Surface analysis of polymer systems. 3.
Zinc sulfide...cadmium sulfide/Nafion

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thin Pt overlayer case, the oxide was also thin, probably highly
defective and attached to bulk Ti. Heating to 760 K caused
migration and segregation of the initially available reduced TiO₂
species which were then easily detected at the Pt surface. Further
incorporation of TiO₂ in the Pt layer requires significantly higher
temperatures and/or longer annealing times. On the basis of the
previous results of Ko and Gorte, a reduced Ti oxide diffuses
deeply than the sampling volume of AES at high temperatures.
Upon cooling it returns to the surface region forming a
uniform layer on the Pt. This would leave a concentration of
TiO₂ beneath the surface as measured here.
Také together, the available data indicates that, once formed, the
reduced TiO₂ (x = 1) species can easily diffuse into and out of the
Pt. Since Ti-Pt alloys are well-known, one possibility for the formation of the reduced titanium oxide is as follows. If we assume
that at high temperature annealing process removes two oxygen
atoms from the TiO₂ unit cell, TiO₂ is formed at the interface. TiO₂
is assumed because it is consistent with the observed stoichiometry and involves breaking the fewest bonds at the interface. In equilibrium with this process, the formation of dilute Pt-Ti and Pt-O compounds are proposed. The formation
of these compounds provides enough energy for the overall process
to be favorable thermodynamically. The diffusion of Ti and O
would then occur through the Pt and away from the interface along the concentration gradient in a correlated but not simultaneous
fashion. Bard and Ross have shown that a reduced TiO₂ species
can diffuse through Pt-Ti. At high temperatures, entropy drives
surface segregation TiO₂ into the bulk. Upon cooling the surface
back to 300 K, enthalpy factors dominate and cause the surface
segregation of the reduced species. For thin films of TiO₂ on Pt,
this process terminates with roughly 1 monolayer of TiO₂ at the
surface with a concentration of TiO₂ distributed throughout the
Pt.
This model also predicts that the small Pt particles present in
Pt/TiO₂ catalysts will incorporate TiO₂ when the substrate is
reduced. In this way, all of the Pt atoms within the particles are
altered and can account for the small Pt BE shifts sometimes
observed in earlier XPS studies. Extended thermal annealing
of the thin film model catalysts supports this conclusion.

Summary

X-ray photoelectron spectroscopy has been used to characterize
TiO₂ overlayers on polycrystalline Pt. The addition of TiO₂
increases (≤ 0.25 eV) the Pt(4f) BE. This is attributed to bonding
between Pt and Ti⁺ at the interface. Annealing to 1300 K under
vacuum causes a significant increase in the Ti³⁺ surface
concentration and a decrease in the total amount of Ti in the XPS
sampling volume. For initial TiO₂ coverages greater than 1
monolayer an equilibrium amount of reduced Ti species is present
on the surface after annealing (between 0.6 and 0.9 monolayer).
Depth profiles indicate that diffusion of a reduced TiO₂ (x = 1)
(27) Y.-M. Sun, D. N. Belton, and J. M. White, to be submitted for publication.

Surface Analysis of Polymer Systems. 3. ZnS-CdS/Nafion

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In Final Form: July 17, 1985)

X-ray photoelectron spectroscopy has been used to characterize the surfaces of Nafion films into which mixtures of CdS
and ZnS have been precipitated by exposing ion-exchanged Nafion films to H₂S. For all the cases studied, precipitation
led to segregation of the metals from interior ion-exchange sites to the surface where small sulfide particles were formed.
Irradiation of the films with visible light in the presence of aqueous 0.1 M Na₂S solution produced H₂ and some Cd⁰.
In the absence of ZnS, there was neither H₂ nor Cd⁰ production. When ZnS and CdS were coprecipitated or when ZnS
was precipitated after CdS, very active films were formed and irradiation changed the surface Zn/Cd ratio to a value near 5.
When CdS followed ZnS precipitation, irradiation did not change the Zn/Cd ratio from its initial value of unity and the
films were inactive for photoassisted hydrogen generation. The results are discussed in light of other measurements on these
materials which point to the importance of CdS surface state alteration by Zn.

