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PHOTOCATALYTIC WATER DECOMPOSITION AND WATER-GAS SHIFT REACTION--ETC(U)

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Photocatalytic Water Decomposition and  
Water-Gas Shift Reactions over  
NaOH-Coated, Platinized TiO<sub>2</sub>

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The photocatalytic decomposition of gaseous water takes place over platinized TiO <sub>2</sub> coated with NaOH (more than 7 wt.%). The quantum efficiency of H <sub>2</sub> and O <sub>2</sub> production reaches about 7% (20 μmole H <sub>2</sub> /hr) at the beginning of the reaction but declines with accumulation of the products due to the thermal back reaction over Pt. The effect of the back reaction can be reduced by increasing the NaOH loading.		

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## 1. Introduction

The photocatalytic decomposition of water is one of the attractive reactions for the direct conversion of light energy into chemical energy and has been achieved in photoelectrochemical (PEC) cells.<sup>1)</sup> Recently some heterogeneous catalytic systems have been found effective for the photolysis of water. Rulakov and Khidekel<sup>2)</sup> have reported the photodecomposition of liquid water using platinumized TiO<sub>2</sub> (Pt/TiO<sub>2</sub>). Other work, with one exception<sup>3)</sup> finds that adsorbed water is not photodecomposed over illuminated pure TiO<sub>2</sub>.<sup>4,5)</sup> Our previous experiments<sup>6)</sup>, while showing that TiO<sub>2</sub> has no photocatalytic activity for the decomposition of gas and liquid phase water, find that Pt/TiO<sub>2</sub> is surely effective for the liquid water photolysis. Pt/TiO<sub>2</sub> also photocatalyzes the reactions of gas phase water with CO,<sup>6)</sup> hydrocarbons,<sup>7)</sup> active carbon<sup>7,8)</sup> and lignite<sup>9)</sup> to produce H<sub>2</sub> and CO<sub>2</sub>. In the liquid water photolysis by Pt/TiO<sub>2</sub>, however, the production of H<sub>2</sub> and O<sub>2</sub> declines rapidly as gas phase products accumulate and finally stops.<sup>5)</sup> When Pt/TiO<sub>2</sub> is illuminated in the presence of gas phase water, no detectable amounts of products are produced because the thermal back reaction (H<sub>2</sub> + 1/2 O<sub>2</sub> → H<sub>2</sub>O) occurs rapidly on Pt.

The photodecomposition of gas phase water has been recently reported by Kawai and Sakata<sup>10)</sup> and Domen et al.,<sup>11)</sup> who employed RuO<sub>2</sub>/TiO<sub>2</sub> and NiO/SrTiO<sub>3</sub>, respectively. The rate of H<sub>2</sub> formation was 0.6 μ mole/hr by a 500 W Hg lamp in the former and 0.2 μ mole/hr by a 450 W Hg lamp in the latter. Wagner and Sauerbrey<sup>12)</sup> have also observed gaseous water photodecomposition over platinumized and metal-free SrTiO<sub>3</sub> crystals, both of which were coated with NaOH. The H<sub>2</sub> formation rate over the NaOH coated Pt/SrTiO<sub>3</sub> was 1.8 μ mole/hr by a 500 W Hg lamp. They also studied the liquid water photolysis over Pt/SrTiO<sub>3</sub> immersed in alkaline solution and found that the reaction rate increases with pH. The maximum H<sub>2</sub> formation rate obtained was 7.5 μ mole/hr.

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## Photocatalytic Water Decomposition and Water-Gas Shift Reactions over NaOH-Coated, Platinumized TiO<sub>2</sub>\*

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### Abstract

The photocatalytic decomposition of gaseous water takes place over platinumized TiO<sub>2</sub> coated with NaOH (more than 7 wt. %). The quantum efficiency of H<sub>2</sub> and O<sub>2</sub> production reaches about 7% (20 μ mole H<sub>2</sub>/hr) at the beginning of the reaction but declines with accumulation of the products due to the thermal back reaction over Pt. The effect of the back reaction can be reduced by increasing the NaOH loading. The photocatalytic activity of platinumized TiO<sub>2</sub> for the water-gas shift reaction increases with increasing NaOH coating. The rates of these photocatalytic reactions are independent of temperature in the range 18-50°C. In NaOH solution, a pH effect on the rate of water photolysis over platinumized TiO<sub>2</sub> is observed.

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The results of Thamer and Smoriat<sup>12)</sup> indicate that the NaOH coating suppresses the back reaction so that the gas phase water photolysis occurs on the Pt/SrTiO<sub>3</sub> even in the presence of Pt and that a pH effect is important in the liquid water photolysis. In preliminary experiments we found that a NaOH coating on Pt/TiO<sub>2</sub> allows detectable amounts of H<sub>2</sub> and O<sub>2</sub> to form when gas phase water is used. Moreover, as with Pt/SrTiO<sub>3</sub>, liquid water photolysis over Pt/TiO<sub>2</sub> becomes faster in NaOH solution. In the present experiments we studied the gas phase water photodecomposition and the photoassisted water-gas shift reactions over NaOH coated Pt/TiO<sub>2</sub> focusing on the effect of NaOH loading and the reaction kinetics. The effect of NaOH concentration on the rate of the liquid water photodecomposition was measured qualitatively. To examine another electrolyte coating, NaCl coated Pt/TiO<sub>2</sub> was also tested for the reactions. The photooxidation of CO was carried out on the TiO<sub>2</sub> samples used to prepare Pt/TiO<sub>2</sub> in order to check their photocatalytic activities for a standard photoreaction.

