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Photoassisted Reactions on Doped Metal Oxide Particles
by
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Photoassisted Reactions on Doped Metal Oxide Particles(a)

Abstract

Photoassisted reactions involving doped metal oxide semiconductor powders are reviewed. The mechanisms, insofar as they are now understood, are discussed for several reactions involving gas phase water near its equilibrium vapor pressure in contact with the oxide. Experimental results are presented along with some discussion of how these processes may be involved in heterogeneous processes in the atmosphere.

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1. Introduction

Solid state photochemistry and photophysics have been studied for a very long time. One outstanding example is the photographic process. The study of gas-solid and liquid-solid photoassisted processes is being pursued with renewed vigor today and must be considered as one of the very exciting topics of surface science and catalysis. Interest has developed along several fronts; one of the significant historical markers is the report in 1972 by Fujishima and Honda (1) that water can be decomposed to H_2 and O_2 in a photoelectrochemical cell using a Pt cathode and an irradiated TiO_2 anode. Prior to that, a significant amount of work on heterogeneous photocatalysis at the gas-solid interface had been reported. Much of this work, and some closely related work, has been recently reviewed (2-4). Reviews of photoelectrochemistry (5-7) and the surface science of irradiated surfaces (8) have also appeared and a recent symposium (9) dealt with interfacial photoprocesses. These, and several other reports from across the international scientific community, indicate a surge in activity, not unlike the chemical activity we hope to see at an irradiated interface. My own interest dates to the mid-sixties when, in the course of a photochemical hot hydrogen atom gas phase reaction study (10), I noticed some interesting iodine atom storage properties of Teflon. This, along with reports that CO could be photodesorbed from nickel surfaces, led to our first work on photo-effects at the gas-solid interface; J. W. McAllister showed that the cross-section for direct photodesorption of CO from polycrystalline nickel was less than 10^{-23} cm^2 (11). In other words, thermal effects

are responsible for most of the observed desorption. To follow up this work, I proposed to study photoassisted reactions on small oxide particles as models for atmospheric reactions. This proposal met with unenthusiastic (i.e. zero) support so we turned to more fashionable topics keeping heterogeneous photoreactions on the "back burner" until about three years ago when Dr. Shinri Sato from the Catalysis Institute at Hokkaido joined our research group and set out to search for gas phase analogs of what had been observed in photoelectrochemistry. Much of the work discussed here is due to Sato.

The purpose of this paper is to review briefly the present status of our research on photoassisted reactions at the gas-solid interface. There are a number of very interesting papers in the literature on this topic; only a few of them are mentioned here.

II. General Considerations

With the possible exception of the conversion of methanol to formaldehyde over silver (12), photoassisted heterogeneous catalytic reactions involve ~~semiconducting metal oxides~~ ^{compound semiconductors} and band gap irradiation.

Figure 1 shows the essential features for an n-type semiconducting oxide like TiO_2 . Absorption of a photon excites an electron from the filled valence band into the conduction band. As shown in the figure, the bands will typically bend upwards at the interface between the n-type semiconductor and either a metal (Schottky diode junction) or an electrolyte. The presence of this electrical field causes spatial separation of the electron in the conduction band and the hole in the valence band. As a result, two excited and charged species exist with which charge transfer (redox) chemistry can be carried out. Although band bending is well established for many systems, the situation is not so clear for small metal oxide particles with or without even smaller metal particles present on their surfaces. In fact, and particularly under illumination, the bands may be nearly flat. Under such conditions electron-hole recombination will compete more favorably with charge transfer reaction channels and, like many of life's experiences, there is more heat produced than chemistry. This does not mean that charge transfer reactions will not occur; it does mean that they must proceed rapidly to be competitive.

The charge transfer reactions will involve oxidation and reduction components and, energetically, the levels of the oxidant and reductant must be appropriately placed with respect to the bands of the solid. Figure 2 shows the proper placement; the oxidation step involves a level placed above the top of the valence band

while the reduction step involves a level lying below the bottom of the conduction band.

Figure 3 shows the actual situation for several compound semiconductors as it relates to charge transfer reactions leading to the decomposition of water into hydrogen and oxygen. The more stable materials, ZnO , TiO_2 , WO_3 and SnO_2 , all have band gaps which are much larger than the 1.23 eV needed to meet the thermodynamic requirements of the water decomposition reaction. The problem is that the potential of the H^+/H_2 reduction reaction lies above the bottom of the conduction band so that electron transfer from this band through the interface to reduce a proton is not very probable and the overall rate will drop to an insignificantly low value. Other materials which have narrower band gaps (which would allow better utilization of the solar spectrum) and proper placement of the bands on the redox energy scale, for example, CdS and CdSe , typically corrode. That is, the lattice is itself reacted away through redox processes involving the cations and ~~anions~~ ^{anions} of the lattice. In photoelectrochemical cells, the problem with the placement of the bands can be overcome by using an external power supply to bias the semiconductor with respect to the redox levels of interest. In the case of TiO_2 , such a bias allows the photoassisted decomposition of water (1).

In examining Fig. 3, it is important to keep in mind that some of these compounds exist in more than one crystalline form and these may have different band gaps. For example, TiO_2 exists in two forms, anatase and rutile. The gap for rutile is shown in Fig. 3 and there

is some evidence that anatase has a slightly lower gap with the bottom of the valence band lying above the H^+/H potential (13) which makes the water decomposition reaction thermodynamically feasible.

Of course, the number of compound semiconductors is large and their properties can not be reviewed in detail here. Table 1, taken from ref. 14, lists those that have been studied in photo-electrochemistry. Iron oxide, with a band gap of 2.0 ± 0.1 eV may be a compound of interest in atmospheric processes. Its conduction band is located at too low a voltage for the water decomposition reaction. However, many other reactions, particularly those involving oxidation of carbon sources, might occur on irradiated iron oxide. Even if the iron oxide is destroyed in the process, so that reactions become heterogeneous stoichiometric processes, as opposed to heterogeneous catalytic processes, the source of the iron oxide will keep its concentration at a steady-state value. The same considerations will apply to other particulates in the atmosphere.

This discussion has focussed on compound semiconductors. Charge transfer reactions on metals are unlikely because the lifetimes of metal excited states are too short to allow chemical reactions to become competitive. Photoassisted reactions could occur by direct excitation of an adsorbed or gas phase species which then reacts or decays through surface interactions. This topic lies outside the scope of this report.

Whether photoassisted heterogeneous reactions are catalytic or stoichiometric is a very important question, particularly if the goal is catalytic production of some product--for example, the

oxidation of solid carbon sources to form carbon dioxide. This problem has been discussed in a paper by Childs and Ollis (15). Establishing photocatalytic activity requires that the measured turnover number per active surface sight be greater than unity.

Since there is no unambiguous method for measuring the number of active sites at a metal oxide surface, estimates must be made and these must be used cautiously. As pointed out by Childs and Ollis (15), a calculated turnover number of 100 is certainly preferable to unity. A number of complications must be considered in demonstrating that more than a stoichiometric reaction is being studied. As one example, consider studies involving TiO_2 substrates. Typically, these substrates are partially reduced prior to their use. The reduction leads to oxygen vacancies and Ti^{3+} species at ^{the} surface and in the sub-surface region. There is considerable evidence to suggest that Ti^{3+} is intimately involved in photodriven processes (6). How should we determine the concentration of these species to be used in turnover number calculations? If those Ti^{3+} species located in the first few layers of the solid participate, then the number of moles of product produced must exceed the total Ti^{3+} concentration, not just the surface Ti^{3+} , before a nonstoichiometric reaction can be unambiguously demonstrated.

III. Experimental

All of the experimental work reported here

was carried out in a glass high vacuum system which contained a sample loop shown in Fig. 4. The sample loop had a volume of 180 cc and was designed so that gases were circulated through the loop by the circulating pump labelled CP. The catalyst, consisting of a fine powder, was placed in the bottom of a quartz reaction vessel labelled RC. Light from a 200 watt high pressure mercury arc lamp which is rich in ultraviolet and visible radiation, was passed through a filter containing nickel sulfate to take out the infrared and was reflected off the mirror into the reaction cell. The reaction cell itself was dipped in a constant temperature bath of water. This constant temperature bath and thermal conduction by means of the gas phase assured that the input energy did not overly heat the solid. Water vapor was stored in a degasable tube and connected into the circulation system through valves as shown in the upper right hand part of the figure. To work with gas phase water this valve assembly was simply opened momentarily and the vapor pressure of water was allowed to expand into the circulation system. When we worked with liquid phase water the reaction cell temperature was lowered to 0°C with an ice bath, the water vessel was opened and vapor was condensed into the reaction cell. Once the reaction had started, samples were periodically taken into the small space between the two valves shown at the lower left part of the figure. Expansion from this small volume into the trap, where water vapor was removed by a suitable liquid nitrogen bath or other cold temperature sources, was used to

prepare the sample for analysis by the mass spectrometer shown schematically at the far left. A typical experiment took several hours so the samples were taken periodically, say at the rate of no more than 1 every 10 minutes.

