JOURNAL OF CATALYSIS **120**, 22–28 (1989)

Hydrogen Uptake by MoS_2 and Sulfided Alumina-Supported Mo Catalysts

JOSEF POLZ, HELMUT ZEILINGER, BARBARA MÜLLER, AND HELMUT KNÖZINGER[1]

Institut für Physikalische Chemie, Universität München, Sophienstrasse 11, 8000 Munich 2, West Germany

Received February 6, 1989; revised June 15, 1989

Volumetric H_2-uptake measurements on polycrystalline MoS_2 (39 m^2 g^{-1}) have been carried out and uptake isotherms in the temperature range 423–573 K have been determined. The equilibrium stoichiometry at 500 mbar and 573 K was $H_{0.035}MoS_2$, and at 473 K the H/Mo ratio increased to 0.051. Alumina-supported sulfided Mo catalysts provided H/Mo ratios that were higher by approximately a factor of 4, indicating either a higher MoS_2 surface area, spillover of H atoms to the support, or both. Two possible mechanisms for H_2 dissociation are discussed, namely, heterolytic dissociation on Mo–S pairs and homolytic dissociation on disulfide $(S–S)^{2-}$ edge groups. The presence of the latter on MoS_2 is documented by Raman spectroscopy which shows the characteristic ν(S–S) mode at 529 cm^{-1}. Although molecular analogs for H_2 activation on disulfide groups are known, it is not yet possible to make a clear distinction between the alternative H_2 dissociation routes. © 1989 Academic Press, Inc.

INTRODUCTION

Polycrystalline molybdenum disulfide is known to catalyze hydrogenation reactions (*1, 2*) and it has frequently been used as a model catalyst in studies related to hydrodesulfurization (*2, 3*). It is also known that microcrystalline MoS_2 takes up significant quantities of hydrogen (*4*). Stoichiometries H_xMoS_2 with x values of up to 0.22 (*5*) were found at H_2 pressures below 1 bar and temperatures below 570 K. However, saturation x values reported by different laboratories often vary by as much as one order of magnitude. Edge planes of the MoS_2 structure have been inferred as responsible for H_2 dissociation, and the H atoms were thought to "spill over" onto the basal planes (*6*). The formation of SH groups during hydrogen uptake has been unequivocally detected by inelastic neutron scattering (INS) (*4, 6–9*). INS also provided evidence for the bonding of hydrogen at two different sites (*7, 8*). SH groups were formed first and the corresponding sites saturated at H_2 pressures below 1 bar and temperatures below 423 K. The nature of the second site, which was found to be occupied at higher temperatures and to saturate around 50 bar, still remains unknown. At least two binding states of hydrogen were observed by Dianis (*10*) by thermal desorption spectroscopy.

In view of the high hydrogen capacity of MoS_2, it is appealing to consider H_xMoS_2 rather than MoS_2 as the true catalytically active component for reactions involving dihydrogen, as has recently been suggested by Anderson *et al.* (*11*). However, the elementary steps leading to dihydrogen activation and dissociation are not understood as yet and the corresponding surface sites are unknown. Also, little information is available on the reactivity of the hydrogen bonded to the MoS_2 matrix. We have initiated experiments using the method of time-differential perturbed angular correlation spectroscopy (*12–14*) which will provide insight into the structure and electronic properties of H_xMoS_2, and which can be applied at high temperatures and pressures under *in situ* conditions. In view of the widely diverging reported hydrogen uptake data, we had first to determine uptake isotherms ac-

---

[1] To whom all correspondence should be addressed.

0021-9517/89 $3.00

curately and reproducibly on our MoS_2 preparation as a basis for spectroscopic studies. In this paper we report on these experiments and on some preliminary results obtained by Raman spectroscopy.

EXPERIMENTAL

Preparation of MoS_2. MoS_2 was prepared from ammonium tetrathiomolybdate (ATTM) by reduction in H_2. For the preparation of ATTM, 20 g of ammonium paramolybdate (APM; puriss, Fluka, Switzerland) was suspended in 150 ml aqueous ammonia solution and H_2S was bubbled through the suspension until the APM was quantitatively consumed. The precipitated dark-red ATTM crystallites were filtered off, washed with ethanol, and dried. They were then placed in a glass tube in flowing H_2 and the tube was abruptly brought into a furnace preheated to 670 K. The material was kept under these conditions for 6 h, then cooled to room temperature and stored under dry, O_2-free N_2 until used. This preparation procedure should yield stoichiometric molybdenum disulfide $MoS_{2.0}$ according to Kathold and Weller (*15*) and Prasad *et al.* (*16*). The resulting material had a BET surface area of 39 ± 2 $m^2\ g^{-1}$.