## 2. Experimental

TiO<sub>2</sub> (MGB anatase, particle size 125-250 μm by sieves) was reduced (doped) at 700°C for 6 hours in flowing H<sub>2</sub> to enhance photocatalytic activity. Platinized TiO<sub>2</sub> (~3 wt. % Pt) was prepared by the photodecomposition of hexachloroplatinic acid.<sup>13)</sup> The BET surface areas of undoped TiO<sub>2</sub>, doped TiO<sub>2</sub> and Pt/TiO<sub>2</sub> were 11, 9 and 10 m<sup>2</sup>/g, respectively. The catalyst (0.25g) was spread uniformly on the flat bottom (14 cm<sup>2</sup>) of a quartz reaction cell. The cell was then connected to an evacuable, circulation system (180 ml volume). Catalysts involving Pt were treated with H<sub>2</sub> at 200°C for about 15 hours and outgassed at the same temperature for 2 hours. NaOH coated Pt/TiO<sub>2</sub> was prepared in the reaction cell, after a series of experiments a calculated amount of NaOH solution (0.1 or 1.0 M) was injected onto Pt/TiO<sub>2</sub> or NaOH/Pt/TiO<sub>2</sub> and the sample was then dried

in flowing He at 500°C. NaOH coated TiO<sub>2</sub> and NaCl coated Pt/TiO<sub>2</sub> were prepared outside the reaction cell by standard impregnation methods.

In experiments involving the photodecomposition of gas phase water, water vapor was introduced into the reaction system from a reservoir of liquid water, which had been outgassed several times at dry ice temperature. For the water-gas shift reaction CO was introduced prior to the introduction of water vapor and for the photodecomposition of liquid water the bottom of the reaction cell was cooled to 0°C so that the catalyst became covered with liquid water (0.2 - 0.3 ml).

After setting the reaction cell temperature with a water bath, reaction was started by illuminating the catalyst with a 200 W high pressure Hg lamp that was filtered through a quartz cell filled with NiSO<sub>4</sub> solution to remove heat. The reaction products were sampled at adequate intervals and, after passage through a cold trap at about -110°C to remove water, were analyzed by a mass spectrometer (CEC 21-614). The analysis system can detect a partial pressure as low as 5 x 10<sup>-4</sup> torr in the reaction system.

In passing, we note the importance of working with a metal-free reaction vessel when using NaOH-coated catalysts. When a cell, previously used for Pt/TiO<sub>2</sub> experiments, was washed in running water, dried and then used with NaOH-coated TiO<sub>2</sub>, activity for the photoassisted decomposition of water was observed. In the absence of NaOH, no activity was noted. The experiment, repeated after thorough ultrasonic cleaning of the cell with alumina powder suspended in the solvent, showed no activity. This suggests that in the earlier experiment, a trace of Pt remained in the cell.

### 3. Results

#### 3.1 Gas phase water decomposition (GMD).

Photocatalytic activity for GMD was tested for undoped and doped  $\text{TiO}_2$  with and without NaOH coating. Undoped  $\text{TiO}_2$  and NaOH/undoped  $\text{TiO}_2$  (3.2 wt. % NaOH) produced neither  $\text{H}_2$  nor  $\text{O}_2$  during 100 min illumination. Doped  $\text{TiO}_2$  and NaOH/doped  $\text{TiO}_2$  (1.6 wt. % NaOH) produced a small amount of  $\text{H}_2$  but no  $\text{O}_2$  was detected even after 15 hour illumination. This  $\text{H}_2$  formation is probably due to the reaction of water with strongly reduced forms of  $\text{TiO}_2$  as concluded previously. 5.6)

NaOH coated  $\text{Pt/TiO}_2$  catalysts produce  $\text{H}_2$  and  $\text{O}_2$  in the GMD reaction when NaOH loading exceeds about 3 wt. % and their formation rates and maximum pressures depend on NaOH loading. The stationary-state  $\text{H}_2$  and  $\text{O}_2$  formation over 3 wt. % NaOH/ $\text{Pt/TiO}_2$  was very small (less than  $1 \times 10^{-2}$  torr); and, after turning off the light, the pressures of  $\text{H}_2$  and  $\text{O}_2$  dropped promptly to zero, indicating a fast back reaction on the catalyst. The initial rates of  $\text{H}_2$  and  $\text{O}_2$  formation were too fast to determine them accurately. When NaOH loading was increased to 7 wt. %, the maximum amounts of  $\text{H}_2$  and  $\text{O}_2$  increased significantly as shown in Fig. 1(a). In repeated runs with the same catalyst, the photocatalytic activity of NaOH/ $\text{Pt/TiO}_2$  for GMD increased slightly by some unspecified mechanism. A stationary activity was usually attained after about 3 hours total illumination and no activity loss was observed in subsequent experiments. All the data presented here were, therefore, obtained after the stationary activity was attained.

