CHEMISTRY LETTERS, pp. 1765-1766, 1993.

Influences of Organic Bases on the Vapor Phase Beckmann Rearrangement Catalyzed by Pentasil-type Zeolite

Hiroshi SATO* and Ken-ichi HIROSE
Organic Synthesis Research Laboratory, Sumitomo Chemical Co., Ltd.
Tsukahara, Takatsuki, Osaka 569

The influences of organic bases on the vapor phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam catalyzed by pentasil zeolite were examined. Almost no influence was observed with amines, and furthermore, even the excess amount of n-Pr_3N (utilized as a solvent for oxime) did not inhibit the reaction greatly. These results indicate that the active site is not the acidic one as generally considered but the neutral silanol group.

In the preceding papers,[1,2] we reported that, in the vapor phase Beckmann rearrangement of cyclohexanone oxime, both high lactam selectivity and long catalytic life (that is, low deactivation by coking) were obtained over high silicious ($Si/Al \geqq 500$) pentasil zeolite having a large external surface area. And we made a new proposal that the active site for this rearrrangement reaction is not the acidic site as generally considered,[3,4] but the neutral silanol on the external surface of zeolite.

In this paper, the influences of organic bases on the rearrangement reaction were investigated from the following viewpoints; 1)To distinguish whether the acidic site contributes to the rearrangement reaction or not. 2)To improve the lactam selectvity by promoting the desoption of produced ε-caprolactam through competetive adsorption of organic bases.

Three kinds of pentasil zeolite with different Si/Al atomic ratios were used as a catalyst. The physical properties of them are listed in Table 1, and the influences of organic bases on them are shown in Table 2.

Although the attempt to improve the selectivity was in vain, almost no influence was observed by co-feeding of pyridine (Py), 4-methylquinoline (4MQ) and R_3N (R=Et, n-Pr, n-Bu). Furthermore, co-feeding of the excess amount of n-Pr_3N (utilized as solvent) did not inhibit the rearrangement reaction greatly (Run No. 11). Considering that the basisity of amines and pyridines are stronger than oxime, the above data strongly support our estimation that the active site for this rearrangement reaction over high-silicious pentasil zeolite is not the acidic one, but the neutral one.

Table 1. Physical properties of pentasil zeolite catalysts

Catalyst	Si/Al	Acidity a) (μmol/g)	Surface area (m^2/g) Total	 External b)	Hydrothermal Synthesis
Z-1	105	138	358	22	A c)
Z-2	1550	13	299	20	B d)
Z-3	147000	≒ 0	364	20	B d)

a) Amount of pyridine adsorbed at 350 ℃ in GC pulse adsorption method.
b) BET value of uncalcined zeolite containing template, $n\text{-}Pr_4N^+$.5)
c) silicone source; sodium silicate, template; $n\text{-}Pr_4NBr$.6)
d) silicone source; $(EtO)_4Si$, template; $n\text{-}Pr_4NOH$.2)

Table 2. Influences of organic bases on the Beckmann rearrangement a)

Run No.	Catal.	Si/Al	Bases	Amount b)	Oxime conv./% c)	Lactam sel./%
1	Z-1	105	—	—	49.5	54.0
2	〃	〃	Py	0.5	38.7	68.4
3	Z-2	1550	—	—	96.0	81.7
4	〃	〃	Py	0.5	94.5	80.7
5	〃	〃	4MQ	0.5	96.9	78.6
6	〃	〃	Et_3N	0.1	89.2	81.5
7	〃	〃	$n\text{-}Pr_3N$	0.1	94.3	81.9
8	〃	〃	$n\text{-}Bu_3N$	0.1	91.1	84.2
9	Z-3	147000	—	—	99.3	80.5
10	〃	〃	$n\text{-}Pr_3N$	0.1	96.9	82.0
11	〃	〃	$n\text{-}Pr_3N$	9.1 d)	91.1	76.1

a) W/F=37g-cat/mol-oxime.h., Temp=350 ℃, Oxime= 8% in benzene. b) Molar ratio to oxime. c) after 5 hour's run. d) oxime= 8% in $n\text{-}Pr_3N$ solvent.

References

1) H. Sato, N. Ishii, K. Hirose, and S. Nakamura, Proceed. of 7th Intern. Zeolite Conf. (1986) p. 755.
2) H. Sato, K. Hirose, and M. Kitamura, Nippon Kagaku Kaishi, 1989, 548.
3) Y. Murakami, Y. Saeki, and K. Ito, Nippon Kagaku Kaishi, 1978, 21.
4) S. Sato, K. Urabe, and Y. Izumi, J. Catal, 102, 99 (1986).
5) H. Sato, A. Sakamoto, K. Hirose, and K. Chikaishi, Chem. Lett., 1989, 1695.
6) T. Yashima, Syokubai (Catalyst), 23 (5), 232 (1981).

(Received July 9, 1993)