

## CO<sub>2</sub> ADSORPTION AND DEHYDRATION BEHAVIOR OF LiNaX, KNaX, CaNaX AND CeNaX ZEOLITES

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In this study, NaX synthetic zeolite was modified by following the conventional cation exchange method at 70°C. 82, 81, 79 and 48% of sodium were exchanged with Li<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Ce<sup>3+</sup>, respectively. Thermal analysis data obtained by TG/DSC was used to evaluate the dehydration behavior of the zeolites. The strongest interaction with water and the highest dehydration enthalpy ( $\Delta H$ ) value were found for Li-exchanged form and compared with the other forms. The temperature required for complete dehydration increased with decreasing cation size (cation size: K<sup>+</sup>>Ce<sup>3+</sup>>Ca<sup>2+</sup>>Na<sup>+</sup>>Li<sup>+</sup>). CO<sub>2</sub> adsorption at 5 and 25°C was also studied and the virial model equation was used to analyze the experimental data to calculate the Henry's law constant,  $K_0$  and isosteric heat of adsorption at zero loading  $Q_{st}$ .  $K_0$  values decreased with increasing temperature and the highest  $Q_{st}$  was obtained for K rich zeolite. It was observed that both dehydration and CO<sub>2</sub> adsorption properties are related to cation introduced into zeolite structure.

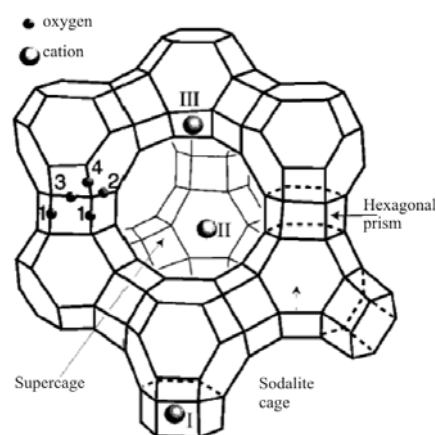
**Keywords:** cation exchange, CO<sub>2</sub> adsorption, dehydration behavior, NaX zeolite

### Introduction

Synthetic zeolites have shown great potential for a number of applications in various fields such as adsorption, separation and ion exchange. They have unique structural properties such as uniform pores, high surface area, high ion exchange capacity and high thermal stability [1]. Synthetic NaX zeolite is composed of eight sodalite cages joined through six-membered oxygen rings in a tetrahedral arrangement. It has also supercage accessible through twelve-membered oxygen rings as seen in Fig. 1 [2]. The negative charges of the AlO<sub>4</sub> units which build the framework are balanced by exchangeable cations. These cations depending heavily on the size, charge density and distribution of cations in the porous structure play a very important role in adsorption, dehydration and ion exchange properties. The water and other adsorbate molecules are loosely bound to these cations. The cations can be introduced into the supercages to affect acid-base properties of zeolite. CO<sub>2</sub> is a small, non-polar, weak acidic molecule and can be adsorbed on the surfaces having basic character. The basic properties can be increased with the aluminum content of the zeolite structure with decreasing cation electronegativity. Besides to the properties mentioned above, the quantitative structural properties of NaX zeolite based on thermal analysis (thermogravimetric analysis (TG), differential scanning calorimetry (DSC)) data are employed to gain quantitative information about the coordinated water in channels and cages of the zeolite [3]. Based on dehydration of zeolites, water is classified as

loosely bound water, zeolitic water and crystal water [4]. The cations located in the cavities and the channel walls are coordinated with water molecules which give rise to dehydration behavior of zeolites. Dehydration behavior of NaX zeolite depends on the amount and type of exchangeable cation, the Al/Si ratio, the presence or absence of H<sub>2</sub>O, time and temperature [5]. Dehydration enthalpy change and thermal stability can be determined by using thermoanalytical techniques [6].

