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# Alkali Metal Cations Influence the CO<sub>2</sub> Adsorption Capacity of Nanosized Chabazite: Modeling vs Experiment

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## Abstract:

The CO<sub>2</sub> adsorption behavior of nanosized chabazite (CHA) containing different compositions of extra-framework alkali metal cations (Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>) with a constant Si/Al ratio of 2.2 was investigated experimentally (adsorption isotherms and *in situ* FTIR spectroscopy) and theoretically by Grand Canonical Monte Carlo (GCMC) modeling. The CO<sub>2</sub> adsorption isotherms were in a good agreement with the GCMC modeling in the pressure range of 0–60 KPa for all samples except the Cs<sup>+</sup> containing nanosized CHA. The GCMC modeling did not consider the kinetics of adsorption thus the CO<sub>2</sub> capacity for the Cs-CHA sample was overestimated; the partial blockage of the pores and inaccessibility of CO<sub>2</sub> to the free voids of the CHA structure was experimentally observed by recording adsorption isotherms and *in situ* FTIR study. The FTIR results revealed the CO<sub>2</sub> adsorbed mainly physically on all samples with the sorption capacity decreasing in the following order: Na-CHA ≈ K-CHA > Cs-CHA. The Na-CHA demonstrated significant micropore volume compared to the other samples as measured by N<sub>2</sub> physisorption due to the inability of Na<sup>+</sup> to effectively occupy the 8MRs. This study implies that the different alkali metal cation forms of the nanosized CHA zeolite are of practical interest for flue gas purification where a high CO<sub>2</sub>/N<sub>2</sub> selectivity is required.

**Keywords:** nanozeolite, chabazite, CO<sub>2</sub> adsorption, extra-framework cations, gas separation, heat of adsorption

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## 1. Introduction

Since the industrial revolution the concentration of atmospheric CO<sub>2</sub> has been continuously increasing.<sup>1</sup> Recent research shows that this value has increased from 280 ppm to approximately 400 ppm in the last two centuries, which is responsible for the current increase in average global temperatures.<sup>2</sup> As a result, capturing CO<sub>2</sub> emitted from various industries in the form of flue gas (3–20% CO<sub>2</sub>, 65–80% N<sub>2</sub>) is a key strategy to reduce anthropogenic global warming and has received significant attention.<sup>3–6</sup> Four technologies are currently employed for CO<sub>2</sub> capture: absorption with amine-based solvents, adsorption by nanoporous solids, cryogenic distillation, and membranes.<sup>7</sup> Adsorption of CO<sub>2</sub> by nanoporous materials is a widely used and attractive technology due to its ease of operation, use of non-corrosive materials, and low energy requirement (specially compared to amine-based absorption).<sup>8–12</sup>

Zeolite-based adsorbents are advantageous compared to other porous materials due to their non-toxic nature, high thermal stability, high selectivity dictated by their structure and chemical composition, and affordability.<sup>13,14</sup> Conventional zeolites, which have particle sizes in the order of micrometers, are composed of aggregates of individual crystals.<sup>15</sup> As a result, micron-sized zeolites suffer from diffusion limitations of guest molecules through their pore networks, however, this can be addressed by decreasing the zeolite particle size.<sup>16</sup> Nanozeolites are typically composed of discrete particles (single crystals) which possess a greater external surface area and number of available active sites compared to micron-sized zeolites.<sup>17,18</sup>

Zeolites can be divided into different categories based on their pore sizes; small (3.0–4.5 Å), medium (4.5–6 Å), large 6.0–8.0 Å), and extra-large (> 8.0 Å).<sup>19</sup> Small-pore zeolites are suitable candidates for CO<sub>2</sub> capture from N<sub>2</sub>-containing mixtures; the kinetic diameters of these small molecules is similar (3.3 and 3.6 Å for CO<sub>2</sub> and N<sub>2</sub> respectively). The CO<sub>2</sub> capacity of different zeolites is already reviewed by Cheung and Hedin,<sup>20</sup> revealing that among the known zeolites the CHA has the highest CO<sub>2</sub> capacities.<sup>20</sup> In addition, the size and shape of the 8-membered rings (8MRs) of the CHA zeolite which control the access to the zeolite pore network can be controlled by the presence of different extra-framework cations (EFCs) and adsorbates.<sup>19,21–24</sup> Two mechanisms for the selective adsorption of CO<sub>2</sub> on small-pore zeolites have been proposed: molecular sieving due to the differences between the zeolite pore size and molecule kinetic diameter, and window-keeping mechanism by extra-framework cations (EFCs).<sup>25</sup> The latter, described by Shang *et al.* as molecular trapdoor behavior, occurs due to the occupation of the zeolite 8MRs by EFCs which control access to the zeolite pore network whereby the EFCs reject or admit different guest molecules based on their interactions with them.<sup>23,26</sup> They showed that the CO<sub>2</sub> guest molecules induced the door-keeper EFCs to move out from the center of 8MRs of the zeolite and selectively admit CO<sub>2</sub> to the CHA supercages compared to non-polar molecules such as

N<sub>2</sub> and CH<sub>4</sub>.<sup>23,24,26</sup> Using thermogravimetric analysis (TGA), we reported selective adsorption of CO<sub>2</sub> over CH<sub>4</sub> due to molecular trapdoor behavior by a nanosized CHA sample (crystal sizes ~ 190 nm) containing a mixture of alkali metal cations (Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>).<sup>27</sup> In that work, the presence of Cs<sup>+</sup> located in the 8MR of the CHA structure was identified as the cation responsible for the selective adsorption of CO<sub>2</sub> evidenced by its ability to displace about the 8MR aperture in the presence of CO<sub>2</sub>.<sup>27</sup>

The CHA structure is described by a three-dimensional pore system containing supercages of 6.7 × 10 Å (*t-cha*) which are accessed by six 8MRs of 3.8 × 3.8 Å connected along the c-axis by double six-membered rings (*d6rs*).<sup>27</sup> Four EFC sites exist in the CHA framework (Fig. 1a): at the center of a *d6r* prism (SI), at the triad axis of a *d6r* prism but displaced inside the *t-cha* (SII), in the *t-cha* at the corner of a four-ring window of a *d6r* (SIII), and at the center of an 8MR window (SIII').<sup>27-</sup>

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Recently we demonstrated the one-pot synthesis of CHA zeolite with small nanocrystals (< 60 nm) using only alkali metal cations (Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup>) as inorganic structural-directing agents, and their behavior during the crystallization stage was studied.<sup>30</sup> Zhang *et al.* have reported on the CO<sub>2</sub> adsorption capacity and separation performance of alkali (Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) and alkaline-earth (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>) metal containing micron-sized CHA zeolites in flue gas streams. From adiabatic simulation calculations it was found that the Na- and Ca-containing CHA zeolites possess advantages for high temperature separation of CO<sub>2</sub> compared to NaX due to their greater capture defined by the product of their adiabatic working selectivity and capacity.<sup>7</sup>

Here we describe the preparation of four different cationic forms of nanosized CHA with different alkali metal compositions as EFCs (Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, and mixed) with a crystal size of 60 nm and Si/Al ratio of 2.2. The CO<sub>2</sub> adsorption capacity of the CHA nanocrystal samples was predicted using Grand Canonical Monte Carlo (GCMC) calculations and was compared to the experimental results from adsorption isotherm measurements and *in situ* FTIR spectroscopy. Good agreement was observed between the modelling and experimental methods when the EFCs do not cause pore blockage demonstrating that GCMC is a powerful tool for predicting zeolite CO<sub>2</sub> adsorption capacities. Experimental CO<sub>2</sub> adsorption measurements showed a higher CO<sub>2</sub> capacity for nanosized K-CHA compared to the micron-sized K-CHA. Following the adsorption of CO<sub>2</sub> on the nanosized zeolite samples using *in situ* FTIR revealed that CO<sub>2</sub> adsorbs mainly by physisorption on all of the samples which was highlighted by three consecutive regeneration cycles by vacuum after CO<sub>2</sub> dosing. The results clearly demonstrated that the CHA nanocrystals are prospective candidates for CO<sub>2</sub> separation from N<sub>2</sub> in vacuum swing applications.

