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# High efficiency of Na- and Ca-exchanged chabazites in D<sub>2</sub>/H<sub>2</sub> separation by quantum sieving

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**Keywords:** quantum sieving; D<sub>2</sub>/H<sub>2</sub> coadsorption; D<sub>2</sub>/H<sub>2</sub> separation; D<sub>2</sub>/H<sub>2</sub> selectivity; chabazite

## **Abstract**

Quantum sieving is a promising approach for separation of hydrogen isotopes using porous solids as sorbents at cryogenic temperatures ( $< 77$  K). In the present work we characterized the properties of two aluminum-rich chabazites: Na-CHA and Ca-CHA (Si/Al = 2.1). The single gas D<sub>2</sub> and H<sub>2</sub> adsorption isotherms were measured and the thermodynamic selectivities were determined through coadsorption experiments in the temperature range 38 – 77 K. We found that at 38 K Na-CHA shows selectivity of 25.8 at the loading of 10.6 mmol·g<sup>-1</sup>. At the same temperature Ca-CHA has slightly lower selectivity (18.3), but its uptake (12.9 mmol·g<sup>-1</sup>) is higher than for Na-CHA. Comparison with the literature shows that the obtained values of selectivity are among the highest reported so far. This property combined with robustness and availability on industrial scale of Al-rich chabazites makes them very promising materials for separation of hydrogen isotopes by quantum sieving.

## 1.Introduction

Separation of hydrogen isotopes by quantum sieving has attracted a considerable research interest in the recent years.<sup>1</sup> This approach is based on the difference in adsorption of hydrogen isotopes at cryogenic temperatures ( $< 77$  K) in the porous solids having pore size comparable with the size of  $H_2$  molecules ( $\sim 3$  Å).<sup>2</sup> Discovery of new classes of porous solids has opened an avenue for improving efficiency of hydrogen isotope separation due to an impressive chemical and structural diversity of these materials. Thus, recently a number of MOFs (Metal Organic Framework) phases have been shown to be efficient in  $D_2$ - $H_2$  quantum sieving through different approaches. High selectivity has been achieved by using the open metal sites,<sup>3-5</sup> by tuning the pore geometry<sup>6-9</sup> or through exploiting the flexibility of the MOF structure.<sup>10-12</sup>

Despite the highly attractive properties of MOFs, these materials possess some shortcomings. Their accessibility at the industrial scale is not guaranteed and their cost can be prohibitive. Another important issue concerns their use for separation of mixtures containing a radioactive tritium isotope. First, the organic part of these materials can be instable under beta radiation emitted by tritium. Second, the tritiation of the organic part through Wilzbach reaction<sup>13</sup> cannot be excluded. Even if this reaction can be rather slow at low temperatures, the use of the organic-containing phases in the presence of tritium is questionable.

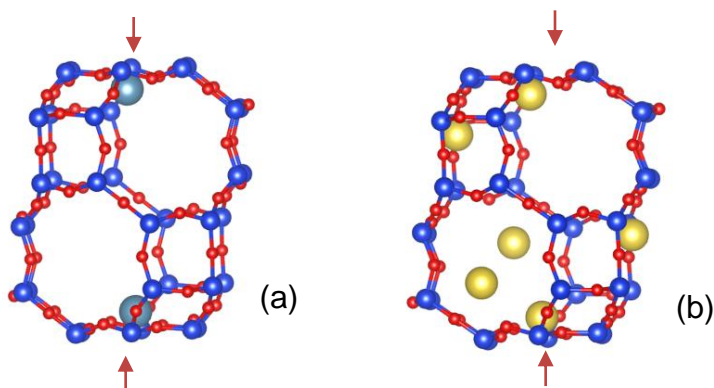
Use of zeolites, porous inorganic aluminosilicates, allows to overcome the limitations related to the radioactivity of tritium. Despite a lower variability of the pore size and surface chemistry than in MOFs, many framework topologies are available containing the pores in the range of 3 – 4 Å suitable for hydrogen isotopes separation. Moreover, variation of Si/Al ratio and of cation composition allows to tune the selectivity of zeolites and to achieve high efficiency in quantum

sieving of hydrogen isotopes. That is why the zeolites have been intensively studied in this application using different techniques.<sup>14 - 22</sup>