The objective of this work is to determine the effect of cation (Li<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Ce<sup>3+</sup>) on the CO<sub>2</sub> adsorption and the dehydration behavior of the NaX zeolite.



**Fig. 1** Faujasite structure showing cation sites (I, II, III) and locations of oxygen atoms (1, 2, 3, 4)

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**Table 1** Experimental conditions for ion exchange at 70°C

The cation introduced	Li <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Ce <sup>3+</sup>
Molarity of solution/M	2	0.085	2	0.085
Solid/liquid ratio/g mL <sup>-1</sup>	5/80	2/20	5/80	3/40
Period of time/day	4	1	4	1

## Experimental

Commercial 13X (NaX) zeolite from Aldrich (Theoretical formula: Na<sub>86</sub>(Al<sub>86</sub>Si<sub>106</sub>O<sub>384</sub>) 264H<sub>2</sub>O, Si/Al:1.23, Cas# 63231-69-6) was used. The conventional exchange procedure with the conditions given on Table 1 was examined [7]. It consists of keeping the NaX zeolite in an aqueous solution of LiCl, CaCl<sub>2</sub>·2H<sub>2</sub>O, KCl or CeCl<sub>3</sub>·7H<sub>2</sub>O at 70°C. By the end of the exchange processes, solid phases were washed and centrifuged several times to obtain the zeolites Cl<sup>-</sup> free. AgNO<sub>3</sub> solution was used to determine existence of Cl<sup>-</sup> ions in zeolites. CO<sub>2</sub> adsorption was studied by using Micromeritics ASAP 2010 model static volumetric adsorption instrument at 5 and 25°C. The characterization studies were done to observe the effect of ion exchange processes on thermal and textural properties of NaX zeolite. The chemical composition of the zeolites was determined using an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES 96, Varian). Textural property such as surface area of the zeolites was determined using a Micromeritics ASAP 2010 model static volumetric adsorption instrument using nitrogen at 77 K. Prior to thermal analysis, zeolites were stored in a desiccator over a saturated ammonium chloride solution at room temperature in order to reach constant water content in zeolites. After that they were heated at a rate of 10 and 15°C min<sup>-1</sup> under nitrogen flow (40 mL min<sup>-1</sup>) for TG (Shimadzu TGA-51) and DSC (Shimadzu DSC-50) analysis, respectively.

## Results and discussion

### *Ion exchange and characterization studies*

Exchangeable cation (Na<sup>+</sup>) which balances the negative charge of the aluminosilicate framework were

**Table 2** Textural properties and percentage of exchange amount for the zeolites

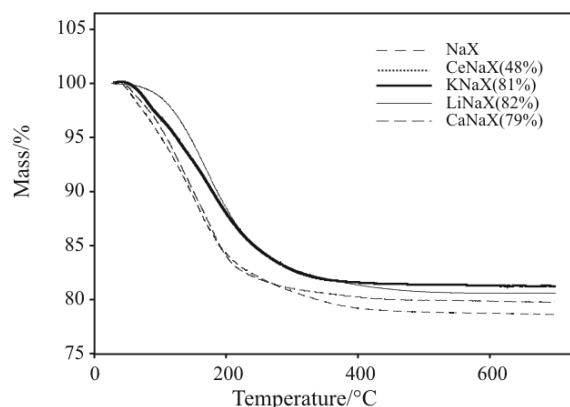
The cation introduced	Zeolite codes	Ionic/ hydrated radius of cation/Å	A <sup>L</sup> /m <sup>2</sup> g <sup>-1</sup>	V <sub>mic</sub> /cm <sup>3</sup> g <sup>-1</sup>
---	NaX	0.95/3.58	1058	0.37
K <sup>+</sup>	KNaX (81%)	1.31/3.31	897	0.33
Ce <sup>3+</sup>	CeNaX (48%)	1.05/9.0	964	0.32
Ca <sup>2+</sup>	CaNaX (79%)	0.99/4.12	1154	0.41
Li <sup>+</sup>	LiNaX(82%)	0.69/3.80	1156	0.40

