



Microreactors based on CuO–CeO₂/zeolite films synthesized onto brass microgrids for the oxidation of CO

Nicolás C. Pérez, Eduardo E. Miró, Juan M. Zamaro*

Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (FIQ, UNL-CONICET) Santiago del Estero 2829, 3000 Santa Fe, Argentina

ARTICLE INFO

Article history:

Received 15 June 2012

Received in revised form

20 September 2012

Accepted 28 September 2012

Available online 8 October 2012

Keywords:

Microreactor

Brass support

Mordenite

Wire mesh

Total CO oxidation

Preferential CO oxidation

ABSTRACT

Microreactors based on Cu, Ce oxides dispersed onto zeolite films grown on brass microgrids were developed. Secondary synthesis conditions were regulated in order to obtain thin, homogeneous and adherent coatings of mordenite to which Cu and Ce were later incorporated. The systems were characterized by XRD, SEM-EPMA, H₂-TPR, LRS and XPS. The catalytic coatings were mechanically and chemically stable under reaction. Cu, Ce/zeolite microreactors were evaluated in the CO total oxidation (COTox) and in the preferential CO oxidation (COProx) showing a superior performance when compared with the same powder catalyst.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The miniaturization of structured catalysts in the micro-scale range offers important advantages when used in industrial catalytic processes. This is due to the great increase in mass and heat transfer coefficients as compared with conventional reactors [1]. In gas phase reactions, this implies controlling highly exothermic or endothermic reactions which are difficult to manipulate in traditional reactors [2]. Moreover, because of their high surface/volume ratios, small reaction volumes are involved, generating short residence times which increase the efficiency and selectivity of processes [3]. Nowadays, with the help of available microfabrication techniques, microreactors can be made in various materials and with diverse design concepts. The use of metallic substrates could bring some advantages, such as the possibility of achieving thin catalytic walls, high mechanical resistance, and versatility to adopt different configurations in the shape and size of the microchannels. Although silicon and stainless steel are the materials most widely reported as supports in the literature [1–3], when exothermic reactions are involved it would be better to employ a material with higher thermal conductivity, as demonstrated by Groppi et al. for structured catalysts of millimetric scale

[4]. For microreactors, molybdenum and aluminum alloys have been employed as supports [5–7], as well as thin brass wires packed into tubular millimeter-sized reactors [8] and brass micromonoliths employed for the ethyl acetate combustion [9]. Brass has high specific thermal conductivity, high thermal diffusivity and low specific heat [10]. Additionally, it is a non-expensive, readily available material.

On the other hand, zeolites are microporous materials that can be employed in a broad variety of reactions and they have high thermal stability and reproducibility of synthesis. Despite these advantages, the coating of microchannels with zeolites [11–16] or the catalytic application of zeolite-based microreactors have not been so widely reported in the literature [5,16–22]. A key factor to successfully design zeolite-based microreactors is the obtention of thin, uniform and adherent zeolite films in the microreactor channels which should be smaller than 500 μm. Subsequently, a variety of active metal species can be introduced in the microporous films, as exchanged metal atoms or dispersed oxide phases. The synthesis of zeolite films on flat substrates of Cu and Cu alloys has been reported in the pioneering works of Davis et al. [23], and Mintova et al. [24–26]. Davis et al. [23] synthesized zeolite Y coatings on Cu foils and analyzed the effect of various treatments on the adherence. Mintova et al. and Valtchev and co-workers [24–26] also studied the synthesis of zeolite films (Zeolite Y, ZSM-5, Silicalite-1 and SAPO-5) on substrates of copper and brass. Furthermore, zeolite 4A has been synthesized on copper foams with small pores [27]. More recently, we have shown the synthesis of uniform and

* Corresponding author. Tel.: +54 0342 4536861; fax: +54 0342 4536861.
E-mail address: zamaro@fiq.unl.edu.ar (J.M. Zamaro).

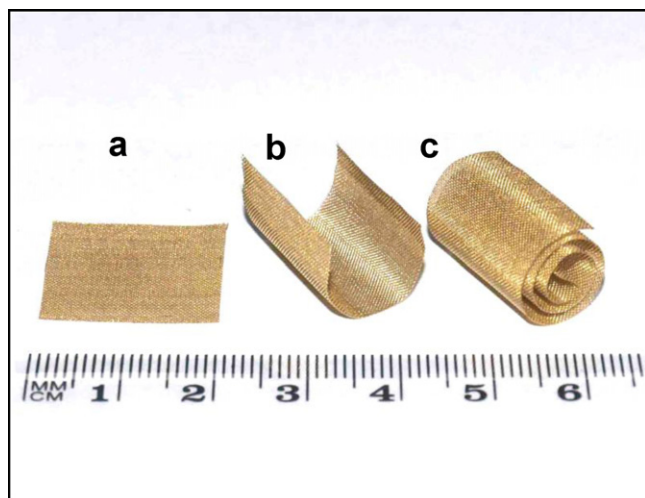


Fig. 1. Pictures of the seeded microgrids before the hydrothermal treatment: (a) planar-shaped, (b) U-shaped and (c) spiral-shaped.

thin mordenite films confined into microchannels formed in brass plates [16].

