

AD-A092 222

TEXAS UNIV AT AUSTIN DEPT OF CHEMISTRY
PHOTOCATALYTIC REACTION OF WATER WITH CARBON OVER PLATINIZED Ti-ETC(U)
OCT 80 S SATO, J M WHITE

F/8 7/2

N00014-75-C-0922

NI

UNCLASSIFIED

1-1
1-1

END
DATE
FILMED
1-8
DTIC

LEVEL II

(II)

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0922

Task No. NR 056-578

TECHNICAL REPORT NO. 17

Photocatalytic Reaction of Water with Carbon
over Platinized Titania

by

S. Sato and J. M. White

Prepared for Publication

in

Journal of Physical Chemistry

Department of Chemistry

University of Texas at Austin

Austin, Texas 78712

October 10, 1980

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

NOV 28 1980

C

AD A092222

DOC FILE COPY

80 11 24 021

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
	AD-A092222	NO.
4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED	
6 Photocatalytic Reaction of Water with Carbon over Platinized Titania.	9 Technical Report, 17 Jan 1980-Dec 1980	
7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)	
10 S. Sato and J. M. White	15 NO0014-75-C-0922	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
J. M. White, Department of Chemistry University of Texas Austin, Texas 78712	Project NR 056-578	
11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE	
Department of the Navy Office of Naval Research Arlington, Virginia 22217	11 10 Oct 1980	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	13. NUMBER OF PAGES	
12 23	33	
15. SECURITY CLASS. (of this report)		16. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
Approved for Public Release: Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
Preprint, accepted, Journal of Physical Chemistry		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
The reaction of gas phase water with active carbon over illuminated, platinized TiO₂ (anatase powder) is studied at room temperature and 60°C. The products are H₂, CO₂, and a small amount of O₂. As the reaction proceeds, the rate declines due to the accumulation of H₂ and the loss of a good contact between the catalyst and carbon. When the reaction is carried out in liquid H₂O, the oxidation of carbon is inhibited and O₂ as well as H₂ evolves.		

DD FORM 1473

JAN 73

EDITION OF 1 NOV 68 IS OBSOLETE
S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

347830

S. Sato and J. M. White

Department of Chemistry
University of Texas at Austin
Austin, Texas 78712

三三三

The reaction of gas phase water with active carbon over illuminated, platinized TiO_2 catalyst powder is studied at room temperature and 600°C . The products are H_2 , CO_2 and a small amount of O_2 . As the reaction proceeds, the rate declines due to the accumulation of H_2 and the loss of a good contact between the catalyst and carbon. The reaction is zero order in H_2O pressure and the activation energy is about 5 kcal./mole. The qualitative wavelength dependence of the reaction rate shows an onset a little shorter than observed in the water-gas shift and the water decomposition reactions over the same catalyst. At room temperature the quantum efficiency is about 2% at the beginning of the reaction. When the reaction is carried out in liquid H_2O , the oxidation of carbon is inhibited and O_2 as well as H_2 evolves.

•Supported in part by the Office of Naval Research.

I. Introduction.

The direct conversion of light energy into chemical energy, i.e., the storage of light energy, has recently received much attention from the viewpoint of the utilization of solar energy. The photocatalytic decomposition of water is one of the most suitable systems for this purpose and has been achieved in photoelectrochemical (PEC) cells ¹⁾ though the efficiency is still too low to use practically ²⁾. Some attempts have been made to photocatalyze water using heterogeneous catalysts. Pulator and Ertl ^{3,4)} have reported the decomposition of water when a suspension of platinumized TiO_2 in 1N H_2SO_4 solution is illuminated; however, their result has received little attention. Sakraizer and Gutting ⁵⁾ claimed the decomposition of adsorbed water over illuminated TiO_2 or Fe_2O_3 doped TiO_2 but Van Parne and Hall ⁶⁾ concluded that the formation of H_2 was not the result of water photolysis but rather arose from the photo-decomposition of hydroxyl groups typically found on TiO_2 .

In connection with the photolysis of water, Hemminger et al.⁷⁾ have reported the reduction of CO_2 by gas phase water to CH_4 over an illuminated SrTiO_3 crystal in contact with a Pt foil, but it is not clear that this was catalytic. Inoue et al.⁸⁾ have observed the formation of formic acid

A

DATE _____
BY _____
DISPOSITION _____
REMARKS _____
ACCESSION NO. _____

etc. when aqueous suspensions of various semiconductors were illuminated under flowing CO_2 . In both experiments, however, O_2 was not detected in the products even though it plays a central role in their mechanistic proposals.

We have recently found that TiO_2 itself has no activity for the photolysis of gas or liquid phase water but illuminated, platinumized TiO_2 (Pt/TiO_2) does.⁹ The continuous photodecomposition of gas phase water does not take place, apparently because the thermal back reaction ($\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$) over Pt overwhelms the photoprocess¹⁰. Continuous H_2 production from gas phase water is attainable when the oxygen formed reacts with CO^{10} , hydrocarbons¹¹, active carbon¹¹ or lignite¹². A similar system has been reported by Kawai and Sakata^{13,14}, who employed a mixture of TiO_2 , RuO_2 and active carbon. Interestingly, they observed that H_2 and CO are the main products when the irradiated mixture is suspended in liquid water¹⁴ while mainly H_2 and CO_2 are produced in the gas phase reaction¹³.

Heterogeneous catalysis systems for water photolysis have disadvantages as compared to PEC cells; the products (H_2 and O_2) are not separated so that the apparent efficiency becomes lower as the products accumulate due to the back reaction ($\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$) on the catalyst and the products must be separated before storage. However,

a heterogeneous catalysis system is less expensive to construct and simpler to use and its disadvantages would be partially overcome by selecting a reaction such as



even though its free energy increase is less than the water decomposition (57 kcal/mole). This reaction is related to another topic of current interest—the gasification of the earth's large reserves of coal. We have already studied the photocatalytic reaction of lignite with gas phase water over Pt/TiO_2 ¹². The reaction rate in this system, however, declined so fast, probably due to impurities in the lignite, that the properties of this system could not be reasonably characterized using our apparatus. For this reason we have studied in detail the reaction of active carbon with gas and liquid phase water over illuminated Pt/TiO_2 .

