CHROMATOGRAPHIC PROPERTIES OF MAGNESIUM-CONTAINING ZEOLITES OF TYPE X

PHYSICAL CHEMISTRY

1965

SovietRxiv

Abstract

Full Text

UDC 543.544

PHYSICAL CHEMISTRY

Academician of the Academy of Sciences of the Georgian SSR G. V. TSITSISHVILI, T. G. ANDRONIKASHVILI,
T. A. CHUMBURIDZE

CHROMATOGRAPHIC PROPERTIES OF MAGNESIUM-CONTAINING ZEOLITES OF TYPE X

The physicochemical properties of zeolites depend substantially on the nature and degree of substitution of the cations compensating the negative charge of the aluminosilicate framework ([1,2]).

When zeolites are used as adsorbents in gas chromatography, depending on the kind and content of cations in them, the separating properties of the packing of the chromatographic column change to a considerable extent ([3–5]). In this respect, zeolites containing magnesium cations have been little studied: only in the work of Janák ([6]) is there an indication of certain chromatographic properties of magnesium-containing zeolites.

For chromatographic studies we used zeolites of the NaX type with different degrees of substitution of sodium ions by magnesium cations. These cation-exchanged forms were prepared by ion exchange according to a method developed in our laboratory ([2]). As the literature data show, despite the comparatively small size of the magnesium ion (its ionic radius is 0.78 Å), it is not possible to replace the sodium ion completely by the magnesium ion in zeolite by the usual methods of cation exchange ([7]). From these data it follows that the maximum substitution of sodium by magnesium in zeolite of type X is possible only up to 70%.

Starting from the sodium form of zeolite of type X (series Ts-202-98), we synthesized three samples of magnesium zeolites of the following composition:

Sample No. 1 $0.20\,MgO \cdot 0.83\,Na_2O \cdot Al_2O_3 \cdot 2.53\,SiO_2$.

Sample No. 2 $0.42\,MgO \cdot 0.60\,Na_2O \cdot Al_2O_3 \cdot 2.58\,SiO_2$.

Sample No. 3 $0.72\,MgO \cdot 0.31\,Na_2O \cdot Al_2O_3 \cdot 2.65\,SiO_2$.

The preservation of the zeolite structures of the samples obtained was confirmed by recording Debye–Scherrer patterns.

Figure 1 and Figure 2 graphs

Figure 1: Figure 1 and Figure 2 graphs

In the study, an artificial mixture of hydrocarbon gases C_1—C_4, carbon monoxide, and hydrogen was used as a model mixture. The conditions for conducting the experiments, as well as the method of preparing the sorbent loaded into the chromatographic columns, were described by us earlier (^{5}).

For the magnesium-substituted forms of zeolites that we studied, a decrease in the retained volumes of all components is characteristic in comparison with the initial sodium form. As the degree of substitution increases, there is a considerable decrease in the values of the retained volumes of all the compounds investigated.

In contrast to the calcium form of the zeolite (^{5}), on this form, as the content of magnesium cations in the zeolite increases, the temperature interval for separation of a mixture consisting of four components—hydrogen, methane, carbon monoxide, and ethane—narrows. Thus, on sample No. 1 this mixture is well separated in the temperature range from room temperature to 80°, on the second sample—from room temperature to 60°, and on the third sample—to 40°. All these data were obtained at a carrier-gas flow rate of 100 ml/min.

All the magnesium-containing zeolites studied (samples Nos. 1, 2, 3) are characterized by the ability to change the elution sequence of individual components of the mixture depending on the heating temperature of the chromatographic column; an increase in the degree of substitution of sodium by magnesium in the zeolite leads to a considerable change in the temperature range of column heating in which inversion of the elution sequence of individual pairs of components of the analyzed mixture occurs.

On sample No. 1 (low content of magnesium cations), complete separation of the propane—ethylene mixture (in the indicated sequence) occurs when the column is heated to 60°. Further increase in the heating temperature of the column leads to poorer separation, and at 100° this mixture is no longer separated. A subsequent increase in the column heating temperature to 280° promotes separation of this pair of components, but with the reverse elution order. On sample No. 2 (intermediate substitution), the propane—ethylene mixture is well separated at a temperature of 60°, but already at 80° column heating their separation deteriorates considerably. A further rise in the column heating

Fig. 1. Dependence of the separation coefficients in the ethylene—propane system on the heating temperature of a column filled with magnesium-containing zeolite. The curve numbers correspond to the sample numbers

Fig. 2. Dependence of the separation coefficients in the propylene—butane system on the heating temperature of a column filled with magnesium-containing zeolite. The curve numbers correspond to the sample numbers

temperature to 280° again improves the separation; in this case inversion of the elution sequence of the propane–ethylene mixture also takes place.

