Vapor-Phase Beckmann Rearrangement of Cyclohexanone Oxime over an HY Zeolite Catalyst Calcined at High Temperature

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The vapor-phase Beckmann rearrangement of cyclohexanone oxime over an HY zeolite calcined at high temperatures was investigated. Cyclohexanone oxime was rearranged into ε-caprolactam with high conversion at 573 K over an HY zeolite calcined at 873 K. The activity decay was slight, while oxime conversion over an HY zeolite calcined at 773 K steeply decreased during the initial stage of the reaction. The catalytic activity for the rearrangement was not correlated with the physical properties of a fresh catalyst, but with those of a used one, especially regarding their porosity and acidity. It was also found that the produced ε-caprolactam was tightly adsorbed on strong aicd sites, filling the micropores of the zeolite during the initial stages of the reaction, and that a large portion of the catalytic reaction proceeded mainly on weak acid sites located in a region near to the external surface of the zeolite.

The vapor-phase Beckmann rearrangement of cyclohexanone oxime has been investigated in order to replace a process using sulfuric acid with a method employing solid acids in manufacturing ε-caprolactam.[1–16] A number of solid acid catalysts, such as mixed boron oxide,[1–6] amorphous silica–alumina,[7–9] and modified zeolites,[10–16] have been proposed. Although strong acid sites on an HY zeolite catalyze the rearrangement of cyclopentanone oxime, even at 393 K, the produced lactam is tightly adsorbed on the zeolite surface.[17] Because a reaction temperature higher than 573 K is required for the desorption of the produced lactam, solid acid catalysts are liable to accompany undesired side reactions, such as decomposition of the reactant oxime and polymerization of the produced lactam, as well as a rapid deactivation by carbon deposition. Recently, a modified H-ZSM-5 zeolite was reported as being a highly selective catalyst; a zeolite having only neutral hydroxyl groups was prepared by treating strong protonic acid sites of the surface with trimethylsilyl chloride; the resulting catalyst was found to be effective for the vapor-phase Beckmann rearrangement.[14]

In the present work, a highly acidic HY zeolite catalyst was investigated regarding the vapor-phase Beckmann rearrangement of cyclohexanone oxime. The HY zeolite was calcined at high temperatures with the view to obtain an effective catalyst by decreasing its acid strength. The acidic property and pore characteristics of the catalyst were measured in order to clarify the relationship between the physical properties and the catalytic behavior of the HY zeolites.

Experimental

A commercial HY zeolite with an Si/Al ratio of 2.8 was supplied by Toso Co., Ltd. (HSZ-320-HOA). The HY sample was calcined at the prescribed temperatures in the atmosphere for 3 h.

The vapor-phase Beckmann rearrangement of cyclohexanone oxime was carried out in a fixed-bed continuous-flow reactor under atmospheric pressure. Prior to the reaction, a catalyst sample was preheated under nitrogen flow at a reaction temperature of 573 K. A mixture of the oxime, benzene, and nitrogen gas with a molar ratio of 1:13:36 was passed through the catalyst bed (0.15 g) at a WHSV of 0.32 h^{-1} in terms of the oxime. The reactor effluent was analyzed by offline GLC using a column of PEG-HT (1 m). The by-products were mainly cyclohexanone and 5-hexenenitrile.

The pore characteristics were obtained with nitrogen physisorption at 77 K. The pore volume was calculated in terms of the amount of physisorbed nitrogen. The adsorption isotherms were classified into the Langmuir or BET type. A specific surface area was evaluated according to the respective adsorption equation.[18] An external surface area was evaluated by the BET equation of the adsorption isotherm after water molecules had been filled in the micropores of the sample at 298 K.[19]

The temperature-programmed desorption (TPD) of adsorbed ammonia was measured through neutralization titration by using an electric conductivity cell containing 0.5 mmol dm^{-3} of a sulfuric acid solution.[20] A sample (10 mg) was preheated in a quartz tube at 773 K for 1 h under reduced pressure (1 Pa). After ammonia had been adsorbed at 298 K for 1 h, physisorbed ammonia was evacuated at 373 K for 1 h. The TPD measurement was started from 373 K at a heating rate of 10 K min^{-1} under a nitrogen flow of 70 ml min^{-1}.

