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Journal of Catalysis 235 (2005) 139–149
JOURNAL OF CATALYSIS
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Active and selective catalyst for liquid phase Beckmann rearrangement of cyclohexanone oxime

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Received 25 February 2005; revised 22 April 2005; accepted 11 July 2005

Abstract

The effect of acid treatment on the catalytic performance of ultrastable Y catalysts in the Beckmann rearrangement of cyclohexanone oxime has been investigated under liquid phase conditions. Over the catalysts treated under mild conditions, enhanced activity was observed due to an increase in the amount of Brønsted acid sites, but a considerable amount of extra-framework aluminum (EFAL) with Lewis acidity remained, resulting in a rapid loss of selectivity to ε-caprolactam. Under relatively severe conditions, the extensive removal of EFAL improved the lactam selectivity, although the extraction of framework aluminum resulted in decreased oxime conversion. Pyridine and benzonitrile adsorption studies indicated the presence of at least two different kinds of Lewis acid sites in the catalysts. The relationships between the catalytic performance and Fourier transform infrared spectroscopy suggested that weak Brønsted acid sites are the active centers for the rearrangement reaction, whereas weak Lewis acid sites due to an extra-framework amorphous phase are responsible for the cyclohexanone formation. Thus the catalyst with weak Brønsted acid sites and a small amount of acidic EFAL species is active and selective for the liquid phase Beckmann rearrangement of cyclohexanone oxime.

Keywords: Beckmann rearrangement; Ultrastable Y; Extra-framework aluminum; Benzonitrile

1. Introduction

The Beckmann rearrangement of cyclohexanone oxime is an important step in the production of ε-caprolactam, a valuable starting material for the manufacture of nylon-6. In the current commercial process, oleum is used mainly stoichiometrically. It carries many serious drawbacks, including high ammonium sulfate formation as a byproduct during the neutralization step to liberate the lactam produced. As a promising solution, replacing this environmentally unfriendly process with heterogeneous catalysis over solid acid materials has been investigated over the last decade [1–19].

Due to a high basicity of lactam, the reaction has been carried out under drastic conditions at temperatures of 300–350 °C, to facilitate the desorption of the lactam product from acid sites [1–17]. This consequently accelerates the side reactions giving various basic compounds and coke formation, often resulting in a rapid decay of catalytic activity. Sumitomo Chemical Company uses a fluidized-bed system to continuously remove carbonaceous deposits from the catalyst in the recently commercialized vapor phase process [20]. Alternatively, performing the reaction under relatively mild liquid phase conditions in the presence of a suitable solvent would minimize the byproducts and prolong the service life of catalysts [18,19]. It would also be expected to provide a more energetically and economically favorable route for the production of caprolactam.

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0021-9517/$ – see front matter
doi:10.1016/j.jcat.2005.07.020

Subjects on the active sites responsible for the formation of ε-caprolactam have been studied extensively [1–19]. Under vapor phase conditions, the weakly acidic hydroxyl groups [5–8] and even the neutral silanols [9] have been suggested to be active and selective, whereas the presence of strong acid sites results in the formation of byproducts [10,11]. In contrast, it has been shown that Brønsted acidity is of importance, whereas silanol sites are involved in cyclohexanone formation at low temperatures [19]. This reflects the superior performance of Brønsted acid sites to weakly acidic hydroxyl groups in the liquid phase rearrangement.

Ultrastable Y (USY) zeolite with the faujasite (FAU) structure, having a three-dimensional network of supercage cavities connected by 12-membered ring windows with a large diameter of 7.4 Å, is commercially prepared by high-temperature steaming of ammonium or proton-form Y zeolite. In addition to the Brønsted and Lewis acidity in the parent material, the formation of a relatively large number of weakly acidic hydroxyl groups and the existence of transient hydroxylated aluminum [21] and various species of extra-framework aluminum (EFAL) (e.g., cationic aluminum ions [22,23] and silica-alumina amorphous phase [24–26]), have been proposed. It is believed that some EFAL species confer Lewis acidity of different strengths [27–30] and that some species have a synergistic effect with Brønsted acid sites, resulting in increased acid strength and catalytic activity [31–33].

Our previous study on the effect of water addition over HUSY catalyst showed that Lewis acid sites are responsible for the formation of cyclohexanone through the hydrolysis of cyclohexanone oxime [34]. A part of these Lewis acid sites is due to EFAL species, which can be leached out by simple acid washing [26,29,31,35]. Moreover, the acidic properties and performance of catalysts can be adjusted by varying the treatment conditions [3,31].

In the present investigation we studied the liquid phase Beckmann rearrangement of cyclohexanone oxime over several samples of USY catalysts prepared by acid treatment. The acidic properties were characterized with Fourier transform infrared (FTIR) spectroscopy. These results were considered in light of catalytic performance, to identify the active sites responsible for the rearrangement and relevant reactions.

2. Experimental

2.1. Catalyst modifications

Commercially available proton-form USY and beta zeolites with the SiO_2/Al_2O_3 ratio of 7 and 25, respectively, were supplied by Tosoh. To dealuminate the parent USY sample (HUSY-7), typically an aqueous solution of HNO_3 or HCl with different concentrations was used. The solid-to-liquid ratio was kept constant at 1:40. As shown in Table 1, reaction temperature and time were also varied to achieve catalysts with a desired Al content. For beta zeolite, it was similarly ion-exchanged using an aqueous solution of NH_4NO_3. The solid products were recovered by filtration, washed many times with distilled water, dried at 120 °C overnight, and calcined at 500 °C for 6 h. The dealuminated samples were designated as DeUSY-*X*, where *X* indicates the SiO_2/Al_2O_3 ratios of the product sample, whereas the obtained beta catalyst with the SiO_2/Al_2O_3 ratio of 36 was designated as HBEA-36.

Table 1
Treatment conditions and structural properties of catalysts used in the present study

Catalyst[a]	Solution	Temperature (°C)	Time[b] (h)	Crystal-linity[c] (%)	Unit cell[d], a_0 (Å)
HUSY-7	–	–	–	100	24.37
DeUSY-11	0.1 M HNO_3	80	3	107	24.37
DeUSY-24	0.2 M HNO_3	25	2	89	24.31
DeUSY-33	0.5 M HNO_3	25	2	56	24.18
DeUSY-35	0.1 M HNO_3	80	2*	98	24.33
DeUSY-40	0.5 M HCl	25	2	67	24.25
DeUSY-63	0.15 M HNO_3	80	2*	62	24.22
HBEA-36	0.5 NH_4NO_3	80	2	–	–

[a] Number after hyphens indicates the SiO_2/Al_2O_3 ratio.
[b] Asterisk means that the treatment was repeated.
[c] Relative to XRD pattern of the parent HUSY-7.
[d] Calculated from the diffraction peak corresponding to (533) reflection plane.