Recently we showed that among the zeolites the highest D<sub>2</sub>/H<sub>2</sub> selectivity is observed in small pore materials of LTA<sup>23</sup> and CHA<sup>24</sup> structure. Moreover, for pure silica CHA a new mechanism of D<sub>2</sub>/H<sub>2</sub> separation was established using experimental measurements combined with molecular simulation<sup>25</sup>. This mechanism is observed at high loading and it is related to the rearrangement of the adsorbed phase in which the molecules occupy new adsorption sites located in the 8MR windows of CHA structure. In the case of adsorption of D<sub>2</sub>/H<sub>2</sub> mixture these sites are preferentially occupied by smaller D<sub>2</sub> molecules and due to this effect the rearrangement results into increase of D<sub>2</sub>/H<sub>2</sub> selectivity.

Despite this interesting effect, the D<sub>2</sub>/H<sub>2</sub> selectivity of pure silica CHA zeolite remains rather low because it does not contain cations which are necessary for high selectivity.<sup>3,4</sup> The question arises if the selectivity of CHA structure can be improved by combining the new (rearrangement – based) mechanism with a classical one based on strong guest – cation interactions. To explore this approach, we decided to study the properties of Ca-exchanged chabazite (Si/Al = 2.1). Due to the higher charge of Ca<sup>2+</sup>, this zeolite contains two times less cations than Na-CHA. Moreover, the cations in Ca-CHA occupy the positions only inside the cage close to 6-membered ring (6MR) windows located at the top and in the bottom of the cages (Fig. 1a). Due the presence of only two Ca<sup>2+</sup> cations the 8-membered ring (8MR) windows remain open<sup>26</sup> (Fig. 1a). In contrast, in Na-CHA four out of six 8MR windows are occupied<sup>27, 28</sup> (Fig. 1b). In addition to Ca-CHA zeolite we studied in more details the Na-exchanged CHA described in our previous work.<sup>24</sup> For both materials the coadsorption measurements at 38 – 77 K were performed in order to determine the equilibrium D<sub>2</sub>/H<sub>2</sub> selectivity. Also, D<sub>2</sub> and H<sub>2</sub> single adsorption isotherms were

measured at different temperatures which allowed to calculate the isosteric heats of adsorption as a function of loading.



**Figure 1** Schematic representation of cation positions in cages of CHA structure: Ca-CHA (a) and Na-CHA (b) (atom colors: red – O, deep blue – Al or Si, light blue – Ca, yellow - Na). The arrows indicate the 6MR windows.

## 2. Experimental

### 2.1 Materials synthesis

KOH and NaCl and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  were purchased from Carl ROTH. Zeolite HY ( $\text{Si}/\text{Al} = 2.55$ ), used for chabazite synthesis, was provided by Alfa Aesar (ref. 45866). Pure silica CHA zeolite was kindly provided by A. Ryzhikov (IS2M laboratory, Mulhouse, France).

Na-CHA and Ca-CHA zeolites ( $\text{Si}/\text{Al} = 2.1$ ) used in the present work were obtained from K-CHA zeolite prepared through conversion of HY material in KOH solution using a known procedure.<sup>29</sup> The detailed procedure of synthesis of K-CHA and Na-CHA materials is given in our previous work.<sup>24</sup> Ca-CHA zeolite was prepared from K-CHA by cationic exchange with  $\text{CaCl}_2$  in the following way: 3.25 g of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  was dissolved in 10 mL of water and 1.25 g of K-CHA zeolite was added to solution. After stirring at room temperature for 8 or 16 h the

suspension was centrifuged and the powder was washed with deionized water. Overall eight stages of cationic exchange were performed and the obtained material was dried in ambient air. The scheme presenting different stages of the preparation of Na-CHA and Ca-CHA zeolites is given in Supporting Information.

### *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. In order to obtain a representative bulk composition of the sample, a large area was chosen (500 x 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.

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. FullProf software package was used for treating the XRD patterns. The cell parameters were refined using DICVOL software.

$\text{N}_2$  adsorption isotherms at 77.4 K were measured using ASAP 2020 setup from Micromeritics. The solids were degassed for 15 h at 673 K before measurements.

