

# Vapour-phase Beckmann rearrangement of cyclohexanone-oxime over Al-MCM-41 type mesostructured catalysts

L. Forni\*, C. Tosi, G. Fornasari, F. Trifirò, A. Vaccari, J.B. Nagy<sup>1</sup>

*Dipartimento di Chimica Industriale e dei Materiali, Università di Bologna, v.le Risorgimento 4, 40136 Bologna, Italy*

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## Abstract

Al-MCM-41 type catalysts with different Al content (Si/Al = 10, 20, 40 as atomic ratio) have been prepared using cetyltrimethylammonium chloride as the organic surfactant and characterised by XRD, NMR, TGA, N<sub>2</sub> sorption, FT-IR, TPD and pyridine adsorption. Different diluents such as methanol, ethanol, isopropanol and water have been used in different compositions for cyclohexanone-oxime (CEOX) selective conversion to  $\epsilon$ -caprolactam over these ordered mesostructures, revealing the positive effect of polar diluents and above all of ethanol on conversion and  $\epsilon$ -caprolactam selectivity. The increase of the weight hourly space velocity (WHSV) decreases the catalyst lifetime, while a better catalytic activity is obtained for a lower Si/Al ratio.

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**Keywords:** Al-MCM-41; Si/Al ratio;  $\epsilon$ -Caprolactam; Vapour phase; Polar diluents

## 1. Introduction

Caprolactam is the starting monomer for the production of nylon-6 which, considering its specific properties, is the ideal starting material for a wide range of products such as carpeting. The current caprolactam manufacturing process is energy intensive and generates considerable wastes. For this reason, alternative paths for the production of caprolactam providing few-step cost effective production and environmentally friendly process are required.

Caprolactam can be obtained by the Beckmann rearrangement reaction of cyclohexanone-oxime in vapour phase. The vapour-phase rearrangement of cyclohexanone-oxime to  $\epsilon$ -caprolactam has been investigated for a wide range of solid catalysts, like B-MFI, SAPO-11, S-1, ALPO 4-11, ZSM-5 and NaY [1–5], hydrotalcite based materials [6,7] and amorphous oxides such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub> and SiO<sub>2</sub>

supported with boron or tantalum oxides [1,3,8–17]. In the past years, it has been suggested that Brønsted acid sites of intermediate strength promoted the formation of  $\epsilon$ -caprolactam [1,17]. However, more recently, it was claimed that the presence of rather weak Brønsted acid sites, such as free surface Si-OH groups (silanol-nests), was suitable for the selectivity to the final product [2,3,18], while strong acid sites accelerate the formation of by-products [9,10]. According to Hölderich and co-workers [18] the presence of Lewis acid sites seems not to affect the reaction, but could modify the strength and activity of Brønsted acid sites.

Crystalline alumino-silicates exhibit the most interesting catalytic activity and the highest selectivity in  $\epsilon$ -caprolactam. Although a rapid catalyst deactivation is often observed, recently Sumitomo claimed a silicalite, for vapour phase rearrangement, showing long time catalytic tests (~2300 and 8000 h) [19] and the start-up of a plant for caprolactam manufacture in Japan in year 2003. However, little is known about the reaction mechanism. For this reason there is a considerable interest in the understanding of the mechanism of reaction, of the dependence on structural parameters and acid sites functionalities.

\* Corresponding author. Tel.: +39 051 2093677; fax: +39 051 2093680.  
E-mail address: [forni@ms.fci.unibo.it](mailto:forni@ms.fci.unibo.it) (L. Forni).

<sup>1</sup> NMR Laboratory, University of Namur, rue de Bruxelles 55, B-5000 Namur, Belgium

In the present paper, we focus on Al-MCM-41 type mesoporous compounds [20,21]. In particular, in the present work we investigate the effect of different methods for catalysts activation on their chemical and physical properties and catalytic activity and also the effect of the polarity of different diluents on the catalytic performances.

