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ABSTRACT

The goal of this research was to evaluate the potential for using reactor wastes to synthesize useful products in quasi-photochemical configuration. It was found that semiconductor oxides act as heterogeneous catalysts for the formation of H_2 in aqueous media under Co^{60} irradiation. The principle of a gamma-ray solar cell was demonstrated experimentally. Experiments with ultra violet irradiated TiO_2 and ZnO grains demonstrated that both H_2 and H_2O_2 were formed, in contrast to the results of work by previous authors. These results were rationalized by energy band diagram representations and by applying principles of semiconductor photo-electrochemistry.

The concept of gamma-ray assisted desulfurization of coal through radiological degradation and heterogeneous catalysis was experimentally demonstrated. The proof-of-concept experiments in the present study provide the basis for further fundamental and applied investigations, particularly in a potentially efficient system with a fresh source and 1.5 m path length.

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1. INTRODUCTION

The goal of this research was to investigate the effective utilization of nuclear reactor wastes for production of new fuels. Another goal was "in order to firmly establish the results obtained to date and to evaluate the potential of radiation photolysis of water versus solar photolysis of water." In order to achieve programmatic objectives, we chose a specific catalyst amongst the wide variety of materials investigated in the previous year and studied the gamma-ray photolytic reaction in further detail. Catalyst mass and transport gas flow rate were studied. Sb_2O_3 was chosen from the present study for two reasons: (a) This material had shown promise in experiments conducted last year and (b) The energy band-gap (3.31 eV) was suitable for the gamma-ray photolysis of water.

The key results which are described in detail in the present report and which pertain to the gamma-ray photolysis of water are: (a) The earlier results of somewhat speculative nature are confirmed by the present data. The feasibility of production of H_2 for water utilizing the principles of heterogeneous catalysis and radioactive nuclear wastes is unequivocally demonstrated by the experiments described below and (b) Arguments in favor of a heterogeneous catalysis mechanism are supported by reassessments carried out in the presence and absence of the solid catalyst. A nominal H_2 yield of 1×10^{-5} mol/hr. was obtained without the catalyst. In the presence of Sb_2O_3 , the yield was increased to 33×10^{-5} mol per gram of catalyst.

For comparison with the gamma-ray photolysis data, the photosynthesis of H_2 and H_2O_2 by UV irradiation of aqueous suspension of TiO_2 and ZnO was investigated. This reaction was chosen because of the recent interest on photocatalytic and photosynthetic processes at the semiconductor/liquid interface.

The synthesis of H_2 and H_2O_2 from water is thermodynamically "uphill" and involves free-energy changes of 2.63 and 1.23 eV per molecule respectively. Photoelectrochemical (PEC) methods have offered a ready means of overcoming the thermodynamic barriers. Several reviews of this field of research have appeared in the recent literature.² The use of the so-called photosynthetic mode¹, in which the semiconductor grains are suspended in the reaction media, however, is more practical. The possibility of H_2 and H_2O_2 production by utilizing the photosynthetic mode was therefore of relevance to the present study. It was also of interest to compare the mechanistic aspects of the production of H_2 from water by the two approaches involving gamma-ray and UV photolysis respectively. Photosynthetic production of H_2O_2 according to reaction (2) has been investigated on various semiconducting materials including ZnO ,^{3,5} CdS ,⁴ HgS ,⁴ ZnS ,⁴ $CdTe$,⁵ $CdSe$,⁴ and Ga_2S_3 .⁴ ZnO , in particular, has been the focus of considerable attention.^{3,5} Notwithstanding the controversies that remain on the mechanism of photosynthesis of H_2O_2 at the ZnO /liquid interface,^{3h} it was particularly of interest to note that previous authors had reported no traces of hydrogen in the reaction products.^{3c} In view of the importance of reaction (1) to energy conversion and storage and the preponderance of this reaction at oxide semiconductor/electrolyte interfaces in general (vide infra), we decided to reexamine the products of UV generated processes at the powdered ZnO /liquid interface.

A second aspect of relevance to the present study concerns the synthesis of H_2O_2 . Previous authors had observed H_2O_2 production at the TiO_2 /electrolyte interface subjected to UV and visible irradiation.⁶ These experiments were, however, conducted in the photoelectrochemical mode. With powdered TiO_2 grains suspended in aqueous solution, no evidence for reaction (2) was obtained in previous studies.^{3a} This finding was surprising particularly

in view of the good correlation that was observed between photoelectrochemical cell reactions of TiO_2 and the corresponding processes on powdered TiO_2 .^{1h,i,j,m,o} We were, therefore, intrigued by the possibility of photosynthesizing H_2 and H_2O_2 at the granular TiO_2 /liquid interface. Our observations on this system are presented along with the results on ZnO mentioned above.

