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Vapor phase Beckmann rearrangement of cyclohexanone oxime on the zeolite catalysts

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Abstract

Effective zeolite catalysts for the vapor phase Beckmann rearrangement of cyclohexanone oxime have the smaller pore window size than cyclohexanone oxime and have very weak acid sites. Ethanol is useful solvent for cyclohexanone oxime to improve the selectivity for ϵ-caprolactam formation.

Keywords: Cyclohexanone oxime; Beckmann rearrangement; Zeolite A; Silicalite; External surface

1. Introduction

It is well-known that ϵ-caprolactam, the monomer of 6-nylon, is produced commercially in large scale by the liquid phase Beckmann rearrangement of cyclohexanone oxime using concentrated sulfuric acid as a catalyst and solvent. This reaction process is excellent, that is, low reaction temperature and high selectivity. However, a lot of ammonia must be required for the neutralization of sulfuric acid to separate ϵ-caprolactam from the product mixture. The amount of ammonium sulfate formed is larger than that of ϵ-caprolactam produced.

In the environmentally benign process any additional reagents and/or products should be avoided. Therefore, many researchers have investigated the vapor phase Beckmann rearrangement of cyclohexanone oxime over solid acid catalysts instead of sulfuric acid. The solid acid catalysts used for this reaction were mixed oxides [1–6] and zeolites [7–14]. Especially, it has been reported that the highly siliceous ZSM-5 zeolite [9,10] and ZSM-5 modified by boron [11–13] showed the high activity and selectivity.

The zeolite catalysts, however, having narrow reaction space in the pore is not profitable for this reaction, because cyclohexanone oxime (6 membered ring compound) converts to ϵ-caprolactam (7 membered ring compound), that is, a reaction from small molecule to large molecule. Therefore, we have proposed a concept that the acidic sites on the external surface of zeolite crystallites which have a smaller pore window than the molecular size of cyclohexanone oxime, are useful for the selective formation of ϵ-caprolactam by this reaction [14]. Moreover, it has also been proposed that the active sites would be the very weak acid sites [14].

The purpose of this study is to clarify our concept mentioned above and to discuss the effect of a kind of solvent for cyclohexanone oxime on the selectivity for ϵ-caprolactam formation.

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2. Experimental

2.1. Catalyst

Mordenite (Si/Al=9), ZSM-5 (Si/Al=20,24,54), silicalite-1 (Si/Al>1000), and ferrierite (Si/Al=10) were prepared hydrothermally. A type (Si/Al=1) and clinoptilolite (Si/Al=9) were supplied from Mizusawa Chem. Ind. and Toso, respectively. Silica gel and magnesium oxide were supplied from Fuji Silicia and Wako Chem., respectively.

2.2. Characterization

The crystallinity and the type of the zeolites used here were checked by XRD. Their chemical composition were measured by atomic absorption spectrophotometry. Gravimetric measurements of cyclohexanone oxime and ϵ-caprolactam adsorption were performed by using a high sensitive thermal balance under 15 Pa of adsorbate vapor pressure at 393 K.

2.3. Reaction

Beckmann rearrangement of cyclohexanone oxime was carried out with a continuous flow reactor system under atmospheric pressure. Cyclohexanone oxime was fed by a micro-feeder as a 15 wt% solution. Helium was used as a carrier gas. The product mixtures were analyzed by gas chromatography using 1,2,4-trimethylbenzene as an internal standard.

3. Results and discussion

The adsorption of cyclohexanone oxime on the various zeolites was measured by using a highly sensitive thermal balance. Changes in the adsorption amount with process time on the various zeolites are shown in Fig. 1. On mordenite with large pore window (12 membered oxygen ring), the adsorption amount increased quickly with process time and reached its equilibrium value soon. On ferrierite with relatively small pore window (distorted 10 membered oxygen ring), the adsorption amount also increased quickly and reached equilibrium state at a short time. However, the amount adsorbed at equilibrium state was very small. These results showed that cyclohexanone oxime could be adsorbed and penetrate into the pore of mordenite, but it could be adsorbed only on the external surface and hardly enter into the pore of ferrierite. On the other hand, on MFI type zeolites with a medium pore window size (10 membered oxygen ring), the adsorption rate of cyclohexanone oxime changed with aluminum content in the framework. The adsorption rate decreased with decreasing the aluminum content. On silicalite-1 with small aluminum content (Si/Al>1000), cyclohexanone oxime could not penetrate into the pore under these experimental conditions. It has been also found that ϵ-caprolactam is adsorbed only on the external surface of ZSM-5 (Si/Al=20) crystallite but could not penetrate into the pore under the same conditions [14].

