VAPOR-PHASE BECKMANN REARRANGEMENT OF CYCLOHEXANONE
OXIME OVER BORIA-HYDROXYAPATITE CATALYST

Yusuke IZUMI,[*] Satoshi SATO, and Kazuo URABE
Department of Synthetic Chemistry, Faculty of Engineering,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464

The boron trioxide coupled with hydroxyapatite was found to
catalyze the Beckmann rearrangement of cyclohexanone oxime in the
vapor phase at 300 °C more selectively than boria-alumina and
silica-alumina. The basic property of hydroxyapatite appears to
play an important role in effecting the rearrangement selectively.

The Beckmann rearrangement of cyclohexanone oxime for the ultimate production
of Nylon-6 has been performed industrially by use of fuming sulfuric acid catalyst
in the liquid phase at 100 - 120 °C. The existing technology poses a significant
problem of co-production of large quantity of ammonium sulfate in addition to
several operational problems of corrosion and waste water disposal. In order to
replace sulfuric acid, a number of solid acid catalysts which work under vapor
phase conditions have been proposed so far: those include boria-alumina,[1] silica-
alumina,[2] modified zeolites,[3] and supported tungsten oxide.[4] The acid function
of catalyst is essential to effecting the rearrangement reaction, but simultane-
ously the acid sites of catalyst will restrain desorption or facilitate re-adsorp-
tion of the product ε-caprolactam due to salt formation. Accordingly, the solid
acid catalysts which usually work at relatively higher temperatures (i,e., 250 -
350 °C) are not always highly selective owing to undesirable catalytic side
reactions such as polymerization and decomposition of the product lactam on the
catalyst surface, and consequently they are often deactivated by rapid carbon
deposit. Higher selectivity and less coking might be expected if it is possible
to design a catalyst which includes not only an acid component but also such a
basic component as can promote desorption of the lactam without impairing the
function of acid. We have recently found that the boron trioxide coupled with
hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), a weakly basic compound, catalyzes the vapor-
phase Beckmann rearrangement selectively. We now report the catalytic performance
of this system, comparing with some typical solid acid catalysts which have previ-
ously been offered to the rearrangement reaction.

A hydrous gel as a precursor of hydroxyapatite was obtained according to the
literature.[5] The boria-hydroxyapatite catalyst was prepared by mixing the
precursor hydrous gel and boric acid in a kneader at 100 °C, drying at 60 °C for
15 h, and finally calcining at 400 °C for 3 h. In the X-ray diffraction spectrum
of this catalyst, there were observed only those diffraction lines which could be

Table 1. Vapor-phase catalytic Beckmann rearrangement of cyclohexanone oxime[a]

Catalyst	Oxime[b] conv., (%)	Selectivity (mol %)			Weight increase[c] of used catalyst (%)
		ε-Capro-lactam	5-Hexene-nitrile	Cyclo-hexanone	
B_2O_3(40 wt%)-hydroxyapatite	67.7	97.1	0.3	2.6	9.6
B_2O_3(25 wt%)-alumina[d]	63.3	89.1	1.0	9.9	28.0
B_2O_3(14 wt%)-silica gel[d]	53.5	85.7	1.8	12.3	41.7
Silica-alumina[e]	71.6	73.3	9.0	17.7	46.9
Zeolite (HX)[f]	27.0	84.6	4.3	11.1	Unmeasured

a) 300 °C, W/F=2.0 g-cat·h/mol , oxime/C_6H_6/N_2=1/13/16 (mole ratio).

b) Average initial conversion at 2 - 3 h after the feed was initiated.

c) After 5 hours' reaction, only N_2 gas was flowed through each catalyst at 300 °C for 30 min. Most of volatile organics were removed, and the recovered catalyst was weighed and compared with its initial weight.

d) Prepared by impregnating γ-alumina or silica gel with boric acid.

e) A reference catalyst of The Catalysis Society of Japan (SAH-1 Al_2O_3 28.61 %).

f) Obtained by calcining NH_4-exchanged X-type zeolite at 350 °C for 40 h.

assigned to boron trioxide (2θ: 14.5° and 27.9°) and hydroxyapatite (2θ: 25.8°, 31.7°, 32.8°, and 34.0°).   The rearrangement reaction was performed by passing cyclohexanone oxime, benzene as a diluent, and nitrogen in a mole ratio of 1:13:16 through the catalyst bed (0.1 g of catalyst as 24 - 60 mesh granules) packed in a Pyrex glass tube reactor. 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.

