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Photoredox Reactions at Semiconductor Particles Incorporated into Clays. CdS and ZnS + CdS Mixtures in Colloidal Montmorillonite Suspensions

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CdS and CdS + ZnS mixtures included into colloidal suspensions of clay were prepared and examined by various methods in connection with their potential use as supports or matrices with specific ionic environments and given interlayer spacings. The physical properties of semiconductor particles incorporated into montmorillonite were studied by X-ray spectroscopy and transmission electron microscopy; they were strongly dependent upon the method of preparation, because of the ion-exchange capacity and ion-segregation characteristics displayed by the clay. An "active" catalyst, formed by small CdS + ZnS particles having a high surface area and intimate contact between these, was obtained by the successive introduction and precipitation of Cd^{2+} and Zn^{2+} ions in the clay. Significant differences were observed for the rate of the photocurrent increase with time ($\Delta i/\Delta t$) vs. pH, for semiconductors included into clay as compared to a physical mixture of equivalent amounts of clay and nonincluded semiconductor particles. The differences in electron trapping and hole scavenging activites displayed by various agents can be rationalized in terms of their ionic or neutral nature in connection with the electrostatic fields existing in clay sheets. Hydrogen was photoproduced (in the absence of a noble metal catalyst) and detected by GC; the rate depended upon the pH and the nature of the hole scavenger used. Mass transfer problems linked to the spacing between clay sheets decrease the efficiency of clay-incorporated semiconductors for the visible-light-induced hydrogen evolution when compared to previously described silica-supported catalysts.

Introduction

Particulate and colloidal semiconductor suspensions, e.g., CdS and ZnS, either alone[1] or supported on silica,[2] or in vesicles,[3] have been utilized as photocatalysts. The desire to construct semiconductor systems with higher efficiencies and which might provide the possibility of product separation by providing a special environment for the supported semiconductor has led to investigation of polymer matrices, such as the perfluorinated sulfonate polymer, Nafion, as support.[1a,4] These also have the advantage of holding the semiconductor dispersions in place in flow systems and provide the possibility of incorporating catalysts and redox couples within the polymer matrix. Although a number of materials have now been used successfully as semiconductor supports, our desire to find an inexpensive support material with interesting structural properties has led us to investigate clays.

Clays are highly stable aluminosilicate materials with definite structures.[5] The appreciable surface areas of typical clays and their ion-exchange and intercalation properties seem to be particularly advantageous for the preparation of semiconductor "integrated chemical systems".[4a,6] Electrochemical and photochemical studies of clay (e.g., montmorillonite) films and suspensions containing $Ru(bpy)_3^{2+}$ have been reported.[7] We report here an investigation of the photoactivity of CdS and CdS/ZnS mixtures incorporated into a montmorillonite suspension. The CdS/ZnS system, either alone[2] or on various supports,[8] has been shown to be capable of hydrogen evolution under irradiation with visible light in the presence of sulfide ion as a sacrificial donor. Studies of the particle energetics by electrochemical measurements of irradiated suspensions at an inert collector electrode as a function of pH, hydrogen evolution, and structural investigations are reported.

Experimental Section

Reagent grade methylviologen (MV^{2+}) chloride trihydrate was procured from Sigma Chemical Co. and propylviologen sulfonate (PVS) was synthesized according to published procedures.[9] Samples of naturally occurring calcium montmorillonite (STX-1, from Gonzalez County, TX) were converted to the Na^+-exchanged form by stirring in 1 N NaCl for 2 days. They were subsequently purified by suspension in cold distilled water, centrifugation (30 min at 9000 rpm), and mechanical separation of the clay gel from the mineral sediment; this whole operation was repeated six times. Finally, the suspension was centrifuged for 5 min at 9000 rpm and only the supernatant containing 3.4 g dm^{-3} of clay was used as a colloidal suspension for further experiments.

Catalysts. Several kinds of catalysts with CdS and ZnS were employed. CdS was introduced into the clay by adding a volume of 0.1 M Cd^{2+} solution containing 0.34 mequiv of Cd^{2+}, a quantity less than the cation-exchange capacity (cec) of the montmorillonite, with stirring, to 250 mL of clay suspension (3.4 g dm^{-3}). This was sonicated for 1 h. The precipitation as CdS was accomplished by keeping the stirred suspension under an H_2S atmosphere about 30 min following the procedure used for very small colloidal CdS particles.[1] The excess H_2S was subsequently removed by bubbling N_2 (previously saturated with water vapor) through the suspension for 24 h. No Cd^{2+} or S^{2-} ions were detected in the supernatant obtained by centrifugation of an aliquot of this suspension. Another suspension containing the same quantities of CdS and clay, but where the CdS was not incorporated into clay, was made for blank tests by mixing the same proportions of a clay suspension and a CdS dispersion in water.

CdS + ZnS mixtures were incorporated into clay by two different methods. (a) The simultaneous coprecipitation of equivalent

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quantities (0.17 mequiv) of Zn^{2+} and Cd^{2+} ions included into clay particles (250 mL of the suspension containing 3.4 g dm^{-3} of clay) following the same procedure as described for CdS particles included into clay. (b) The precipitation with H_2S of 0.17 meq of Cd^{2+} ions introduced by ion exchange into the clay particles (250 mL of 3.4 g dm^{-3}), followed by the removal of H_2S (by N_2 bubbling for 24 h), the introduction of 0.17 mequiv of Zn^{2+} ions, their precipitation as ZnS, and again the removal of the excess of H_2S. This method of preparation, involving successive precipitation of CdS and ZnS, showed higher activity for H_2 evolution under irradiation and will be denoted[2,8] ZnS/CdS and termed the "active catalyst". The catalyst prepared by simultaneous precipitation will be denoted as ZnS·CdS; this material showed a lower activity for H_2 evolution.

