtained which relates pore size, molecular size and D₂/H₂ selectivity⁵:

$$\ln(S_0) = \ln \frac{m(H_2)}{m(D_2)} + \left(\frac{2\gamma_0^2 \hbar^2 (m(D_2) - m(H_2))}{(d - \sigma)^2 k_B m(H_2) m(D_2)} \right) \frac{1}{T} \quad (1)$$

where m is the mass of H₂ or D₂ molecule, γ_0 is the first zero of Bessel functions (equal to 2.4), σ is the molecule diameter, $\hbar = h/2\pi$ (h – the Planck constant), d is the pore diameter, k_B is the Boltzman constant, T is the temperature. Using the σ value for H₂ and D₂ (2.8 Å²⁰) and the aperture size for 4A zeolite (3.8 Å²¹) allows to obtain a good agreement between the calculated and the experimental values (Fig.4b). This result is rather surprising since equation (1) was derived for spherical particles placed in a one-dimensional cylindrical pore at low loading (absence of adsorbate – adsorbate interactions)³. The used zeolite contains quasi-spherical pores connected in three dimensions and the selectivity was measured at high loading (Table S2). Despite these differences the simple quantum sieving model of Beennakker et al. allows to predict the equilibrium D₂/H₂ selectivity in NaA zeolite at any temperature using only one parameter - the size of pore aperture. The same result was obtained in our previous work for Na-CHA zeolite⁵, it would therefore be useful to verify the validity of this correlation for other types of microporous materials.

Another important observation concerning the trend in Fig.4 is the increasing difference between the experimental selectivities and the IAST prediction with lowering temperature. To confirm the deviation from ideality below 77 K, we performed the co-adsorption experiments for different mixture compositions at 48 K (Fig.5). The observed trend corresponds to a strongly non-ideal behavior of the adsorbed D₂/H₂ mixture at 48 K. Similar pattern was previously observed for

different adsorbates and sorbents and it was attributed to the heterogeneous character of the solids²²⁻²⁵. Since NaA is a heterogeneous sorbent (as attested by the variation of the isosteric heat of adsorption, section 3.1.2), we consider that the same explanation of non-ideal character of adsorption is valid in the case of D₂/H₂ mixture on NaA at temperatures below 77 K.

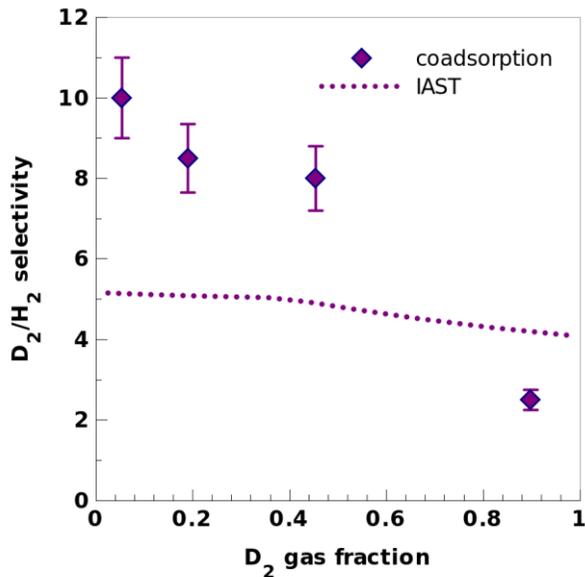


Figure 5 D₂/H₂ selectivity as a function of D₂ gas fraction in NaA (T = 48 K, P = 560 hPa).

Our explanation of non-ideal behavior of D₂/H₂ mixture by heterogeneity of NaA could appear contradictory since at 77 K it behaves as an ideal sorbent while at 48 K strongly nonideal behavior is observed. This apparent contradiction is due to the fact that the deviation from ideality is not an absolute characteristic, but decreases with increasing temperature as it was observed previously in different systems exhibiting non-ideal behavior²⁶. For D₂/H₂ adsorption on NaA the deviation from ideality below 77 K can be related to higher degree of heterogeneity of this system at lower temperature. In fact the degree of heterogeneity of an adsorbent-adsorbate couple is defined not by dispersion of the isosteric heat of adsorption (ΔQ_{iso}) but by the ratio $\Delta Q_{iso}/RT$ ²⁷. Due to this effect the degree of heterogeneity increases with lowering temperature.

