PHOTOEMISSION STUDIES OF RHENIUM DISULFIDE OXIDATION: ALTERED CORE-LEVEL STRUCTURE AND REACTIVITY OF DEFECT SITES

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X-ray photoemission was used to investigate the initial stages of rhenium disulfide oxidation and the altered reactivity and core-level electronic structure of defect sites produced by argon ion sputtering of single crystal and polycrystalline ReS_2-basal plane surfaces. Oxidation of polycrystalline-ReS_2 with O_2 at 100–300 °C produced a mixture of surface oxides containing rhenium in the +4 and +7 oxidation states. Oxidation was facilitated by the presence of low coordination defect sites and was reversible upon resulfidization with H_2S/H_2 at 300 °C.

Rhenium disulfide is among the most active transitional metal sulfide catalysts for hydrodesulfurization of petroleum feedstocks [1], and sulfided rhenium also finds important application as a "promoter" in $PtRe/Al_2O_3$ catalysts for naphtha reforming into high octane gasoline [2]. We have previously reported that defect sites can be produced in ReS_2 basal plane surfaces under the influence of ion bombardment, and that the defect sites exhibit enhanced activity for oxygen chemisorption as measured by low energy ion scattering [3]. In this communication, we report related photoemission studies of the initial stages of ReS_2 oxidation and the defect sites produced by ion bombardment. Production of sulfide vacancy defect sites in single crystal and polycrystalline ReS_2 basal plane surfaces was found to substantially alter the Re(4f) core-level electronic structure as measured by X-ray photoelectron spectroscopy (XPS). The defect sites exhibited enhanced reactivity for oxidation reactions that produced a mixture of surface oxides containing rhenium in the +4 and +7 oxidation states. Oxidation was reversible by treatment with H_2S/H_2 at 300 °C. These results for ReS_2 compliment those previously reported for several forms of molybdenum disulfide (4–6).

Photoemission spectra were collected in a Leybold-Heraeus ultra-high vacuum apparatus using unmonochromatized $Mg(K_\alpha)$ radiation (1253.6 eV) and a hemispherical energy analyzer that was operated at 10 eV pass energy which resulted in an instrumental resolution of 0.8–0.9 eV. Binding energies were referenced to the Au($4f_{7/2}$) core-level (83.8 eV) of gold used either as a part of the sample mounting support or vacuum evaporated in small amounts. Good agreement (±0.1 eV) was obtained by both methods reflecting the conductive, semi-metallic nature of ReS_2. Data acquisition and manipulation were carried out with an HP-1000 computer using the LH-DS5 software package.

Single crystal ReS_2 with a basal plane surface area of about 1 cm^2 was prepared from the elements by chemical vapor transport at 1000–1150 °C using Br_2 as the transport agent. Polycrystalline rhenium disulfide (px-ReS_2, 5.4 m^2/g) was derived from the metathatical reaction of $ReCl_4$ with Li_2S followed by repeated acid washing and sulfidization at 400 °C in 10% H_2S/H_2 as described by Dines and Chianelli [7]. A small microreactor and sample transfer system was used for in situ sulfidization of the samples in 10% H_2S/H_2 at 300 °C and atmospheric pressure prior to XPS analysis. Sulfidization was essential to remove residual traces of surface oxide. Deliberate oxidation studies were carried out in situ using 20% O_2/N_2 in the same apparatus. Research purity gases were employed for all pretreatment studies, and in all cases, the treatment time was 15 minutes. Apart from trace amounts of sodium and carbon, the ReS_2 surfaces were free of contaminants as measured by both XPS and low energy ion scattering [3].

Rhenium (4f) XPS results for ReS_2(0001) and px-ReS_2 before and after sequential ion bombardment studies are compared in fig. 1. Initially stoichiometric surfaces displayed well resolved Re(4f) doublets with Re($4f_{7/2}$) binding energies of 41.5 eV. Sputtering the surfaces with 1.0 keV Ar^+ caused the Re(4f) XPS peaks to continuously broaden, and the peak maxima were shifted to slightly

