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Some aspects of the vapor phase Beckmann rearrangement for the production of ε-caprolactam over high silica MFI zeolites

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Abstract

A high silica MFI zeolite catalyst has been developed for the vapor phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. Methanol fed into the reactor with the oxime improves the yield of caprolactam. Methanol is not converted to dimethylether during the reaction. Moreover, when ammonia is fed to the catalyst with cyclohexanone oxime and methanol, the selectivity remains at a high level, without affecting the conversion. Hence, we conclude that the active sites of high silica MFI are extremely weak acid sites that cannot be detected by ammonia TPD measurement. A fluidized bed reaction system has been developed for the manufacturing process of caprolactam. High quality product is obtained with more than 95% yield. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Vapor phase Beckmann rearrangement; ε-Caprolactam; High silica MFI; Nest silanol

1. Introduction

Caprolactam is an important intermediate used in the production of Nylon 6 fibers and resins. Caprolactam is produced by Beckmann rearrangement of cyclohexanone oxime with oleum or sulfuric acid as reaction medium, and cyclohexanone oxime is mainly produced by the reaction between cyclohexanone and hydroxylamine. The hydroxylamine-phosphate oxime (HPO) process for the cyclohexanone oxime production that DSM developed uses hydroxylamine as its phosphate form [1]. Other manufacturers, except Toray with its photonitrosation (PNC) process, use hydroxylamine in its sulfate form, hence a large amount of ammonium sulfate is produced as a by-product through oximation and Beckmann rearrangement. As the profitability of caprolactam manufacturing strongly depends on the amount of ammonium sulfate, various processes to avoid this drawback have been investigated by many researchers.

Recently, Sumitomo Chemical Co. Ltd. developed the vapor phase Beckmann rearrangement process. In this process, cyclohexanone oxime is converted to caprolactam using a high silica MFI zeolite catalyst [2,3] instead of sulfuric acid. Montedipe SpA (now EniChem SpA) developed the ammoximation process which involves the direct reaction of cyclohexanone with ammonia and hydrogen peroxide on a TS-1 catalyst [4]. None of these processes produces any ammonium sulfate. The combined process of ammoximation and subsequent vapor phase Beckmann rearrangement produces only water as a by-product, as shown in Fig. 1. Therefore, the process can be expected

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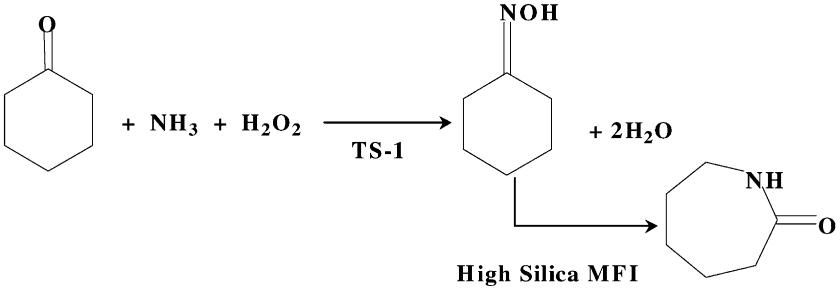


Fig. 1. The combined process between ammoximation and vapor phase Beckmann rearrangement.

to improve the current process to a more competitive and environmentally friendly one. The first combined process will be industrialized in the near future [5].

In this paper, we focus on some aspects of the vapor phase Beckmann rearrangement catalysis.

2. Experimental

The zeolite samples were synthesized in our laboratory as described in patents [2,3,6].

The vapor phase rearrangement reaction tests were carried out with fixed bed type micro-reactors. A mixture of cyclohexanone oxime and methanol and/or benzene was fed into the reactor (10 mm i.d., made of silica glass) with nitrogen as a carrier gas. The reaction product was collected under ice cooling and assayed by gas chromatography (Hewlett-Packard model HP 6890, and Shimadzu model 9A). The conversion of cyclohexanone oxime and the selectivity to caprolactam were calculated as follows: cyclohexanone oxime conversion (%) $= \{$(moles of cyclohexanone oxime charged − moles of unaltered cyclohexanone oxime)/(moles of cyclohexanone oxime charged)$\} \times 100$; selectivity to caprolactam (%) $= \{$(moles of caprolactam in product)/(moles of cyclohexanone oxime charged − moles of unaltered cyclohexanone oxime)$\} \times 100$.

A diffuse reflectance type FT-IR Spectrometer (NICOLET Magne 760-ESP) was used for IR spectra measurements. The catalyst was pretreated at 623 K for 1 h in helium atmosphere or in vacuo. Then, the spectrum was measured at the same temperature as that of pretreatment.

