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## Abstract

## Full Text

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## PHYSICAL CHEMISTRY

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## EFFECT OF VARIOUS TYPES OF RADIATION ON THE PROCESS OF CATALYTIC DEHYDRATION OF *n*-DECYL ALCOHOL

A large number of works have been published devoted to the action of radiation on catalysts of heterogeneous reactions. The influence of  $\gamma$ -rays, neutrons, streams of positive ions, and other types of radiation has been investigated. In some cases the activity of catalysts increased after irradiation (<sup>1-5</sup>), in others it decreased (<sup>6,7</sup>), and in still others it remained unchanged (<sup>8</sup>). Work in recent years has established the important role of radioactive emitters introduced directly into catalysts (<sup>9-11</sup>). However, in the literature there are almost no works in which the effect of different types of radiation on any catalytic process has been compared. The aim of the present investigation was to study this question using, as an example, the dehydration reaction of *n*-decyl alcohol over  $\text{Al}_2\text{O}_3$ . The aluminum oxide used had the following composition:  $\text{Al}_2\text{O}_3$ —99.87%;  $\text{Fe}_2\text{O}_3$ —0.11%;  $\text{SiO}_2$ —traces.

The investigation was carried out in three directions:

- 1) The catalyst was treated in a uranium reactor with neutrons and  $\gamma$ -rays for various periods of time, and then the catalytic process was carried out. In this case, under the action of slow neutrons with a flux intensity of  $\sim 0.8 \cdot 10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$ , certain impurities present in the aluminum oxide were activated and radioactive isotopes were formed— $\text{Na}^{24}$ ,  $\text{Fe}^{59}$ , and  $\text{Cu}^{64}$  (Fig. 1). Aluminum and oxygen do not form long-lived radioisotopes under these conditions, nor does silicon, which was present in the preparation as a minor impurity. The distribution of induced activity was as follows:  $\text{Na}^{24}$ —98%,  $\text{Fe}^{59}$ —2%,  $\text{Cu}^{64}$ —traces. The catalytic activity was studied 3 days after removal of the catalyst from irradiation in the reactor.
- 2) The radioactive isotope  $\text{Ce}^{144}$  was introduced into aluminum oxide in the form of  $\text{CeCl}_3$ , and, in parallel, the reaction was carried out on a non-radioactive catalyst with the addition to it of stable  $\text{CeCl}_3$ . However, it was not possible to prepare catalysts of one and the same chemical com-

position. The radioactive  $\text{CeCl}_3$  contained chlorides of Ca, Ba, Cr, Mn, Mg, and Fe; when the aluminum oxide was impregnated with a solution of  $\text{CeCl}_3$ , the amount of these impurities reached 0.005%, calculated per 1 g of  $\text{Al}_2\text{O}_3$ . The nonradioactive preparation was made with 0.005%  $\text{CeCl}_3$  of “chemically pure” grade per 1 g of  $\text{Al}_2\text{O}_3$ .

- 3) During the reaction, the catalyst and alcohol vapors were irradiated with fast electrons. Their source was a 1 MeV accelerating electron tube. The energy of the electrons at the catalyst surface was 760 keV. The dose, determined by the ferrosulfate method, was of the order of  $10^{20}$  eV/g in 10 min.

The characteristics of the catalysts irradiated in the reactor are given in Table 1. The absolute activity was measured with a gas-flow  $4\pi$ -counter. The degree of conversion of *n*-decyl alcohol was determined by the bromine-number method. The experiments were carried out in a horizontal-type apparatus, volume

the rate of *n*-decyl alcohol was  $0.32 \text{ min}^{-1}$ , and the catalyst weight was 0.3 g. The results of the experiments performed are presented in Fig. 2, A.

**Table 1**

**Irradiation of  $\text{Al}_2\text{O}_3$  in the reactor**  
(neutron flux intensity  $0.8 \cdot 10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$ )

Experiment no.	Duration of irradiation in the reactor, days	Absolute activity, mCi/g	Yield of decylene from dehydrated hydrogen at $340^\circ$ , %	Change in the degree of conversion relative to unirradiated $\text{Al}_2\text{O}_3$ , %
1	—	—	45	—
2	1	0.09	28	−38
2'	1 (aged 49 days)	0.0002	37	−18
3	5	0.13	42	−7
4	10	0.14	51	+13

Aluminum oxide irradiated with neutrons for 1 day showed a sharp decrease in catalytic activity (by 1.5–2 times in the temperature range  $275\text{--}350^\circ$ ). Its induced radioactivity was insignificant (0.09 mCi/g). As is known from previous studies<sup>(9)</sup>, at such a low level of specific radioactivity of catalysts no change in their catalytic activity due to the resulting radioactive radiation is observed.

