

Photocatalytic Water Splitting over ZrO_2 Prepared by Precipitation Method

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Abstract— ZrO_2 prepared by the precipitation method of zirconium oxychloride with various hydrolyzing agents was studied for photocatalytic water splitting reaction under UV light irradiation. The crystal structure as well surface properties were varied with the hydrolyzing agent of KOH, NH_4OH , and NH_2CONH_2 . Especially, the surface area of the prepared ZrO_2 calcined at the same temperature of 750°C for 6 h was dependent highly on the hydrolyzing agent, and thus the highest photocatalytic activity was obtained for ZrO_2 with the highest surface area when KOH was used as a hydrolyzing agent. In the presence of Na_2CO_3 , the photocatalytic activity of ZrO_2 increased by 2-3 fold, which was ascribed to the physically adsorbed carbonate species on the ZrO_2 surface.

Key words: ZrO_2 , Photocatalytic, Water Splitting, Hydrolyzing Agent, Surface Area, Crystal Structure, CO_2 TPD

INTRODUCTION

Hydrogen is an important chemical feedstock and is highly valued as a non-polluting renewable fuel. Among various methods to obtain hydrogen, much attention has been paid to the photocatalytic decomposition of water into H_2 and O_2 using semiconductor photocatalysts because of the potential utilization of abundant solar energy [Domen et al., 2001]. Many semiconductor photocatalysts have been investigated for the photocatalytic decomposition of water under ultraviolet (UV) irradiation such as TiO_2 [Fujishima and Honda, 1972], $\text{K}_4\text{Nb}_6\text{O}_{17}$ [Domen et al., 1990], $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ [Tanaka et al., 1997] and $\text{La}_2\text{Ti}_2\text{O}_7$ [Kim et al., 1999]. Most of these materials are doped with metals such as platinum or metal oxides such as nickel oxide in order to promote the electron-hole separation generated by absorption of photons with energy higher than their band gap energy. ZrO_2 photocatalyst has shown the unique property that its photocatalytic activity is decreased when it is doped with a metal or a metal oxide, which is ascribed to the high potential energy barrier between the metal and the ZrO_2 [Sayama and Arakawa, 1996]. The surface property and crystal structure of ZrO_2 were influenced greatly by the preparation conditions and the hydrolyzing agents [Chuah et al., 1996]. The present authors have found that the photocatalytic activity for water splitting reaction was highly dependent both on the crystallinity and on the surface area [Hwang et al., 2000; Kim et al., 2001; Reddy et al., 2003].

Photocatalytic activity depends heavily on preparation methods of a photocatalyst [Nam and Han, 2003; Jung and Imaishi, 2001]. In the present study, the effect of the physicochemical properties of ZrO_2 prepared by different hydrolyzing agents on the photocatalytic activity for water splitting will be discussed based on the results obtained by X-ray diffraction, UV-diffuse reflectance spectra, BET-surface area and the temperature programmed desorption (TPD) of

CO_2 .

EXPERIMENTAL

1. Catalyst Preparation

ZrO_2 was prepared by the precipitation method from zirconium oxychloride [$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Aldrich, 99.9%)]. A desired quantity of zirconium oxychloride was dissolved in doubly distilled water. To this clear solution with pH 2 a required amount of hydrolyzing agent [NH_4OH , KOH and urea (NH_2CONH_2)] was added slowly until the solution pH reached 9; the hydrolysis by urea took place very slowly. The obtained precipitate was digested for 4 h at 100°C and washed several times with deionized water to make it free from chloride ions. Then the obtained hydroxide was dried at 120°C for 24 h and calcined at 750°C for 6 h. A reference ZrO_2 was obtained by calcination of $\text{Zr}(\text{OH})_4$ (Aldrich, 99.9%) at 750°C for 6 h. The reference ZrO_2 was denoted by standard- ZrO_2 hereafter.

