The study of structure dependence of Ga_2O_3 in photocatalytic reduction of CO_2 to CO with H_2O over the Ga_2O_3

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Abstract: Ga_2O_3 samples were prepared by calcination of $Ga(NO_3)_3 \cdot 8H_2O$ powder at various temperatures from 573 K to 973 K. Structural analyses by XRD and EXAFS measurements revealed the phase transition of Ga_2O_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_2O_3 samples to produce CO, H_2 and O_2. The Ga_2O_3 sample consisting of mixed phases of γ- and β-Ga_2O_3 showed specific high activity for CO production by improving CO_2 adsorption, and the activity was higher than that for Ag loaded Ga_2O_3 sample.

Keywords: Ga_2O_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_2O_3 (Ag/Ga_2O_3) can produce CO, H_2 and O_2 from CO_2 and H_2O under UV light irradiation[1, 2]. However, the production efficiency is too low to use Ag/Ga_2O_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_2O_3 support itself to promote photocatalytic CO_2 reduction with water. In this study, we prepared Ga_2O_3 photocatalysts by calcining $Ga(NO_3)_3 \cdot 8H_2O$ at various temperatures and investigated effects of the Ga_2O_3 structure on the photocatalytic activity.

2. Experimental

Ga_2O_3 samples were obtained by calcining $Ga(NO_3)_3 \cdot 8H_2O$ 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_2O_3 samples prepared by calcination at higher temperatures than 823 K (823, 873, 923, 973-Ga_2O_3) were β-phase Ga_2O_3. 773-Ga_2O_3 was assigned to γ-phase Ga_2O_3 and 573, 673-Ga_2O_3 to ε-phase Ga_2O_3, respectively. The XRD pattern of 823-Ga_2O_3 consisted of very weak and broad peaks. Since the average particle size measured by TEM and BET surface area of 823-Ga_2O_3 were similar to those of 673, 773-Ga_2O_3, the broad XRD pattern of 823-Ga_2O_3 would be due to the low crystallinity of this sample.

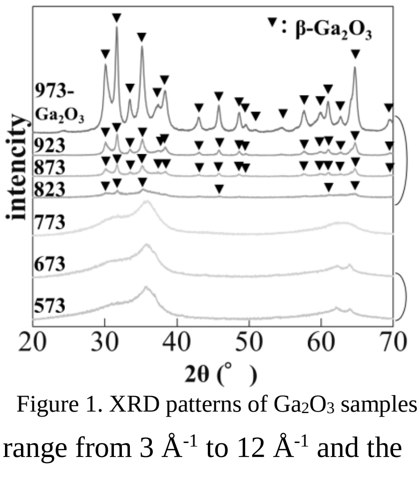

Figure 1. XRD patterns of Ga_2O_3 samples

The local structures of the prepared Ga_2O_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

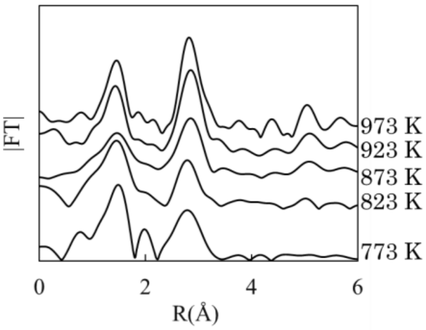

Figure 2. Radial structure functions for Ga K-edge EXAFS spectra of samples

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 -Ga_2O_3 and 973-Ga_2O_3 were coincident with that of a β-Ga_2O_3 reference sample. In the RSF of 823-Ga_2O_3, the first peak is larger than the second one which is similar to that of 773-Ga_2O_3 rather than those of 923-Ga_2O_3 and 973-Ga_2O_3. Considering XRD result, 823-Ga_2O_3 consists of β- and γ-Ga_2O_3phases and γ-Ga_2O_3 phase dominates 823-Ga_2O_3. The RSF of 873-Ga_2O_3 would be corresponding to β-phase Ga_2O_3, however, the amplitudes of first and second peaks of 873-Ga_2O_3 are smaller than those of 923-Ga_2O_3 and 973-Ga_2O_3. The peak reductions are due to the mixture of Ga-O and Ga-(O)-Ga bonds with different atomic distances, suggesting that some γ-Ga_2O_3 phase is remained. Thus, EXAFS analysis clearly demonstrates the phase transition process where the β-Ga_2O_3 phase precipitates and grows in the γ-Ga_2O_3 phase.

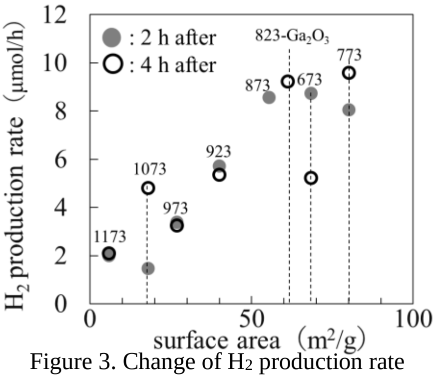

Figure 3. Change of H_2 production rate with the surface area of the sample

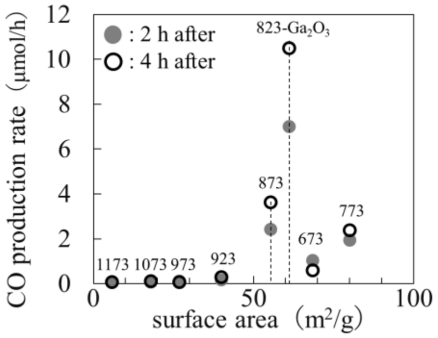

Figure 4. Change of CO production rate with the surface area of the sample

The photocatalytic reduction of CO_2 with water proceeded over all the prepared Ga_2O_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_2O_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_3O_3 gave specific high CO production rate which was even higher than that for Ag loaded Ga_2O_3 (Ag/β-Ga_2O_3) prepared as a reference photocatalyst. Note that 823-Ga_3O_3 which was consisted of the mixed phases of γ- and β-Ga_2O_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_2O_3, not only CO production but also H_2 production should be improved. Therefore, it was presumed that 823-Ga_2O_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_2O_3) was 6 times larger than low active photocatalyst (923-Ga_2O_3).

4. Conclusions

Ga_2O_3 samples were prepared by calcination of $Ga(NO_3)_3 \cdot 8H_2O$ powder at various temperatures from 573 K to 973 K. XRD and EXAFS measurements revealed that Ga_2O_3 samples prepared by calcination at temperatures higher than 923 K were β-phase Ga_2O_3 while those lower than 773 K were γ- or ε-phase Ga_2O_3. The samples prepared by calcination at 823 and 873 K (823-Ga_2O_3 and 873-Ga_2O_3) were assigned to γ, β-mixed phased Ga_2O_3. In particular, the 823-Ga_2O_3 showed low crystallinity and dominated by γ-Ga_2O_3 phase. The photocatalytic reduction of CO_2 with water proceeded over all the prepared Ga_2O_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_2O_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_2O_3 sample.

References

1. N. Yamamoto, T. Yoshida, S. Yagi, *et al.*, e-J Surf. Sci. Nanotech., 12 (2014) 263-268.
2. M. Yamamoto, T. Yoshida, N. Yamamoto, Y. Yamamoto, S. Yagi and H. Yoshida, J. Mater. Chem. A, 2015, 3, 16810-16816
3. M. Yamamoto, S. Yagi, T. Yoshida, Catalysis Today, 2018, 4, 334-340