### *2.3 Adsorption and coadsorption measurements*

The single gas  $\text{D}_2$  and  $\text{H}_2$  adsorption isotherms at different temperatures were measured using the same Micromeritics ASAP 2020 apparatus as for  $\text{N}_2$  adsorption. The samples were degassed at 673 K under secondary vacuum ( $< 10^{-4}$  hPa) for 16 h using a turbomolecular pump. 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 setup for D<sub>2</sub>/H<sub>2</sub> mixture with 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.<sup>24</sup> The reported coadsorption selectivities were corrected for thermal diffusion using the procedure described in the same work.<sup>24</sup> The results of a typical blank experiment, used to calculate the contribution of the thermal diffusion, are presented in Supporting Information.

The adsorption capacities in the present work are expressed using two different units: molec/uc and mmol/g. The first one allows to compare in a correct way the zeolites having different molar weights, while the second unit is more appropriate for applications. These units can be interconverted using the expression: N(mmol/g) = N(molec/uc) x 1000/M (M – molecular weight of the zeolite in g/mol). Given the compositions of the obtained zeolites (see below), the molar weights of 806.38 and 800.59 g/mol were used for Na-CHA and Ca-CHA respectively.

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

#### *3.1 Materials characterization*

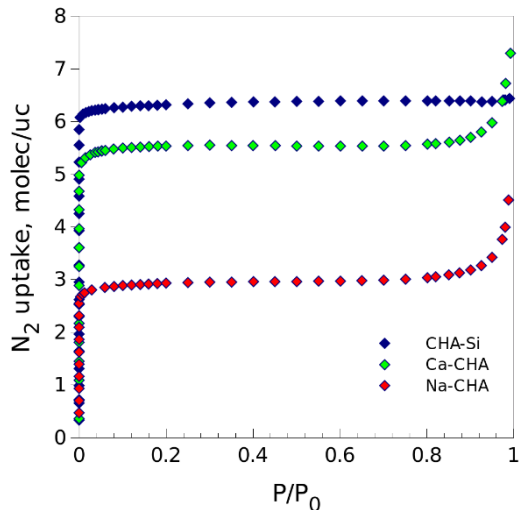
Na-CHA material used in this work is the same one which was described in our previous work with the composition Na<sub>3.9</sub>Al<sub>3.9</sub>Si<sub>8.1</sub>O<sub>24</sub>.<sup>24</sup> Ca-CHA used in the present study was obtained from the same parent K-CHA zeolite which was used for Na-CHA preparation. According to the EDX analysis it has the same Si/Al ratio and the composition Ca<sub>1.8</sub>K<sub>0.3</sub>Al<sub>3.9</sub>Si<sub>8.1</sub>O<sub>24</sub> showing that despite an important number of exchanges the material contains residual K<sup>+</sup> cations. The XRD patterns of Ca-CHA and Na-CHA confirm the preservation of framework after exchange and the



similar crystallinity of the samples (Fig.S1). The refined parameters of the rhombohedral cell ( $a = 9.388 \text{ \AA}$ ,  $\alpha = 94.20^\circ$ ) show that after Ca exchange the cell is slightly retracted in comparison with Na-CHA ( $a = 9.420 \text{ \AA}$ ,  $\alpha = 94.02^\circ$ ).

As mentioned in introduction, higher charge of  $\text{Ca}^{2+}$  cations than  $\text{Na}^+$  results in a twofold decrease of cation number in Ca-CHA. This fact and localization of  $\text{Ca}^{2+}$  close to 6MR windows inside the cages lead to formation of the open 8MR pore apertures (see Fig.1). This configuration should increase the accessibility of the cages in Ca-CHA structure in comparison with Na-CHA. To confirm this fact, the nitrogen adsorption can be used since it is known that cation-free 8MR windows are accessible for  $\text{N}_2$  molecules at 77.4 K while the 8MR containing cations (even as small as  $\text{Li}^+$ ) are not accessible.

