

# Thermodynamics of Carbon (IV)-Oxide adsorption on NaA Zeolite obtained by modification of angren kaolin

Muxlis Oydinov<sup>1\*</sup>, Tolibjon Abdulxayev<sup>2</sup>, Mirzihid Kokhkharov<sup>2</sup>, Eldor Abdurakhmonov<sup>1</sup>, and Firuza Rakhmatkarieva<sup>1</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan, avenue Mirzo Ulugbek, 77A, 100071 Tashkent, Uzbekistan

<sup>2</sup>Namangan Engineering and Technological Institute, 160115 Namangan, Uzbekistan

**Abstract.** Purification of natural gas from carbon dioxide is extremely important for the gas processing industry of Uzbekistan. Type A zeolites are the most suitable for this purpose. The patterns of water adsorption in the NaA zeolite have been considered. It was found that an appreciable amount of water is adsorbed in  $\beta$ -cavities. The carbon dioxide molecule is somewhat larger than the water molecule and, therefore, at room temperature it is unable to penetrate into the  $\beta$ -cavities through the six-membered oxygen windows of 2.6 Å diameter and form there ion-molecule clusters with sodium cations. However, the cations themselves can migrate from the  $\beta$ -cavities to the  $\alpha$ -cavities under the influence of adsorbing molecules.

## 1 Introduction

Carbon dioxide is a strategic gas in many industrial processes. Excessive emission of carbon dioxide into the atmosphere leads to the global greenhouse effect [1]. The solution to this problem is possible and economically profitable if adsorption techniques are applied. One of the potential materials for selective adsorption and separation are nanoporous molecular sieves - zeolites [2-4]. They are of great interest because of the possibility to adjust their texture (pore size and architecture) or chemical properties (Si/Al ratio and nature of extra-lattice cations [5]), which ultimately affect the adsorption properties. Nanoporous zeolites such as NaA [6] and CaA [7] were previously found to be suitable for fluctuating pressure systems [8]. Extra-lattice zeolite cations provide a strong electrostatic interaction with carbon dioxide [9-11].

The sorption properties of microporous carbon, silica-alumina adsorbents with high sorption properties are currently attracting a lot of interest. In particular, a group of scientists is conducting research on sorption processes based on thermodynamic laws [15-26].

Method and materials. NaA zeolite ( $\text{Na}_{12}\text{Al}_{12}\text{Si}_{22}\text{O}_{48}$ ) obtained by modification of Angren kaolin. To dry and purify carbon dioxide, it was passed through a column with

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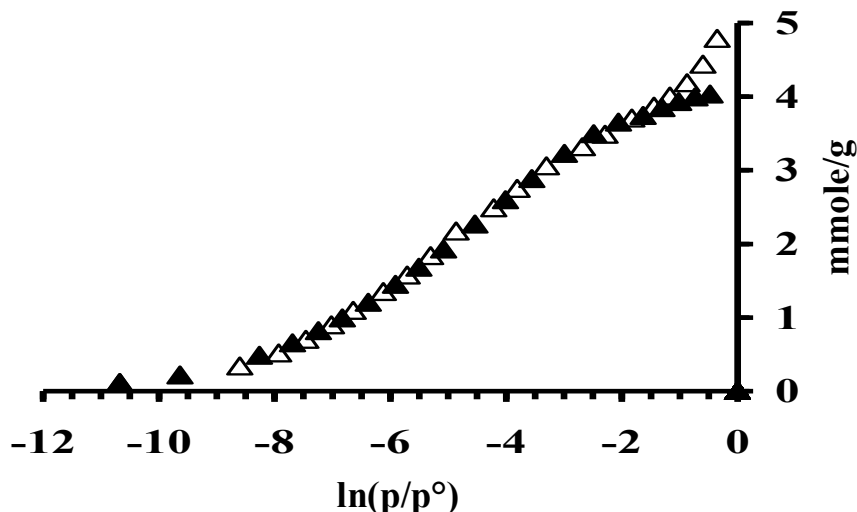
\* Corresponding author: [barnoshka4675@gmail.com](mailto:barnoshka4675@gmail.com)

