A Study of Catalysis by Metal Phosphates. II.[1] A Kinetic Study of the Dehydrogenation of 2-Propanol over the Cadmium Phosphate Catalyst and an Investigation of the Acid-base Character of the Catalyst

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(Received April 12, 1973)

The dehydrogenation of 2-propanol over the *ortho* cadmium phosphate catalyst has been investigated by means of a conventional tubular-flow reactor operating at atmospheric pressure. The adequate temperature for the calcination of catalyst was about 400 °C. The reaction-rate data were approximately arranged by Eq. (3), using the Langmuir-type expression described in the text. The catalytic activity for dehydrogenation to acetone was completely poisoned by the addition of a small amount of CCl_3COOH during the course of the reaction, whereas the activity for dehydration to propylene was greatly enhanced. The behavior of $CH_2ClCOOH$ and C_6H_5COOH as poisons was also investigated. C_5H_5N had no effect on the catalytic reaction. It has been concluded that the cadmium phosphate is to be characterized as a basic catalyst.

A preliminary study of various *ortho* metal phosphate catalysts revealed that two phosphates, $Ca_3(PO_4)_2$ and $Cd_3(PO_4)_2$, had a high and selective activity for the dehydrogenation of 2-propanol to acetone; in this they strongly contrasted with the other phosphates which generally catalyzed the dehydration for propylene formation.[2]

Ishiguro and Ohtsuka[3] have already reported that the cadmium phosphate catalyst selectively promotes the dehydrogenation of 2-propanol; however, they have not presented the detailed reaction kinetics or a characterization of the catalyst.

In this paper, we will describe a further study of the cadmium phosphate catalyst.

Experimental

Materials. The cadmium phosphate catalyst was prepared from $Cd(NO_3)_2$ and Na_3PO_4 according to the method of Ishiguro and Ohtsuka.[3] The catalyst was calcined at the prescribed temperatures between 300 and 600 °C for 4 hr in an air stream. In all cases, the catalysts were white in color.

The N_2 and 2-propanol used in the catalytic tests were the highest pure grade of reagent.

Procedures. The apparatus and procedure for the measurements of the catalytic reaction were the same as those described in the previous report.[1] The experimental data of the catalytic reactions were represented by the total conversion of 2-propanol (x) and the selectivity to acetone (S).[4]

In order to reveal the acid-base character of the catalyst during the course of reaction, the effects of pyridine (C_5H_5N), trichloroacetic acid (CCl_3COOH), monochloroacetic acid ($CH_2ClCOOH$), and benzoic acid (C_6H_5COOH) on the catalytic reaction were investigated by means of the following procedure: 2-propanol with the additive of 0.067 mol/l was prepared for the tests. After we have ascertained that the catalytic reaction for 2-propanol without the additive proceeds at a stationary state, we exchange the feed instaneously with 2-propanol containing the additive and then follow the change in the catalytic activity and in the selectivity.

Results and Discussion

Effect of Reaction Conditions on the Catalytic Activity and Selectivity. The changes in the catalytic activity and in the selectivity with the calcination temperature of the catalyst are shown in Fig. 1. The catalytic activity increased with an increase in the calcination temperature, passed through a maximum at about 400 °C, and then almost disappeared above 500 °C. The catalyst, even when it was calcined at the low temperature of 300 °C, exceeds 80% in selectivity for dehydrogenation to acetone. The selectivity to acetone over the catalyst calcined at 400 °C displayed only a slight decrease of up to 5%, depending on the reaction temperature and the time factor (W/F). Thus, the dehydration of 2-propanol to propylene was negligible in amount under appropriate reaction conditions.

Reaction Rates and Rate Equation. The kinetic studies have been made over the catalyst calcined at 400 °C, wherein the selectivity to acetone was excellent and the activity was almost unchanged throughout the time of the reaction.

In the low range of W/F up to 4 g-cat·hr/mol, the observed conversion of 2-propanol was approximately proportional to W/F, without regard to the reaction temperature. Therefore, one may assume the differential

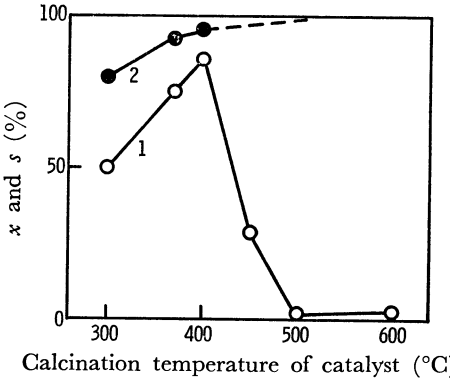

Fig. 1. Effect of the calcination temperature of catalyst on the reaction.
1: Conversion of 2-propanol, x
2: Selectivity to acetone, S
Reaction temperature: 295 °C, Catalyst weight (W): 1.5 g, Feed rate of 2-propanol and N_2 (F): 0.23 mol/hr, Mol-fraction of 2-propanol in feed $\left(y_0 = \frac{IPA}{IPA+N_2}\right)$: 0.26

