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Photocatalytic Water Decomposition and Water–Gas Shift Reactions over NaOH-Coated, Platinized TiO_2[1]

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The photocatalytic decomposition of gaseous water takes place over platinized TiO_2 coated with NaOH (more than 7 wt%). The quantum efficiency of H_2 and O_2 production reaches about 7% (20 μmole H_2/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 platinized TiO_2 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 platinized TiO_2 is observed.

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 (*1*). Recently some heterogeneous catalytic systems have been found to be effective for the photolysis of water. Bulatov and Khidekel (*2*) have reported the photodecomposition of liquid water using platinized TiO_2 (Pt/TiO_2). Other work, with one exception (*3*), has found that adsorbed water is not photodecomposed over illuminated pure TiO_2 (*4, 5*). Our previous experiments (*5*), while showing that TiO_2 has no photocatalytic activity for the decomposition of gas- and liquid-phase water, has found that Pt/TiO_2 is surely effective for the liquid water photolysis. Pt/TiO_2 also photocatalyzes the reactions of gas-phase water with CO (*6*), hydrocarbons (*7*), active carbon (*7, 8*), and lignite (*9*) to produce H_2 and CO_2. In the liquid water photolysis by Pt/TiO_2, however, the production of H_2 and O_2 declines rapidly as gas-phase products accumulate and finally stops (*5*). When Pt/TiO_2 is illuminated in the presence of gas-phase water, no detectable amounts of products are produced because the thermal back reaction ($H_2 + \frac{1}{2} O_2 \rightarrow H_2O$) occurs rapidly on Pt.

The photodecomposition of gas-phase water has been recently reported by Kawai and Sakata (*10*) and Domen *et al.* (*11*), who employed RuO_2/TiO_2 and $NiO/SrTiO_3$, respectively. The rate of H_2 formation was 0.6 μmole/hr by a 500-W Hg lamp in the former and 0.2 μmole/hr by a 450-W Hg lamp in the latter. Wagner and Somorjai (*12*) have also observed gaseous water photodecomposition over platinized and metal-free $SrTiO_3$ crystals, both of which were coated with NaOH. The H_2 formation rate over the NaOH-coated $Pt/SrTiO_3$ was 1.8 μmole/hr by a 500-W Hg lamp. They also studied the liquid water photolysis over $Pt/SrTiO_3$ immersed in alkaline solution and found that the reaction rate increases with pH. The maximum H_2 formation rate obtained was 7.5 μmole/hr.

The results of Wagner and Somorjai (*12*) indicate that the NaOH coating suppresses the back reaction so that the gas-phase water photolysis occurs on the $Pt/SrTiO_3$ 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_2

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allows detectable amounts of H_2 and O_2 to form when gas-phase water is used. Moreover, as with $Pt/SrTiO_3$, liquid water photolysis over Pt/TiO_2 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_2 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_2 was also tested for the reactions. The photooxidation of CO was carried out on the TiO_2 samples used to prepare Pt/TiO_2 in order to check their photocatalytic activities for a standard photoreaction.

2. EXPERIMENTAL

TiO_2 (MCB anatase, particle size ~125–250 μm by sieves) was reduced (doped) at 700°C for 6 hr in flowing H_2 to enhance photocatalytic activity. Platinized TiO_2 (~3 wt% Pt) was prepared by the photodecomposition of hexachloroplatinic acid (*13*). The BET surface areas of undoped TiO_2, doped TiO_2, and Pt/TiO_2 were 11, 9, and 10 m^2/g, respectively. The catalyst (0.25 g) was spread uniformly on the flat bottom (14 cm^2) 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_2 at 200°C for about 15 hr and outgassed at the same temperature for 2 hr. NaOH-coated Pt/TiO_2 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_2 or $NaOH/Pt/TiO_2$ and the sample was then dried in flowing He at ≃40°C. NaOH-coated TiO_2 and NaCl-coated Pt/TiO_2 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 $NiSO_4$ 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 5×10^{-4} 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_2 experiments, was washed in running water, dried, and then used with NaOH-coated TiO_2, 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 (GWD)

Photocatalytic activity for GWD was tested for undoped and doped TiO_2 with and without NaOH coating. Undoped TiO_2 and NaOH/undoped TiO_2 (3.2 wt% NaOH) produced neither H_2 nor O_2 during 100 min illumination. Doped TiO_2 and NaOH/doped TiO_2 (1.6 wt% NaOH) produced a small amount of H_2 but no O_2 was detected even after 15 hr illumination. This H_2 formation is probably due to the reaction of water with strongly reduced forms of TiO_2 as concluded previously (*5*, *6*).