**Fig. 1.** Gamma spectrum of a catalyst aged after irradiation in the reactor for 3 days (A) and 30 days (B).

1 —catalyst ( $\text{Al}_2\text{O}_3$ ), 2 — $\text{Na}^{24}$  (A) and  $\text{Fe}^{59}$  (B)

Fig. 1. Gamma spectrum of a catalyst aged after irradiation in the reactor for 3 days (A) and 30 days (B). 1 –catalyst ( $\text{Al}_2\text{O}_3$ ), 2 –Na24 (A) and Fe59 (B)

Figure 1: Fig. 1. Gamma spectrum of a catalyst aged after irradiation in the reactor for 3 days (A) and 30 days (B). 1 –catalyst ( $\text{Al}_2\text{O}_3$ ), 2 –Na24 (A) and Fe59 (B)

a change in their catalytic activity due to the radioactive radiation produced is not observed. Evidently, bombardment with slow neutrons reduces the number of active centers on the catalyst surface, similarly to what was observed for the sorption capacity of barium sulfate after its irradiation with electrons or positively charged ions<sup>(12)</sup>. Neutron treatment for 5 days also leads to a decrease in the catalytic activity of aluminum oxide, though not such a significant one. Finally, 10 days of irradiation in the reactor somewhat improves the catalytic properties of  $\text{Al}_2\text{O}_3$  in comparison with the unirradiated sample. We believe that under these conditions as well, the observed values of induced radioactivity of the catalyst samples (0.13 and 0.14 mCi/g, respectively) cannot account for the indicated changes in their properties. As noted below, when a foreign radioisotope is introduced into  $\text{Al}_2\text{O}_3$ , even at a specific radioactivity two orders of magnitude higher, the catalytic activity of aluminum oxide increases only slightly.

It should be taken into account that, under prolonged irradiation with slow neutrons, both elements composing aluminum oxide are converted into short-lived radioactive isotopes— $\text{Al}^{28}$  ( $T_{1/2} = 2.3$  min) and  $\text{O}^{19}$

( $T_{1/2} = 29.5$  sec.)—with very high radiation energy. The defects of the crystal lattice that arise during their decay should increase the catalytic activity of the initial preparation. An analogous phenomenon (accumulation of the radiation effect) was observed for solid potassium sulfate as a result of prolonged decay of  $\text{S}^{35}$  in the study of sulfur isotopic exchange in the system  $\text{K}_2\text{SO}_{4\text{tv}}-\text{SO}_{3\text{gas}}$  at high temperature<sup>(13)</sup>. Thus, two factors may exert opposite effects on the catalytic activity of a solid: the formation of defects in the crystal lattice and the appearance of electric charges during radioactive decay, on the one hand; and a decrease in the number of active centers on the surface as a result of a peculiar “polishing” action of radiation<sup>(12)</sup>, on the other. Interesting results were obtained by prolonged aging (49 days) of an  $\text{Al}_2\text{O}_3$  preparation irradiated with neutrons for 1 day. At the comparatively low test temperature ( $280^\circ$ ), the catalytic activity of this sample did not change during aging. It increases rather rapidly with increasing temperature and at  $390^\circ$  approaches the activity of unirradiated alumina. It may be assumed that in this case neutron irradiation was too brief and did not lead to the formation of a significant number of crystal-lattice defects. Heating brings the catalyst surface closer to the normal state, as was observed in the study of the sorption capacity of barium sulfate irradiated with electrons and protons<sup>(12)</sup>.

**Fig. 2.** Dehydration of *n*-decyl alcohol on  $\text{Al}_2\text{O}_3$  in horizontal (A) and vertical

(B) setups.

1— $Al_2O_3$ , 2— $Al_2O_3$  irradiated in the reactor for 1 day, 2'—the same 49 days after irradiation, 3— $Al_2O_3$  irradiated in the reactor for 5 days, 4—the same for 10 days.

B.2— $Al_2O_3 + CeCl_3$  (0.005%), B.3— $Al_2O_3 + Ce^{144}$ , specific activity 11.2 mCi/g, 4,B— $Al_2O_3$  under external electron irradiation. Dose  $10^{20}$  eV/g in 10 min.

The dehydration of decyl alcohol on alumina with an addition of  $Ce^{144}$  and under external irradiation by electrons during the reaction was studied in a vertical catalytic setup. The volumetric flow rate of the alcohol was  $0.68 \text{ min}^{-1}$ . The catalyst weight was 0.15 g. Electron irradiation increases the rate of conversion of decyl alcohol, especially at temperatures of  $250\text{--}300^\circ$  (Fig. 2B). Thus, at  $280^\circ$  the yield of unsaturated hydrocarbons increases 10-fold. With increasing temperature, the annealing of radiation effects produced by fast electrons becomes apparent, and the yield of unsaturated hydrocarbons increases to a lesser degree—at  $390^\circ$ , by only 30%. Evidently, electron bombardment, on the one hand, causes disturbances in the crystal lattice of alumina and, on the other hand, excites the protons present on the catalyst surface, as well as the alcohol molecules, thereby promoting the dehydration reaction.

The degree of conversion of *n*-decyl alcohol on alumina impregnated with a solution of  $Ce^{144}Cl_3$ , despite the fairly high specific radioactivity, increases only slightly in comparison with pure  $Al_2O_3$ . Addition of nonradioactive  $CeCl_3$  to the catalyst gives a more noticeable effect. It is possible that impurities contained in the radioactive  $CeCl_3$  solution exert a poisoning action on the catalyst under study.

Thus, the greatest effect in the reaction studied was produced by irradiation of the catalyst and of the vapors of *n*-decyl alcohol with fast electrons. Ne-

which increase in the catalytic activity of  $Al_2O$  is observed upon introducing a radioactive  $\beta$ -emitter into it. The smallest effect, or even negative results, was produced by irradiating aluminum oxide with neutrons and  $\gamma$ -rays. A more detailed study of the mechanism of radiation catalysis using the dehydration of *n*-decyl alcohol as an example is continuing.

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