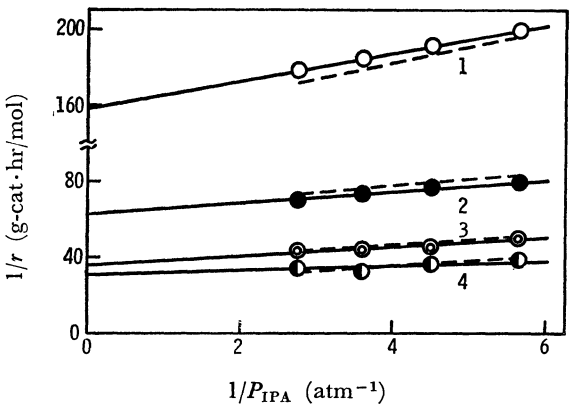

Fig. 2. $1/r$ *vs.* $1/P_{IPA}$ plots.
1: 220 °C, 2: 245 °C, 3: 260 °C, 4: 270 °C
The dotted lines show the correlation between $1/r_{calc}$ and $1/P_{IPA}$, where r_{calc} is the reaction rate computed from Eq. (3).

reactor, in which the reaction rates, $r(=y_0x/(W/F)$ mol/g-cat·hr), can be obtained from the slopes of the linear relationships between y_0x (y_0: mol-fraction of 2-propanol at the inlet of reactor) and W/F.

The observed reaction rates are illustrated in Fig. 2, plotted as reciprocal relations between r and P_{IPA}.

A plot of $1/r$ *vs.* $1/P_{IPA}$ gives a straight line for each of the reaction temperatures. The following equation can be derived and rearranged to the conventional form of the Langmuir-type rate expression:

$$\frac{1}{r} = \frac{1}{k} + \frac{1}{kK}\frac{1}{P_{IPA}} \tag{1}$$

or:

$$r = k\frac{KP_{IPA}}{1+KP_{IPA}} \tag{2}$$

where k is the rate constant (mol/g-cat·hr) and where K is the adsorption equilibrium constant for 2-propanol (atm^{-1}). The intercepts to the ordinate and the slopes of the straight lines give the values of k and K shown in Fig. 3.

Both $\log k$ and $\log K$ are correlated to $1/T$ by straight lines, with slopes of $(-E/R)$ and (Q/R) respectively,

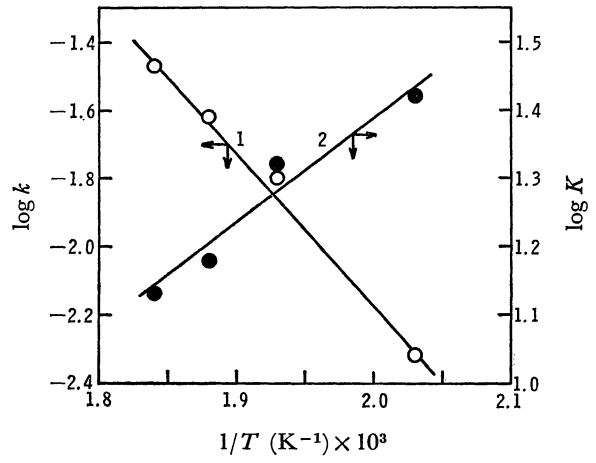

Fig. 3. Arrhenius plots for k and K.
1: $\log k$ *vs.* $1/T$, 2: $\log K$ *vs.* $1/T$

where E is the activation energy for the reaction and where Q is the adsorption heat of 2-propanol. We obtained approximately $E=19$ kcal/mol and $Q=6.7$ kcal/mol. By substituting these values into Eq. (2) and by evaluating the pre-exponential factors of k and K, we obtain:

$$r = 1.84\times10^{-2}\exp\left(\frac{-19000}{RT}\right)\frac{2.3\times10^{-2}P_{IPA}\exp\left(\frac{6700}{RT}\right)}{1+2.3\times10^{-2}P_{IPA}\exp\left(\frac{6700}{RT}\right)} \tag{3}$$

Considering the stoichiometry of the reaction and using Eq. (2) for the rate expression, we obtain Eq. (4) as a conventional integral form for the ideal tubular reactor:[5]

$$W/F = y_0\int_0^x \frac{dx}{r} = \frac{y_0}{k}\left[\frac{1}{K}\left(1+\frac{1}{y_0}\right)\ln\frac{1}{1-x}+x\left(1-\frac{1}{K}\right)\right] \tag{4}$$