## 2. Experimental

Al-containing MCM-41 type catalysts with Si/Al ratios ranging from 10 to 40 are prepared according to the literature [22]. 40 g of a solution (20 wt.%, Aldrich) of cetyltrimethylammonium chloride are added to sodium aluminate (varying, on the basis of Si/Al ratio of interest, from 0.239 to 0.955 g), 20 g of a 20 wt.% solution of tetramethylammonium silicate (99.99%, Aldrich) and 5 g of silica. The mixture is kept under stirring at room temperature for 5 h. The gel is submitted to hydrothermal treatment in an autoclave for 48 h at 150 °C. It is, then, filtered and washed by de-ionized water. The solid is dried and calcined at 540 °C for 7 h. According to this synthesis [21,23] by using such reagents, after calcination and removal of the organics, the formation of Brønsted acid sites occurs at the surface of the channels. However, also two different ionic-exchange solutions are used to activate the Al-MCM-41 in protonic form in order to study the effect of different methods applied to catalyst activation. The first aqueous solution is made of a  $\text{NH}_4\text{Cl}$  salt (pH about 7), while the second one has a pH > 10.0 and is made starting from a  $\text{NH}_4\text{NO}_3$  salt, which according to Masaru Kitamura et al. [24] is a good method for catalysts activation. The powder is then pressed, crushed and sieved in the 40–80 mesh range.

The Si/Al mol ratio of the samples is obtained by atomic absorption using a Philips PU 9100 spectrophotometer. The powder X-ray diffractograms (XRD) are carried out by a Philips diffractometer PW 1050/81 using Cu  $K\alpha$  radiation ( $\lambda = 0.15185$  nm). Catalyst texture is determined by mean of  $\text{N}_2$  adsorption at  $-196$  °C by a Sorptomatic Carlo Erba 1900 series, after evacuation of the samples at 200 °C under vacuum. Surface area is obtained by the BET method, and pore size distribution by BJH method. FT-IR spectra of Al-MCM-41 are collected under vacuum at room temperature, after evacuation at 200 °C with an FT-IR spectrometer Perkin-Elmer model 1750. Catalyst acidity is studied by adsorption of pyridine. At first catalysts are heated under vacuum at

350 °C to remove water and impurities from the surface, then exposed to pyridine vapours for 15 min and finally outgassed under dynamic vacuum at 100 and 300 °C. The concentrations of different types of acid sites are estimated by the integrated absorption bands in the FT-IR spectra at  $1550\text{ cm}^{-1}$  (pyridinium ions formed on Brønsted acid sites) and  $1450\text{ cm}^{-1}$  (pyridine co-ordinated to Lewis acid sites centres) using the extinction coefficients obtained by Dakta et al. [25],  $E_B = 0.73\text{ cm}^2/\mu\text{mol}$  and  $E_L = 1.11\text{ cm}^2/\mu\text{mol}^{-1}$  for Brønsted and Lewis sites, respectively. Thermogravimetric analysis (TGA) is carried out on a TA instrument TGA 2050 model. Weight losses were recorded in air flow, in the range of temperature 30–900 °C with an increasing rate of 5 °C/min.

TPD analysis is carried out on a TPD/RO 1100 ThermoFinnigan. Pre-treatment is carried out with a rate of 20 °C/min from room temperature to 540 °C in a flow of helium. The adsorption step is performed at 150 °C with  $\text{NH}_3$  (10%) in helium. After desorption of physisorbed ammonia, temperature is raised at 540 °C with a 10 °C/min rate, till desorption is complete.

Beckmann rearrangement is carried out in a glass fixed bed reactor (i.d. 8 mm and length 300 mm) operating at 350 °C, and atmospheric pressure (it has been verified that any homogeneous reaction does not occur). Before starting the reaction, the catalyst is treated under  $\text{N}_2$  flow at 350 °C for 2 h. Different feeds were used (Table 1); the feed is injected by a micro-feeder (Inforce) into the reactor, containing 0.20–0.30 g of catalyst, being  $\text{N}_2$  the carrier (15 ml/min). The weight hourly space velocity (WHSV) is 1.21 or  $4.50\text{ h}^{-1}$ , referred to the weight of oxime per hour versus catalyst weight. The effluents are collected in a condenser and the liquid products identified by a capillary column (50% phenyl, 50% methyl silicon) on a Carlo Erba 5300 model gaschromatograph with flame ionisation detector (FID). The qualitative identification of the products is carried out using a GC-MS (HP G1800A) system, equipped with a HP-5 column (length 30 m, i.d. 0.25  $\mu\text{m}$  and film width 0.25  $\mu\text{m}$ ). CEOX conversion and  $\epsilon$ -caprolactam selectivity are calculated on the basis of the moles of reactant converted.

