Characterization of various types of adsorption centres on zeolites using heats of adsorption*

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The importance of various types of adsorption centres on a zeolite of the faujasite type using model adsorbates was tested. The degree of heterogeneity of the zeolite surface was modified by changing the number of cations in the zeolite with the general formula $Na_xH_{1-x}Y$. On the basis of the experimental results, the following conclusions were drawn:

Adsorbates capable of specific interactions (CO, C_2H_4) prefer cationic adsorption centres; a predominant role is played by cations in large cavities.

Non-specifically sorbed molecules (saturated hydrocarbons, C_1—C_3) interact with the zeolite skeleton during adsorption. The values of the heats of adsorption for these substances are not affected by the number of cations.

Active centres formed by the substitution of cations by protons are energetically less pronounced.

С помощью модельных адсорбатов проверялась значимость различных типов адсорбционных центров на цеолите типа фауязита. Степень гетерогенности поверхности измерялась числом катионов в цеолите, который описывается общей формулой $Na_xH_{1-x}Y$. На основе полученных результатов были сделаны следующие заключения:

Адсорбаты, которые обладают специфической адсорбцией (CO, C_2H_4), прежде всего взаимодействуют с сорбционными центрами, образованными катионами; главную роль играют катионы в больших порах.

Молекулы, которые не обладают специфической адсорбцией (предельные углеводороды C_1—C_3), при сорбции взаимодействуют со скелетом цеолита. Теплота адсорбции у этих веществ не зависит от количества катионов.

С энергетической точки зрения менее выразительны активные центры, образованные замещением катионов протонами.

Zeolites — molecular sieves — exhibit outstanding adsorptive and catalytic properties and therefore much attention has been paid to the study of the sorption mechanism of various molecules [1—8]. In Kiselev's classification of adsorbents, zeolites are placed among adsorbents of the second type, *i.e.* adsorbents with strongly

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localized positive charges on the surface (cations, —OH groups) [23]. The walls of cavities in the porous zeolite crystals are composed of silicon—oxygen and aluminium—oxygen tetrahedra. Because of the increase in the aluminium coordination number to four — as compared to its valence state of three — the aluminium—oxygen tetrahedra carry a unit negative charge. These negative charges, appearing in the zeolite lattice wherever the $-\overset{|}{Al}-O-\overset{|}{Si}-$ bonds are located, are compensated by exchangeable cations, mostly with small radii (Na, Ca). Nonuniform charge distribution on the surface of the zeolite lattice causes specificity of the adsorbate--adsorbent interaction for various kinds of molecules.

The zeolite cations can be exchanged analogously as in ion exchangers since they are not fixed components of the lattice. A high degree of exchange can be achieved using a salt of the appropriate cation. From zeolites, whose original sodium cation has been exchanged for an ammonium cation, the so-called H form can be obtained by removing NH_3 at a temperature of about 300°C. Therefore, zeolites with various numbers of cations, depending on the degree of exchange, can be prepared in this way. The —OH groups formed by the removal of NH_3 molecules represent energetically much weaker adsorption centres.

From the zeolite structure it follows that the cations can occupy several positions in the zeolite lattice. Cations located in large cavities are most easily accessible for the adsorbate molecules [9—12]. These cations are also preferably exchanged, as it has been demonstrated using i.r. spectroscopy [13, 14].

Since the protons interact with lattice oxygen and form only weakly polarized covalent bonds, it can be assumed that the intensity of the electrostatic field in the zeolite cavity changes considerably on replacement of the Na^+ cations by the H^+ ions. This change may strongly affect the value of the heat of adsorption for molecules with electrostatic moments.

If the assumption of various localizations of cations in the lattice and thus their varying importance for the adsorbate molecules is considered, then the decrease in the heat of adsorption for molecules of the above type should not depend linearly on the degree of decationization. Assuming a different nature for the adsorption centres with which various molecules interact, we decided to study the adsorption mechanism in a series of zeolites of the faujasite type, differing only in the number of cations, the lattice skeleton being preserved.

Experimental

Zeolites with various cation contents were prepared by the ion exchange from an NH_4NO_3 solution at $t = 80°C$. The ion exchange and analyses of the original NaY zeolite and of individual samples were carried out in the Research Institute for Oil and Hydrocarbon Gases in Bratislava. The results are given in Table 1.

As adsorbates, CH_4, C_2H_6, C_2H_4, and C_3H_8 hydrocarbons and CO were used, all of "research grade" purity from Merck.

