ENTHALPY-ENTROPY COMPENSATION FOR n-HEXANE ADSORPTION ON ZEOLITE X, CONTAINING TRANSITION METAL CATIONS

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ABSTRACT

In this work, the values of entropy changes related to n-hexane adsorption onto ion exchanged X zeolite were calculated from differential heats, obtained from volumetric experiments. The linearity of $-\Delta H$ vs. $-\Delta S$ plots confirmed the existence of enthalpy-entropy compensation effect. Introducing various transition metal cations into the lattice of the NaX the linear compensation relation between ΔH and ΔS was preserved, although its absolute value was not identical for each zeolite considered here. It was found that compensation effect and so the compensation temperature depend on the type of charge-balancing cation (charge, size and electronic configuration).

Keywords: enthalpy-entropy compensation, compensation temperatures, zeolite

INTRODUCTION

In the process of adsorption on zeolites, enthalpy change (ΔH) provides a measure of the energy variations occurring due to the interaction of adsorbate molecules with the zeolite sorbent. The entropy change (ΔS) may be associated with the binding or repulsive forces in the system and is associated with the spatial arrangements at the adsorbate-zeolite interface. Thus, entropy defines the degree of order or randomness existing in the adsorbate-zeolite system. Free energy change (ΔG), based on its sign, is indicative of the affinity of the zeolite as adsorbent for molecules of adsorbate, and provides a criterion as to whether sorption is a spontaneous (-ΔG) or nonspontaneous process (+ΔG). From the Gibbs free energy expression: $\Delta G = \Delta H - T\Delta S$, if ΔH is plotted against ΔS a linear relationship is expected when ΔG is constant or zero. The linear scaling between: enthalpy (ΔH_i) and entropy (ΔS_i) (for a set of related reactions denoted by index i), is known as the "enthalpy-entropy compensation" phenomenon. The values of ΔH_i and ΔS_i are then related by equation:

$$\Delta H_i = \alpha + \beta \Delta S_i \qquad (1)$$

In relation (1), α and β are constants. β is the "compensation temperature", while α has the dimension of free energy. At the "compensation temperature" any variation in enthalpy is balanced by such variation in entropy so that the total change in free energy remains constant.

In the case of adsorption, compensation phenomenon can be physically explained as a loss in entropy (negative value of ΔS_{ads} provoked by the reduction of freedom of motion), that is compensated by a gain in enthalpy (binding energy, negative ΔH_{ads}). Due to the compensation effect of the entropy, the enthalpy of adsorption increases less than it would do if the compensation effect wasn't present.

The investigation of "enthalpy-entropy compensation" effect has importance concerning fundamental studies on gas adsorption [1] and in the investigations related to porous adsorbents useful as catalysts [2]. The existence of the compensation effect and determination

of the compensation temperature enable prediction of the adsorption behavior and the catalytic ability of the system and so provide useful data for the zeolite as a catalyst.

In our previous work [3] "enthalpy-entropy compensation" effect for n-hexane adsorption on ion-exchanged ZSM-5 zeolites was shown. In this work, thermodynamic parameters and the existence of enthalpy-entropy compensatory behavior related to n-hexane adsorption on X zeolite exchanged with transition metal cations (Co^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+}) were investigated. The influence of relevant parameters on compensatory behavior was discussed.

EXPERIMENTAL

The samples used in this work were prepared from synthetic NaX (Union Carbide). The transition metal (Co^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+}) cation-exchanged samples were obtained by conventional ion-exchanged procedures [4]. Chemical compositions of investigated samples are presented in Table 1.

