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Development and Industrialization of the Vapor-Phase Beckmann Rearrangement Process

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The development of a new catalyst effective for the vapor-phase Beckmann rearrangement of cyclohexanone oxime has made it possible to establish a commercial process for the production of ε-caprolactam without producing any ammonium sulfate. Through fundamental studies of the catalyst, it was discovered that an MFI-type zeolite composed exclusively of silica had a high selectivity and activity for the vapor-phase Beckmann rearrangement. Based on acidity measurements and on the reactivity of oximes with different sizes as well as the calculation results of the deprotonation energies of some silanols, we have suggested that the active sites are nest silanols located close to their mouth of the micro pores. By addition of methanol into the reaction system, the selectivity for ε-caprolactam was markedly improved to the levels required for industrialization. A fluidized bed reactor was used for the reaction system in order to maintain a continuous production. By combining the ammoximation process for production of cyclohexanone oxime using the TS-1 catalyst and the vapor-phase Beckmann rearrangement, a commercial plant has been operating on a 60000 tons per year scale since April 2003, without any troubles.

1. Introduction

ε-Caprolactam is mainly produced through the Beckmann rearrangement of cyclohexanone oxime. ε-Caprolactam is an important intermediate in the production of Nylon 6, the world production of which is estimated at about 3.8 million tons per year. Figure 1 shows the widely used current ε-caprolactam production process, which uses benzene as a starting material. Benzene is converted to cyclohexane via hydrogenation and then to cyclohexanone via oxidation. Cyclohexanone oxime is produced by the reaction between cyclohexanone and hydroxylamine. Then, caprolactam is produced by the Beckmann rearrangement of cyclohexanone oxime with oleum or sulfuric acid.

In the current process, a large amount of ammonium sulfate is produced as a by-product through the Beckmann rearrangement. The strong interaction between caprolactam and oleum or sulfuric acid used as a catalyst makes the sulfuric acid recycling difficult, requiring ammonia addition in order to separate the sulfuric acid from the caprolactam.[1] Although ammonium sulfate has been used mainly as a fertilizer, oleum or sulfuric acid and ammonia have a higher value than ammonium sulfate. The amount of ammonium sulfate depends on the way to produce hydroxylamine. In the classical Raschig process, the amount of ammonium sulfate is 2.8 tons per ton of caprolactam in the oximation step, and 1.6 tons in the rearrangement step. Therefore, the total amount of ammonium sulfate is 4.4 tons per ton of caprolactam. In the NO reduction process by

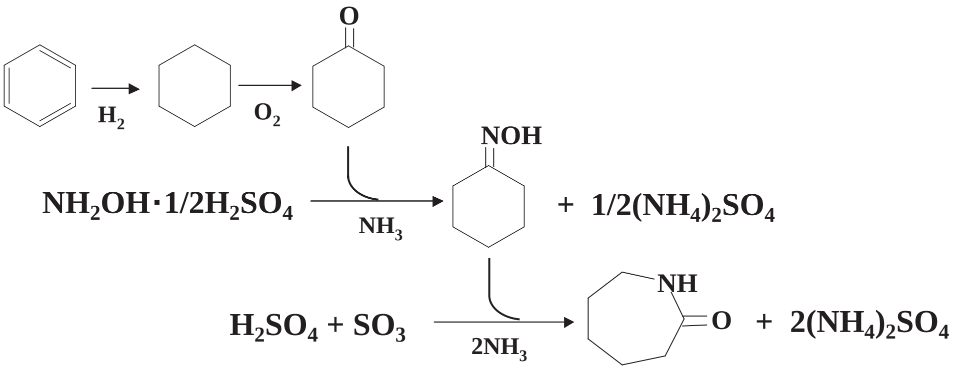


Fig. 1. Current process.

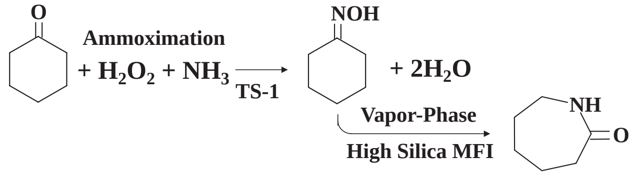


Fig. 2. New process.

BASF, as well as the HPO process by DSM, the amount of ammonium sulfate produced in the oximation step is much smaller. However, the total amount of ammonium sulfate generated in the BASF process is 2.6 tons, and in the DSM process, it is 1.6 tons per ton of caprolactam.[2] Consequently, a new process to avoid the ammonium sulfate generation have been sought by industry and academia for a long time.

