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Improvements in the Beckmann rearrangement process by using highly selective mesoporous catalysts

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The Beckmann rearrangement of cyclohexanone oxime (CHO) into e-Caprolactam (e-C) at 300–380 °C and W/F = 1–60 gh/mol over a Al-MCM-41 catalyst was studied in a flow reactor at atmospheric pressure. Different reaction conditions as well as the nature of the solvents employed in the feed were evaluated. The e-C was the main product on the whole reaction conditions, but temperatures above 360 °C favored its decomposition. A reaction pathway was proposed in order to explain the results obtained at 360 °C. The stability and the possibility of recycling of the catalyst were checked by XRD, N_2 adsorption, FTIR, pyridine adsorption coupled with FTIR and catalytic activity tests. Thus, the catalyst could be used during 3600 min and then recovered and reused three times without significant changes in the active species, catalytic activity and e-C yield. In addition, a modification in the operating conditions, which consisted in pretreating the catalyst with 1-hexanol, allowed to improve the yield to caprolactam by blocking the terminal silanols responsible of the byproduct formation. Thus, the better catalytic performance was observed at 350 °C and W/F = 40 gh/mol, immediately after a catalyst pretreatment with 1-hexanol during 3 h with 1-hexanol, which was also used as reaction solvent. Such conditions allowed us to achieve a high CHO conversion (95%) with a e-C selectivity of around 100%, improving thus results previously reported.

1. Introduction

Over the past years, new policies of sustainable development for the chemical industry are being implemented in order to reconcile the economic activities with environmental protection. However, most commercial production of e-Caprolactam (e-C), starting monomer for the production of nylon-6, is carried out via the classical cyclohexanone oximation and Beckmann rearrangement route in liquid phase. This process is ecologically and economically questionable, due to it is energy intensive and generates considerable wastes [1]. For this reason, alternative paths for the production of e-C that provide few-steps and low cost, an effective production and environmentally friendly, are required. In this sense, the vapor-phase rearrangement of cyclohexanone oxime (CHO) to e-C has been investigated for a wide range of solid catalysts among which the M41S mesoporous materials have focused attention [1–7]. On the other hand, some research groups have also studied how reaction conditions such as temperature, presence of different solvents in the feed, reaction time, etc. affect the e-C yield and the lifetime of the catalyst [1,3,5,8–12]. Thus, Conesa et al. [1] established that the amount of by-products decreases with the increase of the temperature with a concomitant increase in e-C production even up 450 °C. On the contrary, others authors [3,10] reported that, at high temperatures, selectivity to the by-products is increased due to partial decomposition of e-C. Therefore, as it can be seen, opposing views can be found in the literature, so that more research is required for understanding this reaction.

On the basis that, as it was reported by us [6–8], weakly acidic hydroxyls present in silanol nests of the Al-MCM-41 are the actually active sites for the selective rearrangement of CHO toward e-C, in the present work, we have deepened the study of this process searching to optimize the reaction conditions in order to improve the results reported up date. Thus, we analyzed the effect of the reaction temperature, the presence of different solvents in the feed, the contact time (W/F) and the reaction time on the catalytic results. In addition, the catalytic performance, including stability over time on stream and reusability, were investigated. Finally, a modified operating condition was explored in order to increase the selectivity into e-C.

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2. Experimental

2.1. Synthesis

The synthesis of Al-MCM-41 material evaluated in this work was previously reported by us [6,7,13]. According this, cetyltrimethylammonium bromide (CTABr, Merck, 99%) was dissolved in H_2O–NaOH solution and after heating (35–40 °C) to dissolve the surfactant, the tetraethoxysilane (TEOS, Aldrich 98%) was added and stirred for 30 min. After the sodium aluminate (Johnson Matthey) addition, the synthesis gel (molar composition: Si/Al = 20, NaOH/Si = 0.50, CTABr/Si = 0.12 and H_2O/Si = 132) was stirred at room temperature for 7 h and hydrothermal treated at 100 °C for 6 days. The final solid was filtered, washed with distilled water and dried at 60 °C overnight. To remove the template, the sample was heated (heating rate of 2 °C/min) under N_2 flow up to 500 °C and kept at this temperature for 6 h; it was then calcined at 500 °C under air flow for 6 h. The catalyst was named as Al-M(20), where "20" is the Si/Al initial molar ratio.

2.2. Characterization

The fresh catalyst and after using in the catalytic cycles was characterized by XRD, N_2 adsorption and FT-IR and adsorption of pyridine coupled to FT-IR spectroscopy.

The (XRD) X-ray diffraction patterns were recorded in air at room temperature on a Philips PW 3830 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) in the range of 2θ from 2° to 7°.

Specific surface areas were measured using a Pulse Chemisorb equipment by single point at $P/P_0 = 0.3$ through the BET method. The samples were previously heated for 1 h at 300 °C under N_2 flow.

