Mechano-catalytic overall water splitting

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Mechano-catalysis, a novel and simple method to decompose water into H_2 and O_2 in which mechanical energy is directly converted into chemical energy, is demonstrated.

H_2 production from water decomposition is one of the most attractive candidates for future clean energy resources. Electrolysis of water is a familiar way to accomplish overall water splitting. Photoelectrochemical and/or photocatalytic decomposition of water have also been pursued from the viewpoint of solar energy utilization.[1–4] Recently, the authors have been studying the decomposition of water on magnetically stirred Cu_2O powder under visible light irradiation.[5] At the stage when H_2 and O_2 evolved steadily in a stoichiometric ratio, we tentatively concluded that the reaction proceeded 'photocatalytically'.[5] In the subsequent study of the system, however, we found several characteristics of the reaction which are unusual for conventional photocatalytic ones. The most striking aspect of the reaction was the continuous evolution of H_2 and O_2 even after the light was turned off. This cannot be understood by the model of a semiconductor photocatalyst in which photoexcited electrons and holes are postulated to directly react with reactant water molecules (or H^+ and OH^- ions).[1] The lifetime of the photoexcited electronic states is at most of the order of milliseconds. We then hypothesized that photon energy was stored in the Cu_2O particle as some chemical species and the excess energy was gradually released to decompose water. To our surprise, however, the evolution of H_2 and O_2 in the dark continued for several hundred hours, and eventually the amounts of evolved H_2 and O_2 exceeded that of Cu_2O used. Another noticeable feature of this reaction is the marked dependence of the H_2 and O_2 evolution rates on the rate of stirring, *i.e.* the rate of H_2O decomposition increases monotonically with the rate of rotation. Without stirring, no H_2 and O_2 evolution occurred.

From these observations, we ended up with the following working hypothesis: the mechanical energy supplied by stirring was converted to chemical energy of H_2 and O_2 with Cu_2O functioning as a mediator or a catalyst. To work out this hypothesis, we have carried out rather extensive experiments by using various binary oxides. Here we report some phenomenological results which seem to be enough to prove our hypothesis. The detailed and atomic scale mechanism is an open question.

The reaction was carried out in a flat-bottomed reaction vessel made of Pyrex glass. Typically 0.1 g of oxide powder was suspended by magnetic stirring (F205, Tokyo Garasu Kikai) in 200 cm^3 of distilled water. The stirring rod was sealed by PTFE (polytetrafluoroethylene, Teflon®). The reaction vessel was attached to a closed gas circulation system (about 800 cm^3) equipped with an evacuation line. Before the reaction, the gas phase was completely evacuated and only water vapor remained. The evolved gas was accumulated and was analyzed by gas chromatography (TCD, Ar carrier, MS 5A column). When performing reactions in the dark, the reaction vessel was completely covered with aluminium foil, and when performing the reaction under photoirradiation, a 500 W Xe lamp placed at the side of the reaction vessel was used. The reaction temperature was at or somewhat lower than room temperature.

Various kinds of binary metal oxides which are stable in water were surveyed in the dark reaction. Cu_2O, NiO, Co_3O_4, and Fe_3O_4 exhibited H_2 and O_2 evolution. Much lower yet definite activity was also exhibited by RuO_2 and IrO_2. Specifically, CuO and Fe_2O_3 did not show activity for the reaction. Typical photocatalysts such as TiO_2, ZnO and WO_3 were also completely inert.

Fig. 1 shows a typical time course of H_2 and O_2 evolution on NiO in the dark. The NiO sample used was a yellow green powder with a BET surface area of about 1 $m^2\ g^{-1}$ and the particle size was about 0.5 μm [purchased from Kanto Chemical, high purity reagent (3 N)]. H_2 and O_2 kept evolving exactly in the stoichiometric ratio of water decomposition. The rate of H_2 and O_2 evolution gradually decreased with the accumulation of the evolved gas probably due to the effect of O_2 pressure. A similar effect was observed for the other three active oxides, *i.e.* Cu_2O, Co_3O_4 and Fe_3O_4. Almost the same time course was reproduced in the second run after evacuation. The total amount of evolved H_2 after the second run was 1.7 mmol, which exceeded the amount of NiO used, *i.e.* 1.3 mmol (0.1 g). No appreciable degradation of the activity was observed even after the second run. It was thus confirmed that this dark reaction proceeds catalytically.

Another point worth noting is the effect of the shape of the stirring rod: when a stirring rod with a flat bottom was used, the rate of H_2 and O_2 evolution was increased by more than an order of magnitude compared with that obtained when a round bottomed rod was used. This indicates that a mechanical effect such as the rubbing of the catalyst powder by the stirring rod is essential for the decomposition of water.