The powder was typically about 0.25 gram of finely divided and platinized titanium dioxide prepared by following a photochemical method, developed at the University of Texas by Professor Bard and his coworkers (16). It consists of first doping aratase by heating in flowing hydrogen at 700°C for six hours, ~~then heating at 700°C for six hours~~. Once this doped TiO_2 has been prepared it can be stored rather indefinitely and then used to prepare the platinized titanium dioxide. This is achieved by the photodecomposition of chloroplatinic acid in an acetate buffer solution. Temperature of the reaction is 55°C and nitrogen is bubbled through the solution. After a certain irradiation time the material is filtered, carefully washed and the platinized titanium dioxide is then dried. The total BET surface area was typically $11 \text{ m}^2/\text{gm}$ and the Pt composition was typically 2 wt. %. Other preparation procedures were sometimes used; they will be described, as necessary, in the following text.

IV. Photoassisted hydrogen production from titania and water (17).

Schrauzer and Guth (18) concluded that water adsorbed on TiO_2 or Fe_2O_3 -doped TiO_2 was catalytically photolyzed in their system, whereas Van Darme and Hall (19), on the basis of finding only a trace of H_2 , concluded that H_2 formation arose from the non-catalytic photodecomposition of hydroxyl groups originally present on TiO_2 . Kawai and Sakata (20), on the other hand, found that D_2 was formed in the dark when gaseous D_2O was contacted with TiO_2 reduced by CO under UV irradiation. The evolution of D_2 was accelerated by illumination and continued even after evacuating D_2O , but no O_2 was observed. The acceleration was ascribed to the photodecomposition of D_2O over TiO_2 on the assumption that oxygen formed was held at the TiO_2 surface. This assumption is based on the fact that O_2 as well as H_2 was formed by the addition of RuO_2 , a good electrode material for O_2 evolution, to TiO_2 . Rao et al. (21) have recently reported that H_2 and H_2O_2 are produced when reduced TiO_2 (in flowing H_2 for 6 hr at $700-800^\circ\text{C}$) is suspended in liquid water and illuminated in bubbling N_2 . Unreduced TiO_2 produces neither H_2 nor H_2O_2 . We have investigated the activity of reduced anatase for water decomposition (17) and find evidence for a stoichiometric reaction involving oxygen defects.

For these experiments, reduced TiO_2 (0.25g) was spread on the flat bottom of a quartz reaction cell and outgassed at 200°C for 3 hr. After introducing water vapor at room temperature, the sample was illuminated by a 200 W high-pressure Hg lamp and the products were analyzed by a mass spectrometer.

In every case studied, only H_2 was observed in the gas phase and its formation rate dropped to almost zero after a few hrs of illumination. The maximum amount of H_2 formed increased with the reduction temperature and time and it was larger for H_2 -reduced TiO_2 than for CO -reduced samples prepared under the same conditions. The results described below were obtained for H_2 -reduced TiO_2 . For substrates reduced at temperatures above 700°C , H_2 was formed even in the dark in agreement with Kawai and Sakata (20) but its formation stopped within 30 min. When D_2O instead of H_2O was used, the products were dominated by D_2 . Since the amount of H_2 formed did not exceed the value expected from the isotopic purity of D_2O , the hydrogen evolved is believed to come from water added and not from pre-existing surface hydroxyl groups. Support for this also comes from the facts that no increase in HD was observed when D_2 (0.12 Torr) was added to the H_2O reduced TiO_2 system under illumination and that no products were formed when TiO_2 samples were illuminated in vacuo.

Light of energy less than the band gap of TiO_2 produced no H_2 , suggesting that photogenerated electrons and/or holes play an important role. The addition of O_2 (3.2×10^{-3} Torr) completely inhibited H_2 formation and its pressure dropped by a factor of 2 after 1 hr. of illumination. The addition of ^{13}CO (0.25 Torr), on the other hand, had no effect and no $^{13}\text{CO}_2$ was observed. This is significant since CO is oxidized over TiO_2 in the presence of band gap light and oxygen. We find that H_2 is also formed when reduced TiO_2 samples are heated in gaseous water at temperatures higher

than 200°C.

When reduced TiO_2 was immersed in liquid water and illuminated, the amount of H_2 formed was larger than observed in the gas phase process. The liquid water- TiO_2 system was prepared by cooling the bottom of the reactor cell to 0°C in order to cryogenically pump water from the reservoir to the cell. After the sample was covered with 0.2-0.3 ml of water, the cell was warmed to $\approx 23^\circ\text{C}$ and then illuminated. The results are shown in Fig. 5 for variously reduced TiO_2 samples. Just as in the gas phase process, the H_2 evolution rate dropped to zero after a few hrs. and no O_2 was detected. The TiO_2 sample reduced at 750°C for 4 hr. produced 1.3×10^{-2} Torr ($0.13 \mu\text{mole}$) of H_2 in the dark (the pressure at time zero of curve (a) in Fig. 1 is due to this) and H_2 formation was accelerated by illumination.

Although the formation of H_2O_2 was not checked in our experiments, its concentration is limited by photodecomposition to O_2 and H_2O over TiO_2 . Rao et al. (21) observed that the addition of H_2O_2 ($5 \mu\text{mole}$) to their reaction mixture (700 ml) followed by 1 hr. of illumination brought about a two-fold decrease in the H_2O_2 concentration. This implies that the maximum achievable concentration of H_2O_2 over illuminated TiO_2 is very low, less than $4 \mu\text{mole/l}$. Applying this to our system, $1 \times 10^{-3} \mu\text{mole}$, at most, of H_2O_2 could exist in the water. This is much less than the amount of H_2 formed ($0.1 \mu\text{mole}$).

All of these results are consistent with a mechanism in which a reaction between H_2O and oxygen vacancies of reduced TiO_2 is

photoassisted by the production of electron-hole pairs in the solid. This reaction is thermodynamically downhill and not catalytic. In the process proposed here, water reacts slowly with surface oxygen vacancies to evolve H_2 and remove the vacancies by filling them with oxygen or hydroxyl species. This non-catalytic process is significantly accelerated by band gap irradiation. Bulk oxygen vacancies are retained during the photoprocess. Experimental support for this proposal comes from isotope tracing, the effects of reduction temperature and time, and the effects of added O_2 and CO . In the photoprocess, photogenerated holes probably oxidize water to produce some oxygen containing species which react with the oxygen vacancies at the surface.

The fact that TiO_2 alone is inactive for water photolysis can be described, as discussed earlier, in terms of the energy band diagram of illuminated TiO_2 (22). According to a recent study (13) in this area, the flat band potential (electron Fermi level) of TiO_2 (rutile) is about 100 mV more negative than the H^+/H_2 redox potential. This implies that the water photolysis in PEC cells with a TiO_2 photoanode is energetically possible under open circuit conditions. However, there are some potential drops, for example, across the Helmholtz layer, so that the overvoltage available for H_2 evolution becomes lower. Even if anatase has a somewhat more negative flat band potential than rutile, the overvoltage would be too low for efficient evolution of H_2 at the TiO_2 surface (23). Similar overvoltage requirements

for the reduction of protons are found with SrTiO_3 (24). Consequently, these semiconductor catalysts show increased photocatalytic activity for water decomposition when a material, such as Pt, is added which readily evolves H_2 at a lower overvoltage.

V. The Photocatalytic Reaction of Water with Carbon over Platinized Titania

Platinized titania has been used in a large number of photo-assisted reactions (22-30). One of our more detailed studies involved active charcoal and Texas lignite (31, 32). The general conclusion is that solid, liquid and gas phase carbon-hydrogen sources with water as a co-reactant can be converted into CO_2 and H_2 when platinized titania is irradiated. We have not achieved partial oxidation, for example, to CO , but there is one such report using solid carbon with a $\text{RuO}_2/\text{TiO}_2$ semiconductor powder (33).

In these experiments, active charcoal (U.S. Biochemical Co., 0.05g) and Pt/TiO_2 (0.2g) were physically mixed and the mixture was spread uniformly on the flat bottom of a quartz reaction cell. The cell was then connected to the circulation system and the sample was outgassed at 200°C for 2 hrs. before introducing water vapor and starting the reaction.

