Ag-PrO_x dual cocatalysts loaded $CaTiO_3$ for photocatalytic CO_2 reduction with H_2O

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1. Introduction

Calcium titanate ($CaTiO_3$, referred to as CTO) has been studied as an attractive photocatalyst for not only photocatalytic degradation but also water splitting and CO_2 reduction.[1] The simultaneous action of dual cocatalysts on the one photocatalyst has become a new research hotspot.[2-3] Recently, a few studies have been reported the effects of combinations of rare-earth oxides and silver (Ag) on the photocatalytic activity of Ga_2O_3 photocatalyst for the photocatalytic CO_2 reduction by water,[4] and it was concluded that a combination of praseodymium (Pr) and silver (Ag) is the most effective way to promote CO production. In this present study, we examined the combination of Pr species and Ag NPs on the CTO photocatalyst for the CO_2 reduction with water.

2. Experiment

A CTO sample was prepared by a flux method, with a NaCl flux. Pr species was first loaded on the CTO sample by the IMP method, followed by loading Ag species in the PD method, providing the Ag(PD)/Pr(IMP)/CTO sample. The samples were characterized by XRD and diffuse reflectance UV-vis spectra.

The photocatalytic CO_2 reaction test was carried out using a flow system in the inner-irradiation-type reactor with a 400 W high-pressure Hg lamp by using 0.3 g of the photocatalyst sample in an aqueous solution of $NaHCO_3$, and then suspended with magnetic stirring in a bubbling flow of gaseous CO_2. The amount of the gaseous products (H_2, O_2, and CO) were determined using an on-line gas chromatograph.

3. Results and discussion

In this study, four different photocatalytic materials were compared to explore how Pr species and Ag worked (Fig.1A). It was found that the loading both Pr species and Ag NPs much enhanced the production rate of CO and O_2.

To further understand the effect of different amounts of Pr species on the reaction (Fig. 1B). When only 0.5 wt% Pr species (Fig. 1Bb) was added, compared with the cocatalyst only for Ag (Fig. 1Ba), the yield of CO was almost unchanged, but the yield of oxygen was increased. The optimal sample was the one loaded by 1 wt% Pr and 3.5 wt% Ag (Fig. 1Bc). With further increase of the amount of Pr, the gas production decreased. When the amount of Pr was 3 wt% (Fig. 1Be), the gas yield was similar to that only with Ag. Therefore, when a small amount of Pr is present, Pr species may effectively promote the production of O_2, accelerating the CO_2 reduction reaction. Whereas, a large number of Pr species may occupy the formation site of Ag, thus promoting the recombination of electron-hole pairs.

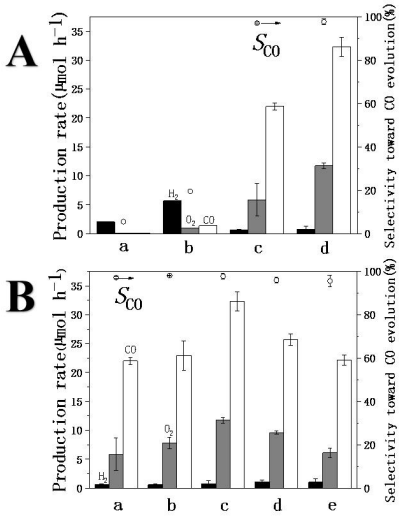

Fig. 1 Results of the photocatalytic activity tests for CO_2 reduction, CO (white bar), H_2 (black bar), and O_2 (gray bar) and the selectivity to CO (S_{CO}%, open circles) in the photocatalytic reaction tests with various samples: (A) (a) bare CTO,(b) Pr(IMP,1.0)/CTO,(c) Ag(PD,3.5)/CTO, and (d)Ag(PD,3.5)/Pr(IMP,1.0)/CTO and (B) (a) Ag(PD,3.5)/CTO, and various Ag(PD,3.5)/Pr(IMP,*y*)/CTO samples, where *y* wt% was (b) 0.5, (c) 1.0, (d) 1.5, and (e) 3.0. The values were recorded after 3.5 h photoirradiation

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