Inorganica Chimica Acta, *72* (1983) 161–163

Factors Affecting Hydrogen Evolution from Hydrated $Ti(OH)_3$: a Model System for Photoassisted Hydrogen Production on Titania

LEONARD KRUCZYNSKI and HYMAN D. GESSER

Department of Chemistry, University of Manitoba, Winnipeg, Man., R3T 2N2 Canada

Received December 7, 1982

Freshly precipitated $Ti(OH)_3$ has been shown to liberate hydrogen by reaction with water:

$$2Ti(OH)_3 + 2H_2O \rightarrow 2Ti(OH)_4 + H_2$$

The rate of this reaction depends on the base used to form the Ti(III) hydroxide, the relative value of $t_{0.2}$ is $NH_4^+ < K^+ < Na^+ < Li^+$. The rate also increased with increase in pH and in the presence of trace metallic ions the effect was $Pt^{4+} \gg Ni^{2+} > Cu^{2+} > Co^{2+} > Fe^{2+}$.

Introduction

The photoassisted electrolysis of water using semiconducting TiO_2, originally as a single crystal photoanode [1] and more recently as suspended particles [2–7] is under intense study. Suspended particles of semiconducting TiO_2 are viewed as short-circuited microcells [2] where conduction band electrons (e^-_{cb}) formed by bandgap illumination, reduce water to form hydrogen:

$$2\,e^-_{cb} + 2H^+ \longrightarrow H_2 \tag{1}$$

Since Ti^{3+} is observed in esr studies of illuminated TiO_2 [8, 9], conduction band electrons are likely trapped as Ti^{3+} species [3–5]. Therefore, the H_2 evolution step becomes [10, 12]:

$$2Ti^{3+}{-}V_o + H_2O \rightarrow Ti^{4+}{-}O{-}Ti^{4+} + H_2 \tag{2}$$

There is some question as to whether this step is photoassisted and requires an oxygen vacancy, V_o [12] since reduction of Pt^{4+} to Pt metal occurs on the non-illuminated face of single crystal semiconducting TiO_2 [13]. Rehydroxylation of the titania surface:

$$Ti^{4+}{-}O{-}Ti^{4+} + H_2O \rightarrow 2Ti^{4+}{-}OH \tag{3}$$

is important for photoactivity at the titania surface [18] and has also been linked to the photoproduction of hydrogen [10]. It appears that H_2 evolution from fully hydroxylated Ti^{3+} [11]:

$$2Ti(OH)_3 + 2H_2O \rightarrow 2Ti(OH)_4 + H_2 \tag{4}$$

as studied in the present work, may be the most facile mode of producing hydrogen on a titania surface.

We have studied H_2 evolution in a model system using hydrated Ti^{3+} formed by adding base to aqueous $TiCl_3$. As in many photocatalytic studies on the TiO_2 surface [3–5], we find that small amounts of platinum greatly enhance the rate of H_2 evolution. Also, the rate of H_2 evolution is sensitive to the type of ions incorporated into the Helmholtz double layer existing at the solid $Ti(OH)_3$/solution interface.

Experimental

Commercial aqueous titanous chloride (Fisher Scientific Co.) was standardized with potassium dichromate and found to contain 19.8% $TiCl_3$ by weight. A 250 ml three-necked round-bottom flask was fitted with a pressure-equalized dropping funnel, an adapter fitted to a nitrogen tank, and an outlet connected to an inverted, water filled 50 ml buret used to collect the evolved hydrogen. After adding a weighed amount of $TiCl_3$ stock solution, 100 ml water and a magnetic stirring bar to the flask, the system was purged with nitrogen for 10 minutes. The dropping funnel was then filled with 50 ml of base solution and flushed with nitrogen for a further 10 minutes. The base was then added dropwise over a period of 2–3 minutes to the stirred $TiCl_3$ solution. The volume of hydrogen evolved was measured with the gas buret at intervals of 5 to 60 minutes. Selected runs are shown in Fig. 1. In experiments where the effect of catalytic

0020-1693/83/$3.00

TABLE I. Rate of Hydrogen Evolution from $Ti(OH)_3$ as a Function of Base.