Infrared analysis of the samples was recorded on a JASCO 5300 FT-IR spectrometer in the 400–1600 cm^{-1} range, named the fingerprint zone of the material, for the KBr-pelletized samples. To examine the presence of silanol groups on the samples, the hydroxyl zone of the FT-IR spectra has been analyzed. For this aim, self-supported wafers of the samples were prepared, placed in a thermostatized cell connected to a vacuum line and evacuated for 7 h at 400 °C under a dynamic vacuum; residual pressure was smaller than 10^{-3} Pa. After cooling to room temperature, the FT-IR spectrum of each sample was recorded (background spectrum). In addition, in order to evaluate the strength and type of acid sites, FT-IR spectral measurements of pyridine adsorbed on the samples were performed. Thus, after the background spectrum was obtained, the solid wafer was exposed to pyridine vapors until saturate the system to 46 mm Hg at room temperature. Then, the spectrum of the adsorbed pyridine was recorded after the pyridine excess was desorbed by evacuation for 1 h at room temperature. It is noteworthy that in order to correctly evaluate the changes in the absolute value of the intensity of the relevant signals all spectra were normalized with respect to the wafer mass used for each measurement.

2.3. Catalytic reactions

The catalytic reactions were carried out in a down flow fixed bed tubular glass reactor (i.d. = 8 mm and 35 cm length) at atmospheric pressure using 0.2 g of the catalyst. The reactor was placed inside a temperature controlled furnace in the 300–380 °C range. A solution of 10 wt.% CHO in toluene, ethanol or 1-hexanol was fed using a syringe pump and nitrogen was used as the carrier gas (30 mL/min). The contact time W/F, referred to the weight of catalyst (g) over the feed rate of CHO (mol/h), was modified between 1 and 60 gh/mol. To check the Al-M(20) recycling ability, the influence of time on stream (TOS = 15–3600 min) over the catalytic activity was studied and several recycling experiments were carried out. Finally, in an additional experiment, the catalyst was pretreated with 1-hexanol vapor at 350 °C for 3 h and subsequently evaluated in the Beckmann rearrangement reaction at 350 °C.

The reaction products and unconsumed reactants were condensed and collected in a properly designed system in order to minimize the loss of organic vapors. In addition, under steady state, we did not observe an apparent net accumulation or depletion of mass in the system, that is, the total mass entering the system (total mass at start) was practically equal to the total mass leaving system (total final mass).

The samples were analyzed using a Perkin Elmer gas chromatograph (Clarus 500) with a capillary column and a flame ionization detector (FID). The product identification was done by GC–MS Perkin Elmer (Clarus 560S). Also the reaction products were analyzed by comparison with chromatographic standards. The conversion was expressed in moles% and the yields calculated as: cyclohexanone oxime conversion × selectivity to reaction products/100.

3. Results and discussion

3.1. Effect of the reaction conditions on the catalytic results

Before testing the catalytic activity and in order to check the reactant stability, blank experiments without catalyst employing 1-hexanol as solvent (solution of 10 wt.% CHO) were carried out in the 300–380 °C temperature range and with a flow rate of 5.6 mL/h. No changes in the CHO molecule were observed.

The effect of the temperature on the CHO conversion and yield to reaction products in the 300–380 °C range over Al-M(20), chosen according to the catalytic results presented in Refs. [6,7], at W/F 40 gh/mol and employing 1-hexanol as solvent is presented in Fig. 1. As it is observed, e-C is the major product and the by-products include cyclohexanone (CH), aniline (AN), 5-hexenenitrile (HEN) and others, which is consistent with other studies already reported [14,15]. The transformation of the oxime was rapid and reached nearly 100% at 380 °C. The e-C yield increased up to 83% when the temperature increased up to 360 °C and then decreased at higher temperatures. These results are in good

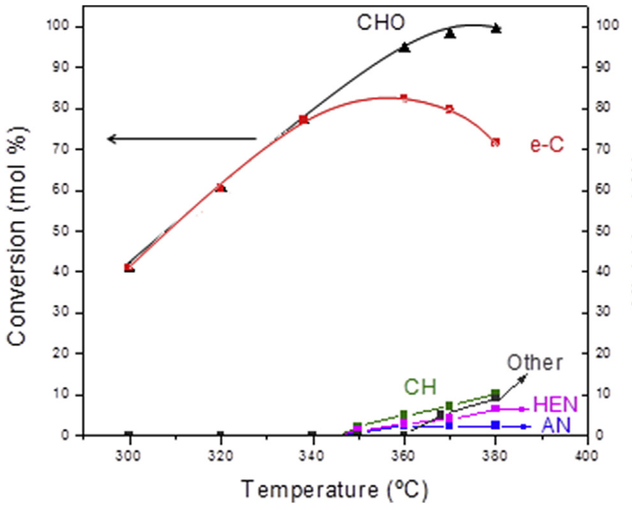


Fig. 1. Effect of the temperature on the CHO conversion and yield to reaction products over Al-M(20). Reaction conditions: W/F = 40 gh/mol, TOS = 15 min, 1-hexanol as solvent.

