

Synthesis of α -Ga₂O₃ by Water Oxidation of Metallic Gallium as a Photocatalyst for CO₂ Reduction with Water

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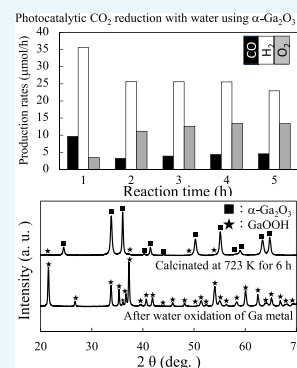
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ABSTRACT: We have succeeded to synthesize gallium oxide consisting of α -phase (α -Ga₂O₃) with the calcination of GaOOH obtained by a direct reaction of liquid Ga metal with water for the first time and found that α -Ga₂O₃ exhibits photocatalytic activity for CO₂ reduction with water and water splitting as well. The calcination above 623 K converted GaOOH to α -Ga₂O₃, and the samples calcined at 723–823 K were well crystallized to α -Ga₂O₃ and promoted photocatalytic CO₂ reduction with water, producing CO, H₂, and O₂. This is observed for the first time that α -Ga₂O₃ without a cocatalyst has shown very high photocatalytic activity for the conversion of CO₂ to CO.



1. INTRODUCTION

Gallium oxide (Ga₂O₃) has been investigated as a photocatalyst for the reduction of CO₂ with water and water splitting as well. Among six polymorphs of Ga₂O₃, i.e., α -, β -, ϵ -, δ -, γ -, and κ -phases,^{1–3} β -Ga₂O₃ has been widely investigated as the photocatalyst for CO₂ reduction with water⁴ owing to its thermodynamical stability. In addition, Ga₂O₃ consisting of two phases, α - and γ -phases or β - and γ -phases, shows the photocatalytic activity for CO₂ reduction, for which their phase boundaries are reported to be active sites for CO₂ reduction.^{5–7} Precipitation of gallium oxide hydroxide (GaOOH) on α - and β -phases is also reported to increase the photocatalytic CO₂ reduction.⁸ In most cases, noble metals such as Ag^{8–13} and Pt¹⁴ have been employed as cocatalysts to enhance CO productivity in photocatalytic CO₂ reduction. However, it has been reported that without a cocatalyst, Ga₂O₃ consisting of two phases, α - and β - or β - and γ -phases, exhibits high activity for the photocatalytic CO₂ reduction.^{5,15,16} It should be noted that except for the β -phase, no single phase of Ga₂O₃ is examined as a photocatalyst for CO₂ reduction with water because of the lack of thermal stability and difficulties in their synthesis.

In this work, we have succeeded to synthesize α -phase Ga₂O₃ (α -Ga₂O₃) 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 α -Ga₂O₃ for CO₂ 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 α -Ga₂O₃

was easily obtained by calcination of GaOOH and was found to show high catalytic activity for the photocatalytic reduction of CO₂ 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 m²/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 α -Ga₂O₃. However, the sample calcined at 623 K was not well crystallized, while the samples calcined above 723 K were well crystallized to α -Ga₂O₃ without any traces of other

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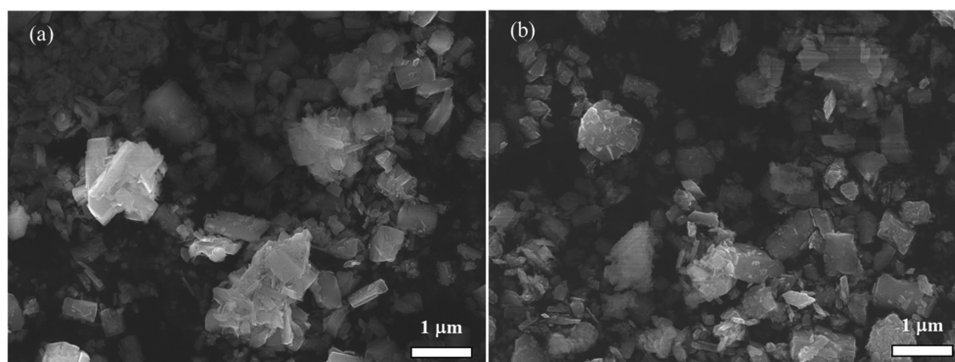


Figure 1. SEM images of samples (a) before and (b) after the calcination at 723 K for 2 h.

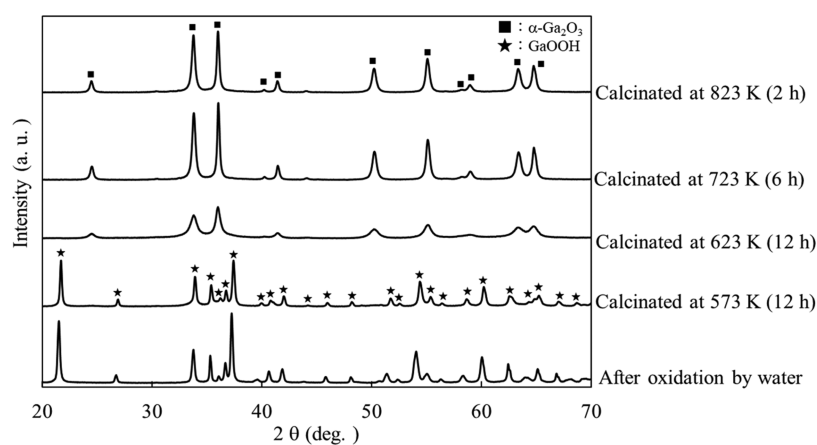


Figure 2. X-ray diffraction patterns for the prepared samples.

