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D₂ and H₂ adsorption capacity and selectivity in CHA zeolites: effect of Si/Al ratio, cationic composition and temperature

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Abstract

The work deals with the effect of composition of CHA zeolites on the adsorption and separation of H₂ and D₂ under cryogenic temperatures. In the first part of this work the effect of Si/Al ratio and cationic composition on single gas adsorption of H₂ and D₂ was studied at 77.4 K. It was found that the adsorption capacities increase with Al content up to Si/Al = 2.1. Unexpectedly, Na-CHA zeolite with the highest Al content (Si/Al = 1.1) adsorbs only negligible amount because of the collapse of the zeolite structure upon dehydration at 400°C. The Na- and Li-containing chabazites with Si/Al = 2.1 possess similar adsorption capacities. In contrast, progressive replacement of Na⁺ with K⁺ results at 77.4 K in decreasing H₂ and D₂ adsorbed amount which becomes negligible for K⁺ content higher than ~ 60 mol. %. In the second part of the work the D₂/H₂ thermodynamic selectivity for Na-, Li- and K-Na chabazites (Si/Al = 2.1) was measured using coadsorption technique at 40 – 77.4 K in the pressure range 530 - 650 hPa corresponding to high loading. The cationic composition is found to have only minor effect on the D₂/H₂ selectivity which increases exponentially with lowering temperature. For example in Na_{3.9}Al_{3.9}Si_{8.1}O₂₄ chabazite it rises from 2.6 at 77.4 K to 13 at 40 K. It is found that variation of D₂/H₂ selectivity with temperature is in a fair agreement with a simple quantum sieving model making use of the aperture size of the chabazite cavity as a unique adjustable parameter.

Keywords: H₂-D₂ coadsorption, H₂-D₂ separation, isotope quantum sieving, chabazite

1. Introduction

Chabazite type zeolites (CHA framework) present interesting structural features making them promising in catalytic and separation applications [1]. CHA type belongs to the group of zeolites whose framework structure can be described by an arrangement of hexagonal rings [2]. In the case of CHA the rings are stacked in AABBC sequence forming a tridimensional structure with cylindrically shaped cavities ($\sim 8 \times 11 \text{ \AA}$) connected through eight-membered oxygen rings (8MR). Interestingly, the Si/Al ratio in chabazite can be varied in a wide range from purely silica material [3] to Si/Al = 1 [4]. In Al rich chabazites the cations occupy different positions, including those in the 8MR windows which separate the cavities. Presence of cations in these sites allows to adjust the adsorption properties through variation of Si/Al ratio and of the nature of cation. Due to these important features CHA materials were studied for different separations involving small molecules [5]. Recently it has been shown that K^+ and Cs^+ exchanged chabazites exhibit special “trapdoor” behavior allowing efficient gas separation [6,7] or encapsulation [8].

Given these properties, CHA zeolites could be interesting candidates for the hydrogen isotopes separation by “quantum sieving” [9]. This approach is based [10] on the difference of zero point energies of the molecules placed in the pores whose size is comparable with the molecular size of hydrogen ($\sim 2.8 \text{ \AA}$ [11]). The aperture size in CHA framework ($\sim 3.8 \text{ \AA}$) makes these zeolites potentially suitable for such separation. Moreover, the high cation content in Al rich materials may allow to achieve high adsorption capacities which are crucial for industrial scale applications. Surprisingly, while numerous studies were realized in this field involving other zeolite types like LTA [12-14], FAU [12,15,16] or MOR [17,18], the chabazites have not been studied for this application to date.

The objective of the present study is to fill this gap by characterizing adsorption of D_2 and H_2 and measuring the D_2/H_2 selectivity of CHA materials as a function of their composition and temperature. First, the single gas adsorption of D_2 and H_2 was measured at 77.4 K on pure silica and

Na-containing chabazites having different Si/Al ratio. Then, for the materials with Si/Al = 2.1 the mixed K-Na and Li-containing zeolites were studied under the same conditions. Based on the obtained data, Na, K-Na and Li exchanged chabazites with Si/Al = 2.1 were chosen for the measurements of D₂/H₂ selectivity between 40 and 77.4 K using co-adsorption technique.

2. Experimental

2.1 Materials synthesis

KOH, NaCl and LiCl were purchased from ROTH. Zeolite HY (Si/Al = 2.55) used for chabazite synthesis was provided by Alfa Aesar (ref. 45866). Aluminum hydroxide was purchased from Sigma-Aldrich (ref. 239186). It contained 60 wt.% of Al₂O₃ as determined by TGA. Chabazite with Si/Al ratio of 13 was kindly provided by F. Batllo from Nalco Water (Naperville, USA) and the pure silica material by J. Patarin from IS2M laboratory (Mulhouse, France).