agreement with those previously reported [4,5] where a decrease in the e-C selectivity was found when the reaction temperature increased. On the other hand, by-products appeared at 350 °C and increased with temperature with a concomitant increase in e-C production up to around 360 °C, beyond which only the by-products yield increased. This behavior is probably due to an increase in the side reactions such as hydrolysis, dehydration and fragmentation of CHO [10,14] as well as to the decomposition of the e-C on the catalyst surface at higher temperatures. Additional experiences were performed in order to analyze the influence of the temperature on the e-C decomposition. Thus, the reactions were carried out for a 10% e-C in 1-hexanol feed, at W/F = 40 gh/mol, in the 340–380 °C range and over the Al-M(20) catalyst. As it could be observed, the e-C decomposed only above 360 °C verifying thus its stability up to this temperature. Therefore, until 360 °C, the by-products appearance can be attributed to side reactions such as hydrolysis, dehydration and fragmentation of CHO. Meanwhile, at higher temperatures, the decrease in the e-C yield with the concomitant increase in the by-products production is due to the e-C decomposition on the catalyst surface. Finally, the results indicate that below 360 °C the main reaction is the Beckmann rearrangement to e-C and beyond this temperature some by-products are also formed due to the decomposition of e-C.

Recently, Conesa et al. [1,16] reported a reaction temperature of 425–450 °C as optimum for obtaining high e-C selectivities in the gas phase Beckmann rearrangement in presence of mesoporous silica alumino phosphate and Al-B-MCM-41 catalysts. Nevertheless, in our present investigations, almost 95% of CHO conversion and 83% of yield to e-C were achieved at far lower reaction temperatures (around 360 °C).

Fig. 2 shows the influence of contact time (W/F) on the catalytic results at 360 °C and employing 1-hexanol as solvent. As the contact time increases up to 10 gh/mol, the CHO conversion increases dramatically to around 80%; thereafter, a continuous increase of CHO conversion with the W/F is observed with a lower slope. Similar trend is observed for the e-C yield, which appears as rearrangement product and is not decomposed at 360 °C in the W/F range studied. Thus, the CHO conversion and the e-C yield reached values of 97% and 85% respectively at W/F = 60 gh/mol.

Fig. 3 shows the reaction products yield versus CHO conversion at 360 °C, according to the standard optimum performance envelope technique [17]. As it is known, a product is regarded as primary if its formation has not been preceded by any intermediates in the gas phase, although many intermediate species may have existed on the catalyst surface. A secondary product is derived from a primary product in a similar sense. The initial selectivity of a product, given by the slope of the OPE at zero conversion, is nonzero for a primary product and zero for secondary or subsequent products. Thus, from Fig. 3, e-C (main reaction product), CH and HEN (by-product) appear as primary products, presenting nonzero initial slopes. In contrast, the zero initial slope observed for AN suggests that this compound is a secondary product [18]. From these results, we can propose, at 360 °C, the reaction mechanism shown in Scheme 1. According to this, e-C (major product), CH and HEN would be primary products arising from rearrangement, hydrolysis, dehydration and fragmentation of CHO and AN would be a secondary product formed from HEN. It should be noted here that, in the whole range of conversions, the e-C yield proportionally increases as the CHO conversion increases. Therefore, e-C is found to be a stable product which does not undergo secondary transformations at 360 °C. This feature has yet been corroborated by additional experiences which demonstrate that e-C is not catalytically decomposed at 360 °C, over the Al-M(20) catalyst.

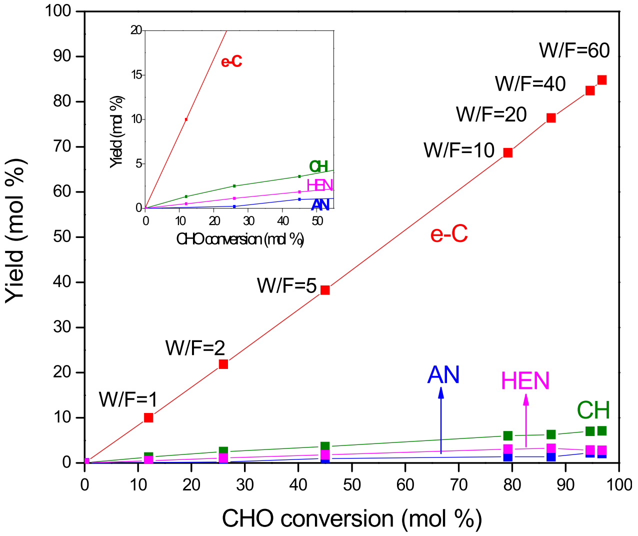


Fig. 3. Reaction product yield as a function of CHO conversion over Al-M(20). Reaction conditions: $T = 360$ °C, TOS = 15 min, 1-hexanol as solvent.

