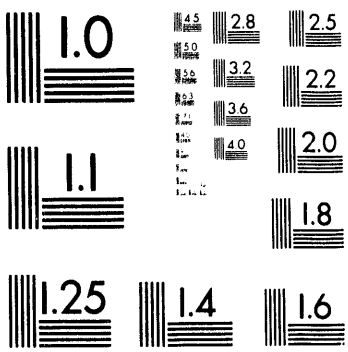
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DOE/ER/13289-7

Summary of Previous Work
DOE Grant No. DE-FG02-84-ER13289
C.M. Friend, Harvard University

The primary focus of our work has been to understand the effect of surface modifiers on the mechanisms and kinetics of desulfurization and deoxygenation reactions. We have focused on the Mo(110) surface because it is the most thermodynamically stable surface and, hence, is the least prone to reconstruction.

Most recently, we have discovered that there are dramatic changes in the kinetics and selectivity for thiol desulfurization on ultrathin cobalt films on Mo(110).[1] The investigation of cobalt and nickel promoters will be the central focus of this proposal. As a result, our results on Co overlayers are discussed in detail.

We have also developed a general methodology for the investigation of complex surface reactions which combines surface spectroscopy and physical organic chemistry. Both chemical and spectroscopic methods are used to probe the nature of surface intermediates. We have employed temperature programmed reaction, X-ray photoelectron, infrared reflection and high resolution electron energy loss spectroscopies in conjunction with isotopic labeling and exchange experiments. In parallel, we are developing methods for analyzing spectroscopic data in order to determine the structure of adsorbed intermediates. This is part of an effort to better understand bonding and reactivity. We have begun a new initiative which combines *ab initio* electronic structure calculations with infrared spectroscopy as a means of describing bonding and testing structural models by direct comparison of theory and experiment.

The Reactions of Thiols and Alcohols on Mo(110)

We have developed a general model for the reactions of organic thiols on Mo(110) which predicts the product distributions and the relative kinetics and selectivity for their desulfurization (Figure 1). The relative rates and selectivity for desulfurization under the

conditions of our experiment are dictated by the C-S bond strength.[2] Hence, thiols with relatively weak C-S bonds, such as *tert*-butanethiol and allyl thiol,[3] react with high selectivity (~85%) for hydrocarbon production and rapid kinetics. In contrast, benzenethiol and methanethiol, both of which have relatively strong C-S bonds, react slowly and with a selectivity of only ~45%.[4]

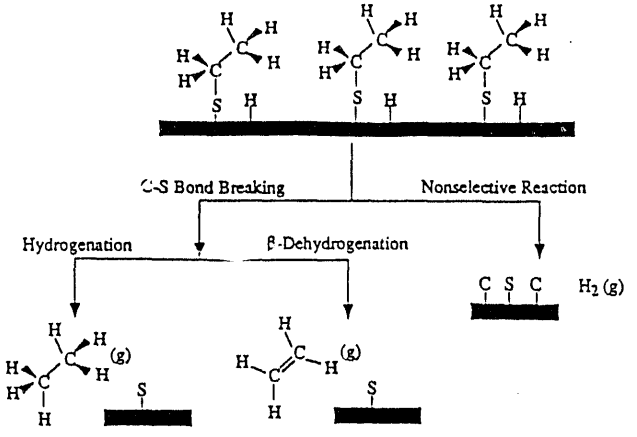

Figure 1: Reaction scheme for ethanethiol on Mo(110).

A systematic investigation of thiols with a range of different alkyl substituents was necessary in order to show that there is a substantial amount of C-S bond breaking in the transition state for thiol hydrogenolysis. Variation in the alkyl substituent produces a systematic change in the homolytic C-S strength. The kinetics for hydrogenolysis on Mo(110) correlate with the relative C-S bond strengths.

Similarly, we showed that the reactions of alcohols on Mo(110) are analogous to the thiols. The O-H bond is cleaved upon adsorption at 120 K, affording an alkoxide intermediate on the surface.[5-11] The C-O bonds in alkoxides are cleaved at a slower rate than their sulfur-analogs due to the relatively stronger C-O bond. The major product is the olefin, produced from C-O bond cleavage and accompanying dehydrogenation.

Using isotopic labelling methods, we have shown that the C-H bond in the γ position is selectively cleaved along the pathway to alkene formation from alkoxides. For example, $(CH_3)C(CD_3)C(H)(OH)$ exclusively produces propene-d_5.[9] The selectivity for γ-C-H bond scission suggests that C-O bond breaking precedes dehydrogenation. An intact C-O bond should result in a preference for β-C-H bond scission.[10]

The thiolate and alkoxide intermediates were identified using a combination of high resolution electron energy loss and X-ray photoelectron spectroscopies. On Mo(110), all of the C_1-C_5 primary thiols[12-18] benzenethiol,[19] and *t*-butanethiol[2] form the corresponding

thiolates upon adsorption at 120 K. The S-H bonds of benzenethiol and methanethiol on Mo(110)-p(4x1)-S[20] and cobalt-covered Mo(110) are also broken upon adsorption. The case of methanethiol on Mo(110) is used to illustrate the experimental approach adopted in our work. Analogous results were obtained for the larger thiols and alcohols.

