ACTIVE SITES OF ALUMINUM PHOSPHATE CATALYSTS FOR THE ISOMERIZATION OF *cis*-2-BUTENE

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Abstract Various aluminum phosphate-alumina mixed catalysts (APA) having different P/Al ratios were prepared, and their activity and selectivity for n-butene isomerization as well as their physical properties were examined. The APA catalysts consisted of crystalline aluminum phosphate and alumina. Some APA catalysts showed infinite selectivity (initial *trans*-2-butene/1-butene ratio) in *cis*-2-butene isomerization; this extraordinary selectivity indicates that the surfaces of the catalysts are occupied by aluminum phosphate featuring such selectivity. Others, however, showed no infinite selectivity, which suggests that alumina involved in them catalyzes the *cis*-2-butene isomerization too. It was also concluded that the active sites featuring the infinite selectivity were located in amorphous aluminum phosphate moiety in the neighborhood of catalytically inactive crystalline aluminum phosphate.

INTRODUCTION

Aluminum phosphate (AP) evacuated at around 750 °C shows a unique catalytic behavior: extremely high *trans*-2-butene/1-butene ratio of products were formed in *cis*-2-butene isomerization. Such a high ratio can be regarded as the characteristic feature which discriminates AP from the other catalysts¹⁾. In amorphous AP, the selectivity (initial *trans*-2-butene/1-butene ratio) usually equals to infinity. On the other hand, in crystalline AP, the selectivity strongly depends on its preparative method¹⁾: The selectivity ranges from a single figure to infinity. Interestingly, certain X-ray crystalline AP (shown as AP-5 in ref. 1) shows the same selectivity value (infinity) as X-ray amorphous AP. In general, similar selectivity may be caused by similar active sites. Thus, we must consider the question where the active sites featuring infinite selectivity are located.

In this study, we prepared various X-ray crystalline aluminum phosphate-alumina mixed catalysts (APA) which have different Al/P ratios, and examined their activity and

selectivity for n-butene isomerization as well as their physical properties.

EXPERIMENTAL

Aluminum phosphate-alumina mixed catalysts (designated as APA-1~10) were prepared by heating mixtures of alumina and phosphoric acid at 80 °C, followed by drying at 120 °C for 20 h. Two kinds of aluminas were used; KHA-24 that was obtained from Nishio Ind. Co. Ltd. was used for APA-1~4, and JRC-ALO-1 kindly supplied from Catalysis Society of Japan was used for APA-5~10. The content (wt%) of phosphoric acid added to each alumina is as follows: APA-1, 17%; APA-2, 34%; APA-3, 51%; APA-4, 68%, APA-5, 8.3%; APA-6, 17%; APA-7, 25%; APA-8, 34%; APA-9, 51%; APA-10, 69%, respectively. Prior to the catalytic reaction, every APA sample was calcined at 300 °C for 3 h, followed by outgassing in situ at 750 °C for 3 h.

The isomerization of n-butene was carried out at 25 °C by using a closed circulation reaction system²⁾. X-Ray powder diffraction patterns were taken with a Rigaku-Electronic diffractometer using nickel filtered CuK α radiation.

RESULTS AND DISCUSSION

Structure and specific surface area of APA-1~4

Figure 1 shows the XRD patterns of APA samples calcined at 400 °C. As the amount of phosphoric acid added increased, the intensity of the diffraction lines due to both tridymite-form and cristobalite-form aluminum phosphates grew, while the intensity of those due to alumina decreased.

The specific surface area of APA prepared from KHA-24 alumina sharply decreased with increase in the amount of the phosphoric acid added (Fig. 2).

Isomerization of n-butene over APA-1~4

Table 1 summarizes the results of the isomerization of 1-butene over APA-1~4. Clearly, the double bond migration to 2-butene easily proceeded over alumina itself.

FIGURE 1 XRD patterns of alumina and APA samples; (a), KHA-24; (b), APA-1; (c), APA-2; (d), APA-3; (e), APA-4. ○; cristobalite form, ●; tridymite form, □; γ -alumina. CuK α , 30 kV, 20 mA.

The activity of the APA for the double bond migration decreased with increase in the amount of phosphoric acid added. This fact indicates that the double bond migration is essentially low over aluminum phosphate. The selectivity of alumina (KHA-24) was 7.1, while the selectivity of the APA decreased to about 2 with increase in the amount of phosphoric acid added.

