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Optical Absorption and Catalytic Activity of Molybdenum Sulfide Edge Surfaces

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The optical and catalytic properties of molybdenum sulfide edge planes have been studied in single crystals and disordered powders. We observe an infrared optical absorption due to the edge planes in the single crystal platelets. This absorption is proportional to the hydrodesulfurization catalytic activity in unsupported powders which were annealed at various temperatures to change their degree of crystallinity. This provides a direct correlation between the electronic structure of these materials as measured by optical absorption and their catalytic activity. This result shows that the optical and catalytic properties of the edge sites are similar in the amorphous and crystalline materials, and we derive turnover numbers and absorption cross sections for these sites.

INTRODUCTION

Industrial catalysts based on MoS_2 have served in hydroprocessing applications for over half a century. Recently, much progress has been made in understanding the physical and chemical basis for the activity, selectivity, and stability of these catalysts but many questions remain (*1*). Part of this progress has been the recognition that the active sites in MoS_2 probably lie on the edge planes (100) and that the basal planes (002) are quite inert. This idea finds a sound intuitive basis when one considers the anisotropic nature of the MoS_2 structure. In this structure the most reactive metal–sulfur bonds occur at the edge planes and the most inactive metal–sulfur bonds occur in the basal planes (*2*). Experimental evidence for this idea comes from several studies on unsupported MoS_2 catalysts. In particular, oxygen chemisorption (*3*), ESR spin density (*4*), and magnetic susceptibility (*5*) have all been correlated with hydrodesulfurization (HDS) activity in these materials, while BET surface area does not in general correlate to activity (*3*). Recent single crystal studies also point to the reactivity of the edge planes (*6*). These physical probes are beginning to yield information regarding the chemical and magnetic nature of the edge planes; however, a clear picture of the electronic nature of the active edge sites is yet to emerge.

In this paper we show that sites on the active edge planes have well-defined optical characteristics. We observe a midgap optical absorption similar to that observed from other semiconductor defects. This absorption is proportional to the catalytic site density in disordered powders providing a direct correlation between the electronic structure of these materials and their catalytic properties. Additionally, we report HDS activity measurements on MoS_2 microcrystallites whose edge area is well defined and directly measurable from SEM micrographs. These measurements allow us to calculate an edge area turnover number for MoS_2 and relate the optical absorption data directly to the MoS_2 edge planes. The data show that edge sites in disordered and crystalline MoS_2 have very similar optical and catalytic properties.

EXPERIMENTAL

A. *Preparation of Platelets*

Molybdenum sulfide microcrystals were grown by chemical vapor transport from

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MoS_2 powder (Alpha Ventron reagent grade). The starting material was placed with an excess of sulfur in one end of a sealed, evacuated quartz tube 25 mm in diameter. That end of the tube was heated to 690°C while the opposite end was kept at 545°C. This process yielded "small" single crystals roughly hexagonal in shape with diameters (~ 1 μm) roughly ten times larger than thickness. These platelets were then reheated at 1100°C for 3 weeks to obtain much larger (~ 30 μm) diameters. This material was sifted through a mesh of ~ 140-μm pore size to eliminate the larger clumps of material.

B. Preparation of Powders

The MoS_2 powders were prepared by the thermal decomposition of $(NH_4)_2MoS_4$ in N_2 at 250°C. The resultant material was separated into batches which were annealed in 15% H_2S/H_2 for 2 h at temperatures ranging from 400 to 900°C (*3*). Scanning electron micrographs of the powders showed what appeared to be platelets and needles between 20 and 100 μm long. The size distribution was independent of the anneal temperature. This is consistent with the previous observation that the annealing process does not change the macroscopic platelet size and the MoS_2 crystals are pseudomorphous with the $(NH_4)_2MoS_4$ precursor (*7*). High-resolution microscopy of the materials showed that they had the "rag" structure (*2*).

