RuS_2/TiO_2-SiO_2 광촉매의 물분해 수소 생성 특성

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Photocatalytic Water Decomposition for Hydrogen Production over RuS_2/TiO_2-SiO_2

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1. Introduction

Photocatalytic water splitting over TiO_2 electrodes was discovered by Fujishima & Honda in 1972 [1]. Since then, not only TiO_2-based catalysts, but also various kinds of photocatalysts for water decomposition were discovered so far with different characteristics and efficiencies. Among such photocatalysts for hydrogen production, ruthenium disulfide (RuS_2) that is due to high stability against photocorosion along with potential electronic properties (E_g and E_{fb}) towards hydrogen formation [2] has been reported by K. Hara el al. [3]. In order to overcome low surface area and band-gap energy of RuS_2, these authors employed SiO_2 and/or TiO_2 as supports [3].

In this study, to further enhance the role of supports we employed gel-derived TiO_2-SiO_2 mixed oxides that are well known as supports and catalysts with excellent properties in comparison with TiO_2 and SiO_2 alone. The detailed investigation of characterization of supports, the effects of support, RuS_2 loading, and sacrificial reagent was conducted and discussed in this publication.

2. Results and Discussion

TiO_2 (P-25, Degussa Co.) and SiO_2 (amorphous, Strem) as supports were used as received. TiO_2-SiO_2 mixed oxides were prepared by sol-gel processes. RuS_2 was loaded on supports at 0.5, 1, 1.5, and 4 wt% by using conventional impregnation and sulfidation method.

The photocatalytic water decomposition was carried out in a batch type reactor (1.5 g of catalyst and 700 ml of diluted water) with an inner cell under UV irradiation at room temperature. The evolution gases were analyzed by GC equipped with TCD and molecular sieve 5 A capillary column (30 m). Photocatalysts were characterized by XRD (Rigaku, with Cu-K_α radiation over a 2θ range of 10 - 80^o), nitrogen adsorption (BET) using Micromeritics ASAP 2100 analyzer, UV-Vis DRS (Shimadzu-UV 525) and Capacitance-Voltage (C-V) technique. The setup of C-V measurement consisted of a lock-in amplifier (EG&G 5210) coupled with potentostat (EG&G 273) and software (EG&G M352). The data of C-V were used for evaluating the flat band potential by means of Mott-Schottky equation: $C^{-2} = 2(V- V_{fb} – KT/e)/\varepsilon\varepsilon_o e N_i$ (1)

where C is the total measured capacitance, ε is the dielectric constant of the material, ε_o the permittivity of the vacuum, e the electron charge, N_i the concentration of donors in n-type semiconductor.

It is apparently that the band-gap energy (E_g) of TiO_2-SiO_2 mixed oxide was higher than that of bare TiO_2 (P-25) and SiO_2 (Table 1). The explanation has been ascribed to the quantum size and support effect [4]. On the other hand, the BET specific surface areas of SiO_2, TiO_2-SiO_2 were substantially higher than that of TiO_2 (P-25) as expectation. On loading RuS_2, the decreasing of surface areas was observed over all of obtained catalysts. These results were ascribed to the high crystallinity and therefore low specific surface area of RuS_2.

It is well-known that the flat band potential (V_{fb}) of a semiconductor can be obtained from the intercept of the Mott-Schottky plot [5] by using the equation (1). Nonetheless, the intercepts of the Mott-Schottky plots did not gather precisely at one potential. On increasing AC frequency above 1 kHz , the intercepts significantly shifted toward more negative potential. For this reason, the AC frequency at which the flat band potential was indicated was fixed at 1 kHz in this work. This frequency is typically used for the measurement of the Mott-Schottky plot [6]. It was determined that the flat band potential of TiO_2-SiO_2 vs NHE was significantly higher than that of bare TiO_2 whereas lower than that of SiO_2 alone.

Table 1 showed the rate of hydrogen formation over various kinds of photocatalysts. The rate of hydrogen evolution as high as 24 μmol/20 h was observed on TiO_2-SiO_2 mixed oxide compared to the trace over TiO_2 and SiO_2. The explanation could be attributable to the band-gap energy of TiO_2-SiO_2 estimated at 3.2 eV while that of bare SiO_2 and TiO_2 determined around 2.3 [7] and 3.0 eV, respectively. Furthermore, TiO_2-SiO_2 mixed oxide showed the flat band potential much higher than that of bare TiO_2. In other words, the reduction power of TiO_2-SiO_2 was energetically favorable for water photolysis in comparison with bare TiO_2. Although SiO_2 alone was higher than TiO_2-SiO_2 in reduction power to reduce water, it was too low in band-gap energy to absorb UV illumination efficiently.

The effect of RuS_2 loading over the rate of hydrogen evolution was presented in Table 1. It was found that 1 wt% RuS_2 over TiO_2-SiO_2 was the optimum loading with the rate of hydrogen formation as high as 518 μmol/20 h. The rate of hydrogen evolution was significantly declined as the loading of RuS_2 over TiO_2-SiO_2 was either decreased or increased beyond 1 wt%. It was well-known that RuS_2 is very stable against photocorrosion along with favorable electronic properties towards hydrogen production [2]. As a consequence, RuS_2 doped on TiO_2-SiO_2 was believed to improve the reduction driving force of derived photocatalyst to reduce water as well as the enforcing of free electron production. Nonetheless, on increasing the amount of RuS_2 over support, the interparticle electron transfer would be suppressed due to the enhanced recombination of photo-excited electrons and holes. In addition, it was known that the E_g in a range of 1.3-1.85 eV [2] along with V_{fb} of -0.48 V versus NHE, pH 0 and –0.56 eV, pH 14 [2] of single-crystal RuS_2 was smaller than that of colloidal RuS_2