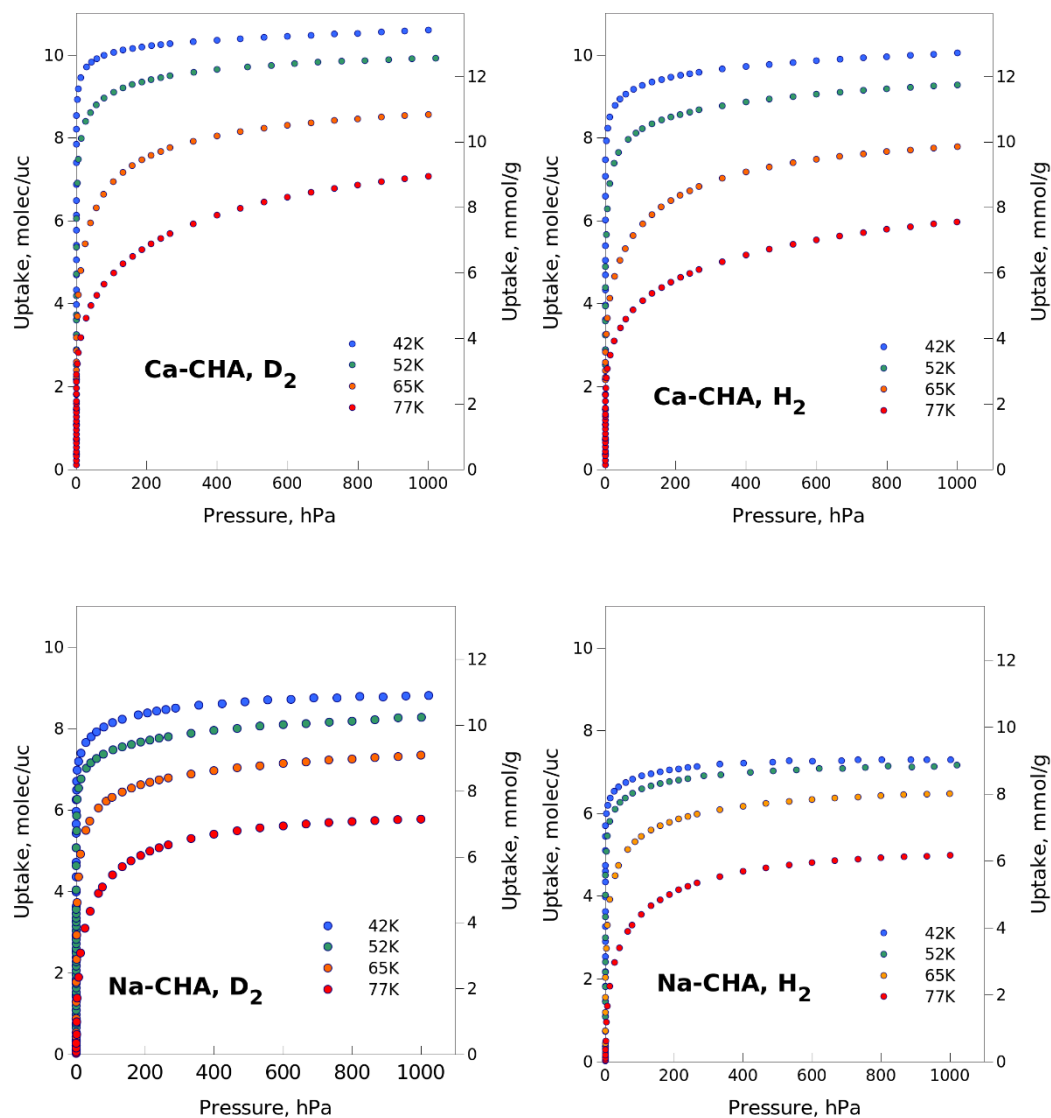
The comparison of  $\text{N}_2$  adsorption isotherms for pure silica CHA, Na-CHA and Ca-CHA confirms that majority of 8MR windows in Ca-CHA are not occupied by cations (Fig. 2). Indeed,  $\text{N}_2$  amount adsorbed by a cation-free pure silica CHA (6.3 molec/uc) corresponds to the maximum amount of nitrogen which can be accommodated in CHA cages at 77.4 K. In Na-CHA the amount adsorbed in the cages (plateau of the isotherm) is much smaller (3 molec/uc) confirming that only a half of cages are accessible to  $\text{N}_2$  molecules because of the blocking of the apertures by  $\text{Na}^+$  cations (four windows out of six). In contrast, the adsorbed amount in Ca-CHA is only slightly lower than in pure silica CHA (5.6 molec/uc). This observation confirms that in Ca-CHA only a small fraction of 8MR apertures is blocked, probably by residual  $\text{K}^+$  cations.