Gases. Argon (99.999%), deuterium (99.6%), hydrogen (99.999%), helium (99.995%), nitrogen (99.999%), hydrogen sulfide (99.8%), and a H_2S/H_2 mixture (1/9) were all Linde products. Ar, N_2, and H_2 were further purified by allowing the gases to flow over Oxisorb.

Uptake measurements. A conventional glass volumetric adsorption apparatus was used for the uptake measurements. The pressure in the system was monitored by means of an MKS Baratron pressure transducer, Type 222B. Predetermined quantities of gases were introduced into the reactor (which could be cooled to 77 K or heated to 770 K) in calibrated volumes. Gas analyses were carried out by mass spectrometry using a quadrupole mass spectrometer of the Vaccum Analyst type from Vacuum Science Workshops, Manchester, UK.

Sample pretreatments. The MoS_2 samples, which were stored under N_2, were brought into the reactor in a procedure that attempted to avoid exposure to air as far as possible. Prior to uptake measurements, the samples were pretreated *in situ* in flowing H_2S/H_2 (1/9) at 573 K for 60 min and subsequently evacuated ($<10^{-3}$ mbar) at 573 K for 60 min. As will be shown below this procedure gave reproducible H_2-uptake data.

Raman spectroscopy. Raman spectra were recorded on an OMARS spectrometer from Dilor, Lille, France, equipped with an optical multichannel analyzer IRY-512/L from Spectroscopy Instruments, Gilching, FRG. The 514.5-nm line of a Spectra Physics Ar^+ ion laser (Model 2025) was used for excitation at approximately 20 mW at the sample position. The spectra were recorded with the sample placed in a specially designed cell in a He atmosphere, the sample holder being cooled to 80 K. The sample was pretreated as described above and then transferred into the Raman cell under a He atmosphere.

RESULTS AND DISCUSSION

The first uptake measurements were highly unreproducible and typically resulted in high uptake values (H/Mo ratios of the order of magnitude of 0.1) which continuously decreased in repeated runs. This phenomenon was clearly due to the presence of chemisorbed oxygen [most probably present as atomic oxygen, as shown earlier by XPS (*17*)]. This chemisorbed oxygen could most probably be eliminated by the pretreatment procedure described under Experimental, as documented by the perfect reproducibility of the uptake measurements after the standard pretreatment. The effect of oxygen to increase the apparent hydrogen uptake has in fact been proved by preadsorption of oxygen on freshly *in situ* pretreated samples. On the other hand, when the oxygen preadsorption was followed by a second standard pretreatment, the initial hydrogen uptake value was perfectly reproduced. It is not clear in which form the extra hydrogen might be bonded. One can only speculate that OH groups are formed when oxygen contamination is present. Inelastic neutron scattering spectra had shown an excitation at 872 cm^{-1} which was tentatively assigned to a Mo–OH deformation mode (*7, 8*) owing to possible surface contamination.

Figure 1 shows hydrogen uptake isotherms at 473 and 573 K. The different symbols in the figure indicate results obtained on different samples, which, however, were given the identical standard pretreatment. The data clearly show the excellent reproducibility of the uptake measurements. When a new charge of MoS_2, the BET surface area of which was 48 m^2 g^{-1} (rather than 39 m g^{-1}), was prepared, the hydrogen uptake under otherwise identical pretreatment and measurement conditions could be reproduced to within 15% of the isotherm data shown in Fig. 1. The isotherms rise steeply below approximately 100 mbar; at higher pressures, the x values increase linearly with a gentle slope. Formally, the isotherms can be reasonably well described by the Langmuir equation.

