

Chemically Prepared Nanocrystalline Films: A Model System for Sulfated Zirconia

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The reasons for the extraordinary activity of sulfated zirconia for acid-catalyzed reactions such as *n*-butane isomerization have not yet been elucidated. Investigation of powders with the standard methods of acidity characterization yielded results which seem to be inconsistent with the catalytic activity [1]. Acidity measurements of oxide surfaces using powdered samples are often of limited value because of experimental problems or complexity of data. Our approach to the characterization of sulfated zirconia is to develop a well-defined model system, which will allow the successful application of techniques such as thermal desorption spectroscopy (TDS) and photoelectron spectroscopies (XPS, UPS).

A new chemical deposition technique to prepare nanocrystalline films of zirconia is described in the literature [2]. The key to this preparation is the use of a self-assembled monolayer (SAM), an ordered array of long chain surfactant molecules, which is anchored to the oxidized surface of a silicon wafer. A sulfonic acid group is then introduced as the functional group at the monolayer-air interface. The wafer is then immersed into an aqueous deposition medium, containing zirconium ions, sulfate and chloride. Within several hours a film, consisting of tetragonal zirconia as well as of sulfate-containing amorphous material, is formed. Calcination at 773K produces a predominantly tetragonal ZrO₂ film with 2-10 nm crystals [2].

We investigated specimens at each preparation step as well as the zirconia film properties in relation to deposition conditions by means of scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). We improved and adapted the method for our purposes, and attempted to identify the mechanism of film growth.

The quality of the self-assembled monolayer is essential for the quality of the film; particularly very thin films reflect inhomogeneities in the SAM. The oxidation step which is necessary to introduce the sulfonic acid groups was identified as a critical step in the preparation. However, zirconia film deposition was observed also without a SAM but the film was patchy and did not appear to adhere well to the substrate (SEM).

Previously reported deposition conditions [2] did not yield the best films for our purposes. The formation of colloids and their agglomeration to precipitates (consisting of basic zirconium sulfates) in the liquid phase during deposition was identified as the cause of flaws in the film. The 200 nm-1 μ m precipitate particles formed in the liquid phase are embedded in the film during growth or adhere to the film surface. They can be removed by washing the films with tissues but the film is detached along with the particles, which creates large defects. Investigations of the deposition media showed [3] that particle growth kinetics can be controlled by varying T, the Zr-, and the HCl-concentration. At 323K, a solution of 4 mmol Zr(SO₄)₂ in 0.4N HCl stays clear for 24h; but nanometer size clusters might be present so that it remains unresolved whether heterogeneous nucleation through the polar groups of the SAM initiates the film growth or whether homogeneously nucleated clusters adhere to the SAM.

Films were deposited from stable solutions with deposition times from 15 min to 48 h. Zirconium could be detected with XPS already after 15 min of deposition. A steady growth of the Zr signal was observed between 30 min and 4 h. Line shape analysis will provide insight into the chemical state of zirconium. The signal of the substrate (Si2p) was not detected anymore after 24 h of deposition, indicating the formation of a continuous film. Transmission electron microscopy (TEM) showed the film to be ca. 12 nm thick with 5 nm tetragonal ZrO₂ [4]. The surface of such a 24h deposited specimen was mostly defect-free (SEM), neither adsorbed particles, nor defective patches, nor cracks could be observed, and the surface was fairly smooth (AFM: $R_{\text{rms}} = 1.3$ nm). Calcination of the film at 773K in vacuum yielded an even smoother surface ($R_{\text{rms}} = 0.6$ nm). Crack formation was not observed.

We are now able to prepare films a few nanometers in thickness, containing sulfate and tetragonal zirconia. Charging problems in XPS are reduced in comparison to powders, and acquisition of interpretable UPS data seems possible, perhaps allowing the investigation of the catalyst valence states as well as the state of adsorbed molecules.

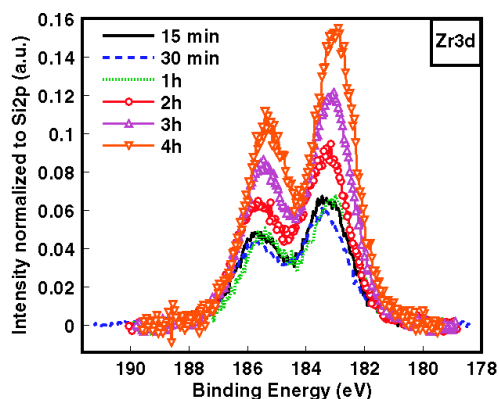


Figure 1: XPS spectra of the Zr3d signal of thin films deposited from a 4 mmol Zr(SO₄)₂ solution in 0.4N HCl at 323K, deposition time varied.

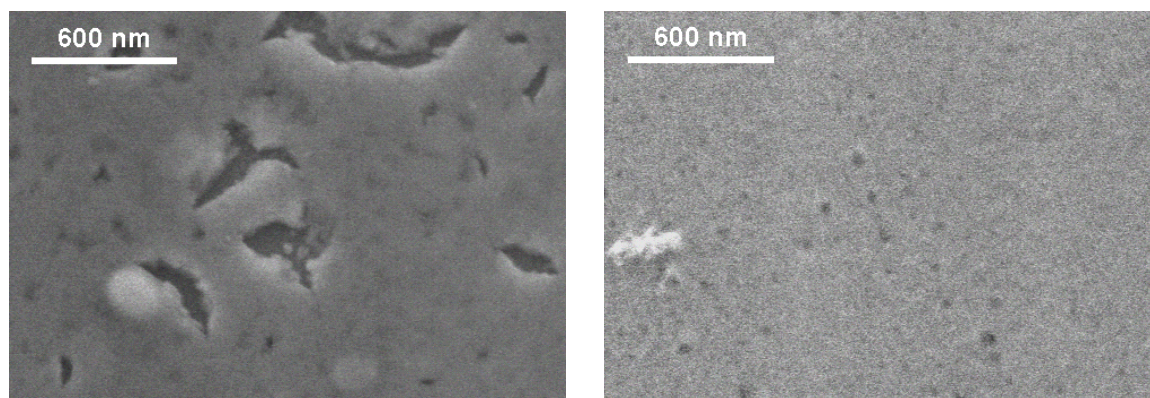


Figure 2: Scanning electron micrograph of a thin zirconia film, deposited from a 4 mmol Zr(SO₄)₂ solution in 0.4N HCl, and calcined at 773K; (left) original preparation method; (right) new improved preparation.

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- [4] A.D. Polli, T. Wagner, M. Rühle, A. Fischer, F.C. Jentoft, R. Schlögl, unpublished results