Thermodynamics of adsorption of hydrocarbons on molecular sieves NaY and CaY by inverse gas chromatography

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Abstract

Inverse gas chromatography (IGC) has been used to measure the surface adsorption of some probes (*n*-alkanes on a series (*n*-C5 to *n*-C8) cyclohexane and benzene) on NaY and CaY zeolites. From the retention volumes at infinite dilution over a range of temperatures, the differential heat of adsorption ($\Delta H°$), the standard free energy of adsorption ($\Delta G°$), and the standard entropy of adsorption ($\Delta S°$) have been determined for the probes on the NaY and CaY zeolites. It was found that interactions of probes with CaY stronger than that on NaY. The dispersive (London) component of the surface free energies (γ_S^d), has also been calculated. The dispersive components of the surface energies for CaY were found to be higher than the values for NaY.
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1. Introduction

One of the advantages of zeolites in comparison with conventional adsorbents lies in the fact that their properties can easily be altered by processes such as ion exchange, extraction of aluminium heat and water stream treatment. Using these methods zeolites can be modified to solve very different separation processes. For example by cation exchange pore diameters can be made to vary in such a way that molecules of different size and shape are separated. Different molecules of comparable size can also be separated by their specific energetic interactions with the zeolite adsorbent.

The openness of structure of type Y zeolites allows them to adsorb larger quantities of gases and larger molecular species. This usually makes separation efficiencies based upon molecular size to have lesser practical importance than the other properties of these zeolites. Since its discovery by Breck nearly five decades ago [1], the Y zeolite has attained prominence both in science and technology. It has become one of the most important industrial adsorbents and catalysts used today. Among the zeolites utilized as catalysts, Y zeolite is probably the most extensively used, essentially as a cracking catalyst [2]. Several researchers have shown that both their adsorption [3–5] and catalytic [6] properties can be strongly influenced by the exchangeable cations.

For a long time, contact angle measurement was the only experimental method used for characterization of the surface energy of solids. This technique can involve serious experimental difficulties and cannot be applied to such solid surfaces as porous and rugous materials. Moreover, this technique cannot be applied to powders and fibers, which do not present film-like surfaces. It is best suited for low surface energy solids, such as polymers, because for such materials, finite contact angles can be achieved with recourse to convenient probe liquids. Mineral surfaces, however, are typically wet out (contact angle close to 0) by most liquids. Although it is possible to use the "two liquid approach" to get a finite contact angle – as in the contact angle of a high energy solid against water in octane – the results pertain to the solids–octane interface, not the solid surface itself [7,8].

Recently, inverse gas chromatography (IGC) has been developed as a new complementary technique for surface

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Nomenclature

a	surface area of the liquid probe molecule (Å^2)
A_s	available area for a molecule in standard adsorbed state ($4.08T \times 10^{-16}\,\text{cm}^2$)
F_a	volumetric flow rate ($\text{cm}^3\,\text{s}^{-1}$)
ΔG°	standard free energy change of adsorption ($\text{kJ}\,\text{mol}^{-1}$)
ΔG^d	dispersive component of the standard free energy change of adsorption ($\text{kJ}\,\text{mol}^{-1}$)
ΔG^{sp}	specific component of the standard free energy change of adsorption ($\text{kJ}\,\text{mol}^{-1}$)
ΔH°	standard differential enthalpy of adsorption ($\text{kJ}\,\text{mol}^{-1}$)
j	James–Martin gas compressibility factor
m	adsorbent mass in the column (g)
N	Avagadro's number
P°	standard state vapor pressure of adsorbate (mmHg)
R	ideal gas constant ($\text{kJ}\,\text{mol}^{-1}\,\text{K}^{-1}$)
S	specific surface area of adsorbent ($\text{m}^2\,\text{g}^{-1}$)
$_2S_t$	two-dimensional translation entropy ($\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$)
$_3S_t$	three-dimensional translation entropy ($\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$)
ΔS°	standard entropy change of adsorption ($\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$)
t_m	dead time (s)
t_R	retention time of the probe (s)
T	column temperature (K)
T_a	ambient temperature (K)
V_N	net retention volume (cm^3)
W	work of adhesion ($\text{mJ}\,\text{m}^{-2}$)

