Beckmann rearrangement of cyclohexanone oxime over mesoporous Si-MCM-41 and Al-MCM-41 molecular sieves

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Abstract

Si-MCM-41 and Al-MCM-41 with different Al contents (Si/Al = 43.9, 23.3 and 14.3) have been prepared using cetyl trimethylammonium bromide as an organic surfactant and characterised by XRD, MAS NMR and N_2 sorption studies. The transformation of cyclohexanone oxime into ε-caprolactam has been studied over these molecular sieves. The influences of temperature and feed rate (WHSV) on the yield of caprolactam over the samples have been investigated at different times on stream. The studies reveal that activity and selectivity increase with Al content (investigated upto Si/Al = 14) and maximum yield of ε-caprolactam is obtained at ∼360 °C. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Beckmann rearrangement; Caprolactam; Cyclohexanone oxime; MCM-41; Mesoporous materials

1. Introduction

Liquid phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam, which is the monomer of Nylon-6, is carried out industrially using concentrated sulphuric acid as the catalyst. Although the process is highly selective, it has several disadvantages such as the production of large amounts of low value ammonium sulphate and corrosion and environmental pollution caused by the use of fuming sulphuric acid. To overcome these problems, many research groups have attempted to carry out vapour phase Beckmann rearrangement using solid acid catalysts like silica–alumina [1], zeolite Y [2,3], mordenite [2,4], ZSM-5 [5], TS-1 [6], ZSM-11 and TS-2 [7].

It has been suggested that the strong Brönsted acidity of the zeolite catalyst enhances the formation of ε-caprolactam [3]. However, a majority of researchers have noticed that acid sites of weak or intermediate strength or even neutral silanol groups present on the external surface of the zeolites are effective for this rearrangement [8–11] and strong acid sites accelerate the formation of by-products [12,13]. It is well known that the mesoporous material MCM-41 possessing a hexagonal array of pores [14], has a large amount of surface SiOH groups and its acidity is considerably weak [15,16]. Considering this characteristic property of the structure of mesoporous molecules, Dai et al. [17] have studied the Beckmann rearrangement of cyclohexanone oxime over H-Al-MCM-41 with a Si/Al ratio of 19. In the present work, we report the conversion of cyclohexanone oxime to ε-caprolactam on Si-MCM-41 and H-Al-MCM-41 with different Si/Al ratios in the range 14–44.

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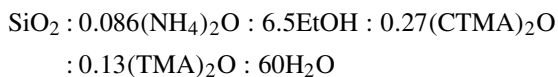*E-mail address:* siva@cata.ncl.res.in (S. Sivasanker).

2. Experimental methods
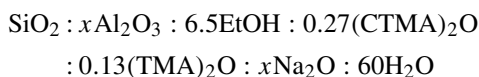
2.1. Preparation of catalysts

2.1.1. Synthesis of catalysts

Si-MCM-41 and Al-MCM-41 with different Si/Al ratios were synthesised as per published procedures [18]. The molar compositions of the synthesis gels in terms of oxides were as follows.

Si-MCM-41:

$$SiO_2 : 0.086(NH_4)_2O : 6.5EtOH : 0.27(CTMA)_2O$$
$$: 0.13(TMA)_2O : 60H_2O$$

Al-MCM-41:

$$SiO_2 : x Al_2O_3 : 6.5EtOH : 0.27(CTMA)_2O$$
$$: 0.13(TMA)_2O : x Na_2O : 60H_2O$$

where $x \leq 0.04$.

Four samples with different Si/Al input ratios of 100, 50, 25 and 12.5 and an Al free sample were synthesised. All the samples were calcined at 550 °C in nitrogen for 1 h and then in air for 6 h. The calcined samples were converted into the catalytically active H-forms by cation exchanging with ammonium nitrate thrice (20 ml of 1 M solution/g of the molecular sieve at 95 °C for 5 h), dried at room temperature and then calcined at 400 °C for 6 h.