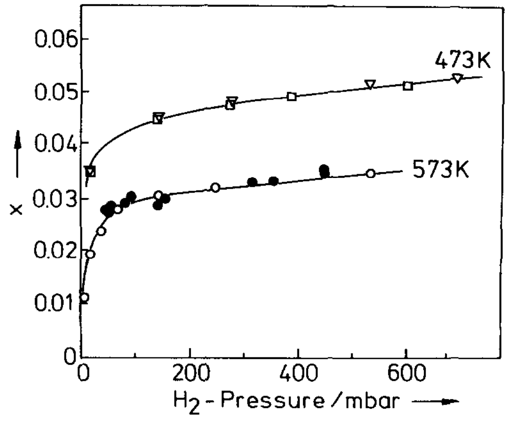


FIG. 1. Hydrogen-uptake isotherms on MoS_2 (39 m^2 g^{-1}) at 473 and 573 K. (The different symbols correspond to measurements on various charges of MoS_2 from the same preparation.)

Isotherms were also measured at 423 and 523 K. As the H_2 uptake is activated (*10*), the uptake at 423 K was extremely slow and equilibrium could presumably not be reached even after several hours (the experimental x value at 500 mbar after 16 h was 0.057). The equilibrium x values at 500 mbar H_2 pressure at 473, 523, and 573 K were 0.051, 0.041, and 0.035, respectively, with an upper experimental error of ±0.002. The isosteric heat of uptake at x = 0.038 was estimated to be 70 ± 5 kJ mol^{-1}.

When the $H_{0.035}MoS_2$ sample obtained after H_2 uptake at 573 K was subsequently evacuated at 573 K (typically for 60 min), a second uptake measurement gave identical x values; this procedure could be reproducibly repeated several times and suggests that the hydrogen uptake was reversible under these conditions and no hydrogen was retained irreversibly. This conclusion is supported by the observation that evacuation of $H_{0.035}MoS_2$ at 673 K and readsorption of hydrogen at 573 K gave again an identical x value of 0.035. Moreover, exposure of the sample after evacuation at 573 K to a D_2 atmosphere at 573 K yielded only small amounts of HD, corresponding to x values of the order of the experimental accuracy. This supports the view that hydrogen is nearly quantitatively desorbed from H_xMoS_2 after evacuation at 573 K and higher temperatures. By contrast, after evacuation at lower temperatures hydrogen was clearly "irreversibly" retained under the experimental conditions applied, as can be seen from the reduced uptakes when a second isotherm was measured. The x values corresponding to the irreversibly held amounts at 523 and 473 K were 0.0086 (±0.004) and 0.0196 (±0.008), respectively.

A comparison is made in Table 1 of our present results with data reported in the literature. It must be noted that the value of 0.014 in row 2 was obtained by Maternova (*28*) by direct determination of SH groups. This value may not be comparable with the remaining total uptakes if hydrogen can be bonded additionally in other forms.

TABLE 1

Reported H/Mo Values as Obtained from Hydrogen Uptake on Molybdenum Disulfide

H/Mo	Pretreatment Conditions	Pressure (bar)	Temperature (K)	S_{BET} ($m^2\ g^{-1}$)	Method	Comments	Ref.
0.089	Evacuation overnight at 573 K	0.9	573	8.4	Volumetry	Deuterium	*(6)*
0.014	H_2 for 2 h at 723 K, then cooled to 300 K in N_2	1.01	300	24	Titration by $AgNO_3$ in pyridine		*(28)*
0.011	Evacuation for 1 h at 723 K		723		Volumetry	Reversible, $x = 0.24$ for first adsorption	*(29)*
0.039	H_2/H_2S at 800 K	0.11	475	85	Dynamic, H_2 pulses in Ar (1 : 9)		*(30)*
0.14	H_2/H_2S (4/1) at 523 K	0.67	≤423	6.9		Amorphous, $MoS_{1.8}$	*(7)*
0.20	Same	0.67	>423	6.9			
0.033	H_2/H_2S (9/1) for 1 h at 623 K		373	89	Volumetry	Irreversibly held portion	*(10)*
0.011			473				
0.22	Flushing with N_2 at 195 K	1.0	325		Volumetry		*(5)*
0.84	Same	1.0	325		Volumetry	Pt on MoS_2	
0.035	H_2/H_2S (9/1) for 1 h at 573 K, evacuation at 573 K	0.5	573	39 ± 2	Volumetry		This study
0.041	Same	0.5	523	39 ± 2	Volumetry		
0.051	Same	0.5	473	39 ± 2	Volumetry		

