

## Production of H<sub>2</sub> and CO from Liquid Water and Carbon using Solar Energy

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**Summary** Gaseous H<sub>2</sub>, CO, and CO<sub>2</sub> were produced from water and carbon by photocatalytic processes using TiO<sub>2</sub>-RuO<sub>2</sub> as a catalyst.

THE utilization of solar energy is of importance in view of the energy and raw material crises, and several photocatalytic reactions have been reported.<sup>1</sup> Coal gasification or liquefaction is also a topic of current interest. We have therefore studied the use of solid carbon (in place of coal or coke) and liquid water as raw materials for the production of gaseous products by a photocatalytic process.

We report here that gaseous H<sub>2</sub> and CO were produced at around room temperature when an aqueous suspension of carbon with TiO<sub>2</sub>-RuO<sub>2</sub> as catalyst was illuminated.

Typically, TiO<sub>2</sub> (30 mg) (Katayama Co.), RuO<sub>2</sub> catalyst (10 mg) (Rare Metallic Co.), and active carbon (0.5 mg) (Katayama Co.) were mixed and rubbed in an agate mortar, and suspended in neutral water (10 ml) in a Pyrex cell which was then evacuated. The mixture was illuminated with a 500 W Xe lamp for 12 h and the gas evolved was trapped at -197 and -78 °C, and analysed by mass spectrometry. The gas was not condensed at -197 °C,

0.05 Torr in a 250 ml vessel, and was shown to be a mixture of H<sub>2</sub> and CO. When D<sub>2</sub>O was used instead of H<sub>2</sub>O, D<sub>2</sub> was detected. Thus the hydrogen evolved must arise from the decomposition of water as shown in equation (1). The



free energy increased by 100 kJ mol<sup>-1</sup> when using light energy. CO<sub>2</sub> was not a main product probably owing to the reducing atmosphere of the ambient gas.

It is well known that illumination of TiO<sub>2</sub> causes the decomposition of water to form hydrogen and oxygen.<sup>2</sup> Since TiO<sub>2</sub> powder can be regarded as a microcell for the photoredox reaction, water will be oxidized at the oxidizing site to form oxygen which reacts with carbon to form CO ( $\Delta G < 0$ ), whereas at the reducing site hydrogen will be formed. RuO<sub>2</sub> may enhance the oxidation of carbon, since it is a good electrode for oxygen evolution.<sup>3</sup> The results are summarized in the Table. When TiO<sub>2</sub> and H<sub>2</sub>O

Thus only the photocatalyst TiO<sub>2</sub> combined with non-corrosive metal oxide retains its initial composition during the reaction. TiO<sub>2</sub> produces only hydrogen when a reducing reagent such as ethylenediaminetetra-acetic acid (EDTA)<sup>4</sup> is added. It should be noted that gaseous water could be decomposed catalytically into H<sub>2</sub> and O<sub>2</sub> on TiO<sub>2</sub>-RuO<sub>2</sub> even without solid carbon. The reaction continued catalytically on this surface, although it terminated on TiO<sub>2</sub> catalyst alone.<sup>1</sup>

When solid carbon is used, the energy required for the dissociation of the C-C bond may reduce the quantity of CO formed. The amount of CO evolved decreased when the powders were not mixed well initially. We therefore heated the TiO<sub>2</sub>, RuO<sub>2</sub>, and C with water vapour to 60–80 °C to assist the oxidation of carbon after which the reaction rate increased >5 times, and CO<sub>2</sub> was also formed (CO<sub>2</sub>/CO = 2–4). This indicates that the photo-driven reaction,  $\text{C} + 2\text{H}_2\text{O} + h\nu \rightarrow \text{CO}_2 + 2\text{H}_2$ , also proceeds, producing more hydrogen from the water. Therefore the use of solar energy as a combination of light and heat energy,

TABLE. Evolution of H<sub>2</sub> and CO from liquid water using light energy with various catalysts and reactants in a 250 ml vessel (500 W Xe lamp).

Catalyst Reactant	TiO <sub>2</sub> H <sub>2</sub> O	TiO <sub>2</sub> C, H <sub>2</sub> O	TiO <sub>2</sub> -RuO <sub>2</sub> H <sub>2</sub> O	TiO <sub>2</sub> -RuO <sub>2</sub> C, H <sub>2</sub> O	TiO <sub>2</sub> EDTA, H <sub>2</sub> O
H <sub>2</sub> produced	a	a	a	b	b
CO produced	a	a	a	b	c

<sup>a</sup> No appreciable D<sub>2</sub> signal was detected by mass analysis when using liquid D<sub>2</sub>O. <sup>b</sup> ≥ 0.05 Torr of H<sub>2</sub> or CO. <sup>c</sup> Decomposition products of EDTA.

only were used, no appreciable quantities of H<sub>2</sub> were observed. Appreciable amounts of H<sub>2</sub> and CO were formed only when TiO<sub>2</sub>, RuO<sub>2</sub>, C, and H<sub>2</sub>O were all present. When Raney Ni or Ru metal was used as the catalyst, the hydrogen produced increased to 5 Torr and 0.4 Torr, respectively, after 12 h illumination. The amount of CO formed, however, was much smaller than that of hydrogen. This is because the metal is oxidized by the oxygen from H<sub>2</sub>O instead of carbon thus aiding the evolution of hydrogen. The dissolution of Ni to give Ni<sup>2+</sup> ( $E^\circ -0.25 \text{ V vs. normal hydrogen electrode}$ ) also assisted H<sub>2</sub> evolution.

will be more useful than light energy alone. When water is photolysed using a powdered photocatalyst<sup>1</sup> the oxygen and hydrogen produced forms an explosive gas. In this system, however, the oxygen is incorporated into carbon compounds to form more stable gases. This method, taking advantage of light energy, may be useful for the gasification of coal and hydrogen evolution from water, although the use of thermal energy, *ca.* 1000 °C, for this reaction is extremely well known.

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<sup>4</sup> W. E. Ford, J. W. Otvos, and M. Calvin, *Nature*, 1978, **274**, 507.