

Fundamental studies of hydrodesulfurization by metal surfaces

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Abstract—Fundamental studies of desulfurization chemistry induced by single-crystal transition-metal surfaces are reviewed with emphasis on recent work. Specifically, the chemistry associated with clean, modified and multimetallic systems is addressed. A brief of our experimental approach, including the use of systematic variation in C—S bond enthalpies for mechanistic studies, is discussed. Studies of thiol reactions on Mo(110) have shown that desulfurization occurs via homolytic C—S bond dissociation in the thiolate intermediate. Furthermore, the relative rates of desulfurization can be correlated with C—S bond strengths. The product distributions for molecules that form radical or cation intermediates and undergo various rearrangement reactions are used to elucidate reaction mechanisms. Adsorbates like oxygen and sulfur passivate the surface toward C—S and C—H bond scission in most cases. However, oxygen substitution also occurs when thiols react on some oxygen-covered surfaces. No synergistic reactivity was observed for thiol chemistry on bimetallic Co—Mo surfaces. © 1997 Elsevier Science Ltd

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The removal of sulfur from fossil fuel feedstock is an extremely important catalytic process and has received considerable attention over the past decade. There has been an extensive effort devoted to modeling desulfurization and related processes using supported catalysts, organometallic complexes and single-crystal transition metal surfaces in ultrahigh vacuum. These studies all provide information about the identity and structure of possible surface intermediates as well as the nature of rate-limiting steps that are important in desulfurization chemistry.

In this article, recent studies of desulfurization chemistry induced by clean and modified transition metal surfaces will be discussed. The scope will be limited to studies on single-crystal materials under ultrahigh vacuum conditions and emphasis will be placed on work performed during the past 5 years. We will specifically use work from our own laboratory to illustrate the experimental approach and to highlight general results. There are several excellent articles on related theoretical and experimental work on supported catalysts, organometallic complexes and clusters, and on the phase behavior of mixed metal sulfides. For a more complete review of the literature, the reader is referred to these comprehensive articles [1–3].

The single-crystal studies have mainly addressed issues related to the mechanisms of reaction on different transition metal surfaces. More recently the effects of additives, such as oxygen and sulfur, and of promoters, such as Co and Ni, have also been studied. Catalysts used for hydrodesulfurization processes in industry are complex materials, typically consisting of a MoS₂-like phase and a transition metal promoter such as Co or Ni on an inert support. While the phases formed on crystalline surfaces are not the same as those on the actual catalyst materials, the investigation of complex, albeit well-defined, phases provides insight into the possible effects of promoters or modifiers on mechanism and rate.

Single-crystal studies are also important in understanding periodic trends in hydrodesulfurization catalysis; the rates and selectivities for dibenzothiophene hydrogenolysis on various metal sulfide catalysts have been investigated, and theoretical modeling of this effect suggests that the metal–sulfur bonding plays an important role in the desulfurization process [4]. Studies on single-crystal surfaces provide a means of comparing mechanism and reactivity under controlled conditions to test for the role of metal–sulfur bond strength in determining the facility for desulfurization. Desulfurization chemistry on clean transition metal surfaces will be discussed first in this article, followed by investigations of the effects of modifiers and promoters.

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THIOL CHEMISTRY ON CLEAN METAL SURFACES

Organic thiols are the most widely studied sulfur-containing molecules on single-crystal surfaces because of their relevance both to desulfurization chemistry and to the formation of self-assembled monolayers. Furthermore, organic thiols react readily on a wide range of transition metal surfaces and are readily characterized using spectroscopic techniques, making them ideal for model studies.

Organic thiols undergo S—H bond dissociation to form thiolates on most transition metal surfaces. Thiolates have been proposed as intermediates in the hydrodesulfurization of cyclic sulfides on Mo(110), and understanding their reactivity is therefore important in modeling product distributions. Methanethiol is the most widely studied thiol because of its relative simplicity. Methanethiol dissociates to methyl thiolate on Ni(111) [5,6], Ni(110) [7], Ni(100) [8], Pt(111) [9], Mo(110) [10], W(001) [11], W(211) [12], Cu(100) [13], Fe(100) [14] and Fe(110) [15]. The C—S bond of the methyl thiolate intermediate is subsequently cleaved, yielding methane and H₂ as gaseous products along with surface carbon and sulfur. Surprisingly, the temperature required for C—S bond cleavage is relatively insensitive to the nature of the metal surface, occurring around 300 K in most cases.

The information regarding S—H and C—S bond breaking in thiols is obtained from vibrational and X-ray photoelectron studies and offers a clear illustration of the use of surface spectroscopies to identify intermediates such as methyl thiolate. There is a downshift for the S(2*p*) binding energies on the order of 1 eV upon cleavage of the C—S bond (Fig. 1) [6,10,16,17]. Hence, the temperature required for C—S bond cleavage is determined by monitoring the S(2*p*) binding energies as a function of surface temperature. Vibrational spectroscopy also provides information about C—S bond breaking. For example, the development of a metal—S stretch at ~350 cm⁻¹ for atomic sulfur has been used as a diagnostic for sulfur removal from thiols and ring compounds bound to several transition metal surfaces. However, there are sometimes other vibrational modes in this energy region for longer-chain thiols, such as the metal-ring stretch in phenyl-containing compounds [18], and the C—S stretch mode is often has low intensity [19]. Therefore, the vibrational spectrum does not always differentiate clearly between intact and broken C—S bonds.

