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Beckmann Rearrangement of Cyclohexanone Oxime over Borate-Pillared LDHs

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Borate-pillared layered double hydroxides (LDHs) were studied as catalysts in vapor-phase Beckmann rearrangement of cyclohexanone oxime to caprolactam under atmospheric pressure. The results were compared with those over the physical admixture of LDH and boria, the co-precipitate of B-Mg-Al hydroxide, and the pristine LDH and boria compounds. Although oxime conversion and caprolactam selectivity declined with time-on-stream over all the catalysts, borate-pillared LDH catalysts could retain activity longer than pure boria or those prepared by other methods. The decay rate however was affected by the Mg/Al ratio, the boron content and the form of LDH precursor used. The LDH itself functioning as a basic catalyst contributed to the formation of side products such as cyclohexanone and 2-cyclohexen-1-one. The physical admixtures of LDH and boria had catalytic properties more close to that of pure boria, which gave high caprolactam selectivities but lost the activity in several hours on stream. The high resistance to decay of the pillared catalysts was attributed to that boria in the interlayer of LDH was stabilized and prevented from structural transformation to a glassy state of no activity.

INTRODUCTION

ε-Caprolactam is a valuable starting material for the manufacture of nylon fibers. The most popular industrial route for its synthesis is through Beckmann rearrangement of cyclohexanone oxime with concentrated sulfuric acid catalyst.[2] However, the use of liquid acid catalysts have caused problems in product separation, corrosion hazard of reactor and the substantial amount of ammonium sulfate formed as by-product in this specific reaction. The environmental regulations and process safety continue to drive the industry to develop solid acids to replace liquid acid processes. Up to now, a wide variety of solid acids has been studied as catalysts in Beckmann rearrangement of cyclohexanone oxime to caprolactam.[3-8] Various factors including catalyst preparation, reaction temperature and surface acidity were shown to have strong influence on oxime conversion, lactam selectivity and the decay rate of the catalysts.[6-10]

The major drawback with solid acid catalysts has been their low selectivities for lactam and rapid deactivation rates. Two main reasons were suggested to account for the loss in activity: the coke formation and irreversible adsorption of the basic reaction products.[7,8] Acid function is essential for the rearrangement reaction, but concomitantly the acid sites of the catalysts will also adsorb caprolactam product strongly due to the acid-base interaction. Takahashi et al.[9] studied the Beckmann rearrangement reaction with high silica HZSM-5 as the catalyst and found that the deactivation rate was proportional to the number of strong acid sites on the zeolite. Izumi et al.[10] therefore suggested that higher selectivity and less coking might be expected if a catalyst contains a basic component in addition to the acid one and if the former can promote the desorption of lactam without impairing the acid function.

Among the various solid catalysts, boron oxide supported on alumina was one of the successful catalysts being used. Good initial activities and high selectivities to lactam were reported.[7,8] Sato et al.[7] reported that a boria catalyst supported on alumina, prepared by vapor deposition, was more efficient than that prepared by impregnation. By examining the external surfaces with SEM images, they observed large B_2O_3 crystallites forming on the impregnated catalyst but not on the vapor deposited catalyst. As a result, pure B_2O_3 was considered to have low catalytic activity for this reaction.

Layered double hydroxide (LDH), generally formulated as $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$, has been reported to be a basic catalyst.[11] It is one of the naturally occurring anionic clay minerals and can be easily synthesized in the laboratory.[11-13] The structure of LDH is similar to that of brucite, where Mg^{2+} is octahedrally coordinated to six hydroxide ions and the octahedra share edges to form a sheet structure. In LDH, a portion of the Mg^{2+} is replaced by Al^{3+}. That results in net positive charges on the metal hydroxide layers. The layer charges are balanced by interlayer anions. For the

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Dedicated to Professor Kung-Tsung Wang on the occasion of his 70th birthday.

synthetic samples, LDH structure was formed with the Mg/Al atomic ratio ranged from 1.5 to ca. 4. Pillaring of layered compounds with bulky inorganic species is one way to prepare materials of high surface area and porosity.[14-16] Our laboratory has been successful in preparing LDH pillared derivatives with tetraborate anions.[17] In contrast to the low thermal stability of pillared derivatives with polyoxometallate anions of groups VB and VIB,[18-20] the structure of borate-pillared LDHs was found to remain intact up to 550 °C. That is attributed to that tetraborate ions are stable in basic environment while the polyoxometallate anions of groups VB and VIB are not. Since supported boria was reported to be an efficient catalyst for Beckmann rearrangement of cyclohexanone oxime to caprolactam, the aim of this study is to examine the catalytic activity and selectivity of borate-pillared LDH in this reaction. Because the borate-pillared LDH has both acidic sites from interlayer boria and basic sites from LDH basal sheet, it is a good candidate to examine whether the basic sites will facilitate the desorption of caprolactam product from the catalyst surface and result in better selectivity of caprolactam.

