

Lawrence Berkeley National Laboratory

LBL Publications

Title

THIOPHENE HYDRODESULFURIZATION OVER TRANSITION METAL SURFACES: STRUCTURE INSENSITIVE OVER MOLYBDENUM AND STRUCTURE SENSITIVE OVER RHENIUM

Permalink

<https://escholarship.org/uc/item/1771k7jk>

Authors

Bussell, M.E.
Gellman, A.J.
Somorjai, G.A.

Publication Date

1987-10-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Chemical
Sciences Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

JAN 8 1988

LIBRARY AND
DOCUMENTS SECTION

Submitted to Journal of Catalysis

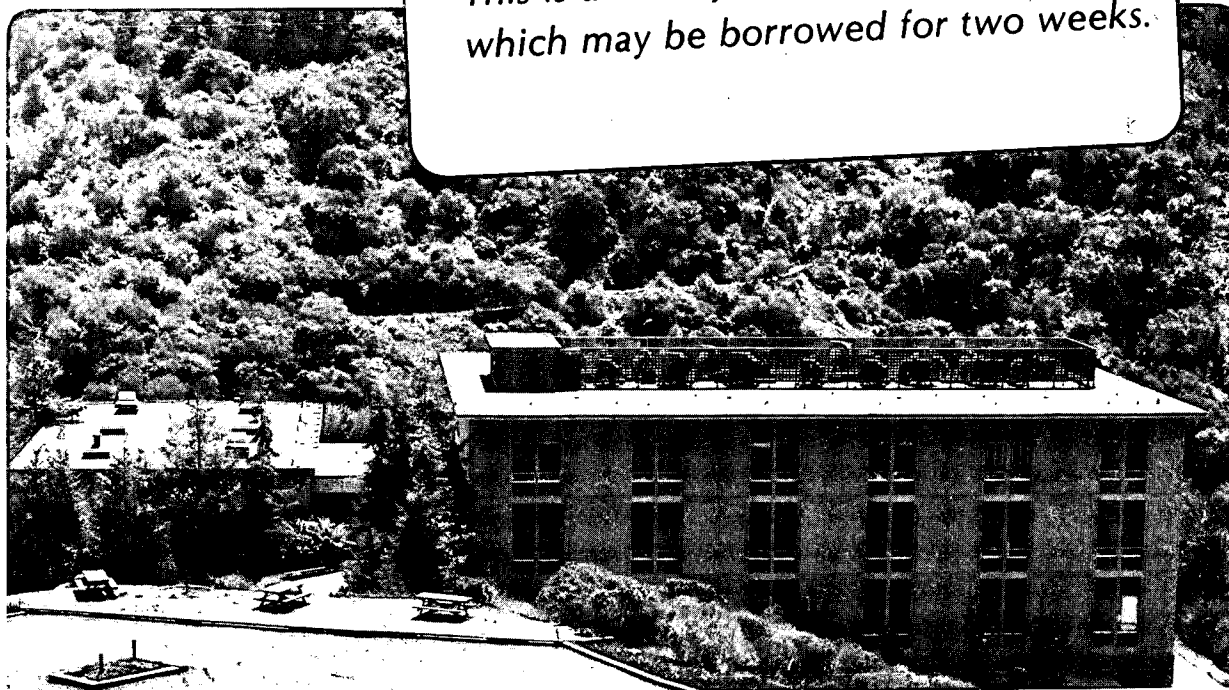
**Thiophene Hydrodesulfurization over Transition
Metal Surfaces: Structure Insensitive over
Molybdenum and Structure Sensitive over Rhenium**

M.E. Bussell, A.J. Gellman, and G.A. Somorjai

October 1987

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.*



LBL-23953
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Thiophene Hydrodesulfurization over
Transition Metal Surfaces: Structure
Insensitive over Molybdenum and Structure
Sensitive over Rhenium

Mark E. Bussell, Andrew J. Gellman*and Gabor A. Somorjai

Department of Chemistry
University of California, Berkeley
and
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

