BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(2), 567—568 (1976)

A Study of Catalysis by Metal Phosphate. III.[1] The Dehydrogenation of Alcohols over Cadmium Phosphate and the Influence of CCl_4 Addition on the Catalytic Reaction

Fumio Nozaki and Yutaka Iimori

Department of Industrial Chemistry, Faculty of Engineering, Chiba University, Yayoi-cho, Chiba 280

(Received June 28, 1975)

Synopsis. Various alcohols were selectively dehydrogenated over the $Cd_3(PO_4)_2$ catalyst. The addition of CCl_4 during the reaction resulted in a rapid decrease in dehydrogenation activity and in an increase in dehydration activity, accompanied by an evolution of CO_2.

In a previous paper,[1] we have reported a kinetic study of the dehydrogenation of 2-propanol over $Cd_3(PO_4)_2$ and an investigation of the acid-base character of the catalyst. In this paper, we will describe an additional result concerning the relative reactivities of various alcohols. In addition, the results of the influence of CCl_4 addition upon the catalytic reaction will be reported and the observations will be discussed.

Experimental

The catalyst was prepared by the same method as has been described in the previous paper[1]. Before use in the tests, the catalyst was calcined at 400 °C for 2 hr in an air stream. The six kinds of alcohols, C_4H_9OH (to be subsequently referred to as *n*-BtOH), $(CH_3)_2CHCH_2OH$ (*i*-BtOH), $CH_3CH_2CH(OH)CH_3$ (*s*-BtOH), C_3H_7OH (*n*-PrOH), $CH_3CH(OH)CH_3$ (*i*-PrOH), and C_2H_5OH (EtOH), were used after they had been dehydrated and distilled in a routine manner.

The procedures for the catalytic tests and for analyzing the reaction products were practically the same as those described in the previous paper[1], except that a 12-m gas-chromatographic column of 30% DMS-chromosorb operating at room temperature was additionally used in this work for the separation and determination of CO_2, 1-butene, *trans*-2-butene, and *cis*-2-butene.

Results and Discussion

For the cases of all alcohols in so far as we have investigated, the catalyst exceeded 95% in selectivity for dehydrogenation and olefine formation attributable to the dehydration was very slight. The conversion data of alcohols were found to be approximately expressed in the zero-th order kinetics. Arrhenius plots for the rate constants are shown in Fig. 1.

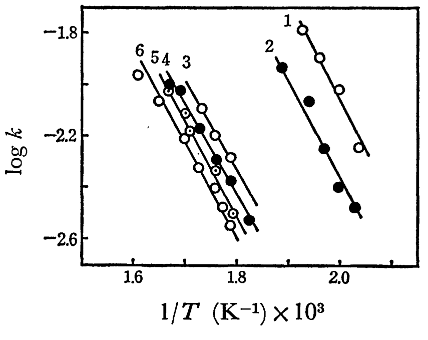

Fig. 1. Arrhenius plots for the rate constants.
1: *s*-BtOH, 2: *i*-PrOH, 3: *i*-BtOH, 4: *n*-BtOH, 5: *n*-PrOH, 6: EtOH.

Figure 1 indicates that the reactivities of the alcohols decrease in this order: *s*-BtOH>*i*-PrOH>*i*-BtOH>*n*-BtOH>*n*-PrOH>EtOH and that the apparent activation energy is about 20 kcal/mol for all the alcohols. The secondary alcohols are much more reactive than the primary alcohols. The observed sequence and regularity in reactivity are similar to that reported in the paper in which the dehydrogenation of alcohols was investigated over metallic catalysts.[2] This fact leads to the speculation that the rate-determining step of the dehydrogenation reaction is an α-hydrogen elimination process.

The changes in catalytic activity upon the addition of CCl_4 are illustrated in Fig. 2, with *i*-PrOH as the example. As CCl_4 had been placed on the catalyst surface, the dehydrogenation to acetone was rapidly retarded and was almost eliminated after the reaction had been continued for about 20 min. In contrast, a dehydration to propylene was generated, with some time-lag. The lag in the appearance of dehydration activity might be a slow response to the acidic sites generated by the reaction of the catalyst with CCl_4. As is shown by Curve 3 in Fig. 2, CO_2 was gradually produced by the addition of CCl_4, although the amount of evolution was so slight that it was difficult to make a quantitative determination. As has previously been reported,[1] the organic acid without a Cl atom, *e.g.*,

