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INVESTIGATION OF CHROMATOGRAPHIC PROPERTIES OF TRANSCARPATHIAN CLINOPTILOLITE

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ABSTRACT

The influence of the concentration and time of action of hydrochloric acid on the chromatographic properties of clinoptilolite was studied. The effect of the degree of dealumination of natural zeolite on the nature of changes in the chromatographic and thermodynamic parameters of the separation of model mixtures containing low-boiling (O_2, N_2) and oxide gases (CO, CO_2, N_2O), gaseous alkanes and olefins, vapours of saturated hydrocarbons, which are permanent components or pollutants, is shown. air. The optimal values of the silicate module were found in the range from 9.8 to 15.1, which ensure the maximum chromatographic retention of the components. Developed silver- and copper-containing modifications of natural clinoptilolite for separation of CO-CO_2 carbon oxides. The possibility of regulating the output sequence of these components from the chromatographic column by changing the temperature and content of exchangeable cations is shown. On copper modifications of clinoptilolite containing 0.85 % of Cu^{2+} cations, the effect of low substitutions was revealed, which is manifested by a sharp increase in retained volumes for CO and C_2H_4, heats of adsorption, changes in Gibbs potentials.

The influence of concentration and exposure time of hydrochloric acid on the chromatographic properties of clinoptilolite was studied. The value of the dealumination of clinoptilolite modifications for the chromatographic analysis of several gases and vapors is shown. The effect of small substitutions of cations was revealed based on the gas chromatographic study of samples of 0.85CuCl for mixtures of CO and C_2H_4.

Keywords: clinoptilolite, gas chromatography, adsorption, the effect of small cation substitutions

1. Introduction

Control of the natural environment is one of the component systems of nature protection measures aimed at supporting the interaction between human activity and the natural environment, the rational use of natural resources, and preventing the direct and indirect impact of the results of society's; activities on nature and human health.

One of the important tasks of modern chromatography is the reliable and accurate analysis of organic substances, often similar in structure and properties. Without it, it is impossible to carry out chemical, physicochemical, biochemical, and medical research, it is largely based on forensic expertise, ecological methods of environmental analysis, as well as chemical, oil, gas, food, medical industries, and many other sectors of the national economy.

The analysis of air pollution is a difficult task of analytical chemistry, because air is a moving system, the composition of which is constantly changing, and one sample can simultaneously contain tens or hundreds of organic and inorganic substances. In addition, the concentration of toxic substances in the atmosphere can be low (10^{-4} % - 10^{-7} % and below).

Laboratory studies use chromatographic, mass spectral, spectral, and electrochemical atmospheric air pollution analysis methods. Physico-chemical methods are used to clean air from gaseous and vapour-like impurities: absorption, adsorption, thermal, catalytic, and biochemical purification. Among the mentioned methods, gas chromatographic analysis is of great importance, with the help of which it is possible to find out with high accuracy the qualitative and quantitative characteristics of substances present in the air with high accuracy.

The development of industry, energy, and road transport is accompanied by emissions into the environment of large amounts of exhaust gases from cars, the use of freons in everyday life causes the appearance of a greenhouse effect on the planet and climate change in general. The annual amount of air pollution is expressed in millions of tonnes (tonne = 10^3 kg = 10^6 g = Mg), in particular: CO, sulphur dioxide, nitrogen oxide, and hydrocarbons. The increase in their concentrations in the air of large cities and industrial centers is of particular concern [1].

The presence of the pollutants mentioned above in the air presented several new and complex problems to chemical science and practice, related to the difficulties of qualitative and quantitative analysis of these pollutants or the need for preliminary air purification before serving to consumers, including the adsorption method as one of the best.

Natural zeolites are of particular interest for their extraction for qualitative and quantitative analysis, as well as for the purification of gases and liquids. The most common natural zeolite is clinoptilolite, large deposits of which are discovered in Transcarpathia. However, its ability to modify and acquire qualitatively new adsorption properties is practically not studied [1-3].

Natural clinoptilolites have an advantage over synthetic zeolites not only in their availability and cheapness but also in several physical and chemical properties. They are heat- and acid-resistant and have high mechanical strength. After modification, clinoptilolites acquire high selectivity in removing hazardous components from polluted air. The study of zeolites is carried out by various methods, among which gas chromatography deserves special attention because it allows you to quickly and with great accuracy obtain valuable information about the physical and chemical properties of adsorbents [2, 4, 5].

Therefore, the study of chromatographic and thermodynamic characteristics of adsorption processes on natural zeolites and their modifications is relevant both from the point of view of their high selectivity for the extraction of individual components from polluted air and for their quantitative analysis [6].

Modification of zeolites with various cations and acid treatment allows to strengthen or weaken the selectivity of retention of components, which is of scientific and practical interest. However, there have been no systematic studies on the effect of acid on the chromatographic retention of air pollutants by zeolites, which contain unequal amounts of exchangeable cations of different natures [6-8].

The aim of the study

Development of new modifications of natural clinoptilolite as a result of their treatment with hydrochloric acid (HCl) solutions and copper and silver salts. Determination of chromatographic and thermodynamic characteristics of these modifications and the possibility of their use for extraction, concentration, and desorption of the main pollutants of the surrounding air.

2. Research methods. The main method was gas chromatography using gas chromatographs of the "Cvet" type (models 4-67 and I62) with a thermal conductivity and flame ionisation detector. Helium, nitrogen, or argon were used as carrier gases. X-ray phase and differential thermal analysis, infrared spectroscopy, flame photometry, and other physicochemical methods are also involved.

Experimental part. The elemental composition of the Sokyrnytskyi clinoptilolite was determined by modern physicochemical research methods, the chemical composition of which corresponds to the formula 1.4 $(Na, K)_2O(Ca, Mg)O_3Al_2O_3 \cdot 28\ SiO_2 \cdot 22\ H_2O$, the Si/Al Si/Al ratio is 4.7 [7-10]. It is shown that during modification (HCl, NaCl, NH_4Cl) the exchangeable ions of clinoptilolite are not completely replaced by cations of the modifier. The biggest structural changes occur when clinoptilolite is treated with hydrochloric acid [2, 11].