2. New Process

Sumitomo Chemical Co., Ltd. established for the first time in the world a new process without using oleum or sulfuric acid, carrying out the Beckmann rearrangement under vapor-phase conditions.[3] Figure 2 shows the outline of this new process. In this new process, the first two steps from Benzene to cyclohexanone are the same as in the current process. However, the oximation and the Beckmann rearrangement steps are new, consisting of ammoximation and subsequent vapor-phase Beckmann rearrangement.

Sumitomo Chemical Co., Ltd. has been studying the vapor-phase Beckmann rearrangement since 1984, and in 1986, discovered the fundamental catalyst based on MFI-type silica zeolite.[4,5] Then, a catalyst with high performance was developed, and the commercial feasibility of this technology was confirmed in a 5000 tons per year demonstrative plant. The combined process with the ammoximation was studied at the same time. Sumitomo Chemical Co., Ltd. industrialized this new process with a production scale of 60000 tons per year in April 2003.

The ammoximation step was developed by Eni Chem[6] (now called Syndial) and was industrialized by Sumitomo Chemical Co., Ltd. In this step, cyclohexanone oxime is produced without producing any amount of ammonium sulfate by the direct reaction of cyclohexanone with ammonia and hydrogen peroxide on a TS-1 catalyst, which consists of titanium silicate with MFI-type structure.[7,8]

In the vapor-phase Beckmann rearrangement process (Fig. 3), cyclohexanone oxime is converted to caprolactam on a high silica MFI zeolite catalyst instead of oleum or sulfuric acid. Thus, this process does not produce any ammonium sulfate. Cyclohexanone oxime is vaporized and is fed together with methanol into the reactor, where the catalyst is loaded. The reaction proceeds at between 350 and 400 °C. The addition of methanol vapor into the reactor is one of the main features of this process. The role of methanol will be explained later. The gaseous products from the reactor are cooled to be condensed, and methanol is recovered and recycled into the reactor. Then, the products are purified, and pure and high quality caprolactam is obtained. In this reaction, high conversion and high selectivity are achieved. Conversion is higher than 99%, while selectivity is higher than 95%. The vapor-phase Beckmann rearrangement process does not require any oleum or sulfuric acid, ammonia manufacturing plants and recovering plant of ammonium sulfate. This means that the investment required for the process with the new vapor-phase Beckmann rearrangement is much lower than that of the current process.

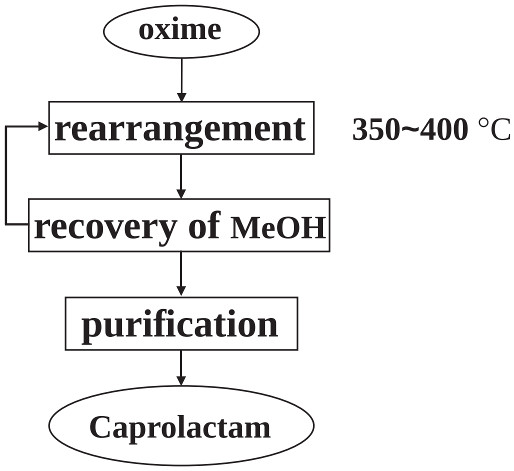


Fig. 3. Beckmann rearrangement process (vapor-phase).

Figure 4 compares the atom economies of the current process with those of the new process, in order to prove that our process is greener. In the current process, the atom economy, which is the weight ratio of target molecule to all products, is 36%. In turn, with the new process, the atom economy is theoretically 100%. We can say that this new process is environmentally friendly, namely a green process.

3. Features of the Catalyst for the Vapor-Phase Beckmann Rearrangement

3.1 Acidity of the Catalyst. At first, we studied how much acidity of the catalyst was effective for the vapor-phase Beckmann rearrangement. Many researchers have studied the relationship between the reactivity and the acidity of catalysts, as the Beckmann rearrangement reaction is believed to be a typical acid-catalyzed reaction. They have insisted that the acidity is very important for achieving a good reaction result. We chose MFI zeolite as a catalyst candidate. The MFI zeolite is one of the most famous acid catalysts, with a unique three-dimensional micropore structure and tunable acidity.[9]

Since the acidity of MFI zeolite depends on the silicon to aluminum atomic ratio,[10] we studied the relationship between the catalytic activity and the acidity of MFI zeolites by using MFI zeolites with a wide range of silicon to aluminum atomic ratio. Figure 5 shows the results of these experiments.[3] The selectivity and the conversion were not enough in the range of the atomic ratios below 100. However, when the ratio became larger, the selectivity and conversion increased, achieving high selectivity and high conversion in atomic ratios larger than 1000. These results show that a zeolite that has a smaller number of acidic sites gives the higher activity and the higher selectivity. We tested then zeolites with atomic ratios above 100000, namely, pure silica, and achieved almost 100% conversion and 80% selectivity.[11]

The acidity of these zeolites was studied by ammonia-temperature-programmed desorption (TPD). Figure 6 shows the results for some MFI zeolites.[3] These TPD spectra were

