Vapour phase Beckmann rearrangement of cyclohexanone oxime catalysed by Hβ zeolite

Lian-Xin Dai,† Raita Hayasaka, Yoshihide Iwaki, Keiko A. Koyano and Takashi Tatsumi*†‡

Department of Applied Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo 113, Japan

When hexan-1-ol was used as the diluent in the vapour phase Beckmann rearrangement of cyclohexanone oxime, Hβ zeolite gave 100% conversion of the oxime with ε-caprolactam selectivity close to 96%.

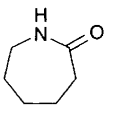
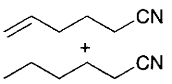
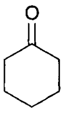
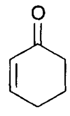
ε-Caprolactam, an important intermediate for the production of Nylon-6, is industrially produced by a liquid phase Beckmann rearrangement of cyclohexanone oxime using highly concentrated sulfuric acid as catalyst.[1] This process has several disadvantages such as the by-production of a large amount of undesired ammonium sulfate, and corrosion and environmental problems caused by the use of fuming sulfuric acid. These problems can be resolved if a solid acid catalyst is used instead of sulfuric acid. A number of attempts have been made to use solid acid catalysts including silica alumina,[2] tantalum oxide[3] and zeolites such as Y[4,5] and mordenite.[4] However, these catalysts gave rise to relatively low selectivity for lactams and rapid decay of activity. It has been reported[6,7] that the HZSM-5 zeolite with high Si : Al$_2$ ($\geqslant$4000) and high external surface area ($\geqslant$10 m^2 g^{-1}) exhibited high activity and selectivity for ε-caprolactam. Titanium silicalites, TS-1 and TS-2, have been reported to be better catalysts for the transformation of cyclohexanone oxime than the other MFI and MEL zeolites, respectively.[8,9]

It has been proposed that the active sites of MFI zeolites for this rearrangement are the weakly acidic or neutral silanol groups present on the external surface of the zeolites.[7] The molecular size of ε-caprolactam is supposedly larger than the diameter of the 10-membered ring channels of the zeolites. Yashima *et al.* suggested that inside the channels the formation of by-products with smaller size could be accelerated at the expense of ε-caprolactam[10] and claimed the catalysts which have a smaller pore size than the molecular size of cyclohexanone oxime showed a high selectivity for ε-caprolactam formation. However, the activity of the catalysts showing the high selectivity was relatively low.[10] Here we report that Hβ zeolites containing interconnected three-dimensional system of 12-ring channels exhibited excellent activity and selectivity for the vapour phase Beckmann rearrangement of cyclohexanone oxime in contrast with other 12-membered ring zeolites such as Y,[4,5] mordenite[4,10] and SAPO-5,[10] which give rise to relatively low selectivity for lactam and rapid decay of activity. The use of β zeolites in this reaction has not been reported so far.

A β zeolite sample (Si : Al$_2$ = 25.6, Tosoh) was ion-exchanged with NH$_4^+$ in 1.0 mol dm^{-3} aqueous NH$_4$Cl and then converted into proton-form by calcination at 773 K. Dealuminated β (Si : Al$_2$ = 650), DA-Hβ, was prepared from the proton-exchanged β zeolite sample by treatment with 9 mol dm^{-3} HNO$_3$ at 353 K for 4 h.[11] Silicalite-1 (JRC-Z5-1000H, Si : Al$_2$ = 1250) was used as received. The catalytic reaction of cyclohexanone oxime was conducted under atmospheric pressure using a continuous flow reactor made of stainless steel. The feed cyclohexanone oxime was dissolved in solvent and injected with a syringe pump along with N$_2$ as a carrier gas. The collected reaction products were analysed by a gas chromatograph equipped with a 4 m long packed column of silicone SE-52 (5%). The liquid product recovery was >98% in all cases.

The results of the reaction of cyclohexanone oxime over β zeolites under different conditions are presented in Table 1. When benzene was used as diluent, Hβ zeolite exhibited a high activity and moderate selectivity for ε-caprolactam formation.