3. Results and discussion

3.1. *Influence of Si/Al ratio*

It is generally accepted that the Beckmann rearrangement of a ketoxime is performed by acids [7], and many attempts to find a high performance solid acid catalyst for the vapor phase Beckmann rearrangement have been done [8–11]. Sato et al. reported very interesting results for the catalyst [12]. They studied the vapor phase Beckmann rearrangement over some MFI zeolites with different Si/Al ratios (8–11,000). Upon experimental data as shown in Fig. 2, the conversion and selectivity are increased with increasing atomic ratio of Si/Al in MFI zeolites. Later, we observed a good performance with a very high silica MFI

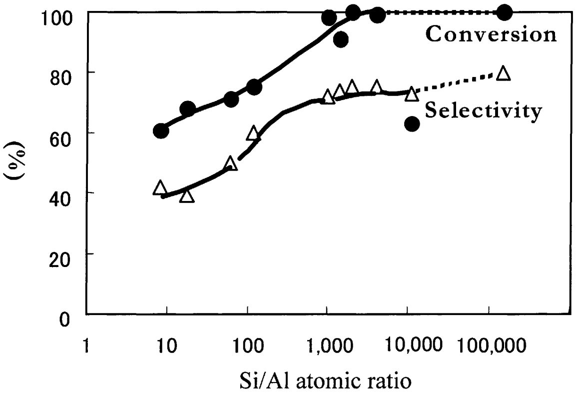


Fig. 2. Influence of Si/Al atomic ratio on: (●) conversion of cyclohexanone oxime, and (△) selectivity to caprolactam. Reaction conditions: cyclohexanone oxime (8 wt.%) in benzene solution, WHSV(oxime) $= 3\,h^{-1}$, temperature $= 623$ K [12].

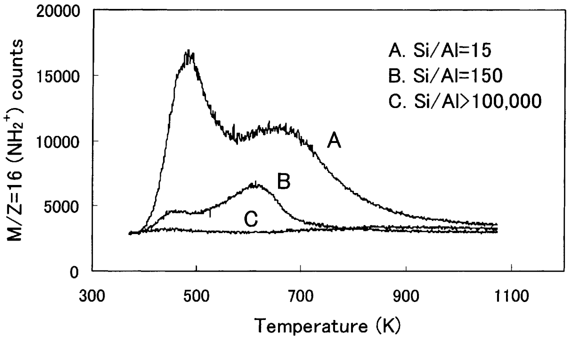


Fig. 3. NH_3 TPD spectra of MFI zeolites: (A) Si/Al = 15, (B) Si/Al = 150, (C) Si/Al > 100,000. Pretreatment: 623 K, 1 h, evacuation. NH_3 adsorption: 373 K, 13 kPa, 30 min.

zeolite; Si/Al atomic ratio = 147,000, in the same reaction conditions as in Fig. 2—conversion = 100%, selectivity = 79.6% [13]. These data are also included in Fig. 2.

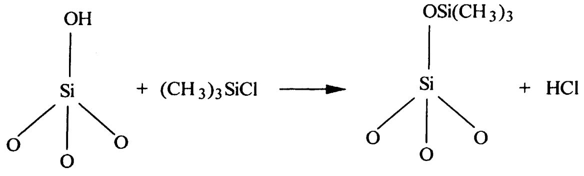
It is known that the acidity of MFI zeolite is a linear function of aluminum content, and no acidity is expected to exist in pure silica MFI zeolite that does not contain aluminum [14]. The ammonia TPD results of some MFI zeolites are shown in Fig. 3. The data clearly indicate that the high silica zeolite does not possess any acidity that can be detected by NH_3 TPD.

We want to emphasize that an extremely high silica MFI zeolite, which is expected to possess almost no acidity, gives very high conversion of oxime and good selectivity to caprolactam.

3.2. Effect of methanol addition into the reaction system

Various kinds of silanols exist in MFI zeolite, namely terminal, geminal, vicinal, and nests. Hölderich and co-workers [15–17] investigated the catalysis of vapor phase Beckmann rearrangement and suggested that the silanol nests were the most favorable sites for the Beckmann rearrangement, while terminal silanols were the least favorable.

Sato et al. [18] tried to modify the terminal silanols on the surface of a high silica MFI zeolite (the Si/Al atomic ratio is larger than 30,000) by treating it with chlorotrimethylsilane vapor, as shown in reaction (1).



(1)

They reported that the selectivity to caprolactam changed drastically from 85 to 95% by such a treatment. This result hints that the selectivity will be improved if the terminal silanols can be blocked in a suitable way.