Table 2 summarizes the results of the isomerization of *cis*-2-butene over APA-1~4. The specific activity (per unit weight) decreased monotonously with increasing amount of phosphoric acid added. On the other hand, the specific activity (per unit surface area) became nearly constant when the amount of phosphoric acid is over 17 wt%. The selectivity (*trans*-2/1) of alumina (KHA-24) itself was ca. 0.5; this finding is inconsistent with its high double bond migration activity described above. The selectivity of the APA increased up to infinity with increasing amount of phosphoric acid added, although alumina remained in the APA. It should be noted that the selectivity (*trans*-2/1) reflects both the degree of

geometrical isomerization (*cis*-2→*trans*-2) and that of double bond migration (*cis*-2→1). These reactions occur on different active sites. If the isomerization was catalyzed by alumina involved in the APA, the selectivity (*trans*-2/1) should be finite value; this prediction will hold for APA-1. However, its contribution to the isomerization over

FIGURE 2 Surface area of APA prepared from KHA-24 alumina as a function of the amount of phosphoric acid.

TABLE 1 Catalytic activity and selectivity in 1-butene isomerization over APA prepared from KHA-24 alumina

Catalyst code	Activity, <i>k</i>		<i>c/t</i> ^{a)}
	/ 10 ⁻⁵ .min ⁻¹ .g ⁻¹	/ 10 ⁻⁷ .min ⁻¹ .m ⁻²	
KHA-24	25500	19200	7.1
APA-1	18.2	20.7	4.9
APA-2	2.93	4.80	2.2
APA-3	1.07	2.62	2.7
APA-4	1.28	6.4	4.6

a) *cis*-2-butene/*trans*-2-butene.

TABLE 2 Catalytic activity and selectivity in *cis*-2-butene isomerization over APA prepared from KHA-24 alumina

Catalyst code	Activity, <i>k</i>		<i>t/1</i> ^{a)}
	/ 10 ⁻² .min ⁻¹ .g ⁻¹	/ 10 ⁻⁴ .min ⁻¹ .m ⁻²	
KHA-24	6.56	4.93	0.5
APA-1	2.24	2.54	280
APA-2	1.58	2.59	∞
APA-3	0.83	2.04	∞
APA-4	0.55	2.76	∞

a) *trans*-2-butene/1-butene.

APA-2~4 was negligible. Therefore, alumina may be almost completely covered with aluminum phosphate when the amount of phosphoric acid is over 34 wt%.

Isomerization of *cis*-2-butene over APA-5~10

Table 3 lists the results of the isomerization of *cis*-2-butene over

TABLE 3 Catalytic activity and selectivity in *cis*-2-butene isomerization over APA prepared from JRC-ALO-1 alumina

Catalyst code	Activity, <i>k</i>		<i>t</i> /1 ^{a)}
	/ 10 ⁻² ·min ⁻¹ ·g ⁻¹	/ 10 ⁻⁴ ·min ⁻¹ ·m ⁻²	
ALO-1	3.9	2.5	1.0
APA-5	4.6	3.6	29
APA-6	5.6	5.4	88
APA-7	5.1	5.8	∞
APA-8	5.9	8.1	∞
APA-9	3.4	6.9	∞
APA-10	1.4	5.8	∞

a) *trans*-2-butene/1-butene.

APA-5~10. When JRC-ALO-1 was used as a reactant for APA preparation, the specific activity expressed in any units increased with increasing amount of phosphoric acid added, and reached a maximum at 34 wt% of phosphoric acid content, and then decreased. This relationship between the activity and the amount of phosphoric acid differs markedly from that for the APA prepared from KHA-24 alumina. The selectivity (*trans*-2/1) of JRC-ALO-1 alumina itself was 1.0, while the selectivity of APA-5~10 increased up to infinity with increasing amount of phosphoric acid added. Such correlation agrees well with that of the APA catalysts prepared from KHA-24 alumina.

Active sites

As described above, the selectivity value of APA-2~4 and 7~10 was infinity, although these APA samples involved at least cristobalite-form of aluminum phosphate. In this sense, APA-2~4 and 7~10 look like a crystalline AP catalyst, AP-5¹⁾. The common features between APA and AP-5 are as follows: Both are mixtures of alumina and aluminum phosphate. The alumina remains in the bulk and the aluminum phosphate can be exposed to a reactant gas. As reported previously¹⁾, amorphous AP catalysts are much more active than crystalline AP catalysts. This fact is crucial for determining which type of AP involves the active sites featuring infinite selectivity (*trans*-2/1). Therefore, we conclude the active sites are located in amorphous aluminum phosphate moiety in the neighborhood of catalytically inactive crystalline aluminum phosphate of the APA catalysts.

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