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Abstract

Full Text

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DEHYDRATION OF PRIMARY DODECYL ALCOHOL OVER MAGNESIUM SULFATE

In previously published works ($^{1-3}$), the influence of radiation from radioactive isotopes introduced into the catalyst (S^{35}, Ca^{45}) on the process of dehydration of cyclohexanol over mixtures of $MgSO_4 + Na_2SO_4$ and $MgSO_4 + CaCl_2$ was investigated. A change was observed in the rate of the catalytic reaction, as well as in the magnitudes of the activation energies of the process. In the present work the effect of β-radiation from S^{35} and of external electron irradiation on the dehydration reaction of a primary aliphatic alcohol (n-dodecanol) over magnesium sulfate was studied. The effect of electron irradiation on the isomerization of the reaction products was also investigated.

Experiments were carried out in a flow-type catalytic apparatus (^{4}). Dodecanol was fed at a space velocity of 0.16 min^{-1} in the case of its dehydration over radioactive catalysts and 0.25 min^{-1} in experiments with external irradiation. The amount of catalyst was 0.4–0.6 g, which corresponds to approximately 1 ml of bulk volume. The dehydration reaction was conducted in the temperature range 250–450°. Magnesium sulfate was prepared by dissolving metallic magnesium in dilute H_2SO_4, reagent grade. For the preparation of radioactive catalysts, radioactive sulfuric acid labeled with S^{35} was used. The magnesium sulfate solution was evaporated to dryness, and the resulting residue was calcined at a temperature of 400° for 2 hr in air. The results of analysis of the preparation (found 65.72% SO_3, calculated for $MgSO_4$ 66.51% SO_3) indicate a salt of composition $MgO \cdot 0.96\, SO_3$. In the present study the following $MgSO_4$ samples were used: 1) a nonradioactive preparation, 2) an $MgSO_4$ preparation with a specific activity of 16.6 mCi/g, 3) the same with an activity of 19.1 mCi/g. In experiments with external irradiation, the source of fast electrons was a direct-acceleration electron tube at 1 MeV, powered by a cascade valve-capacitor voltage multiplier. An electron beam with an energy of 0.8 MeV passed into the reactor with the catalyst through a beryllium membrane 0.3 mm thick. The dose, determined by the ferrous sulfate method, was of the order of 10^{20} eV/g over the experimental time of 10 min.

The total amount of unsaturated hydrocarbons formed according to the scheme

$$C_{12}H_{25}OH - H_2O \to C_{12}H_{24},$$

was determined by bromometric titration. Identification of the dehydration products was carried out by infrared spectrophotometry. Absorption spectra were taken of solutions of undecene-1, undecene-5, and dodecene-1 of various concentrations in mixtures—

IR absorption spectrum of the catalyst obtained during dehydration of *n*-dodecanol over magnesium sulfate. Absorption bands: 1, 2 —*n*-dodecanol; 3, 5 —α-dodecene; 4 —trans-dodecene.

Fig. 1. IR absorption spectrum of the catalyst obtained during dehydration of *n*-dodecanol over magnesium sulfate. Absorption bands: 1, 2 —*n*-dodecanol; 3, 5 —α-dodecene; 4 —trans-dodecene.

with *n*-dodecanol on an IKS-14 infrared spectrophotometer; the α-isomer gives an absorption band at 912 cm^{-1}, and the trans-isomer at 965 cm^{-1}, which is in complete agreement with the literature data (5). In determining the α-isomer, a calibration curve was taken each time for mixtures of *n*-dodecanol with α-dodecene. The linear dependence of the optical density of the solutions on the concentration of α-dodecene indicated the possibility of using the straight line as a calibration curve. Fig. 1 shows the infrared absorption spectrum of the catalyst obtained in the dehydration of *n*-dodecanol over magnesium sulfate.

Dehydration of *n*-dodecanol over magnesium sulfate. **a:** 1—$MgSO_4$, 2—$MgSO_4$, 16.6 mCi/g, 3—$MgSO_4$, 19.1 mCi/g; **b**—under external electron irradiation: I —without irradiation, II—under irradiation. Dependence of the yield of the α-isomer on the radioactive irradiation of the catalyst. 1—$MgSO_4$, 2—$MgSO_4$, 16.6 mCi/g, 3—$MgSO_4$, 19.1 mCi/g.

