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## Abstract

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# INVESTIGATION OF THE CONDITIONS FOR THE FORMATION OF SODIUM ZEOLITES IN LOW-TEMPERATURE HYDROTHERMAL SYNTHESIS *

*(Presented by Academician M. M. Dubinin, 15 XII 1960)*

Recently, artificial zeolites have been finding increasingly wide application as molecular sieves used for the separation of gaseous and liquid mixtures. Industrial samples of molecular sieves of types A and X are synthetic sodium zeolites and their calcium form, in which a significant portion of the $Na^+$ ions compensating the excess negative charge of the aluminosilicate framework is replaced by an equivalent amount of $Ca^{2+}$ ions. In view of the great practical importance of artificial zeolites, the study of the conditions of their formation in hydrothermal synthesis is of particular interest.

Until recently, the conditions for obtaining synthetic zeolites known as Linde molecular sieves A and X remained unknown ($^{1-4}$). Fairly definite information on this subject has been published in the recently issued work of Barrer et al. ($^{5}$). That work reports data on the low-temperature hydrothermal synthesis of crystalline aluminosilicates from alkaline aluminosilicate gels of composition $m\mathrm{Na_2O \cdot Al_2O_3} n\mathrm{SiO_2}$, in which the molar content of excess alkali did not exceed 300% ($\mathrm{Na_2O/Al_2O_3} \leqslant 4$).

In the present work, the conditions for the formation of crystalline sodium aluminosilicates from strongly alkaline aluminosilicate gels were investigated, in which the ratio $\mathrm{Na_2O/Al_2O_3}$ varied from 4 to 6. The content of $SiO_2$ in the gels varied from $n = 1$ to $n = 10$. Studies of the crystallization of aluminosilicates from such strongly alkaline gels were of interest not only because they supplemented earlier results ($^{5}$), covering the region of higher $Na_2O$ concentrations in the initial gels, but especially because increased alkalinity is optimal for the crystallization of the artificial sodium zeolite known as Linde sieve 13 X, the conditions for obtaining which remained unclear from the published data.

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

Alkaline aluminosilicate gels were prepared by mixing alkaline solutions of sodium aluminate and sodium silicate. The starting reagents were NaOH, amorphous $SiO_2$, $NaAlO_2$ or $Al(OH)_3$ of varying degrees of purity. The solutions of silicates and aluminates were mixed with vigorous stirring, and by the moment of gel formation, which most often occurred 30–40 sec after mixing, the solution was fully homogenized.

Synthesis was carried out at temperatures of 70–200°. For temperatures above 100°, stainless-steel autoclaves were used; at temperatures below 100°, synthesis was conducted in glass flasks. In all, there were obtained more than 170 products differing in synthesis conditions (in the composition of the starting gels, temperature, and duration of crystallization). Phase analysis of the synthesized products was carried out from Debyegrams obtained on an ionization X-ray unit. Chemical analysis of typical crystalline products was also carried out*. For identification of the aluminosilicates obtained, X-ray data published in works (5-8) were used. Typical samples of synthetic zeolites were also studied with respect to their adsorption capacity for water, methyl, ethyl, and butyl alcohols, nitrogen, and certain hydrocarbons.

Fig. 1. Temperature and concentration conditions for the crystallization of sodium zeolites: A —analcime, —basic nosean, —synthetic zeolite (zeolite P (5)), —synthetic zeolite (Linde sieve 13X), —synthetic zeolite (Linde sieve 4A)

Fig. 2. Comparison of interplanar spacings for known and obtained synthetic zeolites

In the diagram constructed on the basis of the results of the study of the properties of the synthesized aluminosilicates, the regions of their formation are shown (Fig. 1). Here the abscissa is not simply the molecular content of $SiO_2$ in the starting gel (the quantity $n$), but the ratio $\frac{n}{m-1} = k$, i.e., the ratio of the number of moles of $SiO_2$ in the gel composition to the excess number of moles of $Na_2O$, referred to one mole of $Al_2O_3$. With this method of constructing the diagram, the regions of formation of the various phases are separated under our conditions considerably better than when the diagrams are constructed

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* In the initial stage of the work V. A. Kostrova took part.

in the coordinates $t$ and $n$ (5). This circumstance, generally speaking, is understandable, since the conditions for the formation of aluminosilicates in hydrothermal synthesis are not determined solely by the temperature and the content of $SiO_2$ in the gel or by the ratio $SiO_2/Al_2O_3$, but depend to a considerable degree on the alkali content.

In the temperature range investigated (70-200°), from strongly alkaline silica-alumina gels ($4 \leq m \leq 6$) we obtained at least five crystalline aluminosilicates, initially designated A, , , , and . The last three of these undoubtedly belong to sodium zeolites. As may be concluded from the agreement of the interplanar spacings determined from X-ray data (Fig. 2), and also from the results of adsorption studies,* products and are identical to the synthetic sodium zeolites of types X and A, known under the names Linde molecular sieves 13X and 4A. From the diagram in Fig. 1 it is seen that, under conditions of high excess alkalinity, sodium zeolite of type A is obtained only in the region of small $k$, bounded for temperatures of 70-90° by values $k = 0.20$-$0.70$. For higher temperatures the range of compositions in which formation of zeolite of type A is possible narrows considerably. At temperatures above 110° this synthetic zeolite was not obtained at all. Under the conditions investigated, as also under conditions of lower alkalinity (5), small concentrations of $SiO_2$ in the gel ($n = 1$ and 2) are the most favorable for the formation of this zeolite.