*Permanent Address: Department of Chemistry, University of Illinois, Urbana, IL
61801

In this note we present results of thiophene hydrodesulfurization (HDS) experiments over molybdenum and rhenium single crystals. Previous work in our laboratory showed that a Mo(100) single crystal catalyzes thiophene HDS and that the product distribution is similar to the distribution obtained over an unsupported molybdenum disulfide (MoS_2) catalyst(1,2). The similarity of these results suggests that by determining the effects of surface structure and adsorbate overlayers (C, S) on thiophene HDS over molybdenum single crystals, we can gain insight about the nature of the active sites on MoS_2 based catalysts. This led us to expand our studies to molybdenum single crystals of different surface orientation. We have also begun to investigate thiophene HDS over rhenium single crystals; rhenium disulfide (ReS_2) has been shown to be a more active HDS catalyst than MoS_2 (3).

The experiments reported were performed in a stainless steel, ultrahigh vacuum (UHV) chamber (base pressure = 1×10^{-9} Torr) equipped with a high pressure isolation cell for atmospheric pressure catalytic reactions and is described in detail elsewhere (4). The single crystals were on average 1 cm^2 in area and less than 0.1 cm thick and were cut and polished using standard metallurgical techniques. The cleanliness of the single crystals was verified using AES and LEED. To measure the HDS activity of the single crystal catalysts, the clean single crystal was enclosed in the high pressure isolation cell and the reaction loop pressurized with thiophene and hydrogen ($P_{\text{Th}} = 3.0$ Torr, $P_{\text{H}_2} = 780$ Torr). The reactant gases were circulated in the closed loop batch reactor for 30 min. to ensure mixing, followed by heating the crystal to the reaction temperature ($T = 613$ K). Gas samples were injected into a gas chromatograph every 15 min. and analyzed with a flame ionization detector. Following reaction, the gases were evacuated from the high pressure cell and the cell opened to expose the single crystal to the UHV environment. The accumulation of products was measured for the first two hours of reaction and the reaction rates quoted are for the production of C_4 hydrocarbons in this time period.

Thiophene HDS activities were measured for three low Miller index single crystal planes of molybdenum and four of rhenium and the activities are compared

in Figure 1. The surfaces are illustrated in Figures 2 and 3 along with the coordination numbers of the exposed atoms. Surfaces of comparable openness and corrugation were studied for the two metals yet thiophene HDS was found to be structure insensitive over molybdenum and structure sensitive over rhenium. The rhenium surfaces showed a six-fold variation of HDS activities in the order $(0001) < (11\bar{2}1) < (11\bar{2}0) < (10\bar{1}0)$ while the three molybdenum surfaces studied $((110), (100), (111))$ exhibited almost uniform activities. Comparing the activities of the rhenium and molybdenum surfaces, the least active rhenium surface ($\text{Re}(0001)$) has an activity similar to those of the molybdenum surfaces while the most active rhenium surface ($\text{Re}(10\bar{1}0)$) is six times more active than the molybdenum surfaces. It is interesting to note that our results which show low Miller index planes of rhenium to be one to six times more active than comparable planes of molybdenum agree well with HDS studies over unsupported and supported sulfides of these metals. Chianelli et al. found unsupported ReS_2 to be about four times more active than MoS_2 and Ledoux et al. found ReS_2 supported on carbon to be about two times more active than MoS_2 on the same support (3,5).