Occasionally, H_2-uptake values at elevated temperatures have been compared with the number of N_2 molecules in the monolayer (as determined via the BET procedure). Wright *et al.* *(6)* concluded from their H_2 uptake, which was significantly higher than expected for the given N_2 BET surface area, that considerable proportions of the total hydrogen sorbed must be located in the bulk or bonded at sites inaccessible to N_2 at 77 K. When the area density of H atoms is calculated from the data presented above for 573 and 473 K based on the N_2 BET surface area, one obtains respectively 54 and 78% of the N_2 molecules in the BET monolayer. Wright *et al.* *(6)* compared their hydrogen-uptake data with the density of sulfur atoms in basal and edge planes of MoS_2. Our data for hydrogen uptake are lower than the density values of sulfur atoms by factors of 4 and 2.5, respectively, i.e., much lower than those reported by Wright *et al.* *(6)*. The total number of hydrogen atoms sorbed could thus be accommodated on the surface, provided lattice sulfur atoms were the adsorption sites. If, however, defects and edge sites were the adsorption sites for hydrogen atoms, the site density (estimated from the number of H atoms sorbed and the N_2 BET surface area) appears to be very large. It might then well be, as already suggested by Wright *et al.* *(6)*, that sites exist that are inaccessible to dinitrogen at 77 K.

Molecular dihydrogen will hardly adsorb physically at 77 K on the entire surface as dinitrogen does; rather, it will adsorb on distinct defect sites (e.g., at edges and crevices of molecular dimensions) which might also be involved in atomic hydrogen bonding. Also, sites that are inaccessible to dinitrogen (molecular area 0.162 nm^2) should be accessible to the smaller dihydrogen molecule (0.13 nm^2). An adsorption isotherm for dihydrogen on MoS_2 at 77 K was therefore measured (Fig. 2). The MoS_2 used in this experiment was a new preparation with a surface area of 48 $m^2\ g^{-1}$. The isotherm shown in Fig. 2 gives a saturation value of 6×10^{14} H_2 molecules cm^{-2}, which is almost identical to the monolayer capacity of N_2, which is 6.2×10^{14} N_2 molecules cm^{-2} given a molecular area for the N_2 molecule of 0.162 nm^2. The density of adsorbed H_2

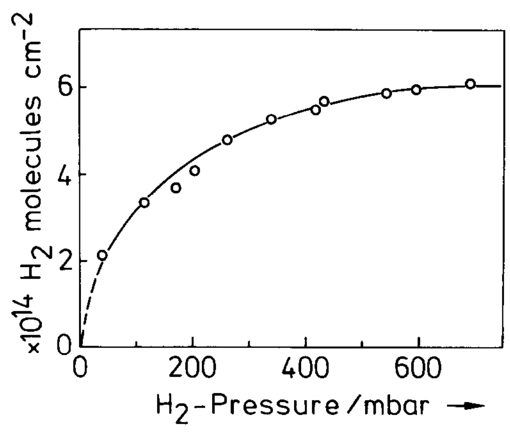
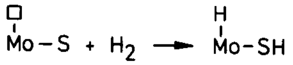


FIG. 2. Adsorption isotherm of dihydrogen on MoS_2 (48 $m^2 g^{-1}$, standard pretreatment) at 77 K.

molecules has been calculated on the basis of the N_2 BET surface area. Considering the fact that H_2, in contrast to N_2, should adsorb only on specific sites at 77 K, the high apparent saturation value for dihydrogen adsorption can be understood only if, in these MoS_2 preparations, there exist sites that remain inaccessible to dinitrogen. We therefore suggest that also atomic hydrogen can probably be adsorbed on these parts of the total surface area that do not contribute to the N_2 BET surface area.

We have also carried out a few hydrogen-uptake measurements on an alumina-supported catalyst. The MoO_3 loading was 12 wt%, and the BET surface area 140 $m^2 g^{-1}$. After calcination in air at 773 K, the catalysts were sulfided *in situ* in flowing H_2S/H_2 (1/9) at 573 K for 2 h followed by evacuation at 573 K for 1 h. The hydrogen uptake measured at H_2 pressures between 300 and 450 mbar and at 573 K corresponded to $x = 0.13 \pm 0.01$. It is interesting to note that this value is higher by a factor of 4 than that obtained on unsupported MoS_2 under comparable conditions. This increased H/Mo ratio may simply reflect the high dispersion of supported MoS_2. However, possible contributions of hydrogen spilled over to the alumina support cannot be excluded. Wright *et al.* (*6*) had suggested on the basis of their INS results that "hydrogenated" alumina was formed when a sulfided alumina-supported Mo catalyst was exposed to H_2. Increased H/Mo ratios for supported catalysts have also been reported in the literature (*4*); however, quantitative comparisons are certainly meaningless unless the state of the catalysts can be clearly specified.