The rates of  $\text{H}_2$  and  $\text{O}_2$  formation were initially high but rapidly dropped to zero after a certain time of illumination. This decrease in the rates is not due to a loss of the photocatalytic activity but due to the back reaction since both  $\text{H}_2$  and  $\text{O}_2$  decreased rapidly in the dark and again increased after re-

illumination as seen in Fig. 1. The  $\text{H}_2/\text{O}_2$  ratio usually exceeds slightly the stoichiometric value of 2. This deviation from the stoichiometric ratio probably arises from the photoadsorption of  $\text{O}_2$  on the catalyst since the ratio dropped to about 2 in the dark period (see Fig. 1(a)) and it was always less than 2 during the early stages of the reaction carried out after a brief evacuation of the reaction system. The maximum pressures of  $\text{H}_2$  and  $\text{O}_2$  increased with the NaOH loading but the initial rate of the reaction decreased (see Fig. 1(b)). The dependence of the initial rate of  $\text{H}_2$  formation,  $v_{\text{H}_2}^0$ , on the NaOH loading is shown in Fig. 6 (to be discussed later).

Temperature, pressure and wavelength dependences of the rate of GMD were examined using 10 wt. % NaOH/ $\text{Pt/TiO}_2$ . Figure 2 shows that  $v_{\text{H}_2}^0$  is almost independent of reaction temperature in the range 18-50°C. On the other hand, the maximum pressures of  $\text{H}_2$  and  $\text{O}_2$ , achieved in these experiments, decrease with increasing temperature, probably because the back reaction becomes fast. For example, at 25°C,  $p_{\text{H}_2}^{\text{max}} = 0.55$  torr while at 50°C it dropped to 0.26 torr. When the reaction was carried out at about 5 torr of  $\text{H}_2$  pressure at room temperature, the initial  $\text{H}_2$  formation rate was about half of the rate at 24 torr of  $\text{H}_2$  pressure, presumably due to decrease in the amount of adsorbed  $\text{H}_2\text{O}$ . The wavelength dependence was qualitatively measured using three cut-off filters. A UV cut-off filter (415 nm cut-off) completely eliminates the reaction. A plexiglass filter (380 nm cut-off) and a Pyrex glass filter (275 nm cut-off) suppress the reaction rate to less than 1% and about 70%, respectively. A similar wavelength dependence has been observed in the water-gas shift reaction over illuminated  $\text{Pt/TiO}_2$ . 6)

The photocatalytic activity of NaCl coated  $\text{Pt/TiO}_2$  for GMD was tested using 10 wt. % NaCl/ $\text{Pt/TiO}_2$ . Although the water-gas shift and liquid water decomposition reactions take place on this catalyst under illumination, the GMD reaction did not occur at all. We assume that NaCl on  $\text{Pt/TiO}_2$  would crystallize

### 3.2. Water-gas shift (WGS) reaction.

The Pt/TiO<sub>2</sub> used in the present experiments showed less photocatalytic activity for the WGS reaction than that used in previous experiments<sup>6</sup>; the reaction rate was 1.1 μ mole/hr for the former and 2.4 μ mole/hr for the latter. This difference in the photocatalytic activity may be due to a lower doping level of the "sieved" TiO<sub>2</sub> used in the present experiments. A relative doping level of TiO<sub>2</sub> can be estimated from the amount of H<sub>2</sub> formed in the reaction of H<sub>2</sub>O with doped TiO<sub>2</sub> under illumination. Although the doping condition is the same, "unsieved" TiO<sub>2</sub> produces more H<sub>2</sub> than "sieved" TiO<sub>2</sub> in this reaction, probably because the former is more easily reduced than the latter.

When Pt/TiO<sub>2</sub> was coated with NaOH, the photocatalytic activity for WGS reaction increased significantly. A summary of these activities is given in Fig. 6 and for 4% NaOH the rate increased by a factor of 2.5. A typical time course of the WGS reaction over NaOH/Pt/TiO<sub>2</sub> is shown in Fig. 3. At the beginning of the reaction, CO<sub>2</sub> formation is very slow because of the reaction of CO<sub>2</sub> with NaOH. As the reaction proceeds, CO<sub>2</sub> formation becomes faster but <sup>12</sup>CO<sub>2</sub> exceeds <sup>13</sup>CO<sub>2</sub> even though <sup>13</sup>CO is used as a reactant. This <sup>12</sup>CO<sub>2</sub> formation probably arises from the exchange reaction of <sup>12</sup>CO<sub>2</sub> with Na<sub>2</sub>CO<sub>3</sub> originally present in NaOH (about 1%). Taking the isotopic purity of <sup>13</sup>CO (90%) into account, the amount of H<sub>2</sub> finally formed agrees well with the initial amount of CO. When the CO pressure falls down to about 0.05 torr, the consumption of CO as well as the formation of H<sub>2</sub> becomes slower presumably because the diffusion of CO through the water layer on the catalyst becomes important. At the same time, a small amount of O<sub>2</sub> is formed. Similar phenomena have been observed in the WGS reaction over Pt/TiO<sub>2</sub><sup>6</sup>. The thermal WGS reaction did not take place at all over NaOH/Pt/TiO<sub>2</sub> catalysts at room temperature.

The kinetics of the WGS reaction were examined using 2.4 wt. % NaOH/Pt/TiO<sub>2</sub>. The reaction is nearly zero (slightly positive) order in CO pressure

between 0.3 and 0.75 torr. When the H<sub>2</sub>O pressure is reduced from 24 torr to about 5 torr by cooling a part (not the catalyst) of the reaction system to 0°C, the rate falls by a factor of 4. When the H<sub>2</sub>O pressure is increased again to 24 torr, the original rate is recovered. The reaction rate is almost independent of catalyst temperature between 18 and 50°C, but drops about a factor of 4 between 18 and 0°C.

