Optimization of silver-loaded sodium titanate photocatalyst for the reduction of carbon dioxide with water

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Abstract: Two types of sodium titanate ($Na_2Ti_6O_{13}$ and $Na_2Ti_3O_7$) with pure structures were synthesized, and loaded with Ag cocatalyst. The former sample exhibited higher photocatalytic activity in the photocatalytic reduction of CO_2 with H_2O. The different fluxes were examined for the preparation of the samples by a flux method. Moreover, the effects of loading method and loading amount of Ag on the photocatalytic conversion of CO_2 were investigated. It was concluded that the Ag/$Na_2Ti_6O_{13}$ sample prepared by the flux method with 1.0wt% of Ag loaded by a photodeposition method exhibited the highest activity (40 µmol h^{-1}) and the highest selectivity toward CO evolution (74%) among the examined samples.

Keywords: Photocatalytic conversion of CO_2, Sodium titanate, Carbon monoxide.

1. Introduction

Heterogeneous photocatalysis has been studied for the reduction of CO_2 with water to produce formate, carbon monoxide (CO), methanol and methane [1]. Prof. Kudo discovered the photocatalytic conversion of CO_2 with H_2O over Ag-modified photocatalysts, where the Ag cocatalyst nanoparticles can function as the active sites for CO_2 reduction to form CO [2]. In our previous studies, we reported that the Ag/$Na_2Ti_6O_{13}$ photocatalyst can exhibit the photocatalytic activity for this reaction with quite low formation rate of CO (0.89 µmol h^{-1}) [3], and clarified that the reaction conditions are also very important [4]. In the present study, the optimization of the photocatalyst was conducted for the CO_2 reduction to CO in the improved reaction conditions, and the reason for the non-stoichiometric O_2 formation was also investigated.

2. Experimental

Sodium titanate ($Na_2Ti_6O_{13}$ and $Na_2Ti_3O_7$) samples were prepared by a flux method and solid state reaction (SSR) method [3]. Ag cocatalyst was loaded on the surface by a photodeposition method (PD), a chemical reduction method (CR), and an impregnation method (IMP). The loading amount of Ag was evaluated by X-ray florescence analysis. The crystal phase and structure of the samples were observed by powder X-ray diffraction. Morphologies of samples were observed by scanning electron microscopy (SEM) image. Diffuse reflectance UV-Vis spectrum was recorded by a JASCO V-670.

The photocatalytic activity test of CO_2 was carried out using a flow system with an inner-irradiation-type reaction vessel. The Ag-loaded titanate sample (0.2 g) was dispersed in ion exchange water (350 mL) containing 0.5 M $NaHCO_3$. Then, CO_2 was bubbled into the solution at a flow rate of 15 mL min^{-1}. Finally, the reaction was conducted using a 100 W high-pressure mercury lamp. The amount of the products (H_2, O_2, and CO) were determined using an on-line chromatograph. The DPD test [5] was used to confirm the formation of hypochlorous acid (HClO) in aqueous solutions after the photocatalytic reactions.

3. Results and discussion

Two types of pure sodium titanates, sodium hexatitanate ($Na_2Ti_6O_{13}$) and sodium trititanate ($Na_2Ti_3O_7$), were prepared and Ag cocatalyst was loaded by the PD method. Among them, the former exhibited much higher CO formation rate (Figure 1.). In addition, the $Na_2Ti_6O_{13}$ samples prepared by the flux method gave the higher CO formation rate and higher selectivity towards CO than that prepared by the SSR method. Moreover, among a series of the mixture of NaCl and KCl fluxes, the pure NaCl flux was found to be the best, indicating that the doped potassium in the $Na_2Ti_6O_{13}$ crystals gave a negative effect on the photocatalytic activity.