**Figure 2**  $N_2$  adsorption isotherms measured at 77.4 K for different CHA zeolites.

### 3.2. Single gas $D_2$ and $H_2$ adsorption isotherms at 42 – 77 K

Comparison of  $H_2$  and  $D_2$  adsorption isotherms in Na-CHA and Ca-CHA at 77 K reveals different patterns in these zeolites in the pressure range below 1 hPa (Fig. S2). In Na-CHA the isotherm is of convex shape (on log pressure scale) and shows a smooth rise with the adsorption beginning at  $\sim 0.1$  hPa. In contrast, in Ca-CHA material the adsorption starts below 0.001 hPa by a step increase of the adsorbed amount followed by a gradual rise attaining 2 molec/uc already at 1 hPa. Such a particular behavior has been observed in our previous work for MgX zeolites.<sup>14</sup> It was attributed to the presence of cations with higher charge ( $Mg^{2+}$ ) which interact with  $H_2$  and  $D_2$  molecules much more strongly than  $Na^+$ . The same explanation is valid for the present case.  $Ca^{2+}$  and  $Na^+$  have similar size (1.00 and 1.02 Å respectively), but the higher charge of calcium results into stronger polarization of the guest molecules. The stronger adsorbate – cation interactions in the case of  $Ca^{2+}$  result into higher uptake in the low pressure range for Ca-CHA.

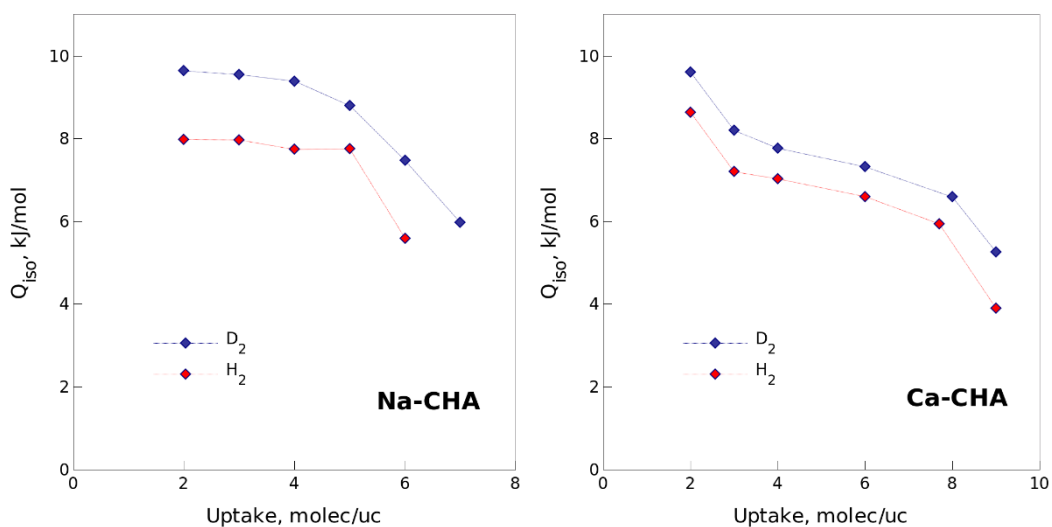


**Figure 3** Single gas D<sub>2</sub> and H<sub>2</sub> adsorption isotherms on Na-CHA and Ca-CHA zeolites at different temperatures.

The isotherms measured at different temperatures show that Ca-CHA adsorbs higher amounts of D<sub>2</sub> and H<sub>2</sub> than Na-CHA (Fig. 3). Thus at 42 K Ca-CHA adsorbs maximum 10.4 molec/uc of D<sub>2</sub> while Na-CHA shows the uptake of 8.8 molec/uc and a similar trend is observed for other temperatures and for H<sub>2</sub>. This significant difference cannot be explained neither by a larger cell

volume in Ca-CHA nor by its higher crystallinity (see section 3.1 and Fig. S1). We suggest therefore that the larger adsorption capacity of Ca-CHA is due to the presence of additional adsorption sites located in the cation-free 8MR windows present in this zeolite. The filling of such adsorption sites at high loadings was demonstrated in pure silica CHA in our previous work.<sup>25</sup>

