A study of the adsorption thermodynamics of *n*-hexane on ion-exchanged X zeolites

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Abstract: In this work, the free eneregy changes and entropy changes of adsorption of *n*-hexane on zeolites of the $M_xNa_{87-2x}X$ (M = Co, Ni, Zn, Cd) type were determined using their isosteric sorption heats. It was found that the exchange of Na^+ ions in NaX with bivalent cations (Co, Ni, Zn, Cd) significantly alters the adsorption characteristics of NaX zeolite. The free energy changes and entropy changes of *n*-hexane adsorption were dependent on the surface coverage and on the nature of the charge-balancing cation. The specific influence of the exchanged cations on the free energy changes and entropy changes of sorption of *n*-hexane originates from the size, location and electronic configuration of the cation.

Keywords: X zeolite, *n*-hexane, adsorption.

INTRODUCTION

Zeolites are widely applied as adsorbents and solid acid catalysts. Being microporous, crystalline structures, zeolites can serve as hosts for active metal ions. Their network can be comprehended as a unique ligand system which provides multiple types for coordination of cations. In this way, the active sites for the catalysis of a variety of reactions are formed. Cation exchanged zeolites offer high catalytic activity for a number of industrially important reactions, such as the selective isomerization of C_5–C_7 paraffins.[1,2] In addition, transition metal ion-containing molecular sieves have been extensively investigated in academic and industrial laboratories because of their promising catalytic behaviour in the oxidation of organic compounds and in the removal of NO_x.[3,4]

The successful application of zeolites as catalysts needs the investigation of the adsorption and diffusion processes which influence the behaviour of guest molecules in these materials. The adsorption of hydrocarbons as probe molecules pro-

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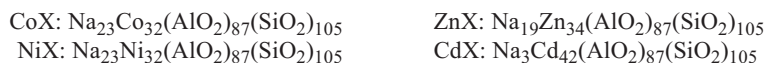\#   Serbian Chemical Society active member.

vides useful information concerning the microscopic and macroscopic aspects of hydrocarbon–zeolite interactions, which can be decisive for further catalyst development. In spite of the efforts devoted for a long time to the investigation of the systems active sites of zeolites – hydrocarbon guest molecules, this subject is still attractive, particularly the case of near room temperature reactions. Among the other hydrocarbons, *n*-hexane, the molecule of which expresses neither a dipolar moment nor a π bond, is often used as a probe.[5–7]

The present work is an extension of a previous study of *n*-hexane adsorption on highly exhanged X-type zeolites ($M_xNa_{87-2x}X$, M = Co, Ni, Zn, Cd). The isosteric adsorption heats were determined and presented as a function of the coverage of the surface area of the zeolites.[8]

Due to the importance of thermodynamic parameters and their possible application in the prediction of catalytic behaviour, the Gibbs energy changes and the entropy changes of *n*-hexane adsorption on a series of cation exchanged X zeolite were calculated in the present work.

EXPERIMENTAL

The samples used in this work were prepared from synthetic NaX (Union Carbide, Si/Al = 1.2). The transition metal (Co^{2+}, Ni^{2+}, Zn^2, Cd^{2+}), cation-exchanged samples were obtained by conventional ion-exchanged procedures[9] and are denoted according to the corresponding cation:

CoX: $Na_{23}Co_{32}(AlO_2)_{87}(SiO_2)_{105}$ ZnX: $Na_{19}Zn_{34}(AlO_2)_{87}(SiO_2)_{105}$
NiX: $Na_{23}Ni_{32}(AlO_2)_{87}(SiO_2)_{105}$ CdX: $Na_3Cd_{42}(AlO_2)_{87}(SiO_2)_{105}$

n-Hexane (Merck, reagent grade) was distilled and stored over calcined NaA zeolite. Its purity (>99.99 %) was controlled by GC and IR analysis.

The experimental procedure for the adsorption measurements is described in detail elsewhere.[10] Briefly, the adsorption measurements were performed in an all-glass BET apparatus, using water as the thermostatic medium. The zeolite samples were preliminarily activated at 573 K and 10^{-3} Pa for several hours, cooled to 298 K, and then the temperature was again raised to 573 K and maintained at this temperature for 48 h. After degassing, the system was cooled down, immersed in the thermostatic bath and the adsorption of *n*-hexane was performed at 298 K. At low pressures, equilibrium was usually attained after 4–6 h, while in the case of higher pressures, the equilibrium was attained after one hour. The adsorption isotherms were measured up to $p/p° = 0.8$ ($p° = 16.8$ kPa at 298 K).