## 2. Experimental and modeling section

### 2.1. Materials and synthesis of CHA nanocrystals

All reagents were used as received unless otherwise specified. Sodium hydroxide pellets (98 wt%), sodium chloride (99 wt%), potassium hydroxide (85 wt%), potassium chloride (99.5 wt%), LUDOX AS-40, and sodium aluminate ( $\text{NaAlO}_2$ , 40–45%  $\text{Na}_2\text{O}$ , 50–56%  $\text{Al}_2\text{O}_3$ ) were purchased from Sigma-Aldrich. Cesium hydroxide hydrate (15–20 wt%  $\text{H}_2\text{O}$ ), and cesium chloride (99.5 wt%) were purchased from Alfa Aesar. Double distilled (dd) water prepared by an Aquatron water still A4000D was used for all syntheses. The synthesis of the CHA nanozeolite has been described previously.<sup>30</sup> 0.54 g of  $\text{NaAlO}_2$  was mixed with 4.2 g of water under rapid stirring. After dissolution, 1.7 g of  $\text{NaOH}$ , 0.824 g of  $\text{KOH}$ , and 0.442 g of  $\text{CsOH}$  (50 wt.%  $\text{Cs}$  in water) were added and stirred for 2 hours to obtain a clear solution. Then, 10 g of LUDOX AS-40 was added dropwise under vigorous stirring. The final composition of the alkali aluminosilicate colloidal suspension was 0.2  $\text{Cs}_2\text{O}$ : 1.5  $\text{K}_2\text{O}$ : 6.0  $\text{Na}_2\text{O}$ : 16.0  $\text{SiO}_2$ : 0.7  $\text{Al}_2\text{O}_3$ : 141.7  $\text{H}_2\text{O}$ . The alkali aluminosilicate colloidal suspension was then aged under vigorous stirring at room temperature for 17 days followed by hydrothermal treatment in a static oven at 90 °C for 7 hours. The CHA nanocrystals were recovered by centrifugation and washed with hot water (90 °C) until a neutral pH (7–8) of the decanted solution was achieved. The recovered CHA nanocrystals were dried in an oven at 60 °C overnight and the final as-prepared CHA nanocrystals were labeled as AP-CHA.

AP-CHA was ion-exchanged to obtain different alkali-metal cation forms as described: 10 mL of 1 M  $\text{NaCl}$ ,  $\text{KCl}$ , or  $\text{CsCl}$  was added to 250 mg of AP-CHA (liquid/solid ratio of 40), and the mixture was stirred for 2 hours. Afterwards, the different alkali-metal forms of CHA nanocrystals were recovered by centrifugation and washed with water three times. This procedure was repeated three times and the recovered CHA nanocrystals were dried in an oven at 60 °C overnight. The ion-exchanged samples with  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$  were labeled as Na-CHA, K-CHA, and Cs-CHA, respectively.

### 2.2. Characterization techniques

Powder X-ray diffraction (PXRD) patterns were collected with a PANalytical X'Pert Pro diffractometer using  $\text{Cu-K}\alpha_1$  radiation ( $\lambda = 1.5406 \text{ \AA}$ , 45 kV, 40 mA). Inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed using a 7900 ICP-MS from Agilent Technologies. Magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra of  $^{29}\text{Si}$  nuclei were recorded with a single pulse on a Bruker Avance 500 MHz (11.7 T) spectrometer using 4 mm-OD zirconia rotors with a spinning frequency of 12 kHz. Single pulse excitation (30° flip angle) of 3  $\mu\text{s}$  was used for  $^{29}\text{Si}$  MAS NMR experiment and 30 s of recycle delay. Tetra-methylsilane (TMS) was used as a reference for  $^{29}\text{Si}$  nuclei.

N<sub>2</sub> adsorption and desorption isotherms were recorded at 77 K and CO<sub>2</sub> adsorption isotherms recorded at various temperatures (248, 283 and 298 K) were measured on a Micromeritics 3Flex Surface Characterization unit (Norcross, GA, USA). The samples were outgassed under vacuum at 623 K for at least 8 h prior to measurement. The specific surface area was calculated using the Brunauer-Emmet-Teller (BET) equation and following the procedure described by Rouquerol *et al.*<sup>31</sup> Micropore volumes were determined by applying an advanced NLDFT method assuming N<sub>2</sub> adsorption at 77 K in cylindrical siliceous zeolite micropores. Isothermic heat of adsorption calculations were computed based on the Clausius-Clapeyron equation applied to CO<sub>2</sub> adsorption isotherms between 248 and 298 K using the ASiQwin 5.2 software provided by Quantatec (Anton Paar, Boynton Beach, FL, USA).<sup>32,33</sup> Thermogravimetric analysis (TGA) was performed using a Setsys SETARAM analyzer. The cycling experiments were performed under heating in the presence of Ar and flowing CO<sub>2</sub> from 298 to 623 K (heating rate of 10 K min<sup>-1</sup>) and held at 623 K for 1.5 hours under Ar, followed by cooling down to 298 K (cooling rate of 20 K min<sup>-1</sup>), followed by flowing CO<sub>2</sub> (40 mL min<sup>-1</sup>) for 2 hours.

*In situ* FTIR spectroscopic measurements of zeolite samples were performed on a self-supported pellet (~20 mg and a diameter of 16 mm); the transmission spectra were recorded with a Thermo Scientific Nicolet iS50 FTIR spectrometer equipped with an MCT detector, at a spectral resolution of 4 cm<sup>-1</sup>. The infrared cell used here for the CO<sub>2</sub> adsorption isotherm experiments is the Carroucell, an *in situ* cell recently developed at the LCS laboratory for concomitant multi-samples analyzes.<sup>34</sup> The specificity of this cell is to be able to accommodate 12 samples simultaneously in a single chamber (same experimental conditions for all samples). While, two of the sample positions can be left unoccupied in order to be able to perform a background or an IR spectrum of the gas phase. The Carroucell IR-cell is equipped with a heating element in order to activate the samples at 623 K prior to the measurements. The cell was connected to a pumping system for the treatment under high vacuum (up to 10<sup>-6</sup> kPa). The samples were activated by heating with a ramp rate of 3 K min<sup>-1</sup> followed by heating at 623 K for 4 h under high vacuum. All IR spectra relating to CO<sub>2</sub> adsorption were recorded at room temperature. The molar absorption coefficients used in this work to obtain the physisorption and chemisorption isotherms were 16 and 40 cm μmol<sup>-1</sup>, respectively.<sup>35,36</sup>

### 2.3. Grand Canonical Monte Carlo calculations of CO<sub>2</sub> adsorption in CHA zeolite

To model the CHA unit cell the structure published by Debost *et al.* was employed.<sup>27</sup> The unit cell was multiplied three times in each direction (x, y, and z) to create a super cell consisting of 27 unit cells upon which all the molecular modeling calculations were performed. For this study, following previous work<sup>37,38</sup>, the Al atoms in the CHA samples were randomly distributed while

respecting Löwenstein's rule<sup>39</sup> and the position of cations were chosen next to the negatively charged Al tetrahedra.

The forcefield parameters used in this work to model the interactions between the alkali cations, the rigid zeolite framework, and the CO<sub>2</sub> molecules are those derived by Jeffroy *et al.* and summarized in Table 1.<sup>40</sup> All interactions between the cations and the framework oxygens (O<sub>zeolite</sub>) were considered as Buckingham interactions. Lennard-Jones interactions were considered for the rest of the atom pairs and the Lorentz-Berthelot combination rules [ $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj}) / 2$  and  $\epsilon_{ij} = (\epsilon_{ii} \times \epsilon_{jj})^{0.5}$ ] were used to estimate forcefield parameters for different atom pairs.

