

Chromatographic properties of zeolites modified for analysis of atmospheric pollutants

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Abstract - Chromatographic properties of different types of synthetic zeolites and samples of natural mordenite, modified by ion-exchange have been studied. The influence of degree of replacement and character of cations of alkali and alkaline-earth metals and also of silver and copper on chromatographic retainment of constant components of air and its most spread pollutants have been shown. Recommendations are made of optimal sorbents and conditions for extraction, concentration, desorption and quantitative chromatographic analysis of oxides of carbon, nitrogen and sulfur and also hydrocarbon gases C₁-C₄.

INTRODUCTION

The present level of industrial development is associated with the disposal of many different types of waste. A serious threat to the environment is posed also by the atmospheric pollution by motor exhaust gases and the outlet from thermal power stations. The first step in the solution of the problems of environmental pollution is the development of analytical methods for the determination of microconcentrations of pollutants. The next step should be the development of effective ways of removing undesirable components from exhaust gases. In this connection adsorbents, especially zeolites, are of great importance for the extraction of components such as the oxides of carbon, nitrogen and sulfur.

The development of physico-chemical methods for the analysis of atmospheric pollutants will also involve the application of zeolites. The aim of the work described here was to develop modified forms of cationic zeolites and to ascertain the optimum conditions for the chromatographic analysis of gaseous pollutants.

METHODS OF INVESTIGATION AND APPARATUS

Powdered synthetic zeolites, produced in USSR, were washed in water and cleaned to pH 8,4 - 8,6. The powder was subjected to ion-exchange with replacement partly (or wholly) of initial ions by cations of respective salts. From the results of chemical analysis was calculated the degree of replacement. The samples were compressed into tablets, heated, pounded and later separated into fractions (0,5-1 and 0,25-5 mm) of granules which were used to fill chromatographic columns (ref. 1) of chromatographs models "Tsvet-4" and "Tsvet-162".

Samples of natural Carpathian zeolites (a solid mineral; ref.2) were directly subjected to compression to the above mentioned sizes, and later to additional acidic treatment by keeping them in solutions of HCl of different concentrations. After cleaning granules from excess acid, they were dried and subjected to additional modification (ref. 3) by treating them with salts (silver nitrate, copper sulfate and others) and later to chromatographic analysis. Granules of zeolites in columns were subjected to further thermal activation (573 K, 3 hours) in a stream of gas-carrier (helium or nitrogen) with a flow rate of 50 cm³/min. Later, the retention times of components of model mixtures containing low-boiling hydrocarbon and oxide gases at temperatures of 273-573 K were taken at intervals of 20 K. From the data obtained were calculated absolute specific retention volumes and their logarithms.

On the basis of logarithmic dependence of experimental values of absolute specific retention volumes V_g on reciprocals of absolute temperatures of chromatographic columns straight lines were obtained. Extrapolations helped to calculate the values of V_g at room temperatures (293 K) for cases of very strong retention of components in zeolites. The ratio of obtained absolute specific retention volumes of the gas and nitrogen (the main component of air) gave a quantitative idea of selectivity of retention of the gas by zeolites.

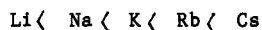
RESULTS AND DISCUSSION

Samples were prepared from the original forms of zeolites NaY, NaX, NaA, KL and natural mordenite by ion exchange. These samples had lower, average and high degree of replacement of initial ions by cations of alkali-(Li, Na, K, Rb, Cs), alkaline-earth (Mg, Ca, Sr, Ba)

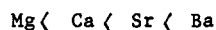
metals and also cations of silver and copper. Introduction of lithium cations into crystal lattices of zeolites lowers specific retention volumes V_g for all chromatographic components, increasing the degree of replacement by lithium cations. This is because the smallest lithium cations are capable of occupying the most screened positions in crystal lattices and weakly interact with molecules of the adsorbate. Apart from this, lithium cations are capable of significant hydration, and most probably be partially surrounded by water molecules. Zeolites, containing lithium, of the Y-type have high affinity to keep widespread pollutants of air like sulfur dioxide, which pollutes air mostly through exhaust gases of thermal power stations.

