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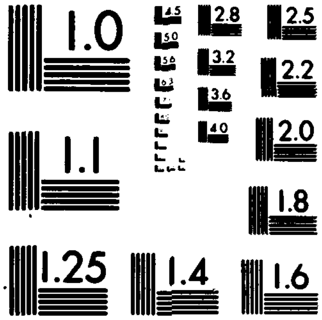

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Photocatalytic Production of Hydrogen from Water and Texas Lignite using a Platinized Titania Catalyst

by

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Photocatalytic Production of Hydrogen from Water and Texas Lignite using a Platinized Titania Catalyst[a]

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Abstract

Using a physical mixture of powdered Texas lignite and platinized titania in the presence of water vapor and ultraviolet light, we show that a catalytic reaction occurs at 23°C to form hydrogen and carbon dioxide. These results are contrasted with a recent electrochemical conversion process.

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I. Introduction.

The conversion of solar energy into chemical energy is a topic of considerable current interest particularly as it has an impact on fuel production and conversion utilizing readily available raw materials. Considerable work has been done on the photo-driven decomposition of water and the notable success of photoelectrochemical cells in achieving this end has recently been reviewed (Maruska and Ghosh, 1978). We have recently reported a photocatalytic system, illuminated platinized titania, which functions at 23°C and in the absence of external potentials, as an ordinary heterogeneous catalyst for the reactions of gaseous water with hydrocarbons, active carbon and carbon monoxide (Sato and White, 1980 a,b). A similar system, using gas or liquid phase water, RuO_2/TiO_2, and light, has also been reported (Kawai and Sakata, 1979a,b). These results extend the interesting work on liquid phase photocatalytic reactions that has been reviewed (Bard, 1979). For example, using platinized titania, liquid phase acetic acid can be converted to methane (Kraeutler and Bard, 1978a). A general review of heterogeneous photocatalysis has also appeared recently (Formenti and Teichner, 1979).

As compared to photoelectrochemical systems, heterogeneous catalyst systems do offer several advantages: (1) they are generally simpler to construct and are less expensive, (2) a wider variety of materials in different forms can be used, (3) because of diffuse light scattering by powders, more efficient light utilization can be achieved, (4) the reactants can be in the gas, liquid or solid phase and (5) a wider range of temperatures are feasible when using gas and/or solid phase reactants. Because of these advantages, heterogeneous photocatalytic systems deserve attention as potential solar-to-chemical energy converters.

Such systems would be helpful in the utilization of lignites. Many processes have been and are under study. For example, an interesting electrochemical process which converts coal and water into hydrogen and carbon oxides, mainly CO_2 has recently been reported (Coughlin and Farooque, 1979). This system operates at electrical potentials significantly lower than the thermodynamic potential of water electrolysis because the oxidation of carbon is claimed. Moreover, they found that lignite and char are more easily oxidized anodically than parent coals. We report here another process producing hydrogen and carbon dioxide from lignite and water vapor in which light, but no electrical power, is used.

II. Experimental.

TiO_2 (anatase) was obtained from MCB, pretreated for 6 hr at 700°C in flowing H_2, cooled in hydrogen and stored in a sample vial. Samples of this material were platinized (2 wt. % Pt) by the photolysis at 55°C of a hexachloroplatinic acid solution containing suspended TiO_2 powder (Kraeutler and Bard, 1978b). After photolysis the sample was washed with distilled water until Cl^- could not be detected. It was then dried in a desiccator until used. The BET surface area, determined using N_2, was 11 $m^2 gm^{-1}$.

Texas lignite, containing 64% C, 17% O, 5% H, 1% N, 0.1% S and small amounts of metals, (Edgar, 1979) was ground in a mortar (estimated average particle size $\simeq$100 μm) and physically mixed (20 wt.%) with the catalyst. A 0.25 gm sample of this mixture was spread uniformly on the bottom flat window of a quartz reaction cell and connected into an evacuable, closed circulation system (180 cm^3). This assembly was linked to a mass spectrometer for product analysis. Distilled water, outgassed several times at dry ice temperature, was stored in a tube on the vacuum line.