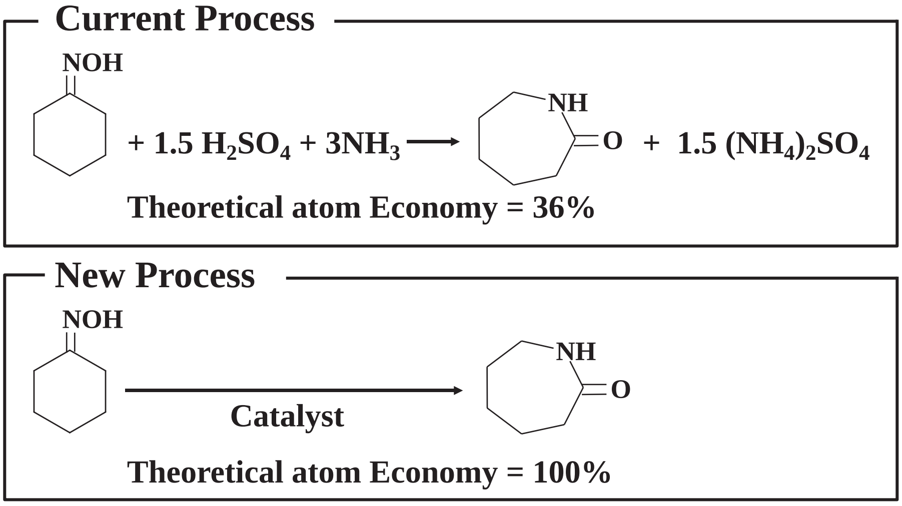


Fig. 4. Comparison between current and new processes.

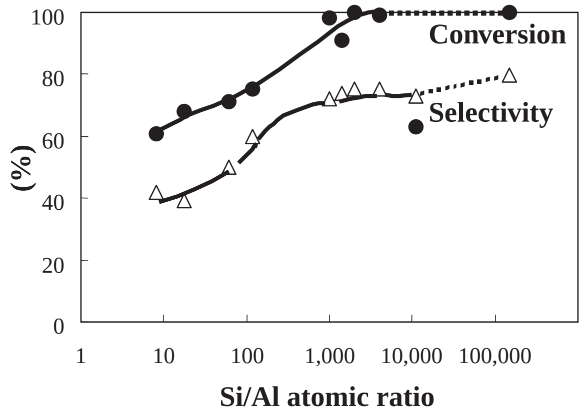


Fig. 5. Influence of Si/Al of MFI zeolites in the Beckmann rearrangement of cyclohexanone oxime. Reaction conditions: 8% oxime in benzene solution; WHSV (oxime) = $3\,h^{-1}$: temp, 350 °C; time, 5 h.[3]

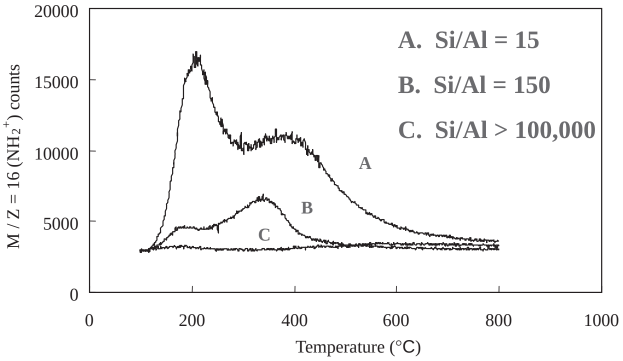


Fig. 6. NH_3 TPD, Pretreatment: 350 °C, 1 h evacuation, NH_3 Adsorption: 100 °C, 100 Torr, 30 min.[3]

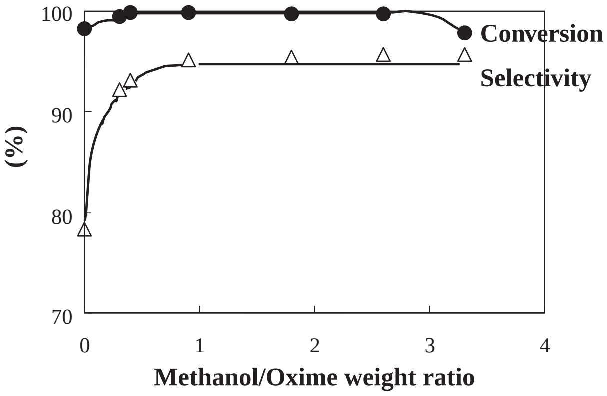


Fig. 7. Effect of methanol addition in the Beckmann rearrangement of cyclohexanone oxime. Reaction conditions: catalyst, high silica MFI zeolite; WHSV (oxime) = $8\,h^{-1}$: temp, 370 °C; time, 6 h.[3]

obtained after ammonia adsorption at 100 °C followed by evacuation at the same temperature. The zeolites with silicon to aluminum atomic ratios of 15 and 150 showed a clear desorption band corresponding to the desorption of ammonia from acidic sites. However, the high silica zeolite, which gives both high selectivity and high conversion, did not show such a clear desorption pattern. Thus, we concluded that the acidity that can be detected by ammonia TPD is not so important for the vapor-phase Beckmann rearrangement reaction and that the acidity generated by the aluminum is unnecessary for this reaction.

