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Abstract

Full Text

PHYSICAL CHEMISTRY

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DEHYDRATION OF ISOPROPYL ALCOHOL ON A RADIOACTIVE TRICALCIUM PHOSPHATE CATALYST

In previously published works ($^{1-4}$) it was established that the β-radiation of the radioactive isotopes S^{35} and Ca^{45}, introduced into the catalysts $\mathrm{Mg\overset{x}{S}O_4} +$ $\mathrm{Na_2SO_4}$, $\mathrm{MgSO_4{+}\overset{x}{Ca}Cl_2}$ and $\mathrm{Mg\overset{x}{S}O_4}$, substantially affects the rate of the alcohol dehydration reaction. It seemed of interest to study the dehydration of an alcohol on a catalyst in which it would be possible partially to replace the stable atoms of one or another constituent element by their radioactive isotopes. Tricalcium phosphate, which is an active catalyst for the dehydration of alcohols ($^{5-9}$), was chosen as the object of investigation.

Tricalcium phosphate was prepared as follows. To a 0.1 M solution of disodium phosphate in an ammoniacal medium, a 48.5% solution of $CaCl_2$ was added dropwise until a negative reaction for phosphate ions was obtained. The precipitate was filtered on a Büchner funnel with a porous filter, washed free of Ca^{2+}, PO_4^{3-} and Cl^- ions, and dried (100-110°) for 1.5 hr. The salt was then calcined for 2 hr at 350°. The radioactive catalysts were prepared in an analogous manner. The radioactive isotope of phosphorus P^{32} was introduced in the form of $\mathrm{Na_2\overset{x}{H}PO_4}$, and Ca^{45} in the form of $\mathrm{\overset{x}{Ca}Cl_2}$. The isotopes Ca^{45} and P^{32} are β-emitters with energies $E(\beta)_{\max} = 0.255$ MeV and $E(\beta)_{\max} = 1.707$ MeV, respectively. For the nonradioactive and radioactive catalyst samples the CaO content was determined: found, 51.57%; calculated, 51.27%.

X-ray examination of the radioactive and nonradioactive salts obtained showed* that they are tricalcium phosphate monohydrate. The sets of interplanar spacings are in full agreement with the literature data (^{10}) for $Ca_3(PO_4)_2 \cdot H_2O$. Debyegrams of the catalysts on which the dehydration reaction had been carried out indicated the absence of changes in the crystal structure of the monohydrate. The characteristics of the prepared tricalcium phosphate samples are given in Table 1.

The catalysts were used on the day after preparation. The investigation was carried out in a flow-type catalytic apparatus described earlier (^{11}).

Figure 1: Kinetics of dehydration of isopropyl alcohol on tricalcium phosphate catalysts containing the radioactive isotope Ca45. The numbers on the curves correspond to the catalyst number.

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Isopropyl alcohol (b.p. 82°; d_4^{20} 0.7860; n_D^{20} 1.3776) was fed at a rate of 0.19 ml/min. Analysis of the gaseous products showed that the gas consisted of 98-99% propylene.

The degree of conversion of the alcohol under the experimental conditions was calculated from the volume of propylene evolved per unit time (NTP). The experimental results for the group of catalysts radioactive with respect to calcium are presented in Fig. 1. The degree of conversion was, with a certain degree of approximation, taken as the rate constant of a zero-order reaction, and from the Arrhenius equation the apparent activation energy of the dehydration process of isopropyl alcohol was determined graphically from the slope of the straight lines obtained. As can be seen from Fig. 1, for the catalyst with a specific radioactivity of 6.2 mCu/g (curve 2) the reaction rate decreased in comparison with the nonradioactive catalyst (curve 1). When the specific activity of the catalyst was increased to 12.2 mCu/g (curve 3), the degree of conversion of the alcohol began to increase.

[*] The X-ray phase analysis was carried out by Yu. P. Simanov and N. A. Shishakov, to whom the authors express their gratitude.

The preparation $Ca_3(PO_4)_2 \cdot H_2O$ with a specific activity of 14.6 mCu/g was divided into two parts, one of which was studied in catalytic experiments in the usual manner, while the other part was kept for 50 days before the experiments were carried out. The resulting curve 4^* lay somewhat lower than curve 4, and close to curve 3, where the catalyst activity was 12.2 mCu/g. As in the study of the dehydration of cyclohexanol on radioactive magnesium sulfate (^{3}), the effect of increasing the catalytic activity in the radioactive—

Fig. 1. Kinetics of dehydration of isopropyl alcohol on tricalcium phosphate catalysts containing the radioactive isotope Ca^{45}. The numbers on the curves correspond to the catalyst number

—catalyst did not intensify with time. This indicates that the catalytic activity of tricalcium phosphate is directly related to its specific radioactivity at the time the experiment is carried out. The degree of conversion of the alcohol on catalyst No. 5 with a specific activity of 23.4 mCu/g proved to be greater than on catalyst No. 4. The catalytic activity increases with the specific radioactivity of the catalytic sample, and on catalyst No. 6, with a specific activity of 58.1 mCu/g, the reaction rate increases by a factor of 5 in comparison with the nonradioactive catalyst.