II. Experimental

TiO_2 powder (anatase, Matheson-Coleman-Bell) was reduced in flowing H_2 for 6 hrs. at 700°C to enhance photocatalytic activity. Platinized TiO_2 (-2 wt%Pt) was prepared by the photodecomposition of hexachloroplatinic acid¹⁵. The BET surface area of Pt/ TiO_2 was about $11 \text{ m}^2/\text{g}$. 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 an evacuable, circulation system (180 ml volume) and the sample was outgassed at 200°C for 2 hrs. After setting the reaction cell temperature with a water bath, water vapor was introduced from a reservoir of liquid water, which had been outgassed several times at dry ice temperature. The reaction was then started by illuminating the sample with a 200W high pressure Hg lamp that was filtered through a quartz cell filled with NiSO_4 solution to remove heat. The gas mixture was sampled at adequate intervals and, after passage through a cold trap at about -110°C to remove H_2O , was analyzed by a mass spectrometer (CEC 21-614).

Hydrogen, oxygen and ^{13}CO (isotopic purity 90%,¹⁶) were used after passing them through a liquid N_2 trap.

III. Results

Figure 1 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 in Fig. 1 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 $0.6 (1.8 \times 10^{-4} \text{ mole/hr.})$ torr/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 pro-

bably due to a decrease in the contact area between the carbon particles and the oxidation sites of the catalyst.

By stoichiometry ($C + 2H_2O \rightarrow 2H_2 + CO_2$) the H_2/CO_2 ratio should be 2, but according to Fig. 2 it was almost 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 catalyst as observed previously¹⁰. The H_2/CO_2 ratio reached 2.9 in the second run and then decreased slightly. When the reaction temperature was raised to 60° C, the ratio approached the stoichiometric value but again increased in the room-temperature reaction (the fifth run). Although the ratio decreased in subsequent room temperature runs (not shown), the stoichiometric ratio was not attained. The formation of O_2 can not account for this deviation of the H_2/CO_2 ratio from the stoichiometric ratio 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 maximizes 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. 3, 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° C prior to this experiment to remove adsorbed species accumulated in the preceding runs. In the dark, the H_2 pressure decrease was relatively slow and became faster with increased H_2 pressure. 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. As a result of the consumption of H_2 , the H_2/CO_2 ratio fell below 2 in the first dark period (Fig. 3) 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. At 60° C the dark loss of hydrogen is not

as pronounced as at room temperature.

The formation of O_2 (Fig. 3) 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. Returning to Fig. 1, the maximum pressure of O_2 was 1×10^{-3} torr in the first run and it increased to 1.3×10^{-3} and 2.4×10^{-3} torr in the second and third runs, respectively. When the reaction temperature was raised to $60^\circ C$ the O_2 pressure dropped quickly to 8×10^{-4} torr and remained there during the reaction. In the fifth run carried out at room temperature the O_2 pressure was 2.6×10^{-3} torr. Thus the O_2 pressure increases with repetitions but never exceeds 1×10^{-2} torr. When the light is turned off, O_2 disappears promptly from the gas phase as shown in Fig. 3.

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. 4). 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 less than observed previously in the reaction of lignite with H_2O^{12} . 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. As shown in Fig. 5, the water-gas shift reaction, $^{13}CO + H_2O = ^{13}CO_2 + H_2$, 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. At the beginning of this reaction, CO_2 exceeded H_2 probably because the addition of CO gave rise to the desorption of CO_2 that had accumulated on the sample in previous runs. 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. Similar phenomena have been observed in the photoassisted water-gas shift reaction over Pt/TiO_2 .

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.

When the pressure of H_2O was reduced to about 5 torr a slight increase in the H_2 formation rate was usually observed. Figure 6 shows the effect of H_2O pressure on the products. In this experiment, H_2O was first introduced at about 24 torr and then a part of the circulation system was cooled to $0^\circ C$ to reduce the H_2O pressure. After 50 min. of illumination the condensed H_2O was released by warming the trap to room temperature, and at 90 min. the H_2O pressure was again reduced. The H_2 formation was not affected by increasing H_2O pressure but accelerated slightly after reducing it to 5 torr at 90 min. The CO_2 formation became slower when H_2O pressure was reduced; an increase in the CO_2 pressure was always observed when H_2O pressure was increased to 24 torr though this effect is not sharp in Fig. 6. When the H_2O pressure was kept at about 5 torr throughout the same run, the H_2/CO_2 ratio exceeded 3 at the beginning but approached values around 2 as the reaction proceeded. Therefore, the slow CO_2 formation shown in Fig. 6 probably arises from increased CO_2 adsorption at lower

H_2O pressures. The O_2 pressure becomes lower when H_2O pressure is reduced, suggesting that an adsorbed H_2O layer on Pt retards the reaction of H_2 with O_2 .

The wavelength dependence of the reaction rate was qualitatively measured using three cut-off filters (Fig. 7). 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 (~275 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 . Prior to the reaction, H_2O was transferred from the storage vessel to the reaction cell by cooling the latter to $0^\circ C$ so that the sample became covered with liquid H_2O (~0.3 ml). This sample was illuminated after warming the cell up to room temperature. The results are shown in Fig. 8. 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.

IV. Discussion

TiO_2 is a typical photocatalyst for the oxidation of CO or hydrocarbons in which the holes and electrons generated by band gap radiation are considered to drive the reactions.¹⁷ In the photolysis of water, however, TiO_2 shows no activity⁹ and in the present study the reaction of active carbon with water did not take place on illuminated TiO_2 at room temperature. The difference between usual photoassisted reactions and the photocatalytic decomposition of water is that in the former mainly oxidation reactions occur presumably owing to the activation of oxygen by holes while in the latter the oxidation of water (or OH^-) by holes and the reduction of protons by electrons take place simultaneously. In addition to possessing both oxidation and reduction capabilities a good photocatalyst for water decomposition must provide for an efficient separation of photo-generated hole-electron pairs over the catalyst.