A surprising result was obtained when methanol was fed over a high silica MFI zeolite catalyst (Si/Al > 100,000) into the reactor with cyclohexanone oxime. Namely, methanol highly enhances the selectivity to caprolactam as shown in Fig. 4. When methanol is not fed into the reactor, the selectivity to caprolactam is less than 80%. However, when a sufficient amount of methanol is in the reaction system, selectivities of around 95% could be achieved.

In order to reveal the cause of the effect of methanol addition, the FT-IR spectra of a catalyst treated with methanol and an untreated catalyst were measured with a diffuse reflectance type apparatus [19]. The data are shown in Fig. 5.

The non-treated catalyst (Fig. 5a) shows a sharp IR absorption at 3740 cm^{-1}, that is attributed to terminal silanols, and a broad IR absorption at around 3500 cm^{-1}, that is assigned to nest silanols [15]. However, this terminal silanol's absorption

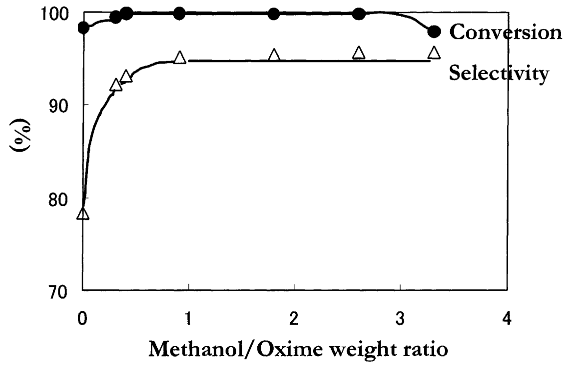


Fig. 4. Effect of methanol addition on: (●) conversion of cyclohexanone oxime and (△) selectivity to caprolactam. Catalyst: high silica MFI (Si/Al > 100,000), WHSV(oxime) = 8 h^{-1}, temperature = 643 K.

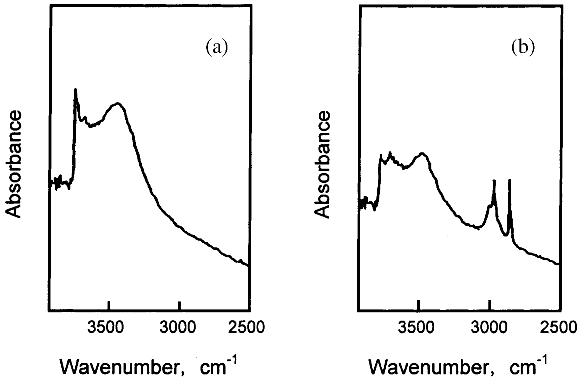
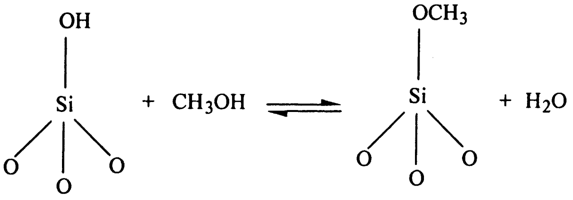


Fig. 5. FT-IR spectra of the catalyst, (a) not treated by methanol, (b) treated by methanol. Treatment by methanol vapor: 4 kPa, 623 K, 30 min, evacuation: 623 K, 1 h, [19].

disappeared in the methanol treated catalyst (Fig. 5b) and two new clear absorption bands were originated by methoxyl groups. The IR absorption bands in the region 2970–2850 $\mathrm{cm^{-1}}$ are attributed to the methyl CH asymmetric and symmetric stretching vibrational bands [20].

The data clearly show that methanol reacts with terminal silanol (3740 $\mathrm{cm^{-1}}$) on the crystal surface of high silica MFI zeolite (Si/Al = 147,000) and converts it to methylsilylether, according to the following reaction (2), at an elevated temperature.



(2)

We think that this modification of the zeolite is responsible for the high selectivity to caprolactam as in the case of chlorotrimethylsilane treatment. The nest silanols remain in the zeolite after methanol treatment. We support a theory that Heitmann et al. proposed recently [15], namely nest silanols are responsible for the Beckmann rearrangement reaction.

The reaction between methanol and terminal silanols is in equilibrium. Therefore, as far as methanol vapor exists in the reaction system, the modification guarantees the high selectivity to caprolactam.

In the Sumitomo Chemical's process, methanol is recovered and recycled without loss. Methanol can be expected to convert to dimethylether, because the dehydration reaction of an alcohol is a typical acid catalyzed reaction. However, we do not have any evidence of dimethylether formation during the Beckmann rearrangement reaction. This evidence strongly suggests that our catalysts possess only an extremely weak acidity.