The photocatalytic activity of NaOH/Pt/TiO<sub>2</sub> for WGS increases with increasing NaOH loading as shown in Fig. 6. When the NaOH loading was increased to 7 wt. %, a considerable amount of O<sub>2</sub> was formed (see Fig. 4). The O<sub>2</sub> pressure reached 0.1 torr and decreased after the CO pressure fell to about 0.05 torr. No appreciable CO<sub>2</sub> was formed during this reaction. The H<sub>2</sub> formation was very fast at the beginning of reaction but declined with time. This decline of the rate and the decrease in H<sub>2</sub> pressure after 45 min. are apparently caused by the reaction of H<sub>2</sub> with O<sub>2</sub>. The initial H<sub>2</sub> production rate in this reaction, 24 μmole/hr, is the highest value obtained in the present experiments.

The WGS reaction over 10 wt. % NaCl/Pt/TiO<sub>2</sub> was very slow (0.24 μmole/hr), indicating the inhibitory effect of NaCl.

### 3.3. Liquid water decomposition (LWD)

The photodecomposition of liquid water over Pt/TiO<sub>2</sub> was slow ( $V_0^{H_2} = 0.9$   $\mu$  mole/hr) as compared to the previous results ( $V_0^{H_2} = 6$   $\mu$  mole/hr).<sup>5</sup> The photocatalytic activity for LWD is much improved by coating Pt/TiO<sub>2</sub> with NaOH as shown in Fig. 6. It should be noted that since the NaOH on Pt/TiO<sub>2</sub> with NaOH as shown water the reaction is carried out in NaOH solution. Assuming the amount of water introduced is 0.25 ml, 1 wt. % NaOH will make 0.25M NaOH solution. Since the amount of water introduced onto the catalyst was not exactly controlled in the present experiments, the observed dependence of the reaction rate on NaOH concentration is qualitative.

The rate of the LWD reaction is quite reproducible when the reaction is repeated after evacuating the products (water is frozen at dry ice temperature during the evacuation). It increases with increasing NaOH concentration up to about 2.5%. In addition to the increase in the initial rate, the maximum pressures of H<sub>2</sub> and O<sub>2</sub> also increase with NaOH concentration while the reaction of H<sub>2</sub> with O<sub>2</sub> in the dark becomes slower. Figure 5 shows the evolution of H<sub>2</sub> and O<sub>2</sub> when 10 wt. % NaOH/Pt/TiO<sub>2</sub> is immersed in liquid water (-0.2 ml) and illuminated. Both the H<sub>2</sub> and O<sub>2</sub> formation rates decline with time but to a lesser extent than for lower NaOH concentrations. The pressure drop in the dark period is also slower even though the pressures of H<sub>2</sub> and O<sub>2</sub> are fairly high.

A further increase in the NaOH concentration from about 2.5M to about 3.2M reduced the rate of the LWD reaction, presumably because the concentrated NaOH solution disturbs the escape of the products from the catalyst surface.

In NaCl solution (~2M), the initial rate of the LWD reaction was 1.4  $\mu$  mole/hr; the reaction is obviously faster than in pure water but much slower than in NaOH solution.

### 3.4. Photooxidation of CO.

To characterize the photocatalytic activity of TiO<sub>2</sub>, a common photocatalytic reaction, photooxidation of CO, was used. Doped and undoped TiO<sub>2</sub> and NaOH coated, undoped TiO<sub>2</sub> were tested. The reaction was carried out at room temperature using a mixture of 54% O<sub>2</sub> and 46% CO at about 0.3 torr total pressure. The initial rate of the reaction over undoped TiO<sub>2</sub> was 0.7  $\mu$  mole/hr and there was no appreciable difference in the photocatalytic activity between undoped and doped TiO<sub>2</sub>. NaOH/TiO<sub>2</sub> showed very slightly less activity (0.6  $\mu$  mole/hr) than TiO<sub>2</sub>. The CO oxidation over Pt/TiO<sub>2</sub> was so fast in the dark that the photocatalytic activity of Pt/TiO<sub>2</sub> for this reaction could not be measured.