This phenomenon can be illustrated for NaA-H₂ couple using the isotherm fit with the Sips model in which parameter n characterizes the degree of heterogeneity²⁷:

$$N = \frac{N_m(Kp)^{1/n}}{1+(Kp)^{1/n}} \quad (2)$$

where N – adsorbed amount, N_m – adsorbed amount at saturation, K – constant, n – heterogeneity parameter. When this model is applied to H₂ adsorption isotherm at 77 K n is equal to 1.9, while the value of 3.1 must be used to describe the isotherm at 48 K (Fig.S4). The increase of n value reflects higher degree of heterogeneity of NaA-H₂ couple at low temperature and the similar trend is observed for NaA-D₂. The molecular scale mechanism of this effect is not clear. It can stem from stronger confinement of the adsorbed molecules due to higher adsorbed amount at lower temperature: 11.8 molec.uc⁻¹ at 77 K viz. 17.7 molec.uc⁻¹ at 48 K (H₂ at 1000 hPa). Another reason can be related to the dynamic behavior of adsorbed H₂ and D₂ molecules which were shown by FTIR to move freely at 77 K but become localized below 60 K in NaA zeolite²⁸. The non-ideal behavior of D₂/H₂ mixture in NaA at low temperature brings two points which are important from a practical point of view. First, our findings show that the selectivity rises upon decrease of D₂ fraction (Fig.5). If this trend holds for lower D₂ fractions, even higher selectivity could be attained in NaA zeolite for mixtures poor in D₂ relevant for industrial applications. Second, the observed deviation from ideality in NaA means that for other heterogeneous sorbents (e.g. cation rich zeolites) the same effect is highly probable. If it is the case, IAST will not be applicable below 77 K and therefore the co-adsorption measurements will be needed for such materials in order to obtain the reliable data necessary for the industrial process design.

3.2. Adsorption properties of KNaA zeolites

3.2.1. Experiments at 77 K

Single gas adsorption. Replacement of Na^+ by K^+ in LTA leads to progressive decrease of adsorbed amounts of H_2 and D_2 at 77 K (Fig.S5 and Fig.6). It follows that the presence of 2 K^+ per unit cell (from 12 cations) is sufficient to block the access of H_2 and D_2 molecules to all α -cages. The same threshold exchange degree ($\sim 17\%$) in KNaA zeolites was reported for N_2 ²⁹ or CH_4 ³⁰ adsorption. The decrease of adsorbed amount is explained by a preferential occupation by K^+ cations of the sites located in the eight-membered oxygen rings (8MR) due to a larger size of potassium in comparison with sodium (1.38 vs. 1.02 Å³¹). Placed exclusively at these sites, two K^+ cations per unit cell occupy four of six windows (1/2 cation per window) interconnecting the α -cages in the LTA framework. Even if two windows remain open in this configuration, this number is not sufficient to achieve percolation through the porous network and to fill the pores from the gas phase³⁰.

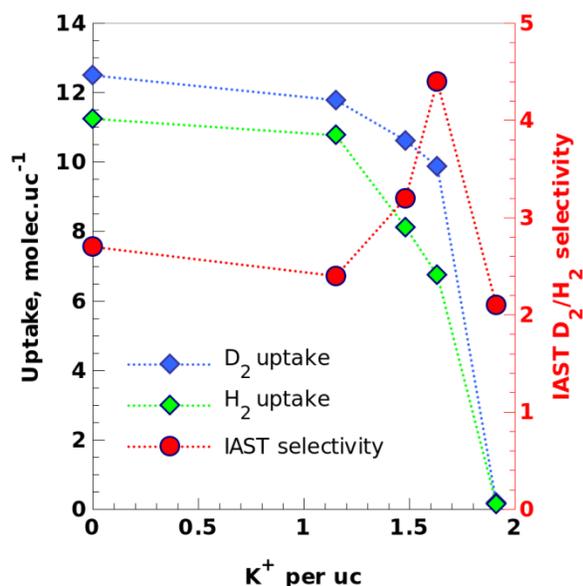


Figure 6 Variation of D_2 and H_2 uptakes and of IAST selectivity as a function of K^+ amount in KNaA zeolites ($T = 77 \text{ K}$, $P = 650 \text{ hPa}$).

