



B-MCM-41 AS NANO-STRUCTURED CATALYST FOR THE IMPROVEMENT OF BECKMANN REACTION CONDITIONS

B-MCM-41 COMO CATALIZADOR NANOESTRUCTURADO PARA OPTIMIZACIÓN DE LAS CONDICIONES DE REACCIÓN DE BECKMANN

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Abstract

The Beckmann rearrangement of Cyclohexanone oxime at 300-380 °C and W/F = 20-60 g h/mol over a B-MCM-41 catalyst was studied at atmospheric pressure. The e-Caprolactam (precursor for nylon-6) was the major product on the whole temperature range studied and Cyclohexanone appeared as the main by-product and was generated probably due to the moderate acidity of these materials. The stability and the possibility of recycling of the catalyst were also analyzed. So, the catalyst could be used during 3600 min and then recovered and reused without significant changes in the active species. A reaction pathway was proposed in order to explain the results obtained. Finally, the better catalytic performance was observed at 320 °C and W/F = 40 g h/mol. Such conditions allowed us to achieve a Cyclohexanone oxime conversion of 54% with an e-Caprolactam selectivity of around 83%. Thus, under this mild reaction condition it could be achieved a high yield to e-Caprolactam with a low proportion of Cyclohexanone. This product mixture (e-Caprolactam and Cyclohexanone) may be separated by vacuum distillation; then the Cyclohexanone could be recycled by reaction with hydroxylamine to form again Cyclohexanone oxime (raw material for e-Caprolactam), marketed for the production of adipic acid, as adhesive in sealing PVC objects or as solvent in several industries.

Keywords: Beckmann rearrangement, reaction conditions, cyclohexanone oxime, catalyst stability, nano-structured catalyst.

Resumen

Se estudió el reordenamiento de Beckmann de ciclohexanona oxima a 300-380 °C y W/F= 20-60 g h/mol sobre un catalizador B-MCM-41 a presión atmosférica. La e-Caprolactama (precursor de nylon-6) fue el producto principal en todo el rango de temperaturas estudiado y la ciclohexanona apareció como principal subproducto (probablemente debido a la acidez moderada de estos materiales). También se analizó la estabilidad y la reutilización del catalizador. Así, el material podría ser usado durante 3600 min y luego recuperado y reutilizado sin cambios significativos en las especies activas. Se propuso un camino de reacción para explicar los resultados obtenidos. Finalmente, el mejor rendimiento catalítico se observó a 320 °C y W/F= 40 g h/mol. Estas condiciones permitieron lograr una conversión de ciclohexanona oxima del 54% con una selectividad a e-Caprolactama de aproximadamente 83%. Por lo tanto, bajo estas condiciones de reacción suaves podría alcanzarse un alto rendimiento de e-Caprolactama con una baja proporción de Ciclohexanona. Esta mezcla de productos (e-Caprolactama y Ciclohexanona) se puede separar por destilación al vacío, y así la Ciclohexanona podría ser reciclada y mediante reacción con hidroxilamina para formar ciclohexanona oxima (materia prima del reordenamiento de Beckmann), comercializada para la producción de ácido adípico, utilizada como adhesivo para sellar objetos de PVC o como disolvente en varias industrias.

Palabras clave: reordenamiento de Beckmann, condiciones de reacción, ciclohexanona oxima, estabilidad catalítica, catalizadores nano-estructurados.

1 Introduction

The conventional method of preparation of the e-Caprolactam (e-C) which is an important precursor for nylon-6, from Cyclohexanone oxime (CHO), results in the formation of a large amount of by-products.

Sumitomo Chemical Co. has combined a process of amoximation and subsequent vapour phase Beckmann rearrangement. Here, CHO is converted to e-C using a high-silica MFI zeolite instead of sulphuric acid as homogeneous catalyst in the conventional Beckmann reaction, Sato *et al.* (1986, 1998) and Conesa *et al.* (2006). Moreover in this process the reaction

