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Efficient volcano-type dependence of photocatalytic CO_2 conversion into methane using hydrogen at reaction pressures up to 0.80 MPa

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ABSTRACT

Photocatalytic conversion of CO_2 into fuels could mitigate global warming and energy shortage simultaneously. In this study, the reaction pressure was optimized for CO_2 reduction by H_2. The major products were methane, CO, and methanol, and the observed catalytic activity order was Cu or Pd on $TiO_2 \gg Ag/ZrO_2 \sim g\text{-}C_3N_4 > Ag/Zn_3Ga$-layered double hydroxide $\sim$ BiOCl. Hot/excited electrons due to surface plasmon resonance could be transferred to CO_2-derived species and the remaining positive charge could combine with excited electrons in the semiconductor. As the levels of hot/excited electrons became more negative, the catalysts became more active, except for Ag/ZrO_2 and Ag/Zn_3Ga-LDH, probably due to lower charge separation efficiency for intrinsic semiconductors or hydroxides. The reaction order was controlled by the partial pressure of H_2, demonstrating preferable adsorption of H on Pd. The photoconversion of CO_2 into methane was optimum at $P_{H2} = 0.28$ MPa and $P_{CO2} = 0.12$ MPa, but the rates gradually dropped at higher partial pressures due to adsorption of CO_2 being hindered by H.

1. Introduction

Photocatalytic conversion of CO_2 into fuels is one of the routes to carbon-neutral fuels, avoiding the net increase in atmospheric CO_2 concentrations associated with fossil fuel-derived alternatives [1–3]. TiO_2 has been investigated most intensively for this purpose and is known to produce methane and/or CO. CuO supported on TiO_2 photoreduced CO_2 into methanol [2,3] or methane [1–3]. However, when isotope-labeled $^{13}CO_2$ was used, C-containing impurities at the TiO_2 surface were likely to be reduced to CO [3,4]. The product using Pd/TiO_2 was carefully confirmed to be $^{13}CH_4$ [3,5].

We recently reported CO_2 photoconversion into methanol using H_2 and layered double hydroxides (LDHs) [6–8]. Industrially, H_2 is produced via cracking and reforming fossil fuels. H_2 can instead be produced sustainably from water utilizing natural light, in a way similar to Photosystem II,

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-, \tag{1}$$

followed by the production of nicotinamide adenine dinucleotide phosphate (NADPH) by Photosystem I [9],

$$NADP^+ + H^+ + 2e^- \rightarrow NADPH. \tag{2}$$

Our analogue of Photosystem I in heterogeneous catalysis is CO_2 photoconversion using LDH and Pd/TiO_2 to form methanol and methane [6–8]:

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \tag{3}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \tag{4}$$

$$2H_2O + 2NADP^+ \rightarrow O_2 + 2NADPH + 2H^+ \tag{1 + 2}$$

$$4H_2O + 2CO_2 \rightarrow 3O_2 + 2CH_3OH \tag{1 + 3}$$

$$2H_2O + CO_2 \rightarrow 2O_2 + CH_4 \tag{1 + 4}$$

Although significant progress has been achieved by many researchers in the photoconversion of CO_2 into fuels [1–3], most studies have evaluated the photoconversion of dissolved CO_2 in aqueous solution, namely Eqs. (1) and (3) or (1) and (4). For example, the critical role of oxygen vacancy (O_V) sites in CO_2/H_2O was suggested [10–13], and enhanced photoconversion of CO_2 was reported at ele-

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vated reaction pressure of CO_2 and moisture [10,11] or liquid water [11,14–19]; however, most of the mechanisms are unknown. Thus, the systematic dependence of CO_2 photoconversion on reaction pressure and an independent understanding of the reduction sites and mechanism for CO_2 conversion (Eqs. (3) and (4)) are still open for discussion.