Base	Mol base/ mol Ti^{3+} [a]	pH[b]	Time (minutes) to evolve 20% H_2 [c]
LiOH	5.4	11.5	120
LiOH	4.8	8.5	280
LiOH	4.2	6.4	690
KOH	4.3	7.9	110
NH_4OH	5.0	7.9	13
$N(CH_3)_4OH$	5.1	12.7	∞(no H_2)

[a] Mol Ti^{3+} is 0.0069 for all trials. [b] Taken 24 hours after mixing. [c] Maximum volume H_2 is 85.3 ml at STP based on mol Ti^{3+} used.

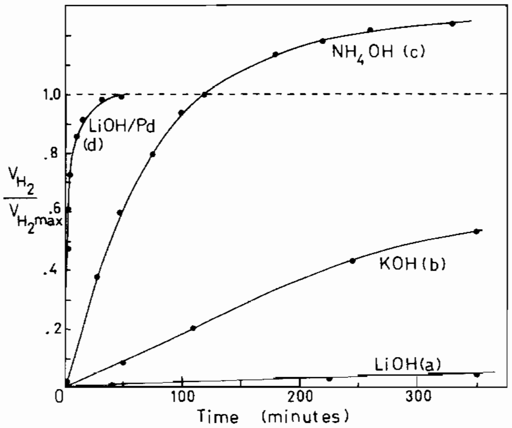

Fig. 1. Kinetic curves for the volume of H_2 produced *vs.* time forTi(OH)$_3$ prepared with various bases: (a) LiOH, 4.2 mol/mol Ti^{3+}; (b) KOH, 4.3 mol/mol Ti^{3+}; (c) NH_4OH, 5.0 mol/mol Ti^{3+}; (d) LiOH, 4.2 mol/mol Ti^{3+}, plus 32 mg H_2PtCl_6 in 1 ml water, Ti/Pt = 1400.

amounts of transition metal ions were studied, lithium hydroxide (4.0 mol LiOH:1 mol Ti^{3+}) was used to precipitate $Ti(OH)_3$. Under these conditions, the precipitate decomposed to a limited extent: less than 10% in 5 hours; as compared to $t_{1/2}$ in the range 1–100 minutes in the presence of metal ions. The metal salt, dissolved in 1 ml of water, was added to the reaction flask containing the freshly precipitated $Ti(OH)_3$.

Results and Discussion

pH and Base Dependence of H_2 Evolution

TABLE II. Correlation of Catalyst Efficiency with Reduction Potential and Current Density for Hydrogen Evolution ($-\log i_o$).

Metal ion	Relative Efficiency[a]	Reduction Potential[b]	Exchange Current[c]
Mn^{2+}	0	−1.18	10.9
Zn^{2+}	0	−0.76	10.5
Fe^{2+}	0.8	−0.44	5.6
Co^{2+}	1.4	−0.28	5.3
Cu^{2+}	3.8	+0.34	7.8
Ni^{2+}	5.0	−0.25	5.2
Pt^{4+}	1400	+0.73	3.0

[a] Calculated from $t_{1/2}/R$ where $t_{1/2}$ is the half time for H_2 evolution in minutes and R is the molar ratio of Ti^{3+}: metal ion. [b] Standard reduction potentials for the reaction $M^{n+} + ne^- \rightarrow M_{(s)}$. [c] Exchange current (in units of $-\log i_o$ where i_o is in amperes/cm^2) for H_2 evolution from the metal in acidic solutions [17].

A 1–3 mol excess of base was used to completely precipitate $Ti(OH)_3$ and bring the pH into the range 3–12. The volume of H_2 evolved after a convenient time (20% of the theoretical yield of H_2) was used as a measure of the reaction rate and is shown in Table I. As noted recently [14], the pH dependence is rather surprising in that a high pH favours H_2 evolution. This behavior has been noted in photocatalytic systems as well [6]. In addition, we find that the rate of H_2 evolution depends on the cation of the base used to precipitate $Ti(OH)_3$: the order of activity being $Li^+ < Na^+ < K^+ < NH_4^+$. Tetramethylammonium hydroxide forms a completely inactive precipitate at any pH. These cations, which may be incorporated into the Helmholtz double layer at the surface of the hydrated precipitate, could control the rate of electron transfer into solution. Rate constants for electron transfer between ferri- and ferrocyanide show a similar cation dependence with H^+ being even less effective than Li^+ [16]. For cases where the rate of H_2 evolution is reasonably fast, theoretical yields of H_2 are at least 95%; except for ammonium hydroxide, where the apparent yield of gas (hydrogen) is over 100% (Fig. 1). We attribute this to the catalytic decomposition of NH_4^+.

