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1962

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Abstract

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PHYSICAL CHEMISTRY

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EFFECT OF IONIZING RADIATION ON THE CATALYTIC ACTIVITY OF ALUMINUM OXIDE IN THE DEHYDRATION REACTION OF *n*-DODECYL ALCOHOL

Aluminum oxide is among the most active catalysts for the dehydration of alcohols ([1-5]). Several points of view exist for explaining the mechanism of this reaction. However, they all reduce to assumptions concerning the formation on the catalyst surface of unstable compounds: in some cases, radicals that can react with neighboring molecules ([6,7]); in others, compounds of the ether type ([4,5]); and, finally, carbonium ions ([1-3]). The latter also explains the phenomenon of isomerization of the double bond in olefins—the products of alcohol dehydration. It is known that the catalytic activity of aluminum oxide in various heterogeneous processes changes after its irradiation. The increase in the catalytic activity of Al_2O_3 observed for the deuterium-hydrogen exchange reaction as a result of the action of slow neutrons, γ-rays, and α-particles is attributed to the formation of a large number of defects in the crystal lattice of Al_2O_3 ([9,10]).

The isomerization of olefins over an aluminosilicate catalyst decreases ([11,12]), while over silica gel it increases ([13]), if the catalyst has previously been subjected to ionizing radiation.

In a number of examples it has been shown that the introduction of significant amounts of radioactive isotopes into catalysts changes the rate of such heterogeneous processes as the dehydration of alcohols and the isomerization of unsaturated hydrocarbons ([14-16]).

In the present work, the effect of ionizing radiation on the dehydration of *n*-dodecyl alcohol and on the isomerization of the reaction products over aluminum oxide was studied. The catalyst was used in the form of grains 1-2 mm in size and had the following composition: 99.87% Al_2O_3; 0.11% Fe_2O_3; and traces of SiO_2. The specific surface area of the aluminum oxide was 245 m^2/g. *n*-Dodecanol had d_4^{30} 0.8286; n_D^{30} 1.4390; MR_D calculated 59.14, found 59.19.

Three series of experiments were carried out.

1. Aluminum oxide was exposed to slow neutrons with a flux intensity of $\sim 0.8 \cdot 10^{13}/cm^2 \cdot sec$ and γ-rays in a nuclear reactor, and was then used in

Fig. 1. Dehydration of n-dodecyl alcohol over Al2O3. Horizontal apparatus. 1 –initial Al2O3; samples irradiated on the reactor: 2–5 days; 3–10 days; 4–30 days

Figure 1: Fig. 1. Dehydration of n-dodecyl alcohol over Al2O3. Horizontal apparatus. 1–initial Al2O3; samples irradiated on the reactor: 2–5 days; 3–10 days; 4–30 days

the catalytic reaction. The characteristics of the catalysts are presented in Table 1.

Table 1

Irradiation of Al_2O_3 in a nuclear reactor. Neutron flux intensity $\sim 0.8 \cdot 10^{13}/\mathbf{cm}^2 \cdot \mathbf{sec}$

No. of preparation	Duration of irradiation in the reactor, days	Absolute activity after removal from reactor, mCi/g for Fe^{59} and Na^{24}	Absolute activity of aged preparations, mCi/g for Fe^{59}	Duration of aging, days	Yield of unsaturated hydrocarbons at 340°, %	Content of α-isomer in the mixture of olefins at 340°, %
1	–	–	–	–	52	68
2	5	0.130	0.001	35	46	50
3	10	0.140	0.002	43	49	60
4	30	0.683	0.002	270	36	–

2. The dehydration reaction was carried out over a mixture of $Al_2O_3 + CaCl_2$. The aluminum oxide was impregnated with a $CaCl_2$ solution, dried, and heated for 2 h at 400°. Some of the experiments were performed with preparations containing the radioactive isotope Ca^{45} (β-emitter, $E_{max} = 0.255$ MeV).

3. The catalyst and dodecanol vapors during the reaction were irradiated with fast electrons with an energy of 800 keV, obtained in an accelerator tube. Data on the catalysts used in this case are given in Table 2.

Fig. 1. Dehydration of *n*-dodecyl alcohol over Al_2O_3. Horizontal apparatus. 1 –initial Al_2O_3; samples irradiated in the reactor: 2–5 days; 3–10 days; 4–30 days.

Fig. 2. Yield of the α-isomer upon irradiation of the catalyst in the reactor. 1 –initial Al_2O_3; irradiated samples: 2–5 days; 3–10 days.

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Figure 2: Fig. 2. Yield of the alpha-isomer upon irradiation of the catalyst in the reactor. 1—initial Al2O3; irradiated samples: 2—5 days; 3—10 days

Fig. 3

Figure 3: Fig. 3

For the experiments, a flow-type catalytic apparatus was used [7]. When working with Al_2O_3 irradiated in the reactor, dodecyl alcohol was fed at a space velocity of 0.16 min^{-1}; the catalyst weight was 0.5 g. In experiments with introduced $CaCl_2$, the space velocity was 0.68 min^{-1} with a catalyst charge of 0.15 g. The degree of conversion of *n*-dodecanol was determined for the catalyst collected during the second 15 min after the start of the experiment.