Table 1 Vapour phase Beckmann rearrangement of cyclohexanone oxime over β and silicalite-1 zeolites[a]

			Selectivity (%)				
Catalyst	Diluent	Conv. (%)					others
Hβ	Benzene	98.8	73.0	7.4	10.6	3.5	5.5
Hβ	Methanol	80.6	86.9	6.6	3.2	1.0	2.3
Hβ	Ethanol	99.5	86.8	4.4	2.9	2.2	3.6
Hβ	Propan-1-ol	99.6	89.6	3.1	2.6	1.7	3.0
Hβ	Butan-1-ol	100.0	91.1	2.9	2.3	1.5	2.2
Hβ	Pentan-1-ol	99.4	92.9	1.8	1.8	1.1	2.4
Hβ	Hexan-1-ol	100.0	95.9	0.0	0.7	0.8	2.6
Hβ	Heptan-1-ol	99.8	92.8	2.6	1.8	1.0	1.8
Hβ	Butan-2-ol	100.0	86.2	5.2	4.3	2.0	2.3
Hβ	2-methylpropan-2-ol	99.2	75.4	5.8	7.9	3.5	3.9
Silicalite-1	Benzene	99.5	80.6	3.3	4.9	6.8	4.4
Silicalite-1	Hexan-1-ol	79.9	96.2	0.3	0.6	0.0	2.9
Silicalite-1[b]	Hexan-1-ol	95.6	94.3	0.9	1.2	0.2	3.4
DA-Hβ	Butan-1-ol	98.7	94.0	2.1	1.3	1.0	1.6

[a] Hβ : Si/Al$_2$ = 25.6, DA-Hβ : Si/Al$_2$ = 650, silicalite-1 : Si/Al$_2$ = 1250, Reaction conditions: 623 K, 0.1 MPa, oxime : diluent : N$_2$ = 1 : 9 : 10 (molar), W/F = 136 g$_{\text{cat}}$ h mol$_{\text{oxime}}^{-1}$, time on stream = 4 h. [b] Time on stream = 1 h.

The selectivity for ε-caprolactam was improved when alcohols were fed with cyclohexanone oxime in place of benzene. The formation of cyclohexanone was effectively retarded by alcohols. With increasing alcohol carbon number, the selectivity for ε-caprolactam formation increased linearly, reaching of a maximum of *ca.* 96% with 100% oxime conversion in the case of hexan-1-ol; the selectivities for 5-cyanopentane and 5-cyanopent-1-ene and cyclohexanone were decreased linearly. Comparison of the effect of C_4 alcohols shows that the selectivity decreased in the following order: butan-1-ol > butan-2-ol > *tert*-butyl alcohol. This is opposite to the order of dehydration reactivity of alcohols; we observed that the addition of a small amount of water to butan-1-ol led to the decrease in the selectivity for ε-caprolactam.

Fig. 1 shows the conversion and selectivity change with time on stream when cyclohexanone oxime was fed with benzene, methanol and hexan-1-ol onto the Hβ catalyst. For benzene as a diluent, there was no significant change in the conversion and selectivity for 4 h. For methanol the conversion decreased rapidly with time on stream, while the selectivity gradually increased and stabilized after 3 h. For hexan-1-ol, high stability was attained together with high activity and excellent selectivity.

It has been reported that alcohols, especially methanol, greatly improved the catalytic performance in the Beckmann rearrangement reaction over silicalite-1.[12] As shown in Table 1, for silicalite-1, the use of hexan-1-ol in place of benzene also resulted in enhancement of the selectivity for ε-caprolactam. However, the catalyst life of silicalite-1 was relatively short in contrast with that of Hβ zeolite; the catalytic activity declined rapidly from *ca.* 95% after 1 h to *ca.* 80% after 4 h of time on stream. This result is consistent with the observation by Kitamura and Ichihashi, who reported that over silicalite-1 the activity decay increased with increasing alcohol carbon number in the range C_1–C_3.[12] This indicates that the effect of diluent on the Beckmann rearrangement reaction was dependent on the kind of zeolites.

