Photocatalytic Hydrogen Production from Liquid Methanol and Water

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Summary Xe-Lamp irradiation of TiO_2 powders mixed with a Pt, Pd, RuO_2, or rhodium complex, leads to the efficient production of hydrogen from liquid methanol and water at room temperature.

HYDROGEN production from methanol and water is an attractive process, since hydrogen gas is a clean fuel in the hydrogen energy system. This reaction has been carried out thermally in the vapour phase at temperatures above 250 °C using a catalyst such as Fe_2O_3.[1] Here we report that H_2 is produced highly efficiently at room temperature from liquid MeOH and H_2O using a TiO_2 powder photocatalyst mixed with a metal (Pt, Pd), metal oxide (RuO_2), or rhodium complex $[(Ph_3P)_3Rh^ICl]$.

Each TiO_2 photocatalyst was prepared by mixing powdered TiO_2 (Katayama Kagaku) with powdered Pt, Pd, or RuO_2 in an agate mortar. $(Ph_3P)_3Rh^ICl$ was supported on TiO_2 by impregnating the TiO_2 powder with a tetrahydrofuran solution of the Rh complex. A mass spectrometer and a manometer were used for the analysis of gaseous reaction products.[2]

When each photocatalyst (300 mg), in a deaerated mixture of H_2O (10 ml) and MeOH (10 ml) in a 280 ml Pyrex glass bulb, was irradiated by a 500 W Xe-lamp, hydrogen gas was evolved. Initially, H_2 was the main gaseous product, but CO_2 began to be evolved after prolonged irradiation. CO and O_2 were not observed. The Table summarizes the amounts of evolved H_2 and the quantum yields at λ 380 nm for the various photocatalysts. The reaction is considered to proceed according to equations (1)—(3). It has been reported that MeOH is oxidized to

$$\mathrm{MeOH} \xrightarrow{h\nu,\ \mathrm{cat.}} \mathrm{HCHO} + \mathrm{H_2} \quad (1)$$

$$\mathrm{HCHO} + \mathrm{H_2O} \xrightarrow{h\nu,\ \mathrm{cat.}} \mathrm{HCO_2H} + \mathrm{H_2} \quad (2)$$

$$\mathrm{HCO_2H} \xrightarrow{h\nu,\ \mathrm{cat.}} \mathrm{CO_2} + \mathrm{H_2} \quad (3)$$

HCHO,[3] HCHO to HCO_2H, and HCO_2H to CO_2[4] on a single-crystal TiO_2 or ZnO photoanode by a current-doubling process. In our experiments using powdered photocatalysts, irradiation of aqueous HCHO (37%) yielded H_2 (3·4 mmol in 10 h for RuO_2–TiO_2–Pt) and CO_2 in the gas phase, the amount of CO_2 increasing gradually. Irradiation of aqueous HCO_2H (40%) produced equal amounts of H_2 and CO_2 from the begining of the reaction (3·8 mmol in 10 h for RuO_2–TiO_2–Pt). In addition, we confirmed the formation of HCHO and HCO_2H in reactions (1) and (2) by mass analysis. Since the TiO_2 powder can be regarded as a photoelectrochemical microcell, holes generated by the light would oxidize MeOH, HCHO, and HCO_2H eventually to produce CO_2, while electrons in the conduction band of the particle would simultaneously reduce protons in the solution to form gaseous H_2.