#### 4. Discussion.

The present experiments have confirmed the inactivity of  $\text{TiO}_2$  for water photolysis even when it is coated with  $\text{RuO}_2$ . In photolyze water, some material such as Pt<sup>5)</sup> or  $\text{RuO}_2$ <sup>10)</sup> must be added. The reason for this has been discussed previously<sup>3)</sup> in terms of the energy band diagram of illuminated  $\text{TiO}_2$ .<sup>14)</sup> Although the flat band potential (electron Fermi level) of  $\text{TiO}_2$  has typically been placed at a position slightly more positive than the  $\text{H}^+/\text{H}_2$  redox potential,<sup>14)</sup> the most recent study by Tomkiewicz<sup>15)</sup> shows that the former is about 100 mV more negative than the latter. This implies that water photolysis in PEC cells with a  $\text{TiO}_2$  photocathode is energetically possible under short circuit conditions, even though actual Pt -  $\text{TiO}_2$  PEC cells require some external potential to decompose water.<sup>14)</sup> The requirement of an external potential in Pt -  $\text{TiO}_2$  PEC cells may arise from some potential loss in the circuit. It seems to us that the flat band potential of anatase is more negative than the  $\text{H}^+/\text{H}_2$  potential as observed by Tomkiewicz,<sup>15)</sup> since water is photolyzed by Pt/ $\text{TiO}_2$  catalysts, which can be modeled as a set of small, short-circuited Pt -  $\text{TiO}_2$  cells. However,  $\text{TiO}_2$  alone would be inactive for the photolysis of water even if 100 mV are available as an overvoltage for  $\text{H}_2$  evolution because  $\text{TiO}_2$  is so inactive for the  $\text{H}_2$  evolution reaction. More than 100 mV are needed for this evolution to proceed at a measurable rate. As compared to Pt -  $\text{TiO}_2$  PEC cells, the potential loss in Pt/ $\text{TiO}_2$  catalyst would be small since Pt is in direct contact with  $\text{TiO}_2$ . It should be noted that a metal-semiconductor contact may give rise to Schottky barrier at the semiconductor surface and such a potential barrier would drive electrons away from the metal. A Schottky barrier is, however, not always formed, it metal-semiconductor interface. If the density of surface states on the semiconductor is high, the potential barrier formed upon contact with a metal would be smaller than Schottky barrier. We assume that our Pt/ $\text{TiO}_2$  samples have many surface states because they were prepared in aqueous solution and, therefore,

the Pt- $\text{TiO}_2$  contact is ohmic.

Photoelectrochemical devices similar to these Pt/ $\text{TiO}_2$  catalysts have been developed by Noziki<sup>16)</sup> as a "Schottky type photoelectrochemical diode", in which a semiconductor crystal such as GaP or CdS is in contact with a Pt plate. The same laboratory has also developed a "p-n type photoelectrochemical diode", which consists of a p-type and n-type semiconductor contact. Using an n- $\text{TiO}_2$ /p-GaP device they successfully photodecomposed liquid water.

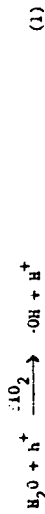
Since adsorbed water is decomposed in both cases, the heterogeneous photocatalytic decomposition of gas phase and liquid phase water is basically the same. The catalyst for the gas phase water photolysis, however, must be relatively inactive for the back reaction of  $\text{H}_2$  with  $\text{O}_2$ . The successful photolysis of gas phase water using  $\text{RuO}_2/\text{TiO}_2$ <sup>10)</sup> or  $\text{NiO}/\text{SrTiO}_3$ <sup>11)</sup> is apparently due to the inactivity of these catalysts for the back reaction. However, their photocatalytic activities are very low. This is attributable to the low activities of  $\text{RuO}_2$  and  $\text{NiO}$  for  $\text{H}_2$  evolution. Although Kawai and Sakata<sup>10)</sup> ascribed the effect of  $\text{RuO}_2$  to enhancement of  $\text{O}_2$  evolution, the catalytic promotion of  $\text{O}_2$  evolution is less important than of  $\text{H}_2$  evolution, because the hole Fermi level of  $\text{TiO}_2$  is sufficiently more positive than the  $\text{O}_2/\text{H}_2\text{O}$  redox potential<sup>14)</sup> so that  $\text{O}_2$  evolves readily at a  $\text{TiO}_2$  electrode. However, since  $\text{RuO}_2$  is even more active for the  $\text{O}_2$  evolution reaction than  $\text{TiO}_2$ , in the actual  $\text{RuO}_2/\text{TiO}_2$  system  $\text{O}_2$  may be evolved from portions of the  $\text{RuO}_2$  surface which are not illuminated.

The photocatalytic activity of Pt/ $\text{TiO}_2$  for the water decomposition<sup>5)</sup> and the water-gas shift<sup>6)</sup> reactions is much improved by reducing  $\text{TiO}_2$  with  $\text{H}_2$ . As noted by Wrighton et al.,<sup>17)</sup> the reduction of a  $\text{TiO}_2$  electrode is also important in Pt -  $\text{TiO}_2$  PEC cells. The  $\text{H}_2$  doping will produce oxygen vacancies in the  $\text{TiO}_2$  lattice so that the resistivity of  $\text{TiO}_2$  is reduced. Since photogenerated electrons must drift through bulk  $\text{TiO}_2$  regions to Pt during the reactions, any increased conductivity of  $\text{TiO}_2$  would enhance the photo efficiency.

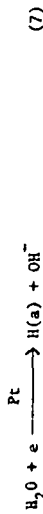
The mechanism of the water photolysis over Pt/ $\text{TiO}_2$  can be described in

analogy with PEC cells. In an acidic solution, a suitable mechanism

is



In neutral and alkaline solution, instead of steps (1) and (4), use



where  $\text{h}^+$  denotes a hole.

In the photoassisted water-gas shift reaction,<sup>6)</sup> CO reacts with  $\text{O}(\text{a})$  formed in step (2) to give  $\text{CO}_2$ .

When water electrolysis (or photolysis) is carried out in neutral water, i.e. with no electrolyte, the diffusion of  $\text{OH}^-$  from cathode to anode would limit the reaction rate. In our previous studies,<sup>5-9)</sup> the rates of most photo-reactions over  $\text{Pt}/\text{TiO}_2$ , 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  $\text{NaOH}/\text{Pt}/\text{TiO}_2$  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 diffu-

sion of  $\text{OH}^-$  from Pt to  $\text{TiO}_2$  and the activation energy observed comes mainly from this diffusion step.