The adsorption isotherms measured at different temperatures were used to calculate the isosteric heat of adsorption for D<sub>2</sub> and H<sub>2</sub> in Na-CHA and Ca-CHA (Fig.4 and S3). For both materials the observed magnitude of Q<sub>iso</sub> and its variation trend are similar to those reported for NaA zeolite.<sup>23</sup> The decrease of the isosteric heat of adsorption with loading for both materials is typical for strongly heterogeneous systems. The reason for such behavior in cationic zeolites is well understood.<sup>30</sup> At low loading the enthalpy is high due to strong cation-guest interactions existing in this range. Upon increase of the adsorbed amount much weaker intermolecular interactions become important which results in decrease of the overall value of the adsorption heat.

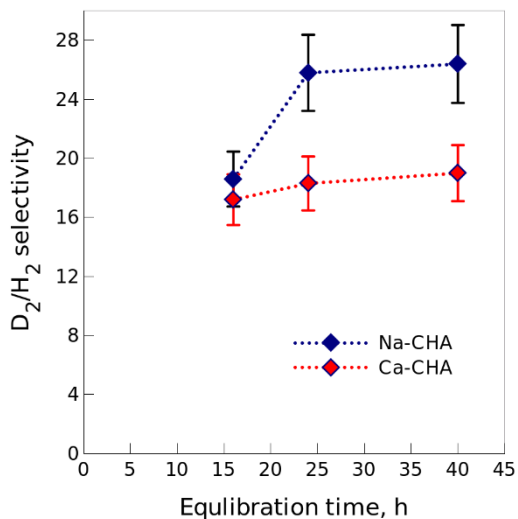


**Figure 4** Isosteric heat of adsorption as a function of uptake in Na-CHA and Ca-CHA zeolites (the lines are guides for the eyes).

The data presented in Fig. 4 seem to contradict our previous conclusion about the presence of very strong guest – cation interactions since the adsorption heat at 2 molec/uc has the same value (9.6 kJ/mol) for Ca-CHA and Na-CHA. This apparent contradiction can be explained by the fact that for Ca-CHA the values of  $Q_{\text{iso}}$  for loadings below 2 molec/uc cannot be calculated in our case because of technical limitations. In fact, for the measurements below 77 K the equilibrium pressures for loadings below 2 molec/uc are close to the low pressure limit of the used apparatus ( $10^{-4}$  hPa) and therefore cannot be measured precisely. Despite this technical limitation we observe that for Ca-CHA the adsorption heat tends to increase at low loadings (Fig. 4) while it is not the case for Na-CHA. This difference appears to suggest that for loadings below 2 molec/uc the isosteric adsorption enthalpy in Ca-CHA should be higher than in Na-CHA.

### *3.3. Coadsorption measurements*

In our previous work we used the equilibration time of 16 h for all temperatures in different CHA zeolites.<sup>24</sup> This time has been chosen on the basis of the coadsorption measurements performed at 77 K and can be insufficient to attain thermodynamic equilibrium at lower temperatures. To verify this point, we measured  $D_2/H_2$  selectivity in Na-CHA and Ca-CHA at 38 K using different equilibration times (Fig.5). It follows that for both Na-CHA and Ca-CHA 24 h interval is sufficient for attaining the equilibrium. Based on these results we chose the equilibration time of 24 h for all coadsorption measurements realized in the present work.



**Figure 5** D<sub>2</sub>/H<sub>2</sub> selectivity at 38 K as a function of equilibration time for Na-CHA and Ca-CHA zeolites for the initial mixture composition: 25%D<sub>2</sub>-75%H<sub>2</sub> (the lines are guides for the eyes).

