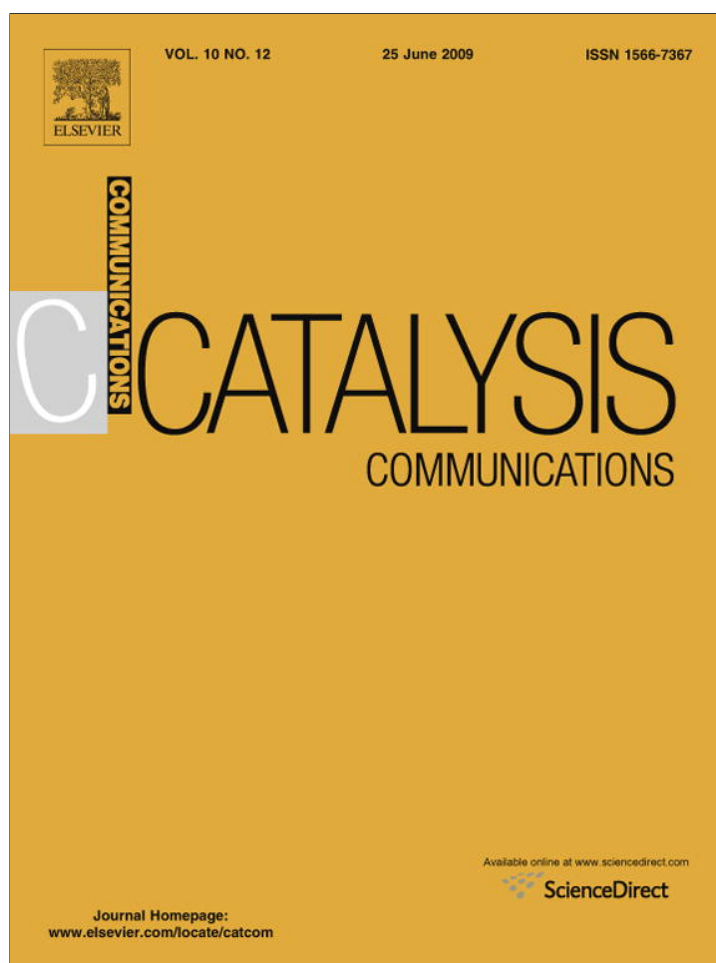


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Confined growth of thin mordenite films into microreactor channels

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ABSTRACT

This communication presents the production of a mordenite film growth totally confined into 350 μm wide microchannels on copper alloy plates for microreactor preparation. The growth is obtained in open channel configuration by secondary synthesis after 12 h of treatment over this highly thermal conductivity support. The confined growth presents a high overall quality. It is crystalline, uniform, and adherent; it totally covers the microchannels surface and has 5 μm . These properties are confirmed by XRD, SEM and EPMA characterizations.

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1. Introduction

Research on microreactors is an emerging, developing field due to the fact that high mass and heat transport rates can be achieved [1]. In gas phase reactions, this implies controlling highly exothermic or endothermic reactions difficult to manipulate in traditional reactors [2]. However, due to their reduced scale, the deposition of the catalytic phase into the microchannels represents a challenge.

Zeolites can catalyze a variety of reactions; they also have good thermal stability and high reproducibility of synthesis. Therefore, they are excellent candidates as active phases. However, to this day few studies have dealt with the production of zeolite-based microreactors. Rebrov et al. [3] obtained MFI growths by direct synthesis on stainless steel plates with 500 μm wide channels which were active for the NO_x SCR reaction. Recently [4,5], zeolite Y, MFI, ETS-10 and mordenite have been grown in the same type of substrates by secondary synthesis and steam assisted crystallization. By means of this latter method, an acceptable selectivity and partial coverage inside the channels could be obtained after 16 days of synthesis. In all cases, the main drawback was to obtain the growth exclusively inside the microchannels and also good homogeneity, coverage, crystallinity and microstructure of the growth along the microchannels. In general, the approach applied in the attempt to obtain selectivity was to modify hydrothermal treatment conditions as time, temperature, reactive concentration and crystal seeding.

On the other hand, despite the fact that one of the main advantages of microreactors is their high heat transfer rate, few articles have reported the use of high thermal conductivity metallic

supports such as aluminum [6]. However, in the case of mordenite growths, the pH necessary for the synthesis is strongly basic, and our experience indicates that aluminum foils are dissolved during the synthesis. This is the reason for the choice of copper alloy in our work. Most published work reports the use of stainless steel [7], although the advantages of using highly conductivity materials were pointed out by Groppi et al. [8].