Figure 6 shows the evolution of H_2 and CO_2 when the sample at room temperature was illuminated by UV light. Small amounts of O_2 and CH_4 ($<10^{-2}$ torr) were the only other products detected. Five repetitions are shown and in each the reaction was repeated after evacuating the reaction system in the dark for 15 min. at the reaction temperature to check reproducibility. Both H_2 and CO_2 formation became slower with time in every run; for example, in the first run the H_2 formation rate dropped from 0.6 Torr/hr. (1.8×10^{-4} mole/hr.) initially to 0.4 Torr/hr. after 2 hr.-illumination. The initial rate of H_2 formation, however, was reproduced

in the second and third runs. During the third run the reaction temperature was raised to 60°C to measure the temperature dependence. The H_2 formation rate increased by a factor of 2.5 from which the activation energy is estimated to be 5 kcal/mole. This rate was reproduced in the fourth run. Returning the cell to room temperature for run 5, the initial rate of H_2 formation was significantly lower and was not restored by outgassing the sample at 200°C . The sample was taken out after the H_2 formation rate had dropped to 0.2 Torr/hr. physically remixed and returned to the reaction cell. The reaction rate was fully restored by this procedure. Therefore, the observed decrease in the rate was not due to intrinsic activity loss but probably due to a decrease in the contact area between the carbon particles and the oxidation sites of the catalyst.

By stoichiometry ($\text{C} + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{CO}_2$) the H_2/CO_2 ratio should be 2, but was always larger for the five runs of Fig. 1. The ratio in the initial stage of the first run, is less than 2, due to CO_2 desorption from the solid. The formation of O_2 can not account for an H_2/CO_2 ratio greater than 2 because it is formed in such small amounts (less than 10^{-2} Torr).

The relative excess of H_2 probably arises because some oxygenated reaction intermediates accumulate on the sample surface. Support for this comes from the fact that an appreciable amount of CO_2 desorbed when the sample was heated to 200°C after the reaction. During heating, CO_2 desorption maximized between room temperature and 80°C , and again increased at temperatures above 120°C . The CO_2 desorption above 120°C may be the result of the decomposition

of reaction intermediates such as carboxyl or the reaction of adsorbed oxygen with carbon. The desorption of H_2 was also observed but in amounts much less than CO_2 .

As shown in Fig. 7, we observed a decrease in the H_2 pressure, when the UV-illumination was stopped during the reaction at room temperature. The sample was outgassed at $200^\circ C$ prior to this experiment to remove adsorbed species accumulated in the preceding runs. The loss of H_2 is thought to arise mainly by its reaction with adsorbed oxygen species located on TiO_2 and carbon. Adsorption of H_2 may also be involved but only to a small extent since very little H_2 was noted in subsequent thermal desorption. The H_2/CO_2 ratio fell below 2 in the first dark period (Fig. 7) probably because of some H_2 adsorption. However, in the second dark period where the reaction proceeded further, the ratio approached 2 but would have fallen slightly below it had the dark period been extended. These results suggest that, in the dark, the H_2/CO_2 ratio would attain the stoichiometric value under conditions where H_2 adsorption can be neglected.

The formation of O_2 during the reaction is tiny but thought to be important because it indicates that the photodecomposition of H_2O may play an important role in the present system. The amount of O_2 formed tends to increase with repetition of the reaction but never exceeds 1×10^{-2} Torr under the conditions of Fig. 6. When the light is turned off, O_2 disappears promptly from the gas phase as shown in Fig. 7.

In this connection the reactivity of gas phase O_2 was examined

in the absence of H_2O and under illumination. The pressure decrease of O_2 was very slow in the dark and increased somewhat upon illumination, but no appreciable amount of CO_2 was formed (see Fig. 6).

After introducing H_2O into the system, the O_2 pressure fell rather sharply to below 10^{-2} Torr and CO_2 appeared in the gas phase. This result shows that gas phase O_2 alone is much less active for the oxidation of carbon than oxygen species produced by the photodecomposition of H_2O . The rapid decrease in the O_2 pressure after introducing H_2O is probably due to its reaction with H_2 formed in the reaction of H_2O with carbon.

The formation of CH_4 was small. It accumulated to a pressure of 6×10^{-4} Torr during the first run with a fresh catalyst but, after a few hours of illumination, its formation rate dropped to zero.

Although no appreciable CO was observed in the reaction products, adsorbed CO is one of the most probable intermediates of the present reaction. In this connection the effect of the presence of CO on the reaction rate was examined using ^{13}CO to discriminate the products. The water-gas shift reaction, $^{13}CO + H_2O \rightarrow ^{13}CO_2 + H_2$, took place simultaneously with the oxidation of carbon, but H_2 formation was considerably suppressed as compared to that observed in the absence of CO . After the CO pressure fell to about 1×10^{-2} Torr, H_2 formation accelerated, indicating the inhibitory effect of CO . At the same time, the O_2 pressure abruptly increased and then slowly decreased to expected values. We have observed similar phenomena in the photoassisted water-gas shift reaction over Pt/TiO_2 (34).

It is still not clear from this result whether adsorbed CO is an intermediate in the carbon/water reaction. However, it is worth noting that adsorbed CO formed in oxidizing carbon would be bound to a carbon particle and would not migrate to a Pt surface where CO inhibits the H_2 evolution (34).

The H_2 formation rate was only slightly dependent on H_2O pressure. Lowering the pressure from 24 to 5 Torr caused a rate increase of no more than 5%.

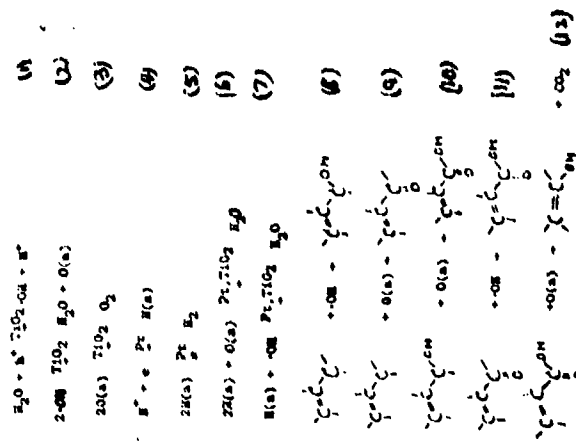
The wavelength dependence of the reaction rate was qualitatively measured using three cut-off filters (Fig. 9). A commercial UV cut-off filter (415 nm cut-off) and a Plexiglass filter (380 nm cut-off) completely eliminated H_2 formation, while a Pyrex glass filter (3275 nm cut-off) reduced its rate to about two thirds of that found with no filter. This measurement includes some experimental error because the reaction rate declines slowly even in the same run.

In another set of experiments, liquid H_2O was used instead of gas phase H_2O . The results are shown in Fig. 10. The formation of H_2 was much slower than in the reaction with gas phase H_2O , and O_2 exceeded CO_2 , indicating that the photodecomposition of H_2O dominates the reaction. The relatively rapid CO_2 formation at the beginning is probably just the desorption of CO_2 accumulated in the previous runs, since the H_2/O_2 ratio is nearly 2. The rate of product formation became faster after 1 hr. illumination for reasons which are not clear. We speculate that local warming by the UV light source may have caused some of the water to evaporate and allowed the rate to increase because the H_2 and O_2 could escape

more readily to the gas phase. No CO was detected in this reaction.

The reason why the oxidation of carbon is inhibited in liquid H_2O is not well understood. The liquid H_2O layer may retard the migration of adsorbed oxygen or hydroxyl radicals formed on TiO_2 to the carbon surface and as a result these species would become O_2 before oxidizing carbon.

Although the mechanism of the oxidation of active carbon is not clear, we assume it involves intermediates similar to those involved in the electrochemical oxidation of graphite electrodes, where hydroxyl, carbonyl and carboxyl groups are typical surface compounds proposed (35, 36). On the basis of the above discussion one mechanism describing the present system can be written as:



According to this mechanism, the surface of carbon would be covered with various oxides of carbon and adsorbed oxygen during the reaction at room temperature. Consequently the H_2/CO_2 ratio in gas phase would exceed the stoichiometric ratio. At 60°C the coverage of these surface species would be lower than at room temperature since they would be decomposed or oxidized effectively as the temperature is raised. Products other than H_2 and CO_2 , such as $HCOOH$ or $HCHO$, might be formed on the surface but would not appear at detectable levels in the gas phase since they would be rapidly oxidized.

The kinetics of the present reaction are similar to those of the photoassisted water-gas shift reaction over Pt/TiO_2 (34). The almost zero order dependence of the rate on H_2O pressure is the same as in the latter and the activation energy (≈ 5 kcal/mole) is close to 7.5 kcal/mole of the latter. As for the wavelength dependence, the present reaction shows a little shorter onset than the shift reaction, but the reason is not clear.

The decline of the H_2 formation rate in a given run is probably due to the accumulation of H_2 which competes with carbon for oxygen species. The long-term decline arises from the loss of a good contact between the catalyst and carbon since the initial reaction rate can be reproduced by remixing the sample.