2.2. Characterisation

Crystalline phase identification and phase purity of the as-synthesised and calcined samples were carried out by XRD (Philips, Holland) using nickel filtered Cu Kα radiation ($\lambda = 1.5406$ Å). The surface areas and pore diameters were determined from N_2 adsorption isotherms using a Coulter (Omnisorp 100 CX) instrument. ^{27}Al MAS NMR spectra of the samples were recorded on a Bruker MSL 300 NMR spectrometer. Temperature programmed desorption of pyridine was studied on H-Al-MCM-41 samples under chromatographic conditions.

2.3. Reaction procedure

The catalytic reactions were carried out in a down flow fixed bed tubular glass reactor (i.d. = 15 mm and 30 cm length) at atmospheric pressure using 2 g of the catalyst. The catalyst was compacted in a hydraulic press, the pellets were broken and then sieved to 16–20 mesh size prior to use. The reactor was placed inside a temperature controlled vertical furnace (Geomécanique, France). The thermocouple tip was centred at the middle of the catalyst bed. A solution of cyclohexanone oxime (20 wt.%) in acetonitrile was fed using a syringe pump. The weight hourly space velocity (WHSV) values have been calculated based on the oxime solution injected. The inert gas (nitrogen gas, 20 ml/min) was introduced using a mass flow controller. Cyclohexanone oxime used was 99% pure (Aldrich, USA). The catalyst was dried in situ in a flow of N_2 (20 ml/min) at 450 °C for 6 h, cooled to reaction temperature prior to start of run. The reaction products were collected in a receiver after cooling with ice cold water and analysed using a Hewlett-Packard gas chromatograph (5880A) with a capillary column (cross-linked methyl silicone gum, HP1, 50 m × 0.2 mm i.d.) and a flame ionisation detector (FID). The product identification was done by GCIR, GCMS and NMR.

3. Results and discussion

3.1. Characterisation

The XRD patterns of the calcined Al-MCM-41 samples with different Si/Al ratios were similar to those reported for MCM-41 materials [14]. Kresge and coworkers [14,19] indexed these peaks for a hexagonal unit cell, the parameter of which was calculated from the equation $a_0 = 2d_{100}/\sqrt{3}$. The unit cell parameter and d-spacing of the Al-MCM-41 samples and Si-MCM-41-B are given in Table 1. On calcination of the samples, the peak is shifted to lower d_{100}-spacing value due to condensation of internal Si–OH groups giving rise to a contraction of the unit cell. The slight increase in d-spacing and unit cell parameters of Al-MCM-41 compared to its pure silica analog (Table 1) suggests the presence of aluminium in the framework.

Chemical analyses of Al-MCM-41 samples obtained from XRF are presented in Table 1. The Si/Al ratios of the samples were 43.9 (sample A), 23.3 (sample B) and 14.3 (sample C). The BET surface areas and pore volumes of the Al containing samples

Table 1
Physicochemical properties of MCM-41 samples

Sample	Si/Al ratio			d_{100}-spacing	Surface area (m^2/g)	Pore volume (ml/g)	Pore diameter (Å)	Acidity (mmole/g)[a]
	Input in gel	Calcined sample	As-synthesised sample	Calcined sample				
Si-MCM-41-B	–	–	36.40	33.00	990	0.60	23	–
Al-MCM-41(A)	50	43.9	37.72	34.48	1025	0.76	24	0.060
Al-MCM-41(B)	25	23.3	38.72	35.39	1072	0.79	25	0.098
Al-MCM-41(C)	12.5	14.3	39.76	36.48	1098	0.82	26	0.152

[a] Pyridine desorbed beyond 100 °C.

are presented in Table 1. The N_2 adsorption isotherms of Si-MCM-41 and Al-MCM-41 samples showed type IV pattern with three stages: monolayer adsorption of nitrogen on the walls of mesopores ($P/P_0 < 0.2$), the part characterised by a steep increase in adsorption due to capillary condensation in mesopores with hysteresis ($P/P_0 = 0.15–0.3$), and multilayer adsorption on the outer surface of the particles. The pore diameters increase with increasing Al content of the samples (Table 1).