Experiments were carried out using a CHROM-2 chromatograph with a flame ionization detector and a simple chromatograph with a catharometer. Glass columns 60 cm long and with an inner diameter of 3.5 mm were employed. In order to obtain a suitable granule size, zeolite pellets were prepared under a pressure of 500 kp/cm² without a binder. The ammonium form was decomposed in a chromatographic column by gradually

Table 1

Elementary composition of the applied zeolites

Sample (abbreviated formula)	Analysis			Composition of idealized elemental cell
$Na-Y'$	$0.96Na_2O$	$0.041CaO \cdot Al_2O_3$	$5.04SiO_2$	$Na_{32.8}Ca(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.88}H_{0.12}-Y$	$0.88Na_2O$	$0.039CaO \cdot 0.079(NH_4)_2O$	$Al_2O_3 \cdot 5.07SiO_2$	$Na_{48.4}Ca(NH_4)_{4.3}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.81}H_{0.19}-Y$	$0.81Na_2O$	$0.035CaO \quad 0.12(NH_4)_2O$	$Al_2O_3 \quad 4.92SiO_2$	$Na_{44.5}Ca(NH_4)_{6.6}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.71}H_{0.29}-Y$	$0.71Na_2O$	$\cdot 0.033CaO \quad 0.25(NH_4)_2O$	$Al_2O_3 \cdot 4.95SiO_2$	$Na_{37.0}Ca(NH_4)_{13.7}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.61}H_{0.39}-Y$	$0.61Na_2O$	$0.028CaO \quad 0.36(NH_4)_2O$	$Al_2O_3 \cdot 4.96SiO_2$	$Na_{33.2}Ca(NH_4)_{19.8}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.54}H_{0.46}-Y$	$0.54Na_2O$	$0.039CaO \quad 0.48(NH_4)_2O$	$Al_2O_3 \quad 4.82SiO_2$	$Na_{29.7}Ca(NH_4)_{26.4}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.43}H_{0.57}-Y$	$0.43Na_2O$	$0.021CaO \quad 0.57(NH_4)_2O$	$Al_2O_3 \quad 4.97SiO_2$	$Na_{23.6}Ca(NH_4)_{31.3}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.30}H_{0.70}-Y$	$0.29Na_2O$	$0.033CaO \quad 0.72(NH_4)_2O$	$Al_2O_3 \cdot 4.95SiO_2$	$Na_{16.4}Ca(NH_4)_{39.6}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.13}H_{0.87}-Y$	$0.13Na_2O$	$0.036CaO \quad 0.88(NH_4)_2O$	$Al_2O_3 \quad 4.92SiO_2$	$Na_{7.1}Ca(NH_4)_{48.4}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.01}H_{0.99}-Y$	$0.012Na_2O$	$0.035CaO \cdot 1.01(NH_4)_2O$	$\cdot Al_2O_3 \cdot 4.95SiO_2$	$Na_{0.6}Ca(NH_4)_{55.5}(AlO_2)_{55}(SiO_2)_{137}$

increasing temperature up to 360°C in a flow of dried He. The completeness of the de-composition was checked using the Nessler reagent.

The optimum operating conditions, *i.e.* the temperature interval, carrier gas flow--rate, and the sample size, were determined for each adsorbate before the measurement. It was confirmed that the carrier gas optimum flow-rate lies in the region of the minimum on the van Deemter curve.

The retention times were measured four times at 5—6 temperatures for each adsorbent and adsorbate. The dead volume of the column was determined from the H_2 retention time at 140°C.

The values of the isosteric heats of adsorption were obtained according to *Greene* and *Pust* [15] from the slope of the linear dependence of the specific retention volume of the adsorbate on the reciprocal of the absolute temperature by the linear regression method with a standard deviation of $\pm 5\%$. Treating the $Na_x(NH_4)_{1-x}Y$ zeolite at 770°C under the vapour pressure, we obtained the so-called ultrastable form. The working conditions of this separation are described elsewhere [16, 17].

Zeolite prepared in this way differs in the number and character of $-OH$ groups due to a decrease in the H^+ mobility, however, the number of cations remains constant.

Results

The nature of the interactions between cations and structural $-OH$ groups was tested by means of the values of the heats of adsorption for adsorbates of various electronic structures. Methane, ethane, and propane were used as adsorbates exhibiting no specific interaction with various adsorption centres of the zeolite, carbon monoxide and ethylene as molecules capable of a specific interaction.