Semiconductors such as TiO_2 usually show much less activity for hydrogenation reactions than metal catalysts and our doped TiO_2 showed no activity for the H_2-D_2 exchange reaction at room temperature.¹⁸ If TiO_2 is used as a cathode in water electrolysis, a large overvoltage would

be necessary to evolve H_2 . It is therefore reasonably assumed that TiO_2 does not effectively catalyze the H_2 evolution reaction in the water photolysis.

When Pt is contact with TiO_2 , Pt would function as a cathode at which H_2 is easily evolved. In addition, Pt would induce bending of both conduction and valence bands at TiO_2 surfaces, resulting in the efficient separation of hole-electron pairs. Since TiO_2 operates as an anode in PEC cells,¹⁾ a combined system of Pt and TiO_2 thus has the features required for water photolysis. A similar system has been reported by Nozaki¹⁹⁾, who has shown that semiconductors (GaP and -CdS single-crystals) in contact with a Pt plate (Schottky-type photochemical diode) operate like their PEC cells.

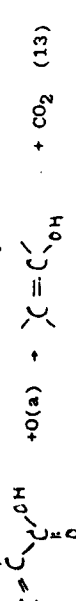
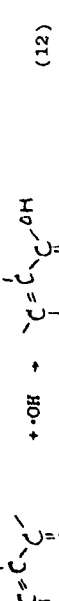
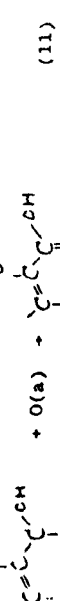
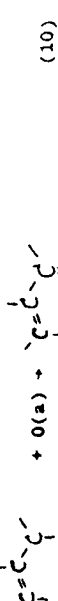
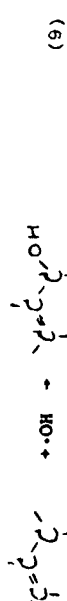
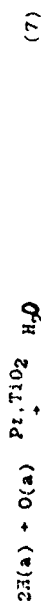
There is, however, a problem in view of the fact that Pt- TiO_2 (usually rutile) PEC cells require some external electrical potential to decompose water^{1,20)} whereas our systems using Pt/ TiO_2 involve no external potential. The requirement of an anodic bias in Pt- TiO_2 PEC cell is explained in terms of the energy-band diagram for TiO_2 under illumination (see Fig. 9). In most experiments the flat-band potential (electron Fermi level) of TiO_2 is observed at a position slightly higher than the H^+/H_2 redox potential and hence the photogenerated electrons are unable to transfer to the H^+/H_2 level²⁰⁾. There is however another experimental result which shows the flat-band potential

to be lower than the H^+/H_2 potential.²¹⁾ It seems to us that the flat-band potential of anatase may be positioned lower than the H^+/H_2 potential. Moreover, the potential necessary for the H_2 evolution in our systems should be lower than the standard H^+/H_2 potential because the reactions are carried out under very low pressure (less than 0.04 atm).

In our systems involving gas phase H_2O , the photodecomposition of H_2O may be the major process over Pt/ TiO_2 and the mechanism is probably analogous to those used to describe PEC cells.¹⁰⁻¹²⁾ That is, the photogenerated holes oxidize H_2O at the TiO_2 surface while the electrons drift to Pt and reduce protons which migrated there from the TiO_2 surface. A characteristic feature of the illuminated Pt/ TiO_2 gas phase H_2O system is its strong oxidation power that is capable of oxidizing even solid carbon as shown in the present experiments. This oxidation power may be attributed to the fact that the hole Fermi level of TiO_2 is positioned far higher than the H_2O/O_2 potential²²⁾ (see Fig. 9). Another possibility is the formation of O^- (a) which is a strong oxidizing agent and is thought to be an important intermediate in the photo-oxidation of CO and hydrocarbons over semiconductors.¹⁷⁾ However, the result of Fig. 4 shows that O_2 is much less active for carbon photo-oxidation than H_2O even though O^- (a) would be formed from O_2 .

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.²² 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.

In Pt-TiO_2 PEC cells, the water photolysis can be achieved without an external electrical bias by placing the TiO_2 electrode in basic solution and the Pt counter-electrode in acidic solution (a salt bridge connects the solutions).²³ Coughlin and Farcoque²⁴, on the other hand, have reported that the electrical potential necessary for the water electrolysis becomes significantly lower when the Pt anode is in contact with coal. These results lead us to suppose that the addition of carbon to the Pt/TiO_2 , H_2O system may give a chemical bias for the photolysis of water. If this supposition is correct it should be possible to utilize semiconductors with higher flat-band potentials than the H^+/H_2 potential for the photocatalytic production of H_2 from H_2O using carbon as a chemical bias reagent.

Kawai and Sakata¹³ have observed H_2 , CO_2 and a small amount of CO when a mixture of TiO_2 , RuO_2 and active carbon is illuminated in the presence of gas phase H_2O . They have also found that CO and H_2 are the major products when the mixture is immersed

in liquid H_2O and illuminated.¹⁴⁾ In our system, however, no CO was detected in either the gas or liquid phase reactions and water decomposition dominated the liquid phase reaction. This difference between these systems is of interest but not understood. It seems to us that the Pt/TiO₂ system has a stronger oxidative force as compared to the RuO₂/TiO₂ system and thus oxidizes carbon completely. Kawai and Sakata¹³⁾ have tested the activities of several kinds of metals (Ru, Ni and Pt) mixed with TiO₂ and carbon and found that the initial H₂ formation is 7-15 times faster for Pt than the RuO₂/TiO₂ system. Although they ascribed this effect to the oxidation of metals, Pt is not easily oxidized and we find no evidence for such in our systems. Their RuO₂/TiO₂ system produced about 4x10⁻⁶ mole of H₂ during 5 hr-illumination by a 500 W Hg lamp at room temperature while in our Pt/TiO₂ system, 9x10⁻⁶ mole of H₂ was produced during 2 hr-illumination by a 200 W Hg lamp. This suggests that the Pt/TiO₂ system has higher activity.

