Vapour phase Beckmann rearrangement of cyclohexanone oxime over MEL type zeolites

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The vapour phase Beckmann rearrangement of cyclohexanone oxime to ϵ-caprolactam is reported over different MEL zeolites viz., silicalite-2, titanium silicate-2 (TS-2), ZSM-11 and alumino-titanium-silicate (Al-TS-2) and fumed silica. TS-2 exhibits 100% conversions with lactam selectivities close to 90%. The titanium containing analogs are also more resistant to deactivation than the parent zeolites. The conversion of cyclohexanone oxime and selectivity for ϵ-caprolactam increase with temperature. The selectivity for ϵ-caprolactam increases with the duration of run at all the temperatures.

Keywords: Beckmann rearrangement; cyclohexanone oxime; ϵ-caprolactam; titanium silicate; TS-2; silicalite-2; MEL

1. Introduction

The Beckmann rearrangement of cyclohexanone oxime to ϵ-caprolactam (precursor to Nylon-6) is an important industrial process. This reaction is now being carried out using concentrated sulphuric acid [1] and is associated with disadvantages like the co-production of 2–3 tons of low-value ammonium sulfate per ton of ϵ-caprolactam and safety hazards, corrosion and environmental problems arising from the use of sulfuric acid.

A number of solid acid catalysts [2] including heteropoly acids [3], silica–aluminia [4] and zeolites like X, Y [5–8], ZSM-5 [7,9] and morderite [5,9] have been tried for this reaction. Sato et al. [10,11] have reported that the Beckmann rearrangement takes place on the external surface of MFI (ZSM-5) zeolites. They found that the active sites for this reaction are the weaker or neutral centers present on the external surface of the crystallites. We now report the Beckmann rearrangement of cyclohexanone oxime over different MEL zeolites viz., silicalite-2, titanium silicate-2 (TS-2), aluminosilicate (ZSM-11) and alumino-titanium-silicate (Al-TS-2). The use of MEL zeolites in this reaction has not been reported so far.

2. Experimental

Silicalite-2 [12], TS-2 [13], ZSM-11 [14] and Al-TS-2 [15] were synthesized as per published procedures. Fumed silica (type S-5005) was obtained from Sigma Chemicals, Mo, USA. All the zeolites are pure analogs of ZSM-11 (MEL) without any MFI impurities (XRD data). The zeolites were calcined at 823 K for 16 h in dry air and exchanged twice with 1 N ammonium acetate and further calcined at 750 K for 10 h to get the catalytically active hydrogen form. The crystallinities of the zeolites were greater than 90%. The physicochemical properties of the zeolites are presented in table 1. Silicalite-2 was prepared in two different crystal sizes by changing the template concentration. Confirmation for the presence of Ti in the lattice of TS-2 and Al-TS-2 samples was obtained from increase in the unit cell dimensions of silicalite-2 and ZSM-11, respectively and the presence of a new IR absorption band at 960 cm^{-1} [16]. Further confirmation for the presence of Ti in the lattice was obtained from a band at 970 cm^{-1} in the Raman spectral region [17,18] and a band at 212 nm in the UV region [19]. Again, the absence of significant amount of bulk TiO_2 in the samples was inferred from the absence of bands characteristic of anatase at 140 cm^{-1} and 330 nm in the Raman and UV regions [16,18,19], respectively. Cyclohexanone oxime was prepared from conventional procedures [20]. Its purity was found to be > 99 wt% by GC analysis.

The catalytic reactions were carried out in a downflow, vertical, tubular, silica reactor (8 mm i.d.) at atmospheric pressure. In a typical experiment 1 g of the catalyst (1–2 mm particle size) was loaded in the reactor. The feed (6 wt% cyclohexanone oxime in benzene) was injected using a syringe pump (Sage Instruments, USA). Nitrogen was passed as a carrier gas. The reactions were

Table 1
Physicochemical properties of the catalysts

Catalyst	Surface area [a] (m^2/g)		Si/M ratio [b]	Average crystallite size [c] (μm)
	total	macro		
SiO_2	(400 ± 20) [d]		–	–
silicalite-2(L)	430	2	> 3000	≈ 3
silicalite-2(S)	440	17	> 3000	≈ 0.5
ZSM-11	420	20	37	≈ 1
Al-TS-2	455	25	(92; 30)	≈ 1
TS-2	460	8	29	≈ 1

[a] Obtained by argon-adsorption from BET equation (Omnisorp CX100, Coulter Corp., USA). Macro pore area obtained from *t*-plot (includes external area of crystallites and amorphous matter, if any).

[b] M = Al, Ti, (Al; Ti).

[c] By SEM.

[d] Manufacturer's data.