Transition Metal Ion Dependence of H_2 Evolution

Platinum, well known for its ability to lower the overpotential for hydrogen evolution, produces large rate enhancements when added to freshly precipitated $Ti(OH)_3$. Catalytic amounts of Pt^{4+} (mole ratio Ti:Pt of 1400:1) reduce $t_{1/2}$ for H_2 evolution to one minute from a value estimated to be weeks without the catalyst. Results for a number of transition metal ions are recorded in Table II, along with exchange current data ($-\log i_o$) for hydrogen evolution from the corresponding metal [17]. From the correlation between H_2 evolution rate and exchange current we believe that the metal ions, initially added to the solution, are probably reduced and become incorporated into the hydrated $Ti(OH)_3$ surface. The metal particles on the surface then can act as centers for H_2 evolution. Reduction potentials, also included in Table II, play a role as well: Cu^{2+}, being more easily reduced than Co^{2+}, is more efficient in evolving H_2 from the precipitate, even though the exchange current for H_2 evolution from copper is less than that for cobalt.

Since many of the factors found to increase the rate of H_2 evolution in titania based photocatalytic water splitting schemes also apply to the 'dark' reaction studied in this work, it appears that reduced titanium species probably play an important role in photocatalytic hydrogen evolution on titania. This is consistent with the observed photoreduction of porous titania glass reported recently [19].

Acknowledgement

We are grateful to the National Science and Engineering Research Council of Canada and INRAD (Winnipeg) for their support of this work.

References

1 K. Honda and A. Fujishima, *J. Chem. Soc. Jpn., 74,* 355 (1971).
2 G. N. Schrauzer and T. O. Guth, *J. Am. Chem. Soc., 99,* 7189 (1977).
3 T. Kawai and T. Sakata, *Chem. Phys. Lett., 72,* 87 (1980).
4 T. Kawai and T. Sakata, *J. Chem. Soc. (Chem. Comm),* 694 (1980).
5 E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca and M. Gratzel, *J. Am. Chem. Soc., 103,* 6324 (1981).
6 S. Sato and J. M. White, *J. Phys. Chem., 85,* 592 (1981).
7 F. T. Wagner and G. A. Somorjai, *Nature, 285,* 559 (1980).
8 P. C. Gravelle, F. Juillet, P. Meriaudeau and S. J. Teichner, *Disc. Faraday Soc., 52,* 140 (1971).
9 E. Serwicka, M. W. Schlierkamp and R. N. Schlinder, *Z. Naturforsch., 36a,* 226 (1981).
10 S. Ferrer and G. A. Somorjai, *J. Phys. Chem., 85,* 1464 (1981).
11 The species present has been formulated as $Ti_2O_3 \cdot H_2O$ by: G. C. Allen, M. B. Wood and J. M. Dyke, *J. Inorg. Nucl. Chem., 35,* 2311 (1973); it will be referred to in this work as $Ti(OH)_3$.
12 H. Van Damme and W. K. Hall, *J. Am. Chem. Soc., 101,* 4373 (1979).
13 H. Yoneyama, N. Nishimura and H. Tamura, *J. Phys. Chem., 85,* 268 (1981).
14 Shortly after the preparation of this manuscript, a study of the pH dependence of H_2 evolution from $Ti(OH)_3$ appeared (Y. Doi, M. Tamaki, *Inorg. Chim. Acta, 64,* L145 (1982)); in that work the authors used NaOH to precipitate $Ti(OH)_3$ and found the rate of H_2 evolution to increase with the amount of base added.
15 S. Sato and J. M. White, *Chem. Phys. Lett., 72,* 83 (1980).
16 M. Shporer, G. Ron, A. Loewenstein and G. Navon, *Inorg. Chem., 4,* 361 (1965).
17 S. Trasatti, *Electroanal. Chem. Interfac. Electrochem., 39,* 163 (1972).
18 G. D. Parfitt, 'The Surface of Titanium Oxide', p. 8, in 'Progress in Surface and Membrane Science', Ed. D. A. Cadenhead and J. F. Danielli, Academic Press, Vol. 11 (1976).
19 L. Kruczynski, H. D. Gesser, C. W. Turner and E. A. Speers, *Nature, 291,* 399 (1981).