



Enhanced CO₂ photocatalytic reduction through simultaneously accelerated H₂ evolution and CO₂ hydrogenation in a twin photoreactor

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ABSTRACT

The photocatalytic reduction of CO₂ utilizes solar energy to mitigate CO₂ emissions and is a promising technology for renewable fuel production. In this study, a novel twin reactor was developed to hydrogenate CO₂ into hydrocarbons by using H₂ directly produced from photocatalytic water splitting. The twin reactor was further modified to simultaneously perform the CO₂ hydrogenation and water splitting reactions in the gas and liquid phases, respectively. Moreover, two photocatalysts, Pt/TiO₂ and Cu/TiO₂, were used to improve the photohydrogenation performance in the reactor. The results indicate that the H₂ produced from water splitting effectively enhanced the CO₂ hydrogenation in the gas phase, and we found that the highest CO₂ reduction activity was achieved by using Pt/TiO₂ and Cu/TiO₂ as the H₂-generating and CO₂ hydrogenation photocatalysts, respectively, which promoted H₂ evolution and CO₂ hydrogenation and resulted in enhanced CO₂ photoreduction.

1. Introduction

Currently, global warming and the energy shortage are two major global issues resulting from rapid industrial development and increasing CO₂ emissions. The photocatalytic reduction of CO₂ into renewable fuels is regarded as a promising route to alleviate and solve both issues, because it utilizes solar energy to reduce atmospheric CO₂ and simultaneously produce useful chemicals as energy sources [1–3].

In 1979, Inoue et al. [4] first reported the photocatalytic reduction of CO₂ with water over various semiconductors, and since, many studies have been performed for CO₂ photocatalytic reduction using water as a reducing agent [5–8]. However, the efficiency of CO₂ photocatalytic reduction with water is still not suitable for practical use because CO₂ is a relatively stable compound [9,10]. The reduction of CO₂ with water is generally thermodynamically unfavorable at equilibrium [11]. However, with amazing achievements in water splitting research [12–14], it is possible and appealing to reduce CO₂ with the H₂ produced through water splitting. CO₂ reduction with H₂ is more thermodynamically feasible. Compared to water, H₂ is a more powerful reducing agent. Guan et al. [15] reported that CO₂ could be reduced by

the H₂ produced through photocatalytic water splitting, where water first decomposed to form H₂ with the assistance of a Pt/K₂TiO₁₃ catalyst, and CO₂ was then converted with the evolved H₂ into hydrocarbons by an Fe-based catalyst. Similarly, our previous work reported enhanced CO₂ photoreduction in a novel reaction model by using the H₂ produced from water splitting to reduce CO₂ through a solid-gas interface reaction [16]. However, O₂ would also be produced as a side-product during the procedure. It would oxidize H₂ or carbon-containing products, leading to a decline in the photocatalytic reduction efficiency.

Recently, a novel twin reactor was developed to convert CO₂ into hydrocarbons with the H₂ produced from photocatalytic water splitting via a thermodynamically favorable hydrogenation reaction [11,17,18]. The twin reactor was divided into two compartments by a membrane, and the compartments contained H₂-generating photocatalysts and O₂-generating photocatalysts, respectively. Therefore, the H₂ and O₂ that evolve from water splitting could be effectively separated [19,20]. Subsequently, the generated H₂ was utilized to directly hydrogenate CO₂ into hydrocarbons. The separation of O₂ evolution and CO₂ hydrogenation prevented the re-oxidation of H₂ and hydrocarbon products. However, the photo-efficiency was below expectation, which

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may be due to the simultaneous H₂ production and CO₂ reduction in the aqueous phase. In this case, the water splitting rather than the CO₂ reduction would occur preferentially because the solubility of CO₂ in water is very low. The CO₂ reduction is less competitive due to the weak adsorption of CO₂ on the active sites of the catalyst [21,22]. However, water splitting provides a hydrogen source to produce hydrocarbons. Therefore, a possible way to enhance the overall efficiency is to enhance the photocatalytic water splitting in the aqueous phase and the CO₂ reduction in the gas phase.

In this study, we developed a modified twin reactor in which the water splitting and CO₂ hydrogenation were performed in the aqueous phase and gas phase, respectively. Different catalysts can enable the simultaneous enhancement of the water splitting and CO₂ hydrogenation processes. Specifically, the photocatalytic activity of Pt- or Cu-loaded TiO₂ for H₂ production and CO₂ hydrogenation were first evaluated in a single batch reactor and then in the twin reactor. The effect of water splitting and CO₂ hydrogenation on the efficiency of CO₂ reduction was analyzed. Finally, a possible mechanism was proposed to demonstrate and explain the resulting enhanced CO₂ hydrogenation activity in the twin reactor.

2. Experimental

2.1. Catalyst preparation

TiO₂ (P25) and WO₃ (99.9%) were commercial products purchased from Degussa and Hayashi Pure Chemical, respectively. The metal species (Pt or Cu) were loaded on the P25 and WO₃ through the reduction of aqueous NaBH₄ using a method similar to that reported by Nie et al. [23]. In a typical preparation process, 1 g TiO₂ was added into 100 mL of a H₂PtCl₆ methanol solution under magnetic stirring for 1 h. Then, 2.5 mL of an aqueous solution of mixed NaBH₄ (0.1 mol/L) and NaOH (0.5 mol/L) were dropped slowly into the suspension under vigorous stirring. After stirring for 0.5 h, the solid samples were collected by centrifugation, then washed with deionized water three times, and finally dried overnight in an oven at 60 °C. Similarly, Cu/TiO₂ was prepared using Cu(CH₃COO)₂ as a metal precursor, and Pt/WO₃ was synthesized by a similar route using WO₃ instead of TiO₂.