The formation of O_2 increases with time but, in any run, its maximum amount is less than observed in the reaction with lignite (32). Although the reaction of H_2 with O_2 occurs rapidly on a clean Pt/TiO_2 even in the presence of gas phase H_2O (37), CO inhibits this reaction to some extent as observed in the water-gas shift reaction

(34). Since CO was not detected in the gas phase of the present reaction, its inhibitory effect is not established. Our results show that a decrease in the amount of adsorbed H_2O on the sample results in decrease in the O_2 pressure. Therefore, it is reasonable to assume that since active carbon adsorbs a large amount of H_2O , the H_2O layer on the Pt that is in contact with carbon thicker than in the absence of carbon. When the H_2O layer is thick, the surface reaction between H_2 and O_2 is inhibited. As the contact area between the catalyst and carbon decreases with the consumption of carbon, oxygen species would have to migrate longer distances to react with carbon; consequently, they would tend to desorb as O_2 .

Assuming, as an upper limit, a flux of 10^{17} photons/sec (32) with energy greater than the band gap energy of TiO_2 (≈ 3.0 eV), the quantum yield of the H_2 production is about 2% at the beginning of the reaction at room temperature and increases with increasing temperature.

VI. The Role of Surface Hydroxyl Groups.

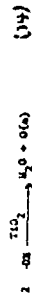
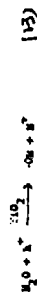
In photoassisted reactions involving water, surface hydroxyl groups are thought to play a central role. Their presence, state, reactivity and replaceability become important in any effort to characterize them. To date results are largely empirical. We have examined the water decomposition and water-gas shift reactions over NaOH-coated platinized TiO_2 (39). Very interesting related work on SrTiO_3 has been reported by Wagner and Somorjai (40).

Figure 11 shows the time evolution of the water decomposition reaction over 2 wt. % Pt on TiO_2 that was coated with 7 and 14 wt. % NaOH. Although gas phase water was introduced, the deliquescent nature of NaOH guarantees that the surface of the powders became wet in these experiments. Figure 11 shows that the initial rate is lower and the ~~photochemical rate~~ ^{rate} is both higher for the larger NaOH. Moreover, the dark back reaction is slowed down for the heavier loading. The reactions were both run at room temperature.

Figure 12 shows how the initial rate of H_2 formation varies with NaOH loading for three reactions, the water-gas shift (WGS), gas phase water decomposition (GWD) and liquid water decomposition (LWD) reactions. The difference in the GWD and LWD reactions is that, in the latter, 0.25 ml of water was condensed to cover the catalyst. A 1 wt. % NaOH loading makes a 0.25M solution. Interestingly, both the LWD and GWD rates are inhibited at high loadings of NaOH.

The mechanism of the water photolysis over Pt/ TiO_2 can be described in analogy with PEC cells. In an acidic solution, a suitable

mechanism is



In neutral and alkaline solution, instead of steps (13) and (16), use

$$\text{OH}^- + \text{h}^+ \xrightarrow{\text{TiO}_2} \cdot\text{OH} \quad (18)$$

$$\text{H}_2\text{O} + \text{h}^+ \xrightarrow{\text{Pt}} \text{H}(\cdot) + \text{OH}^- \quad (19)$$

where h^+ denotes a hole. In the photoassisted water-gas shift reaction, CO reacts with $\text{O}(\cdot)$ formed in step (14) to give CO_2 .

When water electrolysis (or photolysis) is carried out in neutral water, i.e. with no electrolyte, the diffusion of OH^- from cathode to anode would limit the reaction rate. In our other studies, (17, 25, 34, 37) the rates of most photoreactions over Pt/ TiO_2 , in which pure water was used, were temperature dependent (activation energy of 5-8 kcal/mole), while the rates of the GWD and the WGS reactions over illuminated NaOH/Pt/ TiO_2 are independent of temperature between 18 and 50° C. This difference in the temperature dependence leads us to suppose that the reactions involving pure water are rate-limited by the diffusion of OH^- from Pt to TiO_2 and the activation energy observed comes mainly from this diffusion step.

The water photolysis reaction over Pt/ TiO_2 catalysts competes with the thermal back reaction over Pt. Therefore the observed rate, v^{H_2} , of the H_2 formation is given by the equation,

$$v^{\text{H}_2} = 2v^{\text{O}_2} = v_p - v_t$$

where V_p is the rate of the photocatalytic production of H_2 and V_t the rate of the thermal back reaction. The rate V_p would be proportional to the intensity of light with energy greater than band gap energy and independent of the partial pressures of the products under the present experimental conditions. In alkaline solution V_p would be independent of temperature but would depend on the pH of the solution. In the GWD reaction over $NaOH/Pt/TiO_2$ the $NaOH$ coating somewhat reduces V_p while in the LWD reaction the water (solution) layer over the catalyst also limits the escape of the products to the gas phase. On the other hand, V_t is proportional to the Pt surface area and the product pressures, and is temperature dependent. The $NaOH$ coating and liquid water layers considerably suppress V_t .

In the GWD reaction over pure Pt/TiO_2 , neither H_2 nor O_2 are observed because the back reaction occurs even before the products desorb from the catalyst. The LWD reaction takes place because V_t is much suppressed by the water layer. However, V_t increases with product pressures so V_t decays with time and a photostationary state is eventually reached. The present experiments show that the GWD reaction becomes detectable even in the presence of Pt when Pt/TiO_2 is coated with more than 7 wt. % of $NaOH$. This apparently arises because V_p is enhanced by the addition of alkaline electrolyte while V_t is suppressed by the $NaOH$ coating. Increasing $NaOH$ above 7 wt. % gives rise to decreases in both V_p and V_t , but the former is less pronounced than the latter as seen from Fig. 11. As a result the maximum pressures of H_2 and O_2 increase. One may suppose here that the liquid electrolyte layer, formed by coating

the catalyst with a deliquescent material and exposing it to gas phase water, is essential to gaseous water photolysis. Although this deliquescent film is important, we find that gaseous water photolysis does occur over Pt/TiO_2 without such a coating. When the photodecomposition of NO over Pt/TiO_2 is carried out in the presence of gaseous water, H_2 , O_2 , N_2O and a small amount of N_2 are formed (41). Since no H_2 is produced in a control experiment involving no water, the product H_2 is attributed to water decomposition. The formation of O_2 during the water-gas shift reaction also gives another evidence for gaseous water photolysis.

In the WGS reaction V_t is very small since O_2 formed is removed by its reaction with CO to form CO_2 so that V^{H_2} remains constant until the CO pressure falls to about 0.05 Torr (see Fig. 3). The reaction of O_2 with CO , however, is suppressed to some extent when the $NaOH$ coating exceeds 7 wt. %.

Our results may be compared to those obtained by Wagner et al. (40) on single crystal (111) samples of platinized and metal-free $SrTiO_3$. Like our Pt/TiO_2 results, they found, on $Pt/SrTiO_3$, that a $NaOH$ film gave rise to the activity for gas phase water photolysis. As they properly point out the deliquescent character of $NaOH$ makes the surfaces wet in these experiments. Our results involving an aqueous solution of $NaOH$ differ from theirs in that we find a local maximum in the rate versus $NaOH$ concentration (around 2.5 M) whereas they find the rate increases throughout the range 0 - 20 M. Most significantly, they find catalytic activity on $NaOH$ -coated metal-free

SrTiO_3 while we find no activity for the analogous system based on powdered TiO_2 . Yoneyama et al. (42) have also reported the activity of SrTiO_3 powder when its aqueous suspension is illuminated by 1 KW Xe lamp. These results show that metal-free SrTiO_3 , unlike TiO_2 , is active in the photoassisted decomposition of H_2O . This property of SrTiO_3 may come from its higher flat band potential (i.e., 200 mV more negative than the H^+/H_2 potential (43)). Although the mechanism involved is not well understood, a part of SrTiO_3 surface could become the cathode while another part the photoanode. The photoactivity of powdered SrTiO_3 , however, seems to depend on its preparation method. In our preliminary experiments, powdered SrTiO_3 (Alfa) coated with NaOH showed no activity while platinized forms (with and without NaOH coating) were active.

VII. Summary.

These results may be summarized by the following points.

1. We conclude that there is no catalytic reaction of water with any form of titanium dioxide, doped or undoped, unless that titanium dioxide is mixed with some transition metal or other chemical component. This holds for both the gas phase and liquid phase water reactions.
2. In the case of platinized titanium dioxide, we find some photoassisted catalytic activity for water decomposition in the liquid phase. This activity occurs for both reduced and unreduced titanium dioxide but the rates are much higher when a reduced form of titanium dioxide is used. This enhancement may have to do with the increased ability of reduced titanium dioxide to transfer charge from one region to another because of its increased conductivity.
3. The water decomposition reaction cannot be detected over platinized titanium dioxide when gas phase water is used. We believe this is because of the back reaction of hydrogen and oxygen is so facile over platinum. It appears that the forward reaction to decompose water actually does take place.
4. The water-gas shift reaction, which in essence prevents the back reaction of hydrogen with oxygen, occurs readily and catalytically. Interesting effects of CO pressure at low values are observed which indicate that poisoning the Pt surface by small amounts of CO allows the forward reaction of water decomposition to occur to a slight extent.
5. Gas phase water also reacts with carbon sources, both gas

base and solid, to form carbon dioxide and hydrogen.

