Photocatalytic carbon monoxide evolution from carbon dioxide in aqueous solution by the aid of artificial photosynthesis

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Abstract: Stoichiometric evolutions of CO, H_2, and O_2 were achieved for the photocatalytic conversion of CO_2 by H_2O as an electron donor using Ag-loaded Zn-modified Ga_2O_3. The selectivity toward the evolution of CO over H_2 can be controlled by varying the addition of Zn species in the Ag-loaded Zn-modified Ga_2O_3 photocatalyst. The production of H_2 gradually decreased with increasing amounts of Zn species from 0.1 to 10.0 mol%, whereas the evolution of CO was almost unchanged. The XRD, XAFS, and XPS measurements revealed that a $ZnGa_2O_4$ layer was generated on the surface of Ga_2O_3 by modification with the Zn species.

Keywords: Photocatalytic conversion of CO_2; Ga_2O_3; Ca modification

1. Introduction

Reducing the emission of CO_2 has been an extensive and necessary task. Photocatalytic conversion of CO_2 into other valuable feedstocks under ambient temperature and pressure (known as Artificial Photosynthesis) has attracted significant attention as a renewable strategy to recycle CO_2 as a natural resource. Our group has previously reported a series of heterogeneous photocatalysts, such as $ZnGa_2O_4$–modified Ga_2O_3,[1] $ZnGa_2O_4$,[2] and $Sr_2KTa_5O_{15}$[3] with a Ag cocatalyst, which show the higher selectivity for the photocatalytic conversion of CO_2 into CO than the production of H_2 from H_2O. Here we introduce the catalytic performance of Ag/ $ZnGa_2O_4$–modified Ga_2O_3 and the progress thereafter.

2. Experimental

Ga_2O_3 was dispersed in an aqueous solution containing various amounts of $Zn(NO_3)_2$ by ultrasonication. After drying under vacuum at room temperature, the solid mixture of Ga_2O_3 and $Zn(NO_3)_2$ was calcined at 1223 K for 6 h. The amount of Zn species varied from 0 to 10.0 mol% of the total amount of Ga and Zn atoms.

The Zn-modified Ga_2O_3 or Ga_2O_3 photocatalyst (1.0 g) was dispersed in ultra-pure water (1.0 L) containing $AgNO_3$ (9.36×10^{-5} M), and CO_2 (99.999%) was bubbled into the solution at a flow rate of 30.0 mL min^{-1} to purge the air in the reaction system. The Ag cocatalyst (1.0 wt%) was deposited on photocatalyst under UV light irradiation of a 400 W high-pressure mercury lamp for 4 h. Then $NaHCO_3$ (0.1 mol L^{-1}) was added to the same solution, and the suspension was irradiated under the same mercury lamp with a quartz filter connected to a cooling water system. Gaseous products such as H_2, O_2, and CO were analyzed by GC.

3. Results and discussion

Figure 1 shows the formation rates of CO, H_2, and O_2 and selectivity toward CO evolution for the photocatalytic conversion of CO_2 by H_2O over Ag-loaded Zn-modified Ga_2O_3 with various amounts

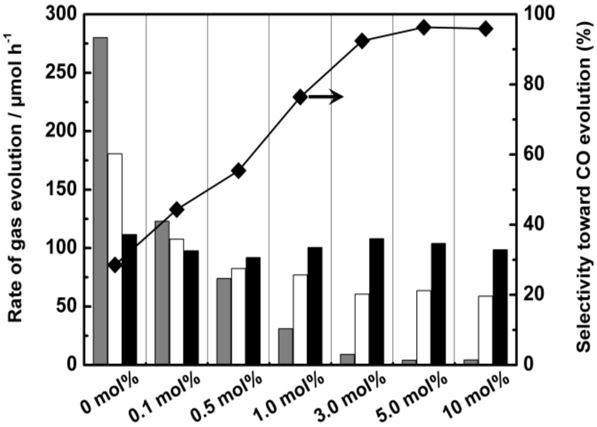

Figure 1. Rates of CO (black), O_2 (white), and H_2 (gray) evolution and selectivity toward CO evolution in the photocatalytic conversion of CO_2 by H_2O over Ag-loaded Zn-modified Ga_2O_3 with various amounts of Zn species.

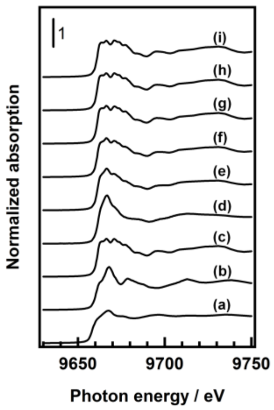

Figure 2. The Zn K-edge XANES spectra of Zn foil (a), ZnO (b), $ZnGa_2O_4$ (c) and Zn-modified Ga_2O_3 with different amount of Zn species: 0.1 mol% (d), 0.5 mol% (e), 1.0 mol% (f), 3.0 mol% (g), 5.0 mol% (h), and 10.0 mol% (i).

of Zn species. All photocatalysts tested could stoichiometrically produce CO, H_2, and O_2 under photoirradiation, indicating that H_2O acted as an electron donor and the number of photogenerated electrons used in the reduction of CO_2 and H^+ was similar to that of photogenerated holes consumed by the oxidation of H_2O. However, the selectivity of the generated electrons toward the reduction of CO_2 was quite different, and depended on the amount of Zn species. The formation rate of H_2 over the Ag-loaded Ga_2O_3 without the Zn species was much higher than that of CO, hence the selectivity of the generated electrons toward the reduction of CO_2 was only 28.5%. When Ga_2O_3 was modified with 0.1 mol% of Zn species, the production of H_2 was suppressed. The H_2 formation rate decreased proportionally with the increase in the amount of Zn species, and was negligible for Zn species concentrations higher than 3.0 mol%. In contrast, the formation rate of CO was not influenced by the amount of Zn species added. Eventually, the selectivity for CO evolution over Ag-loaded Zn-modified Ga_2O_3 gradually increased with elevated amounts of Zn species. When the Zn content was more than 3.0 mol%, the selectivity for CO evolution approached 100%, implying that only the reduction of CO_2 and oxidation of H_2O proceeded on the Ag-loaded Zn-modified Ga_2O_3.

To examine the role of Zn addition, environment around Zn was studied with XAFS spectroscopy. The absorption edge of Zn-modified Ga_2O_3 samples in the Zn-K edge XANES spectra (Fig.2) are similar to those of the ZnO and $ZnGa_2O_4$ references, thus the chemical state of the Zn species is divalent. However, the spectrum of the sample with 0.1 mol% Zn species was quite different from those of ZnO and $ZnGa_2O_4$. Therefore, we speculate that the introduction of a tiny amount of Zn species by the impregnation method resulted in the isolated dispersion of Zn ions in the surface layer of Ga_2O_3 and a different local structure for the Zn species compared to that of $ZnGa_2O_4$. Moreover, as the amount of Zn increased, the XANES spectra became increasingly similar to that of $ZnGa_2O_4$, indicating that further addition of Zn ions could cause a gradual change in the local structure of the Zn species. For samples with more than 3.0 mol% of Zn species, the spectra were identical to that of $ZnGa_2O_4$. We conclude that $ZuGa_2O_3$ is covered with $ZnGa_2O_4$ to preventing the formation of surface proton to be reduced to H_2.

References

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