Synthesis of $\alpha$-Ga$_2$O$_3$ by Water Oxidation of Metallic Gallium as a Photocatalyst for CO$_2$ Reduction with Water

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ABSTRACT: We have succeeded to synthesize gallium oxide consisting of $\alpha$-phase ($\alpha$-Ga$_2$O$_3$) with the calcination of GaOOH obtained by a direct reaction of liquid Ga metal with water for the first time and found that $\alpha$-Ga$_2$O$_3$ exhibits photocatalytic activity for CO$_2$ reduction with water and water splitting as well. The calcination above 623 K converted GaOOH to $\alpha$-Ga$_2$O$_3$, and the samples calcined at 723–823 K were well crystallized to $\alpha$-Ga$_2$O$_3$ and promoted photocatalytic CO$_2$ reduction with water, producing CO, H$_2$, and O$_2$. This is observed for the first time that $\alpha$-Ga$_2$O$_3$ without a cocatalyst has shown very high photocatalytic activity for the conversion of CO$_2$ to CO.

1. INTRODUCTION

Gallium oxide (Ga$_2$O$_3$) has been investigated as a photocatalyst for the reduction of CO$_2$ with water and water splitting as well. Among six polymorphs of Ga$_2$O$_3$, i.e., $\alpha$, $\beta$, $\epsilon$, $\delta$, $\gamma$, and $\kappa$-phases, $\beta$-Ga$_2$O$_3$ has been widely investigated as the photocatalyst for CO$_2$ reduction with water owing to its thermodynamical stability. In addition, Ga$_2$O$_3$ consisting of two phases, $\alpha$- and $\gamma$-phases or $\beta$- and $\gamma$-phases, shows the photocatalytic activity for CO$_2$ reduction, for which their phase boundaries are reported to be active sites for CO$_2$ reduction.5–7 Precipitation of gallium oxide hydroxide (GaOOH) on $\alpha$- and $\beta$-phases is also reported to increase the photocatalytic CO$_2$ reduction.8 In most cases, noble metals such as Ag,9–11 and Pt14 have been employed as cocatalysts to enhance CO productivity in photocatalytic CO$_2$ reduction. However, it has been reported that without a cocatalyst, Ga$_2$O$_3$ consisting of two phases, $\alpha$- and $\beta$- or $\beta$- and $\gamma$-phases, exhibits high activity for the photocatalytic CO$_2$ reduction.5,15,16 It should be noted that except for the $\beta$-phase, no single phase of Ga$_2$O$_3$ is examined as a photocatalyst for CO$_2$ reduction with water because of the lack of thermal stability and difficulties in their synthesis.

In this work, we have succeeded to synthesize $\alpha$-phase Ga$_2$O$_3$ ($\alpha$-Ga$_2$O$_3$) with calcination of GaOOH obtained by a direct reaction of liquid Ga metal with water (referred to as water oxidation of Ga) and examined the photocatalytic activity of the synthesized $\alpha$-Ga$_2$O$_3$ for CO$_2$ reduction with water. It should be mentioned that the formation of GaOOH by the water oxidation of liquid Ga metal was successfully done for the first time. Furthermore, the single phase of $\alpha$-Ga$_2$O$_3$ was easily obtained by calcination of GaOOH and was found to show high catalytic activity for the photocatalytic reduction of CO$_2$ with water. This is also observed for the first time.

2. RESULTS AND DISCUSSION

Figure 1 shows the scanning electron microscopy (SEM) images of samples (a) before and (b) after the calcination at 732 K for 2 h. After the water oxidation of Ga metal to GaOOH, particle sizes of the sample were widely distributed from a few micrometers to a few nanometers. By the calcination, no significant difference appeared in particle sizes, which was confirmed by the specific surface area determined by the Brunauer–Emmett–Teller (BET) method, showing around 7.0 m$^2$/g with no appreciable difference before and after the calcination.

X-ray diffraction (XRD) patterns are given in Figure 2. The diffraction pattern for the sample just after the water oxidation shows that Ga metal was mostly converted to GaOOH with no trace of the diffraction peaks originated from Ga metal. As depicted in Figure 2, calcination above 623 K converted GaOOH to $\alpha$-Ga$_2$O$_3$. However, the sample calcined at 623 K was not well crystallized, while the samples calcined above 723 K were well crystallized to $\alpha$-Ga$_2$O$_3$ without any traces of other
Figure 1. SEM images of samples (a) before and (b) after the calcination at 723 K for 2 h.

Figure 2. X-ray diffraction patterns for the prepared samples.