C. Optical Measurements

The infrared optical absorption was determined using photothermal deflection spectroscopy (PDS) (*8*). This is a calorimetric technique which directly measures the absorption in the sample using the deflection of a laser beam (Fig. 1). It is insensitive to optical scattering and thus ideal for powders, particularly if they are black as in the present study. The sample was distributed on a flat quartz plate and immersed in a solvent, which was either carbon tetrachloride or heptane. The output of a 1-kW xenon arc lamp was dispersed in a grating monochromator and chopped at 15 Hz before illuminating the sample. The light absorbed by the sample caused a small ($>10^{-6}$ K) temperature rise in the adjacent solvent. The accompanying change in index of refraction deflected a He–Ne laser beam grazing the surface of the sample. This deflection was monitored by a position sensitive detector and processed using a lock-in amplifier and computer.

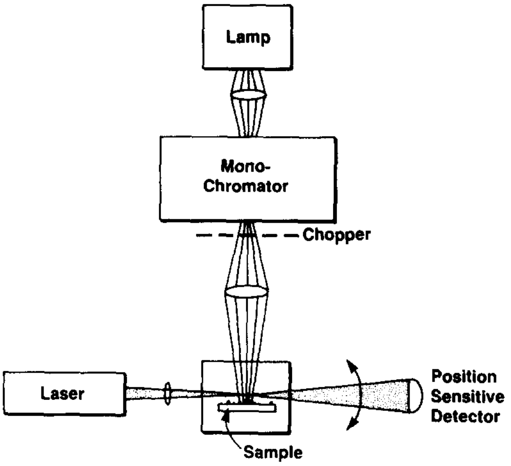

FIG. 1. Diagram of the PDS setup.

The deflection signal was divided by the incident beam intensity, which was monitored simultaneously. The result is proportional to the absorption, or the fraction of light incident on the MoS_2 which is absorbed. This absorption A can be related to the absorption coefficient α by

$$A = 1 - e^{-\alpha l}$$

where l is the average sample thickness. For sufficiently strong absorption coefficients ($\alpha l \gg 1$) the absorption saturates at 1. This was observed in the present samples from 1.8 to 2.5 eV, where there is strong excitonic absorption. This fact can be used to normalize the PDS signal, so that the absolute absorption is known at all photon energies. In the case where the absorption comes from discrete defects, the absorption coefficient can be related to the defect density N and absorption cross section σ by $\alpha = N\sigma$.

Care was taken to ensure that the material was evenly distributed on the substrate and that the MoS_2 particles were well separated. This was confirmed by optical microscopy. Only a small fraction (<20%) of the substrate area was covered, to ensure that light scattered from one particle was not absorbed in another. In the case of the amorphous powders, the size distribution was the same for all the samples studied, so that measured absorption can be directly compared. Several runs were averaged at each anneal temperature to produce the data shown here.

D. Catalytic Activity

Catalytic activity was determined using the hydrodesulfurization of dibenzothiophene in a manner previously reported (*1*). The reaction was performed using roughly 1 g of catalyst in a batch reactor for 8 h at 350°C at 3150 kPa H_2 using a 5 wt% DBT in 100 ml decalin feed. In some cases the catalytic activity was observed to change after several hours; optical absorption measurements taken after the run showed a similar change. In this paper we have used the initial activity for comparison to optical measurements taken before the run.

RESULTS

A. Platelets

The single crystal MoS_2 platelets were analyzed microscopically in order to estimate the area of the edge planes. Typical micrographs of the small and large crystals are shown in Fig. 2. A number of such micrographs were analyzed to generate the platelet diameter histograms shown in Fig. 3. From these data we derive mean platelet diameters of 1.7 μm for the small platelets and 36 μm for the large ones. Using the entire histogram, we can calculate the total edge plane area per gram of catalyst. Assuming that a platelet has a cylindrical shape, the edge area is

$$A = \pi D t$$

where D is the platelet diameter and t is the platelet thickness. The mass of the same platelet is

$$M = \tfrac{1}{4}\pi D^2 t \rho$$

where ρ is the density of crystalline MoS_2. The micrographs indicate that the platelet thickness is proportional to the diameter. Assuming this to be true, the total edge area per unit mass of catalyst is simply

$$\frac{\langle A \rangle}{\langle M \rangle} = \frac{4}{\rho} \frac{\langle D^2 \rangle}{\langle D^3 \rangle}$$

where $\langle . . . \rangle$ indicates the average value taken over the histographs of Fig. 3. Note that this result is not the same as that obtained if it is assumed that all the platelets have the mean diameter.