Among the photocatalysts prepared by the three methods for Ag deposition, the Ag/$Na_2Ti_6O_{13}$ photocatalyst prepared by the PD method exhibited the highest activity (Figure 2.). Since the PD method tends to form the Ag nanoparticles on the reductive facets of the $Na_2Ti_6O_{13}$ crystals, the photocatalytic would take place efficiently. On the other hand, the optimization of the amounts of Ag cocatalyst to be 1.0 wt% drastically improved the CO formation rate and suppressed the H_2 formation rate, indicating that the modification of the Ag cocatalyst on the $Na_2Ti_6O_{13}$ surface leads to increase the reaction sites for the CO formation and to decrease the sites for H_2 evolution. In conclusion, the Ag/$Na_2Ti_6O_{13}$ photocatalysts prepared by the PD method with 1.0 wt% of Ag cocatalyst exhibited initially the highest CO formation rate (40 μmol h^{-1}) and highest CO selectivity (74 %), although the CO production rate gradually decreased with time to became stable (28 μmol h^{-1}) after 7 h

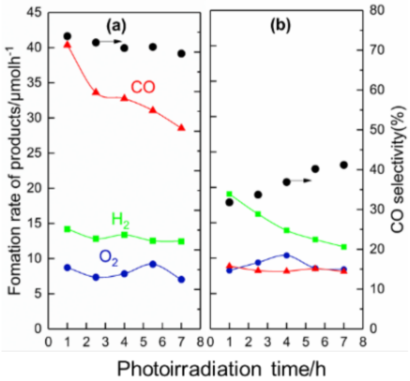

Figure 1. Formation rates of H_2(green square), O_2(blue circle), and CO (red triangle) and the CO selectivity (black circle) in the photocatalytic conversion of CO_2 over Ag/$Na_2Ti_6O_{13}$ (a) and Ag/$Na_2Ti_3O_7$ (b).

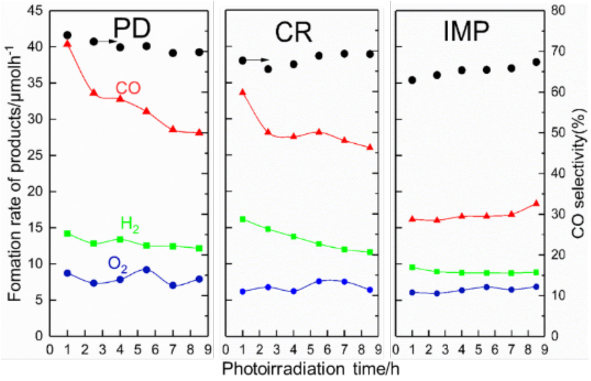

Figure 2. Formation rates of H_2(green square), O_2(blue circle), and CO (red triangle) and the CO selectivity (black circle) in the photocatalytic conversion of CO_2 over Ag/$Na_2Ti_6O_{13}$ prepared by CR, IMP, and PD methods.

In these results, the evolution of O_2 was not enough. i.e., the ratio of the consumed electron and hole estimated from the production rates was not unity, which is not consistent to the stoichiometric ratio. Three possibilities were suggested to explain this phenomenon. The first is that water might be oxidized to hydrogen peroxide, which was, however, denied by the negative result in a starch iodine reaction test. The second is that chloride anion remaining on the surface of the photocatalyst prepared by the flux method with the NaCl flux might react with the hole to form hypochlorite, which would reduce the oxidation of water to form O_2. The result of DPD test clarified that part of Cl^- was oxidized to ClO^-, which competitively consumed holes. The third is that the produced O_2 might be adsorbed on the surface of catalysts to some extent. In the case of the reaction test with the sample prepared by the SSR method, the O_2 evolution increased with irradiation time, and the ratio of e^-/h^+ became to be 1.0 after 22.5 hours. Since this sample should be free from chloride anion, the adsorption of O_2 on the surface of catalysts could explain the initially insufficient O_2 evolution. In summary, two possibilities, the effect of chloride residues and the adsorption of O_2 on the surface, were responsible for the non-stoichiometric amount of O_2 evolution.

4. Conclusions

In conclusion, the Ag/$Na_2Ti_6O_{13}$ photocatalysts loaded with 1.0wt% of Ag by the PD method exhibited the highest formation rate of CO (40 μmolh^{-1}) and the highest selectivity toward CO evolution (74%) initially. And the effect of chloride residues and the adsorption of O_2 on the surface were responsible for the non-stoichiometric ratio of O_2 evolution.

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