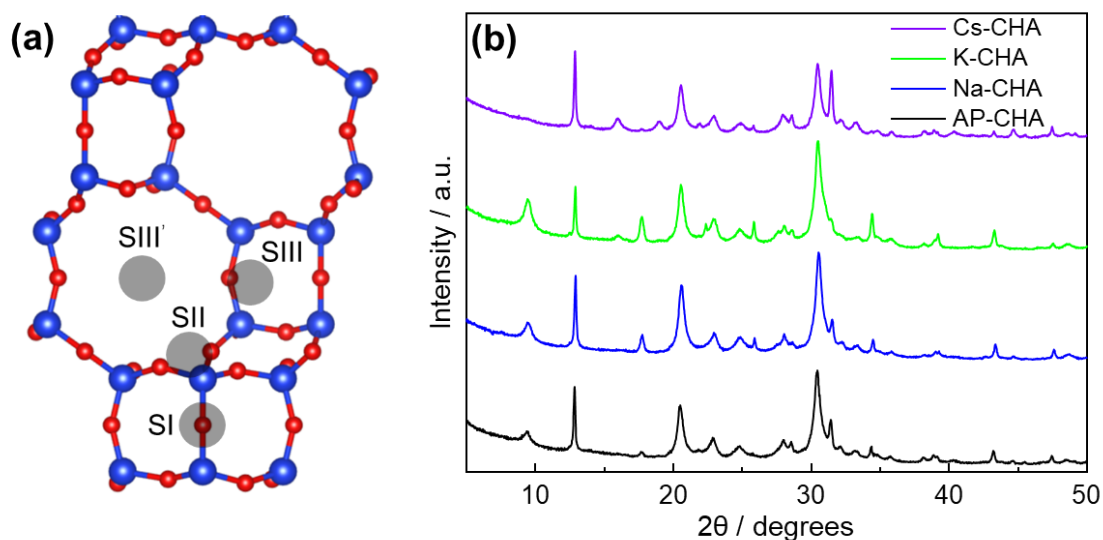
**Table 1.** Force field parameters used in this work

	Lennard-Jones: $-4 \epsilon [\sigma^6 / r^6 - \sigma^{12} / r^{12}]$		
	$\sigma / \text{\AA}$	$\epsilon / \text{K}$	$q / e$
<b>C</b>	2.757	28.13	+0.6512
<b>O</b>	3.033	80.51	-0.3256
<b>Na</b>	2.586	50.27	+1
<b>K</b>	2.820	62.00	+1
<b>Cs</b>	3.165	59.72	+1
<b>O<sub>zeolite</sub></b>	3.000	93.53	-0.8308
<b>Al<sub>zeolite</sub></b>	-	-	+1.1900
<b>Si<sub>zeolite</sub></b>	-	-	+1.3837
	Buckingham: $\alpha \exp(-\beta r) - \gamma / r^6$		
	$\alpha / \text{K}$	$\beta / \text{\AA}^{-1}$	$\gamma / \text{K \AA}^6$
<b>Na ... O<sub>zeolite</sub></b>	$6.11 \times 10^7$	4.05	$7.652 \times 10^5$
<b>K ... O<sub>zeolite</sub></b>	$6.11 \times 10^7$	3.53	$1.800 \times 10^5$
<b>Cs ... O<sub>zeolite</sub></b>	$6.11 \times 10^7$	3.20	$2.831 \times 10^5$

The GCMC simulations of CO<sub>2</sub> adsorbed at 248, 273, and 298 K in CHA nanozeolite samples with different cations were performed consistent with the chemical compositions determined with ICP-MS (see Table 2). The GCMC technique is a stochastic method that simulates a system having a constant volume  $V$  (the pore with the adsorbed phase), in equilibrium with an infinite reservoir of particles imposing its chemical potential  $\mu_{\text{CO}_2}$  for the adsorbed species and its temperature  $T$ . The absolute adsorption isotherm is given by the ensemble average of the number of each adsorbate molecule as a function of the CO<sub>2</sub> fugacities ( $f_{\text{CO}_2}$ ) of the reservoir (the latter are determined from the chemical potential  $\mu$ ).

### 3. Results and Discussion

The CHA nanocrystals containing different alkali metal cations were characterized by PXRD, ICP-MS, and  $^{29}\text{Si}$  MAS NMR and the results are presented in Fig. 1b, Table 2, and Fig. S1, respectively. All ion-exchanged samples contain a small content of co-cations (K and/or Cs) in the CHA unit cell (Table 2). The different alkali forms of CHA show minor differences in XRD patterns (Fig. 1b). For instance, the intensity of the Bragg peak at  $26.62^\circ 2\theta$  with hkl of (2 0 -1) and (2 -1 0) is more intense in the Na-CHA sample.<sup>41</sup> Another example is the diffraction peak at  $9.48^\circ 2\theta$  with hkl value of (1 0 0) disappears in the XRD pattern of Cs-CHA sample, while two diffraction peaks at  $16.02^\circ 2\theta$  and  $19.02^\circ 2\theta$  with hkl of (1 -1 1) and (2 0 0), respectively appear only in this sample.<sup>41</sup> Nevertheless, all the different reflections in the XRD patterns presented in Fig. 1b are attributed to CHA framework.<sup>41</sup> Panezai *et al.*<sup>42</sup> reported similar results for zeolite X in different cationic forms ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ).



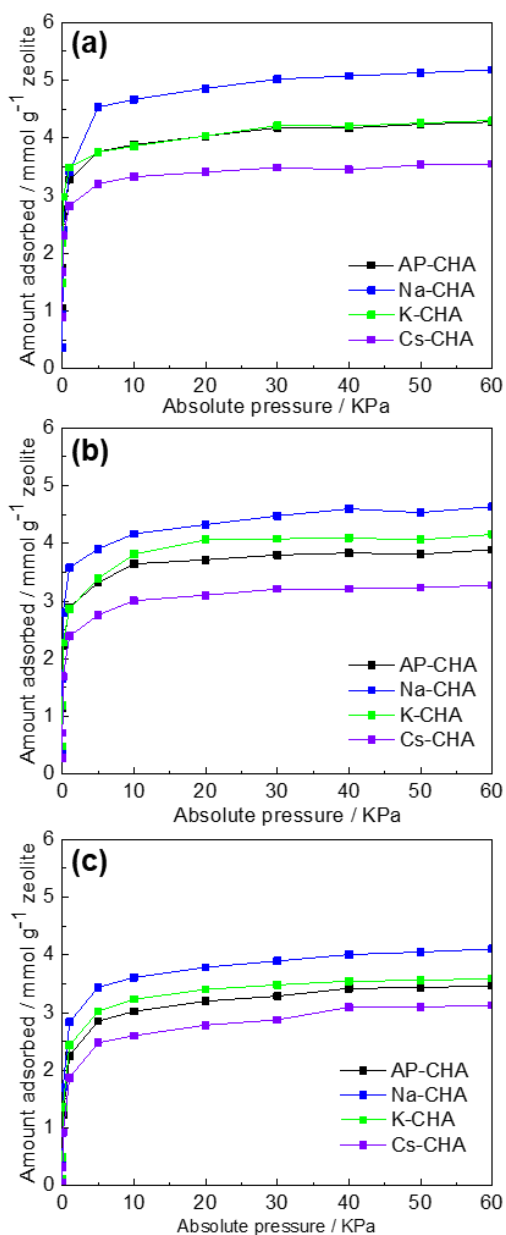
**Fig. 1** (a) Schematic representation of CHA atomic structure and the occupancy sites for extra-framework cations (hollow grey spheres). Four types of cation sites exist: at the center of a  $d6r$  (SI); above a  $d6r$  inside the cavity (SII); next to a 4MR of a  $d6r$  inside the cavity (SIII); at the center of an 8MR (SIII'); T atoms (Si, Al) are depicted by blue spheres, and oxygen atoms by red. (b) XRD patterns of the nanosized AP-CHA, Na-CHA, K-CHA, and Cs-CHA zeolite samples.

**Table 2.** Chemical composition and Si/Al ratio of nanosized AP-CHA, Na-CHA, K-CHA, and Cs-CHA samples.

Sample	Chemical formula (ICP-MS)	Si/Al ( $^{29}\text{Si}$ MAS NMR)
AP-CHA	$\text{Na}_{1.8}\text{K}_{5.7}\text{Cs}_{4.0}\text{Al}_{11.1}\text{Si}_{24.8}\text{O}_{72}$	2.2

<b>Na-CHA</b>	$\text{Na}_{7.3}\text{K}_{1.0}\text{Cs}_{2.3}\text{Al}_{10.6}\text{Si}_{25.4}\text{O}_{72}$	2.1
<b>K-CHA</b>	$\text{K}_{10.4}\text{Cs}_{1.0}\text{Al}_{11.4}\text{Si}_{24.9}\text{O}_{72}$	2.2
<b>Cs-CHA</b>	$\text{K}_{1.8}\text{Cs}_{10.5}\text{Al}_{11.7}\text{Si}_{24.2}\text{O}_{72}$	2.1