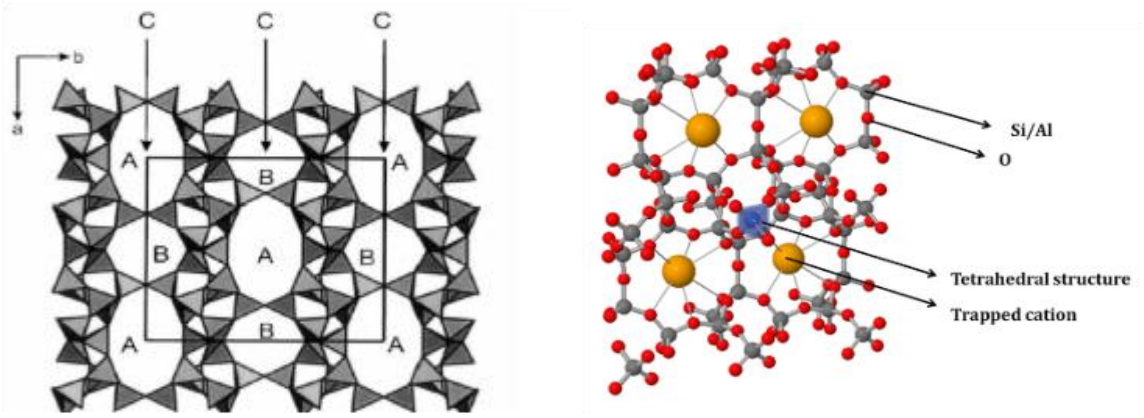

Figure. 1. Tetrahedral model of clinoptilolite along the c axis (ten-membered channels A and eight-membered channels B) [1,6].

The general properties of zeolites are the ability to release zeolite water when heated without destroying the structure and the ability to exchange cations. The basis of the structure of zeolites are rings of tetrahedra formed by $SiO4^{4-}$ and $AlO4^{5-}$, large cavities between which are connected by tubules. Zeolite water is contained in the cavities, and when heated can be lost through these channels. At the same time, the volume of the mineral does not change. Dehydrated zeolite can absorb water again [1, 12].

The crystallochemical parameters of the lattice of natural clinoptilolite of the Sokyrnytsky deposit were calculated using the powder method: monoclinic syngonia, space group C 1 2/m 1, lattice length - a = 17.595 Å, grid width - b = 17.593 Å, lattice height - c = 7.415 Å, angle between lattice lattices - β = 117.010 Å, volume lattice - V = 2044.95 Å^3). Modification of clinoptilolite leads to an increase in the volume of the elementary cell [6]. Crystals of Sokyrnytsk clinoptilolite have a prismatic shape and plate-prismatic appearance [13].

Acid treatment reduces the hydrophilicity of clinoptilolite due to its decationisation and dealumination and leads to a decrease in water content [14, 15]. Treatment of natural clinoptilolite of the Sokyrnytsky deposit with 3 M HCl solution for 30 minutes leads to a decrease in water content from 4.8 % to 3.6 % [6].

Under the action of acids, clinoptilolite undergoes the following changes: 1) cleaning of the material from impurities; 2) ion exchange between the cationic complex of clinoptilolite and the H_3O^+ ion; 3) dealumination, which causes structural modification of clinoptilolite [16].

For the first time, the study of the dealumination of clinoptilolite was carried out by Barrer and Mackie, and since then the idea of the dealumination mechanism has hardly changed [5]. Works [16-18] are devoted to dealumination and decationisation processes. These processes take place according to the scheme (Fig. 2) [16].

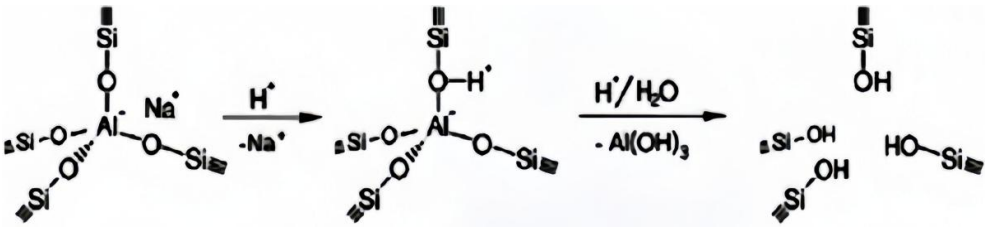

Figure 2. Transformation of clinoptilolite in a solution of hydrochloric acid.

First, exchangeable cations are replaced by hydroxonium ions with the formation of the H-form. As the contact time increases, $[\equiv Si– OH]_4$ clusters are formed, and $Al(OH)_3$ polymer gel is formed in the zeolite channels, which dissolves under the action of acid to form Al^{3+}. Al^{3+} ions leave the channels of clinoptilolite and do not return to the crystal lattice. Tetrahedral Al in the T2 position is removed from the framework, resulting in a vacancy (Fig. 3) [17].

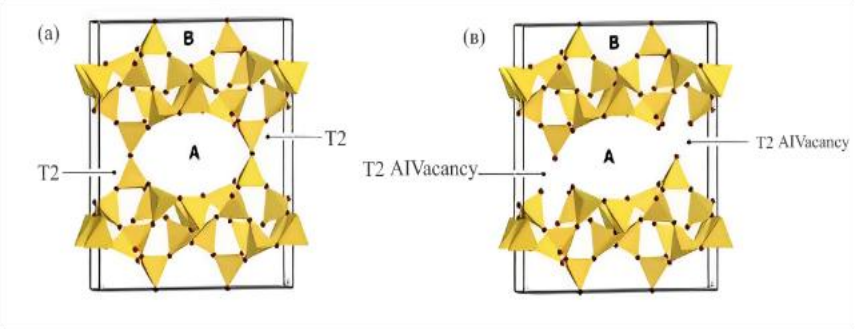

Figure 3. Channel A of clinoptilolite: Al in the T2 tetrahedral position (a) and a vacancy in the T2 position (b) [10].

At degrees of dealumination up to 50%, clinoptilolite does not lose its crystallinity. The order and degree of extraction of exchangeable cations and Al are approximately the same. The elements can be arranged in a series that correlates with the decrease in the strength of the bonds of these elements in the structure of clinoptilolite (Si>Al>>K>Ca>Na) [18].

The interaction of exchangeable cations with adsorptive molecules is determined by the strength of the bond between the cation and the crystal lattice of clinoptilolite: the weaker this bond is, the stronger the interaction [18]. Treatment with acids leads to the most significant change in the properties of clinoptilolite. 2.2.Preparation of zeolite samples. Clinoptilolite from the Sokyrnytsky deposit was used in the work. The zeolite was crushed and sieved through a sieve (0.25 mm). The crystals had dimensions of several micrometers (10^{-6} m). Clinoptilolite was modified by keeping its granules for a long time (from 1 to 16 days) at 293K in solutions of HCI with concentrations of 0.1; 0.2; 0.4; 0.8; 1.6; 3.2; 6.4 mol/l, as well as additional treatment with silver and copper salts [1,2].

The degree of extraction (α) of cations was calculated as the ratio of the difference between their content in the sample before and after treatment to the initial amount in the zeolite. Although there are fewer Na^+ cations in clinoptilolite than Ca^{2+} and K^+, they are removed to the greatest extent and in almost 2-4 days. The extraction of cations is more affected by the concentration of the acid than by the time of its contact with the zeolite (Fig. 4).