Introduction

In previous papers, we have reported on mixed semiconductor
catalysts supported on a variety of materials (particularly co-
precipitated ZnS-CdS/Nafion and ZnS-CdS/SiO₂) that are active
hydrogen evolution catalysts when irradiated with visible light.¹ ²

These catalysts have activities that are comparable with Pt-
Cds/Nafion films and do not depend strongly on the support.
These interesting materials have been studied in a variety of ways
in an effort to understand the key features. In the absorption
spectrum, two onsets were found corresponding to bulk CdS and
ZnS interband transitions. Luminescence measurements indicated
lattice vacancies and interstitials that participated in radiative
relaxation. No evidence for solid solutions has been found.³


The hydrogen production activities of sequentially precipitated (CdS followed by ZnS) catalysts were the same as the coprecipitated catalysts, but the activity was much less when the precipitation order was reversed.1,2 We have also reported the surface characterization of Pt-CdS/Nafion films using X-ray photoelectron spectroscopy (XPS).3,4 This work gave the following results: (1) Adsorbed S2- on Nafion is easily oxidized to sulfate, and the hydrogen generation activity drops with increasing sulfate ion concentration. (2) Under conditions where cubic CdS is formed the surface concentration of CdS is ca. 140 times higher than under conditions where hexagonal CdS is formed. (3) Pt deposited by ion exchange and reduction of a Pt complex ion is concentrated in the surface region of the Nafion. (4) Sputter-deposited Pt (average thickness 100 A) is distributed within the first several hundred angstroms of the Nafion surface. These results are consistent with a model in which Pt particles must be in close contact with CdS particles for highly active photogeneration of hydrogen.

In this paper, we report our surface characterization by XPS of CdS-ZnS/Nafion materials prepared by coprecipitation and sequential precipitation. This work extends previous reports on the CdS-Pt/Nafion.3,4 Here attention is given to changes in the XPS spectra that occur as the result of precipitation of the sulfides and as a result of irradiation with visible light.

Experimental Section

Nafion (117, 0.018 cm thick) membranes were used for all experiments. Films containing coprecipitated sulfides (denoted ZnS-CdS/Nafion) and sequentially precipitated, ZnS followed by CdS (denoted CdS(ZnS/Nafion)), or vice versa, films were prepared according to procedures detailed in previous papers.3,4 The methods involve incorporation of Cd2+ into Nafion by ion exchange and precipitation of the sulfides by addition of H2S. For sequentially precipitated sulfides, the ion-exchange process was also done sequentially. Atomic absorption spectroscopy was used to measure Zn/Cd ratios.

For irradiation and hydrogen production, films (1 x 1 cm when dry) were immersed in Pyrex glass cells containing 3 mL of 0.1 M Na2S. The vessels were degassed under vacuum with sonication to remove gases from the interior of the membrane and were purged with N2. A water-filtered 450-W Xe lamp and a glass filter (Corning 3-72) were used. The latter removes wavelengths shorter than 440 nm. Irradiations lasted at least 2 days to make it easy to detect changes of the ZnS and CdS interfaces by post XPS analysis. After irradiation, the wet films were quickly placed under vacuum and dried overnight to avoid surface oxidation by contact with air.

XPS measurements were carried out using a Vacuum Generators ESCA Lab II system with Al Kα radiation (1486.6 eV). The binding energies (BE) were all referenced to the surface hydrocarbon contamination C(1s) peak (284.5 eV). Auger transitions excited by Al Kα X-rays were also measured. For the work reported here, no variations were detected by XPS across the surface of the sample.

Results and Discussion

Based on the XPS data for a number of Zn and Cd compounds,3,8 it is not possible to clearly identify the oxidation states by using only core level BE’s. However, Auger parameters3 determined by the kinetic energy difference between Auger and XPS transitions show obvious differences. Therefore, Cd(MNN) and Zn(LMM) Auger peaks were measured and used in conjunction with core level BE’s to calculate the Auger parameter.

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References:


When the ZnS-CdS/Nafion film, in aqueous Na$_2$S solution, was irradiated with visible light ($\lambda > 440$ nm) for 2 days, it showed the same hydrogen generation activity as reported earlier. The BE's of Cd(3d$_{3/2}$) and Zn(2p) were equal to those of a fresh film. With irradiation, there was a change in the Cd(MNN) Auger region (Figure 3b) which had two peaks at 381.5 and 383.0 eV. On the basis of measured Auger parameters for cadmium compounds, we assign the low-KE peak (381.5 eV) to the Cd$^+$ ion and the high-KE peak (383.0 eV) to the Cd$^0$ species.