2.2. Reaction procedure

Before applied to the reaction, catalysts were activated at 500 °C for 6 h in a muffle furnace and then allowed to cool down inside a desiccator to prevent adsorption of water in the atmosphere. The Beckmann rearrangement was typically carried out in a 50-ml flask at 130 °C under nitrogen atmosphere, using benzonitrile (PhCN) as a solvent. The amount of catalyst used was 0.1 g, and the catalyst:oxime:PhCN composition was 1:1:200 (weight). The reaction progress was followed by timely sampling and subsequent analysis of product distribution with a gas chromatograph equipped with a 30-m capillary column of PEG.

2.3. Characterizations

FTIR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer with a spectral resolution of 2 cm^{-1}. A 30-mg sample was pressed into a self-supported, 20-mm-diameter wafer. The wafer was set in a quartz infrared (IR) cell that was sealed with CaF_2 windows and connected to a vacuum system. In pyridine and PhCN adsorption experiments, the wafer was evacuated at 500 °C for 1 h, followed by exposure to a desired amount of pyridine and PhCN vapor for 1 h at 100 and 35 °C, respectively. The desorption of pyridine was carried out stepwise at 100 and 150 °C for 1 h at each temperature. The introduction of PhCN vapor and collection of a spectrum were repeated to ensure that a saturated adsorption was achieved. All of the spectra were measured at room temperature in the absorbance mode with 64 scan times.

Crystallinity and unit cell parameter (a_0) were determined by X-ray powder diffraction (XRD), using a MAC Science MX Labo power diffractometer equipped with Cu-K_α radiation. Bulk elemental composition was determined by inductively coupled plasma (ICP) spectroscopy.

3. Results and discussion

As shown in Table 1, for a given treatment temperature, the SiO_2/Al_2O_3 ratio increased with increasing acid concentration or time. This increase was accompanied by a decline in the crystallinity and contraction of the unit cell, indicating the progress of dealumination. Despite the relatively high temperature, the treatment using low acid concentration (0.1 mol HNO_3) preserved the original crystallinity (DeUSY-11 and DeUSY-35). When the reaction was carried out at room temperature, the framework Al was more severely extracted under relatively high acidity conditions (0.2 or 0.5 M HNO_3), resulting in reduced unit cell irrespective of the Al content of DeUSY-24, DeUSY-33, and DeUSY-35. These results suggested that a considerable amount of extracted Al remained on DeUSY-33 as EFAL species.

Hydroxyl groups of various types in the USY catalysts before and after the treatment were observed by FTIR spectroscopy (Fig. 1). The parent HUSY-7 exhibited five distinct absorption bands in the O–H region, at 3740, 3690, 3628, 3600, and 3564 cm^{-1} (Fig. 1a). The bands at 3628 and 3564 cm^{-1} are the characteristic O–H vibrations usually found for proton-form faujasite zeolites, assigned to Brønsted acid sites located in supercages and sodalite cages, respectively. The band around 3740 cm^{-1} was associated with weakly acidic silanol groups, and the band at around 3690 cm^{-1} was assigned to Al–OH groups of EFAL species [36]. The band at 3600 cm^{-1} was attributed to Brønsted acid sites coordinated with EFAL in supercages, having strong acidity [36].

In acid treatment under mild conditions (DeUSY-11), the band at 3628 cm^{-1} increased slightly, whereas the bands at 3600 and 3564 cm^{-1} showed no significant change in intensity (Fig. 1b). This suggests the removal of some extra-framework species, such as amorphous silica-alumina phase [35] and/or debris, rendering Brønsted acid sites in supercages more exposed. It can be seen that the band around 3740 cm^{-1} split into two bands at 3743 and 3738 cm^{-1}, which were assigned to two different silanol groups located at the external surface and in amorphous silica-alumina, respectively [35]. Furthermore, two new bands were detected at 3670 and 3526 cm^{-1}. The former band indicated the formation of new Al–OH groups [36], and the latter was associated with Brønsted acid sites coordinated with EFAL species inside sodalite cages [31], possibly due to the migration of cationic EFAL initially located in the supercages into the sodalite cages on calcination at high temperatures [37].

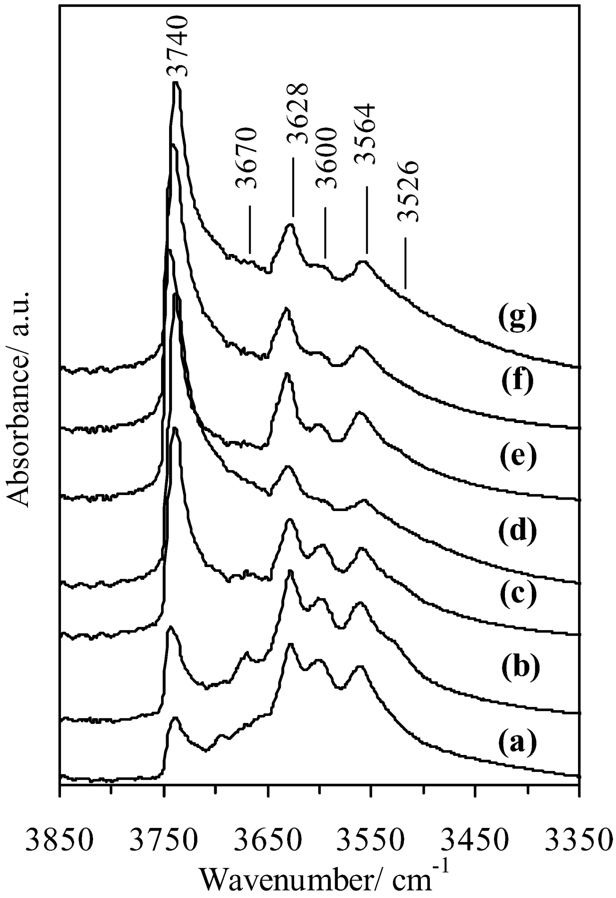


Fig. 1. FTIR spectra of HUSY-7 (a), DeUSY-11 (b), DeUSY-24 (c), DeUSY-33 (d), DeUSY-35 (e), DeUSY-40 (f) and DeUSY-63 (g) in the OH stretching region.