Finally the possibility of using gamma radiation, in conjunction with catalytic modulator materials, to bring about highly selection breakage of chemical bonds, immediately gave hint of the potential utility of this approach in applications related to desulfurization of coal. Organic sulfur in coal is a complex and environmentally important problem at present. This approach, although not outlined in the original proposal, was deemed to be of sufficient importance that gamma-ray assisted desulfurization of model sulfur compounds was evaluated. The results obtained thus far have been extremely encouraging. A ten-fold increase was observed in the amount of H_2S recovered from selected model sulfur compounds. This represents the "worst-possible" case since only the H_2S in the existing gas stream was analyzed in these experiments. No attempt was made to determine the sulfur removed in soluble elemental form. Further research is warranted by the results obtained thus far.

2. EXPERIMENTAL

2.1 Gamma-ray photolysis:

A schematic of the experimental set-up is shown in Figure 1. Details on the various components of the test-set are amplified below:

2.1.1 Gas chromatograph

A Carle analytical gas chromatograph Model No. 111 fitted with automatic sampling accessory, was used for the experiments. A six foot molecular sieve 5 A γ 5/60 column was used for the detection of hydrogen. The

Figure 1: Schematic of setup for Y-ray photolysis experiment

carrier gas was high-purity (99.995 %) dry grade N₂. The nitrogen pressure was 17 psi which produced a flow rate of approximately 10 cc/min. The column and detector in the gas chromatograph were kept at a constant temperature of 40°C by a proportional temperature controller. The automatic sampler allowed sampling of the gas composition at a maximum of 1 hour intervals.

2.1.2 Digital integrators

A digital integrator (Columbia Scientific Industries Model CSI-38) was used for the quantitative determination of H₂ content in the gas stream. The integrator produced a count $\int_{t=t_1}^{t=t_2} (V_{GC} - V_{BC}) dt$ where t_1 and t_2 are the integration on and off times respectively, V_{GC} = chromatograph signed voltage and V_{BC} = baseline correction voltage. The system integrator after every sampling, printed out the number of counts and the sampling time.

2.1.3 Gamma Cell

A U.S. Nuclear Corporation Gamma Irradiator (Model E-0044-A) was used for the irradiation. The radiation source was Co⁶⁰. The cell had entry ports that allowed gas flow via Tygon^R tubing into the reaction vessels in the radiation well. The measured dose rate was approximately 3.6×10^5 rads/hr., corresponding to about 2×10^{13} photon/hr.

2.1.4 Flow controller

A Whitey micrometer valve (+ B-22RSH) and Moore flow controller (Model SD 635UL) were used to adjust and regulate the flow of the N₂ transport gas. The flow controller was a differential-type. Details of the flow controller design are given in a previous report.¹⁵

2.1.5 Flowmeter

Two Fischer Procter (Model # 10 A 2735 B) ball type flowmeters were used

to measure the flow rate of gas in both channels (c.f., Figure 1). The transport gas flow was normally set at 50 cc/min and the gas chromatograph carrier gas flow at 10 cc/min. It was found that the flowmeters were not linear and did not indicate actual flowrates. The flowmeters therefore, were recalibrated by procedures outlined below.

2.1.6 Strip-Chart Recorder

The output of the gas chromatograph was also monitored on a strip-chart recorder (Omnigraphic Model 300). The peak areas were calibrated using standard gas mixtures (vide infra).

2.1.7 Radiation vessel

The radiation vessels, made of Pyrex^R glass were fabricated by R. H. Allen Co., Boulder, Colorado. The cylindrical vessels had typical dimensions of 3.8 cm O.D and 16.3 cm height (Figure 2). A medium size porous glass frit was located 1.5 cm from the bottom of the vessel with an inlet port for N₂ gas located below the frit. A removable cap with a 1/4 inch glass tube for exit gas was provided for loading the vessel with catalyst and solution. The vessel was supported at the bottom by an aluminum holder. Nitrogen flowed through the glass frit, bubbling through the water, suspending the powder catalyst in solution and exiting through the top along with product gases from the photolysis reaction.

2.1.8 Drierite^R filter

To maintain optimum performance in the gas chromatograph column, the transport gas must be free of moisture. A 2-foot X 1 1/2 inch glass tube filled with Drierite^R (#6 and #6) was used to dry the transport gas prior to entry into the gas chromatograph system.

Figure 2: Radiation vessel for Y-ray photolysis experiments.

2.1.9 Calibration

Gas chromatograph and integrator

Two calibration gases were obtained from Union Carbide, Los Angeles, California. Calibration gas #1 was a 45.7 ± 3 % ppm mixture of molecular H_2 and N_2 . Calibration gas #2 was a 48.1 ± 3 % ppm mixture of molecular H_2 in N_2 . Certification of analyses were made by the vendor. The output of the gas chromatograph and integrator was calibrated against these standard gas mixtures. Representative results are assembled in Table 1.

