UHV AND STM STUDIES OF ADSORPTION OF SULFUR ON THE PT(111) ELECTRODE

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We will review electron spectroscopic and diffraction results obtained in ultrahigh vacuum and scanning tunneling results, for sulfur adlayers deposited from aqueous sulfide and bisulfide media on Pt(111) [1-3]. The highest coverage obtained by Auger electron spectroscopy, 0.94 +/- 0.05 ML (monolayers), is very close to the coverage obtained from coulometry, and is associated with a (1 x 1) surface phase. This coverage is much higher than that obtained in previous electrochemical studies by other investigators but is the same as found using S2 beam dosing in vacuum. The near complete sulfur monolayer is characterized by a rapid but incomplete voltammetric oxidation in a narrow potential range near 0.70V vs. a Ag/AgCl reference. Neither the full sulfur monolayer coverage (around 1 ML) nor the sharp voltammetric transition could be obtained when traces of oxygen were present in the electrochemical cell. Oxidation of the (1 x 1) adlayer gave rise to a previously unreported (2 x 2) structure at 1/2 ML. Further voltammetric stripping resulted in two more adlattices: (3 x 3)R30^{o} at 1/3 ML, and p(2 x 2) at 1/4 ML, as reported in previous gas phase studies. The selective stripping procedure provides unique electrochemical control at room temperature of the sulfur structure and coverage, without any change in the long-range surface order of the substrate. When dosing was carried out from bisulfide solution, a ($\sqrt{3}$x 7) phase at 3/5ML was formed. The results of the core-level electron energy loss spectroscopy studies suggest that sulfur adatoms retain some of the negative charge and that this charge plays a major role in controlling hydrogen adsorption coverage in the presence of coadsorbed sulfur on Pt(111).

We believe that our observations are important for several reasons: (i) we found that the electrooxidation of surface sulfur may occur in the form of a narrow voltammetric spike in the potential range preceding surface oxidation. (ii) we found a series of surface structures depending on sulfur coverage, (1 x 1), (2 x 2) at 1/2 ML, etc. and a low coverage (2 x 2). Such a rich structural chemistry has not yet been reported in electrochemical research on simple surface systems. (iii) we provided evidence that a negative charge resides on the Pt(111) bound $S_{adsorbate}$. (iv) we connected the data on sulfur chemical states to a nonlinear suppression effect that the $S_{adsorbate}$ exerts on hydrogen adsorption. (v) we showed evidence that oxygen is permanently incorporated in the S-adsorbate if sulfur adsorption takes place in solutions containing traces of atmospheric oxygen. In summary, we believe our studies provide a detailed picture of sulfur adsorption on Pt(111), connect the structure with typical forms of electrochemical reactivity, and highlight the need for the oxygen-free environment for studies with the S adsorbate in electrochemistry. We conclude that the structure of chemisorbed sulfur, due to its high stability in both aqueous solutions and vacuum, can successfully be investigated by electron spectroscopies and electron diffraction in UHV. The advantage of these techniques is that they reveal surface structure and chemical state in a single solution-vacuum emersion experiment at any level of microscopic insight. New STM data on sulfur adsorption on Pt(111) will be reported.

References:

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