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Novel synthesis of ε-caprolactam from cyclohexanone-oxime via Beckmann rearrangement over mesoporous molecular sieves MCM-48

J.-C. Chang, A.-N. Ko*

Department of Chemistry, Tunghai University, Taichung, Taiwan

Abstract

Vapor-phase synthesis of ε-caprolactam (ε-C) from cyclohexanone-oxime (CHO) has been studied at 1 atm and 300–400 °C using SiMCM-48 and AlMCM-48(*X*) with Si/Al molar ratios *X* in a fixed-bed, continuous flow reactor. The catalysts were characterized with ICP-AES, XRD, TEM, FT-IR, N_2-adsorption, ^{27}Al and ^{29}Si MAS NMR and TPD of ammonia. An increase of *X* value in AlMCM-48(*X*) enhances both the BET surface area and the unit cell parameter but diminishes the acid amount. In the reaction of CHO, benzene, toluene, ethanol and 1-hexanol were utilized as solvents. The CHO conversion increases with the reaction temperature, whereas the ε-C selectivity exhibits the opposite trend due to side reactions. The catalyst stability is greatly enhanced by using ethanol and 1-hexanol as the solvents due to their production of water vapor via dehydration. Excellent catalytic performance of AlMCM-48(10) is attained at 1 atm, 350 °C and *W*/Fc 74.6 g h/mol by using 1-hexanol in the feed; the CHO conversion and the ε-C selectivity exhibit higher than 99% and 90%, respectively, during at least 130 h process time.

Keywords: ε-Caprolactam; Cyclohexanone-oxime; MCM-48; Beckmann rearrangement

1. Introduction

As ε-caprolactam (ε-C) is an important raw material for the manufacture of 6-nylon, much effort has been focused on its preparation from cyclohexanone-oxime (CHO). The traditional process utilizes concentrated sulfuric acid as the catalyst in the liquid phase. However, this homogeneous catalyzed process suffers from corrosion hazards, safety problems and the large amount of ammonium sulfate formed during neutralization of oleum. Consequently, ε-C synthesis via vapor-phase reaction over solid acid catalysts has drawn much attention during the past three decades [1]. A variety of different catalysts have been studied, viz. silica–alumina [2], boria supported on alumina or zirconia [3,4], zeolites such as HY [5,6], PdY [7], ZSM-5 [8–10], [B]-ZSM-5 [11], Beta [10,12,13], [Al]- and [B]-beta [14], alumina pillared montmorillonite [10] and mesoporous molecular sieves [15–17].

In the reaction of CHO over B_2O_3/Al_2O_3[3], the catalyst activity decreased with process time, whereas the ε-C selectivity remained stable during the first 5 h. B_2O_3/ZrO_2 was reported to exhibit high activity and ε-C selectivity at 300–320 °C during 8 h process time; the ε-C yield was associated with the number of intermediate strong acid sites [4]. H-USY zeolites with SiO_2/Al_2O_3 ratios of 27 and 62 exhibited excellent catalytic results by using 1-hexanol as diluent [6]. With H-Beta, HZSM-5 and alumina pillared montmorillonite, the initial catalytic activity correlated well with the total acid amount of various catalysts. The reaction proceeded on both Brönsted and Lewis acid sites and the catalyst deactivation most likely occurred at the strong Brönsted acid sites [10]. For a boron-MFI zeolite, reducing temperature and pressure enhanced the ε-C selectivity at the expense of the catalyst lifetime. However, addition of water up to 6 mol/mol CHO resulted in an increase of catalyst lifetime [11]. Similar effects were observed on aluminum- or boron-containing beta zeolites [14]. Comparing the reaction over H-MCM-41 and H-FSM-16 during 6 h

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* Corresponding author. Tel.: +886 4 23590248; fax: +886 4 23590426.
E-mail address: anko@mail.thu.edu.tw (A.-N. Ko).

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process time, H-MCM-41 exhibited a better performance by using 1-hexanol as diluent [15]. With mesoporous silica FSM-16 catalysts, the ε-C selectivity was improved by supporting Al_2O_3, ZnO and CdO. Furthermore, the acid sites with the heat of adsorption of ethylamine around 135 kJ mol^{-1} were effective for ε-C formation [16]. For the reaction of CHO over Al-MCM-41 at 1 atm and 300–400 °C, both the catalyst activity and stability were enhanced with increasing reaction temperature whereas ε-C selectivity varied only slightly. Ethanol as solvent exhibited much better catalytic results than benzene. The excellent catalyst performance of Al-MCM-41 was attributed to its large surface area and uniform mesopores as well as the weak and medium acidity [17].