A<sup>L</sup>: Surface area from Langmuir method; V<sub>mic</sub>: micropore volume from Howard–Kawazoe Method

substituted with Li<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Ce<sup>3+</sup> ions. The amount of the exchanged Na given in parenthesis with the zeolite codes (Table 2) was about 80% for LiNaX, KNaX and CaNaX. However, its value was 48% for CeNaX due to high hydrated radius of Ce<sup>3+</sup>. Nitrogen adsorption at 77 K is widely used to obtain surface area of zeolites. As seen from Table 2 Langmuir surface area and micropore volume of the cation exchanged zeolites increased with decreasing ionic radius of monovalent cations (R<sub>K<sup>+</sup></sub>>R<sub>Na<sup>+</sup></sub>>R<sub>Li<sup>+</sup></sub>). The surface area decreased with the cation introduction having higher radius (for K<sup>+</sup> and Ce<sup>3+</sup>).

### *Dehydration studies*

Thermal analyses including TG/DSC were used to investigate the change in thermal properties of the zeolites such as dehydration behavior. Zeolites were heated to high temperatures under N<sub>2</sub> flow to complete dehydration. Figure 2 shows the smooth mass loss of the zeolites obtained from TG curves. As seen from the TG data tabulated in Table 3, the required temperature to complete dehydration decreases with increasing the size of the cation introduced. Even though, direct relationship does not exist, Li-rich form has the least amount of water desorbed and the highest energy required to remove the water from the hydrated form. Therefore, Li<sup>+</sup> form presented strong interaction with water compare to the other cations. Number of water molecules desorbed per unit cell as a

**Fig. 2** TG curves of NaX, LiNaX(82%), KNaX(81%), CaNaX(79%) and CeNaX(48%) under N<sub>2</sub> flow

**Table 3** TG and DSC data of the zeolites

Zeolites	Mass loss/%	Number of water molecules desorbed per unit cell	Dehydration temperature/°C	$\Delta H/J\ g^{-1}$ zeolite	$\Delta H/J\ g^{-1}$ water
NaX	21.4	133.4	431	1100	5140
KNaX (81%)	18.8	125.7	407	791	4207
CeNaX (48%)	20.5	155.7	412	847	4131
CaNaX (79%)	20.3	131.3	422	883	4350
LiNaX(82%)	19.4	112	503	1130	5824

measure of hydrophilicity depends also upon the nature of the cations which affect the mass loss and molecular loss of the zeolites [8]. CeNaX(48%) showed the highest hydrophilic property (the order: CeNaX(48%)>NaX>CaNaX(79%)>KNaX(81%)>LiNaX(82%). The DSC curves were used to obtain dehydration enthalpy of the zeolites. Endothermic peak due to desorption of water for all zeolites was obtained below 200°C as shown in Fig. 3. This water desorbed is related to physically adsorbed water by means of cation. The enthalpy change ( $\Delta H$ ) values were obtained by using peak integration method and tabulated in Table 3. LiNaX(82%) zeolite has higher  $\Delta H$  value than the KNaX(81%), CaNaX(79%), CeNaX(48%) zeolites. As seen from the Table 3, the  $\Delta H$  values based on zeolite and water decrease with increasing the size of the cations introduced. Enthalpy change values of water in zeolites were found higher than vaporization enthalpy of pure water ( $\approx 2230\ J\ g^{-1}$ ) which shows how small pores were obtained with Li exchange.