Another TPD was measured for HY zeolites used for the rearrangement at 573 K for 1 h, followed by heating under nitrogen flow for 1 h. The sample was evacuated at 298 K for 1 h under reduced pressure. After ammonia had been adsorbed at 298 K for 1 h, and physisorbed ammonia evacuated at 373 K for 1 h, TPD measurements were carried out from 373 K at a heating rate of 5 K $min.^{-1}$ Individually, a blank TPD spectrum was recorded from 298 K at a heating rate of 5 K min^{-1} under a nitrogen flow of 70 ml min^{-1} without any ammonia adsorption.

Results and Discussion

Catalytic Activities. The vapor-phase Beckmann rearrangement of cyclohexanone oxime has usually been performed within the temperature range from 573 to 653

K for various aluminosilicates.[7—16] In our preliminary tests at a reaction temperature of 623 K, the conversion of cyclohexanone oxime decreased slightly with the process time over an HY zeolite calcined at 773 K; however, little change in catalytic activity was observed with an HY calcined at 873 K (conversion of oxime: 98%, selectivity to lactam: 77%). In order to compare in detail the catalytic performance of HY zeolites at different calcination temperatures, the tests were carried out at 573 K, since oxime conversion at 623 K was too high to discuss the difference in the degradation of catalytic activity.

Figure 1 shows changes in the oxime conversion with the process time at 573 K. The activity loss of HY zeolite calcined at 873 K was very slight, whereas the oxime conversion decreased rapidly with the process time over HY zeolite calcined at 773 K. For HY zeolites calcined at temperatures higher than 873 K, a considerable extent of activity degradation was also observed. Because of the activity decay, the average oxime conversion and selectivity to ε-caprolactam obtained during the initial period (up to 5 h) were adopted as data for catalytic tests (summarized in Table 1). HY zeolite calcined at 873 K showed the highest conversion, owing to a negligibly small activity decay. For each calcination temperature, the selectivity to lactam was invariable, regardless of the process time. Unfortunately, the selectivity slightly decreased from 83 to 77% with an elevation in the calcination temperature from 773 to 1173 K. It should be emphasized that the degradation behavior in the catalytic reaction was significantly altered by changing the calcination temperature of the HY zeolite.

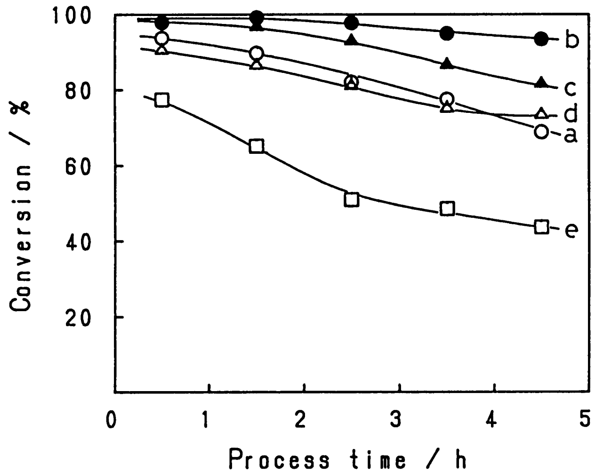

Fig. 1. Changes in the oxime conversion of HY zeolites with the process time. a, Calcined at 773 K for 3 h prior to the reaction; b, 873 K; c, 973 K; d, 1073 K; e, 1173 K. Reaction temperature: 573 K.

Table 1. Catalytic Activities of HY Zeolites Calcined at Various Temperatures[a)]

Calcination temperature	Conversion of oxime	Selectivity to lactam
K	%	mol%
773	82.3	83.1
873	96.6	81.3
973	91.2	79.5
1073	79.3	77.8
1173	57.2	77.3

a) Average activity of 1—5 h at 573 K.

