Preparation of gallium oxide photocatalysts with various crystalline structures and their Ag loading effects on the carbon dioxide reduction with water

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Abstract: Ga_2O_3 prepared by calcination of a gallium nitrate showed high activity for CO_2 reduction with water to produce CO, however, the activity decreased by Ag loading. On the other hand, CO production was enhanced by Ag loading on commercially available Ga_2O_3 (CA-Ga_2O_3). The crystalline structures of the Ga_2O_3 and CA-Ga_2O_3 were coexistence of γ, β- phases of Ga_2O_3 and single β-phase of Ga_2O_3, respectively. The crystalline structure of CA-Ga_2O_3 was maintained after Ag loading with various methods, while that of the prepared Ga_2O_3 changed. The CO production activity increased by Ag loading depended on the crystalline structure of Ga_2O_3 supports.

Keywords: Ga_2O_3 photocatalyst, CO_2 reduction with water, Ag loading effects

1. Introduction

Development of photocatalysts for CO_2 reduction with water might provide a solution for both the storage of usable chemicals and the global warming problem. Gallium oxide (Ga_2O_3) photocatalysts has been the focus of attention, because it can convert CO_2 and water into CO, H_2, and O_2 under UV light irradiation.[1] Recently, we succeeded to prepare a highly active Ga_2O_3 photocatalyst for CO_2 reduction. On the other hand, it was reported the activity for CO production was enhanced by silver loading on the metal oxide photocatalysts.[2-5] In the present study, for further improvement in the CO production, we prepared silver loaded Ga_2O_3 by various methods and investigated the effects of the silver loading on the crystalline structures and photocatalytic activities of the prepared Ga_2O_3.

2. Experimental

Ga_2O_3 was prepared by dissolving a $Ga(NO_3)_3{\cdot}8H_2O$ powder in a distilled water, followed by drying and calcination in air at 823 K for 4 h. Ag/Ga_2O_3 (IMP) was prepared by impregnation of Ga_2O_3 powder with an aqueous solution of $AgNO_3$, followed by drying and calcination in the air at 673 K for 4 h. An aqueous $AgNO_3$ solution was also used for Ag photodeposition on Ga_2O_3 under UV light irradiation (3.5 mW/cm^2) for 3 h (Ag/Ga_2O_3 (PD)). In the preparation of Ag/Ga_2O_3 (PM), nano-sized Ag colloids were physically mixed with Ga_2O_3 and calcined for 1 h in air at 523 K. Ag/CA-Ga_2O_3 (IMP), Ag/CA-Ga_2O_3 (PD) and Ag/CA-Ga_2O_3 (PM) samples were prepared by loading of Ag on commercially available Ga_2O_3 powder (Kojundo Chemical Laboratory Co. Ltd purity 99.99 %) with the same methods mentioned above. The amount of Ag loading was 0.1 wt% for all the samples.

The photocatalytic reduction of CO_2 was conducted in a specially designed gas-liquid-solid three phase reactor. Powder X-ray diffraction (XRD) patterns were recorded by a MiniFlex600 using Cu Kα as the radiation source. XANES measurements were carried out at the beam line 6N1 at Aichi Synchrotron Radiation Center.

3. Results and discussion

Fig. 1 (A) shows CO production rate for each sample. The prepared Ga_2O_3 showed the highest photocatalytic activity for CO production, however the activity decreased by the Ag loading and the deactivation was significant for Ag/Ga_2O_3 (PM). To investigate the chemical states of loaded Ag species, we carried out Ag L_3-edge XANES measurements. XANES features of all Ag loaded Ga_2O_3 samples were broad and fundamentally similar to that of an Ag foil, suggesting the formation of small metallic Ag nanoparticles. Therefore, we concluded that the difference in CO production rate among these Ag loaded Ga_2O_3 samples was not derived from the difference in the chemical state of Ag co-catalysts.

