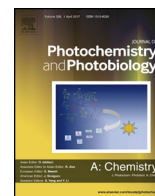




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Invited paper

Photocatalytic CO₂ reduction using water as an electron donor over Ag-loaded metal oxide photocatalysts consisting of several polyhedra of Ti⁴⁺, Zr⁴⁺, and Ta⁵⁺

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ABSTRACT

LaTa₇O₁₉ (BG: 4.1 eV) and CaTa₄O₁₁ (BG: 4.5 eV) with laminated structures consisting of layers of TaO₆ octahedra and TaO₇ decahedra were active for CO₂ reduction to form CO using water as an electron donor when an Ag cocatalyst of an efficient CO₂ reduction site was loaded. In contrast, the activity for the CO₂ reduction of CaZrTi₂O₇ (BG: 3.6 eV) with an anion-defect-type fluorite structure consisting of TiO₄ tetrahedra, TiO₆ octahedra, and ZrO₇ decahedra was negligible even when the Ag cocatalyst was introduced. Selectivity for the CO formation (CO/(H₂ + CO)) over the optimized Ag/LaTa₇O₁₉ photocatalyst reached around 95% in an aqueous NaHCO₃ solution. The rate of CO formation gradually decreased with a reaction time accompanied by an increase in the rate of H₂ evolution. The results of scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS), and X-ray photoelectron spectroscopy (XPS) revealed that aggregation of the Ag cocatalyst during the photocatalytic CO₂ reduction caused the decrease in the CO formation.

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1. Introduction

Photocatalytic CO₂ reduction using water as an electron donor has been paid much attention because it is the reaction that converts photon energy to chemical energy. Furthermore, the reaction has potential for CO₂ fixation to produce raw materials such as C1 chemistry [1,2]. A powdered photocatalyst system is advantageous for a large-scale application because of its simplicity.

A ZrO₂ photocatalyst possessing the ability to split water is active for CO₂ reduction using water as an electron donor without any cocatalysts, giving CO as a reduction product of CO₂, H₂ as a reduction product of water, and O₂ as an oxidation product of water. Moreover, the CO selectivity is enhanced by loading a Cu cocatalyst [3]. BaLa₄Ti₄O₁₅ [4], CaTiO₃ [5], ZnGa₂O₄/Ga₂O₃ [6,7], KMM'Ta₅O₁₅ (M and M' = Ca and Sr) [8–10], NaTaO₃-based

photocatalyst [11], SrO-modified Ta₂O₅ [12], and ZnTa₂O₆ [13], which are active for water splitting [8,14–17], show activity for CO formation by the selective CO₂ reduction even in an aqueous solution when a metallic Ag nanoparticle cocatalyst was loaded. The Ag nanoparticle can be a model cocatalyst for surveying photocatalysts for the CO₂ reduction at the present stage.

The ability of photocatalytic CO₂ reduction strongly depends on a conduction band level. The band structure of a photocatalyst is dominated by the element and the crystal structure. The major crystal structures of photocatalysts reported for the CO₂ reduction are perovskite and tungsten bronze structures as seen in NaTaO₃, CaTiO₃, BaLa₄Ti₄O₁₅, and KMM'Ta₅O₁₅ (M and M' = Ca and Sr). The crystal structures are composed of TaO₆ and TiO₆ octahedra. Therefore, it is important to survey photocatalysts composed of various constituent elements and crystal structures in order to make the photocatalyst library fruitful.

In the present study, the authors have focused on CaZrTi₂O₇ (BG: 3.6 eV) [18], LaTa₇O₁₉ (BG: 4.1 eV) [19], and CaTa₄O₁₁ (BG: 4.6 eV) [20] photocatalysts that have the ability to split water and unique crystal structures composed of MO₇ (M = Zr and Ta) decahedra and TiO₄ tetrahedra in addition to M'O₆ (M' = Ti and