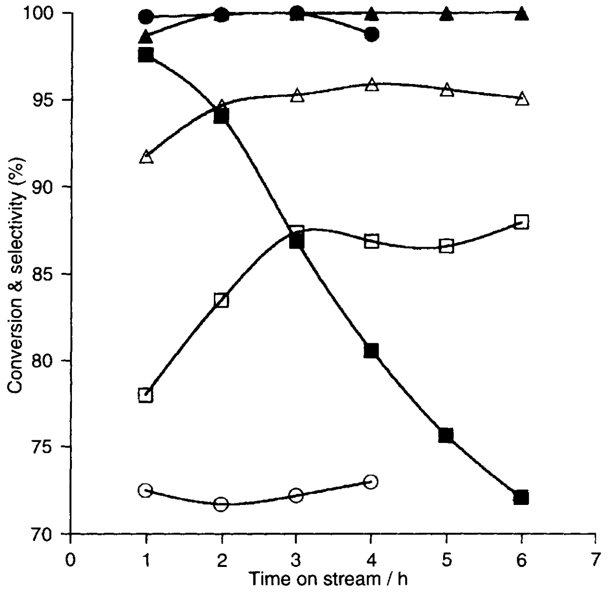


Fig. 1 Change in conversion and selectivity with time on stream in the Beckmann rearrangement of cyclohexanone oxime over Hβ zeolite. Reaction conditions: see footnote in Table 1. Conversion (%) (●) benzene; (■) methanol; (▲) hexan-1-ol. Selectivity (%) (○) benzene; (□) methanol; (△) hexan-1-ol.

The DA-Hβ zeolite (Si : Al_2 = 650), which was prepared by dealumination of Hβ, showed a slightly lower activity but a higher selectivity for ε-caprolactam than the original Hβ. It is noteworthy that Sato and co-workers found both the activity and the selectivity for ε-caprolactam increased along with the increase in Si : Al_2 ($\leqslant$2000) of HZSM-5 zeolite.[6]

The excellent catalytic performance of the Hβ zeolite may be ascribed to its relatively weak acidity[13,14] and unique structure with a three-dimensional pore system containing 12-membered ring apertures but without supercages. Because of its relatively large pores, β zeolite should possess certain free capacity for the transformation of cyclohexanone oxime having six-membered ring into ε-caprolactam having seven-membered ring. The present study has revealed that the Hβ zeolite is a highly active, selective and stable catalyst for the ε-caprolactam formation from cyclohexanone oxime in the presence of primary alcohol with carbon number 4–7.

Footnotes

† Present address: Engineering Research Institute, Faculty of Engineering, The University of Tokyo, Yayoi, Tokyo 113, Japan.

‡ E-mail: tatsumi@komiyama.t.u-tokyo.ac.jp

References

1 J. E. Kent and S. Riegel, *Handbook of Industrial Chemical*, 8th edn., van Nostrand, New York, 1983, p. 402.
2 O. Immuel, H. H. Scwarz, H. Starcke and W. Swoden, *Chem.-Ing.-Tech.*, 1984, **56**, 612.
3 T. Ushikubo and K. Wada, *J. Catal.*, 1994, **148**, 138.
4 P. S. Landis and P. B. Venuto, *J. Catal.*, 1966, **6**, 245.
5 A. Aucejo, M. C. Burguet, A. Corma and V. Fornes, *Appl. Catal.*, 1986, **22**, 187 and references cited therein.
6 H. Sato, N. Ishii, K. Hirose and S. Nakamura, *Stud. Surf. Sci. Catal.*, 1986, **28**, 755.
7 H. Sato, K. Hirose, M. Kitamura and Y. Nakamura, *Stud. Surf. Sci. Catal.*, 1989, **49**, 1213.
8 A. Thangaraj, S. Sivasanker and P. Ratnasamy, *J. Catal.*, 1992, **137**, 252.
9 J. S. Reddy, R. Ravishankar, S. Sivasanker and P. Ratnasamy, *Catal. Lett.*, 1993, **17**, 139.
10 T. Yashima, K. Miura and T. Komatsu, *Stud. Surf. Sci. Catal.*, 1994, **84**, 1897.
11 E. B. Lami, F. Fajula, D. Anglerot and T. D. Courieres, *Microporous Mater.*, 1993, **1**, 237.
12 M. Kitamura and H. Ichihashi, *Stud. Surf. Sci. Catal.*, 1994, **90**, 67.
13 S. G. Hegde, R. Kumar, R. N. Bhat and P. Ratnasamy, *Zeolites*, 1989, **9**, 231.
14 P. G. Smirniotis and E. Ruckenstein, *J. Catal.*, 1993, **140**, 526.

Received, 21st February 1996; Com. 6/01259K