Although the formation of H_xMoS_2 does undoubtedly occur, the elementary steps of dihydrogen activation can be discussed only speculatively at this time. Sulfur vacancies along the edge planes are almost certainly formed during the thermal treatments prior to H_2-uptake measurements (*1*, *2*, *14*). One can therefore envisage heterolytic splitting of dihydrogen on Mo–S pairs

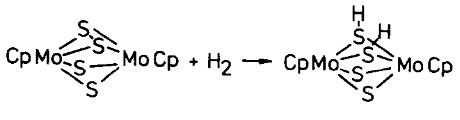


$$\overset{\square}{Mo}-S + H_2 \longrightarrow \overset{H}{Mo}-SH \quad (1)$$

to form Mo–H and S–H groups. Anderson *et al.* (*11*) have recently shown by quantum chemical calculations that this dissociation route would be energetically favorable; however, the INS studies by Wright *et al.* (*6*) had shown for $H_{0.067}MoS_2$ that the H atoms should be bonded to one or more S atoms but not to Mo atoms. It therefore seems appealing to consider an alternative route for H_2 dissociation by reaction with disulfide S_2^{2-} species:

$$S_2^{2-} + H_2 \longrightarrow 2\,SH^- \quad (2)$$

Activation of dihydrogen by S_2^{2-} groups is in fact documented in molecular coordination chemistry (*18*, *19*) (Cp = cyclopentadiene):



(3)

The presence on supported sulfided Mo catalysts of low-valence-state sulfur, i.e., S^- or $(S-S)^{2-}$, has been shown by XPS by Duchet *et al.* (*20*), and Raman spectroscopy (*21*, *22*) has provided evidence for disulfide anions on these catalysts. Figure 3 shows a Raman spectrum obtained on the presently

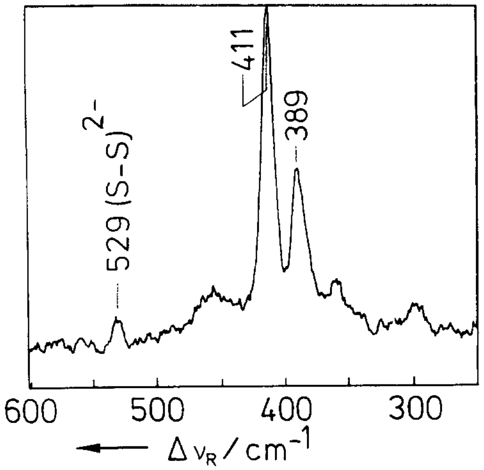


FIG. 3. Raman spectrum of MoS_2 after standard pretreatment.

used MoS_2 after thermal activation as described above. The two bands at 389 and 411 cm^{-1} are characteristic of MoS_2 and the weaker band at 529 cm^{-1} can be assigned to the S–S stretching mode of disulfide anions (*23, 24*). This species was in fact inferred to be connected with catalytic hydrodesulfurization activity (*20, 25, 26*). The tentative mechanism described by Goodenough (*25*) involves reaction of H_2 with disulfide anions as suggested in Eq. (2), and recently Prins *et al.* (*27*) have also pointed toward this possibility.

It is concluded from the results of the present study that hydrogen uptake on MoS_2 at elevated temperatures can be measured reproducibly provided the sulfide is pretreated *in situ* and the access of even traces of oxygen is carefully avoided. Equilibrium uptake data below 1 bar and between 473 and 573 K, when compared to saturation values of dihydrogen adsorption at 77 K and to the monolayer capacity for dinitrogen, suggest that bonding sites for atomic hydrogen must exist on parts of the MoS_2 surface that are inaccessible to dinitrogen. The MoS_2 preparations used therefore appear to be microporous. The nature of sites that activate and ultimately dissociate dihydrogen molecules is not clear as yet. Besides the conventionally suggested cation–anion pair sites [see Eq. (1)], disulfide species located at edge planes must certainly be considered as potential sites of homolytic dihydrogen dissociation. The established reactivity of these groups in organometallic compounds clearly suggests this as a feasible route toward dihydrogen dissociation.