RESULTS AND DISCUSSION

All adsorption isotherms of *n*-hexane on cation-exchanged X zeolite at 298 K have a stepwise character (except in the case of CdX),[10] corresponding formally to type IV of the Brunauer classification.[11] The experimentally obtained sorption isotherms were interpreted by the Dubinin-Radushkevich equation. The stepwise character of the obtained isotherms were interpreted according to literature data:[12] the position of the first and second molecules in the α-cavity is isoenergetic, on the contrary, the adsorption of the third and, especially, of the fourth molecule produce a very large increase in energy, owing to strong absorbate–adsorbate interactions.

TABLE I. Values of $p/p°$ *vs* degree coverage for the investigated samples; $p°$ – standard pressure, p – the equilibrium pressure at 298 K

NaX		CoX		NiX	
$p/p°$	molec./unit cell	$p/p°$	molec./unit cell	$p/p°$	molec./unit cell
0.80	71.40	0.80	81	0.80	64
0.75	69.18	0.75	74	0.75	63
0.70	68.67	0.70	65	0.70	63
0.65	56.67	0.65	52	0.65	62
0.60	48.67	0.60	42	0.60	61
0.55	41.33	0.55	38	0.55	47
0.50	36.67	0.50	36	0.50	40
0.45	32.00	0.45	34	0.45	39
0.40	29.51	0.40	34	0.40	38
0.35	26.30	0.35	33	0.35	37
0.30	23.34	0.30	32	0.30	35
0.25	20.41	0.25	31	0.25	35
0.20	17.17	0.20	30	0.20	32
0.15	15.40	0.15	29	0.15	30
0.10	13.68	0.10	26	0.10	25
0.05	10.67	0.05	20	0.05	13

ZnX		CdX	
$p/p°$	molec./unit cell	$p/p°$	molec./unit cell
0.80	48	0.80	21
0.75	48	0.75	21
0.70	47	0.70	21
0.65	45	0.65	21
0.60	41	0.60	21
0.55	36	0.55	21
0.50	30	0.50	21
0.45	27	0.45	20
0.40	23	0.40	20
0.35	21	0.35	20
0.30	19	0.30	19
0.25	19	0.25	17
0.20	19	0.20	16
0.15	18	0.15	15
0.10	18	0.10	13
0.05	15	0.05	11

The structure of X zeolite is very well known: the unit cell possesses 8 α-cages and 32 sodalite cages of smaller size. Theoretically, the α-cages are the only possible location for the n-hexane molecules. Taking into account the geometry of an α-cage (openings of 0.7 and 0.25 nm, effective cage diameter 1.3 nm and volume of cca 0.8 nm^3)[13] and that of the n-hexane molecule (length 1.03 nm, width 0.49 nm),[14] and bearing in mind the flexibility of the n-hexane molecule due to rotation around the C–C bonds, it is evident that large α cavity can accept four molecules of n-hexane (number of adsorbed molecules, $n = 32$ per unit cell). The values of $p/p°$ *vs.* degree of coverage obtained during the adsorption of n-hexane on the investigated samples, at 298 K are presented in Table I. The adsorbed amounts were expressed in terms of molecules per unit cell, because the number of unit cells per gram of dehydrated zeolite is variable value. It is noteworthy that up to the first inflexion points on the isotherms, the adsorbed amounts of n-hexane correspond to 32 molecules per unit cell.[10] $\Delta G°$, the free energy change of adsorption was calculated in this work, and the obtained values are presented in Fig. 1. If ideal behaviour is assumed, during the isothermal and reversible transfer of one mole of gaseous adsorbate from the gas phase at standard pressure $p°$ into an infinite amount of adsorbent–adsorbate mixture over which the equilibrium pressure is p, the decrease in the Gibbs free energy change, $\Delta G°$, is given as:[15]

$$\Delta G° = -RT \ln (p/p°) \qquad (1)$$

The dependences of the free adsorption energy changes, $-\Delta G°$, on the n-hexane concentration in the case of all investigated X zeolites, at 298 K are presented in Fig. 1. These curves are so-called affinity profiles. It is evident from the figure that the affinities for adsorption decrease with increasing number of adsorbed molecules: the $-\Delta G°$ values decrease from about -15 kJ mol^{-1} to about -6 kJ mol^{-1} with increasing number of n-hexane up to saturation, for all the investigated samples. It is also evident that this effect is dependent on the nature of the charge-balancing cation.

