Selective Production of $\mathcal{E}$-Caprolactam via Liquid-phase Beckmann Rearrangement of Cyclohexanone Oxime over HUSY Catalyst

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$\mathcal{E}$-Caprolactam was selectively produced through the liquid-phase Beckmann rearrangement of cyclohexanone oxime over HUSY catalyst when the by-products formation was effectively retarded by blockage of the corresponding active centers of pre-adsorbed water and benzonitrile molecules.

The Beckmann rearrangement of cyclohexanone oxime is an important step for the industrial production of $\mathcal{E}$-caprolactam, an essential intermediate for Nylon-6 manufacture. The commercial route is nowadays mainly based on classical technologies using highly concentrated sulfuric acid. However, a large amount of ammonium sulfate formed as by-product is a serious drawback. To overcome this problem, the high-temperatures vapor-phase reactions over various heterogeneous catalysts have been developed extensively, but the control of the selectivity and elongation of the catalysts life still present a challenge.[1] Even though the vapor-phase system using silicalite-1 as the catalyst has been industrialized recently,[2] the more energetically and economically favorable route is expected to be provided by the liquid-phase conditions at relatively low temperatures.[3]

From our previous study, weak Brønsted acid sites were suggested to be the active centres for the oxime rearrangement and Lewis acid sites should be responsible for the cyclohexanone formation under the liquid phase conditions.[4] To suppress the latter, the addition of base with energetically preferential adsorption on Lewis sites is an effective way. It was shown that water was a good additive, when it could be directly added into the reaction mixture before heating was performed. Besides the selective adsorption on Lewis sites, water supposed to hydrolyse the oxime could be essentially removed by PhCN hydrolysis giving benzamide and benzoic acid as products. However, control of the amount added is still crucial, since a large amount of benzamide was produced[4] and excess water may hamper the weak Brønsted sites.

Here, we report new procedures for retarding the formation of cyclohexanone and simultaneously improving the oxime conversion. Instead of the direct addition, water was introduced into the reaction system by pre-adsorption on the catalyst followed by heat treatments to optimize the amount added. PhCN solvent itself has a strong interaction with Lewis acid sites, and can be used for their blockage.

Proton-form USY zeolite with the SiO_2/Al_2O_3 ratio of 7 was supplied by Tosoh. Before used as a catalyst, it was calcined at 500 °C overnight in a muffle furnace (HUSY). PhCN dried over molecular sieve 4A was used as solvent. The Beckmann rearrangement was typically carried out in a 50-mL flask at 130 °C

under N_2 atmosphere. Amount of catalyst used was 0.1 g and the catalyst:oxime:PhCN was 1:1:200 (weight). The reaction progress was examined by analysing the products by a gas chromatograph equipped with a 30-m capillary column of PEG.

To investigate the effect of pre-adsorption of water, a freshly calcined catalyst was kept under water vapor over a saturated solution of NH_4Cl at room temperature for a few days, and subsequently heated at various temperatures for 6 h before use for the reaction. The catalysts obtained were designated as H_2O-HUSY-*X*, where *X* denotes heat treatment temperatures. Acid sites were blocked by solvent molecules by suspending a freshly calcined HUSY catalyst in PhCN at room temperature for 2 h prior to an addition of the oxime reactant to afford PhCN-HUSY-rt.

The results of reaction of cyclohexanone oxime over HUSY (7) catalysts treated in various ways are shown in Table 1. Compared to the parent HUSY catalyst, the pre-adsorption of water resulted in a decrease in the oxime conversion. However, it was gradually improved by the treatment with increasing temperatures. This suggested that the adsorbing water lowered the accessibility of oxime reactant to the acid sites, which was removed by heating. The FTIR results indicated that evacuation at around 150 °C for an hour is adequate to eliminate physically adsorbing water. Similar to the direct addition of water,[4] a dramatic enhancement of the selectivity to lactam was found when the catalyst was thermally treated up to 350 °C. Besides the higher oxime conversion, a selectivity as high as 97% together with

Table 1. Products distribution in the Beckmann rearrangement[a] over HUSY (7) catalysts pretreated by various procedures

Catalyst	Conv. /%	Selectivity /%			Yield /%
		![lactam]	![cyclohexanone]	Dimers[b]	![lactam]
HUSY	98.8	75.8	23.8	0.4	67.1
HUSY-H_2O[c]	78.9	94.1	5.7	0.2	73.7
H_2O-HUSY-rt	62.9	95.2	4.6	0.2	60.3
H_2O-HUSY-150	75.8	97.4	2.4	0.2	73.8
H_2O-HUSY-250	80.8	97.6	2.3	0.2	78.9
H_2O-HUSY-350	82.8	97.7	2.1	0.1	80.8
H_2O-HUSY-400	98.3	76.4	23.3	0.3	67.7
H_2O-HUSY-500	98.5	76.0	23.7	0.3	67.3
H_2O-HUSY-600	97.9	72.0	27.7	0.3	63.2
H_2O-HUSY-700	98.1	65.4	34.2	0.4	57.1
H_2O-HUSY-900	97.9	54.6	44.9	0.5	42.5
PhCN-HUSY-rt	77.2	96.8	3.2	0.0	73.5

[a]Reaction conditions: temp., 130 °C; time, 5 h; catalyst amount, 0.1 g; oxime:catalyst:solvent = 1:1:200 (weight). [b]Octahydrophenazine and tetrahydrocarbazole. [c]Water (H_2O/Oxime = 4 (molar)) was added to the reaction mixture directly.

