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H_2 Evolution from Various Aqueous Solutions over Thermally Reduced TiO_2 and Pt–TiO_2 Powder

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The reduction of H_2O (or H^+) to form H_2 by reduced TiO_2 and Pt–TiO_2 was studied in distilled water and aqueous solutions of HCl, H_2SO_4, HNO_3, and NaOH. Over the reduced TiO_2 powder, H_2 evolved moderately in distilled water and Ti^{3+} ions on the surface were presumed to be active sites for the reaction. The reaction in aqueous NaOH solution proceeded similarly to that in water while it was strongly suppressed in aqueous HCl and H_2SO_4 solutions. It was found that the suppression of H_2 evolution is due to protons in the solution. Over reduced Pt–TiO_2, H_2 evolved rapidly from all solutions, except HNO_3. In aqueous HNO_3 solution, NO_3^- was reduced to NH_3 over reduced TiO_2 and Pt–TiO_2.

Recently TiO_2 has been extensively studied from several view points. It is well-known that TiO_2 has a photocatalytic activity under the band gap irradiation.[1] For example, the partial oxidation of hydrocarbons by O_2 on TiO_2 powder,[2,3] the photo-Kolbe reaction of acetic acid in aqueous media on platinized TiO_2,[4,5] the evolution of H_2 from aqueous solution of organic compounds,[6,7] and the photodecomposition of water on Pt–TiO_2[8] and NiO–TiO_2[9] were reported. The photoelectrochemical cell which consisted of a TiO_2 photoanode and a Pt cathode was also proved to decompose water into H_2 and O_2.[10,11] Although detailed mechanisms of these reactions have not been well-understood, the initiation of each reaction is recognized to generate an excited electron-hole pair by the absorption of a photon (>3 ev) in TiO_2. The generation of e^- and h^+ would be also regarded as the formation of Ti^{3+} and O^- species in TiO_2.

TiO_2 has been widely used also as supports for various heterogeneous catalysts, especially in recent years for the purpose of the study of the so-called strong metal support interaction (SMSI).[12] This phenomenon occurs when metals such as Ni and Pt supported on TiO_2 are reduced at high temperatures (>773 K). It is interpreted that the SMSI state is caused by the generation of Ti^{3+} by the high temperature reduction,[13–15] the migration of titanium oxide to metal surfaces[16–19] and so on.

Thus Ti^{3+} ions play an important role in the chemistry of TiO_2. The nature of Ti^{3+} produced by the band gap irradiation[20–25] and also by the thermal reduction[26–28] was investigated by some workers. However, few studies have been reported on the reaction of Ti^{3+} on TiO_2 powder in a liquid phase. In this paper, the behavior of H_2 evolution over thermally reduced TiO_2 and Pt–TiO_2 in various aqueous solutions, liquid water and water vapor was studied in order to reveal the activity of Ti^{3+} on the surface under the dark condition.

Experimental

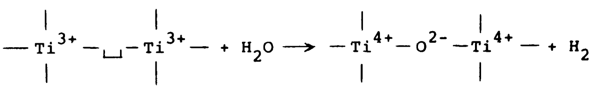
TiO_2 powder (aerosil; P-25) used was a mixture of rutile and anatase, and its surface area was 53 $m^2 \cdot g^{-1}$. Pt(1 wt%)–TiO_2 was prepared by mechanical mixing of Pt black (Kojima Chemical, purity; 99.99%) and TiO_2.

Pretreatments of TiO_2 and Pt(1 wt%)–TiO_2, and reactions with various solutions were carried out in a closed gas circulation system connected to a vacuum line. TiO_2 or Pt(1 wt%)–TiO_2 (1 g) was dispersed on a flat bottom reaction cell made of quartz. They were reduced by H_2 (ca. 40 kPa) at 773 K for 1 h and then H_2 was evacuated at the same temperature. The aqueous solution was degassed thoroughly and then introduced onto the reduced powder in the reaction cell without exposing to air.

The amount of evolved H_2 was determined by gas chromatography (Ar carrier, MS-5A column) directly connected to the circulation system.