3.2 Addition of Methanol. When methanol was added into the reactor with cyclohexanone oxime, the selectivity to caprolactam was greatly improved. Figure 7 shows the relationship between the weight ratio of methanol to cyclohexanone oxime and the activity results.[3] Without methanol in the reaction system, the selectivity was only about 80%. However, when the added amount of methanol was one or two times that of cyclohexanone oxime, the selectivity increased to around 95%. The addition of methanol reduced the formation of all of the by-products, especially coke. The main by-products were 5-cyanopentene (about 2.0%), 5-cyanopentane (about 0.5%), cyclohexanone (about 1.0%), and cyclohexenone (about 0.5%). The reduction of coke formation moderated the drop in the catalytic activity. Even if large amounts of methanol were added, the selectivity remained high, though the conversion decreased slightly. This result opened the way to the industrialization of the new process.

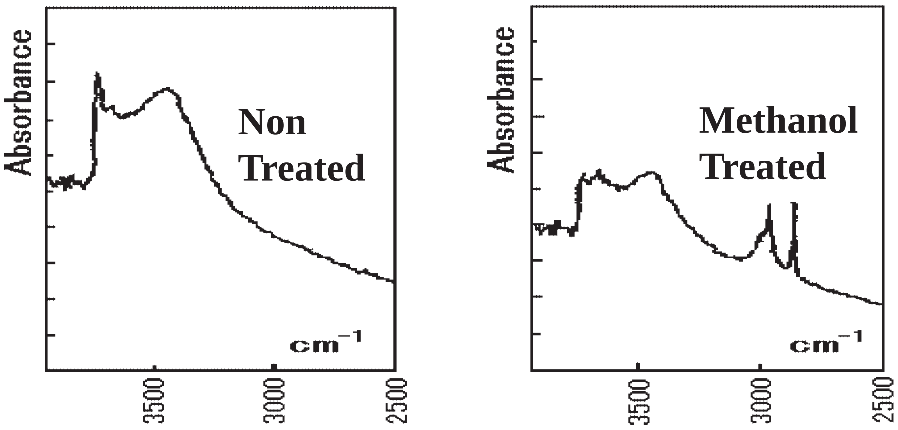


Fig. 8. FT-IR spectra of the catalyst treatment with methanol: 30 torr, 350 °C, 30 min. Evacuation: 350 °C, 1 h.[3]

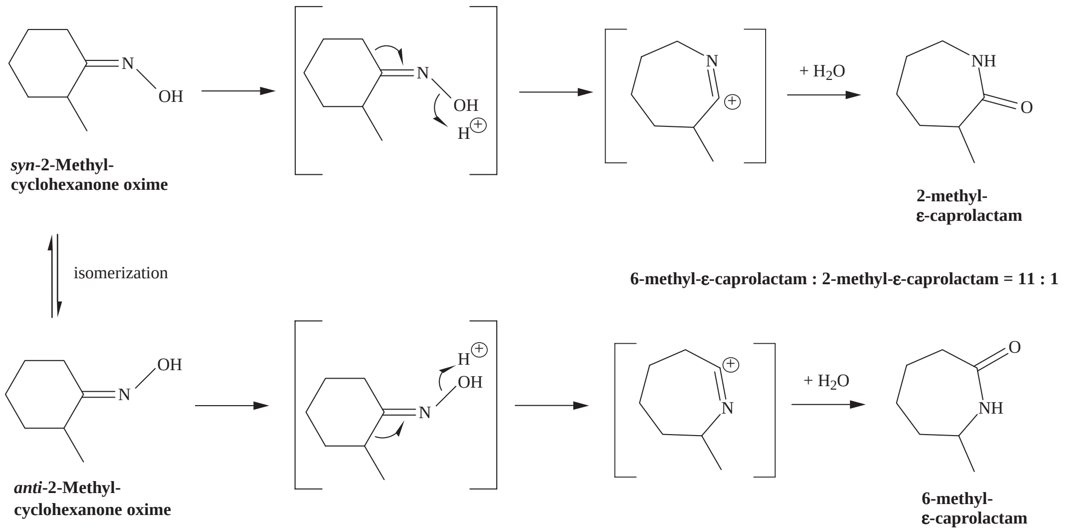
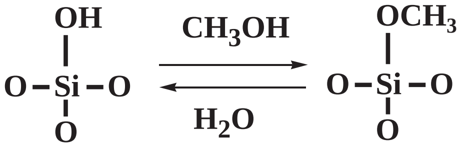


