Acidity versus catalytic activity in bi-structured nanomaterials

Eliana G. Vaschetto, Sandra G. Casuscelli, Griselda A. Eimer*

Centro de Investigación y Tecnología Química (CITeQ-UTN-CONICET), Facultad Regional Córdoba, Maestro López y Cruz Roja Argentina, Ciudad Universitaria, CP: 5016, Córdoba, Argentina

ARTICLE INFO

ABSTRACT

Mesoporous nanomaterials were synthesized from zeolitic precursors and characterized by XRD, adsorption-desorption of N_2, ICP-OES, SEM, TEM, FT-IR and adsorption-desorption of pyridine followed by FT-IR. These materials were catalytically evaluated in the Beckmann reaction, and the reaction products were analyzed by gas chromatography and identified by GC-MS. The activity and the distribution of reaction products were related to the acidic strength of the materials. Thus, it was possible to generate bi-structured catalysts with sites in a certain range of acid strength as potential materials for catalytic processes that require some acidity grade, such as the Beckmann reaction of cyclohexanone oxime for obtaining different products of industrial interest.

1. Introduction

Due to environmental concerns there is growing interest in solid acid catalysts as replacement of liquid acids. The problems associated with the currently used catalysts, such as acids, are their toxicity, corrosivity and effluent disposal. Furthermore, a complete separation of the product and the catalyst is sometimes difficult.

Mesoporous molecular sieves such as hexagonally ordered MCM-41 have attracted considerable attention because of their potential use as versatile catalysts and catalyst supports for the transformation of large molecules [1–5]. Mesoporous materials are characterized by their relatively high surface areas, pore volumes within a small amount of material and uniform channels in the nanometer range.

The enormous diversity in mesoporous structures as well as the fact that their properties can be tuned and modified depending on the type of application have aroused huge interest in these materials among different scientific communities. In fact, mesoporous materials are extensively used on an industrial, pilot, and laboratory scale in different research fields. However, the acidity and hydrothermal stability of these mesostructured materials are relatively low compared with those of microporous materials, which strongly affects their applications.

The structural integrity of Al-MCM-41 and other mesoporous aluminosilicates has been significantly improved in recent years through direct assembly and postsynthesis treatment methods [6]. Nevertheless, their hydrothermal stability and acidity remain lower than those of conventional microporous zeolites and limit potential applications in petroleum refining, petrochemistry and fine chemicals synthesis [7]. One might expect to improve both the stability and acidity of these

materials if a zeolite-like order could be introduced into the pore walls.

Mesoporous molecular sieves [8,9] overcome the pore diameter constraint of microporous materials [10] and allow the diffusion of larger molecules, which are among the many desirable properties that have made such materials the focus of great interest. Then, to upgrade the performance of mesoporous and microporous molecular sieves, attempts have been made to synthesize a new type of material that can combine the advantages of these two kinds of molecular sieves: pores in the mesoporous range with, at the same time, high acidity in order to enhance their activity in acid-catalyzed reactions [11,12].

Micro/mesoporous bi-structured materials are currently under development and, although there are still a relatively small number of published papers in this field, it is growing fast [13–17]. One of the strategies for producing these materials is the assembly of nanoclustered zeolitic precursors in the synthesis gel. According to Perez Pariente et al. [18,19], such approach consists of mimicking the physicochemical conditions prevalent in the synthesis gels from which zeolite materials are obtained, and promoting the surfactant-assisted assembly of the zeolite precursors present in the gel. The resultant micro/mesoporous materials may get the right structural and chemical characteristics for optimum accessibility, stability and acidity. Thus, the first aim of the present work is to prepare catalysts containing pores in the mesoporous range and active sites with enhanced acidity able to convert large molecules.

In addition, the influence of the acid strength of the generated sites on the catalysts synthesized in the Beckmann rearrangement reaction of cyclohexanone oxime (CHO) was studied. It is known that CHO can be catalytically transformed into rearrangement, dehydration-

---

fragmentation and hydrolysis products under different reaction conditions and acidity of the materials. Thus, e-caprolactam (e-C) is obtained by rearrangement, while hexenenitrile (HEN) and cyclohexanone (CH) can be obtained by dehydration-fragmentation and hydrolysis of CHO.

On the other hand, other minor products such as aniline (AN), 5-hexenenitrile (HAN) and cyclohexen-1-one (CHE) can also be obtained by secondary reactions. All these products have relevant industrial applications. As is known, e-C is an important intermediate for the manufacture of synthetic fibers and engineering plastics, being a key starting material for the manufacture of Nylon 6 [20–22]. CH can be used in the production of CHO and adipic acid, as adhesive in sealing PVC objects and as solvent in several industries. HEN can be employed for the functionalization of polymers, which reduces the hysteresis of rubber vulcanization in the manufacture of tires [23]. AN is used to manufacture products such as polyurethane foam, agricultural chemicals, pigments (color precursor) and in the pharmaceutical industry (structural basis for the chemical synthesis of paracetamol). HAN is used in compositions containing carbon black, such as electrically conductive material, paints, cosmetics and batteries [24]. It can also be employed in the manufacture of sulfur crystals and ceramics [25]. CHE is used as building block in organic chemistry synthesis and in multistep synthesis in the construction of polycyclic natural products.