$^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS-NMR spectra are obtained on a MSL-400 Bruker instrument. Repetition time for  $^{29}\text{Si}$  (79.4 MHz) is 60 s and the pulse of 6  $\mu\text{s}$  ( $\theta = \pi/2$ ) with a contact time of 5 ms for cross-polarization (CP-NMR) analysis. The reference is tetramethylsilane (TMS). For  $^{27}\text{Al}$  (104.3 MHz) the

Table 1

Composition of feed solutions: polar agents and diluent gases in molar percentage used during catalytic tests. The molar ratio between cyclohexanone-oxime and toluene (the solvent) is uniform

	Cyclo hexanone-oxime (mol%)	Toluene (mol%)	Methanol (mol%)	Ethanol (mol%)	Isopropanol (mol%)	Water (mol%)	Nitrogen (mol%)
Feed A	4.0	44.0	–	–	–	–	52
Feed B	3.3	35.1	35.1	–	–	0.8	26.5
Feed C	3.3	35.4	35.4	–	–	–	25.9
Feed D	3.4	35.4	–	35.4	–	–	25.8
Feed E	3.4	35.4	–	–	35.4	–	25.8

pulse is 1.0  $\mu\text{s}$  ( $\theta = \pi/12$ ) with repetition time 0.2 s. The reference molecule is  $(\text{Al}(\text{H}_2\text{O})_6)^{3+}$ .

### 3. Results and discussions

Chemical analysis of calcined Al-MCM-41 gives Si/Al ratios higher than the expected ones, see Tables 2 and 3. On the basis of  $^{27}\text{Al}$  MAS NMR, this may be caused by the loss of portions of aluminium atoms (for example octahedral extra framework aluminium) [21] during the washing after hydrothermal treatment. As a matter of facts we observed, the presence of tetrahedral Al atoms at about 50 ppm and a small peak attributed to octahedral aluminium at about 0 ppm [21].

The  $d$ -spacing at  $2\theta \cong 2^\circ$  of the XRD powder patterns of calcined samples decreases with increasing aluminium content ( $d = 4.268, 4.063, 3.845$  nm for Si/Al = 40, 20 and 10, respectively), and a less resolved XRD pattern is observed. In addition the use of solutions of different pH, to obtain the Al-MCM-41 protonic form, leave the layered structure unchanged only when  $\text{NH}_4\text{Cl}$  solution is used. The larger amounts of aluminium incorporated in the structure lead to the decrease of the long range order and of the average distance of the channels [26]. As a matter of facts X-ray diffractogram of sample after exchange with a  $\text{NH}_4\text{NO}_3$  solution do not show the X-ray reflections typical of the MCM-41 ordered structure. We attributed this evolution to the high basicity of the exchange solution which promotes the loss of the high order of the mesostructure. In agreement with Chen et al. [27], thermogravimetric analysis of the dried Al-MCM-41 shows three weight losses: the first between 25 and  $150^\circ\text{C}$  corresponding to the desorption and removal of physisorbed molecules, at  $530\text{--}550^\circ\text{C}$  removal of the organic surfactant molecules (its small amount 0.24% indicates that the template has mainly been removed by washing), at above

$560^\circ\text{C}$  the condensation of adjacent silanol groups. Isothermal analysis on calcined Al-MCM-41 carried out at the reaction conditions ( $350^\circ\text{C}$  in a flow of nitrogen or air) for 6 h, did not point out any relevant weight loss (0.6%), thus a steady thermal stability of the material may be assumed. The  $\text{N}_2$  adsorption isotherms of all the samples (Fig. 1) are of type-IV and characterised by a non-noticeable hysteresis loop. Three well defined stages are identified and explained according to Ko et al. [23]. In agreement with XRD results, by increasing the Si/Al ratio, a shift of the step of capillary condensation towards higher relative pressures is observed as a consequence of the increase of pore size, pore diameter increases (Tables 2 and 3) from 2.78 to 3.16 nm, with furthermore, a narrower pore size distribution with increasing the Si/Al ratio, as a consequence of the increasing long range order.