For convenience in calculating turnover numbers, we wish to calculate the number of Mo atoms exposed on the edge plane. This is done by dividing the edge plane area by the area of an MoS_2 molecular unit (2.0×10^{-15} cm^2). The "edge site" density thus calculated is 6.1×10^{17} sites/g for the small platelets and 7.2×10^{16} sites/g for the large ones.

The optical spectra of these materials are shown in Fig. 4. Also shown for comparison purposes is the absorption spectrum of a 5.2-μm-thick single crystal of millimeter transverse dimensions. The absorption band beginning at 1.2 eV and increasing toward higher energies is due to the indirect bandgap (*9*). Strong excitonic absorption at 1.8 eV saturates the absorption for higher energies. The flat lower energy absorption in the single crystal is from defects in the material and varies strongly from sample to sample.

The spectrum of the large platelets is seen to be very similar to that of the single crystal, except that the defect absorption below 1.2 eV is an order of magnitude higher. The striking similarity of the two curves between 1.3 and 1.6 eV shows that the large platelets are indeed single crystals

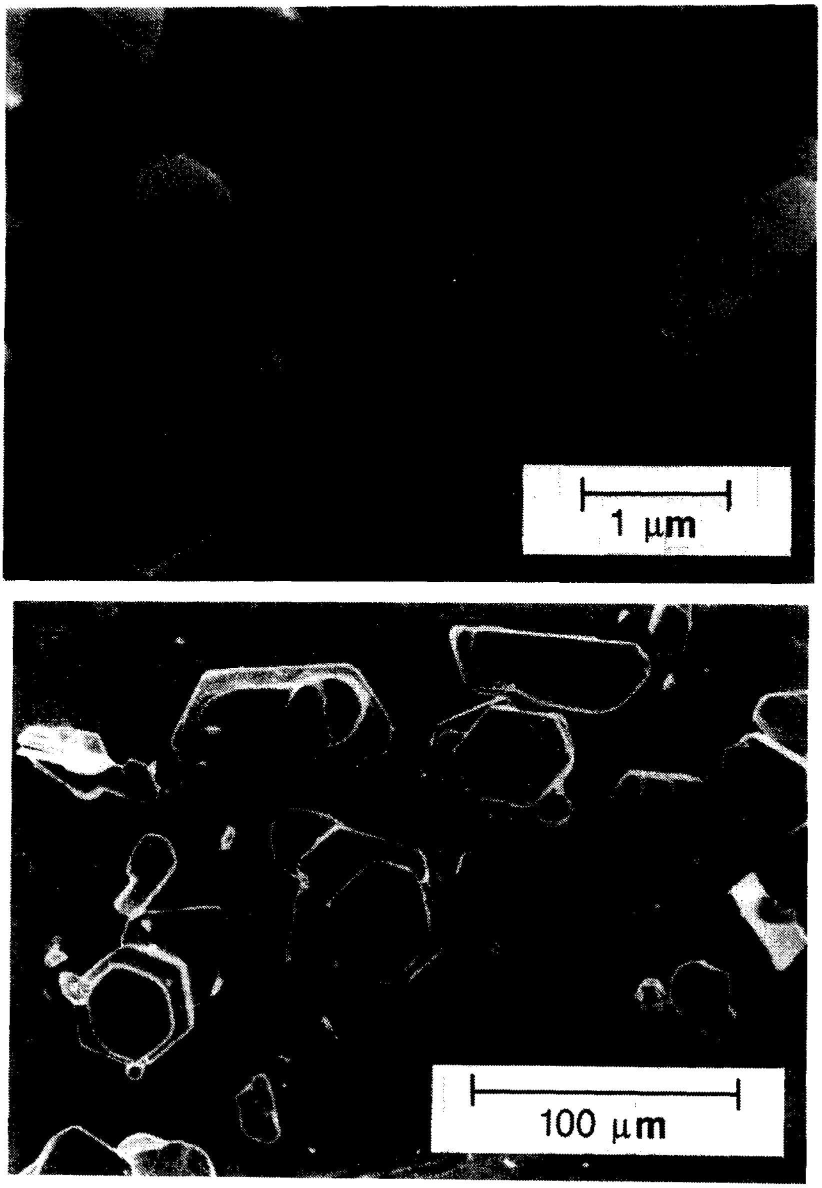

FIG. 2. Scanning electron micrographs of the small (top) and large (bottom) platelets.

with an average thickness of 5 ± 1 μm, because the magnitude of this absorption agrees with that of the 5-μm-thick single crystal.

The absorption spectrum of the smaller platelets is also shown as the upper curve in Fig. 4. This curve cannot be directly compared to the curve for the large platelets because the average sample thicknesses are different. This was accounted for in Fig. 4 by multiplying the small platelet curve by a constant factor of 2 to normalize to the others at 1.5 eV. Because the absorption at this energy is due to the bulk semiconductor, this normalization accounts for the difference in sample thickness so that the low-energy absorption is proportional to the defect density. The low-energy absorption is an order of magnitude greater in the small platelets than it is in the large ones, in good