The reaction on TiO_2 alone was slow compared with that on the supported photocatalysts (Table). This is presumably because electrons and holes cannot be separated efficiently in the TiO_2 solid and/or because of the absence of an effective catalyst for methanol oxidation and hydrogen evolution. In fact, the addition of a hydrogenation catalyst (Pt, Pd, Rh-complex) enhanced the H_2 evolution. The introduction of methylviologen,[5] an electron acceptor and mediator, together with Pt–Al_2O_3 also enhanced H_2 evolution. RuO_2 may provide an oxidation site since the RuO_2 electrode has high catalytic activity for the oxidation of water[6] and carboxylic acid.[7] Interestingly, H_2 evolution was observed even using visible light ($\lambda > 470$ nm) with these photocatalysts (2·9 μmol for RuO_2–TiO_2–Pt, 2·7 μmol for TiO_2–Pt, and 1·2 μmol for TiO_2–Pd in 10 h). Although TiO_2 absorbs light below 400 nm, metal atoms on TiO_2 can form surface states in the band gap, such that irradiation by visible light can inject holes or electrons into the solid catalyst by a mechanism similar to dye sensitization. The details will be discussed elsewhere. TiO_2–Pt in $Ru(bipy)_3^{2+}$ (10^{-3} mol)–water solution (bipy = 2,2′-bipyridyl), which absorbs visible light, also produced hydrogen (4·3 μmol in 10 h) when light of wavelength longer than 470 nm was used. In acidic solutions (1N-H_2SO_4–MeOH, 1 : 1), CH_4 was formed (and *ca.* 1% of H_2), and in basic solutions (6N-NaOH–MeOH, 1 : 1) only H_2 was evolved even after prolonged irradiation, because the CO_2 produced was absorbed by the NaOH solution.

TABLE. H_2 production from MeOH (10 ml) and H_2O (10 ml) on various supported TiO_2 photocatalysts.[a]

Photocatalyst	H_2/mmol	Quantum yield[d] at λ 380 nm/%
TiO_2	0·27	3·2
RuO_2–TiO_2–Pt	5·2	44·0
TiO_2–Pt	4·6	40·0
TiO_2–Pd	2·2	19·0
RuO_2–TiO_2	0·37	4·0
TiO_2–$(Ph_3P)_3Rh^ICl$[b]	0·49	4·2
TiO_2 + MV, Pt–Al_2O_3[c]	0·99	8·6

[a] 500 W Xe-lamp; irradiation for 10 h. TiO_2 powder was mixed with Pt black (5 wt%), Pd black (5 wt%), or RuO_2 powder (10 wt%), and ground in an agate mortar for *ca.* 5 min to form a greyish powder. This powder (300 mg) was used for the experiment without further treatment. [b] TiO_2 powder suspended in a $(Ph_3P)_3Rh^ICl$ (30 mg)—tetrahydrofuran solution was evaporated *in vacuo* to form a brown powder at room temperature. [c] Methylviologen (MV) (20 mg) and Pt (3 wt%)–Al_2O_3 (20 mg) were put into the TiO_2–MeOH–H_2O solution. [d] The quantum yield is defined here as twice the number of hydrogen molecules divided by the number of incident photons, *i.e.* taking into consideration the fact that two electrons are consumed to produce one hydrogen molecule from two protons. We used the number of incident photons here because of the difficulty of measuring the exact number of photons absorbed by the powdered semiconductors.

In these experiments, relatively high quantum yields were obtained using powdered photocatalysts. For example, using the RuO_2–TiO_2–Pt catalyst, 4·5 mmol of H_2 was obtained in 0·5 h using an intense 500 W Hg lamp (Philips), corresponding to a photocurrent of 430 mA. In contrast, the anodic photocurrent was saturated at about 1 mA[3] in the photoelectrochemical oxidation of methanol on a single crystal of TiO_2. This clearly shows the advantage of powdered photocatalysts which have large surface areas and constitute effective catalysts for hydrogen production.

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[1] F. Domka and M. Laniecki, *React. Kinet. Catal. Lett.*, 1978, **8**, 507.
[2] T. Kawai and T. Sakata, *J. Chem. Soc., Chem. Commun.*, 1979, **23**, 1047.
[3] M. Miyake, H. Yoneyama, and H. Tamura, *Chem. Lett.*, 1976, 635.
[4] W. P. Gomes, T. Freund, and S. R. Morrison, *J. Electrochem. Soc.*, 1968, **115**, 818.
[5] T. Kawai, K. Tanimura, and T. Sakata, *Chem. Lett.*, 1979, 137.
[6] K. Doblhofer, M. Metikos, Z. Ogumi, and H. Gerischer, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 1064.
[7] C. Iwakura, F. Goto, and H. Tamura, *Denki Kagaku*, 1980, **48**, 21.