Figure 3. Production rates (μmol/h) for H₂, O₂, and CO for the samples calcined at (a) 723 K and (b) 823 K used for photocatalytic CO₂ reduction tests and (c) the stoichiometric ratio for the two samples.
phases including GaOOH. UV–vis before calcination showed high intensity in the UV region caused by GaOOH, while after the calcination, that became \( \alpha\)-Ga\(_2\)O\(_3\) like and no particular structure related to the catalytic activity was observed. X-ray photoelectron spectra (XPS) for samples before and after calcination also show full conversion of GaOOH to \( \alpha\)-Ga\(_2\)O\(_3\). By comparing the SEM images before and after the calcination, it is revealed that no appreciable sintering occurred, indicating that GaOOH particles were simply converted to \( \alpha\)-Ga\(_2\)O\(_3\) particles. This would be the reason for a small difference in BET surface areas before and after the calcination.

CO\(_2\) reduction tests were conducted for all calcined samples and all of them showed the production of CO, H\(_2\), and O\(_2\). However, for samples calcined below 623 K, among the observed production rates of H\(_2\), CO, and O\(_2\), their stoichiometric mole ratios, i.e., \([\text{H}_2] + [\text{CO}]/(2 \times [\text{O}_2])\), were much higher than 1.0, indicating the existence of Ga metal or hyperstoichiometric Ga\(_2\)O\(_3\). Therefore, the results for the samples calcined at 723 and 823 K are presented in Figure 3a,b, respectively. Both samples showed photocatalytic activity for CO\(_2\) reduction and water splitting. Except for the initial production rates at 1 h, the production rates of H\(_2\), CO, and O\(_2\) stayed nearly constant for up to 5 h, keeping the stoichiometric rates nearly 1, as indicated in Figure 3c. H\(_2\) production rates for both samples were nearly the same as high as 25 \( \mu \text{mol}/\text{h} \). The CO production rates were around 4 and 2 \( \mu \text{mol}/\text{h} \) for the sample calcined at 723 K for 6 h and 823 K for 2 h, respectively. Although the CO production rates are much less than the H\(_2\) production rate, referring to a sample mass of 100 mg, the present production rate of around 5 \( \mu \text{mol}/\text{h} \) is comparable or a little larger than that observed in previous works for the Ga\(_2\)O\(_3\) photocatalyst using the same reaction system.\(^5\) Hence, we can conclude that the synthesized \( \alpha\)-Ga\(_2\)O\(_3\) samples exhibit very high photocatalytic activity for the CO\(_2\) reduction with water.

This is observed for the first time that the single phase of \( \alpha\)-Ga\(_2\)O\(_3\) shows photocatalytic activity for CO\(_2\) reduction with water and water splitting as well. Nevertheless, the selectivity of CO production compared with H\(_2\) production remained low. Because the activity for H\(_2\) production caused by water splitting and simultaneously occurring CO\(_2\) reduction was rather high, the optimization of microparticulation with homogeneous particle distribution would significantly improve the photocatalytic activity, which remains a future study. The Ag cocatalyst could further improve the selectivity.

The XRD patterns of the samples before and after used as photocatalysts are compared in Figure 4, which shows no appreciable difference before and after the calcination, except for the appearance of the traces of GaOOH in the sample calcined at 823 K. Ga\(_2\)O\(_3\) could react with water as follows

\[
\text{Ga}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{GaOOH} \quad \text{(1)}
\]

As found by Kawaguchi et al.,\(^8\) the existence of GaOOH could enhance the photocatalytic activity. However, it is difficult to mention the role of GaOOH for CO\(_2\) reduction because reaction 1 produces neither H\(_2\) nor O\(_2\). The calcination of GaOOH proceeds to the opposite direction of eq 1. There could be some thermodynamic equilibrium as eq 2

\[
\text{Ga}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{GaOOH} \quad \text{(2)}
\]

so that GaOOH could be produced in water during the use of \( \alpha\)-Ga\(_2\)O\(_3\) for the photocatalytic reduction of CO\(_2\). Since the dynamic equilibrium given by eq 2 produces neither H\(_2\) nor O\(_2\), it would not directly contribute to the photocatalytic CO\(_2\) reduction. However, the intermediate state in the dynamic equilibrium could contribute to CO\(_2\) reduction on Ga\(_2\)O\(_3\) and/or GaOOH. Still, the reaction mechanism of CO\(_2\) reduction with water over \( \alpha\)-Ga\(_2\)O\(_3\) is not clear and should be investigated in the future.