The CO oxidation is an exothermic reaction with environmental interest. On the one hand, it is an extremely toxic gas that accumulates indoors and must be eliminated (COTox) [28]. On the other hand, in the field of clean energy, CO must be removed from H₂ streams to be used in power cells (COProx) [29]. Although highly active catalysts based on Au and Pt have been studied for the later reaction [30,31], there is a great interest in using catalysts based on other more abundant and less expensive metals, such as Cu and Ce. Different formulations based on Cu and Ce oxides have been proposed [32–35], all of them presenting an excellent catalytic performance. But, to the best of our knowledge only one study has been published on the use of Cu–zeolite as catalyst for the COProx reaction [36].

The foregoing discussion explains our interest in developing microreactors for the CO oxidation, based on highly dispersed active phases of Cu and Ce on zeolite-coated brass microstructured substrates. The study focuses in first obtaining the dispersed active phase in the powder zeolite and then optimize the synthesis of zeolite coatings on brass microgrids in the search for continuous and stable films. Afterwards, Cu and Ce dispersed phases are introduced into the films and the obtained microreactors are evaluated in the total and preferential oxidation of CO.

2. Experimental

2.1. Support material and synthesis of zeolite coatings

We used strips of brass microgrids (Cu/Zn: 65/35) composed of wires of 100 μm in diameter with spaces of 140 μm between them (see Fig. 1). The substrates were previously washed first with water and then with acetone in an ultrasonic bath. The mordenite

growth was performed by secondary synthesis using a gel containing colloidal silica (Ludox AS-40), Na₂Al₂O (Riedel-de-Häen), NaOH (Cicarelli pro-analysis) and distilled water, varying the dilution from H₂O:SiO₂ = 70:1.15 to 110:1.15. The reactants were aged by stirring for 2 h at r.t. and 100–200 nm sized crystals, extracted from a commercial zeolite powder (Na-Mordenite Zeolyst; Si/Al = 6.5), were used for the seeding. The seeds were obtained from the supernatant generated after centrifuging an aqueous suspension of the as received commercial powders, at 3500 rpm for 30 min. This zeolite was also used for the preparation of powder catalysts. Prior to the seeding, the microstructures were treated with a PDDA, poly(diallyldimethylammoniumchloride), aqueous solution (0.4 wt%). After that, the microgrids were submerged into a suspension of nanometric seeds (2 g L⁻¹) during 10 min. Then, the seeded supports were subsequently dried in N₂ flow (room temperature), and in a stove at 100 °C overnight. After seeding, the supports were placed vertically inside teflon-lined autoclaves and hydrothermally treated at 180 °C for 12–24 h. The internal autoclave was 60 cm³ in volume and 40 mL of gel were used in all syntheses. After synthesis, the vessels were cooled and the samples were withdrawn from the autoclave, washed in water, treated in an ultrasonic bath for 10 min to remove residues from the solution and finally dried at 120 °C for 12 h. Table 1 summarizes the syntheses conditions.

2.2. Zeolite activation: Cu and Ce incorporation

The Cu incorporation in the powder zeolite as well as in zeolite-coated microreactors was carried out by ionic exchange with a 0.05 M Cu(NO₃)₂ solution of (NO₃)₂Cu·6H₂O (Aldrich®) for 24 h at pH = 5 and room temperature. Then, the samples were washed with distilled water and dried at 120 °C for 12 h. The subsequent addition of Ce was performed by impregnation with a colloidal CeO₂ suspension (Nyacol®, 10–20 nm). For the powder catalyst, Ce was added by incipient wetness impregnation whereas for microreactors, by washcoating with a slurry of 2% (w/w), blown with N₂ and drying at 120 °C. Subsequently, some samples were subjected to a reduction-oxidation (redox) treatment, similarly to a previously reported procedure [37]. The aim of this treatment was to generate clusters of copper oxide dispersed in the zeolite matrix. The reduction was carried out in a stream of H₂ in He (50%, v/v; 50 mL min⁻¹) at 350 °C during 2 h. Next, the oxidation was performed with O₂ in He (50%, v/v; 50 mL min⁻¹) for 1 h at the same temperature. Some samples without redox treatment were calcined at 350 °C for 2 h in air. The parent Na-Mordenite (Zeolyst) has a surface area of 409 m² g⁻¹, and after loading the active ingredients this value remained almost constant, due to the low amount of Cu and Ce incorporated by ionic exchange and impregnation, respectively. Table 2 presents a summary of the evaluated catalysts and microreactors.

2.3. Characterizations

2.3.1. Scanning electron microscopy (SEM)

The quality, orientation and microstructure of the zeolite films were examined by SEM with a Jeol JSM-35C equipment, operated

Table 1
Zeolite weight gain on microgrids treated under different synthesis conditions.

Sample	Support shape/size (mm)	Synthesis time (h)	Gel dilution (H ₂ O:SiO ₂)	mg zeolite/cm ² GSA
MZ1	Planar/20 × 20	12	70:1.15	1.02
MZ2	Planar/20 × 20	12	110:1.15	0.24
MZ3	Planar/20 × 20	24	110:1.15	0.98
MZ4	U/20 × 40	24	70:1.15	2.00
MZ5	Spiral/20 × 80	12	70:1.15	0.90
MZ6	Spiral/20 × 80	12+12	70:1.15	1.65
MZ7	Spiral/20 × 80	24	70:1.15	1.82

Download English Version:

<https://daneshyari.com/en/article/46024>

Download Persian Version:

<https://daneshyari.com/article/46024>

[Daneshyari.com](https://daneshyari.com)