CHA zeolite with Si/Al ~ 2 was prepared from zeolite Y according to the known procedure [19]: 8.8 g of KOH was dissolved in 110 mL of deionized water and 12.5 g of zeolite Y was added to the solution. The suspension was placed in polypropylene bottle of 250 mL, shaken for 30 s and placed in an oven at 368 K for 10 days. The obtained product was hot filtered, thoroughly washed with water and dried at 363 K overnight and then stored in ambient air.

The synthesized potassium chabazite was used as a starting material to prepare other cationic compositions. To obtain mixed K-Na materials a partial exchange with NaCl was used. The needed amount of NaCl was dissolved in 5 mL of water to which 0.5 g of chabazite was added. After 24h hours of stirring under ambient temperature (~ 295 K) the solid was separated by centrifugation and washed with water. The fully Na exchanged material was prepared by exchange in 1M NaCl solution under ambient temperature. 50:1 solution to solid ratio was used and five exchanges of 8 to 15 h were realized. In the case of Li higher concentration of LiCl (10 M) and 10:1 ratio were employed with other parameters being the same as for Na exchange.

To obtain the zeolites with Si/Al ratio close to one, the procedure similar to the previously published one was used [4]: 3.72 g of NaOH was dissolved in 24 mL of deionized water and 4.13 g of aluminum hydroxide was added to the solution. This suspension was mixed with 8.93 g of Na exchanged CHA (Si/Al = 2.1) in a round bottom flask which was equipped with an overhead stirrer and heated in an oil bath at 347 K. After heating for 72h the solid was filtered, washed with water and dried at 363 K.

2.2 Materials characterization

The chemical composition of the solids was determined by energy dispersion spectroscopy (EDS) using scanning electron microscope JEOL 7600F. The powdered samples were pressed and some pieces of the obtained pellets were deposited on a carbon tape covering the sample support. Analysis of the pressed powder allowed to avoid interfering EDS signal of the sodium present in the carbon tape. In order to obtain a representative bulk composition of the sample, a large area was chosen (500 x 500 μm^2) and different zones (up to 10) were analyzed inside this area. *Before each analysis the EDS detector was calibrated using the internal standards.* Li cannot be detected by EDS, its content was therefore calculated from the difference between the Al amount and that of the other cations.

XRD patterns of the solids were recorded 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.

N₂ adsorption isotherms at 77.4 K were measured using ASAP2020 setup from Micromeritics. Pore volumes corresponding to the interparticle condensation were calculated using the BJH method.

²⁹Si MAS NMR spectra were recorded at room temperature on a Bruker S3Advance II 300 MHz spectrometer, with a double-channel 7 mm Bruker MAS probe. The recording conditions were the following: frequency = 59.6 MHz, pulse width = 2.3 μs , flip angle = $\pi/6$, recycle time = 80 s, spinning rate = 4 kHz, scan number = 1000.

2.3 Single gas adsorption measurements at 77.4 K

The single gas adsorption isotherms were measured by means of ASAP 2020 sorptometer from Micromeritics using liquid nitrogen to control the temperature. The samples were degassed under secondary vacuum at 673 K for 16 h before the measurements. H₂ and D₂ gases used for these measurements were purchased from Air Liquide (France) and were additionally dried using zeolite filled cartridges from Agilent. The same gases were used for the coadsorption experiments.

2.4 Coadsorption measurements

For coadsorption measurements the home built manometric setup described in detail in our previous work was used [16]. The temperature was maintained using a Gifford – McMahon He cryocooler from Micromeritics. In addition to the temperature measurement integrated in the cryostat, a silicon diode (DT-470 from Lake Shore Cryotronics) was placed directly on the measurement cell wall using the Kapton tape. It was found that the temperature measured on the cell wall was higher than the set point temperature by 1 – 5 K depending on the temperature range. In the present work the temperature measured by the diode was used as a reference temperature. During the coadsorption measurements the cooled cavity of the cryostat in which the cell was placed was continuously purged with He.

The measurements were realized as follows. The sample was degassed under secondary vacuum at 673 K for 16 h, cooled to the room temperature and placed into the cryostat at 90 K under dynamic vacuum. When the the desired temperature has been reached (~ 3 h for 65 K and ~ 16 h for 40 K) the co-adsorption experiment was performed according to the following procedure. First, the sample cell was isolated from the calibrated manifold volume which was filled with 25%D₂ + 75%H₂ mixture by controlling the partial pressure of each gas. This initial mixture was equilibrated for one hour which was found to be necessary for obtaining a homogeneous mixture of H₂ and D₂. After homogenization time, the valve between the sample cell and the manifold volume was opened and

the sample was kept in contact with the mixture until achieving equilibrium.

To determine the time necessary to achieve the equilibrium additional experiments have been realized in which the selectivity was determined after different contact times (Fig. S1). This data shows that in the pressure range used in the present study (530 – 650 hPa) the equilibrium selectivity is attained only after ~ 16 h of contact between the gaseous mixture and zeolite. Based on these experiments we used this contact time in all coadsorption measurements.