Vibrational spectroscopy does provide more detailed information regarding the nature of intermediates present on the surface. In the case of methanethiol reaction, the absence of the ν(S—H) mode near 2570 cm⁻¹ in the electron energy loss spectrum indicates that the S—H bond has been broken (Fig. 2) [6,8,10,14,20]. All of the other losses can be assigned to vibrational modes of the methyl thiolate intermediate. In more complex thiols, isotopic labeling is used to make definitive assignments, as in the case of

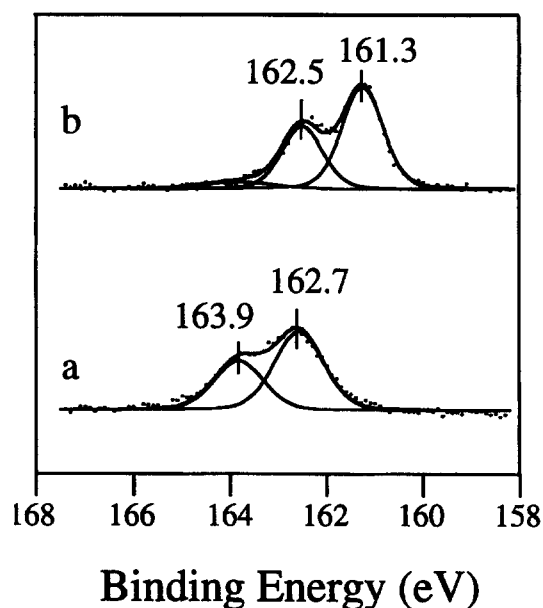


Fig. 1. The S(2*p*) X-ray photoelectron spectrum of condensed methanethiol on Mo(110) annealed to: (a) 200 K and (b) 400 K. The C—S bond is intact at 200 K and broken after heating to 400 K. Reprinted from *Surface Science*, **279**, B. C. Wiegand, P. Uvdal, C. M. Friend, "The Local Structure of Adsorbed Methyl Thiolate: The Reactions of Methanethiol on Mo(110)," 105, 1992, with kind permission of Elsevier Science, NL, Sara Burgerharstraat 25, 1055 KV Amsterdam, The Netherlands.

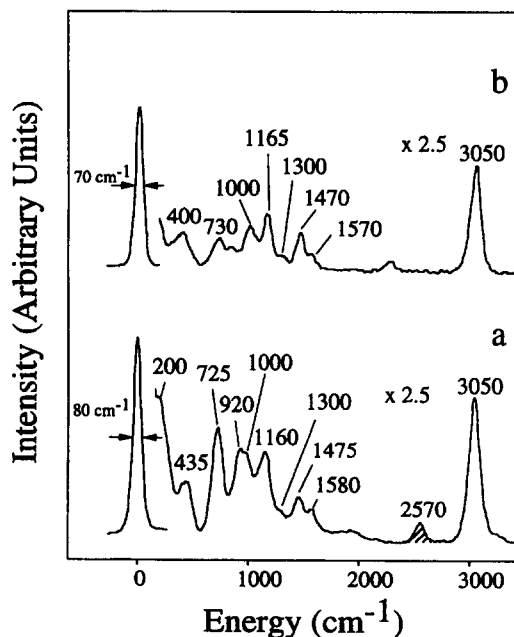


Fig. 2. Electron energy loss data on Mo(110) for: (a) condensed benzenethiol at 100 K showing the S—H stretch at 2570 cm⁻¹ and (b) a saturation exposure of benzenethiol heated to 300 K to form phenyl thiolate [19].

C_6H_5SH and C_6D_5SH on Rh(111) [18] and Mo(110) [19].

Like methanethiol, longer-chain alkane thiols form the corresponding thiolate intermediates at low temperature, based on vibrational and X-ray photoelectron studies. Hydrogenolysis to alkanes competes with nonselective decomposition. However, there is a third path involving selective dehydrogenation to corresponding alkenes for C_2 and higher thiols on Mo(110) [21,22], as illustrate for ethanethiol (Fig. 3). In the reaction of thiolates on Mo(110), C—S bond hydrogenolysis leading to alkane production competes with C—S bond scission and β -dehydrogenation to form the alkene [1,21–25]. Nonselective decomposition to surface carbon and sulfur and gaseous hydrogen is a third pathway. The same type of reactions are observed in other transition metal surfaces, such as for ethanethiol on Fe(100) [26], ethanedithiol on Ni(110) [27] and 2-propanethiol on Rh(111) [28,29].

From the standpoint of catalysis, an enhancement in the selectivity for hydrocarbon production over nonselective decomposition is desirable. A mechanistic model would provide the basis for understanding how selectivity for hydrocarbon production is controlled. There are several different proposed mechanisms for methyl thiolate reactions, even though the product distributions and reaction temperatures are quite similar on many transition metal surfaces. The model proposed for Mo(110) involves homolytic C—S bond cleavage to the corresponding radical species, which rapidly reacts with hydrogen to produce gaseous methane or further decomposes to produce irreversibly-bound hydrocarbon fragments and H_2 (Fig. 4). Indeed, gaseous methyl radicals were evolved during methyl thiolate reaction on Mo(110), providing further evidence for this model [30]. A similar scheme was proposed for reaction on Ni(111) [5,6], although ethane was a minor reaction product, presumably from CH_3 recombination. A slightly different mechanism was suggested for reaction on Fe(100) [4]: methyl radicals were believed to form below the meth-

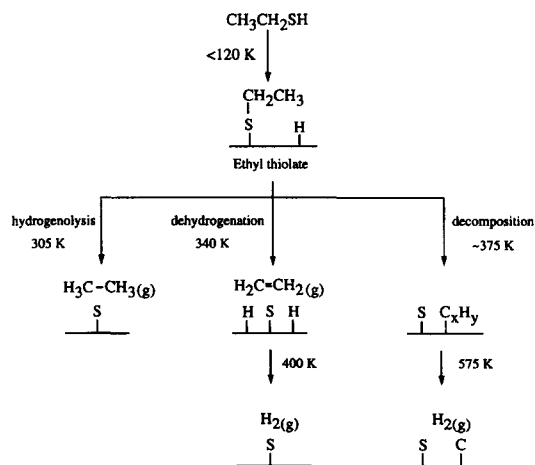


Fig. 3. Scheme for ethanethiol reaction on Mo(110) [21].