2. Characterization

The crystal structures of the obtained samples were determined by X-ray diffractometer (Mac Science Co., M18XHF) with monochromated $\text{Cu K}\alpha$ (1.54 \AA) radiation at 40 kV and 200 mA. Diffraction patterns were recorded with a scanning speed of 4 degree/min in the 2θ range between 10° and 60° . The percentage of tetragonal and monoclinic phases present in the sample was estimated by comparing the area under the characteristic peaks of the monoclinic phase ($2\theta=28.5^\circ$ and 31.6° for the (111) and (11 $\bar{1}$) reflections) and the tetragonal phase ($2\theta=30.4^\circ$ for the (111) reflection), respectively [Chuah et al., 1996].

The band gap energies were determined by UV-Visible diffuse reflectance spectrometer (Shimadzu, UV 2401). The BET surface areas were determined by N_2 adsorption at 77 K in a constant volume adsorption apparatus (Micrometrics, ASAP 1012).

The temperature-programmed desorption (TPD) of carbon dioxide (CO_2) was carried out with an online GC-Mass spectrometer (HP 5890II-HP/5972MSD). Initially, 0.025 g of sample was placed in a quartz reactor and pretreated at 500°C for 2 h in a flow of helium (He). Carbon dioxide was injected at room temperature for 30

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†This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

min and the sample was flushed with helium for 1 h before starting the temperature ramp. The analysis was carried out from 30 °C to 800 °C at a ramping rate of 10 °C/min.

3. Photocatalytic Reaction

The photocatalytic reaction was carried out in a closed gas circulation system. The catalyst (300 mg) was dispersed in distilled water (500 ml) with or without Na_2CO_3 (80 g) addition by magnetic stirring and irradiated by a high pressure mercury lamp (Ace Glass Inc., 450 W) equipped with an inner irradiation quartz reaction cell. The evolved gases were analyzed by on-line gas chromatography (TCD, molecular sieve 5 Å column).

RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction patterns of standard- ZrO_2 ob-

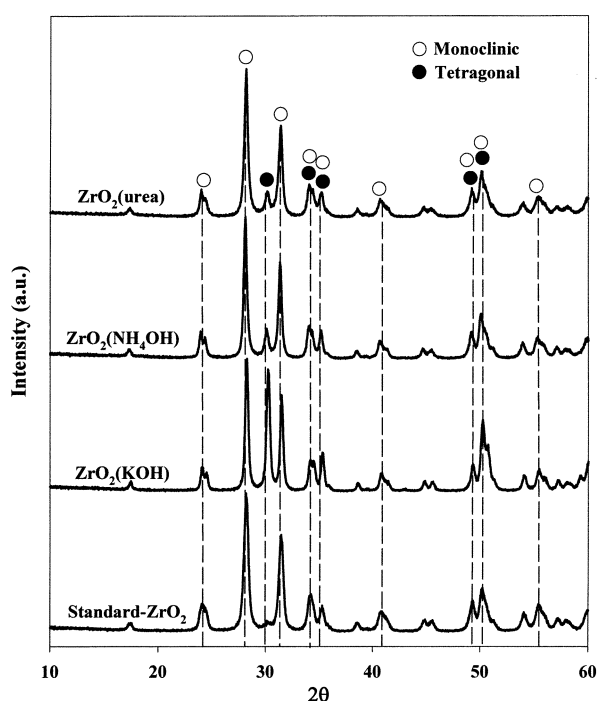


Fig. 1. X-ray diffraction patterns of ZrO_2 with different hydrolyzing agents.

Table 1. The crystal structure and the photocatalytic activity of ZrO_2

Catalyst	Crystal structure (%)		Photocatalytic activity ($\mu\text{mol/gcat.h}$) ^a			
	Monoclinic	Tetragonal	Pure water		Na_2CO_3 solution	
			H_2	O_2	H_2	O_2
Standard- ZrO_2	95	5	60	32	142	72
$\text{ZrO}_2(\text{KOH})$	56	44	112	55	296	150
$\text{ZrO}_2(\text{NH}_4\text{OH})$	78	22	72	38	180	92
$\text{ZrO}_2(\text{Urea})$	82	18	95	48	214	110

^aCatalyst 0.3 g; distilled water 500 ml; inner irradiation-type reaction cell made of quartz, 450 W high-pressure Hg lamp, Na_2CO_3 80 g.

