Quarterly Progress Report for the period 4/01/92- 6/30/92

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1. Background

This project revolves around understanding the fundamental processes involved in the catalytic removal of harmful oxygenated organics present in coal liquids. We are modelling the complex type of sulfided Mo catalyst proposed for these reactions with simple single crystal surfaces. These display a controlled range and number of reaction sites and can be extensively characterized by surface science techniques. We then investigate the reaction pathways for representative simple oxygenates upon these surfaces.

2. Summary

We have successfully solved the structure of Mo(110) p(2x2)-S structure and found the S atom to reside very close to the center-hollow site of a laterally-distorted first Mo layer. Some small vertical distortions in the top two Mo layers are also present.

Preliminary results from experiments carried out with substituted furans indicate that the pattern of reaction is very similar to that of furan itself. The most significant change appears to that substitution beyond the mono stage results in substantial blocking of the adsorption process.

3. Progress

a) determination of the Mo(110) p(2x2)-S structure

We have expanded our investigation of the Mo(110) p(2x2)-S structure using tensor low-energy electron diffraction (TLEED). In the last report we found that the S atom was probably located in the center-hollow (CH) quasi-fourfold symmetric site on the Mo(110) surface at about 1.5Å above the topmost metal layer (Figure 1). However,
the agreement between the experiment and theory was only moderate, which we suspected was due to ignoring the possible reconstruction of the underlying metal atoms due to adsorption. Such adsorption-induced reconstructions are becoming an increasingly common occurrence.

Accordingly we have expanded the calculations to allow the metal atom locations to relax and monitor the changes in the degree of fit, as measured by the Pendry R-factor [1]. The TLEED codes [2] are set up to automatically traverse the multiparameter space (actually 17 parameters are varied) and locate the global minimum. Locating the global as against a local minimum can be checked by starting the calculations from different initial configurations of the adatom. Figure 2 shows how the Pendry R-factor changes with iterations of the program (each iteration varies all the structural parameters to produce the best fit) if we start from either the center-hollow (CH) or 3F sites. The CH site always produces a slightly lower R-factor. The best fit structure shows show significant shifts of the metal atoms (described later). The location of the S atom also changes during the optimization process. One way to view this process is to plot the location of the S atom along the line that joins the 3F and CH sites as shown in Figure 3. Here we see that if we start the S atom at the 3F site, it moves towards the CH site, and the R-factor stabilizes at 0.37. On the other hand, if we start the S atoms at the CH site, its location hardly moves, and the R-factor settles down to a lower value of 0.298. We obtain the atomic locations of all the Mo atoms in the first two layers and well as the S adatom.

The final result is that the p(2x2)-S structure on Mo(110) has the S atom close to
the CH location set in the reference structure, shifted slightly (by 0.03 Å) along the cell diagonal. However, the Mo2 and Mo3 atoms that were closest to the S atom in the reference CH structure move outward (in the x and y directions respectively) by about 0.3 Å, while Mo4 moves along the cell diagonal an equivalent amount to the movement of the S atom (see Figure 3). Also the first Mo layer is rumpled with Mo2 and Mo3 depressed by 0.08 - 0.14 Å relative to Mo1 and Mo4, while the second Mo layer shows less vertical rumpling (see Figure 4). The most significant lateral movement in the second Mo layer is that of Mo5 that moves along the unit cell diagonal by close to 0.2 Å.

The end result of these substrate shifts is that the S adatom is located in a distorted central hollow. This distortion is such that the final coordination of the S atom is rather closer to 3-fold coordinate rather than the 2+2 coordination characteristic of the undistorted CH site. There are now three slightly different Mo-S bond lengths:

\[
\begin{align*}
\text{Mo1 - S} & : 2.78 \text{ Å} \\
\text{Mo2,3 - S} & : 2.49 \text{ Å} \\
\text{Mo4 - S} & : 2.72 \text{ Å}
\end{align*}
\]

The shortest bond-length between Mo2,3 and the S atom is less than the sum of atomic (hard-sphere) radii of 2.65 Å. Mo1 lies slightly deeper than Mo4 and therefore has the longest bond length.

Shih et al [3] have studied the structure of the analogous Fe(110) p(2x2)-S system by a conventional LEED method. Their results placed the S adatom in the middle center hollow site surrounded by 4 Fe atoms that are laterally shifted in a different manner to
that which we have found for Mo. In their structure the Fe atoms remain in the same relative locations to one another as in the bulk, but the unit cell of the top layer is contracted symmetrically with respect to the bulk unit cell. The overall effect is that the Fe atoms are "attracted" to the adatom, leaving more open areas between the S-Fe$_4$ units. We should note they to some extent selected for this structure by only examining structures that preserved the rectangular symmetry of the surface unit cell. In addition they did not allow for surface rumpling of the sort we find for the Mo system.

b) reaction of substituted furans on Mo surfaces

We have started experiments to probe the reactions of methyl substituted furans and tetrahydrofuran on clean and sulfided Mo surfaces. Preliminary results indicate that the pattern of reaction is very similar to that of furan itself. The most significant change appears to be in the amount of materials that absorbs. It seems that substitution beyond the mono stage results in substantial blocking of the adsorption process.

4. Future Work

We will pursue the reactions of the substituted furans in more detail, particularly with regard to their behavior as a Mo surface is progressively sulfided.

5. References


2. M.A. Van Hove, P.J. Rous, A. Wander and A. Barbieri, Lawrence Berkeley Laboratory, Berkeley, CA 94720 (kindly supplied by Dr. Van Hove).

Figures

1. Location of the three-fold (3F) symmetric and center-hollow (CH) adsorption sites on the Mo(110) surface.

2. Variation of the Pendry R-factor with TLEED code iterations starting from either the CH or 3F sites.

3. Variation of the position of the S atom along the line linking the CH and 3F sites with iteration number.

4. The TLEED optimized Mo(110) p(2x2) - S structure. The hatched and dark large circles represent first and second layer Mo atoms respectively. The S adatoms are shown as black circles with diameters smaller than the atomic radius for clarity. Arrowheads show the direction of movement of substrate atoms relative to their locations in the bulk structure.

4. A cross-section through the TLEED optimized Mo(110) p(2x2) - S structure of Figure 3 along the direction linking Mo1 and Mo4. Atoms with dashed outlines lie off this line and are projected onto it. The numbers indicate vertical shifts of atoms in Å from their bulk locations (shown as the long solid lines) e.g. Mo4 has moved down from its bulk location by 0.07 Å.
Figure 2
Figure 3

![Graph showing iteration number vs. Delta R(3F-CH) with two curves labeled CH and 3F, and RPE values of 0.370 and 0.298.](image-url)