Greek letters

γ_S^d	dispersive component of the surface free energy of the solid ($\text{mJ}\,\text{m}^{-2}$)
γ_L^d	dispersive component of the surface free energy of the liquid ($\text{mJ}\,\text{m}^{-2}$)
π_0	surface pressure ($\text{mJ}\,\text{m}^{-2}$)

energy characterization of solid materials. The dispersive component of surface energy of polymers [9], clays [10], zeolites [11], carbon fibers [12], graphite [13], wood [14], glass [15], and cellulose fibers [16] and various other organic [7] and mineral fillers [8] have been reported in the literature. The results obtained were entirely satisfactory

and IGC has thus become a useful and reliable analytical method because of its relative rapidity, simplicity, and good accuracy, as well as the relatively low cost and availability of the equipment associated with its practice essentially in gas chromatography.

In the IGC the molecular sieve zeolite to be characterized is used as the stationary phase, and a solute with well-known properties is injected as a probe. Several thermodynamic quantities, including surface energy, can thus be derived from the retention volume of probe passing through the column filled with zeolites.

This work was thus undertaken in order to investigate how IGC could be applied in estimating dispersive components of surface energies of two alkalies exchanging Y zeolites (NaY, CaY). Another purpose was to determine the variation in adsorption thermodynamic parameters of some hydrocarbons on NaY and CaY by the exchangeable cations.

2. Experimental

2.1. Materials and columns

Two adsorbents were used: Molecular Sieve NaY (Aldrich), and Molecular Sieve CaY which was prepared by a conventional ion exchange technique from NaY with solution of calcium chloride [17]. The surface areas of adsorbents were determined by nitrogen adsorption (BET method) with Micromeritics-Flowsorb II 2300. The measurements were performed in the laboratories of the TÜBİTAK (Scientific and Technical Research Council of Turkey) Research Institute.

A 5.35 mm i.d. and 150 cm long stainless steel column was used in this work. The characteristics of the column and adsorbents were given in Table 1.

The adsorbates (probes) used were *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, and benzene (Merck, reagent grade). They were employed without further purification.

2.2. Instrumentation

The chromatographic experiments were performed with a Unicam 610 gas chromatograph equipped with a flame ionization detector. Retention times were recorded on a Unicam 4815 integrator.

High purity nitrogen was used as carrier gas. The flow rate of carrier gas was measured at the detector outlet with a soap

Table 1
Characterstics of the columns and adsorbents

Adsorbent	Particle size (mm)	Specific surface area (m^2/g)	Packing weight of adsorbent (g)	Column temperature (K)	Carrier gas flow rate (ml/min)
NaY	0.150–0.125	425	2.36	513–543	10, 15, 30
CaY	0.150–0.125	479	2.03	663–693	10, 30

bubble flowmeter and was corrected for pressure drop in the column by using James–Martin gas compressibility factor (j) and correction at column temperature was also made.

The adsorbents were conditioned at 693 K in the nitrogen gas flow for 24 h prior to the measurements. Retention times were calculated from a chart recorder trace of the elution chromatograms and were corrected for column "dead time".

3. Calculations

Chromatographic peaks recorded at infinite dilution concentration region of hydrocarbons on zeolites were symmetrical, with elution times and volumes being independent of the injection size. The fact that the elution times and volumes were independent of injection sizes indicates that, under the experimental conditions used in the present study, adsorption data obeyed Henry's law. The net retention volume (V_N) can be calculated from the following relation [18,19]:

$$V_N = (t_R - t_m)F_a \frac{T}{T_a} j \tag{1}$$

where t_R is the probe retention time, t_m the retention time of the mobile phase (holdup time, dead-time), F_a the volumetric flow rate measured at column outlet and at ambient temperature, T_a the ambient temperature (K), T the column temperature (K) and j is James–Martin gas compressibility correction factor.