To evaluate the influence of cationic composition on the D_2/H_2 selectivity, we calculated the selectivities at 650 hPa using IAST (Fig.6). It appears that, contrarily to uptake, the selectivity

does not change monotonously and for the zeolite containing 1.6 K^+ per unit cell the selectivity is significantly higher than for the other samples. To understand the origin of this effect we realized co-adsorption measurements for D_2/H_2 mixture in the solid containing 1.6 K^+ ($\text{K}_{1.6}\text{Na}_{10.4}\text{A}$).

Co-adsorption. The co-adsorption data for $\text{K}_{1.6}\text{Na}_{10.4}\text{A}$ zeolite at 77 K confirms the higher value of selectivity in this sample in comparison with NaA zeolite: under 650 hPa the selectivity of 2.9 was observed for NaA while it is equal to 4.5 for $\text{K}_{1.6}\text{Na}_{10.4}\text{A}$ (Fig.7). In addition to the increased value of selectivity at high pressure, two other features distinguish these two materials. First, the selectivity in NaA decreases with loading (see Fig.2a), whereas it remains almost constant in $\text{K}_{1.6}\text{Na}_{10.4}\text{A}$. Second, while in NaA the selectivity agrees fairly well with IAST (see Fig.2b), in $\text{K}_{1.6}\text{Na}_{10.4}\text{A}$ the behavior of D_2/H_2 mixture deviates strongly from ideality (Fig.7b). We suggest that the observed effects can be explained by the fact that at 77 K some α -cages in $\text{K}_{1.6}\text{Na}_{10.4}\text{A}$ are accessible only to D_2 molecules having smaller size than H_2 due to quantum effects.

