# A STUDY OF THE CATALYTIC PROPERTIES OF SYNTHETIC ZEOLITES IN THE DEHYDRATION OF BUTANE-1, 4-DIOL

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A study of the catalytic dehydration of butane-1, 4-diol in the presence of synthetic zeolites—NaX, CaX, HNaA, HNaX, and DcX—has shown that the best catalysts for the preparation of tetrahydrofuran (THF) are HNaX and DcX. The maximum yield of tetrahydrofuran (98%) was obtained on HNaX and DcX at 240° C with a space velocity of 0.7 $hr^{-1}$ (ml/ml · hr).

This work deals with the problem of the catalytic dehydration of butane-1, 4-diol on various forms of synthetic zeolites of types X and A for the preparation of tetrahydrofuran (THF) and the determination of the commensurability of the inlet windows of the zeolites with the critical dimensions of the molecules.

The method that we have proposed for the preparation of THF attracts attention because the desired product is obtained in high purity (100%) with high yield (98%). In order to find the optimum reaction conditions, experiments were carried out at various temperatures (from 200° to 350° C) and various space velocities of feed of the butanediol to the reactor. In the experiments with the hydrogen forms of the zeolites, temperatures above 300° C are not recommended because of decationization.

In order to determine the influence of the rate of feed of the butane-1, 4-diol on dehydration and ring closure to THF, it was varied from 0.5 to 1.0 $hr^{-1}$. The maximum yield of THF was found at a velocity of 0.7 $hr^{-1}$. After each experiment, the catalyst was purged at the reaction temperature with nitrogen that had been dried with a synthetic zeolite. The results are given in the table.

At a temperature of 200–280° C, the catalysates obtained on NaX, CaX, and HNaA zeolites were found to contain unchanged butane-1, 4-diol, in addition to THF. With an increase in the temperature of the experiment above 300° C, the yield of liquid catalysates decreased because of a cracking reaction. In experiments at temperatures above 320° C on the NaX and CaX forms of the zeolites, but-1-en-4-ol (identified by its physical constants) [1] was isolated from the catalysate in addition to THF and unchanged butane-1, 4-diol.

On the catalysts HNaX and DcX (Dc = decationized) at 240° C, the dehydration of butane-1, 4-diol gave only THF. At 240–260° C and a space velocity of 0.7 $hr^{-1}$ these catalysts had an activity of 100% and an exceptionally high selectivity in the formation of THF.

The lowest catalytic activity in the dehydration of butane-1, 4-diol was shown by the zeolite HNaA. On this zeolite the degree of dehydration at 240° C was 20.3%, rising to 46.4% at 300° C. In all probability, the low activity of HNaA is explained by the small dimensions of the inlet windows (4–5 Å) into the cavities of the zeolite, since in zeolites the catalytic reactions take place mainly in the intracrystalline cavities. The dimensions of the windows of the HNaA zeolite prevent the passage into them of the molecules of butane-1, 4-diol, the critical diameter of which is approximately 7 Å. It has also been established that the catalytic activity of a type X zeolite is affected by the nature of the ion-exchanged cation, in addition to the size of the inlet windows. Thus, NaX and HNaX have almost the same pore dimensions, but the dehydration of butane-1, 4-diol on them takes place to different extents.

The duration of the effect of the catalyst HNaX under the conditions ensuring the maximum yield of THF was studied. The catalyst worked for 6 hr with practically no change in activity, but after 14 hr the yield of THF had fallen from 98 to 82%. After the catalyst had been blown with dry air at 400° C for 2 hr, its activity rose almost to the original level.

Zeolites in the form of granules manufactured on the semi-industrial scale are supplied mainly with binders. Consequently, we also carried out the dehydration of the butane-1, 4-diol on granules containing binders. It was found that when HNaX was used as catalyst, the addition of a binder did not change the course of the reaction. In the case of HNaA, however, the binder raised the degree of dehydration, and the yield of THF increased by 22.8%. The increase in the yield of THF in this case is explained by the fact that the binder—kaolin—is a dehydration catalyst which, when added to the HNaA catalyst, increases its catalytic activity.

The formation of gas takes place on the catalysts NaX and CaX at 260° C and on the hydrogen and decationized forms at 280° C, and the amount of gaseous products increases with a rise in the temperature. (The analysis of the gaseous products was carried out on a KhL-3 chromatograph by the method that we have described previously [2]). The gas contained 30–35 wt. % of propylene, which could be formed simultaneously with formaldehyde by the cleavage of the terminal C—C bond of but-1-en-4-ol and the redistribution of the hydrogen. But-1-ene and but-2-ene were also found (30%); these could be formed by the partial hydrogenation of butadiene by the hydrogen liberated in the decomposition of the formaldehyde. With a rise in the temperature of the reaction, carbon monoxide (3–4%) and hydrogen (11–16%) appeared in the gases. Among the diene hydrocarbons, butadiene was identified (19–25%).

