GRINDING EFFECTS OF SEVERAL PHOSPHATES ON THEIR CATALYTIC ACTIVITIES

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Abstract The grinding effects of four kinds of phosphates on their catalytic activities for the isomerization and/or oligomerization of n-butene were investigated; activity-enhancing effect was observed for BPO_4 and $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, while activity-depressing effect for AlPO_4 and $\text{Ce}(\text{HPO}_4)_2 \cdot 1.33\text{H}_2\text{O}$.

INTRODUCTION

It is known that the physical and chemical properties of solid substances change when they undergo mechanical treatment such as grinding, pressing, and so on. Mechanochemistry of condensed phosphates has been studied extensively in terms of specific surface area, lattice distortion, crystallite size, acidic property, *etc.*¹ In 1971 Usui *et al.*² have reported that the catalytic activity of crystalline titanium pyrophosphate for the dehydration of 2-propanol strongly depends on its grinding time and its maximum activity is obtained by 50 h grinding. They further studied the dependences of the activity on the crystallite size and lattice distortion, as well as on the annealing temperature. Their conclusion is that the less titanium pyrophosphate catalyst has lattice distortion, the more it is catalytically active. The question, however, has been raised whether this conclusion is correct for other reactions and other phosphates. As to the reaction, the catalyst surface could be changed by interacting with the resulting water. The answer to the above question will help to understand the active sites on phosphate catalysts. A little study, however, has been made on the mechanochemical effect of phosphates on the catalytic activities. In view of this situation, a basic study on the mechanochemistry of a variety of phosphates should precede a detailed study on a specified phosphate, *e.g.* titanium pyrophosphate. Therefore,

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in the present study, four kinds of phosphates were chosen and their catalytic activities for the isomerization and/or oligomerization of n-butene were investigated in terms of grinding effect.

EXPERIMENTAL

Preparation of phosphates.

Two kinds of AlPO_4 , $\text{AlPO}_4\text{-I}$ and $\text{AlPO}_4\text{-III}$ were prepared by the previous methods.³ BPO_4 was prepared by heating an equimolar mixture of boric acid and phosphoric acid.⁴ $\text{Ce}(\text{HPO}_4)_2 \cdot 1.33\text{H}_2\text{O}$ was obtained from Prof. M. Tsuchioka. $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ was prepared by refluxing a mixture of titania and phosphoric acid (mole ratio $\text{P}_2\text{O}_5/\text{TiO}_2 = 20$) at 160 °C for 48 h, filtrating, washing with distilled water, and drying at 120 °C for 20 h.

Grinding was undertaken by using agate mortar and pestle. A granular catalyst sample was prepared as follows: a powdered sample was pressed into a disk under 1250 $\text{kg}\cdot\text{cm}^{-2}$, crushed, and finally sieved (16-30 mesh).

Catalytic reactions.

The isomerization and oligomerization of n-butene (50 Torr, 430 ml) were carried out using a closed circulation system. Prior to use, every phosphate catalyst was evacuated in a reactor at a specified temperature. The gas-phase composition in the reaction system was analyzed by using a gaschromatograph equipped with a 2 m column of propylene carbonate maintained at 25 °C.

RESULTS AND DISCUSSION

AlPO_4

Figure 1a shows the catalytic activities of three $\text{AlPO}_4\text{-I}$ samples evacuated at 750 °C⁵ for the isomerization of *cis*-2-butene. Three samples differ only in grinding time. It should be noted that the activity became lower as the grinding time longer. Since grinding was performed in the atmosphere, a sample was allowed to adsorb moisture. But it will be removed from the surface prior to use for the reaction, when such a sample is evacuated at 750 °C. Nevertheless, the catalytic activity was dependent on the grinding time. This would be

responsible to the change in both surface property and structure. Unfortunately, $\text{AlPO}_4\text{-I}$ sample is amorphous and so the structural change is difficult to be studied. The selectivities (defined as initial ratio of *trans*-2-butene/1-butene) of the three catalysts were infinite, in other words no 1-butene were produced.

When $\text{AlPO}_4\text{-III}$ catalyst was used instead of $\text{AlPO}_4\text{-I}$, the similar tendency to that shown in Fig. 1a between catalytic activity and grinding time was observed (Fig. 1b). These results suggest that the active sites of any AlPO_4 catalyst for *cis*-2-butene isomerization generally diminish whenever the catalyst was ground. $\text{AlPO}_4\text{-III}$ was crystalline and showed the characteristic XRD pattern of cristobalite-form. Grinding of $\text{AlPO}_4\text{-III}$, however, did not bring about noticeable structural change. This result suggests that the active sites of $\text{AlPO}_4\text{-III}$ were not originally involved in the crystalline phase but in the amorphous phase.

BPO₄

Figures 2a and 2b show the catalytic activity of BPO_4 evacuated at 500 °C⁶ for the isomerization of 1-butene and that for the oligomerization of 1-butene, respectively. Unlike AlPO_4 catalysts, the activities of BPO_4 were enhanced by grinding, especially the activity for the isomerization. Figures 3a and 3b show the results of the reactions in which 0.20 g of BPO_4 catalyst was used. The activity of unground BPO_4 (0.20 g) for the

FIGURE 1 Isomerization of *cis*-2-butene over $\text{AlPO}_4\text{-I}$ (a) and $\text{AlPO}_4\text{-III}$ (b). Weight, 0.20 g; evacuation, 750 °C (2 h); reaction temperature, 25 °C.