The water photolysis reaction over  $\text{Pt}/\text{TiO}_2$  catalysts competes with the thermal back reaction over Pt. Therefore the observed rate,  $V^{\text{H}_2}$ , of the  $\text{H}_2$  formation is given by the equation,

$$V^{\text{H}_2} = 2V^{\text{O}_2} = V_p - V_t \quad (8)$$

where  $V_p$  is the rate of the photocatalytic production of  $\text{H}_2$  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  $\text{NaOH}/\text{Pt}/\text{TiO}_2$ , the NaOH coating somewhat reduces  $V_p$  while in the LMD 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  $\text{Pt}/\text{TiO}_2$ , neither  $\text{H}_2$  nor  $\text{O}_2$  are observed because the back reaction occurs even before the products desorb from the catalyst. The LMD reaction takes place because  $V_t$  is much suppressed by the water layer. However,  $V_t$  increases with product pressures so  $V^{\text{H}_2}$  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  $\text{Pt}/\text{TiO}_2$  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. 1.

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.<sup>18</sup> Since no  $H_2$  is produced in a control experiment involving no water, the produce  $H_2$  is attributed to water decomposition. The formation of  $O_2$  during the water-gas shift reaction also gives another evidence for gaseous water photolysis.<sup>6</sup>

In the WGS reaction  $v_k$  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. %.

To estimate the quantum efficiency of our present system, we assume, as an upper limit, the flux of photons with energy greater than band gap irradiation is  $10^{17}/\text{sec}$  using a 200 W Hg lamp.<sup>18</sup> Taking into account that two photons are required to produce one  $H_2$  molecule, the highest  $v_{H_2}^0$ , 20  $\mu$  mole/hr, in the GWS reaction corresponds to a quantum efficiency of 7%. This value is much higher than observed in the photooxidation of  $CO$  over  $TiO_2$  which is a known and typical photocatalytic reaction. We believe, on the basis of earlier work,<sup>7,8</sup> that the quantum yield of  $H_2$  production can be improved by the addition of active carbon or other materials which react with  $O_2$  to form  $CO_2$ .

Our results may be compared to those obtained by Wagner et al.<sup>19</sup> 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  $TiO_2$ . Yonemura et al.<sup>20</sup> have also reported the activity of  $SrTiO_3$  powder when its aqueous suspension is illuminated by 1 kW Xe lamp. These results show that powdered  $SrTiO_3$ , unlike  $TiO_2$ , is active in the photoassisted decomposition of  $CO$ . 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<sup>14</sup>). 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.<sup>21</sup> In our preliminary experiments, powdered  $SrTiO_3$  (Alfa) coated with  $NaOH$  showed no activity while platinized forms (with and without  $NaOH$  coating) were active.

#### Acknowledgment

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Figure Captions

Fig. 1

Time courses of the GWD reaction over illuminated NaOH/Pt/TiO<sub>2</sub> Catalysts:  
(a) 7 wt. % NaOH; (b) 14 wt. % NaOH. H<sub>2</sub>O pressure is ~ 24 torr and catalyst temperature is 25°C.

Fig. 2

Temperature dependence of the initial rate of H<sub>2</sub> formation, v<sub>0</sub><sup>H<sub>2</sub></sup>, in the GWD reaction over illuminated NaOH (10 wt. %)/Pt/TiO<sub>2</sub>.

Fig. 3

Time course of the WCS reaction over illuminated NaOH (4 wt. %)/Pt/TiO<sub>2</sub>. H<sub>2</sub>O pressure is ~ 24 torr and catalyst temperature is 25°C.

Fig. 4

Time course of the WCS reaction over illuminated NaOH (7 wt. %)/Pt/TiO<sub>2</sub>. H<sub>2</sub>O pressure is ~ 24 torr and the catalyst temperature is 25°C.

