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Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE CATALYTIC PROPERTIES OF CALCIUM OXIDE

(Presented by Academician S. I. Vol' fkovich, January 2, 1958)

Several years ago we discovered the strong catalytic action of solid bases—oxides and hydroxides of metals of the second group: CaO, $Ca(OH)_2$, SrO, and BaO —in the dehydration of isopropyl alcohol (1,2). At that time the scant study of heterogeneous alkaline catalysis was also noted. Recently, a number of investigators have discovered the catalytic action of solid bases: oxides and hydroxides (3,4), hydrides (5), amides (6–8), and alcoholates (9) of alkali metals.

Fig. 1. Kinetic curves of dehydration of isopropyl alcohol in the adsorbed layer on CaO

Fig. 2. Kinetic curves of dehydration of cyclohexane on CaO at 350–450°

It is of interest to study the regularities of alkaline catalysis, its differences from acid and from oxidation-reduction catalysis. In the present work, the reactions studied were the dehydration of cyclohexane, the decomposition of isopropyl alcohol, and hydrazine on calcium oxide.

Calcium oxide was obtained by dehydration of $Ca(OH)_2$ at 600° in vacuum in the same vessel in which the catalytic reaction was studied. For the experiments on the decomposition of cyclohexane and hydrazine, 2 g of it were taken; for the experiments on the decomposition of isopropyl alcohol, 1 g. The surface area of CaO, determined from the adsorption of *n*-heptane, was 48.5 m^2/g. The decomposition of *iso*-C_3H_7OH and N_2H_4 was studied in the adsorbed layer, and the decomposition of C_6H_{12} under vacuum static conditions. The reaction

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

products were analyzed by freezing out. In addition, an additional analysis for H_2 was carried out by passing it through a palladium capillary.

Figure 1 gives the kinetic curves for the dehydration of isopropyl alcohol in the adsorbed layer at 100-200°. The amount of desorbed hydrogen at 180-200° is equal to the amount of acetone. At lower temperatures there is 10-20% more hydrogen than acetone. This is explained by the strong adsorption of acetone on CaO. Its study showed that acetone adsorbed at 190° is completely removed by evacuation at the same temperature; at 100° evacuation removes only 4% of the acetone. Adsorption

H_2 was not detected under the experimental conditions (it is less than 0.1% of the filling). The dehydration products amounted to 10-20% of the total amount of reaction products. The reproducibility within a single series of experiments was satisfactory. However, after about 20 experiments had been carried out under standard conditions, the last of them being performed at low temperature (75-100°), an "activation" was observed—an increase in the rate of dehydrogenation by

Fig. 3. Dependence of $\lg k$ on $1/T$ for the dehydrogenation of C_6H_{12} on CaO

Fig. 4. Kinetic curves for the decomposition of hydrazine on CaO in the adsorbed layer

20-30%. The kinetic curves for the dehydrogenation of isopropyl alcohol on CaO become straight lines in the coordinates $\lg p$—$\lg t$. In view of the closeness of the initial fillings of CaO with isopropyl alcohol (0.236 mmol/g at 100°, 0.225 at 150°, and 0.177 at 100°), the activation energy E for the dehydrogenation of iso-C_3H_7OH could be determined by comparing the logarithms of the times required to reach identical conversions with $1/T$. This gives, at low temperatures (100-150°), values of E depending on the filling of 21-30 kcal/mol, and at 180-200°, 32-36 kcal/mol. It is possible that these changes in activation energy are associated with decomposition proceeding on a hydrated surface at low temperatures and on pure CaO at high temperatures. The "activation" of CaO at low temperatures also supports this assumption.