6. In both the water decomposition reaction and the water-gas shift reaction there is a definite wavelength dependence and a definite activation energy. The wavelength dependence indicates that this reaction depends on electron hole pair formation in titanium dioxide. The temperature dependence indicates that there is some kind of thermal barrier occurring with one of the photo-generated intermediates.

7. Adding sodium hydroxide as a coating or in solution, enhances the rate of the water decomposition reaction. This can be understood in terms of the ease with which the charge transfer reactions occur in such media.

8. A simple mechanism has been proposed which is analogous to the mechanisms that have been used in photoelectrochemical cells.

Some possible applications of these concepts to atmospheric processes have been mentioned in section II. In such, stoichiometric reactions may contribute as much as catalytic processes provided a source of particulates is available. Moreover, corrosive processes which plague many catalytic processes, and typically involve narrow band gap semiconductors, should be considered as likely candidates for photoassisted heterogeneous reactions. The particle size of the materials used in our studies have been between 100 and 250 μm diameter. However, much smaller particles are known to be active and use light much more efficiently than our results would indicate. For example, Gratzel and co-workers (44, 45) have shown that colloidal particles of bulk semiconductor powders are very active in water decomposition.

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Table 1. Band gaps and flat band potentials of oxide anodes

Material	Band Gap E_g (eV) (± 0.1 eV)	Flat band potential V_{fb} (V) (± 0.1 V)
SrO_2	3.5	0.5
ZrO_2	5.0	-1.0
Ca_2O_5	4.0	-0.4
Nb_2O_5	3.4	0.0
K_2TaO_3	3.5	-0.2
SrTiO_3	3.2	-0.2
BaTiO_3	3.1	0.15
TiO_2	2.9	0.2
VO_3	2.4	0.5
Fe_2O_3 1.5 W 0.5 O 6.5	2.4	0.4
CdO	2.1	0.8
CdFe_2O_4	2.3	0.8
Fe_2O_3	2.0	0.7
$\text{PbFe}_{12}\text{O}_{19}$	2.3	1.0
$\text{Hg}_2\text{Nb}_2\text{O}_7$	1.8	1.1
$\text{Hg}_2\text{Ta}_2\text{O}_7$	1.8	1.2

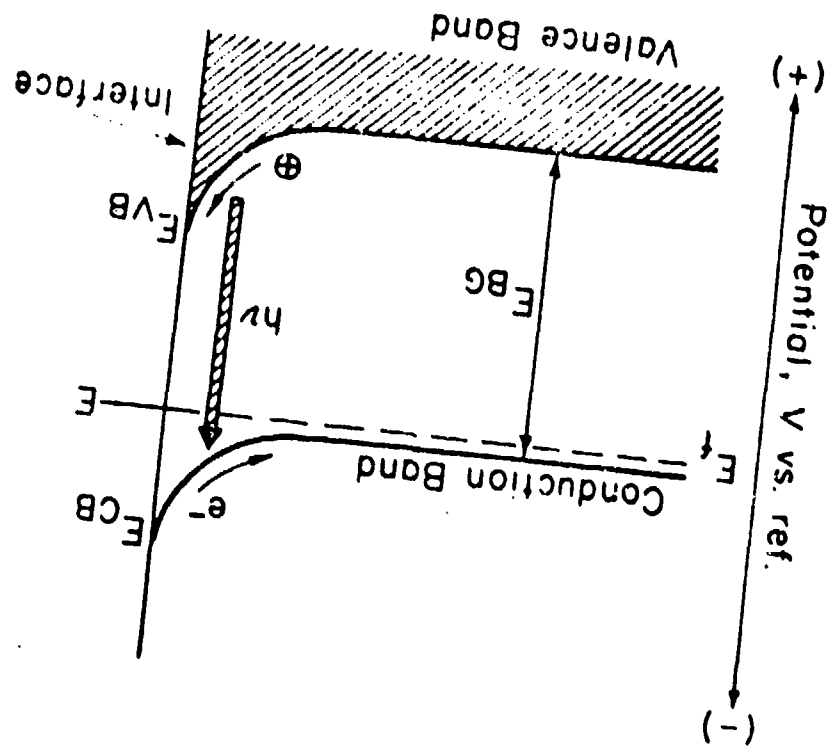
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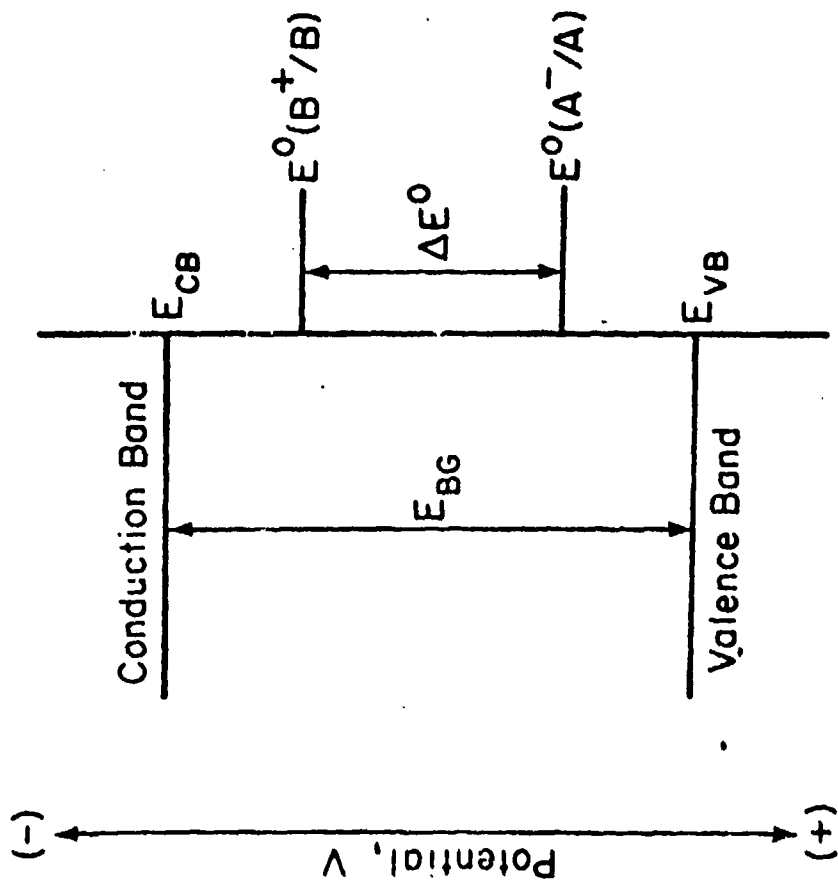
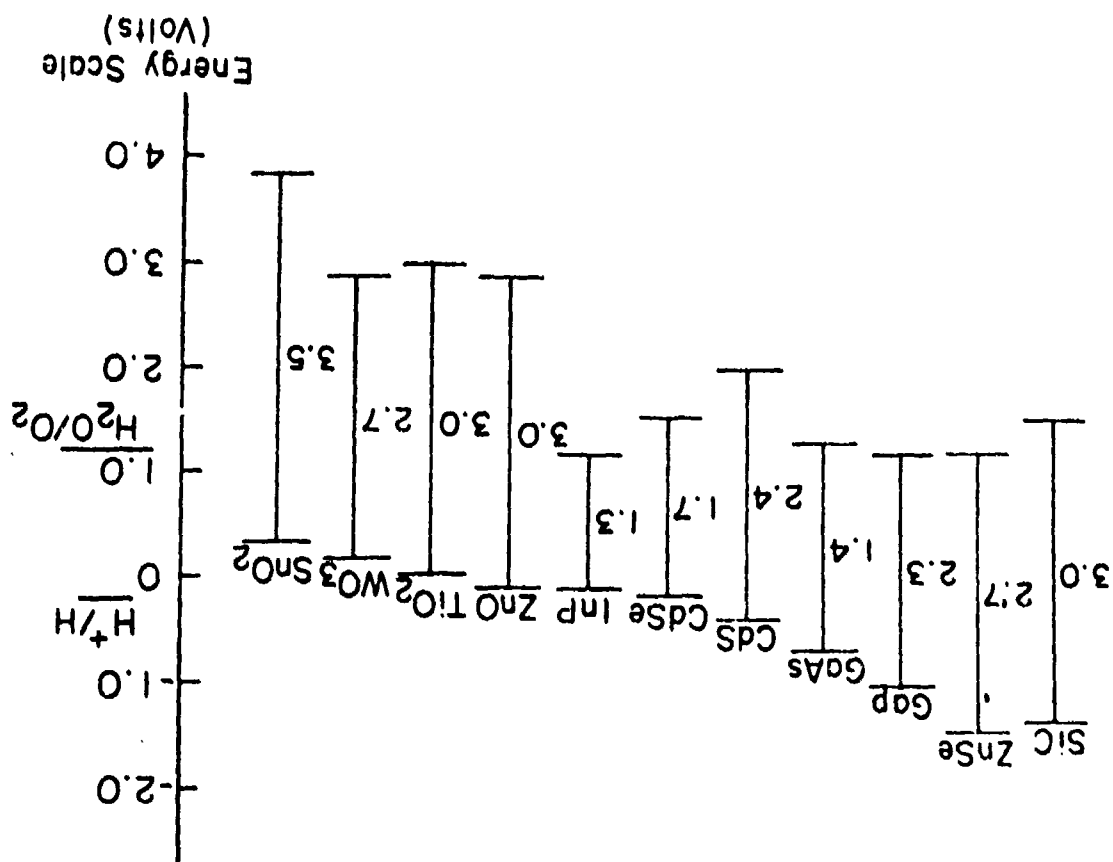
- Figure 1. Schematic energy level diagram for an n-type semiconductor surface.
- Figure 2. Energy level diagram showing desired placement of redox levels with respect to band gap in a semiconducting material.
- Figure 3. Band gap placement of several compound semiconductors with respect to the redox levels involved in water decomposition. Taken from ref. 6.
- Figure 4. Apparatus for studying photoassisted reactions involving H_2O and titania-based powders.
- Figure 5. Evolution of H_2 from illuminated, reduced TiO_2 immersed in liquid water: (a) TiO_2 reduced by H_2 at 750°C for 4 hrs. (b) at 700°C for 6 hrs. (c) at 600°C for 3 hrs. (0.1 Torr = $1\mu\text{mole}$).
- Figure 6. Evolution of H_2 and CO_2 when a mixture of active carbon and Pt/TiO_2 catalyst is illuminated at room temperature in the presence of gas phase H_2O . The reaction was repeated after evacuating the system briefly.
- Figure 7. Change of H_2/CO_2 ratio during the reaction of active carbon with gas phase H_2O .
- Figure 8. Change of O_2 pressure in the absence and the presence of gas phase H_2O over the illuminated active carbon Pt/TiO_2 mixture. H_2O ($\approx 2\%$ Torr) was introduced at 40 min.
- Figure 9. Effects of cut-off filters on the rate of H_2 formation.