The H₂/CO₂ ratio in Kawai and Sakata's experiment¹³⁾ was 1-1.5, much less than the stoichiometric ratio, suggesting the reduction of RuO₂. In preliminary experiments, we find some evidence that Ni or Co mixed with TiO₂ is oxidized in the presence of H₂O and UV-irradiation while the oxides of metals such as Pt and Rh are reduced under the same experimental conditions.¹⁸⁾

The kinetics of the present reaction are similar to those of the photoassisted water-gas shift reaction over Pt/TiO₂.¹⁰⁾ The almost zero order dependence of the rate on H₂O 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 H₂ formation rate in a given run is probably due to the accumulation of H₂ 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 O₂ increases with time but, in any run, its maximum amount is less than observed in the reaction with lignite.¹²⁾ Although the reaction of H₂ with O₂ occurs rapidly on a clean Pt/TiO₂ even in the presence of gas phase H₂O,¹¹⁾ CO inhibits this reaction to some extent as observed in the water-gas shift reaction¹⁰⁾. Since CO was not detected in the gas phase of the present reaction, its inhibitory effect is not established. The result of Fig. 6 shows that the decrease in the amount of adsorbed H₂O on the sample results in decrease in the O₂ pressure. Therefore, it is reasonable to assume that since active carbon adsorbs a large amount of H₂O, the H₂O layer

on the Pt that is in contact with carbon is thicker than in the absence of carbon. When the H_2O layer is thick, O_2 does not react readily with H_2 . As the contact area between the catalyst and carbon decreases with the consumption of carbon, oxygen species would be required to migrate longer distances to react with carbon and consequently they would have an increasing chance to desorb as O_2 .

Assuming, as an upper limit, a flux of 10^{17} photons/sec²⁵ 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.

References

- (1) A. Fujishima, K. Honda and S. Kikuchi, J. Chem. Soc. Japan (Kogyo Kagaku Zasshi), 72, 108 (1969);
A. Fujishima and K. Honda, J. Chem. Soc. Japan, 74, 355 (1971); Nature, 238, 37 (1972).
- (2) J. Manassen, D. Cahen, G. Hodes and A. Sofer, Nature, 263, 97 (1976).
- (3) A. V. Bulatov and M. L. Khidkeel, Izv. Akad. Nauk SSSR, Ser. Khim., 1902 (1976).
- (4) G. N. Schrauzer and T. D. Guth, J. Am. Chem. Soc., 99, 3508 (1977).
- (5) H. Van Damme and W. K. Hall, J. Am. Chem. Soc., 101, 4373 (1979).
- (6) A. H. Boonstra and C.A.H.A. Matsuers, J. Phys. Chem., 79, 1694 (1975).
- (7) J. C. Hemminger, R. Carr and G. A. Somorjai, Chem. Phys. Letters, 57, 100 (1978).
- (8) T. Inoue, A. Fujishima, S. Konishi and K. Honda, Nature, 277, 637 (1979).
- (9) S. Sato and J. M. White, Chem. Phys. Letters, 72, 85 (1980).
- (10) S. Sato and J. M. White, J. Am. Chem. Soc., (in press).
- (11) S. Sato and J. M. White, Chem. Phys. Letters, 70, 131 (1980).
- (12) S. Sato and J. M. White, Ind. Eng. Chem. Prod. Res. Dev. (in press).

- (13) T. Kawai and T. Sakata, *Nature*, **282**, 283 (1979).
- (14) T. Kawai and T. Sakata, *J.C.S. Chem. Comm.*, 1047 (1979).
- (15) B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 4317 (1978).
- (16) We thank Dr. T. N. Taylor of Los Alamos Scientific Lab. for a sample of ^{13}CO .
- (17) M. Forzenti and S. J. Teichner, *Specialist Periodical Reports-Catalysis*, **2**, 87 (1979).
- (18) S. Sato and J. M. White, unpublished result.
- (19) A. J. Nozik, *Appl. Phys. Lett.*, **30**, 567 (1977).
- (20) R. P. Maruska and A. K. Ghosh, *Solar Energy*, **20**, 443 (1978).
- (21) M. Tokkiewicz, *J. Electrochem. Soc.*, **126**, 1505 (1979).
- (22) R. E. Panzer and P. J. Elving, *Electrochim. Acta.*, **20**, 635 (1975); R. W. Coughlin, *Ind. Eng. Chem. Prod. Res. Dev.*, **8**, 12 (1969).
- (23) e.g. A. Fujishima, K. Kohayakawa and K. Honda, *Bull. Chem. Soc. Japan*, **48**, 1041 (1975).
- (24) R. W. Coughlin and M. Farooque, *Nature*, **279**, 301 (1979).
- (25) J. M. White, Ph.D. Thesis, University of Illinois (1966).

Figure Captions

- Fig. 1 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.
- Fig. 2 Change of H_2/CO_2 ratio during the reaction of active carbon with gas phase H_2O (from Fig. 1).
- Fig. 3 Pressure changes of H_2 , CO_2 and O_2 when UV illumination is turned off during the reaction.
- Fig. 4 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 (~24 torr) was introduced at 40 min.
- Fig. 5 Effect of CO on the reaction rate.
- Fig. 6 Dependence of the reaction rate on H_2O pressure.
- Fig. 7 Effects of cut-off filters on the rate of H_2 formation.
- Fig. 8 Evolution of H_2 , O_2 and CO_2 when the sample is immersed in liquid H_2O and illuminated.
- Fig. 9 Schematic energy level diagrams for TiO_2 -Pt PEC cell in the dark and under illumination: CB, conduction band; VB, valence band; E_f , Fermi level; E_{fn} , electron Fermi level; E_{fp} , hole Fermi level.