The gas chromatograph measures the actual number of molecules and not ppm directly. A possible source of error therefore, is variations introduced in the number of H_2 molecules per unit volume of gas due to variations in temperature and pressure. Assuming an average pressure of 62.42 ± 1.96 Torr of Hg, a median temperature of $14 \pm .001^\circ C$ and ideal gas behavior, the total number of molecules per cubic centimeters (n/V) is $1.92 \times 10^{19} \pm 0.01 \times 10^{19}$. To convert integrator counts (C) to number of H_2 molecules per cubic centimeters (n_H), the following equation was used:

$$n_H = \frac{n}{v} \cdot \frac{c}{k} \times 10^6 \times \frac{1}{2} = 9.60 \times 10^{12} \frac{c}{k} \quad (1)$$

where k = counts in ppm.

The factor of $1/2$ is introduced because the gas chromatograph analyzes a 2 ml sample.

Flowmeter

A soap bubble meter was used for calibration of the flow meter. Relevant details on the design of the bubblemeter are found elsewhere.¹⁵ The gas enters the bubble meter and when the bulb is squeezed, a soap bubble is formed. The bubble travels up the tube at the gas flow rate. A stop-watch was used to time the travel of the bubble. By knowing the time and the volume displaced during the bubble's travel, the flow rate was calibrated

Table 1: Calibration of gas chromatograph and integrator

Calibration gas Composition H ₂ in N ₂ (ppm)	No. of Samples	$\bar{C}$ mean value of counts	Δc	K counts/ppm	ΔK^a
45.7 $\pm$ 3%	45	770	110	16.9	2.5
45.7 $\pm$ 3%	41	880	110	19.3	2.5
45.7 $\pm$ 3%	25	800	110	17.5	2.5
48.1 $\pm$ 3%	38	9280	130	19.3	0.6

a) $\Delta K = \left\{ \left(\frac{dk}{dc} \right)^2 (\Delta c)^2 + \left(\frac{dk}{dppm} \right)^2 (\Delta ppm)^2 \right\}^{1/2}$

Figure 3: Representative results for flowmeter calibration

as described elsewhere. Representative calibration results are shown in Figure 3.

2.1.10 Materials

Water deionized by reverse osmosis (specific resistivity = ~ 18 meg ohm/cm) was used for all experiments. The catalyst was anular grade Sb_2O_3 (Ventron) in powder form.

2.2 UV Photolysis

2.2.1 Reaction vessel

The experimental assessment was virtually the same as that described above for gamma-ray photolysis experiments. The only major difference was in the design of the radiation vessel (c.f., Figure 4). A reaction vessel of commercial design (Ace Glass Company, New Jersey) was employed for the UV photolysis measurements. The vessel was made of quartz or Pyrex^R glass. The light source was a Hanovia high pressure Hg lamp and was housed in the double-walled jacket in the vessel as shown in Figure 4. In all the experiments, the reaction mixtures were irradiated with the full output of the lamp. The lamp was cooled by cold water flowing through the double-walled jacket.

2.2.2 UV lamp calibration

The energy output of the light source was measured by an actinometric procedure. The decomposition of monochloroacetic acid in UV light was utilized for this purpose. The Cl ions liberated in the reaction were estimated by the Volhard method.⁸ A value of quantum efficiency equal to 0.62 ± 0.04 was taken from previous work on the UV photolysis of monochloroacetic acid.⁹ An intensity of 11.04×10^{-4} einsteins/min was thus determined for the UV lamp employed in the present study.

Figure 4 Schematic of the setup employed for photosynthetic measurements.

2.2.3 Chemical Analyses

Hydrogen peroxide was analyzed by an iodimetric procedure described elsewhere.⁷ Reduction of peroxide by iodide ions was carried out on 20 ml aliquots of the reaction mixture in $1\text{N H}_2\text{SO}_4$ medium. A few drops of ammonium hydroxide served to catalyze the reduction reaction. The iodine liberated was detected by addition of starch and the solution analyzed spectrophotometrically.

2.2.4 Hydrogen Yields

Hydrogen was analyzed in the gas stream by the gas chromatograph as described in the preceding section for gamma-ray photolysis experiments. Identical procedures were followed for the UV photolysis measurements.

2.2.5 Materials

Titanium dioxide (99.998%) was obtained in powder form from Materials Research Corporation, Orangeburg, New York. Reduction of the starting material was carried out in a conventional furnace by heating for ~6 hr at 700-800°C in a flowing atmosphere of H_2 . The reduced material was light blue in color. Zinc oxide was obtained in granular form from commercial sources (Materials Research Corporation, Orangeburg, New York) and was used as received. Some samples of ZnO from Pfaltz & Bauer Inc., Stamford, were also investigated.

The reaction medium in all experiments was deionized water (resistivity: ~18 MΩ). The initial pH of the reaction mixtures was usually in the range 6.4-6.7 as measured on a Model 701A Orion Research pH meter. The use of buffered solutions to control pH was avoided to preclude effects arising from the UV photolysis of buffer reagents. The results described below also pertain to the case where no organic addi-

tives were intentionally added to the reaction mixture to enhance the photosynthesis of H_2O_2 . $^3\text{O}_2$ gas was, however, passed through the reaction mixture in a few experiments on ZnO_2 which were designed to duplicate measurements previously reported.