EXPERIMENTAL METHODS

Materials

The reagent grade chemicals NaOH, adipic acid (Hanawa), $Mg(NO_3)_2 \cdot 6H_2O$ (Janssen), $Al(NO_3)_3 \cdot 9H_2O$ (Katayama), and ammonium tetraborate nonahydrate ($NH_4B_4O_7 \cdot 9H_2O$, Aldrich) were used as received without further purification.

Preparation of Catalysts

Nitrate-LDH

Layered double hydroxide compounds of the formula $Mg_2Al(OH)_6(NO_3) \cdot xH_2O$, in which the Mg/Al mole ratio is 2 and nitrate ions present in the interlayer was prepared according to the methods described previously.[11,12] To a solution containing 19.9 g of $Mg(NO_3)_2 \cdot 6H_2O$ and 14.8 g of $Al(NO_3)_3 \cdot 9H_2O$ in 200 mL deionized water, a base solution containing 8.0 g NaOH in 300 mL deionized water was added dropwise from a separation funnel. After complete addition of the base, the mixture was heated at 90 °C for 4 h. The precipitate was filtered, washed with deionized water and dried at 50 °C. The characteristic XRD pattern of this nitrate-LDH compound (abbreviated as LDH-N-2) showed $2\theta = 10.3, 20.3°$, corresponding to d-spacing of 8.56 Å.

Adipate-LDH

The adipate-intercalated LDH derivatives were prepared by co-precipitation method according to the procedures described in ref. 17. For sample LDH-A-2, 11.0 g of adipic acid, 14.5 g of NaOH and 100 mL deionized water were stirred in a flask until a homogeneous solution was obtained. A solution of aluminum nitrate (14.8 g) and magnesium nitrate (19.9 g) with the Mg/Al mole ratio of 2 was added dropwise. The mixture was then heated at 90 °C for 4 h under stirring, followed by cooling to room temperature and standing for 18 h. The precipitate was filtered and washed with deionized water. The resultant compound has XRD peaks at $2\theta = 6.4$, 12.6 and 18.9°, corresponding to d-spacing of 14.4 Å.

For sample LDH-A-3, the mole ratio of Mg/Al in solution was increased from 2 to 3 by reducing the amount of aluminum nitrate used. The resultant compound has XRD patterns similar to that of LDH-A-2.

Carbonate-LDH

The sample labeled as LDH-C-2 was prepared by carbonate ion-exchanged with LDH-A-2. To a 3 g portion of LDH-A-2 slurry, a solution containing 0.8 g of sodium carbonate in 20 mL of deionized water was added. The suspension was stirred and heated at 90 °C for 4 h, followed by filtering, washing with deionized water, and drying at 50 °C. The resultant compound has XRD peaks at $2\theta = 11.6$, 23.1 and 34.6°, corresponding to d-spacing of 7.65 Å.

Borate-pillared LDH by ion-exchange

Borate-pillared LDH compounds were prepared by tetraborate ion-exchange with LDHs either with adipate or nitrate anions in the interlayer. For samples B-LDH-A-#, a 16.6 g portion of LDH-A-# slurry was added to a solution of 10.72 g of ammonium tetraborate nonahydrate in 100 mL of deionized water. The suspension was stirred and heated at 90 °C for 4 h, followed by filtering, washing with deionized water, and drying at 50 °C. The resultant B-LDH-A-# compounds have the XRD pattern of $2\theta = 7.9$, 16.1 and 24.2°, corresponding to d-spacing of 11.0 Å.

Similar procedures as those for preparing B-LDH-A-# were followed to prepare B-LDH-N-2 except the slurry of nitrate-precursor (LDH-N-2) was used. The resultant compound B-LDH-N-2 has the XRD pattern of $2\theta = 8.1$, 16.1 and 24.2°, corresponding to d-spacing of 10.9 Å.

Borate-pillared LDH by co-precipitation method

A different borate-pillared LDH compound was prepared by co-precipitation and termed as B-LDH-ppt. A solution containing 15.0 g of ammonium tetraborate nonahydrate, 7.0 g of NaOH and 100 mL deionized water was stirred in a flask until a homogeneous solution was obtained. A solution of aluminum nitrate (9.4 g) and magnesium nitrate (19.2 g) with Mg/Al mole ratio of 3 was added dropwise from a separation funnel. The mixture was then heated at 90 °C for 4 h under stirring, followed by cooling to room temperature and standing for 18 h. The precipitate was filtered and washed with deionized water.