Table 1. Unit cell composition of zeolites

zeolite	unit cell composition
NaX	$Na_{56}(AlO_2)_{87}(SiO_2)_{105}$
CoX	$Na_{23}Co_{32}(AlO_2)_{87}(SiO_2)_{105}$
NiX	$Na_{23}Ni_{32}(AlO_2)_{87}(SiO_2)_{105}$
ZnX	$Na_{19}Zn_{34}(AlO_2)_{87}(SiO_2)_{105}$
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 gas chromatography (GC) and infrared spectroscopy (IR) analysis. The experimental procedure for the adsorption measurements is described in detail elsewhere [5]. The adsorption measurements were performed in an all-glass BET apparatus, using water as the thermostatic fluid. 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 and 288K. The adsorption isotherms were measured up to p/p° = 0.8 (p° = 16.8 kPa at 298 K).

In order to calculate the entropy changes for n-hexane adsorption, ΔS°, the following equation was used:

$$\Delta S^o = R \ln \frac{p^o}{p} + \frac{\Delta H^o}{T} \qquad (2)$$

T is adsorption temperature, p^o is the standard pressure, p is the equilibrium pressure at temperature T and ΔH^o is the standard enthalpy change in the process of adsorption, these values were obtained from isotherms at two temperature ($T_1 = 288$ K and $T_2 = 298$ K).

RESULTS AND DISCUSSION

The heat evolved due to the adsorption of n-hexane on the investigated zeolites is the result of the interactions of adsorbed molecules with the zeolite lattice (i.e., the pore walls), the acid sites and other adsorbed molecules. The values of entropy changes during the adsorption of n-hexane include only the changes in the entropy of the adsorbent. The plots of adsorption enthalpies versus the assigned entropies for the adsorption of n-hexane on parent NaX and all cation-modified zeolites are given in Figure 1.
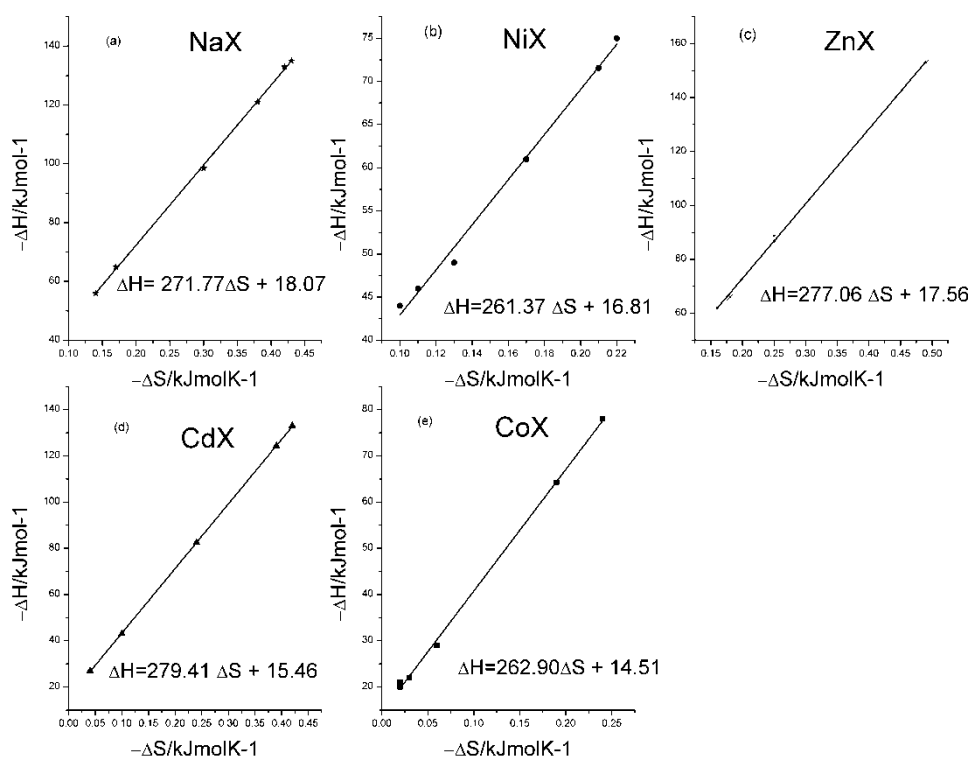
Figure 1. Enthalpy-entropy compensation plots for n hexane adsorption on (a) NaX; (b) CoX; (c) NiX; (d) ZnX and (e) CdX.