FIGURE 2 The isomerization (a) and oligomerization (b) of 1-butene over BPO_4 catalyst. Weight, 0.10 g; evacuation, $500\text{ }^\circ\text{C}$ (2 h); reaction temperature, $0\text{ }^\circ\text{C}$.

FIGURE 3 The isomerization (a) and oligomerization (b) of 1-butene over BPO_4 catalyst. Weight, 0.20 g; evacuation, $500\text{ }^\circ\text{C}$ (2 h); reaction temperature, $0\text{ }^\circ\text{C}$.

isomerization was nearly equal to that of ground BPO_4 (0.10 g). In the oligomerization, however, the activity of the ground BPO_4 (0.10 g) was lower than that of the unground BPO_4 (0.20 g), indicating the requirements of active sites for the two reactions are different. The XRD analysis of BPO_4 evacuated at $500\text{ }^\circ\text{C}$ showed that it was of cristobalite-form, regardless of grinding. The selectivity (defined as initial *cis*-2-butene /*trans*-2-butene) was approximately 2, regardless of grinding.

$\text{Ce}(\text{HPO}_4)_2 \cdot 1.33\text{H}_2\text{O}$

Table 1 shows the activity of $\text{Ce}(\text{HPO}_4)_2 \cdot 1.33\text{H}_2\text{O}$ reaches to a maximum around $800\text{ }^\circ\text{C}$. It is noted that the activity of the catalyst C7 was very lower than that of the catalyst C5, indicating that grinding of as-prepared $\text{Ce}(\text{HPO}_4)_2 \cdot 1.33\text{H}_2\text{O}$ caused the decrease in the activity like in the situation of the AlPO_4 catalysts.

Ti(HPO₄)₂·H₂O

It has been reported that the activity of Ti(HPO₄)₂·H₂O (both weight basis and surface area basis) depends strongly on its evacuation temperature and attains a maximum around 600 °C.⁷ Table 2 lists the catalytic activities of Ti(HPO₄)₂·H₂O-derived catalysts evacuated at 600 °C for the isomerization of 1-butene. It is clear that the activity of the catalyst T2 became almost twice by grinding for 1 h, followed by evacuating at 600 °C. No considerable change in XRD patterns before and after grinding was observed.

Calcining of the catalyst T1 at 900 °C prior to evacuation at 600 °C caused extreme decrease in the activity (see the

result of the catalyst T3). The activity of the catalyst T3 was lower by two orders magnitude than that of the catalyst T1. Like the case of the catalyst T1 (unground), the activity of the catalyst T2 (ground) also decreased sharply by calcining at 900 °C. These results indicate that the activity of ground Ti(HPO₄)₂·H₂O is determined predominantly by its calcination temperature. The activity of the catalyst T5 which had been obtained by grinding the catalyst T3 for 1 h prior to evacuation was still low, being similar to that of the catalyst T4. Grinding the catalyst T3 for 3 h, however, enhanced significantly its activity. This result indicates that grinding has considerable effect of increasing the activity of calcined Ti(HPO₄)₂·H₂O too. The initial ratios of *cis*-2-butene/*trans*-2-butene for all

TABLE 1 Catalytic activities^{a)} and selectivities of Ce(HPO₄)₂·1.33H₂O evacuated at various temperatures for 2 h.

Catalyst	Evacuation temp. / °C	Reaction rate /10 ¹⁶ .molec. ·s ⁻¹ .g ⁻¹	Selectivity <i>cis/trans</i>
C1	200	0	-
C2	500	4.0	2.0
C3	600	2.4	1.8
C4	700	10.1	1.9
C5	800	15.6	2.2
C6	900	1.3	2.0
C7b)	800	2.3	2.1

a) Isomerization of 1-butene was carried out at 50 °C.

b) Catalyst C7 was prepared by grinding as-prepared sample for 1 h, followed by calcining at 800 °C for 2 h.

TABLE 2 Catalytic activities^{a)} of Ti(HPO₄)₂·H₂O evacuated at 600 °C for 2 h.

Catalyst ^{b)}	Pretreatment		Reaction rate /10 ¹⁶ .molec. ·s ⁻¹ .g ⁻¹
	Calcin. temp. / °C	Grinding time / h	
T1	400	0	53.1
T2	400	1	119
T3	900	0	0.3
T4	900	0	1.2
T5	900	1	1.4
T6	900	3	13.1

a) Isomerization of 1-butene was carried out at 25 °C.

b) In order to prepare T4-T6 samples, T2 was used as each starting material.

Ti(HPO₄)₂·H₂O-derived catalysts were about 1.5, regardless of their calcination temperatures and grinding times, suggesting that the nature of their active sites are similar.

The effects of grinding on catalytic activities have been found to differ according to the kinds of phosphates used. The explanation of the change in activity on grinding for each phosphate will be described elsewhere.

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