Despite the intensive research on synthesis, characterization and application of MCM-41 materials, MCM-48, being the cubic member of the M41S family, has received much less attention especially in the field of catalysis. The mesoporous molecular sieves MCM-48 with Si/Al molar ratios of 15–40 were synthesized and characterized. A contraction of the unit cell occurred by substituting the silicon with larger aluminum atoms [18]. MCM-48 possesses bi-continuous and three-dimensional pore channels. Consequently, both the diffusional limitation and the pore blockage are reduced as compared to MCM-41 [18-20]. These characteristic properties show its potential applications in catalysis, adsorption and separation [21]. In this work, SiMCM-48 and AlMCM-48 with different Si/Al molar ratios were prepared and characterized with ICP-AES, XRD, TEM, FT-IR, N_2-adsorption, ^{27}Al and ^{29}Si MAS NMR and TPD of ammonia. The Beckmann rearrangement of CHO to ε-C was investigated using these catalysts. By utilizing SiMCM-48 and AlMCM-48, the acid amount of catalysts was altered so as to examine its effect on the catalytic results. The influence of solvents in the feed, the reaction temperature and the process time on catalytic results was also studied. In addition, the catalytic performance was investigated under optimum reaction conditions.

2. Experimental

2.1. Catalyst preparation

SiMCM-48 was synthesized according to the methods described in the literature [22]. A 1.94 g sodium hydroxide and 17.67 g cetyltrimethyl ammonium bromide were dissolved in 100 ml deionized water. Then 21.05 g tetraethyl orthosilicate was added into the above mixture with stirring 1 h. The solution was then poured into an autoclave and was heated at 100 °C for 72 h. After cooling to 35 °C, the pH value of the gel was adjusted to 7 by adding 2 M HCl solution. In the autoclave, the resulting solution was heated at 100 °C for 24 h. The product was filtered, washed, and dried in air. Finally it was calcined at 550 °C for 6 h. To prepare AlMCM-48(*X*) with Si/Al molar ratio *X*, an appropriate amount of sodium aluminate was used as the aluminum source and similar procedures were followed.

2.2. Catalyst characterization

The Si/Al molar ratio of the sample was measured with an ICP-AES (Kontron S-35). The powder X-ray diffraction patterns of various samples were obtained by an XRD spectrometer using Cu Kα radiation (Shimadzu XRD-6000). The IR spectra of catalysts were recorded at room temperature with an FT-IR spectrometer (Perkin Elmer FT-IR 2000). The mesophases were characterized by transmission electron microscopy (JEOL-2010). The BET surface areas of samples were determined by a sorption analyzer (Quantachrome Quantasorb). The ^{27}Al and ^{29}Si MAS NMR spectra were recorded on a solid-state NMR spectrometer (Bruker DSX 400 WB). The catalyst acidity was obtained by temperature-programmed desorption of ammonia, following the procedures described in the literature [17].

2.3. Catalytic reaction

The catalytic reaction was performed at 300–400 °C under atmospheric pressure by using a fixed-bed, integral-flow reactor. Prior to the reaction, the catalyst was activated with flowing dry air (60 ml/min) at 400 °C for 2 h and then cooled to the reaction temperature with nitrogen gas (99.99%, 60 ml/min). The feed was prepared by dissolving CHO in various solvents (1 mol/l), viz. benzene, toluene, ethanol, and 1-hexanol. It was injected via a microfeeder (Stoelting) into the reactor (1 cm i.d. × 34 cm), containing 0.3 g catalyst sample. Nitrogen was used as the carrier gas (60 ml/min). The value of *W*/Fc refers to the weight of catalyst (g) over the feed rate of CHO (mol/h). The effluents were collected with a condenser. The liquid products were identified with a GC-MS (HP 5989 B) and were periodically analyzed with a GC (China Chromatography Co.) fitted with a flame ionization detector and a megabore column DB-1 (J&W, 0.544 mm × 30 m).