When acid concentration, time, or temperature of the treatment was increased, the band at 3600 cm^{-1} decreased, suggesting the removal of cationic EFAL species (Figs. 1c–g). This coincided with increased SiO_2/Al_2O_3 ratios and enhanced bands at around 3740 cm^{-1}, indicating progressive dealumination. Moreover, the band corresponding to Al–OH groups (3670 cm^{-1}) became less distinct and overlapped with the nearby bands of higher frequencies. The simultaneous broadening of these bands (3740–3670 cm^{-1}) with an increasing band of terminal silanol groups reflected the hydrolysis of Si–O–Al bonds, yielding Al–OH and Si–OH [38]. In the case of DeUSY-24 and DeUSY-35, the species located at extra-framework positions were hydrolyzed mainly because the bridging hydroxyls were increased (Figs. 1c and e).

Compared with DeUSY-35 with a similar SiO_2/Al_2O_3 ratio (Fig. 1e), the intensity of the bridging hydroxyl bands for DeUSY-33 was considerably weaker (Fig. 1d). This result should be related to the difference in dealumination conditions (Table 1). It is also worth mentioning that the band of weakly acidic silanols of DeUSY-33 appeared at lower wavenumber (3738 cm^{-1}), and thus a relatively large amount of amorphous silica-alumina phase was likely present.

Although acidity generated by steaming process has been extensively examined by IR and nuclear magnetic resonance spectroscopic techniques [30,39–41], the structure of Lewis acid sites is still unclear. Using pyridine as a probe molecule in the IR study of adsorption and desorption at elevated temperatures provides details on the types, strength, and amount of acid sites that are accessible to substrates. However, attention is rarely given on weakly acidic species observed by adsorption at relatively low temperatures, due to the high temperatures of relevant catalytic test reactions and the complexity of spectra in the range of interest (1455–1438 cm^{-1}) resulting from physical adsorption of pyridine. Because the reaction temperature in our study is relatively low and the transformation of oxime reactant to cyclohexanone byproduct can occur even over silanol groups [19], determination of weakly acidic sites by pyridine adsorption at relatively low temperatures is of importance.

Fig. 2 illustrates FTIR spectra of HUSY-7 and dealuminated catalysts obtained after the pyridine adsorption at 100 °C followed by desorption at the same temperature (Fig. 2A) and at 150 °C (Fig. 2B). All of the catalysts showed the bands corresponding to Brønsted acid sites at 1545 cm^{-1} and to Lewis acid sites at 1454 cm^{-1} [42]. By a deconvolution technique, other components were found between 1451 and 1438 cm^{-1} (Fig. 3). The band at 1439 cm^{-1} was associated with cationic species like Na^{+} [43], whereas the band at 1447 cm^{-1} was assigned to pyridine hydrogen-bonded to weakly acidic Si–OH groups [42]. Furthermore, the deconvolution resulted in another component at 1450 cm^{-1} observed for the parent HUSY-7 (Fig. 3A), but progressively diminished by the acid treatment with increasing degree of dealumination (Fig. 3B–D). Other bands appeared at 1578, 1596, 1621, and 1634 cm^{-1} (Fig. 2), assigned to the 8a and 8b vibration modes of νCC(N) of pyridine adsorbed on cations, Si–OH groups, and Lewis and Brønsted acid sites, respectively [44].

The amount of acid sites estimated from the bands area and the reported extinction coefficients [45] are summarized in Table 2. The IR intensity of acidic OH groups observed in the O–H stretching region (Fig. 1) was in agreement with the amount of Brønsted acid sites estimated (Table 2). Under mild dealumination conditions (DeUSY-11), some amorphous phase and/or debris was removed, resulting in an increased amount of Brønsted acid. Moreover, most of the components present at 1451–1438 cm^{-1} remained (Fig. 3B), indicating similarity of the corresponding sample and the parent sample. Further dealumination to DeUSY-24 and DeUSY-35 reduced the number of Lewis acid sites in particular (Table 2); this was somewhat consistent with a significant decrease in the species corresponding to the band at 1450 cm^{-1} (Fig. 3C). After treatment under relatively severe conditions (DeUSY-33, DeUSY-40, and DeUSY-63), the band at 1450 cm^{-1} disappeared completely (Fig. 3D), and only the band at 1454 cm^{-1} with a lower intensity was retained. This was concomitant with a loss of Brønsted acid sites and an enhancement of the band at 1447 cm^{-1} (Fig. 2A), indicating extraction of Al from the framework. In contrast, the commercially prepared beta zeolite, HBEA-36, did not exhibit the band at 1450 cm^{-1}, suggesting that this band was associated with acidic EFAL species generated under steaming conditions (e.g., an amorphous silica-alumina) and having structures different from the "true" Lewis acid sites [40] at 1454 cm^{-1}.

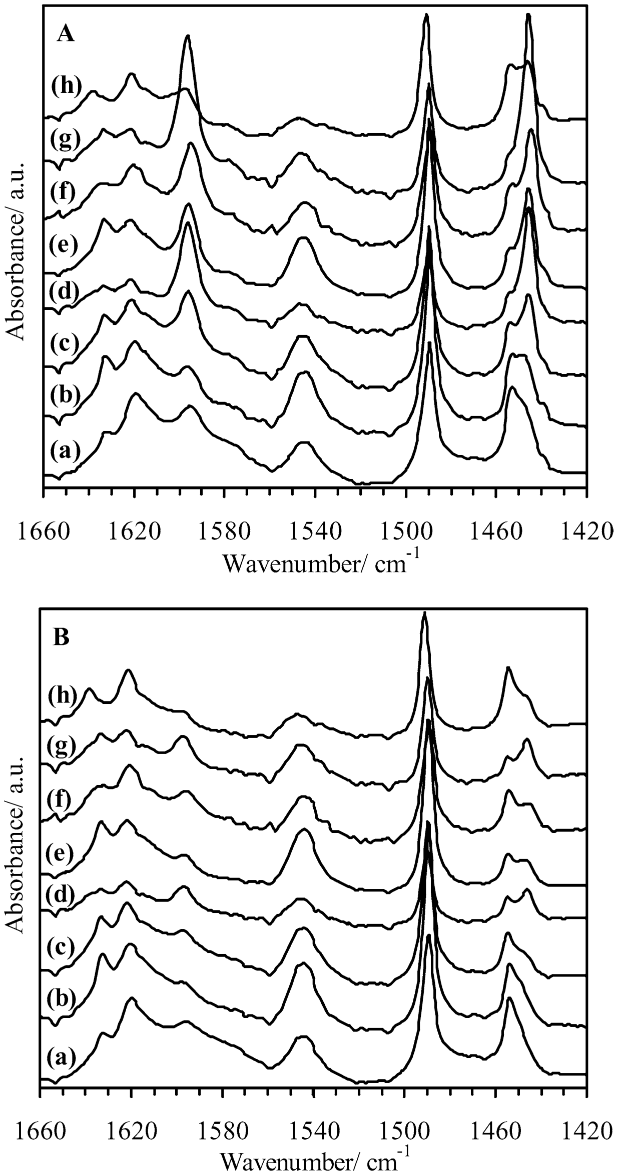


Fig. 2. FTIR spectra of HUSY-7 (a), DeUSY-11 (b), DeUSY-24 (c), DeUSY-33 (d), DeUSY-35 (e), DeUSY-40 (f), DeUSY-63 (g), and HBEA-36 (h) after pyridine adsorption at 100 °C followed by desorption at 100 (A) and 150 °C (B).