Acidity of the H-Al-MCM-41 samples was characterised by the TPD of pyridine. The acid strengths appear to be rather moderate as nearly all the pyridine desorbed below 300 °C. The acidities (mmol/g) based on the pyridine desorbed by the samples beyond 100 °C are presented in Table 1. As the aluminium content increases, the total acidity increases in the samples (Al-MCM-41(A) < Al-MCM-41(B) < Al-MCM-41(C)).

3.2. Beckmann rearrangement

Table 2 presents the product distribution over different catalysts with acetonitrile as the solvent. The major product was ε-caprolactam. The conversion of cyclohexanone oxime (ranging between about 70 and 100%) remained nearly constant (±2%) with time on stream (TOS) up to 5 h over all the catalysts at all the temperatures studied (300–390 °C). However, the selectivity to ε-caprolactam gradually increased with TOS and reached a maximum at about 3 h. The variations in selectivity as a function of duration of run over the different catalysts are presented in Fig. 1. Hence, data were collected at a TOS of 3 h during further studies. The initial increase in selectivity is probably due to deactivation of the strong acid sites.

3.2.1. Influence of temperature

The effect of temperature on selectivity to ε-caprolactam over different catalysts is presented in Fig. 2. The rearrangement was studied in the temperature range 300–390 °C. The transformation of the oxime was rapid over the catalysts and reached nearly 100% at temperatures >350 °C over all the catalysts (Fig. 2). The selectivity for ε-caprolactam increased upto 360 °C and decreased at higher temperatures. At 360 °C, the lactam yield on the catalyst with Si/Al ~ 14 was ~87%. The decrease in selectivity at

Table 2
Product distribution in Beckmann rearrangement over MCM-41[a]

Catalyst	Conversion (wt.%)	Selectivity (wt.%)				
		Caprolactam	Cyanopentane	5-Cyanopentene	Cyclohexenone	Cyclo-hexanone
Si-MCM-41	>99.0	32.4	–	6.8	36.4	24.4
Al-MCM-41(A)	>99.0	48.3	11.1	–	16.6	24.0
Al-MCM-41(B)	>99.0	65.6	8.4	–	12.3	13.6
Al-MCM-41(C)	>99.0	87.6	3.8	–	4.3	4.3

[a] Reaction conditions: temperature = 360 °C; WHSV = 1.88 h^{-1}; TOS = 3 h; cyclohexanone oxime:acetonitrile = 1:5 (wt.%); N_2 = 20 ml/min.
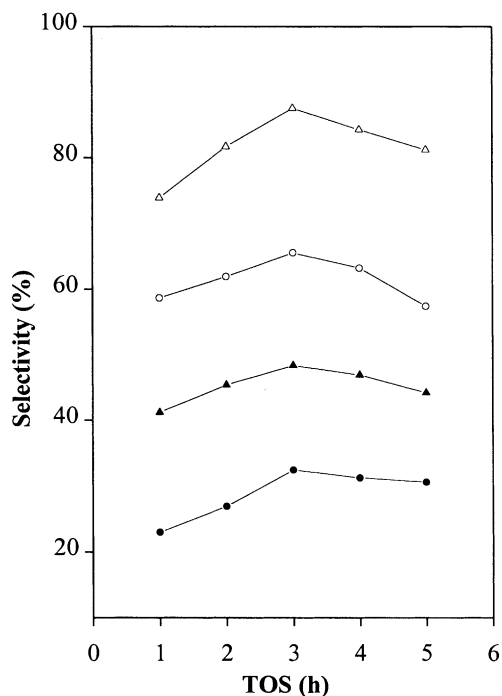
Fig. 1. Effect of time on stream (TOS) on selectivity for caprolactam. Conditions: temperature = 360 °C; WHSV = 1.88 h^{-1}; cyclohexanone oxime:acetonitrile = 1:5 (wt.%); N$_2$ = 20 ml/min ((●) Si-MCM-41; (▲) H-Al-MCM-41(44); (○) H-Al-MCM-41(23); (△) H-Al-MCM-41(14)).