The FT-IR spectra are characterised by a band at about  $3740$  and  $3680\text{ cm}^{-1}$  corresponding respectively to the vibration of isolated and vicinal Si-OH groups, the latter reported as rather selective in caprolactam.

$^{29}\text{Si}$  MAS NMR spectra confirmed the presence of three different kind of silicon sites: chain of silanols such as vicinal and nests of silanols ( $\delta = -90$  ppm), terminal silanols ( $\delta = -100$  ppm) and  $\text{Si}(\text{SiO})_4$  ( $\delta = -108$  ppm). CP-NMR analysis points out the increase of the intensity of Si(OH) groups because such silanols are very close one to the other, see Table 4. Hence, these sites may establish electronic interactions giving rise to a suitable weak acidity for the Beckmann rearrangement. The strong acidity of aluminium mesostructured materials is connected to the presence of accessible interchannel hydroxyl groups associated with tetra coordinated framework Al ions, as well as to the presence of octahedral Al ions [28–31]. The acid properties of Al-MCM-41 samples have been investigated by means of  $\text{NH}_3$ -TPD analysis, results concerning the amount of desorbed ammonia are reported in Table 5. All the samples are basically characterized by a TPD-desorption band centred at about  $300^\circ\text{C}$  with the exception of Al-MCM-41(20) sample exchanged with a  $\text{NH}_4\text{NO}_3$  solution whose desorption maximum is about  $325^\circ\text{C}$ . However, it was not possible to attribute the TPD-desorption peak to the different kind of acid sites of Al-MCM-41 samples. It is very likely that the peaks of acidic-silanols are located under the desorption peak of Al-acid sites. We also observed that, with increasing Si/Al ratio, samples acidity decreases.

The use of different exchange solutions, to get the protonic form for sample Al-MCM-41(20), leaves the acid site distribution unchanged but shows an influence on the global acidity of the samples. As a matter of facts when a  $\text{NH}_4\text{Cl}$  solution is used we observe a slight decrease of the desorbed  $\text{NH}_3$ , while after exchange by a  $\text{NH}_4\text{NO}_3$  solution the difference of acidity has been ascribed to a different structure arrangement. Acid sites distribution of Al-MCM-41 samples has been investigated using FT-IR pyridine adsorption (Table 6). The bands of pyridine bonded on acidic sites are in agreement with an early paper [23] and show an increase of both Brønsted [30] and Lewis acidity with increasing Al content.

Table 2  
Physico-chemical properties of Al-MCM-41 type catalysts

Sample	Si/Al nominal (mol/mol)	Si/Al experimental (mol/mol)	Surface area ( $\text{m}^2/\text{g}$ )	Pore diameter (nm)
Al-MCM-41(10)	10	18	764	2.78
Al-MCM-41(20)	20	28	983	3.06
Al-MCM-41(40)	40	57	795	3.16

Table 3  
Surface area and pore diameters for Al-MCM-41(20) before and after reaction using feed B

	Surface area ( $\text{m}^2/\text{g}$ )	Pore diameter (nm)
Al-MCM-41(20) after reaction (WHSV = $1.21\text{ h}^{-1}$ )	152	3.04
Al-MCM-41(20) after reaction (WHSV = $4.5\text{ h}^{-1}$ )	62	2.20

