PHOTODECOMPOSITION OF WATER OVER Pt/TiO$_2$ CATALYSTS*

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Experiments demonstrate that the decomposition of water is catalytic at 23° C when a platinized, powdered titanium dioxide catalyst, illuminated with band-gap radiation, is used.

1. Introduction

The photoassisted decomposition of H$_2$O in photoelectrochemical (PEC) cells has recently received attention as a potential solar energy conversion and storage system [1−3]. Heterogeneous catalysts have some general advantages as compared to PEC cells because they are less expensive to construct and because they can be made with large surface areas. However, these advantages cannot be realized until photocatalytic activity is demonstrated. The heterogeneous photocatalytic decomposition of gas phase H$_2$O has been reported by Schrauzer and Guth [4], who detected H$_2$ and O$_2$ in the ratio of 2 · 1 when TiO$_2$ or Fe$_2$O$_3$-doped TiO$_2$ was equilibrated with H$_2$O vapor and illuminated by UV light in an Ar atmosphere. The H$_2$ and O$_2$ formation was, however, much slower than in PEC cells, and after a few hours, the rate dropped to almost zero. They ascribed the rate loss to the back reaction This experiment has been repeated by van Damme and Hall [5] using a flow system in order to determine the steady-state photocatalytic activity of TiO$_2$. After 6 h of UV illumination and product collection, only a trace of H$_2$ was detected. Based on this result they concluded that any observed H$_2$ production on TiO$_2$ is not catalytic and probably arises from the photodecomposition of the hydroxylated surface typically found on TiO$_2$ [6].

Metalized semiconductors often show different selectivities in heterogeneous photocatalytic reactions

than semiconductors alone. For example, Kraeutler and Bard [7] have shown that platinized TiO$_2$ catalyzes the decomposition of liquid acetic acid selectively to methane under UV illumination. However, in a PEC cell using TiO$_2$ as the photoanode, the products are dominated by ethane. Bulatov and Khidekel [8] have claimed the photodecomposition of water (1 N H$_2$SO$_4$) in the presence of platinized TiO$_2$.

We report here studies of reactions of H$_2$O over TiO$_2$ and platinized TiO$_2$ (Pt/TiO$_2$) and find no evidence of catalytic activity for water decomposition in the former case while in the latter measurable catalytic activity is found when Pt/TiO$_2$ is wet. Isotopically labelled water, H$_2^{18}$O and D$_2$O, were used to establish some features of the mechanism.

2. Experimental

Reactions were carried out in an evacuable, closed circulation system (180 ml volume) linked to a mass spectrometer. The reaction cell was made of quartz, and during reaction, its temperature was maintained at 23°C by a water bath. The catalyst (0.25 g) was spread uniformly on one face of the reaction cell and outgassed at 200°C for 3 h. After introducing reactants, it was illuminated by a 200 W high-pressure mercury lamp that was filtered through a quartz cell filled with NiSO$_4$ solution to remove infrared. The gas mixture was sampled at various times, and after

passage through a cold trap at about $-110°C$ to re-
move H_2O, was analyzed by the mass spectrometer.

TiO_2 (anatase) was obtained from MCB and plat-
inized TiO_2 (≈ 2 wt% Pt) was prepared by the photo-
decomposition of hexachloroplatinate dissolved in a
Na_2CO_3—acetic acid buffer solution [9]. The total
surface area was about 11 m^2 g^{-1} Oxygen-18 H_2O
(99.3%) was obtained from Prochem and D_2O (99 8%)
from Clini-chem. Distilled H_2O (or the above isotopic
compounds), outgassed several times at dry-ice tem-
perature, was introduced as a gas into the reaction
vessel at 24 Torr, the room temperature vapor pres-
sure (we refer to this catalyst as "dry"). In some ex-
periments the catalyst was cooled to $0°C$ during H_2O
admission in order to enhance the amount of water
adsorbed (we define this as a "wet" catalyst since a
liquid—vapor equilibrium was established after warm-
up to $23°C$).

3. Results and discussion

The TiO_2 sample was variously pretreated (1) Cal-
cined in air at 1000°C for 2 h as recommended by
Schrauzer and Guth [4], (2) reduced (doped) in a H_2
stream at temperatures between 500 and 750°C for
3—10 h and (3) no pretreatment None of these TiO_2
samples were active for the photocatalyzed produc-
tion of H_2 and O_2 from H_2O in either the dry or the
wet state. In the case of strongly doped TiO_2, only
H_2 was formed under UV illumination and the max-
imum amount was about 3×10^{-7} mole (about 10^{17}
molecules m^{-2}). Hydrogen formation was not affect-
ed by the presence of N_2 or CO but was completely
retarded by the addition of 3×10^{-2} Torr of O_2.
These results suggest that H_2 is formed by the non-
catalytic reaction of H_2O with a strongly reduced
form of TiO_2. such as TiO [10] Such a reaction
could increase the surface OH concentration and it is
not unreasonable to expect a change on the order of
$10^{17}-10^{18}$ m^{-2} [6]. This would account for all of
the observed H_2.

