Short communication

Highly selective photocatalytic reduction of carbon dioxide with water over silver-loaded calcium titanate

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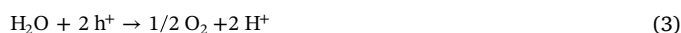
ABSTRACT

The once reported Ag-modified $CaTiO_3$ photocatalyst was reexamined by optimizing the Ag loading amount and using a conventional photochemical reactor. This revealed that the Ag-modified $CaTiO_3$ photocatalyst actually showed both high production rate of CO (54 μmol h^{-1}) and excellent selectivity towards CO formation (94%) by suppressing the H_2 production via water splitting. It is suggested that the high photocatalytic performance originates from not only the optimized amount of cocatalyst and the high irradiation light intensity but also the high concentration of dissolved CO_2 that was achieved by a bubbling flow of CO_2 at the lower reaction temperature. These reaction conditions provided ca. 40 times higher CO formation rate. It was proposed that the deposited small Ag nanoparticles are the selective active sites for CO formation and the $CaTiO_3$ crystal surface produces H_2 preferably.

1. Introduction

Heterogeneous photocatalytic reduction of CO_2 by using water has been widely studied as one of the possible ways to convert CO_2 to other beneficial chemicals such as CO, CH_3OH, CH_4, etc. by using solar energy [1–3], which is called as artificial photosynthesis [4–7]. Recently, various heterogeneous powder photocatalysts that can constantly produce CO, H_2 and O_2 with the stoichiometric ratio of the reductive and oxidative products have been reported [8–16], such as Cu-loaded ZrO_2[8], Ag-loaded $ALa_4Ti_4O_{15}$ (A:Ca, Sr and Ba) [9], Ag-loaded $KCaSrTa_5O_{15}$[10], Ag-loaded $La_2Ti_2O_7$[11], and Ag-loaded $ZnTa_2O_6$[12]. In these photocatalytic reaction systems, the reduction of CO_2 to CO (Eq. (1)) and the reduction of proton to hydrogen (Eq. (2)), and the oxidation of water to O_2 (Eq. (3)) are promoted simultaneously, and thus, the CO_2 decomposition to CO and O_2 (Eq. (4)) and the water decomposition to H_2 and O_2 (Eq. (5)) take place competitively. From Equations (1) and (3), it is obvious that water is necessary for the CO_2 decomposition as an electron source in the oxidation part.

Since the redox potential for proton (0.0 V, vs. SHE) is higher than that for CO_2 to CO (-0.12 V, vs. SHE) [17], H_2 has always been observed as the competitive reductive products through water splitting. When no other reductive products than CO and H_2 are observed in these systems, the CO selectivity, S_{CO} (%), and the ratio of the consumed electron and hole, e$^-$/h$^+$, can be calculated according to Equations (6) and (7), respectively [14], where the production rate of CO, H_2 and O_2

are referred to as R_{CO}, R_{H2} and R_{O2}, respectively.

$$CO_2 + 2\,H^+ + 2\,e^- \rightarrow CO + H_2O \tag{1}$$

$$2\,H^+ + 2\,e^- \rightarrow H_2 \tag{2}$$

$$H_2O + 2\,h^+ \rightarrow 1/2\,O_2 + 2\,H^+ \tag{3}$$

$$CO_2 \rightarrow CO + 1/2\,O_2 \tag{4}$$

$$H_2O \rightarrow H_2 + 1/2\,O_2 \tag{5}$$

$$S_{CO}(\%) = 100 \times R_{CO}/(R_{CO} + R_{H2}) \tag{6}$$

e$^-$/h$^+$ = (electrons consumed for H_2 and CO formation)

$$/(\text{holes consumed for } O_2 \text{formation}) = (R_{CO} + R_{H2})/2R_{O2} \tag{7}$$