3.3. Effect of ammonia addition into the reaction system

Interesting results were obtained when we fed ammonia into the reaction system [21]. Ammonia enhances the selectivity to caprolactam without affecting the conversion of cyclohexanone oxime. The data are shown in the Fig. 6. The experiments were conducted in the following way: a mixture of cyclohexanone oxime/methanol/ammonia/nitrogen (1/6.4/0.35/6.7 in mole ratio) was fed into the reactor with a space velocity of cyclohexanone oxime of 8 $\mathrm{h^{-1}}$ and a temperature of the catalyst bed of 623 K. After the reaction was allowed to proceed for 6.25 h, it was stopped and the catalyst was regenerated by treatment with a gas mixture comprising oxygen, methanol, and nitrogen at 703 K for 23 h. Then, the reaction of cyclohexanone oxime was carried out again. The complete cycle was repeated 30 times under the same conditions. When ammonia was not fed, nitrogen was introduced instead of ammonia.

When ammonia is added to the reaction system (Fig. 6a), the selectivity shows only a slight decrease; however, in the case without ammonia (Fig. 6b), the selectivity decreases with the number of repetitions. It is very important to keep the selectivity to caprolactam in a high level during the production. These results not only suggest that the catalysis is quite different from a usual acid catalyzed reaction, but also give a hint about how to maintain the selectivity on a high level. The mechanism of the phenomena has not yet been revealed.

3.4. Fluidized reaction system

During the vapor phase Beckmann rearrangement reaction, carbonaceous materials are deposited on the catalyst, which have to be eliminated by calcinations

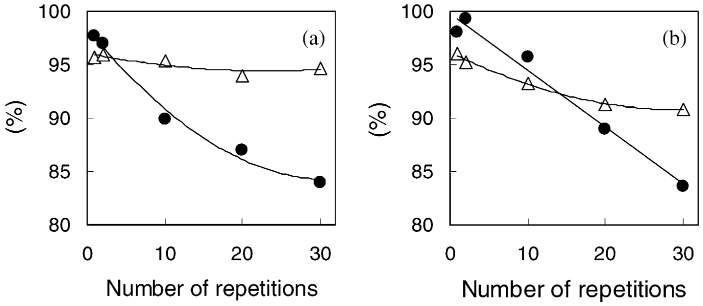


Fig. 6. Effect of ammonia addition into the reaction system: (a) ammonia added, (b) ammonia not added, (●) conversion of cyclohexanone oxime, (△) selectivity to caprolactam. Reaction temperature = 623 K, WHSV(oxime) = 8 h^{-1} [21].

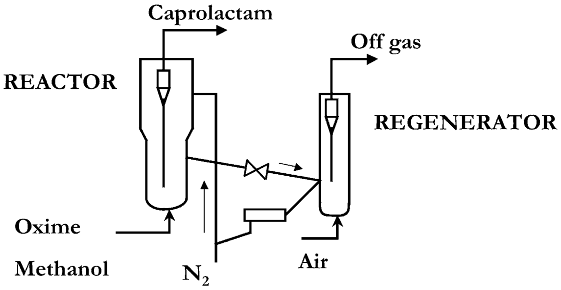


Fig. 7. Fluidized bed reaction system [23].

at an elevated temperature [22]. If the reaction is conducted in a fixed bed system, the reaction to produce caprolactam has to be interrupted for the catalyst regeneration. Hence, the fixed bed system is not effective for the continuous operation.

Our process adopts the fluidized bed reaction system [23]. The mixture of cyclohexanone oxime and methanol vapor is fed into a fluidized bed reactor, in which the catalyst is charged as shown in Fig. 7. Cyclohexanone oxime is converted to caprolactam in good yield and high efficiency. A part of the catalyst is transferred from the reactor to the regenerator and is reactivated. Then, the regenerated catalyst returns from the regenerator to the reactor. The catalyst circulates continuously through the reactor and the regenerator.

4. Conclusions

A catalyst to be used for the vapor phase Beckmann rearrangement process to manufacture caprolactam has been developed. The catalyst and the catalysis have the following characteristics.

1. The selectivity to caprolactam is improved when methanol is added into the reaction system. Methanol can be recycled.
2. An MFI zeolite which has a very high Si/Al atomic ratio can be used for the reaction, resulting in high conversion and good selectivity. Dimethylether is not produced from methanol.
3. Ammonia improves the catalyst performance. It helps to keep the selectivity on a high level through a long period in operation.
4. We conclude that the active sites of the catalyst are extremely weak acid sites, which cannot be detected by ammonia TPD measurements.

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