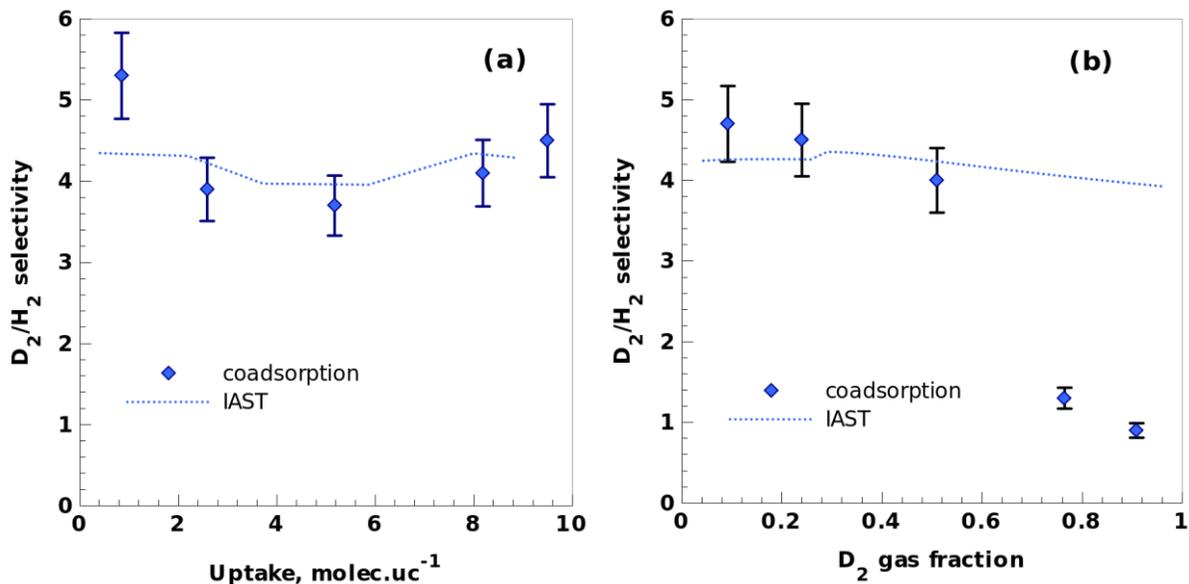


Figure 7 D_2/H_2 co-adsorption selectivity for $\text{K}_{1.6}\text{Na}_{10.4}\text{A}$ zeolite measured at 77 K as a function of total loading for 25 D_2 /75 H_2 mixture (a) and as a function of D_2 gas fraction under 650 hPa (b).

The decrease of D₂/H₂ selectivity with loading in NaA stems from its energetic origin: decrease of the adsorption enthalpy with loading results in drop of selectivity. In K_{1.6}Na_{10.4}A the adsorption enthalpy should also decrease due to similarity of their compositions, but the selectivity remains constant. This behavior suggests that in K_{1.6}Na_{10.4}A the decrease of selectivity, provoked by lower enthalpy at high loading, is compensated by another phenomenon independent of loading. Filling of some pores exclusively with D₂ molecules can be such phenomenon.

The second effect, non-ideality of D₂/H₂ mixture in K_{1.6}Na_{10.4}A, can also be related to the presence of the pores accessible only to D₂. Thus, it was shown that deviation of experimental selectivity from IAST prediction can be due to the presence of very selective sites (such as side pockets in MOR zeolites for CO₂ molecules ³²) which provoke segregation of the adsorbed phase ²⁶. In K_{1.6}Na_{10.4}A the pores accessible only to D₂ molecules may play the same role provoking segregation of D₂/H₂ adsorbed phase and consequently its nonideal behavior.

The fraction of α -cages accessible only to D₂ in K_{1.6}Na_{10.4}A can be roughly estimated by comparing the adsorbed amounts of H₂ and D₂ in NaA and K_{1.6}Na_{10.4}A at 1000 hPa (Fig.S5). It follows that in NaA the ratio between the adsorbed amounts of D₂ and H₂ is equal to 13/11.8 = 1.1. At the same pressure K_{1.6}Na_{10.4}A adsorbs 10.6 molec.uc⁻¹ of D₂ and if the same number of α -cages were accessible both to H₂ and D₂ it should have adsorbed 10.6/1.1 = 9.6 molec.uc⁻¹ of H₂. In contrast, K_{1.6}Na_{10.4}A adsorbs only 7.3 molec.uc⁻¹, that is 24 % less than expected. We suggest that this lack of adsorbed amount of H₂ corresponds to the fraction of α -cages which are inaccessible to H₂, but remain open for D₂ at 77 K.

Partial replacement of Na⁺ by larger K⁺ cations in the LTA structure should hinder the access of adsorbates into the α -cages and therefore slow down the diffusion of the adsorbates. This effect is

indeed observed in KNaA zeolites. We did not measure the diffusion coefficients, but the dynamics of adsorption can be qualitatively evaluated using the time needed to measure the single gas isotherms. Thus in NaA the measurement of complete H₂ adsorption isotherm takes 170 min, while in K_{1.6}Na_{10.4}A this time rises to 838 min. The slower diffusion in K_{1.6}Na_{10.4}A is also responsible for the need to use a longer time to achieve equilibrium in co-adsorption measurements in this zeolite than in NaA (see Fig.S2).

