

Photocatalytic Hydrogen Production from Liquid Methanol and Water

By TOMOJI KAWAI* and TADAYOSHI SAKATA*

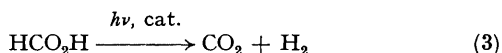
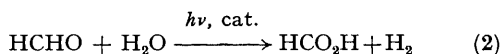
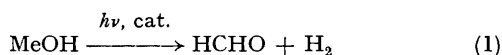
(Institute for Molecular Science, Myodaiji, Okazaki 444, Japan)

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 Fe₂O₃.¹ Here we report that H₂ is produced highly efficiently at room temperature from liquid MeOH and H₂O using a TiO₂ powder photocatalyst mixed with a metal (Pt, Pd), metal oxide (RuO₂), or rhodium complex [(Ph₃P)₃Rh⁺Cl].

Each TiO₂ photocatalyst was prepared by mixing powdered TiO₂ (Katayama Kagaku) with powdered Pt, Pd, or RuO₂ in an agate mortar. (Ph₃P)₃Rh⁺Cl was supported on TiO₂ by impregnating the TiO₂ 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 H₂O (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, H₂ was the main gaseous product, but CO₂ began to be evolved after prolonged irradiation. CO and O₂ were not observed. The Table summarizes the amounts of evolved H₂ 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



HCHO,³ HCHO to HCO₂H, and HCO₂H to CO₂⁴ on a single-crystal TiO₂ or ZnO photoanode by a current-doubling process. In our experiments using powdered photocatalysts, irradiation of aqueous HCHO (37%) yielded H₂ (3.4 mmol in 10 h for RuO₂-TiO₂-Pt) and CO₂ in the gas phase, the amount of CO₂ increasing gradually. Irradiation of aqueous HCO₂H (40%) produced equal amounts of H₂ and CO₂ from the beginning of the reaction (3.8 mmol in 10 h for RuO₂-TiO₂-Pt). In addition, we confirmed the formation of HCHO and HCO₂H in reactions (1) and (2) by mass analysis. Since the TiO₂ powder can be regarded as a photoelectrochemical microcell, holes generated by the light would oxidize MeOH, HCHO, and HCO₂H eventually to produce CO₂, while electrons in the conduction band of the particle would simultaneously reduce protons in the solution to form gaseous H₂.

The reaction on TiO₂ alone was slow compared with that on the supported photocatalysts (Table). This is presumably because electrons and holes cannot be separated efficiently in the TiO₂ 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 H₂ evolution. The

TABLE. H₂ production from MeOH (10 ml) and H₂O (10 ml) on various supported TiO₂ 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 ₃ P) ₃ Rh ⁺ Cl ^b	0.49	4.2
TiO ₂ + MV, Pt-Al ₂ O ₃ ^c	0.99	8.6

^a 500 W Xe-lamp; irradiation for 10 h. TiO₂ powder was mixed with Pt black (5 wt%), Pd black (5 wt%), or RuO₂ 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 TiO₂ powder suspended in a (Ph₃P)₃Rh⁺Cl (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%)-Al₂O₃ (20 mg) were put into the TiO₂-MeOH-H₂O 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.

introduction of methylviologen,⁵ an electron acceptor and mediator, together with Pt-Al₂O₃ also enhanced H₂ evolution. RuO₂ may provide an oxidation site since the RuO₂ electrode has high catalytic activity for the oxidation of water⁶ and carboxylic acid.⁷ Interestingly, H₂ evolution was observed even using visible light (λ > 470 nm) with these photocatalysts (2.9 μmol for RuO₂-TiO₂-Pt, 2.7 μmol for TiO₂-Pt, and 1.2 μmol for TiO₂-Pd in 10 h). Although TiO₂ absorbs light below 400 nm, metal atoms on TiO₂ 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. TiO₂-Pt in Ru(bipy)₃³⁺ (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-H₂SO₄-MeOH, 1:1), CH₄ was formed (and ca. 1% of H₂), and in basic solutions (6N-NaOH-MeOH, 1:1) only H₂ was evolved even after prolonged irradiation, because the CO₂ produced was absorbed by the NaOH solution.

In these experiments, relatively high quantum yields were obtained using powdered photocatalysts. For example, using the RuO₂-TiO₂-Pt catalyst, 4.5 mmol of H₂ 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 mA⁸ in the photoelectrochemical oxidation of methanol on a single crystal of TiO₂. This clearly shows the advantage of powdered photocatalysts which have large surface areas and constitute effective catalysts for hydrogen production.

(Received, 14th April 1980; Com. 384.)

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.