At the end of the equilibration period the valve between sample cell and the manifold volume was closed. Then, the adsorption capacity and selectivity were determined from a mass balance performed with the total pressure and the composition of the gas phase before and after adsorption. The gas mixture composition at equilibrium was determined with a mass spectrometer (Omnistar from Pfeiffer Vacuum) from the ratio of the surface areas of peaks with $m/e = 2$ and 4. To determine from this data the ratio of partial pressures of H_2 and D_2 , the mass spectrometer should be calibrated. We found that reproducible results can be obtained only if the calibration is done after each measurement. Therefore after the analysis of the equilibrium mixture, the manifold volume was evacuated and filled with a fresh 25% D_2 + 75% H_2 mixture, which was then equilibrated for 1 h and analyzed. The response coefficient between ratio of the pressures and ratio of the peak areas thus measured was used to calculate the composition of the gas mixture obtained at the coadsorption equilibrium. Once all these measurements had been done, the cryostat was replaced by a heating mantle, the sample was degassed at 673 K for 2 h and the described procedure was repeated again for another temperature.

In addition to a long equilibrium time, another important effect must be taken into account when measuring selectivity at low temperature: the thermal diffusion [20]. This phenomenon produces the separation of two gases due to the temperature gradient existing between the manifold volume (at room temperature, ~ 295 K) and the sample cell (< 77 K). The thermal diffusion results in the enrichment of the cold volume with heavier species. In our case this phenomenon was quantified

using blank experiments performed in the same operation conditions (including the contact time of 16 h) but without any adsorbent. The selectivity thus obtained is due to the thermal diffusion and it can be expressed in the following way:

$$S_{TD} = \frac{y(D_2)_{cold} \cdot y(H_2)_{hot}}{y(D_2)_{hot} \cdot y(H_2)_{cold}} \quad (1)$$

where $y(i)_{cold}$ and $y(i)_{hot}$ are the mole fractions of component i in the hot manifold volume and cold sample volume. We have found that in our setup the thermal diffusion selectivity is equal to 1.14 ± 0.05 when averaged over the used range of pressure and temperature.

The effect of D_2/H_2 separation through the thermal diffusion should be subtracted from the values obtained with a sorbent in order to obtain the true selectivity values related only to the adsorption-based separation. This was done using the following procedure. The molar fractions of H_2 and D_2 measured in the hot manifold volume ($y(D_2)_{hot}$ and $y(H_2)_{hot}$) were corrected in order to obtain the values existing in the cold sample cell ($y(D_2)_{cold}$ and $y(H_2)_{cold}$) by using the value of the measured selectivity of the thermal diffusion (S_{TD}). This can be done using equations (2) and (3) derived from the definition of S_{TD} and taking into account that both for cold and hot volume $y(H_2) + y(D_2) = 1$:

$$y(D_2)_{cold} = \frac{S_{TD} \cdot y(D_2)_{hot}}{1 - y(D_2)_{hot} + S_{TD} \cdot y(D_2)_{hot}} \quad (2)$$

$$y(H_2)_{cold} = 1 - y(D_2)_{cold} \quad (3)$$

These corrected values of H_2 and D_2 fractions were then used to calculate the adsorbed amount of each species and the corrected adsorption selectivity (equation 4):

$$S = \frac{x(D_2) \cdot y(H_2)_{cold}}{y(D_2)_{cold} \cdot x(H_2)} \quad (4)$$

where $x(i)$ is the molar fraction of component i in the adsorbed phase.

All experimental values of D_2/H_2 selectivity reported in the present study are the corrected values calculated in this way. Using repeated measurements we estimated that the relative standard error of the selectivity value is equal to 10%.

3. Results and discussion

3.1 Solids characterization

The composition of the prepared solids is given in Table 1. While the routine EDS analysis is not well adapted for elemental analysis of powders, the special care taken in our study allowed to obtain accurate results representative of the bulk samples (see section 2.2). It is important to note also that the used cation exchange procedures do not provoke formation of mesopores as follows from the comparison of the N₂ adsorption-desorption isotherms (Fig. S2). At low P/P⁰ the isotherms of Li_r2 and Na_r2 are different from that of K_r2, due to the absence of micropore filling in the latter. In contrast, at high P/P⁰ the shape of the isotherms is similar and it is characteristic of the interparticle condensation with the corresponding volumes being close: 0.1 cm³/g for K_r2 and 0.08 cm³/g for Na_r2 and Li_r2.

The appearance of the XRD patterns of the prepared zeolites (Fig.S3) are slightly different for low silica (Si/Al = 2.1) and high silica (Si/Al > 2.1) materials. For the low silica zeolites the maxima are broader, indicating their lower crystallinity, and the relative intensity of 101 peak ($2\theta = 9.5^\circ$) is smaller than that of 401 ($2\theta = 30.8^\circ$). In contrast, in high silica samples (Na_r13 and CHA-Si) 101 peak is much more intense than 401 peak. Despite these differences, all observed peaks in these materials can be indexed in the rhombohedral cell characteristic of CHA structure (Table 1). It follows however from this data that the cell parameters are strongly influenced by the solid composition: the values of a and of the cell volume decrease with the cation size (for Si/Al = 2.1) and with Al content.