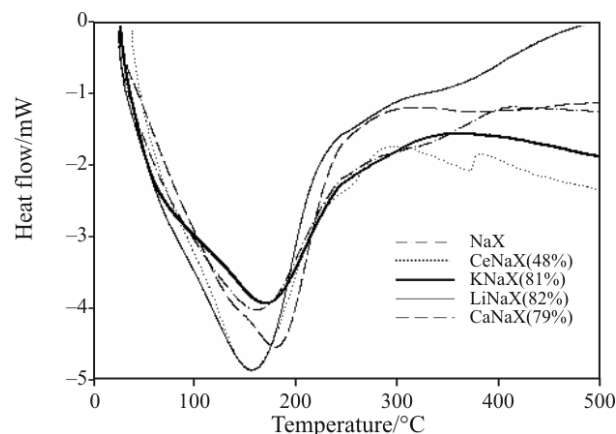
#### CO<sub>2</sub> Adsorption studies

CO<sub>2</sub> adsorption isotherms at 5 and 25°C are given in Figs 4a and b, respectively. From the figures, it is seen that CeNaX (48%) zeolite has the lowest CO<sub>2</sub> adsorption at both temperatures. This can be explained with the low micropore volume given on Table 2. Highly favorable CO<sub>2</sub> adsorption isotherm was obtained at 5°C. The virial equation in the following form was fitted to the experimental data.

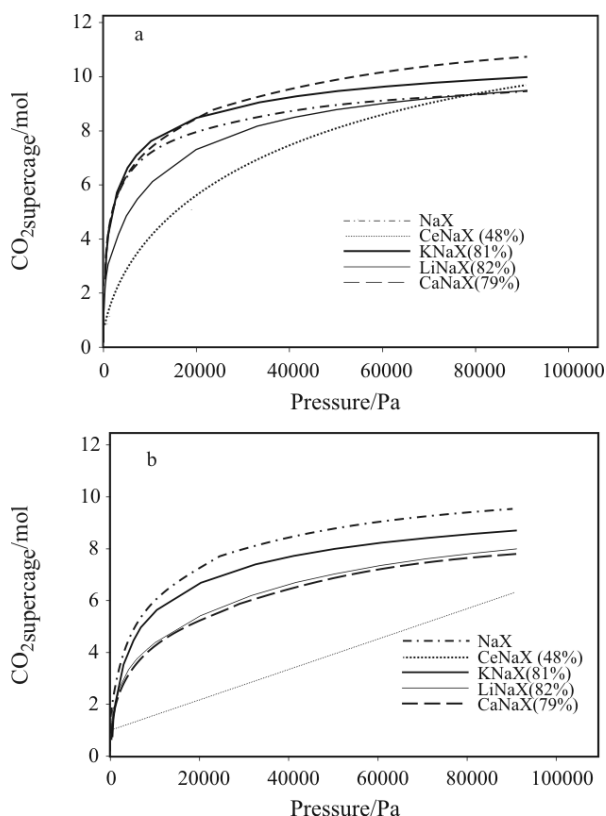
$$\ln(n/p) = A_0 + A_1 n + A_2 n^2 \quad (1)$$

