

HEXADIENE FORMATION FROM 2-PROPANOL OVER CALCIUM PHOSPHATE CATALYST

Toshiaki SODESAWA, Hirotaka NAKAJIMA, and Fumio NOZAKI  
Department of Industrial Chemistry, Faculty of Engineering,  
Chiba University, Yayoi-cho, Chiba 260

Hexadiene formation from 2-propanol over calcium phosphate catalyst was observed and studied from the standpoint of acid-base catalysis. Maximum conversion to hexadiene was obtained at 425°C. The hexadiene formation was suppressed remarkably by the addition of phenol, while its formation was not so much controlled by the pyridine addition.

Generally, it is well known that the acetone formation from 2-propanol occurs easily over the catalysts having strong basicity as follows,  $\text{CH}_3\text{CHOHCH}_3 \longrightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2$ , whereas the propylene formation from 2-propanol progresses predominantly over the catalysts having strong acidity as the following equation,  $\text{CH}_3\text{CHOHCH}_3 \longrightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O}$ . Furthermore, alcohol decomposition over hydroxyapatite catalysts was reported by Hall et al.<sup>1,2)</sup> However, hexadiene formation from 2-propanol has not yet been reported. It has recently been known that calcium phosphate has not only the acidic sites but also the basic sites.<sup>3,4)</sup> We have previously reported on the alkylation of phenol or toluene with methanol over various metal phosphate catalysts.<sup>5,6)</sup> Recently we have found that the hexadiene formation from 2-propanol proceeds readily over the calcium phosphate catalyst. In the present communication, we wish to describe the correlations between the hexadiene forming reaction over calcium phosphate catalyst and its acid-base properties.

The catalytic reaction was carried out using a pulse method in a flow of helium carrier gas. A small amount of liquid 2-propanol was fed by a microsyringe into the upper portion of the pulse reactor where it was readily vaporized. The reaction products were analyzed by means of gas chromatography with a 2.4 m column of 10% polyethylene glycol 1500 on 60/80 mesh Simalite W at 80°C. In addition, in order to confirm the hexadiene formation, the reaction products were collected in the trap with ice using a conventional flow system. Identifications were made from the retention times and by analysis using a gaschromato mass spectroscopy (Shimadzu Seisakusho Ltd., Model LKB-9000). Further identifications were made by fraction using a liquid chromatography with a column of G 2000 HG8 (Toyo Soda Manufacturing Co., Ltd., Model HLC-802 UR) and then by means of IR (Japan Spectroscopic Co., Ltd., Model IRA-1).

The  $\text{Ca}_3(\text{PO}_4)_2$  catalyst was molded from a guaranteed commercial reagent in a

wet method and prepared by the calcination in a stream of air at 400°C for 2 h. All catalysts were activated by the calcination in a stream of helium gas at 500°C for 2 h prior to each catalytic reaction.

Figure 1 shows an effect of pulse number on the conversions to propylene, acetone, and hexadiene in the reaction of 2-propanol over  $\text{Ca}_3(\text{PO}_4)_2$  catalyst at 400 °C. The conversion to propylene remained almost constant over the whole range of the pulse number of 0 to 40. Furthermore, the activity for the acetone formation was almost constant all through the experiment. On the other hand, the conversion to the hexadiene exhibited the highest value at the initial stage of the series of pulse injected, but its conversion decreased rapidly with the increase in the pulse number. The formation of hexadiene was not found in the reaction over  $\text{BPO}_4$  catalyst having the strong acid sites.<sup>6)</sup> When MgO catalyst was used, the hexadiene was not observed in the products. From these results, it seems that the hexadiene formation is not associated with only either of the catalyst functions of acidic sites or basic sites. The hexadiene formation is stoichiometrically considered as the following reaction participating both the dehydration and dehydrogenation,  $2 \text{CH}_3\text{CHOHCH}_3 \longrightarrow \text{C}_6\text{H}_{10} + 2 \text{H}_2\text{O} + \text{H}_2$ . Therefore, it seems that the hexadiene forming reaction occurs readily over  $\text{Ca}_3(\text{PO}_4)_2$  catalyst, having both the acid and basic sites.<sup>6)</sup>

Figure 2 indicates the effect of the reaction temperature on various conversions at the 40th pulse. The conversion to hexadiene increased up to a maximum value at about 425°C and then decreased with the reaction temperature. In the case of acetone, the conversion gradually decreased down to a minimum value at about 400°C, and then increased rapidly with the reaction temperature. On the other hand, the conversion to propylene increased quickly with the temperature. In addition, the total conversion of 2-propanol showed a rapid increase with the reaction temperature. Especially, its value reached almost 95% at 450°C. From these facts, it was found that the profile of the activity change for hexadiene is quite different from those for propylene and acetone in the temperature range 350-450°C.

The characteristic change in conversions by the addition of pyridine to 2-propanol is shown in Fig. 3. In the presence of pyridine, the conversion to acetone remained almost the same value as compared with that in the absence of pyridine. The conversion to hexadiene was not so much controlled at this amount of pyridine addition. However, its conversion was much more decreased with the increase of the amount of pyridine addition. In contrast with this, the conversion to propylene was considerably suppressed by the pyridine addition. From these results, it can be assumed that the hexadiene formation is somewhat related to the propylene formation occurring over the acid sites of  $\text{Ca}_3(\text{PO}_4)_2$  catalyst. Since pyridine is well known as a basic reagent, it seems to be rational that the propylene formation is remarkably suppressed by the pyridine addition. This aspect was observed noticeably by the n-butylamine addition.

