

Summary Abstract: Electronic factors in thiophene adsorption and hydrodesulfurization on MoS₂ surfaces

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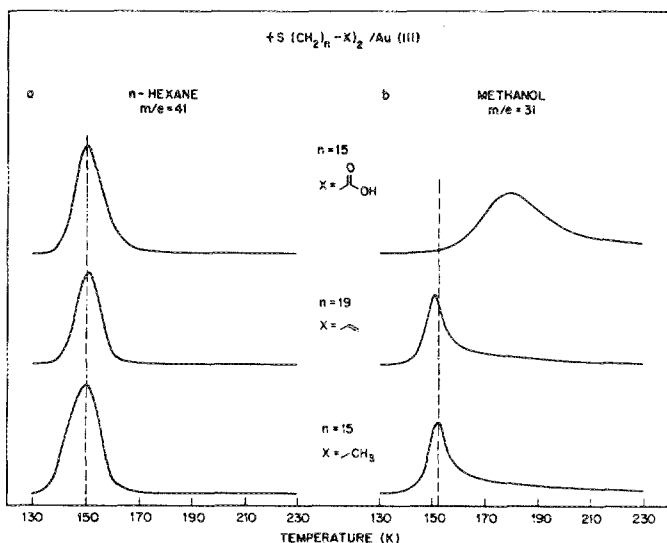


FIG. 1. Temperature programmed desorption traces of (a) n-hexane and (b) methanol desorbing from methyl (bottom), vinyl (middle), and acid (top) terminated surfaces. The substrate materials were prepared by the reaction of a clean Au(111) single crystal with $[\text{CH}_3(\text{CH}_2)_{15}\text{S}]_2$, $[\text{CH}_2\text{CH}(\text{CH}_2)_{19}\text{S}]_2$, and $[\text{HO}_2\text{C}(\text{CH}_2)_{15}\text{S}]_2$, respectively. The strong interaction between the methanol and the acid terminated surface shifts the desorption maximum ~ 30 K. The heating rate was 2.5 K/s in all cases. Only molecular desorption was observed. Gas exposures were 0.2 L.

Temperature programmed desorption studies involving the adsorption of molecules such as hexane, benzene, methanol, and water on top of these model organic surfaces can yield important new insights into the fundamental molecular interactions involved in such technologically important areas as wetting and adhesion. For example, Fig. 1 compares the adsorption of n-hexane and methanol on three different surfaces: methyl, vinyl, and carboxylic acid terminated monolayers. As expected, a nonpolar molecule like hexane inter-

acts only weakly with all three materials. The bonding here is dominated by dispersive forces. As such, one expects, and we find, little coverage dependence in the heat of adsorption of such molecules as n-hexane and other hydrocarbons on these surfaces. In contrast, methanol interacts weakly with the nonpolar surfaces (methyl and vinyl), but bonds much more strongly to the acid terminated material. In addition we find a very strong coverage dependence dominated by interlayer hydrogen bonding.⁶ Similar effects are seen for adsorbed water and formic acid as well. These microscopic observations are exemplified in important macroscopic surface properties. For example, polar liquids, such as water, completely wet polar surfaces such as that of the carboxylic acid terminated monolayer (measured contact angle $\approx 0^\circ$)³ since the molecule-surface interaction is comparable in strength to intermolecular interactions in the liquid. This is not the case with alkyl terminated surfaces, where the contact angle with water equals 104° , as interactions within the adsorbate layer are much stronger than those at the interface. These simple correlations, based on adsorption enthalpies, must be approached with caution, however, as the coverage dependences we observe suggest important contributions which may be entropic in origin.

We will describe additional properties of these model organic surfaces in future publications.⁶

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⁴R. G. Nuzzo, B. R. Zegarski, and L. H. Dubois, *J. Am. Chem. Soc.* **109** (1986).

⁵See, for example, D. L. Allara and R. G. Nuzzo, *Langmuir* **1**, 45 (1985) and references cited therein.

⁶L. H. Dubois, B. R. Zegarski, and R. G. Nuzzo (to be published).

Summary Abstract: Electronic factors in thiophene adsorption and hydrodesulfurization on MoS₂ surfaces

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Hydrodesulfurization, the removal of sulfur in the form of H₂S from petroleum compounds, is a crucial step in industrial refinement processes. In spite of numerous recent experimental and theoretical studies, many aspects of the complex HDS system remain obscure.¹ We will focus on the MoS₂/thiophene system in this work.

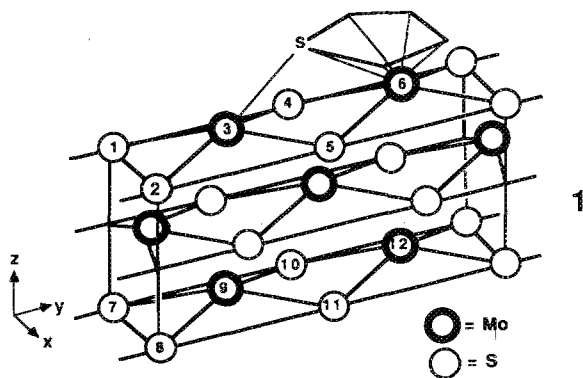
MoS₂ based systems are among the most frequently used and studied catalysts. The microscopic nature of the active

surface is not well defined, although several points can be made. Crystallites of the material are bound to an Al₂O₃ support, which is generally considered to be inert. MoS₂ is a layer compound; the crystals cleave readily between the S-Mo-S sandwiches to expose all-sulfur faces. However, this surface, the basal plane, is believed to be inactive in HDS. The catalytic surface contains exposed Mo atoms. A good candidate is the edge plane perpendicular to the sulfur lay-

ers. Corner sites along the edge and defect sites arising from "missing" surface sulfur atoms, in particular, have been implicated as the active sites.² These Mo atoms are coordinatively unsaturated, thus it is not unreasonable that adsorption may occur here.

