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Abstract

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ADSORPTIVE DEHYDRATION OF LOW-MOLECULAR-WEIGHT FATTY ACIDS BY POROUS GLASSES–MOLECULAR SIEVES

(Presented by Academician M. M. Dubinin on 18 XI 1962)

The ultraporous glasses developed in recent years in the Soviet Union possess molecular-sieve properties (1–5). Appropriate selection of the compositions of the starting glasses and of the conditions of their thermal and chemical treatment makes it possible to obtain a broad range of porous glass molecular sieves, from those close to the synthetic zeolite KA (3A Linde) to those close to zeolites of the faujasite type (CaX, NaX–respectively 10X and 13X Linde) and to more coarsely porous materials. The distribution of pore volumes in porous glasses by pore size may be very narrow (6,7,3). Porous glasses consist practically of pure silica and therefore have certain advantages in chemical stability with respect to acidic media and can be used for solving certain specific adsorption problems that cannot be solved with ordinary sorbents and zeolite-type molecular sieves. The present work sets forth the results of a study whose aim was to determine the fundamental possibility of deep dehydration of low-molecular-weight fatty acids (LMFA) with the aid of porous glass molecular sieves.*

As model mixtures we used concentrated solutions of acetic and propionic acids containing 3-5 wt.% water. The mixtures were analyzed by titrating weighed samples of acid (0.2-0.3 g) with 0.05 *N* KOH solution. The maximum error of determination did not exceed 0.3%. The samples of porous glasses used were prepared from anomalous sodium borosilicate glasses, low-alkali sodium borosilicate glasses, alkali-free borosilicate glasses, and alkali silicate glasses (samples Nos. 1 and 3, described in work (2)). The compositions of the alkali-free and low-alkali glasses were selected on the basis of work (1). For comparison, a sample of fine-pored silica gel ShSM produced by the Voskresensk Chemical Combine named after Kuibyshev was used; it had been washed free of iron impurity with concentrated hydrochloric acid and had an effective pore radius of 8-9 Å. This value was determined from the desorption branch of the hysteresis loop of the water adsorption isotherm. Before the experiments the samples were dried at 120 °C for 2 hours.

For brevity we do not give here the detailed adsorption characteristics of the porous glass samples studied. Some of them have been published (samples Nos.

Fig. 1

Figure 1: Fig. 1

1 and 3 (2); E-7/23 and E-10/30** (3,4)), while others (relating to samples obtained from low-alkali and alkali-free borosilicate glasses) will be included in another, more detailed publication. Judging from

According to the available data on the adsorption of water, methyl and ethyl alcohols, nitrogen, and certain hydrocarbons, samples Nos. 1 and 3 of E-7/23-(I), in terms of the sizes of the constrictions (connecting “windows”) of the pores, are close to zeolite molecular sieves of type A. Sample E-10/30-(I), according to the results of adsorption studies, data on the kinetics of benzene separation from cyclohexane on it (4), and the sizes of the connecting “windows” of the pores, is close to the zeolite molecular sieve CaX (Linde 10X), or is inferior to it.

Fig. 1. Breakthrough curves from dynamic experiments on the dehydration of acetic (A) and propionic (B) acids. Designation of sorbent samples: 1 –silica gel ShSM; 2 –No. 1; 3 –No. 3; 4 –E-7/23-(I); 5 –E-10/30-(I); 6 –0/25 (from alkali-free borosilicate glass)

Preliminary experiments on drying acetic and propionic acids with the described samples at room temperature under static conditions showed the fundamental possibility of adsorption dehydration of the named (and, consequently, also more high-molecular) fatty acids with the aid of porous glasses–molecular sieves, and made it possible to select a number of them for testing under dynamic conditions. The dynamic tests were also carried out at room temperature in columns 300 mm high and 3.5–4.5 mm in diameter, with particle sizes of the tested samples of 0.1–0.25 mm. The flow rate was about 1 cm^3/min per 1 cm^2 of the total cross section of the column.

Figure 1 gives the breakthrough curves for a number of experiments on the dehydration of acetic (Fig. 1A) and propionic (Fig. 1B) acids under dynamic conditions. As can be seen from Fig. 1, the experiments showed the possibility of practically complete dehydration of these (and, consequently, also more high-molecular) fatty acids. The process has a molecular-sieve nature: porous glass E-10/30-(I), close in pore size to zeolite CaX, as well as silica gel ShSM, do not possess the ability to effect efficient dehydration of concentrated acetic and propionic acids.

In the dehydration of propionic acid, the best results were obtained with sample No. 1. With respect to acetic acid, however, the greatest drying capacity was

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* Our attention was drawn to the practical value of such a process by A. I. Levin, to whom we express our gratitude.

** The numerator and denominator of the fraction are, respectively, the mole % of NaO_2 and Ba_2O_3 in the starting glass.

shown by porous glass E-7/23-(I). The reasons for changes in the comparative effectiveness of porous glasses—molecular

sieves upon transition from one acid to another are obviously associated with the molecular-sieve nature of the process and lie in the subtle differences in the sizes of the constrictions of the connecting "windows" of the pores of these samples. Drying of propionic acid on porous glasses—molecular sieves proceeded, under otherwise identical conditions, more effectively than in the case of acetic acid. The reason for this is the greater difference in the sizes of the molecules of water and propionic acid, as compared with the difference between the sizes of the molecules of water and acetic acid.

The degree of utilization of the sorption space in our experiments was not very high and amounted to about 40%. This is probably caused by factors of a kinetic nature (slowing of diffusion in narrow pores under conditions of relatively short contact times). It is also possible, however, that some of the pores of the samples studied prove accessible also to acid molecules (especially acetic acid), which leads to a decrease in the degree of utilization of the sorption space with respect to water.

According to the data of work (8), zeolite NaA made it possible to carry out deep drying of acetic acid. However, according to the results obtained by us, zeolitic molecular sieves proved unsuitable for drying low-molecular fatty acids. 97% acetic acid completely destroyed the granules of zeolite NaA (GrozNII) into powder. In this case a slowly settling suspension formed, and a considerable amount of sodium acetate appeared in the solution. The action of the same acid on powdered zeolite NaA caused destruction of its crystalline structure and led to the formation of an X-ray-amorphous material, likewise accompanied by the appearance in solution of considerable amounts of sodium acetate. It is obvious that any attempt to dehydrate sufficiently strong acids with the aid of cationic forms of ordinary zeolitic molecular sieves will be accompanied by replacement of these cations by a proton, which will lead to an irreversible change (under the conditions of the acid dehydration process) in the composition and structure and, consequently, in the molecular-sieve properties of the zeolite, as well as to contamination of the acid being dehydrated with the corresponding salts.

Thus, the experiments carried out have demonstrated the possibility of molecular-sieve dehydration of low-molecular fatty acids by means of porous glasses—molecular sieves, which is not attainable for sorbents of other types, in particular for ordinary zeolitic molecular sieves. For such purposes, only the use of H-forms of zeolites with increased resistance to acids is possible, achieved by increasing the ratio $SiO_2 : Al_2O_3$. Data from work (9) testify to such a possibility.

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