

CATALYTIC BEHAVIOR OF BORIA-ALUMINA PREPARED
BY CHEMICAL VAPOR DEPOSITION TECHNIQUE

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Catalytic behavior of boria-alumina greatly changed with B_2O_3 content. When $B_2O_3 \leq 12$ wt%, both boria-aluminas ($H_0 \geq -8.2$) obtained by CVD and impregnation methods showed almost the same catalytic activity, but at higher B_2O_3 contents (≥ 15 wt%, $H_0 \geq -3.0$) the CVD boria-alumina exhibited higher catalytic efficiency, e.g. for the vapor-phase Beckmann rearrangement of cyclohexanone oxime.

Boria-alumina is a solid acid which catalyzes the Beckmann rearrangement of cyclohexanone oxime¹⁾ and the hydrocarbon conversion reactions such as toluene disproportionation and xylene isomerization.²⁾ Boria-alumina is usually obtained by impregnating γ - or η -alumina with aqueous boric acid followed by calcination. We have recently reported that the chemical vapor deposition technique (CVD) using $B(OEt)_3$ is very useful to prepare a solid acid boria-silica in which B_2O_3 is uniformly and densely dispersed on the surface of silica.³⁾ In comparison with the boria-alumina prepared by impregnation method (IMP), we now describe an interesting feature of the CVD boria-alumina revealed in the acid catalysis for *m*-xylene isomerization and vapor-phase Beckmann rearrangement of cyclohexanone oxime which require different optimal acid strengths to proceed effectively.

The CVD boria-alumina was prepared by bringing $B(OEt)_3$ vapor into contact with 24-60 mesh granules of γ -alumina (JRC⁴⁾-ALO-1, 0.5 g, surface area $160 \text{ m}^2 \text{ g}^{-1}$, pore volume 0.67 ml g^{-1}) at 300°C for 0.5-5.0 h in the presence of air; the flow rates of $B(OEt)_3$ and air were 3.5 mmol h^{-1} and 113 ml h^{-1} , respectively. B_2O_3 content, which was determined by the alkalimetric titration method using mannitol, attained the maximum value of 33 wt% at 5.0 h of CVD treatment. The test reactions were performed in a flow system which was equipped with a Pyrex glass reactor containing 0.2 g of catalyst. The IMP boria-alumina was calcined at 300°C for 2 h prior to the use in the Beckmann rearrangement of cyclohexanone oxime, and both CVD and IMP boria-aluminas were pretreated at 500°C for 3 h in the case of the isomerization of *m*-xylene. Concerning the rearrangement reaction, an activity declining owing to coking was observed for every catalyst tested, and hence the catalytic efficiency was evaluated on the basis of the initial average oxime conversion and lactam selectivity at 3-4 h after the feed of reactant was initiated.

Figure 1 illustrates the catalytic performance of boria-alumina in the isomerization of *m*-xylene. At a B_2O_3 content of less than 12 wt%, both CVD and IMP boria-aluminas were almost the same in catalytic efficiency: conversion,

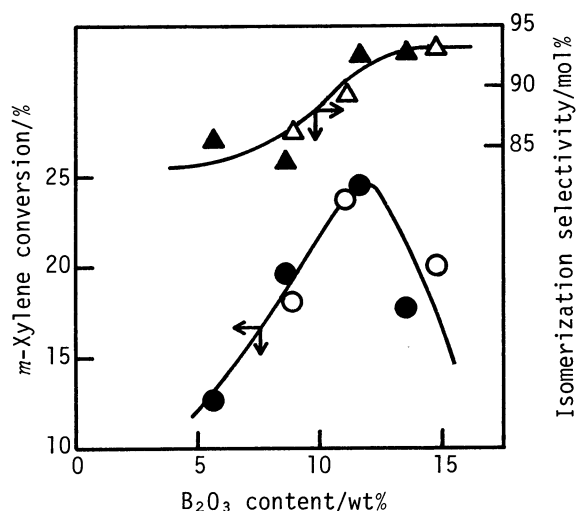


Fig. 1. *m*-Xylene isomerization at 450 °C
 W/F=41.0 g-cat h mol⁻¹; ○, △: CVD;
 ●, ▲: IMP

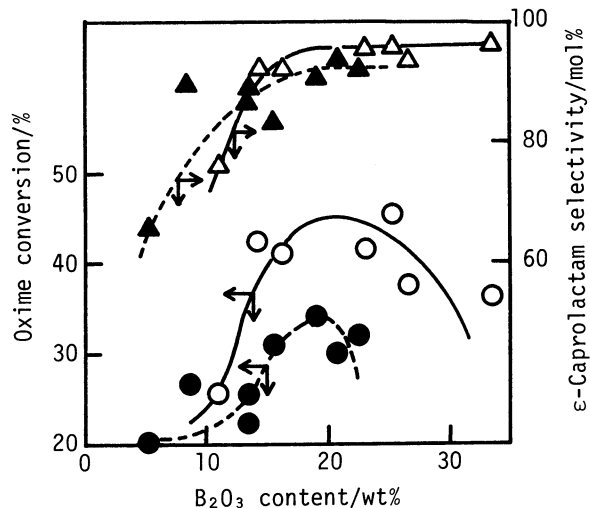


Fig. 2. Beckmann rearrangement at 250 °C
 W/F=143 g-cat h mol⁻¹; oxime:C₆H₆:N₂=
 1:13:16; ○, △: CVD; ●, ▲: IMP

selectivity (85-93 mol%) and *p*-/*o*-xylene isomer ratio (1.1-1.3). On the other hand, as shown in Fig. 2, at a B₂O₃ content of more than 15 wt%, the CVD boria-alumina exhibited higher efficiency than the IMP boria-alumina in catalyzing the Beckmann rearrangement. The same catalytic behavior of CVD and IMP boria-aluminas observed in the isomerization reaction can reasonably be explained by assuming that, until B₂O₃ content does not exceed 12 wt%, all of the B₂O₃ introduced form a surface compound by reacting with alumina independent of the preparation method to develop the strong Brønsted acid sites (H₀≥-8.2) which can effectively catalyze the isomerization.^{2,5} At a B₂O₃ content of more than 15 wt%, the acid sites of free B₂O₃ (H₀≥-3.0) which can selectively catalyze the rearrangement reaction become to dominate over the strong Brønsted acid sites, and the maximum oxime conversions were attained at B₂O₃ contents of between 20 and 25 wt%. It was confirmed by XRD measurement that the characteristic diffraction lines of B₂O₃ appeared at 2θ=14.5 and 28.0° when B₂O₃ content exceeded about 20 wt%. In contrast to the CVD technique, IMP method was inadequate to give the boria-alumina having a high B₂O₃ content of more than 15 wt%, because large crystals of boric acid were deposited on the surface of alumina. Thus the higher catalytic efficiency of CVD boria-alumina revealed in the rearrangement reaction is probably due to the uniform dispersion of B₂O₃ on the surface of alumina which was brought about by applying CVD technique. The study to elucidate the difference in acid property between CVD and IMP boria-aluminas at higher B₂O₃ contents is now under way.

References

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(Received September 4, 1985)