Physical Characterization of Clay and Semiconductor Particles. The crystal structure of sodium montmorillonite and of CdS or CdS + ZnS catalysts incorporated into clay was studied by X-ray diffraction spectroscopy with a General Electric Instrument operated at 35 kV, using a filament current of 20 mA and a Ni filter for Cu Kα radiation. To obtain specific information about the crystal structure of the CdS and ZnS particles, we prepared fresh films of these cast on thin silicon supports (which showed a much better base line than glass supports) and investigated them with a Philips graphite monochromator.

The particle sizes of clay and CdS and ZnS crystals deposited over microgrids reinforced by carbon films were observed by transmission electron microscopy (TEM) with a JEOL 200 CX instrument operated at an accelerating voltage of 120 kV. These experiments were also repeated for other samples prepared on Cu microgrids and observed with a JEOL 200 CX instrument operated at an accelerating voltage of 200 kV, to obtain higher magnifications and selected area X-ray diffraction patterns.

The absorption spectroscopy of suspensions containing similar amounts of CdS or CdS + ZnS mixtures incorporated into clay particles was performed with a Model 270 Cary spectrophotometer.

Apparatus. Electrochemical experiments were performed as previously discussed in a two-compartment Pyrex cell divided by a fine porosity glass frit. The larger compartment (100 cm^3 solution volume) was equipped with a port for placement of a Beckman combination pH electrode and a flat optical window sufficiently large to allow illumination of the entire area of the suspension in the chamber. The collector electrode, a gold flag (10.6 cm^2), was placed in the slurry compartment near a saturated calomel electrode (SCE) used as a reference electrode. The counter electrode, a large platinum flag, was placed in the compartment separated from the slurry.

The pH of the suspension, adjusted to the desired values by addition of small amounts of either 1.0 N H_2SO_4 or 1.0 N NaOH, was measured with a Corning Model 12 pH meter. Photocurrents were recorded with a Princeton Applied Research Model 173 potentiostat/galvanostat and a Houston Instruments Model 2000 X-Y recorder.

The illumination source was a 3.0-kW Xe arc lamp (Christie Corp., Los Angeles, CA, Model CF 30K K) operated at 1.6 kW. In all experiments, a 10-cm water bath and a 420-nm cutoff filter were used to remove IR and UV radiation, respectively.

The photogeneration of hydrogen from water was determined by GC measurements carried out by using two types of illumination devices. In the first, an 80-cm^3 Pyrex cell equipped with a flat optical window sufficiently large to allow illumination of the entire suspension was filled with 50 cm^3 of clay suspension. The samples, whose pH value was initially adjusted to the desired value, were degassed for 1 h with prepurified nitrogen and then irradiated at $\lambda > 420$ nm with constant stirring. The Xe lamp used (Christie Corp., Los Angeles, CA, Model VF 30 K K), operated at 1.6 kW and equipped with a 10 cm water bath, delivered 1.5 W of radiant energy to the cell, as determined with a radiometer/photometer (PAR Model 550-1).

In a second experimental setup, described elsewhere,[2] a 450-W Xe lamp equipped with a water jacket for removing IR radiation was used as a light source of intensity 0.12 W/cm^2. A 19-cm^3 Pyrex vial was filled with 12 cm^3 of clay suspension containing the active mixture of CdS + ZnS, 0.1 M Na_2S, and 0.1 M NaOH. The top of the vial was sealed with a rubber septum, the suspension was purged with prepurified N_2, and the vial was placed to allow the illumination of the unstirred suspension at the bottom. In both types of experiments, gas aliquots (50 to 200 μL) taken from gas phase were analyzed by GC using an Autoprep. A-700 instrument, a 15-ft colum packed with Porapak Q and N_2 as carrier gas.

Results and Discussion

X-ray Diffraction. Sodium montmorillonite is a phyllosilicate having a sheet type of structure with a negatively charged surface.[5] The bidimensional arrangement of one sheet consists of the superimposition of two inverted tetrahedral layers sharing their apical oxygen with the octahedral layer. While the tetrahedral layers are generally silicate sheets, different ions can be found in the octahedral layer. In the case of montmorillonite, two of three octahedral vacancies are occupied by Al(III) and Mg(II), but small quantities of other ions such as Fe(III), Fe(II), etc., may also be present in the octahedral sites. The cation exchange capacity (ca. 1 mequiv per g of dry material) originates from the lack of electroneutrality due to the isomorphic substitutions occurring mainly in the octahedral layer (in montmorillonite ca. 15% Al(III) is substituted by Mg(II)). If one assumes that the isomorphic substitutions are randomly distributed, the statistical distance between negative surface sites is ca 11.5 Å.