the increase in the lactam yield to 80% and a reduction in the amount of benzamide as a hydrolysis product to 0.04% of the solvent were achieved since the water existing in the reaction system could be effectively minimized. Thermogravimetric analysis indicated that the amount of adsorbing water on the catalyst after heating at 350 °C was 0.39 mmol g^{-1}, corresponding to the H_2O/Al ratio of 0.10. However, the treatment at 400 °C resulted in a decrease in the selectivity to lactam although the conversion was totally recovered.
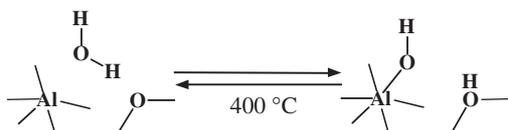
Scheme 1. Reversibly chemical adsorption of water on a Lewis acid site.

The energetically preferential adsorption of water on Lewis acid sites should cause the retardation of oxime hydrolysis and the improvement of lactam selectivity.[4] This type of chemical adsorption on aluminum and other cations was believed to generate the hydroxylated species and protons on basic framework oxygens[5] (Scheme 1, the forward reaction). To completely eliminate the water and regain Lewis acidity, some energy is of necessity.

When the water-adsorbed catalyst was heated at temperature as high as 400 °C, desorption of molecular water and correspondingly dissociated species occurred extensively, recovering substantially Lewis acid sites (Scheme 1, the reverse reaction). Moreover, it is common to consider that these sites are the similar ones originally existing in the parent HUSY catalyst since the comparable results were obtained over the catalysts before and after pre-adsorption of water followed by heat treatment between 400 and 500 °C. However, when the temperature was further increased to 900 °C, the lactam yield was severely reduced whereas the formation of cyclohexanone was enhanced. This result should be ascribed to a loss of Brønsted acid sites, as the active sites for the rearrangement, and a generation of Lewis acid sites, which are the hydrolysis active centers.[6]

A remarkable improvement of the lactam selectivity was also achieved by suspending the catalyst in PhCN prior to the addition of oxime (Table 1). Despite the decrease in the oxime conversion due to an obstruction of the PhCN molecules initially existing on the acid sites, the cyclohexanone formation was retarded with a slight increase in the lactam yield.

Figure 1 shows the FTIR spectra of HUSY (7) catalyst after pre-treating in situ at 500 °C followed by PhCN adsorption at room temperature and further evacuation at various temperatures. At room temperature, there were at least 5 absorption bands of C≡N stretching found at 2230, 2240, 2253, 2272, and 2284 cm^{-1} which respectively associated with silanol groups, weak and strong Brønsted acid sites, and weak and strong Lewis acid sites.[4] The evacuation up to 200 °C mainly removed PhCN adsorbing on silanol groups and on Brønsted sites while most of PhCN on Lewis sites was still intact (Figures 1c–1e). Elevating the temperatures to 300 °C reduced almost entirely the bands relating to Brønsted acid sites with a large decrease in the bands corresponding to Lewis acid sites (Figure 1f). These results indicate that PhCN interact with Lewis acid sites more strongly than with Brønsted ones. As revealed in Figures 1g,
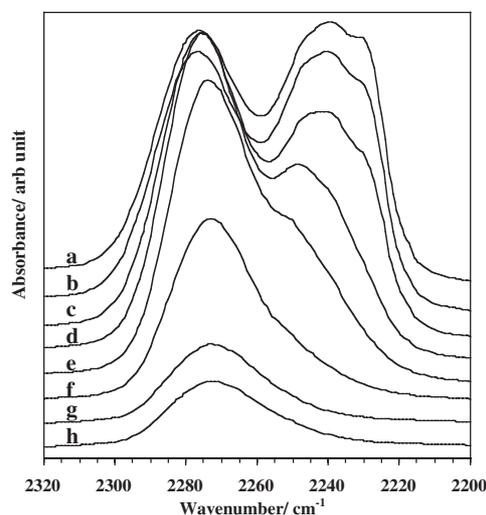

Figure 1. FTIR spectra of HUSY (7) (a) after adsorption of PhCN at room temperature and evacuation at (b) room temperature, (c) 100, (d) 150, (e) 200, (f) 300, (g) 400, and (h) 500 °C.

1h, some Lewis acid sites could hold the PhCN adsorbing even at evacuation temperatures higher than 400 °C.

It is likely that PhCN adsorbs on Lewis acid sites forming more stable intermediate species than the PhCN protonated on Brønsted acid sites. This may be suggested by the relatively large blue shift caused by the former species for about 45 cm^{-1} from the PhCN condensed phase at 2229 cm^{-1}, indicating that the C≡N bond was more strengthened. Hence, probably when the catalyst was allowed to contact with PhCN in the absence of relatively strong bases, both adsorbing species formed on the acid sites. The oxime added afterwards could replace essentially the protonated PhCN species, and the rearrangement to the lactam was catalysed by weak Brønsted acidity. In contrast, the more stabilized species on Lewis acid sites remained and prevented the oxime from hydrolysis.

The advantageous procedures for improving the lactam selectivity in the liquid-phase Beckmann rearrangement of cyclohexanone oxime over HUSY (7) catalyst were presented. A high selectivity up to 97% can be achieved by pre-adsorption of water on the catalyst followed by heating at 150–350 °C or contacting the catalyst with PhCN before the addition of oxime.

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