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Photocatalytic Hydrogen Production with Nanocomposite Photocatalysts

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Hydrogen, which has potential as a clean energy fuel, can be extracted from water, biomass, natural gas and other carbon sources [1]. Methanol has been recommended as the best source for hydrogen fuel among the high energy density liquid fuels [2]. Methanol can be converted to hydrogen by several reactions, containing methanol steam reforming [3,4], partial oxidation of methanol [5,6], oxidative methanol reforming [7], methanol decomposition and photocatalytic oxidation [8,9]. The photocatalytic hydrogen production with the methanol decomposition appears to be very promising method for the practical and low-cost technologies in the hydrogen-based energy system.

Titanium dioxide (TiO_2) is considered as a good photocatalyst for hydrogen generation because of its excellent resistance to chemical and photochemical corrosion in aggressive aqueous environments and due to its activity towards both light and aqueous solutions such as water and methanol. Nobel metal loading onto TiO_2 have been widely investigated for hydrogen generation, and have been presented to be very effective to enhance TiO_2 photocatalytic activity since it can contribute to efficient electron-hole separation. However, considering the high costs incurred by the consumption of novel metals, it is very significant to fabricate a highly efficient and cost-effective photocatalyst, meanwhile, converting them into environment-friendly products. Because copper-containing TiO_2 is cost-effective compared with noble metal loaded TiO_2, its utilization has been energetically studied for the photocatalytic hydrogen production. Sreethawong and Yoshikawa have described that copper-loaded TiO_2 gave about two fold higher hydrogen generation activity compared with the optimum value of the Ni loaded case. Wu and Lee have studied hydrogen generation with TiO_2 with deposited copper, and proven that oxidation of metal copper occurred during reaction induced high hydrogen generation activity. Bandara et al. and Choi el al. have fabricated TiO_2 photocatalysts loaded with CuO, and found that hydrogen production was drastically enhanced by CuO relative to pure TiO_2. However, little information on the photocatalytic hydrogen production with the nanocomposite composed of three components containing TiO_2 and CuO.

The present work deals mainly with the photocatalytic hydrogen production from aqueous methanol solution with $CuO/Al_2O_3/TiO_2$ nanocomposite. Furthermore, the photocatalytic activities of ZnO/TiO_2, SnO/TiO_2, CuO/TiO_2 and Al_2O_3/TiO_2 nanocomposites were evaluated for the comparison with the nanocomposite composed of three components.

TiO_2 P25 photocatalyst was purchased from Degussa Co. Ltd., Germany (anatase 75%, rutile 25%, BET specific surface area 48 m^2/g, mean particle size 25nm). Nanopowders

(ZnO, SnO, CuO and Al_2O_3) were obtained from Sigma□Aldrich. The mean diameter and specific surface area were 50~70 nm and 15~25 m^2/g for ZnO, 18 nm and 47 m^2/g for SnO, 33 nm and 29 m^2/g for CuO and 40~47 nm and 35~40 m^2/g for Al_2O_3. Methanol (99.8%, Nacalai Tesque, Inc., Japan) was used as received without further purification. Laboratory pure water was obtained from an ultrapure water system (Advantec MFS Inc., Tokyo, Japan) resulting in a resistivity > 18 MΩ cm.

A mechanical mixing method was used for the preparation of nanocomposite photocatalyst. The oxide powders were mixed with the mortar. An electric furnace (Koyo Box Furnace, KBF828N, Nara, Japan) was used for sintering at 500 ^oC under an air atmosphere. The furnace was heated from ambient to the final sintering temperature of 500 ^oC at a rate of 4.7 ^oC/min and then the temperature was kept constant for 3 h.