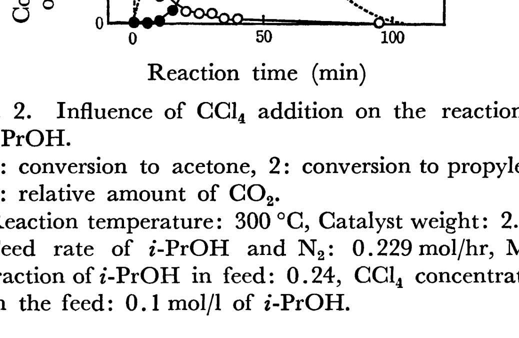

Fig. 2. Influence of CCl_4 addition on the reaction of *i*-PrOH.
1: conversion to acetone, 2: conversion to propylene, 3: relative amount of CO_2.
Reaction temperature: 300 °C, Catalyst weight: 2.0 g, Feed rate of *i*-PrOH and N_2: 0.229 mol/hr, Mol-fraction of *i*-PrOH in feed: 0.24, CCl_4 concentration in the feed: 0.1 mol/l of *i*-PrOH.

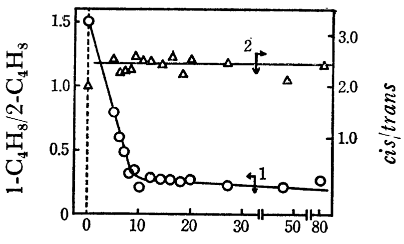

Fig. 3. Changes in the selectivity for dehydration of *s*-BtOH to butene isomers during the course of CCl_4 addition.

1: 1-butene/2-butenes ratio, 2: *cis*/*trans* ratio in 2-butenes. Reaction conditions are the same as for Fig. 2.

C_6H_5COOH, also retarded the dehydrogenation activity of the catalyst, but there was no enhancement of the dehydration activity. In the case of C_6H_5COOH addition, there was absolutely no such evolution of CO_2 as was observed upon the addition of CCl_4.

The influence of CCl_4 addition upon the reaction of *s*-BtOH was quite similar to that shown in Fig. 2; the dehydrogenation to 2-butanone was rapidly retarded, while the dehydration to butene isomers was much enhanced. A characteristic aspect of the behavior to be noted here is that the distribution of butene isomers changes appreciably upon the addition of CCl_4, as is shown in Fig. 3. Before the addition of CCl_4, the 1-butene/2-butenes ratio in butene isomers was about 1.5. In contrast, as CCl_4 is added the ratio decreases rapidly and leads to a value of about 0.25, a value which is quite close to the value of 0.24 in an equilibrium state.[3] The *cis*/*trans* ratio in 2-butenes remains almost unaltered and is kept nearly constant in the range from 2.0 to 2.5. In other words, the most abundant isomer varied from 1-butene to *cis*-2-butene upon the addition of CCl_4. Both the 1-butene/2-butenes and *cis*/*trans* ratios were almost independent of the *s*-BtOH conversion. This indicates that no further isomerization of the butene isomers produced by dehydration is involved. According to the paper reported by Tanabe *et al*,[3] the change in the 1-butene/2-butenes ratio during the course of CCl_4 addition suggests that the reaction pathway of the dehydration has been altered from an acid-base bifunctional mechanism to an *E*-1 mechanism *via* the carbonium-ion intermediate.

The exact mechanism of the CO_2 formation directly attributable to the admission of CCl_4 is still not yet completely elucidated, but we have speculated that the following reaction is involved:

$$CCl_4 + 2OH^- \longrightarrow CCl_2(OH)_2 + 2Cl^- \longrightarrow 2HCl + CO_2 + 2Cl^-$$

where OH^- is the basic site of the catalyst and plays an important role in the dehydrogenation of alcohol. The acidic action of HCl is a likely cause of the appearance and enhancement of the dehydration activity upon the addition of CCl_4. None of the catalyst poisoned with CCl_4 regained its activity for dehydrogenation when the catalytic reaction of alcohol without CCl_4 was continued or when it was passed through N_2 at 300 °C. By a long period of heating in contact with a N_2 stream containing H_2O at 300 °C, the dehydrogenation activity was substantially regenerated. The introduction of CO_2 had no effect on the reaction. A definite correlation between the loss of the dehydrogenation activity upon the addition of CCl_4 and the formation of CO_2 gives a basis for speculation that OH^- is the active site for the dehydrogenation; however, further experimental evidence is necessary to clarify this postulation.

References

1) Part II of this series: F. Nozaki and H. Ohta, This Bulletin, **47**, 1307 (1974).

2) W. G. Palmer and F. H. Constable, *Proc. Roy. Soc. Ser. A*, **107**, 255 (1925); S. Kudo, "Shokubai Kogaku Koza," Vol. 7, ed. by Catalysis Soc. of Japan, Chijin Shokan, Tokyo (1964), p. 212.

3) T. Yamaguchi, T. Kobayashi, and K. Tanabe, *Nippon Kagaku Zasshi*, **92**, 1076 (1971).