A similar picture of the influence of the specific radioactivity of the catalyst was observed for the group of catalysts containing radioactive P^{32} (Fig. 2). At a low specific activity of about 4.3 mCu/g the reaction rate decreased slightly (curve 7). Catalysts with specific activities of 13.8 and 27.6 mCu/g noticeably increase the reaction rate (curves 8 and 9). For the catalyst with a specific activity of 52.2 mCu/g, an approximately eightfold increase in catalytic activity is observed in comparison with the nonradioactive catalyst.

Fig. 3 shows the dependence of the increase in the degree of conversion of isopropyl alcohol on radioactive catalysts on the logarithm of the specific activity and on the power of the absorbed dose of β-radiation. Here $\Delta = 100(a^* - a)/a$, where a is the degree of conversion over the nonradioactive catalyst and a^* is that over the radioactive one.

The calculation of the dose power, under the assumption that all β-particles are absorbed by the catalyst, was carried out according to the formula:

$$M = \frac{A}{m \cdot 1.6 \cdot 10^{-4}} L(\beta) \text{ eV/g} \cdot \text{sec},$$

where A is the radioactivity of the catalyst in mCu/g, m is the weight of the catalyst in grams, and $L(\beta)$ is the dose power absorbed by the substance at a specific activity of 1 mCu/g. The values of $L(\beta)$ for the radioisotopes Ca^{45} and P^{32} were taken from tabular data ([12]).

At low values of the specific radioactivity of the catalysts, the value of Δ for preparations with the introduced isotope Ca^{45} proves to be higher than for catalysts with the isotope P^{32}. Beginning with a specific activity of about

36 mCi/g, a sharp increase in Δ is observed for the catalyst with the radioactive isotope P^{32}. This is apparently connected with the radiation energy of the β-particles of the radioactive isotopes. A similar phenomenon was encountered in the dehydration of various alcohols when comparing [2,12] the action of the radioactive isotopes S^{35} ($E(\beta)_{\text{max}} = 0.167$ MeV) and Ca^{45} ($E(\beta)_{\text{max}} = 0.245$ MeV), P^{32} ($E(\beta)_{\text{max}} = 1.71$ MeV) and $Ce^{144} + Pr^{144}$ ($E(\beta)_{\text{max}} = 2.32$ MeV, $E(\gamma)_{\text{max}} = 2.19$ MeV).

The dehydration of isopropyl alcohol on a tricalcium phosphate catalyst evidently proceeds by a carbonium-ion mechanism:

$$C_3H_7OH \xrightarrow{+H^+} C_3H_7OH_2^+ \xrightarrow{-H_2O} C_3H_7^+ \xrightarrow{-H^+} C_3H_6.$$

Under β-particle irradiation, in the case of the radioactive catalyst the surface of $Ca_3(PO_4)_2 \cdot H_2O$ becomes positively charged, which promotes more rapid occurrence of the first stage of the process. However, the second and third stages of the dehydration reaction, characterized by the interaction of the positive ions ROH_2^+ and R^+ with the catalyst surface, should proceed more slowly. At low

Fig. 2. Kinetics of dehydration of isopropyl alcohol on tricalcium phosphate catalysts containing the radioactive isotope P^{32}. The numbers by the curves correspond to the catalyst number

Figure 2: Fig. 2. Kinetics of dehydration of isopropyl alcohol on tricalcium phosphate catalysts containing the radioactive isotope P^{32}. The numbers by the curves correspond to the catalyst number

specific activities of the catalyst we observe this phenomenon. In the case of high specific radioactivity of the catalysts, the rate of protonation apparently increases considerably. At the same time, excitation of the ROH_2^+ molecules increases owing to the larger number of emitted fast electrons. In such a state of the ions, the elimination of a water molecule and the subsequent deprotonation with formation of an olefin evidently proceed more readily.

Fig. 2. Kinetics of dehydration of isopropyl alcohol on tricalcium phosphate catalysts containing the radioactive isotope P^{32}. The numbers by the curves correspond to the catalyst number.