The surface areas of nanocomposite photocatalysts were determined by the three points BET method with di-nitrogen at 77 K (Autosorb-1-C, chemisorption and physisorption analyzer, Qnantachrome Instruments, USA). The structure and crystalline phases of nanocomposite photocatalysts were characterized by X-ray diffractometer (XRD, RIGAKU Ultima IV, sample horizontal type) with Cu K_α radiation (λ=0.15406 nm) at 40 kV and 50 mA. The diffraction patterns were taken over the 2θ angle range from 10^o to 80^o with a scan speed of 4^o/min and a stepsize of 0.02^o. The microstructure and morphology of the nanocomposite photocatalysts were analyzed by transmission electron microscope (TEM, Hitachi H-7000, 125 kV accelerating voltage).

The pyrex column vessel reactor (inner volume: 55.6 mL) was used for the photocatalytic production of hydrogen from aqueous methanol solution. The pyrex glass cuts off all wavelength below 300 nm. Typically, 20 mg of the nanocomposite photocatalysts were added to 30 mL of 10 vol% methanol solution in the photoreactor. A 15 W black light (Toshiba Lighting & Technology Corp) with a maximum emission of ~352 nm was applied as light source, which was positioned on the side of photoreactor. The light intensity was measured by a UV radio meter with a sensor of 320 to 410 nm wavelengths (UVR-400, Iuchi Co., Osaka, Japan), and the value was 1.0 mW/cm^2. The nanocomposite photocatalysts were continuously dispersed in the aqueous methanol solution by a magnetic stirrer during the irradiation. The temperature of the suspension in the photoreactor was kept constant by the water bath. The irradiation time was 3 h. The hydrogen product from the aqueous methanol solution was analyzed by gas chromatography (GL Sciences, GC□3200) with thermal conductivity detector (TCD). The stainless column (4 m long, 2.17 mm i.d.) packed with Molecular Sieve 5A was used for the separation. The carrier gas was high purity argon gas. The temperature conditions of GC were 50 ^oC for injection, column and detector.

The quick recombination of photogenerated electrons (e^-) and holes (h^+) decreases the photocatalytic efficiency of TiO_2. The use of a charge transfer catalyst (CTC) to prepare a binary photocatalyst is an alternative way to achieve better photocatalytic activities because the charge transfer catalyst is able to trap the photogenerated electrons (e^-) and holes (h^+) in its domain. Therefore, the effect of metal oxide cocatalysts on the photocatalytic hydrogen production over TiO_2 was investigated for the simple mixing preparation methods. The photocatalytic hydrogen production over TiO_2 tended to increase in the addition of metal oxide cocatalysts, compared with those in the absence of them. The optimum contents were

1.5, 0.5, 1.0 and 0.5 wt% for ZnO, SnO, CuO and Al_2O_3 cocatalysts, respectively. The photocatalytic activity for hydrogen formation increased in the order ZnO, SnO, CuO and Al_2O_3. The Al_2O_3/TiO2 photocatalytic activity was approximately 6 times better than that obtained with TiO_2. Wu et al. have studied the photocatalytic hydrogen evolution over Cu□deposited TiO_2 from the aqueous methanol solution (42%), and presented that the optimum Cu loading was approximately 1.2 wt%. The incident radiation produces electrons from the valence band to the conduction band, the band gap energy being lowered by copper incorporation. A photo-induced electron reduces water to hydrogen while methanol, the sacrificial reagent for hole, gets oxidized. Because the CuO conduction band is located below that of TiO_2, electron transfer to the conduction band of CuO is possible. The phenomenon becomes important when a part of incident radiation has wavelength in the UV range. The hole transfer from the valance band of TiO_2 to that of CuO is also allowable for the same reason. The combined effects of CuO with TiO_2 are responsible for the enhanced hydrogen evolution.

When the electron–hole (e–h) pair is formed by the UV light, the activated energy is large enough to excite the photogenerated electron ($e^{\square}$) from the TiO_2 band (3.2 eV) into the Al_2O_3 band (>5.0 eV). Nevertheless, the photogenerated hole (h^+) in the TiO_2 cannot shift the Al_2O_3 region energetically. Therefore, the recombination of the photogenerated electron (e^-) and hole (h^+) pair is hindered by the separation. Hence, the estimated phenomenon may be attributable to the enhanced hydrogen formation.