Figure 10. Evolution of H_2 , O_2 and CO_2 when carbon, liquid H_2O and Pt/TiO_2 are illuminated.

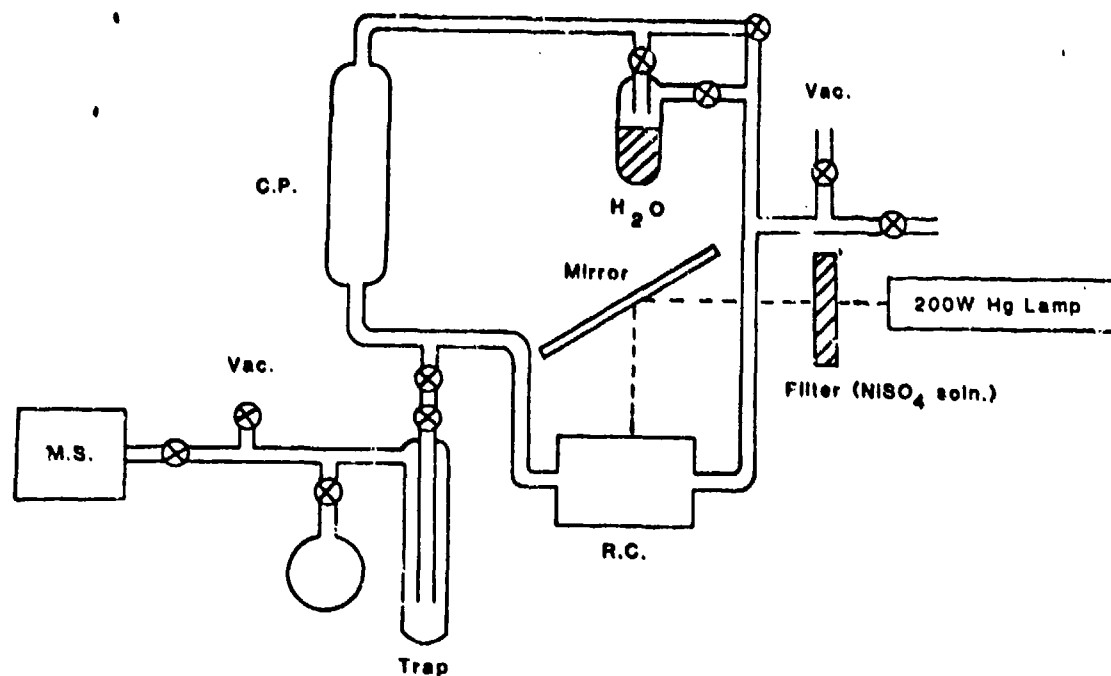
Figure 11. Time courses of the CWD reaction over illuminated $NaCH/Pt/TiO_2$ catalysts: (a) 7 wt. % $NaOH$; (b) 14 wt. % $NaOH$. H_2O pressure is ≈ 24 Torr and catalyst temperature is $25^\circ C$.

Figure 12. Initial H_2 formation rates, $V_0^{H_2}$, in the CWD (○), WGS (□) and LWD (●) reactions over illuminated Pt/TiO_2 as a function of $NaOH$ loading (See text for the definition of the abscissa for the LWD reaction).