tained by calcination of $\text{Zr}(\text{OH})_4$ and the ZrO_2 prepared by precipitation of zirconium oxychloride at pH 9 with KOH , NH_4OH and urea (NH_2CONH_2) as hydrolyzing agents. The standard- ZrO_2 showed almost exclusively the monoclinic phase while the ZrO_2 prepared by the precipitation method showed both monoclinic and tetragonal phases as summarized in Table 1. However, the relative amount of monoclinic and tetragonal phases present in the prepared ZrO_2 was highly dependent on the hydrolyzing agent, although all samples were calcined at the same temperature of 750 °C.

Fig. 2 shows the UV-Visible diffuse reflectance spectra of standard- ZrO_2 and the ZrO_2 prepared by the precipitation method using various hydrolyzing agents. All samples showed an absorption edge of 315 nm corresponding to band gap energy of 3.93 eV. Thus, the

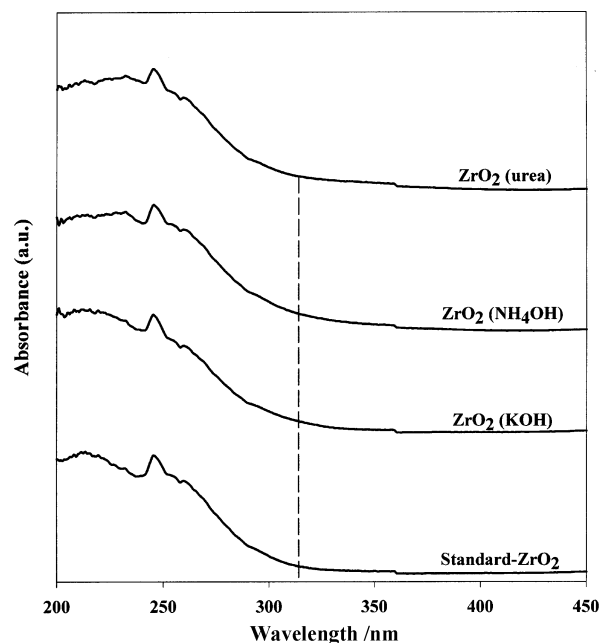


Fig. 2. UV-visible diffuse reflectance spectra of ZrO_2 with different hydrolyzing agents.

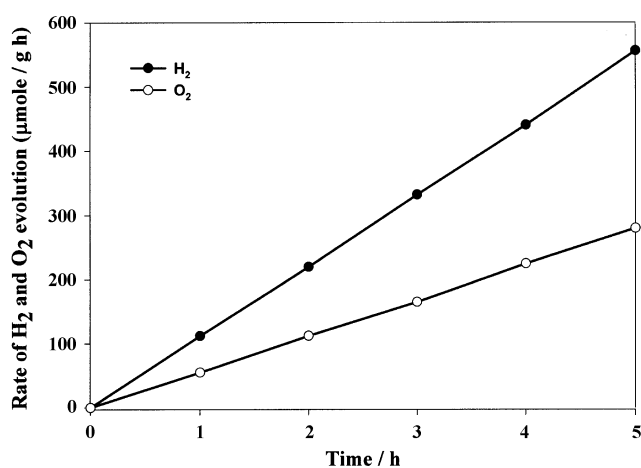


Fig. 3. Rates of H_2 and O_2 evolution on ZrO_2 (KOH) in pure water under UV irradiation. Catalyst 0.3 g; distilled water 500 ml; inner irradiation-type reaction cell made of quartz, 450 W high-pressure Hg lamp.

difference in photocatalytic activity of ZrO_2 prepared by the different hydrolyzing agents was not originating from the difference in the optical property.