ACKNOWLEDGMENTS

This research was financially supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie.

REFERENCES

1. Tanaka, K., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 33, p. 99. Academic Press, New York, 1985.
2. Mitchell, P. C. H., "Catalysis," Vol. 4, p. 175. Roy. Soc. Chem., London, 1981.
3. Delmon, B., *in* "Proceedings, Climax 3rd International Conference on Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 73. Climax Molybdenum Company, Ann Arbor, MI, 1979.
4. Moyes, R. B., *in* "Hydrogen Effects in Catalysis" (Z. Paál and P. G. Menon, Eds.), p. 583. Dekker, New York, 1988.
5. Blackburn, A., and Sermon, P. A., *J. Chem. Technol. Biotechnol.* **33A,** 120 (1983).
6. Wright, C. J., Sampson, C., Fraser, D., Moyes, R. B., Wells, P. B., and Riekel, C., *J. Chem. Soc. Faraday Trans. 1* **76,** 1585 (1980).
7. Sampson, C., Thomas, J. M., Vasudevan, S., and Wright, C. J., *Bull. Soc. Chim. Belg.* **90,** 1215 (1981).
8. Vasudevan, S., Thomas, J. M., Wright, C. J., and Sampson, C., *J. Chem. Soc. Chem. Commun.*, 418 (1982).
9. Jones, P. N., Knözinger, E., Langel, W., Moyes, R. B., and Tomkinson, J., *Surface Sci.* **207,** 159 (1988).
10. Dianis, W. P., *Appl. Catal.* **30,** 99 (1987).
11. Anderson, A. B., Al-Saigh, Z. Y., and Hall, W. K., *J. Phys. Chem.* **92,** 803 (1988).
12. Lerf, A., and Butz, T., *Angew. Chem. Int. Ed. Engl.* **26,** 110 (1987).
13. Butz, T., Lerf, A., Vogdt, C., and Knözinger, H., *J. Catal.* **116,** 31 (1989).
14. Knözinger, H., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 5, p. 20. Chem. Inst. Canada, Ottawa, 1988.
15. Kathold, D. G., and Weller, S. W., *J. Catal.* **98,** 572 (1986).
16. Prasad, T. P., Diemann, E., and Müller, A., *J. Inorg. Nucl. Chem.* **35,** 1895 (1973).

17. Zhuang, S., Hall, W. K., Ertl, G., and Knözinger, H., *J. Catal.* **100,** 167 (1986).
18. Rakowski Du Bois, M., van Dervear, M. C., Du Bois, D. L., Haltiwanger, R. C., and Miller, W. K., *J. Amer. Chem. Soc.* **102,** 7456 (1980).
19. Rakowski Du Bois, M., *Chem. Rev.* **89,** 1 (1989).
20. Duchet, J. C., van Oers, E. M., de Beer, V. H. J., and Prins, R., *J. Catal.* **80,** 386 (1983).
21. Schrader, G. L., and Cheng, C. P., *J. Catal.* **80,** 369 (1983).
22. Payen, E., Kasztelan, S., and Grimblot, J., *J. Mol. Struct.* **174,** 71 (1988).
23. Mennemann, K., and Mattes, R., *Angew. Chem. Int. Ed. Engl.* **16,** 260 (1977).
24. Müller, A., Nolte, W.-O., and Krebs, B., *Angew. Chem. Int. Ed. Engl.* **17,** 279 (1978).
25. Goodenough, J. B., *in* "Proceedings, 4th International Conference on Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 1. Climax Molybdenum Company, Ann Arbor, MI, 1982.
26. Stiefel, E. I., *in* "Proceedings, 4th International Conference on Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 56. Climax Molybdenum Company, Ann Arbor, MI, 1982.
27. Prins, R., de Beer, V. H. J., and Somorjai, G. A., *Catal. Rev. Sci. Eng.*, in press.
28. Maternova, J., *Appl. Catal.* **3,** 3 (1982).
29. Vasudevan, P. T., and Weller, S. W., *J. Catal.* **99,** 235 (1986).
30. Hou, P., and Wise, H., *J. Catal.* **78,** 469 (1982).