The XRD pattern of CHA with Si/Al ratio of 1.1 is different from that of the materials with the ratio 2.1 (Fig.1A). It contains additional maxima ($2\theta = 17.0, 23.9, 29.6, 34.9$) and the observed peaks cannot be indexed in the rhombohedral cell used for other zeolites. These differences have already been described in the article of Thrush et al. [4] and to the best of our knowledge no structural information or even XRD pattern indexation has been reported for this material. This fact makes the

XRD pattern insufficient for conclusion about the formation of a single phase CHA material with the framework Si/Al ratio of 1.1. To obtain additional information on this point we measured ^{29}Si MAS NMR spectra of Na_r2 and Na_r1 samples (Fig.1B). The spectrum of the parent solid having Si/Al ratio of 2.1 (Na_r2) contains five peaks (-88.24, -92.57, -98.01, -103.53 and -108.40 ppm) which correspond to Si atoms surrounded by different number of Al atoms in the framework from $\text{Q}^4(4\text{Al})$ to $\text{Q}^4(0\text{Al})$ [4]. In contrast, the spectrum of Na_r1 sample contains only one intense peak whose shift (-85.9 ppm) is characteristic of $\text{Q}^4(4\text{Al})$ configuration [4, 21] proving formation of the solid with the framework Si/Al ratio close to unity.

3.2 Effect of Si/Al ratio in CHA zeolites on D_2 and H_2 adsorption at 77.4K

The isotherms of H_2 and D_2 adsorption at 77.4 K on pure silica and different Na – containing chabazites are displayed in Fig.2. It shows that both the affinity and the maximum amount adsorbed increase with decreasing Si/Al ratio down to Si/Al = 2.1. This effect is clearly due to the presence of cations strongly interacting with H_2 and D_2 molecules. The similar behavior has been observed in our previous work for FAU type zeolites [16]. It should be noticed however that in CHA framework this trend does not hold for the solid with Si/Al = 1.1 which adsorbs very small amount of H_2 and D_2 . This fact is rather unexpected given that Na-containing LTA zeolite (4A), which also contains 8MR windows occupied by Na^+ cations, adsorbs significant amount of H_2 and D_2 at 77.4 K [22]. We supposed that such behavior of Na_r1 sample is due to deterioration of its porous structure during degassing at 673 K. The XRD pattern of this solid recorded after the activation (Fig. S4) confirms this hypothesis. It shows the transformation of the CHA structure into a mixture of an amorphous phase and a sodalite type phase [23]. Given this result, Na_r1 sample was excluded from the further study.

The D_2 and H_2 adsorption isotherms were used to estimate by IAST the D_2/H_2 selectivity at 77.4 K as a function of Si/Al ratio (Fig.3). The highest selectivity is observed for Na_r2 sample having the

lowest Si/Al ratio similarly to the trend previously observed for FAU zeolites [16]. Due to this property and to their higher adsorption capacity the zeolites with Si/Al = 2.1 were chosen to study the effect of cationic composition on adsorption capacity and D₂/H₂ selectivity.

3.3 Effect of cationic composition of CHA zeolites (Si/Al = 2.1) on H₂ and D₂ adsorption at 77.4 K

The potassium-containing CHA with Si/Al ratio 2.1 (K_r2) does not adsorb H₂ or D₂ at 77.4 K and the same effect was reported for 3A zeolite (K – exchanged LTA) in which K⁺ occupies 8MR windows [24]. The exact reason for this effect is not clear. The size of H₂ molecule is about 2.8 Å [11] and it should be able to pass through the aperture of 3 Å. However this value was determined at the room temperature and at 77.4 K it should be slightly smaller. This decrease may thus make impossible the passage of H₂ and D₂ molecules through 8MR windows occupied by K⁺.

The partial exchange of K⁺ by Na⁺ allows to adjust the molecular sieving properties of LTA zeolites and thus to obtain high selectivity in N₂/CO₂ separation [25]. Therefore we tried the same approach and studied the properties of mixed K-Na chabazites with Si/Al = 2.1 in adsorption of H₂ and D₂. The single gas adsorption isotherms presented in Fig. 4 show that the maximum adsorbed amounts decline with potassium content. The threshold value seems to be close to two K⁺ per unit cell above which no adsorption is observed. Given that K⁺ cations occupy preferentially the positions in 8MR in CHA framework [26, 27], at this exchange degree four out of six windows in CHA supercage should be occupied by potassium cations. Even if two windows remain open in these conditions, the connectivity between the supercages is no longer sufficient to fill them from the exterior (this phenomenon is known as the percolation threshold [28]). In contrast to amounts adsorbed, the D₂/H₂ selectivity at 77.4 K estimated by IAST is only slightly influenced by the amount of K⁺: the values obtained both for low and high pressure range are close to two for all materials (Fig. 5).