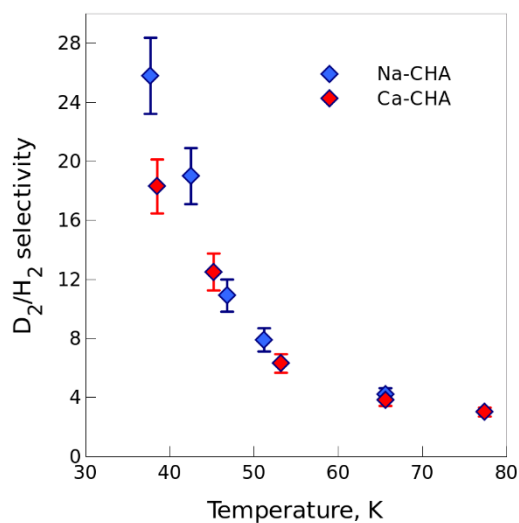
The increase of D<sub>2</sub>/H<sub>2</sub> selectivity with the equilibration time is related to a particular arrangement of our setup and it can be explained in the following way. The coadsorption experiment starts by the preparation of the initial D<sub>2</sub>/H<sub>2</sub> mixture in the reference cell at ambient temperature. Then this mixture is admitted to the sample cell (length ~ 26 cm, diameter - 1.2 cm) which contains in its bottom part the degassed zeolite under vacuum and at measurement temperature. Since H<sub>2</sub> diffuses in the gas phase faster than D<sub>2</sub>, the gas mixture arriving at the zeolite surface contains more H<sub>2</sub> than the initial mixture. Consequently, the adsorbed phase formed at this moment is richer in H<sub>2</sub> than it should be under equilibrium. Then, during the equilibration time, D<sub>2</sub> molecules from the gas phase replace the excess adsorbed H<sub>2</sub> molecules. As a result, the fraction of D<sub>2</sub> in the adsorbed phase increases and the selectivity becomes higher with time. The low rate of this exchange process is thus the reason of the long time needed to achieve the equilibrium in our coadsorption measurements.

Because of the effect described above it is not possible in our case to measure the kinetic  $D_2/H_2$  selectivity. The data shown in Fig. 5 allow however to compare qualitatively the “equilibration rate“ reflecting the rate of replacement of excessive  $H_2$  by  $D_2$ . Indeed, for Ca-CHA the increase of the contact time from 16 to 24 h results in selectivity change of only 6 % (from 17.2 to 18.3), that is the equilibrium state is almost attained after 16 h of contact. In contrast, for Na-CHA the selectivity increases from 18.6 to 25.8 (i.e. by 39 %) when increasing the time from 16 to 24 h. The shorter time needed to attain the equilibrium in Ca-CHA can be attributed to a faster exchange between the gas phase and the adsorbed phase during the equilibration which is due to the presence of cation-free 8MR windows in this material (see Fig.1).

Comparison of selectivities for Na-CHA after 24 h of equilibration with the previously published values <sup>24</sup> (measured after 16 h of contact) shows that in our previous study the thermodynamic equilibrium was not achieved for the temperatures below 50 K (Fig.S4). The new, truly equilibrium, values of  $D_2/H_2$  selectivity are much higher and attain the value of 25.8 at 38 K. Moreover, this high value of selectivity is achieved at the loading of 10.6 mmol/g. These parameters make Na-CHA the most efficient material for  $D_2/H_2$  separation at this temperature reported so far. Thus the value of 26 was also reported for selectivity in Co formate MOF material, but it was obtained at 25 K and at 7 mmol/g loading <sup>6</sup>. The selectivity of 24 was found for HKUST-1 MOF at 20 K (loading - 18.2 mmol/g).<sup>8</sup> In the same work an exceptional selectivity of 53.8 at 20 K was reported for SIFSIX-3-Zn MOF, but at low loading (0.96 mmol/g). Similarly, the high value of selectivity (41.4) observed in Fe-based AHEFAU MOF was measured at 20 K and at  $\sim 2.7$  mmol/g.<sup>9</sup>

$D_2/H_2$  selectivities for Ca-CHA and Na-CHA at different temperatures are compared in Fig. 6. It follows that the properties of Ca-CHA material are similar to those of Na-CHA. Thus, at 38 K