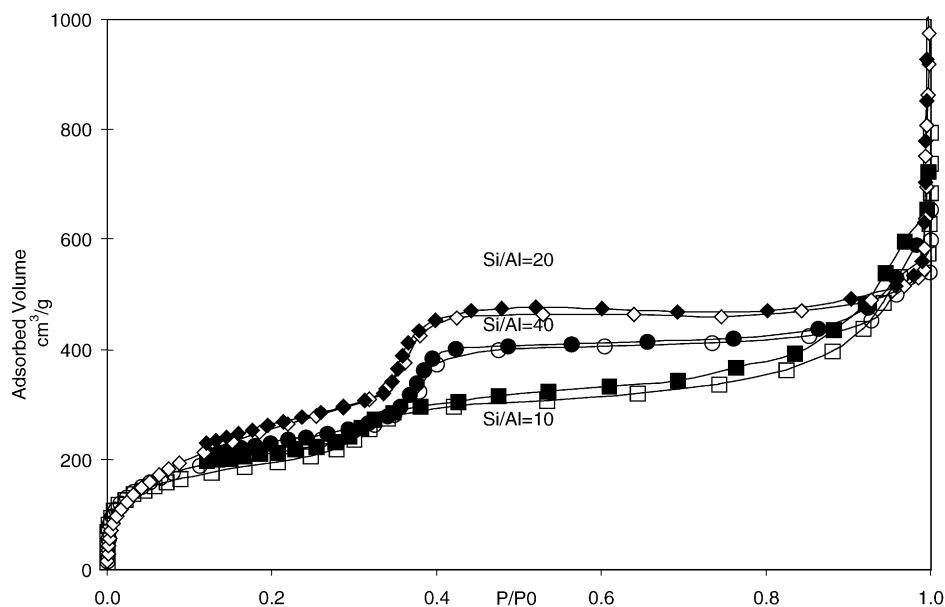


Fig. 1.  $N_2$  isotherm at  $-196^\circ\text{C}$  of Al-MCM-41(10), Al-MCM-41(20), Al-MCM-41(40).

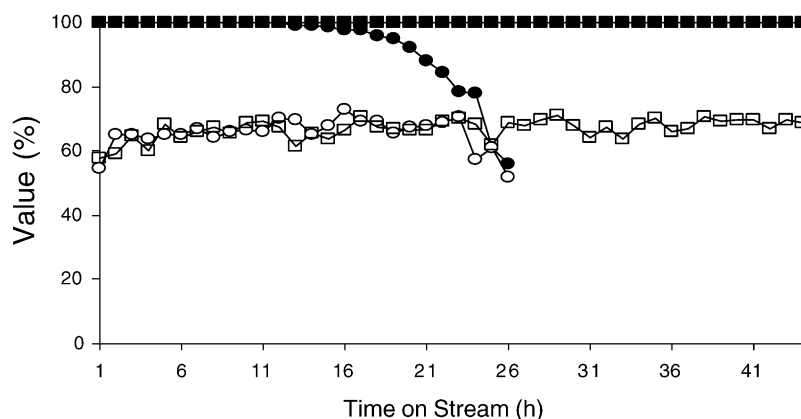


Fig. 2. Effect of space velocity (WHSV) on oxime (CEOX) conversion and  $\epsilon$ -caprolactam selectivity of sample Al-MCM-41(20) as a function of time on stream. (■) CEOX conversion for  $\text{WHSV} = 1.21\text{ h}^{-1}$ , (●) CEOX conversion at  $\text{WHSV} = 4.5\text{ h}^{-1}$ , (□)  $\epsilon$ -caprolactam selectivity at  $\text{WHSV} = 1.21\text{ h}^{-1}$ , (○)  $\epsilon$ -caprolactam selectivity at  $\text{WHSV} = 4.5\text{ h}^{-1}$ .

Brønsted acid sites are characterized by a weaker acidity than Lewis acid sites, as we observe in Table 5 after desorption at  $300^\circ\text{C}$ .

Vapour phase Beckmann rearrangement of cyclohexanone-oxime (CEOX) over Al-MCM-41 type catalysts leads mainly to  $\epsilon$ -caprolactam, with cyclohexanone, cyclohexen-

1-one, hexanenitrile, 5 hexenenitrile, aniline, tars and heavy volatile products as by-products [5,8,23].