Dehydration of Butane-1, 4-diol on Various Forms of Synthetic Zeolite

| Experiment number | Catalyst | Temperature of the experiment, °C | Space velocity, hr$^{-1}$ | Degree of dehydration, % | Yield of tetrahydrofuran, % |
|---|---|---|---|---|---|
| 1 | NaX | 200 | 0.5 | 67.1 | 66.5 |
| 2 | NaX | 220 | 0.5 | 72.3 | 70.9 |
| 3 | NaX | 240 | 0.5 | 77.9 | 76.3 |
| 4 | NaX | 260 | 0.5 | 82.1 | 79.6 |
| 5 | NaX | 280 | 0.5 | 85.7 | 82.5 |
| 6 | NaX | 300 | 0.5 | 88.9 | 80.0 |
| 7 | NaX | 320 | 0.5 | 94.5 | 78.4 |
| 8 | NaX | 350 | 0.5 | 98.4 | 73.1 |
| 9 | NaX | 280 | 0.7 | 85.9 | 83.0 |
| 10 | NaX | 280 | 1.0 | 81.8 | 81.2 |
| 11 | CaX | 220 | 0.7 | 73.4 | 72.0 |
| 12 | CaX | 240 | 0.7 | 80.2 | 79.1 |
| 13 | CaX | 260 | 0.7 | 85.1 | 82.1 |
| 14 | CaX | 280 | 0.7 | 91.8 | 83.4 |
| 15 | CaX | 300 | 0.7 | 93.3 | 81.2 |
| 16 | CaX | 350 | 0.7 | 99.0 | 72.0 |
| 17 | HNaX | 220 | 0.7 | 93.2 | 92.2 |
| 18 | HNaX | 240 | 0.7 | 100.0 | 98.0 |
| 19 | HNaX | 260 | 0.7 | 100.0 | 97.0 |
| 20 | HNaX | 280 | 0.7 | 100.0 | 96.1 |
| 21 | HNaX | 300 | 0.7 | 100.0 | 94.9 |
| 22 | HNaX | 240 | 1.0 | 98.4 | 97.3 |
| 23 | DcX | 220 | 0.7 | 94.0 | 92.9 |
| 24 | DcX | 240 | 0.7 | 100.0 | 98.0 |
| 25 | DcX | 260 | 0.7 | 100.0 | 97.1 |
| 26 | DcX | 280 | 0.7 | 100.0 | 96.4 |
| 27 | HNaX binder | 220 | 0.7 | 95.2 | 93.6 |
| 28 | „ | 240 | 0.7 | 100.0 | 98.0 |
| 29 | HNaX | 260 | 0.7 | 100.0 | 97.6 |
| 30 | HNaA | 240 | 0.7 | 20.3 | 10.6 |
| 31 | HNaA | 260 | 0.7 | 32.6 | 30.3 |
| 32 | HNaA | 300 | 0.7 | 46.4 | 44.1 |
| 33 | HNaA binder | 300 | 0.7 | 78.3 | 66.9 |

## EXPERIMENTAL

**Preparation of the catalysts.** As catalysts we used NaX and CaX synthetic catalysts in the form of powders (samples from the Gor'kii Experimental Base of VIINP [All-Union Scientific-Research Institute for the Treatment of Petroleum and Natural Gas and the Preparation of Synthetic Liquid Fuel]) and the types HNaX, HNaA, and DcX which we synthesized ourselves. All the catalysts mentioned above were prepared without a binder, and the HNaX and HNaA types were also studied with a binder—kaolin, 20%. From the powdered synthetic zeolites, tablets with dimensions of 3 × 4 mm were formed by pressing. The hydrogen forms of the synthetic zeolites of types X and A were obtained by means of the ion-exchange reaction between NaX and NaA synthetic zeolites and 0.1 N ammonium chloride solution. The zeolites were treated with the ammonium chloride solution five times. The solid matter that was filtered off was dried in a thermostated oven at 120° C. At the end of the ion-exchange process, the catalyst was dried at 300° C for 5 hr. By heating to 300° C, the ammonia was driven off from the zeolite, giving the hydrogen form. The initial NaX zeolite contained 10.8% sodium and the NaA zeolite 12.6%. After treatment with ammonium chloride, the amounts of sodium in the zeolites were for HNaX about 2.7% and for HNaA about 4.5%. To obtain the decationized catalyst, the hydrogen form of the zeolite was heated at 500° C for 5 hr.

X-ray structural analysis of the forms obtained showed that the crystal structures of all the forms of zeolites synthesized were retained, and after the dehydration reaction structure had not changed significantly.

**Dehydration of butanediol.** The dehydration of butanediol to tetrahydrofuran was carried out in a continuous-flow apparatus at atmospheric pressure. The length of the reactor was 100 cm and its diameter, 20 mm. The reactor was charged with a bulk volume of 70 $cm^3$ of catalyst. The constancy of the rate of feed of the butane-1, 4-diol was maintained automatically by means of a syringe and a reducing valve. In each experiment 20 g of butane-1, 4-diol was passed. The catalysate obtained was collected in a receiver provided with a reflux condenser and in a trap cooled with ice.

The initial butane-1, 4-diol, after distillation through a column with an efficiency of 52 theoretical plates, had bp 120° C (10 mm), $n_D^{20}$ 1.4480, $d_4^{20}$ 1.018.

Bourns and Nichols [3] have stated that in the presence of alumina butane-1, 4-diol forms propylene and formaldehyde. To detect any formaldehyde formed in our experiments, the latter was trapped by cooling. At the end of the experiments the specific gravity of the aqueous solution proved to be 1.010 (the solution smelled of formaldehyde), which corresponds to 3.7 g of formaldehyde in the solution [4].

The reaction products were dried and fractionated through a column with an efficiency of 52 theoretical plates. The THF was characterized by the following physical indices: bp 64–65° C (742 mm), $d_4^{20}$ 0.8889, $n_D^{20}$ 1.4080. The THF was identified by gas-liquid chromatography. Chromatographic analysis showed that the THF was 100% pure.

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