Physical admixture of tetraborate and LDH

0.3 g of ammonium tetraborate nonahydrate and 0.33 g of LDH-N-2 were mixed well by milling with mortar and pestle. The catalyst was termed as B/LDH-N-2. Similarly, catalyst B/LDH-C-2 was prepared by physically mixing tetraborate and LDH-C-2.

Characterization

X-ray powder diffraction patterns were obtained by using a Scintag X1 diffractometer automated with a DMS 2000 system. Cu Kα operated at 40 kV and 30 mA was the x-ray source. Samples were scanned from $2\theta = 3$ to 70°. Surface area was measured based on nitrogen adsorption at liquid nitrogen temperature using a volumetric system. Thermal gravimetric analysis (TGA) was done by using a Du Pont 9900 thermal analysis system. IR spectroscopy was performed on a Bomem DA 3.02 FT-IR spectrometer. The elemental contents of B, Al, and Mg were determined by ICP-AES (Allied Analytical Systems JARREL-ASH, Model ICAP 9000) with the solutions of samples dissolved in 6 M HCl. The surface acidity and basicity of the samples were determined by temperature programmed desorption of NH_3 and CO_2, respectively, using a Du Pont 951 thermogravimetric analyzer. Samples were preheated at 450 °C under a flow of N_2 (100 mL/min) and cooled to 200 °C before introducing NH_3 or CO_2. The desorption profiles were obtained from 200 to 450 °C with a heating rate of 10 °C/min.

Catalytic Reaction

2-Propanol decomposition

The reactions were performed in a plug-flow type reactor operating at 300 °C under atmospheric pressure. Saturated 2-propanol vapor at 18 °C (controlled with a thermostat) was fed with a nitrogen gas carrier (20 mL/min) to the catalyst bed. About 0.3 g of the catalyst was preheated under a nitrogen stream at 350 °C for ca. 2 h before starting the reaction. The products were analyzed by a HP 5890 gas chromatograph with a FID detector.

Beckmann rearrangement

The vapor phase Beckmann rearrangement of cyclohexanone oxime was carried out at atmospheric pressure in a plug-flow type reactor. The catalyst, 0.3 g in powder form, was packed in a Pyrex glass tube reactor of 15 mm O.D. The reaction temperature was read through a thermocouple placed in the thermowell right above the catalyst bed. All catalysts were pre-heated under nitrogen for 2 h before the reaction. The reactant containing 10 weight percent cyclohexanone oxime in benzene was introduced with a syringe pump in a liquid flow-rate of 0.75 mL h^{-1}. Nitrogen gas in a flow-rate of 10 mL min^{-1} controlled by a KORFLOC flowmeter was introduced into the reactor as a diluent. The gas products downstream from the reactor were collected by passing through a cool trap at liquid nitrogen temperature. The products collected in 20 min intervals were analyzed with an off-line HP 5890 gas chromatograph equipped with a 0.32 ID, 30 m length DB-1 capillary column and a FID detector. The product identification was assisted with a HP 5971 mass selective detector and NIST mass spectral database.

RESULTS

Catalyst Characterization

The XRD patterns of some representative LDH compounds are shown in Fig. 1. The interlayer spacings are varied with the size of interlayer anions. The d-spacing of nitrate-LDH is 8.8 Å, while long chain adipate anion expanded the d-spacing to 14.4 Å. After pillaring with tetraborate anions, the d-spacing shrank to 11 Å. By subtracting the layer thickness of 4.6 Å, the free interlayer

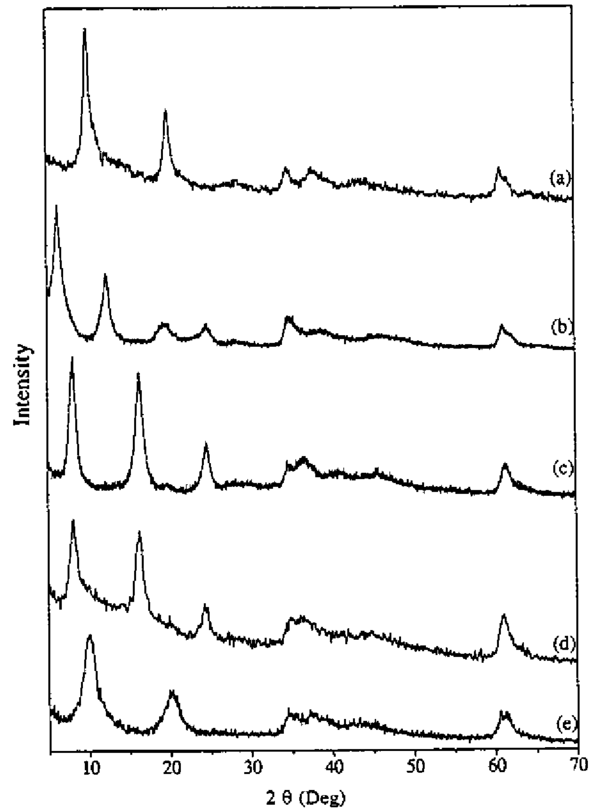

Fig. 1. XRD patterns of (a) LDH-N-2, (b) LDH-A-2, (c) B-LDH-2, (d) B-LDH-3, and (e) B-LDH-ppt.