The structure insensitivity of thiophene HDS over molybdenum suggests that the reaction occurs on an adsorbate overlayer which masks the influence of the structure of the metal, or that the single crystals reconstruct to a common surface in the high pressure environment. Previous work in our laboratory investigated the role of adsorbed sulfur and carbon in thiophene HDS over the $\text{Mo}(100)$ surface (6,7). Radiotracer ^{14}C and ^{35}S studies showed that both sulfur and carbon are strongly bound to the $\text{Mo}(100)$ surface and are hydrogenated from the surface at a rate much slower than the rate of thiophene HDS. Preadsorbed sulfur decreases the rate of thiophene HDS while adsorbed carbon has no effect on the activity of the catalyst. Furthermore, the initially clean $\text{Mo}(100)$ single crystal becomes covered primarily with adsorbed carbon ($\theta_c \approx 0.80$) during the initial stages of reaction, indicating that the active catalyst surface is covered with adsorbed carbon. These results along with the structure insensitivity of thiophene HDS over Mo single crystals suggest that the active catalytic surface of the Mo single crystals studied is covered

with adsorbed carbon and that this overlayer blocks the influence of the metal's surface structure on the catalyst's activity. The possibility of adsorbate induced reconstruction of the single crystals to a common surface cannot be ruled out; however, LEED experiments before and after reactions showed the symmetry of the metal surface to be unchanged.

In contrast, thiophene HDS over Re single crystals is structure sensitive with a six-fold increase in activity on going from the hexagonal close packed Re(0001) surface to the more corrugated Re(10 $\bar{1}$ 0) surface. These results indicate that thiophene's interaction with the metal surface is not moderated by an overlayer of carbon as was found with molybdenum. In fact, preliminary experiments studying the effect of adsorbed carbon on thiophene HDS over the Re(0001) and Re(10 $\bar{1}$ 0) surfaces indicate that the carbon is graphitic in nature and is a strong poison of the HDS activity of the catalysts (8). The trend of increasing HDS activity of the rhenium surfaces (0001) < (11 $\bar{2}$ 1) < (11 $\bar{2}$ 0) < (10 $\bar{1}$ 0) does not mirror the increase in surface openness (0001) < (10 $\bar{1}$ 0) < (11 $\bar{2}$ 0) < (11 $\bar{2}$ 1) which indicates that surface openness is not the determining factor in catalyst activity. The ammonia synthesis reaction over iron and rhenium single crystal surfaces has been found to be very structure sensitive (9,10). Strongin et al. correlated the activity of a surface to the density of highly coordinated atoms (Fe: C₇ sites, Re: C₁₀, C₁₁ sites) exposed at the surface of the single crystals (9). Theoretical calculations by Falicov and Somorjai suggest that the highly coordinated metal atoms exposed at the surface have high catalytic activity because these sites experience the largest charge fluctuations in the solid(11). However, steric effects must also be examined when considering the catalytic activity of a site. For a surface atom to be catalytically active, it must be accessible for adsorption of the reactant species. It is generally accepted that dissociation of molecular nitrogen is the rate limiting step in the ammonia synthesis reaction. N₂ is a relatively small molecule (van der Waal's radii = 1.5 Å) and is expected to be accessible to exposed second and third layer metal atoms at the surface. These are believed to be the most active sites for ammonia synthesis as they are the most highly coordinated surface atoms and are accessible for adsorption of

the reactant molecules.

In the HDS reaction, thiophene's relatively large size (vertical adsorption: v.d.W. radius = 1.85 Å, horizontal adsorption: v.d.W. radius = 3.5 Å) probably limits its accessibility to metal atoms in the top layer of the surface. Using this assumption, examination of the coordination numbers of the top layer atoms of the surfaces studied may help explain the observed trend in activity. Except for the close-packed Re(0001) surface which exposes C₉ sites and is the least active, a trend is apparent for the remaining Re surfaces: the higher the coordination number of the top layer atoms, the higher the activity of the surface for thiophene HDS. This is in agreement with the theory of Falicov and Somorjai discussed above. The anomalous behavior of the Re(0001) surface can be rationalized in two ways: a C₉ Re atom is incapable of breaking C-S bonds in the high pressure environment, or, the close-packed structure of the surface sterically hinders adsorption of thiophene in the geometry required for reaction.