X-ray photoelectron data clearly show that the C-S bonds of thiols remain intact when adsorbed on Mo(110). The C-S bond remains intact up to temperatures where gaseous reaction products are evolved, ~250 K for the case of methanethiol. A single C(1s) peak with an energy of 284.7 eV is observed following methanethiol adsorption on Mo(110) at 120 K. A set of two peaks in the sulfur region correspond to the $S(2p_{1/2})$ and $S(2p_{3/2})$ states and have binding energies of 162.7 and 163.9 eV, respectively. These values are in the range expected for intact C-S bonds and are substantially higher than those measured for atomic sulfur and adsorbed hydrocarbon fragments. Atomic sulfur has $S(2p_{1/2})$ and $S(2p_{3/2})$ binding energies of 161.3 and 162.5 eV, respectively. Hydrocarbon fragments bound to Mo have C(1s) binding energies in the range of 283-284 eV.

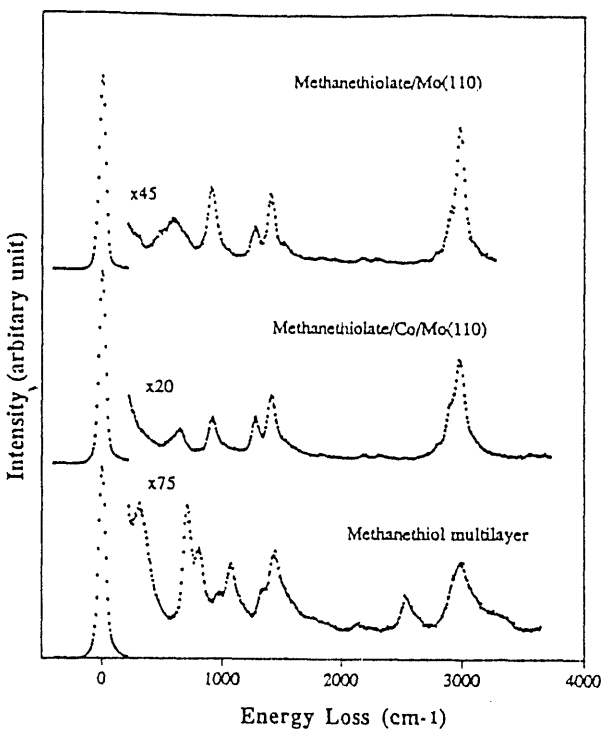

Figure 2: Electron energy loss spectra for: methane thiol multilayers; methyl thiolate on Co-covered Mo (θ_{Co} = 5 ML); and clean Mo(110).

The maximum (saturation) coverage of methyl thiolate was also determined to be 0.3±0.05 per Mo atom based on S(2p) intensities. Coverage information is important for theoretical modeling of the bonding of the thiolates on the surface. The thiolate coverage is determined by comparing the S(2p) intensity following reaction to that of the Mo(110)-p(4x1)-S surface, which has a sulfur coverage of 0.5. The saturation coverage for other

thiolates is somewhat different and generally correlates with the steric bulk of the alkyl group.

Electron energy loss data indicate that methyl thiolate is the majority intermediate formed when methanethiol reacts with Mo(110) at 100 K (Figure 2). This intermediate persists on the surface up to the ~300 K, the temperature at which methane is formed. Methyl thiolate is identified by comparing the vibrational spectra for condensed methane thiol and the intermediate present after heating. The primary changes in the vibrational spectrum induced upon reaction with the surface are the disappearance of the ν(S-H) and δ(S-H) modes, indicating S-H bond cleavage.[21] The vibrational spectra for the condensed thiol and the intermediate formed on the surface are otherwise similar, providing evidence that the methyl group remains intact.

The only other notable change upon thiolate formation is that the C-S stretch frequency is shifted to lower energy. The ν(C-S) mode is observed at 640 cm^{-1} in the thiolate compared to 715 cm^{-1} in CH_3SH, indicating a substantial weakening of the C-S bond. Similar effects have also been observed for other thiolates[20] and alkoxides on Mo(110).[4]

This example illustrates the importance of using complementary chemical and spectroscopic methods when investigating surface reactions. Even for the relatively simple case of methanethiol, several types of experiments were necessary to define the nature of the intermediate leading to methane formation. In more complex, longer-chain thiols and alcohols, the complementarity of these methods assumes greater importance.