**Table 4** Virial constants and isosteric heat of adsorption values

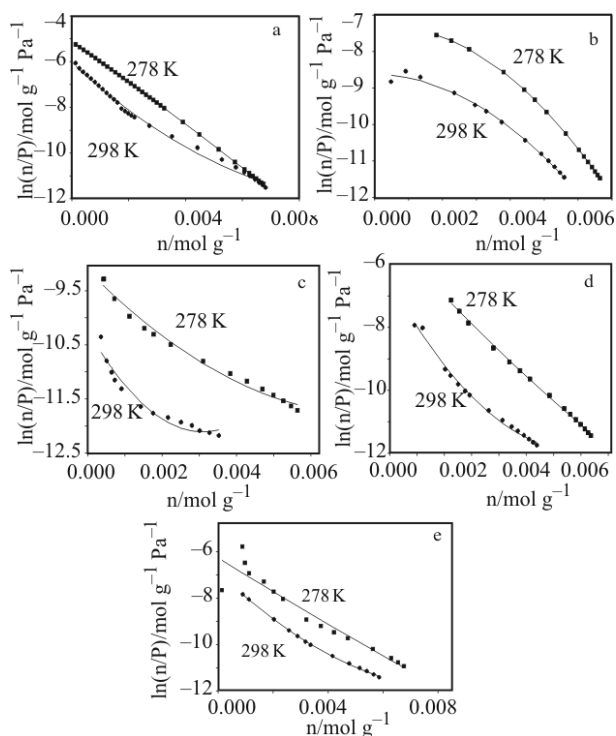
Zeolites	$A_0$	$A_1$	$R^2$	$K_0 \cdot 10^{-4}$	$Q_{st}/kJ\ mol^{-1}$				
					Temperature: 5°C		Temperature: 25°C		
NaX	-5.10	-863	0.999	60.97	-6.06	-1135	0.996	1.84	83.0
KNaX(81%)	-7.33	-572	0.98	36.98	-8.6	-851	0.960	3.32	120.5
CeNaX(48%)	-9.11	-698	0.988	1.11	-10.3	-1214	0.957	0.33	41.7
CaNaX(79%)	-5.14	-960	0.999	58.58	-6.5	-1562	0.996	14.59	87.9
LiNaX(82%)	-6.26	-732	0.910	19.11	-6.8	-1138	0.999	11.14	18.6


**Fig. 3** DSC curves of NaX, LiNaX(82%), KNaX(81%), CaNaX(79%) and CeNaX(48%) under N<sub>2</sub> flow

where  $n$  is the amount adsorbed at pressure  $p$ . As seen from Figs 5a–e, the experimental data are in good agreement ( $R^2 > 99.999$ ) with the virial model. The first virial coefficient  $A_0$  is related to the Henry's law constant,  $K_0$  ( $\exp(A_0)$ ) which depends on the interaction between the adsorbent surfaces and the adsorbed gas molecules. As given in Table 4,  $K_0$  value increases with decreasing temperature. For both temperatures, the lowest interaction between the adsorbent surfaces and the adsorbed gas molecules was obtained with the Ce-rich zeolite. The heat of adsorption at zero loading,  $Q_{st}$  was calculated from the Van't Hoff equation. The heat of CO<sub>2</sub> adsorption for K-rich zeolite was found as the greatest value ( $120.5\ kJ\ mol^{-1}$ ) due to the contribution of the energy of specific interaction with the zeolite cations [9]. The heat of adsorption was ob-



**Fig. 4** CO<sub>2</sub> adsorption isotherm of the zeolites at a – 278 K and b – 298 K



**Fig. 5** Virial plots for the adsorption of carbon dioxide on modified zeolites a – NaX, b – KNaX(81%), c – CeNaX(48%), d – CaNaX(79%) and e – LiNaX(82%) (line: model; points: experimental)

served in the same order increased with increasing ionic radius of monovalent cations introduced: KNaX(81%)>NaX>LiNaX(82%).

## Conclusions

The results of this study clearly show that the introduction of cations having different charge and ionic radius by cation exchange modified the textural properties and dehydration behavior of the zeolite. Langmuir surface area of the zeolites was increased with decreasing ionic radius of cations and the highest surface area was obtained with the LiNaX(82%) zeolite as 1156 m<sup>2</sup> g<sup>-1</sup>. Li-rich form zeolite had the highest dehydration enthalpy, whereas the least heat of CO<sub>2</sub> adsorption. For monovalent cations the dehydration enthalpy change values ( $\Delta H$ ) decreased with the increase in the size of cations while the heat of CO<sub>2</sub> adsorption was in the reverse order. Adsorption of CO<sub>2</sub> decreased with temperature. The lowest interaction between the adsorbent surfaces and the adsorbed CO<sub>2</sub> molecules was obtained with the CeNaX(48%) zeolite at both temperatures according to Henry's constant value.

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DOI: 10.1007/s10973-008-9117-9