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takes place between 350 and 400 °C, Izumi *et al.* (2007). Since this process is economically questioned by the high operating temperatures and catalyst deactivation, research on this field continues to be intense. Among the solid materials investigated, for this reaction MCM-41 appears as very interesting. These mesoporous materials exhibit high specific surface and a pore hexagonal structure with long-range ordering, Dai *et al.* (1998), Chaudhari *et al.* (2002), Martínez *et al.* (2006), Ramos-Ramírez *et al.* (2015) and Campelo *et al.* (2005). Moreover these materials can often exhibit a high concentration of sites catalytically active by incorporating heteroatoms into the siliceous framework. Thus, incorporation of foreign atoms in the framework of silica-based MCM-41 such as Al, Reddy *et al.* (1996), Ti, Gabelica *et al.* (1995), B, Trong On *et al.* (1995), Sayari *et al.* (1995), Chenite *et al.* (1995), Oberhagemann *et al.* (1995), Zhang *et al.* (2011) and Vaschetto *et al.* (2018), has been reported.

The substitution of Si by B during the synthesis of MCM-41 is expected to modify the acidic properties of these materials and therefore their catalytic properties. Many reports are available in the literature on synthesis of B-MCM-41. In a previous report, we have synthesized B-MCM-41 materials with different contents of boron. On the basis that acid hydroxyls exist in the silanol nests of materials B-MCM-41, Vaschetto *et al.* (2018), these species could be proposed as the active sites for the selective rearrangement of CHO toward e-C.

Herein, we wish that mesoporous borosilicate (B-MCM-41) behave as an efficient nano-ordered solid catalyst for the reaction of Beckmann rearrangement, given the presence of possible active sites such as silanol nests. In the present work, we have evaluated B-MCM-41 catalysts for this process in order to search optimized reaction conditions. Thus, the effect of the reaction temperature and the contact time on the catalytic results were analyzed. In addition, the catalytic performance, including stability over time on stream (TOS) and reusability, was investigated. The results of this study prove the feasibility of the reaction under smooth reaction conditions which minimized by-product formation and coke, generating a Caprolactam improved yield.

2 Experimental

2.1 Synthesis

The mesoporous materials (B-MCM-41) were prepared by hydrothermal synthesis using cetyltrimethylammonium bromide (CTABr, Merck, 99%) as template and tetraethoxysilane (TEOS, Aldrich, 98%) as silicon source. Ammonium hydroxide (NH₄OH, Cicarelli, 30%) was used for hydrolysis and pH adjustment, and boric acid (H₃BO₃, Cicarelli) was used as source of boron. The catalysts were synthesized from a synthesis gel of molar composition: OH/Si = 0.50, CTABr/Si = 0.12, H₂O/Si = 132 and Si/B = 10-80. A typical synthesis was reported by us else were, Vaschetto *et al.* (2018). The final solid was filtered, washed with distilled water and dried at 60 °C overnight. To remove the template, the samples were heated (heating rate of 2 °C/min) under N₂ flow up to 500 °C and kept at this temperature for 6 h; they were then calcined at 500 °C under air flow for 6 h. The samples obtained were named as B-M(x), where "x" is the Si/B initial molar ratio.

2.2 Characterization

The X-ray diffraction (XRD) patterns were recorded in air at room temperature on a Philips PW 3830 diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å) in the range of 2θ from 1.5° to 7°. Specific surfaces were measured using a Pulse Chemisorb equipment by single point at P/P₀ = 0.3 through the BET method. The samples were previously heated for 1 h at 300 °C under N₂ flow. The Boron content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), using a VISTA-MPC CCD Simultaneous ICP-OES-VARIAN.

Infrared analysis of the samples was recorded on a JASCO 5300 FT-IR spectrometer. The FT-IR spectra in the lattice vibration region were performed using the KBr 0.05% wafer technique. In addition, in order to evaluate the strength and type of acid sites, FT-IR spectral measurements of pyridine adsorbed on the samples were also performed.

2.3 Catalytic reactions

The catalytic reactions were carried out in a down flow fixed bed tubular glass reactor (i.d.= 8mm and 35 cm length) at atmospheric pressure using 0.2 g of the catalyst.