Physical Properties of Fresh HY Zeolite. The physical properties of fresh HY zeolites calcined at various temperatures are summarized in Table 2. Both the surface area and the pore volume were unchanged up to 973 K upon changing the calcination temperature. Above 973 K, however, they gradually decreased with an elevation of calcination temperature. Destruction of crystalline structure of HY zeolite was initiated at 1073 K; a sample calcined at 1173 K was found to be completely amorphous by observations using X-ray diffraction spectroscopy.

Figure 2 illustrates the TPD profiles of ammonia adsorbed on various HY zeolites calcined at different temperatures. The number of acid sites, evaluated from the amount of desorbed ammonia, decreased significantly with increasing calcination temperature. However, the acid strength appreciated by the desorption temperature was almost unchanged, irrespective of the calcination temperature. The change in the number of acid sites with the calcination temperature was correlated with the surface area and pore volume (Table 2). Unfortunately, these physical properties of fresh zeolites do not show any direct proportionality to the catalytic behavior for the vapor-phase Beckmann rearrangement, as is shown in Fig. 1 and Table 1. Only the external surface area, however, seemed to be correlated with the catalytic behavior. This is discussed later.

Physical Properties of HY Zeolite Used for the Reaction. Figure 3 illustrates a typical TPD profile of HY zeolite used for the vapor-phase Beckmann rearrange-

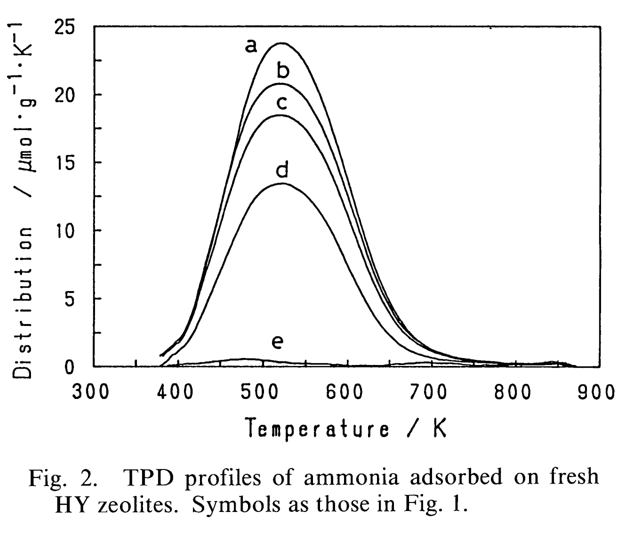

Fig. 2. TPD profiles of ammonia adsorbed on fresh HY zeolites. Symbols as those in Fig. 1.

Table 2. Physical Properties of Fresh HY Zeolites Calcined at Various Temperatures

Calcination temperature	Pore volume	Surface area m^2 g^{-1}		Total number of acid sites[c]	Acid site density[c]
K	ml g^{-1}	Total	External	μmol g^{-1}	μmol m^{-2}
773	0.32	865[a]	19[b]	3990	4.6
873	0.36	893[a]	21[b]	3690	4.1
973	0.37	863[a]	24[b]	3250	3.8
1073	0.26	607[a]	21[b]	2260	3.7
1173	0.02	26[b]	7[b]	100	3.8

a) Specific surface area was calculated by Langmuir equation. b) By BET equation. c) Calculated from the total amount of desorbed ammonia with TPD measurement.

Table 3. Physical Properties of HY Zeolite after Being Used for a Beckmann Rearrangement[a]

Calcination temperature	Pore volume	Surface area[b]	Weight increase[c]	Adsorbed lactam[d]	Residual acid sites	
K	ml g^{-1}	m^2 g^{-1}	g/g-cat.	μmol g^{-1}	μmol g^{-1} [e]	%[f]
773	0.05	33	0.23	470	19	0.5
873	0.08	104	0.20	501	58	1.6
973	0.07	85	0.18	439	48	1.5
1073	0.07	74	0.19	417	37	1.6
1173	0.02	15	0.01	20	8	8.0

a) Each catalyst was used for the vapor-phase Beckmann rearrangement of cyclohexanone oxime at 573 K for 1 h followed by heating under nitrogen flow at 573 K for 1 h. b) Calculated by BET equation. c) Weight increase of catalyst after use. d) Calculated from the TPD spectrum without ammonia adsorption. e) Calculated from the difference between the TPD spectrum of adsorbed ammonia and the TPD spectrum before adsorption. f) Fraction of residual acid sites with regard to the total acid sites of fresh HY zeolite.