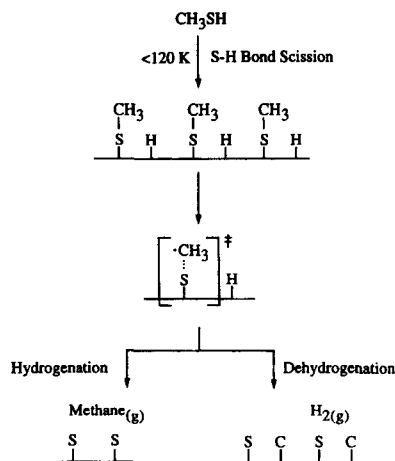


Fig. 4. Scheme for methanethiol reaction on Mo(110). Reprinted from *Surface Science*, **279**, B. C. Wiegand, P. Uvdal, C. M. Friend, "The Structure of Adsorbed Methyl Thiolate: The Reactions of Methanethiol on Mo(110)," 105, 1192, with kind permission of Elsevier Science, NL, Sara Burgerharstraat 25, 1055 KV Amsterdam, The Netherlands.

ane evolution temperature, trap on the surface and produce methane after combining with surface hydrogen. However, the direct reaction of methyl thiolate to form methane could not be ruled out as a contributing pathway. On Pt(111), the major reaction products were hydrogen, methane and ethylene; both methyl thiolate and methylene sulfide ($CH_2=S$) were proposed as intermediates, but there was no evidence for gaseous $CH_2=S$ [9,31]. Hydrogen, methane and ethane were also produced on Cu(100) [13]. Recombination of $CH_{5(a)}$ and $H_{(a)}$ was proposed as a mechanism for methane formation, similar to the Fe(100) case.

Experimentally, the reaction mechanism can be deduced by using an approach that is traditionally associated with solution-phase physical organic chemistry, as illustrated for the case of thiol desulfurization on Mo(110). Specifically, we employed alkyl substitution as a means of varying the C—S bond strength in order to test the proposed mechanism involving homolytic C—S bond breaking. A series of studies showed that the facility for hydrogenolysis from alkane thiol reaction on Mo(110) correlates with the respective C—S bond strengths. The C—S Bond strengths for thiols with different alkyl constituents are related to the stability of the various alkyl radicals. For example, allyl thiol has a very low C—S bond enthalpy due to the resonance stabilization of the allyl radical. Accordingly, allyl thiol [32] reacts upon adsorption at 100 K yielding propene as the primary product, whereas benzenethiol [33] and methanethiol [10] react at ~ 350 K, affording benzene and methane, respectively. The correlation between C—S bond strength and the temperature required for hydrogenolysis also holds for a range of other thioliates. In

particular, *tert*-butanethiol [23] reacts more rapidly than primary thiols, such as ethanethiol, 1-propanethiol and 1-butanethiol [21,24,34].

Notably, such a relationship between homolytic C—S bond strength and hydrogenolysis temperature did not hold for Ni(111) [35,36] and Ni(110) [7,37]. The onset temperature for benzene evolution was lower than that of methane and ethane from the corresponding thiols, suggesting the possibility of hydrogen-assisted C—S bond cleavage. A similar lack of correlation between C—S bond strength and hydrogenolysis rate would also be expected if C—S bond breaking were not the rate-determining step, as was proposed for methanethiol reaction for Fe(100) [14].

The effect of fluorine substitution on the reaction selectivity of alkane thiols provided further insight into alkane thiol reaction mechanisms. Specifically, the reactions of 4,4,4-trifluorobutanethiol [38] and 2,2,2-trifluoroethanethiol [39] on Mo(110) were investigated. Both react *via* a thiolate intermediate, in a manner analogous to the unfluorinated thiols on Mo(110). Gaseous trifluoroethyl radicals are produced during the reactions of 2,2,2-trifluoroethanethiol on Mo(110), suggesting that homolytic C—S bond scission is generally induced in thiols by Mo(110).

The trifluoroethyl radical is only produced over a very narrow coverage range, 0.24–0.26 monolayers. The radical evolution is associated with a reorientation of the trifluoroethyl group as the coverage is increased, based on intensity changes in the infrared spectrum, and is attributed in part to steric inhibition of radical trapping by the surface. Otherwise, the reactions of 2,2,2-trifluoroethanethiol are analogous to those of ethanethiol [21]. The radical evolution pathway causes a ~30% increase in the overall selectivity of hydrocarbon evolution relative to the ethanethiol. The decrease in nonselective decomposition is explained on a thermodynamic basis since the C—H and C—C bond strengths are increased by the presence of the fluorine atom; the C—H and C—C bond strengths in CF₃CH₃ are 6.5 and 13 kcal mol⁻¹, respectively, greater than those in CH₃CH₃ [40].

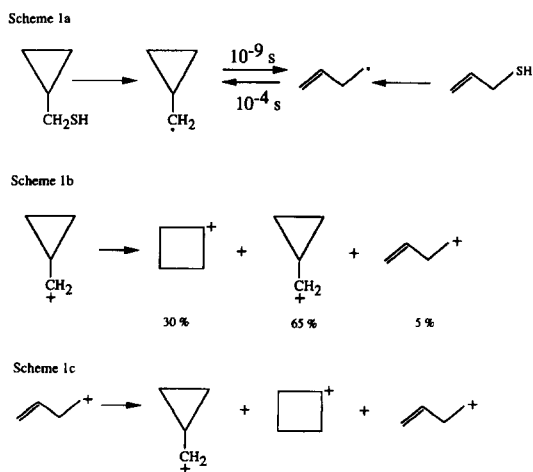
On the other hand, no radical evolution is observed in the reactions of 4,4,4-trifluorobutanethiol on Mo(110). This is consistent with the fact that the terminal C—H and C—C bonds in a transient 4,4,4-trifluorobutyl radical are relatively unperturbed compared with those in 1-butanethiol and ethanethiol. Therefore, these bonds are weaker compared with the 2,2,2-trifluoroethanethiol case and allow for more nonselective decomposition. 4,4,4-Trifluorobutanethiol also produces difluoroethylene, a trace amount of ethylene and HF from CF₃(CH₂)₃S— at 540 K, whereas no high-temperature ethylene or any other hydrocarbon products were observed from CH₃(CH₂)₃S— [21]. This reaction pathway is attributed to a combination of energetic and structural factors introduced by the presence of the terminal trifluoro group [38].