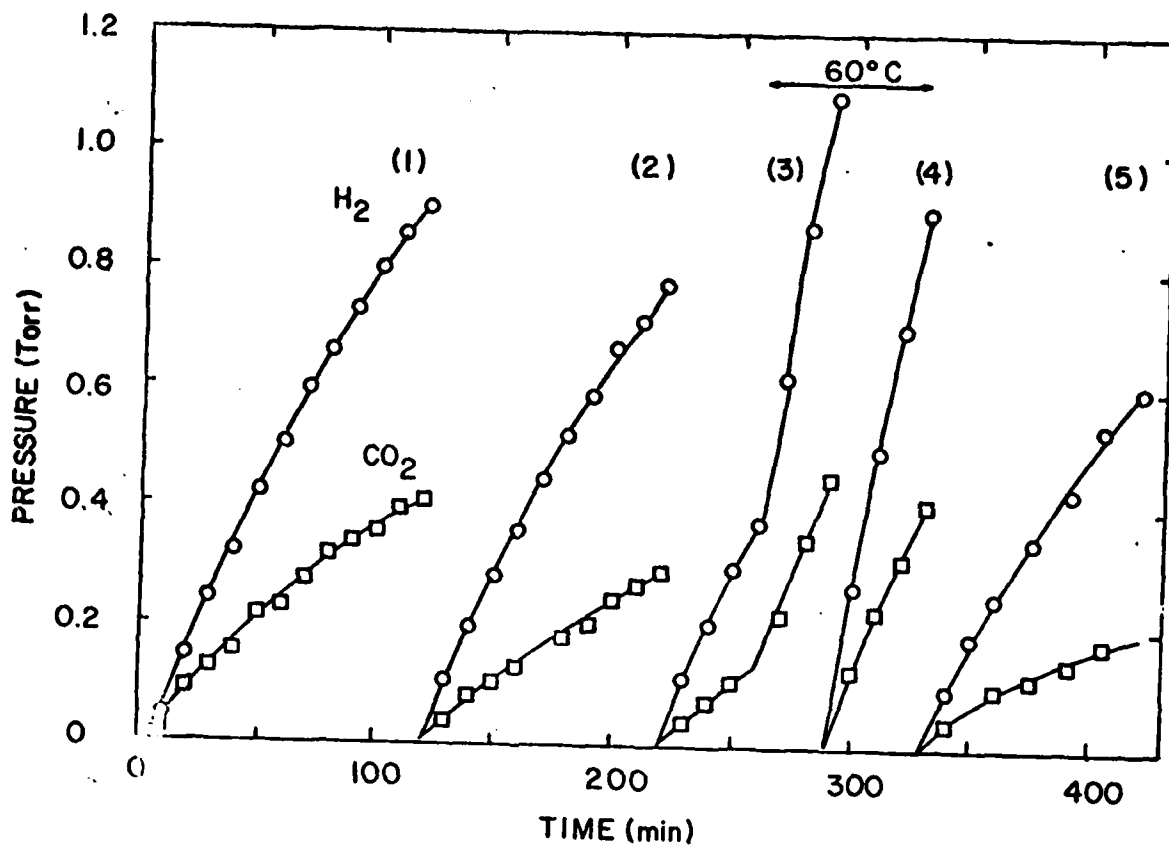
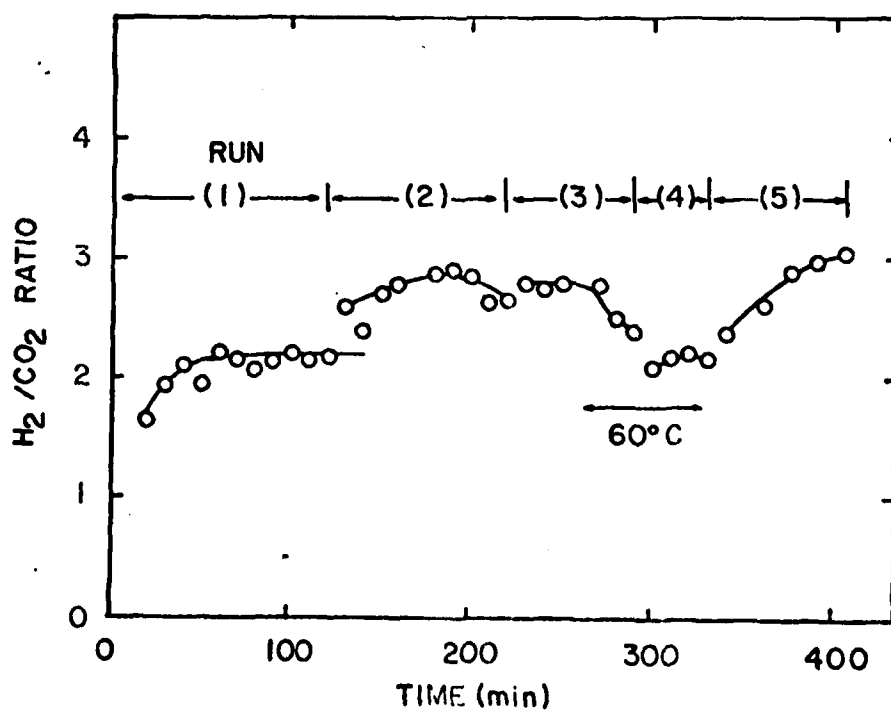


Fig. 2



See and ref. 1.