2.3 Gamma Ray - Assisted Desulfurization

2.3.1 Materials

$\text{NH}_2(\text{CH}_2)_2\text{SH}$, $\text{C}_6\text{H}_5\text{SH}$ and CH_3SSCH_3 were used as model sulfur compounds for the proof-of-concept experiments. All these materials were of reagent grade purity and were obtained from the Chemistry Department stockroom. 75ml amounts of these chemicals dissolved either in alcohol and water, were used for the irradiation experiments. The catalyst employed for the desulfurization experiments was annular grade SiO_2 (Alfa Ventron).

2.3.2 Analytical Procedures

The outlet from the gamma-ray irradiation chamber was connected to a gas washing tube containing ammoniacal H_2O_2 solution. After an irradiation "run," the contents of the gas washing tube were transferred to a clean beaker. The tube was washed separately and the washings added to the clean beaker to ensure complete removal of product gases from the desulfurization reaction. The solution in the beaker was boiled for 30 minutes, acidified with HCl and a hot - 5% solution of BaCl_2 added, a white precipitate of BaSO_4 immediately separated out. The precipitate was allowed to settle and then transferred to a Whatman ashless filter paper. Subsequent ignition of the filter paper allowed gravimetric determination of BaSO_4 . The amount of sulfur removed from the original compound was then computed from the weight of BaSO_4 .

3. RESULTS AND DISCUSSION

3.1 Gamma-Ray Photolysis of Water

A series of thirteen experiments were carried out in which the amount of Sb_2O_3 catalyst was varied from 0 to 3.0 gm. Each experiment lasted 12 to 16 hours. The exit gas stream was sampled every 12 minutes by the autosampling accessory. Three control experiments were made without catalyst or irradiation. The results from these experiments are assembled in Table 2 and graphically shown in Figure 5.

The results unequivocally demonstrate the feasibility of production of H_2 from water by gamma-ray assisted catalysis. One point worthy of note in the data in Table 2 and Figure 5 is that catalyst mass seems to exercise only a minor influence on H_2 yield. This immediately suggests that surface area limitations were not a factor in the overall H_2 yields, in the range of catalyst mass levels included in the present study. The influence of surface area would have manifested itself in a linear correlation between H_2 yield and catalyst mass at low mass ranges followed by a saturation effect. The fluctuations in the integrator output, however, are disturbing (Table 2). The stability of the integrator output constituted a serious problem in the gamma-ray photolysis experiments. Direct measurement of H_2 yield for example, by peak area determinations from the strip-chart recorder output would have been preferable. Such an approach, however, was impractical because of the exceedingly long irradiation times that were employed. Shorter irradiation times were attempted. The H_2 yields, in these cases, however, were rather insignificant. The absorption length for 1 MeV protons in water is $106/3.3 \times 10^4 = 30\text{cm}$.¹⁷ This exceeded the path length in our sample cell. Moreover, our source had decayed from 5000 to 500 curies, further reducing signal strength.

Table 2: γ -ray photolysis of water using Sb_2O_3 catalyst

Run No.	Catalyst Mass (gm)	Integrator Counts			H_2 yield (md/hr) $\times 10^{-5}$
		Max	Min	Avg	
1 a)	0	0	0	0	0
2 b)	0	0	0	0	0
3 c)	0	0	0	0	0
4 d)	0	2902	2197	2622.8	1.01
5	0.2	3371	2958	3208.4	1.23
6	0.4	3523	2956	3305.9	1.26
7	0.6	4024	2951	3473.4	1.33
8	0.8	3575	3035	3303.9	1.26
9	1.0	4163	2945	3513.7	1.34
10	1.5	3317	2845	3046.1	1.32
11	2.0	3596	2972	3196.4	1.22
12	2.5	3259	2913	3093.0	1.18
13	3.0	3968	2666	3185.4	1.28

a) unirradiated, cell above irradiation chamber

b) unirradiated, cell in place in irradiation chamber

c) irradiated, cell bypassed

d) irradiated, no catalyst

Figure 5: Hydrogen yield from γ -ray photolysis of water versus mass of catalyst

In spite of the scatter in the data, we can definitely conclude that the introduction of a catalyst in the reaction visual results in a significant increase in H_2 yield. This is compelling argument in favor of a heterogeneous catalytic mechanism for the photolysis reaction.

We propose the following mechanism to account for the data in Table 2 and Figure 5: Absorption of gamma-ray energies such that with $E \gg E_g$ by the solid catalyst. (E_g is the energy band-gap of the catalyst) generates non-equilibrium electron hole pairs by direct excitation of electrons from the valence band into the conduction band of the catalyst material. The non-equilibrium electrons relax back to the conduction band edge by a radiationless process (i.e., by dissipation of energy as heat). These electrons subsequently recombine with a gamma-ray generated hole leading to the release of a photon with an energy equivalent to that of the band-gap, E_g . Emission of photons with lower energies is also possible through mediation of electron-hole recombination processes by states lying within the energy band-gap (e.g. impurity levels) caused by the irradiation. These processes may be represented by the following equations:

where Z = catalyst, Z^* = excited catalyst and S = surface state or bulk state lying within the energy band-gap.