NaOH-coated Pt/TiO_2 catalysts produce H_2 and O_2 in the GWD reaction when NaOH loading exceeds about 3 wt% and their formation rates and maximum pressures depend on NaOH loading. The stationary-state H_2 and O_2 formation over 3 wt% NaOH/Pt/TiO_2 was very small (less than 1×10^{-2} Torr) and, after turning off the light, the pressures of H_2 and O_2 dropped promptly to zero, indicating a fast back reaction on the catalyst. The initial rates of H_2 and O_2 formation were too fast to determine them accurately. When NaOH loading was increased to 7 wt%, the maximum amounts of H_2 and O_2 increased significantly as shown in Fig. 1a. In repeated runs with the same catalyst, the photocatalytic activity of NaOH/Pt/TiO_2 for GWD increased slightly by some unspecified mechanism. A stationary activity was usually attained after about 3 hr 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 H_2 and 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 H_2 and O_2 decreased rapidly in the dark and again increased after reillumination as seen in Fig. 1. The H_2/O_2 ratio usually exceeds slightly the stoichiometric value of 2. This deviation from the stoichiometric ratio probably arises from the photoadsorption of O_2 on the catalyst since the ratio dropped to about 2 in the dark period (see Fig. 1a) and it was always less than 2 during the early stages of the reaction carried out after a brief evacua-

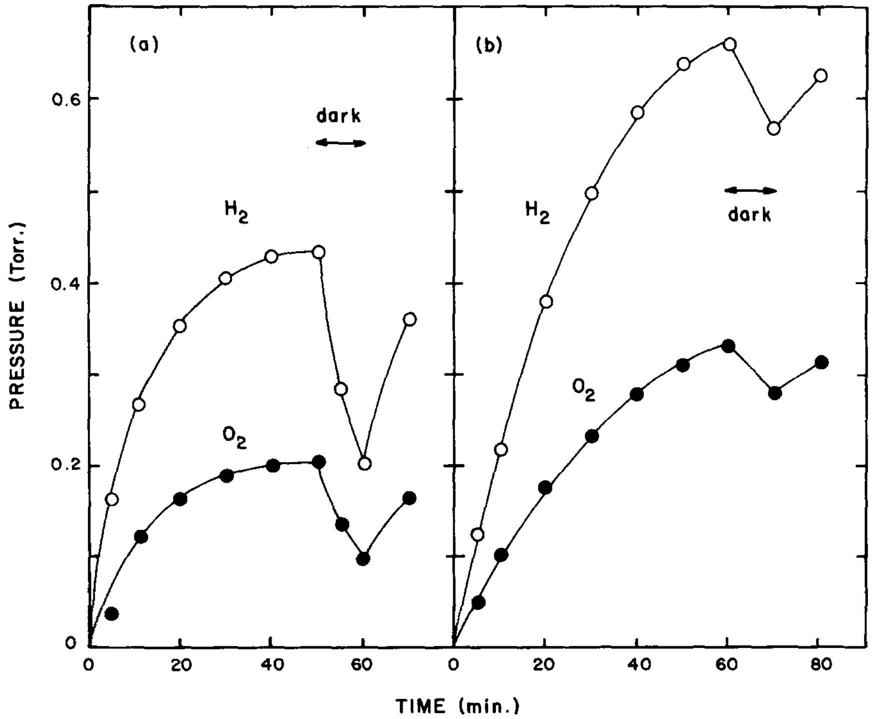

FIG. 1. Time courses of the GWD reaction over illuminated NaOH/Pt/TiO_2 catalysts: (a) 7 wt% NaOH; (b) 14 wt% NaOH. H_2O pressure is ~24 Torr and catalyst temperature is 25°C.

tion of the reaction system. The maximum pressures of H_2 and O_2 increased with the NaOH loading but the initial rate of the reaction decreased (see Fig. 1b). The dependence of the initial rate of H_2 formation, $V_0^{H_2}$, on the NaOH loading is shown in Fig. 6 (to be discussed later).