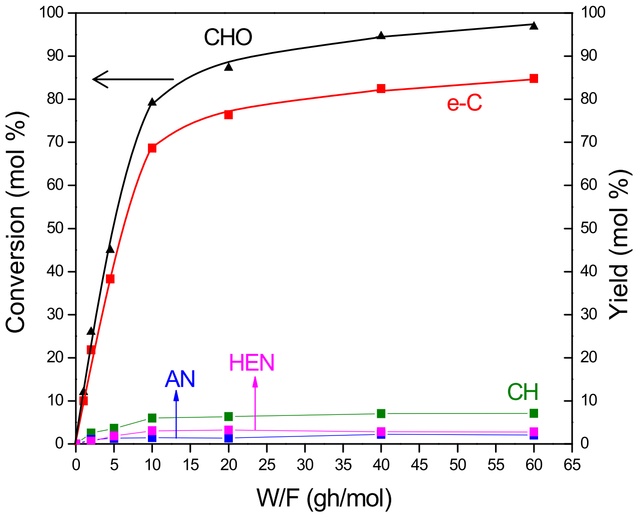
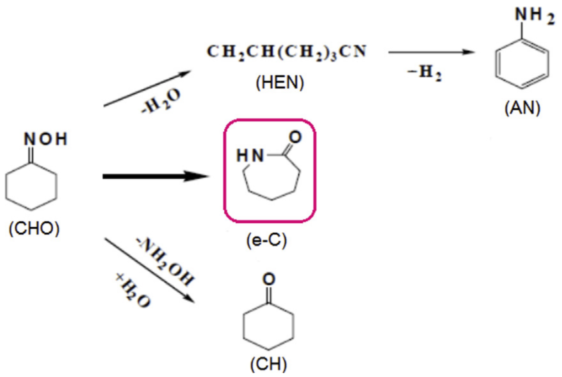


Fig. 2. Influence of contact time (W/F) on the catalytic results over Al-M(20). Reaction conditions: $T = 360$ °C, TOS = 15 min, 1-hexanol as solvent.

To investigate the nature of the solvent on the catalytic activity, nonpolar (toluene) and polar (1-hexanol and ethanol) solvents were utilized at 360 °C and W/F = 40 gh/mol over Al-M(20)



Scheme 1. Proposed reaction pathway for the CHO transformation over Al-M(20) at 360 °C and employing 1-hexanol as solvent.

Table 1
Influence of different solvents on the catalytic activity over Al-M(20). Reaction conditions: $T = 360$ °C, W/F = 40 gh/mol.

Solvent	CHO conversion (mol%)	Product yield (mol%)				
		e-C	CH	AN	HEN	Others
Toluene	100	8.38	21.71	5.71	2.54	61.66
1-Hexanol	94.57	82.47	7.78	2.24	2.04	–
Ethanol	61.93	34.15	10.26	4.65	3.41	9.46

(Table 1). Thus, although the initial CHO conversion decreases in the order of toluene > 1-hexanol > ethanol, the e-C yield is much higher by using 1-hexanol as compared with toluene and ethanol.

The catalytic performance observed by using 1-hexanol can be explained taking into account the effect of the alcohols as solvents during the reaction. In this sense, it is known that the most effective solvents in the Beckmann rearrangement reaction in vapor phase, using MFI type zeolites [19–21], are the short chain alcohols such as methanol and ethanol. These solvents increase the conversion and selectivity towards the formation of e-caprolactam. Some authors suggest that this effect is due to their ability to methylate terminal silanol groups, responsible of the formation of byproducts [19–21]. Likewise, such methylation would increase the silanol hydrophobicity, facilitating the rapid desorption of the lactam [22,23]. An opposite effect is observed in the conversion by using long chain alcohols over zeolite type catalysts [21]. Meanwhile, for materials of higher pore size, the 1-hexanol seems to be the best alternative [24–27]. This solvent blocks active centers of the catalyst that promote the formation of secondary products, producing an increase in the activity and selectivity to e-C. In contrast, by using short chain polar solvents such as methanol or ethanol, the cyclohexanone conversion and caprolactam selectivity decrease since these solvents can be competitively adsorbed on the acid centers of the catalyst, blocking the accessibility to the reagents [24–27]. Therefore, alcohols with different number of carbon atoms have different effects in terms of conversion and selectivity, depending on the type of material used as catalyst in the rearrangement reaction [11,21,25–27].

In the case of our mesoporous catalyst and in agreement with the literature, we think that the 1-hexanol reacts with the terminal silanols responsible for the side reactions to undesired by-products. The blocking of these species leads to high yield to e-C observed in this work when this alcohol is used as solvent. Likewise, the formation of coke and polymers on the catalyst surface during the reaction is inhibited and consequently the extent of deactivation of surface active sites reduced.