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Ta) octahedra being different from perovskite and tungsten bronze structures. $\text{CaZrTi}_2\text{O}_7$ has an anion-defect-type fluorite structure with TiO_4 tetrahedra, TiO_6 octahedra, and ZrO_7 decahedra (Fig. S1) [21]. $\text{LaTa}_7\text{O}_{19}$ and $\text{CaTa}_4\text{O}_{11}$ have laminated anisotropic structures consisting of layers of TaO_6 octahedra and TaO_7 decahedra (Figs. S2 and S3) [22,23]. Assuming the levels of valence band maxima formed by O 2p orbitals are +3.0 V vs. NHE at pH0 [15], the levels of conduction band minima estimated from those band gaps are quite negative compared with the potential to reduce CO_2 to CO (−0.12 V vs. NHE at pH0). In other words, those band structures, which are composed of Ti 3d, Zr 4d, and Ta 5d orbitals to form the conduction bands and O 2p orbitals to form the valence bands, are thermodynamically preferable for CO_2 reduction to form CO accompanied by extraction of electrons from water. Therefore, these three metal oxides motivate us to evaluate those photocatalytic performances for the CO_2 reduction and examine what the main factor affecting those performances is.

In the present study, effects of loading the Ag cocatalyst on photocatalytic performances of $\text{CaZrTi}_2\text{O}_7$, $\text{LaTa}_7\text{O}_{19}$, and $\text{CaTa}_4\text{O}_{11}$ for CO_2 reduction were examined and the relationship between the band structures and the photocatalytic performances was discussed. Additionally, conditions of the Ag cocatalyst were investigated by SEM, DRS, and XPS.

2. Experimental

Amorphous precursors of $\text{CaZrTi}_2\text{O}_7$, $\text{LaTa}_7\text{O}_{19}$, and $\text{CaTa}_4\text{O}_{11}$ photocatalysts were prepared by a polymerized complex method according to the literatures [18–20]. The precursor of $\text{CaZrTi}_2\text{O}_7$ was calcined with Cs_2CO_3 of a flux reagent at 1273 K in air to obtain a nanocrystalline $\text{CaZrTi}_2\text{O}_7$ photocatalyst [18]. The obtained photocatalyst was washed with water to remove the flux reagent. The precursors of $\text{LaTa}_7\text{O}_{19}$ and $\text{CaTa}_4\text{O}_{11}$ were calcined at 1273 K and 1373 K in air, respectively [19,20]. The obtained samples were identified to be almost single-phase photocatalysts by X-ray diffraction patterns (XRD: Rigaku; MiniFlex (Cu $K\alpha$)) and diffuse reflectance spectra (DRS: Jasco; V-570) (Figs. S4–S6). The reflectance was converted to absorption using Kubelka-Munk function. An Ag cocatalyst was loaded on the surface of the obtained photocatalysts by photodeposition *in situ*, liquid-phase reduction [4], and impregnation. AgNO_3 was employed as the Ag cocatalyst source. Photodeposition was conducted *in situ* at the beginning stage of a photocatalytic reaction. In the impregnation, photocatalyst powder was dispersed in an aqueous AgNO_3 solution in a porcelain crucible. The slurry solution was stirred with a glass rod during evaporation using a hot plate. Obtained powder was calcined in air at 723 K for 1 h. In the liquid-phase reduction [4], an aqueous AgNO_3 solution was added to an aqueous suspension

containing of the photocatalyst. After addition of an equimolar amount of NaPH_2O_2 with respect to Ag^+ to the suspension, the mixture was stirred at 333 K for 1 h. The obtained powder was washed with water and dried at ambient temperature in air. The Ag cocatalyst was characterized using scanning electron microscopy (SEM: JEOL; JSM-7600F), DRS, and X-ray photoelectron spectroscopy (XPS: JEOL; JPS-9010MC, Mg anode). The binding energy of powder samples was corrected using a binding energy of C 1s of contamination (284.3 eV) on Au foil. The binding energy of the Au foil was corrected using the reference datum of Au foil (Au $4f_{7/2}$: 84.0 eV) [24] after contamination on the surface of the Au foil was carefully removed by Ar etching.

Photocatalytic CO_2 reduction and water splitting were conducted using a gas-flow system equipped with an inner irradiation quartz cell and a 400 W high-pressure mercury lamp. Photocatalysts were dispersed in water. NaHCO_3 was added into the aqueous solution, if necessary. CO_2 or Ar gas was continually bubbled into the aqueous suspension. The amounts of gaseous products were determined by gas-chromatographs (Shimadzu, GC-8A; TCD, MS-5A, Ar carrier; FID, MS-13X, a methanizer, N_2 carrier). An isotope experiment was conducted using $^{13}\text{CO}_2$ gas (99.5 atom %). The product of ^{13}CO was analyzed using a GC–MS (Shimadzu; GC–MS Plus, RESTEK; RT–Msieve 5A).