Fig. 9. Plausible reaction mechanism of the vapor-phase Beckmann rearrangement.



$$\mathrm{O{-}\overset{\displaystyle OH}{\underset{\displaystyle O}{Si}}{-}O}\ \underset{H_2O}{\overset{CH_3OH}{\rightleftarrows}}\ \mathrm{O{-}\overset{\displaystyle OCH_3}{\underset{\displaystyle O}{Si}}{-}O}$$

Scheme 1.

The effect of methanol was investigated with the help of FT-IR measurements.[12] Figure 8 shows the spectrum of the same zeolite with or without methanol treatment.[3] A high silica MFI zeolite was treated with methanol vapor at 350 °C, then the IR spectra was measured after evacuation. The zeolite that was not treated with methanol showed a sharp IR absorption at 3740 cm^{-1}, which was assigned to terminal silanols. However, after the methanol treatment, two new clear absorption bands assigned to methoxy groups[13] appeared, while the terminal silanol's absorption band disappeared. We think that this change of the spectrum follows the exchange shown in Scheme 1, where methanol reacts with the terminal silanols and converts them to methoxy groups. This blocking of the terminal silanols leads to high selectivity for caprolactam. From this point of view, we concluded that the terminal silanols are the active sites for the side reaction to undesired by-products. The reaction between methanol and terminal silanols continued as long as methanol vapor existed in the reaction system, because of the equilibrium. Therefore, the existence of methanol guarantees high selectivity for caprolactam.

3.3 Reaction Mechanism of the Vapor-Phase Beckmann Rearrangement. In general, it is considered that the liquid-phase Beckmann rearrangement proceeds via typical S_N2 mechanism, where the alkyl group at anti position to the oxime OH group migrates.[14] We examined the vapor-phase Beckmann rearrangement of *anti*-2-methylcyclohexanone oxime. The main product was 6-methyl-ε-caprolactam, and the molar ratio of 6- and 2-methyl-ε-caprolactam was 11:1. This result indicates that the migration of the alkyl group at the anti position to the OH group takes place in the same way as the liquid-phase Beckmann rearrangement (Fig. 9). It was also confirmed that *syn*-2-methylcyclohexanone oxime was produced by the isomerization of a part of *anti*-2-methylcyclohexanone oxime through a non-catalytic reaction. Thus, small amounts of 2-methyl-ε-caprolactam were possibly produced via this isomerization. We concluded that the reaction mechanism of the vapor-phase condition is the same as in the liquid phase.[15]

3.4 The Catalyst Active Site for the Vapor-Phase Beckmann Rearrangement. From the results of ammonia TPD and FT-IR measurements for the zeolite treated with methanol, it was concluded that the active sites are neither the acidic sites originating from aluminum of the zeolite framework nor the terminal silanols. Several kinds of silanols exist in zeolite as shown in Fig. 11: terminal, geminal, vicinal, and nests. Nest silanols, generated at defect sites, are formed by removing a silicon atom from the zeolite framework, as shown in Fig. 10.[16] The broad band around 3400 $\mathrm{cm^{-1}}$ in Fig. 8 is attributed to nest silanols. The FT-IR spectra of the zeolite demonstrate that most of the nest silanols remain after the methanol treatment.

Hölderich et al. have investigated the relationship between the catalytic activity and types of silanol in the silicalite using FT-IR spectroscopy and have proposed that nest silanols are the most favorable sites for the vapor-phase Beckmann rearrangement.[17] We also think that the catalytic activity of the zeolite for the vapor-phase Beckmann rearrangement can be ascribed to the nest silanols. Thus, the structure of nest silanols should play an important role for the vapor-phase Beckmann rearrangement.

3.5 Deprotonation Energies of Each Silanol in Zeolite. In order to confirm if nest silanols are active sites for the vapor-phase Beckmann rearrangement, the deprotonation energies of some silanols were studied and compared by means of molecular orbital calculation with the help of D mol cube modeling. All geometry optimization and energy calculations with D mol cube modeling were performed with GGA-PW91 exchange correlation functionals and double numerical plus polarization (DNP) basis set including p- and d-orbital as porlarization function. The size of the DNP basis set is comparable to conventional 6-31G** Gaussian basis sets.