space of borate-pillared LDH is ca. 6.4 Å. The diffraction patterns are similar for borate-pillared samples with Mg/Al ratio being 2 or 3. On the other hand, the sample prepared by co-precipitation (B-LDH-ppt) has a pattern closer to that of nitrate-LDH than that of the pillared samples, indicating that either the boron atoms are mixed into the framework of LDH or the tetraborate ions are transformed to other smaller species.

The FTIR spectra of the pillared and co-precipitated samples were compared with those of nitrate-LDH and ammonium tetraborate (Fig. 2). The presence of the ν_3 BO_3 stretching bands at 1300-1500 cm^{-1} and the ν_3 BO_4 stretching bands at 1000-1150 cm^{-1} with an intensity ratio similar to that of ammonium tetraborate confirms that the major boron species present in the as-prepared borate-pillared LDH are tetraborate.[21] The spectrum of co-precipitation sample (B-LDH-ppt) also has absorption in these regions but the peaks are weaker and more broadening. Besides, an intensive nitrate (NO_3^-) group vibration appears at 1384 cm^{-1},[22] implying that quite a large amount of NO_3^- ions was incorporated in the interlayer of LDH during co-precipitation. For the borate-pillared LDH prepared by borate ion-exchange with adipate-LDH, there also was presented a small sharp peak of NO_3^- group on top of the ν_3 BO_3 stretching band in the 1300-1500 cm^{-1} region. Hence, a small amount of nitrate ions may also incorporate into the adipate-LDH sample and be retained even after borate ion-exchange.

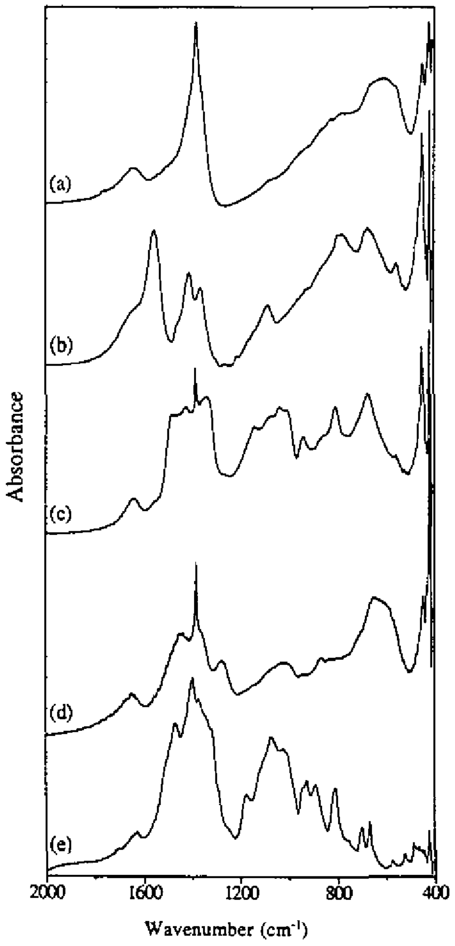

Fig. 2. IR spectra of (a) LDH-N-2, (b) LDH-A-2, (c) B-LDH-A-2, (d) B-LDH-ppt, and (e) $(NH_4)_2B_4O_5(OH)_4$.

Pillaring condition was found to have strong influence on the boron content and the surface area of the borate-pillared products. Table 1 lists the bulk chemical compositions and surface areas of the catalysts. The Mg/Al mole ratios of the as-prepared borate-LDH catalysts are generally lower than that in the parent liquids. The B/Al ratios in boria-containing compounds vary in a relatively large range, from 2.0 to 3.8. For the physical admixtures, the boron contents have a direct correlation with the masses of ammonium tetraborate and LDH used. However, in samples prepared by ion-exchange, that ratio varied with reaction conditions. Different B/Al ratios imply that different boron species may present in the interlayer. In aqueous solution, borate of low concentration forms mainly mononuclear species, such as $B(OH)_3$ and $B(OH)_4^-$, while those in concentrated solutions are polymeric ions, such as $B_5O_6(OH)_4^-$, $B_3O_3(OH)_4^-$ and $B_4O_5(OH)_4^{2-}$, formed successively with an increase in pH.[23] The theoretical B/Al ratio of borate-pillared LDH would be 1, 2, 3 and 5, corresponding to the interlayer borate in the form of monoborate ($B(OH)_4^-$), tetraborate (in the form of $B_4O_7^{2-}$ or $B_4O_5(OH)_4^{2-}$), triborate ($B_3O_5^-$) and pentaborate ($B_5O_6(OH)_4^-$), respectively.[17,24] Because the ion-exchange reaction was started with tetraborate, the B/Al ratio in borate-pillared LDHs of values greater than 2 implies that triborate or pentaborate ions are probably also present in the interlayer.