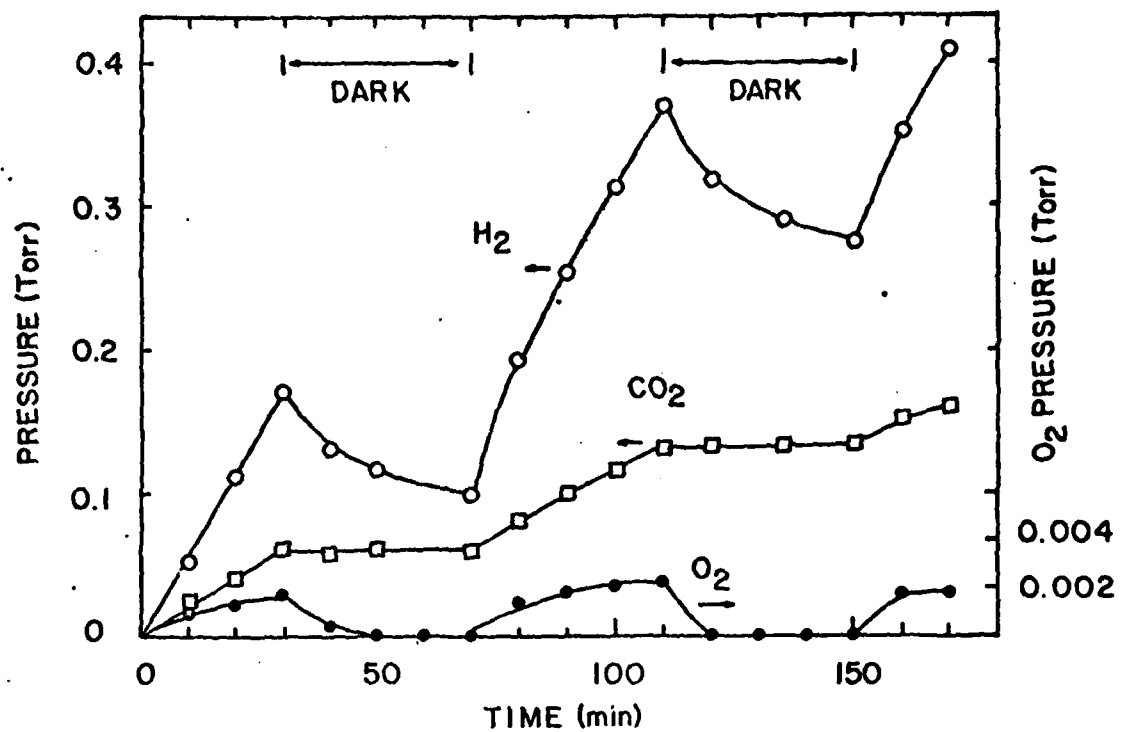


Fig. 3
Sato and White

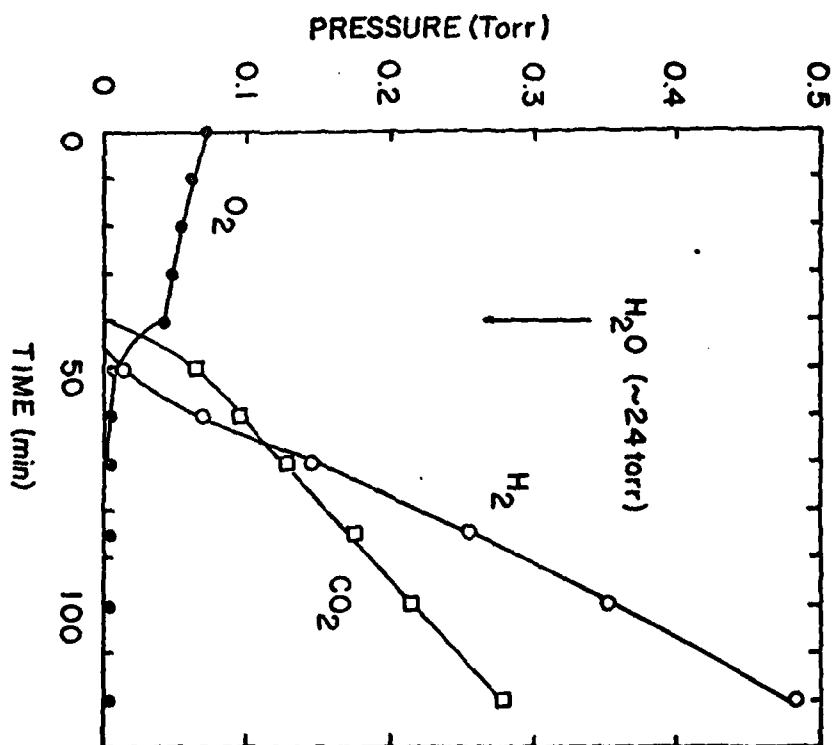
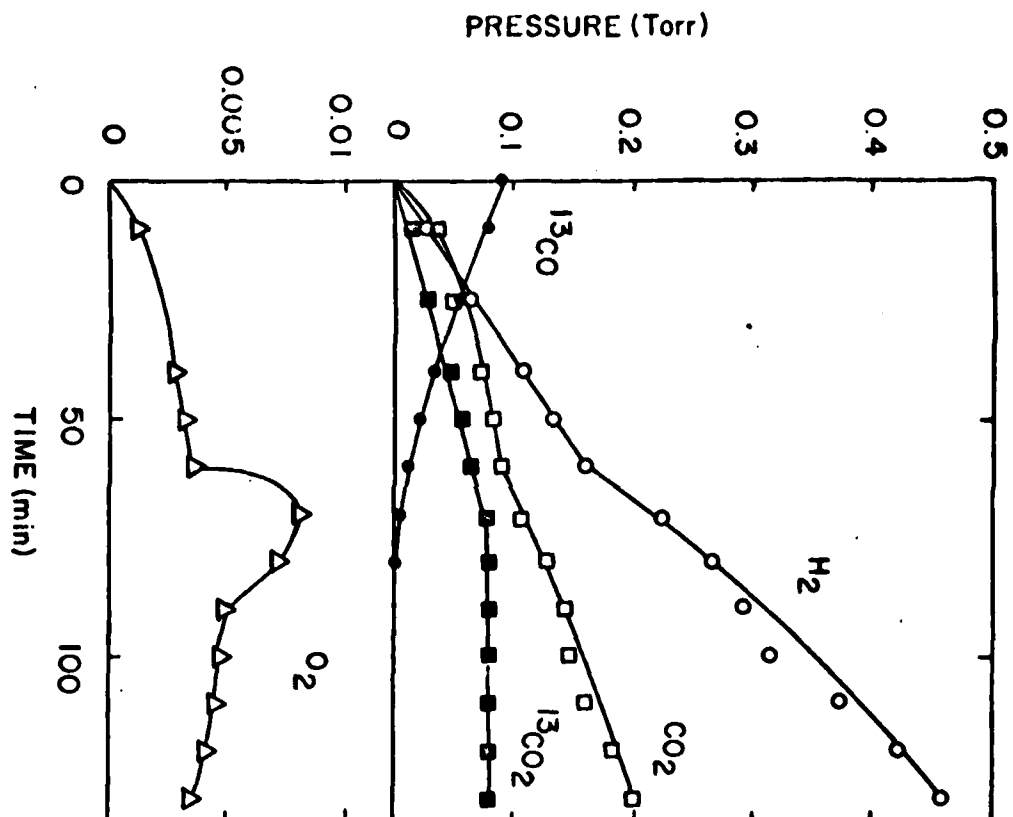