These sheets are superimposed, forming microcrystals which can be expanded by absorbing polar molecules, such as water, in the interlamellar space. Consequently, the phyllosilicate sheets, stacked together in the solid state (presumably due to van der Waals interactions), tend to swell and break apart into isolated platelets when suspended in water. This delamination process is not complete, so that the rectangular platelets in a suspension contain at least 3–5 sheets. In our TEM experiments we detected clay particles of 0.1 to 0.15 μm, in agreement with the effective spherical diameter of 0.22 μm found for the colloidal particles by photon correlation spectroscopy.[7d]

Exchangeable cations can reside on the outer surfaces and edges of platelets and can be intercalated between the sheets; this can be significant with respect to the incorporation of photoactive species or of semiconductor particles into clays. The clay platelets also contain water molecules adsorbed in the interlamellar space both in and out of the coordination sphere of the interlamellar cations. As a consequence of the strong local crystalline field of the exchangeable cations, the number of dissociated molecules of water in the interlayer space is much larger than bulk water (the order of the dissociation constant of water, K_w, becomes ca. 10^{-7} instead of ca. 10^{-14}).[10] But whereas the hydroxyl ions remain immobilized in the coordination shell of the hydrated exchangeable cation, M^{z+}, protons are highly mobile (as H_3O^+) in the network of the other water molecules. On nearly dehydrated clay surfaces, the fraction of water molecules in the form of H_3O^+ may be as high as 10^{-2}, while the environment of the exchangeable cations becomes increasingly hydroxide-like. This property is often described in terms of surface acidity, because it is shown by the protonation of adsorbed organic weak bases.

If the interlayer thickness increases, as occurs when Na^+ cations are exchanged for divalent or trivalent cations, the quantity and the mobility of interlamellar water increases as the fraction of liquidlike molecules becomes greater compared to those having an icelike character. Changing the interlayer water content also affects the basal spacing, which can be measured by X-ray diffraction. The X-ray diffraction spectra recorded for clay films (dried 24 h at 300 K cast on silicon supports) exhibit a prominent peak in the region of $2\theta < 10°$ (Figure 1). For sodium montmorillonite this (001) reflection corresponds to a basal spacing of $d_{001} = 12.44$ Å, allowing only one water monolayer intercalated between clay sheets. For CdS + ZnS mixtures included into clay,

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[10] Estimated from IR (Fripiat, J. J.; Jelli, A.; Poncelet, G.; Andre, J. *J. Phys. Chem.* **1965**, *69*, 2185) and NMR (Touillaux, R.; Salvador, R.; Van der Meersche, C.; Fripiat, J. J. *Isr. J. Chem.* **1968**, *6*, 337) data.

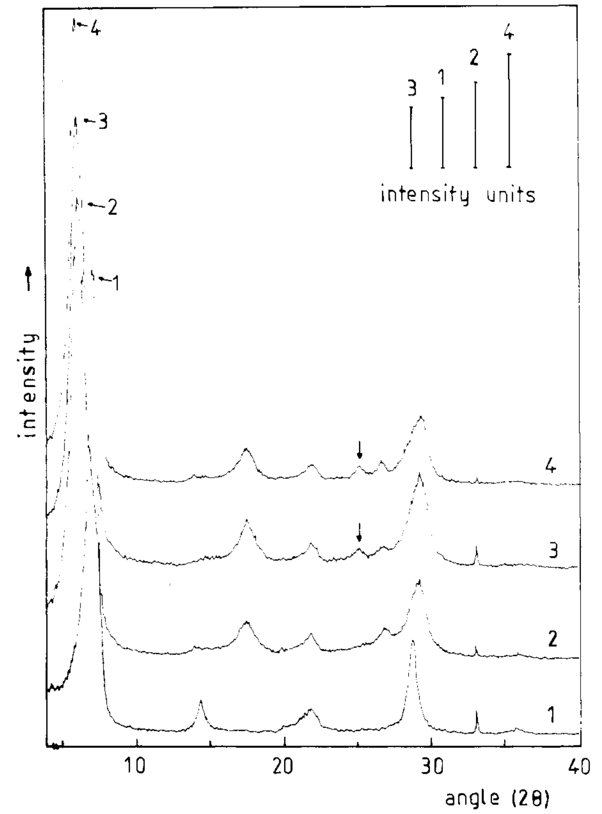


Figure 1. X-ray diffraction spectra of films prepared on silicon supports: (1) sodium montmorillonite; (2) less-active ZnS·CdS mixture; (3) and (4) two different batches of the active ZnS/CdS mixture incorporated into clay.

the spacing d_{001} = 14.24 Å corresponds to two water monolayers. Therefore, if CdS and ZnS particles are formed on the internal sites between sheets, they must be very thin and consist of a relatively small number of molecules. Unfortunately, it is difficult to examine such particles by TEM. Particles smaller than ca. 50 Å diameter disappear in less than 10 s under electron irradiation because of thermal decomposition or photodecomposition. Nevertheless, TEM pictures at 170 000 magnification show a significant difference between the size of particles observed for the less active catalyst ZnS·CdS (particles larger than 200 Å diameter) and active catalyst ZnS/CdS (mostly of particles smaller than ca. 50 Å diameter).

An obvious loss of the ordered crystalline structure of the clay when CdS and ZnS particles were incorporated, as shown by the broadening of clay peaks in the X-ray spectra (Figure 1), was also confirmed by X-ray diffraction patterns obtained in TEM experiments.