Fig. 2. Effect of temperature on conversion of cyclohexanone oxime and selectivity for caprolactam. Conditions: TOS = 3 h; WHSV = 1.88 h^{-1}; cyclohexanone oxime:acetonitrile = 1:5 (wt.%); N$_2$ = 20 ml/min ((●) Si-MCM-41; (▲) H-Al-MCM-41(44); (○) H-Al-MCM-41(23); (△) H-Al-MCM-41(14)).

higher temperatures is probably due to the decomposition of the ε-caprolactam on the catalyst surface and increase in the side reactions [10]. The product break up at different temperatures over two typical catalysts Al-MCM-41(14) and Si-MCM-41 are presented in Fig. 3. The yield of the by-products decreases with temperature with a concomitant increase in caprolactam production upto about 360 °C, beyond which they increase again. At higher temperatures, additional by-products are formed due to decomposition of caprolactam. The yields of cyclohexanone and cyclohexenone are very high over Si-MCM-41. As these are hydrolysis products, it appears that surface Si–OH groups in Si-MCM-41 catalyse this reaction.

3.2.2. Influence of space velocity

The influence of contact time on conversion and caprolactam selectivity at 360 °C is presented in Fig. 4(a) and (b), respectively. Increasing the con-
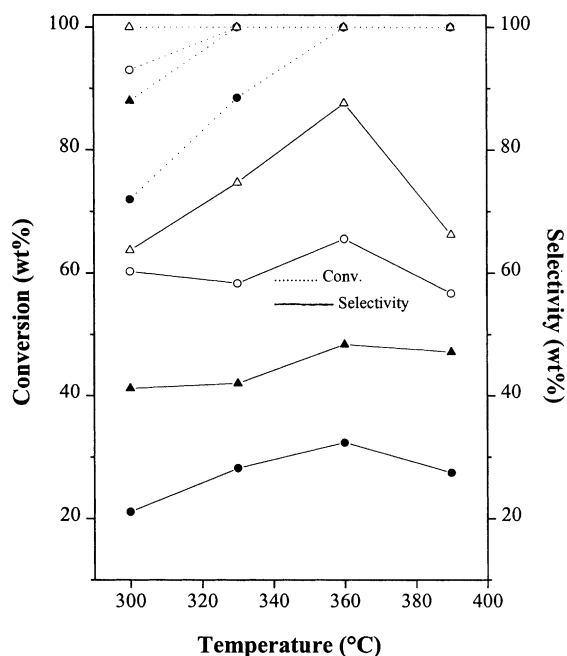
tact time increases conversion over the catalysts (Fig. 4(a)). In the case of Al-MCM-41(C), conversion increases to nearly 100%, even at the lowest contact time investigated; the selectivity for caprolactam goes through a maximum at an intermediate contact time (∼0.5 h). The product distribution at different contact times over the Si-MCM-41 and Al-MCM-41(C) are presented in Fig. 5. It is noticed that the yield of caprolactam increases rapidly with contact time while the by-products decrease upto a contact time of about 0.5 h. At higher contact times, the caprolactam yield decreases. A rapid increase in yield of cyclohexanone and cyclohexenone is also noticed beyond 0.5 h in the case of Al-MCM-41(C).