Thiol Reactions on Ultra-thin Cobalt Films: Structural Flexibility in Surface Reactions

Our most recent work provides strong evidence that structural and morphological changes in cobalt overlayers on Mo(110) are important in determining the kinetics and selectivity of thiol desulfurization.[1] Most importantly, sulfur produced during thiol desulfurization induces segregation of the cobalt and hence a roughening of the cobalt overlayer (Figure 3). The kinetics of thiolate hydrogenolysis are increased as the sulfur is deposited suggesting that the rougher cobalt phases are more active for the desulfurization process. These preliminary results provide the framework for this proposal.

Previous work, reproduced by our group, demonstrated that 3-D crystallites of Co

grow on top of first 2-D cobalt layer when it is deposited on Mo(110).[22,23] Hence, the surface is rougher for intermediate coverages ($1.3 < \theta_{Co} < 5$) where the 3D crystallites are formed. As the coverage is increased above 5 ML, the 3-dimensional clusters coalesce, thereby decreasing the surface roughness. Thick copper films on W(110) likewise have a lower defect density than thin 2-D layers based on He diffraction data, lending credibility to our assertion that the cobalt films become smoother in the thick film limit. [24]

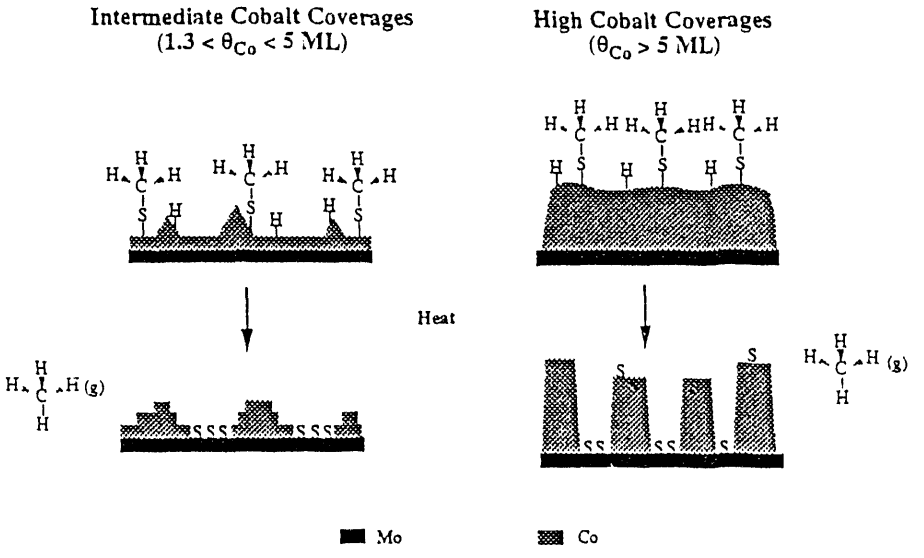

Figure 3: Reaction scheme for methanethiol on Co-covered Mo(110) in the thick- and thin-film limits.

The desulfurization of benzenethiol and methanethiol were investigated on the cobalt-modified Mo(110) surfaces. The thiolate intermediates were identified using electron energy loss spectroscopy (Figure 2). The vibrational spectra for methyl thiolate on the clean and Co-covered surface are essentially identical, indicating that there are not dramatic differences in the thiolate bonding (Figure 2).

The total amount of reaction and the selectivity for hydrogenolysis are higher on Co-covered Mo(110) compared to clean Mo(110) for all cobalt coverages investigated.[25] The total amount of methanethiol reaction also increases with Co coverage, reaching a maximum at ~2.5 ML. The maximum amount of reaction is ~1.8 times that of the clean molybdenum surface. For cobalt coverages above 2 monolayers, the total amount of reaction decreases, maintaining a nearly constant value of ~1.3 times larger than the clean Mo(110) surface for cobalt coverages above ~6 monolayers. The increase in the amount of reaction

generally correlates with surface roughness and is attributed to changes in surface area.

The selectivity for methane production increases with Co coverage up to ~2.5 ML, after which it remains constant within experimental error. The selectivity for methane production is low, ~45%, on clean Mo(110).[4,19] The relatively low selectivity made this an excellent test case for investigating enhanced performance of the mixed metal systems. The selectivity is derived from temperature programmed reaction yields of methane and referenced to the selectivity for clean Mo(110). We plan to investigate the underlying reason for the increase in selectivity in the next grant period.