The emitted photon can be released directly to water molecules absorbed on the surface of the catalyst. Since the energy of the emitted photon (3.31 eV) approaches the bond energy of water molecules (3.79 eV), an additional decomposition path over the normal direct photolysis mode is possible as represented by the following equations:

Radiation catalysis

Direct gamma-ray photolysis

It may be shown that the yields of molecular H_2 by direct photolysis (Eqn. 4) are insignificant in comparison with the levels produced in the presence of the catalyst.¹⁵

In summary, the proof-of-concept experiments shown in Table 2 and Figure 5, have unequivocally demonstrated the enhanced production of H_2 from water in the presence of a suitable catalyst. The results furnish compelling proof for the existence of a heterogeneous catalytic mechanism for the photolysis reaction. However, the relatively small ratio of path length/ coupled with low radiation intensities caused by a weak vessel absorption length led to poor quantum efficiencies. Overall quantum yields and commercial feasibilities were difficult to estimate. Nevertheless, the magnitude of the observed increases even under these conditions point to the need to perform a demonstration under simulated commercial conditions where the source is fresh and low cm path lengths are obtained. Source strength is as critical as path length since free radical concentration increases as the square root of the intensity.¹⁸

3.2. UV PHOTOLYSIS OF WATER

Contrary to the results of a previous study,^{3c} hydrogen production on UV irradiation of ZnO/water mixtures seemed to be quite facile. In the absence of ZnO, however, no traces of H_2 or H_2O_2 could be found. Figure 6a illustrates typical results which show that a limiting rate of H_2 evolution is attained after approximately an hour of irradiation.¹⁰ This limiting rate is proportional to the mass of ZnO as shown in Figure 6b, although at high levels of solid content in the reaction mixture (>10 g in 700 ml of water), this dependence falls off and the rate becomes insensitive to a further increase in ZnO concentration. A gradual decay in the rate of H_2 evolution was also noted on prolonged irradiation (Figure 6a). Analysis of the reaction mixtures at various stages of the illumination, revealed the presence of H_2O_2 in all cases. Passage of O_2 through the reaction mixture also brought about a substantial increase in the concentration of H_2O_2 . Addition of $\sim 5 \mu$ mole of H_2O_2 to the reaction mixture followed by one hour of illumination brought about a two-fold decrease in the concentration of H_2O_2 . These results are in essential agreement with those of previous workers.³ The maximum quantum yield for production of H_2 on ZnO was calculated to be 1.13×10^{-3} for the conditions employed in the present set of experiments.

Figure 7 illustrates the rate of H_2 evolution on TiO_2 for these levels of solid content in the reaction mixture. A limiting rate of H_2 production is attained after ~ 2 hr of illumination. The behavior is similar to the case of ZnO discussed above. This limiting rate is directly proportional to the concentration of TiO_2 as shown in Figure 8. Figure 9a illustrates the concentration of H_2O_2 in the illuminated TiO_2 /water suspensions as a function of time. A limiting concentration of

Figure 6 (a) Rate of H_2 evolution as a function of irradiation time for ZnO /water suspensions; g of ZnO in 700 ml of water; (b) Limiting rate of H_2 evolution as a function of the amount of ZnO . The solution volume in all cases was 700 ml.

Figure 7. Rate of evolution of H₂ in TiO₂/water suspensions for three levels of solid content (a) 10 g (b) 20 g and (c) 30 g. Solution volume in all cases was ~700 ml.

Figure 8 Dependence of limiting rates of H_2 and H_2O_2 formation on the amount of TiO_2 in 700 ml of solution.

Figure 9 (a) Amount of H_2O_2 formed in TiO_2 /water suspensions as a function of irradiation time and (b) Rate of H_2O_2 formation in TiO_2 /water suspensions as a function of irradiation time. Data are shown for three levels of solid content in 700 ml of water: (○) 10 g (Δ) 20g and (□) 30 g.

H_2O_2 is attained after ~ 3 hr of illumination and concomitantly the rate drops gradually to zero as shown in Figure 9b. Control experiments carried in the absence of TiO_2 revealed no traces of either H_2 gas or H_2O_2 . The behavior seen in the case of TiO_2 in the present study is similar to that reported by previous authors for ZnO .^{3a,d,h} The quantum yields for production of H_2 and H_2O_2 on TiO_2 were calculated to be 3.09×10^{-6} and 3.17×10^{-4} respectively. These values refer to the maximum concentrations of H_2 and H_2O_2 that were observed in the present study. The estimates, however, reflect the lowest limits of quantum yield under the particular conditions employed since the light intensities were not corrected for solid attenuation and scattering effects.