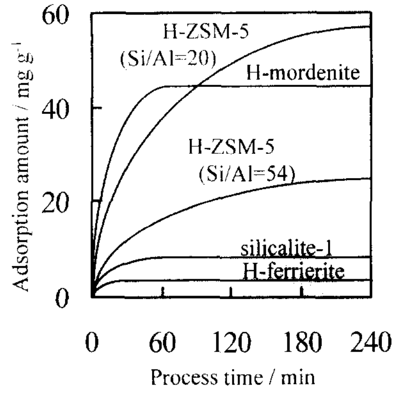

Fig. 1. Adsorption of cyclohexanone oxime on various zeolites. Adsorption conditions: temperature, 393 K; vapor pressure, 15 Pa.

Fig. 2 shows the changes in the conversion of cyclohexanone oxime and the selectivity for ϵ-caprolactam formation over H-ZSM-5 (Si/Al=24) with time on stream. The conversion decreased quickly with time on stream, while the selectivity kept the initial value for 3 h of time on stream. The by-products of this reaction were cyclohexanone, cyclohexenon, 1-cyanopentane, 1-cyanopentene, and polymer of ϵ-caprolactam. The polymer of ϵ-caprolactam could not be detected by gas chromatography. Therefore, its amount was calculated from material balance between reactant and the detectable products. The following results would be discussed based on the data at 105 min of time on stream.

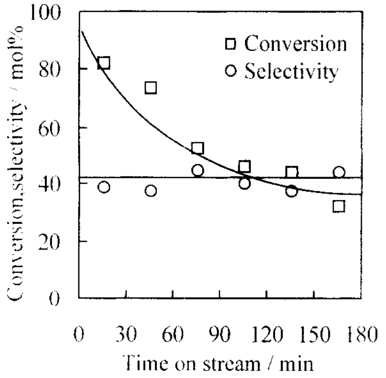

Fig. 2. Changes of conversion and selectivity over H-ZSM-5 (Si/Al=24) catalyst with time on stream. Reaction conditions: temperature, 593 K; W/F=10.2 g h mol^{-1}; solvent, benzene.

Table 1
Conversion of cyclohexanone oxime and selectivity for ϵ-caprolactam over various zeolites and oxide catalysts

Catalyst	Conversion[a] (%)	Selectivity[a] (mol%)
H-Mordenite	32	33
H-ZSM-5 (Si/Al=24)	46	40
Silicalite-1	66	93
H-Ferrierite	76	61
Na-, K-Clinoptilolite	26	86
Ca-A	34	89
Na-A	19	5
Silica gel	100	11
MgO	54	0

Reaction conditions: temperature, 593 K; W/F=10.2 g h mol^{-1}; solvent, benzene.
[a] Data obtained at 105 min of time on stream.

Table 1 shows the conversion of cyclohexanone oxime and the selectivity for ϵ-caprolactam formation over zeolite catalysts which have various pore window size and various solid acid properties. H-mordenite and H-ZSM-5, which have enough size of pore window to swallow cyclohexanone oxime, showed rather low conversion and selectivity. The activity of these catalyst decreased quickly with time on stream by coke formation on the external surface of crystallite and in the pore. So, the data shown in this table are relatively low. The selectivity of these catalysts was also low. Because a part of cyclohexanone oxime reacted in the zeolite pore, the by-products with small molecular size were produced preferentially. And on these catalysts polymerization of ϵ-caprolactam proceeded. On the other zeolite catalysts having small pore window hard to adsorb cyclohexanone oxime in their pore, the activity drop with time on stream was moderate. These zeolite catalysts except for Na-A, showed relatively high selectivity for ϵ-caprolactam formation. These results suggest that the zeolite catalysts having large pore window to swallow cyclohexanone oxime would not be favorable for this reaction.

On the other hand, H-ferrierite having strong acid sites, showed not so high selectivity, while silicalite-1 having a very small amount of acid sites and many hydroxyl groups, which have very weak acidity, showed the very high selectivity. And Ca-A having weak acid sites, and Na, K-clinoptilolite with both very weak acid sites and very weak base sites, showed also high selectivity. However, Na-A having rather strong base sites because of excess sodium ion, showed very low selectivity. Silica gel having a lot of neutral hydroxyl groups, showed high activity but low selectivity. MgO, a typical solid base catalyst, had no catalytic activity for ϵ-caprolactam formation. From these results, it is concluded that the catalytically active sites would not be base sites nor neutral hydroxyl groups but be acid sites including very weak acid sites, and the higher selectivity could be obtained on the weaker acid sites. It is concluded that the very weak acid sites on the zeolites are the active sites for the selective Beckmann rearrangement of cyclohexanone oxime as predicted before [14,15].