Recently, several photocatalysts have been found to exhibit high CO selectivity, i.e., higher production rate of CO than that of H_2, for example, Ag-loaded $NaTaO_3$:Ba [13], Ag-loaded $Sr_2KTa_5O_{15}$[14], and Ag-loaded Zn-doped Ga_2O_3[15,16]. Among them, especially, Ag/$ZnGa_2O_4$ recorded a very high CO selectivity such as 96% [16]. In these studies, some reasons for the high CO selectivity has been proposed, e.g., the bubbling CO_2 in the presence of sodium bicarbonate ($NaHCO_3$) would increase the concentration of CO_2 as a reactant around the photocatalyst [13,14], and the number of the active sites for H_2 formation would be decreased by the loaded Ag cocatalyst [15] or the inactive surface layer such as $ZnGa_2O_4$ on Ga_2O_3 photocatalyst [16].

Calcium titanate has been studied as a photocatalyst for water splitting [18,19], photocatalytic steam reforming [19,20] and so on. The $CaTiO_3$ photocatalyst has a conduction band with a high potential enough to reduce both CO_2 and proton to produce CO and H_2, respectively [21]. Previously, we once reported that Ag-loaded $CaTiO_3$ polyhedral crystals can promote the photocatalytic reduction of CO_2 to produce CO and O_2 along with the water splitting to form H_2 and O_2[22], where the CO selectivity was not so high such as 45% at the steady state [22]. In the present study, we examined the Ag-loaded $CaTiO_3$ photocatalyst by optimizing Ag-loading amount and changing the reactor. As a results, the original photocatalytic activity of the Ag-loaded $CaTiO_3$ photocatalyst was uncovered, i.e., the new reaction condition much improved the photocatalytic activity of the Ag-loaded $CaTiO_3$ photocatalyst for the CO_2 reduction, not only the CO production rate but also the CO selectivity, compared to those in the previous study [22].

2. Experimental

2.1. Catalyst preparation

$CaTiO_3$ sample was similarly prepared via a flux method [22] from $CaCO_3$ (Kojundo 99.99%) and TiO_2 (rutile, Kojundo 99.99%) as starting materials with NaCl (Kishida 99.5%) as a flux. The starting materials and the flux were physically mixed by a mortar, where the molar ratio of $CaCO_3$ to TiO_2 was 1:1 and that of the starting materials to the flux was 4:6. The mixed powder in an aluminum crucible was heated by an electric muffle furnace up to 1373 K at a rate of 200 K h^{-1}, held at this temperature for 10 h, cooled down to 773 K at a rate of 100 K h^{-1} and then naturally cooled down to room temperature. The resulting powder was washed four times with hot water (353 K, totally 2 L). Ag cocatalyst was loaded on the surface of the $CaTiO_3$ photocatalysts by a photo-deposition method. The $CaTiO_3$ powder of 1.0 g was introduced to a quartz tube with 20 mL of aqueous $NaHCO_3$ solution (1.0 mol L^{-1}) and required amount of aqueous $AgNO_3$ solution. Bubbling with a helium gas, photoirradiation was carried out using a 300 W xenon lamp for 24 h, where the light intensity was measured to be 50 mW cm^{-2} at 365 $\pm$ 20 nm in wavelength. The irradiation wavelength was limited to the range from 350 to 500 nm by using both a UV cold mirror and an ultraviolet-cut filter. The loading amount of Ag was confirmed by X-ray florescence analysis. The obtained samples were referred to as Ag(*x*)/$CaTiO_3$, where *x* means the loading amount of Ag cocatalyst in weight %.

2.2. Characterizations

Scanning electron microscopy (SEM) image was recorded by a JEOL JSM-890 in a secondary electron detection mode. Powder X-ray diffraction (XRD) pattern was recorded by a Shimadzu Lab X XRD-6000 with Cu Kα radiation (40 kV, 30 mA). Diffuse reflectance UV–Vis spectrum was recorded on a JASCO V-670 equipped with an integrating sphere covered with $BaSO_4$ as the reference.