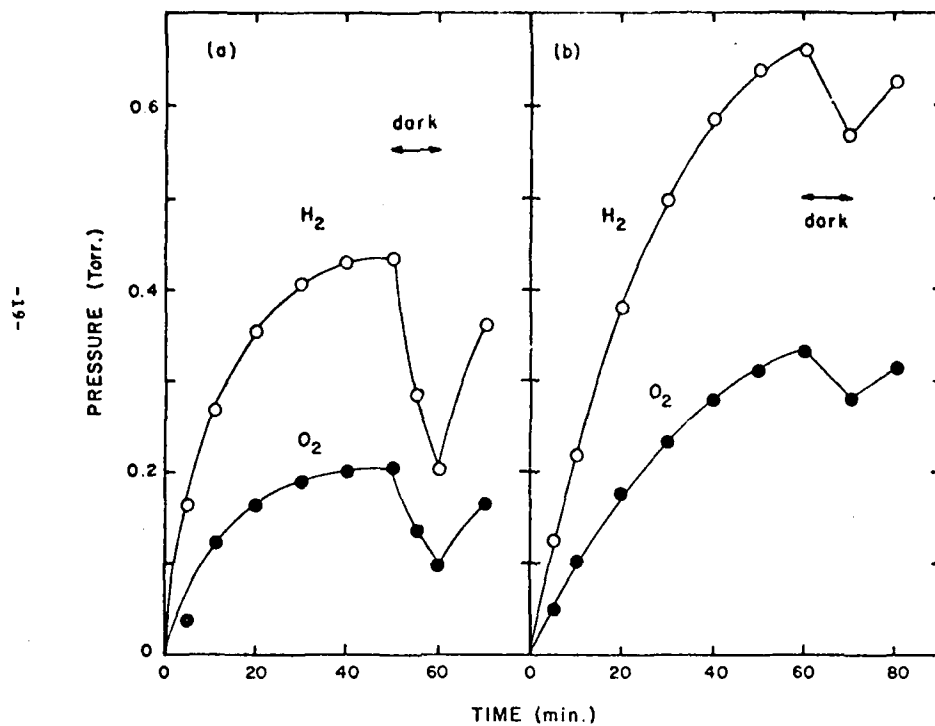
Fig. 5

Time course of the LMD reaction over illuminated Pt/TiO<sub>2</sub> immersed in NaOH solution (~2.5M).

Fig. 6

Initial H<sub>2</sub> formation rates, v<sub>0</sub><sup>H<sub>2</sub></sup>, in the GWD (○), WCS (□) and LMD (●) reactions over illuminated Pt/TiO<sub>2</sub> or NaOH/Pt/TiO<sub>2</sub> as a function of NaOH loading. (See text for the definition of the abscissa for the LMD reaction).

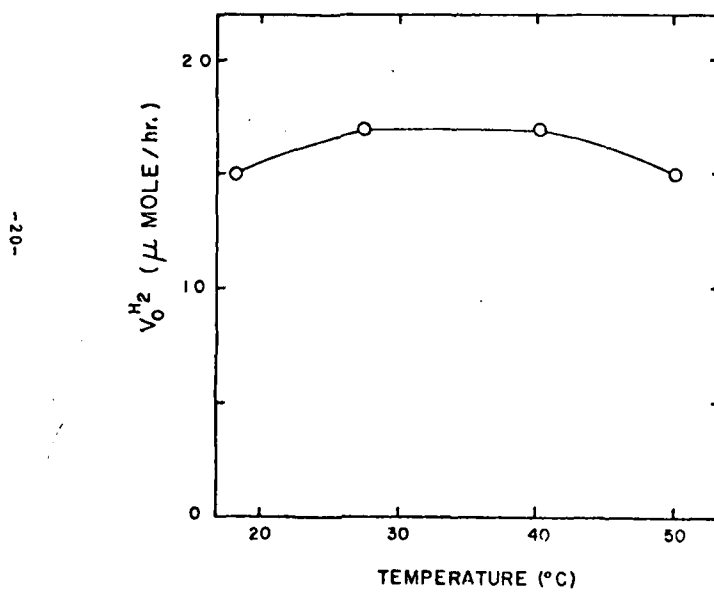
Fig. 1



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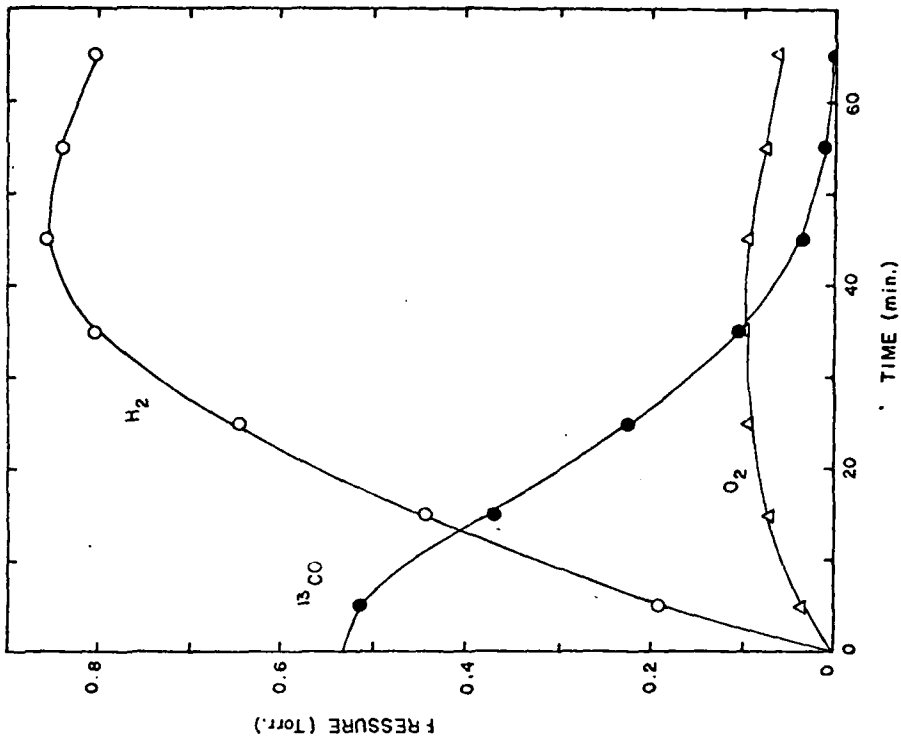
Fig. 2