On desorption of pyridine at 150 °C, there was no reduction in the intensity of the band assigned to Brønsted acid sites (Fig. 2); the major change was found in the region of Lewis acid sites and other components nearby, at

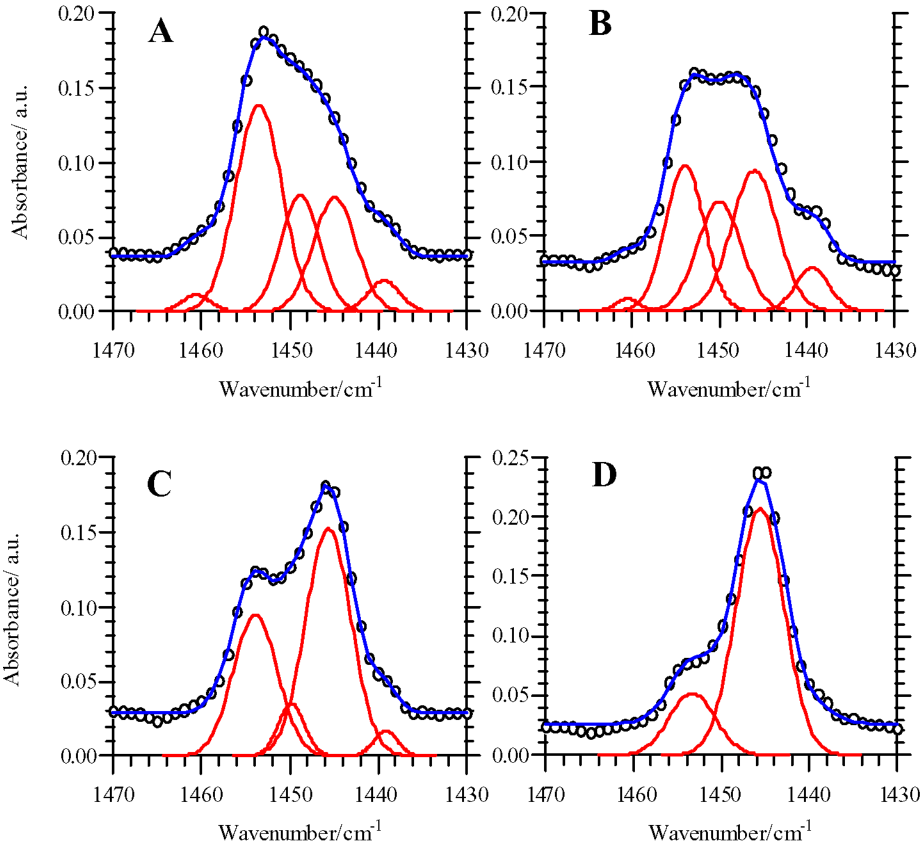


Fig. 3. Deconvolution curves of FTIR spectra in the range of 1460–1440 cm^{-1} of HUSY-7 (A), DeUSY-11 (B), DeUSY-24 (C), and DeUSY-33 (D) after pyridine adsorption and desorption at 100 °C.

Table 2

Amount of acid sites[a] in the catalysts determined from pyridine adsorption study by FTIR spectroscopy

Catalyst[b]	Brønsted acid sites[c] ($\mu\text{mol g}^{-1}$)	Lewis acid sites[d] ($\mu\text{mol g}^{-1}$)		
		100 °C	150 °C	Difference[e]
HUSY-7	138	130	95	35
DeUSY-11	192	95	77	18
DeUSY-24	172	70	44	26
DeUSY-33	112	36	23	12
DeUSY-35	209	60	32	28
DeUSY-40	128	70	44	27
DeUSY-63	125	36	19	17
HBEA-36	91	59	54	5

[a] Calculated using the extinction coefficients given by Emeis [45].

[b] Number after hyphens indicates the SiO_2/Al_2O_3 ratio.

[c] Determined at 100 °C from the band appeared at 1545 cm^{-1}.

[d] Determined from the bands appeared between 1454 and 1450 cm^{-1}.

[e] Difference between the amount of Lewis acid sites determined at 100 and 150 °C.

1455–1438 cm^{-1}. A noticeable decrease in the intensity of the bands at 1447 and 1596 cm^{-1} indicated weakly acid silanol groups. Pyridine also desorbed from Lewis acid sites at 150 °C, as evidenced by a decrease in the band at 1454 cm^{-1}, suggesting the presence of weak Lewis acidity. The quantitative determination revealed that USY catalysts had relatively large amount of weak Lewis acid sites compared with HBEA-36 (Table 2). Although the band corresponding to Lewis acid sites observed over HUSY-7, dealuminated catalysts, and HBEA-36 was found at the same wavenumber, 1454 cm^{-1}, the difference in the acid strength reflected the existence of Lewis acid sites with different chemical natures.

Fig. 4 shows the dependence of the oxime conversion and selectivity to the lactam on time over HUSY-7 and its dealuminated catalysts. Compared with the parent sample, here, regardless of Al content, the reaction was catalyzed more actively by DeUSY-11, DeUSY-24, DeUSY-35, and DeUSY-40, with lower conversions obtained by DeUSY-33 and DeUSY-63 (Fig. 4A). However, HBEA-36 with a similar SiO_2/Al_2O_3 ratio to DeUSY-35 gave a much lower conversion. Because all Al is not incorporated into the zeolitic framework, and some may exist as nonacidic EFAL species, these results should be directly related to the amount of acid sites present; the more acid sites present in the catalyst, the higher the oxime conversion attained. The conversion curves leveled off at 1 h and stabilized after 2 h.