The kinetics for methane production are also significantly different on Co-covered Mo(110) compared to the clean surface (Figure 4). The leading edges of the methane formation peaks are similar for thin Co films (θ < 5 ML) and clean Mo (Figure 4). However, above 200K, the reaction rate on the cobalt films is faster than for initially clean Mo(110). For example, the rate of methane production is ~2 times higher at 225 K and nearly 4 times greater at 250 K on the cobalt film with ~2.5 monolayers of cobalt. Furthermore, the peak temperature is lower by ~25 K on the cobalt-covered surfaces relative to clean Mo(110). This behavior is

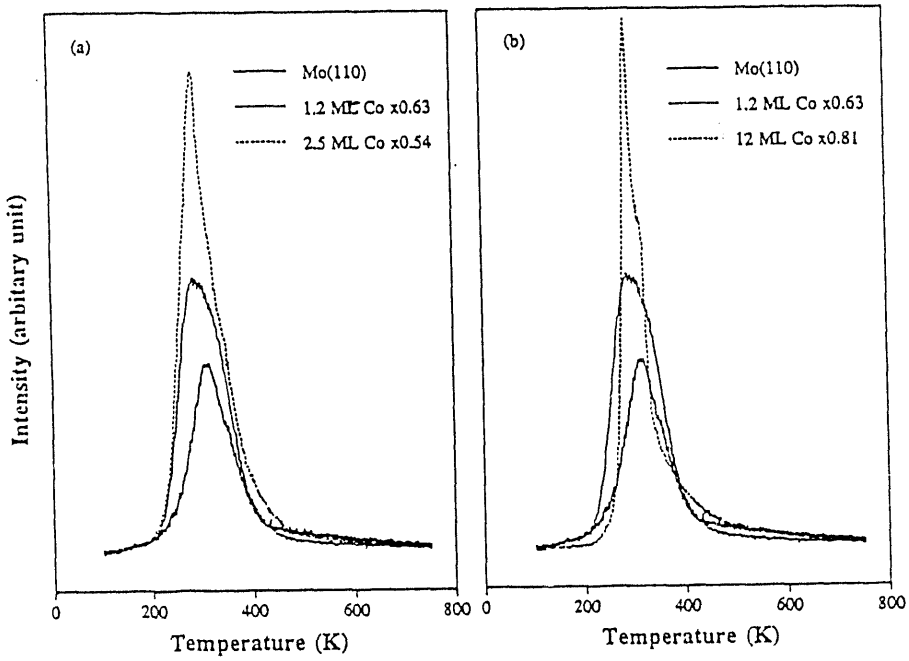

Figure 4: Methane production during temperature programmed reaction of methyl thiolate on Co-covered Mo(110) illustrating the differences in kinetics for different Co coverages.

qualitatively similar for all coverages where the cobalt film is composed of 3-D crystallites on top of a pseudomorphic first layer of cobalt; i.e., in the range of 1.2-5.0 ML.

The acceleration in the rate of methane production is even more pronounced for thicker cobalt films, $\theta > 5$ ML, which have a smoother, more 3-dimensional structure. Although the leading edge of the methane peak is shifted to higher temperature for the thick Co films, the rate rapidly overtakes that on the Mo(110) surface once it is initiated (Figure 4). The rate of methane production is equal on clean Mo(110) and a 3-D cobalt film (θ = 12 ML) at 260 K, for example. At a temperature of 275 K, the methane production rate on the cobalt film is ~2.3 times that on Mo(110), however (Figure 4). As for the thinner cobalt films, the methane peak temperature is ~25 K lower than on clean Mo(110).

Cobalt is forced into 3-dimensional crystallites when sulfur is deposited during the course of desulfurization. This conclusion is based on a quantitative comparison of the Auger electron signals for Co, Mo and S before and after reaction (Figure 5).[1]

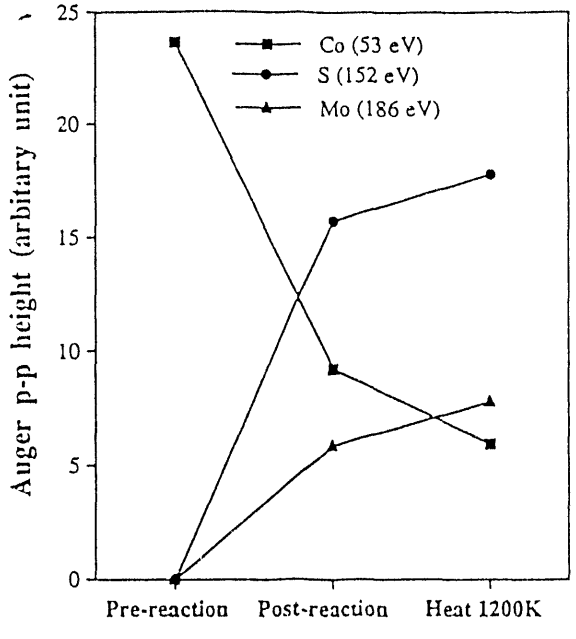

Figure 5: Auger electron intensities for Co, Mo and S before and after methanethiol desulfurization on Mo(110) covered with ~9ML of cobalt.