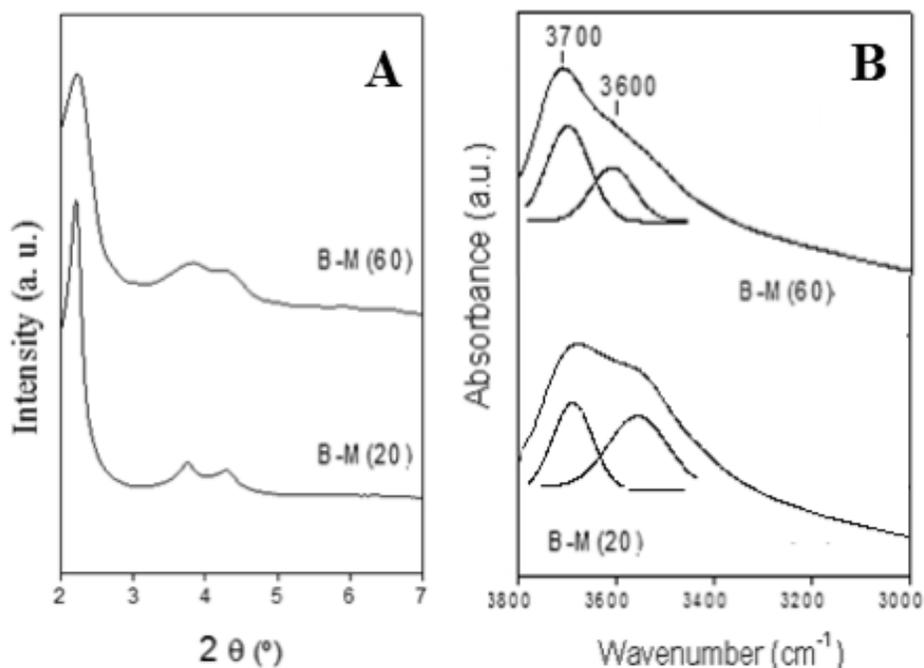


Fig. 1. A) XRD patterns for the samples B-M(60) and B-M(20). B) FT-IR spectra in the hydroxyl stretching region after degassing at 400 °C for B-M(60) and B-M(20).

The reactor was placed inside a temperature controlled furnace in the 300-380 °C range. A solution of 10 wt.% CHO in 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 20 and 60 g h/mol. To check the selected material 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. 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 x selectivity to reaction products/100.

3 Results and discussion

The characterization of these materials was shown by us elsewhere, Vaschetto *et al.* (2018). According to the XRD patterns, shown in Figure 1A for representative samples, mesoporous structures with characteristic peaks corresponding to the (100), (110) and (200) planes, were obtained.

It is known that there are several types of surface silanol groups with different acidic properties: terminal, geminal, vicinal and nests, Izumi *et al.* (2007), Hölderich *et al.* (1997), Ichihashi (2002), Jentys *et al.* (1999) and Zholobenkoet *et al.* (2001). The Figure 1B depicts the FT-IR spectra of the samples more representative in the hydroxyl range that were deconvoluted into two contributions at about 3700 and 3590 cm⁻¹.

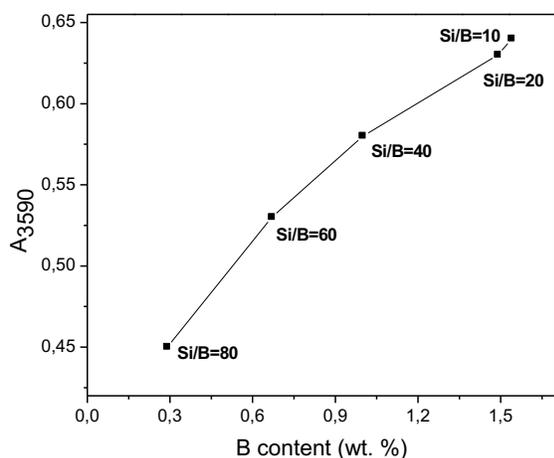


Fig. 2. A_{3590} integrated absorbance vs. B content (wt. %).