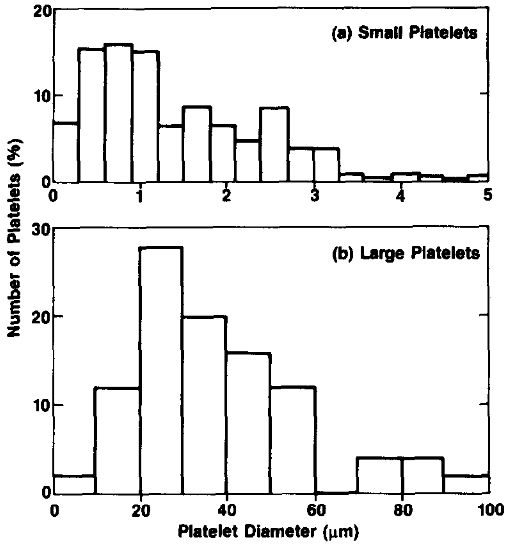

FIG. 3. Histograms of the size distribution in the MoS_2 platelets.

agreement with the greater density of edge sites.

From these data it is evident that the optical absorption observed below 1.2 eV in the platelets is due to the exposed edge planes. "Dangling bonds," vacancies, or other similar surface defects would be expected to have electronic states in midgap and thus increase the optical absorption in this region. From the known density of edge sites we can calculate the average optical absorption of a single edge site. The answers obtained from the data of Fig. 4 (at 0.8 eV) are 6.1×10^{-17} cm^2 for the small platelets and 8.4×10^{-17} cm^2 for the large ones. The agreement between these two numbers is excellent considering the approximations going into the diameter calculations and shows that the low-energy absorption is indeed proportional to the edge plane area.

It is tempting to ascribe the very low level of absorption observed in the macroscopic crystal to similar edge defects at grain boundaries in the bulk of the material. This absorption was observed to be proportional to the crystal thickness over more than an order of magnitude, showing that it is not a surface effect. The low absorption coefficient (5 cm^{-1}) corresponds to a defect density of 7×10^{16} cm^{-3}. This is consistent with our knowledge of these crystals, although we have not directly measured the defect density and it is difficult to eliminate the possibility of impurities at the parts-per-million level. It is possible that part of this absorption is due to the exposed basal plane surface. However, even if all of the absorption we have observed in a thin (0.5 μm) sample were due to these surfaces, the absorption cross section of an exposed basal plane site would still be only 10^{-19} cm^2. This is more than two orders of magnitude smaller than we have observed from the ex-

