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Metal loaded zeolite films with bi-modal porosity for selective detection of carbon monoxide



Louwanda Lakiss^a, Sébastien Thomas^a, Philippe Bazin^a, Vincent de Waele^b, Svetlana Mintova^{a,*}

^aLaboratoire Catalyse et Spectrochimie (LCS), ENSICAEN, Université de Caen-CNRS, 6 Bd. Maréchal Juin, 14050 Caen, France

^bLaboratoire de Spectrochimie Infrarouge et Raman (LASIR), CNRS, Université de Lille 1, 59655 Villeneuve d'Ascq Cedex, France

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This article we dedicate to the 60th Birthday of Professor Thomas Bein.

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ABSTRACT

The assembly of metal containing (Pt and Pd) zeolite Beta nanocrystals in thin films retaining a bi-modal porosity (micropores of 0.73 nm and mesopores of 2.3–2.6 nm) is presented. The high porosity of metal loaded films was examined by adsorption of probe molecules (water and toluene). Besides, the optical properties of the films including surface roughness (10 nm), thickness (200–500 nm), and mechanical stability (Young's modulus of 0.7–1 GPa) are determined. The zeolite films are further used for detection of carbon monoxide as a single analyte and in a mixture with methanol at different temperatures; it is found that 70% of the Pt and Pd surfaces remain accessible for the CO, but higher partial pressure of the analytes is needed to reach the saturation level.

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1. Introduction

Nanosized zeolite crystals have been manufactured and assembled in thin-to-thick films using different approaches including direct crystallization, seeding, spin and dip coating, and sol-gel technique [1–3]. The variety of polycrystalline zeolite films deposited on porous and nonporous supports determine their application, which mainly depend on their hydrophobicity, thickness, and porosity. The porosity of zeolite films is complicated because it comprises interparticle and intraparticle porosity. Depending on the deposition method, zeolite films with variable properties can be prepared [4–7]. Besides, several types of metal and semi-conducting clusters in the zeolites can be incorporated and deposited in films with different optical properties [8,9]. The metal containing zeolites assembled in films with variable porosity and chemical composition have shown a great promise as size selective chemical sensors, anti-bio-fouling films, biocompatible layers, wear-resistant coatings, and de-humidifiers [10].

The porosity of powder zeolite samples is commonly probed via experimental determination of the adsorption isotherm of an inert gas, in particular, nitrogen or argon. Such a determination of the porosity practically involves the confinement of the porous sample

in vacuum and exposing it to an inert gas at increasing partial pressure and fixed temperature. Adsorption isotherms are determined using either volumetric or gravimetric methods. However, this sorption characterization cannot be directly applied to porous thin films since the film/support ratio is very low and thus the detection limit is low as well. Several non-destructive on-wafer methods such as positronium annihilation lifetime spectroscopy (PALS), small angle neutron scattering spectroscopy combined with specular X-ray reflectivity (SANS-SXR), and ellipsometry-porosimetry (EP) have been developed to determine the porosity, pore size, and pore size distribution of thin films [11–16]. The ellipsometry-porosimetry is a method that relies on the optical property changes of a film during the adsorption and desorption of an adsorbate. Toluene is commonly used as an adsorbate, and information for the pore size and pore size distribution in the film can be obtained. In addition, the ellipsometry-porosimetry approach has allowed modeling of the mesopore void space of pure silica zeolite films [17,15]. It is rather difficult to determine the porosity of zeolite films due to the limitation in characterization techniques applicable to self-standing and supported films. Besides, additional functionality in the films coming from the presence of metal clusters predominantly located in the pores is difficult to be characterized with the methods listed above.

This paper presents the preparation of metal loaded zeolite nanocrystals (zeolite Beta with Pt and Pd nanoparticles) assembled

* Corresponding author. Tel.: +33 2 31 45 27 37; fax: +33 2 31 45 28 21.

E-mail address: svetlana.mintova@ensicaen.fr (S. Mintova).

in films with bi-modal porosity. The properties of the metal loaded zeolite films including porosity, thickness, refractive index, and mechanical stability are determined and also their performance in detection of carbon monoxide and methanol in the presence of water is evaluated.

2. Experimental section

2.1. Preparation of zeolite suspensions

Zeolite Beta nanocrystals were prepared from Cab-O-Sil fumed silica as silica source, aluminum isopropoxide as aluminum source, and tetrapropylammonium hydroxide (TEAOH) as a structure directing agent. The synthesis mixture with a molar composition: 100 SiO₂:1.43 Al₂O₃:64.45 TEAOH:1500 H₂O, was first heated at 70 °C for 2 days, and then transferred to 100 °C for 8 days. After completing the synthesis, the crystalline suspension was purified by high-speed centrifugation (20,000 rpm for 1 h) in three subsequent cycles and re-dispersed in water. The crystalline zeolites were loaded with Pd and Pt by one step ion exchange treatment at 60 °C for 24 h using 0.01 wt.% (NH₄)₂-PdCl₆ and [Pt(NH₃)₄](NO₃)₂ solutions. The ion-exchanged samples were washed two times with water in order to remove the excess of metals prior to the reduction process.