Hexagonal crystals of CdS (d = 3.58 Å) and of ZnS (d = 3.31 Å) were identified in both X-ray spectra from peaks displayed by active CdS + ZnS mixtures (see small arrows in Figure 1) at 2θ = 25.2° and 2θ = 26.8°, corresponding respectively to d = 3.532 Å and d = 3.32 Å. The less active mixture displays only a peak at 2θ = 26.8°, corresponding to ZnS (Wurtzite). Note that for CdS + ZnS mixtures precipitated on colloidal SiO_2, no crystallinity of either CdS or ZnS particles having less than 30 Å diameter was found.[8] However, unsupported CdS + ZnS particles having larger sites were found to be cubic.[8] Hexagonal crystals of CdS and ZnS formed between clay sheets are probably very thin (a few ångstroms) but quite long (ca. 25–50 Å).

The absorption spectra of the active and less-active CdS + ZnS mixtures included into clay were similar to those obtained for CdS + ZnS co-catalysts.[2,8] There are two onsets in absorption, at 320 and 530 nm, corresponding to the bandgaps of ZnS (3.7 eV) and CdS (2.4 eV), respectively, but no evidence for the formation of solid solutions.

Electrochemistry. Anodic photocurrents produced by the illumination at $\lambda > 420$ nm of the stirred clay suspensions containing CdS or CdS + ZnS particles included into clay (1 g dm^{-3}) were collected as previously reported.[11,13] at a gold flag (10.6 cm^2) electrode held at −0.4 V/SCE. The addition of 0.1 M potassium sodium tartrate as a hole scavenger[12] was necessary to decreased e^-h^+ recombination and to prevent the reaction of holes with lattice S^{2-} leading to S formation and loss of CdS. Other hole scavengers investigated, such as acetate or polyvinyl alcohol (PVA), were not useful, especially at neutral pH values, in preventing decomposition.

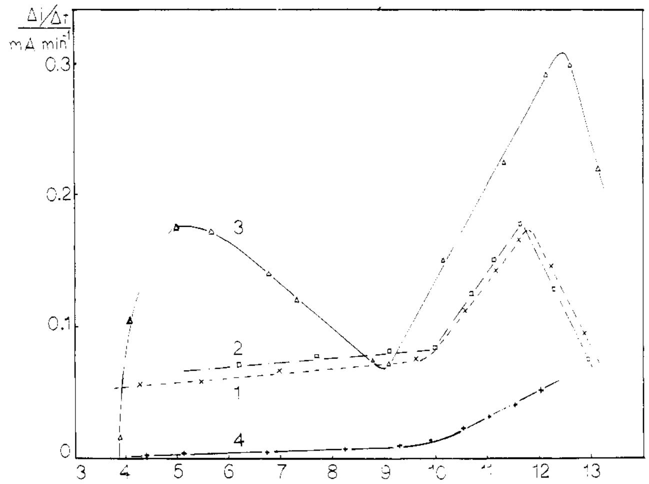
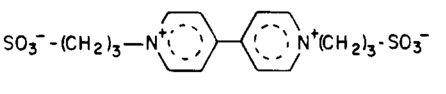


Figure 2. The dependence of the rate of the change of photocurrent with time, $\Delta i/\Delta t$, vs. pH for CdS susensions: (1) CdS particles; (2) CdS mixed with clay; (3) CdS incorporated into clay; (4) CdS incorporated into clay, same conditions as above, except with 0.1% polyvinyl alcohol instead of tartrate. Cell conditions: CdS 0.257 mg/100 cm^3, 1 g dm^{-3} clay, 0.1 M tartrate, 2 × 10^{-4} M PVS, gold (10.6 cm^2) electrode held at −0.4 V vs. SCE illumination at $\lambda > 420$ nm with a 1600-W lamp.

Preliminary experiments with different electron trapping agents showed that methylviologen, MV^{2+} used previously with CdS systems, was not useful, because a large fraction of the $MV^{+}\cdot$ radicals were sequestered by the cation-exchange sites of clay and their photogenerated charge could not be collected at the inert electrode. Previous experiments have also demonstrated that $MV^{+}\cdot$ is strongly held in montmorillonite.[14] Consequently in most of our experiments, the neutral viologen, PVS, was used as mediator.



PVS

The PVS/$PVS^-\cdot$ system has a redox potential of −0.8 V vs. SCE. The blue photoreduced $PVS^-\cdot$ is adsorbed to a much lower extent compared to $MV^{+}\cdot$, presumably because the anion-exchange capacity of the clay is at least 20 times smaller than its cation-exchange capacity. Most of the photoproduced $PVS^-\cdot$ can therefore reach the collector electrode where it is reoxidized to neutral PVS and consequently significant anodic photocurrent levels are observed.