Finally, in order to evaluate the mesoporous catalysts synthesized from microporous precursors, the Beckmann rearrangement reaction was carried out. Although there are reports on the synthesis of these materials [26–29], they have not yet been studied for this reaction. Therefore, in this work we analyze the influence of the materials acidity on the reaction products in the rearrangement of cyclohexanone oxime in vapor phase.

2. Experimental

The synthesis method of the solids consists of first developing zeolitic precursors, promoting their assembly through the molecules of a surfactant.

To prepare the initial synthesis gel containing the zeolitic precursors, tetraethoxysilane (TEOS, Aldrich, 98%) was used as the source of Si, sodium aluminate (Johnson Matthey, 98%) as the aluminum source, and an aqueous solution of tetrapropyl ammonium hydroxide (TPAOH, Merck, 40% solution) as the template agent of the precursor solution. The hydrothermal treatment time between 6 and 48 h at 80 °C for this precursor solution in autoclave under autogenous pressure was analyzed as the first synthesis variable (*variable 1*). The zeolitic precursor was then cooled to room temperature and added to an aqueous solution of cetyltrimethyl ammonium bromide (CTABr, Merck, 99%) under stirring. Subsequently, this final gel with molar composition: Si:Al:TPAOH:CTABr:H2O = 1: 0.017 or 0.05: 0.24: 0.15: 21.2 was aged at room temperature for 12 h or heated in autoclave at 100 °C for 9–16 h, in order to analyze the hydrothermal treatment of the final gel (*variable 2*).

In all the cases, the resulting solids were filtered from the reaction medium, washed with a solution of ethanol in water and dried at 60 °C overnight. The surfactant was evacuated from the samples under continuous N_2 flow and the samples were then calcined in air flow at 500 °C. The calcined samples were named as MP(x)-y-z(e) or MP(x)-y-z (h), where "MP" refers to the materials synthesized from zeolite precursors, "x" is the Si/Al molar ratio, "y" is the hydrothermal treatment time (in hours) of the precursor gel at 80 °C, "z (e)" are the hours of aging at room temperature and "z (h)" the hours of hydrothermal treatment of the final gel at 100 °C.

2.1. Characterization

The X-ray diffraction (XRD) patterns were recorded in air at room temperature on a Philips PW 3830 diffractometer with Cu Kα radiation (λ = 1.5418 Å) in the range of 2θ from 1.5° to 35°. Specific surfaces

were measured using Pulse Chemisorb equipment by single point at $P/P_0 = 0.3$ through the BET method. The samples were previously heated at 300 °C for 1 h under N_2 flow. The aluminum content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), using a VISTA-MPC CCD Simultaneous ICP-OES-VARIAN. The infrared analysis of the samples was recorded on a JASCO 5300 FT-IR spectrometer. The scanning electron microscopy (SEM) images of the materials were obtained in a JEOL JSM-6380 LV. Gold coverage was applied to make the samples conductive. The acceleration voltage was 20 kV.

Moreover, the solids were analyzed by Transmission Electron Microscopy (TEM) with a JOEL JEM-1200 EX II, working voltage: 120 kV. A small drop of the dispersion (sample in a 50% water–ethanol solution) was deposited on a copper grid and then evaporated in air at room temperature. 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 performed.

Self-supported wafers of the samples (∼20 mg and 13 mm of diameter) were prepared, placed in a thermostated cell with CaF_2 windows connected to a vacuum line and evacuated for 7 h at 400 °C under dynamic vacuum; the residual pressure was smaller than 10^{-3} Pa. After cooling to room temperature, the spectrum of each sample was recorded (background spectrum). After the background spectrum was recorded, the solid wafer was exposed to pyridine vapors (Sintorgan, 99% purity) until the system saturated to 46 mm Hg at room temperature; the contact time at this pressure was 12 h. After an IR spectrum of the adsorbed pyridine at room temperature was recorded, the subsequent IR spectra were obtained following the pyridine desorption by evacuation for 1 h at 25, 50, 100 and 200 °C. Finally, the difference spectrum for each sample was obtained by subtracting the background recorded previously.

2.2. Catalytic reactions

The catalytic reactions were carried out in a fixed-bed down flow 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 at 360 °C. A solution of 10 wt% cyclohexanone oxime in 1-hexanol was fed using a syringe pump and nitrogen as the carrier gas (30 mL/min). The contact time (W/F), referred to the weight of catalyst (g) over the feed rate of cyclohexanone oxime (mol/h), was 40 gh/mol. 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 conditions, we did not observe an apparent net accumulation or depletion of mass in the system, that is, the total mass entering the system (total initial mass) was practically equal to the total mass leaving the 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 products were identified by GC-MS Perkin Elmer (Clarus 560S). Mass spectral data (m/z/intensity ratio) for the identified products are the following: **5- hexenenitrile:** 27/25, 41/70, 55/100, 67/12, 80/10, 95/10 [M+]; **e-caprolactam:** 30/50, 42/50, 55/100, 67/20, 85/45, 113/75 [M+]; **cyclohexanone:** 27/25, 42/75, 55/100, 69/35, 83/20, 98/50 [M+]; **aniline:** 39/20, 52/15, 66/45, 78/5, 93/100 [M+]; **hexanenitrile:** 29/35, 41/100, 54/78, 68/28, 82/25, 96/15; **cyclohexen-1-one:** 27/18, 40/25, 55/15, 68/100, 96/30 [M+]. Also the reaction products were analyzed by comparison with chromatographic standards. The conversion was expressed in moles %, and the yields were calculated as cyclohexanone oxime conversion x selectivity to reaction products/100.