3.1. Adsorption thermodynamics

When adsorption takes place in the Henry's law region, the standard free energy change of adsorption (ΔG°), as a function of V_N, can be determined from:

$$\Delta G^\circ = -RT \ln \left(\frac{V_N P_0}{mS\pi_0} \right) \tag{2}$$

where R is the ideal gas constant, m the mass of adsorbent in the column, S the specific surface area of adsorbent, P_0 the adsorbate vapor pressure in the gaseous standard state having a value of 101.3 kPa (1 atm) and π_0 is the reference two-dimensional surface pressure whose standard state is arbitrary. The standard reference state was taken as $\pi_0 = 0.338$ mJ/m^2 proposed by de Boer [20]. Therefore, ΔG° can be written:

$$\Delta G^\circ = -RT \ln V_N + \text{constant} \tag{3}$$

At zero surface coverage ΔH° can be identified by the differential heat of adsorption of the probe. It is estimated from the changes in V_N with temperature, i.e.:

$$\Delta H^\circ = -R \frac{d \ln V_N}{d(1/T)} \tag{4}$$

Since ΔH° is temperature independent, Eq. (5) predicts a linear relationship between ΔG° and ΔH°.

Then, the standard entropy change of adsorption of the probe at zero coverage, ΔS°, can be calculated by Eq. (5) [21–24]:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{5}$$

3.2. Dispersive component of surface energy

Depending on the nature of the probes injected, ΔG° will be the result of nonpolar and polar interactions. Nonpolar probes such as n-alkanes would interact by dispersion interactions only:

$$\Delta G^\circ = \Delta G^d \tag{6}$$

For a polar probe, additional specific interactions with the solid would give a higher free energy of adsorption due to the contribution of the specific free energy change of adsorption:

$$\Delta G^\circ = \Delta G^d + \Delta G^{sp} \tag{7}$$

Since nonpolar liquids interact by dispersive interactions only, the free energy change of adhesion, ΔG° of a nonpolar probe can be related to the work of adhesion by

$$\Delta G^\circ = NaW \tag{8}$$

where W is the work of adhesion, N the Avogadro's number and a is the cross-section area of the liquid probe molecules.

The work of adhesion, W of a nonpolar liquid onto a solid can be expressed as the geometric mean of the dispersive components of the solid (γ_S^d) and the liquid (γ_L^d). Thus,

$$W = 2(\gamma_S^d \gamma_L^d)^{1/2} \tag{9}$$

Combining Eqs. (3), (8) and (9):

$$RT \ln V_N = 2N(\gamma_S^d)^{1/2} a(\gamma_L^d)^{1/2} + \text{constant} \tag{10}$$

A straight line was obtained from a plot of the free energy change of adsorption of liquid probes onto solids $RT \ln V_N$ as a function of the product of the alkane the cross-section area and the dispersive component of the alkane surface energy $(a(\gamma_L^d)^{1/2})$. The dispersive component of the solid, γ_S^d can thus be obtained from the slope of the line [25–27].

4. Results and discussion

4.1. Adsorption thermodynamics

In this study, thermodynamic parameters for adsorption of all hydrocarbons (n-alkanes on a series (n-C$_5$ to n-C$_8$), cyclohexane and benzene) on NaY and CaY were determined in the infinite dilution region. Standard free energy changes of adsorption (ΔG°) were calculated by Eq. (2). Differential heats of adsorption (ΔH°) were calculated from plots of $\ln V_N$ against $1/T$. The slopes of the lines are $[-(\Delta H^\circ/R)]$ according to Eq. (4). These plots are given in Fig. 1. Standard entropy
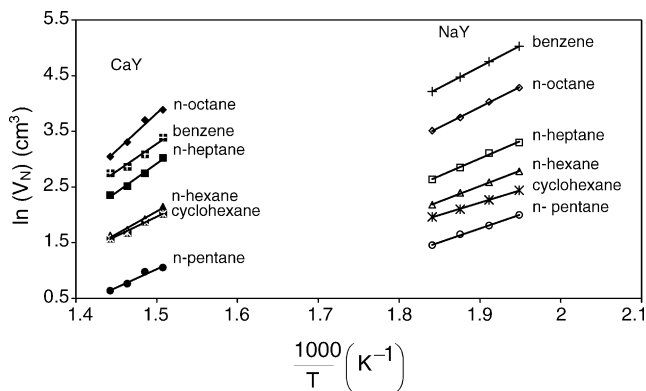
Fig. 1. The plot of $\ln V_N$ vs. $1/T$ for the adsorption of the probes on NaY and CaY.

changes of adsorption (ΔS°) were calculated by Eq. (5). The values of $-\Delta H^\circ$, $-\Delta S^\circ$ and $-\Delta G^\circ$ increase with increasing carbon number and that the linear increase was obtained for the *n*-alkanes.