Results and Discussion

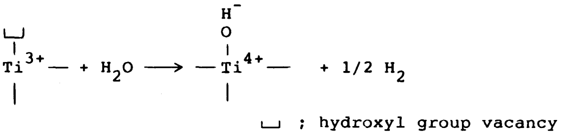
H_2 Evolution in the Reaction of Reduced TiO_2 and Pt–TiO_2 with Water. Behavior of H_2 evolution at 300 K from liquid and vapor water over reduced TiO_2 and Pt(1 wt%)–TiO_2 is shown in Fig. 1. The Pt–TiO_2 powder shows higher activity than TiO_2 and there is almost no difference in the activity between the reactions of liquid and vapor water. The evolution of H_2 on reduced TiO_2 is slow while that on reduced Pt–TiO_2 occurs immediately after the introduction of water. It is well-known that the reduced TiO_2 powder has Ti^{3+} ions and oxygen vacancies. When H_2 evolved from H_2O over the reduced TiO_2 powder the oxygen vacancies would be occupied by oxygen derived from H_2O. Therefore, a mechanism of H_2 evolution over the reduced TiO_2 surface is proposed as follows;



$$-\overset{|}{\underset{|}{Ti^{3+}}}-\sqcup-\overset{|}{\underset{|}{Ti^{3+}}}- + H_2O \longrightarrow -\overset{|}{\underset{|}{Ti^{4+}}}-O^{2-}-\overset{|}{\underset{|}{Ti^{4+}}}- + H_2$$

$\sqcup$; oxygen vacancy

and/or



$$-\overset{\sqcup}{\underset{|}{Ti^{3+}}}- + H_2O \longrightarrow -\overset{\overset{H^-}{O}}{\underset{|}{Ti^{4+}}}- + 1/2\ H_2$$

The driving forces are the reducing power of Ti^{3+} ions and stabilization energy of oxygen from water into the lattice oxygen. When TiO_2 powder is irradiated in aqueous solution containing a reducing agent such as alcohol, it is often observed that the color of TiO_2 changes from white to blue or gray, and a small amount of H_2 evolves. In this case, TiO_2 was reduced by a reducing agent with formation of oxygen vacancies on the surface and H_2 seems to evolve by a similar mechanism as stated above. On the other hand, in the case of Pt–TiO_2, the evolution of H_2 proceeds on the Pt surface after the electron transfers from reduced TiO_2 to Pt. This phenomenon is similar to that of the photocatalytic reaction for H_2 evolution from aqueous solutions. It was reported that the SMSI state of the Pt–TiO_2 system disappears when water exists.[29,30] This phenomenon may be explained by the oxidation of reduced TiO_2 by water via a similar process.

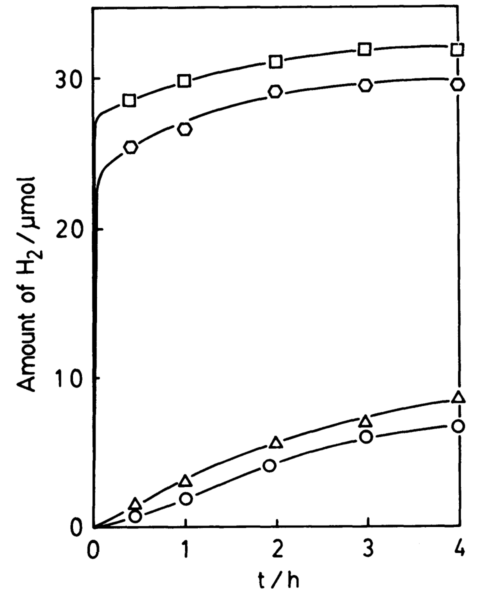


Fig. 1. H_2 evolution from liquid (10 ml) and vapor (3.2 kPa) water over reduced TiO_2 (1 g) and Pt(1 wt%)-TiO_2 (1 g) at room temperature.
□; liquid and ○ ; vapor over Pt-TiO_2, O; liquid and △; vapor over TiO_2.