with 2.8 eV for E_g and 0.6 V versus NHE for V_{fb} [8] as well as that of supported RuS_2 in this report with 2.0 eV for E_g. These results have been ascribed to the size effect [3]. Accordingly, it was proposed that on increasing the loading of RuS_2 over TiO_2-SiO_2 the lower dispersion of RuS_2 on the support would lead to the formation of single-crystal RuS_2 thereon and consequently, diminish the E_g and V_{fb} of RuS_2. In other words, the reduction power of RuS_2 was too weak to reduce water and therefore, the trace of hydrogen was observed over $RuS_2(4)/TiO_2$-SiO_2.

It has been suggested that the V_{fb} (0.6 V) of colloidal RuS_2 was hardly changed with the change in the E_g thereof [3]. From the E_g value of TiO_2-SiO_2, the energy band levels of photocatalysts in aqueous solution of Na_2SO_3 0.1 M, pH 9 in relation to the redox potential of water were presented in Fig. 1 and accordingly, it was proposed that the charge transfer processes of photo-excited electrons on the conduction band of TiO_2-SiO_2 to RuS_2 and holes on the valence band of TiO_2-SiO_2 to RuS_2 were possible. For that reason, possible charge transfer processes between RuS_2 and TiO_2-SiO_2 were believed to improve the efficiency of charge separation, resulting in the enhancement of reduction and oxidation over the photocatalyst.

EDTA, Na_2SO_3, Na_2S, and CH_3OH employed as electron donors showed almost similar effects on the rate of hydrogen evolution. Meanwhile, the combination of Na_2SO_3 and Na_2S in a aqueous solution was found to substantially improve the formation of hydrogen over the $RuS_2(1)/TiO_2$-SiO_2 photocatalyst as high as 1.303 mmol/h. This result was in consistence with the previous report [3] in which Na_2S/Na_2SO_3 was found as the best electron donors on RuS_2/TiO_2 and RuS_2/SiO_2 towards hydrogen production. It has been reported that the flat band potential of RuS_2 would be shifted towards a more negative potential in an Na_2S aqueous solution [3]. As a result, hydrogen formation is energetically enhanced. On the other hand, it also reported that the addition of SO_3^{2-} ions to an S_2^{2-} solution enhanced hydrogen formation over RuO_2/CdS photocatalyst [3].

In summary, the highest rate of hydrogen formation was observed on RuS_2 supported over TiO_2-SiO_2-mixed oxide that was ascribed to the higher band-gap energy and/or stronger reduction driving force of TiO_2-SiO_2 support in comparison with bare TiO_2 and SiO_2. The flat band potential along with the band-gap energy of TiO_2-SiO_2 was higher than that of supported RuS_2 that was believed to bring about the charge transfer processes of photo-excited electrons on the conduction band of TiO_2-SiO_2 to RuS_2 and holes on the valence band of TiO_2-SiO_2 to RuS_2. Consequently, it was believed to increase the efficiency of charge separation, resulting in the enhancement of reduction and oxidation over the photocatalyst. On increasing RuS_2 over TiO_2-SiO_2 beyond the optimum loading (1 wt%), the photoactivity of catalyst was substantially declined that was due to the decreasing of reduction power of RuS_2 towards hydrogen production.

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Table 1: E_g, BET specific surface area and rate of hydrogen formation of photocatalysts

Photocatalyst	E_g (eV)	BET specific surface area (m^2/g)	Rate of hydrogen formation (μmol/h)
SiO_2	2.3 [7]	292	Trace
TiO_2	3.0	48	Trace
TiO_2-SiO_2	3.2	220	1.2
RuS_2(1)/SiO_2	-	-	7.76
RuS_2(1)/TiO_2	-	-	18.36
RuS_2(1)/TiO_2-SiO_2	-	180	25.9
RuS_2(0.5)/TiO_2-SiO_2	-	-	14.8
RuS_2(1.5)/TiO_2-SiO_2	-	-	11.2
RuS_2(4)/TiO_2-SiO_2	-	-	0.5

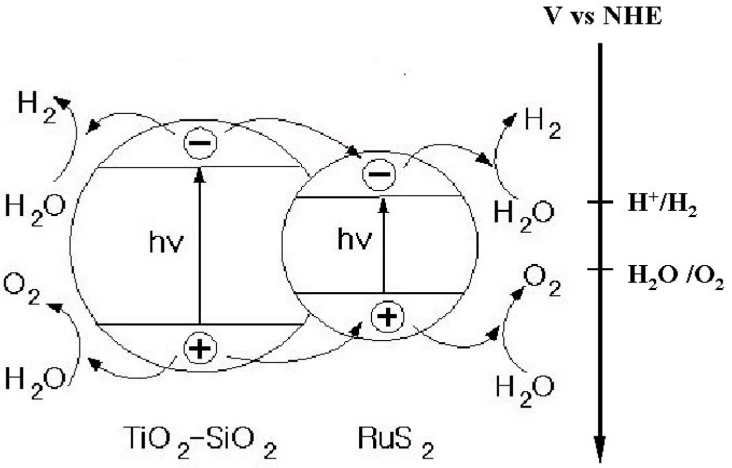

Fig.1. Schematic diagram of band energy levels of TiO_2-SiO_2-supported RuS_2 in an Na_2SO_3 aqueous solution, pH 9.