The chromatographically determined values of the heats of adsorption obtained with a series of samples with the general formula $Na_xH_{1-x}Y$ and their standard deviations are given in Table 2. The two groups of adsorbates differ qualitatively

Table 2

Chromatographic heats of adsorption (kcal mol^{-1}) for model adsorbates in dependence on decationization degree of NaHY zeolite adsorbents

Adsorbate	Decationization degree of the sample (mole %)									
	0%	12%	19%	29%	39%	46%	57%	70%	87%	99%
CH_4	4.33	4.10	4.39	4.30	4.12	4.05	4.11	4.17	3.75	4.12
	±0.14	±0.20	±0.11	±0.04	±0.10	±0.05	±0.16	±0.11	±0.08	±0.17
C_2H_6	6.16	5.92	6.17	6.14	5.72	5.78	5.77	6.33	6.20	5.69
	±0.35	±0.21	±0.21	±0.25	±0.18	±0.14	±0.16	±0.35	±0.26	±0.15
C_3H_8	8.12	8.03	8.15	8.11	7.84	7.95	7.44	8.08	7.92	7.60
	±0.30	±0.30	±0.27	±0.25	±0.29	±0.21	±0.28	±0.20	±0.14	±0.32
CO	5.79	5.71	5.47	5.66	4.92	4.84	5.19	5.26	4.85	4.76
	±0.13	±0.25	±0.23	±0.12	±0.11	±0.17	±0.20	±0.18	±0.20	±0.10
C_2H_4	11.26	10.05	9.64	9.33	9.03	9.11	9.29	9.50	9.15	8.87
	±0.37	±0.24	±0.22	±0.24	±0.18	±0.21	±0.25	±0.21	±0.12	±0.27

Table 3

Heats of adsorption for model adsorbates on zeolites with various types of $-OH$ groups
(kcal mol^{-1})

Adsorbate	$Na_{0.3}H_{0.7}Y$	
	Original	Partially dehydroxylated
CH_4	4.17 ± 0.11	3.93 ± 0.10
C_2H_6	6.33 ± 0.35	5.88 ± 0.28
C_3H_8	8.08 ± 0.20	6.97 ± 0.31
CO	5.26 ± 0.18	4.85 ± 0.18
C_2H_4	9.50 ± 0.21	8.62 ± 0.20

in the shape of the dependence of the heat of adsorption on the zeolite composition. For molecules exhibiting a specific interaction the heats of adsorption decreased significantly with increasing decationization, while no significant change in the heats of adsorption was found for molecules with non-specific interaction. In Table 3, the heats of adsorption on the Na_3H_7Y zeolite are compared with those for identical sorbates on a zeolite in the so-called ultrastable form. The minute decrease in the heats of adsorption due to partial dehydroxylation of this zeolite verifies our assumption on negligible contribution of interaction with $-OH$ groups for both adsorbate types.

Discussion

As it follows from our results, the heats of adsorption for C_1-C_3 saturated hydrocarbons do not change significantly with the degree of decationization. The average values, 4.14 kcal mol^{-1} for methane, 6.00 kcal mol^{-1} for ethane, and 7.92 kcal mol^{-1} for propane, are in a good agreement with our assumption on non-specific interaction and are close to the values obtained for adsorbents with a homogeneous surface [18]. This results is easy to explain, since the most important component of the adsorption energy of these molecules if formed by dispersion forces, which are not substantially affected by the number of Na^+ cations. The contribution of electrostatic component in these molecules is given by a change in their polarization energy alone and does not represent any substantial contribution to the overall adsorption energy. The heats of adsorption of these adsorbates increase linearly with increasing number of C, the increment per CH_2 group being 1.9 ± 0.1 kcal mol^{-1}, this being in agreement with the published data [8, 19, 20] for adsorbents with homogeneous surface.

Specifically sorbed molecules of carbon monoxide and ethylene cause a statistically significant decrease in the values of the heat of adsorption with increasing decationization. The effect of the electrostatic field was expressed by means of the $\Delta H\ C_2H_4 - \Delta H\ C_2H_6$ or $\Delta H\ CO - \Delta H\ CH_4$ dependences on the degree of zeolite decationization. These function are shown in Fig. 1, together with the calculated standard deviations of the ΔH differences.

A statistically significant decrease in both functions was demonstrated, however, the parabolic shape of the function is statistically significant only for the ethylene—ethane couple. The scatter of the values of the difference in the heats of ad-

sorption for the carbon monoxide—methane couple and the relatively low heats of adsorption for the two adsorbates render unambiguous conclusions about the function shape impossible. Basic molecules with larger dipole moments, exhibiting substantially higher heats of adsorption were not used, since it has been shown [21] that they may cause delocalization of cations or protons.
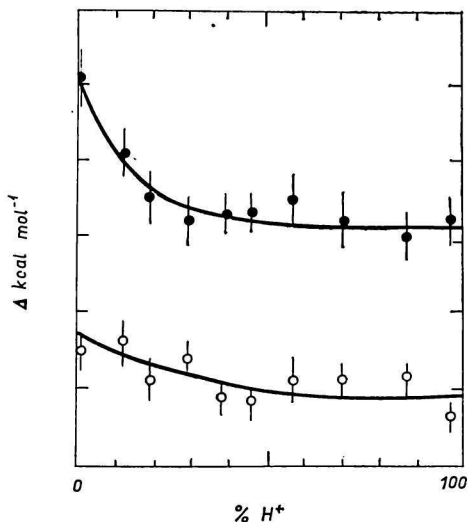