3. Results and discussion

3.1. Catalyst properties

Fig. 1 shows the powder X-ray diffraction patterns of calcined samples of SiMCM-48 and AlMCM-48 ($X = 10$, 20 and 40). The calcined SiMCM-48 exhibits a strong peak at a d_{211}-spacing of 3.65 nm as well as seven small peaks, in agreement with another report [18]. Before calcination, larger *d*-spacings were observed for all these peaks due to the existence of organic templates. Therefore, lattice contraction occurred but the structure remained stable after calcination, in accordance with the literature [18,22]. Increasing the aluminum content in AlMCM-48(*X*) causes a slight decrease of d_{211}-spacing, implying the substitution

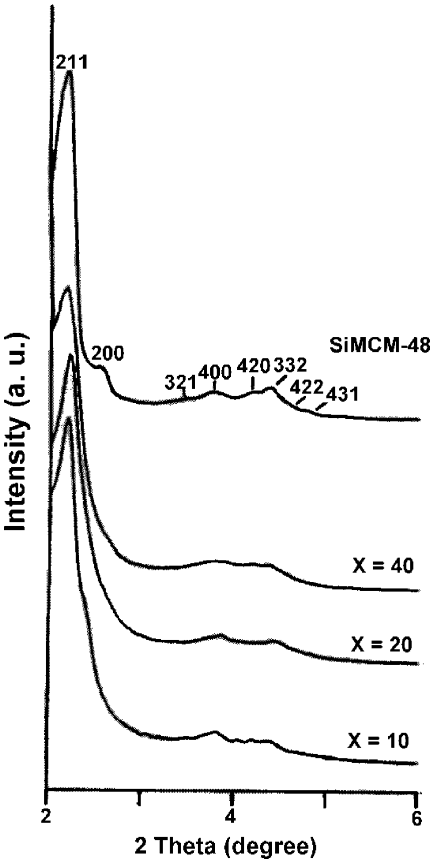


Fig. 1. Powder XRD patterns of calcined SiMCM-48 and AlMCM-48(*X*).

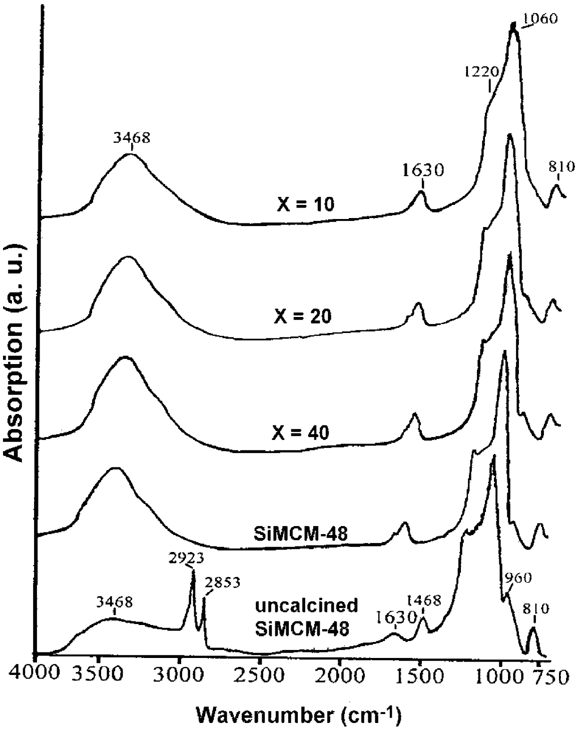
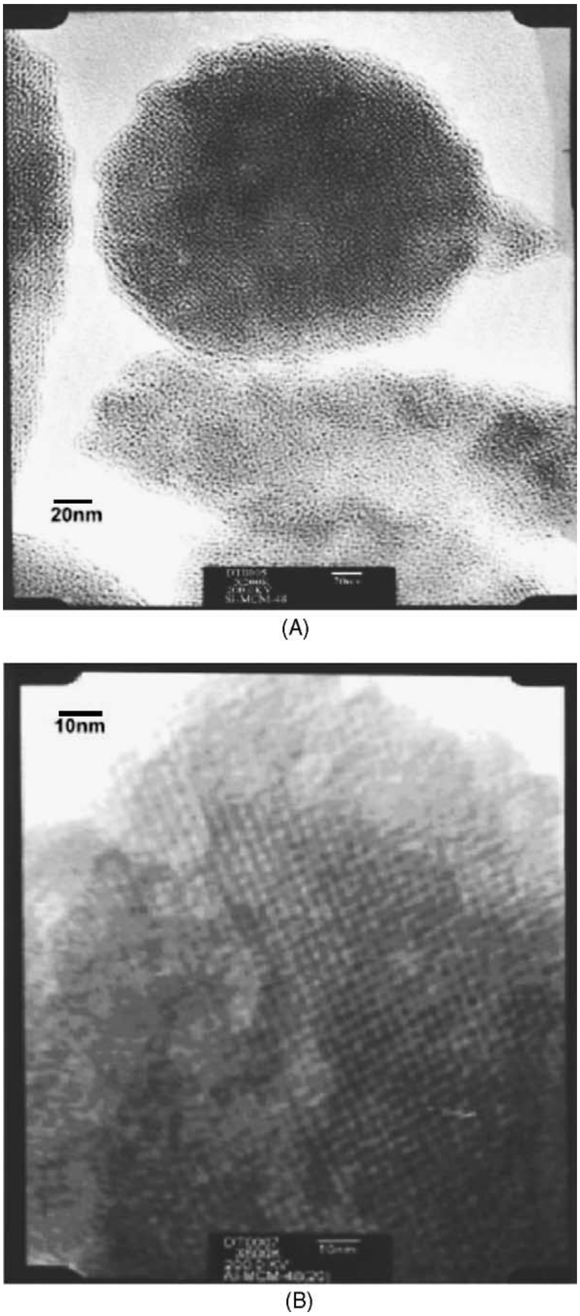


