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Adsorption of Methanethiol on Stoichiometric and Defective TiO₂(110) Surfaces: A Combined Experimental and Theoretical Study

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Introduction: Self-assembled monolayers (SAMs) of alkanethiol on metal and semiconductors are receiving a lot of attention due to possible technical applications in areas of biosensing, catalysis, tribology, and microelectronics [1]. In this respect, it is important to establish the nature of the interactions between the substrates and S groups in the monolayer interface, including the identification of sites for molecular adsorption and dissociation, and the possible formation of lateral S-S bonds [1,2]. A complete understanding of these basic issues is necessary for tailoring the physical and chemical properties of SAM functional materials in a controlled manner [1].

Methods and Materials: The chemistry of methanethiol on stoichiometric TiO₂(110) and defective TiO_{2-x}(110) was investigated using synchrotron-based soft X-ray photoemission (SXPS), thermal desorption spectroscopy (TDS) and first-principle density-functional (DF) slab calculations.

Results: On the Ti and O sites of a perfect TiO₂(110) substrate there is no dissociation of CH₃SH. The molecule bonds to Ti sites via its S lone pairs and desorbs at temperatures below 300 K. TDS experiments show molecular desorption peaks in the range 206-160 K (corresponding to desorption energies of ~ 13-10 kcal/mol) that can be attributed to CH₃SH chemisorbed on terraces of TiO₂(110). From defect sites, methanethiol desorbs at relative high temperature, ~ 288 K, with a desorption energy of ~ 18 kcal/mol. The presence of O vacancies in the oxide surface produces electronic states that facilitate the cleavage of the S-H bond and the deposition of CH₃S. The bond between CH₃S and O-vacancy sites is mainly covalent, but the bonding interactions are very strong and can induce the migration of O vacancies from the bulk to the surface of the oxide. In systems with a limited number of O vacancies, adsorbed CH₃S and H can recombine and desorb as CH₃SH into gas phase. For surfaces with a large concentration of O vacancies and defects, there is extensive decomposition of CH₃SH at 100 K, producing a mixture of SO_x, CH_x, S, and CH₃S on the oxide. The C-S bond in adsorbed CH₃S breaks in the 250-750 K temperature range, with CH₃ or CH₄ desorbing into gas phase and leaving S and CH_x fragments on the surface. These results illustrate the important role played by O vacancies in the chemistry of a thiol over an oxide surface.

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