If we consider the adsorbate as an ideal gas, its three-dimensional translation entropy can be written as

$$_3S_t = R \ln(M^{3/2} T^{5/2}) - 9.62 \tag{11}$$

where M is the molecular weight of adsorbate. The two-dimensional translation entropy is calculated by

$$_2S_t = R \ln(MTA_s) + 275.32 \tag{12}$$

where A_s is the available area for a molecule in standard adsorbed state ($4.08T \times 10^{-16}$ cm^2). Therefore, the theoretical entropy change upon the adsorption of a vapor on a solid surface can be calculated from the difference between $_2S_t$ and $_3S_t$ [22,28].

The differential heats of adsorption (ΔH°) at zero surface coverage, the free energy changes (ΔG°), the experimental entropy changes (ΔS°) and theoretical entropy changes ($_3S_t - _2S_t$) are given in Table 2 (these parameters are average values for the temperature range studied).

When 1 mol gas goes across the gas phase to the adsorbed phase, a decrease in translational entropy occurs. This change

can be expressed by: ($_3S_t - _2S_t$). The values for the *n*-alkanes are from -53.49 for *n*-pentane to -55.41 J mol^{-1} K^{-1} for *n*-octane on NaY and from -54.55 for *n*-pentane to -56.46 J mol^{-1} K^{-1} for *n*-octane on CaY. The theoretical entropy change is of the same order as the experimental value (Table 2). The entropy change decrease of *n*-alkanes upon adsorption results in part from the loss of one degree of translational freedom. When the number of carbon atoms increases, the values of $-\Delta S^\circ$ are higher than the values of theoretical entropy change. This additional entropy loss that is found experimentally may result from a restriction of rotational and vibrational freedom on the surface.

Table 2 also shows that $-\Delta H^\circ$ values of all studied probes are higher on zeolite CaY than on zeolite NaY. For Y zeolites exchanged with di-valent cation like Ca^{2+}, a higher adsorption capacity could be expected than that with Na$^+$ because two mono-valent cations are replaced by a single di-valent cation and the ionic radii of calcium are not greater than that of sodium. Therefore, the net volume occupancy by these di-valent cations would be less than one half as with sodium.

The results obtained from the differential heat of adsorption (ΔH°) measurements in different studies are summarized in Table 3. As can be seen from this table, the ΔH° measurement results obtained by using the chromatographic method are in agreement with the results obtained by static measurement methods (gravimetric and calorimetric) in the previous studies found in literature except in the case of benzene which is a large molecule for which the gas chromatographic ΔH° values deviate from the static ones as reported by Kiselev and Yashin [34].

It is evident from the data that benzene exhibits more negative ΔH° than the corresponding values for aliphatic and alicyclic hydrocarbons with the same carbon atom number (i.e. *n*-hexane and cyclohexane). The more negative the heat, the greater the interaction between the adsorbate and the adsorbent. This can be explained by the specific interactions between benzene's π electrons and the surfaces. It was observed that on NaY and CaY the adsorption strength increases in the following sequence: cyclohexane < *n*-hexane < benzene. This is in agreement

Table 2
Thermodynamic parameters for the adsorption of the probes on NaY and CaY

Adsorbent	Probe	$-\Delta H^\circ$ (kJ mol^{-1})	$-\Delta G^\circ$ (kJ mol^{-1})	$-\Delta S^\circ$ (J mol^{-1} K^{-1})	$-(_2S_t - _3S_t)$ (J mol^{-1} K^{-1})
NaY	*n*-Pentane	41.35	2.25	74.0	53.5
	n-Hexane	46.13	5.59	79.6	54.2
	n-Heptane	52.12	7.51	84.1	54.8
	n-Octane	60.32	11.76	91.9	55.4
	Cyclohexane	37.05	4.30	62.0	54.1
	Benzene	62.84	14.93	90.7	53.2
CaY	*n*-Pentane	55.12	1.98	78.3	54.5
	n-Hexane	66.89	3.69	93.2	55.3
	n-Heptane	85.40	8.31	113.6	55.9
	n-Octane	111.11	12.96	144.7	56.5
	Cyclohexane	57.60	3.56	79.7	55.2
	Benzene	81.70	10.40	105.1	54.9