3. CONCLUSIONS

We have succeeded to synthesize \( \alpha\)-phase Ga\(_2\)O\(_3\) with the calcination of GaOOH obtained by the water oxidation of liquid Ga metal and examined the photocatalytic activity of the synthesized \( \alpha\)-phase Ga\(_2\)O\(_3\) for the CO\(_2\) reduction with water. \( \alpha\)-Ga\(_2\)O\(_3\) samples obtained by the calcination at 723 and 823 K exhibited the photocatalytic activity for CO\(_2\) reduction and water splitting. Compared to the H\(_2\) production rate, the CO\(_2\) production rate was rather small. Nevertheless, referring to a sample mass of 100 mg, we can conclude that \( \alpha\)-Ga\(_2\)O\(_3\) without a cocatalyst has very high activity for the photocatalytic reduction of CO\(_2\) with water.

It has been reported that without the cocatalyst, Ga\(_2\)O\(_3\) consisting of two phases, \( \alpha\)- and \( \beta\)-phases or \( \beta\)- and \( \gamma\)-phases, exhibits high activity for the photocatalytic CO\(_2\) reduction,\(^9\)\(^10\) while the present study indicates that the single phase of \( \alpha\)-Ga\(_2\)O\(_3\) exhibits very high photocatalytic activity for...
the CO₂ reduction with water and water splitting as well. At present, the reaction mechanism is not clear. However, GaOOH produced during the reaction could have a certain role. This suggests that the existence of two phases of α-Ga₂O₃ and GaOOH are required for the CO₂ reduction as observed in previous works for the two phases, i.e., α- and β-phases or β- and γ-phases.

It should also be noted that the structure and particle sizes of α-Ga₂O₃ were not optimized. Microparticulation with homogeneous particle distribution would significantly improve the photocatalytic activity and remain as a future work together with clarification of the active sites and mechanism of the photocatalytic reaction.

4. EXPERIMENTAL SECTION

α-Ga₂O₃ was obtained by calcination of GaOOH produced by the water oxidation of liquid Ga, which is the first trial except for one report on the formation of GaOOH by ultrasonic irradiation of molten gallium in water.¹⁷ Liquid Ga metal (4.5 g. Kojundo Chemical Laboratory Co., Ltd., purity 99.999%) and 20 mL of distilled water were placed in a plastic beaker and agitated in a stirred bath at 343 K until Ga was mostly dispersed in water as GaOOH, the reaction product with water. After filtered and dried in air, the product was calcined in air at temperatures ranging from 573 to 823 K for 2–12 h.

The photocatalytic CO₂ reduction tests were carried out in a fixed-bed flow reactor cell. One hundred grams of the calcined sample was dispersed in an aqueous solution of 10 mL of NaHCO₃ (1 M). The air in the cell was replaced with CO₂ gas at a flow rate of 50 mL/min for 45 min. Then, the tests were conducted with UV irradiation under CO₂ gas at a flow rate of 3.0 mL/min. A 300 W Xe lamp was used as a UV source and its light intensity was about 40 mW/cm² in a wavelength range of 254–300 nm. The reaction products (mainly CO, H₂, and O₂) were analyzed by a gas chromatograph equipped with a thermal conductivity detector.

The characterization of samples was performed by scanning electron microscopy (SEM), X-ray diffraction (XRD), XPS, and UV–vis diffuse reflectance spectroscopy. SEM images of the samples were acquired using a JSM-6500F, operating at 15 kV. XRD patterns of the samples were recorded on a MiniFlex600 (Rigaku) using Cu Kα as a radiation source with an operating voltage of 40 kV and a current of 15 mA. The XRD patterns were collected at a 2θ angle range of 20–70°. The 2θ step size was 0.02°, and the scanning rate was 5°/min. The specific surface areas (SSAs) of the samples were determined by Brunauer–Emmett–Teller (BET) SSA measurements at 77 K (liquid N₂ temperature) using a Monosorb (Quantachrome). Before the BET measurements, the samples were heated at 573 K for 3 h in a N₂ atmosphere as a pretreatment.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Roy, R.; Hill, V. G.; Osborn, E. F. Polymorphism of Ga₂O₃ and the System Ga₂O₃–H₂O. J. Am. Chem. Soc. 1952, 74, 719–722.

(2) Yoshioka, S.; Hayashi, H.; Kuwabara, A.; Oba, F.; Matsunaga, K.; Tanaka, I. Structures and energetics of Ga₂O₃ polymorphs. J. Phys.: Condens. Matter 2007, 19, No. 346211.