Temperature, pressure, and wavelength dependences of the rate of GWD were examined using 10 wt% NaOH/Pt/TiO_2. Figure 2 shows that $V_0^{H_2}$ is almost independent of reaction temperature in the range 18–50°C. On the other hand, the maximum pressures of H_2 and O_2, achieved in these experiments, decrease with increasing temperature, probably because the back reaction becomes fast. For example, at 25°C, $p_{max}^{H_2} = 0.55$ Torr, while at 50°C it dropped to 0.26 Torr. When the reaction was carried out at about 5 Torr of H_2O pressure at room temperature, the initial H_2 formation rate was about half of the rate at 24 Torr of H_2O pressure, presumably due to decrease in the amount of adsorbed H_2O. The wavelength dependence was qualitatively measured using three cutoff filters. A uv cutoff filter (415 nm cutoff) completely eliminates the reaction. A Plexiglas filter (≈380 nm cutoff) and a Pyrex glass filter (≈275 nm cutoff) 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 Pt/TiO_2 (*6*).

The photocatalytic activity of NaCl-coated Pt/TiO_2 for GWD was tested using 10 wt% NaCl/Pt/TiO_2. Although the water–gas shift and liquid water decomposition reactions take place on this catalyst under illumination, the GWD reaction did not occur at all. We assume that NaCl on Pt/TiO_2 would crystallize when outgassed and, after introducing gaseous water, it would not absorb enough water to form a liquid electrolyte layer. Under such conditions the Pt surface would not be well covered with a NaCl film and the back reaction would overwhelm the photoprocess. In addition, a specific adsorption of Cl^- ions on Pt may inhibit the hydrogen evolution reaction since a NaCl coating has an inhibitory effect on the water–gas shift reaction as will be described later.

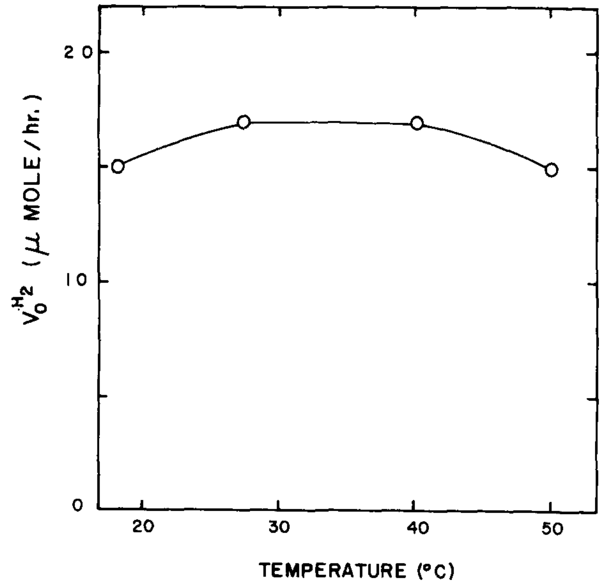

FIG. 2. Temperature dependence of the initial rate of H_2 formation, $V_0^{H_2}$, in the GWD reaction over illuminated NaOH (10 wt%)/Pt/TiO_2.

3.2. *Water–Gas Shift (WGS) Reaction*

The Pt/TiO_2 used in the present experiments showed less photocatalytic activity for the WGS reaction than that used in previous experiments (*6*); the reaction rate was 1.1 μmole/hr for the former and 2.4 μmole/hr for the latter. This difference in the photocatalytic activity may be due to a lower doping level of the "sieved" TiO_2 used in the present experiments. A relative doping level of TiO_2 can be estimated from the amount of H_2 formed in the reaction of H_2O with doped TiO_2 under illumination. Although the doping condition is the same, "unsieved" TiO_2 produces more H_2 than "sieved" TiO_2 in this reaction, probably because the former is more easily reduced than the latter.