The models of silanols for the calculation are shown in Fig. 11.[16] The dimensions of Si–O bonds in each silanol were based on the structure of MFI zeolite, and silicon atoms next to these silanols were substituted by hydrogen atom in the calculation. The deprotonation energy of each silanol to release a marked proton boundlessly was calculated, and Table 1 shows the results of each deprotonation energy, compared to water.[16] The silanols were deprotonated with a lower energy than water, thus, they can release a proton easier than water. This means their acidity is stronger than water. The ease of proton escape from silanols was in the order: nest, vicinal, geminal, and terminal. These results suggest that the nest silanol's acidity is the strongest of all silanols in a zeolite, and the nest silanols can give a proton to cyclohexanone oxime easier than water or the other silanols. Therefore, we think that nest silanols act as the active sites for the vapor-phase Beckmann rearrangement.[17]

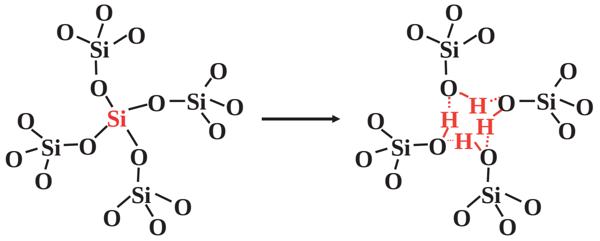
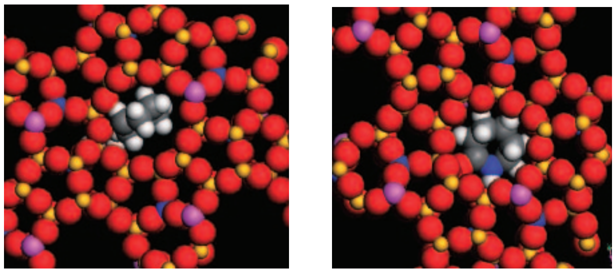


Fig. 10. Nest silanols.[16]

3.6 Location of Active Site. MFI zeolite has a unique three-dimensional micropore structure. In addition, most of the surface for the catalytic reaction is inside the pore structure. Therefore, it is natural to think that the active sites are located inside the micropores.[18] In order to confirm this possibility, we compared the molecule's size and the size of the pore mouth. Figure 12 shows a comparison of the cyclohexanone oxime or caprolactam molecule's size and that of the pore mouth.[18] The geometries of the molecules were fixed by the help of D mol cube quantum mechanical program.[19] Cyclohexanone oxime seemed to be able to enter the micro-

Table 1. Deprotonation Energy Differences of Silanols[16]

	H_2O	Terminal	Geminal	Vicinal	Nest
$\Delta E/\mathrm{kcal\,mol^{-1}}$	0.00	−40.96	−54.24	−55.49	−64.64



Cyclohexanone oxime in straight channel

Caprolactam in straight channel

Fig. 12. Comparison of the size of cyclohexanone oxime and that of zeolite aperture.[18]

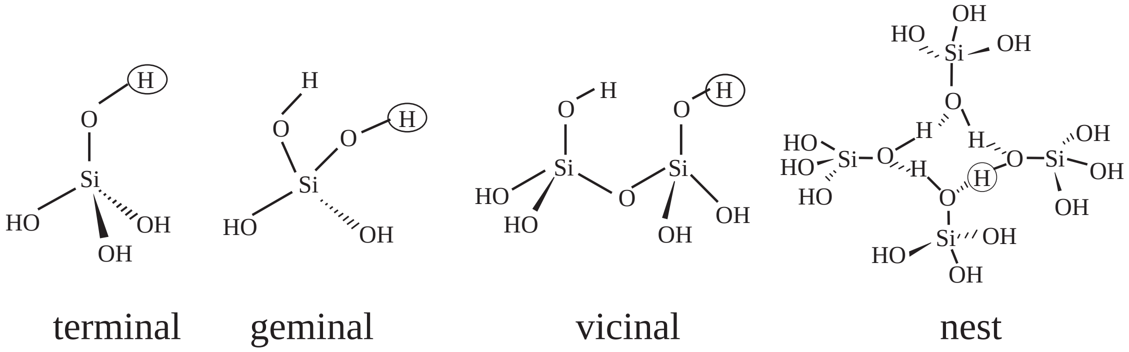


Fig. 11. Silanols in the zeolite.[16]

Table 2. Reaction Results of Some Oximes over High Silica MFI Zeolite (Si/Al > 30000)[a)]

Oximes	Conversion /%	Selectivity /%
Cyclohexanone oxime	100	71
Cyclopentanone oxime	100	83
Cyclooctanone oxime	20	0
4-Methylcyclohexanone oxime	100	71
3-Methylcyclohexanone oxime	98	47
2-Methylcyclohexanone oxime	99	39
2,6-Dimethylcyclohexanone oxime	98	36

a) Reaction conditions: temp, 350 °C; time, 5 h.[18]

pore, but it seemed impossible for caprolactam to go through the pore mouth, indicating that caprolactam is not formed in the inner part of the micropores. We believe that the active sites are not in the inner and deep parts of micropores, but on the external surface or in the inner parts close to the mouth of the micropores.[15]

In order to ascertain where the active sites are located, we tried the vapor-phase Beckmann rearrangement of some oximes over a high silica MFI zeolite. Table 2 shows the results of these reactions.[18] In this experiments, methanol was not used, and therefore, selectivities were low. Cyclopentanone oxime, which is smaller than cyclohexanone oxime, gave the amide product with a high selectivity. In turn, cyclooctanone oxime, which is larger than cyclohexanone oxime, did not react. When oximes that are larger than the zeolite micropore were used, these reactions did not take place. Therefore, we conclude that the active site is not on the external zeolite surface.