Two further experiments were conducted. First, double-sided adhesive tape was stuck to the flat bottom of the stirring rod and

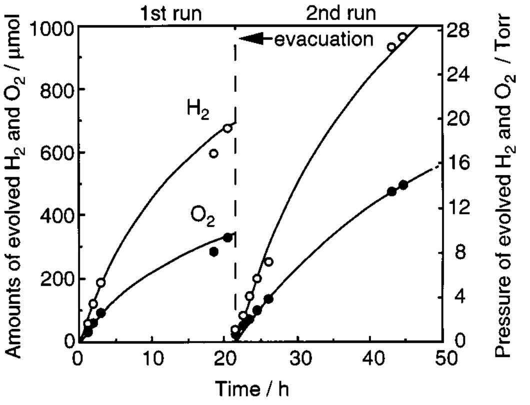

Fig. 1 Time course of H_2 (open circles) and O_2 (filled circles) evolution on NiO in the dark. The gas phase was evacuated at a reaction time of 22 h. Catalyst (NiO): 0.1 g, H_2O: 200 cm^3.

ca. 0.01 g of NiO powder was stuck onto the other side of the tape. The stirring rod was rotated in distilled water without any suspended NiO powder in it, and almost the same rate of H_2 and O_2 evolution as seen in Fig. 1 was achieved. This indicates that at least the major part of the water splitting reaction proceeded in between the stirring rod and the bottom of the glass reaction vessel. This result also excluded the possibility that the Teflon which coated the stirring rod took part in the reaction. Second, a Ni metal foil (35 mm × 9 mm × 0.2 mm) was oxidized at 800 °C for 1 h in air and was rotated in distilled water at the bottom of the reaction vessel by using a stirring rod attached on top of the foil. Again H_2 and O_2 evolution was observed with a rate of about half that obtained in the above experiment using adhesive tape. These results suggest that the rubbing of the oxide materials against the bottom wall of the glass reaction vessel is essential, but the collisions between the oxide particles or at the stirrer surface are not.

In the above experiments, we did not pay much attention to the influence of magnetic fields generated by the stirring device. To avoid magnetic field effects, a motor driven mechanical stirrer was used for the abrasive stirring. The motor rotated the catalyst powder (NiO) stuck on the tip of the driving shaft, which was pressed on the bottom of the reaction vessel. Even in the reaction cell, stoichiometric H_2 and O_2 evolution was observed. Therefore, the magnetic field exerted by the stirrer has nothing to do with the present phenomenon.

From all the above experimental results, we conclude that the H_2 and O_2 evolution is regarded as ‘mechano-catalytic’ overall water splitting. Because of the first and second laws of thermodynamics, it is not probable that heat of friction leads to the observed water decomposition. We, therefore, consider that these catalysts directly convert mechanical energy to chemical energy.

We now turn to the influence of photoirradiation. When the reaction vessel containing a suspended powder catalyst was irradiated with a Xe lamp, essentially no appreciable change in H_2 and O_2 evolution rate was observed for NiO, Co_3O_4, and Fe_3O_4. However, in the case of Cu_2O, a difference of the rate of H_2 and O_2 evolution was observed as shown in Fig. 2. During the first 50 h, the reaction was carried out under irradiation (> 460 nm) and then the reaction was continued in the dark for another 50 h after the evacuation of the gas phase. The rate of H_2 and O_2 evolution under the irradiation was faster by about 3 times than that in the dark. Because of the difference of the activity between reaction in the dark and under photoirradiation, we previously concluded the observed phenomenon as photocatalysis, which should be corrected. At present, we do not have a satisfactory explanation for the effect of photoirradiation on Cu_2O.

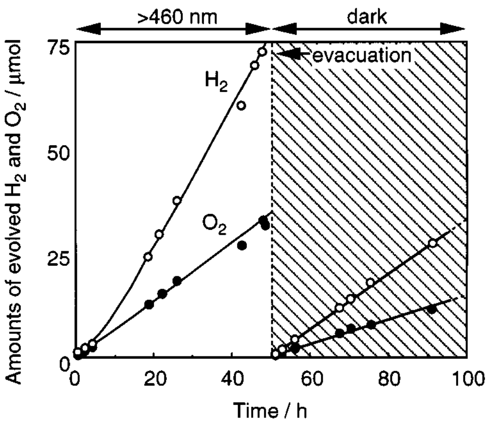

Fig. 2 Time course of H_2 (open circles) and O_2 (filled circles) evolution on Cu_2O under visible light (> 460 nm) irradiation and in the dark. The reaction system was evacuated at a reaction time of 50 h. Catalyst (Cu_2O): 0.1 g, H_2O: 200 cm^3.

As we have shown, the rate of H_2 and O_2 evolution strongly depends on the rubbing method of the catalytic materials, and thus much more efficient systems could be constructed by a suitable reactor design.

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