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Scanning Tunneling Microscopy of Sulfur and Benzenethiol Chemisorbed on Ru(0001) in 0.1 M $HClO_4$

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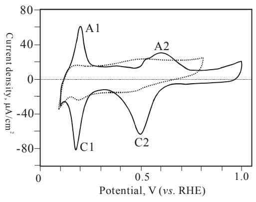
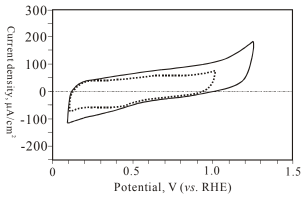
The adsorption of sulfur adatoms (SA) on Ru(0001) has been extensively examined to reveal its interfacial structure for its applications in catalysis. Five ordered structures, $p(2 \times 2)$, $(\sqrt{3} \times \sqrt{3})R30°$, $c(4 \times 2)$, $\begin{pmatrix} 7 & 0 \\ 3 & 6 \end{pmatrix}$, and $(\sqrt{7} \times \sqrt{7})R19.1°$, have been identified to form at gas-solid interfaces with increasing coverage from 0.25 to 0.57. Depending on the coverage, interaction between SA's can be repulsive or attractive. In particular, repulsive interaction was observed for $p(2 \times 2)$ and $(\sqrt{3} \times \sqrt{3})R30°$, as SA's were adsorbed as individual atoms at hcp 3-fold hollow sites at the coverage of 0.25 and 0.33, respectively. In contrast, pairwise or three-body interaction prevails to produce apparent atomic clusters in $c(4 \times 2)$ and $(\sqrt{7} \times \sqrt{7})R19.1°$ at the coverage of 0.5 and 0.57, respectively. From the perspective of catalysis, Ru is of great importance for its role in reducing the poisonous effect of carbon monoxide on the Pt anode of a fuel cell, but this property is greatly obstructed by the adsorption of SA. The passivation effect of SA on transition metals seems to arise from the formation of a strong covalent bond between S and metal surfaces, which depletes the charge density of *d* orbitals needed for the metal atoms to bind with other species. Furthermore, sulfides of Ru can selectively perform hydrodesulfurization (HDS) on dibenzothiophene, a molecule particularly difficult to desulfurize. HDS is an important reaction in processing petroleum.

The electrochemistry of sulfur at a few single crystal electrodes such as Au(111), Cu(111), and Pt(111) has been reported. Results show that the redox process of sulfur varies substantially with chemical identity of the electrode. On Au(111) sulfur is changed slowly from $(\sqrt{3} \times \sqrt{3})R30°$ to S_8 octomers at potentials positive of -0.7 V in 0.1 M NaOH. On Cu(111) ordered adlattices of sulfur adatoms, $(\sqrt{3} \times \sqrt{3})R30°$ and (19×19), are produced before the formation of sulfide at the onset potential of Cu dissolution. On Pt(111) SA is oxidized to sulfate, without being converted to the S_8 octomer or sulfide species. Ruthenium, being a member of the platinum group, it is possible that sulfur on Ru would behave similarly to that on Pt. However, the electrochemistry of sulfur at Ru electrode has not been investigated. Because sulfur can act as a poison to Pt and Ru electrodes, it is important to gain better understanding of sulfur adsorption at electrified interfaces of these materials.

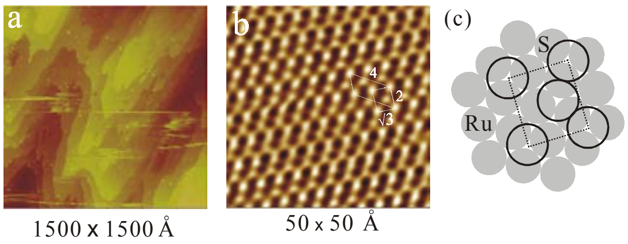
In situ scanning tunneling microscopy (STM) combined with linear sweep voltammetry was used to examine spatial structures of sulfur adatoms (SA) and benzenethiol (BT) molecules adsorbed on an ordered Ru(0001) electrode in 0.1 M $HClO_4$. The Ru(0001) surface, prepared by mechanical polishing and electrochemical reduction at –1.5 V (vs. RHE) in 0.1 M $HClO_4$, contained atomically flat terraces with an average width of 20 nm. Cyclic voltammograms (Fig.1 and 2) obtained with an *as-prepared* Ru(0001) electrode in 0.1 M $HClO_4$ showed characteristics nearly identical to those of Ru(0001) treated in high vacuum. High-quality STM images were obtained for SA and BT to determine their spatial structures as a function of potential (Fig. 3 and 4). The structure of the SA adlayer changed from $(2 \times \sqrt{3})rect$, to domain walls, to $(\sqrt{7} \times \sqrt{7})R19.1°$, and then to disordered, as the potential was scanned from 0.3 to 0.6 V. In contrast, molecules of BT were arranged in $(2 \times \sqrt{3})rect$ between 0.1 and 0.4 V, while they were disordered at all other potentials. Adsorption of BT molecules was predominantly through the sulfur headgroup. Sulfur adatoms and adsorbed BT molecules were stable against anodic polarization up to 1.0 V (vs. RHE). These two species were adsorbed so strongly that their desorption did not occur even at the onset potential for the reduction of water in 0.1 M KOH.





Figs. 1. Cyclic voltammograms of Ru(0001) recorded at 50 mV/s in 0.1 M $HClO_4$. The Ru(0001) electrode was prepared by mechanical polishing with aluminum oxide particles measuring down to 0.1 μm (dotted trace), followed by reduction at –1.5 for 5 min (solid trace).

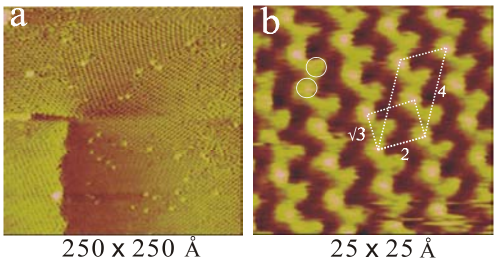
Fig. 2. Voltammograms for Ru(0001) coated with a monolayer of sulfur adatoms recorded at 50 mV/s in 0.1 M $HClO_4$



1500 x 1500 Å

50 x 50 Å

Fig. 3. In situ STM topography scan (a) and atomic resolution of sulfur adatoms revealing surface morphology and atomic structure of Ru(0001) pre-treated with mechanical polishing and reduction at –1.5 V for 5 min. The potential of Ru(0001) was 0.2 V, and the STM imaging conditions were 200 mV and 2 nA.



250 x 250 Å

25 x 25 Å

Fig. 4. In situ STM molecular resolution of benzenethiol adsorbed on Ru(0001). The potential of Ru(0001) was 0.2 V, and the STM imaging conditions were 200 mV and 2 nA

Reference:

Ou Yang et al *Langmuir* 2004 in print.