Table 1. Chemical Composition and Surface Area of the Catalysts

Catalyst	Mg/Al molar ratio Parent liq.	Mg/Al molar ratio Solid	B/Al molar ratio	BET S.A.[a] (m^2/g)
Boria	-	-	-	8
LDH-N-2	2	1.6	0	62
LDH-C-2	2	1.8	0	131
B-LDH-A-2	2	1.5	2.6	145
B-LDH-A-3	3	2.5	3.5	90
B-LDH-N-2	2	1.6	3.0	162
B-LDH-ppt	3	2.8	3.7	42
B/LDH-N-2	2	1.6	2.0	48
B/LDH-C-2	2	1.7	3.8	73

[a] Pre-condition temperature = 350 °C

The surface areas of borate-pillared LDH samples prepared with either adipate- or nitrate-LDH slurry were all around 130-160 m^2g^{-1} (Table 1), which was about twice greater than that of unpillared LDH-N-2 (62 m^2g^{-1}). The surface areas of most LDH samples were almost unchanged upon heating at temperatures from 200 to 450 °C. However, heat treatment of carbonate-LDH (LDH-C-2) at temperatures higher than 350 °C increased the surface area from 75 to 131 m^2g^{-1}. This phenomenon is commonly recognized due to the structural disorder accompanying the decarboxylation of interlayer carbonate ions.[11]

The surface acidity and basicity of nitrate- and borate-pillared LDHs were determined by temperature programmed desorption of NH_3 and CO_2, respectively. NH_3 is supposed to be chemisorbed on the acid sites, while CO_2 is chemisorbed on the basic sites. However, all the desorption profiles were found to cover over the temperature range of 200-450 °C and it is difficult to distinguish the acid strength from the profiles. Moreover, because of the amphoteric character of alumina, the amounts of NH_3 and CO_2 chemisorbed could not reflect the true acid-base properties of LDH samples. Table 2 shows the total amounts of NH_3 and CO_2 chemisorbed by the samples. Nitrate-LDH adsorbed the greatest amounts of both NH_3 and CO_2 among the samples. The fact that more CO_2 than NH_3 was adsorbed might imply that more basic sites than acidic sites were present. Over borate-pillared samples, the amounts of CO_2 chemisorbed were markedly suppressed, implying the decrease in basic sites. However, the total amounts of NH_3 chemisorbed decreased as well. When the Mg/Al molar ratio of LDH increased from 2 to 3, the ratio of acidic to basic sites is decreased as expected.

Catalytic Reactions

2-Propanol decomposition

2-propanol decomposition was used as an indicator reaction to study the acid-base properties of the catalysts. It is well accepted that dehydration of alcohol is mainly catalyzed by acid sites while dehydrogenation is catalyzed by basic sites.[25] As shown in Table 3, the major product over nitrate-LDH (LDH-N-2) was acetone, while the major products over borate-pillared LDHs was propene. The propene selectivity is higher for B-LDH-A-2 than for B-LDH-A-3 because the amount of borate incorporated in LDH increases as the Mg/Al molar ratio decreases. It is also noticeable that borate-pillared LDH, prepared by tetraborate ion-exchange with nitrate-LDH, has propene selectivity as high as that over the physical admixture (B/LDH-N-2). The high acidity is an indication that the boria formed after calcination is probably covering the outer surfaces of the LDH particles in both samples. In contrast, the catalytic behavior of B-LDH-ppt prepared by co-precipitation is similar to that of nitrate-LDH, and shows more basic character than acidic. Hence, most of the boron species in B-LDH-ppt are probably hidden inside the framework and play little role in the catalytic reaction. These results demonstrate that boria can enhance the acidity and weaken the basicity of LDH when it is either pillared in the interlayer of LDH by ion-exchange or physically admixed with LDH, but barely effective when prepared by co-precipitation.