Table 1 indicates that the boria-hydroxyapatite catalyst is as active as typical solid acids such as boria-alumina and silica-alumina despite its relatively small specific surface area (34 m^2/g). As shown in Fig. 1, there was observed a considerable decline in the oxime conversion during the reaction over every catalyst tested under the present reaction conditions. But the boria-hydroxyapatite revealed the highest selectivity giving the best yield of ε-caprolactam. Since the percent weight increase of used catalyst shown in Table 1 represents the amount of heavy by-products which remain in the catalyst, it probably reflects an extent of carbon deposit. As expected, the boron trioxide coupled with a pertinent basic compound of hydroxyapatite was less polluted with carbonaceous material even at higher conversions of the oxime, and as a result it gave a good selectivity to the lactam. On the other hand, the boron trioxide combined with acidic silica gel was less selective and more polluted with unvolatile organics during the reaction. Considering that silica-alumina, which possesses also base sites inherently in addition to its major acid sites, is less selective than the boria-hydroxyapatite, there will be needed an appropriate balance between acid and base sites on catalyst with respect to both quantity and strength for effecting the
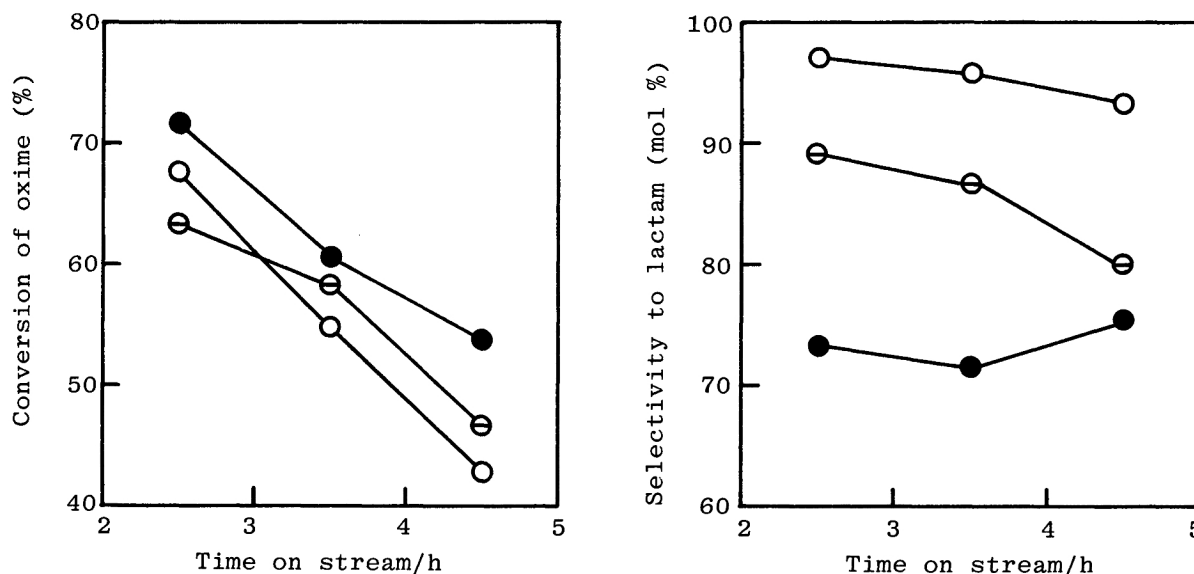
Fig. 1. Change in catalytic activity with time on stream. ○: boria-hydroxyapatite, ⊖: boria-alumina, ●: silica-alumina; 300 °C; W/F=2.0 g-cat·h/mol; oxime/C_6H_6/N_2= 1/13/16 (mole ratio).

Table 2. TPD of chemisorbed ammonia and acetic acid

Catalyst	Desorption temperature (°C)	
	Ammonia	Acetic acid
Boria-hydroxyapatite	278	268
Silica-alumina	327	320

rearrangement reaction selectively. The temperature-programmed desorption data of chemisorbed ammonia and acetic acid which are listed in Table 2 verified that the acid and base strengths of the boria-hydroxyapatite catalyst were both weaker than the counterparts of silica-alumina, because higher desorption temperatures of chemisorbed ammonia or acetic acid reflect greater strengths of acid or base, respectively. The strong base sites of silica-alumina presumably promote the conversion of the adsorbed cyclohexanone oxime to 5-hexenenitrile and water through proton abstraction of 5-cyanopentyl carbenium ion (an intermediate formed by the cleavage of the activated oxime on the acid sites), and consequently the hydrolysis of the oxime to cyclohexanone is accelerated.