From Fig. 1, it can be seen that the exchange of Na$^+$ with either Co^{2+}, Ni^{2+} and Zn^{2+} causes a decrease in the profiles $-\Delta G°$ *vs.* degree of coverage. Indeed, the values of $-\Delta G°$ obtained for a particular degree of coverage and compared with the corresponding value obtained in the case of the pure sodium form are lower. These larger negative values of $-\Delta G°$ indicate stronger exothermic adsorption processes than in the case of adsorption on NaX. On the contrary, ion exchange with Cd^{2+} ions produces increases of the $-\Delta G°$ value in comparison with the value obtained for a NaX sample. The main specific interaction between a cation in the lattice and a hexane molecule is the ion-induced dipole interaction; this interacion is dependent on the charge, size and location of the cations. Co^{2+}, Ni^{2+} and Zn^{2+}, which have a similar and smaller ionic radius and a higher charge compared to those of the Na$^+$ ion, evidently generate a stronger electrostatic field in the α-cage of a zeo-
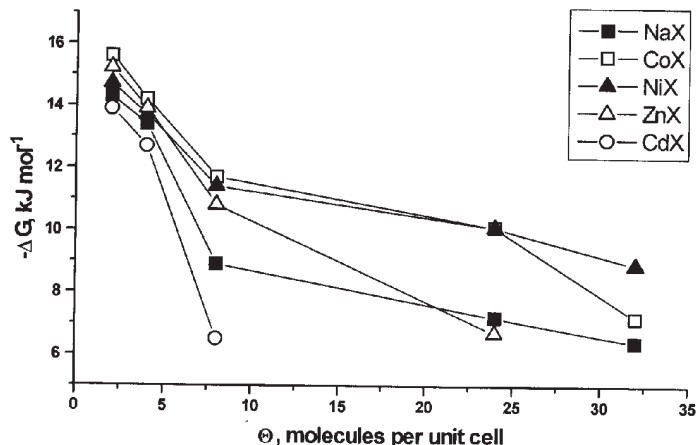
Fig. 1. Gibbs energy change for *n*-hexane adsorption at 298 K.

lite, where the *n*-hexane molecules are adsorbed. The interactions of these divalent cations with *n*-hexane molecules are therefore stronger than the corresponding interaction of Na^+. The values of $-\Delta G°$ obtained for CdX, higher than in the case of NaX and the other cation exchanged zeolites, can be attributed to the larger ionic radius of Cd^{2+} and the "peripheral" location of Cd^{2+} ions in the α–cages of CdX[16] and to the consequential depopulation of the cationic sites distributed within the α-cage.

For all coverages, CoX has the largest $-\Delta G°$ values, except for the adsorption of 32 molecules per unit cell, in which case the largest value is found with NiX. Such a behaviour is due to the fact that there are more Ni^{2+} ions in the α-cages of NiX than Co^{2+} ions in CoX.[17] Since the ionic radii of Co^{2+} and Ni^{2+} are about the same, the free volume of the α-cages of CoX is larger than those of NiX, which makes the diffusion of adsorbed molecules in CoX zeolites easier. After attaining a high density of adsorbed molecules ($n = 32$) the diffusion possibility becomes strongly reduced and the influence of charge density prevails, thus making the value for $-\Delta G°$ for the adsorption of *n*-hexane on NiX higher than for the case on CoX.

As the Gibbs free energy change characterizes the natural tendency of a system to spontaneous change, it can be concluded that the adsorption of *n*-hexane on CoX, NiX and ZnX are easier than on the X zeolites with Na^+ and Cd^{2+} ions.

Additional information concerning the nature of the adsorbed phase can be obtained from a detailed analysis of the entropy change of adsorption. In order to calculate the entropy changes for *n*-hexane adsorption, $\Delta S°$, the following equation was used:

$$\Delta S° = R \ln(p°/p) + \Delta H°/T \qquad (2)$$

where $\Delta H°$ is the standard enthalpy change in the adsorption process.

The value of $\Delta S°$ obtained for initial coverage varies between –20 (obtained for CoX) and –160 J mol^{-1} K^{-1} (obtained for ZnX). The entropy change produced
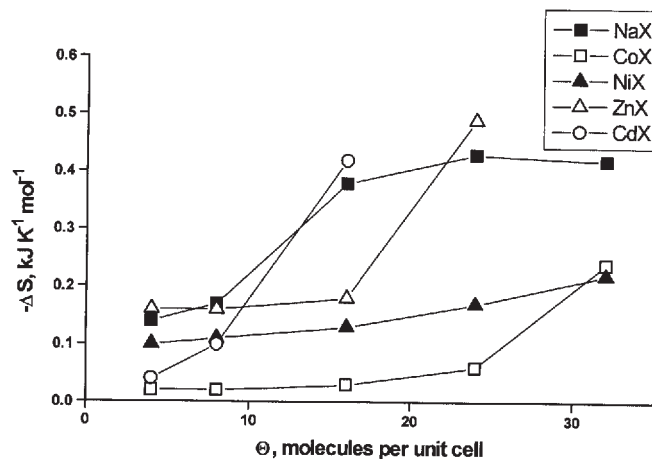
Fig. 2. Entropy change for *n*-hexane adsorption at 298 K.