As shown in Fig. 1 (B), XRD measurement for the prepared Ga_2O_3 exhibited the crystalline structure of the coexistence of β- and γ-phase Ga_2O_3. Diffraction peaks for Ag/ Ga_2O_3 (IMP) were assigned to mixed phases of α-, β- Ga_2O_3, and those for Ag/Ga_2O_3 (PD) to mixed phases of β-, γ- Ga_2O_3 and GaOOH (2). These results suggested that lower CO production for Ag/Ga_2O_3 (IMP) and Ag/Ga_2O_3 (PD) was caused by the changes in crystalline structure. On the other hand, the crystalline structure of Ag/Ga_2O_3 (PM) maintained that of Ga_2O_3. In addition, there were no remarkable difference in the surface area and the amount of chemisorbed CO_2 among Ga_2O_3 and Ag/Ga_2O_3 (PM). In-situ FT-IR measurements suggested that surface chemical state of the Ga_2O_3 had changed by the Ag loading process and promoted the formation of the other CO_2 adsorbates not used for CO production.

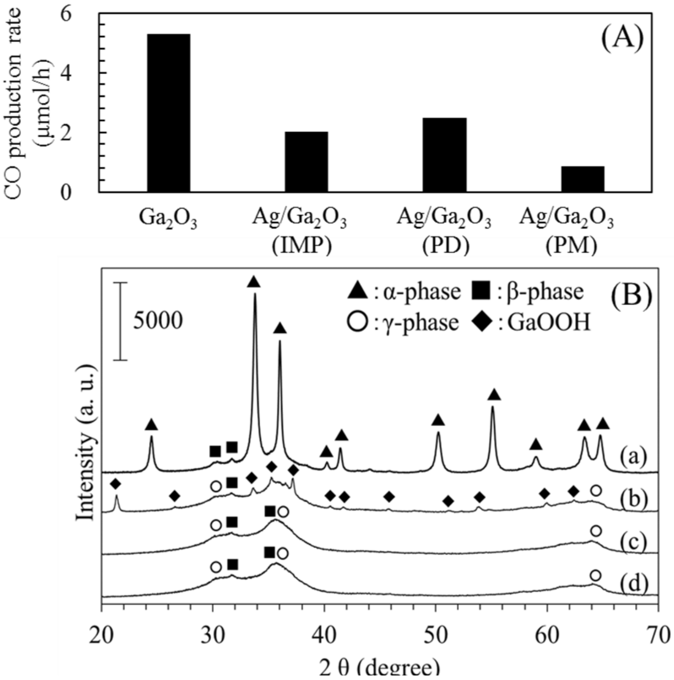

Figure 1. (A) CO production rates after 5 h for CO_2 reduction tests over prepared samples. (B) X-ray diffraction patterns of (a) Ag/Ga_2O_3 (IMP), (b) Ag/Ga_2O_3 (PD), (c) Ag/Ga_2O_3 (PM) and (d) Ga_2O_3.

4. Conclusions

In summary, the coexistence of γ- and β-phase Ga_2O_3 showed the high activity for CO production in the photocatalytic CO_2 reduction with water under UV light irradiation. However, the CO production activity decreased after Ag loading with impregnation and photodeposition methods probably due to the change in the original crystalline structure of the Ga_2O_3. The photocatalytic deactivation of the Ga_2O_3 after Ag loading with physically mixed method would be caused by the surface structural change of the Ga_2O_3 since the formation of CO_2 adsorbates not used for CO production increased.

On the other hand, the crystalline structure of β-Ga_2O_3 was maintained and the activity of β-Ga_2O_3 for CO production increased by Ag loading. From these results, it was revealed that the CO production activity increased by Ag loading depended on the original crystalline structures of Ga_2O_3. In addition, the Ga_2O_3 with mixed phases of γ- and β- not loaded with Ag showed much higher activity than all the Ag loaded Ga_2O_3 samples.

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