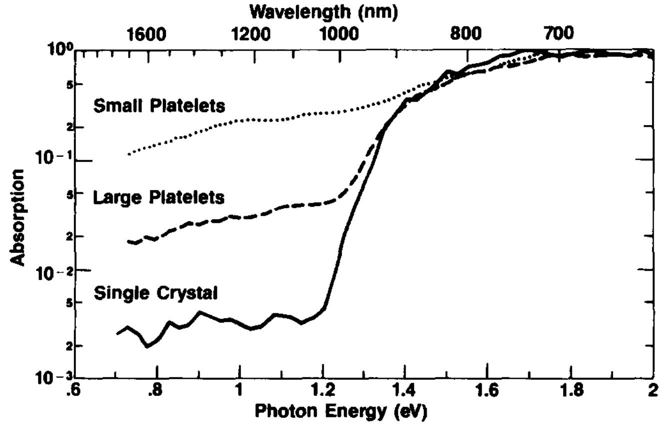

FIG. 4. PDS absorption spectra of the platelets, as well as of a macroscopic MoS_2 single crystal 5.2 μm thick. The small platelet spectrum has been shifted upward to account for its smaller thickness.

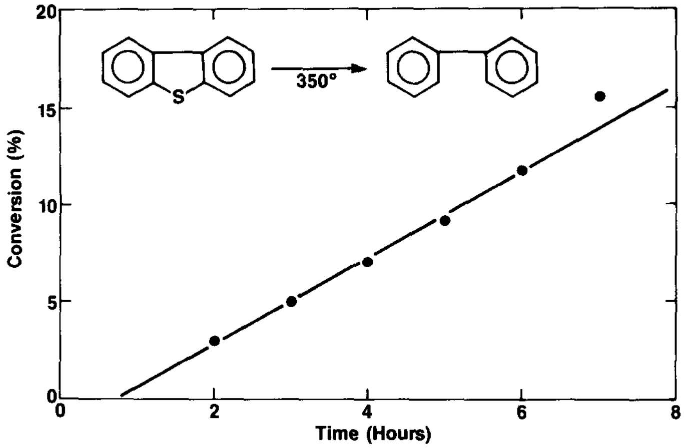

FIG. 5. Catalytic conversion of DBT into BP observed on the small platelets.

posed edge sites. The fact that we fail to observe optical activity from the basal surfaces is consistent with the chemical inactivity of these planes. Further study is necessary to understand the electronic structure of basal planes and other defects in MoS_2 single crystals.

Figure 5 shows the catalytic conversion of dibenzothiophene measured on the small platelets. Biphenyl was the only product observed; no hydrogenation occurred on the crystalline materials. The slope gives a hydrodesulfurization activity of $R = 4.8 \times 10^{16}$ molec/g-s. From this and the density of edge sites in this material we can calculate the turnover frequency to be 7.9×10^{-2} molec/site-s. This calculation assumes that each exposed Mo atom is catalytically active; it is, of course, possible that only a fraction of the edge sites is active in which case the appropriate turnover number would be higher.

B. Powders

X-Ray diffraction patterns for the MoS_2 powders are shown for several anneal temperatures in Fig. 6; these results are typical for poorly crystalline MoS_2 (*2*). It is clear

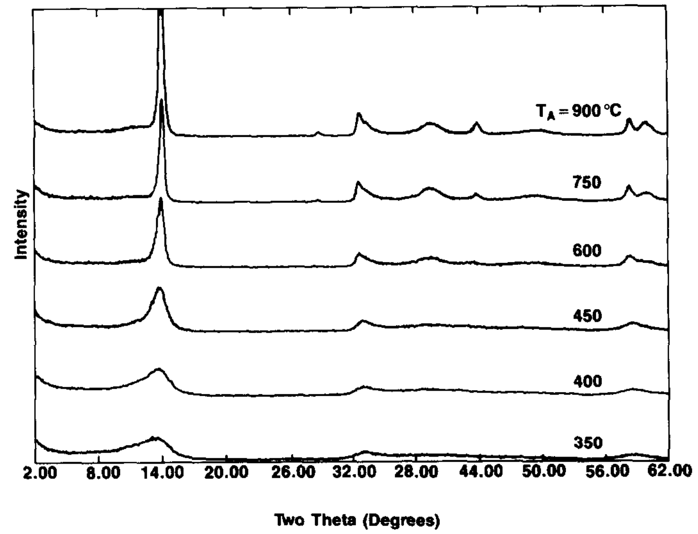

FIG. 6. X-Ray diffraction patterns observed from the disordered MoS_2.

that higher anneal temperatures yield more crystalline material; the decrease in the (002) linewidth shows that the layer stacking increases dramatically.