3.2. Stability and reusing of the catalyst

An important aspect to be studied in a catalytic process is the stability of the catalyst over the time on stream and the possibility of recycling. Then, the effect of time on stream (TOS) on the CHO conversion and e-C yield, over Al-M(20) at 360 °C and W/F = 40 gh/mol is shown in Fig. 4. As it can be seen, although the CHO conversion and e-C yield initially decreased, beyond a TOS = 180 min, the steady state seems be reached and both CHO conversion and e-C yield remained almost constant. In addition, in order to check the recycling ability of catalyst under the reaction conditions, three recycling experiments were carried out for Al-M(20). After each reaction, the catalyst was recovered, calcined at 500 °C and weighed for then to be reused. It should to be noted that a negligible difference in the catalyst mass was determined after each cycle, suggesting that the presence of non-volatile species adsorbed on catalyst surface, which could poison the active sites, is very low [13]. In addition, it is noteworthy that, for all the cycles, the CHO conversion decreased in the first 180 min. and then it maintained an almost constant value under steady state of around 76% until 3600 min. This value was not significantly modified from the first to the third cycle. The e-C yield showed the same behavior on the three catalytic cycles.

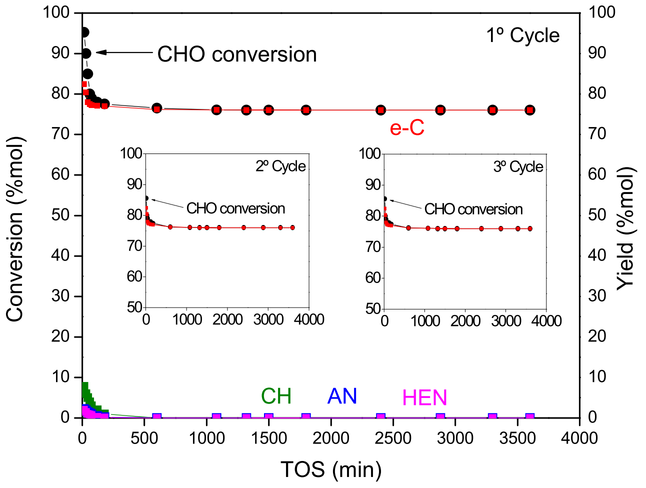


Fig. 4. Effect of time on stream (TOS) on the CHO conversion and e-C yield over Al-M(20). Reaction conditions: $T = 360$ °C, W/F = 40 gh/mol, 1-hexanol as solvent.

Then, the catalyst used for three catalytic cycles of 3600 min process time each one, was characterized by XRD, N_2 adsorption, FT-IR and FT-IR-Py after calcination.

The XRD pattern of the reused catalyst indicates the retention of the mesoporous structure after the three cycles (Fig. 5A). However, although the average pore diameter was remained constant around 2.74 nm, a decrease in the specific area and pore volume from 1242 to 924 m^2 g^{-1} and from 0.83 to 0.72 cm^3/g, respectively, was observed. This feature is generally indicative of the blockage of some mesopores with certain loss of structural ordering. In addition, a comparison of the FT-IR spectra (Fig. 5B) of the reused and fresh catalyst gives account for a slight decrease, after reusing, in the area of the 960 cm^{-1} peak representative of the incorporation of Al in tetrahedral coordination replacing to Si into the framework [6].

As it was reported in our previous papers [6,7] FT-IR spectra of our Al-MCM-41 catalysts in the hydroxyl range exhibited a broad and intense band, attributed to hydrogen bonded hydroxyl groups [28,29], that can be deconvoluted into two contributions at about 3700 and 3590 cm^{-1}. These two contributions are assigned to terminal silanol groups and silanol nests, respectively, generated at framework defect sites. Meanwhile, FT-IR spectra of adsorbed pyridine over our materials shows bands at 1597 and 1447 cm^{-1} assigned to pyridine bonded to silanol groups whose hydroxyls are not capable to protonate pyridine [6,7,29–35] as well as to some contribution to from pyridine bonded to Lewis acid sites, arising from the presence of extra-framework aluminum oxide [6,7,36–38]. Meanwhile, the presence of a band at 1632 cm^{-1} is attributed to pyridine interacting with acid hydroxyls [6,7,38–40], such as the nest silanols associated with the 3590 cm^{-1} band.

In this work, FT-IR spectra of self-supported wafers of the reused and fresh samples in the hydroxyl zone (Fig. 6A) and of pyridine adsorbed on the same at room temperature (Fig. 6B), reveal a slight decrease in the amount of nest silanols (band at 3590 cm^{-1}) and consequently in the acidity (band at 1632 cm^{-1}) of reused catalyst with respect to the fresh catalyst [6,7,13]. Such changes are clearly reflected in the integrated absorbance ratios, used to the normalization purpose, between the following bands: 3590 cm^{-1}/ 2100–1500 cm^{-1} region (corresponding to overtones and