as a result of the adsorption of *n*-hexane in the case of the investigated zeolites with different extra framework cations for initial pressures of *n*-hexane is the highest in the case of CoX. The corresponding values of the entropy change obtained for the other investigated samples can be ordered as: CoX > CdX > NiX > NaX > ZnX. The values of $\Delta S°$ obtained for the initial coverage indicate that *n*-hexane molecules are strongly bound in α-cages of CoX zeolite.

The dependencies of the adsorption entropy changes $-\Delta S°$ on the degree of coverage, for the investigated zeolites are presented in Fig. 2. It is evident that the values of $-\Delta S°$ for hexane adsorption for all the investigated samples increase with surface coverage. Such a behaviour could be ascribed to strong adsorbate–adsorbate attractive interactions with increasing surface coverage, leading to a decrease in the mobility of the adsorbed phase. In addition, large uptakes on *n*-hexane cause a decrease in the free volume in the α-cages, which hinders the mobility of the adsorbate molecules.

The entropy change accompanying the adsorption process can be expressed as:

$$\Delta S° = S_g° - S_s^* \tag{3}$$

where $S_g°$ is the molar entropy of *n*-hexane vapour at standard pressure $p°$ and temperature T, while S_s^* is the differential molar entropy of adsorbed *n*-hexane. The values of the differential molar entropy of the adsorbed *n*-hexane, S_s^*, for all the investigated cationic forms of X zeolite were calculated, and plotted as a function of degree of coverage. The obtained results are presented in Fig. 3.

The differential molar entropies decrease with increasing degree of coverage, in all the investigated systems. The analysis of the results presented in Fig. 3 proves that the S_s^* values for NaX and CdX decrease at the very beginning of the adsorption process ($n < 1$). The S_s^* values for CoX, NiX and ZnX remain unchanged during the adsorption of the first and second *n*-hexane molecule in an α-cage. The adsorption of the third and the fourth molecule makes the density of
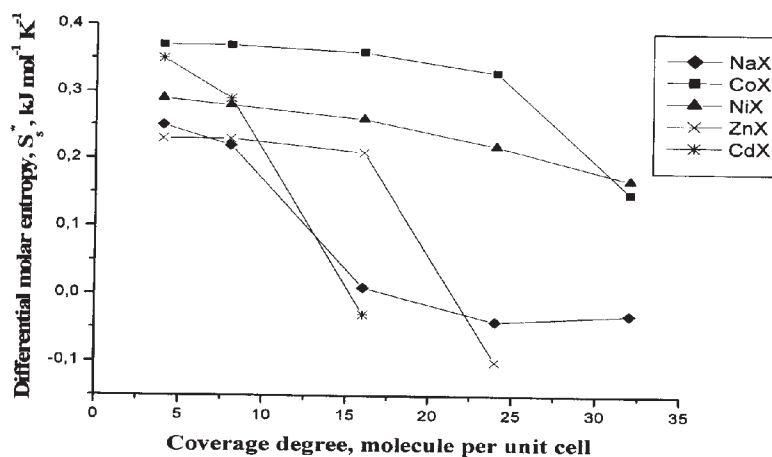
Fig. 3. Differential molar entropy change for *n*-hexane adsorption.

adsorbed molecules in an α-cage higher, which causes a sudden increase of adsorbate–adsorbate interactions. As a result, a decrease of the differential molar entropy is evident.

The differential molar entropy of the adsorbed *n*-hexane, S_s^*, can be further considered

$$S_s^* = S_c^* + S_{th}^* \tag{4}$$

where S_c^* denote the differential molar configurational and thermal entropies of the adsorbed phase. This equation may be used when the density of the molecules adsorbed in the α-cages of a zeolite is high enough; then, it is generally assumed that these molecules attempt to pack closely together and take up the space to the walls of the anion framework.