In Table 1, the amount of consumed H_2 by the reduction at 773 K and that of evolved H_2 from water are summarized. The extent of the reduction of TiO_2 by H_2 is different from that of Pt-TiO_2. In both cases, the amount of evolved H_2 is less than that of H_2 consumed during the reduction. The rate of H_2 evolution and the total amount of evolved H_2 increased with increasing the reaction temperature. The color of reduced TiO_2 was blue indicating the existence of Ti^{3+}, which was confirmed by ESR. After the reaction, the color was not completely recovered to original white at room temperature and even at 773 K. Furthermore, the evolution of H_2 was completely suppressed by the contact with O_2 (ca. 40 kPa) for 5 min at room temperature. The color was still blue in this case while it was rapidly turned into white by exposing to O_2 at 773 K. These results suggest that only Ti^{3+} existing close to the surface can react with H_2O, and the most of Ti^{3+} accompanied by oxygen vacancies in the bulk remains unchanged at room temperature. On the other hand, Ti^{3+} in the bulk can also react partially at 773 K. The apparent activation energy calculated from the initial rate of H_2 evolution over reduced TiO_2 was about 21 kJ·mol^{-1} below 473 K and about 50 kJ·mol^{-1} above 473 K. The activation energy is probably required for the H_2 evolution on reduced TiO_2 and the diffusion of a lattice oxygen from H_2O into the oxygen vacancy of the bulk respectively.

H_2 Evolution from the Reactions over Reduced TiO_2 and Pt-TiO_2 with Various Aqueous Solutions. The evolution of H_2 on the reactions of distilled water and aqueous solutions of NaOH, HCl, H_2SO_4, and HNO_3 over reduced TiO_2 is shown in Fig. 2. The evolution of H_2 from acidic solutions is much slower than those from distilled water and aqueous alkaline solution.

The rates of H_2 evolution at various concentrations of NaOH over reduced TiO_2 are shown in Fig. 3. The rate of H_2 evolution is moderately suppressed with increacing the NaOH concentration. On the contrary, in the case of reduced Pt-TiO_2, a large amount of H_2 evolves at the beginning of the reaction.

The evolution of H_2 from aqueous HCl solution

Table 1. The Amount of Ti^{3+} and That of Evolved H_2

	Consumed H_2 by the reduction at 773 K	Degree of reduction	Ti^{3+} total	Ti^{3+} surface[a)]	Evolved H_2 at r.t.	Evolved H_2 at 773 K
	µmol	%	µmol	µmol	µmol	µmol
TiO_2	70	1.1	140	9	7	33
Pt-TiO_2	130	2.1	260	17	30	52

a) The amount of titanium ions on the surface was estimated to be ca. 800 µmol g^{-1} from a surface area by assuming a rutile (110) surface.

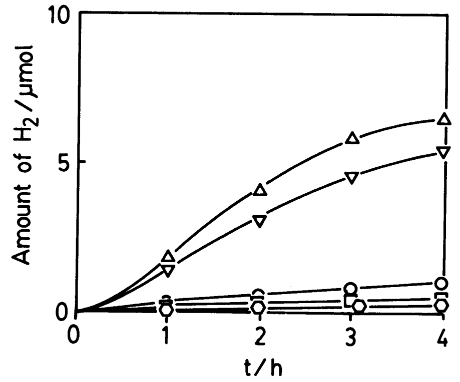


Fig. 2. H_2 evolution from various aqueous solutions (10 ml) over reduced TiO_2 (1 g) at room temperature. △; distilled water, ▽; 0.1 mol·dm^{-3} NaOH, ○; 0.1 mol·dm^{-3} HCl, □; 0.1 mol·dm^{-3} HNO_3, ○; 0.1 mol·dm^{-3} H_2SO_4.

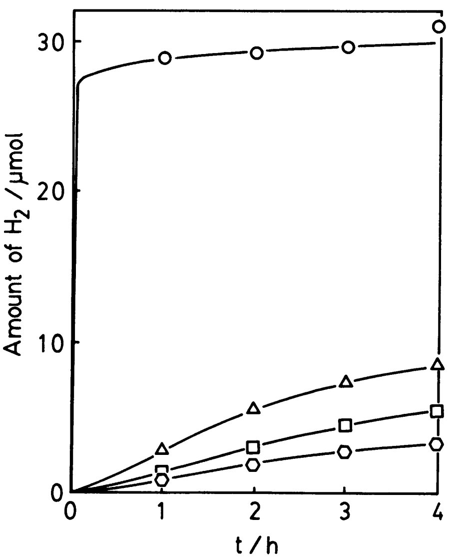


Fig. 3. H_2 evolution from aqueous NaOH solutions (10 ml) over reduced TiO_2 (1 g) and Pt(1 wt%)–TiO_2 (1 g) at room temperature.
○; 1 mol·dm^{-3} over Pt–TiO_2, △; 0.01 mol·dm^{-3}, □; 0.1 mol·dm^{-3}, ○; 1 mol·dm^{-3} over TiO_2.