Finally, it is interesting to compare the great difference in magnitude of the structure sensitivity of ammonia synthesis and thiophene HDS over the same rhenium surfaces. Ammonia synthesis shows a 10³ fold variation in activity with the Re(11 $\bar{2}$ 1) surface the most active, while thiophene HDS shows only a six-fold variation in activity. For NH₃ synthesis, the activity of a surface increases in order of increasing coordination number of rhenium atoms exposed in the second and third layers of the surface. The Re(11 $\bar{2}$ 1) surface is the most active as it has exposed C₁₀ and C₁₁ atoms while the next most active rhenium surface (Re(11 $\bar{2}$ 0)) surface exposes only C₁₁ atoms. The Re(10 $\bar{1}$ 0) surface is third in activity, it exposes C₁₀ sites, and finally the least active surface is the Re(0001) plane which exposes only C₉ atoms. The greater magnitude of the structure sensitivity for ammonia synthesis can be explained by molecular nitrogen being accessible to all the exposed surface atoms including second and third layer atoms so it is very sensitive to which sites are exposed by a particular surface. Thiophene on the other hand, can adsorb only on top layer atoms which have a lower variation in coordination number which results in thiophene HDS being less sensitive to the structure of the rhenium single

crystals. Our results for thiophene HDS and the ammonia synthesis results over rhenium single crystals suggest that the activity of a surface correlates with the coordination number of exposed surface and near surface atoms that are accessible to the adsorbed reactant molecules. For HDS, thiophene is accessible to only the top layer atoms while in the ammonia synthesis reaction molecular nitrogen is accessible to exposed second and third layer atoms as well.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the help of G. S. Blackman in preparing the drawings of the surfaces. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-ACO3-76SFOO098.

REFERENCES

1. Gellman, A. J., Neiman, D., and Somorjai, G. A., *J. Catal.* **106**, (1987).
2. Kolboe, S., *Can. J. Chem.*, **47**, 352 (1969).
3. Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **67** 430 (1981).
4. Gellman, A. J., Farias, M. H., Salmeron, M., and Somorjai, G. A., *Surf. Sci.* **136** 217 (1984).
5. Ledoux, M. J., Michaux, O., Agostini, G. and Panissod, P., *J. Catal.* **102** 275 (1986).
6. Gellman, A. J., Bussell, M. E., and Somorjai, G. A., *J. Catal.*, **106** (1987).
7. Bussell, M. E., and Somorjai, G. A., *J. Catal.*, **106** 93 (1987).
8. Strongin, D. R., Carrazza, J., Bare, S. R., and Somorjai, G. A., *J. Catal.* **103** 213 (1987).
9. Bussell, M. E., Kelly, D. G., and Somorjai, G. A., to be published.
10. Asscher, M., Carrazza, J., Khan, M. M., Lewis, K. B., and Somorjai, G. A., *J. Catal.*, **98** 277 (1986).
11. Falicov, L. M., and Somorjai, G. A., *Proc. Nat. Acad. Sci.*, **82** 2207 (1985).

FIGURE CAPTIONS

Figure 1: a) Thiophene HDS activities for three low miller indice planes of molybdenum ($P_{Th} = 3.0$ Torr, $P_{H_2} = 780$ Torr, $T = 613$ K). b) Thiophene HDS activities for four low miller indice planes of rhenium ($P_{Th} = 3.0$ Torr, $P_{H_2} = 780$ Torr, $T = 613$ K).

Figure 2: Drawings of the three molybdenum surfaces studied. The coordination numbers of the surface atoms are shown.

Figure 3: Drawings of the four rhenium surfaces studied. The coordination numbers of the surface atoms are shown.

