



## Reactivity of Nanocrystalline Sulfated Zirconia Model Thin Films



**R. Lloyd, H. Sauer, F.C. Jentoft, R. Schlögl**

Department of Inorganic Chemistry, Fritz Haber Institute, Max Planck Society,  
Faradayweg 4-6, 14195 Berlin, Germany

lloyd@fhi-berlin.mpg.de

Sulfated zirconia (SZ) is a catalyst for isomerization of *n*-butane at room temperature [1]. Previous studies of SZ have so far been unable to satisfactorily describe the nature of its active sites [2]. To improve the application of surface characterization techniques to the catalyst, a model system consisting of a nanocrystalline SZ thin film supported on a silicon wafer has been developed [3]. The present investigations address the role of the atmosphere during thermal treatment and validation of the model through interaction with probe molecule ammonia and reactant *n*-butane.

Oxidized silicon wafers are used as the substrate, onto which a film is grown from an aqueous acidic solution of zirconium sulfate via self-assembled monolayer (SAM) mediated deposition. Film thickness is controlled by deposition time; a linear growth rate of approx. 1 nm/h is observed for up to 192 h [4]. Thermal treatment of the films results in decomposition of the SAM and crystallization of zirconia with retention of sulfate; here the films are treated at 823 K in either N<sub>2</sub> or air. Interaction of the calcined films with *n*-butane and ammonia is investigated using thermal desorption spectroscopy (TDS). Comparative runs of an oxidized silicon wafer are used as a blank. For catalytic tests a low dead volume reactor is being

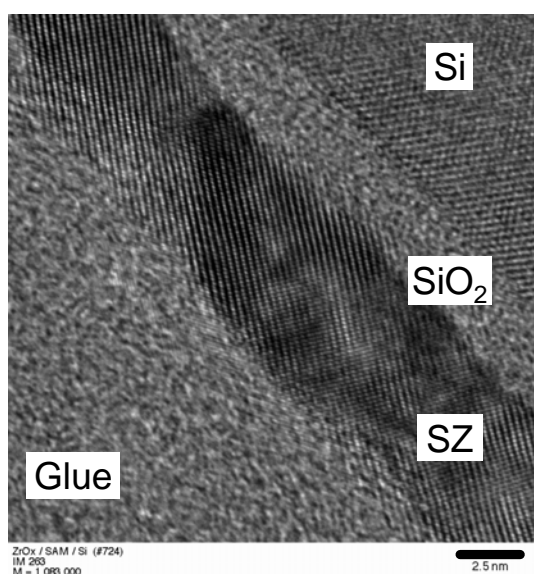


Figure 1: HRTEM cross section of a film treated in air at 823 K.

constructed, which allows flow and batch mode operation.

Analysis of high resolution transmission electron micrographs (Fig. 1) of the thermally treated films reveals structures consistent with that of the reported tetragonal phase [5]; although contributions from the cubic phase cannot be excluded. Scanning electron and atomic force micrographs of the thermally treated films show the surfaces to be continuous and crack free; although, films treated in air are slightly rougher. X-ray photoelectron spectra indicate the treatment atmosphere also influences the surface chemistry.

The O 1s signal comprises of at least two overlapping peaks - one at 532.0 eV attributed to sulfate and hydroxyl groups, and one at 530.2 eV due to the oxide. The relative intensity of the high binding energy species decreases during thermally treatment (more significantly for the N<sub>2</sub> treated films); concurrently the S content is reduced. Overall chemical compositions after thermal treatments are comparable to that of a typical SZ powder catalyst. Although treatment in N<sub>2</sub> produces smoother films, calcination in air is favored as it is analogous to commonly accepted powder synthesis.

*n*-Butane TDS show no typical hydrocarbon fragment signals, such as  $m/z = 43$  (C<sub>3</sub>H<sub>7</sub><sup>+</sup>), significantly exceeding those of the blank experiment. This preliminary result suggests there are no detectable amounts of strongly adsorbed butane species on the SZ surface at room temperature. From calorimetric measurements on powders it is known that the interaction of *n*-butane with the majority of sites on SZ is weak ( $\approx 45$ – $60$  kJ/mol [6]). Hence, from most of the sites butane molecules are easily removed in vacuum, and our TDS result confirms this scenario. Fragments indicative of sulfate decomposition ( $m/z=64$ ) are detected at temperatures over 723 K. NH<sub>3</sub> TDS profiles (Fig. 2) exhibit a broad peak from 373 to 423 K and a sharp peak centered at ca. 637 K for  $m/z = 15$ . Sulfate fragments are detected concomitant with the high temperature peak.

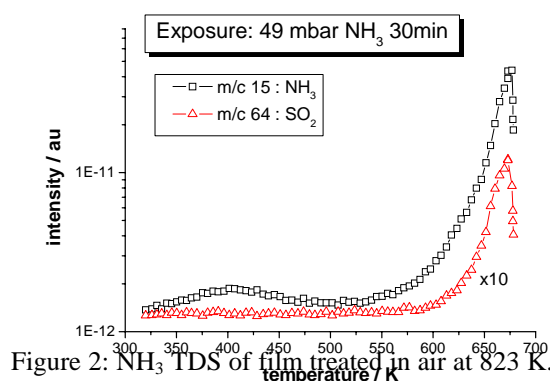


Figure 2: NH<sub>3</sub> TDS of film treated in air at 823 K.

This is consistent with earlier reports of sulfated oxides undergoing oxidative decomposition upon exposure to basic probe molecules at elevated temperatures [2].

The tetragonal nanocrystals, the surface composition, the weak interaction of most of the sites with butane and the reactive interaction with ammonia are properties that make the described films a suitable model for SZ catalysts.

Financial support through DFG priority program 1091 is kindly acknowledged.

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