At a constant temperature of 260 °C, a series of the conversion data was obtained under conditions in which W/F varied widely from 1.5 to 22.3, and y_0, from 0.183 to 0.383. Fig. 4 shows a plot of W/F *vs.* y_0 $[\{(1+1/y_0)/K\}\ln(1/1-x))+x(1-1/K)]$ for $K=13.0$, which is evaluated from Eq. (3) for K at 260 °C. A good linear correlation is shown in Fig. 4. Consequently, it can be concluded that Eq. (3) is satisfactory for the rate equation under all the present experimental conditions.

When comparing 2-propanol which contained much acetone and 2-propanol without acetone for the feed of the reaction, no essential differences in reaction rates could be detected. Thus, the retardation effect of acetone on the reaction rate was found to be negligible.

Acid-base Character of the Catalyst. The coexistence of C_5H_5N in the reactant flow had no effect on the catalytic reaction within the limits of experimental error, whereas CCl_3COOH showed a remarkable influence on the catalyst activity, as is shown in Fig. 5. Dehydrogenation to acetone was retarded rapidly and was poisoned completely after the reaction had been continued for about 30 min by using 2-propanol with 0.067 mol/l CCl_3COOH. In contrast, dehydration to

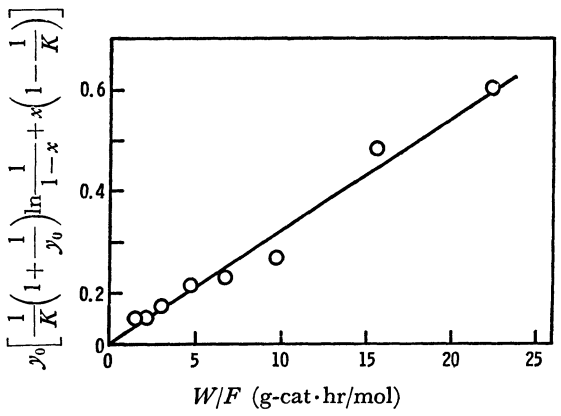

Fig. 4. Test of the Langmuir-type rate equation by integral method.
Reaction temperature: 260 °C, y_0: 0.183~0.383

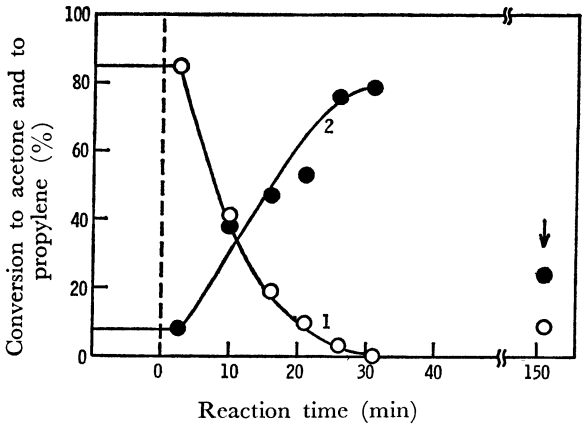

Fig. 5. Influence of CCl_3COOH addition on the catalytic reaction.
1: Conversion to acetone
2: Conversion to propylene
Reaction temperature: 305 °C, Concentration of CCl_3COOH in the feed of 2-propanol: 0.067 mol/l, The other reaction conditions are the same as noted in Fig. 1. The dotted line shows the time when the feed of 2-propanol without the additive was exchanged with 2-propanol containing CCl_3COOH. The data marked by an arrow show the result after the catalyst has been reactivated by passing through N_2 at 350 °C for 2 hours.

propylene increased remarkably, as CCl_3COOH had been accumulated on the catalyst surface. The disappearance of the dehydrogenation activity upon the addition of a small amount of CCl_3COOH to the catalyst indicates that the active sites of the catalyst contributing to the dehydrogenation reaction are basic. The required quantity of CCl_3COOH which completely poisoned the dehydrogenation activity of the catalyst was almost unchanged with the change in the reaction temperature or in the concentration of CCl_3COOH; it was estimated to be about 0.05 mmol/g-cat from the results shown in Fig. 5. However, it was difficult to determine the exact amount of CCl_3COOH for the complete poisoning because of the presence of poison

