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## Abstract

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# RADIOACTIVE CATALYSTS

## DEHYDRATION OF CYCLOHEXANOL OVER MAGNESIUM AND SODIUM SULFATES

In recent years, works have appeared in which irradiation with gamma rays or neutrons was used to affect processes of heterogeneous catalysis (1–3).

In contrast to this, in our study the source of ionizing radiation for the reaction of heterogeneous catalysis of gaseous substances was the catalyst itself, containing different amounts of a radioactive isotope, a beta emitter. It was assumed that continuous bombardment by beta particles would have an energetic effect on the processes occurring at the solid-gas boundary (adsorption of reactant molecules on the catalyst, chemical reactions between them, exchange of atoms or, possibly, molecules from the adsorption layer with the boundary gas zone). Also not excluded was the influence of radiation on the structure of the catalyst, in particular a change in its surface, and the radiation-chemical action of the radiation on the gaseous reactants even before their contact with the catalyst.

The object of the study was the reaction of catalytic dehydration of cyclohexanol over magnesium and sodium sulfates, in which sulfur was replaced by varying amounts of radioactive sulfur $S^{35}$.

The investigation was carried out in a flow-type catalytic apparatus with an insert reactor (4), in a horizontal tubular furnace equipped with automatic feed; the temperature was measured by a thermocouple in a sheath located in the catalyst. The cyclohexanol had b.p. 70°/20 mm; $n_D^{30} = 1.4625$; $d_4^{30} = 0.9445$.

Radioactive preparations of $MgSO_4$ were prepared from inactive recrystallized magnesium sulfate (chemically pure) and an addition of sodium sulfate radioactive with respect to sulfur together with stable sodium sulfate (chemically pure) as carrier. The ratio of $S^{35}$ to ordinary sulfur was $1.8 \cdot 10^{-10}$. A weighed portion of magnesium sulfate was dissolved in water, a definite amount of the solution of active sodium sulfate was introduced there as well, and ion exchange took place. The solution was evaporated, and the salt was gradually heated to 400° (5) and kept at this temperature for 1.5 hr. As was established in preliminary experiments, the catalyst prepared in this way was completely dehydrated. To obtain comparable results, radioactive and nonradioactive catalysts were prepared with one and the same content of sodium sulfate, in one case stable (chemically pure), in the other radioactive. In addition, the process of dehydration of cyclohexanol over anhydrous magnesium and sodium sulfates was studied.

The radioactivity of the catalysts was measured with the aid of an end-window counter (6). A definite volume of solution, usually 0.1 ml, was applied to a disk of filter paper placed in an aluminum cup and evaporated. The activity of the preparation was always measured under identical geometrical conditions with respect to the counter.

Kinetic experiments on the dehydration of cyclohexanol were carried out over 0.5 ml of each of the prepared catalysts (whose weight was known and varied within the limits from 0.14 to 0.30 g) in the temperature interval 355–415°, with a constant space velocity of cyclohexanol of 0.4 $\text{min}^{-1}$. Constant catalytic activity was established after 3 hr of operation, which con—

was confirmed by the reproducibility of the degree of conversion of cyclohexanol at the same temperature. After each experiment the catalyst was regenerated for 45 min with a stream of dry air passing at a rate of 9 L/h. Each experiment lasted 30 min. The catalyst collected during the first 15 min was not examined. The degree of conversion of cyclohexanol was determined by titration according to Kaufmann' s bromine-number method (7) of a weighed portion of catalyst obtained during the second 15 min after the start of the experiment. The correctness of this method was confirmed by titration of mixtures of $C_6H_{11}OH$, $C_6H_{10}$, and $H_2O$ prepared in advance. Cyclohexene was isolated and had b.p. 81.5°; $n_D^{20} = 1.4472$; $d_4^{20} = 0.8117$.