As discussed previously,[11-13] measurement of the anodic photocurrent for semiconductor suspensions as a function of pH can provide information about the particle energetics, since the relative energies of the semiconductor bands are usually pH-dependent, while the potential of the mediator couple, PVS/$PVS^-\cdot$, is not. The rate of increase of the anodic photocurrent with time, $\Delta i/\Delta t$,

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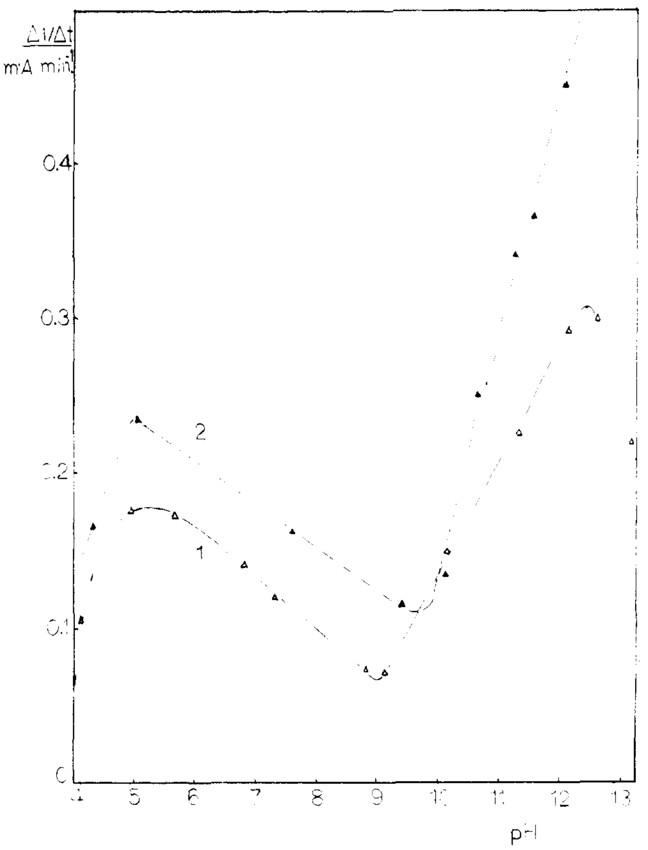


Figure 3. $\Delta i/\Delta t$ vs. pH dependences for CdS into clay with two electron-trapping agents: (1) 2×10^{-4} M PVS; (2) 2×10^{-3} M MV^{2+}. Same cell conditions as Figure 2.

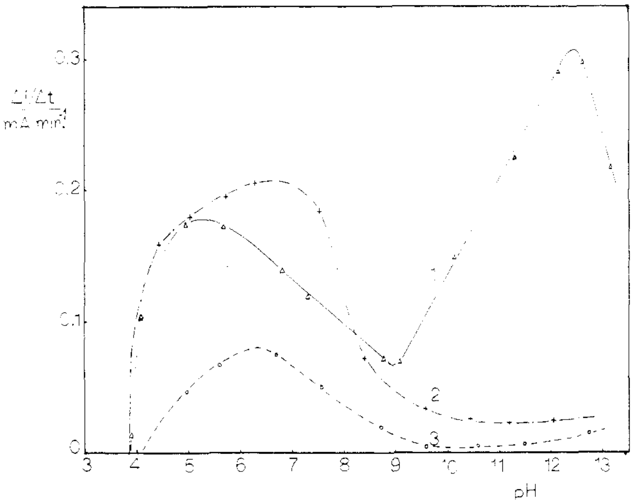
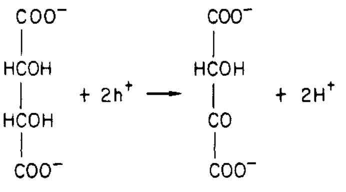


Figure 4. $\Delta i/\Delta t$ vs. pH dependences for (1) CdS into clay; (2) the active ZnS/CdS mixture in clay; (3) the less-active ZnS·CdS mixture in clay. Same cell conditions as Figure 2.

depends upon the pH of the suspension (see Figures 2–4). The $\Delta i/\Delta t$ vs. pH dependence for the unincorporated CdS/tartrate/PVS system has a first intersection point at pH 9.85 and is somewhat similar to the dependence described earlier[12] for the maximum steady-state photocurrent values, i_{ss}, plotted vs. pH, observed in the absence of tartrate ions for the CdS/OH⁻/PVS system. The shift of the intersection point from pH_0 11.1, where the onset of photocurrent mediated by PVS was observed in the absence of tartrate, to pH_0 9.85 in our case, as well as the higher photocurrent values found, can be explained by the more efficient trapping of holes by the tartrate ions. A significant decrease in the $\Delta i/\Delta t$ vs. pH curves after pH 11.8 was observed (see curve 1 in Figure 2). This can be attributed to an excess of OH^- near the surface of the CdS particles, which perhaps makes the approach of negatively charged ions like tartrate, or zwitterionic neutral molecules like PVS that have two localized negative charges, to the CdS more difficult. the $\Delta i/\Delta t$ vs. pH dependence determined for a simple mixture of clay colloid and CdS particles (not incorporated into the clay) was very similar to that observed for the CdS suspension without clay (compare curves 1 and 2 in Figure 2). Incorporation of CdS into the montmorillonite produces significant changes in the electrochemical response of irradiated systems (Figure 2, curve 3). For unsupported (or silica-supported) CdS the mediated photocurents at high pH decrease as the pH is decreased to a background level attributed to direct electron transfer from particle to electrode. For CdS/clay, the $\Delta i/\Delta t$ values also decrease with a decrease in pH for pH's > 9. However, at smaller pH values the photocurrent and $\Delta i/\Delta t$ values increased, attaining a maximum around pH 5 and then decreasing sharply at pH 4. The same qualitative behavior was observed with MV^{2+} as an electron scavenger (Figure 3) and for ZnS + CdS incorporated into the clay (Figure 4). The presence of photocurrents at more acidic pH values implies that the conduction band edge at a given pH lies at more negative values for the clay-incorporated CdS compared to unicorporated material. A photocurrent onset of pH 4 for CdS/clay vs. an onset at pH 10 for CdS alone is equivalent to a shift of about −0.3 V in the band edge position. We have recently discussed the energetics of particulate CdS and CdS·ZnS suspensions compared to single crystal and thin film measurements[15] and proposed that the "apparent" band-edge position found for suspensions was significantly more positive than that for CdS electrode materials because of a high density of surface states in the particulate CdS. If this model can be applied here, it suggests that clay-incorporated CdS more closely displays the actual band positions. Whether this can be attributed to differences in the structure of the incorporated CdS itself or to the nature of the environment around the incorporated particles, and the reasons for the decrease in photocurrent at higher pH values, requires further study. The nature of the ionic charge on the clay and that of the tartrate species as a function of pH may be of significance.

