TRANSFORMATION OF n-BUTYRALDEHYDE ON ZEOLITE CATALYSTS

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Most of the reactions catalyzed by zeolites belong to the carbonium ion type, and their acceleration is explained by the acid properties of the decationized and multivalent cationic forms of the crystalline aluminosilicates [1-3]. As a rule, the monovalent cationic modifications (with the exception of Li and Ag) are not active in the indicated reactions. Water extracts of these zeolites, representing the salts of strong bases and weaker aluminum–silicon heteropoly acids, have an alkaline reaction [4-6]. It is natural to expect that they should exhibit a catalytic activity in reactions that are accelerated by bases. Some examples of such reactions are given in [2, 7], but they have received little study, and neither have the catalytic properties of the monovalent cationic forms of zeolites.

In the present communication are given the results that were obtained when n-butyraldehyde was transformed on some zeolite catalysts in the presence of hydrogen and also without it. At the present time isooctyl alcohol (2-ethylhexanol) is obtained from butyraldehyde, the esters of which with various acids are valuable plasticizers [8]. The methods used are the direct (one-step) catalytic conversion of the aldehyde to isooctane, or its condensation to 2-ethylhexenal and the hydrogenation of the latter to octyl alcohol. A search for new catalysts for these processes is of practical interest.

The catalysts were prepared from zeolite NaY with $SiO_2/Al_2O_3 = 4.4$, and the pH of the water extract (100 ml of distilled water per 2 g of crystallite) was 9.7. By washing it with distilled water we obtained a NaY sample with pH 7.7, while by ionic exchange with KCl, NH_4Cl and $Nd(NO_3)_3$ we obtained the cationic modifications (the degrees of Na^+ exchange are indicated in Table 1). The decomposition of NH_4NaY to

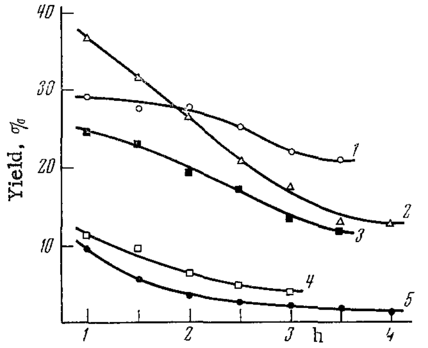

Fig. 1

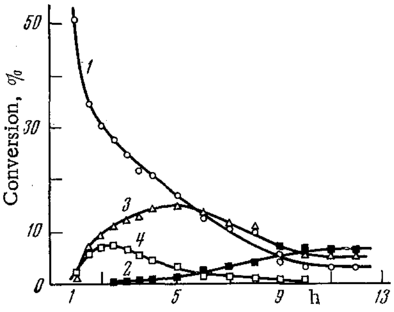

Fig. 2

Fig. 1. Change in yield of 2-ethylhexenal with time on zeolites NaY (1), KNaY (2), NaY with pH 7.7 (3), NdNaY (4) and HNaY (5). The conditions are indicated in Table 1.

Fig. 2. Conversion of butyraldehyde to butanol (1), 2-ethylhexenal (2), 2-ethylhexanal (3) and 2-ethyl-1-hexanol (4) on 4% Ni/NaY as a function of the time of catalyst operation at 200°, molar ratio $n\text{-}C_4H_8O : H_2 = 1 : 1.4$, feed rate of mixture 0.144 M/h ($0.53\ h^{-1}$ in aldehyde).

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TABLE 1. Condensation of n-Butyraldehyde on Zeolite Catalysts at 200°C, Feed Rate 6 M/liter·h (0.53 h^{-1}), Data Obtained after the Catalysts had Operated for 1 Hour

Catalyst	pH of water extract	Amount in "organic" layer, %				Conversion of n-butyraldehyde %	Yield of 2-ethylhexenal, % of theory
		butanol	2-ethylhexanal + butyl butyrate	2-ethylhexenal	n-butyric acid		
NaY	9,7	0,9	0,5	31,2	—	46,8	29,1
		0,3*	0,3	27,5	—	40,0	26,0
		1,6†	1,0	23,7	1,7	41,0	21,9
NaY	7,7	0,8	0,5	26,3	0,6	41,7	24,5
0,70 KNaY	7,9	0,5	0,8	37,7	—	48,6	36,5
0,63 NdNaY	—	1,3	0,9	12,6	1,1	33,5	11,4
0,68 HNaY	—	0,9	0,9	10,0	1,3	29,6	9,5
5% NiO/NaY	9,7	0,6	0,8	30,4	1,1	45,8	29,9

*After running four experiments and regeneration.