In Fig.1 is shown the absolute specific retention volumes V_g for oxides of sulfur(IV) which decrease with increase in temperatures of chromatographic columns as in contents of lithium cations in crystal lattice Y-type zeolites. Therefore lithium-rich zeolites are proposed as column fillings for chromatographic determination of SO_2 in polluted air.

After introducing other heavier alkali metals into crystal lattice of zeolites, it was noted that affinity of the zeolite to sulfur dioxide increases with increasing atomic mass of these cations. This increase intensifies by increasing polarizability parts in interaction energy of dipole molecules of SO_2 with cations in the following order



In an analogous manner is observed increase of absolute specific retention volumes V_g of SO_2 in Y-type zeolites containing maximum amount of ion-exchange cations of alkaline-earth metals.



Consequently, zeolites of the Y-type containing cations of alkali and alkaline-earth metals display high affinity to adsorption of SO_2 and can serve as good adsorbing filters to remove SO_2 .

Synthetic and natural zeolites are capable of adsorbing and keeping also oxides of nitrogen - useful for cleaning industrial outlets in nitric acid production (ref. 5).

But the nature of cations and degree of ion-exchange have great influence on retaining different oxides of nitrogen. In lithium containing Y-type zeolite, by increasing content of Li^+ cations absolute specific retention volume falls not only for oxides of nitrogen (NO and N_2O) but also for hydrocarbon gases (Fig.2). At the temperatures of chromatographic columns the hydrocarbon ethane is poorly retained than both oxides of nitrogen owing to the absence of dipole moment in molecules of ethane. But under the same conditions NO is the last to elute from the chromatographic column because of its dipole moment.

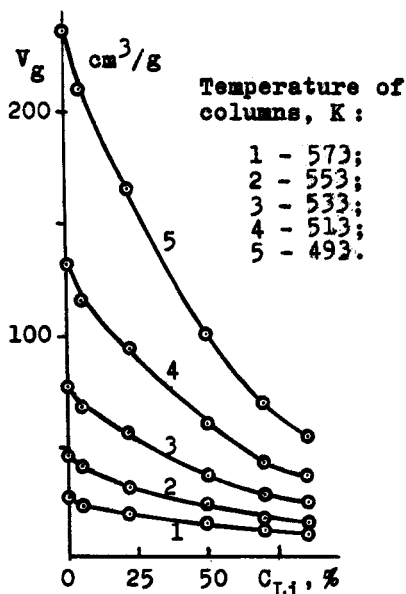


Fig.1. The influence of degree of the substitution of sodium cations by lithium on the absolute specific retention volumes V_g for SO_2 .

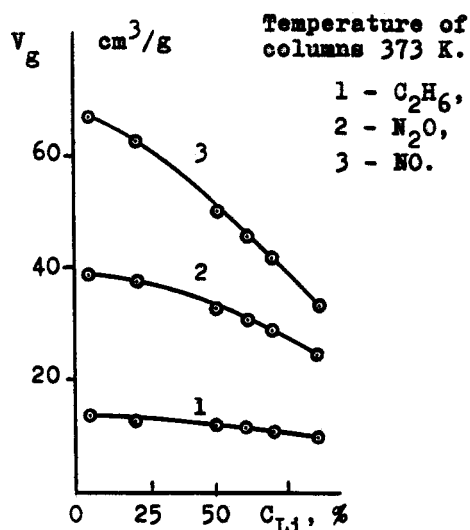


Fig.2. Change of retention volumes V_g for gases with increase in degree of Na^+ by Li^+ (C_{Li}).