Dry, platinized TiO_2, prepared from TiO_2 doped
in H_2 at 700°C for 6 h, also produced H_2 in the pres-
ence of gas phase H_2O under UV illumination, with
concomitant formation of CO_2 and a small amount
of CH_4‡, but no O_2 was observed. This H_2 is thought
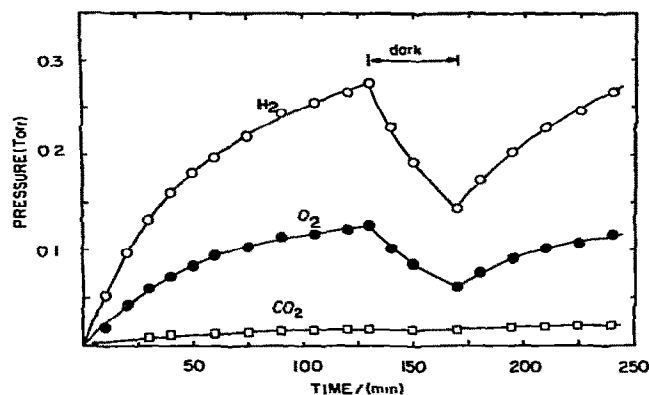
‡ The details of this reaction will be reported elsewhere.

Fig. 1. Time dependence of H_2, O_2 and CO_2 production in a
system comprised of Pt/TiO_2, H_2O (ℓ) and band gap radiation
at 23°C. During the period 130—170 min, the light source
was off.

to form in the same way as for strongly doped TiO_2
alone (see above). When a fresh Pt/TiO_2 sample was
illuminated in vacuum (3×10^{-7} Torr), no detectable
products were formed. This suggests that, in the ab-
sence of H_2O, hydroxyls present on TiO_2 are not de-
composed by UV light.

When Pt/TiO_2 was outgassed at 200°C for 2 h, wet
at $0°C$ with enough H_2O (0 2 ml) to cover its surface,
and irradiated by UV light at 23°C, H_2 and O_2 were
formed in the ratio of nearly 2 : 1 (see fig. 1). The ini-
tial rate of H_2 formation was 3.5×10^{-7} mole/h but
decreased to about 1×10^{-7} mole/h after 2 h of ir-
radiation. As a check on the source of this decline in
the rate, the light source was turned off after 130 min
(fig. 1). Over the next 40 min, H_2 and O_2 were slowly
consumed. When the light source was turned on at
170 min, the H_2 and O_2 pressures rose again. These
results clearly point to the back reaction of H_2 and
O_2 on Pt as the source of the declining net rate of H_2
and O_2 evolution. The rate of the back reaction is
much slower than on dry Pt/TiO_2 probably because
it is diffusion-controlled in the wet system. As shown
in fig. 2, when $H_2{}^{18}O$ was used H_2 and ^{18}O, were
formed. A small amount of $C^{18}O_2$ was also formed.
The amount of $^{18}O^{16}O$ formed was about 2% of
$^{18}O_2$ and no $^{16}O_2$ was observed. The $C^{18}O_2$ forma-
tion is ascribed to the oxidation of a variable amount
of adsorbed carbon present as a result of the decom-
position of acetic acid during the preparation of cat-
alyst. As a result, the H_2/O_2 ratio in figs. 1 and 2 is
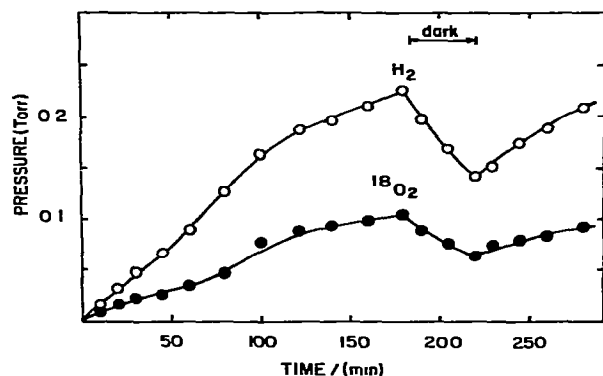slightly greater than 2. This result clearly shows that

Fig. 2. Time dependence of H_2 and $^{18}O_2$ production over an illuminated Pt/TiO_2 catalyst wet with $H_2^{18}O$ at $23°C$. During the period $180-220$ min, the light source was off.

