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Hierarchical silicalite-1 structures based on pyrolized materials

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ABSTRACT

The synthesis of silicalite-1 layers on pyrolyzed wood bodies with a desired shape was studied. The synthesis procedure is based in an "in situ" hydrothermal treatment of a precursor gel in which the support is immersed. Two different calcination methods were carried out, using a flow of air or N_2 and air. Samples were characterized by means of X-ray diffraction, thermogravimetric analyses and N_2 adsorption/desorption isotherms, revealing the existence of a micro/mesoporous hierarchical silicalite-1 structure.

1. Introduction

Mesoporosity in zeolites is of interest, as the sole presence of micropores often imposes diffusion limitations because of the restricted access and slow intracrystalline transport to and from the active sites [1]. In this context, Christensen et al. [2] reported the performance of zeolites with a hierarchical pore structure in the ethylation of benzene, concluding that the hierarchical zeolite was significantly more active than the conventional one.

One method to prepare hierarchical zeolites is the synthesis of zeolite layers over a carbon source. After the synthesis, carbon and template are burned away resulting in intracrystalline mesopores in the zeolite. Thus, carbon supports with different shapes [3–5], activated carbon [6], and carbon–ceramic [7] or carbon–silica [8] composites have been used.

On the other hand, pyrolysis of waste biomass is an interesting method to obtain carbonaceous supports for the synthesis of zeolites. Several vegetal wastes have been used. Katsuki et al. carried out the synthesis of ZSM-5 [9], and zeolites NaA and NaX [10] over carbonized rice husk, one of the most important byproducts (from rice) of biomass globally available. Onyestyák et al. synthesized zeolite Na-X [11] and mordenite [12] over wood char. This is a way to use the porous structure of wood to obtain a zeolite monolith using a natural resource instead of the typical ceramic supports. Other carbonized waste materials used for the synthesis of zeolites are corrugated paper [13], coal fly ash [14–16] or petroleum pitch [17].

The aim of this work is the preparation of hollow self-supporting zeolitic bodies with a hierarchical porous structure and a predefined shape. To this aim, a piece of wood, with the desired macroscopic shape, was pyrolyzed and used as macrotemplate-support for the synthesis of silicalite-1. After the synthesis of zeolite, support material as well as zeolite template were removed by calcination, thus obtaining a shaped polycrystalline zeolitic material without other materials.

2. Experimental

2.1. Support material pyrolysis

Cylindrical bodies of beech wood, with a length of 30 mm, an outer diameter of 6 mm and a wall thickness of 1 mm, were heated at 15 °C/min up to 500 °C for 2 h with a nitrogen flow of 1 L/min. Fig. 1a shows a cylinder before and after being pyrolyzed. As can be seen, after pyrolysis there is a reduction of 20% of the initial dimensions of the material.

2.2. Synthesis of zeolite

The method for the synthesis of silicalite-1 layers was that previously developed in our group for the synthesis of zeolite H-ZSM-5 films over alumina tubular supports [18]. The pyrolized body was immersed in a synthesis gel with a molar composition 19.46 SiO_2: 438 H_2O: 1 TPAOH. Briefly, the silica source was Ludox AS-40®, while TPAOH, the structure directing agent (SDA), is tetrapropylammonium hydroxide. The hydrothermal synthesis was carried out at 170 °C for 72 h. Two synthesis steps were carried out to get a thicker zeolite layer and then to increase the mechanical strength of the zeolitic body.