3. Results and discussion

Table 1 shows CO_2 reduction in an aqueous solution with/without NaHCO_3 over $\text{LaTa}_7\text{O}_{19}$, $\text{CaTa}_4\text{O}_{11}$, and $\text{CaZrTi}_2\text{O}_7$ photocatalysts loaded with an Ag cocatalyst. CO formation over Ag-loaded $\text{LaTa}_7\text{O}_{19}$ (Ag/ $\text{LaTa}_7\text{O}_{19}$) was observed. The CO formation hardly depended on the loading methods of the Ag cocatalyst regardless of the presence or absence of NaHCO_3 . It has been reported that the rate of CO formation over metal oxide photocatalysts loaded with the Ag cocatalyst decreases with an increase in the particle size of the Ag cocatalyst [4–13]. Since the Ag cocatalyst aggregated immediately during the CO_2 reduction even if the initial particle size of the Ag cocatalyst depended on the loading methods as mentioned later, the rate of the CO formation was insensitive to the initial condition of the Ag cocatalyst loaded by different methods. An impregnation method was slightly superior to liquid-phase reduction and photodeposition *in situ* regardless in the presence or absence of NaHCO_3 . When NaHCO_3 was added into the reactant solution, Ag/ $\text{LaTa}_7\text{O}_{19}$ prepared by impregnation gave 74% of relatively high selectivity for the CO formation. Consequently, the impregnation method was employed for evaluation of photocatalytic performances of $\text{CaTa}_4\text{O}_{11}$ and $\text{CaZrTi}_2\text{O}_7$ loaded with the Ag cocatalyst in an aqueous NaHCO_3 solution. Ag/ $\text{CaTa}_4\text{O}_{11}$ showed high activity for CO_2 reduction as

Table 1

Effects of loading methods of an Ag cocatalyst and addition of NaHCO_3 on photocatalytic CO_2 reduction over $\text{LaTa}_7\text{O}_{19}$, $\text{CaTa}_4\text{O}_{11}$, and $\text{CaZrTi}_2\text{O}_7$ photocatalysts.

Photocatalyst	Band gap /eV	Loading method	NaHCO_3	Initial rate/ $\mu\text{mol h}^{-1}$			e^-/h^+	Selectivity %
				H_2	O_2	CO		
$\text{LaTa}_7\text{O}_{19}$	4.1	PD	No	15	9	2	0.9	12
$\text{LaTa}_7\text{O}_{19}$	4.1	PD	Yes	13	18	23	1.0	64
$\text{LaTa}_7\text{O}_{19}$	4.1	LPR	No	22	10	2	1.2	8
$\text{LaTa}_7\text{O}_{19}$	4.1	LPR	Yes	16	20	24	1.0	60
$\text{LaTa}_7\text{O}_{19}$	4.1	IMP	No	16	9	3	1.1	16
$\text{LaTa}_7\text{O}_{19}$	4.1	IMP	Yes	9	17	25	1.0	74
$\text{CaTa}_4\text{O}_{11}$	4.5	IMP	Yes	31	30	35	1.1	53
$\text{CaZrTi}_2\text{O}_7$	3.6	IMP	Yes	Trace	Trace	Trace	–	–

Photocatalyst: 0.5 g, Ag cocatalyst: 1 wt%, reactant solution: 360 mL of water and an aqueous NaHCO_3 solution (0.1 mol L^{-1}), system: a CO_2 flow system, reactor: an inner irradiation cell made of quartz, light source: a 400 W high-pressure mercury lamp. t: trace, LPR: liquid-phase reduction, IMP: impregnation, PD: photodeposition *in situ*. $e^-/\text{h}^+ = [(\text{The sum of the rates of } \text{H}_2 \text{ and CO formations})/(\mu\text{mol h}^{-1}) \times 2]/[(\text{Rate of } \text{O}_2 \text{ formation})/(\mu\text{mol h}^{-1}) \times 4]$. Selectivity% = $(\text{Rate of CO formation})/(\mu\text{mol h}^{-1})/[(\text{The sum of the rates of } \text{H}_2 \text{ and CO formations})/(\mu\text{mol h}^{-1}) \times 100]$. Band gaps were estimated from the onsets of those diffuse reflectance spectra (Figs. S4–S6).

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