† 250°, in a H_2 stream, v = 2 liters/h n-C_4H_8O : H_2 = 1 : 1.4 mole.

HNaY was run at 500° in a stream of air. The catalyst 4% Ni/NaY was prepared by impregnating the starting zeolite with a solution of the calculated amount of nickel acetylacetonate in methanol and subsequent treatment (in the reaction tube) with H_2 at 450° for 5 h, while the 5% NiO/NaY was prepared by heating the Ni/NaY catalyst in air at 500°. The powdery catalysts were molded without a binder into tablets 4 × 4 mm, which were dehydrated at 500° and then charged in an amount of 10 ml (4.95-5.20 g) into a Pyrex reactor. The products were analyzed chromatographically using the conditions given in [9]. The principal condensation products of the aldehyde on all of the catalysts were 2-ethylhexenal and water. The catalyzate contained small amounts of butyl butyrate (0.3-1.0%), and also butanol and butyric acid, which were apparently formed as the result of the hydrolysis of the ester. The acid was absent in the products in the case of NaY (pH 9.7) and KNaY at 200°, which is explained by its being bound by the basic zeolites. The latter can be one of the reasons for the decrease in the activity of the samples with time (Fig. 1).

In the presence of NdNaY and HNaY, and also NaY, at temperatures above 200°, was observed the progress of side reactions for the decomposition of the starting aldehyde and 2-ethylhexanal, which were accompanied by considerable gas formation, especially in the first 10-40 min of catalyst operation.

When based on their activity in the crotonic condensation, the investigated catalysts can be arranged in the order (Table 1): KNaY > NaY (pH 9.7) ~ 5% NiO/NaY > NaY (pH 7.7) > NdNaY > HNaY. On the basic zeolites the total conversion of the aldehyde and the yields of 2-ethylhexanal are higher than on acid catalysts (HNaY and NdaY). The latter are more active in the side reactions (decomposition, hydrogen redistribution, etc.), and lower their activity more rapidly (see Fig. 1). A highly stable catalyst was zeolite NaY (pH 9.7), while KNaY was a highly active catalyst. The conversion of the butyraldehyde and the yield of 2-ethylhexenal, when based on the starting NaY sample, decreased slightly after washing it to pH 7.7 or after running several experiments (washing the reaction mixture with NaOH solution and, in particular, one of the products with water). This gives reason to believe that the catalytic action is inherent to the zeolites themselves, and not to the adsorbed alkali, in which connection their properties depend on the nature of the cation. The addition of 5% NiO is practically without effect on the properties of the NaY sample. In contrast to Nd_2O_3 [10], dipropyl ketone was not obtained on zeolite NdNaY.

We attempted the one-step synthesis of 2-ethylhexanol from butyraldehyde and H_2 in the presence of the two-component catalyst 4% Ni/NaY (zeolite NaY failed to exhibit a hydrogenating activity even at 250°, Table 1). However, in this case, together with isooctanol, we obtained butanol, 2-ethylhexanal, 2-ethylhexenal and water, the yield of which changed with time (Fig. 2). The yields of the condensation products increased with decrease in the catalyst activity in the hydrogenation of the aldehyde to butanol, in which connection the conversion of butyraldehyde to 2-ethylhexanol and 2-ethylhexanal was at a maximum after 2.5 and 5 h of catalyst operation, respectively, while the conversion to 2-ethylhexenal increased up to 9 h and then remained constant. The total degree of aldehyde conversion in 12 h dropped from 90 to 40%. The above-mentioned relationships are apparently associated with a difference in the adsorption coefficients of the starting aldehyde and the transformation products, and can change when the temperature and pressure are varied.

CONCLUSIONS

1. On the zeolites NaY, KNaY, HNaY and NdNaY, at 150-250°, butyraldehyde undergoes mainly the crotonic condensation with the formation of 2-ethylhexenal. The most active catalyst is KNaY, the most stable is NaY, and the least selective are HNaY and NdNaY.

2. Butanol, 2-ethyl-1-hexanol, 2-ethylhexanal, and 2-ethylhexenal are obtained in the presence of 4% Ni/NaY in a hydrogen atmosphere, the ratio in the yields of which changes during the course of catalyst operation.

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