The study of structure dependence of Ga$_2$O$_3$ in photocatalytic reduction of CO$_2$ to CO with H$_2$O over the Ga$_2$O$_3$

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Abstract: Ga$_2$O$_3$ samples were prepared by calcination of Ga(NO$_3$)$_3$·8H$_2$O powder at various temperatures from 573 K to 973 K. Structural analyses by XRD and EXAFS measurements revealed the phase transition of Ga$_2$O$_3$ with increasing calcination temperature, i.e., ε-phase → γ-phase → β-phase. The photocatalytic reduction of CO$_2$ with water proceeded over all the prepared Ga$_2$O$_3$ samples to produce CO, H$_2$ and O$_2$. The Ga$_2$O$_3$ sample consisting of mixed phases of γ- and β-Ga$_2$O$_3$ showed specific high activity for CO production by improving CO$_2$ adsorption, and the activity was higher than that for Ag loaded Ga$_2$O$_3$ sample.

Keywords: Ga$_2$O$_3$ photocatalyst, CO$_2$ reduction with water.

1. Introduction

Since we will continue to release much carbon dioxide into the atmosphere, we must establish a new technology for the conversion of carbon dioxide into renewable energies. It has been reported that Ag loaded Ga$_2$O$_3$ (Ag/Ga$_2$O$_3$) can produce CO, H$_2$ and O$_2$ from CO$_2$ and H$_2$O under UV light irradiation$^{1,2}$. However, the production efficiency is too low to use Ag/Ga$_2$O$_3$ as an effective method of removing atmospheric CO$_2$. Although some works focusing on the effects of Ag co-catalysts on the photocatalytic activity have been reported$^{2,3}$, we tried to improve Ga$_2$O$_3$ support itself to promote photocatalytic CO$_2$ reduction with water. In this study, we prepared Ga$_2$O$_3$ photocatalysts by calcining Ga(NO$_3$)$_3$·8H$_2$O at various temperatures and investigated effects of the Ga$_2$O$_3$ structure on the photocatalytic activity.

2. Experimental

Ga$_2$O$_3$ samples were obtained by calcining Ga(NO$_3$)$_3$·8H$_2$O in the air at temperatures from 573 K to 973 K for 4 h. Photocatalytic activities of the prepared samples for CO$_2$ reduction with water were examined as follows: the sample (0.1 g) was dispersed in an aqueous solution of NaHCO$_3$ (0.1M) in the fixed-bed flow reactor cell under CO$_2$ gas with a flow rate at 3.0 mL/min and irradiated by UV-light (Xe lamp). The reaction products (CO, H$_2$ and O$_2$) were analyzed with gas chromatography. The samples were characterized with XRD, XAFS and BET surface area measurements and CO$_2$ adsorption experiment.

3. Results and discussion

XRD measurement (Fig. 1) showed that Ga$_2$O$_3$ samples prepared by calcination at higher temperatures than 823 K (823, 873, 923, 973-Ga$_2$O$_3$) were β-phase Ga$_2$O$_3$. 773-Ga$_2$O$_3$ was assigned to γ-phase Ga$_2$O$_3$ and 573, 673-Ga$_2$O$_3$ to ε-phase Ga$_2$O$_3$, respectively. The XRD pattern of 823-Ga$_2$O$_3$ consisted of very weak and broad peaks. Since the average particle size measured by TEM and BET surface area of 823-Ga$_2$O$_3$ were similar to those of 673, 773-Ga$_2$O$_3$, the broad XRD pattern of 823-Ga$_2$O$_3$ would be due to the low crystallinity of this sample.