Recently, we have used rearrangement reactions to further investigate the nature of the transient alkyl

radical intermediates formed during thiol desulfurization. This investigation not only addresses the nature of the intermediate in thiol desulfurization, but also establishes a method for probing transient intermediates of organic transformations on surfaces. Specifically, we studied the reactions of cyclopropanemethanethiol and 3-butene-1-thiol on Mo(110) to probe for radical and cationic intermediates by exploiting the rapid isomerizations of the cyclopropyl carbinyl radical and cation [Scheme 1(a)] [41].

The fact that methylcyclopropane and hydrogen are the primary products from cyclopropanemethanethiol reaction shows that the reaction mechanism involves homolytic C—S bond scission. Furthermore, the product distribution indicates that hydrogenolysis without rearrangement is the major reaction pathway (Fig. 5). Carbon–sulfur bond homolysis to a radical species would lead to rapid conversion (10⁻⁹ s) to an allyl carbinyl radical in the gas phase [42,43]. The allyl carbinyl radical can then hydrogenate to form 1-butene, dehydrogenate to 1,3-butadiene or trap on the surface and nonselectively decompose. The lack of rearrangement in cyclopropylmethyl thiolate indicates that C—S bond scission and C—H bond formation occur nearly simultaneously. However, the production of a minor amount of 1,3-butadiene *via* rearrangement of cyclopropylmethyl carbinyl group in the reaction of cyclopropylmethyl thiolate indicates that homolytic C—S bond scission to afford the radical does occur to some extent. Related studies of cyclopropylmethylbromide confirm that rearrangement is possible, but that trapping of the cyclopropylmethyl carbinyl radical is favored over hydrocarbon evolution [44].

Heterolytic C—S bond scission leading to a cationic intermediate during cyclopropanemethanethiol desulfurization is excluded based on the absence of cyclobutane or cyclobutene. Heterolytic C—S bond cleavage would yield the cyclopropyl carbinyl cation,



Scheme 1.

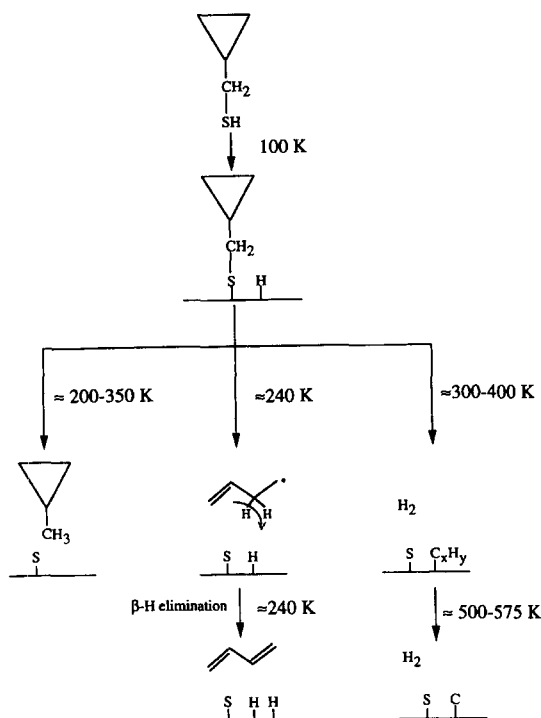


Fig. 5. Scheme for cyclopropanemethanethiol reaction on Mo(110) [41].

which is in equilibrium with both the allyl carbanyl cation and cyclobutyl cation [Scheme 1(b)] [45–47]. Hydrogenation would yield a mixture of cyclobutane, methylcyclopropane and 1-butene, whereas dehydrogenation would yield a mixture of cyclobutene and 1,3-butadiene.

The product distribution for 3-butene-1-thiol reaction also demonstrated that the dominant reaction pathway involves homolytic C—S bond dissociation without rearrangement. The major gaseous products observed were 1-butene, 1,3-butadiene and hydrogen (Fig. 6). The absence of rearrangement products like methylcyclopropane, cyclobutane and cyclobutene rule out a cationic mechanism. Heterolytic C—S bond scission would form the allyl carbanyl cation, which rearranges to a mixture of cyclopropyl carbanyl, cyclobutyl and allyl carbanyl cation [Scheme 1(c)] [48]. Hydrogenation would yield a mixture of methylcyclopropane, cyclobutane and 1-butene, whereas dehydrogenation would yield a mixture of cyclobutene and 1,3-butadiene. If C—H bond formation occurs more rapidly than rearrangement after sulfur elimination, only methylcyclopropane would be produced. However, neither the rearrangement products from this cationic mechanism nor methylcyclopropane were observed. Notably, trapping of the alkyl radical followed by hydrogenation is expected to lead to rearrangement based on the fact that cyclopropyl bromide rearranges on oxygen-covered Mo(110) [49].

A better understanding of the mechanism of C—S

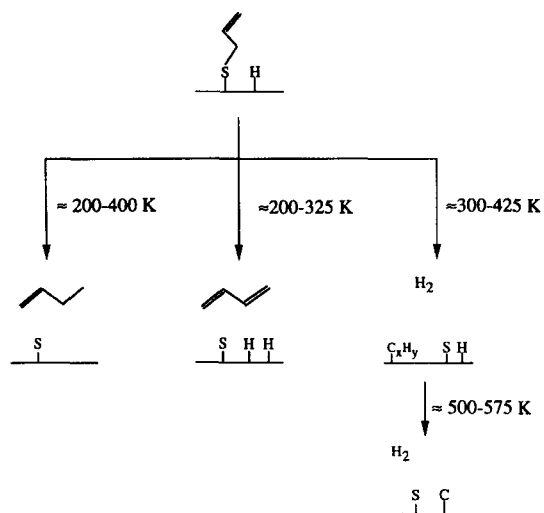


Fig. 6. Scheme for 3-butene-1-thiol reaction on Mo(110) [41].

bond activation also requires knowledge of the bonding of thiolates to the surface. The first step in modeling bonding is to probe the geometry of the thiolate. At coverages approaching saturation, the alkyl groups are nearly perpendicular to the surface. For example, the orientation of the ring in phenyl thiolate at saturation coverage is estimated to be $\sim 20^\circ$ away from the surface normal using near edge X-ray adsorption fine structure [33]. It is interesting to note that this is similar to the orientation of long-chain thiols that form self-assembled monolayers on Au [50], indicating that intermolecular interactions dictate orientation at high coverage. Indeed, the alkyl orientations of trifluoroethyl thiolate on Mo(110) [39] and phenyl thiolate on Rh(111) [18] depend on coverage; these species assume a more upright geometry at higher coverages based on an analysis of vibrational intensities. The reactivity of the thiolates are also dependent on coverage and therefore on intermolecular interactions. These results suggest that detailed studies of structure and reactivity will provide great insight into the desulfurization process.