To our knowledge, the results reported here represent the first instance where H_2 evolution in the case of ZnO and H_2 and H_2O_2 production in the case of TiO_2 have been observed in the photosynthetic mode. H_2O_2 formation was, however, noted by previous authors on TiO_2 electrodes in PEC cells.⁶ Photoproduction of H_2 on TiO_2 electrodes in PEC cells is also a well-documented result.¹ The present results, however, seem to be contradictory to those obtained by previous investigators. Markham and Laidler^{3a} report that "under the conditions described in this paper, no peroxide can be found in irradiated suspensions of titanium dioxide either in presence or absence of phenolic compounds." No mention is made in this paper on the nature of the TiO_2 samples that were employed, i.e., whether they were reduced or not prior to irradiation. Our experience with TiO_2 which was not subjected to prior reduction indicates that the negative results in the above mentioned study could be rationalized on the basis that the samples employed by Markham and Laidler were not sufficiently conductive. No H_2O_2 or H_2 , for that matter, could be detected

in the present study with unreduced TiO_2 . Calvert et al.^{3c} also report that H_2 could not be detected in irradiated O_2 -free ZnO /water suspensions. The reason for this observation is not presently clear but may well be linked to the closed nature of their reaction system and the rather stringent requirements imposed therein on the sensitivity of the H_2 detection system. (These authors employed a mass-spectrometric procedure for their analysis. We believe that our gas chromatographic system is more sensitive to H_2 at the concentration levels that are commonly encountered in these studies.)

The results obtain in the present study are compelling proof for the existence of a direct correlation between photoelectrochemical processes on semiconducting electrodes and the corresponding photo-synthetic reactions on the same materials in granular form. Such a correlation, however, hinges to a large extent on the relative positions of the semiconductor band edges and the energy levels corresponding to the individual local cell (redox) reactions. For the water-splitting reaction, the semiconductor conduction and valence band edges (E_{CB} and E_{VB} respectively) should ideally straddle the levels corresponding to the half-reaction:¹¹

For reaction (6), the interfacial energetics will have to be such that the conduction and valence band edges straddle respectively, the level corresponding to reaction (7) i.e. H^+/H_2 redox energy and the $\text{O}_2/\text{H}_2\text{O}_2$

redox level. It is pertinent to note that the above criterion will hold independent of the pH of the reaction medium since the band-edges and the redox levels move in a manner relative to each other on the pH scale. The apparently facile production of H_2 that was observed for rutile electrodes in PEC cells where a small bias is required to sustain H_2 evolution.² This bias is necessitated by the fact that the H^+/H_2 equilibrium potential lies slightly negative of the flat-band potential, V_{fb} ($V_{fb} \approx E_{CB}/e_0$ for heavily doped material) for rutile. The anatase form of TiO_2 , however, has a slightly larger energy band-gap (E_g) than rutile ($E_g = 3.23$ vs 3.02 eV, respectively).¹¹ This would presumably shift the flat-band potential in a more negative direction with the result that E_{CB} now becomes more negative than the H^+/H_2 level. An X-ray diffractogram of the TiO_2 samples that were used for the experiments revealed the material to be a mixture of both rutile and anatase forms. The interfacial energetics is illustrated in Figure 10 for both TiO_2 (anatase and rutile) and ZnO . The energetics are shown for the case where no band-bending exists at the grain/liquid interface. Data for construction of the band-edges for TiO_2 and ZnO and the various energy levels were obtained from references 11 and 12. Several features of the energy diagram are worthy of note: (i) The conduction band-edge for ZnO overlaps the H^+/H_2 energy level unlike in the case of TiO_2 (rutile). (ii) Oxidation of water can proceed on TiO_2 since the O_2/H_2O level (c.f. reaction (8)) is negative with respect to E_{VB} . (iii) The O_2/H_2O_2 level is also negative with respect to E_{VB} for TiO_2 ; photosynthesis of H_2O_2 is therefore thermodynamically feasible. (iv) Both the O_2/H_2O and O_2/H_2O_2 levels lie negative of the decomposition Fermi energy, E_D for TiO_2 .

Reactions (6) and (8) therefore will occur more readily than corrosion of TiO_2 for kinetic reasons which have been discussed by Gerischer.^{12a}

(v) Although the $\text{O}_2/\text{H}_2\text{O}_2$ and $\text{O}_2/\text{H}_2\text{O}$ levels are negative with respect to E_{VB} for ZnO , the decomposition Fermi energy also lies more negative than the corresponding level for TiO_2 with the result that corrosion reactions become more important for this material.

The above predictions are consistent with the findings of the present study. While corrosion of ZnO cannot be unequivocally proved by the present results, two findings are relevant in this regard: (i) A gradual decay in the rate of H_2 evolution was observed for ZnO but not for TiO_2 , (compare Figure 6a and Figure 7), and (ii) an infra-red spectrum of the material after the irradiation experiments and subsequent drying at $\sim 110^\circ\text{C}$ showed intense bands corresponding to OH^- groups. These bands were virtually absent in the spectra for the starting material and for material kept in contact with water for approximately the same period as the irradiation experiments and subsequently dried. These results are consistent with a corrosion reaction of the type:

The Fermi energy level corresponding to this reaction has been calculated by Gerischer^{12b} and is shown in Figure 10. Photocorrosion reactions of the type represented by equation (9) could account for the complex trends in the dependence of H_2 evolution rate on the mass of ZnO (c.f. Figure 6b). We postulate the following sequence of processes to explain photosynthetic production of H_2 and H_2O_2 on TiO_2 and ZnO . Many features in the proposed mechanism are common to the scheme previously described by Harbour and Hair for ZnO .^{3h} Light of energy greater than the band-

Figure 10 Semiconductor band energies and solution redox levels for reduction of H^+ ions, oxidation of OH^- ions and reduction of O_2 .