Table 2. Amount of CO_2 and NH_3 Chemisorbed on LDH and Borate-pillared LDHs (in unit of mg/100 mg catalyst)

Catalyst	NH_3	CO_2	acidic:basic sites (%)
LDH-N-2	1.84	2.30	44:56
B-LDH-A-2	1.21	0.67	64:36
B-LDH-A-3	0.45	0.74	38:62

Table 3. Results of 2-Propanol Decomposition over Various Catalysts at 300 °C

Catalyst	Conversion (%)	Selectivity (%) Propene	Acetone
LDH-N-2	12.9	33.9	60.5
B-LDH-A-2	35.5	86.1	13.9
B-LDH-A-3	20.8	62.6	37.4
B-LDH-N-2	67.8	94.7	5.3
B/LDH-N-2	52.9	94.0	6.0
B-LDH-ppt	8.0	31.1	68.9

Beckmann rearrangement

In Beckmann rearrangement of cyclohexanone oxime, the oxime conversion and product selectivity vary tremendously for different catalysts. Table 4 shows the results obtained after 4 h on stream. Over pure boria, although the conversion was low, caprolactam was the major product. In contrast, little caprolactam was formed over nitrate- or carbonate-LDH compounds (LDH-N-2 and LDH-C-2, respectively). Instead, the major products are cyclohexanone, 2-cyclohexen-1-one and coke. These side products are probably catalyzed by the basic sites on LDH since the latter has more basic character than acidic. The reaction scheme proposed by Landis and Ventuto[3] is therefore modified and shown in Scheme I. On the other hand, the physical admixtures (B/LDH-C-2 and B/LDH-C-3) behaved similarly to pure boria, and caprolactam was the major product. The similarity in product selectivities between boria and the physical admixtures implies that the LDH particles in the latter catalysts are encapsulated by a layer of boria. It is in-

Table 4. Product Distribution in Beckmann Rearrangement of Cyclohexanone Oxime over Various Catalysts at 340 °C and after 4 h on Stream

Catalyst	Boria	LDH-N-2	LDH-C-2	B-LDH -A-2	B-LDH -A-3	B/LDH -C-2	B/LDH -C-3
Conversion (%)	3.4	15.3	42.9	96.1	54.6	53.8	57.8
Product Select. (%)							
Caprolactam	87.0	2.6	0	40.7	25.7	90.0	96.8
Cyclohexanone	13.0	21.0	44.0	6.1	13.0	0.5	0.6
2-Cyclohexen-1-one	0	66.8	4.8	17.2	23.2	0.9	2.2
Aniline	0	0	0	0	7.7	1.2	0
Hexanenitrile	0	0	3.2	0	1.1	0.2	0.4
Coke	0	9.8	48.0	36.0	29.3	7.2	0

[a] The physical admixture of ammonium tetraborate and B-LDH-A-2 in 1:2 weight ratio.

teresting to find that borate-pillared LDH catalyst shows mixed characters of pure boria and LDH in product selectivities. Caprolactam of ca. 30-40% selectivities was obtained in addition to the base-catalyzed products.

Similar to that observed over other solid acid catalysts, the oxime conversion and caprolactam yield decrease with time-on-stream. Table 5 shows that the deactivation is enormous over pure boria. The oxime conversion of 13% was observed first at 20 min; it declined to 3.4% in 4 h, and eventually there was no detectable catalytic activity after 20 h on stream. Over the physical admixtures, the activities declined in a rate similar to but slower than that of pure boria. The resistance to decay (R value) is estimated by the ratio of caprolactam yield after 20 h on stream to that of 4 h. The co-precipitated catalyst (B-LDH-ppt) was the worst catalyst, which gave low lactam selectivity and a short lifetime.

The borate-pillared LDH samples were distinguished in their greater resistance to decay. It was also noticed that the R value increases with the decrease of Mg/Al molar ratio, or the increase in boron content. Among the pillared catalysts under investigation, B-LDH-A-2 was best performed with only 80% decay in activity after 20 h on stream. In comparison, B-LDH-N-2 prepared with nitrate-LDH slurry instead of adipate-LDH slurry, gave lower conver-

Scheme I Proposed reaction scheme of Beckmann rearrangement over borate-pillared LDH