zeolite. Differential molar adsorption-calorimetric studies of carbon dioxide adsorption in a NaA molecular sieve were performed using the apparatus described in [12,13]. Dissolved gases were removed by freezing the adsorbent with subsequent pumping. Using the method of heat flux compensation by the Peltier effect made it possible to increase the accuracy of adsorption heat measurements by an order of magnitude. The calorimeter makes it possible to measure the heat released over an unlimited period of time. Adsorption measurements were carried out on a universal high-vacuum volumetric unit that allowed adsorption measurements and adsorbate dosing to be carried out with great accuracy.

Results and discussion. Figure 1 shows the adsorption isotherm (a) of carbon dioxide in NaA at 303 K in the coordinates  $a-f(p/p_0)$  ( $p_0$  is the  $\text{CO}_2$  pressure, at 303 K  $p_0 = 54806$  torr, the adsorbed amount is expressed in units of  $\text{CO}_2$  per pseudo-elemental unit cell (e.y.) (the real unit cell is 8 times larger). The isotherm of water adsorption in NaA is initially slightly concave to 0.3 mmol, then grows straight up to  $\sim 4.2$  mmol/g, after which it bends towards the ordinate axis and grows linearly. The isotherm of  $\text{CO}_2$  adsorption in NaA is satisfactorily described by the two-term equation of the theory of volume filling of micropores (TOZM)

$$a = 4,06 \exp[(A/14,21)2] + 0,16 \exp[(A/12,95)5] + 2,89 \exp[(A/0,6)1],$$

where  $a$  is adsorption in micropores, mmol/g,  $A = RT \ln(P^\circ/P)$  - work of transfer of 1 mmol of vapor from the surface (pressure  $P^\circ$ ) into the equilibrium gas phase (pressure  $P$ ),

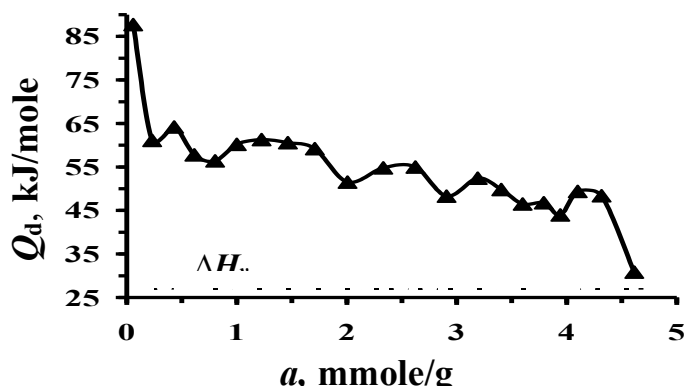


kJ/mol.

**Fig. 1.**  $\text{CO}_2$  adsorption isotherm in the NaA zeolite at 303C.  $\Delta$ -experimental data;  $\blacktriangle$ -calculated with TOSM.

Figure 2 shows the differential heat of adsorption ( $Q_d$ ) of  $\text{CO}_2$  in NaA at 303 K. The dashed line is the condensation heat of carbon dioxide at 303 K ( $\Delta H_v = 27$  kJ/mol). For NaA,  $Q_d$  starts at  $\sim 82$  kJ/mol and decreases to 57.4 kJ/mol at 0.4 mmol/g. Then  $Q_d$  forms a step, decreasing from 57.4 to 52.91 kJ/mol at 1 mmol/g. Further adsorption is accompanied by the formation of another step (wave) extending 1.0 mmol/g in the N interval from 1.0 to 2.0 mmol/g with  $Q_d$  varying from 52.91 to 52.78 kJ/mol. This is followed by an extended step extending from 2.0 to 5.0 mmol/g, followed by another step extending 1.0 mmol/g (from 5.0 to 6.0 mmol/g). The process ends with the curve passing through 2 maximums with the length of 1.0 mmol/g. The NaA zeolite accommodates a total of 7.3 mmol/g.