Fig. 1. The effect of the degree of zeolite decationization on the sorption specificity.
● $\Delta H\ C_2H_4 - \Delta H\ C_2H_6 = \Delta_{spec}$;
○ $\Delta H\ CO - \Delta H\ CH_4 = \Delta_{spec}$.

The specificity of the interaction of carbon monoxide and ethylene molecules is considered in electrostatic approximation as the contribution of quadrupole moment of the C_2H_4 molecule and the dipole moment of the CO molecule. This specific component of the interaction is generally affected by the zeolite composition, i.e. it depends on the number of cations and their location. The initial decrease in the number of Na^+ cations, given by preferential decationization of large cavities, is most pronounced, as follows from Fig. 1. At a higher degree of exchange, when less easily accessible cations occupying the I, I', and II' positions according to Smith's notation [22] are removed, the decrease in the values is less significant, since these cations affect the sorption of molecules in large cavities to a substantially lesser degree.

The contribution of —OH groups formed to specific interaction is almost negligible.

The results of our experiments confirm directly the importance of the contribution of specific interaction in adsorption of substances possessing an electrostatic moment.

It has been proved that in adsorption on zeolites these substances prefer cationic sorption centres.

The nonlinear decrease in the values of the heats of adsorption in dependence on the degree of decationization is, in our opinion, another illustration of the effect of the cation position in the lattice on its properties as a sorption centre during the specific interaction.

References

1. Barrer, R. M., *J. Colloid Sci.* **21**, 415 (1966).
2. Yates, D. J. C., *Catal. Rev.* **2**, 113 (1968).
3. Turkewich, J., *Catal. Rev.* **1**, 1 (1967).
4. Kiselev, A. V. and Lopatkin, A. A., *Molecular Sieves*, p. 252. Papers from the Conference Society of Chemical Industry, London, 1968.
5. Barrer, R. M. and Stuart, W. L., *Proc. Roy. Soc.* **A249**, 464 (1958).
6. Barrer, R. M. and Gibbons, R. M., *Trans. Faraday Soc.* **59**, 2569 (1963).
7. Barrer, R. M. and Gibbons, R. M., *Trans. Faraday Soc.* **61**, 948 (1965).
8. Kiselev, A. V., *Gas Chromatography 1964*, Proc. 5th Symposium Held in Brighton. Elsevier, Amsterdam, 1965.
9. Bosáček, V., *Molecular Sieves*, p. 164. Papers from the Conference Society of Chemical Industry, London, 1968.
10. Barry, T. I. and Lay, L. A., *J. Phys. Chem. Solids* **27**, 1821 (1966).
11. Barry, T. I. and Lay, L. A., *J. Phys. Chem. Solids* **29**, 1395 (1968).
12. Angell, C. L. and Schaffer, P. C., *J. Phys. Chem.* **70**, 1413 (1966).
13. Ward, J. W., *J. Phys. Chem.* **73**, 2086 (1969).
14. Jacobs, P. A. and Uytterhoeven, J. B., *Trans. Faraday Soc.* **69**, 373 (1973).
15. Greene, S. A. and Pust, H., *J. Phys. Chem.* **62**, 55 (1958).
16. Bosáček, V., Patzelová, V., and Tvarůžková, Z., unpublished results.
17. Patzelová, V *The IV Colloquium on Adsorption*. Kazimierz, Poland, November 1974.
18. Kiselev, A. V., *Discuss. Faraday Soc.* **40**, 205 (1965).
19. Barrer, R. M. and Sutherland, J. W., *Proc. Roy. Soc.* **A237**, 439 (1956).
20. Kiselev, A. V., *Molecular Sieves. II. Advances in Chemistry Series*, Vol. 102. Amer. Chem. Soc., Washington, D.C. 1971.
21. Uytterhoeven, J. B., Jacobs, P., Makay, K., and Schoonheydt, R., *J. Phys. Chem.* **72**, 1728 (1968).
22. Smith, J. V., *Molecular Sieves. I. Advances in Chemistry Series*, Vol. 101, p. 171. Amer. Chem. Soc., Washington, D.C., 1971.
23. Kiselev, A. V. and Yashin, Ya. I., *Gazo-adsorptsionnaya khromatografiya*. Nauka, Moscow, 1967.