After outgassing the sample for 3 hrs. at 200°C, it was cooled to 23°C and approximately 24 torr of water was added. This system was illuminated with a 200w high pressure mercury arc that was filtered through a $NiSO_4$ solution to remove most of the infrared light. Small aliquots of the gas phase were taken at various times and, after passage through a cold trap (about -110°C) to remove water, were analyzed with the mass spectrometer.

III. Results.

Figure 1 shows a typical time evolution of products. The rate of hydrogen production over the first twenty minutes is about 2×10^{-2} torr min^{-1} but this drops to a nearly constant value of 9×10^{-3} torr min^{-1} over the subsequent eighty minutes. The other major product was CO_2 and over the time interval 20-100 min, the ratio H_2/CO_2 drops slowly from 2.75 to 2.55. Minor amounts of O_2 and CH_4 were also found; after 100 min, $p_{O_2} = 10^{-3}$ torr and $p_{CH_4} = 6 \times 10^{-3}$ torr. No other products were detected, in particular H_2S was not produced from sulfur impurities in the lignite. The hydrogen formation rate and its time dependence compares favorably with that observed in the active carbon reaction. For example, at 100 min. the H_2 rate in the active carbon reaction is 7×10^{-3} torr min^{-1} However, no oxygen was detected and the H_2/CO ratio was very nearly 2 in the latter (Sato and White, 1980). Here the ratio is greater than two probably because hydrogen in the lignite is partly converted to H_2.

Significantly, the catalyst only slowly lost its activity during repeated runs involving system evacuation followed by restoration of the water pressure. Irradiation of Pt/TiO_2 in the absence of lignite produced limited amounts of H_2($<10^{-1}$ torr) over extended periods. This was accompanied by even smaller amounts of CO_2 but no oxygen was observed. These products are thought to arise from the oxidation of residual carbon on the catalyst. It is also of interest to consider whether the observed H_2 could arise from the non-catalytic reaction of surface hydroxyl groups present on the TiO_2. According to the literature (Boonstra and Mutsaers, 1975) the number of OH groups on both anatase and rutile declines with increasing outgassing temperature. Based on their results, we estimate a surface hydroxide concentration of less than 2×10^{18} m^{-2}.

If all these were converted to hydrogen then we would expect to produce less than 0.5 torr of H_2. Figure 1 shows that 1.2 torr of hydrogen is produced in 110 min with no evidence of a rapidly declining rate. Moreover, eight hours of production time (see below) involved in Fig. 2 and the rate is never less than 0.75×10^{-2} torr min^{-1}. The total H_2 production over this period is thus greater than 3.6 torr. From these results we conclude that surface hydroxide initially present on these TiO_2 samples can not account for the observed amounts of hydrogen.

Figure 2 shows the H_2 formation rate and the O_2 pressure as a function of reaction time for six consecutive experiments involving the same catalyst/lignite sample. Between each experiment, the system was evacuated, treated in some way and the water pressure restored. Prior to experiments (1) and (4) the sample was treated by outgassing for 3 hr at 200°C. Prior to the other four experiments the sample was outgassed at 23°C for 10 min. The dotted line in Fig. 2 connects the initial rates for the six experiments and shows that the activity declines with use and is not fully reactivated by outgassing at either 23 or 200°C. During the course of a single run the activity drops rapidly over the first twenty minutes and then declines much more slowly (as in Fig. 1). This trend is followed in each of the six experiments. After one hour into experiment 5, the temperature was raised from 23 to 60°C. This gave no increase in rate over a time interval of 30 min.

In the lower part of Fig. 2, the O_2 pressure as a function of time is shown for each experiment. In general these results show (1) that the oxygen accumulation rate increases with the number of experiments that involve outgassing at 23°C, (2) that outgassing at 200°C reduces the subsequent oxygen production rate, (3) that oxygen accumulation is limited and in some cases goes through a maximum and (4) that increasing the temperature accelerates the rate of oxygen removal.