over reduced TiO_2 and Pt(1 wt%)–TiO_2 is shown in Fig. 4. It was found that the reaction over reduced TiO_2 is strongly suppressed by HCl. Only a small amount of H_2 evolves in aqueous HCl solution (1 mol·dm^{-3}). The suppression effect of HCl on H_2 evolution is more remarkable than that of NaOH. The reaction in aqueous NaCl solution shows similar behavior to that in distilled water, which means the suppression was not owing to Cl^- ions. To examine the effect of HCl in more detail, the neutralization of aqueous HCl solution by NaOH solution was carried out during the reaction as shown in Fig. 5. Over reduced TiO_2 only a small amount of H_2 evolved in aqueous HCl solution (1 mol·dm^{-3}) in contrast to Pt which is a better catalyst for H_2 evolution. As soon as aqueous NaOH solution (1 mol·dm^{-3}) was added into the system, H_2 evolved rapidly. The resultant solution was in alkaline condition. From these results, it is inferred that H^+ suppresses the H_2 evolution over reduced TiO_2. Excess protons seem to poison the basic site which works as an electron donar center for H_2 evolution. Grätzel et al.[16)] reported that Ti^{3+} species are produced when colloidal TiO_2 in acidic and alkaline solutions are irradiated, and ESR signals are different in acidic and in alkaline solutions. On the basis of these results it is concluded that the state of

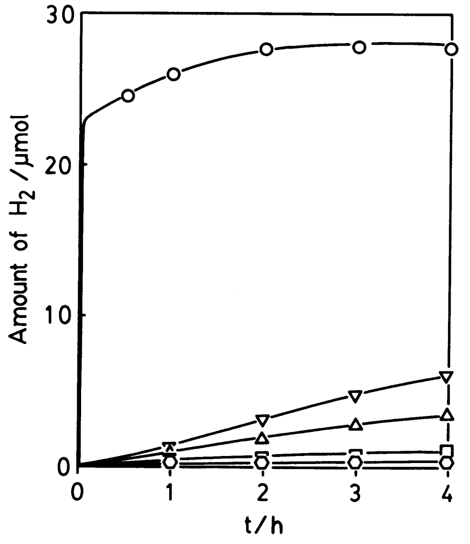


Fig. 4. H_2 evolution from aqueous HCl solutions (10 ml) over reduced TiO_2 (1 g) and Pt(1 wt%)–TiO_2 (1 g) at room temperature.
○; 1 mol·dm^{-3} over Pt–TiO_2, ▽; 0.01 mol·dm^{-3} (NaCl), △; 0.01 mol·dm^{-3}, □; 0.1 mol·dm^{-3}, ○; 1 mol·dm^{-3} over TiO_2.

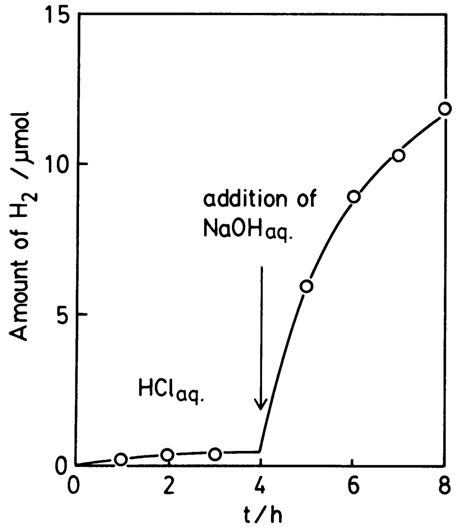


Fig. 5. Effect of addition of aqueous NaOH solution (1 mol·dm^{-3}, 10 ml) on H_2 evolution from aqueous HCl solution (1 mol·dm^{-3}, 5 ml) over reduced TiO_2 (1 g).

Ti^{3+} on TiO_2 in acidic solution differs from that in alkaline solution. However, the detailed mechanism of the suppression of H_2 evolution by protons is not clear at present.

