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1963

SovietRxiv

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Abstract

Full Text

PHYSICAL CHEMISTRY

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SEPARATION OF ISOTOPIC HYDROGEN MOLECULES ON SYNTHETIC TYPE-A ZEOLITES IN THE COBALT ION-EXCHANGED FORM

(Presented by Academician M. M. Dubinin, July 27, 1963)

At present there are relatively few works devoted to the study of the separation of isotopic hydrogen molecules on molecular sieves. Japanese investigators ($^{1-3}$), using gas chromatography, showed (^{2}) that on a Linde 5A-type molecular sieve, at the temperature of liquid nitrogen and an initial-gas pressure of 330 mm Hg, considerable separation occurred when a mixture of isotopic hydrogen molecules was passed through. For example, if the initial mixture consisted of 45% H_2, 23% HD, and 32% D_2, then at the outlet from the column the amounts were 70, 27, and 3%, respectively. Separation was also carried out on a Linde 13X sieve (^{3}). In work (^{4}) the comparative separating ability of various sorbents was studied, including three samples of Linde molecular sieves of types 4A, 5A, and 13X. The author indicates that relatively high separation factors were obtained ($\alpha_{D_2/H_2} > 2$); however, the separation of hydrogen isotopes apparently is not connected with the sieve effect, since type-13X sieves with a pore diameter of 13 Å give the same enrichment as the type-4A sieve, whose pore size is close to the van der Waals size of hydrogen (2.4 Å). A sample of 3A sieve had a small capacity for both hydrogen isotopes. The authors note that the chemical composition of the adsorbent should apparently have a marked influence on the separation factor.

Fig. 1. Sorption isotherms of nitrogen vapor at −195.8°. Curves for sieves NaA *(1)*, Co_6A *(2)*, and $Co_{12}A$ *(3)*.

Fig. 2

Figure 2: Fig. 2

The aim of the present work was to study the influence of cobalt-substituted forms of zeolites on the separation of isotopic hydrogen molecules. The initial form of the NaA sieve had a crystal composition typical for this form of zeolite. Cobalt-substituted forms of molecular sieves were synthesized by a procedure based on repeated exchange of the initial form of the zeolite with a salt of the cation introduced into the zeolite (^{5}). In the present case sodium ions were replaced by cobalt ions from a 0.05 N solution of cobalt chloride. Sieve samples were obtained with cobalt-ion contents from 3.69 to 14.20 wt. %. In particular, in the sample containing 14.20 wt. % cobalt ions, 67.7% of the sodium ions had been replaced. Preservation of the zeolite framework after ion exchange was monitored by X-ray diffraction. The parameters of the elementary cubic cell were 12.32 ± 0.01 Å for the initial NaA form, 12.29 ± 0.01 Å for Co_1A, Co_3A, and Co_6A, and 12.28 ± 0.01 Å for $Co_{12}A$.

It was shown that the cation-exchanged forms obtained are characterized by molecular-sieve properties, i.e., they sorb vapors well.

water and nitrogen and do not absorb benzene vapor. As a standard characteristic of the capacity of the sieves, Fig. 1 gives the sorption isotherms of nitrogen vapor at a temperature of $-195.8°$.

The efficiency of the separation process is determined by the value of the single-stage separation coefficient, which was calculated from mass-spectrometric data by the formula $\alpha = I_1/I_2$, where I_1 is the ratio of the intensities of the ion currents HD/H_2 in the adsorbed phase; I_2 is the ratio of the intensities of the ion currents HD/H_2 in the gas phase.

Experiments on isotope separation were carried out in static and circulation apparatuses, both with a gas mixture in which only H_2 and HD molecules were present and with mixtures of H_2, HD, and D_2 at the temperature of liquid nitrogen. The sorbent, diluted with crushed quartz or molded with an addition of kaolin from 10 to 15 wt.%, before the experiments conducted under static conditions, was evacuated with a fore-vacuum pump for 24 hours at a temperature of 117°.

Fig. 2. Change in the single-stage separation coefficient as a function of the amount of cobalt ions introduced into the zeolite. $\varepsilon_0 = \alpha_{\mathrm{Co1A}} - 1$; $\varepsilon_i = \alpha_i - 1$

The kinetics of isotopic exchange was studied in a circulation apparatus with a magnetic pump (^{6}). Before the experiment, the sorbents were evacuated with a fore-vacuum pump while heated to a pressure of $5 \cdot 10^{-3}$ mm Hg. Before the experiment, the sorbent was cooled with liquid nitrogen, then the isotope mixture was admitted and the magnetic pump was switched on. Gas samples taken at definite time intervals were analyzed for isotopic composition. Analy-

Fig. 3

Figure 3: Fig. 3

sis of the isotopic composition of hydrogen was carried out on an MI-1305 mass spectrometer. The results of the experiments are shown in Figs. 1-3. All experiments were reproduced, and the graphs give average data. For the Co_4A sample, experiments were carried out with different HD contents in the initial mixture, from 0.94 to 9.14 mol.%, and for Co_6A—from 0.26 to 2.14 mol.% D_2. The independence of the single-stage separation coefficient from the concentration of isotopes in the initial mixture is shown. From Fig. 1 (curves 1, 2, 3) it is seen that with an increase in the content of cobalt ions in the sorbent its sorption capacity increases. The single-stage separation coefficient has a maximum value for NaA. When cobalt ions are introduced, it first drops sharply and then increases, reaching a value equal to α_{NaA} only when 61% of the sodium ions are replaced by cobalt ions. In Fig. 2, the black points present data on the single-stage separation coefficients obtained under circulation conditions, which agree satisfactorily with the data obtained under static conditions. The somewhat underestimated values of the single-stage separation coefficients obtained in experiments with gas circulation are apparently associated with a certain rise in temperature in the sorption zone owing to insufficiently complete cooling of the circulating gas.

Fig. 3. Dependence of the degree of isotopic exchange of hydrogen on molecular sieves Co_4A (1) and $Co_{12}A$ (2) on time.

The kinetics of hydrogen isotope separation on molecular sieves with different contents of cobalt ions is described by the curve in Fig. 3. The rate of isotope exchange is high at the initial moment of the reaction, but already 4–15 min after the start of the experiment the isotopic composition of the gas phase, within the accuracy of mass-spectrometric analysis, practically does not change. At the same time, no appreciable influence of the cobalt-ion content on the rate of isotope exchange is observed.

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Received
2 VII 1963

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