The Mo(MNN) peak at 186 eV is not attenuated to the extent expected when sulfur is deposited from methanethiol decomposition on the Co-covered surfaces. For example, the Mo(MNN) line is attenuated by 19% when 0.3 monolayers of sulfur are deposited on clean Mo(110) in a uniform layer. In contrast, there is only an 11% attenuation of the Mo(MNN) signal following deposition of ~0.5 monolayers of sulfur on to a cobalt film (θ_{Co} ~ 2 ML) deposited onto Mo(110). These data are strong evidence that there is <u>not</u> growth of a uniform layer of sulfur on top of the cobalt and that

instead the cobalt is forced into 3-dimensional crystallites, as sulfur is deposited. Crystallite growth results in less attenuation of the Mo signal due to cobalt. The decreased attenuation partially compensated by a reduction in the Mo signal due to the presence of the sulfur.

The structural change is even more apparent for very high Co coverages. Before reaction, the Mo(186eV) Auger signal is completely attenuated by the thick Co layer (9 ML). Following reaction, the Mo(MNN) peak reappears reaching a value that is essentially the same as for a cobalt coverage of 2 ML (Figure 5).

Changes in the cobalt and sulfur Auger electron intensities corroborate the proposal that cobalt is forced into 3-dimensional crystallites during the course of reaction. For example, for 2 monolayers of Co, the MVV peak is attenuated to $\sim 60\%$ of its original value following methanethiol reaction, while the molybdenum peak is only attenuated to 89% of its original value. At the same time, the sulfur signal increases. The decrease in Co(53eV) signal is consistent with segregation of the Co into three-dimensional crystallites with a higher aspect ratio after sulfur is deposited.

Cobalt desorption data substantiate the assertion that sulfur induces segregation of the cobalt into 3-D crystallites and provides evidence that cobalt is <u>not</u> dissolving into the molybdenum. The cobalt desorption temperature is ~ 60K lower when sulfur is present compared to the pure cobalt layers on Mo(110).

Additional evidence of a structural change in the cobalt overlayers is obtained from low energy electron diffraction patterns obtained following methanethiol reaction. Following temperature programmed reaction of methane thiol to 700 K, a diffraction pattern similar to that observed for thick Co layers ($\theta > 5$ ML) was observed for all cobalt coverages investigated (1.1 to 6 ML). This pattern is characterized by spots attributed to both thick Co layers and the underlying substrate. Notably, the double-scattering spots are absent suggesting that the first, pseudomorphic layers are forced into the 3-D crystallites. If the cobalt overlayers are sufficiently thick, the double-scattering spots will not be observed. These data suggest that all cobalt has segregated into relatively thick Co crystallites. In addition, a hint of c(2x2) pattern can be discerned, which is ascribed to ordered S overlayer on Mo(110). A c(2x2)-S pattern is formed when sulfur is deposited from methanethiol hydrogenolysis on Mo(110).

The dependence of the methane formation kinetics on the cobalt coverage specifically suggests that formation of 3-D crystallites enhances the rate of methane thiol hydrogenolysis. The kinetics are strongly dependent on surface structure with the most rapid production of methane occurring for cobalt coverages in the range where 3-D crystallites are present, $1.3 < \theta_{Co} < 5$. The very early stages of methanethiol hydrogenolysis are similar for the intermediate cobalt coverages and the clean Mo(110) surface. We attribute this similarity to a small fraction of exposed molybdenum, perhaps at grain boundaries, in the cobalt films. Earlier studies of CO adsorption onto cobalt films also suggested that there are exposed molybdenum sites at intermediate Co coverages.[26,27] Once the reaction is initiated, the rate of methane hydrogenolysis is clearly more rapid on the cobalt films than on clean Mo(110).

Our data suggest the initial rate of reaction is lower for the smoother structure of 3-D Co layer than for the rougher Co crystallites. Once the reaction is initiated on the 3-D layer surface, sulfur forces the cobalt into 3-D crystallites for which the reaction rate is higher. Hence, the narrower peak shape observed for methane production from thick, 3-D layers of cobalt. More detailed investigations of the changes in surface structure and the temporal evolution of the hydrogenolysis rates are planned to understand this effect in more detail. We also plan to probe for the generality of these phenomena in our future work.

The Effect of Sulfur: 2,5-Dihydrothiophene on Mo(110) and Mo(110)-(4x1)-S

Understanding the role of surface sulfur in desulfurization reactions is exceedingly important since it is a byproduct of desulfurization and is an integral component of the catalyst. We investigated the effect of sulfur on the reactivity of Mo(110) in order to build-up our model of the desulfurization process. These data will also be important in interpreting our reactivity studies of the mixed metal phases.