To check the possible influence of the β-radiation of the introduced radioactive isotopes on the magnitude of the specific surface area of the catalysts, it was

Table 1

Dehydration of isopropyl alcohol on $Ca_3(PO_4)_2 \cdot H_2O$

Catalyst No.	Introduced isotope	Absolute activity, mCi/g	Absorbed dose rate, eV/g · sec	Specific surface area, m^2/g	Increase in surface area, %	Degree of alcohol conversion (350°), %	Specific catalytic activity per unit surface area	Apparent activation energy ε, kcal/mol
1	–	0.0	0.0	71.3	0.0	12	0.1683	17.8
2	Ca^{45}	6.2	$2.0 \cdot 10^{13}$	74.5	4.5	10	0.1342	18.0
3	Ca^{45}	12.2	$3.8 \cdot 10^{13}$	91.3	28.0	33	0.3614	15.5
4	Ca^{45}	14.6	$4.5 \cdot 10^{13}$	68.0	–4.6	35	0.5147	15.5
4*	Ca^{45}	11.6	$3.6 \cdot 10^{13}$	68.2	–4.6	32	0.4691	15.5
5	Ca^{45}	23.4	$7.3 \cdot 10^{13}$	74.1	4.0	42	0.5667	12.8

Catalyst No.	Introduced isotope	Absolute activity, mCi/g	Absorbed dose rate, eV/g • sec	Specific surface area, m^2/g	Increase in surface area, %	Degree of alcohol conversion (350°), %	Specific catalytic activity per unit surface area	Apparent activation energy ε, kcal/mol
6	Ca^{45}	58.1	$1.8 \cdot 10^{14}$	74.1	4.0	58	0.7827	11.9
7	P^{32}	4.3	$1.1 \cdot 10^{14}$	109.6	53.7	8	0.0730	17.0
8	P^{32}	13.8	$3.6 \cdot 10^{14}$	67.0	−6.0	23	0.3433	17.8
9	P^{32}	27.6	$7.2 \cdot 10^{14}$	89.7	24.8	30	0.3168	17.0
10	P^{32}	52.2	$1.4 \cdot 10^{15}$	62.7	−12.1	95	0.5140	7.3

* Aged 50 days before the catalytic experiments.

their surface area was measured by the BET method from krypton adsorption ([13]). The results are presented in Table 1. With a determination accuracy of 5-10%, the specific surface area of catalysts Nos. 2, 4, 5, 6, and 8 proved to be practically the same as the surface area of the nonradioactive catalyst No. 1. The greatest increase in surface area reached 53.7% relative to the surface of the nonradioactive catalyst (sample No. 7 with a specific radioactivity of 4.3 mCi/g); however, the catalytic activity of this sample proved to be the lowest.

Table 1 presents the values of the apparent activation energy of the dehydration process, ε. For the nonradioactive sample, ε is equal to 17.8 kcal/mol. Catalysts with a specific radioactivity of 10-20 mCi/g have a somewhat lower activation energy. On catalysts with high specific radioactivity, up to 58.1 for Ca^{45} and 52.2 mCi/g for P^{32}, the activation energy of the reaction is, respectively, 6 and 10.5 kcal/mol lower than in the case of the nonradioactive catalyst. Thus, in the present study an example has been shown of a stronger influence of the energy of radioactive radiation on the value of the apparent activation energy of the reaction of alcohol dehydration than was observed by us earlier ([1]-[3]).

Fig. 3. Change in the degree of conversion of isopropyl alcohol on radioactive catalysts (350° C): **a** —influence of the specific radioactivity of the catalysts, **b** —influence of the absorbed dose rate. **1** —catalysts with Ca^{45}, **2** —catalysts with P^{32}.

Fig. 3. Change in the degree of conversion of isopropyl alcohol on radioactive catalysts (350° C): a —influence of the specific radioactivity of the catalysts, b —influence of the absorbed dose rate. 1 —catalysts with Ca^{45}, 2 —catalysts with P^{32}

Figure 3: Fig. 3. Change in the degree of conversion of isopropyl alcohol on radioactive catalysts (350° C): a —influence of the specific radioactivity of the catalysts, b —influence of the absorbed dose rate. 1 —catalysts with Ca^{45}, 2 —catalysts with P^{32}

The data obtained confirm the previously expressed assumption (1) about the utilization of the energy of radioactive decay by catalytically active centers and once again indicate a direct connection between the process of radioactive decay and the change in catalytic activity. Assumptions about an indirect effect of radiation through an increase in the surface area of the catalyst were not confirmed.

The degree of enhancement of the catalytic properties apparently depends on the intensity of the action of radioactive radiation on the catalytically active surface centers that have adsorbed molecules of the reacting substance.

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