The aim of the present work is to develop a method for obtaining a uniform, thin layer of mordenite confined into microchannels formed in copper alloy substrates.

2. Experimental

2.1. Support treatment and film growth

A brass plate was used (Cu/Zn: 70/30) of 1 mm thickness with microchannels 350 μm wide and 200 μm deep which were formed using the acid-etching method. The bottom of the microchannels presented high roughness. The support was conditioned by washing with water and soap and then with ultrasound in water and acetone. Later, the inside of the microchannels was seeded with mordenite nanocrystals (200 nm; 5 g/l; Na-Mor Zeolyst Si/Al = 6.5). The seeding was assisted with PDDA[poly(diallyldimethylammoniumchloride)] previously infiltrated into the microchannels. The successive infiltrations were performed by capillarity with the microchannels in closed configuration, applying a plastic film. For the seed growth, a gel containing colloidal silica (Ludox AS40), sodium aluminate, sodium hydroxide and water was employed with composition $\text{H}_2\text{O}:\text{SiO}_2:\text{Na}_2\text{O}:\text{Al}_2\text{O}_3 = 70:1.12:0.38:0.025$. The plate was placed with the microchannels in open configuration. The gel was aged 2 h at room temperature while stirring and the

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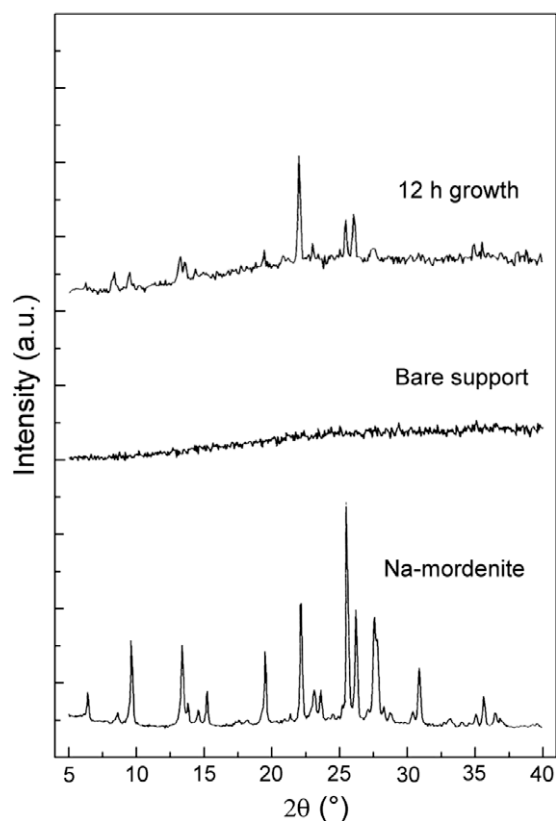


Fig. 1. XRD patterns of the microchannel support before and after the secondary mordenite growth.

hydrothermal treatment was performed under static conditions at 180°C during 12 h. The sample was washed and subject to ultrasound to remove waste and poorly adhered material. Finally, the sample was dried in a stove at 120°C .

2.2. SEM, XRD and EPMA characterization

Through X-ray diffraction (XRD) it was possible to identify the crystalline phase of the growths obtained on the supports. A Shimadzu XD-D1 instrument operated at 40 kV and 30 A was employed with a scanning rate of 2°min^{-1} between $2\theta = 5^\circ$ and 40° which is the range where the most important signals of the mordenite can be found. The diffraction patterns obtained were compared to those of pure mordenite powders.

The growth development on the support, its crystalline microstructure and the spatial ordering of the crystals was determined by Scanning Electron Microscopy (SEM). A SEM Jeol JSM-35C instrument, operated at 20 kV acceleration voltages was employed. The samples were glued to the sample holder with Ag painting and due to the low electrical conductivity of the zeolite, they were then coated with a thin layer of Au in order to improve the images. In addition, for knowing with accuracy the microchannels coverage and the confinement degree of the growth inside microchannels, SEM analysis in backscattering mode was employed.

Electron probe micro analysis (EPMA) were performed with a dispersive instrument coupled to the SEM in order to analyze the elemental composition of the growths. The analyses were performed at different depths in the thickness of the zeolite growth.