ment for only 1 h at 573 K both with and without ammonia adsorption. In a blank TPD spectrum of the sample without ammonia adsorption (dotted line), the products adsorbed on the used sample were desorbed from 500 K. The molecules desorbed above 500 K were found to be mainly ammonia formed by decomposition of the adsorbed molecules during the TPD process at high temperature. It was confirmed by indophenol-color development in an aqueous solution of desorption product collected individually.[21] The adsorbed molecules were probably ε-caprolactam, since the oxime contacted with an acid site was easily rearranged into lactam.[17] In the TPD spectrum of adsorbed ammonia (solid line in Fig. 3), another desorption peak at around 400 and 550 K appeared, together with a high peak at 700 K. The small peak at 450 K in the solid line was ascribed to an ammonia adsorbed on residual acid sites of the used sample. The difference in the signal intensity between the two curves corresponds to the residual acid sites of zeolite after being used for the catalytic reaction. The other zeolite samples calcined at various temperatures also had two desorption peaks in a similar manner as that shown in Fig. 3.

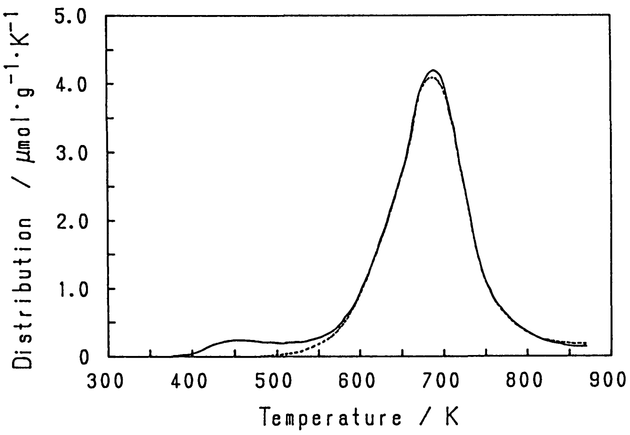

Fig. 3. Typical TPD profile of ammonia adsorbed on a used HY sample. An HY zeolite calcined at 773 K was tested for a Beckmann rearrangement at 573 K for 1 h. Solid line, a TPD spectrum of adsorbed ammonia; dotted line, a blank TPD spectrum without ammonia adsorption.

Table 3 summarizes the number of residual acid sites, together with the physical properties of HY zeolites after being used for the reaction. The number of residual acid sites was maximized for a catalyst sample calcined at 873 K, whereas the number of adsorbed lactam remained constant, regardless of the calcination temperature except for 1173 K. Because the adsorbed lactam was decomposed into ammonia at high temperatures during the course of the TPD process, the product lactam was tightly adsorbed on the acid sites of zeolite during the catalytic reaction. Thus, the pore volume was allowed to drastically decrease.

The amount of ammonia adsorbed on fresh HY zeolites (Table 2) was about five- or seven-times as large as that of adsorbed product lactam (Table 3). Since the molecular size of lactam is much larger than that of ammonia, the amount of desorbed ammonia is not directly reflected by the number of effective acid sites. Both the amounts of desorbed ammonia and adsorbed lactam, however, are affected by the number of acid sites. As shown in Table 2, a sample calcined at 773 K had a high acid-site density, the number of acid sites per unit of surface area, which would result in both rapid product deposition and coke formation. Thus, the residual acid sites of a sample calcined at 773 K were less than those of the other samples. Calcination at high temperatures results in a slight decrease in the acid density (Table 2). The low acid-site density possibly leads to a desorption of the product lactam. These findings suggest that calcination at 873 K induces an optimum acid-site density which would be hardly poisoned by coking. Thus, the slight activity decay of a catalyst calcined at 873 K was tentatively interpreted in the same way.

