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CHROMATOGRAPHIC SEPARATION OF LOW-BOILING INORGANIC AND HYDROCARBON GAS MIXTURES ON ZEOLITES

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SUMMARY

The possibility of using different types of zeolites of both synthetic and natural origin for the chrornatographic separation of low-boiling inorganic and C_1-C_4 hydrocarbon gas mixtures is shown. A large effect of the zeolite structure and its cation modification on the character of the separation of individual model mixtures was found, in particular, on the elution sequence of separate components of the mixtures. It was established that the use of surface layer sorbents (zeolites coated on the solid support) allows a better separation of hydrocarbon gas mixtures and at lower column temperatures than on ordinary volumetric zeolite chromatographic columns.

INTRODUCTION

Zeolites of synthetic and natural origin are used as adsorbents in gas-adsorption chromatography in addition to activated carbons, fine porous carbons of the sarane type, graphitized black carbons, silica gels, aluminas, Aerosils, porous glasses and porous polymers[1-5].

Zeolites were first used as adsorbents in gas chromatographic columns about 20 years ago[6,7]. Janak[6] utilized sodium zeolite (Alusil) and a series of its cation-substituted forms as an adsorbent for the separation of C_1-C_7 hydrocarbon mixtures. He showed that the introduction of silver cations into the zeolite structure changed the elution sequence considerably, giving a high selectivity for olefins. Our work[7] was devoted to the possibility of using a natural zeolite (natrolite from the Khibin deposits, U.S.S.R.) for the separation of C_3-C_7 hydrocarbon mixtures.

In gas chromatography, zeolites can be used as molecular sieves and sorbents. The molecular sieve properties of the zeolites are used in combination with gas liquid chromatography when there is a risk of overlapping of the separate chromatographic zones and poor separations. A system of two successive columns is used, one filled with zeolite and the other with stationary phase. In the zeolite column, depending on the type, normal hydrocarbons are strongly adsorbed and in some instances other compounds also, and the remaining fraction of the mixture passes into the second column, operating by gas-liquid chromatography[8-11]. Such a method is used for the separation of complex petroleum mixtures[9-12]. However, most of the papers on the use of zeolites in gas chromatography have involved cases where the molecules of the

compounds in the mixtures can easily penetrate into the zeolite cavities. These papers can be divided into the following eight subgroups[5], depending on the composition of the mixtures to be separated: (1) hydrogen isotope mixtures; (2) inert gas mixtures; (3) binary mixtures of oxygen and nitrogen; (4) mixtures of oxygen and argon; (5) mixtures of hydrogen, oxygen, nitrogen, methane and carbon monoxide; (6) the above mixtures, but also containing carbon dioxide or other compounds strongly sorbed on zeolites; (7) hydrocarbon gas mixtures and (8) widely boiling liquid hydrocarbon mixture.

In later papers it was shown that the separation of many mixtures can be performed more rapidly by using surface-layer adsorbents than by the method of volumetric filling of gas chromatographic columns'[3–15]. Bombaugh[16] used a column of powdered zeolite (about 20%) coated on a coarse porous solid support.

Our aim was to study the possibility of using different types of zeolites of both synthetic and natural origin for the chromatographic separation of mixtures of low-boiling inorganic and hydrocarbons gases, and the effects of the nature of the cation, in the zeolites, temperature of adsorbent activation, column temperature and some other parameters on the character of the separation of model systems.

EXPERIMENTAL

Zeolites

We studied synthetic zeolites of the X, Y and L types, erionite and mordenite, synthesized at the Gorky Pilot Plant, and natural zeolites, mordenite and clinoptilolite, containing tuffs of Ratevani and Khekordzula deposits, respectively (Georgian S.S.R.).

Cation-exchange modification of the zeolites was achieved by treatment of the original sodium form of the zeolite with aqueous solutions of salts of $Li^+, K^+, Rb^+,$ $Cs^+, Ag^+, Mg^{2+}, Ca^{2+}, Sr^+, Ba^{2+}$ and Cd^{2+}. The degree of replacement of the original cations was controlled by the number of treatments. Conservation of the zeolite structure in all the synthesized specimens was monitored by Debyegrams. Photographs were taken in RKD chambers on the URS-55" installation with the use of unfiltered copper radiation. The Debyegrams showed that all the specimens studied had a zeolite crystalline lattice.

The synthetic zeolite powder was pressed into tablets without adding any binder, then the tablets were crushed and the fraction of 15–30 mesh (0.5–1 mm) was used. With natural zeolites, the exchange was conducted on crushed granules of definite size. All specimens were activated by heating at 450°C for 4–5 h. The zeolites were loaded into chromatographic columns. where they were activated again. Both "strong" activation (heating at 500°C for several hours) and "weak" activation (heating at 300°C for several hours) were used.

In certain instances surface-layer sorbents were used for filling the chromatographic columns. The zeolite powder was mechanically mixed with Chromaton N-AW-5, grain size 0.43–0.6 mm as the solid support[16], which can retain about 17% of zeolite on its surface.