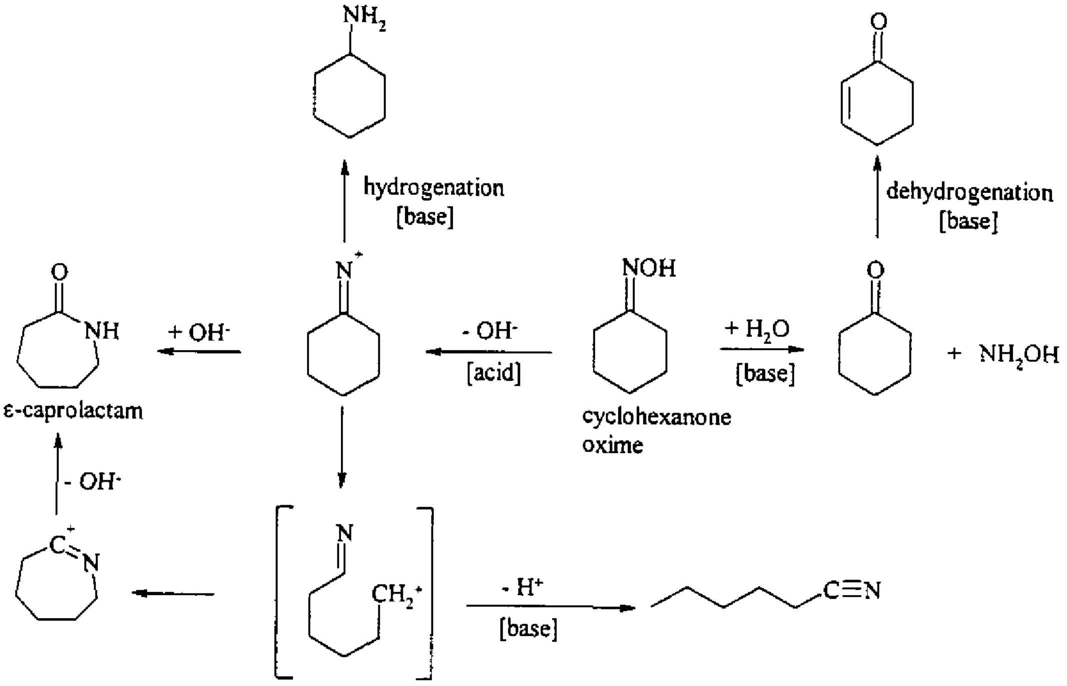

Table 5. Beckmann Rearrangement of Cyclohexanone Oxime over Boria-containing LDHs as a Function of Time-on-stream

Catalyst \ Time on stream	4 h conv.	4 h selec.[a] (%)	4 h yield[b]	20 h conv.	20 h selec.[a] (%)	20 h yield[b]	R[c]
Boria	3.4	87.0	3.0	0	0	0	0
LDH-N-2	15.3	0	0	4.6	0	0	-
LDH-C-2	42.0	0	0	11.7	0	0	-
B-LDH-A-2	96.1	40.7	39.1	95.0	33.0	31.3	0.80
B-LDH-A-3	54.6	25.7	14.0	14.9	41.0	6.1	0.44
B-LDH-N-2	41.8	56.7	23.7	27.0	51.4	13.9	0.59
B/LDH-N-2	29.3	68.3	20.0	3.2	65.9	2.1	0.10
B/LDH-C-2	53.8	90.7	48.8	10.9	83.9	9.1	0.19
B/LDH-C-3	57.8	92.9	53.7	19.4	74.8	14.5	0.27
B-LDH-ppt	21.9	22.3	4.9	12.3	7.7	0.95	0.19

[a] Selectivity of caprolactam. [b] Yield of caprolactam.
[c] R (resistance to decay) = caprolactam yield at 20 h/yield at 4 h.

sion, shorter lifetime, but relatively higher selectivity of lactam. These results are consistent with those of 2-propanol decomposition. They are elucidated by that more boria species are retained on the superficial surface of LDH when the LDH with nitrate instead of larger adipate ions in the interlayer was used for ion-exchanged with tetraborate. The interlayer boria species sandwiched in between the LDH layers were stabilized during the Beckmann rearrangement reaction, while the boria species present on the outer surface lost activity easily. Hence, among pillared catalysts B-LDH-A-2 has higher resistance to decay than B-LDH-N-2. In turn, the latter has higher resistance to decay than B/LDH-N-2 which was prepared by physical mixing.

Table 6 shows the effect of pre-condition temperature. Over B-LDH-A-2 catalyst, when the pre-condition temperature was raised from 350 to 450 °C, the cyclohexanone conversion decreased and the caprolactam selectivity increased. However, that was compensated by a poor resistance to decay. When the pre-condition temperature was raised to 750 °C, the catalyst lost most of the activity. That is primarily due to the collapse of the pillared structure and the decrease in surface area from 145 to < 10 m^2/g during high temperature calcination. For comparison, pure boria lost its catalytic activity completely when it was pre-heated to temperatures higher than 400 °C.