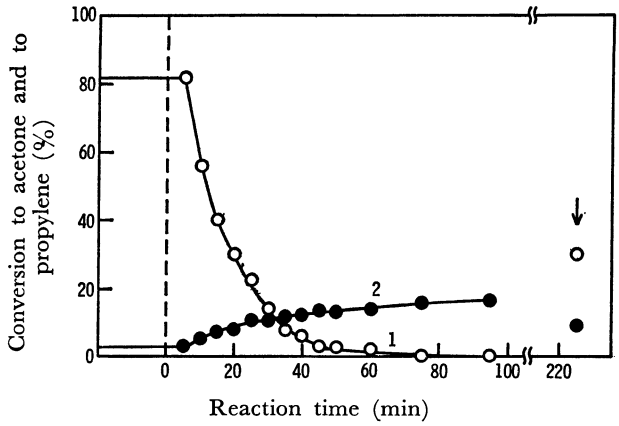

Fig. 6. Influence of $CH_2ClCOOH$ addition on the catalytic reaction.
Reaction temperature: 300 °C, The other reaction conditions and the notes are the same as described in Fig. 5.

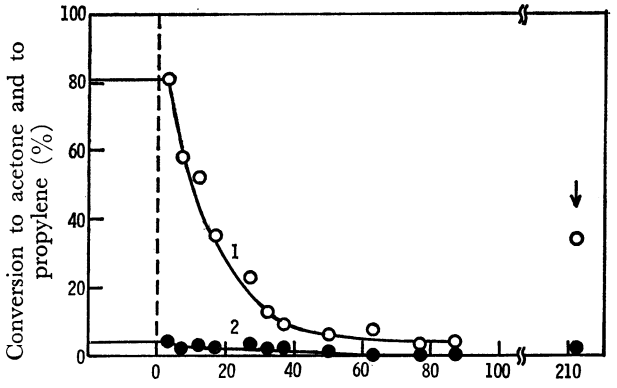

Fig. 7. Influence of C_6H_5COOH addition on the catalytic reaction.
Reaction temperature: 300 °C, The other reaction conditions and the notes are the same as described in Fig. 5.

adsorbed on the sties which are not active for the catalytic reaction.

To make sure that the catalyst can be characterized as basic, the influences of $CH_2ClCOOH$ and C_6H_5COOH on the catalytic reaction were also investigated. As is shown in Figs. 6 and 7, the dehydrogenation to acetone was explicitly poisoned by the addition of the organic acids, although their rates of poisoning the dehydrogenation and also their degree of enhancing the dehydration are somewhat different from that of CCl_3COOH.

None of the catalysts poisoned with CCl_3COOH, $CH_2ClCOOH$, or C_6H_5COOH regained their catalytic activity for dehydrogenation when the catalytic reaction of 2-propanol without the additive was continued at the reaction temperature of 300 °C for two hours, or when it was passed through N_2 at 300 °C for two hours. By passing it through N_2 at such a slightly higher temperature as 350 °C, however, some of the catalytic activity for dehydrogenation was restored, although the degree of the recovery depended primarily on the species of the poisons, as is shown in Figs. 5—7. The enhanced dehydration activity directly attributable to the addition of CCl_3COOH or $CH_2ClCOOH$ readily disappeared when it was passed through N_2; in contrast, the recovery of dehydrogenation activity was rather difficult. The detailed role of CCl_3COOH or $CH_2ClCOOH$ in the appearance of dehydration activity during the poisoning test is not yet clear. However, a feasible and tentative explanation is that Brönsted acid molecules adsorbed on the catalyst surface catalyze the dehydration to propylene. The reason for this is that the decreasing order of dehydration activity of the catalysts poisoned with the organic acids is as follows: $CCl_3COOH > CH_2ClCOOH > C_6H_5COOH$; this order is in accord with expectations based on the acid strength. Since the acid molecules adsorbed on the catalyst surface other than basic sites would be rapidly desorbed, the ready recovery of dehydration activity is understandable, as has been described above.

The effect of H_2O on the catalytic reaction was not observable under the same conditions as those studied for the poisoning of CCl_3COOH, except that the concentration of H_2O varied over a wide range between 0.098 and 0.65 mol/l.

On the basis of the observations presented above, it appears clear that the cadmium phosphate is intrinsically a basic catalyst. However, the catalyst structure which causes this basic character must remain the subject for a future study.

References

1) Part I of this series: F. Nozaki, T. Itoh, and S. Ueda, *Nippon Kagaku Kaishi*, **1973**, 674.
2) Unpublished work.
3) T. Ishiguro and A. Ohtsuka, *Yakugaku Zasshi*, **78**, 1383 (1958).
4) Selectivity to acetone=Conversion to acetone/Total conversion of 2-propanol (x).
5) At the point in the reactor where the conversion is x, P_{IPA} may be written as $P_{IPA}=y_0(1-x)/(1+y_0x)$.