

PRONOUNCED CATALYTIC ACTIVITY AND SELECTIVITY OF HIGH-TEMPERATURE  
EVACUATED ALUMINIUM PHOSPHATE FOR THE ISOMERIZATION OF n-BUTENES

Hidenobu ITOH, Akio TADA, and Kozo TANABE\*

Department of Environmental Engineering, Kitami Institute of  
Technology, Kitami 090\*Department of Chemistry, Faculty of Science, Hokkaido University,  
Sapporo 060

Aluminium phosphate evacuated at 750 °C catalyzed only the cis-trans isomerization of cis-2-butene without double bond migration, but that evacuated at 1000 °C catalyzed the double bond migration of 1-butene with cis-trans isomerization. The activity of aluminium phosphate evacuated at 750 °C for the cis-trans isomerization was at least 10 times higher than that of silica-alumina.

The nature of active sites on aluminium phosphate (AP) has been investigated by infrared spectroscopy<sup>1)</sup> and by means of a tracer technique which consisted of isomerization over deuterated catalyst and co-isomerization of light and perdeuterated butene.<sup>2)</sup> These results suggest that the nature of active sites on AP is sensitive to its evacuation temperature. But little study has been made on the dependency of its catalytic activity and selectivity on the evacuation temperature. For this reason, we investigated the isomerization of n-butenes on AP evacuated at temperatures ranging from 300 ° to 1100 °C.

AP was prepared as follows. A solution of 75.0 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 23.0 g of 85%  $\text{H}_3\text{PO}_4$  in 400 ml of water was neutralized to pH 7 by adding 160 ml of 10% ammonia water at the rate of 0.1 ml/min with stirring at room temperature. The precipitate was allowed to stand at room temperature for 17 h. After filtration it was washed with 200 ml each of water three times, dried at 120 °C for 20 h, and heated in air at 300 °C for 2 h. Isomerization reactions were carried out in a closed recirculation apparatus with an initial pressure of 48 mmHg. A 0.2 g charge of preheated AP was used for almost all experiments, and prior to use it was activated by evacuating in situ for 2 h at different temperatures.

The catalytic activity of AP for cis-2-butene isomerization at 25 °C is shown as a function of the evacuation temperature in Fig. 1. The activity is expressed in terms of first order rate constant on a unit surface area basis. The activity appears on evacuation at 500 °C and increases sharply to a maximum at 750 °C, above which a rapid decline occurs up to 1100 °C. Only trans-2-butene was produced on every AP catalyst. 1-Butene was not detected before cis-trans rotation (CTR) had nearly attained to equilibrium. In order to get an information about double bond migration (DBM) the isomerization of 1-butene was also investigated using 0.5 g of AP. The other reaction conditions were similar to those in the cis-2-butene isomerization. It was revealed that the rate of CTR was  $10^3$  times that of DBM on AP evac-

uated at 750 °C. For comparison, Fig. 1 also shows catalytic activities of a typical solid acid, silica-alumina (Nikki Kagaku, N631(L)) evacuated at various temperatures. The catalytic behavior of silica-alumina is much different from that of AP. 1-Butene was considerably formed on silica-alumina, initial trans-/1- ratio being 3.0 when evacuated at 750 °C. Additionally, the activity decreases monotonously with increasing evacuation temperature. It is also noteworthy that the maximum activity of AP for CTR is at least 10 times higher than the largest activity of silica-alumina.

Figure 2 shows the influence of evacuation temperature on the activity and selectivity (initial cis-/trans- ratio) of AP for the isomerization of 1-butene at 100 °C. The activity shows a maximum at 1000 °C, which is 250 °C higher than the optimum evacuation temperature for cis-2-butene isomerization. The cis-/trans- ratio is approximately unity for all evacuation temperatures. This is considered to be caused by fast CTR of cis- and/or trans-2-butene produced primarily by the DBM of 1-butene.

The difference between the optimum evacuation temperature for DBM and that for CTR suggests that the two reactions occur independently on different active sites. Sakai and Hattori<sup>2)</sup> investigated the nature of active sites on AP evacuated at 600 °C and concluded that Lewis acid sites where intramolecular hydrogen transfer occurs are characteristically active for CTR. In the CTR starting from cis-2-butene, neither catalyst deactivation nor induction period was observed, but the both were clearly found in DBM starting from 1-butene. Probably a small amount of surface residue would provide protonic sites like the situation with silica-alumina,<sup>3)</sup> which are considered to be active sites for the DBM. Results of a separate experiment demonstrated that the catalytic activity of AP for the skeletal isomerization of cyclopropane to propylene in which the protonation of cyclopropane has been reported to be a key step,<sup>4)</sup> came also to a maximum on evacuation at 1000 °C.<sup>5)</sup> This is an additional evidence for the existence of induced protonic sites on AP evacuated at 1000 °C.

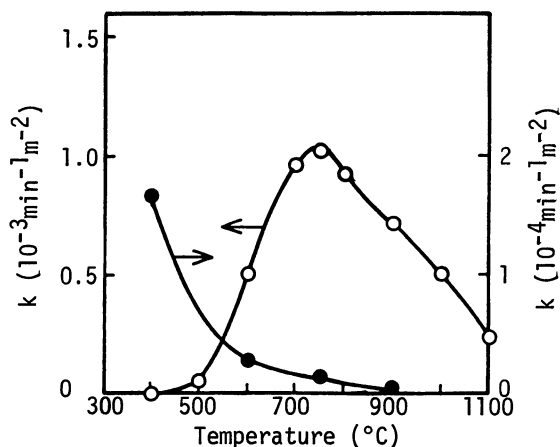


Fig.1 Dependence of the activity on evacuation temperature in the isomerization of cis-2-butene over aluminium phosphate (O) and silica-alumina (●). (Reaction temperature: 25 °C)

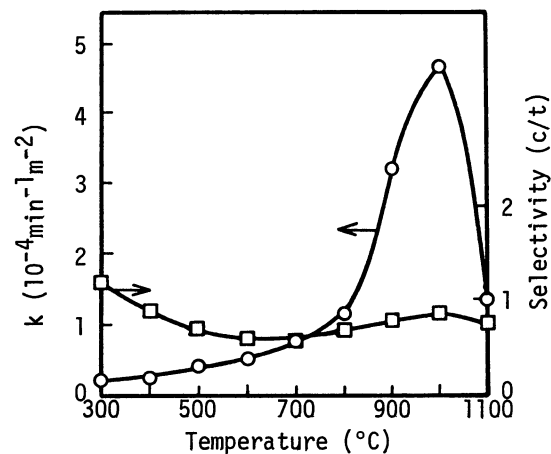


Fig.2 Dependence of the activity and selectivity on evacuation temperature in the isomerization of 1-butene over aluminium phosphate. (Reaction temperature: 100 °C)

#### References

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(Received July 16, 1981)