(3) Stepanov, S. I.; Nikolaev, V. I.; Bougov, V. E.; Romanov, A. E. Gallium Oxide: Properties and applications — a review. Rev. Adv. Mater. Sci. 2016, 44, 63–86.

(4) Huang, Z.; Teramura, K.; Asakura, H.; Hosokawa, S.; Tanaka, T. Recent progress in photocatalytic conversion of carbon dioxide over gallium oxide and its nanocomposites. Curr. Opin. Chem. Eng. 2018, 20, 114–121.

(5) Akatsuka, M.; Kawaguchi, Y.; Itoh, R.; Ozawa, A.; Yamamoto, M.; Tanabe, T.; Yoshida, T. Preparation of a high active Ga₂O₃ photocatalyst for CO₂ reduction with water. Appl. Catal., B 2020, 262, No. 118247.

(6) Kawaguchi, Y.; Akatsuka, M.; Yamamoto, M.; Yoshioka, K.; Ozawa, A.; Kato, Y.; Yoshida, T. Preparation of gallium oxide photocatalysts and their silver loading effects on the carbon dioxide reduction with water. J. Photochem. Photobiol. A 2018, 358, 459–464.

(7) Ito, R.; Akatsuka, M.; Ozawa, A.; Kato, Y.; Kawaguchi, Y.; Yamamoto, M.; Tanabe, T.; Yoshida, T. Photocatalytic Activity of Ga₂O₃ Supported on Al₂O₃ for Water Splitting and CO₂ Reduction. ACS Omega 2019, 4, 5451–5458.

(8) Kawaguchi, Y.; Yamamoto, M.; Ozawa, A.; Kato, Y.; Yoshida, T.; et al. Effects of the crystalline structure of Ga₂O₃ on the photocatalytic activity for CO production from CO₂. Surf. Interface Anal. 2019, 51, 79–84.

(9) Yamamoto, N.; Yoshida, T.; Yagi, S. The influence of the preparing method of a Ag/Ga₂O₃ catalyst on its activity for photocatalytic reduction of CO₂ with water. Surf. Sci. Nanotechnol. 2014, 12, 263–268.

(10) Yamamoto, M.; Yoshida, T.; Yamamoto, N.; Nomoto, T.; Yamamoto, Y.; Yagi, S.; Yoshida, H. Photocatalytic reduction of CO₂ with water promoted by Ag clusters in Ag/Ga₂O₃ photocatalyst. J. Mater. Chem. A 2015, 3, 16810–16816.

(11) Yamamoto, M.; Yoshida, T.; Yamamoto, N.; Nomoto, T.; Yagi, S. The loading effect of silver nanoparticles prepared by impregnation and solution plasma methods on the photocatalysis of Ga₂O₃. Nucl. Instrum. Methods Phys. Res., Sect. B 2015, 359, 64–68.

(12) Han, C.; Mao, W.; Bao, K.; Xie, H.; Jia, Z.; Ye, L. Preparation of Ag/Ga₂O₃ nanofibers via electrospinning and enhanced photocatalytic hydrogen evolution. Int. J. Hydrogen Energy 2017, 42, 19913–19919.

(13) Kato, Y.; Yamamoto, M.; Akatsuka, M.; Ito, R.; Ozawa, A.; Kawaguchi, Y.; Tanabe, T.; Yoshida, T. Study on carbon dioxide reduction with water over metal oxide photocatalysts. Surf. Interface Anal. 2019, 51, 40–45.

(14) Pan, Y.; Sun, Z.; Cong, H.; Men, Y.; Xin, S.; Song, J.; Yu, S. Photocatalytic CO₂ reduction highly enhanced by oxygen vacancies on Pt-nanoparticle-dispersed gallium oxide. Nano Res. 2016, 9, 1689–1700.
(15) Teramura, K.; Tsuneoka, H.; Shishido, T.; Tanaka, T. Effect of H₂ gas as a reductant on photoreduction of CO₂ over a Ga₂O₃ photocatalyst. *Chem. Phys. Lett.* 2008, 467, 191–194.

(16) Park, H.; Choi, J. H.; Choi, K. M.; Lee, D. K.; Kang, J. K. Highly porous gallium oxide with a high CO₂ affinity for the photocatalytic conversion of carbon dioxide into methane. *J. Mater. Chem.* 2012, 22, 5304–5307.

(17) Hirano, M.; Sakoda, K.; Hirose, Y. Direct formation and phase stability of Luminescent γ-Ga₂O₃ spinel nanocrystals via hydrothermal method. *J. Sol–Gel Sci. Technol.* 2016, 77, 348–354.