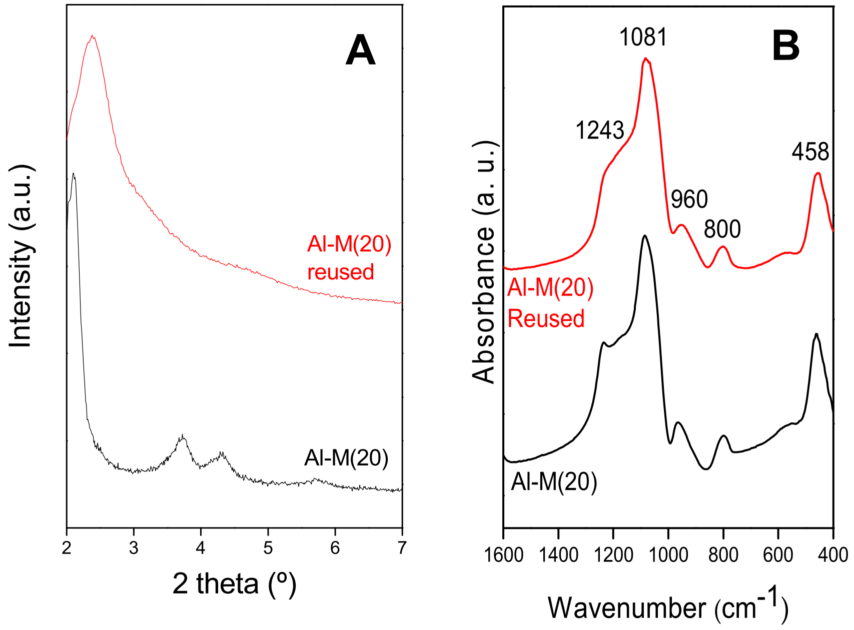


Fig. 5. XRD pattern of the reused and fresh catalyst (A) and FT-IR spectra in the 400–1600 cm^{-1} range of the reused and fresh catalyst (B).

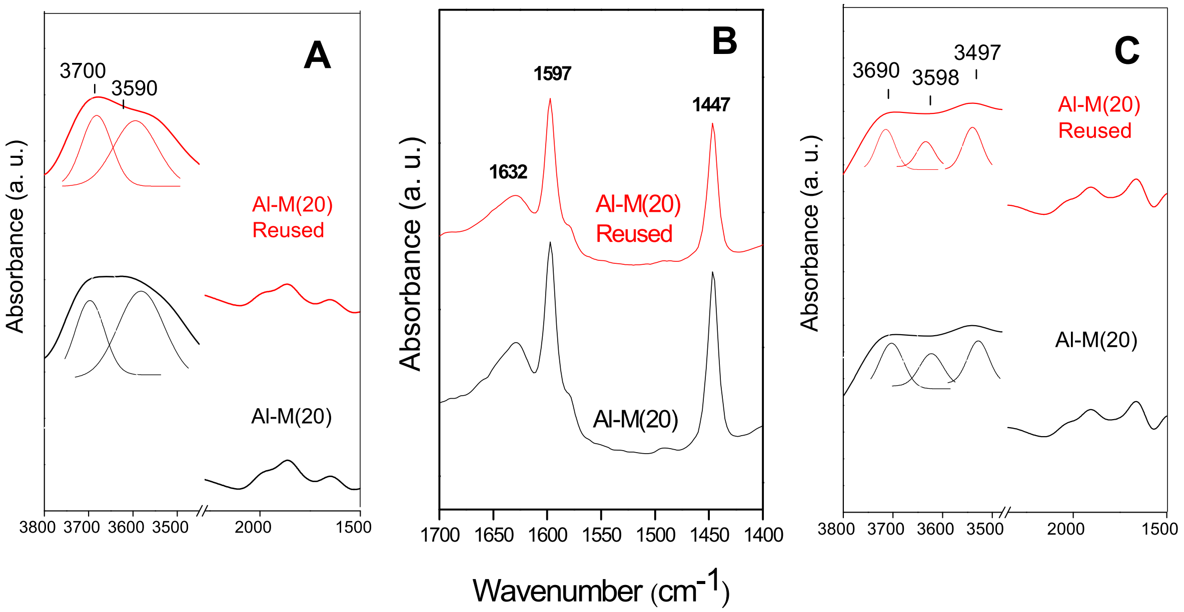


Fig. 6. FT-IR spectra in the hydroxyl region of the reused and fresh catalyst (A); FT-IR of pyridine adsorbed at room temperature on the reused and fresh catalyst in the 1700–1400 cm^{-1} region (B) and in the hydroxyl region (C).

combination modes of the silica network) and 1632 cm^{-1}/1447 cm^{-1}. These $A_{3590/(2100-1500)}$ and $A_{1632/(1447)}$ values are summarized in Table 2.

On the other hand, Fig. 6C shows the modification of the OH stretching patterns of silanols (hydroxyl region) when interacting with adsorbed pyridine on the reused and fresh catalysts at room temperature. Comparing the spectra shown in Fig. 6C with respect to those in Fig. 6A, it is observed that the adsorption of pyridine causes a decrease in the area of the band at 3590–3598 cm^{-1} corresponding to the nest silanols, due the formation of pyridinium ions. The other band at 3690–3700 cm^{-1} corresponding to terminal silanol groups is also decreased. This fact would lead to the appearance of a band at approximately 3497 cm^{-1}. This presence can be explained by a shift of a part of the IR band corresponding to terminal silanols to lower frequencies owing to hydrogen bonding between pyridine molecules and these OH groups which are not capable to protonate pyridine. The integrated absorbance ratios of these bands are also shown in Table 2.

