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VAPOR-PHASE BECKMANN REARRANGEMENT OF CYCLOHEXANONE OXIME OVER SILICA-BORIA CATALYST PREPARED BY CHEMICAL VAPOR DEPOSITION METHOD

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Cyclohexanone oxime was converted to ε-caprolactam in a high yield of 93% at 250 °C over a silica-supported boron oxide catalyst which was prepared by means of chemical vapor deposition. This catalyst was much more efficient than silica-boria and alumina-boria which were obtained by the usual impregnation method.

Several types of solid acids have been proposed as the catalysts for the vapor phase Beckmann rearrangement of cyclohexanone oxime into ε-caprolactam in order to improve the conventional liquid-phase process in which a large quantity of sulfuric acid is consumed.1-4) Among those solid acids, alumina-boria1) has been studied most extensively in view of practical application. Even alumina-boria, however, is not necessarily high selective because it works effectively only at high reaction temperatures above 300 °C at which undesirable side reactions become noticeable. In this context, it is desirable to develop more selective catalysts or such active catalysts as can be applied at lower reaction temperatures. We have recently reported a new type of selective rearrangement catalyst of boria-calcium hydroxyapatite which was designed on the basis of an idea that a weakly basic substance such as hydroxyapatite might enhance the selectivity by facilitating the desorption of the basic product ε-caprolactam from the catalyst surface without impairing the acid function of boria which is essential to effecting the rearrangement.5) We now report another approach to the design of active rearrangement catalyst which involves dispersing boron oxide uniformly and densely over silica gel by means of chemical vapor deposition (CVD).

The CVD silica-boria catalyst was prepared by contacting $B(OEt)_3$ vapor with 24-60 mesh granules of silica gel (Fuji Davison ID type) at 350 °C for 3 h in the presence of air: the flow rates of $B(OEt)_3$ and air were 3.5 mmol h^{-1} and 100-450 ml min^{-1}, respectively. The boria content of catalyst was determined by measuring the weight increase of silica gel after the CVD treatment. Little deposition of boria was observed when N_2 was employed in place of air in the CVD procedure followed by hydrolysis to decompose the surface organic moieties. The rearrangement reaction was performed at 250 °C by passing the oxime, benzene and N_2 in a mole ratio of 1:13:16 through the catalyst bed (0.2 g of catalyst as 24-60 mesh granules) packed in a Pyrex glass reactor at a WHSV of 0.81 h^{-1} in terms of the oxime. The reactor effluent was collected in a trap and analyzed by means of GLC using a PEG 20M column (1 m). The major by-products detected were cyclohexanone and 5-

hexenenitrile. Since during the reaction there was observed a decline in the oxime conversion by about 10% every one hour for every catalyst tested including alumina-boria, the catalytic efficiency was evaluated on the basis of the average initial oxime conversion and lactam selectivity at 3-4 h after the feed was started.

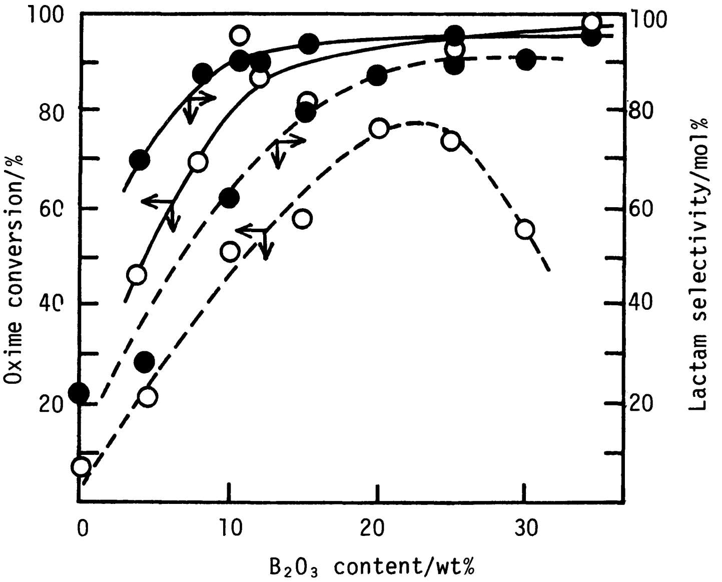

Fig. 1. Rearrangement activity of SiO_2-B_2O_3.
——: CVD catalyst, ---: impregnation catalyst
250 °C, WHSV=0.81 g-oxime/g-cat./h.

Figure 1 illustrates the change in catalytic efficiency with boria content, together with the activity change of the comparative silica-boria catalyst which was prepared by impregnating silica gel with an aqueous boric acid followed by evaporation and calcination at 350 °C for 3 h. The CVD technique unambigously surpassed the usual impregnation method with respect to preparing active and selective boria catalysts. It should be noted that, compared with the impregnation catalyst, the CVD catalyst exhibited much higher catalytic efficiency at lower boria contents. The result suggests the boria of CVD catalyst may be reasonably different from that of impregnation catalyat in its dispersion state and acid property. In addition, the CVD silica-boria was also experimentally confirmed to be far more effective than alumina-boria, because under the present reaction conditions at most 31% of the oxime was converted with a lactam selectivity of 83.9% over an alumina-boria (B_2O_3 content 26.3 wt%) which was obtained by impregnating γ-alumina with aqueous boric acid. Table 1 summarizes the influence of the physical properties of silica gel support on the rearrangement activity of CVD silica-boria. A silica gel having a larger surface area could be loaded with more boria under the same CVD treatment (350 °C, 4 h) to give higher catalytic efficiency.

Table 1. Effect of support on rearrangement activity of CVD silica-boria

Silica gel support					
Surface area	Pore volume	Pore size	B_2O_3 content of catalyst	Oxime conv.	Lactam select.
m^2g^{-1}	ml g^{-1}	nm	wt%	%	mol%
281	1.35	19.2	34	98.6	96.4
70	1.02	58.3	32	66.3	94.0
585	0.74	5.1	15	69.6	91.0
649	0.59	3.6	7.2	22.3	58.5
166	0.58	14.0	2.0	11.1	35.6

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