When Pt/TiO_2 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_2 is shown in Fig. 3. At the beginning of the reaction, CO_2 formation is very slow because of the reaction of CO_2 with NaOH. As the reaction proceeds, CO_2 formation becomes faster but $^{12}CO_2$ exceeds $^{13}CO_2$ even though ^{13}CO is used as a reactant. This $^{12}CO_2$ formation probably arises from the exchange reaction of $^{13}CO_2$ with Na_2CO_3 originally present in NaOH (about 1%). By taking the isotopic purity of ^{13}CO (90%) into account, the amount of H_2 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_2, 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_2 is formed. Similar phenomena have been observed in the WGS reaction over Pt/TiO_2 (*6*). The thermal WGS reaction did not take place at all over NaOH/Pt/TiO_2 catalysts at room temperature.

The kinetics of the WGS reaction were examined using 2.4 wt% NaOH/Pt/TiO_2. The reaction is nearly zero (slightly positive) order in CO pressure between 0.3 and 0.75 Torr. When the H_2O pressure is reduced from 24 Torr to about 5 Torr by cooling a part (not the catalyst) of the

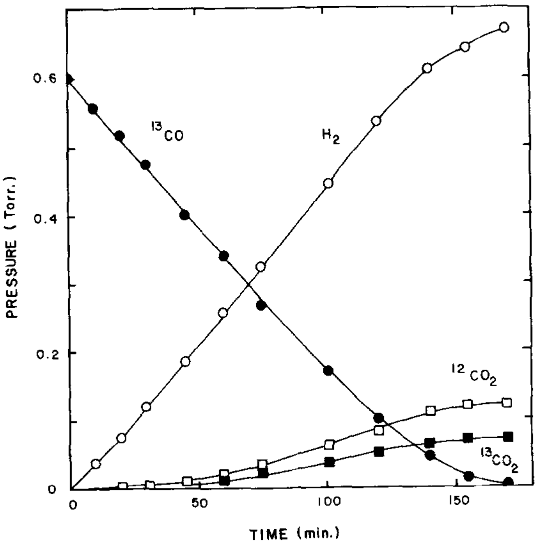

FIG. 3. Time course of the WGS reaction over illuminated NaOH (4 wt%)/Pt/TiO_2. H_2O pressure is ~24 Torr and catalyst temperature is 25°C.

reaction system to 0°C, the rate falls by a factor of 4. When the H_2O 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 $NaOH/Pt/TiO_2$ 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_2 was formed (see Fig. 4). The O_2 pressure reached 0.1 Torr and decreased after the CO pressure fell to about 0.05 Torr. No appreciable CO_2 was formed during this reaction. The H_2 formation was very fast at the beginning of reaction but declined with time. This decline of the rate and the decrease in H_2 pressure after 45 min are apparently caused by the reaction of H_2 with O_2. The initial H_2 production rate in this reaction, 24 μmole/hr, is the highest value obtained in the present experiments.

The WGS reaction over 10 wt% $NaCl/Pt/TiO_2$ 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_2 was slow ($V_0^{H_2} = 0.9$ μmole/hr) as compared to the previous