IV. Discussion.

The data shown in Figs. 1 and 2 clearly demonstrate the photocatalytic reaction of water and lignite to produce hydrogen and carbon dioxide. The thermodynamics of this process are not known since the lignite is not well-characterized chemically. Based on the thermodynamics of solid carbon, ethane, ethylene and other small C,H molecules we expect $\Delta G^o > 0$. Thus, through the use of light we have successfully driven this thermally uphill reaction and have done so in a catalytic sense.

The quantum efficiency, although it could be improved with a different cell design, is not high. Assuming an upper limit of 10^{17} photons sec^{-1} irradiate the catalyst, based on HI actinometry and thermopile measurements (White, 1966), then the H_2 production rate of 9×10^{-3} torr min^{-1} corresponds to a quantum yeild of 0.01. The energy efficiency, that is the net increase in energy stored per unit of light energy input, is estimated as 0.0003 assuming conservatively that the free energy increase per mole of H_2 formed is 10 kJ $mole^{-1}$. This calculation is based on the conversion of olefinic material (Sato and White, 1980).

The results reported here can be compared qualitatively with electrochemical conversions (Coughlin and Farooque, 1979). These authors observed a gradual decrease of the reaction rate in their coal-water process which they ascribed to the accumulation of surface functional groups, such as carboxyl groups, on coal. They also found that the initial high anodic current could be regained if the coal was removed from the electrolyte (after the current had decreased to low value), heated to about 200°C, and then returned to the system. In our process, however, an outgassing treatment of the sample at 200°C had no effect on the reaction rate (see Run 4 in Fig. 2). The temperature dependence of the H_2 production was also slight as seen from the last part of Run 5 in Fig. 2. The apparent activation energy in the electrochemical experiments was 40-48 kJ mole^{-1} and that in the RuO_2/TiO_2 system was also significant (Kawai and Sakata, 1979). In a separate experiment we outgassed a sample at 60°C and then measured the reaction rate at 60°C. The rate was somewhat less than observed at 23°C.

The O_2 data are very interesting because they indicate that the Pt is covered by some species which inhibits (poisons) the reaction of O_2 and H_2 on Pt. In the absence of poisoning the back reaction with oxygen is far faster than the O_2 formation rate (Sato and White, 1979a). These results are distinct from those on active carbon (Sato,and White, 1979b) where no O_2 was observed. Perhaps sulfur accumulates at Pt as the reaction proceeds and allows the accumulation of oxygen. Heating to 200°C may cause the migration or desorption of this sulfur-containing species and subsequently the clean Pt serves to suppress O_2 formation.

The mechanism of the reaction can not be established from the data reported here. However, our other work (Sato and White, 1979) makes it clear that band gap radiation is involved so we conclude, as expected, that the incident photons activate the catalyst by forming electron-hole pairs near the surface. Due to band bending, the hole will stay at (or migrate to) the surface while the electron will move away from the surface and eventually arrive at a neighboring Pt particle.One possible product formation mechanism involves the interaction of water with holes at TiO_2 sites to form O(a) and/or OH(a) wit

concomitant formation of H^+ which moves to a neighboring Pt site where it picks up an electron and is recombined to form H_2. The active oxygen species are used to oxidize carbon which is in contact with the catalyst; the products expected are CO_2 and H_2O.

A mechanism involving desorbed gas phase O_2 reacting with lignite can be ruled out because CO_2 production was very slow in systems where the catalyst/lignite mixture was illuminated in the presence of O_2. An additional comment on the mechanism can be made on the basis of the following experiment. The addition of 0.3 torr of ^{13}CO to the catalyst/lignite/water system reduced the rate of H_2 production by about a factor of 2 and the water-gas shift reaction took place at about 20% of the rate of H_2 production. This result indicates an inhibitory effect of CO probably because H_2 recombination on Pt is retarded by adsorbed CO. During this experiment there was no significant dilution of ^{13}CO with ^{12}CO (i.e. insignificant isotope exchange) and no O_2 was formed.