Sulfur inhibits both C-S and C-H bond cleavage on Mo(110). However, C-H bond activation is inhibited to a greater extent than C-S bond scission. The net result is an increase in the selectivity for hydrocarbon production accompanied by a decrease in the reaction probability and rate. This effect is illustrated with the reactions of 2,5-dihydrothiophene on clean and sulfur-covered Mo(110).[28,29]

2,5-Dihydrothiophene is desulfurized to 1,3-butadiene on both clean and sulfur-

covered Mo(110).[28,29] Butadiene is facilely eliminated in an intramolecular process, as demonstrated using isotopic labeling methods. Furthermore, a significant fraction of the butadiene is produced upon adsorption at 100 K on the clean surface, indicating very rapid kinetics for the desulfurization. The selectivity for butadiene elimination is high, ~67% on the clean surface. The relatively high selectivity is attributed to the lack of reorganization of the hydrocarbon framework necessary in the transition state for butadiene elimination and the fact that no C-H bonds are broken or formed during the course of reaction.

The selectivity for butadiene elimination is increased to ~83% on the Mo(110)-(4x1)-S surface.[29] In addition, the kinetics for butadiene elimination are decreased so that molecular 2,5-dihydrothiophene remains on the surface up to 225 K. Consequently, desorption of 2,5-dihydrothiophene competes with desulfurization so only ~1/3 as much reaction occurs on the Mo(110)-(4x1)-S surface eompared to clean Mo(110).

The decrease in reactivity on the sulfur-covered surface reflects both the lower site availability and the decreased heat of adsorption for sulfur at coverages above 0.5 monolayers. Previous work showed that the heat of sulfur desorption is lower for coverages above 0.5 so that the thermodynamic driving force for desulfurization is less when substantial amounts of sulfur are present. Furthermore, the sulfur on the Mo(110)-(4x1)-S surface is packed rather densely on the surface so that few sites are available for sulfur deposition during reaction.

Sulfur dramatically retards C-H bond activation on Mo(110), accounting for the enhanced selectivity. Dehydrogenation processes lead to nonselective reaction on Mo(110) and sulfur generally inhibits these reactions. Theoretical investigations are necessary to fully understand this effect but it is probable that both electronic and steric effects are at work.

The pattern of decreased reactivity and increased selectivity for hydrocarbon production on the sulfur-covered surfaces is repeated in studies of thiols, such as benzenethiol on Mo(110)0(4x1)-S overlayers.[20] Hence, sulfur is expected to generally serve to slow down desulfurization processes but to inhibit nonselective reactions involving C-H bond activation to a greater extent than C-S bond cleavage. These observations are important in our investigations of the mixed Co-S-Mo phases because sulfur-covered Mo is exposed by the cobalt segregation.

Structural Tools and Theoretical Modeling

Structural determinations are key to understanding bonding and bond activation in surface reactions. We have developed several experimental approaches to determining the structure of adsorbed intermediates during the past grant period and are beginning collaborations that will allow us to incorporate theoretical approaches to describing the bonding of surface intermediates.

We have used high resolution electron energy loss and infrared reflection absorption spectroscopies in conjunction with near edge x-ray absorption fine structure measurements to determine molecular orientation. Theoretical studies promise to be a powerful means of interpreting the vibrational spectra in more detail so that site coordination may be obtained. Our goal is to directly compare vibrational spectra with frequencies calculated using a force-field analysis of *ab initio* electronic structure calculations in order to gain a detailed understanding of bonding and reactivity.

A significant amount of our effort has been expended on investigation of alkoxide intermediates on Mo(110) because of their importance in deoxygenation and oxidation catalysis and the availability of isotopically-labeled forms of the parent alcohols. Isotopically labeled compounds are critical in making valid vibrational assignments and in evaluating the accuracy of vibrational frequencies derived from theoretical studies. The investigation of alkoxides is used as a prototype for developing vibrational spectroscopy as a means of determining the structure of adsorbed species.

Infrared spectroscopy is emerging as a powerful method for relating molecular orientation to vibrational energies. Only dipole active modes are observed in infrared spectroscopy and the spectral resolution is extremely high. Consequently, the C-H stretch region can be scrutinized in detail in order to probe for tilting of the terminal methyl groups in thiolates and alkoxides, for example. If the C_3 axis of an alkoxide or thiolate is oriented along the surface normal, only the symmetric C-H stretch would be observed in their infrared spectra. The asymmetric C-H stretches are not allowed in dipole scattering since their dipole moment would be parallel to the surface plane. For a tilted geometry, both the symmetric and asymmetric ν(C-H) modes are dipole-allowed. Furthermore, degeneracy of the asymmetric stretches would be broken due to a lowering of the molecular symmetry in a

tilted state. High resolution electron energy loss spectroscopy cannot be applied in this case because of its inferior resolution and the predominance of short-range, impact scattering (Figure 6).