Furthermore, the profile of the activity change for various products in the addition of phenol are illustrated in Fig. 4. As can be seen from Fig. 4, the conversion to propylene in the phenol addition remained almost the same value as

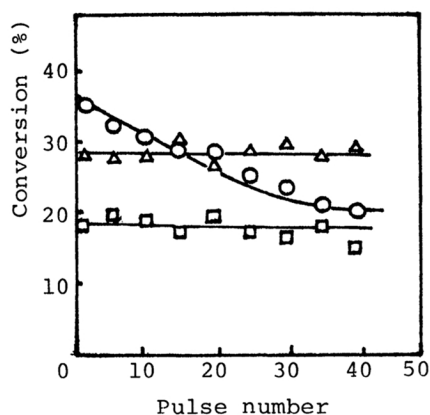


Fig. 1. Change in conversion with the repeated injections of 2-propanol.

○: Conversion to hexadiene,  
 ▲: Conversion to propylene,  
 □: Conversion to acetone.

Catalyst weight(W): 0.2 g, He gas flow rate(F): 30 ml/min, Pulse size: 2  $\mu$ l, Reaction temperature: 400 °C.

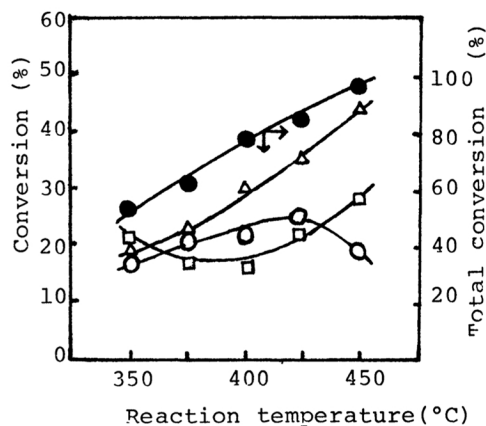


Fig. 2. Conversion as a function of reaction temperature.

The symbols and the other reaction conditions except temperature are the same as for Fig. 1.

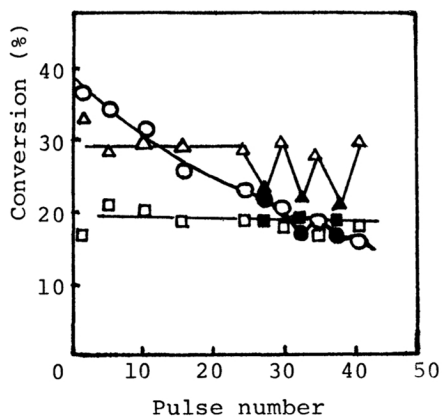


Fig. 3. Effect of pyridine addition.

●: Conversion to hexadiene in the pyridine addition,  
 ▲: Conversion to propylene in the pyridine addition,  
 ■: Conversion to acetone in the pyridine addition.

Pulse size: 2.4  $\mu$ l (2-propanol: pyridine=5:1), the other reaction conditions are the same as for Fig. 1.

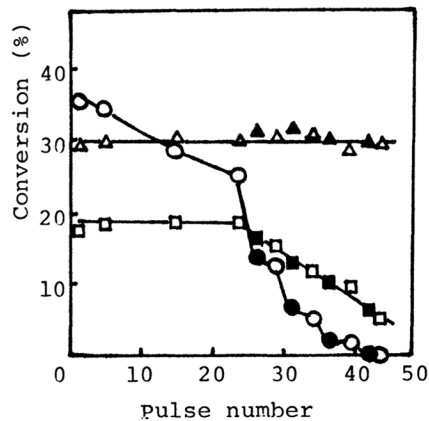


Fig. 4. Effect of phenol addition.

●: Conversion to hexadiene in the phenol addition,  
 ▲: Conversion to propylene in the phenol addition,  
 ■: Conversion to acetone in the phenol addition.

Pulse size: 2.4  $\mu$ l (2-propanol: phenol=5:1), the other reaction conditions are the same as for Fig.1.

compared with that in the absence of phenol. On the other hand, the formations of hexadiene and acetone rapidly decreased by the phenol addition and was completely suppressed at last. Especially, the conversion for hexadiene formation was reduced to almost 0% at the 40th pulse. From these results, it seems that hexadiene formation is at least parallel to acetone formation which occurs over the basic sites. This trend was found even by the chloroform addition. This behavior was quite different from that by the pyridine addition.

From the experimental results described above, the hexadiene formation may be considered as the reaction participating both the dehydration and dehydrogenation, it may be therefore concluded that both the acidic and basic sites over  $\text{Ca}_3(\text{PO}_4)_2$  catalyst play an important role in the hexadiene formation from 2-propanol. Furthermore, its formation seems to be more strongly related to the basic sites of  $\text{Ca}_3(\text{PO}_4)_2$ .

Further studies on characterization of the calcium phosphate catalyst for the hexadiene formation from 2-propanol and the mechanism are now in progress.

#### References

- 1) J.A.S.Bett and W.K.Hall, *J. Catal.*, 10, 105(1968).
- 2) C.L.Kibby and W.K.Hall, *J. Catal.*, 29, 144(1973).
- 3) T.Imanaka, Y.Okamoto, and S.Teranishi, *Bull. Chem. Soc. Jpn.*, 45, 1353(1972).
- 4) A.Tada, *Bull. Chem. Soc. Jpn.*, 48, 1391(1975).
- 5) F.Nozaki and I.Kimura, *Bull. Chem. Soc. Jpn.*, 50, 614(1977).
- 6) T.Sodesawa, I.Kimura, and F.Nozaki, submitted for publication in *Bull. Chem. Soc. Jpn.*

(Received March 12, 1979)