3. Results and discussion

After treating the support under hydrothermal conditions for 12 h, the main XRD mordenite signals can be observed onto the

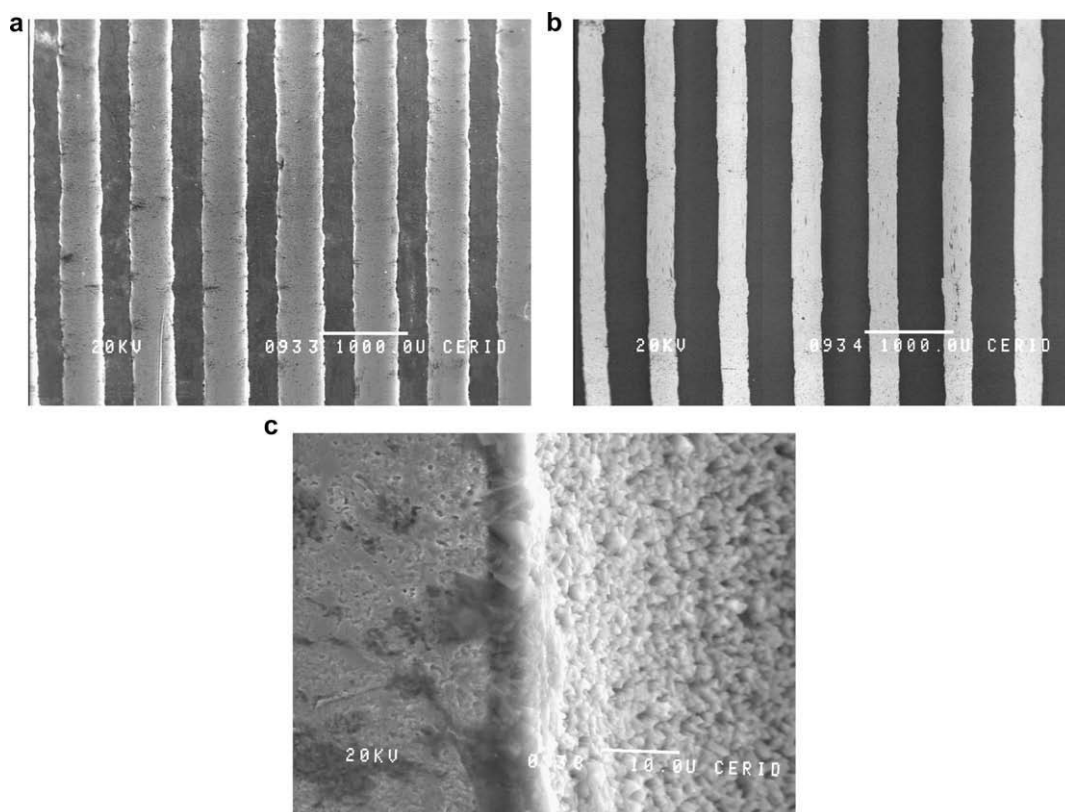


Fig. 2. SEM micrographs (top views) of a confined mordenite growth into microchannels; (a) general view (the bright zones are the mordenite covered microchannels); (b) image in backscattering mode (the dark zones are the mordenite covered microchannels); (c) close view of the growth in the border of a microchannel.

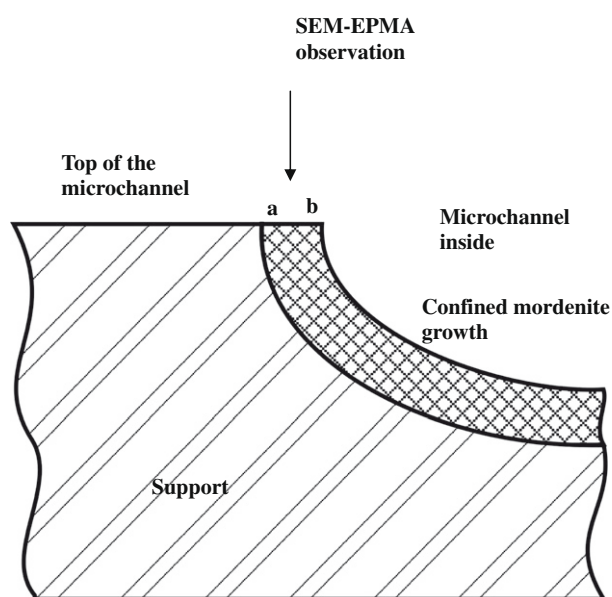


Fig. 3. Scheme of the selective mordenite growth into the copper alloy microchannel. The arrows indicate the zones analyzed by EPMA.