Both the symmetric and asymmetric C-H stretch modes are observed for methoxide bound to Mo(110), demonstrating that it is tilted toward the surface (Figure 6).[30] The tilt is estimated to be $-20°$ with respect to the surface normal based on NEXAFS data.[30] The C-H stretch regions for methoxide and methyl thiolate are compared in electron energy loss and infrared spectra obtained in our laboratory to illustrate the superior resolution of the infrared method and the splitting of the degeneracy of the asymmetric stretches (Figure 6). Furthermore, electron energy loss spectroscopy is more sensitive to the asymmetric modes due to impact scattering. The additional modes in the C-H stretch region of methoxide are assigned to combination and overtones associated with the symmetric and asymmetric methyl deformation modes at 1420 and 1450 cm^{-1} (Table 1).[31] We plan to test our assignments by performing high-quality electronic structure calculations for the methoxy-Mo(110) system.

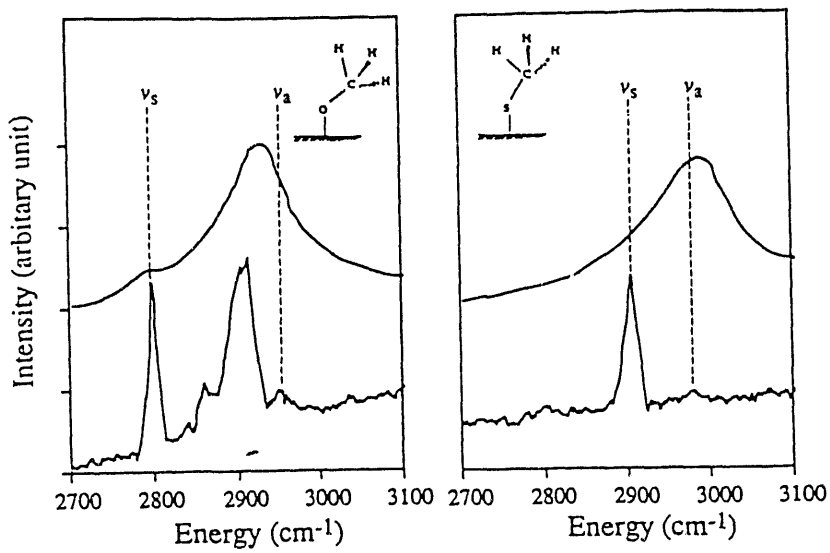

Figure 6: Comparison of electron energy loss and infrared reflection spectra in the C-H stretch region for methoxy and methyl thiolate on Mo(110).

Table 2: Tentative Vibrational Assignments for Methoxy on Mo(110)

Frequency (cm^{-1})		Assignment
CH_3O	CD_3O	
1040	1020	ν(C-O)
1420	1086	$\delta_a(CH(D)_3)$
2798	2050	$\nu_s(CH(D)_3)$
2857	----	$2\delta_s(CH_3)$
----	2060	$2\delta_a(CD_3)$
2900	----	$2\delta_a(CH_3)$
----	2106	$2\delta_a(CD_3)$ or ν_s(C-O)x$\delta_s(CD_3)$
2910	----	$2\delta_a(CH_3)$
----	2150	$\delta_s(CH_3)$ x $\delta_a(CD_3)$
2949	2211	$\nu_a(CH(D)_3)$

We have also shown that surface-induced changes in intramolecular coupling are important for larger molecules, such as 2-propoxide on Mo(110).[11,33] These effects must be taken into account when making vibrational assignments for longer-chain alcohols and thiols. Otherwise, the assignments will be incorrect, invalidating intensity analyses. Mode coupling is well-documented in the gas phase for long-chain alcohols and thiols because there are often several modes with similar energies and the same symmetry. If several modes are coupled in the free molecule, there will likewise be coupling in the adsorbed state or in closely related intermediates derived from the free molecule.

We have used a combination of isotopic labeling experiments and theoretical modeling of the vibrational spectra of 2-propoxide on Mo in order to make definitive vibrational assignments.[4] 2-Propanol forms 2-propoxide upon interaction with the surface and deoxygenates to eliminate propene in a process similar to the desulfurization of thiols.[9] Intramolecular coupling in gaseous 2-propanol is well-documented. The extent of coupling is dramatically changed when 2-propoxide is formed on the surface, however.[34] Vibrational data were obtained for four different 2-propanol isotopomers and were modelled by *ab initio* force field calculations in order to explain the vibrational data. There are substantial intensity redistributions in the vibrational peaks of the different isotopomers of 2-propoxide

because the C-O stretch, which is oriented near the surface normal, is coupled to the C-C stretch and methyl deformations. The force field calculations accurately modeled the intensity redistributions and peak shifts due to isotopic labeling.[21] Isotopic labeling changed the degree of coupling because it perturbed the symmetry of the molecule and the vibrational energies. All changes were modeled accurately by our calculations. The calculations demonstrated that the primary reason for the change in coupling was that the C-O stretch was shifted to lower energy by more than 100 cm^{-1}. Without the isotopic labeling experiments and force field calculations, the vibrational modes would have been incorrectly assigned and the C-O bond weakening would not have been evident.