The effect of the different Si/Al ratio (from 10 to 40) was investigated using feed B (methanol and water) and  $\text{WHSV} = 4.5\text{ h}^{-1}$ . Si/Al ratio affects caprolactam selectivity which increases with increasing aluminium content (and increasing

Table 4

$^{29}\text{Si}$  MAS NMR and  $^{29}\text{Si}$  CP NMR spectra of MCM-41 activated by  $\text{NH}_4\text{Cl}$  aqueous solution (MCM-41(20)- $\text{NH}_4\text{Cl}$ ) and  $\text{NH}_4\text{NO}_3$  basic aqueous solution (MCM-41(20)- $\text{NH}_4\text{NO}_3$ )

Sample	MAS NMR $\delta$ (ppm)			CP NMR $\delta$ (ppm)		
	Si(OH) <sub>2</sub>	SiOH	Si(SiO) <sub>4</sub>	Si(OH) <sub>2</sub>	SiOH	Si(SiO) <sub>4</sub>
MCM-41(20) $\text{NH}_4\text{Cl}$	7	17	76	22	64	14
MCM-41(20) $\text{NH}_4\text{NO}_3$	11	13	76	13	79	8

Both samples have a nominal Si/Al molar ratio = 20.

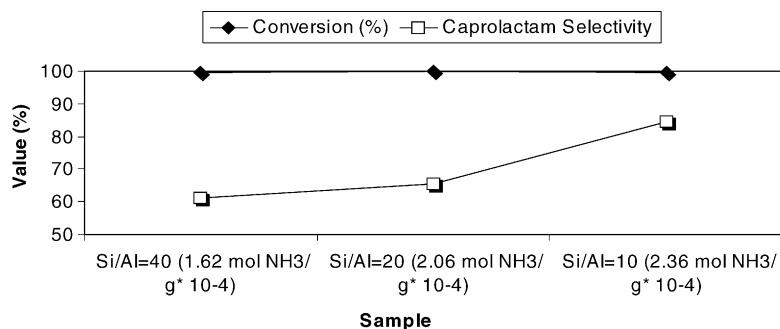


Fig. 3. Cyclohexanone oxime conversion (◆) and caprolactam selectivity (□) as a function of acidity and Si/Al molar ratio. The values are referred to feed B (cyclohexanone-oxime, methanol, water and nitrogen), WHSV = 4.5 h<sup>-1</sup> and to time on stream 3 h.

acidity) from about 61–84% values, as displayed in Fig. 3 and unlike the results of Chaudari et al. [32] it remains unchanged, in all cases, for almost 20 h of reaction. On its hand, cyclohexanone oxime conversion remains nearly constant, at values higher than 99.8%, for the first 4 h of reaction, then it progressively decreases for Al-MCM-41(40), Al-MCM-41(20) and Al-MCM-41(10), respectively, this latter showing an almost complete CEOX conversion for at least 16 h. This behaviour is explained by the different acidity introduced by the aluminium content. Catalytic performances of samples having different Si/Al ratio are attributed to the different acidic characteristics. The higher the acidity is, the better the catalytic performances are. Such results are in agreement with Corma and co-workers [33] who attributed this behaviour to the presence of internal silanol groups and framework aluminium.

According to the method of preparation of Al-MCM-41, calcination allows the formation of Al-MCM-41 protonic form. However, we verified the effect of two exchange solutions which are (i) aqueous solution at pH ≈ 7 with an NH<sub>4</sub>Cl salt and (ii) aqueous solution at pH > 10 with an

NH<sub>4</sub>NO<sub>3</sub> salt. According to TPD results the activated samples have similar profiles as Al-MCM-41(20) and the acidity little differs from the 2.06 × 10<sup>-4</sup> mol NH<sub>3</sub>/g of sample Al-MCM-41(20). However, because of this little difference of acidity we also observe slight differences in catalytic activity as reported in Fig. 4. The exchange procedure induces a lowering of the catalytic performances (caprolactam yield is 58.8% with NH<sub>4</sub>Cl and 60.0% with NH<sub>4</sub>NO<sub>3</sub> while its value is 65% with direct calcination). The different acidity, after exchange at high pH (NH<sub>4</sub>NO<sub>3</sub>) can be ascribed to the disorganization of the long range ordered structure.