Table 3
Comparison of the obtained and literature data on heat of adsorption

Adsorbent	Probe	$-\Delta H^\circ$ (kJ mol^{-1})	Method[a]	Reference
NaY	n-Pentane	41	Grav.	[29]
		39.4, 46	Chrom.	[30,31]
		41.35	Chrom.	Obtained
	n-Hexane	47, 46	Grav., Calor.	[29,2]
		45.5, 50.2	Chrom.	[30,31]
		46.13	Chrom.	Obtained
	n-Heptane	51.9	Chrom.	[30]
		52.12	Chrom.	Obtained
	n-Octane	61	Grav.	[29]
		57.5	Chrom.	[30]
		60.32	Chrom.	Obtained
	Cylohexane	51, 54.42	Calor.	[32,2]
		48	Chrom.	[32]
		37.05	Chrom.	Obtained
	Benzene	79.5, 71.16, 74.92	Calor.	[32,2,33]
		62.84	Chrom.	Obtained
CaY	n-Hexane	39.76	Calor.	[2]
		66.89	Chrom.	Obtained
	Cylohexane	58.60	Calor.	[2]
		57.60	Chrom.	Obtained
	Benzene	92.09	Calor.	[2]
		81.70	Chrom.	Obtained

[a] Grav., Calor., Chrom. = determined by gravimetric, calorimetric and chromatographic.

with the literature results for NaY, NaX, alumina and silica surfaces [35–37]. Any chromatographic ΔH° measurement values could not be found for CaY in literature. Thus, the measurements were performed in this study for CaY and the obtained results fitted the increasing adsorption strength sequence mentioned above. There is only one study on ΔH° measurements of CaY with static methods which could be found in literature and, as can be seen in Table 3, there is a deviation in static measurement results considering the increasing order of adsorption strength values [2].

The synthetic faujasite analogues, zeolites X and Y, are used extensively as catalysts in variety of reactions and in separation processes. They are much more open than zeolite A. Their largest windows have free diameters of ≈7.4 Å; for zeolite A, it is 4.2 Å [2]. The 12-ring windows of the faujasites can admit molecules as large as benzene, mesitylene, and tertiary amines.

It was reported [38,39] that benzene molecules interact both with Na$^+$ ions (acting as Lewis acids) and highly negative charged framework oxygen atoms (intrinsic basic sites) of 12-ring windows of NaY, synthesized from the sodium aluminosilicate gel. The amount of benzene adsorbed in a supercage has led to the conclusion that about four Na$^+$ ions were located in each supercage and others are in the hexagonal and sodalite cages.

By studying adsorption on zeolite Y, it becomes possible to compare the properties of zeolites X and Y and thus to explore the influence of charge density on the physical adsorption of gases in the same aluminosilicate structure. Such a comparison is also relevant to the different catalytic activities of the two forms of synthetic faujasite [40].
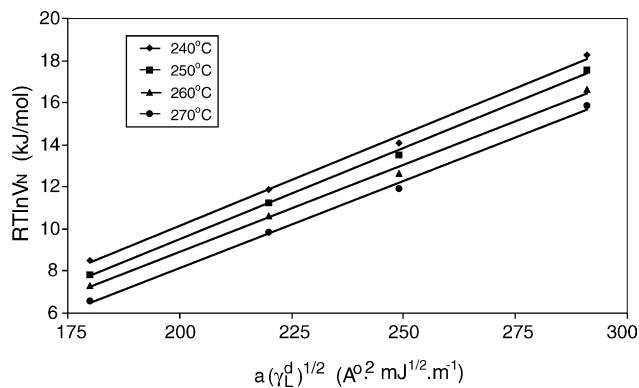

Fig. 2. $RT \ln V_N$ vs. $a(\gamma_L^d)^{1/2}$ plot for the adsorption of n-alkanes on NaY.

The thermodynamic parameters for the adsorption of some hydrocarbons on NaX were found in our previous study [36,41]. In this study, it was observed that the $-\Delta H^\circ$ values of the studied hydrocarbons on NaY were lower than those obtained for NaX. Since the dispersion interactions are similar in both zeolites, this implies that the electrostatic field does not increase with increase in the Si/Al ratio. In spite of this, the adsorption heat decreased as Si/Al ratio increased (for NaY Si/Al = 2.45, for NaX Si/Al = 1.25).