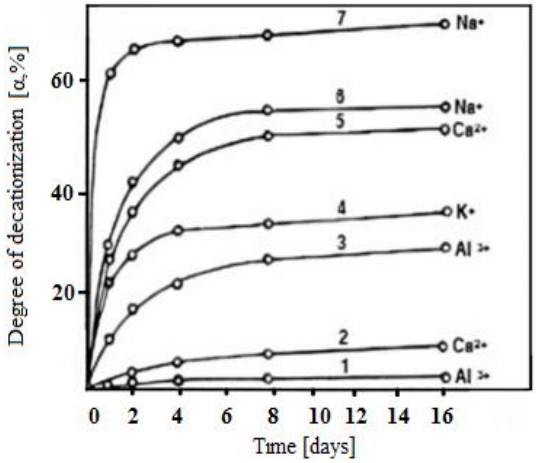

Figure 4. Dependence of the degree (α) of decationization and dealumination of clinoptilolite on time at different concentrations of HCI: 0.1 M HCI - (1, 2, 6); 6.4 M HCI (3, 4, 5, 7).

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At the same time, the degree of dealumination of clinoptilolite in a 6.4 M solution of HCl does not exceed 28.7 % with a simultaneous increase in the silicate module (SiO_2/Al_2O_3) from 9.8 to 15.1. The sample with a modulus of 15.1 was additionally modified with Ag^+ cations, the content of which did not exceed 10 %. High-silica clinoptilolite (module 14.4) was used to prepare a series of copper-containing (up to 5 %) derivatives.

Later, samples of such zeolites were chemically analysed for the content of exchangeable cations Na^+, and K^+, as well as Al_2O_3, SiO_2, and water. The content of alkali metal cations was determined by the method of flame photometry from the solutions obtained after the treatment of zeolites with hydrochloric acid. The content of Al_2O_3 and SiO_2 was determined by the weight method.

Natural clinoptilolite and its deionised Ag^+ and Cu^{2+} modifications were studied by the methods of IR spectroscopy, X-ray phase, and differential thermal analysis (DTA), which proved the complete invariance of the parameters of the crystal structure of all modifications of clinoptilolite after decation and significant dealumination [19].

IR spectra were recorded on a UR-20 spectrophotometer in the wavenumber range of 400 cm^{-1} - 5000 cm^{-1}. A slight shift of the 1070 cm^{-1} band toward higher wave numbers is associated with the release of aluminium from the tetrahedra when the modulus (SiO_2/Al_2O_3) increases from 9.8 to 15.1 (Fig.5, lines 1 and 4).A slight shift of the 3450 cm^{-1} band (lines 2 and 3) confirms the significant strength of the samples modified with Ag^+ and Cu^{2+} cations.

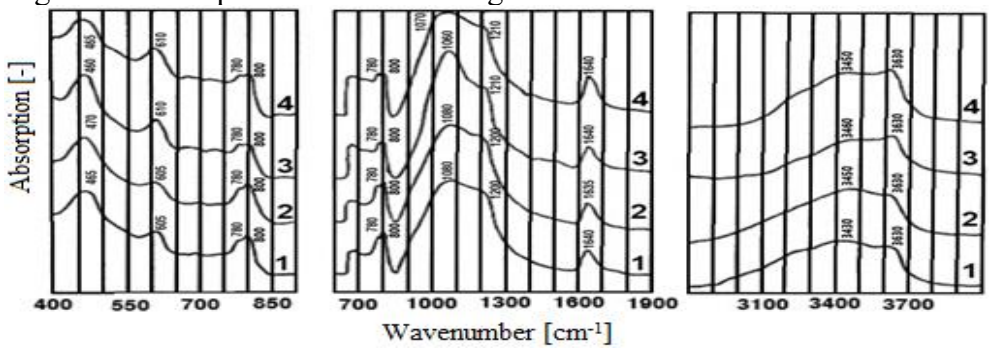

Figure 5. IR spectra of some modifications of clinoptilolite. SiO_2/AI_2O_3 ratio in the samples: 15.1 – (1 and 3); 14.4 – (2); 9.8 – (4). Content of cations, %: 5.0 Cu^{2+}- (2); 9.7 Ag^+ - (3).

The IR spectroscopy method is one of the most informative for studying some properties of zeolites [19]. The high sensitivity of the spectrum of the crystal framework to structural changes allows the use of IR spectroscopy to obtain information about the localisation and migration of cations in zeolites and the deformations of the crystal lattice related to them.

For IR spectral studies, the samples were tableted by pressing highly dispersed zeolite powder. The thickness of the tablets varied from 0.8 mg/cm^2 to 2 mg/cm^2, which made it possible to obtain spectra of good quality in the entire spectral range. Tablets were pressed under a pressure of 15 MPa. The preparation of samples in this way made it possible to obtain informative spectra in the range of 4000 cm^{-1} - 400 cm^{-1}, so we can simultaneously observe changes in the surface coating and changes in the region of crystal lattice vibrations.

The diffractograms (Fig. 6) were taken on the DRON-3 device under copper radiation using a Ni filter, and the parameters of their crystal lattices were also calculated (Table 1).

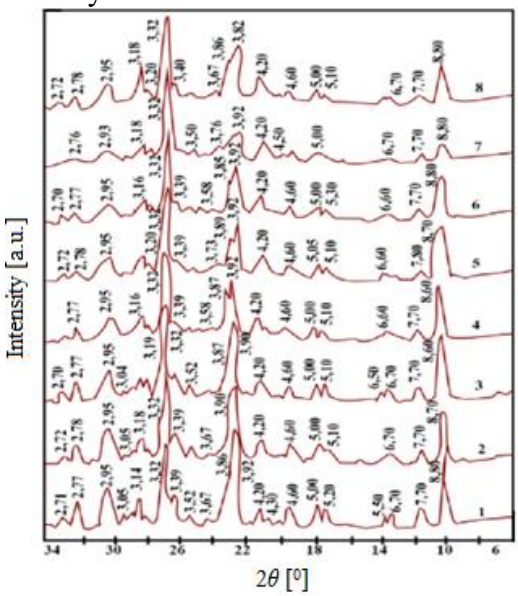

Figure 6. Diffraction patterns of clinoptilolite and its modifications at different ratios of SiO_2/AI_2O_3 9.8 – 1; 11.3 – 2; 12.4 – 3; 13.4 – 4; 15.1 - 5; 15.1 (9.7 Ag^+) – 6; 9.8 (5.2 Ag^+) – 7, 14.4 (5.0 Cu^{2+}) – 8.

After dealumination and cationic treatment, the parameters of the crystal cells of the clinoptilolite modifications practically do not change (Table 1). Only a weak (up to 0.5%) framework compression is observed as the modulus increases from 9.8 to 15.1 in the presence of cations. In the presence of Ag+ and Cu2+, there is a tendency for the framework to expand (by 0.15 and 0.6%, respectively). The stability of all samples of clinoptilolite 1 was also confirmed on the derivatograph using the recorded DTA curves [1].