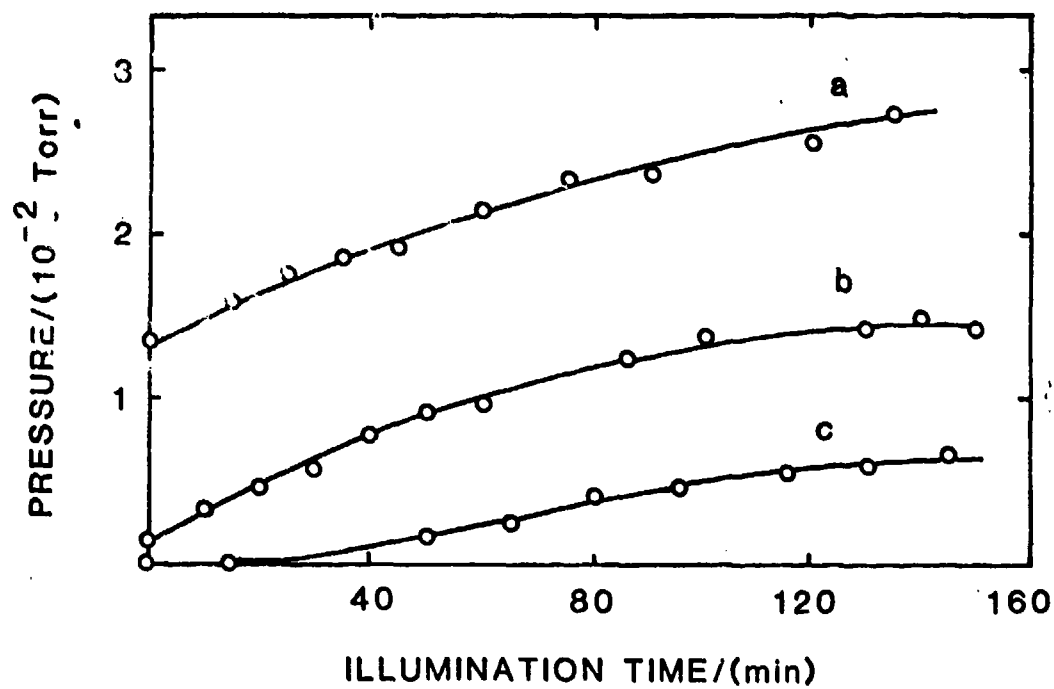




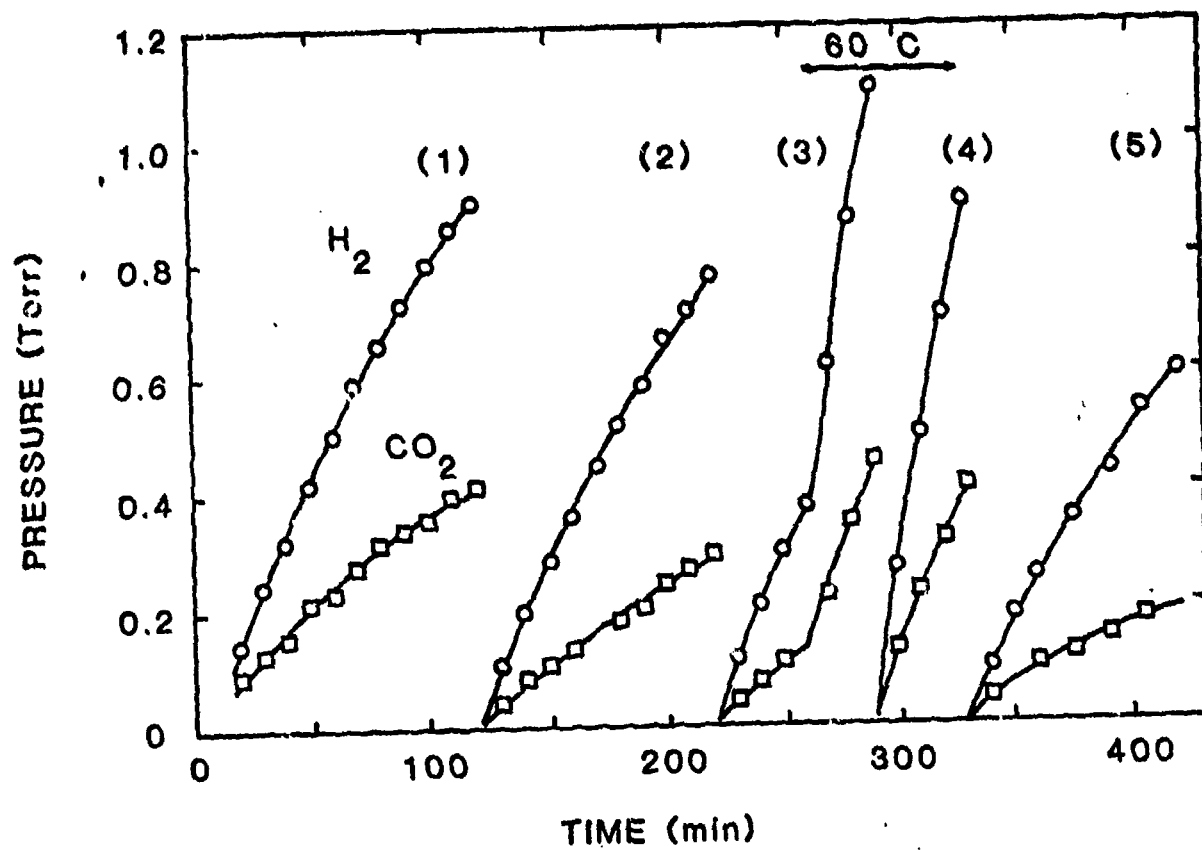
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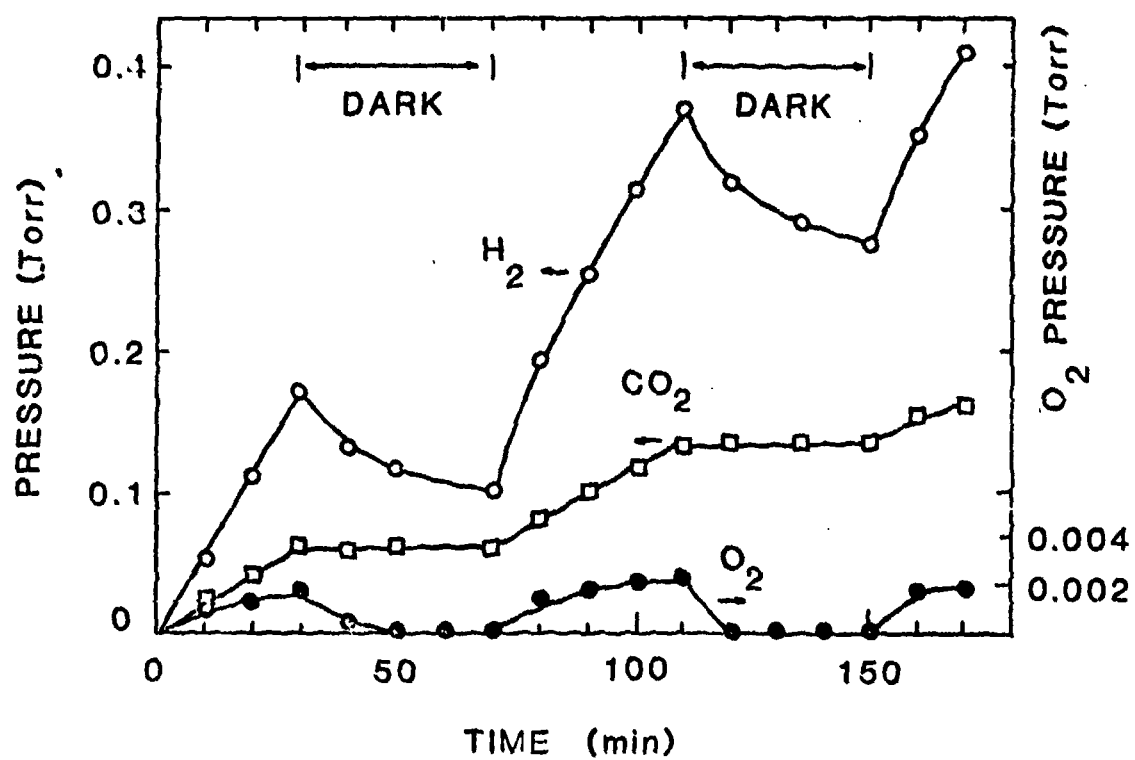
White Fig. 4