Figure 2 illustrates the temperature dependence of catalyst efficiency of the boria-hydroxyapatite together with those of the comparative silica-alumina and boria-alumina catalysts. There are no significant differences in catalytic activity at each reaction temperature among these three catalysts, but the boria-hydroxyapatite reveals evidently higher selectivity at any temperatures. The boria-hydroxyapatite might therefore be expected as one of selective catalysts from the practical viewpoint. The present study suggests that not only acid
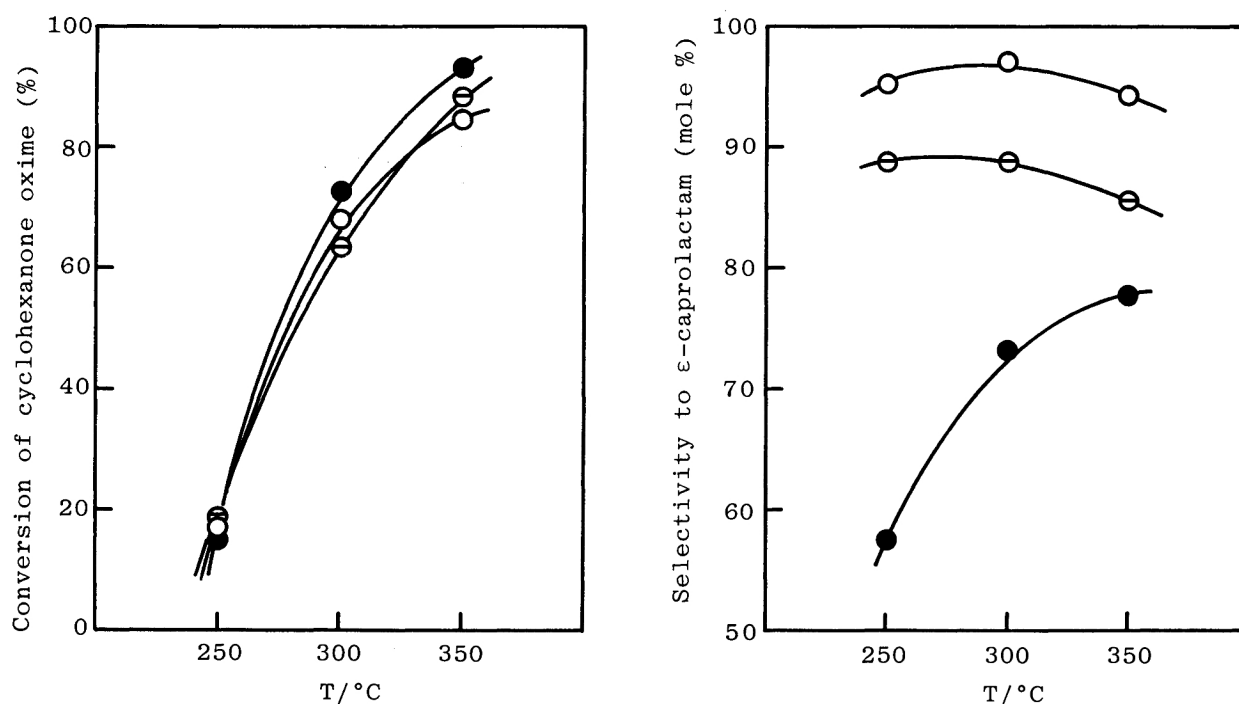
Fig. 2 Temperature dependence of catalyst efficiency of vapor-phase Beckmann rearrangement of cyclohexanone oxime. ○: boria-hydroxyapatite, ⊖: boria-alumina, ●: silica-alumina; W/F=2.0 g-cat·h/mol; oxime/C_6H_6/N_2=1/13/16 (mole ratio); data were obtained for 2 - 3 h after the feed was initiated.

property but also base property of catalyst should be investigated in more detail in order to design an effective catalyst system which will be actually applicable to vapor-phase Beckmann rearrangement process.

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