As reported previously,[12] no photocorrosion of the incorporated CdS was observed in the presence of tartaric acid as a sacrificial donor. Only very small amounts of CO_2 were detected by GC; this is supplementary evidence about the low activity of carboxylate groups as hole scanvengers when tartrate is used (acetate is not an efficient hole scavenger for CdS). The proposed mechanism for tartrate is



$$\begin{array}{c}COO^-\\|\\HCOH\\|\\HCOH\\|\\COO^-\end{array} + 2h^+ \longrightarrow \begin{array}{c}COO^-\\|\\HCOH\\|\\CO\\|\\COO^-\end{array} + 2H^+ \qquad (1)$$

involving one or both)COH groups and producing two protons. This is consistent with the decrease of the initial pH value during the long time irradiation of neutral unbuffered suspensions. (A similar process $OH^- + h^+ \rightarrow OH\cdot$ as that found to promote the photooxidation process of ethylene glycol and other polyalcohols[16] might also be considered.)

A small quantity of PVS (0.2 mM) was very efficient in trapping the photoproduced electrons

$$CdS(e^-) + PVS \rightarrow CdS + PVS^{-}\cdot \qquad (2)$$

$PVS^-\cdot$ is oxidized back to PVS at the Au collector electrode held at −0.4 V vs. SCE. A much larger (ca. 10 times) amount of MV^{2+} was necessary for the same level of photocurrent, because many of the photoproduced $MV^{+}\cdot$ radicals were trapped on clay sites. When $\Delta i/\Delta t$ vs. pH curves determined for CdS included into clay/tartrate/PVS or MV^{2+} systems are compared (see curves

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(15) Finlayson, M.; Wheeler, B. L.; Kakuta, N.; Park, K. H.; Bard, A. J.; Campion, A.; Fox, M. A.; Webber, S. E.; White, J. M.; *J. Phys. Chem.*, in press.

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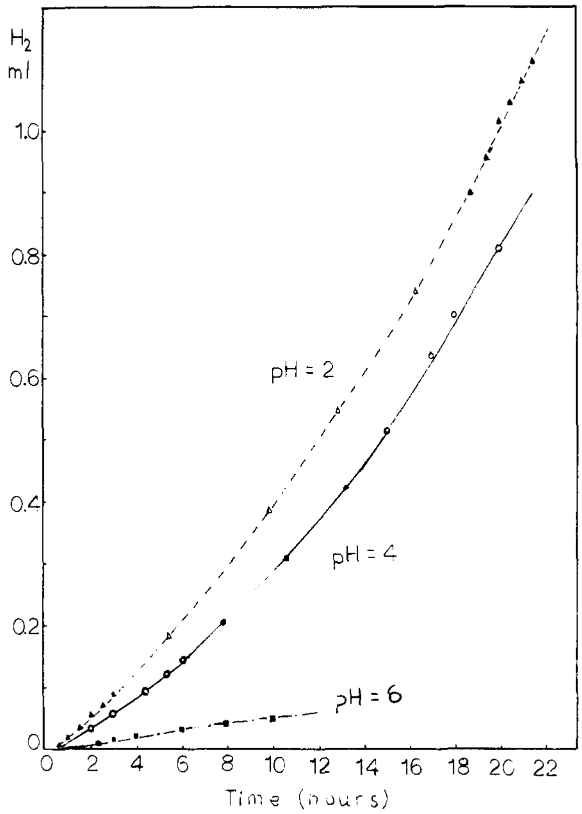

Figure 5. Effect of pH on the production of hydrogen under continuous illumination at $\lambda > 420$ nm with a 1600-W Xe lamp. Cell conditions: 5.35 mg of active ZnS/CdS mixture in 50 cm^3 of stirred clay (1 g dm^{-3}) suspensions containing 0.1 M tartrate.

1 and 2 in Figure 3), very different behavior of these electron relays in alkaline media occurs. The decrease of $\Delta i/\Delta t$ values at pH > 12 with PVS can be attributed to the negative charges localized on $-SO_3^-$ groups of the PVS molecules, making their approach to the surface of the CdS particles more difficult as the surface concentration of OH^- increases.

