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**Quarterly Progress Report for the period 6/30/91 - 09/30/91
to the US Department of Energy**

Project title: "Fundamental Studies of Catalytic Processing of Synthetic Liquids"

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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

Our previous work has shown that an important component of furan reactions on sulfided Mo surfaces are dehydrogenation reactions of adsorbed hydrocarbon fragments. The desorption of hydrogen occurs in several steps and is strongly influenced by the amounts of sulfur and carbon on the surface. In order to understand this complex behavior during this period we have performed a complete series of adsorption/desorption experiments for hydrogen (deuterium) on Mo(110) that has been prepared with varying amounts of carbon and sulfur on the surface. Hydrogen adsorption is blocked by preadsorbed sulfur with a dramatic weakening of the strength with which hydrogen is bound to the surface. Hydrogen adsorption is totally blocked by 0.5 ML of preadsorbed sulfur.

3. Progress

a) Adsorption/desorption of hydrogen on clean Mo(110)

Figure 1 shows a series of deuterium thermal desorption spectroscopy (TDS) traces after various exposures of Mo(110) to deuterium. Deuterium is used rather than hydrogen itself as the TDS signal is much cleaner than that from hydrogen because of the very low background at AMU 4 compared to AMU 2; experience with other systems has shown that deuterium TDS is almost identical to hydrogen TDS and we shall refer to deuterium and hydrogen interchangeably. Our data is very similar to that of Mahnig and Schmidt [1] if we allow for the slower heating rate in our case. Above 10L exposure to hydrogen the amount of material that desorbs, as measured by the area under the TDS curve, does not

change indicating that the surface has saturated. The saturation coverage hydrogen cannot be directly measured from these experiments, but we can estimate it in the following manner. Zaera et al [2] have shown that on Mo(100) the saturation coverage of hydrogen corresponds to 2 H/Mo. Mahnig and Schmidt [1] found that the maximum hydrogen TDS yield from Mo(110) was just 1/2 of that from Mo(100), indicating a saturation coverage of 1 H/Mo. Given the close agreement between our data and that of Mahnig and Schmidt, we therefore will assume that the saturation coverage that occurs at about 10L exposure corresponds to a hydrogen coverage equal to 1.0 ML. With this assumption we can construct an uptake curve for hydrogen on the clean Mo(110) surface as shown in Figure 2.

The D₂ TDS curves shown in Figure 1 can be interpreted in the following manner. At the lowest hydrogen coverages, hydrogen desorbs in a single symmetric peak (designated β_2 by Mahnig and Schmidt) centered at about 230°C. As the hydrogen coverage is increased this peak increases in area and shifts to lower temperature. At about 1L exposure this peak saturates and a second β_1 peak appears at about 165°C that also shifts to lower temperature with increasing hydrogen coverage. The behavior of these peaks are indicative of second-order desorption processes. In the case of the low-coverage data, where we can easily isolate the β_2 peak, we can analyze the data to extract the kinetic parameters. The simplest approach is that of Redhead [3], who showed that if the energy of desorption (E_d) and the frequency factor (ν) are independent of the hydrogen coverage (Θ_H), then the peak maximum (T_m) is related to the coverage by:

$$\ln(T_m^2 \Theta_H) = (E_d/R)(1/T_m) + \ln(\beta E_d/R\nu)$$

This relationship is plotted in Figure 3 and yields a value of $E_d = 19$ kcal/mol. The curve is not a true straight line because of the assumption of no changes in the kinetic parameters with coverage. More complex procedures are available [4] to more accurately evaluate these parameters.

The origin of the high-coverage peak is not clear. It could result from occupation of a second type of adsorption site, but King [4] has argued for the H/W(110) system that

the occurrence of two peaks at high hydrogen coverages is due to interactions among the adsorbate atoms that become important as the surface concentration of hydrogen increases.

b) Adsorption/desorption of hydrogen on sulfided Mo(110)

Preadsorption of sulfur on the Mo(110) surface has a dramatic effect on the amount of hydrogen that can be adsorbed, and on the position of the hydrogen TDS peaks. Figure 4 contrasts the TDS signals from the clean Mo(110) surface with that from a surface with 0.4 ML of sulfur on the surface. We can see that the amount of hydrogen adsorbed is greatly reduced, at about 0.5 ML of sulfur no hydrogen can be adsorbed - that is the surface is completely blocked towards hydrogen adsorption. The hydrogen that does desorb does so with similar peak shapes to that from the clean surface, but at much lower temperatures. The severity of these effects scales with the sulfur coverage as is demonstrated in Figure 5. Here the saturation coverage and peak maximum can be seen to move to lower values as the amount of sulfur on the surface increases.