**Fig. 1.** Dependence of catalytic activity on additions of $Na_2SO_4$ (380°)

**Fig. 2.** Effect of the radiation intensity of the catalyst on its catalytic activity

**Fig. 3.** Dependence of the increase in the degree of conversion of cyclohexanol on the logarithm of the specific radioactivity of the catalyst (410°)

No gaseous products were obtained in the reaction process. In the apparatus, after the receiver with the catalyst, an IMA-1 labeled-atom intensimeter was placed, intended for determining the soft beta radiation of $S^{35}$. The instrument showed no evidence of any radioactive contamination.

The catalytic activity was characterized by the degree of dehydration of cyclohexanol, referred to 0.1 g of catalyst. It turned out that, as nonradioactive sodium sulfate was added to magnesium sulfate, the catalytic activity decreased. It is seen from Fig. 1 that anhydrous sodium sulfate is also a catalyst for the dehydration of cyclohexanol, although considerably less active than magnesium sulfate.

Therefore, in order to determine how the introduction of $S^{35}$ into the catalyst instead of ordinary sulfur affects the catalytic activity, the experiments were carried out in pairs. In the catalysts of each pair of experiments the ratio $Na_2SO_4 : MgSO_4$ was the same, but in one of these experiments the sodium sulfate introduced was nonradioactive, while in the other it was radioactive, with a known content of $S^{35}$. The catalysts in such pairs were assigned identical numbers, but the number of the radioactive catalyst was supplied with an asterisk. It is very important that in all experiments with radioactive catalysts an increase in catalytic activity was observed in comparison with experiments with nonradioactive catalysts at the same sodium sulfate content (Fig. 2).

Let us denote the degree of conversion of cyclohexanol into cyclohexene under the given conditions with a nonradioactive catalyst by $a$, and with a radioactive catalyst by $a^*$. We shall call the quantity

$$\Delta = 100(a^* - a)/a.$$

the increase in the degree of conversion.

It turned out that the quantity $\Delta$ increases with increasing radioactivity

catalyst, but not proportionally. The degree of conversion in kinetic experiments usually did not exceed 15%, only in individual cases reaching 23%.

At the same time, as was shown in previous works ($^8$), with a small error one may equate the degree of conversion to the reaction-rate constant $k$ and then, from the Arrhenius equation $K = k_0 e^{-\varepsilon/RT}$, determine graphically the activation energy of the dehydration process $\varepsilon$ (Fig. 4, Table 1).

It can be seen that, in the cases studied for the action of radioactive catalysts, the Arrhenius equation proves valid: all the lines in Fig. 4 are straight. For radioactive catalysts this fact had not been evident beforehand. As is seen from Table 1, the apparent activation energy increases with increasing addition of sodium sulfate and, although only slightly, nevertheless decreases quite definitely upon introduction of the radioactive isotope $S^{35}$.

**Fig. 4.** Dependence of the logarithm of the rate constant on reciprocal temperature in the dehydration of cyclohexanol.
1 $-MgSO_4$ (nonradioactive), 2 $-Na_2SO_4$ (nonradioactive), 3 $-MgSO_4 +$ 2.07% $Na_2SO_4$ (nonradioactive), 4 $-MgSO_4 +$ 21.87% $Na_2SO_4$ (nonradioactive), 4* $-MgSO_4 +$ 21.87% $Na_2SO_4$ (radioactive), 5 $-MgSO_4 +$ 4.06% $Na_2SO_4$ (nonradioactive), 5* $-MgSO_4 +$ 4.06% $Na_2SO_4$ (radioactive), 6 $-MgSO_4 +$ 0.52% $Na_2SO_4$ (nonradioactive); 6* $-MgSO_4 +$ 0.52% $Na_2SO_4$ (radioactive).

Thus, in the present work it has been established experimentally that the radioactive radiation of the catalyst affects the catalytic activity and the activation energy.

