

Wet-Chemical Preparation and Characterization of Nanocrystalline Thin Films of Sulfated Zirconia

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Sulfated zirconia is a promising catalyst for the isomerization of *n*-butane [1]. The products after isomerization on powdered material indicate acid-catalyzed reactions, but the function of characterized acid sites (Brönsted, Lewis) in the reaction course have not yet been fully understood. Additionally the catalytic reactivity of the powdered oxide material cannot be explained with the acid strength of sulfated ZrO₂ as measured by standard methods of acidity characterization. The aim of this work is to develop a less complex system than the powdered material, a well-defined model system of a nanocrystalline thin film of sulfated zirconia. Such model systems will allow the application of surface sensitive techniques such as thermal desorption spectroscopy (TDS) and photoelectron spectroscopy (XPS).

Based on a biomimetic approach a stepwise wet-chemical deposition technique used generally for the preparation of ceramic oxide thin films is used to produce high quality specimens [2]. We investigated samples at each preparation step by means of scanning electron microscopy (SEM), atomic force microscopy (AFM), high resolution transmission electron microscopy (HRTEM), and XPS to elucidate the influence of the deposition conditions in relation to the film properties.

A cleaned and oxidized silicon wafer serves as the substrate, on whose surface a hydrophilic sulfonic acid terminated self-assembled monolayer (SAM) is anchored in order to obtain a well adherent and continuous zirconia film. Film deposition is performed in an acidic stock solution of zirconium sulfate (0.4 N HCl, 4 mM [Zr]) at 323-343 K between 3 h and 4 d. It has been shown that the colloid chemistry in the liquid phase plays an essential role during film formation [3]. Investigations with SEM indicate that the formation of precipitates at 343 K are the cause of flaws due to particles ($d = 0.2\text{-}1\ \mu\text{m}$) that are embedded in the film during growth or are adherent to the film surface. These films did not yield high quality samples for our purposes. In contrary, film deposition at 323 K takes place without visible bulk precipitation and film surfaces from such clear stable solutions are extensively defect-free and smooth ($R_{\text{rms}} = 1.3\ \text{nm}$, AFM) [4].

Structural properties and film thickness of the as-deposited and heat treated films from stable solutions were characterized by HRTEM. Cross sectional images of as -deposited films from stable solutions indicate an amorphous layer consisting of Zr, O, and S throughout the thickness of approx. 6 nm and 33 nm after a deposition procedure of 12 h and 48 h, respectively. Upon thermal

treatment a decrease in film thickness is measured and for films treated in Ar above 823 K a significant amount of t-ZrO₂ is observed.

Films calcined in an O₂:N₂ mixture (1:4 mixing ratio) at 773 K and subsequently transferred into the high vacuum chamber of a photoelectron spectrometer without exposure to the ambient were carbon-free. The maximum of the S 2p signal is detected at 168.8 eV revealing sulfur (+VI). Additionally, two oxygen species are distinguished (peak maxima at 531.9 and 530.2 eV), consistent with the presence of sulfate and oxide, suggesting that the films resemble sulfated zirconia. Adsorption experiments with ammonia (NH₃) to characterize acidic sites have been carried out, the results are promising in that two different adsorbed species were found [5].

Literature:

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