The relatively rapid decrease of the H_2 production rate at the beginning of a reaction is not understood. Perhaps as H_2 accumulates, back reactions with oxygen species formed on TiO_2 become relatively more important. Other possibilities include inhibitory effects of traces of CO formed in the reaction or the loss of excellent contact between lignite and catalyst particles. Interestingly, the H_2 formation does increase with the lignite/catalyst ratio; a 20% increase was noted when the weight ratio was doubled from 0.1 to 0.2. This observation points to the real possibility of substantially improving the efficiency. Because of its importance as a fuel, the formation of CH_4 (6×10^{-3} torr at 100 min, Fig. 1) is of interest in spite of the fact that the yield is small. Repeated experiments, as in Fig. 2, were characterized by a rapid decrease in the rate of CH_4 production. Moreover, these rates were not affected by the addition of CO_2 (55 torr) to the system thus eliminating the possibility that CH_4 arises from hydrogenation of CO_2. One possible mechanism involves the contact of lignite particles with Pt sites where hydrogenation can occur. If this conjecture has any merit, then the rate of CH_4 formation could be improved by modifying the catalyst-lignite contact.

V. Summary and Conclusions.

The results of these experiments demonstrate that lignite coal and gas phase water can be catalytically converted to CO_2 and H_2 over a Pt/TiO_2 catalyst illuminated with band-gap light. Significantly, the reaction occurs readily at 23°C. The quantum efficiency is only about 0.01 but can be significantly improved through the use of a different reactor design and through changes in the lignite/catalyst ratio.

The success of these experiments, coupled with the electrochemical results (Coughlin and Farooque, 1979) which demonstrate hydrogen production rates at oxidation potentials well below one volt, suggests that narrower band gap semiconductors that are doped with transition metals offer some promise as catalysts for the gasification of lignite. Hopefully, by using gaseous water some of the semiconductor decomposition and oxidation problems encountered in photoelectrochemical cells can be avoided.

Acknowledgement

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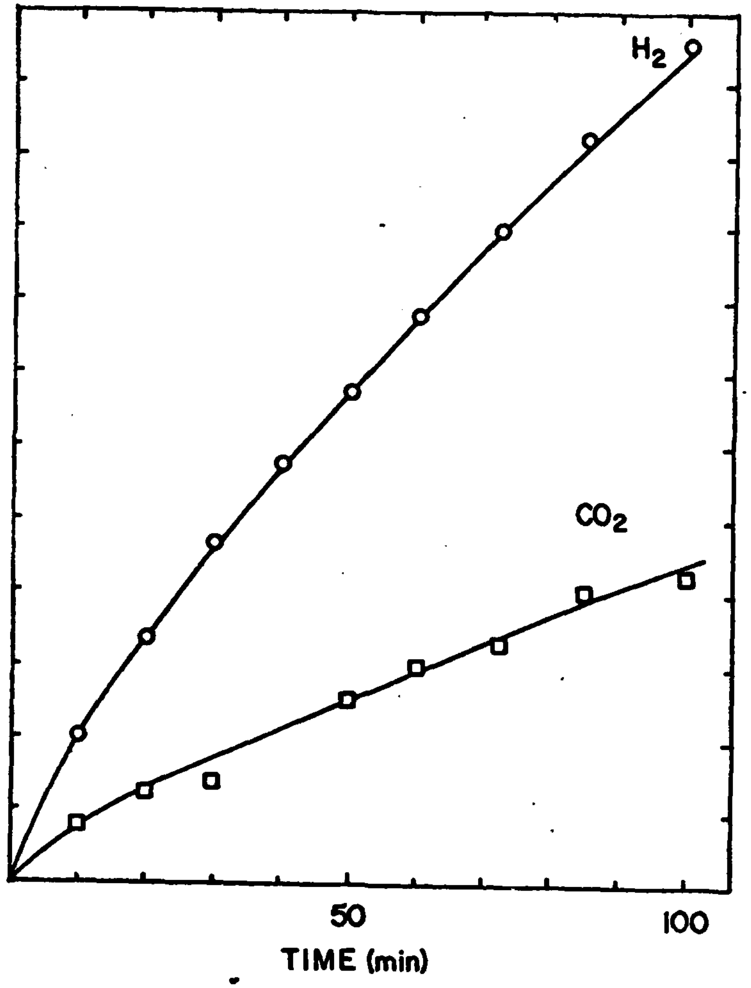
Figure Captions