As shown in Fig. 4B, the catalysts that gave a high conversion exhibited a severe drop in lactam selectivity (ca. 17%) within the first hour of the reaction. This is harsher than the drop for the parent HUSY-7 catalyst (14%). In contrast, the drop was <10% over DeUSY-33 and DeUSY-63. There was only a slight change in the selectivity after 2 h, corresponding to the plateau region of the oxime conversion–reaction

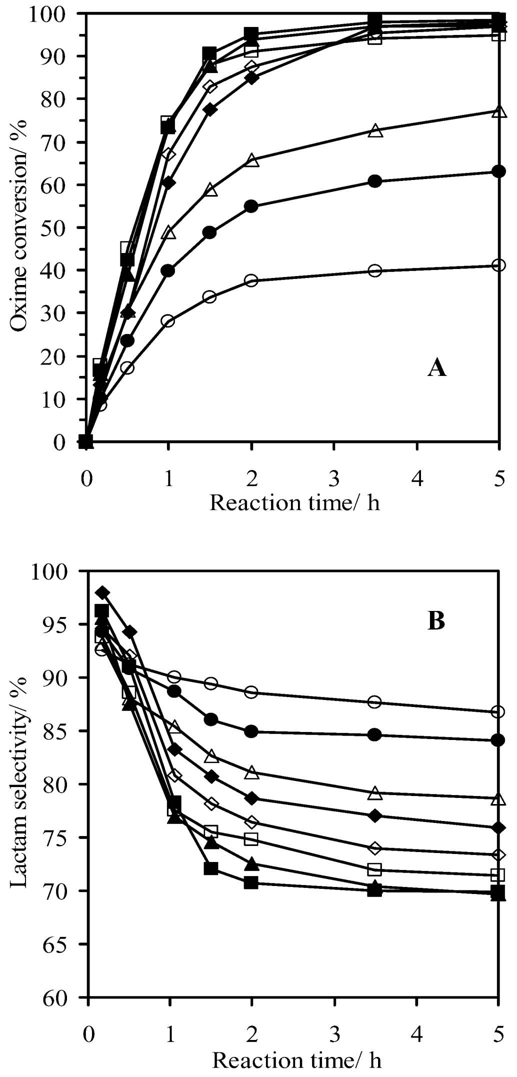


Fig. 4. Dependence of the oxime conversion (A) and the lactam selectivity (B) on reaction time over HUSY-7 (◆), DeUSY-11 (■), DeUSY-24 (▲), DeUSY-33 (●), DeUSY-35 (◇), DeUSY-40 (□), DeUSY-63 (△), and HBEA-36 (○) in the liquid-phase Beckmann rearrangement of cyclohexanone oxime. Reaction conditions: see Table 4.

time plot in Fig. 4A. At 5 h, lactam selectivity was 70–73% over DeUSY-11, DeUSY-24, DeUSY-35, and DeUSY-40, 78.4% over DeUSY-63, and 84.5% over DeUSY-33. However, such a severe drop was not seen when HBEA-36 was used as a catalyst; lactam selectivity decreased by only 5% after 5 h.

The initial rate of reaction and products distribution at a given conversion obtained over USY and beta catalysts are summarized in Table 3. At 25% oxime conversion, there was no noticeable difference in lactam and cyclohexanone formation among the catalysts used. However, there was a rough correlation among the amount of acid sites (Table 2), rate of reaction, and lactam yield. The more acid sites, the higher the reaction rate and the lactam yield attained. It is also likely that with decreasing Al content, anone formation increased. This may be related to the generation of weakly acidic silanol groups on the dealumination. Such sites have been suggested to catalyze the hydrolysis of oximes to the corresponding ketones under liquid phase conditions [19].

When oxime conversion reached 50 and 80%, the rough trends toward the amount of acid sites observed at 25% conversion no longer existed. The catalyst that early showed a high lactam yield exhibited a rapid increase in cyclohexanone and dimer/polymer formation. In contrast, the lactam yield achieved over DeUSY-33 and DeUSY-63, both of which had a relatively small number of acid sites, was comparable to that obtained over other catalysts with high acid content. These results should be related to catalyst deactivation. As indicated in Fig. 4B, a significant decrease in lactam selectivity occurred during 50–80% oxime conversion.

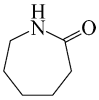
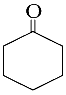
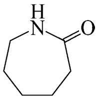
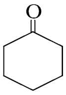
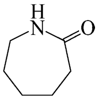
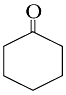
These results suggest that the active sites responsible for lactam formation were gradually deactivated and mostly lost when the conversion reached 80%. Consequently, the surviving relatively weak acid sites catalyzed the reaction instead at the subsequent stages [46]. Our previous study over MCM-41 catalysts found inferior performance of abundantly present silanol groups [47]. Due to insufficient acidic strength, the rearrangement of cyclohexanone oxime to lactam was not effectively catalyzed, producing low oxime conversion and lactam selectivity. Substantial cyclohexanone formation over MCM-41 did not occur, however.

Figs. 5 and 6 show the plots of the initial rate of reaction and the lactam yield, respectively, at 25% oxime conversion with the corresponding number of Brønsted acid sites. A linear relationship could be established in both cases, indicating that Brønsted acid sites are active and selective for the liquid phase Beckmann rearrangement of cyclohexanone oxime; no direct correlations could be found between the lactam yield achieved at higher oxime conversion and the Brønsted acid amount, suggesting a deactivation of Brønsted acid sites.

The relationship between the cyclohexanone yield and number of Lewis acid sites is illustrated in Fig. 7. With an increasing number of Lewis sites, cyclohexanone formation over USY catalysts increased, but it declined in high acidity conditions. In contrast, the data of HBEA-36 greatly deviated from this relationship. These results indicate that Lewis acid sites present mainly in beta zeolite are less harmful to rearrangement, and thus should have a different structure and acidity than those sites responsible for the hydrolysis reaction. The drop in the cyclohexanone yield over HUSY-7 with a high Lewis acid content implied that some Lewis sites were not involved in the cyclohexanone formation. Because the hydrolysis occurred mostly in the late stages, suggesting generation of water in the reaction system, Lewis sites with strong acidity were likely associated with the dimerization or formation of high-molecular-weight compounds, yielding water as a byproduct.