With irradiation, the Cd/F ratio decreased to 7% of the fresh sample value (Table I). The Zn/Cd ratio changed from 0.32 to 0.26, suggesting that the surface becomes zinc-rich during irradiation but that it does so through the loss of Cd. The Cd/F ratio increased with Ar$^+$ bombardment. No zinc or cadmium species were found in the sulfide solution after irradiation by XPS before and after sulfiding (Table I). The Zn/Cd ratio changed only slightly during irradiation.

Irradiation, as for the other films, changed the Cd(MNN) Auger region, indicating the formation of Cd$^0$. Unlike the other films, both the Zn/F and Cd/F ratios increased and the Zn/Cd ratio changed only slightly during irradiation.

**Effect of Sulfiding**. In another set of measurements, the films were examined by XPS before and after sulfiding (Table II). For both ZnS/CdS/Nafion and CdS/ZnS/Nafion films, the results labeled "before" were measured with the first species sulfided and the second ion exchanged but not sulfided. These results indicate that the Cd$^+$ and Zn$^{2+}$ ions which are bound to cation-exchange sites tend to move to the surface during sulfiding. It is not clear whether the migration of sulfide occurs before or after the cation leaves the exchange site. However, in particular, the ZnS/CdS/Nafion case, the surface contains a layer of which the Zn$^{2+}$ migrates through and over the CdS that is present before it forms particles of ZnS. Table II also indicates that, before sulfiding, the Zn/Cd ratio for ZnS/CdS/Nafion and the Cd/F ratio for CdS/ZnS/Nafion are both higher than expected based on either the pure or the mixed semiconductor/Nafion systems. Most likely, this is due to adsorption of Zn$^{2+}$ or Cd$^+$ on the previously formed sulfide.

After ion exchange and before sulfiding, the ZnS-CdS/Nafion film had a Zn/Cd ratio near unity consistent with the solution mole ratio used. Thus, there is no strong preference for one of the ions at the exchange sites. After H$_2$S treatment, the surface was enriched in CdS. Qualitatively, in single-component films CdS was much more quickly formed (e.g. turned yellow) than ZnS (turned white). These results are consistent with our previous work on ZnS-CdS/SiO$_2$.

X-ray diffraction (XRD) showed strong α-CdS peaks in CdS/Nafion, but ZnS-CdS/Nafion had small broad peaks with intensities too weak to make a positive identification. No XRD

![Figure 3. Cd(MNN) XAES spectra of ZnS-CdS/Nafion soaked in Na$_2$S (a) without and (b) with visible light irradiation.](image)

**TABLE I: Surface Zn and Cd Content**

<table>
<thead>
<tr>
<th>system</th>
<th>irradiated</th>
<th>Zn/Cd</th>
<th>Zn/F</th>
<th>Cd/F</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS-CdS/Nafion</td>
<td>no</td>
<td>0.32</td>
<td>0.23</td>
<td>0.71</td>
</tr>
<tr>
<td>ZnS(CdS)</td>
<td>yes</td>
<td>0.26</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>CdS(ZnS)</td>
<td>no</td>
<td>19.2</td>
<td>20.7</td>
<td>1.08</td>
</tr>
</tbody>
</table>

*Account has been taken of atomic sensitivity factors.*

**TABLE II: XPS Peak Area Analysis of Surface Atomic Ratios before and after Sulfiding**

<table>
<thead>
<tr>
<th>sample</th>
<th>sulfiding</th>
<th>Zn/Cd</th>
<th>Zn/F</th>
<th>Cd/F</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS-CdS/Nafion</td>
<td>before</td>
<td>1.07</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>CdS(ZnS)</td>
<td>after</td>
<td>0.92</td>
<td>0.23</td>
<td>0.71</td>
</tr>
<tr>
<td>CdS(CdS)</td>
<td>after</td>
<td>0.10</td>
<td>0.97</td>
<td>0.01</td>
</tr>
<tr>
<td>ZnS(CdS)</td>
<td>after</td>
<td>1.92</td>
<td>20.7</td>
<td>1.06</td>
</tr>
</tbody>
</table>