Table 1. Parameters and volumes of elementary cells of the original and modified clinoptilolite samples (angle β = 116 o35')

Ratio SiO_2/Al_2O_3	**Content of cations [%]**	**Lattice parameters [nm]**			**Unit cell volume [nm^3]**
		***a* ± 0.0003**	***b* ± 0.0002**	***c* ± 0.0001**	
9.8	-	1.7522	1.7728	0.7420	2.0650
11.3	-	1.7492	1.7801	0.7386	2.0621
12.4	-	1.7497	1.7721	0.7413	2.0591
13.4	-	1.7521	1.7678	0.7412	2.0570
15.1	-	1.75212	1.76676	0.7404	2.0542
15.1	9.7 Ag^+	1.7585	1.7649	0.7399	2.0571
9.8	5.2 Ag^+	1.7522	1.7729	0.7429	2.0682
14.4	5.0 Cu^{2+}	1.7577	1.7733	0.7398	2.0661

The selected modifications of zeolites were converted into granules (fractions of 0.5-1.0 and 0.25-0.5 mm) after pressing the powders into tablets, strengthening them by heating and subsequent grinding and sifting through sieves. Granules were poured into columns for chromatographic analysis. Carrier gas (He, Ar, N_2) was blown through columns (100x0.3 cm) at a flow rate of 50 cm^3/min.

Under these conditions, at 573K, the granules were first dehydrated for at least 3 hours, and then samples of model mixtures, the components of which are part of the air or are its pollutants, were introduced into the columns (with a syringe or a dosing faucet): inert gases, carbon and nitrogen oxides, SO_2, alkanes C_1-C_4, C_2H_4, C_2H_2, C_3H_6, isomers of butene, pairs of aromatic and saturated hydrocarbons C_6-C_{10}.

With the participation of the thermal conductivity detector, each component was recorded on the chromatogram after leaving the zeolite column as a peak, for which the elution time, width, and other parameters were measured. The temperature of the column was lowered each time by 20K to record new chromatograms up to 273K. Based on the obtained chromatograms and elution times of the components at all temperatures with an interval of 20 K, the main chromatographic and thermodynamic characteristics of the adsorption processes were calculated [2].

3. Results and their discussion

As a result of acid treatment and increasing the degree of dealumination, the chromatographic properties of clinoptilolite change so much that it becomes possible to separate low-boiling gases, carbon and nitrogen oxides, volatile alkanes, and olefins. After reaching a silicate module of 11-12.5, the main components of air O_2-N_2 are separated at room temperature temperatures At the same time, there are such optimal values (SiO_2/Al_2O_3 in clinoptilolites), which achieve not only the best chromatographic separation of components, but also the maximum value of their retention volumes.

This is a sample with a modulus of 10.5 when carbon and nitrogen oxides are retained, and for C2-C10 alkanes, the maximum retention moves toward higher degrees of decationisation. This is the result of a combination of the geometric and electronic structure of the adsorbate molecules and the size and structure of the cavities, the nature, and the available number of cations in the unit cells of clinoptilolite.

A similar picture was also observed when changing the width of the chromatographic zones for the extraction of other gases, but for C_6-C_{10} hydrocarbon vapours, the molecules of which can be adsorbed only on the outer surface of clinoptilolite crystals, there is a constant expansion of the peaks on the chromatograms. Clinoptilolite samples modified with silver cations show an increased affinity for carbon monoxide CO and olefins (Fig. 7), the molecules of which are polar or contain π-bonds [1, 2].

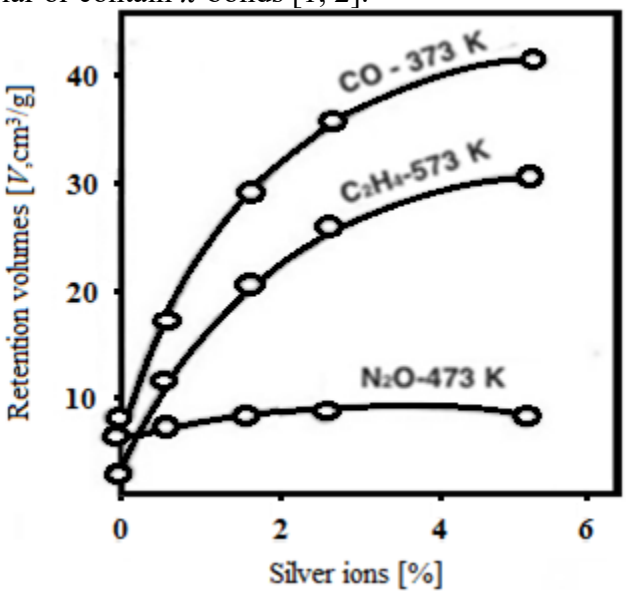

Figure 7. Dependence of retention volumes V on the content of silver (ratio SiO_2/AI_2O_3) = 9.8).

Chromatographic properties of clinoptilolite depend not only on the number of cations but also on the SiO_2/Al_2O_3 ratio in the zeolite. A mixture of C_2-C_4 alkanes and CO-CO_2 carbon oxides (which are not separated on samples with a modulus of 9.8) can be separated on high-silica Ag-clinoptilolites. The nature of the separation of the CO-CO_2 mixture depends on the amount of silver (Fig. 8). The point of intersection of the two curves shows that from a column filled with clinoptilolite containing about 3 % Ag^+, both oxides emerge as a common peak [2, 20].

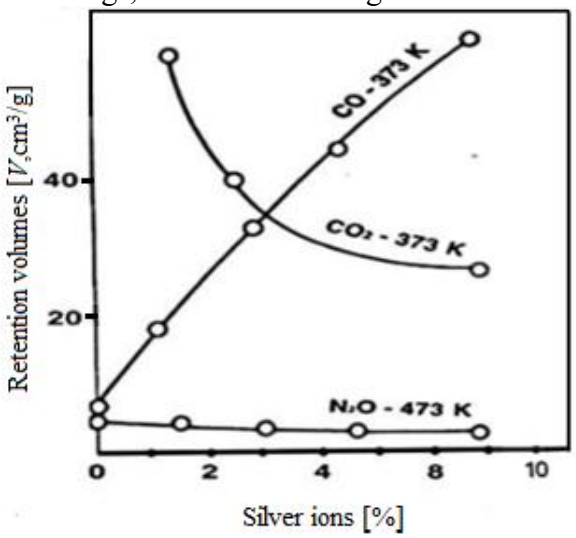

Figure 8. Effect of silver content in clinoptilolite on retention volumes (ratio (SiO_2/AI_2O_3) = 15.1).