The graphs of enthalpy vs. entropy changes for the adsorption of n-hexane on NaX and all its cation-modified samples express highly linear trends, with the correlation coefficients R^2 higher than 0.99. As the values of correlation coefficient are normally used as a criterion to judge if compensation effect exists, it means that the enthalpy-entropy compensation effect was found during the process of adsorption of n-hexane on NaX and its cation-modified forms. The values of correlation coefficients and the compensation temperatures are summarized in the Table 2.

Table 2. Characteristic parameters for enthalpy-entropy relationship

Zeolite	R^2	α / kJmol^{-1}	β /K
NaX	0.9995	18.33	271.66
CoX	0.9986	14.51	262.90
NiX	0.9930	16.81	261.37
ZnX	0.9987	17.56	277.06
CdX	0.9999	15.46	279.41

From the data presented in Table 2, it is evident that the introducing the transition metal cations in zeolite lattice alter the compensation temperature (β, equation 1). The higher slope of the -ΔH vs. -ΔS plot, i.e. the higher the compensation temperature, means that the same change in ΔH is accompanied by the larger change in ΔS. The presence of Co^{2+} and Ni^{2+} cations in zeolite causes decrease of the compensation temperature in comparison to the parent NaX. On the contrary, Zn^{2+} and Cd^{2+} cations cause the increase of the compensation temperature (Table 2). The change of enthalpy of adsorption of n-hexane on the X zeolite is the result of the ion-induced dipole interaction (through electrostatic and dispersion forces)

between highly polarizing cationic centers in zeolite and un-polar molecules of n-hexane. The cations Co^{2+} and Ni^{2+} have the same charge as Zn^{2+} and Cd^{2+}, but smaller ionic radii, so electrostatic field of Co^{2+} and Ni^{2+} should be stronger than that of Zn^{2+} and Cd^{2+} ions. In spite of that, compensation temperatures show that the interactions of adsorbate and zeolite are stronger in ZnX and CdX than in CoX and NiX. Obviously, the size and charge of the charge balance cation are not the only factors which determine the compensation temperature. Transition metal cations used in this work differ in electron configuration. The cobalt and nickel cations are spin unpaired, while the zinc and cadmium cations are spin paired. As the consequence, Co^{2+} and Ni^{2+} can behave as electron acceptors, so they can form bonds with oxygen atoms from the lattice, as well as with the adsorbed n-hexane molecules. If d electrons of the cation "react" with the oxygen of the lattice, the reaction of n-hexane with the oxygen atoms is reduced, while the cations partly lose the possibility of interaction with n-hexane. Both effects cause the smaller increase of the entropy change for the appropriate values of the enthalpy change and the compensation temperature decrease. For Zn^{2+} and Cd^{2+}, being spin paired cations, ion-induced dipole interactions are not reduced and are the only kind of interactions with the adsorbed n-hexane molecules. As the charge of Zn^{2+} and Cd^{2+} is the twice the charge of Na^+, ion-induced dipole interactions in ZnX and CdX are stronger than in NaX. Because of that the loss of entropy for the same value of the enthalpy is higher and the compensation temperatures of ZnX and CdX are the highest between all investigated zeolites.

CONCLUSION

The results presented in this paper confirmed existence of the enthalpy-entropy compensation effects during the process of adsorption of n-hexane on faujasite zeolite NaX and its transition metal modified forms: CoX, NiX, ZnX and CdX. It was shown that the main characteristic parameter of the compensation effect, the compensation temperature, depends on the nature of the type of the extra-framework cation (charge, size and electronic configuration). Charge balance cations Co^{2+} and Ni^{2+} being spin unpaired decrease the compensation temperature, while the spin paired cations Zn^{2+} and Cd^{2+} increase the compensation temperature comparing to that of the parent NaX.

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