Fig. 3. Time dependence of H_2 and O_2 production at 0 and $23°C$.

under conditions where H_2, O_2 and CO_2 are formed, the oxygen is derived from H_2O, not from surface OH present at the beginning of the reaction. A separate experiment shows that oxygen isotope exchange is slow. When D_2O was substituted for H_2O, the products were D_2, O_2 and a small amount of HD. No strong conclusions can be drawn from this data since D for H exchange at the surface is relatively fast.

In repeated experiments with the same catalyst, the time evolution of H_2 was reproducible to within ±25% as long as the products were evacuated for only a short time However, the activity slowly declined if extensive evacuation was done at room temperature or $200°C$. Apparently the catalyst is poisoned but the mechanism is unknown.

Fig. 3 shows that the rate dropped by about a factor of two when the catalyst was cooled to $0°C$ by an ice—water mixture; the apparent activation energy is estimated to be 5 kcal/mole. The use of a 415 nm cut-off filter completely stopped the reaction (fig. 4), while a Plexiglass filter (380 nm cut-off) suppressed the rate lo less than 1/20 and a Pyrex glass filter (275 nm cut-off) had little effect. The energy efficiency during the initial stages of the water decomposition reaction is roughly 5×10^{-4}. It is also noteworthy that Pt/TiO_2 prepared from undoped TiO_2 is much less active than Pt/H_2-doped TiO_2.

After the total amount of H_2 formed in the present experiments exceeded 10^{-5} mole the catalyst still showed significant activity for the photodecomposition of H_2O. This is additional evidence that the pho-
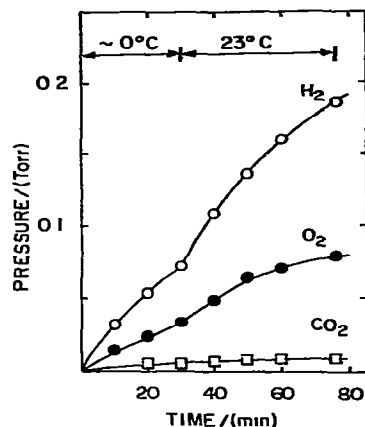
tolysis of H_2O on Pt/TiO_2 is catalytic. If only initially present surface OH groups on TiO_2 were photodecomposed, the amount of H_2 should never exceed 9×10^{-6} mole because the Pt/TiO_2 outgassed at $200°C$ has at most 4.4×10^{19} OH/g, which was determined by hydrogen exchange between D_2 and the surface OH groups.

The mechanism of the present process is not understood but probably involves features similar to those of PEC cells or Schottky barrier type photochemical diodes [11], in which Pt functions as a cathode and TiO_2 as a photoanode. Differences do exist, however, since the operation of a $Pt-TiO_2$ PEC cell requires some external electrical potential in addition
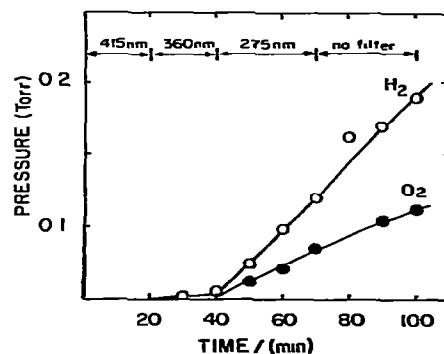
Fig. 4. Effect of cut-off filters on the production of H_2 and O_2 from a wet, illuminated Pt/TiO_2 catalyst at $23°C$.

to band-gap radiation to decompose H_2O [2] while the Pt/TiO_2 powder catalyst works using only light. The Schottky barrier at a $Pt-TiO_2$ interface may play an important role in electron—hole separation

4. Summary and conclusions

These results demonstrate that the thermally up-hill water decomposition reaction can be driven at $23°C$ using band-gap illumination of a Pt/TiO_2 powder covered with liquid water. As H_2 and O_2 accumulate, the back reaction becomes important and a photostationary state is reached. Isotopic labelling experiments show that liquid phase water is utilized and total yield measurements confirm that the products are not limited to a stoichiometric reaction of hydroxyl groups initially present at the surface. In the case of dry catalysts where small amounts of H_2 and no O_2 are formed, it is not clear whether the basic mechanism changes or the back reaction dominates The mechanism, in either case, is not well-understood and many experiments must be done involving other catalysts, reactants and conditions Some of these have been done or are underway in our laboratory For example, the water-gas shift reaction [12] and the reactions of ethylene [13], and Texas lignite [14] with gas phase water are photocatalytic.

Acknowledgement

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