CO is poorly retained on unmodified clinoptilolites and its chromatographic peak leaves the column together with air. However, on AgCl samples, the picture changes, since CO molecules are more strongly retained by sorbents not only due to dispersion interactions but also additional specific π-bonds [21] by silver cations. After preliminary processing of HCl and reaching the ratio SiO_2/Al_2O_3 = 15.1, silver-containing clinoptilolite allows the separation of gas mixtures containing components of different nature in a wide range of temperatures (573 K - 313 K) [2].

It should be noted that on columns filled with granules of such modifications, it was possible to separate such a CO-CO_2 mixture, but at 573 K these components are partially separated and CO is retained worse than CO_2. When the temperature of the chromatographic column changes in the elution sequence of the CO-CO_2 components, a temperature inversion is observed: in the range of 533 K - 493 K, the CO peak is the first to leave the column. As the temperature increases, the order of peak elution changes to the reverse (Fig. 9). The reason for the inversion lies in the strengthening of specific interactions of CO with silver cations in clinoptilolite at low adsorbent temperatures [21, 25].

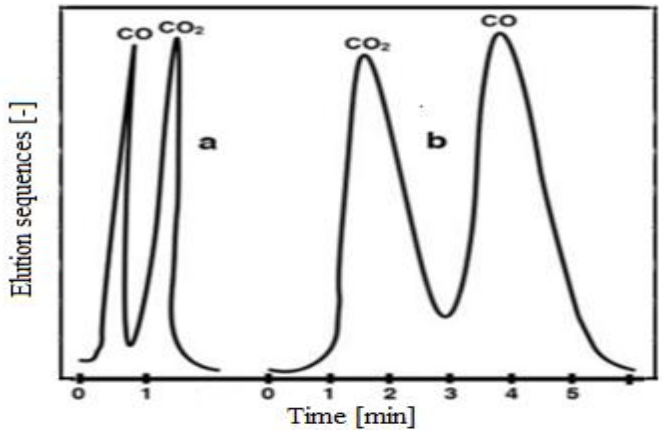

Figure 9. Inversion chromatograms: elution sequences of CO and CO_2 (on clinoptilolites with a ratio of SiO_2/AI_2O_3 = 15.1; 2.9% Ag. Column temperature: a) 533K, b) 473K).

On Ag-clinoptilolites in the range of 373 K - 273 K, a temperature inversion of the order of CO and CO_2 components exit from the chromatographic column is observed [1]. If the silver content in Ag-clinoptilolite is lower, CO oxide elutes first, and on samples with higher silver content, the reverse sequence of elution is observed components (inversion) (Fig. 10).

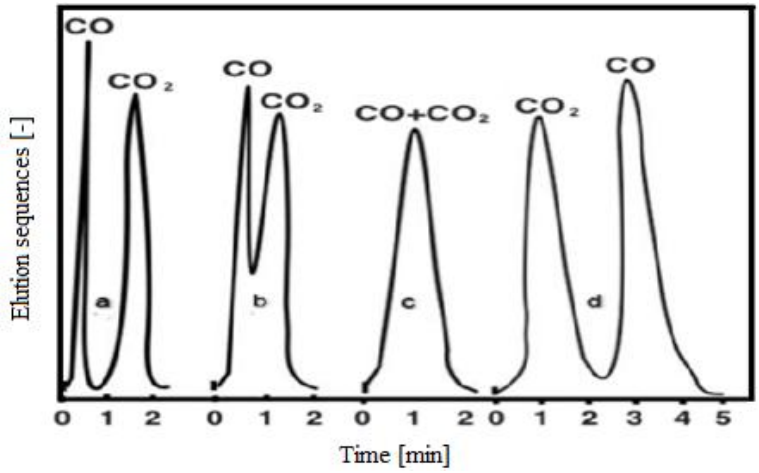

Figure 10. Chromatograms of inversion of the elution sequence of the components of the $CO+CO_2$ mixture under the influence of silver cations. The temperature of the columns is 373K. Ag^+ content (%): a) 0.96; b) 2.9, c) 4.8; d) 9.6.

Cases of inversion are of some interest because they open up new possibilities for the separation and analysis of this mixture of oxides. Copper is an analog of silver in terms of the electronic structure of atoms, therefore CuCl (Cuclinoptilolite) modifications are of interest for their chromatographic analysis to develop cheaper highly efficient sorbents. A series of such samples was prepared by ion exchange based on modifications of Sokyrnitsy clinoptilolite after preliminary acid treatment, in which the ratio SiO_2/Al_2O_3 = 14.4. Some results of the gas chromatographic study of Cucl are shown in the Table 2.

Table 2. Specific retained volumes of gases and vapors (cm^3/g) on Cucl

Component	Temperature [K]	Content of copper cations [%]				
		0.10	0.42	0.85	1.70	5.0
O_2	333	1.4	1.3	1.5	1.3	1.2
N_2	333	4.7	3.6	3.2	2.9	2.5
Kr	333	5.6	5.4	5.3	5.2	5.1
CO_2	573	-	9.6	9.9	10.0	11.5
C_2H_4	573	2.1	3.6	4.7	35.3	68.4
C_2H_6	373	-	30.0	28.0	26.3	25.9
C_3H_8	333	-	36.4	36.0	35.6	35.0
н-C_4H_{10}	573	-	18.6	18.2	18.0	16.3
C_6H_{14}	473	1.1	2.2	2.3	3.6	3.8
C_7H_{16}	473	1.6	6.6	6.8	7.2	8.2
C_8H_{18}	473	7.8	10.3	12.2	13.6	14.8
C_9H_{20}	493	60	12.0	13.0	13.4	14.5
$C_{10}H_{22}$	513	3.0	10.6	11.5	11.8	13.6
C_6H_6	573	1.3	2.0	2.1	2.6	2.7
C_7H_8	513	5.8	6.5	9.1	10.8	12.3

Data Table 2 illustrates the drop in retention volumes for gaseous alkanes and low-boiling gases as Cu^{2+} cations increase. This becomes clear if we take into account that divalent cations Cu^{2+} replace two monovalent cations Na^+ and K^+, which leads to a decrease in the total number of adsorption cationic centers, respectively, as on Agcl, and to a weakening of adsorption. Among clinoptilolite samples, zeolite derivatives with high modulus SiO_2/Al_2O_3 = 14.4, containing up to 5 % Cu cations, are the most important. It is shown that the chromatographic retention values for alkanes and low-boiling gases (except CO) decrease as the Cu^{2+} content increases due to a decrease in the total number of cationic adsorption centers after replacing two singly charged cations with copper.

For vapours of saturated and aromatic C6-C10 hydrocarbons, there is an increase in retained volumes under the same conditions, since their relatively large molecules are adsorbed mainly on the outer surface of the crystals. Due to steric hindrances, they cannot penetrate the middle of the cells, but they are noticeably polarised by cations, not only of the cavities but also of the surface [22, 23].

Similarly to silver-containing samples, a rapid drop in the retained volumes for N_2O oxide is observed on copper modifications of clinoptilolite as the exchangeable cations of the zeolite are replaced by copper (Fig. 11).

