Enhancement of CO Evolution by Modification of Ga_2O_3 with Rare-earth Elements for the Photocatalytic Conversion of CO_2 by H_2O

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Abstract: Modification of the surface of Ga_2O_3 with rare-earth elements enhanced the evolution of CO as a reduction product in the photocatalytic conversion of CO_2 using H_2O as an electron donor under UV irradiation in aqueous $NaHCO_3$ as a pH buffer, with the rare-earth species functioning as a CO_2 capture and storage material. Isotope experiments using $^{13}CO_2$ as a substrate clearly revealed that CO was generated from the introduced gaseous CO_2.

Keywords: reduction of CO_2, photocatalysis, rare earth.

1. Introduction

Photocatlaytic conversion of CO_2 has recently drawn increased attention due to allowing direct solar-to-chemical energy conversion. Kudo and his colleagues published a cutting-edge paper in the history of the photocatalytic conversion of CO_2 by H_2O, in which Ag-loaded $ALa_4Ti_4O_{15}$ (A = Ca, Sr, Ba) exhibited a higher formation rate of CO than H_2 and evolved a stoichiometric amount of O_2.[1] In this case, more of the CO reduction product was generated than H_2. We found that Ag-loaded Zn-modified Ga_2O_3 demonstrated high conversion and good selectivity toward CO evolution in the photocatalytic conversion of CO_2 with H_2O as an electron donor, compared to several other recently reported photocatalysts.[2] X-Ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) analyses revealed that $ZnGa_2O_4$ was formed on the surface of the Ga_2O_3, where it suppressed only the evolution of H_2 derived from water splitting. Actually, we reported that Ag-loaded $ZnGa_2O_4$ also exhibited photocatalytic activity with high selectivity toward CO evolution.[3] The selectivity for CO evolution was dependent on the loading of the $ZnGa_2O_4$, and reached nearly 100% in the case of 3.0 mol% Zn-modified Ga_2O_3 with 1.0 wt% Ag co-catalyst. The rate of H_2 formation decreased exponentially with increased $ZnGa_2O_4$ loading, although the rate of CO formation was not changed. Thus, the next objective in this field is to enhance the rate of CO formation. We have already demonstrated that the solid base materials have an important role in the surface-capture of CO_2 molecules for the photocatalytic conversion reaction. It is well-known that rare-earth (RE) oxides react with H_2O and CO_2 to form carbonate species. On the basis of these very interesting features of RE elements, in this study, we used REs to modify the surface of Ga_2O_3 in order to more effectively capture and enhance the concentration of CO_2 near the surface for subsequent photocatalytic reduction.

2. Experimental

Ga_2O_3 was obtained by the calcination of gallium hydroxide ($Ga(OH)_3$), prepared via the hydrolysis of $Ga(NO_3)_3$ with an aqueous solution of NH_3, at 1273 K for 6 h. RE-modified Ga_2O_3 was prepared by an impregnation method. Ga_2O_3 was introduced to an aqueous solution of 0.1–10 mol% $RE(NO_3)_3$ (RE = Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Yb, or Lu). The suspension was stirred at room temperature for 1 h with ultrasonication, and then gradually evaporated to dryness at 323 K. The sample was calcined from 1023 to 1423 K for 6 h in air. Samples are designated according to their elemental composition as follows: 1.0 wt% Ag-loaded *x* mol% RE-loaded Ga_2O_3 is referred to as Ag/*x* RE/Ga_2O_3. The photocatalytic conversion of CO_2 using H_2O, including the Ag co-catalyst modification of the photocatalysts, was carried out in a quartz innerirradiation type reaction vessel (1.0 L) in a quasi-flow batch system. The synthesized photocatalyst (0.5 g) was dispersed in an aqueous solution of $NaHCO_3$ (0.1 M). CO_2 gas (99.999%) was bubbled into the solution at a flow rate of 30 mL min^{-1}. The suspension was irradiated with a 400 W high-pressure mercury lamp through a quartz filter equipped with a cooling water system. The CO, H_2, and O_2 products were analyzed by TCD-GC and FID-GC with a methanizer.