The photocatalytic activities of the prepared ZrO_2 were measured in a closed gas circulation system at room temperature under UV irradiation. A typical time course of H_2 and O_2 evolution is shown in Fig. 3 and the photocatalytic activities of all catalysts are summarized in Table 1. All the catalysts showed photocatalytic activity in water splitting, producing hydrogen and oxygen in a stoichiometric ratio ($\text{H}_2/\text{O}_2=2:1$). There was no indication of catalyst deactivation for 10 h during which the catalyst had turned over many times, making this overall water splitting a catalytic reaction. It should be noted that these ZrO_2 samples do not contain other metals or metal oxides as co-catalysts, which are indispensable for other known photocatalysts [Fujishima and Honda, 1972; Domen et al., 1990; Tanaka et al., 1997; Kim et al., 1999]. ZrO_2 with KOH as a hydrolyzing agent, which had the highest surface area than any other catalysts, showed the highest activity.

In Table 1, the photocatalytic activities in the presence of Na_2CO_3 are also shown. For all ZrO_2 , the addition of Na_2CO_3 (80 g) as an external additive to the reaction solution containing 500 ml of distilled water showed increase in the rates of both H_2 and O_2 evolutions by a factor of 2-3, while maintaining the evolution of H_2 and O_2 nearly stoichiometric (2 : 1). Enhancement of the photocatalytic activity in the presence of Na_2CO_3 was ascribed to acceleration of O_2 desorption from ZrO_2 surface, as demonstrated by Sayama and Arakawa [1996]. In photocatalytic water splitting over a semiconductor, excited electron-hole pairs are generated when the catalyst is illuminated with light having energy equal to or greater than its band gap. The principal challenge is how to suppress the energy-wasteful recombination of the formed electron-hole pairs. The car-

bonate ions (CO_3^{2-}) on the ZrO_2 surface could accelerate the charge separation of electron and hole by trapping holes, resulting in the increased photocatalytic activity. In order to elucidate the role of carbonate species on the ZrO_2 surface, temperature programmed desorption (TPD) experiments of CO_2 were performed and the results are shown in Fig. 4. Among three peaks from 30 °C and 800 °C, the first peak between 30 °C and 300 °C was ascribed to the physically adsorbed CO_3^{2-} on the ZrO_2 surface, which could act as the trapping sites for holes. Although the shape this peak for four ZrO_2 catalysts showed considerable differences, the area under this peak did not vary markedly, which indicated that the number of sites on ZrO_2 surface for CO_2 adsorption was nearly the same. On the other hand, the area of high temperature peaks varied significantly depending on the catalysts, i.e., $\text{ZrO}_2(\text{KOH}) > \text{ZrO}_2(\text{urea}) > \text{ZrO}_2(\text{NH}_4\text{OH}) > \text{standard } \text{ZrO}_2$.

Thus, different hydrolyzing agents employed to prepare ZrO_2 catalysts by precipitation affect significantly crystal structure and surface properties that eventually affect their catalytic activity. Then, what is the most important factor responsible for the different photocatalytic activities of ZrO_2 for water splitting? From Table 1, it is obvious that crystal structure of ZrO_2 has little effect on the activity. ZrO_2 catalysts show a wide variation in the composition of monoclinic and tetragonal structures. But it has no correlation with the catalytic activity for pure water as well as for water containing Na_2CO_3 . The crystallinity of photocatalysts is also an important parameter that determines their photocatalytic activities [Hwang et al., 2000; Kim et al., 2001; Reddy et al., 2003]. However, there was not much difference in crystallinity among four ZrO_2 catalysts as indicated