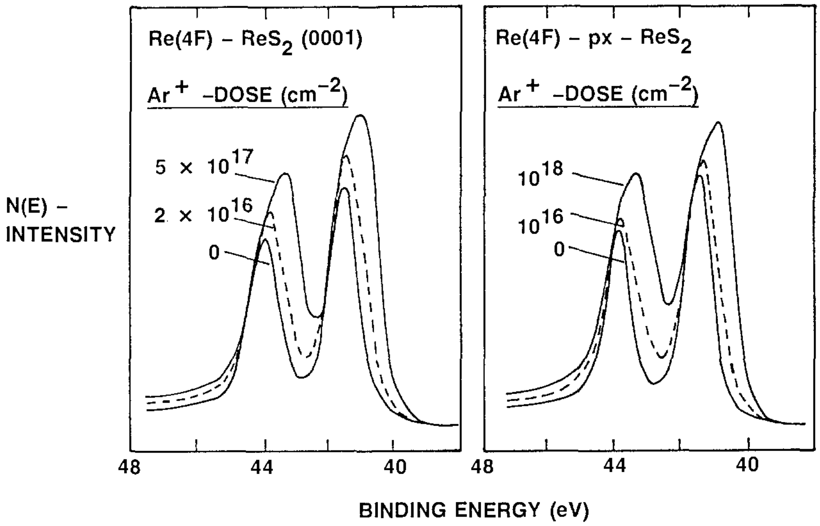

Fig. 1. Rhenium (4f) photoemission spectra are compared for ReS_2(0001) and polycrystalline ReS_2 before and after sputtering the initially stoichiometric surfaces with a variable dose of 1 keV Ar^+. Relative intensities have been adjusted slightly to more clearly illustrate the displacement of Re(4f) doublet to lower binding energy with increasing ion dose.

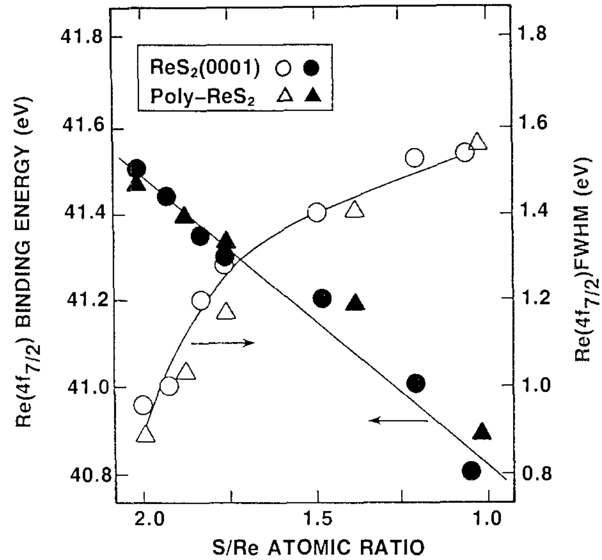

Fig. 2. Rhenium ($4f_{7/2}$) binding energies and full widths at half maxima are shown as a function of the average $ReS_2(0001)$ and px-ReS_2 surface composition as determined from the S(2p) and Re(4f) XPS intensities corrected with photoionization cross sections.

lower binding energies. These changes occurred without significant alteration of the S(2p)-lineshape, although the S(2p) XPS intensity was attenuated substantially. This is shown more clearly in fig. 2 where the Re($4f_{7/2}$) full width at half maximum and binding energy are displayed as a function of the (S/Re) atomic ratio as estimated from the S(2p) and Re(4f) peak areas corrected with photoionization cross sections [8] assuming uniform atomic distributions. Ion bombardment clearly resulted in preferential sputtering of sulfur from the near surface region. In this process, surfaces containing high concentrations of defect sites were produced. The defect containing surfaces exhibited altered Re(4f) lineshapes and binding energies indicating that the local electronic structure is changed. In the limit of a high ion dose (ca. 10^{18} cm^{-2}), the composition of the near surface region approached "ReS" and the Re($4f_{7/2}$) binding energy was shifted well toward that (40.0 ± 0.1 eV) for metallic rhenium.

The Re(4f) core-level shifts for sputtered ReS_2 surfaces can be interpreted, at least qualitatively, on the basis of a simple initial state bonding model in which the Re($4f_{7/2}$) binding energy reflects the local chemical environment. In this model, production of defect sites is presumably accompanied by charge redistribution wherein the electron density in valence orbitals of rhenium atoms adjacent to sulfide vacancies is increased. Precedent for this interpretation is provided by ultraviolet photoemission data for sputtered MoS_2 surfaces and the XPS spectra for MoS_2 edge planes [9]. In simple chemical terms, sputtered surfaces are expected to contain rhenium atoms with lowered formal oxidation states (FOS) which is consistent with the lowered binding energies and reduced sulfer content detected for defect containing surfaces. The true situation for the ReS_x surface electronic structure is probably complicated by surface disordering and the possible formation of small metallic clusters, especially at the highest ion dosages. As such, surface restructuring is also likely to contribute to the altered ReS_2 XPS lineshapes. More detailed structural studies would be valuable to investigate this possibility.