Stepped nature of the adsorption heat curve is considered in connection with stoichiometric interaction of CO<sub>2</sub> molecules with Na<sup>+</sup> coordination-unsaturated cations in different energy homogeneous centers of NaA zeolite cavities.



**Fig. 2.** Differential of CO<sub>2</sub> adsorption in NaA zeolite at 303C. The horizontal dotted line is the heat of condensation of water at 303C.

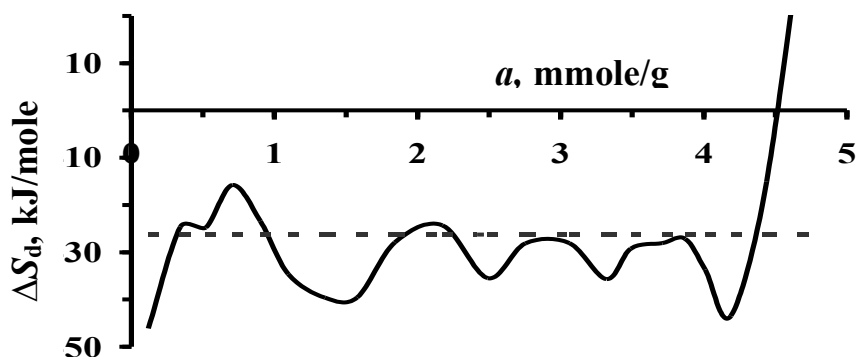
The interpretation of the results is a model of the molecular pattern. In the initial adsorption region, we observe two sections extending 1.3 CO<sub>2</sub>/eu each. Obviously, for the quadrupole CO<sub>2</sub> molecule, the SIII and SII centers are more favorable than SI due to the ion-dipole interaction with Na<sup>+</sup> cations because the degree of coordination unsaturation (k.n.) of H<sup>+</sup> and Na<sup>+</sup> cations in SIII and Na<sup>+</sup> in SII far exceeds the k.n. degree of cations in SI, where they are surrounded by six strongly shielding oxygen atoms cation. In addition, the energy of CO<sub>2</sub> adsorption with sodium cations in the NaX and NaY zeolite in a similar position is 36 kJ/mol [14], while the curve Qd in the main filling region is located much higher. In addition, in this position sodium is somewhat advanced toward the β-cavity, as shown by studies of water adsorption on NaA [10]. Consequently, we should exclude SI cations as the main centers of adsorption.

But we cannot exclude them as additional adsorption centers. Therefore, the formation of high-energy complexes should be associated with cations in positions SIII and SII. Since the cations in position SIII are 1.7 Å away from the adsorbent wall and are the most accessible to the adsorbing molecules, they should apparently be energetically preferable to the SII cations in the eight-membered oxygen windows. And, indeed, the first two sections correlate with the number of cations in the SIII position, hence, their appearance is related to the adsorption of CO<sub>2</sub> on them and the formation of high-energy complexes. As in the case of water, we attribute the strongly overestimated heat at the smallest fills to the adsorption of CO<sub>2</sub> on protons (H<sup>+</sup>), followed by adsorption on Na<sup>+</sup> cations. But unlike water, carbon dioxide is a quadrupole molecule with weak charges at the ends as compared with water. In addition, the distance between the cations in SIII and SI, as well as between SII and SI is about the size of the carbon dioxide molecule. And if we consider that the cations in positions SIII and SII have high mobility, the most likely configuration is that the carbon dioxide forms a bidentate complex with a proton or sodium in positions SIII and sodium in position SI at the ends. (H<sup>+</sup> or Na)IIIIO=C=ONaI).