In Figure 4 we compare $\Delta i/\Delta t$ vs. pH dependencies for active or less-active CdS + ZnS mixtures incorporated into clay. These curves have a quite different shape (especially in alkaline media) as compared with that of the curve obtained for CdS alone in clay. Significantly higher $\Delta i/\Delta t$ values were observed at neutral pH values for the active (ZnS/CdS) catalyst (curve 2) while those of the less-active ZnS·CdS catalyst showed a lower maximum in the same pH range. No significant amounts of hydrogen were produced during the long-term irradiations of suspensions at alkaline or neutral pH values. Some H_2 was detected only when the pH was more acidic than pH 4.

Hydrogen Evolution. The amounts of hydrogen produced by the active ZnS/CdS mixture in clay when tartrate, but no PVS, was present depended upon the pH of the suspension (Figure 5). At pH 2 the product of hydrogen was significantly higher than at pH 4; similar results were obtained with the TiO_2/glucose/Pt-SiO_2 systems.[13] When S^{2-} was used as a hole scavenger instead of tartrate, 0.73 cm^3 h^{-1} of hydrogen was produced continuously by the active catalyst at pH 12.9 (see curve 1 in Figure 6). As found with other ZnS + CdS systems,[8] an induction period of 10–30 min, during which no H_2 was detected, was seen. This behavior can be related to the low $\Delta i/\Delta t$ values (measured as initial slopes) as soon as the illumination of the suspension starts. This induction period was attributed to the formation of cadmium metal that acts as a catalyst for hydrogen evolution from sulfide solutions.[17] Henglein and Guttierrez[1d] explained the production of hydrogen on CdS + ZnS co-catalysts in sulfite solutions by the formation of a layer of reactive Zn metal on the colloidal particles. Only after a certain concentration of the metal had been built up did the evolution of hydrogen become noticeable.

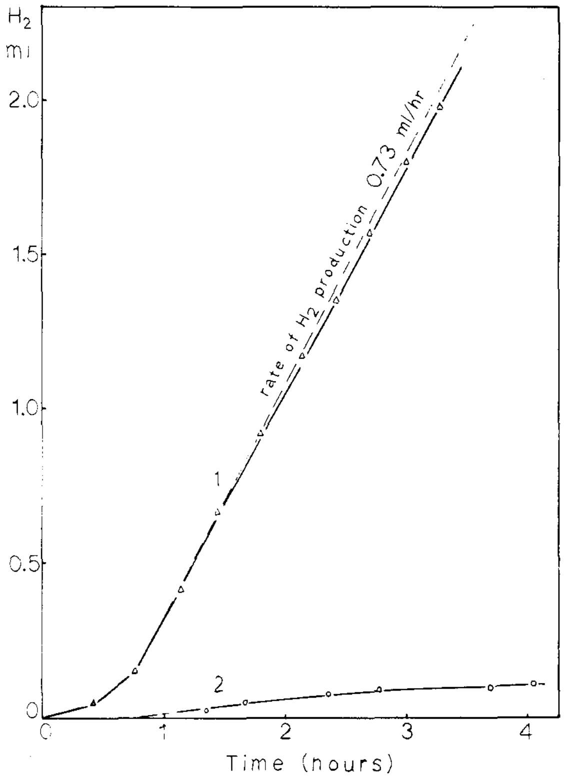

Figure 6. Hydrogen production as a function of illumination time with a 1600-W Xe lamp at $\lambda > 420$ nm for (1) the active ZnS/CdS mixture in clay; (2) the less-active ZnS·CdS mixture in clay. Cell conditions: 5.35 mg of CdS + ZnS in 50 cm^3 of stirred suspensions of clay (1 g dm^{-3}), containing 0.1 M Na_2S and 0.1 M NaOH.

The method of preparation of mixed CdS + ZnS incorporated into clays appears to have a strong effect on the rate of production of hydrogen in alkaline (pH 12.9) sulfide solutions (compare curves 1 and 2 in Figure 6). The simultaneous coprecipitation of equivalent amounts of Zn^{2+} and Cd^{2+} ions introduced by ion exchange into clay leads to the less-active ZnS·CdS mixture. This is different from the results found with silica-supported[8] or unsupported[2] catalysts prepared by coprecipitation, in which ZnS·CdS showed about the same activity as ZnS/CdS. On the contrary, the catalytic activity (for H_2 production) of CdS + ZnS mixtures incorporated into clay by a successive ion exchange and precipitation of Cd^{2+} ions followed by that of Zn^{2+} ions (ZnS/CdS) was larger for two different batches of active catalyst prepared in this way.

This difference in behavior can perhaps be attributed to ion segregation, i.e., to the nonrandom distribution of Zn^{2+} and Cd^{2+} ions simultaneously introduced into clay.[7d] A given interlayer of a clay platelet would either be completely saturated with Cd^{2+} (or Zn^{2+}) ions or not be occupied at all. Thus, after the first Cd^{2+} (or Zn^{2+}) ion is incorporated between or on the clay layers, the energy to incorporate a second ion of the same size next to the first is lower than that to place it randomly in the particle. Such segregation has been proposed previously[7d,9] to result from differences in sizes and solvation energies of the ions; rather different ions like MV^{2+} and $Ru(bpy)_3^{2+}$ were segregated in the clay layers while similar ions like $Ru(bpy)_3^{2+}$ and $Zn(bpy)_3^{2+}$ were not. If most of the Zn^{2+} and Cd^{2+} ions are segregated in different layers or surfaces, then the ZnS and CdS particles formed by their precipitation would be separated (except at edge sites) and therefore behave as a physical mixture of individual particles, having no catalytic properties for the production of hydrogen under visible light irradiation. Blank tests have shown that CdS alone in clay does not produce hydrogen under illumination.