Oxidation of both stoichiometric and sputtered px-ReS_2 in flowing oxygen at 100–300 °C resulted in drastic changes in the O(1s), S(2p), and Re(4f) XPS spectra that are exemplified in figs. 3 and 4. Digital subtraction of the ReS_2 component from the Re(4f) spectra for partially oxidized surfaces, as illustrated by the lower spectrum in fig. 3, indicates that at least two new chemical states of rhenium were produced by oxidation. The three line spectrum for oxidized rhenium can be easily resolved into two doublets with Re($4f_{7/2}$) intensity maxima near 42.4 and 45.3 eV. These species are attributed to ReO_2 and Re_2O_7-like oxides as their binding energies agree closely with those for (42.0 and 45.5 eV) for ReO_2 and ReO_4^-, respectively. All spectra for partially oxidized surfaces showed evidence for both oxide species, and the Re^{+4}/Re^{+7} intensity ratio estimated

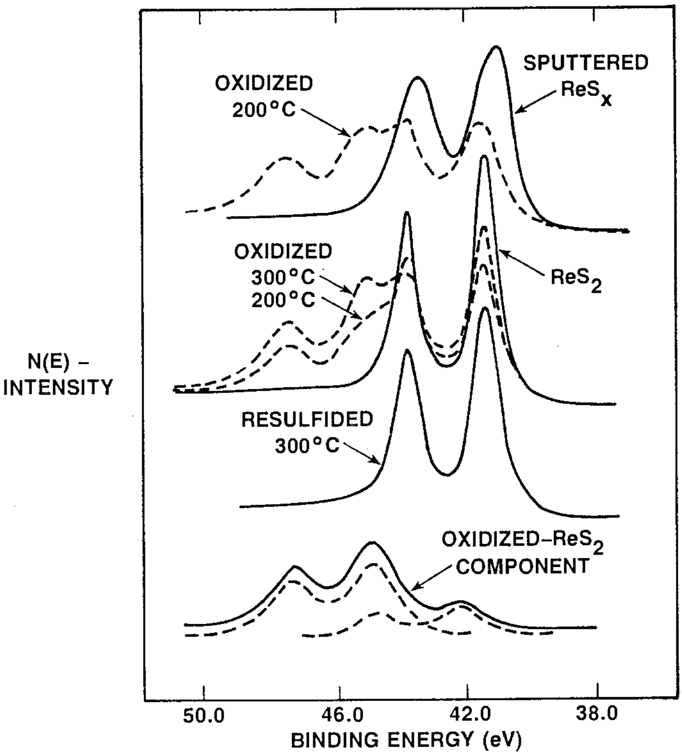

Fig. 3. Rhenium (4f) photoemission results are compared for stoichiometric and sputtered px-ReS_2 surfaces following reactive treatment with O_2 or H_2S/H_2 at 200–300 °C. The lower spectrum which has been deconvoluted into two oxide components was obtained by digital subtraction of the ReS_2 component from the spectrum for px-ReS_2 partially oxidized at 300 ° C.

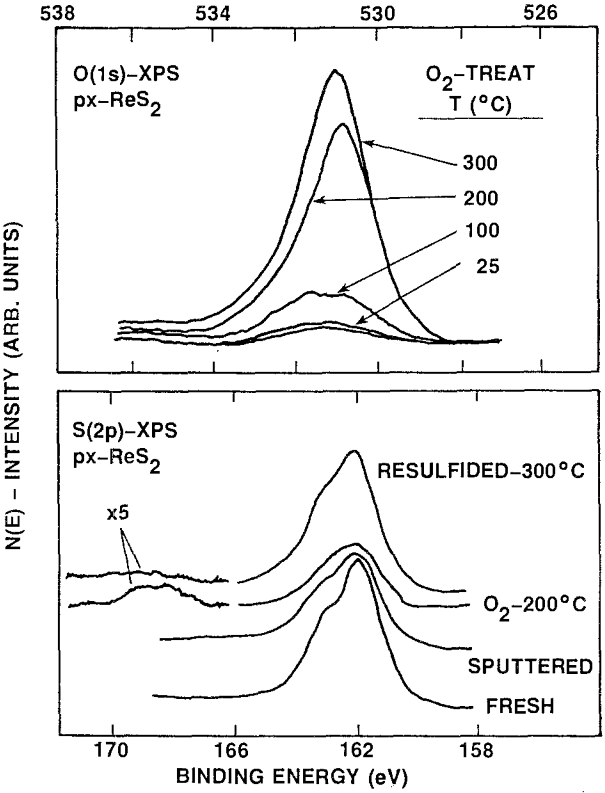

Fig. 4. Oxygen (1s) XPS results are shown for px-ReS_2 after oxygen treatment for 15 min. at 25–300 °C (top frame). Also shown are S(2p) XPS results for px-ReS_2 after several treatments (lower frame).

from deconvoluted spectra varied between about 0.2 and 0.4 with increasing extent of oxidation. Further support for this interpretation is provided by the average O/S/Re stoichiometries of the near surface region which could be closely approximated as a linear combination of ReS_2, ReO_2 and Re_2O_7. The mixed-valence Re(4f) line-shape for oxidized rhenium corresponds closely with that for ReO_3 [11].