plate as shown in Fig. 1. The pattern observed indicates the growth of a crystalline phase in view that the bare support presents no diffraction signals in the range analyzed. The small thickness of the zeolite film and the absence of zeolite growths outside the microreactor channels are the causes of the relatively low XRD signals observed. This is a usual fact in XRD analysis of thin films, see for example the work by Valtchev and Mintova [9]. Anyway, the presence of various of the main mordenite diffractions ($2\theta = 22.2^\circ$, 25.5° and 26.2°) indicates that pure and crystalline mordenite effectively grows at the microreactor plate. A dense mordenite growth covering all the microchannels surface was confirmed by SEM (Fig. 2a). Notably, the growth was produced only inside the microchannels (light gray in Fig. 2a) and was practically null on top of them (dark gray in Fig. 2a). The zeolite confinement into the microchannels and their coverage are eloquent if the sample is observed by SEM in backscattering mode (BS) (Fig. 2b). The top of the channels is observed bright by the highly retrodispersion of the metal substrate highlighting an absence of zeolite in these sectors. The synthesis variables employed were selected not only in order to minimize the zeolite growth in solution but also to maximize the growth on the microchannels. The effect was obtained by the combined action of various factors. The electrically charged additive infiltrated into the microchannels fixed the seeded mordenite crystals, avoiding their migration outside the channels. The short ageing time of the gel diminished the nuclei formation in solution, reducing the possibility of nuclei attachment and growth on the non-seeded microchannel outside and privileging the growth on the seeded zones. The high roughness of the microchannels bottom surface helped to develop the growth inside them because it is known that these surface defects can promote zeolite nucleation. The channels position in the synthesis medium decreases crystal addition by gravity outside the microchannels. A more exhaustive study and discussion on the impact of these variables will require performing additional experiments to these preliminary results.

In addition to the high selectivity achieved, the images (Fig. 2a and b) show a very high homogeneity and coverage in all microchannels extension. A close view of the microchannels edge is presented in Fig. 2c. The growth has been suppressed at the top of the microchannels and is densely and homogeneously produced in-

Table 1

EPMA analysis at different depths in the mordenite growth into microchannel (atomic ratios).

Sample	Si/Al	Al/Cu	Cu/Zn
Support	–	–	2.6
Ext. growth ^b	6.3	3.0	–
Int. growth ^a	5.5	1.1	–

^a Analysis performed on the growth, $1\ \mu\text{m}$ above the mordenite-support interphase.

^b Analysis performed on the growth $1\ \mu\text{m}$ below the mordenite growth surface.

side. The crystallinity is high, the morphology corresponds to mordenite crystals and the thickness is about $5\ \mu\text{m}$. The sample sonicated in water for 10 min shows no zeolite detachment, which means that the film also presents high adherence. EPMA analyses at different depths (see Fig. 3) are presented in Table 1. The support corresponds to a 70/30 type alloy. The mordenite growth has a Si/Al ratio between 5 and 6 that decreases toward the interphase with the support. This implies a high exchange capacity. The amount of aluminum was constant at any thickness. The theoretical ratio of the synthesis gel was Si/Al = 22.5, indicating differences in the Si incorporation in the growth as in mordenite films on other substrates [10]. Besides, Cu and Zn coming from the support are incorporated into the growth. Their concentration decreases toward the film surface.

4. Conclusions

The selective growth of mordenite inside copper alloy microchannels is of relevance in microreactor preparation. The confined growth leaves the channel tops uncovered thus allowing a close contact between the stacked catalytic plates in this type of microreactor. This fact and the high adherence of the confined growth onto the highly conductive support material improve the heat transfer and allow a precise control of the reaction temperature. The total confinement of the gaseous flow inside the microchannels also assures a suitable flow regime to achieve the high mass transfer properties characteristic of a catalytic microchannel. Additionally, the film is thin and uniform, it totally covers the microchannels and has a high exchange capacity, properties that are all necessary to achieve high catalytic efficiency.

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