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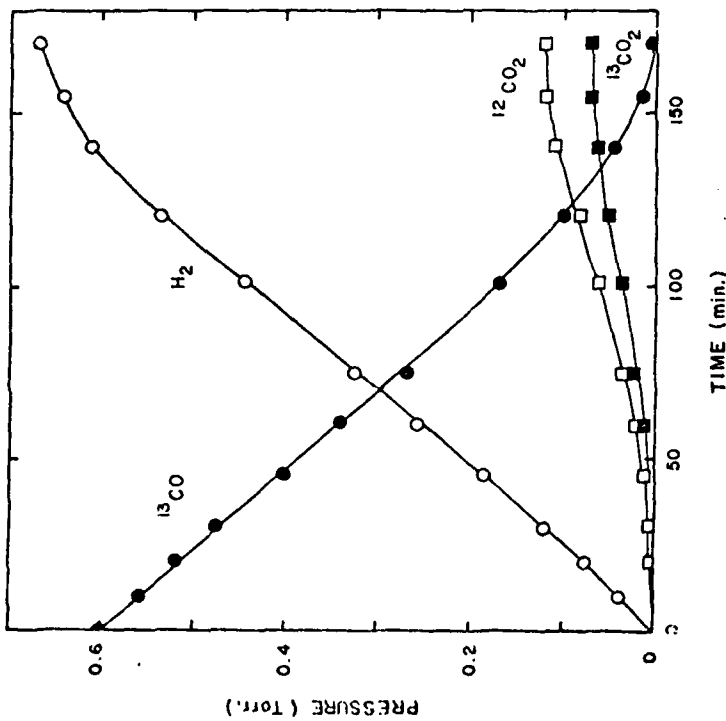
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Fig. 4



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Fig. 3



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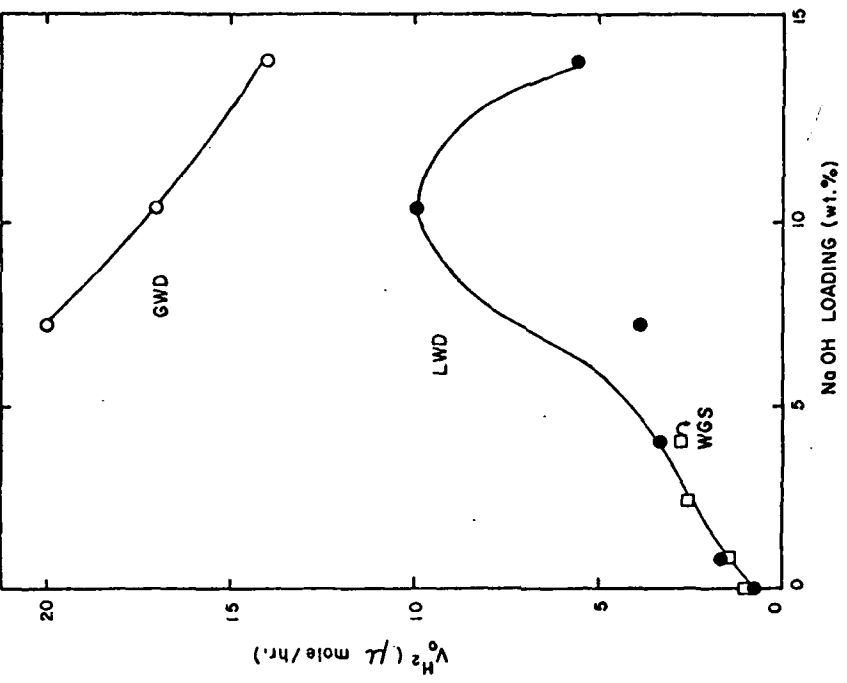
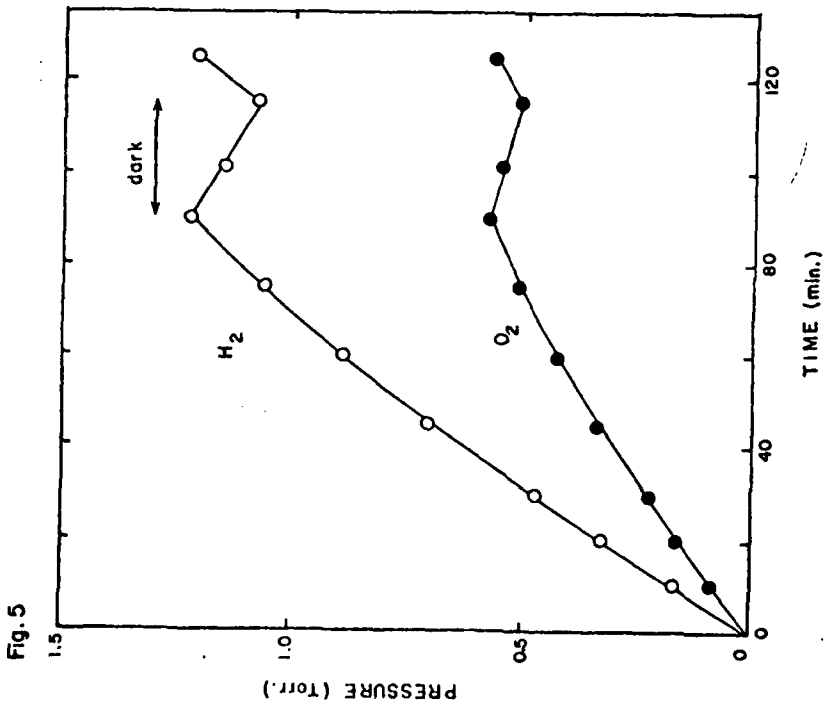


Fig. 5

Fig. 6

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