Nevertheless, taking into account the above results, which show light variations in the physicochemical and catalytic properties of the catalyst after three catalytic cycles, it is possible to suggest that the most of sites responsible of the Beckmann rearrangement remain available and active for the reaction.

However, in order to elucidate the possible cause of deactivation of catalyst observed during the first 180 min and taking into account the effect of the solvent on the reaction, a pretreatment of the

Table 2
Integrated absorbance ratios of IR bands for the reused and fresh catalyst.

		Al-M(20)	Al-M(20) reused
FT-IR spectra in the hydroxyl region	$A_{3700/(2100-1500)}$[a]	1.84	1.81
	$A_{3590/(2100-1500)}$[a]	2.21	2.05
FT-IR of pyridine adsorbed at room temp.	$A_{1632/(1447)}$[b]	0.59	0.55
	$A_{3700/(2100-1500)}$[c]	1.61	1.58
	$A_{3590/(2100-1500)}$[c]	1.24	1.18

[a] From Fig. 6A.
[b] From Fig. 6B.
[c] From Fig. 6C.

catalyst with 1-hexanol for 3 h was performed immediately before the start of reaction. In this regard, we think that the selectivity to e-C can be initially improved if the terminal silanols appear blocked in a suitable way from the start of reaction.

In this sense Sato and coworkers [41] have already reported a modification of terminal silanols on the surface of a high-silica MFI by treating it with chlorotrimethylsilane vapor where the silanols are converted to trimethylsilyl groups. Another authors have reported interesting results by using a zeolite pretreated with methanol for enhance the selectivity to caprolactam [9,12,23].

Here, we previously investigate the effect of a pretreatment with 1-hexanol on the catalyst surface properties by FT-IR spectroscopy. Thus, the catalyst, previously degassed at 350 °C for 1 h in vacuo, was treated with 1-hexanol vapor at 350 °C for 3 h and evacuated for 1 h at the same temperature. Fig. 7 shows FT-IR spectra of catalyst not treated (as reference) and treated with 1-hexanol.

As it can be observed, the nontreated catalyst shows a IR absorption at 3700 cm^{-1} that is attributed to terminal silanols and other around 3590 cm^{-1} that is assigned to nest silanols [6,7,13]. Then, the terminal silanols absorption (normalized with respect to the 2100–1500 cm^{-1} region) decreased in a 26% for the 1-hexanol treated catalyst and new IR absorptions were originated from O–R groups in the 3000–2800 cm^{-1} and 1200–1000 cm^{-1} regions. The jagged peak in the first region with maxima at 2940 and 2860 cm^{-1} is attributed to alkyl CH asymmetric and symmetric stretching vibrations characteristic of tetrahedral carbon–hydrogen bonds [11,42]. The second region analyzed is a part of the called "fingerprint region". Here, a band of medium intensity at 1016 cm^{-1} characteristic of the C–O stretching vibration, can be distinguished [43]. Such features clearly show that 1-hexanol reacts with terminal silanols leading to formation of alkoxy species over the catalyst surface, according to Scheme 2. In addition, the normalized IR absorption around 3590 cm^{-1} remained without changes for the treated catalyst, indicating that most of the nest silanols are not affected by 1-hexanol vapor and stays available for the rearrangement reaction.

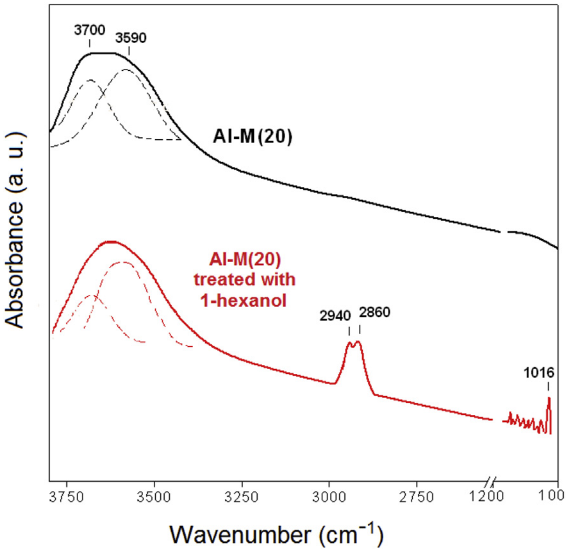
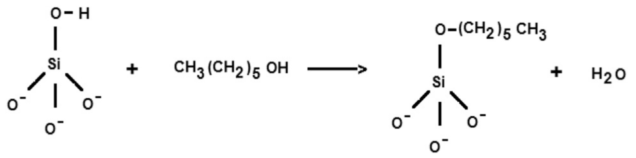


Fig. 7. FT-IR spectra in the hydroxyl region of catalyst not treated and treated with 1-hexanol.