3.2.2. Experiments at 48 - 77 K

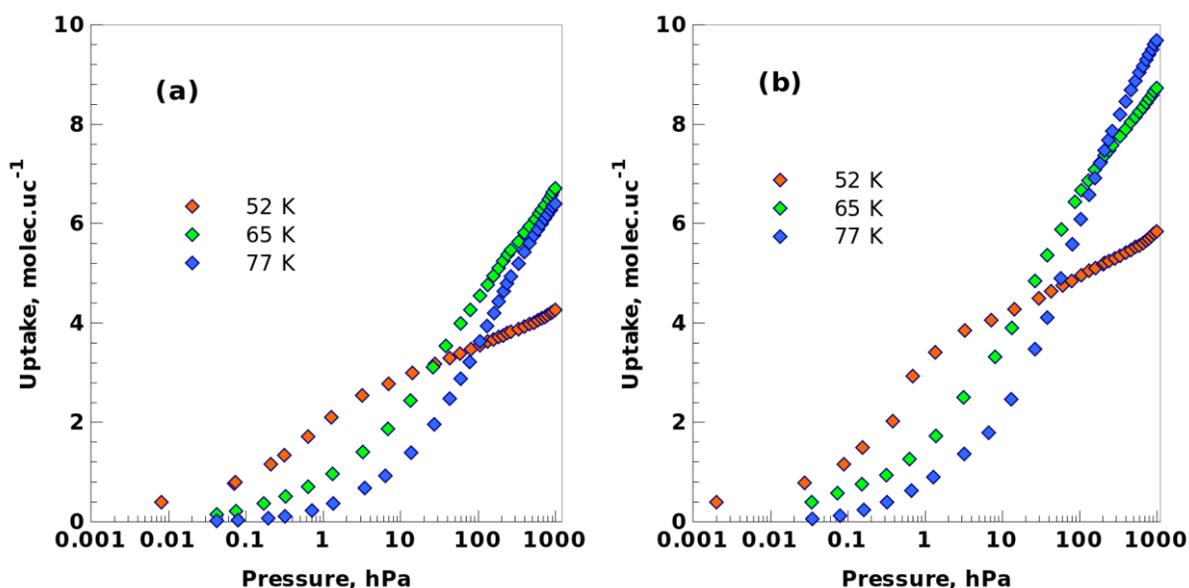


Figure 8 H₂ (a) and D₂ (b) adsorption isotherms for K_{1.6}Na_{10.4}A zeolite at different temperatures.

Single gas adsorption. The shape of the adsorption isotherms of H₂ and D₂ in K_{1.6}Na_{10.4}A changes with temperature in a complex fashion (Fig.8). In the low pressure range the adsorbed amount slightly increases with lowering temperature, but at higher pressure the opposite trend is observed. Such variation of the isotherms shape with temperature is characteristic of the zeolites showing pore closure with decreasing temperature^{33,34}. Presence of this effect in K_{1.6}Na_{10.4}A is

thus in line with the adsorption of H₂ and D₂ in KA zeolite³⁵ in which similar behavior was observed but in different temperature range: at ~ 150 K both molecules can enter the pores, while at 77 K this zeolite does not adsorb hydrogen isotopes. More generally, the phenomenon of pore closure at low temperature in cationic zeolites has been known for a long time³³. If the temperatures of pore closure for species in mixture are sufficiently different, this effect can be used for separation. Thus, variation of aperture size with temperature has been recently applied for efficient separation of CO₂/CH₄ mixture in “trapdoor” CHA zeolites^{36,37}. The origin of this phenomenon was attributed to variation with temperature of the amplitude of thermal displacement of the cations localized in the pore aperture³⁴.

Co-adsorption. The co-adsorption data for K_{1.6}Na_{10.4}A sample as a function of inverse temperature is compared with that for NaA in Fig.9a (cf. the logarithm scale of the selectivity axis). Along with the selectivity the variation of the total uptake is depicted for both samples (Fig.9b and Tables S2 and S3).

