



## Adsorption of probe molecules and reactants on a sulphated zirconia thin film model system



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Sulphated zirconia (SZ) is catalytically active for the isomerization of *n*-butane at room temperature [1]. Numerous investigations of the catalyst have been performed; however, no consistent theories have been devised to satisfactorily describe its active sites [2]. To improve surface characterization, a model system consisting of a nanocrystalline SZ thin film supported on a silicon wafer has previously been developed [3]. We now present results on the interaction of such films with the probe molecule NH<sub>3</sub> and the reactant *n*-butane.

Oxidized silicon wafers are used as the substrate, onto which a self-assembled monolayer (SAM) is deposited. The SAM terminal group functionality is then changed such that it initiates film deposition from an aqueous acidic solution of zirconium sulphate [3]. Film thickness is controlled by deposition time; a linear growth rate of approx. 1 nm/h is observed for up to 192 h [4]. Calcination of the films at 823 K results in decomposition of the SAM and crystallization of zirconia with retention of sulphate. For thermal desorption spectroscopy (TDS) the calcined films were exposed to *n*-butane or ammonia at pressures from 5x10<sup>-2</sup> mbar to 0.5 bar, for up to 1 h at 298 K. TDS was performed in vacuum with heating rates of 15 to 30 K/min. Comparative runs of an oxidized silicon wafer were used as a blank. For catalytic tests a low dead volume reactor is

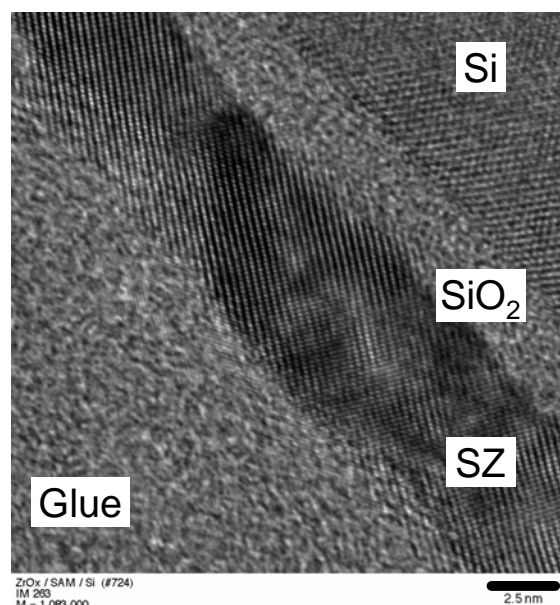


Figure 1: HRTEM cross section of a calcined film.

being constructed, which allows flow and batch mode operation under conditions of up to 723 K and 5 bar.

A high resolution transmission

electron micrograph of a calcined film is presented in Figure 1. The elucidated structure is 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 film show the surface to be overall smooth and crack free. The O 1s signal in X-ray photoelectron spectra is comprised of at least two overlapping peaks - one at 532.0 eV attributed to sulphate and hydroxyl groups, and one at 530.2 eV due to the oxide. The relative intensity of the high binding energy species decreases during calcination, concurrently the S content was reduced. The elemental composition of the calcined film is similar to that of a typical SZ powder catalyst (see table).

XPS quantification of surface composition

At%	Zr	O	S
as deposited	14.7	80.6	4.7
calcined	18.6	77.7	3.6
powder [6]	27	68	5

TDS results from *n*-butane showed no typical hydrocarbon fragment signals, such as  $m/z = 43$  ( $C_3H_7^+$ ), that significantly exceeded the signals in the blank experiment. These initial results suggest there are no detectable amounts of strongly adsorbed butane species on the SZ surface at room temperature. This observation is consistent with the small heats of adsorption ( $\approx 45$ -60 kJ/mol) obtained for butanes in calorimetric experiments for the majority of sites [7]. Fragments indicative of sulphate decomposition ( $m/z=64$ ) were detected at temperatures over 723 K.  $NH_3$ -TDS profiles exhibited a broad peak from 373 to 423 K and a sharp peak centred at ca. 637 K for  $m/z = 15$ . Furthermore, sulphate fragments are detected concomitant with the high temperature peak. This is consistent with earlier reports of sulphated oxides undergoing oxidative decomposition upon exposure to basic probe molecules at elevated temperatures [2].

The tetragonal phase, the chemical composition, the weak affinity of butane to most of the sites, and the intense interaction with ammonia correspond to the properties of typical active sulphated zirconia powders. Hence, the thin films produced are viable model catalysts.

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