In contrast, the plot of cyclohexanone yield with number of weak acid sites exhibited an approximately linear relationship (Fig. 8). This result suggested that Lewis acid sites

Table 3
Products distribution in liquid-phase Beckmann rearrangement[a] of cyclohexanone oxime over various USY and beta catalysts

Catalyst[b]	Initial rate of reaction $(\mathrm{mmol\,g^{-1}\,h^{-1}})$	Yield (%)								
		At 25% conversion			At 50% conversion			At 80% conversion		
				Others[c]			Others[c]			Others[c]
HUSY-7	7.4	23.5	1.2	0.3	43.2	4.6	2.2	61.8	13.3	4.8
DeUSY-11	10.2	23.8	0.9	0.3	43.1	4.9	2.0	60.1	14.8	5.1
DeUSY-24	8.9	23.6	1.1	0.3	41.8	5.8	2.4	58.4	16.3	5.3
DeUSY-33	5.4	22.6	2.4	0.0	43.6	6.3	0.1	–	–	–
DeUSY-35	11.0	23.9	0.9	0.2	43.1	5.1	1.8	62.6	13.7	3.7
DeUSY-40	7.1	22.9	1.9	0.2	41.2	7.4	1.4	61.2	15.0	3.8
DeUSY-63	5.8	22.2	2.8	0.0	42.9	6.9	0.2	–	–	–
HBEA-36	4.1	22.4	2.6	0.0	–	–	–	–	–	–

[a] Reaction conditions: temperature, 130 °C; catalyst amount, 0.1 g; oxime:catalyst:PhCN = 1:1:200 (weight).
[b] Number after hyphens indicates the SiO_2/Al_2O_3 ratio.
[c] Mostly dimers and polymers.

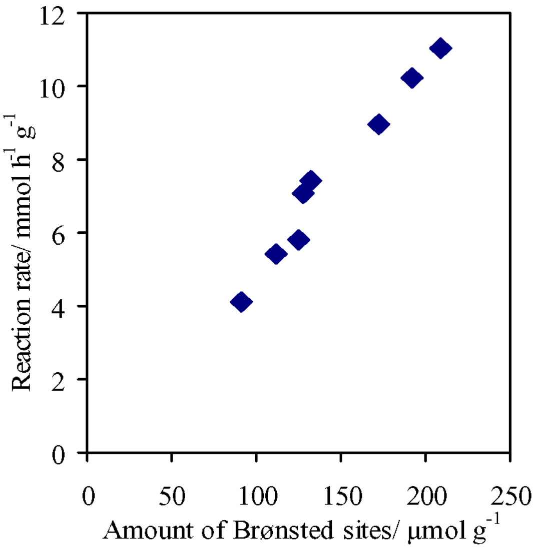


Fig. 5. Plot of the initial rate of reaction against the amount of Brønsted acid sites.

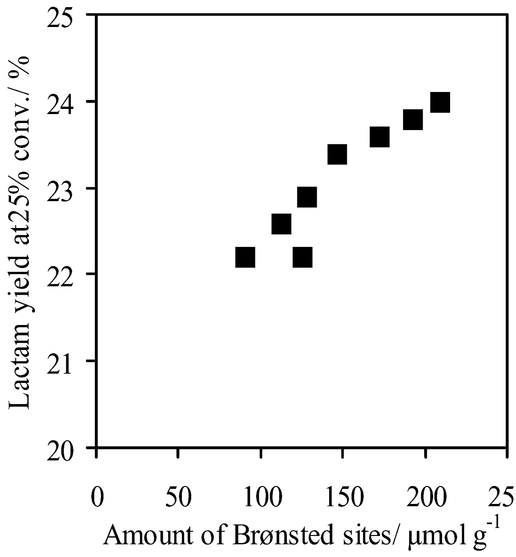


Fig. 6. Plot of the lactam yield at 25% oxime conversion against the amount of Brønsted acid sites.

of weak strength are the active centers for the hydrolysis of cyclohexanone oxime. However, the parent HUSY-7 and catalysts dealuminated under mild conditions (DeUSY-11 and DeUSY-24) showed a deviation from the linear trend, likely attributable to the presence of various types of weak Lewis sites generated during high-temperature steaming treatment, which may act differently in the reaction system.

FTIR spectroscopic study of PhCN adsorption has been performed to more thoroughly investigate the characteristics of Lewis acid sites in the catalysts. It was reported that the shifts of the C≡N stretching mode caused by an interaction of lone pair electrons of nitrogen with acids can be used to discriminate between Brønsted and Lewis acid centers, as well as between those centers of different strengths [48]. Fig. 9 shows FTIR spectra of the catalysts used in the present study after PhCN adsorption at 35 °C. The adsorption of PhCN on the catalysts gave rise to the broad band of C≡N stretching vibration at 2300–2220 cm^{-1}, corresponding to PhCN adsorption on various types of acid sites [34]. Deconvolution of the spectra indicated that this band comprised at least five distinct components (Fig. 10A). The band at 2229 cm^{-1} corresponded to PhCN molecules hydrogen-bonded to weakly acidic silanol groups. The band at 2239 cm^{-1} was assigned to PhCN adsorbing on the weak Brønsted acid sites, whereas the band at 2253 cm^{-1} was associated with relatively strong Brønsted acidity. Furthermore, in accordance with the results from pyridine adsorption (Fig. 3A), two other components related to Lewis acid sites were observed at 2272 and 2284 cm^{-1}. It is commonly believed that the higher the shift of the C≡N stretching band, the stronger the Lewis acidity. As reported previously [49], the band appearing around 2280 cm^{-1} was assigned to Lewis acid sites, such as cationic EFAL species.

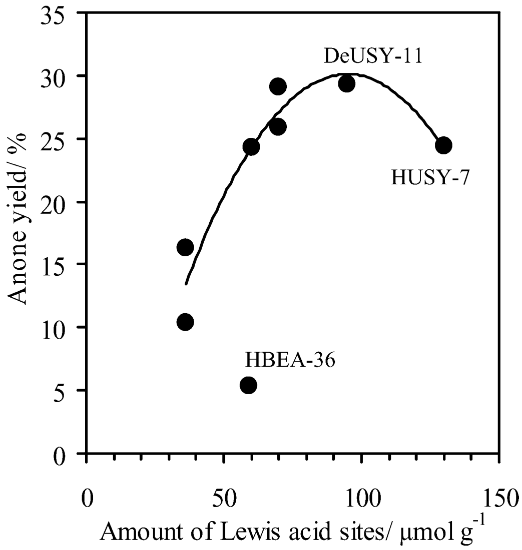


Fig. 7. Plot of the cyclohexanone yield obtained at 5 h of the reaction course against the amount of Lewis acid sites determined from pyridine adsorption–desorption at 100 °C.

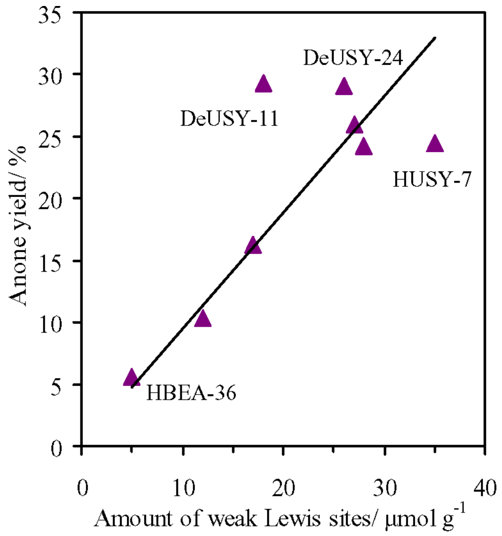


Fig. 8. Plot of the cyclohexanone yield obtained at 5 h of the reaction course against the amount of weak Lewis acid sites.