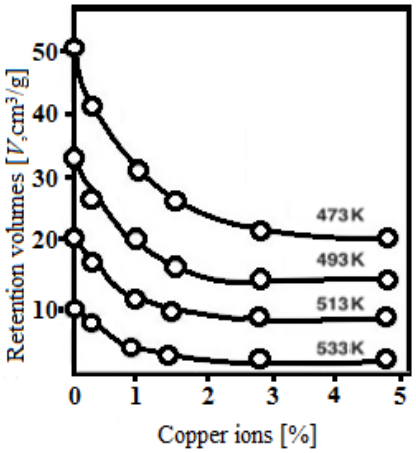

Figure 11. Retained volumes for N_2O at different copper contents.

The presence of copper leads to an increase in retention values for carbon oxides. However, for CO_2 this increase is smooth, and for CO a maximum is observed on the 0.85 Cucl sample at all temperatures (Fig. 12).

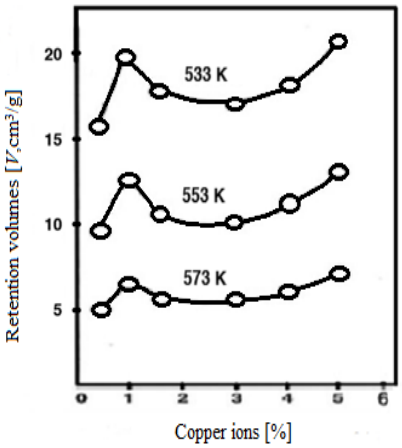

Figure 12. Effect of low substitutions for CO on 0.85Cucl.

This dependence is also observed for ethene on the same 0.85Cucl (Fig. 13)

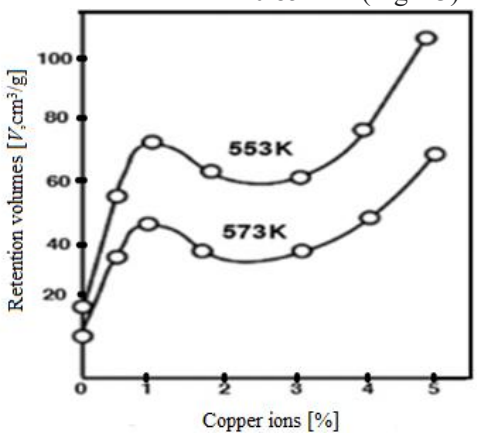

Figure 13. The effect of the content of Cu^{2+} cations on the retained volumes for C_2H_4.

Such a phenomenon was discovered on Y-type zeolites containing cations of alkali metals and copper and was called the "small substitution effect" [3, 21]. The latter is classified as a poorly studied phenomenon and is associated with the following features:

- the presence of narrow channel cavities in which a strong sorption field is created as a result of overlapping adsorption potentials of opposite walls;
- certain sizes of adsorbate molecules (critical diameter, length, spatial configuration, etc.);
- spatial placement of cations and their migration, which interact with adsorbate molecules with increased energy;
- the temperature of the system, capable of slightly changing the kinetic sizes of the adsorbate molecules, as well as the diameter of the input windows.

On AgCl, the effect of small substitutions was not observed either for CO or for olefins. Unlike other unsaturated hydrocarbons, it was possible to elute C_2H_4 from CuCl with any degree of substitution at high temperatures. However, higher olefins (C_3H_6, C_4H_8) from a 1-meter column could not be eluted even at 573 K, since the retention volume exceeds 30 min.

The effect of small substitutions is also evident on the 0.85 CuCl sample when measuring the width of the chromatographic zones, the heat of adsorption changes in Gibbs potentials, and the entropy of the transition of CO and C_2H_4 gas molecules to the adsorbed state. This effect is an important indicator in the development of clinoptilolite adsorbentsfor the absorption of the above-mentioned components from various gas mixtures, including from polluted air.

Based on the logarithmic dependence of *V* values on the inverse temperature (1/T), the absolute retained volumes and relative retention for carbon monoxide compared to nitrogen, the main component of air on Ag- and Cu-clinoptilolites, were calculated (Table 3).

All the given facts clearly illustrate the effect of small substitutions, reflecting a complex process of interaction, the result of which depends both on the geometric structure of gas molecules and the nature of interatomic bonds in them, and on the nature of cations and the specificity of their location in different energy positions in the elementary cells of zeolite.

Table 3. Retention volumes CO and N_2 on Agcl and Cucl at 293K

Agcl samples (SiO_2/Al_2O_3 = 15,1)			**Cucl samples (SiO_2/Al_2O_3 = 14.4)**		
Contents Ag^+, %	**N_2**	**CO: N_2**	**Contents, Cu^{2+}, %**	**N_2**	**CO: N_2**
	±0.2	± 10 %		±0.2	± 10 %
0	5.4	13.7	0	5.4	13.7
0.96	10.5	$1.9\cdot10^3$	0.42	9.6	$6.6\cdot10^4$
2.90	12.3	$8.1\cdot10^3$	0.85	12.3	$2.6\cdot10^5$
4.80	14.5	$1.1\cdot10^4$	1.70	13.2	$7.6\cdot10^5$
9.60	15.5	$6.5\cdot10^4$	5.00	14.8	$2.7\cdot10^6$

As can be seen from the third and last column of the table (Table 3), carbon monoxide (CO) is retained on natural clinoptilolite 13.7 times longer than nitrogen (N_2). After the introduction of 0.96 % Ag^+ and 0.42 % Cu^{2+} into the zeolite, this selectivity index increases to $1.9\cdot10^3$ and $6.6\cdot10^4$, respectively. If the content of these cations is increased by 10-12 times, then samples of 9.6 % Ag and 5.0 % Cu^{2+} zeolite are capable of filtering out 66,000 and 2.7 million nitrogen molecules before the passage of one CO molecule.

These highly selective modifications of clinoptilolite have been investigated as fillers of concentrating traps, which allow the extraction of minimal amounts of CO, as well as C_2H_4 at room temperature for their subsequent chromatographic analysis.

For analytical purposes, it is convenient to use copper zeolites with lower degrees of substitution (5 % - 8 %), because with an increase in temperature to 573 K, these modifications can desorb absorbed CO, as can be seen from the Table 2, and at low temperatures without additional cooling, they reliably remove small amounts of it from the air. Therefore, they can be used to control the CO content in the air, as well as in the atmosphere of closed rooms and printing facilities.

Change in thermodynamic functions of adsorbed gases and vapors.

1. Change in adsorbate enthalpy

Based on the chromatographic data, the heats of adsorption (with an accuracy of ± 0.5 kJ) of the monitored gases and vapors (Table 4) were calculated depending on the degree of dealumination of clinoptilolite.