The optical absorption spectra of these materials are shown in Fig. 7. We observe a strong, broad absorption tail below the band-to-band absorption which is dependent on the anneal temperature. This absorption is very similar to that observed from edge plane defects in the platelets with a slight difference in shape which will be discussed below.

The above spectra were taken in carbon tetrachloride on samples which were air-oxidized at room temperature. We also performed experiments on samples which had not been exposed to oxygen. The powders were mounted in airtight PDS cells and treated in H_2S/H_2 at 350°C for 2 h to sulfide the surface. The cells were filled with distilled spectral grade heptane and sealed in a glove box. A small (<20%) increase was observed in the PDS absorption relative to the oxidized samples. Oxygen is known to react with the edge sites (*3*, *6*, *13*). The relatively small change observed upon oxidation might be due to the fact that not all of the defects seen optically lie on the surface; edge-like defects in the bulk of the material could be inaccessible to oxygen. Alternatively, it is possible that the oxide formed in these materials also absorbs in the infrared.

In Fig. 8 we plot the absorbance at 0.8 eV (= ln[1 − A], where A is the absorption from Fig. 7) against the anneal temperature. Also shown is the total hydrodesulfurization activity observed. This activity is plotted directly against the absorbance in Fig. 9. The line is a least-squares fit to the data points. An excellent fit is observed going through

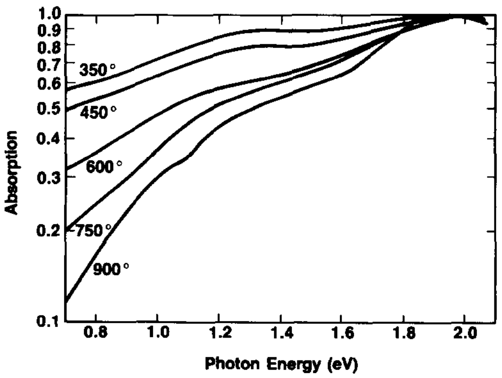

FIG. 7. Optical absorption spectra of the MoS_2 powders.

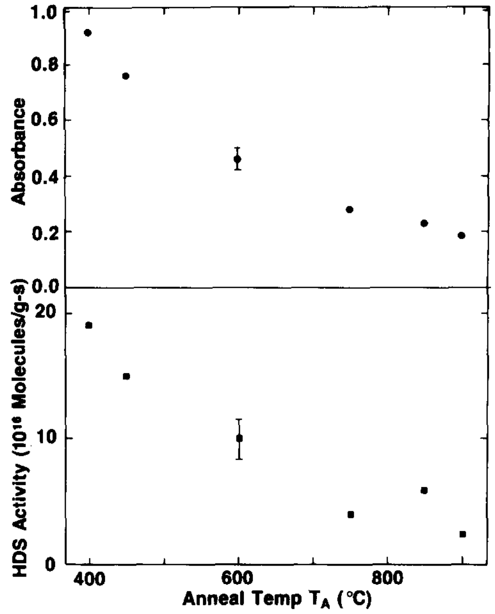

FIG. 8. Optical absorbance at 0.8 eV and HDS activity versus anneal temperature for the powders.