In contrast to gels with a low $Na_2O$ content (5), under the conditions of our experiments zeolite X was obtained quite reproducibly at 70° in the region of compositions for which $k$ varied from 0.75 to 1.33. From gels with values $k > 1.33$, at 70°, even on prolonged holding (more than 7 days), crystalline products were not obtained. At higher temperatures, for example already at 90°, zeolite X did not crystallize reproducibly. Within the same range of variation of $k$, zeolite X formed at this temperature together with product . At temperatures above 100° zeolite X probably does not form at all.

Product differs in the character of its Debye patterns from zeolites A and X; at the same time this aluminosilicate has a considerable adsorption capacity with respect to water, can release it on heating without destruction of the crystal-lattice structure, and undoubtedly is also a zeolite. Apparently, this zeolite is identical to zeolite P, recently described by Barrer (4), as may be concluded from the closeness of the interplanar spacings of these products and of the temperature region of their formation. The composition of the zeolite synthesized by us corresponds to the formula
$0.94\,Na_2O \cdot Al_2O_3 \cdot 3.52\,SiO_2 \cdot 4.55\,H_2O$
and lies within the range of variation of the compositions of zeolite P according to Barrer' s data. The optimum temperatures for the formation of zeolite lie within 90-120°. In this temperature range zeolite forms reproducibly at $k$ varying within $1.33 \leq k \leq 4$. The possibility of formation of this zeolite in the region of still larger $k$ has not been traced.

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* The analyses were carried out in the laboratory of Professor Yu. V. Morachevskii.

Fig. 3. Adsorption isotherms on synthesized zeolites: 1 –$H_2O$ on G (13X), 2 –$H_2O$ on D (4A), 3 –$H_2O$ on B (at 18°), 4 –$C_2H_5OH$ on B at 18°, 5 –$N_2$ on B at –196°, 6 –H-$C_5H_{12}$ on B at 18°

Figure 3: Fig. 3. Adsorption isotherms on synthesized zeolites: 1 –$H_2O$ on G (13X), 2 –$H_2O$ on D (4A), 3 –$H_2O$ on B (at 18°), 4 –$C_2H_5OH$ on B at 18°, 5 –$N_2$ on B at –196°, 6 –H-$C_5H_{12}$ on B at 18°

To characterize the adsorption properties of zeolite , adsorption of $H_2O$, $C_2H_5OH$, $N_2$, and $n$-$C_5H_{12}$ was investigated. The adsorption isotherms obtained are shown in Fig. 3. For comparison, this figure shows the isotherms of adsorption of $H_2O$ on samples of sodium zeolites A and X synthesized by us. Before adsorption, all the synthetic zeolites were heated in vacuum at 200°. From the isotherms in Fig. 3 it is seen that zeolite has a considerable adsorption capacity with respect to water vapor and exhibits a clearly expressed selectivity of adsorption.

The calcium form of zeolite , obtained by ion exchange, in which 73% of Na$^+$ is replaced by Ca$^{2+}$, in its adsorption properties differs hardly at all from the original sodium form. This fact requires special explanation, since it is known that the capacity for selective adsorp—

···of zeolites of types A and X changes to a significant degree as a result of the replacement of Na$^+$ ions by Ca$^{2+}$. In the temperature range 150-200°, under the conditions studied, analcime and basic nosean are formed almost exclusively (products A and B, Fig. 1). Here the basic nosean crystallizes predominantly from more alkaline gels, or from gels with a lower $SiO_2$ content (small $k$). In many cases the joint formation of these aluminosilicates was observed.

**Fig. 3.** Adsorption isotherms on synthesized zeolites: 1 –$H_2O$ on G (13X), 2 –$H_2O$ on D (4A), 3 –$H_2O$ on B (at 18°), 4 –$C_2H_5OH$ on B at 18°, 5 –$N_2$ on B at –196°, 6 –H–$C_5H_{12}$ on B at 18°.

Sodium zeolites A, X, and B, under certain conditions, during synthesis can recrystallize with the formation of other crystalline phases. Such transformations were observed predominantly in those cases when the compositions of the initial gels corresponded to values located near the boundaries of the formation regions of different zeolites. Thus, for example, with prolonged holding, cases of the following transitions were noted: A→X, X→B, B→analcime.

A transition to the analcime of basic nosean was also noted.

For a more complete determination of the optimal conditions for zeolite crystallization and characterization of their properties, further investigations are necessary. Such investigations may lead to the discovery of new synthetic zeolites

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* The results of the adsorption studies are not presented in full in this work.

possessing useful properties, and will help answer a number of still unresolved questions that are not only of purely scientific but also of considerable practical interest.

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