The present study screened semiconductor photocatalysts for efficient photoreduction of CO_2 into fuels using H_2 as a reductant at 0.12–0.80 MPa in order to clarify the role of Eq. (3) and/or (4). The band gap (E_g) values of the semiconductors were varied between 2.6 and 5.6 eV by employing ZrO_2, g-C_3N_4, BiOCl, TiO_2, and $[Zn_3Ga(OH)_8]_2CO_3{\cdot}mH_2O$ LDH while keeping the conduction band (CB) minimum more negative than the reduction potential ($E°$) for CO_2 to methane, CO, or methanol (−0.32 to −0.11 V against the standard hydrogen electrode (SHE)) [3,8]. The reaction pressure dependence for Reaction (3) and/or (4) was carefully investigated.

Sastre et al. reported CO_2 conversion using H_2 and Ni-based catalysts irradiated by a solar simulator, and the rates were surprisingly as high as those using a photocatalyst: 55 mmol h^{-1} g_{cat}^{-1} [20]. The temperature and gas pressure reached 423 K and some hundreds of kPa due to the exothermic nature of Eq. (4). On the basis of blank tests below 453 K in the absence of light, photocatalytic activation of H_2 to form Ni–H species followed by thermal hydrogenation of CO_2 to formate on metallic Ni was suggested [2,20]. The possibility of a thermal assist for activation is also discussed in this study.

The reason that a volcano-type dependence of CO_2 photoconversion on reaction pressure is obtained using the most active Pd/TiO_2 photocatalyst was investigated by monitoring the mass balance of reactions, the oxidation state of Pd, and the concentration of O_V sites in TiO_2 by X-ray absorption fine structure (XAFS). This paper is the first of several in which the sites and mechanism for reaction in $CO_2 + H_2$ are compared with those for reaction in $CO_2 + H_2O$. As site separation between photo-oxidation (H_2 or moisture) and photoreduction (CO_2), and the concentrations and roles of O_V sites on the catalysis are complicated issues, the photoconversion of CO_2 using moisture is reported separately [21].

2. Experimental

2.1. Catalyst synthesis

An aqueous solution (1.0 mM) of Ag nitrate (>99.8%, Wako Pure Chemical) was stirred with ZrO_2 {JRC-ZRO-3, Catalysis Society of Japan, specific surface area (SA) 94 m^2 g^{-1}} for 24 h. An aqueous solution of 40 mM of $NaBH_4$ (>95%, Wako Pure Chemical) was then added in the molar ratio Ag:$NaBH_4$ = 1:4 and the solution was stirred for 1 h. The solution was filtered using a polytetrafluoroethene-based membrane filter (Omnipore JVWP04700, Millipore; pore size 0.1 μm) and the collected yellow precipitate was washed with deionized water (<0.055 μS cm^{-1}) supplied by a model RFU424TA (Advantec). The powder was dried under vacuum at 290 K for 24 h. The obtained yellow powder is denoted as Ag/ZrO_2. The loading of Ag was 0.5 wt.% (Table 1a).

Ten grams of urea (>99%, Wako Pure Chemical) was heated at 823 K for 3 h and the resultant yellow powder was washed with 0.1 M of nitric acid (Wako Pure Chemical) and deionized water to obtain g-C_3N_4 [22].

BiOCl was synthesized via a solvothermal procedure described in Ref. [23]. Briefly, 2.0 g of Bi nitrate pentahydrate (>99.5%, Wako Pure Chemical) and 1.3 g of cetyltrimethylammonium chloride (>95%, Wako Pure Chemical) were dissolved in 80 mL of ethylene glycol (EG, >99.5%, Wako Pure Chemical). The solution was stirred for 1 h and 1.0 M of KOH (85%, Wako Pure Chemical) in EG was added. The reaction solution was maintained at 433 K for 12 h. The solution was filtered and the collected white powder was washed with deionized water and ethanol.