TABLE II. Configurational entropies, S_c^*, and thermal entropies, S_{th}^*, obtained for different degrees of coverage

Zeolite	Molec./unit cell	S_c^*/kJ mol^{-1}K^{-1}	S_{th}^*/kJ mol^{-1}K^{-1}
NaX	4	−17.62	0.27
	8	−10.58	0.23
	16	−1.96	0.01
	24	5.88	−0.03
	32	17.37	−0.01
CoX	4	−17.37	0.38
	8	−10.04	0.38
	16	−1.33	0.36
	24	6.65	0.32
	32	19.23	0.13

TABLE II. Continued

Zeolite	Molec./unit cell	S_c^*/kJ mol^{-1}K^{-1}	S_{th}^*/kJ mol^{-1}K^{-1}
NiX	4	−18.26	0.31
	8	−11.52	0.29
	16	−3.37	0.26
	24	3.37	0.22
	32	11.52	0.16
ZnX	4	−11.52	0.24
	8	−3.37	0.23
	16	11.52	0.20
	24	26.41	−0.13
CdX	4	−12.05	0.36
	8	−4.07	0.29
	16	9.58	−0.04
	24	24.47	−0.19

The value of the configurational entropy S_c^* can be further presented as:

$$S_c^* = R \ln x / (1-x) \qquad \text{and} \qquad (5)$$

$$S_s^* = S_{th}^* + R \ln x /(1-x) \qquad (6)$$

where $x = W/W_0$. Here W is the amount of adsorbed *n*-hexane at equilibrium pressure p and W_0 is the total sorption capacity (molecules per unit cell) of the zeolites at 298 K.[10] The values of S_c^* and S_{th}^* were calculated and are presented in Table II. Since the thermal entropy remains constant for low degrees of coverage, the adsorptive behaviour is governed by the configurational component. This is not the case for large uptakes of *n*-hexane, where a continuous decrease in the thermal entropy is noticed. The value S_{th}^* may be compared with the molar entropy of liquid *n*-hexane (0.30 kJ mol^{-1} K^{-1} at 298 K). The entropy of liquid *n*-hexane is greater than S_{th}^* for *n*-hexane adsorbed in X zeolites. The obtained results confirm that an *n*-hexane molecule within the zeolite crystal has less freedom than in the liquid phase. The better regularity of the arrangement of *n*-hexane molecules within the X zeolite lattice than is the case in its bulk liquid can be attributed to the cation–adsorbate and adsorbate–adsorbate interactions, as well as to the influence of the zeolite framework. The highest value (the state in which *n*-hexane is most similar to the bulk liquid) is found for *n*-hexane adsorbed on CoX and NiX. The spin-unpaired cations Co^{2+} and Ni^{2+} in the zeolite lattice co-ordinate the electrons from the lattice oxygen atoms thus diminishing the chances of interactions of these cations with the adsorbed molecules. Since the cation–adsorbate interactions contrib-

ute to the regularity of the arrangement of adsorbed molecules, it could be expected that the decrease of Co^{2+} and $Ni^{2+}-$ adsorbate interactions could yield higher S_{th}^{*} values as compared to the other cationic forms of the investigated X zeolites. However, although the S_{th}^{*} values for CoX and NiX are higher than the corresponding values for NaX, CdX and ZnX, they are still considerably lower than the molar entropy of liquid *n*-hexane. It follows that the adsorbed *n*-hexane has the lowest loss of degree of freedom, relative to the corresponding value for its bulk liquid state, if it is adsorbed on CoX and NiX zeolites.

CONCLUSION

The analysis of the results obtained in this work, the changes of Gibbs free energies and differential and thermal molar entropies, confirm that the X type zeolite exchanged with transition metal cations: Co^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} exhibits a different behaviour with respect to *n*-hexane sorption. The substitution of the sodium ions in NaX with divalent cations alters profoundly the adsorption of *n*-hexane. Their influence is primarily exerted through the ion-induced dipole interaction, in which the size and charge of the cation is of great importance, as well as through its electronic configuration (especially vacant d-orbitals) and the number and the locations in the lattice.

ИЗВОД

ТЕРМОДИНАМИКА АДСОРПЦИЈЕ *n*-ХЕКСАНА НА ЈОНСКИ ИЗМЕЊЕНИМ X ЗЕОЛИТИМА

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У овом раду су одређене промене слободне енергије и промена ентропије адсорпције *n*-хексана на зеолитима типа $M_xNa_{87-2x}X$ (M = Co, Ni, Zn, Cd) на основу изостерних топлота сорпције. Показано је да измена Na^+ јона у NaX зеолиту двовалентним катјонима (Co, Ni, Zn, Cd) значајно мења адсорпционе карактеристике NaX зеолита. Такође је утврђено да промена слободне енергије и промена ентропије адсорпције *n*-хексана зависи и од степена покривености површине зеолита.

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