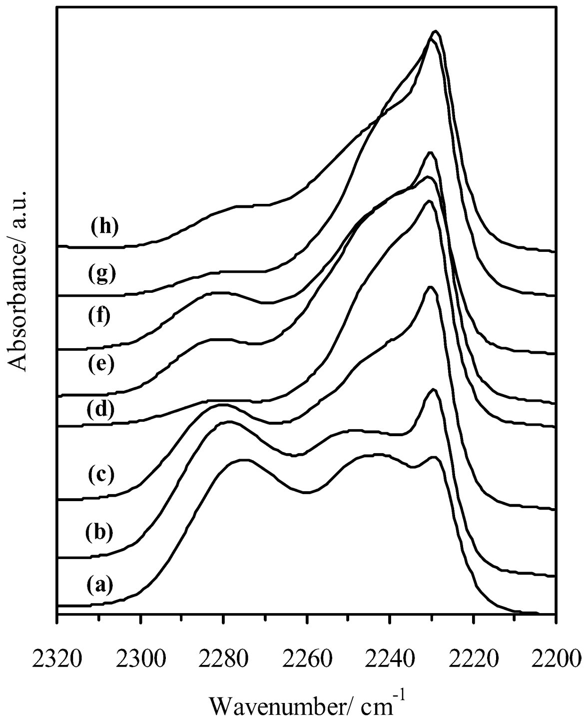


Fig. 9. FTIR spectra of HUSY-7 (a), DeUSY-11 (b), DeUSY-24 (c), DeUSY-33 (d), DeUSY-35 (e), DeUSY-40 (f), DeUSY-63 (g), and HBEA-36 (h) in the CN stretching region after PhCN adsorption at 35 °C.

Figs. 10A–D illustrate the representative deconvolution curves of FTIR spectra shown in Fig. 9. The mild acid treatment of HUSY-7, yielding DeUSY-11, resulted in a decrease in the band associated with relatively weak Lewis acid sites at 2272 cm^{-1} but enhancement of the component of strong Lewis acid sites centered at 2283 cm^{-1}. Moreover, the band related to strong Brønsted acid sites (2253 cm^{-1}) and weakly acidic silanol groups (2229 cm^{-1}) increased slightly. These findings are in agreement with results obtained from an FTIR study of pyridine adsorption (Fig. 2). With an increasing degree of dealumination (i.e., increased SiO_2/Al_2O_3 ratio), both of the bands assigned to Lewis acid sites gradually decreased (see also Fig. 9) concomitantly with a decrease in strong Brønsted acid sites at 2253 cm^{-1}.

The numbers of acid sites quantitatively determined in terms of relative band area are given in Table 4. The table shows that DeUSY-33 and DeUSY-63, which exhibit increased lactam selectivity, have large relative areas for Brønsted acid sites of weak strength (2239 cm^{-1}) and small relative band areas for both Lewis acid species (2283 and 2272 cm^{-1}). Moreover, these catalysts have a high ratio of bands area of strong-to-weak Lewis acid sites ($A_{2283\ \text{cm}^{-1}}/A_{2272\ \text{cm}^{-1}}$), suggesting that the relatively weak Lewis sites promote cyclohexanone formation. The Lewis acid sites at 2272 cm^{-1}, abundantly present in the parent HUSY-7, may belong to an extra-framework aluminum-rich amorphous phase generated during the ultrastabilization process. The similarities between EFAL in USY zeolites and transition aluminas have been reported previously [41,50]. In contrast, the Lewis acid sites appearing at 2283 cm^{-1}, which exist as dominant species in acid-treated USY and HBEA-36, should be related to transient hydroxylated Al that partially attaches to the framework by one or two Si–O–Al bonds. These species are present mainly in beta zeolite as octahedral Al coordinated with water molecules [51,52]. Therefore, the weak Lewis acid sites responsible for the hydrolysis of the oxime are probably located in an aluminum-rich amorphous phase.

Although DeUSY-33, DeUSY-63, and HBEA-36 have a relatively high percentage of weakly acidic silanol groups at 2229 cm^{-1} (Table 4), their cyclohexanone formation was not

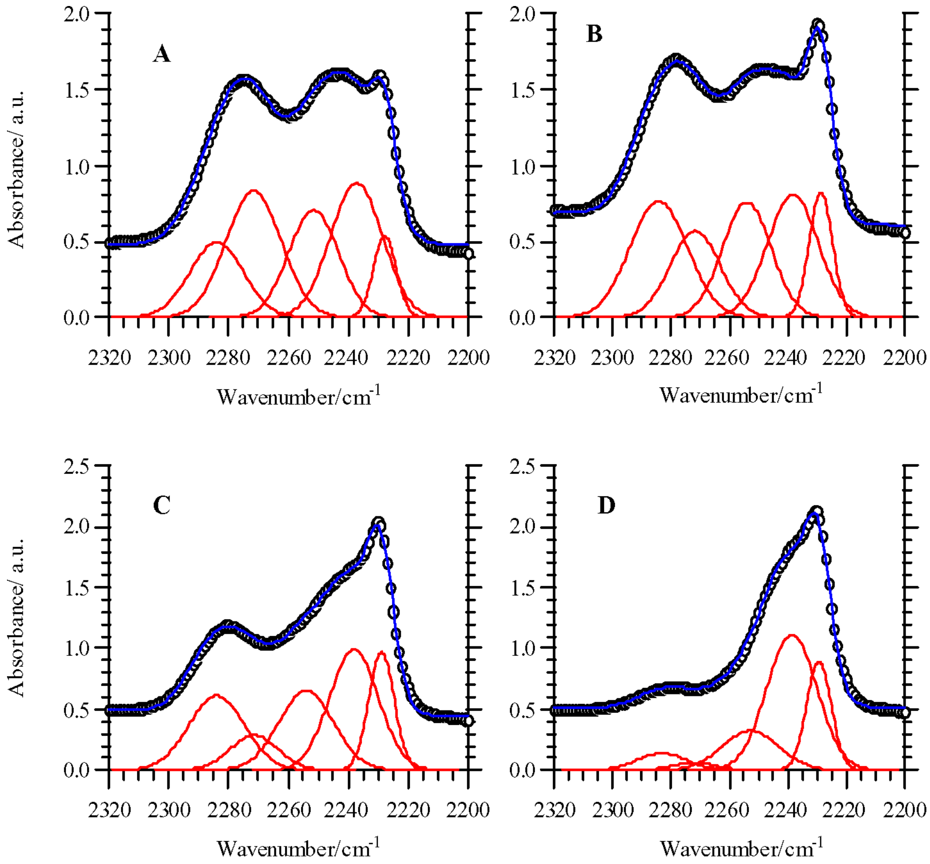


Fig. 10. Deconvolution curves of FTIR spectra in the CN stretching region of HUSY-7 (A), DeUSY-11 (B), DeUSY-24 (C), and DeUSY-33 (D) after PhCN adsorption at 35 °C.