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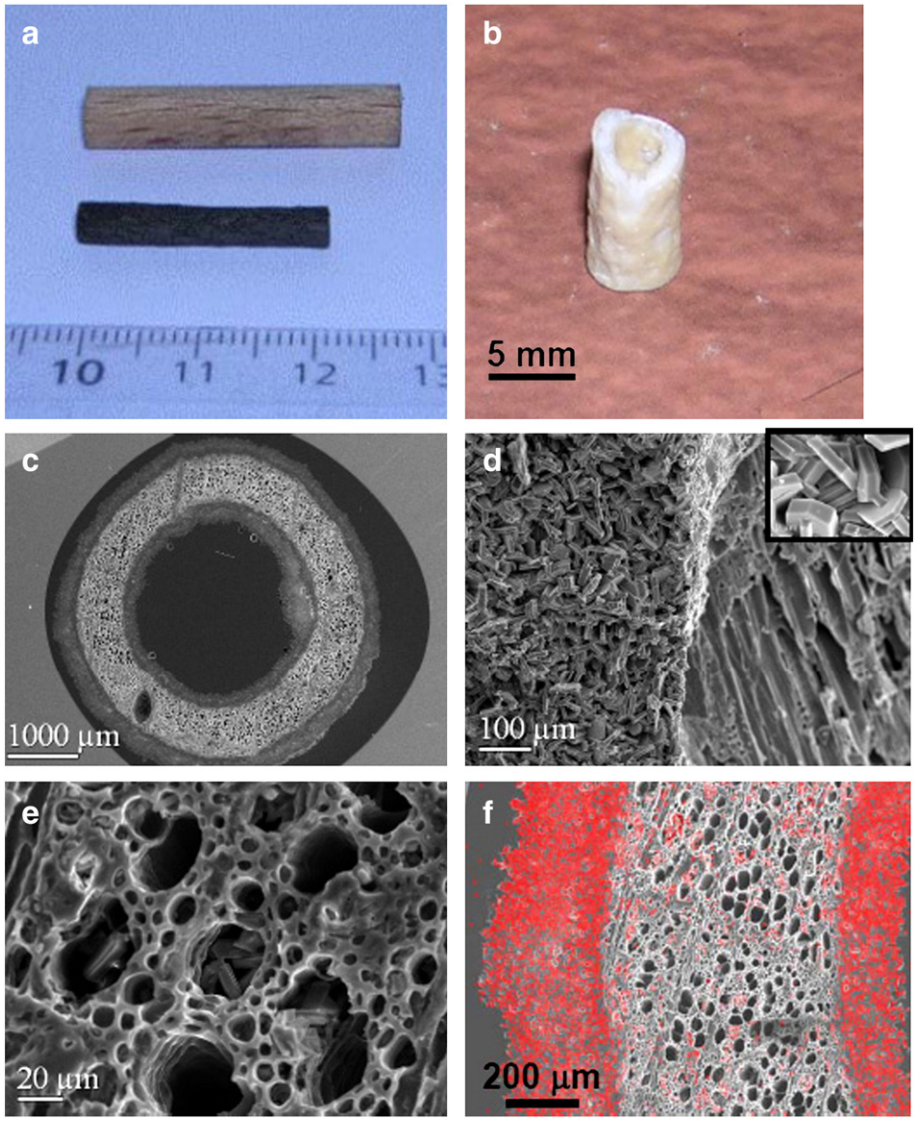

Fig. 1. Photograph of (a) wood cylinder before and after pyrolysis and (b) hollow zeolite piece after calcination with N_2 and air. SEM images of silicalite-1 layer over wood cylinders: (c) cross-sectional view; (d) front view of inner surface with inset showing silicalite-1 crystals in detail; (e) silicalite-1 crystals inside support pores. (f) Cross-sectional Si (red) EDX analysis.

2.3. Calcination

SDA and carbonaceous support were eliminated by calcination at 480 °C for 8 h with a heating rate of 0.5 °C/min. It was carried out by using either an air flow of 100 mL/min during all the calcination process or a 100 mL/min nitrogen flow during heating, which was replaced by air once the temperature of 480 °C was reached.

2.4. Characterization

The samples obtained before and after calcination were characterized by X-ray diffraction (XRD) analysis (Rigaku/Max diffractometer Cu Kα radiation and graphite monochromator); N_2 adsorption/desorption isotherms (Micromeritics ASAP 2020); scanning electron microscopy and EDX analysis (JEOL JSM-6400 operating at 20 kV); and thermogravimetric analysis (TGA, Mettler Toledo TGA/SDTA851e).

3. Results and discussion

X-ray diffractograms of silicalite-1 crystals and film over a carbonaceous support are shown in Fig. 2. Both diffractograms correspond with a MFI-type morphology and no other zeolitic phases are present.

Fig. 1b is a general view of the final product once calcined, no appreciable change was observed in the size of the body. SEM image 1c reveals a homogeneous layer of intergrowth crystals on both inner

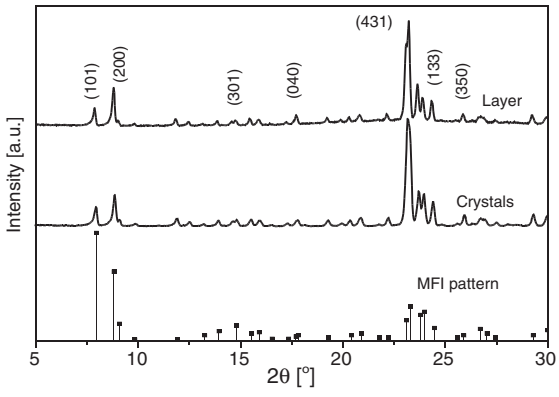

Fig. 2. X-ray diffractograms of the outer layer of silicalite-1 body and silicalite-1 crystals.