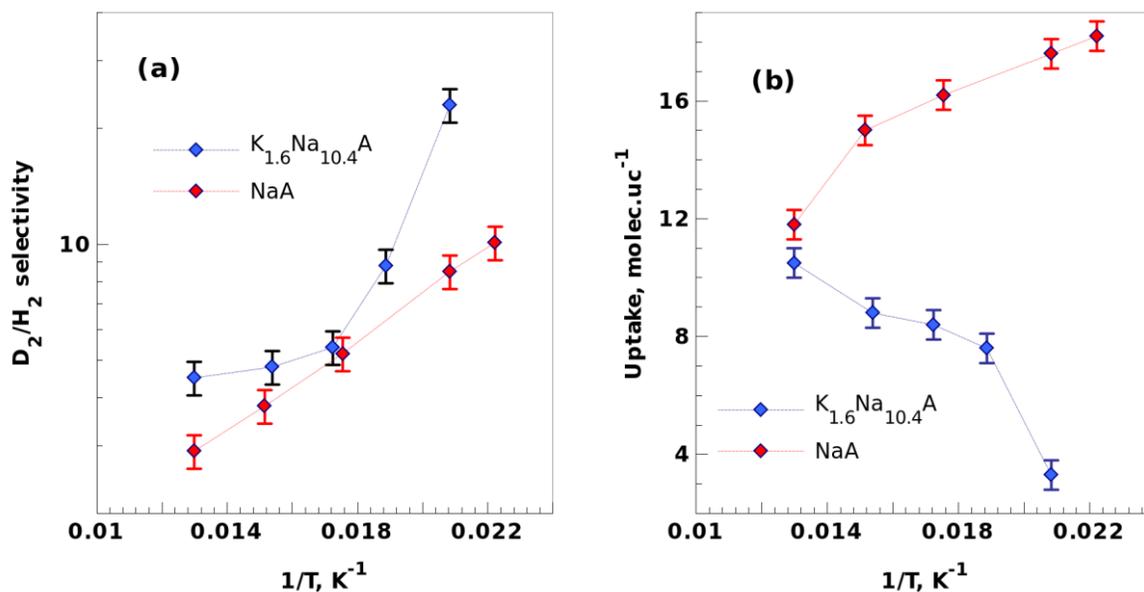


Figure 9 Variation of D₂/H₂ adsorption selectivity (a) and of mixture uptake (b) as a function of the inverse temperature for K_{1.6}Na_{10.4}A (blue) and NaA (red). Initial mixture composition: 25D₂/75H₂. The values of equilibrium pressure for each point are given in Tables S2 and S3.

Two important differences between $K_{1.6}Na_{10.4}A$ and NaA can be noticed. First, the selectivity for $K_{1.6}Na_{10.4}A$ does not follow an exponential trend as observed for NaA (Fig.9a, a linear dependence of logarithm of selectivity on the inverse temperature). A stronger increase of selectivity for $K_{1.6}Na_{10.4}A$ with the inverse temperature results in a higher selectivity at low temperature: at 48 K it equals 23.0 for $K_{1.6}Na_{10.4}A$ and 8.5 for NaA. Second, the adsorbed amount of mixture increases with the inverse temperature for NaA, while it decreases for $K_{1.6}Na_{10.4}A$ as it can be expected from the single gas adsorption isotherms (Fig.9b). As in the case of pure gases these findings can be explained by the progressive pore closure with lowering temperature which decreases the accessibility of the pores both for D_2 and H_2 . However, even at 48 K $K_{1.6}Na_{10.4}A$ contains a fraction of pores accessible only to D_2 providing higher D_2/H_2 selectivity than in NaA. From the practical point of view it can be noticed that the increase of selectivity obtained in $K_{1.6}Na_{10.4}A$ at 48 K is not a spectacular one. Thus, using the definition of selectivity, one can obtain that for a gaseous mixture 25% D_2 +75% H_2 , the increase of selectivity from 8.5 to 23.0 corresponds to the rise of D_2 fraction in the adsorbed phase from 0.739 to 0.885. It should be noted however that K^+ content in the studied zeolites was optimized at 77 K and LTA zeolites with other K^+ exchange rates can be even more efficient at lower temperatures. Another possible way to further increase the selectivity can be the use of mixed cation small pore zeolites, but of other framework types like e.g. CHA or GIS which have different shape of pore aperture.