Table 2

Dehydration of *n*-dodecanol over Al_2O_3 + 19.4% $CaCl_2$ under the action of radioactive radiation and external electron irradiation at 350°

No. of preparation	Absolute activity, mCi/g	Dose absorbed by the catalyst upon electron irradiation, eV/g	Change in degree of conversion relative to nonradioactive catalyst, Al_2O_3 + $CaCl_2$, %	Content of α-isomer in the olefin mixture, %
1	–	–	–	28
2	39.1	–	155	100
3	–	10^{20}	67	64
4	39.1	10^{20}	39	53

As can be seen from the results obtained (Fig. 1), preliminary irradiation of aluminum oxide with neutrons causes a decrease in its catalytic activity. The greatest negative effect was observed for the preparation that had remained for 30 days in the reactor, despite prolonged holding after irradiation (Table 1). Isomerization of the reaction products as a result of neutron irradiation of the catalyst increases (Fig. 2).

Treatment with slow neutrons does not change the magnitude of the surface area of Al_2O_3. Thus, a sample irradiated for 5 days had a specific surface area of 249 m^2/g. Evidently, under the action of slow neutrons the number of active centers in the catalyst decreases, and a kind of "smoothing" of its surface occurs. The longer this treatment is carried out, the more strongly the catalytic activity of Al_2O_3 decreases. The induced radioactivity that arises is undoubtedly too small to exert its own effect. These same causes apparently lead to the fact that electrons

Fig. 3. Dehydration of *n*-dodecyl alcohol over Al_2O_3 + 19.4% $CaCl_2$. Vertical apparatus.

Fig. 4

Figure 4: Fig. 4

1 $-Al_2O_3$ + 19.4% $CaCl_2$; 2 $-Al_2O_3$ + 19.4% $CaCl_2$ (specific activity 39.1 mCu/g); 3 $-Al_2O_3$ + 19.4% $CaCl_2$ under external irradiation with electrons, dose 10^{20} eV/g; 4 $-Al_2O_3$ + 19.4% $CaCl_2$ (specific activity 39.1 mCu/g) under external irradiation with electrons, dose 10^{20} eV/g.

Fig. 4. Yield of the α-isomer in the dehydration of *n*-dodecyl alcohol over Al_2O_3 + 19.4% $CaCl_2$.
1 –nonradioactive catalyst; 2 $-Al_2O_3$ + 19.4% $CaCl_2$ (specific activity 39.1 mCu/g); 3 –nonradioactive catalyst under external irradiation with electrons, dose 10^{20} eV/g; 4 $-Al_2O_3$ + 19.4% $CaCl_2$ (specific activity 39.1 mCu/g) under external irradiation with electrons, dose 10^{20} eV/g.

of the double bond, not retained by charges on the catalyst surface, already in the course of the reaction readily migrate toward the middle of the molecule. A decrease in catalytic activity was previously observed by us also in the dehydration of *n*-decyl alcohol over alumina irradiated in a nuclear reactor ([16]).

In carrying out the dehydration reaction of *n*-dodecanol over a catalyst of composition Al_2O_3 + $CaCl_2$, with a molar ratio of 1.00 Al_2O_3 : 0.18 $CaCl_2$, a decrease in the degree of conversion of the alcohol was noted in comparison with pure alumina. Introduction of a radioactive isotope into the catalyst and irradiation with fast electrons during the reaction increase the rate of the catalytic process (Figs. 3 and 4). The results of experiments with the radioactive catalyst Al_2O_3 + $CaCl_2$ under the simultaneous action of fast electrons made it possible to decide unambiguously the question of the influence of surface charge on the catalytic process. Upon emission of β-particles, the surf-

the activity of the catalyst $Al_2O_3 + CaCl_2$ acquires localized positive charges, which evidently facilitates the initial stage of the reaction—the adsorption of alcohol vapor on alumina. Irradiation of the radioactive catalyst with electrons from outside will lead to neutralization of the positive charges that arise and should consequently reduce the rate of the process under study. Indeed, in Fig. 3, curve 4 lies below curve 2. It should be noted that the action of fast electrons on the nonradioactive catalyst $Al_2O_3 + 19.4\% CaCl_2$ increases the degree of conversion of *n*-dodecanol (curve 3, Fig. 3). Apparently, electron bombardment produces excitation and ionization of atoms on the surface of Al_2O_3. It is possible that localized charges of different sign arise simultaneously, including those favoring acceleration of the catalytic process.

Isomerization of the reaction products decreases when radioactive or external electron radiation acts on the catalyst and on the vapors of *n*-dodecanol (Fig. 4). The yield of α-dodecene (Fig. 4) proves to be greatest in the case of the radioactive catalyst: a 100% content of the α-isomer in the olefin mixture is retained up to a temperature of 420°. A similar effect was observed in the dehy-

dration of *n*-dodecanol over $MgSO_4$ (15), but with a lower yield of unsaturated hydrocarbons than over nonradioactive magnesium sulfate. The occurrence of positive charges on the catalyst surface probably hinders the movement of electrons along the chain of carbon atoms, which causes displacement of the double bond.

Irradiation with fast electrons has a less pronounced effect on the catalytic process. Electron bombardment of the radioactive catalyst sharply increases the rate of isomerization, from which it may once again be concluded that positive charges on the catalyst surface play an exceptionally important role in inhibiting the isomerization process.

Thus, the introduction of a radioactive emitter into Al_2O_3 and the use of external electron irradiation make it possible to influence effectively the rate of dehydration of *n*-dodecanol and the composition of the products obtained.

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Received
6 I 1962

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