The fact that the hydrogen TDS peak temperatures are shifted to lower temperatures relative to the clean surface indicates that the bond between the surface and adsorbed hydrogen is less strong when adsorbed sulfur is present. Thus, if desorption of hydrogen were to be the rate-limiting step during a dehydrogenation process involving hydrocarbon moieties on the surface, then the sulfided surface would allow the reaction to proceed more easily than the clean surface.

The range of the blocking effect of sulfur on hydrogen adsorption can be investigated in the following manner. If we accept that the desorption is second-order, then the area under a TDS trace should follow a modified Langmuirian form of the type:

$$\text{Area} = (1 - n\Theta_s)^2$$

where Θ_s is the surface coverage of sulfur atoms that block the adsorption of n H_2 molecules each. Figure 6 shows the fit of some of the TDS data (for a 5L deuterium exposure) for various assumed values of n . Our experimental data does not seem to follow the expected smooth curves, having something of a stepped appearance, but does seem to fit best for $n = 1-1.5$. Examination of similar plots for other exposures shows that the apparent stepped appearance of the data is found in all cases and we are pursuing the

possible origin of this feature.

It is interesting to speculate about the adsorption processes at work here. It is likely by analogy with other systems, but not yet proven, that sulfur adsorbs either in the pseudo-fourfold hollow (4F) sites (A in Figure 7), or the 3-fold (3F) sites (B in Figure 7) on the Mo(110) surface. It is also most probable by analogy that the hydrogen atoms adsorb on the bridge sites on this surface. The site where the hydrogen molecule dissociates is probably the 3F site, from where the two H atoms can easily move to two nearby bridge sites. Now, if a sulfur atom were already present in the site where a hydrogen molecule would normally dissociate then clearly that molecule would be blocked from adsorption. If we further allow for the size of the adatom then it is possible for one adatom to block more than one such adsorption site. Thus, for instance an S atom adsorbed in the 4F site could block two 3F sites and all four potential H atom bridge sites (Figure 7 site A). On the other hand, a sulfur atom adsorbed in the 3F site would still leave some access to the other 3F site (Figure 7 site B) and would leave at least two bridge sites open. The present data tends to support the latter possibility more than the former, but further analysis is needed to clarify this issue.

c) Adsorption/desorption of hydrogen on carbided Mo(110)

The preadsorption of carbon on the Mo(110) surface also blocks the adsorption of hydrogen as can be seen in Figure 8, where a carbided surface is compared with the clean surface. At this time we do not have a good calibration for the surface carbon coverage, but experiments to determine this are underway. As Figure 9 shows, the preadsorption of carbon results in a lowering of both peak area and temperatures. The shifts in temperature maximum with are less dramatic than we saw for sulfur preadsorption. Once we have reliable estimates of the surface carbon coverage we can pursue this topic.

4. Future Work

Research during the next quarter will concentrate on the establishing the surface coverage of carbon that occurs in furan adsorption via ethylene and CO adsorption experiments. When we have that information in hand we will use the hydrogen TDS data

on sulfided and carbided surfaces that we have generated here to illuminate the hydrogen evolution that occurs during furan reactions on these surfaces.

5. References

1. M. Mahnig and L.D. Schmidt, Z. fur Physik. Chem. NF 80,71 (1972).
2. F. Zaera, E.B. Kollin and J.L. Gland, Surf. Sci. 166, L149 (1986).
3. P.A. Redhead, Vacuum 12, 203 (1962).
4. D.A. King, Surf. Sci. 47, 382 (1975).

Figure 1. Deuterium TDS spectra for various exposures on Mo(110)

Figure 2.
Uptake of deuterium
on Mo(110)

Figure 3.
2nd order Redhead
plot for the low-
coverage data of
Figure 1.

TPRS Plot: D_2 (0.05 - 10 L) on Mo(110)

Figure 4. D_2 TDS from clean and sulfided Mo(110)

TPRS Plot: D_2 (0.1 - 20 L) on S/Mo(110) $\Theta_S \approx 0.40$

TPRS Plot: D₂ (5 L) on S/Mo(110)

Figure 5. D₂ TDS data for various S coverages on Mo(110)

Figure 6. Fit of D₂ TDS data for sulfided Mo(110)

Figure 7. Possible adsorption sites for S and H on Mo(110)

TPRS Plot: D_2 (0.05 - 10 L) on Mo(110)

Figure 8. Contrasts for D_2 TDS from clean and carbided Mo(110) surfaces,

TPRS Plot: D_2 (0.02 - 5 L) on C/Mo(110) $R_{C/Mo} = 0.15$

TPRS Plot: D₂ (5 L) on C/Mo(110)

Figure 9. Changes in D₂ TDS spectra from carbided Mo(110) surfaces.

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