Analysis of the single gas and co-adsorption data obtained for $K_{1.6}Na_{10.4}A$ zeolite at 48 – 77 K allows to hypothesize about the origin of the exclusive admission of D_2 to some α -cages in this material. The important fact in this context is that in $K_{1.6}Na_{10.4}A$ the pores remain open at much lower temperature than in KA zeolite. This finding can be explained by the fact that the positions

of K^+ in the 8MR windows in our material are not the same as in KA. Indeed, it is known that the exact positions of cations in 8MR windows in LTA zeolites depend on cation repulsion and therefore on composition³⁸. Thus, it was shown that in K_2Zn_5A some K^+ cations are displaced from the plane of 8MR window into the cavity creating a larger aperture than in KA zeolite³⁹. We suggest that a similar phenomenon exists in our $K_{1.6}Na_{10.4}A$ material due to the presence in each α -cage of different cations (3.2 windows are occupied by K^+ and 2.8 by Na^+). In some α -cages a particular arrangement of cations may result in displacement of K^+ cations from the “gate keeping” positions in the plane of 8MR windows towards the center of the α -cage similarly to K_2Zn_5A . Such a displacement will modify the effective size of 8MR windows making it intermediate between the sizes of D_2 and H_2 and allowing thus the exclusive access of D_2 molecules.

4. Conclusions

Using the single gas and binary mixture adsorption we showed that partial substitution of Na^+ by K^+ in LTA zeolite strongly impacts the properties of the zeolite in D_2/H_2 separation. Increase of K/Na ratio results in progressive decrease of the adsorbed amounts both for H_2 and D_2 , but not to the same extent. Due to this effect the D_2/H_2 selectivity rises with K/Na ratio achieving at 77 K the maximum value for the material having the composition $K_{1.6}Na_{10.4}A$. For this zeolite the selectivity is equal to 4.5 while it is 2.9 for NaA (650 hPa, 25 D_2 /75 H_2). At 77 K the IAST describes fairly well the adsorption of D_2/H_2 mixture in NaA zeolite, but a strong non-ideality is observed in $K_{1.6}Na_{10.4}A$.

The detailed co-adsorption study between 48 and 77 K showed that at low temperature both in NaA and $K_{1.6}Na_{10.4}A$ the adsorption deviates from ideal behavior. As expected, the adsorbed

amounts in NaA increase with the inverse temperature, while they decrease in $K_{1.6}Na_{10.4}A$ due to progressive pore closure. In NaA the rise of D_2/H_2 selectivity with the inverse temperature can be described by a simple quantum sieving model, but it is not the case for $K_{1.6}Na_{10.4}A$ for which the selectivity rise is steeper than for NaA. Due to this effect at 48 K the D_2/H_2 selectivity of 23.0 is attained in $K_{1.6}Na_{10.4}A$ whereas the value of 8.5 is obtained in NaA. This increase of selectivity is however achieved at the price of lower adsorbed amount in similar pressure range: 10.3 mmol.g^{-1} for NaA ($P = 574 \text{ hPa}$) and 1.9 mmol.g^{-1} for $K_{1.6}Na_{10.4}A$ ($P = 648 \text{ hPa}$). The particular behavior of $K_{1.6}Na_{10.4}A$ revealed in our work is explained by the fact that in this zeolite a fraction of α -cages is accessible only to D_2 molecules through 8MR windows partially blocked by K^+ cations.

Associated content

Supporting information

The Supporting Information is available free of charge at:

Description of IAST calculations; SEM image of NaA zeolite; amounts of KCl and NaCl used for preparation of different KNaA zeolites; amounts adsorbed, selectivities, and equilibrium pressures for D_2/H_2 mixtures at different temperatures in NaA and $K_{1.6}Na_{10.4}A$ zeolites; variation of selectivity as a function of contact time for NaA and $K_{1.6}Na_{10.4}A$ zeolites; H_2 and D_2 adsorption isotherms for NaA at different temperatures; Sips fits of H_2 isotherms in NaA at 77 and 48 K; H_2 and D_2 adsorption isotherms at 77 K for KNaA for different K/Na ratios.

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TOC graphics

Properties of NaA and $K_{1.6}Na_{10.4}A$ in D_2/H_2 separation