Replacement of Na⁺ with Li⁺ has no significant effect on the maximum amount adsorbed for H₂ and D₂ (Fig.4). In contrast, the initial part of the adsorption isotherms is strongly influenced by the

nature of cation in this case. For Li-exchanged sample the initial slope of the isotherm (the Henry constant) is much larger pointing to stronger interactions with guest molecules (Fig.6). Thus for H₂ adsorption the Henry constant in Na_r2 is equal to 0.45 molec.uc⁻¹.hPa⁻¹ while for Li_r2 it is 35 molec.uc⁻¹.hPa⁻¹. This increase for Li_r2 sample can be attributed to smaller radius of Li⁺ (0.76 Å) in comparison with Na⁺ (1.02 Å) [29]. This difference brings two features in the Li-containing zeolites: i) the molecule – cation distance is shorter and ii) the induced dipole moment in the adsorbed molecule is larger due to higher polarization ability of Li⁺ [30]. Both these effects provide much stronger cation-guest interactions for Li-containing zeolite and result in higher D₂/H₂ selectivity at low loading. Thus at 77.4 K and loading of 1 molec.uc⁻¹ the selectivity is equal to 4.3 for Li_r2 sample while its value is 2 for Na_r2. The observed increase of the selectivity with the interaction strength seems to be a general phenomenon for different porous materials. Thus it was observed in Li- and Mg-exchanged FAU zeolites [16] and also in MOFs materials containing coordinatively unsaturated cations (CUS) strongly interacting with H₂ and D₂ molecules like MOF-74 [31, 32] or Cu(I)-MFU-4l [33] .

According to the quantum sieving models [34], temperature is the key parameter for high D₂/H₂ selectivity. That is why in the next part of our study we used the coadsorption technique to measure the adsorption selectivity of Na_r2, Li_r2 and NaK_r2 (1.9) samples between 40 and 77.4 K.

3.4 D₂/H₂ selectivities of CHA zeolites (Si/Al = 2.1) as a function of temperature

The selectivities of different exchanged chabazites measured by coadsorption of 25D₂/75H₂ mixture are presented in Fig.7A. As temperature decreases the selectivity rises attaining at 40 K the value of 13 for the sodium exchanged chabazite. This value is rather high in comparison with other materials characterized in similar temperature range. Indeed it is higher than that reported for 5A zeolite (5 at 40 K and 50 hPa [35]) and it is comparable to the best selectivities recorded previously for MOF materials. Thus for MIL-53(Al) at 40 K the value of 13.6 has recently been reported [36] or 12 at 60

K in MOF-74(Co) [31]. It should be noticed however that the values reported for MOFs were measured at low pressure and thus at low loading (e.g. 2.9 mmol.g⁻¹ for MIL-53(Al) [36]). In contrast, the selectivities obtained in our study were measured at high loadings: the selectivity for Na-CHA at 40 K was obtained at 12 mmol.g⁻¹ (P_{eq} = 536 hPa). Given that industrial separations are realized at high loadings, our data show that chabazites and possibly other small pore zeolites are promising candidates for separation of H₂-D₂ mixtures on a large scale.

The general quantum sieving model suggests an exponential dependence of D₂/H₂ selectivity on the inverse temperature [34]:

$$S_0 = \frac{m_2}{m_1} \exp\left(\frac{E_2 - E_1}{k_B T}\right) \quad (5)$$

where S_0 is the zero pressure selectivity, m_i is the molecular mass of component i , E_i is the ground state energy of component i , k_B is the Boltzmann constant and T is the absolute temperature. Despite the fact that in our study the selectivities were measured at high loading, the exponential dependence is also observed since for all three zeolites the logarithm of selectivity changes linearly as a function of $1/T$ (Fig. 7B).

The obtained data was further used to check if the observed variation of selectivity can be predicted using some structural parameters of the studied zeolites. In order to do so, the values of the ground state energies (E_i) entering equation (5) should be related to some structural properties of the solid. The simplest model allowing to obtain such relationship was proposed by Beenaker et al. [11] and it is based on a particle in an infinite potential well. Combining the expression for E_i obtained for this model with equation (5) one obtains:

$$\ln(S_0) = \ln\left(\frac{m(H_2)}{m(D_2)}\right) + \left(\frac{2\gamma^2 \hbar^2 \Delta m}{(d-\sigma)^2 k_B m(H_2) m(D_2)}\right) \frac{1}{T} \quad (6)$$

where m is the mass of H₂ or D₂ molecule, γ is the constant equal to 2.4, σ is the molecule diameter, k_B is the Boltzmann constant, $\hbar = h/2\pi$ (h – Planck constant), d is the well diameter. While

σ value for H₂ and D₂ is known (~ 2.8 Å [11]), the choice of d value is ambiguous since for CHA structure one can apply either the aperture size (3.8 Å) or one of the dimensions of the supercage (8 x 11 Å). Comparison between our data and the model fits based on two different d values (3.8 and 8 Å) (Fig.7b) shows clearly that the use of the aperture size gives a much better agreement with the experimental points. Given the extreme simplicity of the model, the agreement is rather surprising and it suggests a simple approach for estimating the achievable D₂/H₂ selectivity at different temperatures for other porous materials using only the size of the pore aperture.