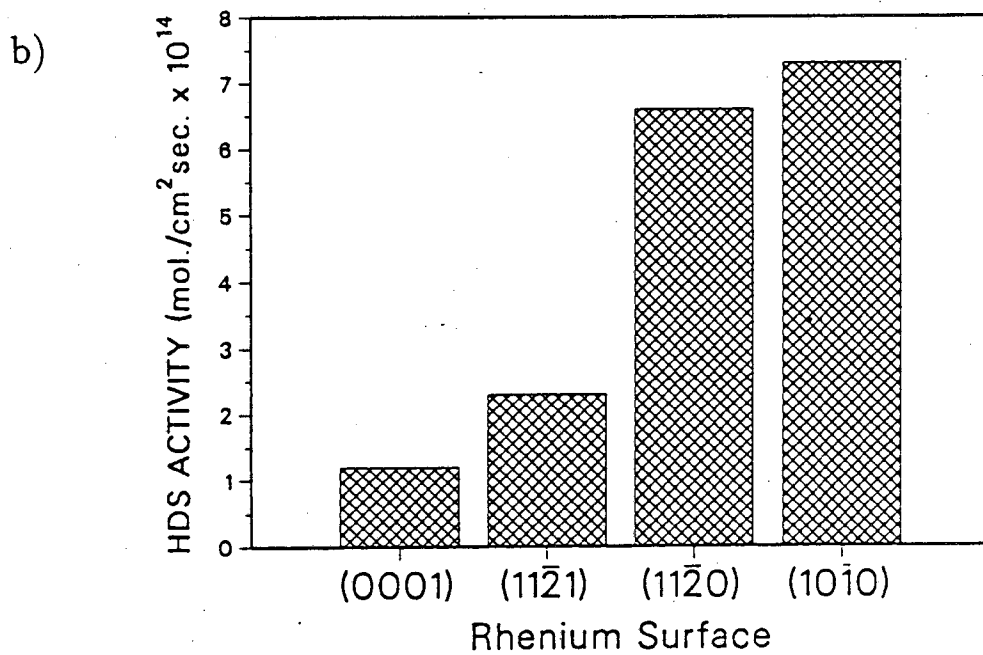
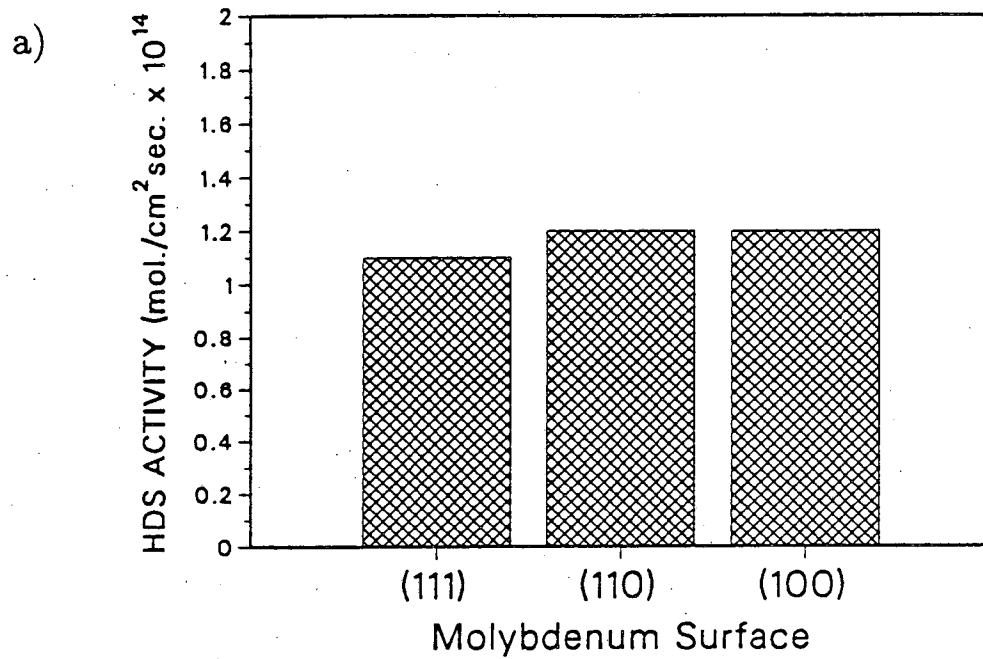
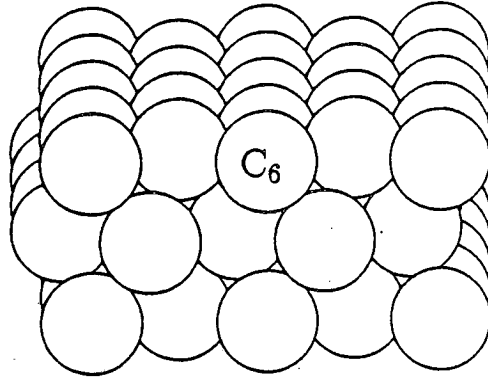