An increase in the lifetime of photogenerated electron–hole pairs in the coupled oxides, due to the hole and electron transfer between the two coupling oxides, seems to be very critical to the catalytic activity enhancement for the hydrogen production. Therefore, the photocatalytic hydrogen production with the nanocomposite composed of three components, TiO_2, CuO and Al_2O_3, were investigated in the aqueous methanol solution. When the Al_2O_3 doping concentration was 0.2 wt%, the maximum hydrogen formation was obtained in the doping concentration of CuO 0.4 wt%. As the doping concentration of Al_2O_3 increased to 0.3 and 0.4 wt%, the optimal doping concentrations for CuO shifted to 0.2 wt%. On the CuO doping concentration of 0.2 wt%, the best hydrogen production was observed with 0.3 wt% Al_2O_3 doping concentration. With increasing the CuO doping concentration, the peak of convex curves moved to the lower Al_2O_3 content. Therefore, the photocatalytic hydrogen production proved a close relationship between the CuO and Al_2O_3 doping concentrations. The maximum hydrogen formation (1200 μmol $g^{\square 1}$·cat) was obtained using 0.2 wt% CuO/0.3 wt% Al_2O_3/TiO_2 nanocomposite photocatalysts. Wang et al. have fabricated $ZnO/TiO_2/SnO_2$ mixtures with the molar ratio of $ZnO:TiO_2:SnO_2$ = 4:1:1 from the component oxide powders ZnO, TiO_2 and SnO_2 by solid-state reaction at elevated temperature. In the photocatalytic degradation of methyl orange, the mass photocatalytic activity of $ZnO/TiO_2/SnO_2$ mixture was 2.0 times that of TiO_2, 16.4 times that of SnO_2 and 0.92 times that of ZnO, i.e. $ZnO/TiO_2/SnO_2$ composite was photocatalytically more active than the pure TiO_2 and SnO_2 but less active than ZnO. In the present work, the photocatalytic activity for hydrogen production was approximately ten times that of pure TiO_2.

Little information of the temperature effect on the photocatalytic hydrogen production from the aqueous solution has been presented. Therefore, the effect of reaction temperature on the photocatalytic hydrogen formation from the aqueous solution with $CuO/Al_2O_3/TiO_2$

nanocomposites was investigated in the range of 40 to 70 ^{o}C. Formic acid potassium supporting electrolyte was added into the aqueous methanol solution for the enhancement of hydrogen production. The H_2 yield increased gradually with increasing in the reaction temperature. The hydrogen production yield at 70 ^{o}C was about three times that near room temperature (40 ^{o}C). Korzhak et al. have reported the influence of temperature on the quantum yield of photocatalytic hydrogen production in the presence of TiO_2/Cu nanocomposites. In the study, the quantum yield was proportional to the temperature, and it could be postulated that the temperature dependences of quantum yield (hydrogen production) originate from the thermal activation of desorption of acetaldehyde which was the oxidation product from a sacrificial reagent ethanol. In the present work, the affect of temperature on the photocatalytic hydrogen production may similarly be attributable to the thermal activation of desorption of formaldehyde which was produced by the oxidation of methanol. Consequently, it was found that the reaction temperature is a significant factor for the photocatalytic hydrogen formation from the aqueous solution.

In summary, it was found that the deposition of CuO and Al_2O_3 into TiO_2 greatly enhance the photocatalytic activity of TiO_2 toward hydrogen production from aqueous methanol solution. The photocatalytic activity with 0.2 wt% CuO/0.3 wt% Al_2O_3/TiO_2 for hydrogen production was about 10 times that of pure TiO_2. Methanol dehydrogenation has application in indirect methanol fuel cells, where methanol is first reformed to hydrogen in an energy-consuming step. Photocatalytic dehydrogenation of methanol has the advantage of supplying the reforming energy from sunlight.

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