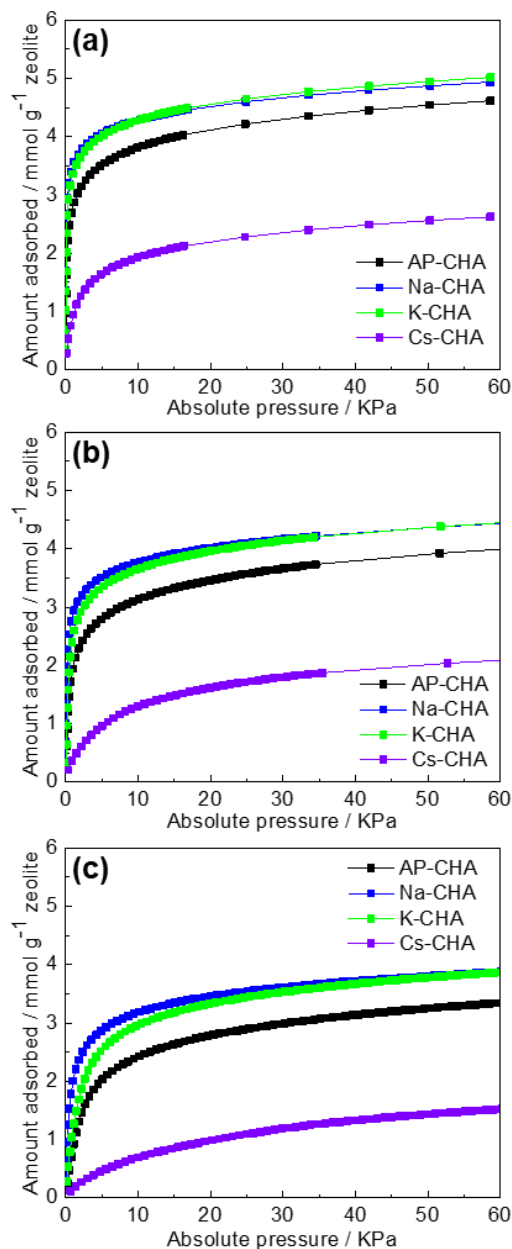
The CO<sub>2</sub> adsorption isotherms predicted for the CHA nanocrystals with different cations using GCMC calculations at 248, 273, and 298 K are presented in Fig. 2. The GCMC results reveal that the CO<sub>2</sub> capacity of the CHA nanozeolite decreases upon increasing the size of extra-framework alkali metal cations (Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup>). This is expected as less free space is available in the CHA cages occupied by larger cations.



**Fig. 2** CO<sub>2</sub> adsorption isotherms of nanosized AP-CHA, Na-CHA, K-CHA, and Cs-CHA zeolite samples at (a) 248 K, (b) 273 K, and (c) 298 K calculated using the GCMC method.

The experimentally measured adsorption isotherms of CO<sub>2</sub> on the CHA nanocrystals at the same temperatures (248, 273, and 298 K) as the GCMC modelling are presented in Fig. 3. All CO<sub>2</sub> isotherms were fully reversible; the adsorption curves associated with less potential cumulative errors are presented in Fig.3. Similar to the GCMC results, increasing the adsorption temperature was found to lead to a decrease in the CO<sub>2</sub> adsorption capacity of the CHA nanocrystals. However, unlike the GCMC results the K-CHA sample shows similar CO<sub>2</sub> adsorption behavior to the Na-CHA sample, as well as the highest CO<sub>2</sub> adsorption capacity. Nanosized Na-CHA and Cs-CHA samples showed CO<sub>2</sub> capacities of 4.5 and 2.1 mmol g<sup>-1</sup> respectively at 60 kPa and 273 K which is similar to their micron-sized counterparts.<sup>7,23</sup> While in the nanosized K-CHA sample an increase of CO<sub>2</sub> capacity was observed compared to the micron-sized K-CHA counterpart (4.5 vs 4.1 mmol g<sup>-1</sup> at 60 kPa and 273 K).<sup>24</sup> The experimentally measured CO<sub>2</sub> adsorption capacity for the nanosized CHA samples decreases in the following order: Na-CHA ≈ K-CHA > AP-CHA > Cs-CHA (Fig. 3). To address the effect of small amounts of co-cations in the nanosized CHA samples, the CO<sub>2</sub> adsorption capacity at 50 kPa of CO<sub>2</sub> and 273 K vs the amount of alkali EFCs (i.e. Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup>) in the different nanosized alkali forms of CHA is presented (Fig. S2). As shown in Fig. S2c, the CO<sub>2</sub> capacity is linearly influenced by the Cs amount present in the CHA. By increasing the content of Cs<sup>+</sup> EFC (ionic diameter of 3.4 Å) more space within the CHA framework is occupied and hence, the overall CO<sub>2</sub> capacity decreases.<sup>43</sup> While such correlations are not seen for the samples with increased amount of Na<sup>+</sup> and K<sup>+</sup> EFCs with ionic diameters of 1.9 and 2.7 Å, respectively<sup>43</sup> (Fig. S2a,b). The CO<sub>2</sub> adsorption capacity is significantly higher (over 4 mmol g<sup>-1</sup> at 50 kPa and 273 K) for Na-CHA, K-CHA, and AP-CHA samples compared to the Cs-CHA sample (2 mmol g<sup>-1</sup> at 50 kPa and 273 K). This suggests that the Cs content strictly restrict the access of CO<sub>2</sub> to the adsorption sites. Moreover, the nanosized Cs-CHA sample show a significantly lower experimentally measured CO<sub>2</sub> adsorption capacity as compared to the other samples and to the theoretically predicted values by GCMC (Fig. 2 vs Fig. 3). Such discrepancies are discussed in more detail below. GCMC calculations are an effective tool to predict CO<sub>2</sub> adsorption in different CHA zeolite samples. However, perfect zeolite crystals without defects are used to describe the zeolite structure and adsorbate. Inconsistencies between experimentally measured and theoretically calculated results may arise from the fact that the defects in zeolites effect the adsorption of CO<sub>2</sub>. Additionally, large EFCs such as Cs<sup>+</sup> located within the zeolite pores can affect the CO<sub>2</sub> diffusion to the adsorption sites while GCMC calculations do not take into consideration these diffusion limitations. In the case of the nanosized Cs-CHA sample, all SIII' sites in the 8MRs are occupied by Cs<sup>+</sup> EFCs and the remaining Cs<sup>+</sup> and K<sup>+</sup> EFCs most likely occupying the SII sites (see cationic sites in Fig. 1a).<sup>27-29,44</sup> The occupation of the SII site by Cs<sup>+</sup> would significantly decrease the available space within the CHA cages due to the cation

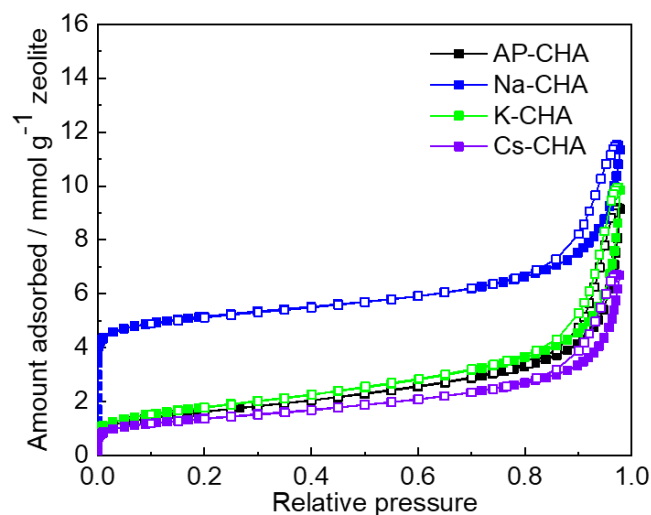
size, however, those free spaces are available for the GCMC simulations and resulted in overestimation of CO<sub>2</sub> adsorption capacities comparing to the experimental adsorption measurements (Fig. 2 vs Fig. 3).



**Fig. 3** CO<sub>2</sub> adsorption isotherms for nanosized AP-CHA, Na-CHA, K-CHA, and Cs-CHA zeolite samples measured at (a) 248 K, (b) 273 K, and (c) 298 K.

