Enhancement of CO evolution by a Ca modification technique for photocatalytic conversion of CO_2 by H_2O

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Abstract: CO was generated at a high rate of 646 μmol h^{-1} for the photocatalytic conversion of CO_2 by H_2O over Ca-modified Ga_2O_3 with Ag−Cr dual cocatalyst, which was prepared in an aqueous solution of $CaCl_2$ (0.001 mol L^{-1}). The XRD, XPS, SEM and TEM measurements revealed that a $CaGa_4O_7$ layer was generated on the surface of Ga_2O_3. The selectivity toward the evolutions of CO and H_2 could be controlled by varying the concentrations of $CaCl_2$ during the preparation of Ga_2O_3.

Keywords: Photocatalytic conversion of CO_2; Ga_2O_3; Ca modification

1. Introduction

For the past centuries, due to the combustion of carbon–rich fossil fuels, such as coal, oil, and natural gas, the concentration of CO_2 in the atmosphere has dramatically increased. The emission of CO_2 arguably contributes to the increase in global temperatures and climate changes. 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. However, the photocatalytic activity toward CO evolution is still not promising due to the high–energy barrier of CO_2 reduction, easy recombination of photocarriers, and so forth. Very recently, we proposed an Ag−Cr dual cocatalyst modification strategy which offers a facile approach for remarkably enhancing the photocatalytic efficiency for the conversion of CO_2 into CO with H_2O as an electron donor. In this work, we further increased the formation rate of CO by a Ca modification technique for the photocatalytic conversion of CO_2 by H_2O over Ag–Cr/Ga_2O_3.

2. Experimental

Ca–modified Ga_2O_3 was prepared by an ammonia precipitation method as reported previously.[4] Generally, $Ga(NO_3)_3 \cdot nH_2O$ was dissolved in the de-ionized water or various concentrations of $CaCl_2$ ultra-pure water solution (200 mL). Hydroxylation was carried out by dripping ammonium hydroxide solution until the pH value reached to 9. The produced hydroxide was centrifuged and dried overnight. Ga_2O_3 was obtained by calcining the precursor at 1273 K for 10 h. Ca–modified Ga_2O_3 prepared using different concentration of $CaCl_2$ was denoted as Ga_2O_3_Ca_x. Ag−Cr/Ga_2O_3 was fabricated using a photodeposition method, the loading amount of Ag and Cr were 1.0 mol% (Ag/Ga) and 1.0 mol% (Cr/Ga), respectively.

The photocatalytic conversion of CO_2 was carried out in an inner−irradiation−type reaction vessel using a quasi-flow batch system. The fabricated photocatalyst (0.5 g) was dispersed in an aqueous solution of $NaHCO_3$ (0.1 M). CO_2 was bubbled into the H_2O solution at a flow rate of 30 mL min^{-1}. 400 W high−pressure Hg lamp was used as the light source. The amounts of products evolved were detected by TCD–GC and FID–GC.

3. Results and discussion

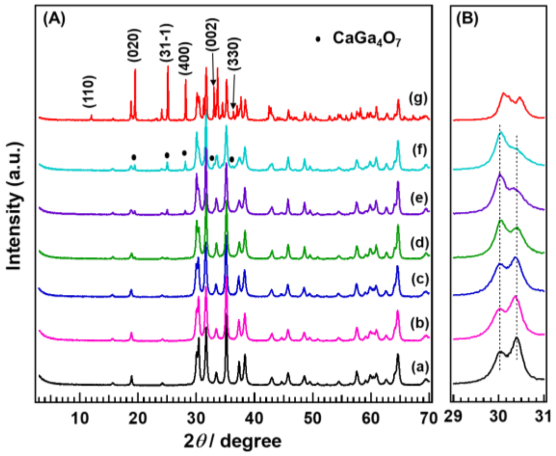

Figure 1. (A) XRD patterns and (B) the enlarged areas at 2θ ranged from 29° to 31° of (a) bare Ga_2O_3, various Ga_2O_3_Ca_x: x = (b) 0.0005, (c) 0.001, (d) 0.002, (e) 0.005, (f) 0.01, and (g) $CaGa_4O_7$.