2.3. Photocatalytic reduction of CO_2

Photocatalytic reaction test was carried out in a commercially obtained conventional inner irradiation photochemical reactor equipped with a 100 W high pressure mercury lamp, where the light intensity was measured to be 44 mW cm^{-2} at 254 $\pm$ 10 nm in wavelength (Table S1, Reactor B). The reaction temperature was 288 K. The irradiation area was 154.5 cm^2. The Ag(*x*)/$CaTiO_3$ photocatalyst powder of 0.3 g was dispersed in 360 mL of an aqueous $NaHCO_3$ solution (1.0 mol L^{-1}), where bicarbonate ion (HCO_3^-) derived from $NaHCO_3$ works as a buffer to enable the dissolution of much more CO_2 into the solution [23]. The photocatalyst was suspended with magnetically stirring in a bubbling flow of gaseous CO_2 at a flow rate of 30 mL min^{-1} for 4 h in
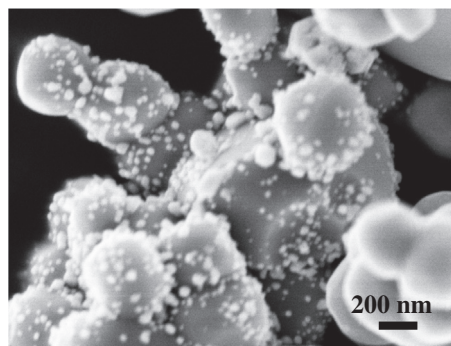

Fig. 1. SEM image of the Ag(3.5)/$CaTiO_3$ sample before use for the photocatalytic reaction test.

the dark, and then the lamp was switched on to start the photocatalytic reaction. The light intensity became the maximum in a few minutes. The reaction temperature was around 288 K. The produced gases were carried with the bubbling flow of CO_2 from the reactor and a portion was periodically sampled to be analyzed by an on-line chromatograph (Shimadzu, GC-8A, TCD, Shincarbon ST, He carrier). In order to find the other products in the liquid phase, a part of the liquid phase was sampled and analyzed by GC–MS (GCMS-Q5050).

3. Results and discussion

3.1. Characterization of photocatalysts

Fig. 1 shows a SEM image of the Ag(3.5)/$CaTiO_3$ photocatalyst before the reaction test. The $CaTiO_3$ particles had a polyhedral crystal shape covered with flat facets. The particle size of the $CaTiO_3$ crystals observed was in the range of 0.2–3 μm. The Ag nanoparticles with the size of 10–120 nm were deposited preferably on the selected facets. Fig. S1 shows a XRD pattern of the sample, confirming the presence of $CaTiO_3$ crystallites and Ag metal particles. The average crystallites size of the Ag nanoparticles was estimated to be 31.5 nm from the diffraction line width at 38.1° by using Scherrer equation, which consists with the SEM observation. These observations are almost consistent with those in the previous study [22].

3.2. Photocatalytic reduction of CO_2

Fig. 2 shows the time course of the production rates in the photocatalytic CO_2 reduction with water over the Ag(3.5)/$CaTiO_3$ sample in the standard condition with the CO_2 bubbling flow at 288 K. The products were mainly CO and O_2 as well as a small amount of H_2. The production rate of CO and O_2 gradually increased and that of H_2 decreased for initial 6 h. After that, the production rates became constant to be 54 μmol h^{-1} for CO and 25 μmol h^{-1} for O_2, where the former is
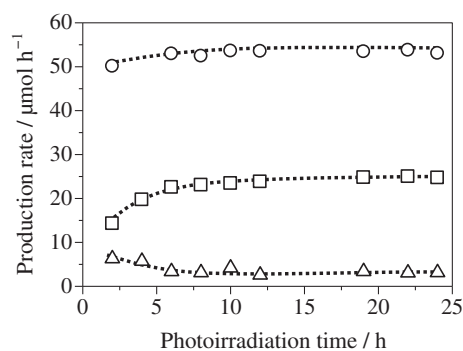

Fig. 2. Time courses of the production rates of CO (circle), H_2 (triangle), and O_2 (square) in the photocatalytic reduction of CO_2 with water over the Ag(3.5)/$CaTiO_3$ sample.