An intimate contact between ZnS and CdS particles was found to be an important requirement for good catalytic activity.[8,15] With clays, such an active CdS + ZnS mixture could be obtained only by the successive incorporation and precipitation of Cd^{2+} and Zn^{2+}

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(17) Itaya, K.; Bard, A. J. *J. Electroanal. Chem.*, in press.

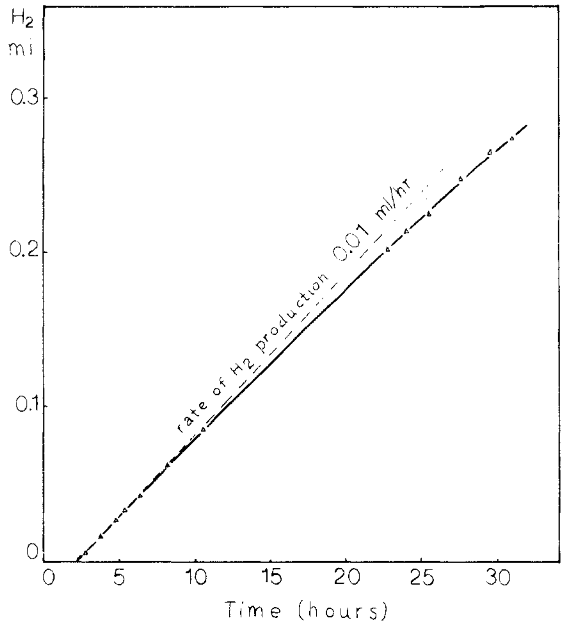

Figure 7. Amounts of hydrogen produced under the illumination at λ > 420 nm with a 450-W Xe lamp. Cell conditions: 3.15 mg of ZnS/CdS active mixture in 12 cm^3 of unstirred suspension of clay (1 g dm^{-3}) containing 0.1 M Na_2S and 0.1 M NaOH.

ions. We assume that the clay recovers at least some of its ion-exchange capacity once the precipitation with S^{2-} of the Cd^{2+} ions initially incorporated is finished. Precipitation of CdS may also expand the interlayer spacing in the clay particle so that Zn^{2+} ions can be incorporated in proximity to the CdS particles and be in turn precipitated near them. Such small CdS + ZnS particles intercalated in an interlayer space probably have a high surface area, as needed for active photocatalysts. Moreover, since the Cd^{2+} was introduced and precipitated before the Zn^{2+}, subsequently formed ZnS crystals form as an outside layer; this was effectively shown to be the best arrangement for ZnS + CdS mixtures supported on silica particles.[8]

Larger (more than ca. 50 Å) CdS + ZnS particles observed by TEM and probably located on edge sites or on outside sites may contribute to the photoelectrochemical and catalytic properties observed, but they cannot explain the observed differences in the ZnS/CdS and ZnS·CdS forms. The rate of hydrogen production on the most active ZnS/CdS/clay mixture was about four times smaller than that found with a ZnS/CdS/SiO_2 system under similar conditions (Figure 7). This perhaps can be attributed to greater difficultly of the hole scavenger, S^{2-}, accessing the intercalated semiconductor, or equally to problems with hydrogen evolution.

Conclusions

Photoredox reactions of CdS and ZnS + CdS mixed particles examined in this study are affected by their incorporation into clay colloids. The rate of increase of anodic photocurrents measured vs. time, $\Delta i/\Delta t$, as well as the amounts of hydrogen photoproduced, depend upon the pH and on the nature of electron-trapping agents (PVS or MV^{2+}) or of the hole scanvengers used (PVA, tartrate, S^-). The behavior of observed dependencies can be explained by assuming that most CdS + ZnS mixed particles are intercalated between the clay layers. Unfortunately, it is difficult to observe such thin particles by scanning or transmission electron microscopy. Only particles larger than ca. 50 Å for the active catalyst and ca. 200 Å for the less-active one were observed by TEM. The hexagonal CdS or ZnS particles located between the clay layers are probably quite flat and only a few ångstroms thick.

Our results confirm previous conclusions obtained for CdS + ZnS mixtures supported by silica[8] concerning the importance of particle size, the need of intimate contact, and the position of ZnS in the outer layer on a CdS core. In contrast to silica supports, the structure and localized charges of clay influence both the preparation and the properties of the incorporated semiconductor particles.

The efficiency of the best ZnS/CdS/clay catalysts for H_2 evolution in a S^{2-} medium was somewhat lower than that for SiO_2 supported semiconductors, perhaps because of mass transfer and accessibility problems in the clay. We are currently investigating free-standing films of pillared clays[17] and the design of "integrated chemical systems" involving clay/semiconductor/catalyst/relay assemblies with the aim of producing systems that can provide vectorial charge transfer and product separation under irradiation.

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Registry No. PVS, 77951-49-6; MV, 1910-42-5; PVA, 9002-89-5; CdS, 1306-23-6; ZnS, 1314-98-3; Na_2S, 1313-82-2; H_2, 1333-74-0; potassium sodium tartrate, 304-59-6; montmorillonite, 1318-93-0.