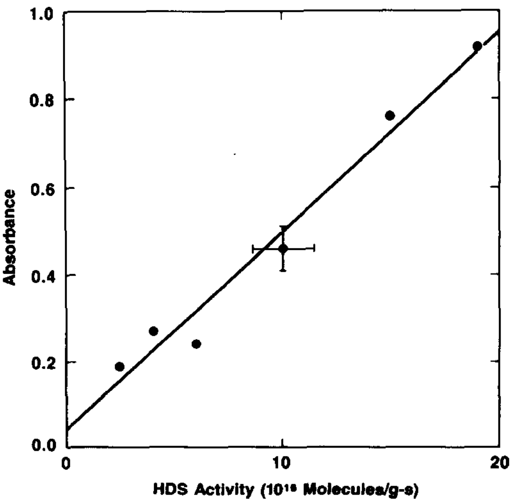

FIG. 9. Correlation between the optical absorbance and catalytic activity. The line is a least-squares fit to the data points.

the origin, confirming a direct correlation between the optical absorption and the catalytic activity. Given the similarities to the platelets, we attribute the optical absorption to edge site defects. Assuming that the absorption cross section is the same in both materials, the turnover frequency calculated from the slope of the line in Fig. 9 is 3 (±1) × 10^{-2} molec/site-s. This value is approximately two times lower than that obtained from the platelets, an agreement which is reasonable given uncertainties in the size and density of the disordered material.

DISCUSSION

The similarity in turnover frequency between the disordered and microcrystalline materials indicates that the active sites for desulfurization in each are similar and are located on the edge surfaces. Optical absorption due to similar surface and bulk defects has been studied in more conventional crystalline (*10*) and amorphous (*11, 12*) semiconductors. Such defects, particularly those which are catalytically active, would generally be expected to have energy levels lying between the conduction and valence bands and thus absorb photons with below bandgap energies. This is indeed the behavior observed, and the $\approx 10^{-16}$-cm^2 cross section observed is typical of such defects.

A broadening of the valence band edge in poorly crystalline MoS_2 materials has previously been observed in ultraviolet photoemission spectroscopy (UPS) (*13*). The effect there is barely resolvable due to the relatively poor energy resolution of this technique. Those observations are consistent with the optical measurements observed here and show that the defects are close to the valence band and below the Fermi level. Interestingly, the UPS signal was shown to be decreased significantly upon brief exposure to oxygen. Because the oxygen chemisorption has been related to activity, this implies that these tail states are chemically and catalytically active. However, because of the small escape depth for photoemitted electrons, UPS only observes states near the surface. The fact that the PDS data are less sensitive to oxygen might be due to a significant fraction of the absorbing sites being away from the surface and unaccessible to oxygen. A similar effect is observed in the ESR spin density, which is also insensitive to oxygen (*4*).

The turnover number derived here for the disordered MoS_2 (3 × 10^{-2} molec/site-s) is a factor of 3 larger than that calculated (*3*) on similar materials using oxygen chemisorption (1.2 × 10^{-2} molec/site-s, assuming one molecule O_2 adsorbed per edge site). However, the chemisorption experiment is subject to difficulties such as its dependence on measurement temperature. In view of this, we feel that the chemisorption measurement, while proportional to the edge site density, is not a reliable quantitative measure of these sites. In any case, the microcrystalline platelet materials examined here did not have a high enough density of edge sites to allow an accurate O_2 chemisorption measurement.

A careful comparison of the shape of the optical absorption below 1.4 eV shows that the crystal defect absorption is much flatter than that of the disordered powders; i.e., it increases less with increasing energy. It is well known that disorder in an amorphous material will broaden the band-to-band absorption to produce an exponential tail (*11*), as we observe in our disordered MoS_2. This effect can be viewed as a variation in the defect energy from site to site. Such a variation should be considerable given the extreme disorder present in this "rag" structure.

The effect of disorder can be seen in the catalytic activity as well. We have already commented that the MoS_2 platelets yielded only unhydrogenated product. The powders, on the other hand, gave cyclohexylbenzene as up to 50% of the total product. This hydrogenated fraction increased in the more disordered material. This shows that hydrogenation is linked in some way to disorder in MoS_2. We plan to study this relationship in more depth in the future.

CONCLUSIONS

We have shown that HDS catalytic activity for unsupported MoS_2 platelets and powders is directly correlated with the density of edge surface sites. These sites have a characteristic optical absorption in the near infrared. The turnover frequency for hydrodesulfurization of DBT is roughly 5×10^{-2} molec/site-s in both amorphous and crystalline materials.

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