The N<sub>2</sub> adsorption and desorption isotherms of nanosized CHA samples with different cations measured at 77 K are presented in Fig. 4; the corresponding specific BET surface area and micropore volume are summarized in Table 3. In samples K- and Cs-CHA, all Na<sup>+</sup> cations were removed and replaced by the bigger and heavier K<sup>+</sup> and Cs<sup>+</sup> cations which occupy the SIII' positions

acting as door-keepers and prevent the diffusion of  $N_2$  molecules efficiently inside the network at 77 K (Table 2). This phenomenon is not observed for sample Na-CHA with higher BET surface areas ( $439 \text{ m}^2 \text{ g}^{-1}$ ). The nanosized AP-, K-, and Cs-CHA zeolite samples exhibit a low micropore volume ( $0.01 \text{ cm}^3 \text{ g}^{-1}$ ) compared to the Na-CHA sample ( $0.14 \text{ cm}^3 \text{ g}^{-1}$ ). This value is comparable to that of micron-sized Na-CHA with a similar Si/Al ratio and similar EFC composition reported by Ridha *et al.*<sup>45</sup> In the case of the nanosized Na-CHA sample, a small difference between the GCMC and experimental results is observed (Fig. 2 vs Fig. 3). This can be explained with the presence of co-cations ( $K^+$  and  $Cs^+$ ) in the sample determined experimentally (Table 2). The Na-CHA sample has a significantly higher micropore volume compared to the AP-, K- and Cs-CHA samples due to the preference of  $Na^+$  occupying the SII site within the supercage (Fig. 4 and Table 3).<sup>46</sup> This behavior is consistent with the results reported previously for micron-sized Na-CHA with similar Si/Al ratios.<sup>24,45</sup> The observation of a high micropore volume and BET surface area determined by  $N_2$  adsorption analysis at 77 K as well as a high  $CO_2$  adsorption capacity measured at 273 K for the nanosized Na-CHA indicates that the sample does not exhibit molecular trapdoor behavior. For the nanosized K-CHA sample the GCMC results (Fig. 2) are in good agreement with the experimental adsorption isotherms (Fig. 3). The observation of a low micropore volume determined by  $N_2$  adsorption analysis at 77 K and a high  $CO_2$  adsorption capacity measured at 273 K for the nanosized K-CHA indicates that the sample exhibits molecular trapdoor behavior, consistent with the observations reported previously for micron-sized K-CHA.<sup>23,24</sup> The discrepancy between the experimental and theoretical results for the nanosized Cs-CHA sample can be explained by the restricted accessibility of  $CO_2$  guest molecules to the CHA cages due to the presence of  $Cs^+$  EFCs (*vide supra*). In the GCMC calculations,  $CO_2$  molecules can be inserted and displaced freely subject to the available cavities in order to minimize the grand potential of the system at a given chemical potential (or fugacity) and temperature. However, in real samples, a significant part of the structure is inaccessible due to the presence of large  $Cs^+$  cations. As a consequence, the theoretical results deviate from the experimental data for this specific case (Cs-CHA). The modeled  $CO_2$  adsorption isotherm of the AP-CHA sample was calculated with respect to the experimentally determined chemical composition (see Table 2). As shown (Fig. 2 vs Fig. 3), the modeled and experimental  $CO_2$  adsorption isotherms for the AP-CHA nanocrystals are in a good agreement. The good agreement can be explained by the low  $Cs^+$  content in this sample (Table 2).



**Fig. 4** Nitrogen adsorption/desorption isotherms of nanosized AP-CHA, Na-CHA, K-CHA, and Cs-CHA zeolite samples measured at 77 K (the filled squares represent the adsorption branch while the empty squares represent the desorption branch of the experiments).

**Table 3.** BET specific surface area and micropore volume of nanosized AP-CHA, Na-CHA, K-CHA, and Cs-CHA zeolite samples determined from N<sub>2</sub> adsorption measurements at 77 K and the corresponding CO<sub>2</sub> capacities measured at 50 kPa CO<sub>2</sub> at 273 K.

Sample	$S_{\text{BET}} / \text{m}^2 \text{g}^{-1}$	$V_{\text{micro}} / \text{cm}^3 \text{g}^{-1}$	CO <sub>2</sub> capacity* / mmol g <sup>-1</sup>
AP-CHA	132	0.01	4.0
Na-CHA	439	0.14	4.5
K-CHA	146	0.01	4.5
Cs-CHA	111	0.01	2.1

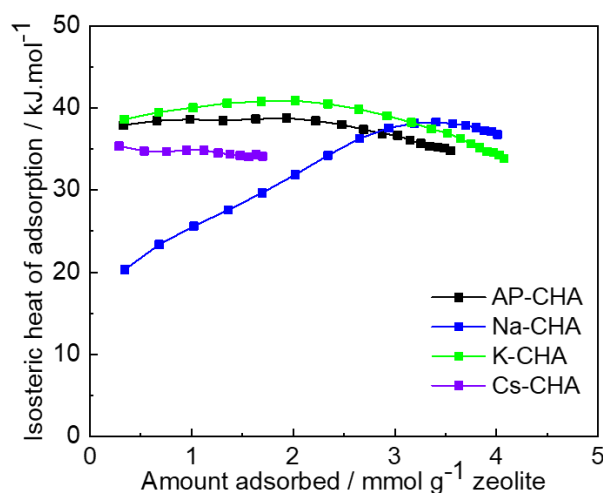
\* At 60 kPa of CO<sub>2</sub> and 273 K.

In order to better understand the interaction of the CO<sub>2</sub> molecules with the different EFCs, the isosteric heats of CO<sub>2</sub> adsorption ( $\Delta H_{\text{iso}}$ ) for the CHA nanocrystals were calculated as a function of CO<sub>2</sub> uptake by applying the Clausius-Clapeyron equation to the experimentally measured CO<sub>2</sub> adsorption isotherms between 248 to 298 K (Fig. 5).<sup>32,33</sup> Between the four different nanosized CHA samples, three different types of  $\Delta H_{\text{iso}}$  behavior can be distinguished due to the different EFC content. (i) For nanosized AP- and K-CHA, the heat of adsorption initially increases slightly from 37.9 kJ mol<sup>-1</sup> at 0.3 mmol g<sup>-1</sup> loading to 38.7 and 40.8 kJ mol<sup>-1</sup> at 1.6 mmol g<sup>-1</sup> of CO<sub>2</sub> surface coverages, which is consistent with the presence of specific heterogeneous cationic adsorption sites interacting with the quadrupole moment of the CO<sub>2</sub> molecules (*i.e.* strong adsorbate-adsorbent interactions). As the amount of adsorbed CO<sub>2</sub> increases, steric (*i.e.* repulsive) adsorbate-adsorbate interactions become more substantial resulting in  $\Delta H_{\text{iso}}$  slow decrease to lower values (around 30–35 kJ mol<sup>-1</sup>). Eventually, a slow decreasing asymptote-like decay is

observed. This  $\Delta H_{\text{iso}}$  behavior is well understood and documented for small pore zeolites.<sup>47</sup> The similar  $\Delta H_{\text{iso}}$  values for AP- and K-CHA samples is likely a consequence of the similar cations location within the CHA structure;  $\text{Cs}^+$  and  $\text{K}^+$  prefer to occupy the SIII' site in the 8MR while the remaining  $\text{Na}^+$  and  $\text{K}^+$  occupy the SII site above the S6R. This provides similar coordination environments for  $\text{CO}_2$  which will preferentially orientate along the c-axis (dual-cation site) as discussed by Pham *et al.* for CHA zeolite with a high Al content.<sup>48</sup> Previously we showed that the adsorbed  $\text{CO}_2$  was coordinated along the c-axis of the supercage in high Al-containing nanosized CHA.<sup>27</sup> (ii) The Cs-CHA sample shows an almost constant  $\Delta H_{\text{iso}}$  value with  $\text{CO}_2$  loading. This sample reaches almost immediately a balance between decreasing adsorbate-adsorbent and increasing attractive adsorbate-adsorbate interactions at a  $\Delta H_{\text{iso}}$  of about  $35 \text{ kJ mol}^{-1}$ . A small decrease to lower  $\Delta H_{\text{iso}}$  ( $34.1 \text{ kJ mol}^{-1}$ ) is observed at higher coverages ( $1.7 \text{ mmol g}^{-1}$ ) and compared to K-CHA, access to the pore network of Cs-CHA is more restricted. This is due to the larger size of the  $\text{Cs}^+$  EFCs which can interact more strongly with the framework oxygens of the 8MRs, as well as  $\text{Cs}^+$  located at the SII site in the CHA cage, restricting the deviation of  $\text{Cs}^+$  from the 8MR to allow the rapid uptake of  $\text{CO}_2$ .<sup>23,26</sup> The lower  $\Delta H_{\text{iso}}$  value of Cs-CHA compared to K-CHA is likely due to the lower charge density of  $\text{Cs}^+$  compared to  $\text{K}^+$  despite the presumably shorter coordination distance for  $\text{CO}_2$  at the dual-cation site, *i.e.* coordination between cations at either the SII/SII or SII/SIII' sites.<sup>48</sup> The almost constant  $\Delta H_{\text{iso}}$  is likely due to the limited number of  $\text{CO}_2$  molecules reaching the CHA supercage, resulting in an overall low adsorption uptake with a fast equilibrium followed. This is followed by a minor decrease of  $\Delta H_{\text{iso}}$  values at higher coverages due to repulsive adsorbate-adsorbate interactions. For sample Cs-CHA, the cation reversible position deviation due to the trapdoor effect may also play a role on the  $\Delta H_{\text{iso}}$  and might not be exclusively be related with the  $\text{CO}_2$  adsorption. (iii) Finally, for the Na-CHA sample, the initial  $\Delta H_{\text{iso}}$  ( $20 \text{ kJ mol}^{-1}$ ) is significantly lower compared to the other samples. This is followed by a continuous increase in  $\Delta H_{\text{iso}}$  up to a maximum of  $38.3 \text{ kJ mol}^{-1}$  at  $3.4 \text{ mmol g}^{-1}$  of  $\text{CO}_2$  loading, then followed by a small decrease to  $36.8 \text{ kJ mol}^{-1}$  at  $4.0 \text{ mmol g}^{-1}$  loading (Fig. 5). A similar shape of the  $\Delta H_{\text{iso}}$  curve has been observed for Na-Rho (however, the maximum was at half the surface coverage reported here) and, to a lesser degree, for Na-CHA samples.<sup>7,49</sup> The evolution of the heat of adsorption curve suggests that the surface is "homogeneous" (similar to K-CHA) with a very accessible and open micropore structure being consistent with the smaller size of the  $\text{Na}^+$  ion.<sup>50</sup> The increase is thus due to the growing contribution of the adsorbate-adsorbent interactions until higher surface coverage is reached.

