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

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ABSTRACT

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

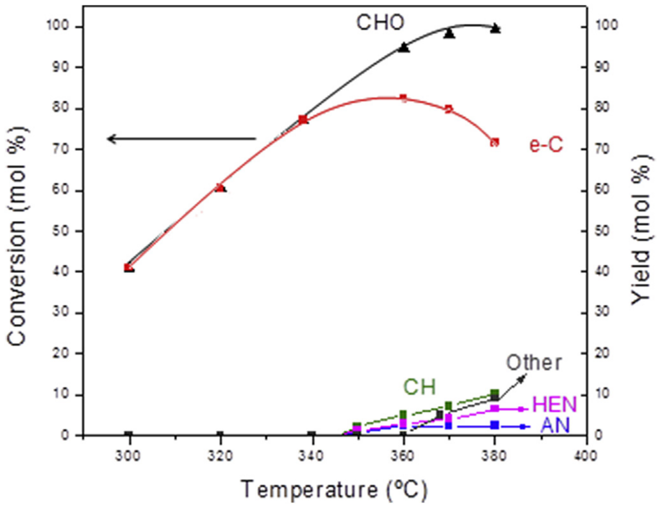

Fig. 1. Effect of the temperature on the CHO conversion and yield to reaction products over Al-M(20). Reaction conditions: W/F = 40 gh/mol, TOS = 15 min, 1-hexanol as solvent.