Chromatography

Studies were carried out on Tsvet-3 and LHM-8MD chromatographs, column

TABLE I

SELECTIVITY CRITERIA (K_s) OF $O_2 N_2$ BINARY MIXTURE ON DIFFERENT TYPES OF ZEOLITES IN THE SODIUM FORM

Column temperature, 20°C. Thermal activation regime, 450°C.

NaX	NaY	NaL	NaE	NaM
0.50	0.42	0.30	0.24	0.57

length 100 cm, I.D. 0.3 cm. Helium was used as the carrier gas at a flow-rate of 50 ml/min. The column was operated at 20–260°C and a thermal conductivity detector was used.

The selectivity criterion K_s (ref. 17), the quantitative characteristic of the efficiency of separation of binary mixtures, was determined by using the equation $K_s = (V_{g_2} - V_{g_1}/V_{g_2} + V_{g_1})$, where V_g are the retention characteristics and 1 and 2 are the components being separated. The uniformity of separation of multi-component mixtures was determined by means of the uniformity criterion[17], $\bar{A} \equiv n_K \tau K/t$, where n_K is the number of peaks, τ is the width of the least diffused peak, K is the degree of separation of the worst separated component pair and t is the duration of analysis.

RESULTS AND DISCUSSION

Zeolites are especially effective for the chromatographic separation of oxygen-nitrogen mixtures with the indicated elution sequence at room and elevated temperatures. The character of this separation, however, is greatly dependent on the type of zeolite and the nature of the metal cation. Compared with industrial synthetic zeolites in the same cation form (sodium), the separation is most effective on the sodium form of mordenite (Table I).

A decrease in the cation density in the unit cell of the zeolite leads to poorer separations, whereas the best separation is given by mordenite, which has the lowest cation population. Obviously, in this instance the peculiarities of the mordenite structure affect the character of the separation of oxygen-nitrogen mixtures.

The nature of the cation in the zeolite affects the separation of mixtures. With most heavier cations the separation of oxygen-nitrogen mixtures worsens. However, the silver forms of zeolites differ as the silver cations have filled and free sp orbitals and interact with molecules of compounds that have quadrupole moments, such as nitrogen. Table II shows the coefficients of selectivity for oxygen-nitrogen on various cation forms of type Y zeolites. It can be seen that the introduction of silver cations

TABLE II

SELECTIVITY CRITERIA (K_s) OF O_2–N_2 BINARY MIXTURE ON CATION FORMS OF ZEOLITES OF TYPE Y

Column temperature, 20°C. Thermal activation regime, 450°C.

LiY	NaY	KY	RbY	CSY	AgY
0.33	0.42	0.32	0.27	0.23	0.89

TABLE III

SELECTIVITY COEFFICIENT (K_s) OF O_2–N_2 BINARY MIXTURE

Column temperature, 20°C.

Mordcnite containing tuff (Ratevani deposits)				Clinoptiolite containing tuff (Khekordzula deposits)		Synthetic mordenite		
Natural specimen, calcium form	Alkali and alkaline-earth metal cation-enriched specimens			Natural specimen, calcium potassium form	Treated with 0.1 N HCl	Original sodium-form specimen	Calcium form	Strontium form
	NaM	CaM	SrM			NaM	CaM	SrM
0.84	0.76	0.86	0.90	0.43	0.59	0.57	0.81	0.84

into the zeolite structure doubles the coefficient of selectivity. Oxygen-nitrogen mixtures are also separated well by the natural zeolites clinoptilolite and mordenite containing tuffs, which in some instances are more advantageous than the synthetic mordenite in the sodium form (Table III).

The good separating ability of natural mordenite is obviously connected both with its structure and with the presence of calcium cations, as the sodium form gives a poorer separation. Natural clinophilolite, despite the large number of calcium cations present, does not give good separations of oxygennitrogen mixtures; acidic modification improves the efficiency but it is still considerably lower than that with mordenite. This demonstrates again the effect of the specific structure of mordenite on this separation.

For application to oxygen-nitrogen mixtures the high siliceous silver-substituted forms of zeolites, such as erionite, mordenite, zeolites of type L and, to a lesser extent, zeolites of type Y possess very interesting properties. At room temperature even higher (100°C) they separate oxygen-nitrogen mixtures in that elution sequence. However, if the silver form of zeolites is impregnated with the vapours of saturated hydrocarbons (pentane, hexane, etc.), unsaturated hydrocarbons, starting from propene, and also with benzene, at 200–300°C they can separate the mixture with the reverse elution sequence, which ism not characteristic of ordinary zeolites.

The nature of the zeolite cation strongly affects the separation of methane–carbon monoxide mixtures, that results in the inverse elution sequence of individual components of the mixture in the process of their separation at the heating temperature of the column, being 20°C. Janak et al. showed[18], however, that the effect of the nature of the cation in a zeolite on the character of chromatographic separations is greatly emphasized when the specimens are dehydrated. On zeolites of type X containing sodium and lithium cations, first methane and then carbon monoxide are eluted. On specimens in which sodium ions are replaced by rubidium or caesium cations, and on zeolites with a high potassium content, the order of elution of these components changes. Silver-containing zeolites show the greatest selectivity towards carbon monoxide, the selectivity decreasing in the order Ag > Li > Na > K > Rb > Cs. The same effect occurs with these cations in zeolites of type Y and L. However, in erionite univalent cations do not cause a reversed elution sequence and in all

TABLE IV

UNIFORMITY CRITERION ($\bar{\Delta}$) FOR Ar–Kr–Xe–O_2–N_2–CH_4

Column temperature, 40°C.