Figure 1

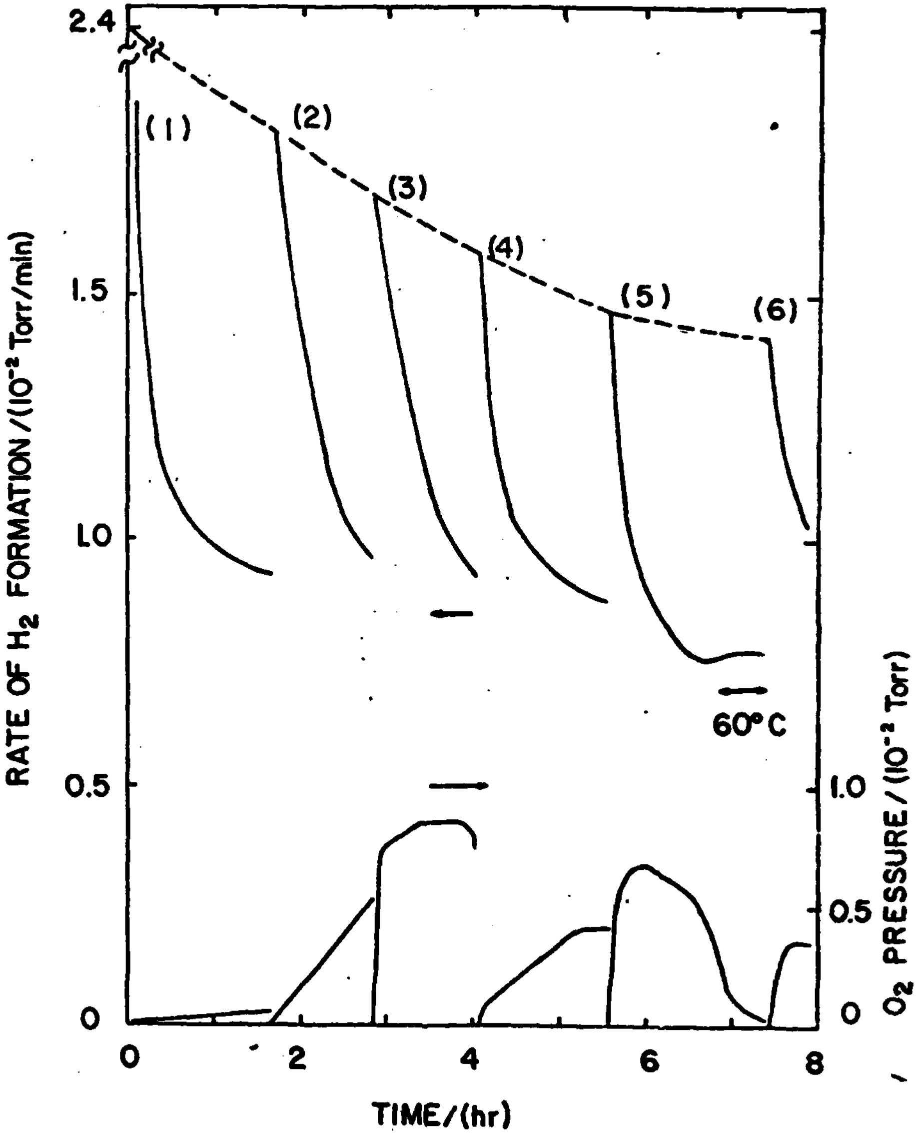
Photocatalytic production of H_2 and CO_2 from gaseous H_2O and Texas lignite by Pt/TiO_2.

Figure 2

Changes in the rate of H_2 formation (upper) and the pressure of O_2 (below) during the reaction of Texas lignite with gaseous H_2O over UV-illuminated Pt/TiO_2. The products were evacuated at 23°C for 10 minutes before each run except runs 1 and 4, in which cases evacuation was at 200°C for 3 hr. Notice that in run 5, there is a segment during which the temperature was 60°C. The H_2 production rates are scaled on the left-hand ordinate while the oxygen pressures are on the right.



Sato and White, Fig. 1



Sato and White, Fig. 2

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