the selectivity of Ca-CHA (18.3) is slightly lower than for Na-CHA, but the corresponding loading (12.9 mmol/g) is higher in accordance with the single gas adsorption data (section 3.2). The higher selectivity of Na-CHA seems to contradict the fact that in Ca-CHA the guest-cation interactions are much stronger at low loading (see section 3.2). It should be noted however that the difference of zero point energies (ZPE) between D<sub>2</sub> and H<sub>2</sub>, which determines the D<sub>2</sub>/H<sub>2</sub> selectivity<sup>2</sup>, depends not only on the interaction strength, but also on the pore size. In fact, D<sub>2</sub> can be separated from H<sub>2</sub> without strong interactions with cations, e.g. by using pure silica zeolites<sup>25</sup> or organic cages<sup>31</sup>. We suggest that the smaller pore size in Na-CHA explains why this zeolite shows higher D<sub>2</sub>/H<sub>2</sub> selectivity than Ca-CHA. Indeed, in Na-CHA Na<sup>+</sup> cations partially block the 8MR windows and therefore their size is significantly smaller than that of cation-free 8MR present in Ca-CHA.



**Figure 6** D<sub>2</sub>/H<sub>2</sub> selectivity as a function of temperature for Na-CHA and Ca-CHA zeolites (initial mixture composition – 25%D<sub>2</sub> - 75%H<sub>2</sub>, equilibration time – 24 h).



Given the presence of cation-free 8MR windows in Ca-CHA, we suppose that D<sub>2</sub>/H<sub>2</sub> separation in Ca-CHA could occur through a combination of two mechanisms. The first one is based on strong guest – cation interactions which favor D<sub>2</sub> adsorption as shown previously (so called Chemical Affinity Quantum Sieving, CAQS).<sup>1, 3, 4, 15</sup> The second one is related to the molecular rearrangement of the adsorbed phase similar to that described in our previous work.<sup>25</sup> This rearrangement was observed in pure silica CHA at high loading and it results in appearance of new adsorption sites located inside the 8MR windows. Since these new sites have higher affinity for D<sub>2</sub> molecules, the rearrangement results in the rise of D<sub>2</sub>/H<sub>2</sub> selectivity. We suggest that a similar phenomenon can take place in Ca-CHA zeolite which also contains cation – free 8MR windows having the same shape as in pure silica CHA. Due to this similarity, 8MR windows in Ca-CHA at high loading can become new adsorption sites adsorbing preferentially D<sub>2</sub> molecules and allowing thus to increase D<sub>2</sub>/H<sub>2</sub> selectivity.

The results obtained in our work allow to draw a more general conclusion. They suggest that D<sub>2</sub>/H<sub>2</sub> selectivity in zeolites depends not only on the window size and on the strength of cation – guest interactions as generally accepted. 8MR window having a particular geometry, as in the case of CHA zeolites, can become a new adsorption site showing strong selectivity towards heavier hydrogen isotopes at high loading. This finding suggests that other zeolite frameworks with cation - free 8MR windows can demonstrate even higher efficiency in hydrogen isotope separation than the studied CHA – based materials.

## **Conclusions**

D<sub>2</sub>/H<sub>2</sub> quantum sieving was studied in Na- and Ca-exchanged chabazites (Si/Al = 2.1) in 38 – 77 K temperature range. The influence of the contact time on the selectivity was studied in order

to determine the duration needed to achieve a coadsorption equilibrium. Using the established duration (24 h for our setup) the thermodynamic selectivities were determined from the coadsorption data. We found that Na-CHA is one of most selective sorbents reported so far: at 38 K it shows selectivity of 25.8 at the loading of 10.6 mmol/g. Ca-CHA has slightly lower selectivity (18.3), but its uptake (12.9 mmol/g) is higher than for Na-CHA. These properties combined with robustness and availability on industrial scale make Al-rich chabazites very promising materials for separation of hydrogen isotopes by quantum sieving.

### **Supporting information**

The supporting information is available free of charge at <https://pubs.acs.org/doi/10.1021> ...

Scheme of zeolites preparation; description of blank coadsorption experiment; XRD patterns of Na-CHA and Ca-CHA zeolites; adsorption isotherms of H<sub>2</sub> and D<sub>2</sub> on Na-CHA and Ca-CHA zeolites at 77.4 K; the isosters for D<sub>2</sub> and H<sub>2</sub> adsorption on Na-CHA and Ca-CHA zeolites used for the calculation of the adsorption enthalpies as a function of loading; D<sub>2</sub>/H<sub>2</sub> selectivity as a function of temperature in Na-CHA zeolite measured after equilibration for 16 h and 24 h.

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## Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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