From the reaction results of methyl-substituted cyclohexanone oximes, the selectivity of 4-methylcyclohexanone oxime was the same as that of cyclohexanone oxime. In turn, when methyl-substituted cyclohexanone oximes, such as 2-methylcyclohexanone oxime, 3-methylcyclohexanone oxime, and 2,6-dimethylcyclohexanone oxime, were used for the vapor-phase Beckmann rearrangement, the selectivity decreased. As the position of the methyl group became closer to the NOH group of oxime, the selectivity decreased. These methyl-substituted oximes cannot enter easily the zeolite pore. They give lower selectivities, because of steric hindrance between the pore and them. According to these results, we conclude that the active site is in the inner parts close to the mouth of the micropores, and not in the deep parts of the micropores.[20]

Figure 13 shows our image of the active site.[18] This figure is a view of a cyclohexanone oxime molecule coordinated to nest silanols in a straight channel, seen from its side section. About half of the cyclohexanone oxime molecule is outside of the aperture. We think that the Beckmann rearrangement takes place in this situation, and in this way, the reaction product, i.e., caprolactam, can escape easily into the gas phase.

4. Industrialization

In order to produce caprolactam and to regenerate the catalyst continuously, a fluidized bed reaction system was adopted (Fig. 14).[3,21] When the vapor-phase Beckmann rearrangement reaction was continued for a long time, carbon-like materials deposited on the catalyst, leading to a drop in the catalytic activity. We think this carbon-like material comes from the polymerization of cyclohexanone oxime. Therefore, it was necessary to stop the reaction and remove the carbon-like material through the regeneration in air at high temperature, repeating the reaction–regeneration cycle again and again. In this reaction system, a mixture of oxime and methanol was fed into a fluidized bed reactor, in which the catalyst was loaded. Cyclohexanone oxime was converted to caprolactam in the reactor, and caprolactam was sent through a cyclone from the reactor to the purification zone. A part of the catalyst was carried continuously from the reactor to the regenerator and was regenerated in air at high temperature. Then, the regenerated catalyst returned to the reactor. In this way, the catalyst circulates continuously between the reactor and the regenerator. In order to keep the best performance of the catalyst, in other words, to keep high conversion and high selectivity for a long time, we developed a catalyst suitable for the fluidized bed reaction, and optimized the reactor and its operational conditions by operating a demonstrative plant of 5000 tons per year.[22]

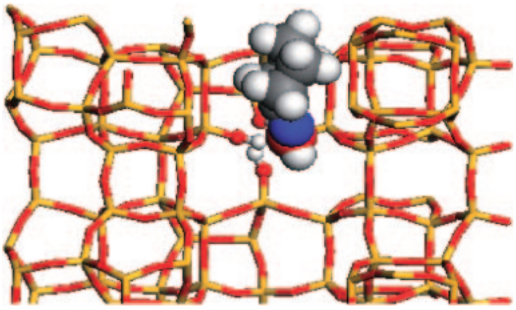


Fig. 13. A model of coordination of cyclohexanone oxime on the active site.[18]

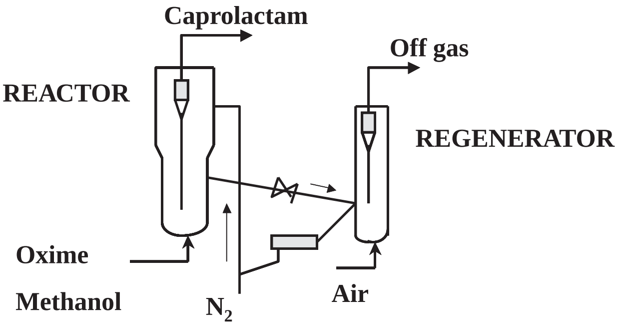


Fig. 14. Fluidized bed reaction system.[3]

In April 2003, the new process was industrialized with a production scale of 60000 tons per year. A picture of the new plant for the production of caprolactam is shown in Fig. 15. This New plant is in the Ehime factory of Sumitomo Chemical Co., Ltd. This commercial plant has been operating without any problem.[23]