Fig. 2. FT-IR spectra of SiMCM-48 and calcined AlMCM-48(*X*).

of silicon by larger aluminum atoms. Such a result is consistent with another report [18].

Fig. 2 displays the FT-IR spectra of MCM-48 materials. For all samples, a broad band at ca. 3468 cm^{-1} is ascribed to water. The weak band at 1630 cm^{-1} corresponds to the bending mode of water [23]. The broad band at 1060 cm^{-1} with a shoulder at 1220 cm^{-1}, and the band at 810 cm^{-1} are attributed to Si–O stretching and Si–O–Si bending, respectively [18,24]. With as-synthesized SiMCM-48, three additional bands occur at 1468, 2853 and 2923 cm^{-1} that are ascribed to C–H bending and C–H



(A)

(B)

Fig. 3. TEM images of calcined MCM-48 catalysts: (A) SiMCM-48; (B) AlMCM-48(10).

stretching, respectively. Lack of these bands for the calcined samples implies the removal of organic templates upon calcination. The band at 960 cm^{-1} is possibly due to the SiO_4 structure. Its intensity diminishes with the aluminum content in AlMCM-48(*X*), showing the substitution of silicon by aluminum.

Fig. 3 illustrates the TEM images of MCM-48 catalysts. The cubic structure and a regular pattern are observed for the MCM-48 materials as reported elsewhere [25]. Fig. 4 shows the ^{27}Al and ^{29}Si MAS NMR spectra of calcined MCM-48 samples. The peak at 52 ppm corresponds to tetrahedral-coordinated structural aluminum, whereas the peak at ~0 ppm is attributed to the aluminum expelled from the AlMCM-48(*X*) structure. Furthermore, the aluminum content *X* has no apparent effect on the extent of dealumination (Fig. 4A). The environment of silicon in the skeletal structure of molecular sieves is usually written as Q^n to represent $Si(OSi)_n(OH)_{4-n}$. For the calcined AlMCM-48(40), three resonances (Q^2–Q^4) appear at −93, −103, −111 ppm, respectively (Fig. 4B). An increase of aluminum content in AlMCM-48(*X*) samples diminishes the Q^3 and Q^2 peak intensities due to the replacement of silicon with aluminum, resulting in a decrease of the Si–OH content in the samples. In addition, a small shift of these peaks toward lower resonance occurs.