Based on these observations, we propose to rationalize all the heat of adsorption patterns using a general data interpretation hypothesis: It is very likely that all  $\text{CO}_2$  adsorption data should display a so-called "bell-shaped" curve for  $\Delta H_{\text{iso}}$  as a function of the surface coverages. However, depending on the chemical nature of the adsorbent and the cation, we may not be able to measure

accurately the full bell with respect to the technical and kinetic limits associated with volumetric instrumentation up to 1 bar. The substantial presence of the so-called “door-keeping” cations may also affect the  $\Delta H_{\text{iso}}$  curve shape to some extent. Despite this potential effect, we consider that the general bell curve assumption holds. Therefore, the experimental position of the maximum and our ability to measure it here depends on the cation size. For Na-CHA, the small size of  $\text{Na}^+$  cations results in adsorption of several  $\text{CO}_2$  molecules before reaching the turning point where the loading is sufficient enough for the repulsive part of the  $\text{CO}_2$ - $\text{CO}_2$  contribution to be statistically dominant. While for Cs-CHA, it is the opposite case. Because  $\text{Cs}^+$  is a large cation there is not enough room for the adsorption of many  $\text{CO}_2$  molecules, even at low  $\text{CO}_2$  loading, leading to an immediate impact of repulsive steric effects. In other words, with such large cations, much lower relative pressures would be necessary to see the increasing part of the bell curve. As mentioned above, the importance of the heat of adsorption component coming from the reversible molecular trapdoor effect is still unclear and will require further in-depth investigations. Finally, AP- and K-CHA represent more ideal systems where the intermediate cation size and gating effects allow for observing the “full bell”. Further in-depth investigations are currently ongoing on this topic to strengthen our hypothesis. However, these investigations go beyond the scope of the present manuscript and will be reported in a dedicated high-resolution low- and high-pressure adsorption study.

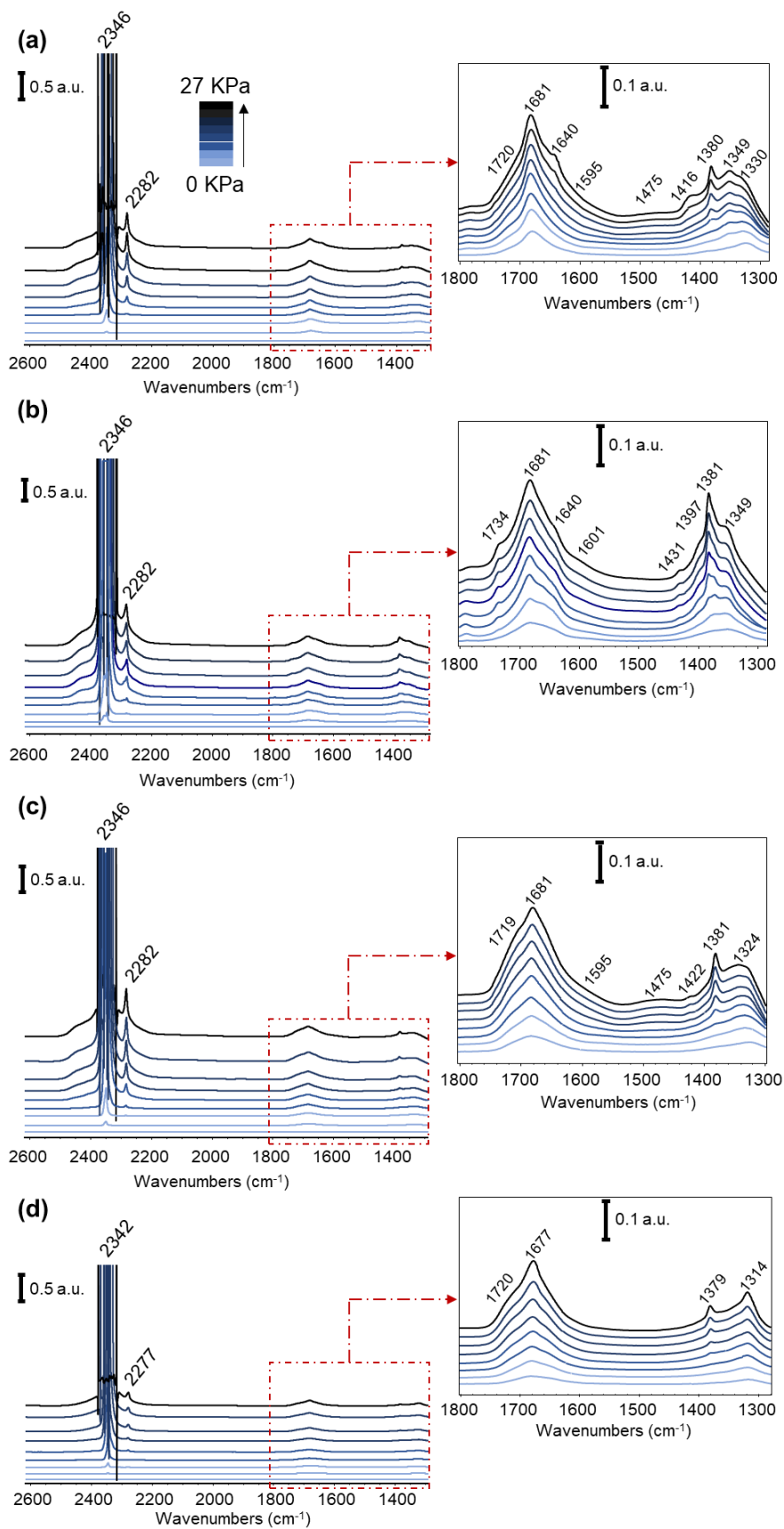


**Fig. 5** Isosteric heat of adsorption of  $\text{CO}_2$  on nanosized AP-CHA, Na-CHA, K-CHA, and Cs-CHA zeolite samples vs  $\text{CO}_2$  surface loading.

To shed further light on the  $\text{CO}_2$  adsorption behavior, the nanosized CHA samples were studied by *in situ* FTIR spectroscopy. The IR spectra of these samples under an atmosphere of  $\text{CO}_2$  at different pressures at 298 K are presented in Fig. 6. Upon exposing the samples to  $\text{CO}_2$ , bands at