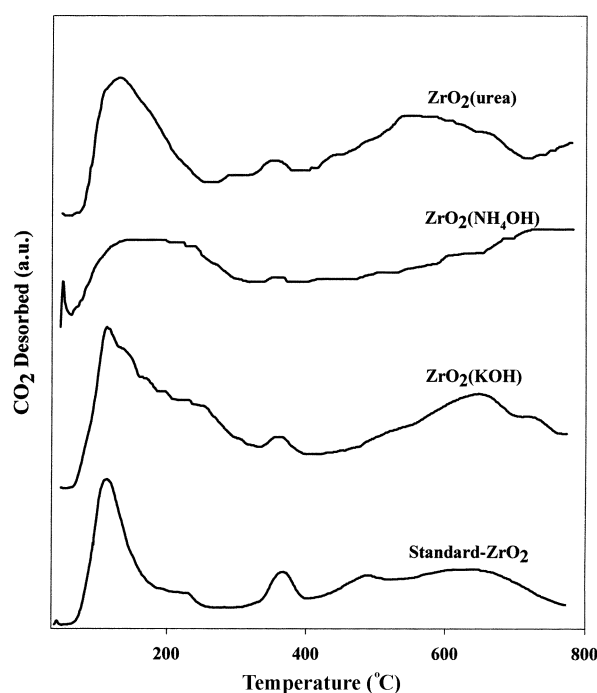


Fig. 4. CO_2 -TPD profiles of ZrO_2 prepared by precipitation with different hydrolyzing agents.

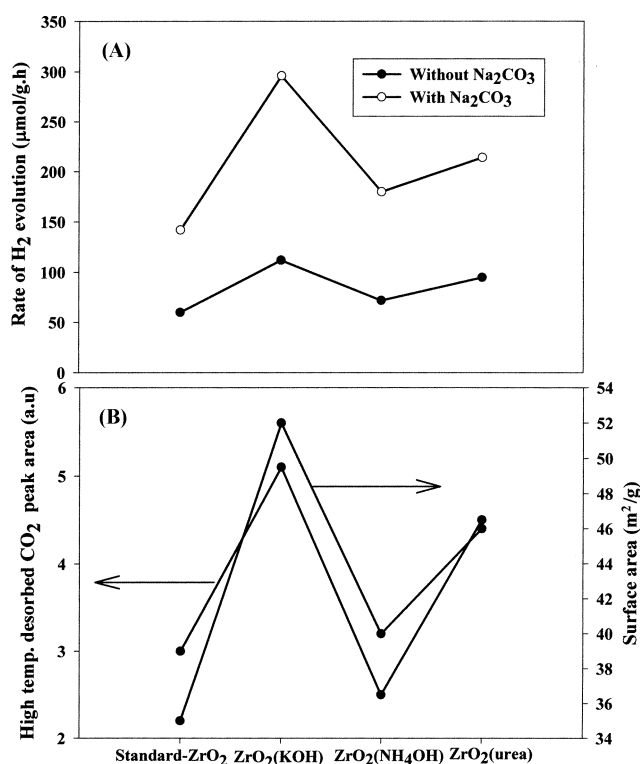


Fig. 5. Correlations among the high temperature CO_2 desorption peak areas, surface areas, and rates of H_2 evolution with and without Na_2CO_3 .

by similar XRD peak intensity in Fig. 1.

Fig. 5 shows plots of two other parameters that appear to affect catalytic activity represented by the rates of H_2 evolution: the area of high temperature CO_2 desorption peaks and the BET surface area. Both parameters show good correlations with the rates of H_2 evolution. The effects of surface area on photocatalytic activity are well documented. The water-splitting reaction involves surface processes like adsorption and desorption of the reactant (H_2O) and products (H_2 and O_2), and the rates of these processes depend on the surface area. The TPD of CO_2 is often used to titrate the surface basicity by means of adsorption of acidic CO_2 molecules. Indeed, the surface basicity could promote the rate of water-splitting reaction by accelerating O_2 desorption due to a repulsive interaction of basic sites and O_2 . Furthermore, the sites titrated by CO_2 could become the adsorption sites for carbonates which are shown to promote the water-splitting reaction. However, the variation in the area of high temperature CO_2 desorption peaks may simply represent the variation in surface area because two parameters show exactly the same trend. In any case, the hydrolyzing agent influences both structure and the surface properties, but the surface area appears to be the key variable that changes the rates of H_2 and O_2 evolution.

As a conclusion, the ZrO_2 prepared by precipitation method with various hydrolyzing agents (KOH , NH_4OH , and NH_2CONH_2) showed differences in the surface area and crystal structure. The difference in the surface area of each ZrO_2 was found to be a dominating factor contributing to the difference in the photocatalytic activity for water splitting. In the presence of Na_2CO_3 , the photocatalytic activity of ZrO_2 increased by a factor of 2-3 folds, which was ascribed to the physically adsorbed carbonate species on the ZrO_2 surface.

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