Fig. 5 displays the ammonia-TPD profiles from the calcined MCM-48 catalysts. The relative acid amount of various catalysts was estimated by comparing the peak areas under the curves with reference to SiMCM-48. The acid amount follows the decreasing order of AlMCM-48(10) > AlMCM-48(20) > AlMCM-48(40) > SiMCM-48. Such a trend shows that the acid amount enhances with the

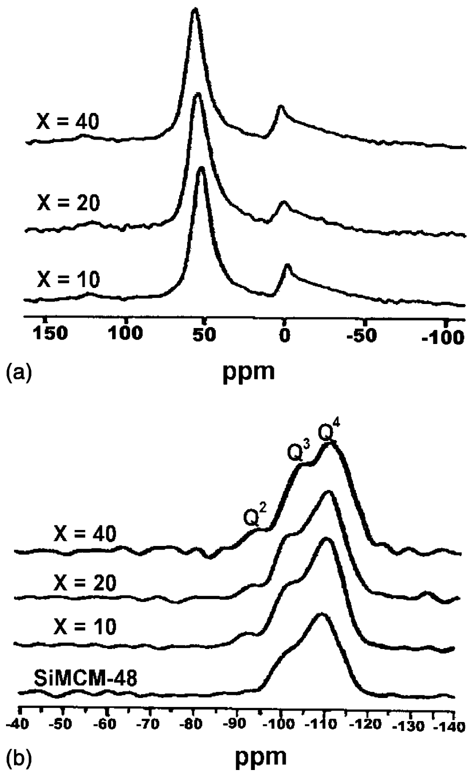


Fig. 4. MAS NMR spectra for calcined SiMCM-48 and AlMCM-48(*X*): (A) ^{27}Al; (B) ^{29}Si.

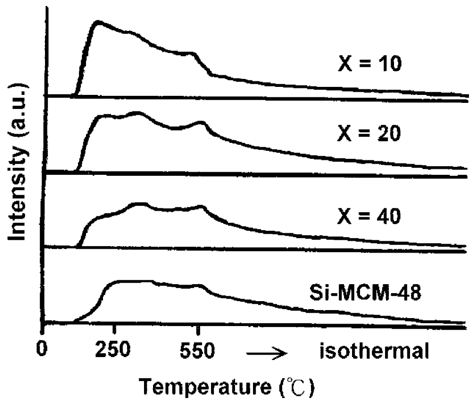


Fig. 5. NH_3-TPD profiles from calcined SiMCM-48 and AlMCM-48(*X*).

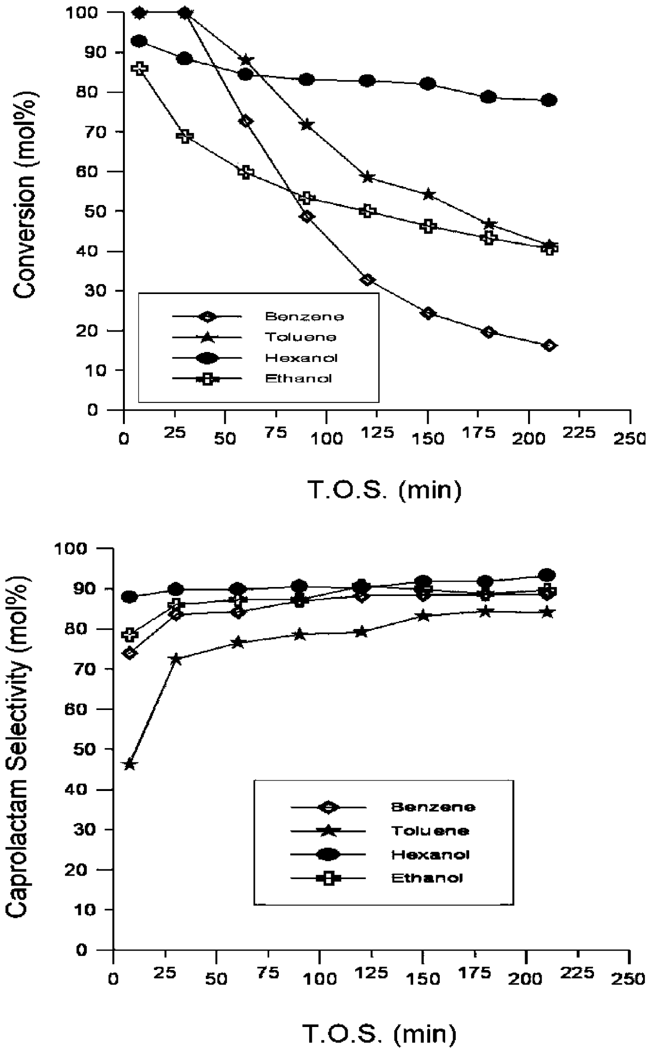


Fig. 6. Influence of solvents on catalytic results over AlMCM-48(10) at 300 °C and *W*/Fc 74.6 g h/mol.