3. Results and discussion

Table 1 shows the rates of product formation in the photocatalytic conversion of CO_2 in an aqueous solution of 0.1 M $NaHCO_3$ over Ag/Ga_2O_3 with or without modification by 3.0 mol% RE under UV irradiation. As seen the XRD patterns of all the RE/Ga_2O_3, RE species could be observed in addition to the Ga_2O_3. As shown in the UV-Vis DRS of RE-modified Ga_2O_3, the band gap energies of the Ga_2O_3 and RE/Ga_2O_3 (except Ce/Ga_2O_3) are nearly the same. This indicates that the RE species do not influence the band structure of Ga_2O_3. In all cases, CO and H_2 are evolved as the reduction products from CO_2 and H^+ by the generated electrons, respectively; in addition, stoichiometric amounts of O_2 are observed. Over all the RE-modified Ag/Ga_2O_3 catalysts, except La and Ce, the CO formation rate is higher than that over Ag/Ga_2O_3, and the selectivity for CO evolution exceeds 50%. With Ce modification, the rates of H_2, O_2, and CO formation decline compared to unmodified Ga_2O_3, whereas only a slight decrement is observed in the case of La. Relatively high rates of CO formation are obtained after modification with Yb, Dy, and Sm, although the other RE elements also enhance the rate. With the exceptions of Ce and La, RE modification largely enhances the activity of the photocatalyst, affording CO formation rates ~2.0–2.6 times that of Ag/Ga_2O_3. Thus, the modification with RE elements effectively enhances the evolution of CO.

Table 1 Rates of product formation in the photocatalytic conversion of CO_2[a]

Photocatalyst	Rate of gas evolved / μmol h^{-1}			Selectivity toward CO evolution (%)	e^-/h^+
	H_2	O_2	CO		
Ga_2O_3	141	67.3	4.8	3.3	1.08
Ag/Ga_2O_3	169	116	80.7	32.3	1.08
Ag/3.0 Y/Ga_2O_3	118	136	161	57.7	1.03
Ag/3.0 La/Ga_2O_3	123	68.3	51.7	29.6	1.28
Ag/3.0 Ce/Ga_2O_3	4.09	12.1	32.6	88.9	1.52
Ag/3.0 Pr/Ga_2O_3	29.5	82.9	182	86.1	1.28
Ag/3.0 Nd/Ga_2O_3	84.8	117	167	66.3	1.08
Ag/3.0 Sm/Ga_2O_3	131	149	200	60.4	1.11
Ag/3.0 Gd/Ga_2O_3	110	136	172	61.0	1.04
Ag/3.0 Dy/Ga_2O_3	169	187	197	53.8	0.98
Ag/3.0 Ho/Ga_2O_3	141	143	156	52.5	1.04
Ag/3.0 Er/Ga_2O_3	93.0	151	194	67.6	0.95
Ag/3.0 Yb/Ga_2O_3	144	171	209	59.2	1.03
Ag/3.0 Lu/Ga_2O_3	144	151	160	52.6	1.01

[a] Photocatalyst weight: 0.5 g; CO_2 flow: 30 mL min^{-1}; solution volume: 1.0 L; additive: 0.1 M $NaHCO_3$; light source: 400 W Hg lamp; Ag loading: 1.0 wt%, RE loading: 3.0 mol%.

4. Conclusions

The modification of the surface of Ga_2O_3 with rare-earth (RE) elements improved the rate of CO formation in the photocatalytic conversion of CO_2 using H_2O as an electron donor. An experiment using isotopically labeled $^{13}CO_2$ and five blank tests clarified that the CO_2 introduced in the gas phase is reduced to CO under photoirradiation.

References

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