

Synthesis and characterization of mesoporous silica thin films as a catalyst support on a titanium substrate

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Available online 11 January 2007

Abstract

Mesoporous silica films with a thickness of 500–900 nm were synthesized on a titanium substrate by the evaporation-induced self-assembly method (with 900–1200 rpm for 90 s) using cetyltrimethylammonium bromide (CTAB) as structure-directing agent and tetraethyl orthosilicate as the silica source. Prior to coating deposition, the titanium substrate was oxidized to increase the surface roughness up to 500 nm and to produce a thin titania layer. Just before the synthesis, the titania layer was made super hydrophilic by an UV treatment for 2 h to provide a better adhesion of the silica film to the substrate. Films with hexagonal and cubic mesostructures with a uniform pore size of 2.8 nm and a surface area of 1080 m²/g were obtained and characterized by different methods. An alternative approach for surfactant removal by gradual heating up to 250 °C in vacuum was applied. Complete removal of CTAB from the as-synthesized silica films was confirmed by infrared spectroscopy.

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Keywords: Mesoporous silica; Evaporation-induced self-assembly (EISA); DRIFT spectroscopy

1. Introduction

The preparation of mesostructured silica thin films attracts considerable attention due to the potential industrial applications in sensors [1,2], microelectronics [3,4], optics [5,6] and separation [7]. Mesoporous silica thin coatings supported on (micro-) structured substrates are promising candidates for fine chemicals catalytic applications because of their large surface area, narrow pore size distribution and precisely tailored pore morphology, which decreases residence time distribution and increases the product yield. These materials are prepared using sol–gel chemistry in combination with texturation imposed by the physical chemistry of the surfactant and are deposited as thin films in an evaporation-induced self-assembly procedure (EISA) [8].

Most characterization studies are performed on glass, however depending on the application of the films, silicon for low-*k* applications [5], alumina for sensor applications [9], or porous alumina for membranes [7] are used as a substrate. Many

catalytic reactions proceed with large heat generation or absorption and from this point of view a metal support seems to be more preferable. In our work titanium is chosen as metal substrate. The surface of this metal can be oxidized to create titania which provides better adhesion of the silica film to the support. The distinctive feature of this support is that it represents super hydrophilicity of the surface containing more than 15 OH-groups per nm² [10].

In most of published studies the films were prepared from a mixture containing cetyltrimethylammonium bromide (CTAB) as a surfactant and a silica sol obtained by hydrolysis of an alkoxysilane in ethanol. During the rapid evaporation of the solvent, the micelle domains form and grow from the air–sol interface to the interior of the films. By changing the surfactant/silica ratio, different micellar structures were stabilized by the silica network formed during the rapid evaporation of the solvent: lamellar [11,12], 2D-hexagonal [12–14], 3D-hexagonal [15], and cubic [11,12,15]. The phase diagram proposed in [16] provides a basis for reproducible preparation of silica thin films with different mesostructures.

The objective of the present work is to develop highly ordered mesoporous silica films on a titanium substrate. The preparation of mesoporous thin films [11–17] and the formation

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mechanism are nowadays extensively documented [15,16]. However there is a limited number of published studies concerning the specific removal of the organic template. Among them are plasma and supercritical fluid extraction [18], solvent extraction [19], ozone treatment [20], and photocalcination using UV-light in vacuum [21]. Removal of surfactant from the inorganic–organic composite materials after synthesis is generally conducted via calcination in an air flow at high temperatures. However, this procedure often leads to film distortion or even cracks formation because of the considerable amount of internal stress generated by film shrinkage. Therefore, an alternative approach was applied to remove the organic components from as-synthesized silica thin films by gradual heating in vacuum up to 250 °C.

2. Experimental

2.1. Support pretreatment and characterization

Prior to the experiments, the titanium substrates of $1 \times 1 \text{ cm}^2$ and with thickness of 0.05 cm (99.6+ wt.%, GoodFellow) were ultrasonically treated in acetone. Then the plates were oxidized at 60 °C for 6 h in an aqueous hydrogen peroxide solution (30 vol.%, Fluka) and calcined at 500 °C to remove peroxide species. Just before the synthesis, the titania layer was made super hydrophilic by an UV treatment for 2 h to provide a better adhesion of the silica film to the substrate. The average surface roughness of the oxidized titanium substrates determined by Laser Scanning Confocal Microscopy was 500 nm. The wettability of the titania layer after the UV treatment was investigated on a Dataphysics OCA 30 device. Oxidized samples showed the water contact angle below 5° and no changes in wettability were observed on storage in air for 1 h after UV-irradiation.