All energies are referred to the electrochemical energy scale (Normal Hydrogen Electrode). Decomposition Fermi energies for ZnO and TiO₂ are also shown and the data are those calculated by Gerischer (reference 12a,b). The band positions and redox levels are adjusted for pH = 7.

gap of the oxide creates electron-hole pairs. For n-type semiconductors, the interfacial energetics are such that the bands are bent upward; holes therefore move to the grain surface where they are available for oxidation reactions and electrons move to the bulk of the grain.

Therefore, the various steps in the sequence will consist of:

followed by reaction (4) and

The subscript "s" above denotes a surface adsorbed state. Evidence for formation of O_2^- and HO_2^1 radicals is found in a recent study by Harbour and Hair.^{3h} The reduction reactions represented by (11) and (13) could be mediated through surface states in the band-gap of the material. In fact, recent work on the chemisorption of O_2 on TiO_2 reports evidence for the transfer of electrons from the conduction band of TiO_2 to absorbed O_2 to create a chemisorbed O_2^- state.¹³ The formation of such a state could introduce a level with the band-gap of the host material. Additional source of surface states would be defects which are preponderant in polycrystalline materials such as the samples employed in the present study. The oxygen required for the formation of H_2O_2 by reaction (14) is provided either by reaction (8) or externally e.g. by bubbling O_2 through the reaction mixture. The reduction process represented in equation (7) also effectively competes with reaction (11) and (13) for the photogenerated electrons. Photogenerated

electrons. Photocorrosion reactions (e.g. reaction 9), particularly in the case of ZnO, compete with reaction (8) for the photo-generated holes in the semiconductor.

The data shown in Figure 9b on the gradual decay in the rate of H_2O_2 production on TiO_2 are similar to the results obtained by previous workers on ZnO.^{3a,3d} This fall-off in rate merely reflects the increased contribution from back-reactions of the type:

The saturation observed in the rate of H_2O_2 and H_2 production as a function of TiO_2 content (Figure 4) is probably related to factors originating from surface coverage limitations at high levels of solid content. More work is needed to unravel the origin of this effect.

Back-reactions of the type represented by equation (15) and radical reactions such as:

become especially important in the photosynthetic mode. A clear advantage of PEC cells in this regard lies in an efficient means of separating the reaction products, i.e., oxidation and reduction reactions are carried out at different sites (at the photoanode and counter-electrode respectively for the case of semiconducting electrodes) rather than on the same grain as in the case of the photosynthetic mode. Other loss mechanisms such as recombination of photogenerated carriers also become more predominant in the photosynthetic mode particularly because

a field-assisted means of separating the carriers (e.g., by means of an external bias) does not readily exist unlike in the case of PEC cells. Partial metallization of the semiconducting grains would, however, serve to reduce recombination losses in the bulk.¹² This approach has worked well with other photocatalytic and photosynthetic reactions on TiO_2 and SrTiO_3 .¹⁴ Work is continuing in this laboratory on the effect of metallization on H_2O_2 and H_2 yields utilizing various semiconducting materials.

3.3. X-RAY ASSISTED DESULFURIZATION OF COAL

As outlined in the experimental section, the sulfur recovered from the model compound was monitored as H_2S in the exit gas stream from the reaction chamber. No attempt was made in these proof-of-concept experiments to measure the total amount of sulfur removed from the compound (i.e. both as H_2S and as soluble sulfur which would presumably remain in the solution phase).

The results are shown in Table 3. From the data shown in this table, we note a tenfold increase in the formation of H_2S in the presence of the irradiated solid catalyst. We interpret these results in terms of the following reaction sequence:

Table 3: γ -ray desulfurization of model sulfur compounds

Compound	Mass (gm)	Sulfur Content (gm)	SiO ₂ (gm)	irradiation Time (hr)	Sulfur recovered (gm)	Sulfur recovered %
NH ₂ (CH ₂) ₂ SH	3.7	1.5376	0	24	.00122	0.079
NH ₂ (CH ₂) ₂ SH	3.7	1.5376	0.75	24	0.01276	0.82
C ₆ H ₅ SH	3.3	0.989	0	24	0	0
C ₆ H ₅ SH	3.3	0.989	0.37	24	0.0079	0.80
CH ₃ SSCH ₃	4.04	2.75	0	24	0	0
CH ₃ SSCH ₃	4.04	2.75	0.75	24	0.03	1.11

The principle underlying the desulfurization scheme is similar is that outlined above for γ -ray photolysis of water. The emitted photon serves to impart sufficient energy to break the organic-sulfur bonds in the compound. Organic sulfur in coal occurs mainly as R-SH, R-S-R, R-S-S-R, and Ar-SH linkages. Bond energies of C-S, S-H, and S-S bonds are 175, 82.2 and 101.9 k cal/mol respectively. Since an energy of ~ 230 kcal is available in SiO_2 the emitted photons will have energies well in excess of those corresponding to the C-S, S-H, and S-S bonds. Direct fragmentation of Sulfide linkages by γ -ray also occurred, as shown by the control experiments

in Table 3. These processes are attributed to the direct generation to free radicals by gamma-ray impact (c.f. . .).