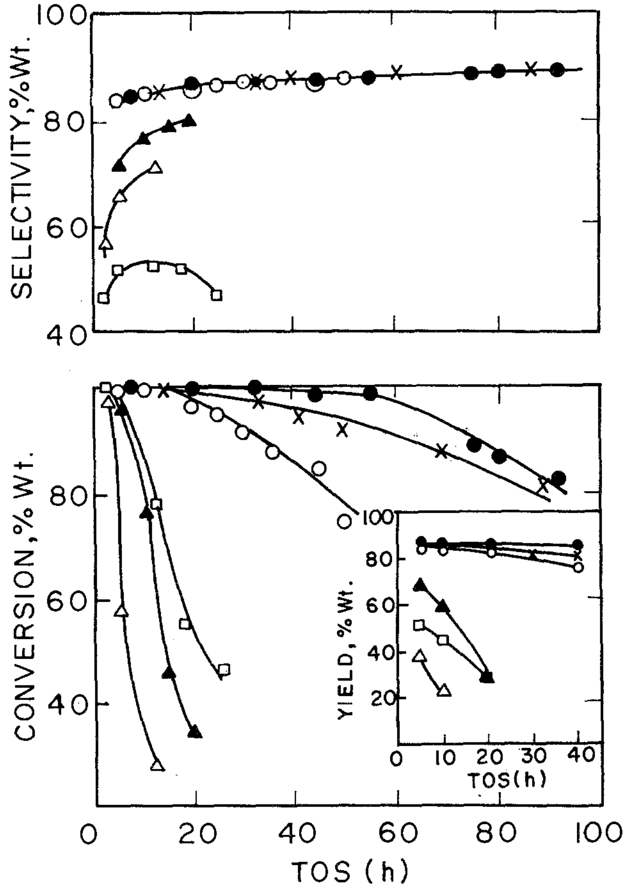

Fig. 1. Influence of time on stream on conversion and selectivity over various MEL-analogs and fumed silica. (△) ZSM-11; (▲) Al-TS-2; (□) fumed silica; (○) silicalite-2(L); (×) silicalite-2(S); (●) TS-2. Conditions: temp. (K) = 613; press. = 1 atm.; WHSV (h^{-1}) = 7; oxime concentration in feed = 6 wt% in benzene; N_2 flow rate = 5 ml min^{-1}.

carried out at different temperatures between 543 and 643 K. The products collected at different time intervals were analyzed in a gas chromatograph (Hewlett–Packard 5880 A) equipped with a capillary column (50 m × 0.25 mm cross linked methyl silicone gum). The liquid product recovery was > 90% in all cases.

3. Results and discussion

The results obtained over different catalysts viz., silicalite-2, TS-2 ZSM-11, Al-TS-2 and silica are reported in fig. 1. The major product obtained is ε-caprolactam. By-products formed are cyclohexanone, cyclohexenone,

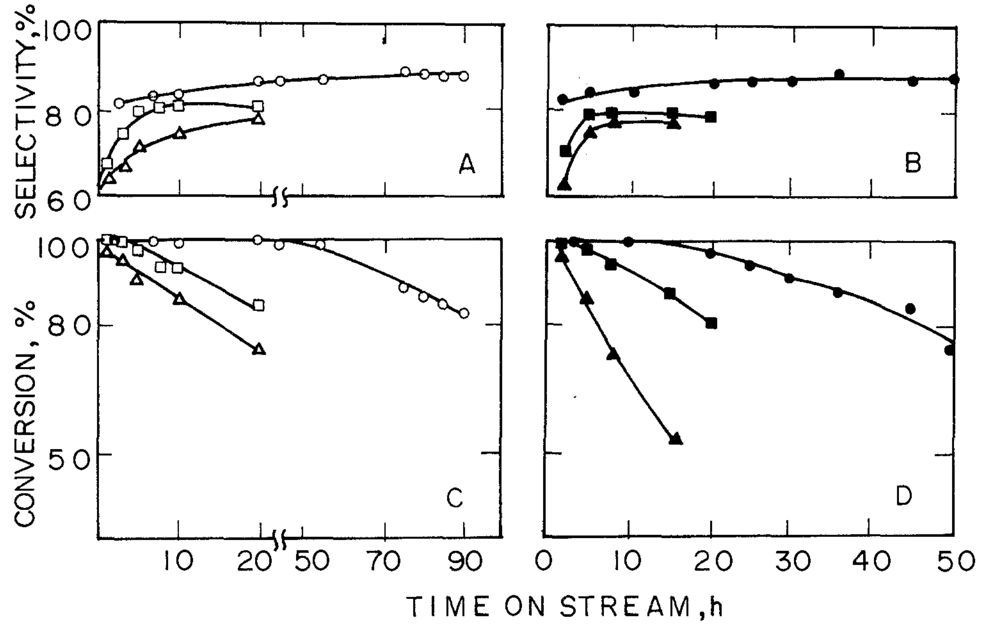

Fig. 2. Influence of temperature on conversion and selectivity over silicalite-2 and TS-2. (A,C) TS-2; (B,D) silicalite-2. (△, ▲) 543 K; (□, ■) 573 K; (○, ●) 613 K. Conditions: press = 1 atm.; WHSV (h^{-1}) = 7; oxime concentration in feed = 6 wt% in benzene; N_2 flow rate = 5 ml min^{-1}.

cyanopentane and cyanopentene, the major by-product being cyclohexanone. The catalysts can be arranged in the following decreasing orders for the conversion of cyclohexanone oxime, selectivity for ε-caprolactam and deactivation rate:

activity: TS-2 > silicalite-2 > SiO_2 > Al-TS-2 > ZSM-11
selectivity: TS-2 $\approx$ silicalite-2 > Al-TS-2 > ZSM-11 > SiO_2
deactivation rate: TS-2 < silicalite-2 < SiO_2 < Al-TS-2 < ZSM-11.

