Study of the influence of gel composition in the synthesis of self-supported silicalite-1 layers

O. de la Iglesia [a,b,*], P. Hrabanek [c], A. Zikanova [c], M. Kocirik [c]

[a] Centro Universitario de la Defensa. Academia General Militar, Ctra. de Huesca s/n 50.090 Zaragoza, Spain
[b] Institute of Nanoscience of Aragon (INA), Universidad de Zaragoza, Mariano Esquillor s/n, 50018 Zaragoza, Spain
[c] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Praha 8, Czech Republic

ARTICLE INFO

ABSTRACT

In this work, the synthesis of self-supported layers over mercury was carried out. Influence of the amount of water, TPA^+, OH^- and Na^+ in the precursor gel was investigated for this kind of synthesis. Layers were characterized by X-ray diffraction to study their crystallographic structure, scanning electron microscopy to determine their thickness and crystal properties, and mercury porosimetry for the determination of layer density.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Zeolite films have attracted the attention of many authors during the past 20 years [1] because they have a pore size similar to that of many molecules of interest (0.7 to 1.5 nm), coupled with their extraordinary properties of adsorption and catalysis. These qualities make them ideal for applications such as separations, membrane reactors, microreactors or sensors. Zeolite and related materials polycrystalline films have been grown on different solid surfaces as stainless steel [2], alumina [3] or silicon wafers [4].

The use of a solid support provides mechanical strength and morphology control, nevertheless it produces nonuniform interactions with the zeolite film during the synthesis, modifying its properties. Mercury provides an uniform interaction with the film, then allowing the study of zeolite films growth without any extern agent during the synthesis. The synthesis of silicalite-1 films [5–10] or discrete crystals [11,12] over mercury have been already carried out.

The study of the growth of silicalite-1 crystals and films has the aim of understanding the mechanism of synthesis and the influence of different parameters in the growth of crystals. In this topic, Hayhurst et al. [13,14] studied the effect of the concentration of NaOH and TPA^+ in the growth of silicalite-1 crystals; other authors treated the influence of the structure directing agent [15,16]. The synthesis parameters of Al- and Ge, Al-silicalite-1 [17] or V-silicalite-1 [18] have been also studied. The mechanism of crystal growth has been also investigated using atomic force microscopy [19,20].

In the case of films, Wang and Yan [21] carried out the synthesis of MFI thin films over alumina and stainless steel supports, studying the size and orientation of crystals. In this work, we have studied the influence of the composition of the gel in the synthesis of self-supported silicalite-1 films over mercury, which has not been reported before.

2. Experimental

The synthesis of the films was carried out in a 25 mL Teflon vessel placed in a stainless steel autoclave. The bottom of the vessel was covered with mercury, that is the support of the film, and an amount of 18 mL of synthesis gel was poured in the autoclave. Then a hydrothermal treatment was done at 170 °C and for 20 h. The molar compositions of the different gels used were 1 SiO_2: 0–0.2 NaOH: 0.2–0.3 TPA^+: 80–400 H_2O. The silica source was tetraethyl orthosilicate (TEOS). After the synthesis, layers were washed with distilled water and dried at room temperature overnight. Afterwards, structure directing agent was eliminated by calcination at 480 °C for 8 h in air.

Different characterization techniques were used: scanning electron microscopy (JEOL JSM-6400 operating at 20 kV) was used in order to study the morphology and thickness of layers; X-ray diffraction analyses (Rigaku D-Max diffractometer with Cu-Kα radiation at 40 kV and 80 mA) were carried out also to study the crystallographic structure of layers; and mercury porosimetry (Autopore IV 9520) was done for the determination of layer density.

3. Results

Table 1 summarizes all the layers synthesized in this work with the thickness, weight and SiO_2 yield, and the composition of gel

---

* Corresponding author at: Chemical and Environmental Engineering Department, Universidad de Zaragoza, Zaragoza, Spain. Tel.: +34 976 761000x5439; fax: +34 976 761879.
E-mail address: oiglesia@unizar.es (O. de la Iglesia).

Table 1
Properties of the synthesized layers and gel composition.

Sample	Molar composition TEOS:NaOH:TPAOH:H$_2$O	Thickness (μm)	Weight (mg)	SiO$_2$ yield (%)
S1	1:0:0.25:80	272.2 ± 2.5	258.2	11.7
S2	1:0:0.25:165	178.8 ± 1.9	169.6	14.6
S3	1:0:0.25:240	94.9 ± 1.5	90.0	11.0
S4	1:0:0.25:300	43.7 ± 1.6	41.5	6.3
S5	1:0:0.2:165	352.3 ± 2.1	334.2	28.7
S6	1:0:0.28:165	99.3 ± 3.6	94.2	8.1
S7	1:0.04:0.2:165	297.0 ± 3.7	281.7	23.6
S8	1:0.08:0.2:165	261.3 ± 6.9	247.9	20.2
S9	1:0.2:0.2[a]:165	349.9 ± 1.8	331.0	28.4

[a] TPABr used as structure directing agent.

used in each case. The weight was calculated by means of the volume of the layer by means of the layer thickness. Density was determined by mercury porosimetry of calcined samples, obtaining a value of 1.905 ± 0.052 g/cm^3.

