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**Abstract**

**Full Text**

## CHEMISTRY

**P. TETENI and L. BABERNICH**

### THE EFFECT OF IRRADIATION ON THE CATALYTIC PROPERTIES OF COPPER

*(Presented by Academician A. A. Balandin, 30 XI 1961)*

The study of the effect of irradiation on the catalytic properties of solids is of theoretical and practical interest. Investigations of this kind may help to solve the question of the relationship between the bulk and surface properties of solids; on the other hand, changes in catalytic properties upon irradiation of catalysts may become a highly effective method of utilizing nuclear radiation.

In the present work the effect of irradiation on the catalytic properties of a copper catalyst in the dehydrogenation reaction of cyclohexane was studied. The catalyst was prepared from copper nitrate by the method described earlier <sup>(1)</sup>. Kinetic experiments were carried out in a flow apparatus. The experimental procedure is described in <sup>(2)</sup>. The extent of conversion of cyclohexane into benzene was determined from the refractive index of the liquid catalyzate. For this purpose an immersion refractometer was used, permitting determination of the refractive index with an accuracy of  $\pm 0.00002$ . Catalyst samples were irradiated in an argon atmosphere in a nuclear reactor with a neutron flux of  $10^{13}$  neutrons/cm<sup>2</sup> · sec. The irradiation time was of the order of 100 hours, so that the integral neutron flux was  $3 \cdot 10^{18}$  neutrons/cm<sup>2</sup>. The specific activity of the samples immediately after irradiation was 2.5-3.5 Cu/g. Catalytic experiments were usually carried out with samples having an activity below 1  $\mu$ Cu/g.

**Table 1**

Data characterizing the catalytic activity of various samples.

Rate of passage of cyclohexane vapor: 11.7 ml/min. Weight of samples: 6 g

No. of samples	$k$ , ml/min (310°C)	$\varepsilon$ , kcal/mol	$k_0$ , ml/min
1	0.040	41.0	$1.36 \cdot 10^{14}$
2	0.050	—	—
3	0.148	17.5	$5.26 \cdot 10^5$
4	0.100	18.1	$5.86 \cdot 10^5$
5	0.376	17.2	$1.36 \cdot 10^6$
6	0.510	20.3	$1.78 \cdot 10^7$
7	0.043	45.7	$1.45 \cdot 10^{15}$

Fig. 1. Arrhenius straight lines for various samples of the copper catalyst (for sample numbers, see Table 1)

Figure 1: Fig. 1. Arrhenius straight lines for various samples of the copper catalyst (for sample numbers, see Table 1)

*Note.* 1—unirradiated sample; 2—sample irradiated for 24 hr; 3,4—samples obtained during 103 hr; 5—sample irradiated by recrystallization of sample 3; 6—sample obtained by recrystallization of sample 4; 7—sample irradiated with  $\gamma$ -rays.

A copper catalyst, as is known from the literature, catalyzes the dehydrogenation of cyclohexane only weakly (<sup>3</sup>). Samples examined before irradiation also showed some, though very weak, catalytic activity with respect to this reaction (Table 1). The value of the apparent activation energy, 41 kcal/mol, was considerably higher than in the case of other catalysts (10–20 kcal/mol for transition metals and 25–30 kcal/mol in the case of oxide catalysts). As a result of neutron irradiation the catalytic activity of copper increased significantly (Table 1). This change is especially clearly expressed in the values of the activation energy of the reaction, which for two different samples decreased to 17.5 and 18.1 kcal/mol.

The observed change in catalytic activity may be caused by: a) structural changes that took place under neutron irradiation; b) radioactivity of the sample; c) a promoting action of micro-

amounts of nickel and zinc formed as a result of the decay of radioactive copper. In the course of the present investigation it was established that the observed change in catalytic activity is not connected with structural changes arising in the catalyst upon irradiation. This is proved by the following facts:

- a) Upon irradiation with  $\gamma$  rays, the catalytic activity of copper did not change. A catalyst sample which, upon irradiation with a cobalt source, had received a total dose of  $7 \cdot 10^8$  rad had practically the same catalytic activity as before irradiation (Table 1). The value of the activation energy of dehydrogenation for this sample proved to be close to the value observed for the unirradiated sample. It should be noted that the energy received by the sample upon irradiation with a cobalt source is approximately only one order of magnitude lower than the energy received by the sample during 100-hour irradiation in the reactor ( $5 \cdot 10^9$  rad).

**Fig. 1.** Arrhenius straight lines for various samples of the copper catalyst (for sample numbers, see Table 1)

- b) The sample irradiated with neutrons was dissolved in nitric acid, and from this solution a new sample was obtained by exactly the method described. The data characterizing the catalytic activity of this sample are given in Table 1. From these data it is evident that the catalytic activity of the

sample did not decrease but, on the contrary, increased as a result of the procedure described, while the activation energy of dehydrogenation remained practically the same as in the case of the neutron-irradiated sample. All this shows that the cause of the changes in catalytic activity cannot be sought in structural changes that took place during irradiation, since all possible strain defects in the lattice that arose upon irradiation should have disappeared as a result of such “recrystallization” of the catalyst.

Thus, the cause of the observed phenomenon may be either the radioactivity of the catalyst or the promoting action of the decay products of radioactive atoms. The solution of this question requires further investigations.

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

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