Fig. 4

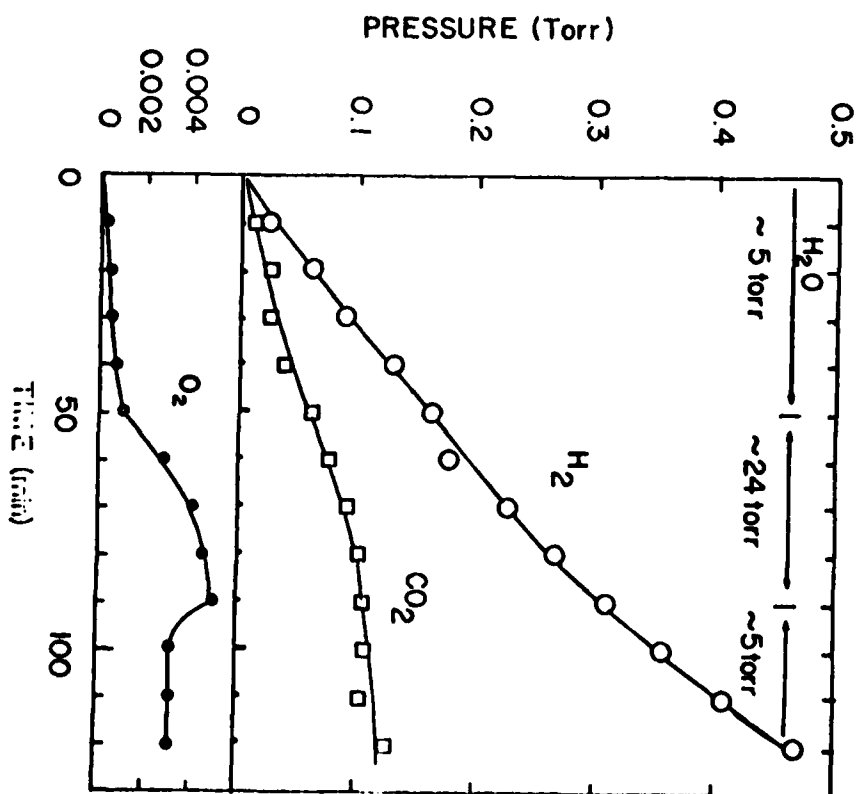
Sato and White

Fig. 5



Sale and White

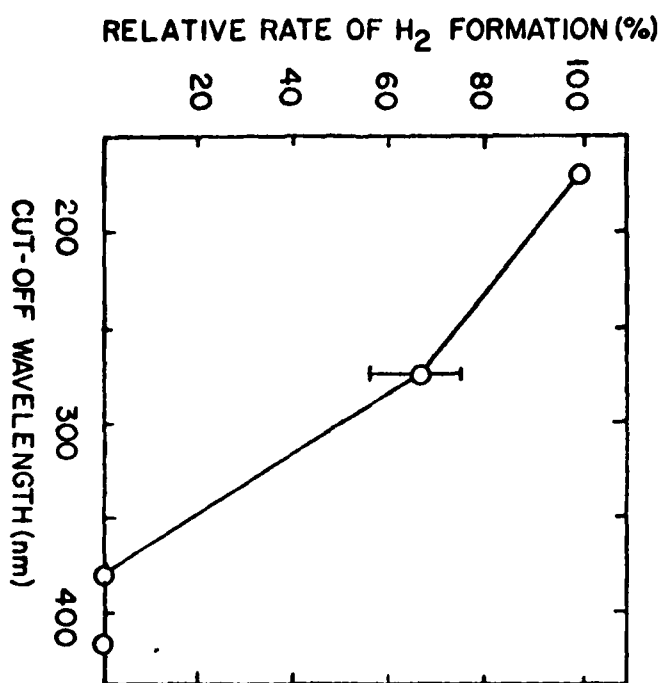
Fig. 6



Sale and White

Fig. 7

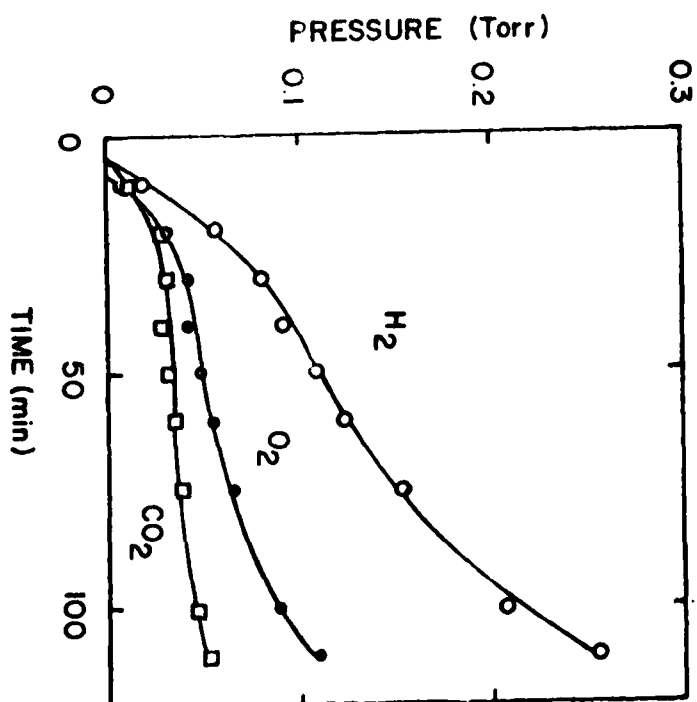
31



Sato and Uchida

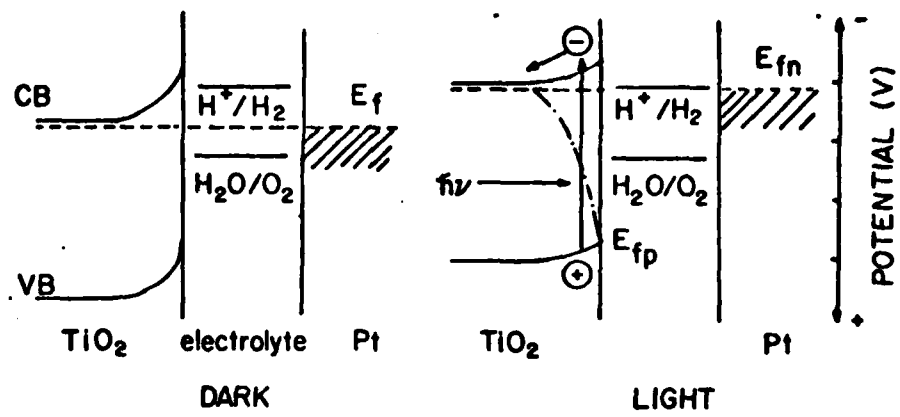
Fig. 8

32



Sato and Uchida

Fig. 2



Sato and White

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GENNo.
Copies

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco 96503

1

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland 21402

1

TECHNICAL REPORT DISTRIBUTION LIST, 056

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. D. A. Vroom IRT P.O. Box 80817 San Diego, California 92138	1	Dr. C. P. Flynn Department of Physics University of Illinois Urbana, Illinois 61801	1
Dr. G. A. Somorjai Department of Chemistry University of California Berkeley, California 94720	1	Dr. W. Kohn Department of Physics University of California (San Diego) LaJolla, California 92037	1
Dr. L. N. Jarvis Surface Chemistry Division 4555 Overlook Avenue, S.W. Washington, D.C. 20375	1	Dr. R. L. Park Director, Center of Materials Research University of Maryland College Park, Maryland 20742	1
Dr. J. B. Hudson Materials Division Rensselaer Polytechnic Institute Troy, New York 12181	1	Dr. W. T. Peria Electrical Engineering Department University of Minnesota Minneapolis, Minnesota 55455	1
Dr. John T. Yates Surface Chemistry Section National Bureau of Standards Department of Commerce Washington, D.C. 20234	1	Dr. Narkis Tzoar City University of New York Convent Avenue at 138th Street New York, New York 10031	1
Dr. Theodore E. Madey Surface Chemistry Section Department of Commerce National Bureau of Standards Washington, D.C. 20234	1	Dr. Chia-wei Woo Department of Physics Northwestern University Evanston, Illinois 60201	1
J. M. White Department of Chemistry University of Texas Austin, Texas 78712	1	Dr. D. C. Mattis Polytechnic Institute of New York 333 Jay Street Brooklyn, New York 11201	1
Dr. Keith H. Johnson Department of Metallurgy and Materials Science Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. Robert M. Hexter Department of Chemistry University of Minnesota Minneapolis, Minnesota 55455	1