The dehydrogenation of cyclohexane, as shown by the kinetic curves in Fig. 2, at an initial C_6H_{12} pressure of 0.2 mm proceeds at a satisfactory rate at 300-450°. At this initial pressure, cyclohexane is adsorbed on CaO, according to adsorption measurements on a Mac-Bain balance, at 300° in an amount of 0.044 mmol/g, and at 350°—0.030 mmol/g, i.e., one C_6H_{12} molecule corresponds to 300-400 Å^2 of surface. Benzene is adsorbed under these conditions in still smaller amounts. Adsorption ends rapidly; on evacuation, the adsorbed amounts are removed. At such fillings, adsorption of the components does not hinder the reaction, and its kinetics obey a first-order law. The dependence of the initial reaction rate on the pressure of cyclohexane is also linear. The amount of H_2 in the reaction products at temperatures of 350-400° is 52-59% (in different experiments), and at 450° 69-74%. The reproducibility of the results is good. After a series of experiments (12 experiments at 300-450° and $p_{\text{init}} = 2$ mm), the decrease in rate was only 5-8%.

In Fig. 3 the dependence of the logarithm of the first-order rate constant for the decomposition of cyclohexane on CaO on $1/T$ is plotted. The activation energy of dehydrogenation calculated from this straight line is 30.5 kcal/mol. This is considerably higher than the E for the dehydrogenation of C_6H_{12} on metals, and is close to the values found by Balandin and Brusov (^{10}) and by Kagan and Flid (^{11}) for the dehydrogenation of cyclohexane on Cr_2O_3. According to these authors, on oxide catalysts, in contrast to metals, the formation of cycloolefins and cracking products is possible. Our data also show that stoichiometric decomposition of C_6H_{12} into C_6H_6 + $3H_2$ is not observed.

Some kinetic curves for the decomposition of hydrazine in the adsorbed layer on CaO at 50-200° are shown in Fig. 4. The activity of CaO with respect to the decomposition of hydrazine is unstable, and fluctuations in activity when the experiment was repeated in individual cases reached 20-25%. In the decomposition products, ammonia was determined (the volume of gas condensing in liquid nitrogen), the amount of which varied from 11.1% at 100° to 20.4% at 200°; hydrogen (the noncondensing gas passing through the Pd capillary), whose content changed little with temperature, ranging from 46.8 to 55.7%; and nitrogen (the residual noncondensing gas)—from 31.1 to 35.5% at temperatures of 100-200°. Thus, the decomposition of hydrazine on CaO proceeds according to the same equation as in solutions of strong alkalis (^{12}):

$$(3+x)\,N_2H_4 \to 2NH_3 + (2+x)N_2 + (3+2x)H_2$$

and differs from decomposition on metals and semiconductors, on which, as was shown by experiments specially carried out by us, only ammonia and nitrogen are formed:

$$3N_2H_4 \to 4NH_3 + N_2.$$

The kinetic curves for hydrazine decomposition in the coordinates p—$\lg t$ become straight at temperatures of 150-200° and do not become straight at 50-100°. Calculation of the dependence of E on coverage gives values of E varying from 6200 to 7400 cal/mole at 50-100° and from 12,000 to 28,000 cal/mole at 100-200°. It should be pointed out, however, that these values are only approximate, in view of the large fluctuations in the activity of CaO. It is possible that the different activation energies and the different form of the kinetic curves for the decomposition of N_2H_4 on CaO at high and low temperatures are also caused by hydration of the CaO surface at low temperatures by water, which may have been an impurity in the initial hydrazine.

The investigation carried out shows the possibility of carrying out on CaO three reactions involving the elimination of hydrogen, which are customarily assigned to the oxidation-reduction or homolytic type. Of these reactions, two—the dehydrogenation of alcohol and of cyclohexane—proceed in the same direction as on electronic semiconductors, while the third—the decomposition of hydrazine—proceeds in a direction different from its course on metals and semiconductors.

Comparison with a closely related oxide in the secondary subgroup of Group 2 of the periodic system (a typical electronic semiconductor)—zinc oxide ([13])—shows the closeness of the activation energies for the decomposition of isopropyl alcohol both under flow conditions (12-16 kcal/mole on CaO, 12-13 on ZnO) and in the adsorbed layer (21-36 and 25-46, respectively), while the occurrence of the reaction in one and the same temperature interval indicates close values of the pre-exponential factor k_0.

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