The role of different weight hourly space velocity values (WHSV), using feed B (Table 1), on CEOX conversion and ε-caprolactam selectivity at 350 °C on Al-MCM-41(20) is shown in Fig. 2. Said effect is almost negligible for the first 15 h of reaction, with a complete CEOX conversion and value of the selectivity in ε-caprolactam set around 65%. The difference arises at higher time on stream: for space velocity = 1.21 h<sup>-1</sup>, ε-caprolactam selectivity and CEOX conversion remain unchanged over 40 h, while for higher WHSV (4.5 h<sup>-1</sup>), a strong decrease of the conversion is observed, but ε-caprolactam selectivity values remain almost unchanged. This behaviour is attributed to a faster deactivation at high WHSV due to the higher amount of reactant (about four times) fed per hour and, as a consequence, to the larger amount of tars formed (no shape-selective tars limitations occurs on these mesoporous materi-

Table 5

Al-MCM-41 with different Si/Al ratio and Al-MCM-41(20) with different activation treatment

Sample	Desorbed NH <sub>3</sub> (mmol/g)
Al-MCM-41(10)	0.236
Al-MCM-41(20)	0.206
Al-MCM-41(40)	0.162
Al-MCM-41(20) NH <sub>4</sub> Cl	0.196
Al-MCM-41(20) NH <sub>4</sub> NO <sub>3</sub>	0.224

All samples are calcined at 540 °C.

Table 6

Acid properties of Al-MCM-41 type catalysts as determined by FT-IR spectroscopy of adsorbed pyridine, after evacuation at 100 and 300 °C

	C <sub>L</sub> (μmol/g)		C <sub>B</sub> (μmol/g)		C <sub>L</sub> /C <sub>B</sub>	
	100 °C	300 °C	100 °C	300 °C	100 °C	300 °C
Al-MCM-41(10)	124	136	0.91	3.11		
Al-MCM-41(20)	78	149	0.52	2.66		
Al-MCM-41(40)	35	90	0.39	1.28		

Note: C<sub>L</sub>: concentration of Lewis acid sites, C<sub>B</sub>: concentration of Brønsted acid sites.

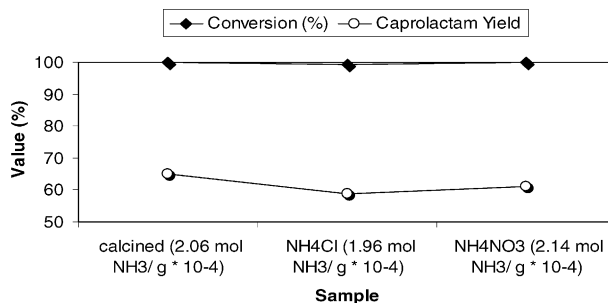
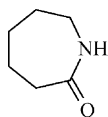
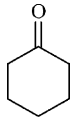


Fig. 4. Cyclohexanone oxime conversion (◆) and caprolactam yield (○) as a function of acidity and activation methods. Values are referred to feed B (cyclohexanone oxime, methanol, water and nitrogen), WHSV = 4.5 h<sup>-1</sup> and time on stream 3 h.

Table 7  
Effect of different polar diluents on cyclohexanone oxime conversion, caprolactam and cyclohexanone selectivities

	Conversion (%)	Selectivity (%)		Tars yield (%)
				
CEOX, Tol. (feed A)	95.4	54.3	6.2	5.3
CEOX, Tol., water, methanol (feed B)	>99.8	65.0	4.6	0.52
CEOX, Tol., methanol (feed C)	>99.8	66.6	5.3	1.3
CEOX, Tol., ethanol (feed D)	>99.8	71.0	3.2	/
CEOX, Tol., isopropanol (feed E)	>99.8	67.5	3.6	0.97

Reference catalyst is Al-MCM-41(20) and TOS = 3 h.

als), in agreement with the decrease of surface area observed (Table 3).