Our investigations of substituted thiols on Mo(110) indicate that homolytic C—S bond cleavage is the first step in hydrocarbon elimination. The facility for C—S bond cleavage partly determines the selectivity and temperature for desulfurization on the surface. We have shown that product distributions may be used in some cases for distinguishing radical *vs* cationic mechanism for desulfurization. Although there is a less extensive set of studies on other surfaces, the differences in thiol reactivity on Mo and Ni suggest there may be slight mechanistic variations on transition metal surfaces, perhaps reflecting differences in hydrogenation activity. In order to address this issue, systematic studies of the effect of alkyl substitution on thiol reactivity on other surfaces are necessary.

RING DESULFURIZATION

Although desulfurization of ring compounds is more directly relevant to industrial hydrodesulfurization processes, there have been few recent investigations on single-crystal surfaces. Ring compounds, in particular thiophene, are generally less reactive than thiols and are therefore less likely to selectively produce gaseous hydrocarbon products under ultrahigh vacuum conditions. In most studies of thiophene on transition metal surfaces, nonselective decomposition to H_2 , S_a and C_a is the major reaction pathway. The lack of hydrocarbon production from thiophene reaction on Mo(110) [51] and Ni(100) [52] makes detailed mechanistic studies on these surfaces impossible.

The approach we have taken to understanding the reactivity of sulfur-containing ring compounds on Mo(110) is to investigate partially and fully hydrogenated rings, such as 2,5-dihydrothiophene. We were specifically interested in the reactions of 2,5-dihydrothiophene because it was proposed as an intermediate for thiophene hydrodesulfurization, based on model studies using organometallic complexes [53]. Furthermore, this provided us with an opportunity to test for similar reactivity on surfaces and in complexes. 2,5-Dihydrothiophene readily reacts on Mo(110), eliminating butadiene at 120 K with a selectivity of ~67% [54]. The butadiene elimination reaction is qualitatively similar to the reactions of 2,5-dihydrothiophene in metal complexes, suggesting a correspondence between the reactivity of organometallic models and the surface. However, the generality of butadiene elimination has not been tested on other surfaces, probably because 2,5-dihydrothiophene is not commercially available.

THE EFFECT OF SULFUR

Since sulfur is an integral part of working Mo-based desulfurization catalysts [55], we have performed studies of desulfurization reactions on sulfur-covered Mo(110). We found that sulfur inhibits C—S and C—H bond breaking on Mo(110), thereby leading to a lower reactivity but higher selectivity in most cases. Indeed, related studies on other surfaces, such as Fe(100) [14,56], Ni(110) [7], Ni(111) [5] and W(001) [57], indicate that surface sulfur generally inhibits thiol reaction. The optimal conditions for desulfurization require a sulfur concentration on the surface which factors high selectivities but allows for reasonable reaction rates.

In all cases investigated, the selectivity of hydrocarbon production over nonselective decomposition was higher when sulfur was present on the Mo(110) surface. For example, the selectivity for gaseous butadiene elimination from 2,5-dihydrothiophene is ~85% on Mo(110)-p(4 × 1)-S compared to 70% on clean Mo(110) [58]. Similarly, the selectivity for hydrocarbon production from benzenethiol reaction

is ~80% for Mo(110) covered with 0.35 monolayers of sulfur compared with 50% on clean Mo(110) [19].

We also established that the probability for desulfurization over desorption of thiols [44] and cyclic sulfides [58] is decreased on sulfur-covered Mo(110) compared with initially clean Mo(110), reflecting a higher barrier for S—H and C—S bond dissociation. The decrease in desulfurization activity for most cases investigated is probably due to blocking of the Mo surface by sulfur; less of the sulfur-containing intermediates and the sulfur produced during their desulfurization can be accommodated on the surface.

Sulfur has a similar effect on the reactions of thiols on other transition metal surfaces. For methanethiol reaction on c(2 × 2)S-Fe(100), almost all the methanethiol desorbs without decomposition; only trace amounts of methane are detected and hydrogen is not observed [14]. The reduction in reactivity of ethanethiol on Fe(100) by sulfur is attributed to the blocking adsorption sites [56]. On Ni(110), sulfur also stabilized methyl thiolate with respect to decomposition such that the methane yield increased while the hydrogen yield decreased [7]. Similarly, 0.25 monolayers of sulfur on Ni(111) was found to inhibit methanethiol desulfurization and dehydrogenation [5].