Table 1
Physical properties of MCM-48 catalysts

Catalysts	Si/Al molar ratio (gel)	Si/Al molar ratio (sample)	Surface area (m^2/g)	d_{211}-Spacing (nm)	a[a] (nm)	Relative acid amount
SiMCM-48	–	–	1351	3.65	8.94	1.00
AlMCM-48(40)	40	36.2	1014	3.65	8.94	1.29
AlMCM-48(20)	20	18.5	971	3.54	8.67	1.85
AlMCM-48(10)	10	9.8	774	3.47	8.49	2.10

[a] $a = d_{211} \times 6^{1/2}$ is the cubic unit cell parameter.

aluminum content in the samples. In addition, these catalysts own acid sites of weak and intermediate strength; the relative amount of intermediate to weak acid sites enhances with a decrease of aluminum content. Similar results were observed for the dependence of catalyst acidities on the Si/Al ratio of H-beta [10] and HZSM-5 zeolites [10,26]. The physical properties of MCM-48 catalysts are summarized in Table 1.

3.2. Catalytic reactions

In the Beckmann rearrangement of CHO over various catalysts, the major product is ε-C and the side products include cyclohexanone (CHA), cyclohexen-1-one (CHE), 5-hexenenitrile (HEN), hexanenitrile (HAN) and aniline (AN) that is consistent with other studies [10,15,17]. The CHO conversion and the product selectivity are calculated with respect to the moles of CHO converted.

3.2.1. Effect of solvents

Fig. 6 shows the influence of various solvents on the catalytic results. The initial CHO conversion decreases in the order of benzene ≈ toluene > 1-hexanol > ethanol. The decay rate exhibits the following trend: benzene > toluene > ethanol > 1-hexanol. The ε-C selectivity follows the order of 1-hexanol > ethanol ≈ benzene > toluene. The reasons for the good catalyst stability with alcohols as solvents are explained as follows [10,27]: the alcohol dehydrates to alkene, dialkyl ether and water over these acid catalysts. During the reaction, both the alcohol and the continuously produced water inhibit the formation of coke and polymers on the catalyst surface. Accordingly, the extent of deactivation of surface active sites is reduced. This argument was verified by feeding water together with the solvent into the reactor; the decay rate became significantly diminished for the reaction over Hβ zeolite [10]. Based on the above discussion, the best catalytic results are attained by using 1-hexanol as the solvent due to its highest ε-C selectivity and lowest decay rate. With Al-MCM-41, the polar solvent ethanol exhibited better catalytic results than nonpolar benzene [17].

3.2.2. Effect of catalysts

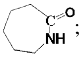
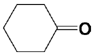
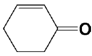
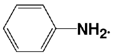
Table 2 shows the catalytic results for the reaction of CHO/1-$C_6H_{13}OH$ at 300 °C and W/Fc 74.6 g h/mol. The catalyst activity diminishes as follows: AlMCM-48(10) > AlMCM-48(20) > AlMCM-48(40) > SiMCM-48. Such a trend is consistent with the relative acid amounts of these catalysts. However, the catalyst decay rate enhances with Si/Al molar ratio of AlMCM-48; that implies catalyst deactivation is occurring at intermediate acid sites rather than weak acid sites. Fig. 7 shows the influence of the catalyst total acidity on catalytic results. Both the CHO conversion and the ε-C yield correlate well with the total acid amounts of these catalysts. In the reaction of CHO over H-β, HZSM-5 and alumina pillared montmorillonite, similar results were reported [10].