Figure 1A shows the XRD patterns of bare Ga_2O_3, Ga_2O_3_Ca_x and $CaGa_4O_7$. The diffraction peaks assigned to the (020), (31−1), (400), (002), and (330) facets of $CaGa_4O_7$ gradually appeared with the increasing of Ca species. Addition of higher amount of Ca species was in favor of the formation of $CaGa_4O_7$. Figure 1B shows the enlarged XRD patterns of all samples at 2θ ranging from 29° to 31°. The diffraction peaks of all Ga_2O_3_Ca_x samples did not shift obviously as compared with those of bare Ga_2O_3. Since the ionic radius of Ca^{2+} (0.099 nm) is larger than that of Ga^{3+} (0.062 nm), the unshifted peak position in the XRD pattern implies that Ca ion does not act as a dopant in the bulk Ga_2O_3 lattice. However, an obvious increase at 2θ equal to 30.1° and decrease at 2θ equal to 30.5° were observed with the increase of Ca species, which indicates that the addition of Ca species could alter the structure of Ga_2O_3. XPS spectra, SEM and TEM images of various Ga_2O_3_Ca_x samples further confirmed that $CaGa_4O_7$ was generated on the surface of Ga_2O_3.

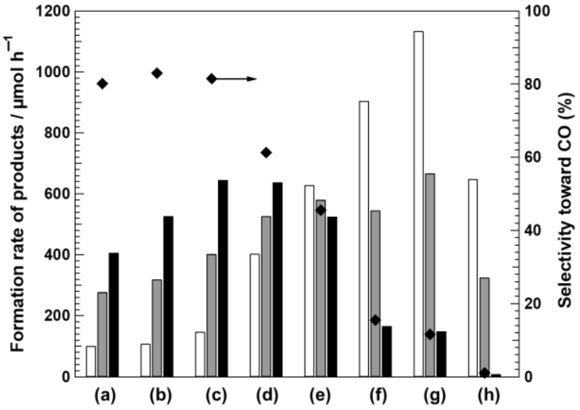

Figure 2. Formation rate of CO (black), O_2 (grey), and H_2 (write) evolutions and selectivity toward CO evolution (black diamond) over (a) Ag–Cr/Ga_2O_3, various Ag–Cr/Ga_2O_3_Ca_x: x = (b) 0.0005, (c) 0.001, (d) 0.0015, (e) 0.002, (f) 0.005, (g) 0.01, and (h) Ag–Cr/$CaGa_4O_7$ for the photocatalytic conversion of CO_2 by H_2O.

Figure 2 shows the formation rates of CO, H_2, O_2 and selectivity toward CO evolution for the photocatalytic conversion of CO_2 by H_2O over various Ag–Cr/Ga_2O_3_Ga_x. Stoichiometric amount of H_2 and CO as reduction products and O_2 as oxidation product were obtained, which indicates that H_2O is used as an electron donor. The amount of Ca species showed great effect on the formation rates of H_2 and CO. The formation rate of CO increased with an increasing of Ca from 0 to 0.001, then decreased with further increase in the amount of Ca from 0.0015 to 0.01. The formation rate of H_2 increased continuously with the addition of Ca species, since bare $CaGa_4O_7$ showed activity only for the H_2 evolution derived from overall water splitting (Figure 2h). The highest formation rate of CO (646 µmol h^{-1}) was observed over Ag–Cr/Ga_2O_3_Ga_0.001.

4. Conclusions

A $CaGa_4O_7$ layer was generated on the surface of Ga_2O_3 by a Ca modification technique. The formation rate of CO and H_2 could be controlled by adjusting the amount of $CaGa_4O_7$ on the surface of Ga_2O_3. The highest formation rate of CO (646 µmol h^{-1}) was obtained over Ag–Cr/Ga_2O_3_Ga_0.001 with a selectivity toward CO evolution higher than 80%.

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