Table 4. Heats of adsorption (kJ/mol) on acid-modified clinoptilolites

Component	**Temperature interval [K]**	**Silicate module (SiO_2/Al_2O_3)**							
		9.8	**10.1**	**10.5**	**11.0**	**11.7**	**12.5**	**13.6**	**15.1**
C_2H_6	473-553	30.4	32.5	33.1	34.1	36.2	39.1	40.2	39.0
C_6H_{14}	473-553	41.1	45.4	47.9	50.6	534	56.6	57.0	55.1
C_7H_{16}	473-553	54.1	55.5	56.4	56.5	56.6	57.0	56.5	53.0
C_2H_4	473-553	66.3	65.9	64.0	62.6	58.4	51.5	30.6	27.4
C_3H_6	493-573	82.5	79.1	77.6	76.1	71.1	57.0	38.1	32.9
C_6H_6	493-573	34.0	35.9	37.1	37.5	38.0	39.6	39.5	376.
CO	513-533	44.5	44.0	44.0	43.6	43.5	42.0	38.0	30.0
N_2O	473-553	57.3	56.6	56.0	52.0	50.0	48.1	43.4	38.2

The heat of adsorption represents important information about the energy of interaction in the adsorbent-adsorbate system [24]. On deionised zeolites, the adsorption of polar molecules is less than on the original ones following the decrease in the electrostatic field strength in their cavities. Therefore, for CO and N_2O gases, the molecules of which have dipole moments and can penetrate deeply into the cavities of the crystal lattices of clinoptilolites, the enthalpy value decreases significantly with an increase in the silicate modulus.

This confirms the opinion that interactions between CO dipoles and exchangeable cations make a significant contribution to the energy of the adsorbent-adsorbate interaction. In the course of dealumination and growth of the SiO_2/Al_2O_3 ratio, this effect decreases against the background of dispersion interactions (Table 4).

The values of gas chromatographic retention of various components of model gas mixtures make it possible to calculate changes in the enthalpy of adsorbed gases and vapours on silver-containing modifications of clinoptilolite. Not only the nature and electronic structure of the adsorbate molecules, the content of silver cations in the cavities of clinoptilolite, but also the ratio of SiO_2/Al_2O_3 in it, which manifests itself due to certain sizes of the entrance windows and the cavities inside the crystals, have the main influence on the value of heats of adsorption of zeolite after dealumination and dedication.

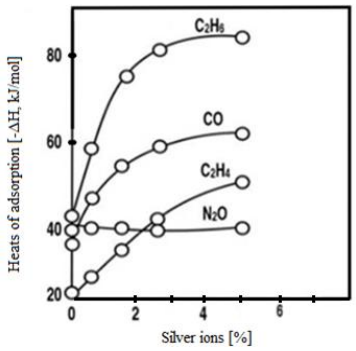

Figure 14.The effect of silver content in clinoptilolite on the heats of adsorption (-ΔH) with the ratio $SiO_2/Al_2O_3 = 9.8$

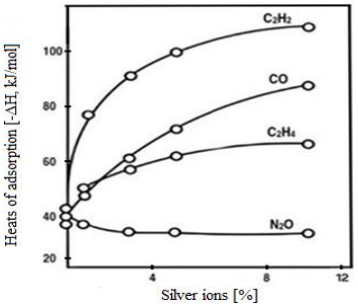

Figure 15. Dependence of heats of adsorption (-ΔH) on the amount of silver in clinoptilolite with the ratio $SiO_2/AI_2O_3 = 15.1$.

For all studied components, except for N_2O, the heat of adsorption increases with an increase in the silver content in the zeolite (Figs. 14, 15), since then the dispersion interaction is further strengthened by polarisation under the action of cations. The latter is also induced by temporary dipoles in alkane molecules if they can diffuse into the channels of clinoptilolite. Therefore, an increase in heat of adsorption is observed for C_2H_6 (Fig. 14).

The heat of adsorption of C_4H_{10} alkane vapours also increases as the clinoptilolite is enriched with silver (Table 5). With the increase in the content of exchangeable silver cations in the zeolite, an increase in heat in the homologous series of alkanes and benzene is followed. For columns filled with AgCl granules with a higher silica modulus $SiO_2/Al_2O_3 = 9.8$, the heat of adsorption for all the studied substances exceeds the values (-ΔH) obtained on the original clinoptilolite. This fact is explained by the ability of adsorbate molecules to penetrate inaccessible cavities of clinoptilolite after its acid treatment and decationisation.

Table 5. The heat of adsorption (-ΔH, Kj/mol) of hydrocarbons on clinoptilolite modified with Ag^+ cations, %.

Component	Temperature [K]	Silicate modulus and silver content [%]							
		SiO_2/Al_2O_3= 9.8				SiO_2/Al_2O_3 =15.1			
		0	1.60	2.60	5.20	0.96	2.90	4.80	9.60
C_6H_{14}	413-553	32.0	37.2	39.3	40.9	40.5	57.3	58.7	65.0
C_7H_{16}	433-573	35.6	40.5	43.6	46.7	47.5	50.1	51.0	56.9
C_8H_{18}	453-573	37.6	48.9	52.6	56.0	55.8	58.7	59.7	69.0
$C_{10}H_{22}$	453-573	47.0	50.3	57.6	68.5	59.5	62.8	70.0	77.3
C_6H_6	433-573	19.5	31.3	38.5	50.0	68.0	75.0	80.5	85.1

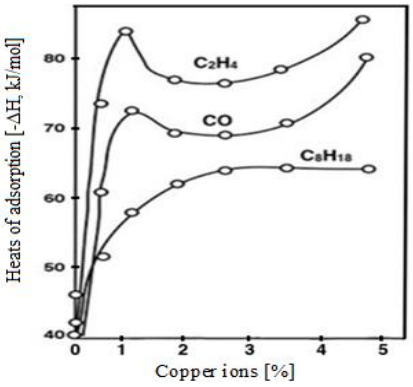

Figure 16. Dependence of heats of adsorption (-ΔH) on the amount of copper in clinoptilolite with the ratio SiO_2/Al_2O_3 = 15.1

Therefore, based on the heat of adsorption, it is possible to give preference to silver-containing modifications of clinoptilolite, obtained after pre-treatment with acid and increasing the silicate module. They can serve as effective absorbers for removing carbon and nitrogen oxides, hydrocarbon vapours, and other substances from polluted air.

On the copper 0.85 CuCl modifications of clinoptilolite, the effect of small substitutions is also evident when determining the heat of adsorption (Fig. 16).

Change of Gibbs potentials

For adsorbed components on zeolites, changes in the Gibbs potential were determined as the temperature increased for every 20 K. As Table 6 illustrates, the Gibbs potentials increase for all adsorbates after the transition to the adsorbed state as the silver content in clinoptilolite increases.