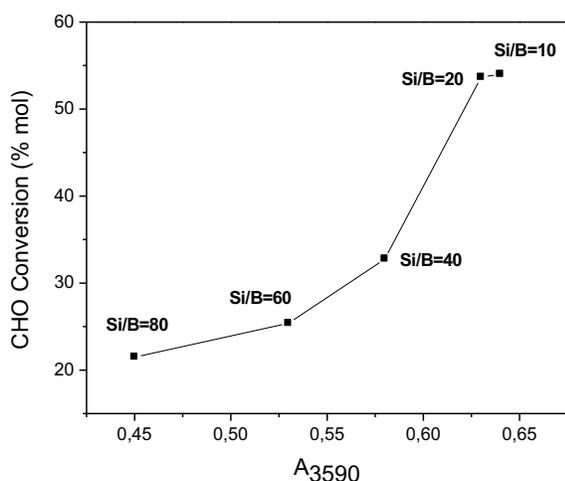


Fig. 3. CHO conversion vs. A_{3590} integrated absorbance. Reaction conditions: Temperature= 320°C, W/F= 40 g h/mol, TOS= 15 min and 1-hexanol as solvent.

These have been assigned to hydrogen bonded to terminal/vicinal silanol groups (3700 cm^{-1}) and silanol nests (3590 cm^{-1}), generated at framework defective sites. Comparing the integrated absorbances of this last band (A_{3590}) for samples synthesized with initial molar ratios in the synthesis gel Si/B= 10-80 (Figure 2), it is possible to observe that the relative proportion of silanol nests increases for the samples with higher B contents. This fact indicates that increasing the B amount inside the framework, the formation of structural defects is increased, Jentys *et al.* (1999), leading to a higher proportion of silanol nests, Vaschetto *et al.* (2018).

In this work, initially we show the catalytic results for this reaction over B-MCM-41 catalysts synthesized with different B contents in the synthesis gel, which are able to introduce different concentrations of silanol nests into the structure. These materials were evaluated under mild reaction conditions (temperature= 320°C, W/F= 40 g h/mol, TOS= 15 min and 1-hexanol as solvent). Thus, the CHO conversion vs. the integrated absorbance of the IR band at 3590 cm^{-1} (A_{3590} , associated to silanol nests) is shown in Figure 3 and the data in the Table 1. As it is observed, the conversion values are increased according with the silanol nests density increasing. Nevertheless, a strictly linear behavior was not observed; thus from a molar ratio Si/B = 40 the increasing of the conversion is more pronounced, probably due to the higher amount of boron in the structure and a consequent greater amount of silanol nests.

Then, varying the B content in the synthesis gel we have achieved to increase the acid silanol nests density on the material and to reach a conversion about 55% for a Si/B initial ratio between 20 and 10 (Table 1). In addition, the selectivity to e-C was maintained in 83% for all the B contents, but it is important to note that in all cases, Cyclohexanone (CH) was generated probably due to the moderate acidity of these materials, Vaschetto *et al.* (2018). The B-M (10) and B-M(20) are the most active reaching a yield of e-C about 44%.

To continue the studies the catalyst B-M(20) was chosen, given its high catalytic activity and lower requiring of B in the initial gel compared to B-M(10). In order to verify the formation of coke, in one of our experiments carried out under mild reaction conditions, the catalyst B-M(20) was recovered and heated at 500 °C. A negligible difference in the weight was determined. Therefore, it is evidence that under our reaction conditions the coke formation is insignificant. Therefore, the presence of species adsorbed on catalyst surface, which could poison the active sites, could be discarded under the mild reaction conditions employed.

To determine the conditions that maximize the yield to e-C, the temperature, W / F and TOS were modified and analyzed. The effect of the temperature on the CHO conversion and yield to reaction products in the 300-380 °C range over B-M(20), at W/F 40 g h/mol and employing 1-hexanol as solvent is presented in Figure 4. As it is observed, e-C is the major product and the byproducts include Cyclohexanone as main by-product, and also Aniline (AN), 5-hexenenitrile

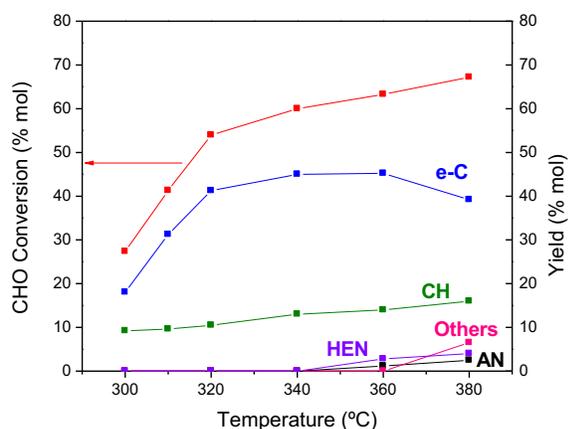


Fig. 4. Effect of the temperature on the CHO conversion and yield to reaction products over B-M(20). Reaction conditions: W/F=40 g h/mol, TOS=15 min, 1-hexanol as solvent.