2.2. Catalyst characterization

The X-ray diffraction (XRD) patterns of the prepared Pt/TiO₂ and Cu/TiO₂ were identified on a PANalytical X'Pert PRO diffractometer using Cu K α radiation ($\lambda = 0.1542$ nm) at a scan rate of 1° min⁻¹. The specific surface area of the prepared samples was estimated by N₂ adsorption–desorption isotherms at 77 K using a Micrometrics ASAP 2020 surface area and porosity analyzer. The surface morphology of the catalysts was investigated using a field-emission scanning electron microscope (FE-SEM, FEI Nova NanoSEM 450). X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Shimadzu/KRATOS AXIS-ULTRA DLD-600 W equipped with Al/Mg K α radiation. The UV–vis absorption spectra of the catalysts were obtained with a UV–vis spectrophotometer (Perkin Elmer, Lambda 950). The photoluminescence (PL) spectra of the catalysts were recorded at room temperature on a confocal laser Raman microscope (Horiba JobinYvon, LabRAM HR800). A 325-nm He-Cd laser source was used to excite the material in the PL test.

2.3. CO₂ Photocatalytic reduction

2.3.1. Photocatalytic hydrogenation of CO₂ in a modified twin reactor

The photocatalytic hydrogenation of CO₂ was carried out in a modified twin reactor (as shown in Fig. 1). Details of the reactor have been described elsewhere in the cited literature [11,17]. First, 200 mL of a 2 mM Fe₂(SO₄)₃ and a 2 mM FeSO₄ solution were adjusted to a pH of 2.6 by adding concentrated H₂SO₄, and then placed in the O₂-

generation and CO₂-hydrogenation sides, respectively. A Nafion membrane (Nafion 117) was used to divide and connect the two compartments. Pt/WO₃ (300 mg) was dispersed in the Fe₂(SO₄)₃ solution as an O₂-photocatalyst. Metal (Pt or Cu)-loaded TiO₂ (20 mg) was suspended in the FeSO₄ solution as a H₂-photocatalyst and spread on an elevated rectangular quartz plate (6 cm²) in the gaseous phase as a CO₂-photocatalyst. The aqueous phase of both sides was under agitation during the reaction. Prior to irradiation, ultra-pure Ar (99.9995%) and CO₂ (99.9992%) were bubbled into the solutions of O₂-generation and CO₂-hydrogenation compartments, respectively. Two 300 W xenon lamps (Newport, Model 66902) with AM 1.5G filters installed were placed on the side of the reactors and utilized as the light source in this study. The measured light irradiance was approximately 90 mW/cm², and the irradiation time was 4 h.

The gas samples were taken at 1 h intervals using a 1 mL gas-tight syringe. The oxygen, nitrogen, and hydrogen were analyzed by a gas chromatograph equipped with a thermal conductivity detector (TCD) and a Molecular Sieve 5A column. The CO and hydrocarbons were analyzed by another gas chromatograph equipped with a flame ionization detector (FID), a methanizer, and a Porapak QS packed column.

2.3.2. Photocatalytic H₂ production and CO₂ reduction with H₂/water in a batch reactor

The photocatalytic H₂ production and CO₂ hydrogenation with H₂ was also performed in a batch cylindrical reactor (internal volume: 275 mL, Fig. 2), which was illuminated by a 9 W Hg lamp ($\lambda = 254$ nm, UVP, Pen-Ray 11SC-1) located in the center of a quartz tube. In the case of the hydrogen evolution (Fig. 2A), 20 mg of the catalyst was suspended in deionized water (100 mL) under magnetic stirring. Prior to irradiation, the solution was pre-purged by ultra-pure Ar for 30 min to expel the air from the reactor.

In the case of CO₂ reduction with H₂ and water, the catalyst was placed in a 25-mL beaker and set at the bottom of the reactor (Fig. 2B). H₂ was injected into the reactor by using a syringe, and the concentration of H₂ was analyzed by GC-TCD to ensure that 1 vol.% of H₂ was in the reactor. Deionized water (5 mL) was added in the region between the beaker and the reactor. The analytical method was the same as that used in the twin reactor. No water was added in the reactor in the case of CO₂ reduction with H₂ in the absence of water,

3. Results and discussion

3.1. Characterization of as-prepared catalysts

XRD was used to investigate the crystalline structure of the as-prepared catalysts. As illustrated in Fig. 3, all the peaks of the Cu/TiO₂ and Pt/TiO₂ catalysts are assigned to the anatase (JCPDS, No. 21-1272) and rutile TiO₂ phases of P25. For Pt/WO₃, the XRD pattern was similar to that of the orthorhombic WO₃ phase (JCPDS, No. 20-1324). No peaks corresponding to Pt can be observed in the XRD patterns of all samples due to the low loading content and the fine dispersion of Pt on the supported surface [17,23].

N₂ adsorption-desorption was applied to explore the textural properties of the prepared catalysts. The specific surface area, S_{BET}, was calculated based on the classical Brunauer-Emmett-Teller (BET) theory and are summarized in Table 1. We observed that the loading of Pt and Cu had no significant influence on the surface area of P25, indicating that P25 is stable during the reduction process in an aqueous solution of NaBH₄.

Fig. 4 shows the FE-SEM images of the P25, Cu/TiO₂ and Pt/TiO₂ catalysts. The TiO₂ particles of all samples were uniformly distributed, and the average particle size was approximately 25 nm. This indicates that the metal loading has no obvious influence on the particle size of TiO₂. In all images, no metal or metal oxide particles were observed, which was attributed to the high dispersion or low loading content of the metallic species.

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