Scheme 2. Formation of surface alkoxy species on the catalyst treated with 1-hexanol.

Subsequently the Al-M(20) material pretreated with 1-hexanol for 3 h was catalytically evaluated, where the mixture of 1-hexanol with 10 wt.% CHO was fed to reactor at 350 °C and W/F = 40 gh/mol immediately after the pretreatment. The results are shown in Fig. 8. As it can be seen, the activity does not initially decay, and both CHO conversion and e-C yield remain constant from the beginning of the reaction. These results, consistent with FT-IR analysis of the catalyst treated with 1-hexanol, confirm that the modification of terminal silanols by 1-hexanol plays a very important role to improve the catalytic activity. Thus, when 1-hexanol vapor is initially fed in the reaction system, the terminal silanols being the active sites for the formation of by-products, are effectively covered by this solvent, ensuring a high selectivity toward the Beckmann rearrangement.

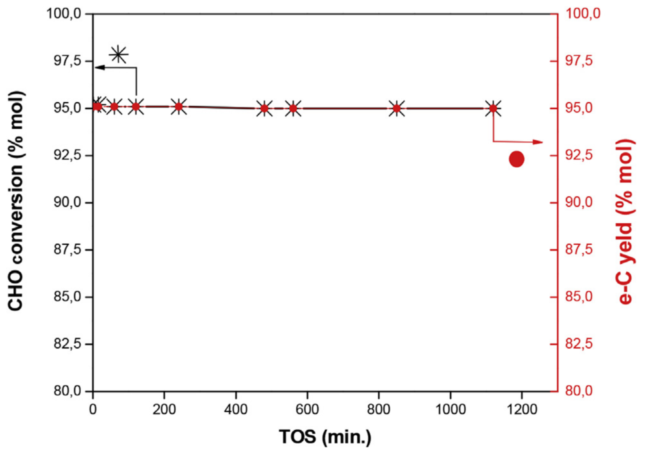


Fig. 8. Effect of time on stream (TOS) on the CHO conversion and e-C yield over Al-M(20) treated with 1-hexanol vapor for 3 h. Reaction conditions: $T = 350$ °C, W/F = 40 gh/mol and 1-hexanol as solvent.

In this manner, with the implementation of this new operating condition (pretreatment with 1-hexanol) the Al-MCM-41 catalyst revealed a excellent catalytic performance, showing high conversion of cyclohexanone oxime (~95%), high stability, lifetime and reusability. Likewise no formation of coke and caprolactam selectivities around 100% were observed, avoiding following purifications. All these features lead to an interesting and workable process to be carried out industrially. In addition the catalytic results presented here improve the patent published by Sumitomo Chemical Co. [8] and the results reported by Ichihashi and Sato [9] (CHO conversion ~99% and lactam selectivity ~92%, using methanol as solvent).

4. Conclusions

The rearrangement of CHO to e-C was studied by using Al-M(20) as catalyst in the 300–380 °C temperature range, $W/F = 1–60$ gh/mol and $TOS = 0–3600$ min, and the feed was prepared by dissolving CHO in various solvents: toluene, ethanol, and 1-hexanol. By increasing temperature, the CHO conversion quickly achieved nearly 100% at 380 °C. e-C was the major product on the whole temperature range studied and the by-products include cyclohexanone (CH), aniline (AN), 5- hexenenitrile (HEN) and others. The e-C yield reached a maximum value of 83% at 360 °C and then decreased at higher temperatures due to its decomposition on the catalyst surface. By varying W/F at 360 °C and according to the OPE curves, the e-C (major product), CH and HEN (yields lower than 10%) appear as primary products arising from rearrangement, hydrolysis, dehydration and fragmentation of CHO, while AN (yield lower than 3%) appears as secondary product formed from HEN. In addition, a new operating condition (catalyst pretreatment with 1-hexanol vapor) was explored in order to increase the e-C selectivity. Thus, an initial modification of catalyst with 1-hexanol played an important role in the Beckmann rearrangement reaction. Such solvent can block the terminal silanols, responsible of the generation of byproducts, leading to the formation of surface alkoxy species which was corroborated by FTIR. Meanwhile, the nest silanols remained active to selectively produce e-C. The quantification of the same by IR experiments supports this asseveration.

Moreover, the stability and reusability of the catalyst was tested. In this sense, the permanence of the active species on the fresh and used solids was also corroborated by FTIR of adsorbed pyridine. Finally, the Al-M(20) pretreated with 1-hexanol showed the highest catalytic performance at 350 °C, $W/F = 40$ gh/mol and by using 1-hexanol as solvent, exhibiting a CHO conversion of 95% and e-C selectivity around 100%. The high catalytic efficiency on Al-M(20) is attributed to its uniform mesopores and large specific area, as well as to its weakly acidic character arising from hydroxyl groups present at silanol nests on the catalyst surface.

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