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: Ga2O3 prepared by calcination of a gallium nitrate showed high activity for CO2 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 Ga2O3 (CA-Ga2O3). The crystalline structures of the Ga2O3 and CA-Ga2O3 were coexistence of γ, β- phases of Ga2O3 and single β-phase of Ga2O3, respectively. The crystalline structure of CA-Ga2O3 was maintained after Ag loading with various methods, while that of the prepared Ga2O3 changed. The CO production activity increased by Ag loading depended on the crystalline structure of Ga2O3 supports.

Keywords: Ga2O3 photocatalyst, CO2 reduction with water, Ag loading effects

1. Introduction

Development of photocatalysts for CO2 reduction with water might provide a solution for both the storage of usable chemicals and the global warming problem. Gallium oxide (Ga2O3) photocatalysts has been the focus of attention, because it can convert CO2 and water into CO, H2, and O2 under UV light irradiation.1 Recently, we succeeded to prepare a highly active Ga2O3 photocatalyst for CO2 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 Ga2O3 by various methods and investigated the effects of the silver loading on the crystalline structures and photocatalytic activities of the prepared Ga2O3.

2. Experimental

Ga2O3 was prepared by dissolving a Ga(NO3)3·8H2O powder in a distilled water, followed by drying and calcination in air at 823 K for 4 h. Ag/Ga2O3 (IMP) was prepared by impregnation of Ga2O3 powder with an aqueous solution of AgNO3, followed by drying and calcination in the air at 673 K for 4 h. An aqueous AgNO3 solution was also used for Ag photodeposition on Ga2O3 under UV light irradiation (3.5 mW/cm2) for 3 h (Ag/Ga2O3 (PD)). In the preparation of Ag/Ga2O3 (PM), nano-sized Ag colloids were physically mixed with Ga2O3 and calcined for 1 h in air at 523 K. Ag/CA-Ga2O3 (IMP), Ag/CA-Ga2O3 (PD) and Ag/CA-Ga2O3 (PM) samples were prepared by loading of Ag on commercially available Ga2O3 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 CO2 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$_2$O$_3$ showed the highest photocatalytic activity for CO production, however the activity decreased by the Ag loading and the deactivation was significant for Ag/Ga$_2$O$_3$ (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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ exhibited the crystalline structure of the coexistence of β- and γ-phase Ga$_2$O$_3$. Diffraction peaks for Ag/ Ga$_2$O$_3$ (IMP) were assigned to mixed phases of α-, β- Ga$_2$O$_3$, and those for Ag/Ga$_2$O$_3$ (PD) to mixed phases of β-, γ- Ga$_2$O$_3$ and GaOOH (2). These results suggested that lower CO production for Ag/Ga$_2$O$_3$ (IMP) and Ag/Ga$_2$O$_3$ (PD) was caused by the changes in crystalline structure. On the other hand, the crystalline structure of Ag/Ga$_2$O$_3$ (PM) maintained that of Ga$_2$O$_3$. In addition, there were no remarkable difference in the surface area and the amount of chemisorbed CO$_2$ among Ga$_2$O$_3$ and Ag/Ga$_2$O$_3$ (PM). In-situ FT-IR measurements suggested that surface chemical state of the Ga$_2$O$_3$ had changed by the Ag loading process and promoted the formation of the other CO$_2$ adsorbates not used for CO production.

4. Conclusions

In summary, the coexistence of γ- and β-phase Ga$_2$O$_3$ 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$_2$O$_3$. The photocatalytic deactivation of the Ga$_2$O$_3$ after Ag loading with physically mixed method would be caused by the surface structural change of the Ga$_2$O$_3$ since the formation of CO$_2$ adsorbates not used for CO production increased.

On the other hand, the crystalline structure of β-Ga$_2$O$_3$ was maintained and the activity of β-Ga$_2$O$_3$ 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$_2$O$_3$. In addition, the Ga$_2$O$_3$ with mixed phases of γ- and β- not loaded with Ag showed much higher activity than all the Ag loaded Ga$_2$O$_3$ samples.

References