The metal containing zeolite samples were subjected to gamma irradiation in order to reduce the metal cations (Pt⁺ and Pd²⁺) to metal nanoparticles (Pt⁰ and Pd⁰) following the procedure reported before [9]. The suspensions were subject to γ -irradiation provided by a panoramic ⁶⁰Co γ -source at the dose rate of 2000 Gy h⁻¹. Prior to irradiation, both suspensions Pt-BEA and Pd-BEA were introduced in a Pyrex cell along with 0.2 M *iso*-propanol, degassed and kept under N₂ atmosphere. The total dose delivered was 10 kGy. For simplicity, the zeolite Beta samples containing Pt⁰ and Pd⁰ will be further abbreviated as BEA-Pt and BEA-Pd, respectively.

2.2. Preparation of zeolite films

Zeolite films with a thickness of 250 nm from suspensions BEA-Pt and BEA-Pd were deposited on silicon wafers. The silicon wafers with a dimension of 10 × 10 mm were first cleaned in ultrasonic bath containing ethanol for 15 min, and then placed in a WS-400B-6NPP-LITE spin coater system. In order to ensure the preparation of smooth and homogenous films, the BEA-Pd and BEA-Pt zeolite crystals were re-dispersed in ethanol (coating suspensions) with a solid content of 2 wt.%. For the preparation of zeolite films, 1 ml of the coating suspensions were filtered (filters diameter of 200 nm), and then spin coated with a spinning rate of 3600 rpm s⁻¹ for 60 s. The spin coating process was performed 3 times (after each coating step, the films were dried at 250 °C for 60 min. The substrates were vacuum-locked under nitrogen atmosphere during spinning process. Finally, the mechanical stability of the films is increased and the organic template and solvents from the zeolite are removed under annealing at 450 °C for 1 h (heating rate of 3 °C/min). Both the BEA-Pt and BEA-Pd films with a thickness of 250 nm were subjected to detailed characterization. The BEA-Pt and BEA-Pd films with a thickness of 250 nm were then subjected to detailed characterization.

2.3. Characterization

The size and stability of the metal containing zeolite Beta particles in the colloidal suspensions were determined by dynamic light scattering (DLS) using a Malvern Zetasizer-Nano instrument equipped with a 4 mW He-Ne laser (633 nm). Besides, high-resolution transmission electron microscopy (TEM) using FEI 300

TEM microscope operated at 300 kV was applied to study the size and crystallinity of zeolites as well as the size and location of metal clusters. The chemical composition of the samples was measured by X-ray Fluorescence (XRF) analysis with a MagiX PHILIPS PW2540 (Si/Al ratio of zeolite Beta 12; content of Pt and Pd in samples BEA-Pt and BEA-Pd was 0.8 wt.% and 1.2 wt.%, respectively).

The reduction of metal cations in the zeolite suspensions was followed by UV-visible spectrophotometer using a Hewlett-Packard 8453A.

The morphology and average size of the zeolite crystals and the thickness of the films were measured by scanning electron microscopy (SEM) using a Philips XL30 microscope.

The thickness, refractive index (*n*), Young's module, contact angle (degree of hydrophilicity), and porosity of the films were characterized by ellipsometry-porosimetry (EP) in a vacuum chamber using a SOPRA instrument. The adsorption and desorption of water and toluene used as probe molecules in the films were performed at room temperature. In addition, some films were activated at 300 °C for 1 h prior to the measurements in order to remove the water completely.

The detection of carbon monoxide (CO) and methanol (CH₃OH) as pure compounds and in a mixture by BEA-Pt and BEA-Pd films were followed by *in situ* IR spectroscopy. A reactor-cell for characterization of films working in the temperature range 25–300 °C connected to *operando* gas-system was used to study the films (Fig. S1, Supplementary information). The entire process including activation of samples (removal of adsorbed water and contaminants at 300 °C) and controlled adsorption and desorption of pure CO, CH₃OH, and mixtures were performed in the *operando* IR cell. The experiments on the BEA-Pt and BEA-Pd films at 25, 75 and 100 °C were performed under argon flow. All experiments were performed in the presence of water with a concentration of 100 ppm coming from the carrier gas (Ar).

3. Results and discussion

3.1. Metal-loaded BEA zeolite in suspensions

The crystallinity and presence of metal nanoparticles in the Beta suspensions (BEA-Pt and BEA-Pd) were studied by TEM microscopy. As shown in Fig. 1, the BEA-Pt and BEA-Pd crystallites have well resolved crystalline fringes, and metal particles within the channels can be seen (Fig. 1a and b). The lattice fringes of the Beta crystals confirm the stability of the Beta zeolite nanocrystals after ion exchange and reduction process. Besides, the Pt and Pd nanoparticles randomly distributed within the Beta crystals were observed. There were no isolated pure metal nanoparticles in the suspensions or on the surface of the zeolite crystals observed. Additionally, the crystals size distribution of suspensions of BEA-Pt, BEA-Pd and pure BEA was measured by DLS at a constant pH = 9, and a constant concentration of solid particles (2 wt.%) (Fig. 1c). The crystals size distribution curve of pure Beta suspension contains only one peak centered at 120 nm. However, the metal loaded suspensions (BEA-Pt and BEA-Pd) exhibited a peak centered at 55 nm with an additional shoulder at 100 nm. These can be explained with a dynamic aggregation of metal containing zeolite nanocrystals. During the reduction process resulting in the formation of metal nanoparticles (Pt, Pd) in zeolite Beta crystals, disintegration of the aggregates was detected, resulting in the change of the position of the main peak in the DLS curves (Fig. 1c). The stability of the samples was investigated by measuring the zeta potential value for the three suspensions (BEA, BEA-Pt and BEA-Pd); the zeta potential value for all samples was between -27 mV and -32 mV. These results correspond to crystals having negative surface charge resulting in low to negligible agglomeration.

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