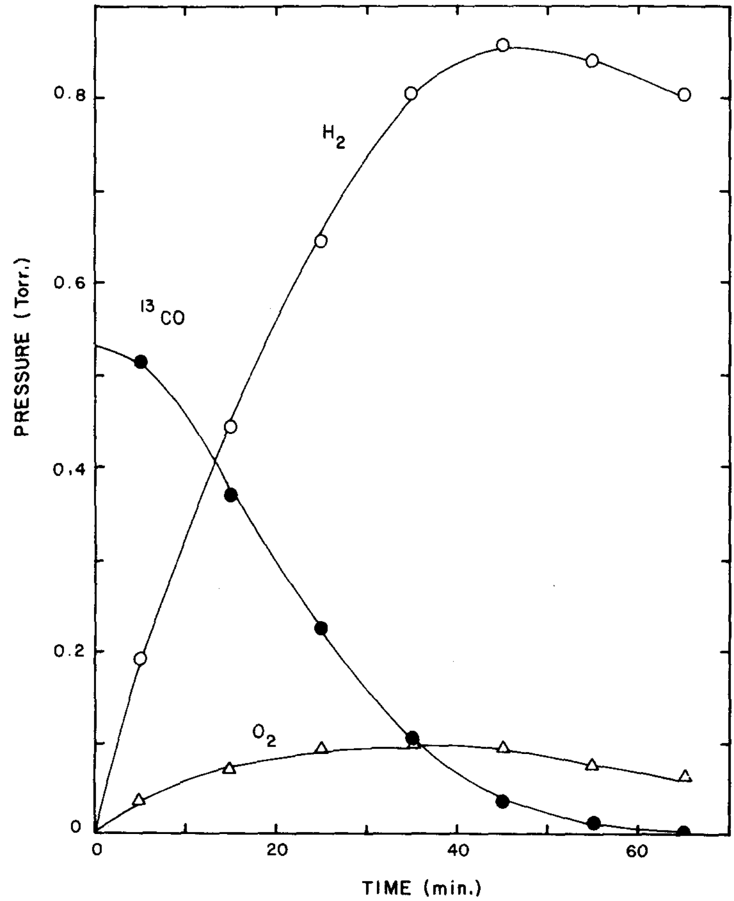

FIG. 4. Time course of the WGS reaction over illuminated NaOH (7 wt%)/Pt/TiO_2. H_2O pressure is ~24 Torr and the catalyst temperature is 25°C.

results ($V_0^{H_2}$ = 6 μmole/hr) (5). The photocatalytic activity for LWD is much improved by coating Pt/TiO_2 with NaOH as shown in Fig. 6. It should be noted that since the NaOH on Pt/TiO_2 dissolves into water the reaction is carried out in NaOH solution. Assuming the amount of water introduced is 0.25 ml, 1 wt% NaOH will make 0.25 *M* 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 *M*. In addition to the increase in the initial rate, the maximum pressures of H_2 and O_2 also increase with NaOH concentration while the reaction of H_2 with O_2 in the dark becomes slower. Figure 5 shows the evolution of H_2 and O_2 when 10 wt% NaOH/Pt/TiO_2 is immersed in liquid water (~0.2 ml) and illuminated. Both the H_2 and O_2 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_2 and O_2 are fairly high.

A further increase in the NaOH concentration from about 2.5 *M* to about 3.2 *M* 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 (~2 *M*), the initial rate of the LWD reaction was 1.4 μmole/hr; the reaction is obviously faster than in pure

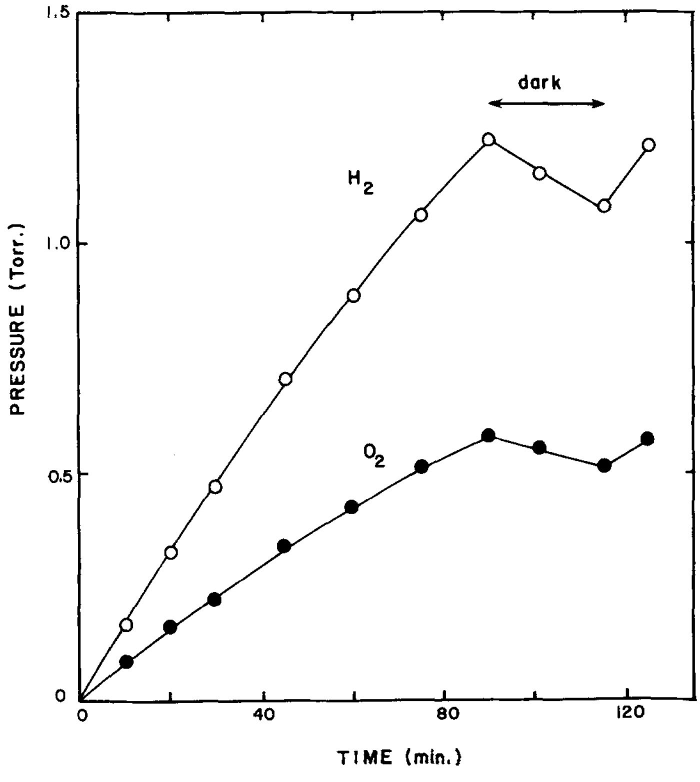

FIG. 5. Time course of the LWD reaction over illuminated Pt/TiO_2 immersed in NaOH solution (~2.5 *M*).

water but much slower than in NaOH solution.