3.2.3. Effect of reaction temperature

The influence of reaction temperatures on the catalytic reaction of CHO/C_6H_6 over AlMCM-48(20) was studied as illustrated in Fig. 8. An increase of reaction temperature enhances the CHO conversion with concomitant decrease in both the ε-C selectivity and the catalyst deactivation. For the reaction at 350 °C and 4 h time on stream, the CHO conversion and the ε-C selectivity are 94.2% and 78.1%, respectively. With Al-MCM-41(25), the corresponding values are 78.7% and 70.8% [17]. Therefore, AlMCM-48(20) exhibits better catalytic performance than Al-MCM-41(25).

Table 2
Catalytic results for the reaction of CHO/1-$C_6H_{13}OH$ at 300 °C and W/Fc 74.6 g h/mol

Catalysts	Conversion[a] (mol%)	Selectivity[a] (mol%)				
		ε-C	HEN	CHA	CHE	AN
SiMCM-48	10.6/4.7	77.0/91.1	11.2/3.1	0/0	11.8/5.8	0/0
AlMCM-48(40)	80.9/45.7	91.7/90.3	4.7/5.4	1.6/1.9	0.9/1.6	1.1/0.8
AlMCM-48(20)	94.5/71.7	82.8/86.6	11.3/9.0	4.2/3.0	0/0	1.7/1.4
AlMCM-48(10)	92.8/77.9	88.1/91.6	8.5/4.2	1.7/1.9	1.0/1.9	0.7/0.4

[a] Time-on-stream: 7.5 min (left) and 210 min (right); ε-C:  ; HEN: $CH_2CH(CH_2)_3CN$; CHA: ; CHE: ; AN: .

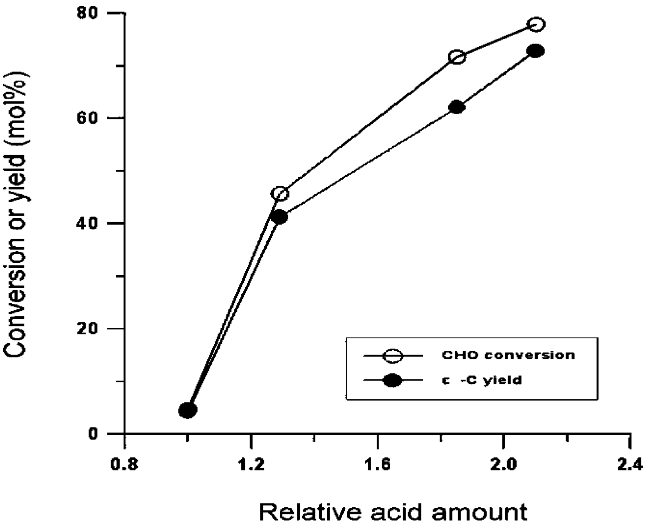


Fig. 7. Influence of total acid amount of catalysts on catalytic results. Conditions: CHO/1-$C_6H_{13}OH$; 300 °C; *W*/Fc 74.6 g h/mol; time-on-stream 210 min.

