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Effect of Ag co-catalyst on CO_2 adsorption states over Ga_2O_3 photocatalyst

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ABSTRACT

Ag species in the Ag loaded Ga_2O_3 (Ag/Ga_2O_3) photocatalysts were investigated with regard to changes in their structures and the chemical states before and after the photocatalytic CO_2 reduction with water. Ag clusters with the size of around one nanometer in as prepared 0.1 wt% Ag/Ga_2O_3 sample became larger metallic Ag nanoparticles with the size of several nanometers after the reaction. In the 1.0 wt% Ag/Ga_2O_3 sample, Ag nanoparticles having the $AgGaO_2$ interface structure decomposed to aggregated Ag metal particles after the reaction. Such transition in the morphology and chemical states of Ag species could explain the variations in photocatalytic activities of these samples during the reaction, and suggested that at least metallic Ag particles would function as effective co-catalysts.

In-situ FT-IR measurements of the Ag/Ga_2O_3 samples before and after the reaction, we could not detect CO_2 molecules adsorbing on metallic Ag nanoparticles in dark. Under light irradiation, however, the absorption bands originated from the photo-adsorbed CO_2 species on Ag metal nanoparticles appeared. Thus, we detected the interaction of CO_2 molecules and metallic Ag nanoparticles as the effective co-catalysts for CO_2 reduction.

1. Introduction

In recent years, exhaustion of carbon resources and global warming due to CO_2 emissions brought about by the large consumption of fossil fuels have become a worldwide problem. As a solution to address these problems, photocatalytic reduction of CO_2, which reduces CO_2 and creates carbon resources by using clean solar energy, has attracted much attention [1–8]. In particular, when water is used as the electron donor, the reduction of CO_2 is also interesting from the viewpoint of realizing artificial photosynthesis. Therefore, heterogeneous semiconductor photocatalysts effective for oxidizing water have been widely studied on the CO_2 reduction with water [9–20].

Recently, it has been reported that the photocatalytic activity for CO_2 reduction to CO is enhanced by the loading of Ag as co-catalyst [9]. Since then, several studies have shown the photocatalytic CO_2 reduction using Ag co-catalysts [10–12,15,17,19]. The Ag co-catalyst has been considered to be one of the effective electron receiving sites to promote the separation of photogenerated electron-hole pairs as well as the possible CO_2 reduction sites to produce CO [9,10,12,15]. It has been also proposed that the particle size and chemical state of the Ag co-catalyst should affect the photocatalytic activity, and metallic Ag nanoparticles with a small size and uniform distribution contribute to the enhancement in the photocatalytic conversion of CO_2 with water [9]. However, the reaction mechanism involving the functions of Ag co-catalysts has not yet been revealed in detail.

In our previous study, we had carried out in-situ FT-IR measurements of as-prepared Ag loaded Ga_2O_3 (Ag/Ga_2O_3) photocatalysts at each reaction step, and proposed the following reaction mechanism; CO_2 molecules are adsorbed as carbonate and bicarbonate species on the catalyst surfaces and these species change to bidentate formate species under photoirradiation. The formate species interact with H_2O molecules to produce CO under photoirradiation [21]. We also revealed that the formation of the bidentate formate species as a reaction intermediate of CO_2 reduction would take place at the perimeters of the Ag clusters on the Ga_2O_3 surface [22]. However, we could not explain the difference in photocatalytic activity for CO production between a high active 0.1 wt% Ag/Ga_2O_3 photocatalyst and a low active 1.0 wt% Ag/Ga_2O_3 photocatalyst by the difference in the amount of the formed bidentate formate species. This may indicate another unclarified reaction mechanism of CO_2 reduction proceeding just on the Ag co-catalyst. Considering the results reported in the previous works [9,10], during the photocatalytic reaction, Ag co-catalyst would be oxidised by the photogenerated holes and dissolved as Ag^+ cation, followed by re-photodeposition with the photoexcited electron. Since these changes of

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the structural and chemical state of Ag co-catalysts would affect the reaction mechanism, in-situ FT-IR measurements for the Ag/Ga_2O_3 samples after a period of reaction time should also be important to understand the reaction mechanism in detail.

Therefore, in this study, we carefully confirmed the change in the CO_2 reduction mechanism by monitoring the photocatalytic activity and selectivity with reaction time, and investigated the transitions of morphology and chemical states of Ag co-catalysts in Ga_2O_3 photocatalysts during the reaction by HAADF-STEM and XAFS analyses. Then, we compared the chemical states of the adsorbed CO_2 species in Ag/Ga_2O_3 photocatalysts before and after the reaction by FT-IR measurements. Moreover, in order to clarify the reaction mechanism proceeding on the Ag co-catalysts, we examined the dynamic adsorption process of CO_2 on the Ag co-catalyst by conducting in-situ FT-IR measurements under light irradiation.

2. Experimental

2.1. Preparation of Ag/Ga_2O_3 photocatalysts

Ag/Ga_2O_3 samples were prepared by an impregnation method and a photodeposition method as reported previously [23]. For the impregnation method, a mixture of a Ga_2O_3 powder (Kojundo Chemical Laboratory Co. Ltd. purity 99.99%) and an aqueous solution of $AgNO_3$ (Kishida Chemical Co. Ltd. purity 99.8%) was magnetically stirred and dried up, followed by calcination at 673 K for 2 h, which provided the Ag/Ga_2O_3 samples. The loading amounts of Ag were 0.1 and 1.0 wt%. We also prepared Ga_2O_3 samples loading metallic Ag nanoparticles by a photodeposition method. For the photodeposition method, a mixture of a Ga_2O_3 powder and an aqueous solution of $AgNO_3$ with about 12 vol% of methanol was magnetically stirred and photoirradiated with a 300 W Xe lamp for 3 h, followed by filtration. The loading amounts of Ag were 1.0 and 2.0 wt%.