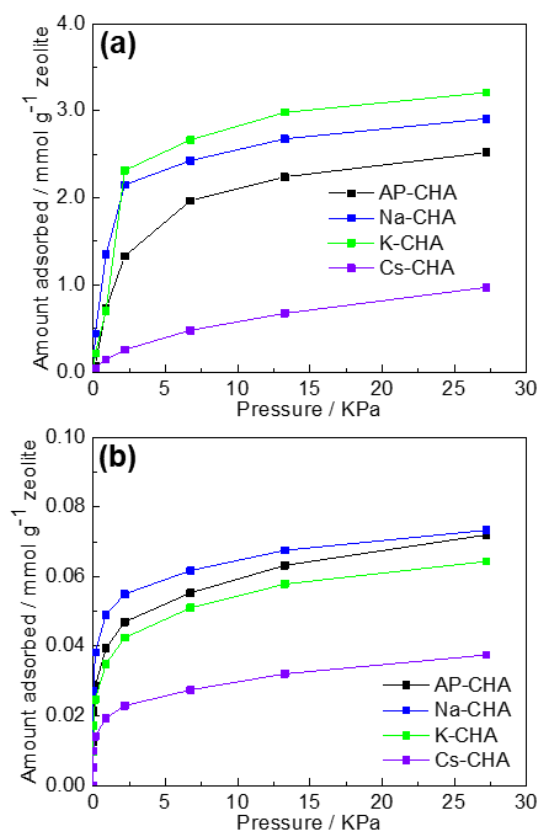
$\sim 2346$  and  $\sim 2282$   $\text{cm}^{-1}$  related to physisorbed  $\text{CO}_2$  and a series of bands from  $1314$  to  $1734$   $\text{cm}^{-1}$  related to chemisorbed  $\text{CO}_2$  species appear.<sup>51,52</sup> The band at  $2346$   $\text{cm}^{-1}$  corresponds to the physisorption of  $^{12}\text{CO}_2$ , however, due to the high  $\text{CO}_2$  concentration applied to all samples, a saturation of the FTIR signal prevents the utilization of this band for evaluation. As a consequence, the  $^{13}\text{C}$  isotope (from natural abundance; 1.11 %) variant of  $\text{CO}_2$  which can be detected by FTIR at  $2282$   $\text{cm}^{-1}$  was used to quantify the physisorbed  $\text{CO}_2$ .

Upon exposing the samples in different alkali forms to  $\text{CO}_2$ , four carbonate species are detected (Fig. 6). The AP-CHA nanosized sample shows a band at  $1416$   $\text{cm}^{-1}$  assigned to the free carbonate species, a pair of bands at  $1475$  &  $1595$   $\text{cm}^{-1}$  ( $\Delta\nu_3 = 120$   $\text{cm}^{-1}$ ) assigned to unidentate carbonates, two pairs at  $1349$  &  $1640$   $\text{cm}^{-1}$  ( $\Delta\nu_3 = 291$   $\text{cm}^{-1}$ ) and  $1380$  &  $1681$   $\text{cm}^{-1}$  ( $\Delta\nu_3 = 301$   $\text{cm}^{-1}$ ) assigned to two slightly different chemisorbed bidentate carbonate species, and a pair of bands  $1330$  &  $1720$   $\text{cm}^{-1}$  ( $\Delta\nu_3 = 390$   $\text{cm}^{-1}$ ) related to the bridged bidentate carbonates.<sup>51-54</sup> Similar to the AP-CHA sample, in sample Na-CHA the formation of free carbonates at  $1397$   $\text{cm}^{-1}$ , unidentate carbonates at  $1431$  &  $1601$   $\text{cm}^{-1}$  ( $\Delta\nu_3 = 170$   $\text{cm}^{-1}$ ), two slightly different chemisorbed bidentate carbonate species at  $1349$  &  $1640$   $\text{cm}^{-1}$  ( $\Delta\nu_3 = 291$   $\text{cm}^{-1}$ ) and  $1381$  &  $1681$   $\text{cm}^{-1}$  ( $\Delta\nu_3 = 300$   $\text{cm}^{-1}$ ), and a band at  $1734$   $\text{cm}^{-1}$  assigned to bridged bidentate carbonate species are observed.<sup>51-54</sup> While the IR spectrum of sample K-CHA reveals the presence of free carbonate at  $1422$   $\text{cm}^{-1}$ , unidentate carbonates at  $1475$  &  $1595$   $\text{cm}^{-1}$  ( $\Delta\nu_3 = 120$   $\text{cm}^{-1}$ ), only one type of bidentate carbonates at  $1381$  &  $1681$   $\text{cm}^{-1}$  ( $\Delta\nu_3 = 300$   $\text{cm}^{-1}$ ), and bridged bidentate carbonates at  $1324$  &  $1719$   $\text{cm}^{-1}$  ( $\Delta\nu_3 = 395$   $\text{cm}^{-1}$ ).<sup>51-54</sup> The IR spectrum of Cs-CHA sample shows the formation of only bidentate carbonates at  $1379$  &  $1677$   $\text{cm}^{-1}$  ( $\Delta\nu_3 = 298$   $\text{cm}^{-1}$ ) and bridged bidentate carbonate species at  $1314$  &  $1720$   $\text{cm}^{-1}$  ( $\Delta\nu_3 = 406$   $\text{cm}^{-1}$ ).<sup>51-54</sup> The intensity of the peaks in this region ( $1314 - 1734$   $\text{cm}^{-1}$ ) were used to quantify the chemisorbed  $\text{CO}_2$  species.<sup>52</sup>



**Fig. 6** *In situ* FTIR spectra of nanosized (a) AP-CHA, (b) Na-CHA, (c) K-CHA, and (d) Cs-CHA zeolite samples under increasing of CO<sub>2</sub> pressure (0–27 kPa) at 298 K; all samples were pretreated at 623 K under high vacuum (10<sup>-6</sup> kPa) prior to measurement.

Fig. 7a shows the isotherms corresponding to physisorbed CO<sub>2</sub> recorded for different nanosized CHA samples at 298 K based on the integration of the <sup>13</sup>CO<sub>2</sub> FTIR band at 2282 cm<sup>-1</sup> which was corrected with respect to the natural abundance of <sup>13</sup>C (1.11%) to include both <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> (Table S1). Fig. 7b presents the isotherms corresponding to CO<sub>2</sub> chemisorption on the nanosized CHA samples at 298 K based on the FTIR chemisorption region of 1314-1734 cm<sup>-1</sup> (Table S2 and Table S3). These results are consistent with the work by Polisi *et al.*<sup>52</sup> in studying CO<sub>2</sub> adsorption on sodium forms of zeolites X and Y. Moreover, these results suggest that the CO<sub>2</sub> chemisorption is inversely related to the size of the alkali cations. The main mode of CO<sub>2</sub> adsorption for the different alkali forms of nanosized CHA is physisorption since this mode consist over 96 % of the adsorption based on the *in situ* FTIR (Fig. 7a,b Table S4). This also explains the saturation of the main <sup>12</sup>CO<sub>2</sub> adsorption band at 2346 cm<sup>-1</sup> presented in Fig. 6 under CO<sub>2</sub> adsorption with pressures as low as 6 kPa.

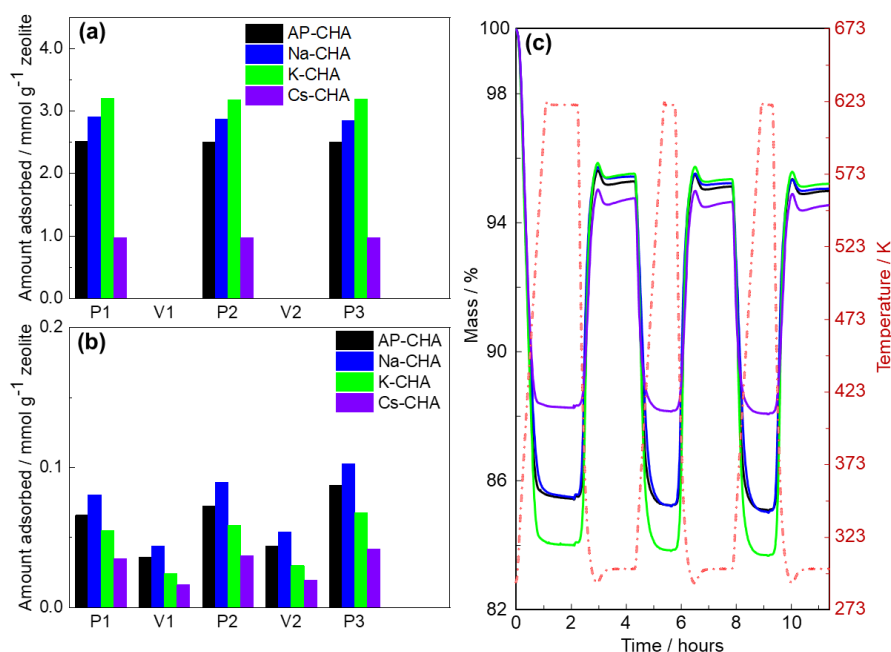


**Fig. 7** CO<sub>2</sub> (a) physisorption and (b) chemisorption isotherms for nanosized AP-CHA, Na-CHA, K-CHA, and Cs-CHA zeolite samples based on *in situ* FTIR spectra recorded at 298 K.