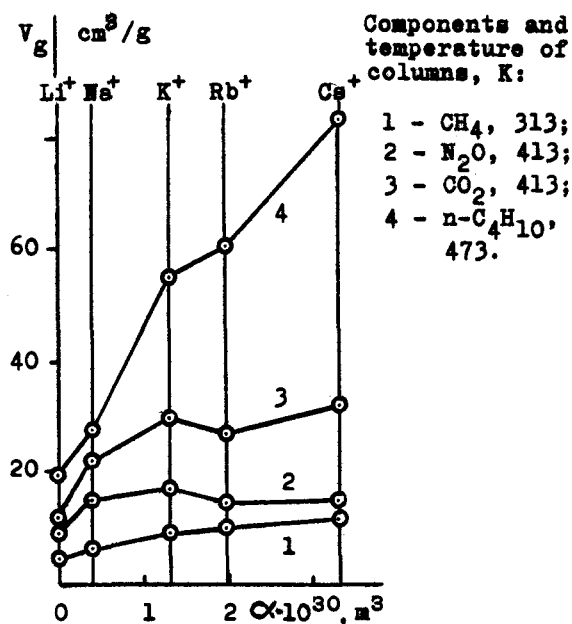


Fig. 3. Dependence of retention volumes V_g on electronic polarizability (α) of cations in zeolites Y-type.

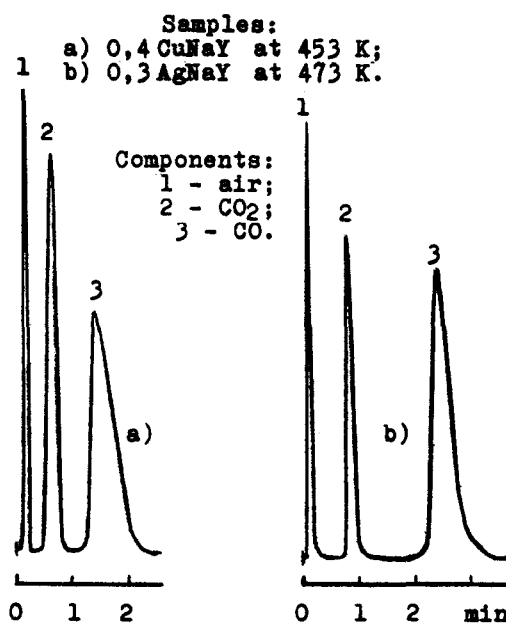


Fig. 4. Chromatograms of separation mixture of CO - CO₂. Columns 100 x 0,3 cm, the flow-rate 50 cm³/min for gas-carrier He, thermoconductivity detector.

Decisive influence on chromatographic retention of separating gases is displayed by the nature as well as individual ability of cations. In one sample with maximum content of exchanged cations (ref. 6), electronic polarizability raised chromatographic volumes V_g of hydrocarbons as well as of gaseous oxides (Fig. 3).

In contrast to ions of alkaline-earth metals, cations of silver display high inclination especially to unsaturated and polar compounds. This is noticed on zeolites of the X-type which, in the presence of even a trace of Ag⁺ cations have excessive affinity to molecules of olefins. In Table 1 are shown absolute specific retention volumes V_g for isomers of butane and butene (ref. 7).

The data in Table 1 illustrate a sharp rise in the V_g volumes of unsaturated hydrocarbons by a small increase in cation content of silver in the zeolite. Each Ag⁺ cation even if surrounded by 200 cations of Na⁺ (with degree of replacement of 0,5%) at 573 K raises retention volumes V_g for butenes substantially to two times whilst insignificantly for both isomers of butane C₄H₁₀. After displacing every hundredth cation of sodium by silver in zeolite, retention time for butenes C₄H₈ at 573 K becomes significant in that it is impossible to eluate from a metre high column at a flow rate of gas-carrier at 50 cm³/min. Hence the particular sorbent behaves like adsorption filters for extracting unsaturated hydrocarbons and sifting alkanes and low boiling gases. Selectivity of such a sifting can be illustrated by values of relative retention, in comparison with nitrogen, at composing at 293 K of samples of NaX (5,1-7,24) · 10⁴ for isomers of butene. After displacing only 2,5% of Na⁺ cations of this zeolite by silver, values of selectivity rise by 10-20 times. This means that under these conditions retention of butene on a silver-containing sample was 20 thousand times stronger than atmospheric nitrogen.