While only small levels ($\leq 15\%$) of oxide were detected at 100 °C, significant oxidation became apparent after oxygen treatment at 200–300 °C. Significant concentrations of ReS_2-like material persisted after O_2-treatment at 300 °C which was the highest temperature investigated. Oxidation was accompanied by the growth of a sharp O(1s) XPS peak at about 530.8 eV (fig. 4) which compares favorably with those reported for a variety of metal oxides [12].

As indicated in figs. 3 and 4, the oxidation reaction of px-ReS_2 appears to be highly reversible as sulfidization of partially oxidized surfaces in 10% H_2S/H_2 at 300 °C consistently restored Re(4f) and S(2p) photoemission spectra indicative of stoichiometric ReS_2. The S(2p) XPS results shown in fig. 4 also indicate that ReS_2

surface oxidation occurs without significant retention of oxidized surface sulfur species. Only trace levels of sulfate (S(2p)$^{\sim}$ 168 eV) could be detected after oxidation, and these species were eliminated beyond easy detection limits upon resulfidization at 300 ° C. It should also be noted that the total S(2p) intensity and S(LMM)/S(2p) intensity ratio were both lowered by 20–40% during oxidation of stoichiometric and sputtered px-ReS2 at 200–300 ° C. These changes indicate that oxidation is accompanied by partial elimination of sulfur from the near surface region [13] and/or formation of an oxidized rhenium overlayer. Previous studies of MoS_2 films by Stewart and Fleischauer [4] revealed similar behavior wherein the surface sulfide concentration was lowered during oxidation with little or no sulfate formation.

Defect containing surfaces produced by ion bombardment displayed enhanced reactivity for oxidation at 100–200 ° C (cf. fig. 3). In addition fig. 3 shows that the defect sites were preferentially oxidized. The enhanced reactivity of these sites appears to be closely related to their ability to strongly chemisorb oxygen which is not detectable on stoichiometric basal plane surfaces [3]. Controlled atmosphere electron microscopy studies could be valuable to better clarify this behavior. In any event, the present results appear to support the concept that defect sites (edge planes [5] or "edge-like" basal plane defects [6] are especially effective for initiating oxidation reactions of layered transition metal sulfides.

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References

[1] T.A. Pecoraro and R.R. Chianelli, J. Catal. 67 (1981) 430.
[2] J.H. Sinfelt, *Bimetallic Catalysts* (Wiley and Sons, New York, 1983).
[3] S.M. Davis and J.C. Carver, Appl. Surface Sci. 20 (1984) 193.
[4] T.B. Stewart and P.D. Fleischauer, Inorg. Chem. 21 (1982) 2426.
[5] R.R. Chianelli, A.F. Rupert, S.K. Behal, A. Wold and R. Kershaw, J. Catal. 92 (1985) 56.
[6] O.P. Bahl, E.L. Evans and J.M. Thomas, Proc. Roy. Soc. London Ser. A. 306 (1968) 53.
[7] R.R. Chianelli and M.B. Dines, Inorg. Chem. 17 (1978) 2758.
[8] J.H. Scofield, J. Electron. Spec. 8 (1976) 129.
[9] J.L. Gland and E. Kolin, to be published.
[10] J.C. Widervenck and F. Jellinek, J. Less Common Metals 24 (1971) 73;
A.F. Wells, *Structural Inorganic Chemistry*, 5th Ed. (Clarendon Press, Oxford, 1984).
[11] G. Hollinger, F.J. Himpsel, M. Martensson, B. Reihl, J.P. Doumerc and T. Akahane, Phys. Rev. B 27 (1983) 6370.

[12] *Handbook of X-ray Photoelectron Spectroscopy* (Physical Electronics, Eden PK, MN, 1979).

[13] Because of the different attenuation lengths for S(LMM) and S(2p) photoelectrons (ca. 8 and 20 Å, respectively) the S(LMM)/S(2p) intensity ratio is sensitive to the sulfur atomic distribution of the near surface region. Specifically, a decreased intensity ratio reflects depletion of sulfur from the outer surface layers; see also M.P. Seah and W.A. Dench, Surf. and Interface Anal. 1 (1979) 2.