Sodium tetrachloropalladate (>98%, Sigma Aldrich) solution (1.0 mM) was stirred with TiO_2 (P25, Degussa; anatase phase:rutile phase = 8:2, specific SA 60 m^2 g^{-1}) at 290 K for 24 h. Then 40 mM of $NaBH_4$ aqueous solution was added in the molar ratio Pd:$NaBH_4$ = 1:8 and the suspension was stirred at 290 K for 1 h. The solution was filtered using a JVWP04700 filter and the collected yellow precipitate was washed with deionized water before drying under vacuum at 290 K for 24 h. The obtained gray powder was denoted as Pd/TiO_2. The loading of Pd was 0.5 wt.% (Table 1d).

$Cu(NO_3)_2{\cdot}3H_2O$ (0.078 g; >99.9%, Wako Pure Chemical) and urea (2.5 g) were dissolved in 50 mL of deionized water. A quantity of 1.0 g of TiO_2 (P25) was added to this solution. Thereafter, the temperature of the suspension was increased to 353 K and kept constant for 4 h while stirring as a deposition–precipitation step. The sample was then washed with deionized water (50 mL each) and filtered five times using a JVWP04700 filter. After drying, the sample temperature was elevated at a rate of 1.25 K min^{-1} and kept at 673 K in air for 2 h [24]. The loading of Cu was 3.2 wt.% (Table 1e).

The synthetic procedure for preparing LDH $[Zn_3Ga(OH)_8]_2CO_3{\cdot}mH_2O$ has been described previously [8]. A quantity of 1.0 mM of Ag nitrate solution was stirred with $[Zn_3Ga(OH)_8]_2CO_3{\cdot}mH_2O$ powder at 290 K for 24 h and then 40 mM $NaBH_4$ aqueous solution was added in the molar ratio Ag:$NaBH_4$ = 1:4 and stirred for 1 h. The solution was filtered using a JGWP04700 filter and the collected yellow precipitate was washed with deionized water. The obtained yellow powder is denoted as Ag/Zn_3Ga-LDH. The loading of Ag was 0.5 wt.% (Table 1f).

2.2. Characterization

X-ray diffraction (XRD) patterns were observed using a D8 ADVANCE diffractometer (Bruker) at the Center for Analytical Instrumentation, Chiba University, at a Bragg angle (θ_B) of $2\theta_B$ = 5.0–60° with a scan step of 0.02° and a scan rate of 3 s per step. The measurements were performed at 40 kV and 40 mA using Cu Kα emission (wavelength λ = 0.15419 nm) [25,26] and a nickel filter. Crystallite sizes (t) were estimated using the Scherrer equation

$$t = \frac{0.9\lambda}{\text{Peak width} \times cos\theta_B}. \qquad (5)$$

Ultraviolet (UV)–visible spectra were measured using a Model V-650 (JASCO) spectrophotometer equipped with an integrating sphere (ISV-469, JASCO) for diffuse reflectance measurements in the wavelength range 200–800 nm. The E_g values were estimated via simple extrapolation of the absorption edge or by fitting to the Davis–Mott equation,

$$\alpha h\nu \propto (h\nu - E_g)^n, \qquad (6)$$

where α, h, and ν are the absorption coefficient, Planck's constant, and the frequency of light, respectively, and n is 1/2, 3/2, 2, or 3 for allowed direct, forbidden direct, allowed indirect, and forbidden indirect electronic transitions, respectively [8,27,28]. Fits to Eq. (6) were performed assuming each n value, or using the n value evaluated based on fits to the log–log form of Eq. (6) using the E_g value obtained by simple extrapolation of the absorption edge to the wavelength axis in the UV–visible spectra.

Transmission electron microscopy (TEM) images were observed using a Model H-7650 transmission electron microscope (Hitachi) at an accelerating voltage of 100 kV. A tungsten filament was used in the electron gun and samples were mounted on conducting carbon with a Cu grid mesh (150 mesh per inch). The magnification