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Abstract

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RADIOACTIVE CATALYSTS

DEHYDRATION OF CYCLOHEXANOL OVER MAGNESIUM SULFATE AND CALCIUM CHLORIDE

In a previous communication ([1]) it was shown that the process of catalytic dehydration of cyclohexanol is substantially affected by the presence in the catalyst ($MgSO_4$) of the radioactive isotope sulfur-35.

In the present work the dependence of the reaction yield on the radiation energy of the isotope used was studied at the same values of the absolute activity of the radioactive catalyst. For comparison with the action of S^{35} ($E_{max} = 0.167$ MeV), a β-emitter, Ca^{45} ($E_{max} = 0.254$ MeV), was also chosen. Ca^{45} of high specific activity was obtained by irradiation with slow neutrons, at a flux density of $0.8 \cdot 10^{13}/cm^2 \cdot sec$, of calcium carbonate enriched with the stable isotope Ca^{44}. Identification of the radioactive isotopes formed was carried out on a scintillation spectrometer with a 100-channel amplitude analyzer. The β-spectrum obtained showed the presence of Ca^{45}. However, the preparation also exhibited weak γ-activity not characteristic of calcium-45. Measured by the relative method against a radium standard, it proved to be equal to 0.010 mg/eq Ra per 1 g of $CaCO_3$. The γ-activity detected is due to the presence of a small amount of Fe^{59}.

Table 1

Dehydration of cyclohexanol over $MgSO_4 + CaCl_2$

Catalyst No.	Catalyst characteristic: $CaCl_2$ content, wt. %	Catalyst characteristic: absolute activity, mCu/g	Apparent activation energy of the cyclohexanol dehydration process, kcal/mol
1	0	0	15.1
2	100	0	–
2*	100	93.7	–
3	13.82	0	17.8

Catalyst No.	Catalyst characteristic: $CaCl_2$ content, wt. %	Catalyst characteristic: absolute activity, mCu/g	Apparent activation energy of the cyclohexanol dehydration process, kcal/mol
3*	13.93	12.0	14.2
4	27.05	0	18.2
4*	26.99	24.6	18.3
5	49.87	0	16.4
5*	49.82	45.1	15.5

Radioactive calcium chloride was obtained by adding 18% HCl to $CaCO_3$ until it dissolved, followed by evaporation to dryness and calcination of the resulting salt at 400°. Measurement of the absolute activity of $CaCl_2$ was carried out with end-window and 4π-counters.

The dehydration reaction of cyclohexanol was studied over a mixture of the salts $MgSO_4$ and $CaCl_2$. The radioactive catalysts were prepared as follows: to non-radioactive magnesium sulfate was added a definite amount of a $CaCl_2$ solution, so that the $MgSO_4$ preparation would be wetted by it. The salt mixture was then heated to 400° and kept at this temperature for 2 hours. Nonradioactive catalysts were prepared under analogous conditions and with the same $CaCl_2$ content.

The characteristics of the catalysts used are presented in Table 1.

The dehydration of cyclohexanol was studied in the temperature range 350-420°. The scheme of the apparatus used is described in ([1]). Cyclohexanol was fed at a rate of 0.2 ml/min. A catalyst charge of about 0.25 g, in the form of grains 1-2 mm in diameter, was placed in a quartz flow reactor. The reaction products were collected in a water-cooled receiver. The content of unsaturated hydrocarbons in the catalyzate was determined by bromometric titration.

Fig. 1

Fig. 2

Fig. 1. Dependence of the catalytic activity of $MgSO_4$ on additions of $CaCl_2$ (383°)
Fig. 2. Effect of radioactive irradiation of the catalyst on its catalytic activity

In comparing the catalytic activity of the samples, which could be judged from the degree of conversion of the alcohol at a given temperature, it was found that pure magnesium sulfate is the most active. Additions of calcium chloride to magnesium sulfate caused a considerable decrease in catalytic activity (Fig. 1). Calcium chloride without magnesium sulfate proved to be inert in this reaction.

Fig. 3

Fig. 4

Fig. 3. Increase in the degree of conversion of cyclohexanol as a function of the specific radioactivity of the catalyst (*a*) and the dose rate received by the catalyst (*b*) (410°). 1 —$MgSO_4$ + $CaCl_2$, 2 —$MgSO_4$ + Na_2SO_4.

Fig. 4. Dependence of the reaction rate constant on reciprocal temperature

In all the $MgSO_4$—$CaCl_2$ mixtures studied, after introduction into them of the radioactive isotope Ca^{45}, an increase in catalytic activity was observed. However, pure $CaCl_2$, even with a high Ca^{45} content (93.7 mCi/g), like the nonradioactive preparation, proved to be indifferent in this reaction. Thus, it may be asserted that it is not the β-radiation itself of the radioactive isotope that affects the kinetics of the dehydration process.

cyclohexanol, but excitation by β-particles and by the secondary electrons knocked out by them of the atoms of the catalyst, such as $MgSO_4$, does take place.

Figure 2 presents data on the dependence of the degree of conversion of cyclohexanol on the reaction temperature. Catalysts of the same composition are designated by the same numbers, but the radioactive sample is marked with an asterisk. It can be seen that, for example, at 410° catalyst 3* increased the degree of conversion of cyclohexanol, compared with catalyst 3, by 87%, catalyst 4* compared with catalyst 4 by 170%, and catalyst 5* compared with catalyst 5 by 486%. The dependence of the degree of conversion on the logarithm of the specific activity of the catalyst is shown in Fig. 3a. The dashed line in this figure denotes the dependence of the increase in the degree of conversion of cyclohexanol on the logarithm of the specific activity, which we established earlier ([1]) on magnesium and sodium sulfates with radioactive sulfur-35. The different form of the curves obtained is apparently associated with the difference in the radiation energies and, consequently, with the secondary effects caused by the action on the catalyst of β-particles of higher energy. Figure 3b shows the dependence of the increase in the degree of conversion on the dose rate of irradiation received by a catalyst containing sulfur-35 or calcium-45. The dose rate was calculated on the assumption that all emitted β-particles were absorbed by the catalyst. It may be concluded that, in both cases, the increase in the degree of conversion depends linearly on the logarithm of the radiation dose absorbed by the catalyst, but at the higher β-particle energy the corresponding straight line rises more steeply upward.

On the basis of the data obtained on the dependence of the reaction yield on temperature, the apparent activation energies were calculated (see Fig. 4 and Table 1). They increase appreciably with increasing addition of $CaCl_2$. In the case of radioactive catalysts, the value of E_{app} decreases somewhat.

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1. A. A. Balandin, Vikt. I. Spitsyn, N. P. Dobrosel' skaya, I. E. Mikhailenko, DAN, **121**, 495 (1958).

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