3.2.3. Influence of Si/Al ratio

The effect of Al content in the H-Al-MCM-41 samples was investigated over the catalysts having different Si/Al ratios (Si/Al of 44, 23 and 14). The selectivity
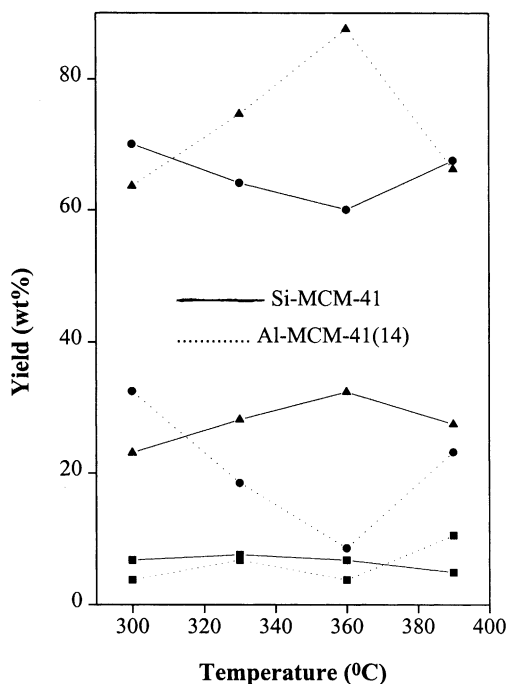
Fig. 3. Break up of products at different temperatures. Conditions: WHSV = 1.88 h^{-1}; cyclohexanone oxime: acetonitrile = 1:5 (wt.%); TOS = 3 h; N$_2$ = 20 ml/min (($\blacksquare$) cyanopentane + 5-cyanopentene; ($\bullet$) cyclohexanone + cyclohexenone; and ($\blacktriangle$) caprolactam).

for ε-caprolactam is more over the Al-MCM-41 samples than over Si-MCM-41. It increases with increase in Al content. The highest yield of ε-caprolactam of 87.6% is obtained over the sample with a Si/Al ~ 14. It is observed that by-products decrease with increasing Al content in the catalysts (Table 2). Apparently, the silanol groups present on Si-MCM-41 are not sufficiently acidic to catalyse the rearrangement though they are able to catalyse the formation of the by-products. More hydrolysis products are obtained over Si-MCM-41 probably due to the reaction of the surface –OH groups with the oxime. This observation is different from that of earlier workers who observed an increase in selectivity with decreasing Al content [6] in the case of MFI type materials. This difference is probably due to the different strengths of the acid sites in the two systems (MFI and MCM-41) and the relatively small amounts of –OH groups in MFI.
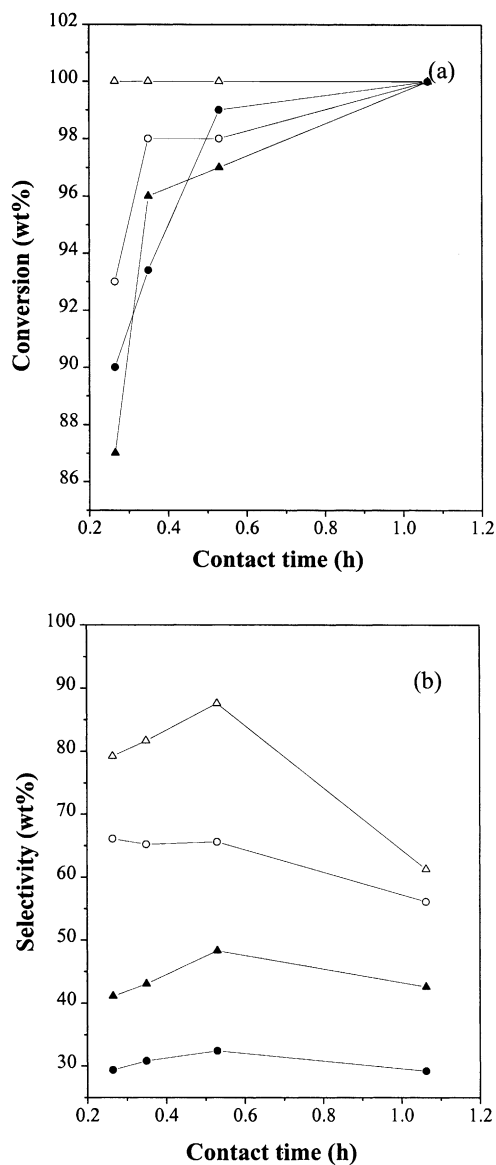

Fig. 4. Effect of contact time on (a) conversion and (b) selectivity. Conditions: temperature = 360 °C; cyclohexanone oxime:acetonitrile = 1:5 (wt.%); TOS = 3 h; N$_2$ = 20 ml/min (($\bullet$) Si-MCM-41; ($\blacktriangle$) H-Al-MCM-41(44); ($\bigcirc$) H-Al-MCM-41(23); and ($\triangle$) H-Al-MCM-41(14)).