**Table 1**

**Apparent activation energies of the process of dehydration of cyclohexanol over $MgSO_4$ with various additions of $Na_2SO_4$**

| Catalyst No. | Catalyst characteristic: $Na_2SO_4$ content, wt. % | Catalyst characteristic: absolute activity, mc/g | Number of experiments | Apparent activation energy, kcal/mole |
|---|---|---|---|---|
| 1 | 0 | 0 | 6 | 15.2 |
| 2 | 100 | 0 | 11 | 23.8 |
| 3 | 2.07 | 0 | 11 | 20.1 |
| 4 | 21.87 | 0 | 11 | 20.8 |
| 4* | 21.87 | 105.2 | 9 | 19.2 |
| 5 | 4.06 | 0 | 8 | 21.4 |
| 5* | 4.06 | 9.2 | 9 | 19.2 |
| 6 | 0.52 | 0 | 9 | 16.4 |
| 6* | 0.52 | 1.26 | 9 | 15.5 |

It is necessary to consider possible explanations of the results obtained. One might have supposed that the observed effect is due to collisions of electrons (beta particles) with cyclohexanol molecules in the gas phase adjacent to the catalyst. This supposition is not justified because, in such a case, the cyclohexanol molecules would decompose in different directions, as in pyrolysis. Besides dehydration, for example, dehydrogenation would also have to occur. The preservation of the selectivity of the process indicates the predominance of phenomena occurring on the surface of the catalyst.

Therefore one might suppose that the elements arising in

as a result of radioactive decay, or the products of their secondary chemical interaction, promote the catalyst. However, the effect was also observed when the fraction of S^35 (catalyst No. 6*) was only $1.8 \cdot 10^{-10} \times 0.52 \cdot 142/(100 \cdot 120) = 1.1 \cdot 10^{-12}$, and the fraction of decay products was, obviously, still considerably smaller. As is known, however, such an insignificant impurity cannot exert a promoting action on the catalyst.

One might further suppose that the surface of the solid is loosened under the influence of impacts by beta particles. However, such an effect is unlikely, since, as is known, it becomes noticeable only in the case of bombardment by heavy particles.

The action of a radioactive impurity is in a certain sense analogous to an increase in temperature. For example, as can be seen from Fig. 3, a degree of conversion equal to 3.3% is reached in the case of nonradioactive catalyst No. 4 at 410°, and in the case of radioactive catalyst No. 4* at a lower temperature, 365°. Hence it becomes possible to suppose that individual acts of radioactive decay can create local overheatings, with the rise in temperature also accelerating the reaction. However, such an assumption is likewise not justified. First, a simple increase in temperature (by 45°) should not affect the reaction mechanism and, consequently, the activation energy, which should have remained unchanged upon introduction of the radioactive component into the catalyst. Experiment shows, however, that $\varepsilon$ does not retain its value in this case (20.8 kcal), but decreases somewhat (to 19.2 kcal in the experiments indicated above; see Table 1). This argues against the assumption made above. Second, on the basis of the data obtained in the present work, it can be shown that the energy of radioactive decay is in general far from sufficient to provide the observed acceleration of a reaction requiring a definite activation energy. In connection with this, the number of overheating sites will be insufficient for the required temperature increase, which also compels rejection of the assumption of the decisive role of local overheatings.

Thus, in the present work we are dealing with an entirely new effect of the joint action of electrons and the active centers of the catalyst. It should be thought that the beta particles here act on catalytically active centers that have adsorbed cyclohexanol molecules. The action of the beta particles consists in lowering the activation energy of the chemical reaction of cyclohexanol dehydration. In this case, for activation of the molecules it becomes possible to utilize the energy of particles possessing a lower velocity of motion, the number of which is greater according to the Maxwell—Boltzmann law for the equilibrium distribution of energy. Calculation by the Arrhenius equation shows that, with $k_0$ constant and at $410^\circ$, the observed decrease in $\varepsilon$ by 1.6 kcal (from 20.8 to 19.2 kcal) provides an increase in the reaction rate by a factor of 3.3 by calculation, as against a factor of 2.8 observed experimentally.

The possibility of activating the chemical action of catalysts while preserving their selectivity by introducing radioactive components is undoubtedly of great interest. The investigation is being continued.

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