3.4. Photooxidation of CO

To characterize the photocatalytic activity of TiO_2, a common photocatalytic reaction, photooxidation of CO, was used. Doped and undoped TiO_2 and NaOH-coated, undoped TiO_2 were tested. The reaction was carried out at room temperature using a mixture of 54% O_2 and 46% CO at about 0.3 Torr total pressure. The initial rate of the reaction over undoped TiO_2 was 0.7 μmole/hr and there was no appreciable difference in the photocatalytic activity between undoped and doped TiO_2. $NaOH/TiO_2$ showed very slightly less activity (0.6 μmole/hr) than TiO_2. The CO oxidation over Pt/TiO_2 was so fast in the dark that the photocatalytic activity of Pt/TiO_2 for this reaction could not be measured.

4. DISCUSSION

The present experiments again confirmed the inactivity of TiO_2 for water photolysis even when it is coated with NaOH. To photolyze water, some material such as Pt (*5*) or RuO_2 (*10*) must be added. The reason for this has been discussed previously (*8*) in terms of the energy band diagram of illuminated TiO_2 (*14*). Although the flat band potential (electron Fermi level) of TiO_2 has typically been placed at a position slightly more positive than the H^+/H_2 redox potential (*14*), the most recent study by

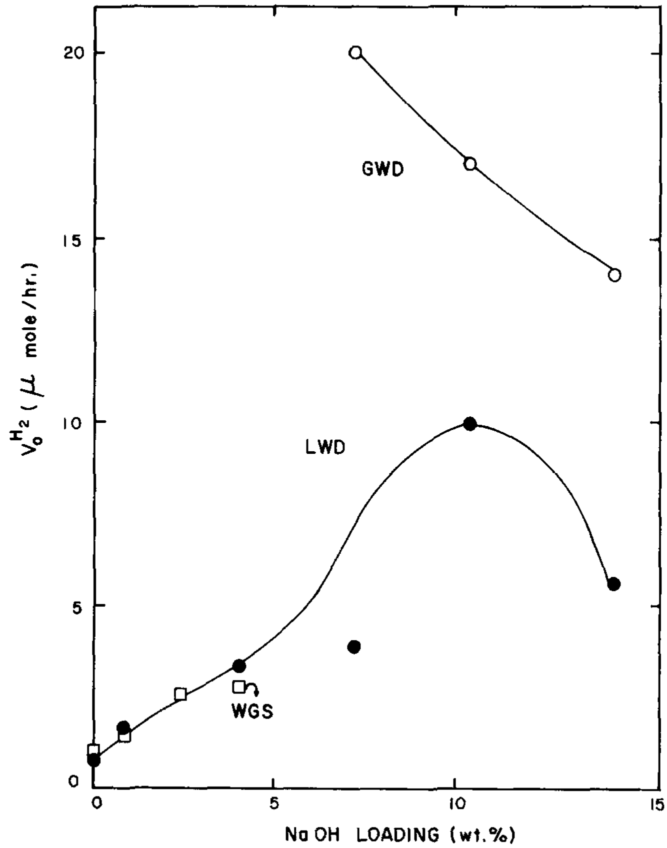

FIG. 6. Initial H_2 formation rates, $V_0^{H_2}$, in the GWD, WGS, and LWD reactions over illuminated Pt/TiO_2 or $NaOH/Pt/TiO_2$ as a function of NaOH loading. (See text for the definition of the abscissa for the LWD reaction.)