4. Conclusions

In the first part of this study the single gas adsorption isotherms of H₂ and D₂ were measured in CHA zeolites as a function of material composition at 77.4 K. It was shown that adsorption capacity increases strongly with Al content up to Si/Al = 2.1. In contrast, the Na-exchanged chabazite with higher Al content (Si/Al ratio of 1.1) show only very small adsorption capacity because of the structure collapse after activation in vacuum at 673 K. In the second part of the work the D₂/H₂ equilibrium selectivity was measured by coadsorption in CHA zeolites with Si/Al = 2.1 in a wide temperature range (40 – 77.4 K). As predicted by quantum sieving models, the selectivity exponentially increases with lowering temperature. Moreover, we found that its evolution can be predicted with fair precision using only one parameter - the aperture size of CHA framework. The maximum value of D₂/H₂ selectivity in our study was obtained for Na_{3.9}Al_{3.9}Si_{8.1}O₂₄ chabazite at 40 K and it is equal to 13. It is worth noting that this value is obtained at a rather high loading of 12 mmol.g⁻¹ and it suggests thus a good potential of small pore zeolites for cryogenic separation of D₂/H₂ mixtures.

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Figure captions

Figure 1 XRD patterns (A) and ^{29}Si NMR spectra (B) of Na_r1 (a) and Na_r2 (b) chabazites.

Figure 2: Adsorption isotherms at 77.4 K of H_2 (A) and D_2 (B) for chabazites with different Si/Al ratio.

Figure 3: D_2/H_2 (25/75) selectivity at 77.4 K calculated by IAST at 10 hPa (blue) and 800 hPa (red).

Figure 4 Adsorption isotherms at 77.4 K of H_2 (A) and D_2 (B) for chabazites with Si/Al = 2.1 and different cationic composition.

Figure 5 Uptake of H_2 and D_2 at 77.4 K (top panel) and D_2/H_2 selectivity estimated by IAST (bottom panel) as a function of number of K^+ cations in the unit cell of the chabazite $\text{K}_x\text{Na}_{3.9-x}\text{Al}_{3.9}\text{Si}_{8.1}\text{O}_{24}$ (lines are guides for eye).

Figure 6 Low pressure range of H_2 isotherms measured at 77.4 K for Na_r2 and Li_r2 samples (lines are guides for eye).

Figure 7 D_2/H_2 (25/75) coadsorption selectivity for chabazites with Si/Al = 2.1 as a function of temperature (A) and logarithm of selectivity vs. $1/T$ (B). Straight lines in plot (B) correspond to the model fits with different d values (see text for details).