Self-supported zeolite films (see Fig. 1a) were characterized by scanning electron microscopy for the determination of layer thickness and the size and morphology of crystals. Fig. 1 shows SEM photographs of sample S1. In all cases, the films were formed by crystals with a silicalite-1 morphology (see Fig. 1e and f). In Fig. 1f crystals of different sizes can be observed. The mean size was 7 ± 3.7 μm, indicating a high variation in crystal size. Crystals observed in the mercury side are a/b-oriented (Fig. 1d), while in the solution side (Fig. 1e) there is no preferential orientation. This fact indicates that crystals are formed by homogeneous synthesis, and the first layer of crystals is a/b-oriented to compensate the surface tension of mercury, and afterwards there is no interaction with the support and crystals are deposited with a random orientation.

Fig. 2 shows the X-ray diffractograms of sample S1 for the mercury side and the solution side. In both cases the diffractograms correspond to the MFI pattern, typical morphology of silicalite-1. In agreement with SEM photographs, the peaks corresponding to planes (020) and (040) in the mercury side diffractogram are very intense, which is in accordance with an orientation of crystals type b. This can not be observed in the solution side.

3.1. Influence of gel composition

Fig. 3 shows the influence of gel composition in the growth of silicalite-1 layer. The use of a more diluted gel reduces the growth rate (Fig. 3B) and therefore the thickness (Fig. 3A), because the formation of crystals needs a high concentration of nutrients in the
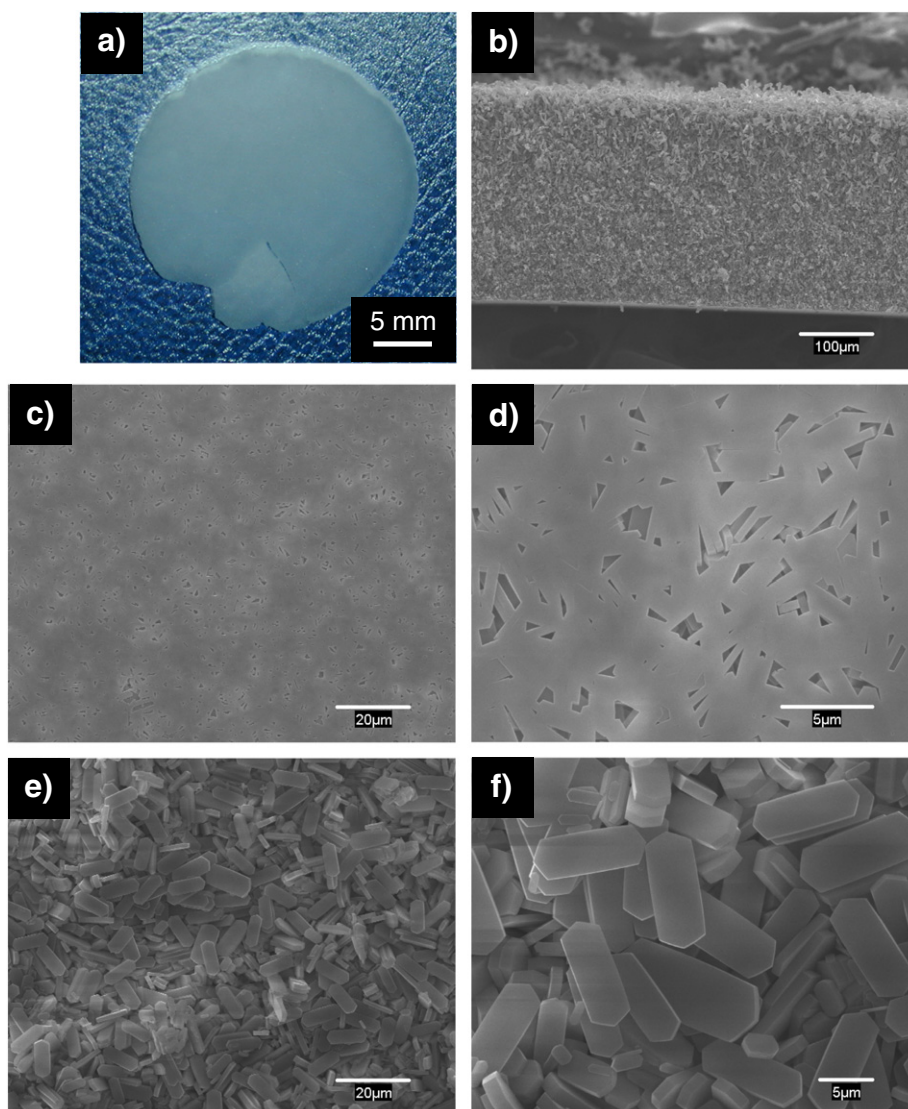

Fig. 1. a) Image of the layer S1. SEM photographs of sample S1: b) Cross section; c) Mercury side; d) Magnification of mercury side; e) Solution side; f) Magnification of crystals in solution side.