The specific surface area of the used zeolite was drastically decreased by a closure of the micropores of zeolite, ascribed to adsorption of the produced lactam (Table 3). The surface area of HY zeolite calcined at 773 K was 33 $m^2 g^{-1}$, fairly approaching the value of the external surface area of fresh zeolite (Table 2). The surface area of HY zeolite calcined at 873 K, however, was maintained at a high level (104 $m^2 g^{-1}$) which was five-times higher than the value of the external surface area of fresh zeolite. Interestingly, the change in the surface area as a function of the calcination temperature well correlated with the change in the number of residual acid sites (Fig. 4). Moreover, the changes in these two factors with the calcination temperature was quite similar to that regarding catalytic activity (Fig. 4). In addition, the weight increase of the catalyst was ca. 0.3 g/g-catalyst, even after it had been used for a reaction at 573 K for 1 h. It was not increased after the reaction had been carried out for 5 h. During the initial stages of the reaction, a great portion of the micropores of HY zeolite was found to be readily filled with the product lactam, accompanying a drastic decrease in the pore volume.

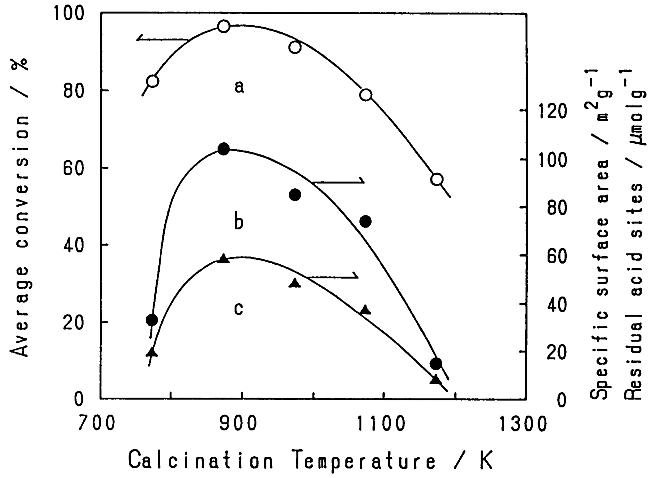

Fig. 4. Comparison between the catalytic activity and physical properties of used HY catalysts. a, Average oxime conversion of 1—5 h at 573 K; b, specific surface area; c, residual acid sites.

Although the rearrangement of cyclopentanone oxime is substantially catalyzed, even at 393 K over an HY zeolite surface, the product lactam is strongly adsorbed at the zeolite surface.17) Strong acid sites located in micropores seemed to be ineffective for the catalytic reaction; since the product lactam was impossible to desorb from the strong acid sites, it was allowed to decompose into ammonia in a similar manner as in the TPD process. A fraction of the residual acid sites to the total acid sites was about 1.5% (Table 3), which is smaller than that of external surface area to the total surface area (ca. 2.5%, Table 2). The values of the surface area of the used zeolite were higher than those of the external surface area of fresh zeolite (Tables 2 and 3). After the strong acid sites located on both external and internal zeolite surfaces had been covered with lactam, weak acid sites located near the external surface catalyzed the rearrangement reaction. Over a protonic ZSM-5 zeolite, the pore-opening size of which is 0.51—0.56 nm, the vapor-phase Beckmann rearrangement of cyclohexanone oxime proceeds not on internal acid sites, but on external neutral hydroxyl groups.14,15) In the present study, the reactant cyclohexanone oxime can readily invade micropores of HY zeolite, since the molecular diameter of cyclohexanone oxime (0.65—0.70 nm)14) is smaller than the pore-opening size of HY zeolite (0.74 nm).22) However, the product ε-caprolactam, the molecular size of which is 0.70—0.75 nm, is tightly adsorbed on strong acid sites, and is hardly desorbed. The title reaction over HY zeolite was found to be allowed to take place mainly on weak acid sites which are located in a region near to the external surface.

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