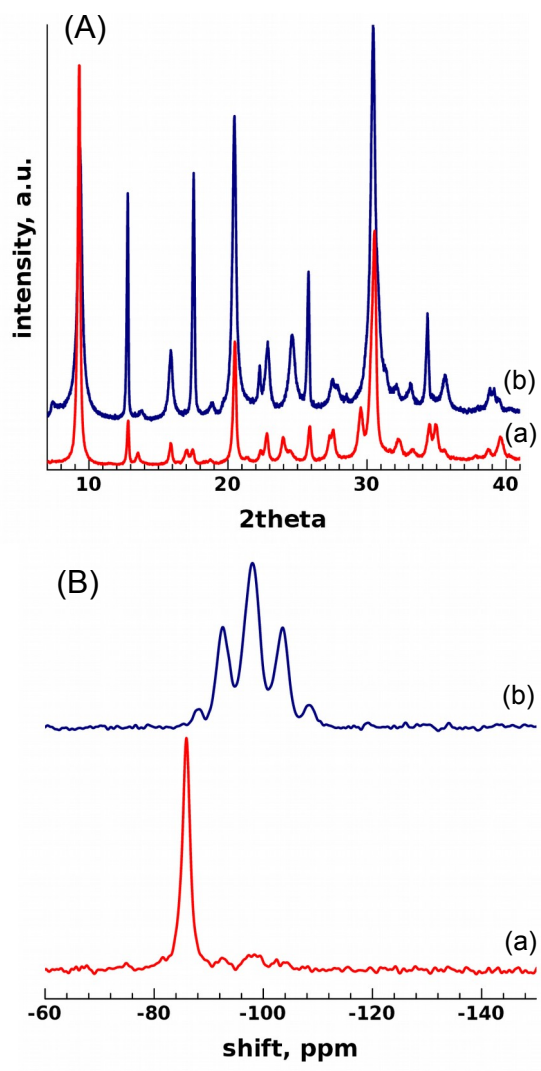


Figure 1

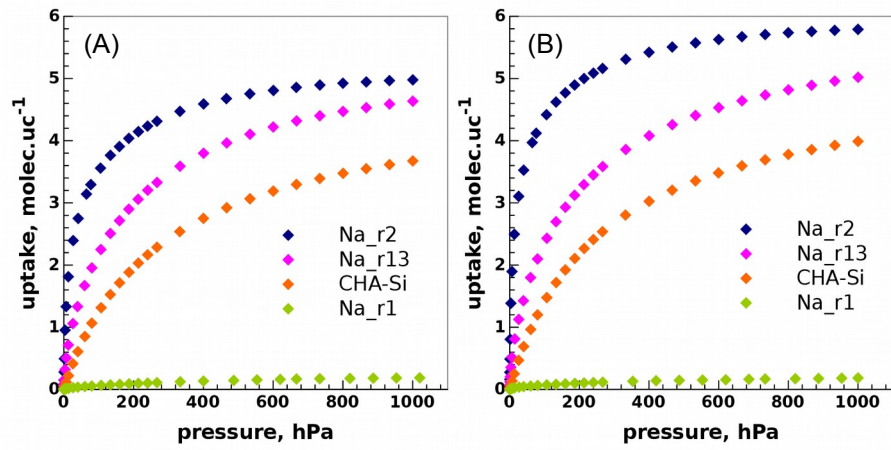


Figure 2

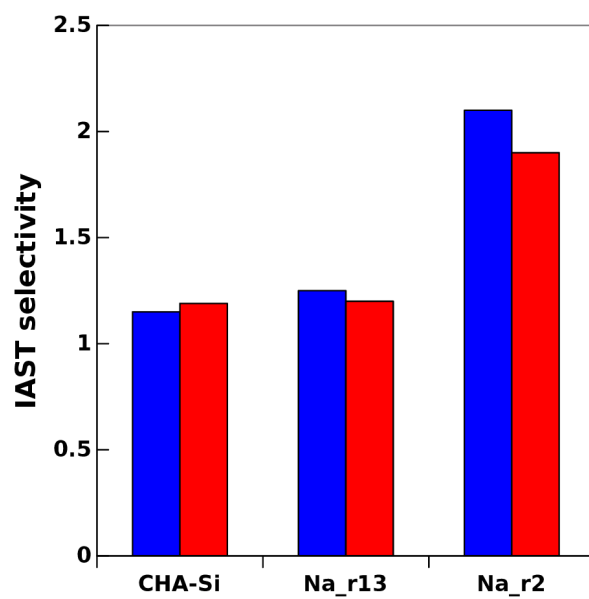


Figure 3

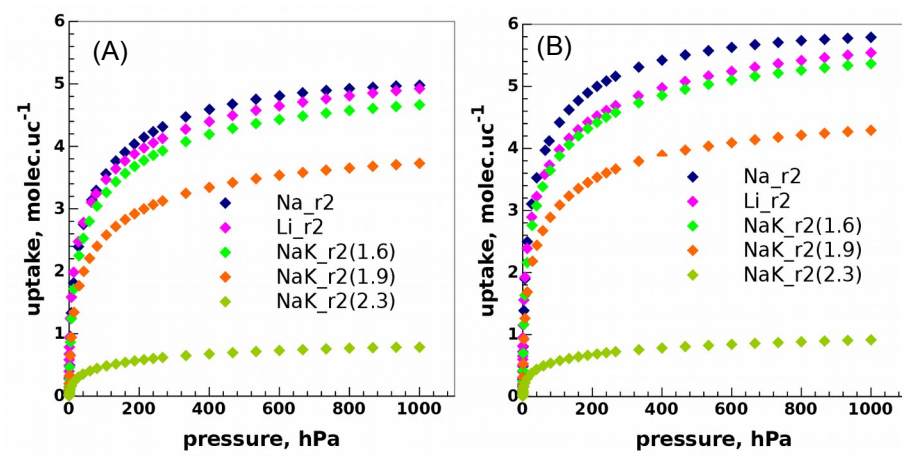


Figure 4

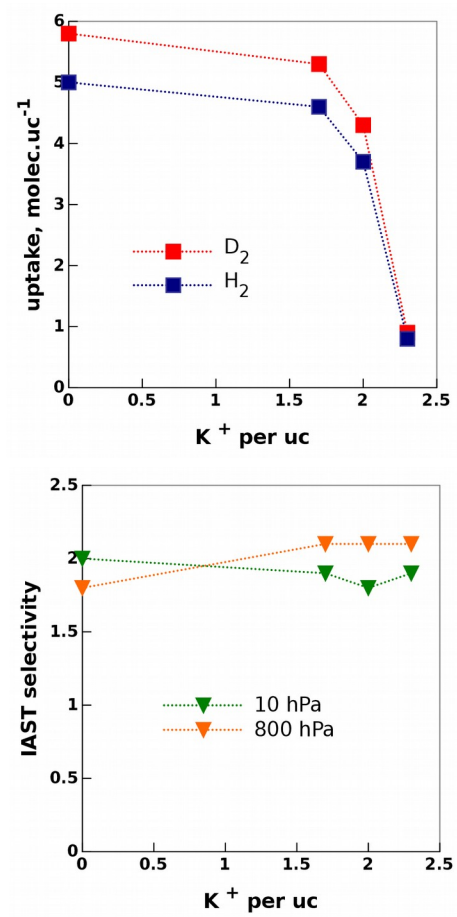


Figure 5

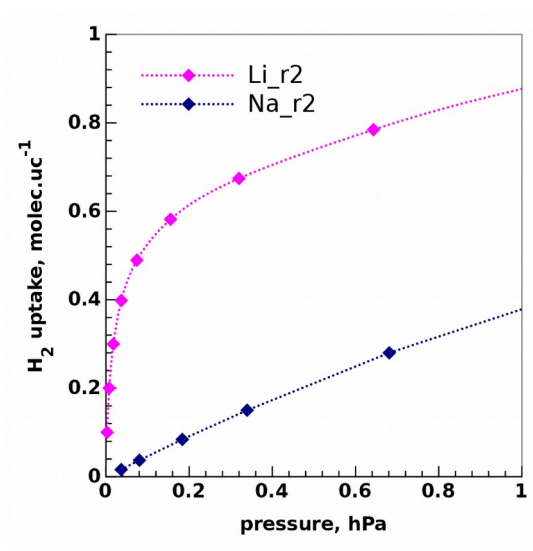


Figure 6

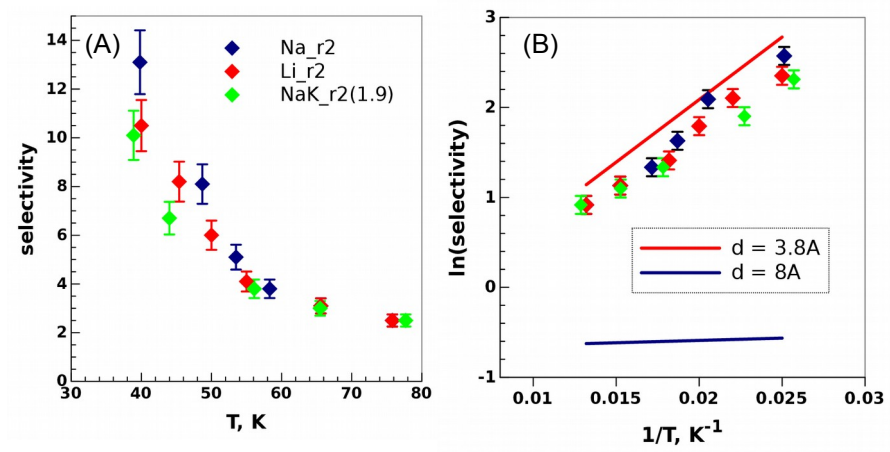


Figure 7

Table 1 Composition and structural parameters of the chabazites used in the work

	Designation	Composition ^a	Si/Al ratio	Rhombohedral unit cell parameters		
				a, Å	α	V, Å ³
1	Na_r1	Na _{5.7} Al _{5.7} Si _{6.3} O ₂₄	1.1			
2	K_r2	K _{3.9} Al _{3.9} Si _{8.1} O ₂₄	2.1	9.438	94.00	834
3	Na_r2	Na _{3.9} Al _{3.9} Si _{8.1} O ₂₄	2.1	9.420	94.02	830
4	Li_r2	Li _{3.6} K _{0.3} Al _{3.9} Si _{8.1} O ₂₄	2.1	9.402	94.84	822
5	NaK_r2(1.6) ^b	K _{1.6} Na _{2.3} Al _{3.9} Si _{8.1} O ₂₄ (0.801) ^c	2.1			
6	NaK_r2(1.9) ^b	K _{1.9} Na ₂ Al _{3.9} Si _{8.1} O ₂₄ (0.605) ^c	2.1			
7	NaK_r2(2.3) ^b	K _{2.3} Na _{1.6} Al _{3.9} Si _{8.1} O ₂₄ (0.290) ^c	2.1			
8	Na_r13	H _{0.6} Na _{0.26} Al _{0.86} Si _{11.14} O ₂₄	13	9.264	94.24	788
9	CHA-Si	Si ₁₂ O ₂₄	∞	9.233	94.27	780

^a Determined by the EDX analysis.

^b Number of K⁺ cations per unit cell is given in the parenthesis for mixed Na-K chabazites.

^c Weight of NaCl (g) used in the cation exchange (see Experimental part for details).