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Interaction of Sulfur with TiO₂(110): O↔S Exchange and Sulfide Formation

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Introduction: In chemical feedstocks derived from petroleum or other natural sources, sulfur containing molecules are common impurities [1] and are responsible for the poisoning of catalysts used in many chemical and petrochemical processes [2,3]. TiO₂ is employed on a large industrial scale for the removal of H₂S in the Claus process [4]. Understanding on a molecular level of the sulfur interaction with TiO₂ surfaces may lead to design of better catalysts for hydrodesulfurization and/or sulfur tolerant catalysts.

Methods and Materials: A single crystal TiO₂(110) is employed for Sulfur adsorption and interaction using synchrotron-based high resolution photoemission spectroscopy (PES), Auger electron spectroscopy (AES), Temperature programming desorption (TPD), and first-principles density functional (DF) slab calculations.

Results: Sulfur adsorption on TiO₂(110) gives rise to multilayer at 100 K. S₂ and S_n species are detected on the surface by high-resolution PES and AES. At 300 K there is less than one monolayer on the TiO₂(110) surface. PES shows the presence of the at least three different types of sulfur species associated with SO_x groups and S atoms bonded to the Ti rows or O vacancies in the bridging oxygen rows. After annealing this surface to 600 K, only S atoms bonded to O vacancies remain on TiO₂(110). A desorption state at ~ 460 K for S₂ (mass 64) was observed in TPD spectra, in good agreement with PES results. The introduction of O vacancies in TiO₂(110) generates new occupied states at ~ 2 eV above the top of the {O 2p + Ti 3d} valence band, which are ideal for electron-donor interactions with S. TiO₂(110) bonds sulfur much stronger than highly ionic oxides like MgO or Al₂O₃. This trend can be explained with a simple model based on band-orbital mixing. When the TiO₂(110) surface was kept at above 600 K during the sulfur adsorption, all surface oxygen was replaced by S. PES shows a complete loss of oxygen from the surface. At the same time a large binding energy shift of Ti 2p core levels by 2.5 eV towards lower binding energy suggests complete reduction of the Ti⁴⁺ surface layer. The intensity of Ti core levels is lowered by one half and the S 2p data show the presence of three different S species. These S species desorb at ~ 1100 K, leaving a clean and defective TiO₂(110) surface. The TPD result indicates S₂ as the major desorption product.

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