2.2. HRTEM measurements

In the HRTEM measurements, samples were mounted directly on a carbon covered copper mesh. A Cs-corrected S/TEM (JEOL, JEM-ARM 200F Cold) equipped with a thermal field-emission gun was operated at 200 kV. HAADF-STEM images were taken at almost just focus at a resolution of 1024 × 1024 pixels ($0.021 \times 0.021\ nm^2\ pixel^{-1}$).

2.3. XAFS measurements

XAFS measurements were carried out at the beam line 6N1 at the Aichi Synchrotron Radiation Center as previously reported [23]. Ag L_3-edge XANES spectra of the samples were measured using a two crystal Ge(111) monochromator at room temperature in an atmospheric chamber with He gas. The data were recorded in a fluorescence X-ray yield mode with a silicon drift detector (Vortex Electronics) and in a total electron yield mode.

2.4. XRD measurements

Powder X-ray diffraction (XRD) patterns were recorded at room temperature on a MiniFlex600 (Rigaku) using Cu Kα as the radiation source with an operating voltage of 40 kV and current of 15 mA.

2.5. DRS measurements

Diffuse reflectance (DR) UV–visible spectrum was recorded at room temperature on a JASCO V-670 equipped with an integrating sphere covered with $BaSO_4$, where the $BaSO_4$ was used as the reference.

2.6. In situ FT-IR measurements

FT-IR spectra were recorded with a FT/IR-6100 (JASCO) in a transmission mode at room temperature. A sample (ca.20 mg) was pressed into a disk (diameter: 10 mm) at 50 MPa and placed in an in-situ IR cell equipped with CaF_2 windows. The cell allowed us to obtain the spectra of the samples in a CO_2 atmosphere as well as under light irradiation. Before the measurements, the samples were evacuated at room temperature for 2 h. For each spectrum, the data from 6 scans were accumulated at a resolution of $4\ cm^{-1}$.

2.7. Reaction tests for photocatalytic CO_2 reduction with water

Reaction tests for photocatalytic CO_2 reduction with water were conducted in a specially designed gas–liquid–solid three phase reactor as follows: Before the reaction test, the Ag/Ga_2O_3 powder (0.1 g) in the reactor was irradiated from a 300 W Xe lamp for one hour under CO_2 gas with a flow rate of 3.0 mL/min, where the light intensity measured in the range of 254 ± 10 nm was $11\ mW/cm^2$. Then 10 mL of 1.0 M $NaHCO_3$ aqueous solution was added to this reactor cell in dark. After one hour, the background was measured with an online gas chromatograph with thermal conductivity detector (GC-TCD, Shimadzu GC-8APT). Subsequently, photocatalytic reduction of CO_2 under photoirradiation was started and CO, H_2 and O_2 production rates were measured every hour with the GC-TCD up to five repetitions. Selectivity for CO in the reduced products was defined as follows: CO selectivity (%) = 100 × (production rate of CO)/(Sum of production rates of CO and H_2).

3. Results and discussion

3.1. Photocatalytic activity on the CO_2 reduction with water

The prepared 0.1 wt% Ag/Ga_2O_3 and 1.0 wt% Ag/Ga_2O_3 samples were examined for the photocatalytic reduction of CO_2 with water. The products observed in the present study were CO, H_2 and O_2, where CO was the reduction product from CO_2 and H_2 was produced by water splitting as a competitive reaction [9,10]. Fig. 1 shows the time courses of CO, H_2 and O_2 production rates over the 0.1 wt% Ag/Ga_2O_3 sample. The evolution of O_2 was lower than a half of total rates of H_2 and CO. However, the production rates of O_2 was higher than that produced by water splitting, supporting that photocatalytic CO_2 reduction using water as the electron donor actually proceeded. Oxygen might be dissolved in the aqueous solution or adsorbed on the surface of the photocatalyst in the present reaction condition. As shown in Fig. 1, CO production rate gradually decreased while the production rates of H_2 and O_2 gradually increased with reaction time, and they became almost

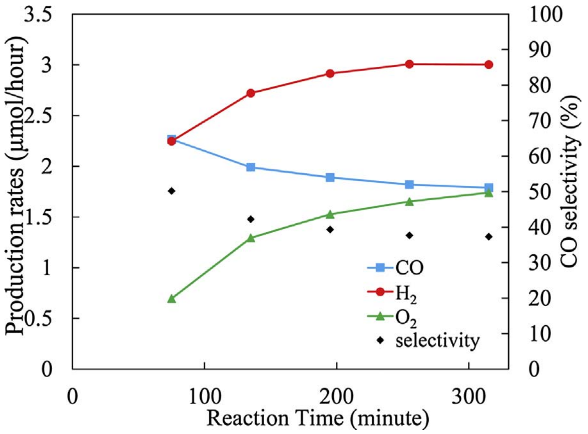

Fig. 1. The time courses of CO, H_2 and O_2 production rates in the photocatalytic reduction of CO_2 with water over the 0.1 wt% Ag/Ga_2O_3 photocatalyst.