5. Conclusion

A vapor-phase Beckmann rearrangement was established for the first time in the world. This new process and the catalyst have the following features. (1) The new process is completely free from ammonium sulfate. Therefore, this process can reduce the investment of plant and equipment, as well as reduce the consumption of resources. (2) The main component

Fig. 15. The new plant for the production of caprolactam.

of the catalyst for the vapor-phase Beckmann rearrangement is silica. So, it is not toxic, and it is stable during reaction and regeneration. (3) The selectivity for caprolactam is greatly improved by adding methanol into the reaction system, and the methanol can be recovered quantitatively and recycled. (4) The active sites of the catalyst appear to be nest silanols located in the inner parts close to the mouth of the micropores. (5) The fluidized bed reaction system keeps the best performance of the catalyst.

The combined process of ammoximation and vapor-phase Beckmann rearrangement, is a green and sustainable process. Considering the above-mentioned points, this new technology is expected to be widely accepted in the world in the future.

References

1 J. Ritz, H. Fuchs, H. Kieczka, W. C. Moran, *Ullman's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, Federal Republic of Germany, **1986**, Vol. A5, pp. 31–50.

2 G. Petrini, G. Leofanti, M. A. Mantegazza, F. Pignataro, *Caprolactam via Ammoximation, American Chemical Society Symp. Ser.*, American Chemical Society, Washington, **1996**, Vol. 626, pp. 33–44.

3 H. Ichihashi, M. Kitamura, *Catal. Today* **2002**, *73*, 23.

4 H. Sato, K. Hirose, N. Ishii, Y. Umada, U.S. Patent 4,709,024, **1987**; *Chem. Abstr.* **1988**, *108*, 113126.

5 H. Sato, K. Hirose, M. Kitamura, Y. Umada, N. Ishii, H. Tojima, U.S. Patent 4,717,769, **1988**; *Chem. Abstr.* **1988**, *109*, 38401.

6 V. Alessi, R. Penzo, S. Pattaro, R. Tessari, M. J. Slater, Proceedings of Value Adding through Solvent Extraction at ISEC'96, Melbourne, **1996**, Vol. 2, pp. 1673–1678.

7 A. Zecchina, G. Spoto, S. Bordiga, F. Geobaldo, G. Petrini, G. Leofanti, M. Padovan, M. Mantegazza, P. Roffia, *Stud. Surf. Sci. Catal.* **1993**, *75*, 719.

8 P. Roffia, G. Leofanti, A. Cesana, M. Mantegazza, M. Padovan, G. Petrini, S. Tonti, P. Gervasutti, *Stud. Surf. Sci. Catal.* **1990**, *55*, 43.

9 H. Sato, *Catal. Rev. Sci. Eng.* **1997**, *39*, 395.

10 D. H. Olson, W. O. Haag, R. M. Lago, *J. Catal.* **1980**, *61*, 390.

11 H. Sato, N. Ishii, K. Hirose, S. Nakamura, Proceedings of the 7th IZC, Tokyo, **1986**, pp. 755–762.

12 M. Kitamura, H. Ichihashi, *Stud. Surf. Sci. Catal.* **1994**, *90*, 57.

13 L. H. Little, *Infrared Spectra of Adsorbed Species*, Academic Press, London, **1966**, p. 174.

14 A. H. Blatt, *Chem. Rev.* **1933**, *12*, 215.

15 H. Kajikuri, M. Kitamura, H. Ichihashi, Proceedings of the Kyushu International Symposium on Physical Organic Chemistry KISPOC-VII, Japan, **1997**, p. 507.

16 H. Ichihashi, *Sci. Tech. Catal.* **2002**, 73.

17 W. F. Hölderich, J. Roseler, G. Heitmann, A. T. Liebens, *Catal. Today* **1997**, *37*, 353.

18 H. Ichihashi, M. Ishida, A. Shiga, M. Kitamura, T. Suzuki, K. Suenobu, K. Sugita, *Catal. Surv. Asia* **2003**, *7*, 261.

19 H. Kath, R. Glaser, J. Weitkamp, *Chem. Eng. Technol.* **2001**, *24*, 150.

20 *Materials Studio 2.1 Molecular Modeling System and DMol3 Quantum Mechanical Program*, Accelrys Inc., San Diego.

21 H. Kajikuri, M. Kitamura, H. Ichihashi, The 4th Japan-Korea Symp. Catal. Tokyo, Japan, **1993**, p. 12.

22 M. Kitamura, Y. Shimazu, M. Yako, JP 2000-229939, **2000**; *Chem. Abstr.* **2000**, *133*, 151072.

23 Y. Izumi, H. Ichihashi, Y. Shimazu, M. Kitamura, *Chem. Eng. Jpn.* **2004**, *68*, 48.

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