Table 4
Amount of acid sites represented in terms of IR band area from PhCN adsorption

Catalyst[a]	Relative area of CN stretching bands[b] (%)					$A_{2283\ cm^{-1}}/A_{2272\ cm^{-1}}$ band area ratio
	2283 cm^{-1}	2272 cm^{-1}	2253 cm^{-1}	2239 cm^{-1}	2229 cm^{-1}	
HUSY-7	16.0	27.8	21.2	27.6	7.3	0.58
DeUSY-11	26.0	16.8	21.8	24.2	11.2	1.54
DeUSY-24	21.8	8.8	22.7	30.9	15.7	2.50
DeUSY-33	6.5	0.8	17.9	53.7	21.0	7.52
DeUSY-35	14.5	7.7	25.8	35.7	16.3	1.90
DeUSY-40	15.1	9.7	21.2	37.1	16.9	1.56
DeUSY-63	6.6	0.9	19.8	47.5	25.2	7.09
HBEA-36	9.8	3.3	26.7	33.8	26.3	2.91

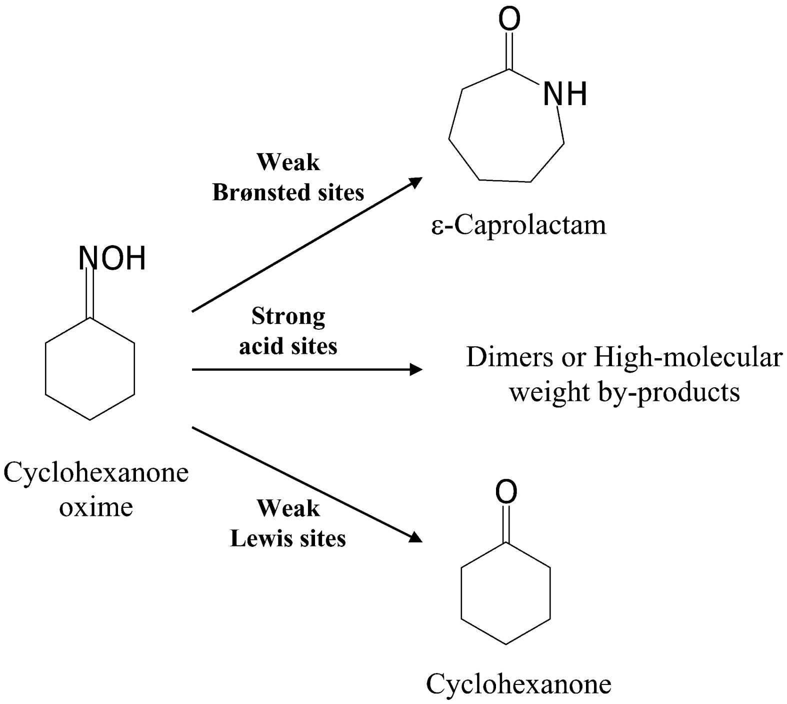
[a] Number after hyphens indicates the SiO_2/Al_2O_3 ratio.

[b] For assignments, see text.

as remarkable as that achieved using other USY catalysts. These results suggest a low activity of silanol groups under liquid phase conditions related to their extremely weak acidity, not only in the rearrangement reaction [19,47], but also in the hydrolysis of the oxime under liquid phase conditions. Scheme 1 shows the proposed active sites for the reaction system of cyclohexanone oxime–PhCN in the presence of USY catalysts. ε-Caprolactam is produced actively and selectively over the weak Brønsted acid sites, whereas the Lewis acid sites of weak strength belonging to EFAL are responsible for cyclohexanone formation. Furthermore, water, used in the hydrolysis reaction, may be generated through the dimerization or formation of high-molecular-weight compounds over strong acid sites.

4. Conclusions

The effect of acid treatment on the catalytic performance of USY catalysts in the liquid phase Beckmann rearrangement of cyclohexanone oxime at 130 °C in PhCN solvent has been investigated. Dealumination using mild acids (0.1–



Scheme 1. Proposed active sites for the reaction of cyclohexanone oxime over USY catalysts in PhCN solvent.

0.15 mol) without repetition at 80 °C did not extract the framework Al, and did retain the crystallinity of solid products. Although the activity was enhanced due to the increase in the number of Brønsted acid sites, considerable acidic EFAL species remained, demonstrating a rapid drop in lactam selectivity. Performing dealumination under relatively severe conditions, using 0.5 mol HNO_3 at room temperature or 0.15 mol HNO_3 at 80 °C with repetition, resulted in extensive removal of extra-framework species at the expense of framework Al and crystalline structure. As a result, the number of Lewis acid sites decreased noticeably, mitigating cyclohexanone formation and improving selectivity to lactam.

At least two types of Lewis acid sites of different strengths can be observed from the FTIR spectroscopic study of pyridine and PhCN adsorption. One of these exists mainly in the parent HUSY-7 prepared by high-temperature steaming and may be related to an extra-framework alumina-rich amorphous phase; the other, which is the predominant species in the dealuminated catalysts, is probably associated with transient hydroxylated Al. It has been suggested that the weak Lewis acid sites located in an amorphous phase are the active sites for cyclohexanone formation, whereas oxime rearrangement is suitably catalyzed over weak Brønsted acid sites. In addition, the strong acid sites may be involved in the generation of water through the formation of high-molecular-weight byproducts, causing catalyst deactivation. Thus, the catalyst with particularly weak Brønsted acid sites and a small amount of acidic EFAL species is active and selective for the liquid phase Beckmann rearrangement of cyclohexanone oxime.

Acknowledgments

The authors are grateful to Dr. Weibin Fan, a research fellow of Japan Society for the Promotion of Science, for helpful discussions on the catalyst characterizations. This work was partially supported by a Core Research for Evolutional Science and Technology (CREST) grant from JST Corporation (to T.T.).

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