In accordance with earlier reports [10] over MFI zeolites, the presence of Al^{3+} in the MEL framework decreases the activity as well as the selectivity. However, the incorporation of Ti into the framework improves the life of the catalyst without significantly affecting the selectivity of the catalyst. Al-TS-2, where Al^{3+} and Ti^{4+} are substituted into the MEL framework has conversion and selectivity between that of silicalite-2 and ZSM-11. The inset in fig. 1 presents the yield (conversion × selectivity/100) of the lactam obtained over the different catalysts at different times on stream. Though similar yields of lactam are obtained over TS-2 and silicalite-2 upto about 20 h, there is a yield loss in the case of silicalite-2 beyond this time. The loss in yield is a result of a decrease in conversion and not selectivity. It is observed that the small particle silicalite (silicalite-2(S); $\approx$ 0.5 μm) deactivates at a slower rate than the large particle version, its deactivation still being more than that of TS-2 with a larger particle size (≈ 1 μm). Apparently, the incorporation of Ti decreases catalyst deactivation. As expected, the incorporation of Al^{3+} in both silicalite-2 and TS-2 decreases both conversion and selectivity of both catalysts. Even amorphous SiO_2 yields more lactam than the aluminosilicate, ZSM-11.

The influence of temperature on the conversion of cyclohexanone oxime and selectivity for ϵ-caprolactam over TS-2 and silicalite-2 is presented in fig. 2. The studies were carried out in the temperature range 543–613 K. Higher conversions and selectivities are obtained at higher temperatures over both the catalysts. The selectivity for lactam increased with time on stream at all the temperatures in the range studied (543–613 K). The increase in selectivity with time may be because of the deactivation of strong acid sites, by coke deposition, which cause the formation of by-products. TS-2 is more resistant towards deactivation at all the temperatures vis-á-vis silicalite-2, though both exhibit similar selectivities for lactam formation.

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References

[1] J.E. Kent and S. Riegel, *Handbook of Industrial Chemistry*, 8th Ed. (Van Nostrand, New York, 1983) p. 402.

[2] O. Immel, H.H. Schwarz, K. Starke and W. Swodenk, Chem. Eng. Technol. 56 (1984) 612.

[3] D.C. England, US Patent 2,634,269 (1953).

[4] P.B. Venuto and P.S. Landis, Adv. Catal. 18 (1968) 259.

[5] P.S. Landis and P.B. Venuto, J. Catal. 6 (1966) 245.

[6] W. Hölderich, M. Messe and F. Näumann, Angew. Chem. Int. Ed. 27 (1986) 187.

[7] A. Corma, H. Garcia, J. Primo and E. Sastre, Zeolites 11 (1991) 593.

[8] A. Aucejo, M. Burguet, A. Corma and V. Fornes, Appl. Catal. 22 (1986) 187.

[9] W.K. Bell and C.D. Chang, EP 056,698 (1985).

[10] H. Sato, N. Ishii, K. Hirose and S. Nakamura, Stud. Surf. Sci. Catal. 28 (1986) 755.

[11] H. Sato, K. Hirose, N. Ishii and Y. Yamada, EP 234,088 (1987).

[12] D.M. Bibby, N.B. Milestone and L.P. Aldridge, Nature 280 (1979) 664.

[13] J.S. Reddy, R. Kumar and P. Ratnasamy, Appl. Catal. 58 (1990) L1.

[14] G.T. Kokatailo, P. Chu, S.L. Lawton and W.M. Meier, Nature 275 (1978) 119.

[15] J.S. Reddy and R. Kumar, in: *Recent Developments in Catalysis: Theory and Practice*, eds. B. Viswanathan and C.N. Pillai (Narosa, New Delhi, 1990) p. 156.

[16] J.S. Reddy, Thesis, University of Poona, India (1992).

[17] M.R. Boccuti, K.M. Rao, A. Zecchina, G. Leofonti and G. Petrini, Stud. Surf. Sci. Catal. 48 (1989) 133.

[18] A. Zecchina, G. Spoto, S. Bordiga, M. Padovan, G. Leofonti and G. Petrini, Stud. Surf. Sci. Catal. 65 (1991) 671.

[19] A. Zecchina, G. Spoto, S. Bordiga, A. Ferrero, G. Petrini, G. Leofonti and M. Padovan, Stud. Surf. Sci. Catal. 69 (1991) 251.

[20] I. Vogel, *A Text Book of Practical Organic Chemistry*, 3rd Ed. (ELBS/Longmann, London, 1971) p. 343.