(HEN) and others, which are consistent with other studies already reported, Ko *et al.* (2001) and Souro *et al.* (2001). The transformation of the oxime reached a value close to 70% at 380 °C. The e-C yield increased up to 45% when the temperature increased up to 360 °C and then decreased at higher temperatures. These results are in good agreement with those previously reported, Chang *et al.* (2004) and Maheswari *et al.*

(2003), where a decrease in the e-C selectivity was found when the reaction temperature increased. On the other hand, by-products such as AN, HEN and others, appeared after 340 °C and increased with temperature with a small increase in e-C production up to around 360 °C, beyond which only the byproducts yield increased. This behavior is probably due to an increase in the side reactions such as hydrolysis, dehydration and fragmentation of CHO, Ko *et al.* (2001) and Singh *et al.* (1996), as well as to the decomposition of the e-C on the catalyst surface above 360 °C. Therefore, until 360 °C, the by-products appearance can be attributed to side reactions such as hydrolysis, dehydration and fragmentation of CHO, while the main reaction is the rearrangement of the CHO to obtain e-C (Figure 5). Meanwhile, at high temperatures, the decrease in the e-C yield with the increase in the by-products production would be due to the e-C decomposition on the catalyst surface. Additionally, in order to confirm the decomposition of e-C on the catalyst BM(20), some experiences in which a solution of e-C (10 wt.% in 1-hexanol) was fed to the reactor in the 320-380 °C range at W/F = 40 g h/mol were performed. It was observed that the e-C decomposed only above 360 °C in CH and HEN, thus verifying their stability up to this temperature.

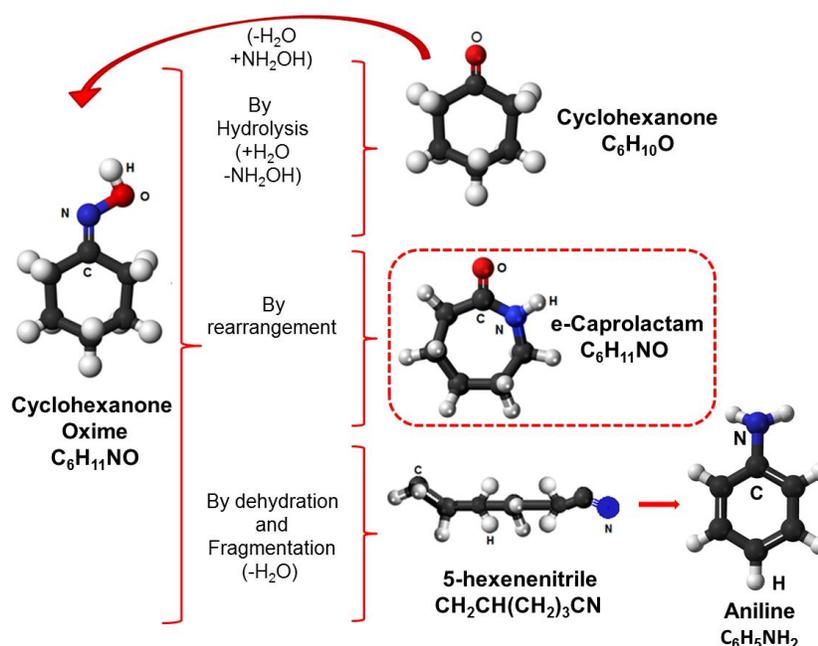


Fig. 5. Proposed reaction pathway for the CHO transformation over B-M(20) at 360 °C and employing 1-hexanol as solvent.

Table 1: Catalytic activity of the synthesized materials. Reaction conditions: TOS=15 min, T=320 °C and 1-hexanol as solvent.