On sample No. 3 (high content of magnesium cations), separation of these components also occurs at 60° column heating, but worse than on samples Nos. 1 and 2. Beginning at 80° column heating, separation ceases, and a further rise in the column heating temperature causes inversion of the elution sequence of the components of the propane–ethylene mixture with a gradual increase in the degree of their separation.

Figure 1 presents the dependence curve of K_1–the coefficients of complete separation of ethylene and propane according to Zhukhovitskii (8)–and of the δ-coefficients of partial separation according to Struppe (9) on the heating temperature of the chromatographic column on zeolites with different degrees of exchange of sodium cations for magnesium (samples Nos. 1, 2, 3). As can be seen from Fig. 1, all three samples are characterized by inversion of the elution sequence of propane–ethylene; moreover, with an increase in the degree of substitution of sodium by magnesium, the separation coefficients of propane–ethylene, at one and the same column heating temperature, decrease, while with the inverted elution order of these components, on the contrary, the separation coefficients increase up to a certain temperature limit (160°). At higher column heating temperatures the separation coefficients of this mixture are almost identical on all three samples. Increasing the magnesium content in the molecular sieves also causes a shift of the regions corresponding to the temperature ranges in which no separation occurs into the region of lower column heating temperatures.

Unlike the calcium form of zeolite (5), where the inversion of the elution sequence of the components of the butane–propylene mixture is very weakly expressed and is not accompanied by their separation, on the magnesium form of zeolites this is manifested considerably more clearly, and these components are separated. Figure 2 gives the curve of the dependence of the separation coefficients on the heating temperature of the chromatographic column on magnesium-containing

Table 1

Heat of adsorption (kcal/mol)

Component	Sample No. 1	Sample No. 2	Sample No. 3	Component	Sample No. 1	Sample No. 2	Sample No. 3
CO	6.2	5.9	5.9	C_2H_4	9.5	9.2	9.1
CH_4	4.6	4.2	4.2	C_3H_6	11.4	10.4	9.9
C_2H_6	6.4	6.1	6.1	C_4H_8	12.9	11.7	11.3
C_3H_8	7.7	7.9	7.8	C_2H_2	11.6	9.9	8.7
n-C_4H_{10}	9.1	9.1	9.1				

zeolites. In this case as well, just as for the propane–ethylene mixture, with an increase in the content of magnesium cations in the zeolite the separation coefficients decrease, while after inversion of elution the values of the separation coefficients increase. At the same time, the temperature ranges in which no separation of this mixture occurs are broader than for the propane–ethylene mixture.

On the basis of gas-chromatographic data, the heats of adsorption of the investigated components on magnesium-substituted forms of zeolites were calculated (Table 1).

The heats of adsorption were calculated for those temperature ranges of column heating in which symmetrical separation peaks are obtained, i.e., equilibrium chromatography takes place.

It follows from these data that the magnitudes of the heats of adsorption of unsaturated compounds decrease with increasing content of magnesium cations in the zeolite. As for the heats of adsorption of saturated hydrocarbons and carbon monoxide, they practically do not change, or else there is a slight decrease with increasing degree of substitution of sodium by magnesium in the zeolites.

Institute of Physical and Organic Chemistry
named after P. G. Melikishvili
Academy of Sciences of the Georgian SSR

Received
2 IV 1965

CITED LITERATURE

1. M. M. Dubinin, *Izv. AN SSSR, ser. khim.*, No. 7, 1359 (1964).
2. G. V. Tsitsishvili, T. G. Andronikashvili, *Synthetic Zeolites*, Publishing House of the Academy of Sciences of the USSR, 1962, p. 117.
3. T. G. Andronikashvili, Sh. D. Sabelashvili, G. V. Tsitsishvili, *Neftekhimiya*, 2, 2, 248 (1962).
4. G. V. Tsitsishvili, T. G. Andronikashvili, Sh. D. Sabelashvili, Z. I. Koridze, *Soobshch. AN GruzSSR*, 35, 1, 87 (1964).
5. G. V. Tsitsishvili, T. G. Andronikashvili, A. Dumbradze, Z. I. Koridze, *DAN*, 156, 4, 932 (1964).
6. Janak, *Vapour Phase Chromatography*, London, 1957, p. 247.
7. P. E. Eberly Jr., *J. Phys. Chem.*, 66, 5, 812 (1962).

8. N. M. Turkeltaub, A. A. Zhukhovitskii, *Gas Chromatography*, Publishing House of the Academy of Sciences of the USSR, 1960, p. 144.

9. H. G. Struppe, I Symp. Uber Gas Chromatography, DDR, Berlin, 1959, S. 28.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.