Tomkiewicz (*15*) shows that the former is about 100 mV more negative than the latter. This implies that water photolysis in PEC cells with a TiO_2 photoanode is energetically possible under short-circuit conditions, even though actual Pt–TiO_2 PEC cells require some external potential to decompose water (*14*). The requirement of an external potential in Pt–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 H^+/H_2 potential as observed by Tomkiewicz (*15*), since water is photolyzed by Pt/TiO_2 catalysts, which can be modeled as a set of small, short-circuited Pt–TiO_2 cells. However, TiO_2 alone would be inactive for the photolysis of water even if 100 mV is available as an overvoltage for H_2 evolution because TiO_2 is so inactive for the H_2 evolution reaction. More than 100 mV is needed for this evolution to proceed at a measurable rate. As compared to Pt–TiO_2 PEC cells, the potential loss in Pt/TiO_2 catalyst would be small since Pt is in direct contact with TiO_2. It should be noted that a metal–semiconductor contact may give rise to a 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 at a 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 a Schottky barrier. We assume that our Pt/TiO_2 samples have many surface states because they were prepared in aqueous solution and, therefore, the Pt–TiO_2 contact is ohmic.

Photoelectrochemical devices similar to these Pt/TiO_2 catalysts have been developed by Nozik (*16*) 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*-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 H_2 with O_2. The successful photolysis of gas-phase water using RuO_2/TiO_2 (*10*) or $NiO/SrTiO_3$ (*11*) 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 RuO_2 and NiO for H_2 evolution. Although Kawai and Sakata (*10*) ascribed the effect of RuO_2 to enhancement of O_2 evolution, the catalytic promotion of O_2 evolution is less important than that of H_2 evolution, because the hole Fermi level of TiO_2 is sufficiently more positive than the O_2/H_2O redox potential (*14*) so that O_2 evolves readily at a TiO_2 electrode. However, since RuO_2 is even more active for the O_2 evolution reaction than TiO_2, in the actual RuO_2/TiO_2 system O_2 may be evolved from portions of the RuO_2 surface which are not illuminated.

The photocatalytic activity of Pt/TiO_2 for the water decomposition (*5*) and the water–gas shift (*6*) reactions is much improved by reducing TiO_2 with H_2. As noted by Wrighton *et al.* (*17*), the reduction of a TiO_2 electrode is also important in Pt–TiO_2 PEC cells. The H_2 doping will produce oxygen vacancies in the TiO_2 lattice so that the resistivity of TiO_2 is reduced. Since photogenerated electrons must drift through bulk TiO_2 regions to Pt during the reactions, any increased conductivity of TiO_2 would enhance the photoefficiency.

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

$$H_2O + h^+ \xrightarrow{TiO_2} \cdot OH + H^+, \qquad (1)$$

$$2 \cdot OH \xrightarrow{TiO_2} H_2O + O(a), \qquad (2)$$

$$2\,O(a) \xrightleftharpoons{TiO_2} O_2, \qquad (3)$$

$$H^+ + e \xrightarrow{Pt} H(a), \qquad (4)$$

$$2\,H(a) \xrightleftharpoons{Pt} H_2. \qquad (5)$$

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

$$OH^- + h^+ \xrightarrow{TiO_2} \cdot OH, \qquad (6)$$

$$H_2O + e \xrightarrow{Pt} H(a) + OH^-, \qquad (7)$$

where h^+ denotes a hole. In the photoassisted water–gas shift reaction (*6*), CO reacts with O(a) formed in step (2) 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 previous studies (*5–9*), 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

$$V^{H_2} = 2V^{O_2} = V_p - V_t, \qquad (8)$$

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^{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 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. 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 (*18*). 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 additional evidence for gaseous water photolysis (*6*).

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%.

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}/sec using a 200-W Hg lamp (*19*). By taking into account that two photons are required to produce one H_2 molecule, the highest $V_0^{H_2}$, 20 μmole/hr, in the GWD reaction corresponds to a quantum efficiency of 7%. This value is much higher than that 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 (*7*, *8*), 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 and Somorjai, (*12*) 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.* (*20*) have also reported the activity of $SrTiO_3$ powder when its aqueous suspension is illuminated by a 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 (*14*)). Although the mechanism involved is not well understood, a part of the $SrTiO_3$ surface could become the cathode while another part the photoanode. The photoactivity of powdered $SrTiO_3$, however, seems to depend on its preparation method (*21*). In our preliminary experiments, powdered $SrTiO_3$ (Alfa) coated with NaOH showed no activity while platinized forms (with and without NaOH coating) were active.

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