4.2. Dispersive component of surface energy

This parameter (γ_S^d) is very important for the determination of surface characteristics of adsorbent materials, providing an knowledge of the force field of the high energy sites. According to general knowledge, γ_S^d is proportional to the surface density of atoms, their polarizability and their ionization energy [42].

Plots of $RT \ln V_N$ versus $a(\gamma_L^d)^{1/2}$ were found to be linear for both zeolites at all studied temperatures thereby confirming the validity of Eq. (10). Figs. 2 and 3 illustrate typical results. The dispersive components of the zeolites (γ_S^d) were calculated from slopes which are $2N(\gamma_S^d)^{1/2}$. The values of a and γ_L^d were obtained from the literature (Table 4). The dispersive components of NaY and CaY (γ_S^d) are tabulated at experimental temperatures in Table 5. It was observed that,
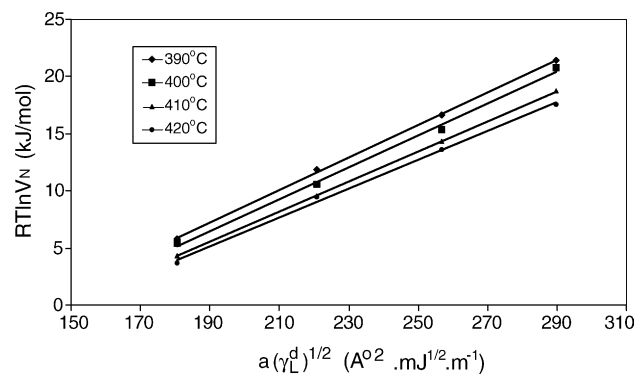

Fig. 3. $RT \ln V_N$ vs. $a(\gamma_L^d)^{1/2}$ plot for the adsorption of n-alkanes on CaY.

Table 4
Properties of the probe [43,44]

Probe	a (Å^2)	γ_L^d (mJ m^{-2})
n-Pentane	45.0	16.1
n-Hexane	51.5	18.4
n-Heptane	57.0	20.3
n-Octane	62.8	21.3

Table 5
Values of γ_S^d measured on adsorbents at various temperatures

Adsorbent	γ_S^d (mJ m^{-2})			
	240 °C	250 °C	260 °C	270 °C
NaY	52.6	51.8	47.4	47.3

Adsorbent	γ_S^d (mJ m^{-2})			
	390 °C	400 °C	410 °C	420 °C
CaY	139	133	120	110

γ_S^d values decrease with temperature. The variation of γ_S^d as a function of temperature is linear and hence γ_S^d at room temperature can be obtained by extrapolation. No value of γ_S^d has been found published for NaY and CaY to compare to our results.

CaY presents a higher value of γ_S^d than does NaY. CaY shows a high γ_S^d varying between 139.5 and 109.9 mJ/m^2 with temperatures between 390 and 420 °C. These values are characteristic for high energy inorganic surfaces and are in accordance with the values obtained for the differential heat of adsorption.

5. Conclusion

From the results obtained in this study, the following conclusions can be drawn:

(1) IGC at infinite dilution is a convenient method for the evaluation of the adsorption thermodynamic magnitudes (ΔH°, ΔG°, ΔS°, γ_S^d) of zeolites.

(2) In CaY, the specific interactions are greater for the exchanged zeolite containing divalent ion than for NaY. It is concluded that the interaction strength increases with increasing cation charge and decreasing cation size.

(3) The weaker adsorption of the investigated probes on the NaY in comparison with the respective NaX zeolites shows that the aluminium content of the zeolites modifies the energetic state of the adsorption sites.

(4) The adsorption strength on NaY and CaY zeolites increases according to the following sequence: cyclohexane < *n*-hexane < benzene. The interaction between the adsorbed molecules on the charge condensing cations is of an electrostatic nature. The polar molecules are generally more strongly adsorbed than the non-polar ones. The adsorption strength of non-polar molecules is modified by their electric polarizability.

(5) The diffusion of a particular species in the zeolite is, therefore, expected to be strongly dependent on the chemical environment of the diffusing species, which in turn depends on the zeolite parameters (Si/Al ratio, nature of the cation and its degree of exchange and pretreatment conditions, etc.).

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