The reactions of benzenethiol on sulfur-covered Mo(110) are an exception to the more generally observed decreased reactivity. The amount of benzenethiol that reacts on clean and sulfur-covered Mo(110) is essentially the same up sulfur coverages of 0.35 monolayers [19]. The persistence of the reactivity of benzenethiol is attributed to its ability to form an S—S bond upon adsorption (Fig. 7). The disulfide

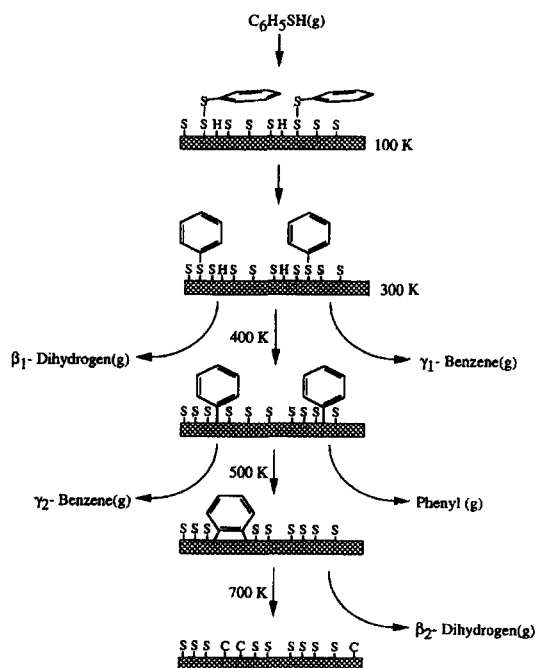


Fig. 7. Scheme for benzenethiol reaction on Mo(110) covered with 0.35 monolayers of sulfur [19].

species provides an intermediate stage in the desulfurization reaction that circumvents the steric inhibition of thiolate formation. The disulfide decomposes to the thiolate at ~ 300 K as the sulfur layer rearranges to accommodate the thiolate. Sulfur is known to rearrange on Mo(110) near 300 K in order to achieve higher coverages. Note that a benzyne intermediate was observed on the surface upon heating to 500 K [19].

Electron energy loss investigations of different isotopes of benzenethiol were used to demonstrate unequivocally that a disulfide linkage forms upon adsorption at low temperature. The isotopic labeling studies verified the assignment of a strong mode at 470 cm^{-1} as the S—S stretch of phenyl formed from reaction of benzenethiol with sulfur on the Mo(110) surface [19]. In particular, the small shift of $\sim 5\text{ cm}^{-1}$ in this peak upon ring deuteration rules out other possible assignments, such as the C—H bending or C—S stretching modes.

The formation of disulfide linkages is specific to benzenethiol to Mo(110) and does not occur for other thiols that we have investigated, including methanethiol [10], ethanethiol [21], butanethiol [38] and allyl thiol [32]. In all other cases, the absence of disulfide linkages results in substantially reduced reactivity when sulfur is present. For example, the amount of methanethiol that reacts on Mo(110) covered with ~ 0.3 monolayers of sulfur is approximately 20% that on the clean surface. The formation of the disulfide linkage appears to be related to the aromaticity of the phenyl in benzenethiol. It is possible that there is a stabilization of the disulfide *via* interaction between sulfur lone pairs and the π -electron system of the ring. Carbon-carbon bond unsaturation is itself not sufficient to promote disulfide formation, since the disulfide linkage is not formed in the reactions of allyl thiol.

THE EFFECT OF OXYGEN

The reactions of sulfur-containing molecules with oxidized metals offer the possibility for new reaction pathways involving oxygen substitution for sulfur. Furthermore, the reactivity of oxidized materials are of interest because metal oxides such as MoO_3 are often used as the starting catalyst material, which subsequently reacts with the sulfur-containing feed to generate the working catalyst.

Oxygen substitution reactions occur for thiol reactions on Rh(111) [28,29,59]. For example, 2-propanethiol reacts *via* a thiolate intermediate on oxygen-covered Rh(111), ultimately yielding acetone and propene, *via* a transient 2-propyl radical (Fig. 8). Propene formation *via* hydrogen elimination from the radical competes with oxygen addition to the radical species, which yields 2-propoxide. The 2-propoxide further reacts to produce acetone. Oxygen substitution is also observed in the reaction of benzenethiol on oxidized

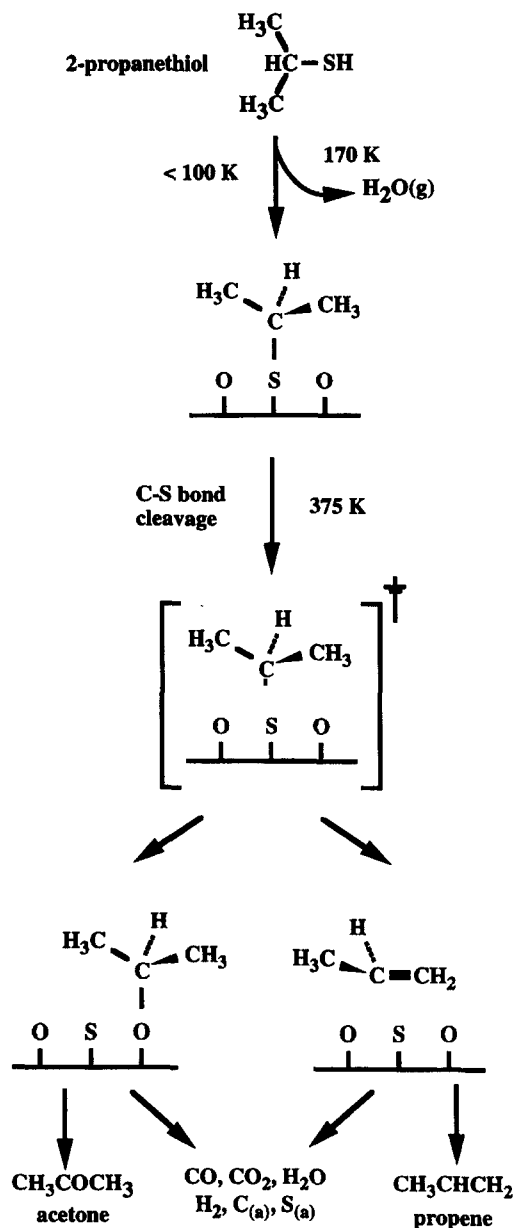


Fig. 8. Scheme for 2-propanethiol reaction on oxygen-covered Rh(111) [29].

Mo(110), which produced trace amounts of phenol, in addition to the major reaction products: hydrogen, water and benzene [60].

The investigations of other alkyl substituents and alkyl iodides provide additional evidence for a radical mechanism in the reactions of thiols on oxygen-covered Rh(111). For example, *tert*-butanethiol is predicted to react at lower temperature than 2-propanethiol if homolytic C—S bond cleavage is rate-determining [59]. Furthermore, addition of the resulting *tert*-butyl radical to oxygen should yield surface-stable *tert*-butoxide, which is known to react at higher temperatures than 2-propoxide because of the absence of C—H bonds at the carbon adjacent to oxygen [61].