Once reliable vibrational assignments are made, intensities of dipole-scattered vibrational modes can be related to the orientation of a specific functional group in a molecule. For example, we have used the relative intensities of the symmetric and asymmetric methyl deformation modes to determine the orientation of the methyl group in several alkoxides on Mo(110).[3] In these cases, the methyl deformations were experimentally determined to be dipole scattered.[34]

The relative intensities of the two different methyl deformations is related to the orientation of the methyl group since they have different polarizations and are both dipole-scattered. The doubly degenerate asymmetric mode has a dynamic dipole moment perpendicular to the C_3 axis of the methyl group whereas the dipole moment of the symmetric deformation lies along the symmetry axis.

The methyl groups of 2-propoxide were determined to be oriented at an angle of 67° with respect to the surface normal based on an analysis of the relative intensities of the methyl deformations. Hence, the C-O bond is oriented near the surface normal, assuming that there are no significant changes in the bond angles of 2-propoxide compared to free 2-propanol. This assumption is justified on the basis of the *ab initio* force field calculations.[21] More accurate theoretical modeling is necessary for a more quantitative determination of the C-O bond tilt.

In several other cases, we have used near edge X-ray absorption fine structure (NEXAFS) measurements to probe the orientation of surface intermediates. In the near edge X-ray absorption fine structure experiment, core level electrons are excited to unfilled

molecular states as they are ejected into the vacuum. The polarization dependence of these excitations is related to the molecular orientation.[33]

Near edge X-ray absorption fine structure measurements were used to determine the orientation of the 2,5-dihydrothiophene on Mo(110)-p(4x1)-S.[12] The orientation of the ring was determined to be $\sim 9°$ with respect to the surface normal using NEXAFS for high coverages of 2,5-dihydrothiophene. Due to limitations on experimental time, the orientation of 2,5-dihydrothiophene in the low-coverage phase was not determined.

High resolution electron energy loss data[29] complemented the NEXAFS data by showing that the orientation of 2,5-dihydrothiophene with respect to the Mo(110)-p(4x1)-S surface depends on its coverage. The intensity of the HC= out-of-plane bending mode was used to infer the approximate orientation. At high coverage, the ring was nearly upright with respect to the surface, in accord with the NEXAFS results. At lower coverage the C-C=C-C plane tilts towards the surface plane.

The reactivity of 2,5-dihydrothiophene on Mo(110)-p(4x1)-S correlates with its coverage. The more tilted state at low coverage reacts to eliminate butadiene whereas desorption predominates from the high coverage overlayer. Electronic structure calculations are also necessary to understand the coverage dependence in reactivity.

We plan to further investigate 2,5-dihydrothiophene using infrared spectroscopy and *ab initio* electronic structure calculations. These planned studies will give us additional insight into the bonding and structure of 2,5-dihydrothiophene on Mo(110) and will set the stage for detailed investigations of the mixed-metal systems.

Summary

We have developed a general method for determining the mechanisms for surface reactions and have specifically modeled desulfurization and deoxygenation processes on clean and S-covered Mo(110). Recent efforts have been aimed at accurately describing the bonding and structure of adsorbed reactants.

Most recently, we have investigated thiol desulfurization on Co-covered Mo(110). The kinetics and selectivity for thiol hydrogenolysis depend strongly on the structure and composition of the interface. These studies have opened a new and exciting area of research

which serves as the basis for our renewal proposal.

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$$R = \text{Total Reaction} = \theta_S\{[Y(CH_4)/Y(CH_4)^\circ] + [S(CH_4)/S(H_2)(Y(H_2)/Y(H_2)^\circ]\} \quad (1)$$

where θ_S is the thiolate coverage on clean Mo(110),[4] $Y(CH_4)$ and $Y(H_2)$ are the integrated intensities of methane and H_2 temperature programmed reaction peaks, and $S(CH_4)$ and $S(H_2)$ correspond to the mass spectrometer sensitivities for methane and hydrogen, respectively. The superscript, °, refers to the yields measured for the clean Mo(110) surface. The sensitivity factors are calibrated according to the known selectivity of methanethiol hydrogenolysis on clean Mo(110) as measured by Auger electron spectroscopy.

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