Thiophene (C_4H_4S) is the simplest, and most reactive, aromatic species in the HDS feedstock. Neither the geometry of adsorption nor of the active site is known. Coordination of the planar five-membered ring species directly to a surface Mo is generally assumed for both. In organometallic chemistry, both η^5 -bound (coordinated to all five atoms of the ring) and η^1 -sulfur bound (coordinated perpendicularly to the sulfur) species exist.³ However, on the MoS_2 surface, η^2 coordination via the β carbons, which are furthest from the sulfur, or via the S-C bond cannot be excluded. The severe experimental difficulties associated with a direct analysis of the reaction mechanism on the catalytically important surfaces have been prohibitive. However, model studies have been performed on various transition-metal surfaces. On $Mo(100)$ and $Ni(100)$, evidence for a metallocycle formation has been found,⁴ whereas on $Mo(110)$ the proposed intermediate is an η^1 -coordinated surface butyl thiolate.⁵

As the organic products are mainly butanes and butenes, the S-C bonds must be severed in any case. Bonding modes which induce partial occupation of the thiophene LUMO, $3b_1$, will weaken the bond. It is a π^* orbital antibonding between S and C, and localized mainly on the α carbon (adjacent to the sulfur). The extent of $3b_1$ occupation, as measured by the integrated projected density of states, is one criteria we can use to identify possible active sites. The orbital lies 4.4 eV above the HOMO, thus sites which produce substantial occupation are also likely to be high-energy sites.



To simplify our examination of the HDS active sites, our extended Hückel calculations were performed on a three layer, one-dimensional infinite chain MoS_2 sandwich such as **1** (shown in with one particular thiophene coordination mode). The geometric specifications are taken from the real crystal structure. Interadsorbate interactions were minimized by using a unit cell containing six atoms, four sulfur, and two molybdenum, per layer. One such cell is shown; y is the direction of propagation. Atomic charges agree to within $0.005e$ - and overlap populations to 0.005 with those calculated for a two-dimensional MoS_2 slab (propagated in both x and y directions) with the bulk geometric parameters. The one-dimensional model is appropriate for this problem as

"intersandwich" interactions are negligible (at the extended Hückel level) due to the $3.17\text{-}\text{\AA}$ spacing between the sulfur layers. Similar agreement in the calculated parameters is found between one- and two-dimensional slabs with thiophene adsorbed at several test sites. The atomic parameters used can be found in Ref. 6.

Our model exposes two types of surface Mo atoms. Mo_3 protrudes from the surface and, with only four neighboring sulfur atoms, is coordinatively unsaturated. Mo_6 is recessed into the face and has the full bulk complement of six neighboring sulfurs. Both are electron deficient, even with respect to the bulk ($Mo: +0.66$, $S: -0.33$); the net charges are $+0.80$ for Mo_3 and $+1.13$ for Mo_6 . Seven geometries were considered for thiophene adsorption onto a pristine face (no defect sites). For the first set the thiophene sulfur S_i is bound on top of Mo_3 such that (1) the ring is perpendicular to the surface in the xz plane; (2) the ring is at 45° to the surface, and (3) the ring is parallel to the surface. The same ring orientations are selected for (4), (5), and (6) such that S_i is bridging Mo_3 and Mo_6 . The sixth is an η^5 species and is shown in the schematic. The coordination of (7) is as for (1), but to the receding Mo_6 . The S_i -Mo distance is 1.90 \AA for all modes, which is the minimum found in Mo organometallic species.⁷ Similar surface-adsorbate calculations indicate that the choice of chemisorptive bond length will alter the magnitude, rather than the direction and type, of interaction.⁸

On the basis of both the S-C overlap population (o.p.) and the S-C antibonding $3b_1$ occupation, the bridging sites are substantially more effective at weakening the S-C bond than the on-top modes in any given ring orientation. Coordination to the recessed Mo has the smallest effect on this bond. The η^5 species (6) experiences the most severe S-C bond weakening; the o.p. drops from the molecular value of 0.887 to 0.778 . The thiophene $3b_1$ occupation of $0.719e$ - is the largest calculated. By matching the peaks in the $3b_1$ density of states (DOS) to those of the surface Mo levels, we find the primary source of backdonation to be the $Mo_6 x^2-y^2$ levels. The xy states are involved in the MoS_2 surface bond formation; $\sim 40\%$ are found in the sulfur p block. In a true C_{5v} fragment, CpM ($Cp = \text{cyclopentadienyl}$, C_5H_5), the xy and x^2-y^2 orbitals are degenerate and both interact with the degenerate $Cp \pi^*$ orbitals,⁹ which become the $3b_1$ and $2a_1$ of thiophene. If sulfur atoms are sequentially removed from the surface to model defect sites, the xy levels shift out of the sulfur p block and into major peaks of the thiophene π^* states.

The $3b_1$ occupation increases for the bridging set in the order perpendicular, 45° and parallel, but much less so for the on-top set. As described earlier, the binding energies become less favorable as well. One must keep in mind, however, that our calculations produce reasonable relative energies, but unreliable absolute energies.

Chemisorptive bonds typically have two components: adsorbate-to-surface donation and surface-to-adsorbate backdonation. The two sulfur lone pair orbitals, $2b_1$ perpendicular to the ring and $9a_1$ in the ring plane, figure prominently in the former. Thiophene is a much better donor than acceptor adsorbate, as the LUMO is not only localized at the α carbon