In the case of H-FSM mesoporous materials, Dai et al. [17] have earlier reported an increase in selectivity with increase in Al content as reported by us for Al-MCM-41 catalysts. In their studies, Dai et al. [17] have also investigated MCM-41 with a Si/Al
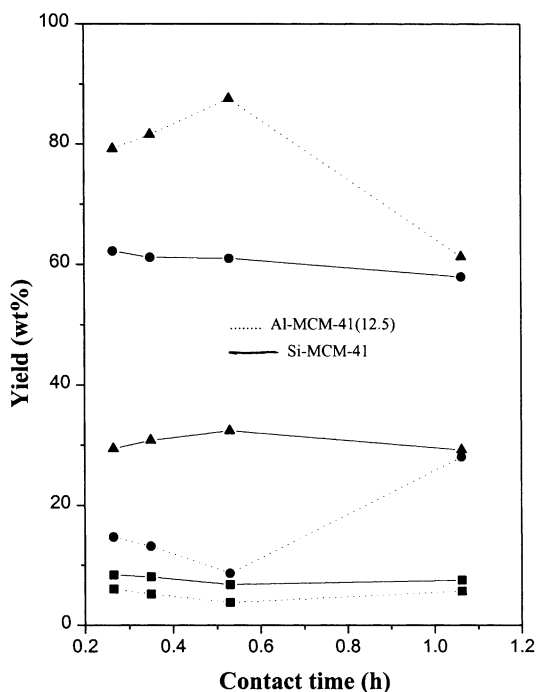
Fig. 5. Effect of contact time on product distribution. Conditions: temperature = 360 °C; cyclohexanone oxime: acetonitrile = 1:5 (wt.%); TOS = 3 h; N_2 = 20 ml/min ((■) cyanopentane + 5-cyanopentene; (●) cyclohexanone + cyclohexenone; and (▲) caprolactam).

ratio of 19 for the rearrangement of cyclohexanone oxime. They have reported a higher selectivity (92% using 1-hexanol as the solvent at 350 °C) than us (87.6% over Al-MCM-41(C) (Si/Al ~ 14) using acetonitrile as the solvent at 360 °C) at a similar conversion (~100%). The higher selectivity obtained by Dai et al. [17] with 1-hexanol is probably due to the attenuation of strong acidity by the water formed during the dehydration of the solvent, 1-hexanol.

The above studies reveal that formation of caprolactam (rearrangement) is mainly favoured over moderate acid centres present on Al-MCM-41. The large yields of the deaminated product cyclohexenone over Si-MCM-41 suggest that it is formed more over the neutral surface silanol groups. Similarly, the formation of cyclohexanone (hydrolysis product) is also favoured over SiOH groups. C–C bond cleavage products, cyanopentane and cyanopentene are formed in smaller amounts over both Si-MCM-41 and Al-MCM-41. Apparently, these are produced from dehydration and cracking and could also be from thermal reactions. The probable sequence of the different reactions is shown in Scheme 1. The rearrangement to caprolactam is catalysed by the acid sites in Al-MCM-41. SiOH groups may be responsible for the hydrolysis of oxime.
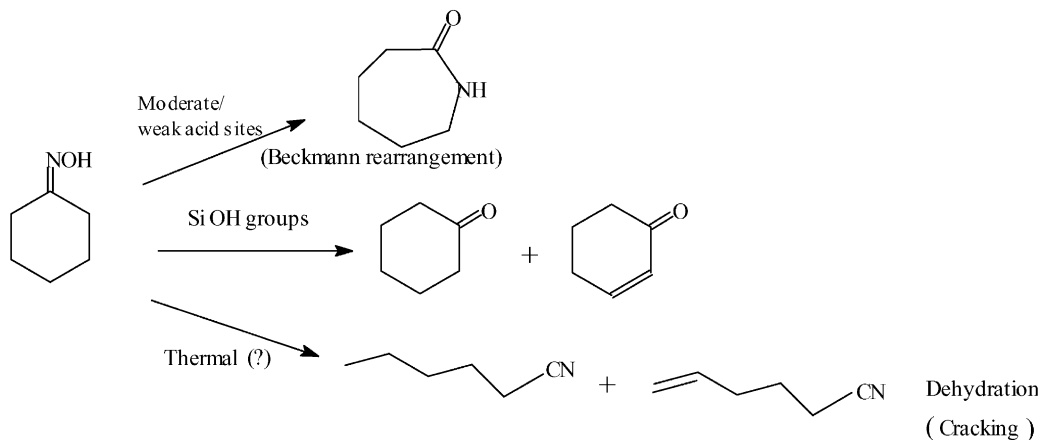
Scheme 1. Reactions occurring on MCM-41 catalysts.