NaX	NaY	CaX	CaY	SrX	SrY	BaX	BaY
0.016	0.025	0.020	0.023	0.024	0.039	0.032	0.055

instances carbon monoxide is eluted before methane. Obviously, this is associated with the small cation density of this zeolite and steric hindrance of the cations.

On the bivalent cation zeolites there is no inverse sequence of component elution and the carbon monoxide is eluted after methane, as electrostatic interactions with these cations are stronger, except for the barium for of erionite. Probably this is connected with the specific structure of erionite. Selectivity towards carbon monoxide for all zeolites (excluding the barium form of erionite) containing bivalent cations and subjected to "strong" thermal activation decreases in the order Cd > Ca > Sr > Mg > Ba > Na.

It was established that with a decrease in the cation density in the zeolite, the symmetry of the peaks of the separated substances on the chromatograms increases, as the effect of the nature of the cation is weaker, This is apparent from Table IV, where the uniformity criteria for multi-component mixtures of low-boiling gases (Ar–Kr–Xe–O_2–N_2–CH_4) separated on zeolites of types X and Y containing Ca^{2+}, Sr^{2+} and Ba^{2+} cations are given. Thus, for zeolites of type Y modified by cations of the heavy metals strontium and barium, the above mixture is separated better.

The nature of the cation in the zeolite has an important effect on the chromatographic separation of mixtures of hydrocarbon gases, especially the inverse elution of the pairs ethylene-propane and butane-propylene. On zeolites of types X and Y with a high content of calcium, lithium and strontium cations at all column temperatures ethylene is eluted after propane and propylene after butane. On potassium-, rhubidium-, caesium- and barium-containing zeolites at any column temperature, each saturated hydrocarbon is eluted before the corresponding unsaturated compound with the same number of carbon atoms. On NaX and NaY zeolites at lower column temperatures (140–160°C) first propane and then ethylene are eluted. At higher temperatures this elution sequence changes, which can be explained by a stronger dependence on temperature of specific interaction of ethylene with cation surface of the zeolite, since such type of intermolecular forces is directed at greater extent.

A decrease in the cation density in the unit cell of the zeolite causes a decrease

TABLE V

SEQUENCE OF ELUTION OF C_3H_8–C_2H_4 AND C_4H_{10} C_3H_6 AND TEMPERATURES CORRESPONDING TO THE START OF INVERSE ELUTION ON NaX, NaY, NaL AND NaE ZEOLITES

NaX	NaY	NaL	NaE
C_3H_8–C_2H_4, 160°C	C_3H_8–C_2H_4, 180°C	C_3H_8–C_2H_4, 80°C	C_2H_4–C_3H_8
C_4C_{10}–C_3H_6, 240°C	C_4H_{10}–C_3H_6, 220°C	C_4H_{10}–C_3H_6, 120°C	C_3H_6–C_4H_{10}

TABLE VI

COMPARISON OF UNIFORMITY CRITERIA ($\bar{A}$) WITH THE USE OF SURFACE-LAYER (SLS) AND VOLUMETRIC SORBENTS (VS)

Adsorbent: zeolite of type X modified by alkaline-earth metal cations.

Model mixture (with elution sequence as shown)	Column temperature ($^\circ C$)	Zeolite	$\bar{A}$
C_2H_6–C_2H_4–C_3H_8–C_3H_6–C_4H_{10}	2 0 0	MgX (VS)	0.087
	100	MgX (SLS)	0.093
C_2H_6–C_3H_8–C_2H_4–C_4H_{10}–C_3H_6	200	CaX (VS)	0.039
	100	CaX (SLS)	0.042
C_2H_6–C_3H_8–C_2H_4–C_4H_{10}–C_3H_6	200	Sr (VS)	0.027
	100	Sr (SLS)	0.0364
C_2H_6–C_2H_4–C_3H_8–C_3H_6–C_4H_{10}	2 0 0	BaX (VS)	0.0309
	100	BaX (SLS)	0.0544

in the temperature of the start of the inverse elution sequence of propane-thylene and butane-propylene. For erionite, owing to the negligible concentration of sodium cations in the unit cell there is no inverse elution sequence, as the electrostatic interaction of ethylene and propylene with cations is weakened and they are eluted at all column temperatures before propane and butane, respectively (Table V). The sodium cation-enriched erionite is thus closer to silica gel in performance.

Chromatographic separations on surface-layer sorbents, i.e., with zeolite coated on the solid support (Chromaton N-AW), of a model mixture of C_2–C_4 hydrocarbons were better than those obtained using volumetric sorbents (Table VI).

It follows from the results that separations of hydrocarbon gas mixtures are better and occur at lower column temperatures on surface-layer sorbents than on volumetric zeolites.

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