Fig. 2. Dehydration of *n*-dodecanol over magnesium sulfate. **a:** 1—$MgSO_4$, 2 —$MgSO_4$, 16.6 mCi/g, 3—$MgSO_4$, 19.1 mCi/g; **b**—under external electron irradiation: I—without irradiation, II—under irradiation.

Fig. 3. Dependence of the yield of the α-isomer on the radioactive irradiation of the catalyst. 1—$MgSO_4$, 2—$MgSO_4$, 16.6 mCi/g, 3—$MgSO_4$, 19.1 mCi/g.

The catalytic activity of $MgSO_4$ in the dehydration reaction of primary dodecyl alcohol decreases when S^{35} is introduced into the catalyst, compared with non-radioactive magnesium sulfate (Fig. 2a). External irradiation with electrons during the reaction had no effect (Fig. 2b).

In previous work we used, for the cyclohexanol dehydration reaction, a mixture of $MgSO_4 + Na_2SO_4$ salts as the catalyst. The yield of cyclohexene increased with increasing specific radioactivity of the catalyst. Since the study of the dehydration of *n*-dodecanol over radioactive catalysts led to opposite results in comparison with the dehydration of cyclohexanol, the dehydration of cyclohexanol over radioactive magnesium sulfate was investigated. The experiments were carried out in a vertical furnace using a reactor of smaller dimensions. As can be seen from the results obtained, in this case the yield of unsaturated hydrocarbons increases:

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Dehydration of cyclohexanol over $MgSO_4$

Nonradioactive catalyst, 0.1 g

Temperature, °C	283	348	385	425
Yield of unsaturated hydrocarbons, %	13	22	25	29

Radioactive catalyst, 0.1 g

Temperature, °C	295	350	388	425
Yield of unsaturated hydrocarbons, %	10	26	36	54

It may be concluded that the structure of the alcohol molecule whose vapors are adsorbed on the catalyst surface is of great importance in carrying out heterogeneous catalytic processes, especially with the use of radioactive catalysts.

Fig. 3 presents data on the isomerization of olefins formed during the dehydration of *n*-dodecanol on nonradioactive and radioactive preparations of magnesium sulfate. The results show that the isomerization process, like the dehydration reaction itself, proceeds more slowly on radioactive catalysts. In this case, a change in the specific radioactivity of magnesium sulfate by 2.5 mCi/g has a stronger effect on the dehydration of dodecanol than on the isomerization of the unsaturated hydrocarbons obtained.

As already noted, the yield of olefins in the dehydration of *n*-dodecanol under irradiation with fast electrons does not change. However, irradiation with electrons during the reaction has a noticeable effect on the isomerization of unsaturated hydrocarbons; namely, the yield of the α-isomer decreases appreciably (Fig. 4).

Yield of the α-isomer under external electron irradiation. Dose 10^{20} eV/g in 10 min.: 1—without irradiation, 2—under irradiation.

Fig. 4. Yield of the α-isomer under the action of external electron irradiation. Dose 10^{20} eV/g in 10 min.: 1—without irradiation, 2—under irradiation.

Thus, when a radioactive catalyst containing S^{35} is used, the yield of the α-isomer increases owing to a decrease in olefin isomerization. The action of external irradiation with fast electrons produces the opposite effect. These observations make it possible to suppose that the surface charge of the catalyst affects the catalytic processes of alcohol dehydration and olefin isomerization. Under β-particle emission the catalyst surface becomes positively charged, whereas under external electron irradiation it becomes negatively charged. It is possible that the isomerization process proceeds by a carbonium-ion mechanism

$$CH_3-(CH_2)_8-CH_2-\overset{\oplus}{C}H=\overset{\ominus}{C}H_2 \xrightarrow{+H^+} CH_3-(CH_2)_8-CH_2-\overset{\oplus}{C}H-CH_3 \rightarrow$$

$$\rightarrow CH_3-(CH_2)_8-\overset{\oplus}{C}H-CH_2-CH_3 \xrightarrow{-H^+} CH_3-(CH_2)_8-CH=CH-CH_3$$

and the resulting positive carbonium ion interacts more readily through its hydrogen atom with the negatively charged surface of the catalyst.

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