Table 6 . The effect of silver content in clinoptilolite on the change in Gibbs potentials [kJ/mol]

Component	Temperature [K]	Content of silver cations [%]				
		0	0,52	1,60	2,60	5,20
C_6H_{14}	373	8.2	7.8	8.9	10.2	12.4
C_7H_{16}	473	2.6	5.7	6.8	7.7	8.8
C_8H_{18}	473	5.4	6.3	7.5	7.8	8.9
C_9H_{20}	473	7.1	9.0	10.1	11.0	12.2
$C_{10}H_{22}$	573	2.6	2.7	3.5	4.3	5.5
C_7H_8	533	2.8	10.6	13.9	17.7	19.8

Especially the growth of Gibbs potentials is visible for those gases whose molecules have a dipole moment or π-bond (Fig. 17 and Fig. 18) at different values of the ratio.

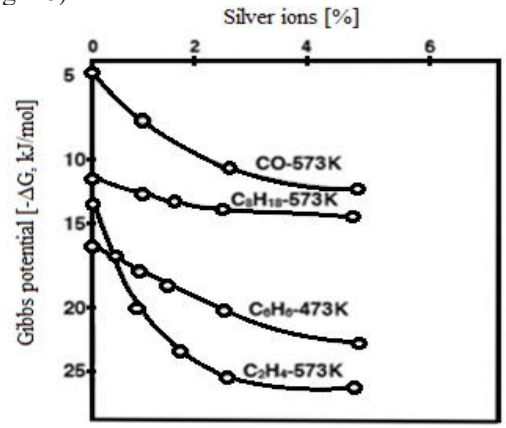

Figure 17. Change in Gibbs potentials for gases depending on the content of silver in clinoptilolite at 573K (SiO_2/Al_2O_3) = 9.8).

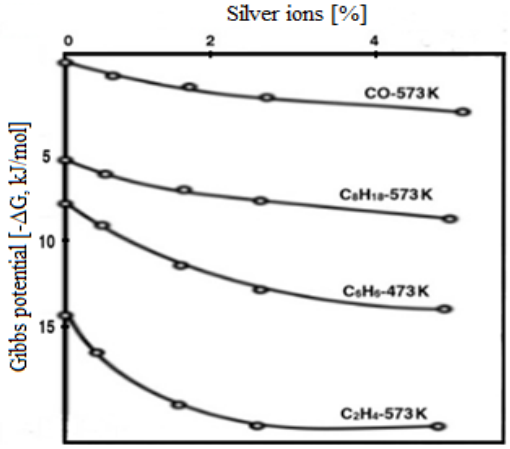

Figure 18. Change in Gibbs potentials (-ΔG, Kj/mol) depending on the silver content in clinoptilolite at SiO_2/AI_2O_3 = 15.1.

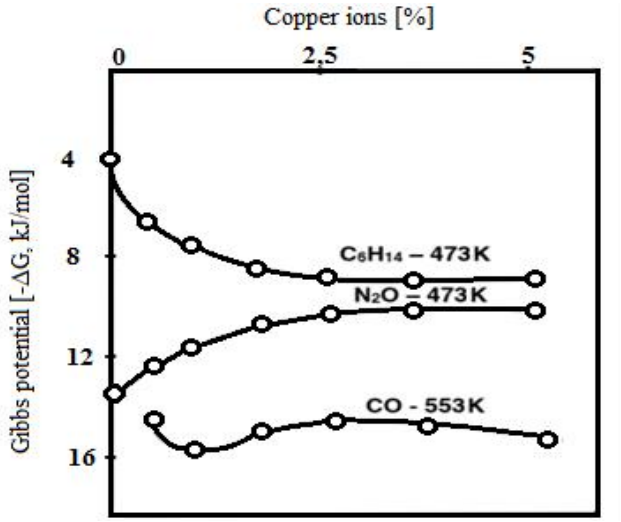

Figure 19. Influence of Cu^{2+} cation content in clinoptilolite on Gibbs potentials (-ΔG).

The calculated changes in Gibbs potentials after the transition of gas and vapour molecules to the adsorbed state are in full correlation with the chromatographic retention values and reach a maximum at the corresponding SiO_2/Al_2O_3 ratios.

Changes in the Gibbs potentials of low-boiling, oxide, and hydrocarbon gases C_1-C_2 on copper modifications of clinoptilolite (Fig. 19) indicate a decrease in the mobility of their molecules as the zeolite is enriched with cations of its elementary lattices and, accordingly, their interactions with the adsorbate increase. The considered regularities served as a theoretical basis for the use of dealuminated zeolites for extraction, concentration, and analysis of the mentioned gases and vapours.

Copper modifications of clinoptilolite (at 0.85 Cu^{2+}) show the effect of small substitutions on the Gibbs potentials for CO and C_2-C_4 olefins. The obtained chromatographic regularities are interpreted with the help of calculated thermodynamic functions, adsorbed gases, and vapours (changes in Gibbs potentials, enthalpy of adsorption).

4 Conclusions

1. According to the results of the chemical analysis of modifications of clinoptilolite obtained after long-term treatment of granules at 293 K with solutions of HCI of various concentrations (from 0.1 to 6, mol/l), the ratio SiO_2/Al_2O_3 (silicate module) was calculated, which increases as the concentration of the acid and its time increase impact.
2. Chromatographic separation of the difficult-to-analyse CO-CO_2 mixture from one sample was performed on silver-containing samples of clinoptilolite. At the same time, two types of inversion were found - changes in the sequence of elution of components from the column under the influence of temperature and due to the different content of silver cations in the zeolite. This allows you to control the sequence of appearance of components during the quantitative analysis of impurities of one gas in another.

3. On copper modifications of clinoptilolite containing 0.85 % of Cu^{2+} cations, the effect of low substitutions was revealed, which is manifested by a sharp increase in retained volumes for CO and C_2H_4, heats of adsorption, changes in Gibbs potentials.
4. Developed and tested modifications of clinoptilolite containing 4.8 % of Argentum cations and 5.8 % of copper cations, which show high selectivity of chromatographic retention of carbon dioxide(II). It was established that at a temperature of 293 K, they can pass 11 thousand and 2.7 million nitrogen molecules, respectively, before the passage of one carbon monoxide (CO) molecule. These modifications of clinoptilolite are recommended as adsorption filters for extraction from air, concentration, and gas chromatographic analysis of micro impurities of carbon oxide(II).
5. The effect of the degree of dealumination of natural clinoptilolite on the nature of the change in the chromatographic and thermodynamic parameters of the separation of model mixtures containing low-boiling and oxide gases, alkanes and olefins, and vapours of saturated and aromatic hydrocarbons is shown. The optimal values of the silicate module were found in the range of 9.8 to 15.1, which ensures the maximum chromatographic retention of the components. It was established that as the structure of the adsorbate molecules becomes more complicated, the maximum of its retention shifts towards large values of the silicate modulus.

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