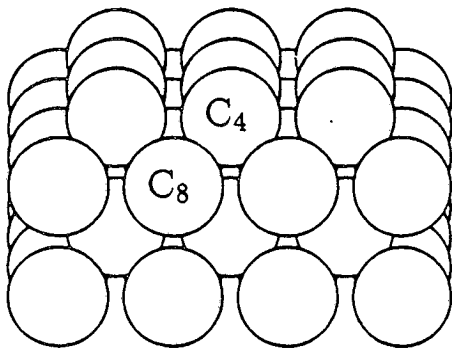
Fig. 1

XBL 878-3473

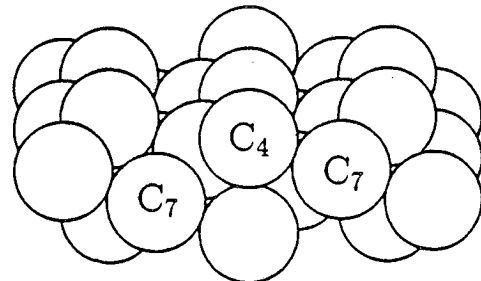
Mo(110)



Mo(100)



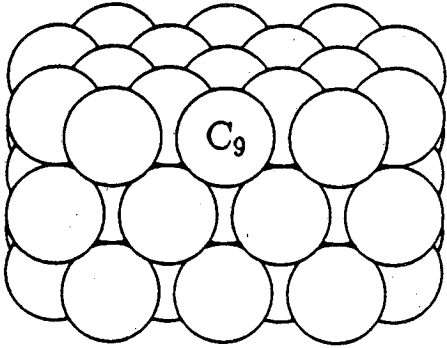
Mo(111)



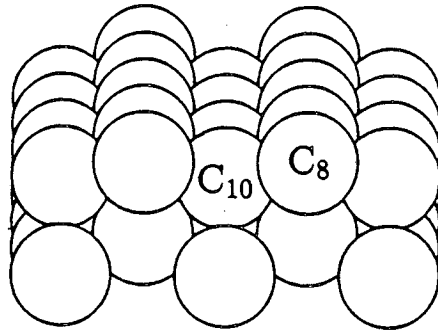
XBL 878-3470

Fig. 2

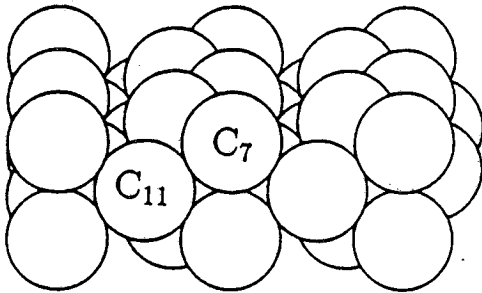
Re(0001)



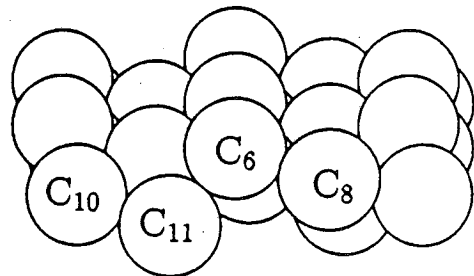
Re(10 $\bar{1}$ 0)



Re(11 $\bar{2}$ 0)



Re(11 $\bar{2}$ 1)



XBL 878-3563

Fig. 3

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720