Sample	Si/B(a)	W/F (g h/mol)	Conversion CHO (% mol)	Yield (% mol)	
				e-C	CH
B-M(10)	10	40	53.95	44.16	9.56
B-M(20)	20	40	53.72	44.24	9.7
B-M(40)	40	40	31.76	25.34	6.42
B-M(60)	60	40	25.36	21.21	4.15
B-M(80)	80	40	21.48	18.39	3.09
B-M(20)	20	20	27.17	17.26	9.9
B-M(20)	20	60	55.56	43.98	11.58

Table 2: Effect of time on stream (TOS) on the CHO conversion and e-C yield over B-M(20). Reaction.

TOS (min)	Conversion CHO (% mol)	Yield (% mol)	
		e-C	CH
15	53.72	44.24	9.71
60	51.15	43.64	7.51
120	50.35	43.08	7.27
240	49.88	42.68	7.2
480	49	42.15	6.85
960	49	42.15	6.85
1920	49	42.15	6.85
3600	49	42.15	6.85

Therefore, this fact confirms that in the Beckmann rearrangement reaction, the decrease in the e-C yield with the increase in the by-products production at high temperatures is due to the e-C decomposition on the catalyst surface. Finally a temperature of 320 °C was chosen to continue the study of the other reaction variables, given that at this value a high production of e-C with a low proportion of by-products (CH) was achieved.

The influence of contact time (W/F) on the catalytic results at 320 °C, using 1-hexanol as solvent is shown in Table 1. As the contact time increased from 20 to 60 g h/mol, the conversion of CHO increased up to 55.56%. Meanwhile, e-C yield remained almost constant from to W/F = 40 g h/mol, while the yield to CH increased. Thus, CHO conversion and yield to e-C reached maximum values of 54% and 44.24% respectively, using B-M(20), W/F = 40 g h/mol and a temperature of 320 °C, being CH the main by-product with a low yield of 9.7%. Then this product mixture may be separated by vacuum distillation to obtain CH which can be used for different purposes, among them to obtain CHO for producing e-C. Thus, the reusing of this by-product (CH) can be performed by reaction

with hydroxylamine to form CHO (raw material for e-C) (Figure 4). In addition, CH can also be used in the production of adipic acid, as adhesive in sealing PVC objects and as solvent in several industries (cellulose acetate, nitrocellulose, natural resins, vinyl resins, rubber, waxes, fats, shellac).

Finally, an important aspect to consider is the stability of the catalyst with the reaction time and reusability. Thus, the effect of time on stream on activity B-M(20) at 320 °C and W/F = 40 g h/mol was investigated through experiments with the TOS extended (15 - 3600 min). Table 2 shows conversion of CHO and yield to e-C and CH. As it can be seen on approximately 120 min, both the conversion of CHO as yields to products remained almost constant and the catalyst showed very good activity up to 3600 min TOS, in the first catalytic cycle.

After this experience, in order to verify the formation of coke, the catalyst was recovered and heated at 500 °C. A negligible difference in the weight was determined. Therefore, it is evidenced that under our reaction conditions the coke formation is insignificant. Subsequently, the catalyst was reused and presented the same behavior that the reported

in Table 2. Thus, in the second reaction cycle, the conversion of CHO and yields to products remained almost constant until 120 min, showing good activity up to 3600 min TOS. This evidences the high stability and reusability of the catalyst.

In this manner, the implementation of this catalyst revealed a good catalytic performance, with high conversion of cyclohexanone oxime, high stability, lifetime and reusability.

Conclusions

B-MCM-41 type nano-structured catalysts with different B contents were prepared by direct hydrothermal synthesis and evaluated in the rearrangement of CHO to e-C under different reaction conditions: 300-380 °C, W/F = 20-60 g h/mol and TOS = 15-3600 min. The e-C was the major product on the whole temperature range studied and CH appeared as the main by-product. The e-C yield reached a maximum value of 45% at 360 °C and then decreased at higher temperatures due to its decomposition on the catalyst surface.

The B-M(20) showed the highest catalytic performance at 320 °C, W/F= 40 g h/mol and by using 1-hexanol as solvent, exhibiting a CHO conversion of 54% and e-C selectivity around 83%. Moreover, the stability and reusability of the catalyst was corroborated, under the reaction conditions mentioned. Thus, under this mild reaction condition it could be achieved a high yield to e-C with a low proportion of CH. The product mixture (e-C and CH) obtained at 320 °C may be separated by vacuum distillation and the CH be recycled by reaction with hydroxylamine to form again CHO (raw material for e-C).

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