2.2. Initial sols and thin film preparation

The initial sol was prepared by addition of cetyltrimethylammonium bromide [$\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$] (CTAB, Aldrich) dissolved in ethanol (96 vol.%, Merck) to a silica sol prehydrolyzed at 70 °C below the isoelectric point of silica (pH=2). The prehydrolyzed silica sol was prepared by mixing tetraethyl orthosilicate (TEOS, 98%, Merck), ethanol, water, and HCl (pH value of silica sol was kept below 2 by addition of HCl) and heating the mixture at 70 °C for 1 h. The typical molar ratios were as follows: 1 TEOS:34 EtOH:0.12–0.24 CTAB:2.8 H_2O :0.6 HCl. After an aging period of 2 h at room temperature the sol (100 μl) was deposited onto a titanium plate which was placed in a spin coater (with 900–1200 rpm for 90 s). The resulting films were dried at 80 °C for 1 h. The surfactant was removed from as-synthesized films by gradual heating with 1 °C/min up to 250 °C in vacuum.

2.3. Film characterization

Small-angle X-ray diffraction (SA-XRD) patterns were obtained on a Rigaku Geigerflex Diffractometer with $\text{CuK}\alpha$ radiation operated at 40 kV, 40 mA. The diffraction patterns

were recorded at a 0.02° step size and 1–10 s step time in $1-7^\circ 2\theta$. The surface morphology was investigated by a Field Emission Scanning Electron Microscope (FE-SEM, JEOL). The morphology of the films was determined by High Resolution Transmission Electron Microscopy (HR-TEM). HR-TEM was performed using a Philips CM30T microscope equipped with a LaB6 filament and operated at 250 kV. The films were scratched from the substrate. The collected powders and flakes were grinded and dispersed in ethanol. Then the suspensions were dropped gently to a holey amorphous carbon film on a Ni or Cu grid. N_2 adsorption/desorption isotherms of the mesoporous silica films were measured at -196°C on a Micromeritics ASAP 2010 instrument. A sample for one experiment ($\sim 18 \text{ mg}$ of films) contained 70 substrates with mesoporous silica films. Surfactant removal from the as-synthesized mesoporous silica films was studied by Diffuse-Reflectance Infrared Fourier Transform (DRIFT) spectroscopy (Nicolet Nexus FTIR). The surface properties of mesoporous silica films were investigated in a vacuum cell by DRIFT spectroscopy using the adsorbed CO. Prior to adsorption, the sample was pretreated in vacuum at room temperature for 2 h. DRIFT spectra of the initial sample and those after CO injection were registered at -196°C on a FTIR-8300 Shimadzu spectrometer with an attached device of diffusion reflection DRS-8000 in the region of $400-6000 \text{ cm}^{-1}$ with 4 cm^{-1} resolution and accumulation of 100 scans. The signal/noise ratio was above 10,000.

3. Results and discussion

The structure of the deposited films was determined by SA-XRD. Fig. 1 shows the SA-XRD pattern for the mesoporous silica film supported on the oxidized titanium substrate. The pattern indicates the intense (100) diffraction peak and a much weaker (200) peak. These peaks could be assigned to the 2D-hexagonal structure ($P6mm$) of the mesoporous silica film in which the channels aligned to the surface. Films with this type of mesostructure were found to form on the substrate at a

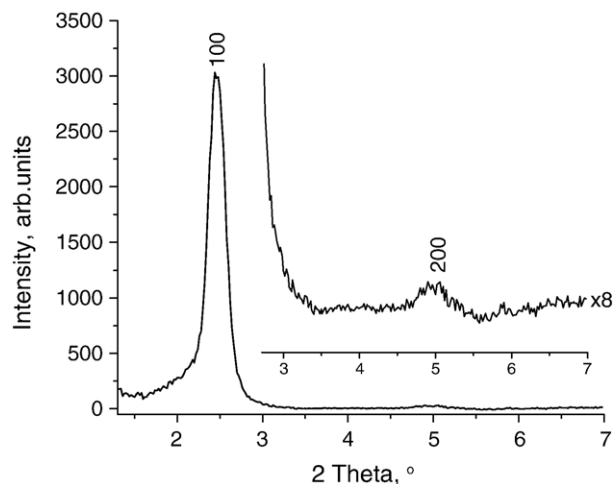


Fig. 1. XRD pattern for hexagonal mesoporous thin film supported on titanium obtained from a gel with CTAB/Si=0.20.

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