3.4 Gamma-Ray Photovoltaic Cells

The possibility of generating electricity by gamma-ray irradiation of solid-state solar cells was checked on p-Si/SiO₂/indium Tin Oxide devices. These solar cells were 250 μ thick. Currents of the order of 5 to 10 microamperes and photovoltages in the range of 10-15 millivolts were observed. The levels of power conversion are low, but considering the incident flux (10^{14} photons/sec), the resulting current densities were respectable for the devices used. The electron-hole pairs generated by gamma-ray photons apparently behave similarly to the solar photon. Increased, or multiplicative quantum yields due to gamma irradiation were not observed. Further work is necessary to design a gamma-cell that can efficiently generate electricity. A wide gap semiconductor with a reasonable diffusion length seems best since the bandgap will be 5 orders of magnitude over the proton energy. For example, if our source were charged to 5000 curies and Cds instead of silicon was used, power outputs of 1 mA at 300mV are possible, or $1/3 \text{ mW/cm}^2$. Because the irradiation is continuous, this would be roughly equivalent to $1/3 \times 6$ or 2.0 mW/cm^2 . These power levels are somewhat low by photovoltaic standards, but perhaps useful if a gamma-ray reactor waste system can be configured in an optimum way. Also, the efficiency noted above is a "guesstimate" and should not be taken as a fundamental limit on this type of device. Efficient equivalent solar conversion of 10 mW/cm^2 of electrode is not to be ruled out on the basis of these data. Also, since gamma-irradiation causes degradation of solar cells, a requirement

of periodic or continual annealing of this damage must be established before gamma-voltaic conversion can have commercial feasibility.

4. SUMMARY AND CONCLUSIONS

- 1) The feasibility of generating H_2 from water using radioactive wastes in the presence of solid catalysis is demonstrated by the results obtained in the present study.
- 2) The drastic improvement noted in H_2 in the presence of the solid catalyst provides a compelling argument for the heterogeneous catalysis mechanism proposed for the photolytic reaction.
- 3) No evidence for H_2O_2 was found in the case of the gamma-ray photolytic reaction. This behavior contrasts that observed for UV photolysis of water where significant amounts of H_2O_2 were observed in addition to H_2 .
- 4) The present experiments have shown for the first time that H_2 generation can be sustained on UV irradiated ZnO/water suspensions. Photosynthesis of both H_2 and H_2O_2 has been demonstrated in UV-irradiated TiO_2 /water suspensions. Previous authors were unable to find evidence for H_2O_2 formation in irradiated suspensions of TiO_2 . These results have implications in the possibility of storing solar energy by mediating appropriate redox processes at the semiconductor/solution interphase.
- 5) The concept of gamma-ray assisted desulfurization of coal by heterogeneous catalysis and radiological degradation of polymeric sulfur is demonstrated by proof-of-concept experiments on model sulfur compounds. A tenfold increase in conversion of indigenous sulfur to H_2S was noted in the presence of SiO_2 in gamma-ray irradiated alcohol and water suspensions. A reaction scheme is proposed to explain the results. The mechanism is shown to be similar

to the reaction pathways postulated for the gamma-ray photolysis of water.

6) A general conclusion from the present research is that radioactive wastes may be utilized in a constructive manner in the production and processing of fuels.

5. RECOMMENDATIONS FOR FUTURE WORK

The present study has identified at least two major areas where further research may be of particular relevance to the utilization of radioactive wastes. First, the mechanistic aspects of the gamma-ray photolysis of water need to be understood. Specifically, identification of the radicals formed in intermediate steps in the overall reaction sequence, is critical to confirm the reaction schemes postulated in the present report. Spin-trapping techniques and subsequent identification by ESR may prove useful. Second, the desulfurization reaction needs to be characterized in more detail. The effects of variables such as temperature, pH, catalyst content, and gamma-ray irradiation dose (time) need to be further explored. Intensity is a critical variable since desulfurization depends upon chain cleavage radical formation and bond reforming. Thus, increased intensity would have an "autocatalytic" effect through a free radical density which increases as the square root of the intensity. In the experiments demonstrated in this report, only the effluent H_2S was monitored. It is entirely possible that a substantial fraction of the sulfur in the parent compound would have been solubilized as elemental sulfur. Analysis of the solution in the reaction vessel is necessary to obtain a complete material balance. These experiments would further enhance the relevance of the present results for practical applications.

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