The reactions of aqueous HNO_3 solution over reduced TiO_2 and Pt(1 wt%)–TiO_2 were quite different from those of aqueous HCl and H_2SO_4 solutions. Instead of H_2 evolution, NH_3 was detected by the Nessler reagent in the solution after the reactions in both cases. This means that NO_3^- was preferentially reduced to NH_3 by Ti^{3+}. The photocatalytic reduction of NO_3^- into NH_3 by water over Pt–TiO_2 powder has already been reported.31)

References

1) M. A. Grätzel, "Energy Resources through Photochemistry and Catalysis," Academic Press, Inc., New York (1983).

2) M. Formenti, F. Juillet, and S. J. Teichner, *C. R. Acad. Sci.*, **C270**, 138 (1970).

3) M. Formenti, F. Juillet, P. Meriaudeau, and S. J. Teichner, *Chem. Tech.* **1971**, 680.

4) B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 2239 (1978).

5) B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 5985 (1978).

6) T. Kawai and T. Sakata, *Nature (London)*, **286**, 474 (1980).

7) T. Kawai and T. Sakata, *Chem. Lett.*, **1981**, 81.

8) K. Yamaguchi and S. Sato, *J. Chem. Soc., Faraday Trans. 1*, **81**, 1237 (1985).

9) A. Kudo, K. Domen, K. Maruya, and T. Onishi, *Chem. Phys. Lett.*, **133**, 517 (1987).

10) A. Fujishima and K. Honda, *Nature (London)*, **238**, 37 (1972).

11) M. S. Wrighton, D. S. Ginley, P. T. Wolczanski, A. B. Ellis, D. L. Morse, and A. Linz, *Proc. Natl. Acad. Sci. U. S. A.*, **72**, 1518 (1975).

12) S. J. Tauster, S. C. Fung, and R. L. Garten, *J. Am. Chem. Soc.*, **100**, 170 (1978).

13) S. C. Fung, *J. Catal.*, **76**, 225 (1982).

14) J. M. Herrmann and P. Pichat, *J. Catal.*, **78**, 425 (1982).

15) J. M. Herrmann, *J. Catal.*, **89**, 404 (1984).

16) D. E. Resasco and G. L. Haller, *J. Catal.*, **82**, 279 (1983).

17) H. R. Sadeghi and V. E. Henrich, *J. Catal.*, **87**, 279 (1984).

18) S. Takatani and Y.-W. Chung, *J. Catal.*, **90**, 75 (1984).

19) J. A. Dumesic, S. A. Stevenson, R. D. Sherwood, and R. T. K. Baker, *J. Catal.*, **99**, 79 (1986).

20) W. J. Lo, Y. W. Chung, and G. A. Somorjai, *Surf. Sci.*, **71**, 199 (1978).

21) S. Ferrer and G. A. Somorjai, *Surf. Sci.*, **94**, 41 (1980).

22) F. T. Wagner, S. Ferrer, and G. A. Somorjai, *Surf. Sci.*, **101**, 462 (1980).

23) M. Anpo, T. Shima, and Y. Kubokawa, *Chem. Lett.*, **1985**, 1799.

24) R. F. Howe and M. Grätzel, *J. Phys. Chem.*, **89**, 4495 (1985).

25) J. Kiwi, *J. Phys. Chem.*, **90**, 1493 (1986).

26) P. C. Gravelle, F. Juillet, P. Meriaudeau, and S. J. Teichner, *Disc. Faraday Soc.*, **52**, 140 (1971).

27) S. Sato and J. M. White, *J. Phys. Chem.*, **85**, 592 (1981).

28) S. Ferrer and G. A. Somorjai, *J. Phys. Chem.*, **85**, 1464 (1981).

29) K. Kunimori, H. Abe, E. Yamaguchi, S. Matsui, and T. Uchijima, The Proc. of the 8 th International Congress on Catalysis (Berlin), *V*, 251 (1984), Verlag Chemie.

30) K. Kunimori, S. Matsui, and T. Uchijima, *Chem. Lett.*, **1985**, 359.

31) A. Kudo, K. Domen, K. Maruya, and T. Onishi, *Chem. Lett.*, **1987**, 1019.