

DEHYDRATION AND DEHYDROGENATION OF *sec*-BUTANOL
OVER ZINC PHOSPHATE CATALYST

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The dehydration and dehydrogenation of *sec*-butanol were carried out on zinc phosphate catalyst. The catalyst was found to show a very high selectivity for the dehydrogenation, when calcined at 650 °C, though it showed a high selectivity for the dehydration when calcined at 300 °C. The active sites for the dehydrogenation were confirmed to be basic sites by a poisoning experiment.

Not much work has been reported on the dehydration and dehydrogenation of *sec*-butanol over metal phosphates, although some works have been done recently on the dehydration and dehydrogenation of isopropanol over the phosphates of $\text{Ca}^{1)}$ or $\text{Cd}^{2)}$. In the present work, we examined the selectivity, as well as the activity, for the title reaction, and found that the dehydrogenation selectivity increased with the increase of the temperature of calcination.

The reaction was carried out at 300 °C using a usual pulse reactor. The amount of each pulse was 2 μl , helium or hydrogen being used as a carrier gas (flow rate: 26 ml/min). The zinc phosphate catalyst was prepared as follows. Zinc phosphate ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$; E.P., Kanto Chemical Co.) was pressed at 1600 kg/cm^2 into tablets and stored in a tightly sealed glass bottle. Prior to use the catalyst sample was crushed, sieved (16-30 mesh), and calcined at temperatures ranging 300 to 650 °C in air for 3 hr. The acidic and basic strengths of the catalyst were measured by the conventional indicator method. The structure of the catalyst was identified by X-ray analysis.

The structure, acidic and basic strengths, and surface area measured by the BET method are given in Table 1. All the catalyst samples showed fine patterns in X-ray diffraction. Figure 1 shows the dependence of the yield to butene and methyl ethyl ketone on the calcination temperature. It can be seen that the higher the calcination temperature, the higher the dehydrogenation activity and the lower the dehydration activity. Generally, it is known that alcohols are converted to olefins by acidic sites and to aldehydes or ketones by basic sites.³⁾ However, in our catalyst system no basic property was detected by the indicator method. Thus, the poisoning effects with pyridine and dichloroacetic acid on the decomposition of *sec*-butanol were investigated in order to confirm this conclusion. Figure 2 shows the effects of poisoning.

Table 1. Structure and properties of the zinc phosphate catalyst

Calcination temp. (°C)	Structure	Surface area (m ² /g)	Maximum acidic strength (Ho)	Maximum basic strength (Ho)
200	dihydrate	1.1	1.5	-
300	anhydride	5.4	1.5	-
400	"	9.1	1.5	-
500	"	4.4	3.3	-
600	"		4.8	-
650	"		4.8	-

Addition of pyridine brought a decrease in the dehydration activity. On the other hand, dichloroacetic acid inhibited the dehydrogenation reaction and promoted the dehydration reaction. These results indicate that the dehydration needs acidic sites and the dehydrogenation basic sites. It is obvious from Fig. 1 that the ratio of cis- to trans-2-butene is substantially higher than the equilibrium value, 0.625,⁴⁾ in all cases. The ratio increased with the addition of pyridine, but decreased with that of dichloroacetic acid. These facts can not be explained by an alkoxonium-carbonium ion mechanism⁵⁾ catalyzed by acid sites.

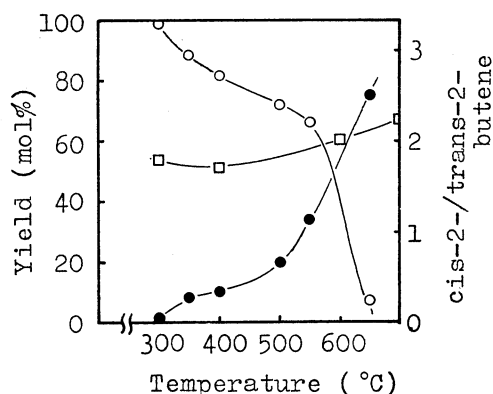


Fig. 1. Decomposition of sec-butanol over zinc phosphate catalyst.

●: Ketone, ○: n-Butene, □: cis-2-/trans-2-Butene

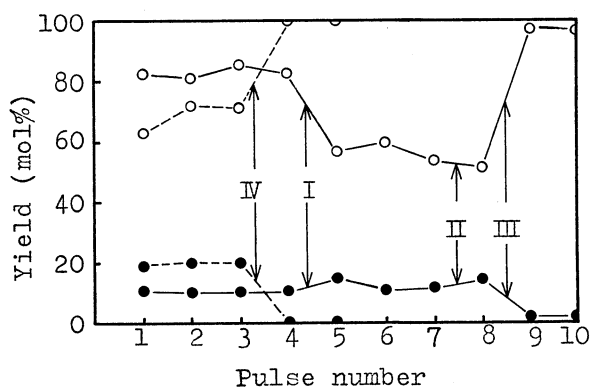


Fig. 2. Poisoning effect on sec-butanol decomposition.

—: Calcined at 400°C, ---: Calcined at 500°C, ●: Ketone, ○: n-Butene, I: pyridine injection 2μl, II: pyridine injection 4μl, III, IV: dichloroacetic acid injection 2μl

References

- 1) Y. Sasaki, H. Ohta, and F. Nozaki, Ann. Meet. Chem. Soc. Jap., 30th, Higashiosaka, Prepr. 4B13 (1974).
- 2) H. Ohta and F. Nozaki, Symp. Catal. Soc. Jap., 33rd, Hiroshima, Prepr. 1W13 (1973).
- 3) H. Niiyama and E. Echigoya, Bull. Chem. Soc. Jap., 44, 1739 (1971).
- 4) E. F. Meyer and D. G. Stroz, J. Amer. Chem. Soc., 94, 6344 (1972).
- 5) T. Yamaguchi, H. Shimizu, T. Matsuda, K. Takagaki, and K. Tanabe, Kogyo Kagaku Zasshi, 74, 1302 (1971).

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