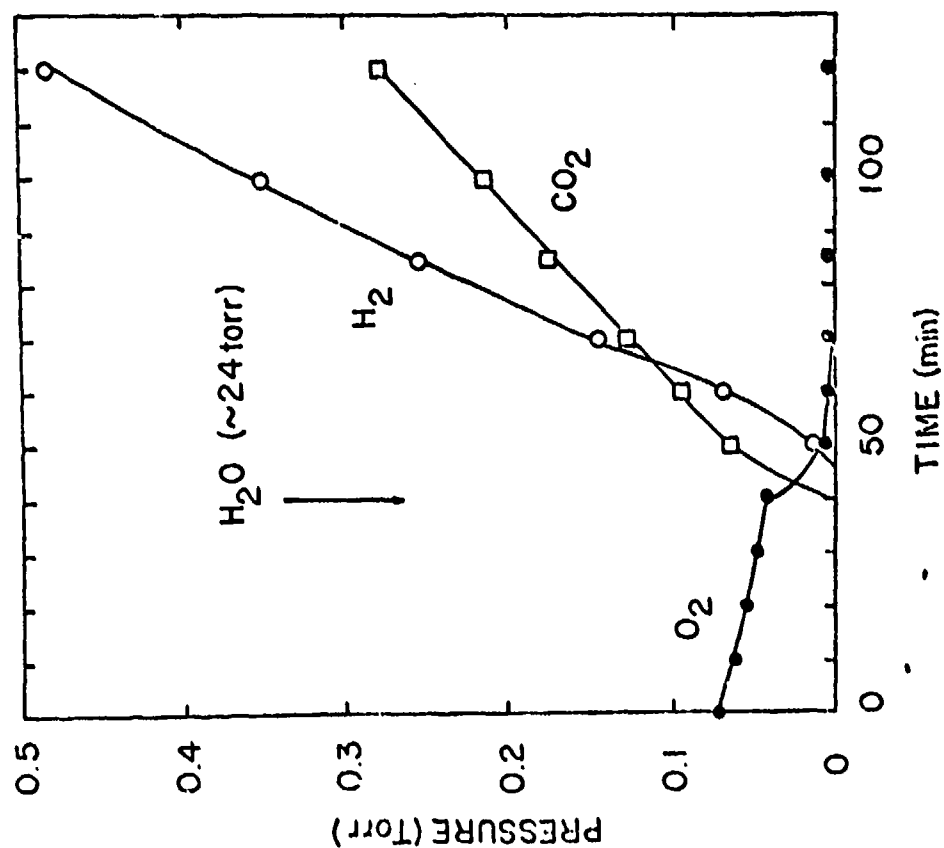
White Fig. 5



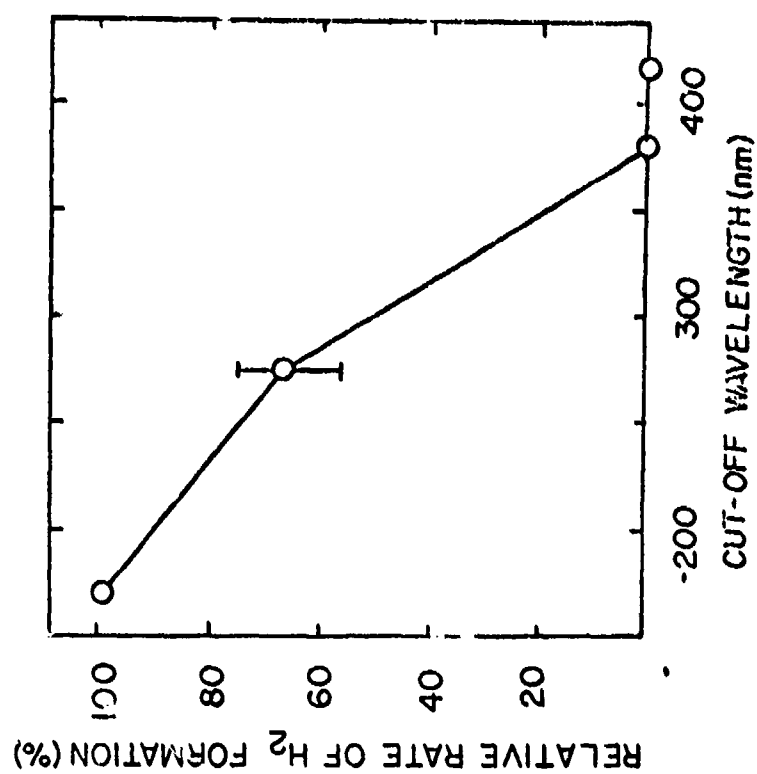
White Fig. 6



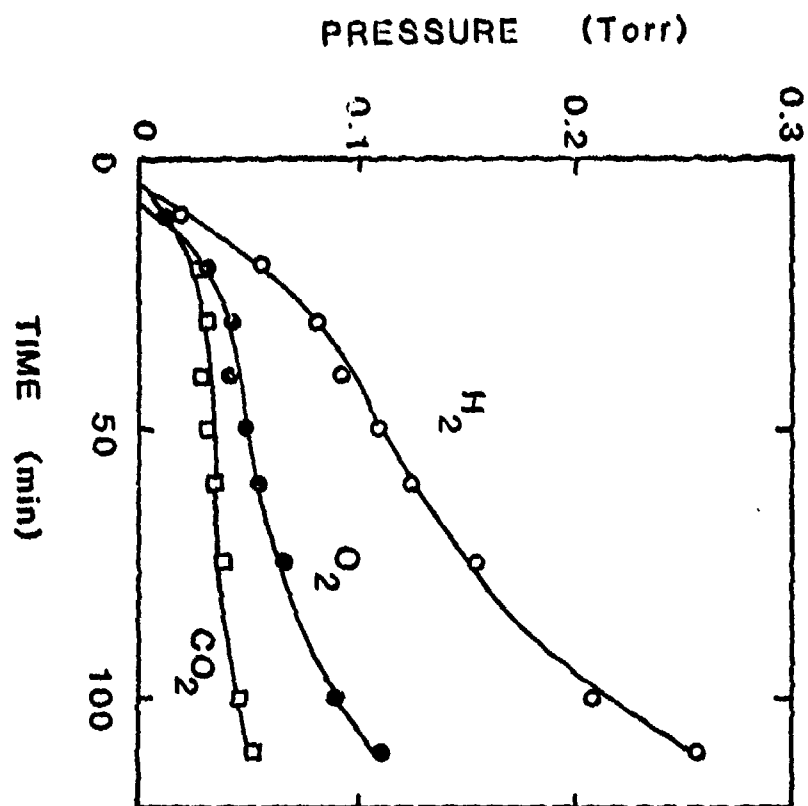
White Fig. 7



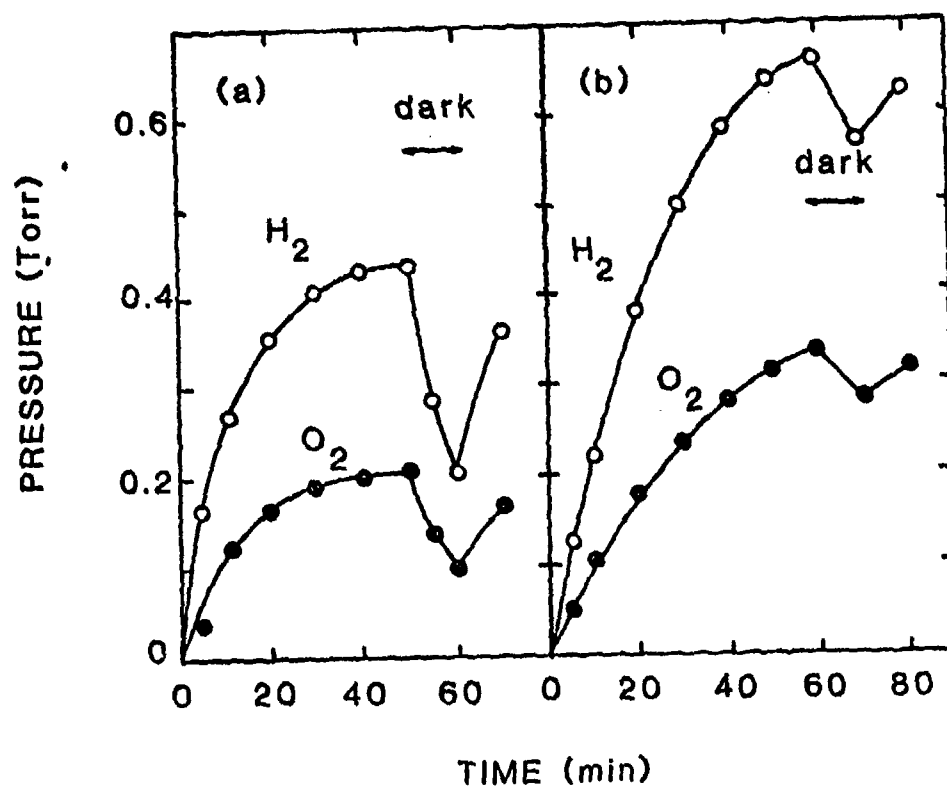
White Fig. 8



White Fig. 9



White Fig. 10



White Fig. 11

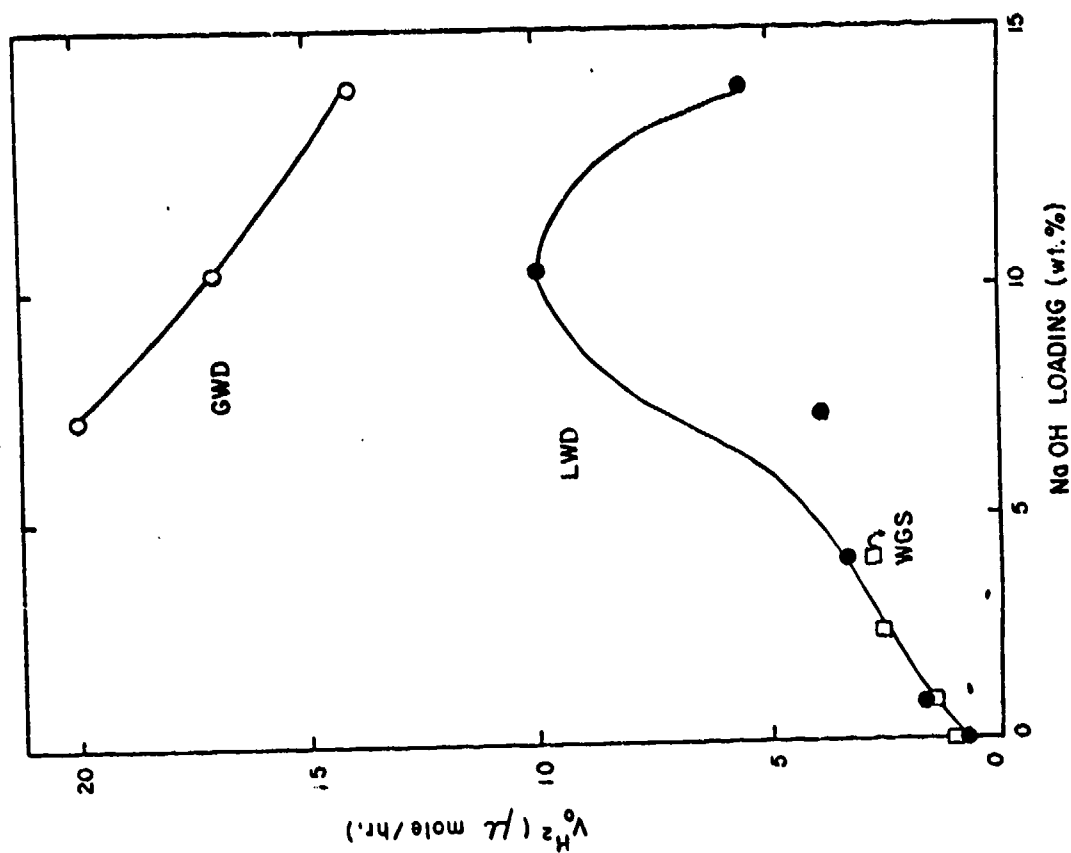


Table. Fig. 12.

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