Table 1. Influence of cations Ag⁺ on volumes V_g of hydrocarbons at 573 K (zeolites AgNaY)

Component	Degree of displacement of cations Na ⁺ by Ag ⁺ , %				
	0	0,25	0,5	1,0	2,0
C ₄ H ₁₀ - normal	9,1	9,3	9,4	9,6	10,8
C ₄ H ₁₀ - iso	9,0	9,1	9,2	9,5	10,6
C ₄ H ₈ {	1	29,9	46,5	72,3	-
	cis	30,1	43,2	72,8	-
	trans	29,2	44,7	74,1	-
	iso	38,7	50,5	75,8	-

Table 2. Influence of temperature on selectivity of CO retention on zeolite NaY

Degree of ion-exchange, %	Temperature of column, K					
	573	533	473	373	313	293
0	1,2	1,3	1,5	2,2	2,9	3,2
8,5	7,6	7,6	13,5	$2,0 \cdot 10^2$	$1,4 \cdot 10^3$	$5,0 \cdot 10^3$
16,9	10,0	11,9	32,0	$5,5 \cdot 10^2$	$1,5 \cdot 10^4$	$1,6 \cdot 10^4$
34,1	17,2	35,9	118,5	$2,0 \cdot 10^3$	$3,0 \cdot 10^4$	$1,3 \cdot 10^5$
60,4	79,3	134,5	591,5	$1,9 \cdot 10^4$	$4,6 \cdot 10^5$	$4,0 \cdot 10^6$

Table 3. Influence of silver nitrate on selectivity of retention of CO by zeolites at temperature 293 K

Type of zeolite	Expenditure (mass %)	Selectivity	
		relative volume	logarithm
NaY (synthetic)	0	3,2	0,51
	5,1	$5,0 \cdot 10^3$	3,70
	10,2	$1,6 \cdot 10^4$	4,20
Mordenite (natural)	0	4,8	0,68
	1,6	$6,5 \cdot 10^5$	3,81
	6,7	$9,6 \cdot 10^5$	5,98

Air always contains both oxides of carbon which are difficult to separate using natural unmodified zeolites. But, after displacing significant parts (average displacement) of Na⁺ cations by ions of silver or copper, retention times of both oxides become different and this makes it possible chromatographically to separate CO and CO₂ (Fig.4). Metre high columns (Fig. 4) filled with copper containing zeolite types Y or L, achieved good separation of carbon oxides within a shorter time than on zeolite samples containing silver.

Analysing micro concentrations of oxides of carbon(II) of polluted air give rise to a difficult problem. Usually concentrated CO is eluted in special adsorption traps cooled with liquid nitrogen; although cooling can be avoided if silver containing zeolites are used (ref. 7). The ratio of absolute specific volumes or corrected times of retention of CO and nitrogen can serve as a quantitative measure of selectivity of adsorption of CO.

In Table 2 are shown the influence of temperature and degree of ion exchange on selectivity of CO retention. In a Ag⁺-free sample of NaY at room temperature (293 K) the carbon monoxide was retained 3,2 times stronger than nitrogen. After displacing 8,5% of sodium by silver ions the CO was found to be retained 5000 times longer, but at temperature interval of 533-573 K only 7,6 times longer than nitrogen. Increasing degree of ion-exchange to 60,4% the value of selectivity at 293 K rises to 4 million, but heating up to 533-573 K, drops to almost 100. This is helpful to sample AgNaY to concentrate traces of CO at room temperature for subsequent chromatographic analysis on sample NaY.

An analogous problem is solved with the help of modified natural zeolite (mordenite) from the Carpathian mountains (ref. 2). Silver containing ion-exchange forms of this mordenite (ref. 3) in comparison with analogous synthetic zeolite Y-type has higher selectivity of adsorption of CO (Table 3).

The data in Table 3 show that to attain almost the same (3,70 and 3,81) logarithmic values of selectivity of extraction of CO from air, 3,19 times less silver salt is needed for natural than for synthetic samples. Therefore, there is no need for pressing the zeolite into tablets and further caking, when preparing granules of adsorbent for filling column-concentrator. After heating up to 513-553 K concentrated substances desorb and are carried with the gas-carrier flow to analysing chromatographic column, which is filled with zeolites NaY, NaA or CaA. This is then subjected to quantitative analysis by any known method (ref. 7).

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