The local structures of the prepared Ga$_2$O$_3$ samples were also investigated by the EXAFS measurement of Ga K-edge spectra. The Fourier transform was performed on each EXAFS spectrum in the range from 3 Å$^{-1}$ to 12 Å$^{-1}$ and the
radial structure function (RSF) was obtained as shown in Fig. 2. In the RSFs, the first peak appeared at 1.2 Å is assigned to the backscattering from adjacent oxygen atoms (Ga-O bond) and the second peak around 2.7 Å shows the presence of the second-neighboring gallium atoms (Ga-(O)-Ga bond). The RSFs of $\gamma$-Ga$_2$O$_3$ and 973-Ga$_2$O$_3$ were coincident with that of a $\beta$-Ga$_2$O$_3$ reference sample. In the RSF of 823-Ga$_2$O$_3$, the first peak is larger than the second one which is similar to that of 773-Ga$_2$O$_3$ rather than those of 923-Ga$_2$O$_3$ and 973-Ga$_2$O$_3$. Considering XRD result, 823-Ga$_2$O$_3$ consists of $\beta$- and $\gamma$-Ga$_2$O$_3$ phases and $\gamma$-Ga$_2$O$_3$ phase dominates 823-Ga$_2$O$_3$. The RSF of 873-Ga$_2$O$_3$ would be corresponding to $\beta$-phase Ga$_2$O$_3$, however, the amplitudes of first and second peaks of 873-Ga$_2$O$_3$ are smaller than those of 923-Ga$_2$O$_3$ and 973-Ga$_2$O$_3$. The peak reductions are due to the mixture of Ga-O and Ga-(O)-Ga bonds with different atomic distances, suggesting that some $\gamma$-Ga$_2$O$_3$ phase is remained. Thus, EXAFS analysis clearly demonstrates the phase transition process where the $\beta$-Ga$_2$O$_3$ phase precipitates and grows in the $\gamma$-Ga$_2$O$_3$ phase.

The photocatalytic reduction of CO$_2$ with water proceeded over all the prepared Ga$_2$O$_3$ samples to produce CO, H$_2$ and O$_2$. As shown in Figs. 3 and 4, H$_2$ and CO production rates after 2 and 4 h CO$_2$ reduction tests over the Ga$_2$O$_3$ samples were plotted against their surface areas. H$_2$ production rate of the samples showed a tendency to increase with surface area of them. On the other hand, CO production rate didn’t show any tendency and 823-Ga$_2$O$_3$ gave specific high CO production rate which was even higher than that for Ag loaded Ga$_2$O$_3$ (Ag/$\beta$-Ga$_2$O$_3$) prepared as a reference photocatalyst. Note that 823-Ga$_2$O$_3$ which was consisted of the mixed phases of $\gamma$- and $\beta$-Ga$_2$O$_3$ showed high activity for CO production. If the charge separation of electron-hole pairs and/or photo-absorption efficiency was enhanced for 823-Ga$_2$O$_3$, not only CO production but also H$_2$ production should be improved. Therefore, it was presumed that 823-Ga$_2$O$_3$ enhanced the CO$_2$ adsorption process, and our CO$_2$ adsorption experiments actually confirmed that the amount of CO$_2$ chemisorption on high active photocatalyst (823-Ga$_2$O$_3$) was 6 times larger than low active photocatalyst (923-Ga$_2$O$_3$).

4. Conclusions

Ga$_2$O$_3$ samples were prepared by calcination of Ga(NO$_3$)$_3$ $\cdot$ 8H$_2$O powder at various temperatures from 573 K to 973 K. XRD and EXAFS measurements revealed that Ga$_2$O$_3$ samples prepared by calcination at temperatures higher than 923 K were $\beta$-phase Ga$_2$O$_3$ while those lower than 773 K were $\gamma$- or $\epsilon$-phase Ga$_2$O$_3$. The samples prepared by calcination at 823 and 873 K (823-Ga$_2$O$_3$ and 873-Ga$_2$O$_3$) were assigned to $\gamma$-, $\beta$-mixed phased Ga$_2$O$_3$. In particular, the 823-Ga$_2$O$_3$ showed low crystallinity and dominated by $\gamma$-Ga$_2$O$_3$ phase. The photocatalytic reduction of CO$_2$ with water proceeded over all the prepared Ga$_2$O$_3$ samples to produce CO, H$_2$ and O$_2$. H$_2$ production rate of the samples showed a tendency to increase with their surface area. On the other hand, the 823-Ga$_2$O$_3$ showed specific high activity for CO production by improving CO$_2$ adsorption on the sample, and the activity was even higher than that for Ag loaded Ga$_2$O$_3$ sample.

References