Table 2 shows the effect of various solvents for cyclohexanone oxime on the catalytic performance of H-ZSM-5. The activity and selectivity of H-ZSM-5 (Si/Al=24) catalyst was strongly influenced by the kind of solvent. The effect of solvent seems to be complex. We cannot arrange the effect of solvent

Table 2
Effect of various solvents for cyclohexanone oxime on the catalytic performance of H-ZSM-5 (Si/Al=24)

Solvent	Conversion[a] (%)	Selectivity[a] (mol%)
Benzene	46	40
Ethanol	82	88
Acetone	42	71
Cyclohexane	60	60
THF	63	38
Chloroform	82	5

Reaction conditions: temperature, 593 K; W/F=10.2 g h mol^{-1}.
[a] Data obtained at 105 min of time on stream.

Table 3
Conversion of cyclohexanone and selectivity for ϵ-caprolactam over various zeolite catalysts under the presence of ethanol as a solvent

Catalyst	Conversion[a] (%)	Selectivity[a] (mol%)
H-Mordenite	8	88
H-ZSM-5 (Si/Al=24)	82	88
Silicalite-1	80	98
H-Ferrierite	54	84
Ca-A	34	91

Reaction conditions: temperature, 593 K; W/F=10.2 g h mol^{-1}; solvent, ethanol.

[a] Data obtained at 105 min of time on stream.

based on the polarity. It was found that among the solvents used here, ethanol was the best solvent to improve the conversion of cyclohexanone oxime and the selectivity for ϵ-caprolactam formation. In this case, the polymer formation of ϵ-caprolactam decreased very much to increase the material balance to nearly 100%.

The effects of ethanol as a solvent for cyclohexanone oxime were checked over the other zeolite catalysts and the results obtained are shown in Table 3. In all catalysts used here, the selectivity for ϵ-caprolactam formation was improved by ethanol as compared with benzene. On the other hand, over the most catalysts, except for MFI-type zeolites, the conversion of cyclohexanone oxime was depressed by ethanol solvent. From these results, it is suggested that ethanol can wash out ϵ-caprolactam produced from active site effectively, to avoid the successive reaction of ϵ-caprolactam, polymerization. However, the reactant, cyclohexanone oxime, was also washed out from active site by ethanol, to decrease the conversion. On the H-mordenite, H-ferrierite and H-ZSM-5(Si/Al=24) having strong acid sites, a part of ethanol is converted to diethyl ether and ethylene, while no diethyl ether nor ethylene can be detected over silicalite-1 and Ca-A. From the results obtained here, it is concluded that silicalite-1 shows high activity and selectivity under the presence of ethanol for vapor phase Beckmann rearrangement of cyclohexanone oxime.

The results obtained over silicalite-1 under the presence of ethanol as a solvent for cyclohexanone oxime are shown in Fig. 3, when the reaction temperature increased to 623 K to get higher conversion of cyclohexanone oxime. Both conversion and selectivity were higher than 95% and kept the high values at longer than 3 h of time on stream.

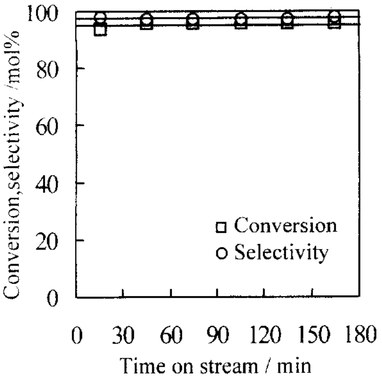

Fig. 3. Changes of conversion and selectivity over silicalite-1 catalyst with time on stream. Reaction conditions: temperature, 623 K; W/F=10.2 g h mol^{-1}; solvent, ethanol.

4. Conclusion

The vapor phase Beckmann rearrangement of cyclohexanone oxime on the zeolite catalysts is studied under atmospheric pressure at 593–623 K. The zeolite catalysts with smaller pore window size than reactant molecular size, such as silicalite-1, ferrierite and A type zeolite, showed high selectivity for ϵ-caprolactam formation, while mordenite and ZSM-5 having larger pore window size than reactant, showed not so high selectivity. From this result it is concluded that Beckmann rearrangement of cyclohexanone oxime to ϵ-caprolactam proceeds selectively on the active sites on the external surface of zeolite crystal.

The base sites and the neutral hydroxyl groups of silica gel did not accelerate effectively this reaction. The acid sites with any acid strength could accelerate this reaction. The weaker acid sites showed the higher selectivity for ϵ-caprolactam formation, because on the strong acid sites, many side reactions, ring opening, decomposition and polymerization, were also accelerated.

It was found that the kind of solvent for cyclohexanone oxime strongly affected the activity and the selectivity. In the solvents tested in this study, ethanol was the most suitable solvent and it improved the selectivity for ϵ-caprolactam formation. Under the optimum conditions, the conversion of cyclohexanone oxime and the selectivity for ϵ-caprolactam formation over silicalite-1 were more than 95% for longer than 3 h of time on stream.

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