Indeed, surface-bound *tert*-butoxide is formed from *tert*-butanethiol on oxygen-covered Rh(111) and is identified using vibrational spectroscopy [59]. The *tert*-butoxide disproportionates to gaseous isobutene and *tert*-butanol at ~ 350 K.

Investigations of the corresponding alkyl iodides on oxygen-covered Rh(111) also substantiate the proposed radical mechanism. The relatively weak C—I bonds are expected to lead to facile elimination of a transient radical, which should undergo reactions that are similar to the respective thiols. Both 2-propyl iodide [62] and *tert*-butyl iodide [59] yield similar products to the corresponding thiols when they react on oxidized Rh(111). The fact that the C—I bonds are approximately 15 kcal mol^{-1} weaker than the C—S bonds in the thiols leads to somewhat different product distributions and reaction temperatures. For example, 2-propyl iodide forms propene and acetone at 335 K, compared with 375 K for 2-propyl thiolate reaction on Rh(111)-p(2×1)-O. The observed lower temperature for C—I *vs* C—S bond breaking further supports the model involving homolytic bond breaking.

The oxygen substitution reactions on Rh and Mo require a balance between the driving force for C—S bond breaking, i.e. the metal–sulfur bond strength, and the barrier to oxygen addition which depends on metal–oxygen bond strength. Hence, the intermediate metal–oxygen bond strength for Rh ($\sim 97 \text{ kcal mol}^{-1}$) compared with Mo(110) ($\sim 130 \text{ kcal mol}^{-1}$) [40] is consistent with the more facile oxygen substitution on Rh. However, a more extensive set of work is required to substantiate this assertion.

Oxygen substitution was not observed for thiolate reaction on a number of other transition metal surfaces. Instead, the oxygen inhibited C—S and C—H bond breaking on the surface, similar to the effect of sulfur. For example, on Ni(110) [7] and W(211), [12] oxygen stabilized the methyl thiolate intermediate such that methane production was favored over decomposition and the total reactivity of the surface was decreased. Oxygen also decreased the reactivity of the surface by site-blocking in the reaction of ethanethiol on O-covered Fe(100) [56]; however, this effect did not become significant until the oxygen coverage was 0.5 monolayers or higher. The presence of oxygen in the reactions of coadsorbed benzenethiol and methanethiol on Ni(111) altered the product distribution. Surprisingly, C—C bond formation resulted in toluene formation [27]. Benzene, methane and hydrogen were also produced. Toluene production was significantly enhanced on oxygen-covered Ni(111) because the competing hydrogenolysis to benzene and methane was hindered by the loss of atomic hydrogen, which combined with surface oxygen to form water. The lack of oxygen substitution during reaction of methanethiol on Ni(110) and ethanethiol on Fe(100) is somewhat unexpected since both have intermediate metal–oxygen bond strengths; metal–oxygen bond strengths are $\sim 91 \text{ kcal mol}^{-1}$ for

Ni, $\sim 93 \text{ kcal mol}^{-1}$ for Fe and $\sim 97 \text{ kcal mol}^{-1}$ for Rh [40]. Therefore, oxygen addition should be facile if the respective alkyl radicals were produced from the thiol reaction. Indeed, recent studies of 2-propyl iodide on oxygen-covered Ni(100) [63] demonstrated that oxygen readily added to 2-propyl, in this case forming 2-propoxide, which further reacted to form acetone, similar to what was observed on oxygen-covered Rh(111). Hence, the lack of oxygen substitution in the thiols on Ni(110) and Fe(100) is most likely due to the inability of oxygen on these two surfaces to activate S—H bonds and/or site-blocking of the thiolate by the oxygen. Both effects would prevent thiolate formation and therefore oxygen-substitution reactions.

REACTIONS ON BIMETALLIC SURFACES

Recently, there has been an increasing interest in the properties of bimetallic surfaces related to desulfurization reactions. There is an extensive body of work regarding coadsorbed sulfur and metals that act as promoters, such as Ni, Co and Fe, on early transition metals, such as Mo(110) and W(110), which is discussed in the companion article by Rodriguez in this issue. Understanding the reactivity of such complex phases is important in discerning the role of promoters, like Co, on the selectivity and rate of desulfurization. To this end, we have investigated the reactions of selected thiols on well-defined overlayers of Co deposited on Mo(110). One of our goals in this work was to probe for special reactivity associated with mixed Co–Mo sites and for sensitivity to surface structure. Special reactivity associated with mixed Co–Mo sites has been suggested based on previous theoretical work which indicates that there is an electronic effect that accounts for the promotion [64]. Our investigations were aimed at probing for this unique reactivity.

Cobalt thin films grown on Mo(110) are ideal for chemical investigations because they offer a range of Co–Co lattice spacings and morphologies that can be systematically varied and because their structure and growth mode are known from previous work [65–67]. For coverages up to 1 monolayer, the Co atoms adopt the structure of the underlying Mo(110) lattice (Fig. 9). As the Co coverage is increased above 1 monolayer, compression along the [001] direction occurs in order to incorporate more Co atoms into the first layer and achieve a packing density similar to that of the Co(0001) surface; additional low energy electron diffraction (LEED) spots, due to double scattering between the substrate and overlayer, appear along the [001] direction in this coverage regime. Above 1 monolayer, the Co assumes an (8×2) commensurate structure. The periodicity changes continuously from eight-fold to about 7.2-fold as the Co coverage