Dr. J. E. Demuth IBM Corporation Thomas J. Watson Research Center P.O. Box 218 Yorktown Heights, New York 10598	1	Dr. R. P. Van Duyne Chemistry Department Northwestern University Evanston, Illinois 60201	1

TECHNICAL REPORT DISTRIBUTION LIST, 056

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. M. G. Lagally Department of Metallurgical and Mining Engineering University of Wisconsin Madison, Wisconsin 53706	1	Dr. J. Osteryoung Chemistry Department SUNY, Buffalo Buffalo, New York 14214	1
Dr. Robert Gomer Department of Chemistry James Franck Institute 5640 Ellis Avenue Chicago, Illinois 60637	1	Dr. G. Rubloff I.B.M. Thomas J. Watson Research Center P. O. Box 218 Yorktown Heights, New York 10598	1
Dr. R. G. Wallis Department of Physics University of California, Irvine Irvine, California 92664	1	Dr. J. A. Gardner Department of Physics Oregon State University Corvallis, Oregon 97331	1
Dr. D. Ramaker Chemistry Department George Washington University Washington, D.C. 20052	1	Dr. G. D. Stein Mechanical Engineering Department Northwestern University Evanston, Illinois 60201	1
Dr. P. Hansma Chemistry Department University of California, Santa Barbara Santa Barbara, California 93106	1	Dr. K. G. Spears Chemistry Department Northwestern University Evanston, Illinois 60201	1
Dr. P. Hendra Chemistry Department Southampton University England SO9JNH	1	Dr. R. W. Plummer University of Pennsylvania Department of Physics Philadelphia, Pennsylvania 19104	1
Professor P. Skell Chemistry Department Pennsylvania State University University Park, Pennsylvania 16802	1	Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 41106	2
Dr. J. C. Hemminger Chemistry Department University of California, Irvine Irvine, California 92717	1	Professor George H. Morrison Cornell University Department of Chemistry Ithaca, New York 14853	1
Dr. Martin Fleischmann Department of Chemistry Southampton University Southampton SO9 5NH Hampshire, England	1	Professor N. Winograd Pennsylvania State University Chemistry Department University Park, Pennsylvania 16802	1
		Professor Thomas F. George The University of Rochester Chemistry Department Rochester, New York 14627	1