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CHROMATOGRAPHIC SEPARATION OF A MIXTURE OF HYDROCARBON GASES C_1-C_4 ON TYPE-X ZEOLITES WITH DIFFERENT CONTENTS OF CALCIUM CATIONS

It is known that the adsorption capacity of zeolites depends on the degree of replacement of sodium by other cations ([1,2]). Consequently, the degree of cation replacement in zeolites will also exert a definite influence on their chromatographic properties ([3]).

We investigated the chromatographic properties of three samples of calcium zeolites of type X, obtained by an ion-exchange reaction from the corresponding sodium forms. The composition of these samples may be expressed by the following chemical formulas: sample No. 1 —$0.25\,CaO \cdot 0.67\,Na_2O \cdot Al_2O_3 \cdot 2.66\,SiO_2$; sample No. 2 —$0.56\,CaO \cdot 0.50\,Na_2O \cdot Al_2O_3 \cdot 2.51\,SiO_2$; sample No. 3 —$0.83\,CaO \cdot 0.09\,Na_2O \cdot Al_2O_3 \cdot 2.45\,SiO_2$.

Granules were prepared from the zeolite powders without the use of a binder (kaolin), and were activated by heating at a temperature of 450° for 5–6 hours. These sorbents, with a particle size of about 15–30 mesh, were then loaded into the columns of a KhT-2M chromatograph. The flow rate of the carrier gas (air) was varied within the range 30–120 ml/min, and the heating temperature of the column was varied from room temperature to 300–400°. The model mixture used in the study was a mixture consisting of hydrocarbon gases C_1-C_4, carbon monoxide, and hydrogen. Examination of the experimental data gave the following results.

With an increase in the degree of replacement of sodium by calcium, the temperature interval for separation of a mixture consisting of the four components hydrogen, methane, carbon monoxide, and ethane becomes broader. Thus, on sample No. 1 this mixture is well separated in the temperature interval from room temperature to 80°; on the second sample, from room temperature to 100–120°; and, finally, on the third sample, up to 140°. These data were obtained at a carrier-gas flow rate of 100 ml/min.

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

On the calcium forms of the zeolites (samples Nos. 1 and 2), as on the initial sodium form, a change is observed in the elution sequence of the ethylene-propane components as a function of the heating temperature of the chromatographic column. However, the character of this dependence is also determined to a greater extent by the content of calcium ions in the zeolite. On sample No. 1 (a zeolite with low sodium replacement), the following elution sequence of ethylene-propane is observed as the column heating temperature is increased. At a temperature of 80-100° the retained volume of propane is smaller than the retained volume of ethylene, while at 120° an interchange takes place in the elution sequence of these components. A further increase in temperature up to a certain limit promotes better separation of this binary mixture while preserving the order of elution.

On sample No. 2 (medium replacement), at a column heating temperature of 100-120° the elution order is propane-ethylene; at 140-180° separation does not occur. A further increase in temperature to 240° leads to inversion of the elution sequence of this pair.

On sample No. 3 (high content of calcium ions), at all tempera-

temperature intervals of column heating (100-220°), the following elution sequence is preserved: propane is eluted first, and then ethylene.

Figure 1 presents the curve of the dependence of the separation coefficients of these components according to Zhukhovitskii K_1 (4) and the coefficients according to Struppe δ (5) on the heating temperature of the chromatographic column on zeolites with different calcium-ion contents (samples Nos. 1, 2, 3). As can be seen from Fig. 1, for samples Nos. 1 and 2 an inversion of the elution of ethylene and propane is characteristic, whereas in the case of sample No. 3 it is absent, i.e., no change in the order of elution of the components occurs over the entire temperature range studied. A similar pattern is also characteristic of such a pair as butane–propylene. The influence of the calcium content in the zeolite on the order of elution

Fig. 1. Dependence of the separation coefficients in the ethylene–propane system on the heating temperature of a column packed with calcium-containing zeolite. The numbers of the curves correspond to the sample numbers.

Fig. 2. Influence of the carrier-gas flow rate on the catalytic conversion of propylene. Adsorbent–the calcium form of zeolite (sample No. 2). Heating temperature of the chromatographic column: 300°. Carrier-gas flow rate: 1–30, 2–50, 3–70, 4–100 ml/min.

of saturated and unsaturated compounds can, in all probability, be explained by the stronger polarizing properties of this ion compared with the sodium ion

(6).

Molecular sieves also exhibit catalytic properties with respect to certain compounds; thus, for example, on the nickel form of type 13X zeolite during chromatography of cyclopropane its isomerization to propylene occurs (7). We have observed that the calcium form of zeolites also possesses catalytic ability with respect to unsaturated hydrocarbons C_3–C_4.

When propylene is chromatographed on a column heated to 300° and packed with calcium zeolite, the propylene begins to undergo catalytic action by the sorbent, and instead of one peak on the chromatogram two peaks appear, the peak of an unknown substance beginning to be eluted earlier than propylene. Reducing the carrier-gas flow rate from 100 to 30 ml/min leads to the disappearance of the propylene peak (Fig. 2). Raising the heating temperature of the chromatographic column to 400° at a carrier-gas flow rate of 100 ml/min also leads to the disappearance of the peak corresponding to propylene.

It may be assumed that this phenomenon is connected with the simultaneous polymerization and isomerization of propylene, which is manifested more strongly at elevated temperatures and reduced carrier-gas flow rates; the compound formed as a result of isomerization has a smaller retention volume than propylene and, apparently, is cyclopropane. On the other hand, since the retention volumes of cyclopropane and propane

are very close (7), and their separation on zeolite is difficult; it is therefore permissible that on this sorbent as well, owing to disproportionation of hydrogen, instead of isomerization of propylene, self-hydrogenation of the latter to propane takes place.

In chromatography on these cation-exchanged forms, *n*-butylene also undergoes change. The peak corresponding to butylene on the chromatogram, when the column-heating temperature is raised from 200°, gradually begins to decrease, and at 300° it disappears completely (carrier-gas flow rate 100 ml/min). Along with this, another substance appears, which is eluted before butylene. The zeolite with a low sodium replacement (sample No. 1) is characterized by this property. On zeolites with a high content of calcium ions (samples Nos. 2 and 3), butylene is not eluted during chromatography, but in all cases, beginning at a column-heating temperature of 220°, a peak appears corresponding to the product of catalytic conversion of butylene. Apparently, an increase in the calcium content in the zeolite promotes polymerization of butylene.

Table 1

Heat of adsorption (kcal/mol)

Component	Sample No. 1	Sample No. 2	Sample No. 3
CH_4	4.7	4.2	4.1
CO	6.5	7.0	7.9

Component	Sample No. 1	Sample No. 2	Sample No. 3
C_2H_6	6.6	6.3	6.2
C_2H_4	8.5	8.8	10.9
C_3H_8	7.3	7.3	7.2
C_3H_6	10.8	11.2	13.9
C_4H_{10}	9.9	9.5	9.2

On the basis of gas-chromatographic data (8), the heats of adsorption of the compounds studied on three zeolite samples were calculated. The heats of adsorption of methane, carbon monoxide, and ethane correspond to the temperature intervals 20–140°; those of propane and ethylene, 120–240°; and those of butane and propylene, 160–300°.

As is evident from the data of Table 1, an increase in the degree of replacement of sodium by calcium leads to an increase in the heats of adsorption of unsaturated hydrocarbons and carbon monoxide, whereas the heats of adsorption of saturated compounds change little.

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