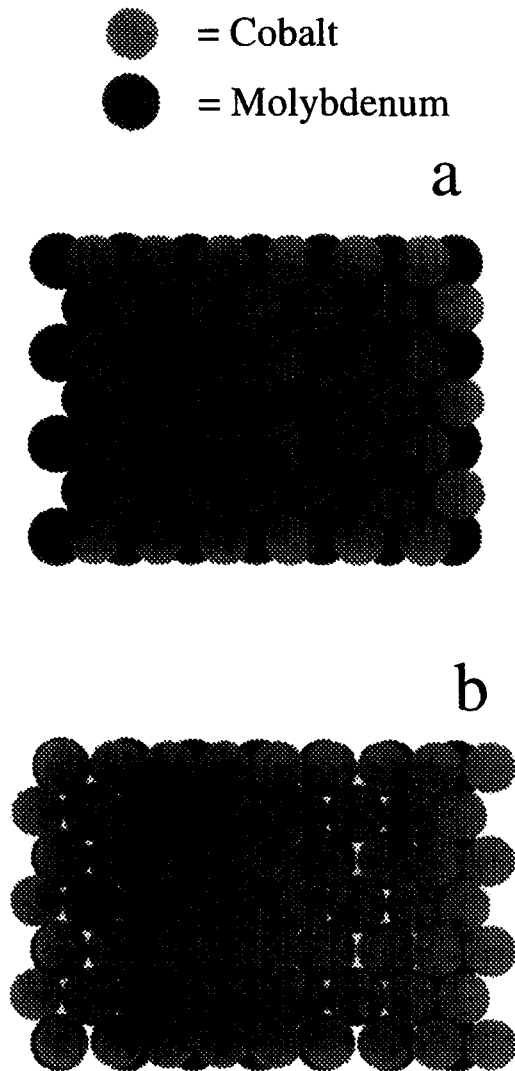


Fig. 9. Schematic representation of various Co overlayers deposited on Mo(110) for: (a) a pseudomorphic structure at a Co coverage of 1.0 monolayer; (b) a close-packed, incommensurate structure at a Co coverage of 1.3 monolayers.

increases to 1.3 monolayers, and the Co–Co spacing approaches that of bulk Co.

The different regimes of overlayer structure accessible in the Co on Mo(110) system offer an excellent opportunity to test for the sensitivity of thiol desulfurization to the Co geometric and electronic structure. In particular, the Co–Co lattice constant varies from 2.73 Å in the pseudomorphic layer ($\theta_{\text{Co}} = 1$ monolayer) to 2.52 Å, which is the lattice constant of bulk Co, for coverages greater than 1.3 monolayers. Hence, variations in reactivity for any process sensitive to the geometric structure of the Co overlayers are expected. In addition, mixed Co–Mo sites are present at low coverages.

We have shown that the surface reactions of methanethiol on uniform Co overlayers on Mo(110) are remarkably insensitive to the geometric and electronic structure of the surface [30]. The reactions on Co-covered Mo(110) are similar to those on Mo(110) itself in that no new products are formed and that the total amount of reaction, as well as the selectivity for hydrocarbon formation, is similar for all Co coverages up to 2.5 monolayers. The lack of sensitivity to Co structure in the reactions of methanethiol is not surprising due to the similarity in methanethiol reactions on a variety of transition metal surfaces. Indeed, the saturation coverage of methanethiol is also similar on Ni(111) [5,6], Ni(100) [8], Ni(110) [7], Fe(001) [14], Ru(0001) [17] and W(001), which represent a range of different packing densities. Furthermore, the reactions of methanethiol on the Co overlayers are qualitatively similar to those on Fe(100) [14], Cu(100) [13], W(001) [11], W(211) [12], Ru(0001) [17] and Mo(110) itself [10], since the thiolate intermediate is formed upon adsorption at 100 K, and methane formation competes with nonselective decomposition. Even the selectivity for hydrocarbon formation is similar on different surfaces: $48 \pm 5\%$ on the Co films compared with $\sim 50\%$ on Mo(110) itself [30] and $\sim 40\%$ on Pt(111) [31]. Systematic variation in the alkyl group is necessary to probe the mechanism of thiolate reaction on the Co overlayers, and preliminary investigations of benzenethiol have been performed as part of this effort.

The reactions of benzenethiol on the Co overlayers are similar to those on Mo(110), in that phenyl thiolate is identified as the intermediate formed by S–H bond cleavage at low temperature, and C–S bond hydrogenolysis to yield benzene and hydrogen competes with nonselective decomposition to atomic carbon and hydrogen [33]. However, unlike the methanethiol case, the reactivity of benzenethiol is different on Co compared with Mo. Benzene is evolved at considerably lower temperature (215 K) from a 1.3 monolayer compared with on Mo (310 K) [33,68]. Furthermore, the selectivity for benzene formation is 20% higher and the total amount of phenyl thiolate formed is $\sim 10\%$ higher on the Co overlayer. As observed on Ni(111) [35], the relative C–S bond strengths for benzenethiol and methanethiol do not correlate with the evolution temperatures of the hydrogenolysis products. Benzene from benzenethiol is evolved at a *lower* temperature than methane from methanethiol on the Co overlayer [30], even though the C–S bond is stronger in the former case. These results suggest the C–S bond homolysis does not control the desulfurization of thiols on the Co overlayers; perhaps hydrogen-assisted desulfurization occurs as was suggested for Ni(111) [35]. Changing from the pseudomorphic to close-packed overlayer structure has little effect on benzenethiol reactivity, except for a slight change in benzene evolution peak shape. The reactivity on Co coverages less than 1 monolayer do not demonstrate any evidence for syn-

ergy; benzene and hydrogen are the only gaseous products for all Co coverages investigated.

SUMMARY

Recent work involving sulfur-containing molecules on transition metal surfaces has provided a better understanding of desulfurization processes. Sulfur removal for thiols on the Mo(110) surface occurs *via* homolytic C—S bond cleavage, and the kinetics for this process are correlated with the stability of the transient radical species. Furthermore, reactions involving sulfur-containing radical or cationic intermediates that undergo various rearrangement processes can be used as a mechanistic probe. Sulfur has been found to inhibit the reactivity of transition metal surfaces and to also increase the selectivity for hydrocarbon production over decomposition. Oxygen plays a similar role to sulfur on many surfaces, but may also lead to oxygen substitution reactions on surfaces such as Rh(111). Thiols on bimetallic Co—Mo surfaces so far have not exhibited any unique reactivity, but more work in this area is forthcoming.

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