*See text for definition of systems.*

References:

signals of ZnS were observed in either ZnS/Nafion or ZnS-CdS/Nafion. This indicates that the character of the CdS changes in the presence of Zn even though optical absorption measurements are dominated by features due to bulk CdS and ZnS. \(^1\) We speculate that there may be a significant concentration of zinc ions in the CdS lattice. For the sequentially precipitated films, all the results are consistent with a physical mixture of the two sulfides with large interfacial areas of intimate contact. Based on the XRD of single-component films mentioned above, the crystal size of CdS was larger than that of ZnS. Thus, ZnS-(CdS/Nafion) films might have large CdS particles covered with small ZnS particles. For CdS(ZnS/Nafion) similar particle sizes might lead to clusters of small ZnS particles covered with a shell of CdS or to clusters of ZnS particles contacting larger CdS particles. In either case, the contact area would be lower than for the ZnS(CdS/Nafion). This might account for the poor hydrogen generation activity and the relatively small change in the Zn/Cd ratio that occurs with irradiation.

For unknown reasons, Cd\(^0\) was observed in all three kinds of films after irradiation. Cd\(^0\) did not form in single-component CdS/Nafion films. Thus, we conclude that the presence of ZnS is required for Cd\(^0\) production. Gutierrez and Henglein\(^1\) reported that Cd metal catalyzes hydrogen formation on CdS colloids. The presence of Cd\(^0\) does not necessarily produce an active hydrogen generation catalyst since under our conditions irradiated CdS-(ZnS/Nafion) films contain Cd\(^0\) and have very low activity. Consistent with other findings, including high quantum yields for irradiated CdS(Nafion) films, this indicates that the character of the CdS changes on the XRD of single-component films mentioned above, the crystal size of CdS was larger than that of ZnS. Thus, ZnS-(CdS/Nafion) films might have large CdS particles covered with small ZnS particles. For CdS(ZnS/Nafion) similar particle sizes might lead to clusters of small ZnS particles covered with a shell of CdS or to clusters of ZnS particles contacting larger CdS particles. In either case, the contact area would be lower than for the ZnS(CdS/Nafion). This might account for the poor hydrogen generation activity and the relatively small change in the Zn/Cd ratio that occurs with irradiation.

Dynamics of Excited-State Reactions in Reversed Micelles. 2. Proton Transfer Involving Various Fluorescent Probes according to Their Sites of Solubilization

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Reversed micelles of bis(2-ethylhexyl)sulfosuccinate (AOT) in heptane were investigated with three acid fluorescent probes: 2-naphthol (NOH), sodium 2-naphthol-6-sulfonate (NSOH), and potassium 2-naphthol-6,8-disulfonate (NDSOH). These probes, which tend to undergo porosity in the excited state, are well suited to the investigation of the acid–base reactivity of water molecules forming the aqueous core. The rate constants for deprotonation and back-recombination were determined by phase fluorometry as a function of the water content \(w = [H_2O]/[AOT]\). These rate constants together with the spectroscopic properties of the probes provide information on their localization and the corresponding ability of the microenvironment to accept a proton. (i) NSOH is localized around the center of the water pool and, at water contents, \(w\), greater than about 10, its behavior regarding protolysis is identical with that in bulk water. (ii) NOH resides in the vicinity of the interface and an amount of water of \(w \approx 40\) is required for observing the same deprotonation rate as in bulk water whereas the rate of back-recombination is still much faster. (iii) NOH is localized at the interface and does not undergo deprotonation in the excited state whatever the water content. Efficiency and kinetics of proton transfer are thus strongly dependent on localization. The ability of water to accept a proton is related to its H-bonded structure and its protolytic reactivity is an image of its structure which changes as a function of the distance with respect to the interface.

Introduction

Owing to their ability to solubilize large amounts of water, reversed micelles offer a peculiar reaction medium, a kind of microreactor which exhibits, in some cases, catalytic effects.\(^1\)\(^3\) Reversed micelles are thought to behave as membrane mimetic systems, their water core being similar to water pockets of bio aggregates.\(^4\)\(^6\) Moreover, there is some analogy with the active