In Table 7, the conversion of cyclohexanone-oxime, caprolactam and cyclohexanone selectivity are reported when different alcohols are used as diluents. Sample Al-MCM-41(20) was used as the reference and the effect of the following diluents investigated: toluene (feed A) as the solvent, methanol and water (feed B), methanol (feed C), ethanol (feed D), isopropanol (feed E). Space velocity is set at  $4.5 \text{ h}^{-1}$  to increase the rate of deactivation. We observed a relevant difference of catalytic performance between the use of toluene and other polar diluents since the beginning of the reaction. Cyclohexanone-oxime conversion and caprolactam selectivity are sensibly lower with toluene than with polar solvents (see Table 7), and deactivation rate is much faster with toluene (when only toluene is used, after 5 h of reaction, cyclohexanone-oxime conversion decreases to 80% while with polar diluents it is still about 100%). In agreement with Ko et al. [23] we confirm that this behaviour is ascribed to solvent effect: the solvent reacts with the catalyst to give dehydration products (such as dimethylether and water) and protects silanols according to the mechanism reported by Ichihashi and Kitamura [34]. Polar solvents and the small amounts of water formed would prevent the formation of large molecules on the catalyst active sites. The good effect of water, mentioned by Röseler et al. [5] is also confirmed by the introduction of a small amount of water in the feed (feed B). In this case a slight decrease of caprolactam selectivity is observed, however a lower deactivation rate occurs. As a matter of facts tars yield is sensibly reduced when water is co-fed with a polar solvent (methanol), tars yield undergoes a relevant decrease from 5.3% (feed A), 1.26 (feed C) to 0.5% (feed B). Also the use of solvents with a different polarity promotes a different caprolactam selectivity leaving cyclohexanoneoxime conversion almost unvaried. Best results are obtained with ethanol as the diluent as reported in Table 7. This has been explained [35] by the good balance between the dielectric constant of polar solvent and its competitiveness of absorption with the substrate (larger polar molecules may hinder the access of cyclohexanone oxime to active sites and thus prevent its rearrangement). This phenomenon has a good effect on cyclohexanone formation in fact its selectivity

is reduced by the use of polar diluents with a minimum value for ethanol, as displayed in Table 7. Cyclohexanone selectivity is 5.3% with methanol, 3.2% with ethanol and 3.6% with isopropanol. In addition the good balance between dielectric constant of polar solvents and the absorption on the catalyst plays a relevant role for it decreases catalyst deactivation rate. As a matter of fact at 10 TOS, Al-MCM-41(20) with feed E has a cyclohexanoneoxime conversion of 66.6% while the same sample with feed C has a cyclohexanoneoxime conversion of 98.2%.

#### 4. Conclusions

Rearrangement of cyclohexanone-oxime carried out on Al-MCM-41 with different Si/Al molar ratios showed that catalysts are active but for highest Si/Al ratio, catalyst deactivation runs faster and  $\epsilon$ -caprolactam selectivity is lower. Thus, catalyst acidity is deeply affected by aluminium content. The effect of different exchange solutions, on the reported catalyst preparation does not improve catalytic performances because they do not modify catalyst properties ( $\text{NH}_4\text{Cl}$ ) or modify the long range structure of the mesopores ( $\text{NH}_4\text{NO}_3$ ). Space velocity, in the range tested, does not show any difference in oxime conversion and  $\epsilon$ -caprolactam selectivity. However, at higher WHSV values, due to the higher flow of CEOX introduced in the reactor, catalyst lifetime is dramatically shortened. The effect of polar diluents is rather important because of the competitiveness of said diluents with the substrate on the catalyst surface acid sites. This competition deeply affects caprolactam and cyclohexanone selectivity, tars formation and hence catalysts deactivation rate. However, the presence of water slightly decreases  $\epsilon$ -caprolactam selectivity, but promotes longer catalyst lifetime.

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