In the second section, the number of CO<sub>2</sub> molecules adsorbed on SIII cations doubles (CO<sub>2</sub>)<sub>2</sub>/H<sup>+</sup> and (CO<sub>2</sub>)<sub>2</sub>/Na<sup>+</sup>. The third section corresponds exactly to the number of cations in the SII position, 3.7. Carbon dioxide forms three (CO<sub>2</sub>)/Na<sup>+</sup> complexes with the SII cations in the supercavity, each of which is also closed on the SI cation at the opposite end (NaIIO=C=ONaI).

The fourth section, one molecule long (CO<sub>2</sub>)/e.y., corresponds to the addition of a third molecule of carbon dioxide to the double complex to form (CO<sub>2</sub>)<sub>3</sub>/H<sup>+</sup> and (CO<sub>2</sub>)<sub>3</sub>/Na<sup>+</sup> complexes oriented at the opposite end to Na<sup>+</sup> in the SI. Finally, the fifth section of one molecule per e.i. is characterized by the curve passing through two high maxima. Attachment of the fourth CO<sub>2</sub> molecule to the sodium cation in SIII, is impossible due to steric considerations. Therefore, we explain the appearance of the maxima by the reorientation of CO<sub>2</sub> molecules to complete the formation of a polydentate cluster in the center of which the H<sup>+</sup> cation (first maximum) and Na<sup>+</sup> (second maximum) from position SIII are tetrahedrally surrounded by four carbon dioxide molecules, each of which at the opposite end adjoins sodium in position SI. Taking into account the distance between the opposite cations at the SI position of the  $\alpha$ -cavity and the size of the cluster, as well as the energy gain from bidentate interaction, it can be argued that such a cluster can be located only in the center of the supercavity of the NaA zeolite.

Thus, when the NaA zeolite is saturated with carbon dioxide, out of 12 sodium cations per eq. 11 are involved in the adsorption interaction, only one cation in the SI position is not involved in the adsorption process. This is due to the lack of a partner cation, and there is no opportunity for monodentant interaction, since the relatively large carbon dioxide molecule is unable to get close to the cation strongly shielded by oxygen atoms to form a strong enough bond, although the space around this center is sufficient to accommodate this complex.



**Fig. 3.** Differential entropies of CO<sub>2</sub> adsorption in NaA zeolite at 303K. The horizontal dashed line is the mean integral entropy.

Figure 3. shows the molar differential entropy of adsorption ( $\Delta S_d$ ) of carbon dioxide in NaA zeolite. Entropy of liquid carbon dioxide is taken as zero. In general,  $\Delta S_d$  curve is located above the entropy of liquid carbon dioxide except for a small section at the end of the curve. According to the shape of the differential heat curve of adsorption, the entropy of carbon dioxide adsorption in NaA grows rapidly up to 48.65 J/mol\*K in the initial region, then passes through the maximum and minimum in the first two sections, and decreases almost linearly in the third section.

At the end of the adsorption process the entropy decreases sharply, crossing the zero line and reaches - 27J/mol\*K and also grows sharply into the positive region. The deep minimum at the final stage indicates a strong localization of a four-dimensional cluster of four adsorbed carbon dioxide molecules and five Na<sup>+</sup> cations at the ends of CO<sub>2</sub> molecules. The average integral entropy of carbon dioxide adsorption in the NaA zeolite is 24 J/mol\*K, which implies that the mobility of adsorbed CO<sub>2</sub> molecules is markedly higher than that of carbon dioxide molecules in the liquid.

Conclusion. Thus, at saturation NaA zeolite holds 4.8 mmol/g of carbon dioxide molecules per unit cell. All of them are located in  $\alpha$ -cavities. The  $\beta$ -cavities are not involved in the adsorption process. Of the seven adsorbed molecules, four form a cluster in the center of which the Na<sup>+</sup> cation (originally located in position SIII) is surrounded by four carbon dioxide molecules, the opposite ends of which are closed on Na<sup>+</sup> cations in position SI. The three remaining carbon dioxide molecules form three bidentate complexes with cations in positions SII and SI. There is enough space in NaA to form the eighth complex, but for the monodentate complex, the last cation not involved in adsorption in position SI does not have enough strength to hold the carbon dioxide molecule.

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