Fig. 8 shows three consecutive vacuum regeneration ( $\sim 10^{-6}$  kPa) and CO<sub>2</sub> dosing (27.2 kPa) cycles of different nanosized CHA sample recorded using *in situ* FTIR spectroscopy by integration of the <sup>13</sup>CO<sub>2</sub> band at 2282 cm<sup>-1</sup> corresponding to physisorbed species corrected with respect to the

natural abundance of  $^{13}\text{C}$  (1.11%) (Fig. 8a) and chemisorbed species in the region of 1314 – 1734  $\text{cm}^{-1}$  (Fig. 8b). Upon applying the first vacuum (V1), all physisorbed species are successfully removed from the samples as shown in Fig. 8a and Fig. S3. While some chemisorbed species still remain in the zeolites after regeneration using the primary vacuum (Fig. 8b and Fig. S3). The following  $\text{CO}_2$  dosing and vacuum regeneration (P2 and V2) show that the  $\text{CO}_2$  physisorption capacity of the samples did not change (Fig. 8a). The third  $\text{CO}_2$  dosing (P3) reveals that the  $\text{CO}_2$  physisorption capacity does not decrease (Fig. 8b and Fig. S3) despite the minor accumulation of the chemisorbed species. In fact, after quantification of chemisorption using *in situ* FTIR results (Table S5), this accumulation only corresponds to less than 0.8 % of the whole adsorption which is the reason why no loss of  $\text{CO}_2$  capacity was observed.

The adsorption behavior of different alkali forms of nanosized CHA was investigated further by performing multiple thermogravimetric (TG) cycles of heating (623 K) and flowing  $\text{CO}_2$  at 298 K (Fig. 8c). Similar to the regeneration of samples using a high vacuum, no  $\text{CO}_2$  capacity loss was observed when heating was used for the regeneration. The XRD patterns of different alkali forms of nanosized CHA were collected after the  $\text{CO}_2$  cycling experiments and presented in Fig. S4. The crystallinity of the samples is fully preserved thus confirming their high stability under cycling  $\text{CO}_2$  experiments. The materials can be excellent candidates for the separation of  $\text{CO}_2$  from  $\text{N}_2$  or  $\text{CH}_4$  in both vacuum swing or temperature swing processes.



**Fig. 8** Amount adsorbed  $\text{CO}_2$  on nanosized AP-CHA, Na-CHA, K-CHA, and Cs-CHA zeolite samples under consecutive vacuum regeneration at 298 K represented by the (a) physisorbed (based on the  $^{13}\text{CO}_2$  band) and (b) chemisorbed  $\text{CO}_2$  based on *in situ* FTIR at 298 K. (V) stands for high vacuum of  $10^{-6}$  kPa and (P) stands for  $\text{CO}_2$  dosage of 27.2 kPa, and (c) TG cycles of  $\text{CO}_2$  adsorption under flow ( $40 \text{ mL min}^{-1}$ ) at 298 K and regeneration by increasing the temperature to 623 K for

The type and content of alkali metal cations ( $\text{Na}^+$ ,  $\text{K}^+$ , or  $\text{Cs}^+$ ) in the nanosized CHA zeolite samples significantly changes both the  $\text{CO}_2$  adsorption behavior and the  $\text{CO}_2$  separation performance in the presence of  $\text{N}_2$ . This is due to the different sizes of the cations which dictates their ability to occupy the 8MRs and control the selective uptake of  $\text{CO}_2$  in the presence of non-polar small molecules such as  $\text{N}_2$  and  $\text{CH}_4$ . For the nanosized Na-CHA sample, the micropore volume based on  $\text{N}_2$  adsorption at 77 K ( $0.14 \text{ cm}^3 \text{ g}^{-1}$  at 77 K, Table 3) as well as the high  $\text{CO}_2$  adsorption capacity ( $4.0 \text{ mmol g}^{-1}$  at 298 K, Fig. 3c) are consistent with the previously published results for micron-sized Na-CHA. The results show that  $\text{Na}^+$  is unable to effectively occupy the 8MRs of the supercages and to control the selective adsorption of small molecules.<sup>24</sup> Hence, an open porosity can be imagined for this sample which can be further supported by the  $\Delta H_{\text{iso}}$  results (Fig. 5) with a wide range of adsorption sites with different energies being available. Conversely, in the nanosized AP-CHA and K-CHA samples, molecular trapdoor behavior is observed due to the extremely low micropore volume in the presence of  $\text{N}_2$  ( $0.01 \text{ cm}^3 \text{ g}^{-1}$ , Table 3) while possessing high  $\text{CO}_2$  capacity (Fig. 3). The nanosized Cs-CHA sample shows similar behavior to the K-CHA sample, however, the  $\text{CO}_2$  capacity is lower ( $1.7 \text{ mmol g}^{-1}$  at 298 K, Fig. 3c) due to the larger size of the  $\text{Cs}^+$  cation. Comparing the  $\text{CO}_2$  adsorption isotherms obtained from the adsorption measurements and from *in situ* FTIR spectroscopy (Fig. 3c vs Fig. 7a), one can conclude that all samples mainly contained physisorbed  $\text{CO}_2$  (over 96 % of the  $\text{CO}_2$  adsorption) with minor formation of carbonate species (Fig. 6).

#### 4. Conclusions

The adsorption of  $\text{CO}_2$  in four different alkali metal cationic forms of nanosized chabazite (CHA) zeolite (AP-, Na-, K-, and Cs-CHA) were studied using GCMC modeling, experimental adsorption isotherm measurements, isosteric heat of adsorption calculations and *in situ* FTIR spectroscopy. Comparing GCMC predictions for  $\text{CO}_2$  adsorption isotherms with those obtained experimentally for the different alkali metal cationic forms of nanosized CHA samples revealed that this method is a powerful tool to predict the  $\text{CO}_2$  adsorption capacity of different CHA samples with various cationic compositions where diffusion restrictions of guest molecules due to the size of the extra-framework cations are not foreseen. Experimental adsorption measurements showed that the  $\text{Na}^+$  cations in nanosized Na-CHA sample do not block the CHA pore openings (8MRs) to guest molecules ( $\text{CO}_2$  or  $\text{N}_2$ ). The Na-CHA sample exhibits an open porosity in contrast to the other samples. This sample shows high  $\text{CO}_2$  uptake ( $4.5 \text{ mmol g}^{-1}$  at 60 kPa and 273 K) and high micropore volume upon  $\text{N}_2$  adsorption ( $0.14 \text{ cm}^3 \text{ g}^{-1}$  at 77 K) which is similar to micron-sized zeolites with comparable Si/Al ratios and cation populations. In comparison, the nanosized K-CHA

sample shows a high CO<sub>2</sub> adsorption capacity (4.5 mmol g<sup>-1</sup> at 60 kPa and 273 K) and significantly lower micropore volume based on N<sub>2</sub> adsorption measurements (0.01 cm<sup>3</sup> g<sup>-1</sup> at 77 K), hence molecular trapdoor behavior is observed for this sample. Similar to the K-CHA sample, the nanosized Cs-CHA sample shows negligible N<sub>2</sub> adsorption (0.01 cm<sup>3</sup> g<sup>-1</sup>), however, the CO<sub>2</sub> capacity decreases by half (2.1 mmol g<sup>-1</sup> vs 4.5 mmol g<sup>-1</sup>) compared to the K-CHA sample due to the larger size of the Cs<sup>+</sup> cations and the restricted diffusion of guest molecules. A general bell-shaped model is proposed for the isosteric heat of CO<sub>2</sub> adsorption with the position of the curve maximum and extent of each part of the bell curve being dependent on the nature of the cations. Moreover, *in situ* FTIR CO<sub>2</sub> adsorption results revealed that CO<sub>2</sub> is mainly physically adsorbed on all nanosized CHA sample, and the chemisorption of CO<sub>2</sub> can be decreased by exchanging smaller for larger cations. The CHA nanocrystals may be considered as an excellent candidate for CO<sub>2</sub> capture from a mixture containing N<sub>2</sub> and possibly CH<sub>4</sub> in vacuum swing (especially for low-temperature regeneration processes) or temperature swing applications.

### **Author Contributions**

S. G.: synthesis, analysis, validation, visualization, writing of original draft, review & editing; B. C.: theoretical study, supervision of theoretical section, validation, writing – review & editing; E. B. C.: validation, writing – review & editing; R. G. N.: analysis, methodology, validation, writing – review & editing; P. B.: investigation, validation, supervision of the FTIR section; M. D.: analysis; L. J. A.: analysis; V. R.: analysis; S. M.: funding acquisition, project administration, resources, supervision of the whole work, validation, writing – review & editing

### **Conflicts of interest**

There are no conflicts to declare.

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