4. Conclusions

Transformation of cyclohexanone oxime to ε-caprolactam was carried out on Si-MCM-41 and H-Al-MCM-41 samples with different Si/Al ratios. Conversion of cyclohexanone oxime was nearly constant with TOS upto 5 h over all the catalysts at the temperatures studied (300–390 °C). Selectivity for ε-caprolactam increased with TOS and reached a maximum at about 3 h. Caprolactam yield was highest (87%) for Al-MCM-41 with Si/Al ∼ 14 at a temperature of 360 °C and contact time of 0.53 h. While acidic sites appear to catalyse the rearrangement, SiOH groups catalyse the formation of by-products.

Acknowledgements

References

[1] P.B. Venuto, P.S. Landis, Adv. Catal. 18 (1968) 259.
[2] P.S. Landis, P.B. Venuto, J. Catal. 6 (1966) 245.
[3] A. Aucejo, M.C. Burguet, A. Corma, V. Fornés, Appl. Catal. 22 (1986) 187.
[4] W.K. Bell, C.D. Chang, European Patent 056,698 (1985).
[5] H. Sato, K. Ishii, K. Hirose, Y. Nakamura, Stud. Surf. Sci. Catal. 28 (1986) 755.
[6] A. Thangaraj, S. Sivasanker, P. Ratnasamy, J. Catal. 137 (1992) 252.
[7] J.S. Reddy, R. Ravishankar, S. Sivasanker, P. Ratnasamy, Catal. Lett. 17 (1993) 139.
[8] L.-X. Dai, R. Hayasaka, Y. Iwaki, K.A. Koyano, T. Tatsumi, Chem. Commun. (1996) 1071.
[9] T. Yashima, K. Miura, T. Komatsu, Stud. Surf. Sci. Catal. 84 (1994) 1897.
[10] P.S. Singh, R. Bandopadhyay, S.G. Hegde, B.S. Rao, Appl. Catal. A: Gen. 136 (1996) 249.
[11] H. Sato, K. Hirose, M. Kitamura, Y. Nakamura, Stud. Surf. Sci. Catal. 49 (1989) 1213.
[12] H. Sato, S. Hasabe, H. Sakurai, K. Urabe, Y. Izumi, Appl. Catal. 29 (1987) 107.
[13] T. Ushikub, K. Wada, J. Catal. 148 (1994) 138.
[14] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10835.
[15] M. Busio, J. Jänchen, J.H.C. van Hooff, Micropor. Mater. 5 (1995) 211.
[16] A. Corma, V. Fornes, M.T. Navarro, J. Perez-Pariente, J. Catal. 148 (1994) 569.
[17] L.-X. Dai, K. Koyama, T. Tatsumi, Catal. Lett. 53 (1998) 211.
[18] K. Chaudhari, T.K. Das, A.J. Chandwadkar, S. Sivasanker, J. Catal. 186 (1999) 81.
[19] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.