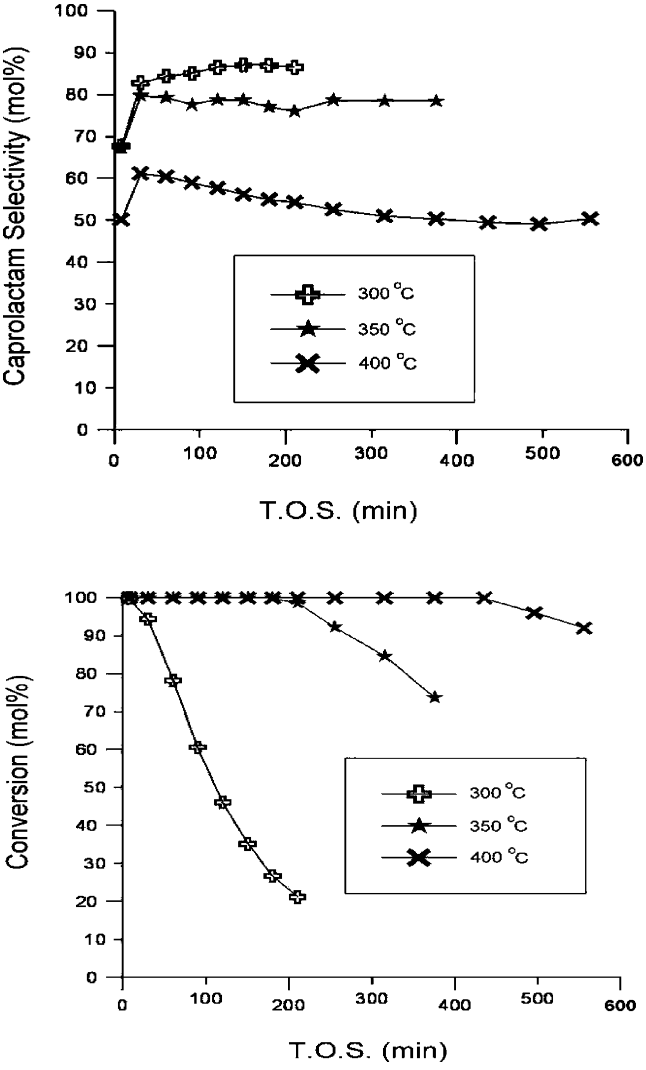


Fig. 8. Influence of reaction temperature on catalytic results. Conditions: AlMCM-48(20); CHO/C_6H_6; *W*/Fc 74.6 g h/mol.

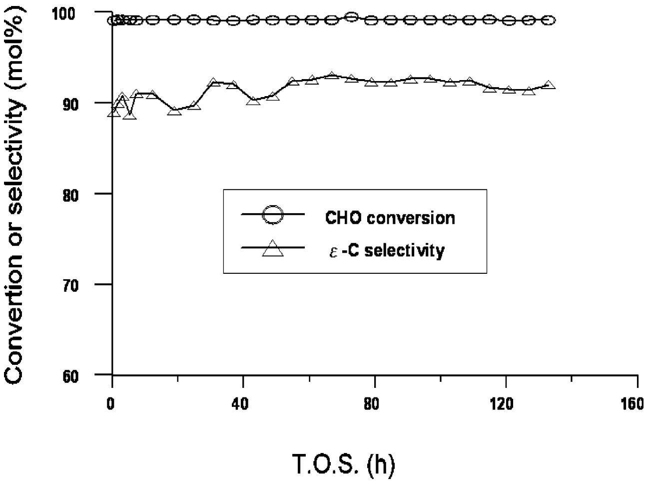


Fig. 9. Catalytic results for the reaction of CHO/1-$C_6H_{13}OH$ over AlMCM-48(10) at 350 °C and *W*/Fc 74.6 g h/mol.

3.2.4. The optimum conditions

Based on the above results, the optimum reaction conditions are proposed as follows: AlMCM-48(10), 1-hexanol, 350 °C and *W*/Fc 74.6 g h/mol. Fig. 9 displays the catalytic performance under these conditions. The CHO conversion and the ε-C selectivity attain larger than 99% and 90%, respectively, during at least 130 h process time. In the reaction of CHO/C_2H_5OH over Al-MCM-41(25) at 350 °C and *W*/Fc 74.6 g h/mol, the CHO conversion and the ε-C selectivity are 63.9% and 90.5%, respectively, at 26 h process time [17]. Apparently, AlMCM-48(10) shows much better catalytic results than Al-MCM-41(25) under these reaction conditions. The excellent catalytic results on this catalyst are attributed to its large surface area and three-dimensional mesopore channels as well as the weak and intermediate acidity. Accordingly, AlMCM-48(10) is a potential catalyst for the synthesis of ε-C.

4. Conclusions

In this work, the following conclusions are obtained:

- Both calcined samples of SiMCM-48 and AlMCM-48(*X*) exhibit the characteristic structure of mesoporous molecular sieves MCM-48.
- A decrease of the Si/Al molar ratio in AlMCM-48 results in the decrease of surface area and the increase of acid amounts. Both the CHO conversion and the ε-C yield correlate well with the catalyst total acid amount.
- In the reaction of CHO, increasing reaction temperatures enhances the CHO conversion with concomitant decrease of both the ε-C selectivity and the catalyst decay.
- The catalyst deactivation by using different solvents follows the order of benzene > toluene > ethanol > 1-hexanol.

- AlMCM-48(10) is an excellent catalyst for the synthesis of ε-C from CHO at 350 °C and *W*/Fc 74.6 g h/mol; the CHO conversion and ε-C selectivity attain higher than 99% and 90%, respectively, during at least 130 h process time.

Acknowledgement

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