DISCUSSION

The catalytic activities of borate-pillared LDHs were strongly dependent on the LDH precursor used. The Mg/Al ratio in LDH, adipate- or nitrate-LDH, and slurry or dried powders were all important factors. The adipate-LDH with the d-spacing expanded by the organic chains to 14 Å facilitates the tetraborate ion-exchange and results in pillared products with boria more homogeneously distributed in the interlayer. On the other hand, using the nitrate-LDH of d-spacing 8.5 Å as the precursor results in borate-pillared derivatives containing a considerable portion of boria accumulated on the superficial surfaces. Similarly, a slurry precur-

Table 6. Effect of Precondition Temperature on Beckmann Rearrangement of Cyclohexanone Oxime over Boria-containing Catalysts

Catalyst \ Time-on-stream	Pre-cond. temp (°C)	4 h conv.	4 h select. (%)	4 h yield	20 h conv.	20 h select. (%)	20 h yield	R
B-LDH-A-2	350	96.1	40.7	39.1	95.0	33.0	31.4	0.80
	450	80.3	51.8	41.6	33.7	50.4	17.0	0.41
	750	6.3	28.3	1.8	4.3	6.7	0.3	0.17
Boria	350	3.4	87.0	3.0	0	0	0	0
	400	0	0	0	0	0	0	-

sor containing more interlayer water is better than dried powders for tetraborate ion-exchange.

The catalytic behaviors of the physically admixed samples suggest that the boria species are distributed mainly on the outer surface of the LDH particles. The cover-up of the surface of LDHs with boria decreases the surface area of pristine LDH as well as the basic sites. As a result, high caprolactam selectivity and fast decay rate were observed, and that is a pattern similar to what was observed over pure boria. In the case of a co-precipitated sample, most of the boron species are probably mixed in the framework of Mg/Al hydroxide and not accessible by the reactant molecules.

Aucejo et al.[4] reported that Beckmann rearrangement of cyclohexanone oxime was catalyzed by Bronsted acid sites, while Curtin et al.[8,26] who studied supported boria catalysts, proposed that acid sites of intermediate acid strength were enough. From the results of chemisorption of NH_3 and CO_2 (Table 2) as well as 2-propanol decomposition (Table 3), Mg/Al LDHs own mainly basic character and some acidic sites. These acidic sites are not strong enough to catalyze Beckmann rearrangement of cyclohexanone oxime to caprolactam; however they may adsorb the reactant or products strongly. As a result, only a trace amount of caprolactam but a considerable amount of coke were formed over LDH-N-2 and LDH-C-2 catalysts. On the other hand, boria itself has high selectivity of caprolactam, but the oxime conversion is low and the activity decreases abruptly with time-on-stream. Besides, the glassy boria, obtained by heating ammonium tetraborate at 400 °C for more than 1 h, has no catalytic activity in a rearrangement reaction (Table 6). These results explain why pure B_2O_3 is reported to have little activity in Beckmann rearrangement reactions.[7,11] Curtin et al.[26] studied the deactivation and regeneration of B_2O_3/Al_2O_3 catalysts and suggested that the deactivation was associated with the diffusion of boron into the alumina lattice and the formation of an amorphous phase. Therefore, the transformation of boria structure from an active form to a glassy form or other phases during reaction should account for the loss in activity of supported boria. In contrast, the activity should be retained if the transformation of boria structure could be prevented. The present study shows that pillaring of LDH compounds with borate ions is one way to prepare boria containing catalysts of rather good stability. Because the layer structures of borate-pillared LDHs were found to remain intact up to 550 °C,[17] the boria species sandwiched in between the interlayer of LDHs have a relatively higher thermal stability than pure boria or supported boria toward sintering or phase transformation. That is considered to be the key factor for the higher resistance to decay of borate-pillared LDHs in Beckmann rearrangement reactions. However, the drawback of borate-pillared LDHs as catalysts in this reaction is that relatively large amount of side products catalyzed by the basic sites present on the LDHs was found.

The caprolactam selectivities over borate-pillared LDHs were in the range of 30-56%, which was lower than that over pure boria or the physical admixture (68-90%). The acid site of boria and the basic site of LDH seem to act independently in catalyzing the oxime rearrangement reaction. These results contradict to the proposal suggested by Izumi et al.[10] that a basic component might suppress the strong adsorption of the basic products on the acid catalytic sites and result in higher caprolactam selectivity.

CONCLUSIONS

It is concluded that borate-LDH catalysts prepared by pillaring the layer double hydroxide with tetraborate ions can retain activity longer than pure boria or those prepared by other methods. The stability of the pillared catalysts is due to that boria is stabilized in the interlayer of LDH and is prevented from structural transformation to a glassy state of no activity. Higher catalytic activity of borate-pillared LDH is observed when boria is more homogeneously distributed in the interlayer. Moreover, the catalytic activity is proportional to the amount of boria accessible by the reactants. LDHs of lower Mg/Al ratio have higher boron content and are more active in Beckmann rearrangement reactions. On the other hand, the physical admixture of borate and LDH results in catalysts with boria mainly covering on the surface of the LDH particles. Similar to that of over pure boria, the physical admixture gives higher lactam selectivity than pillared LDHs; however the catalytic activity decays more quickly.

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Key Words

Beckmann rearrangement; Boria; LDH; Pillaring; Catalyst.

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