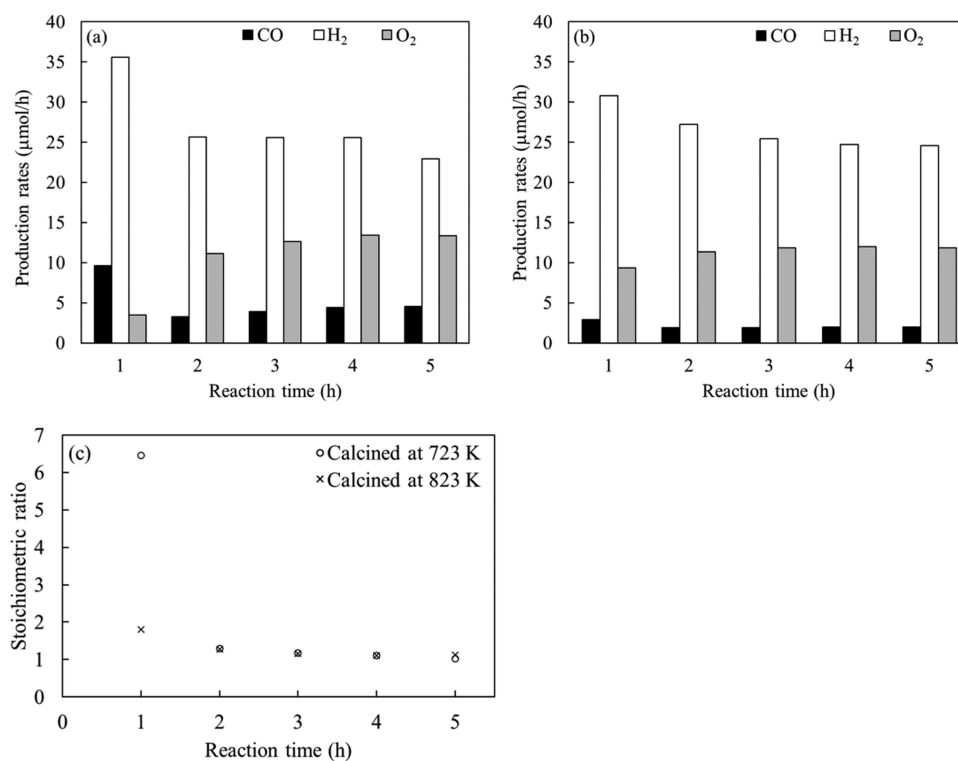


Figure 3. Production rates ($\mu\text{mol/h}$) for H_2 , O_2 , and CO for the samples calcined at (a) 723 K and (b) 823 K used for photocatalytic CO_2 reduction tests and (c) the stoichiometric ratio for the two samples.

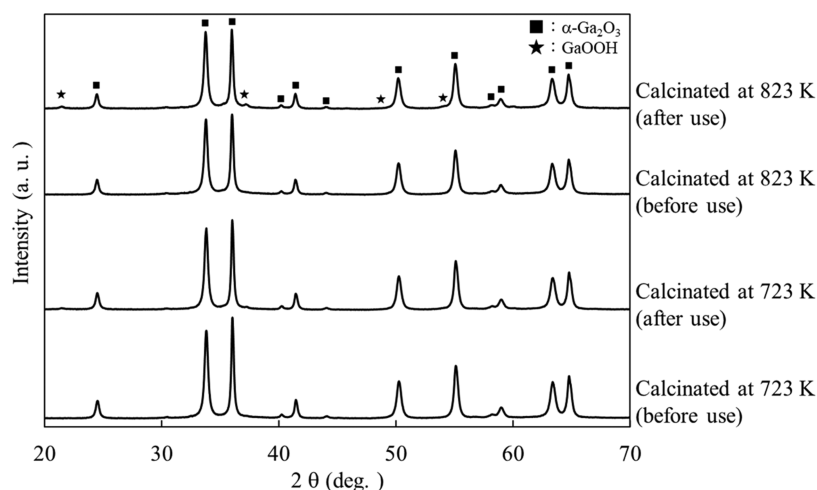


Figure 4. Comparison of X-ray diffraction patterns before and after the use of samples exhibiting high photocatalytic activity.

phases including GaOOH. UV–vis before calcination showed high intensity in the UV region caused by GaOOH, while after the calcination, that became Ga_2O_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 $\alpha\text{-Ga}_2\text{O}_3$. 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 $\alpha\text{-Ga}_2\text{O}_3$ 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_2O_3 . Therefore, the results for the samples calcined at 723 and 832 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 $25 \mu\text{mol/h}$. The CO production rates were around 4 and $2 \mu\text{mol/h}$ 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 $5 \mu\text{mol/h}$ is comparable or a little larger than that observed in previous works for the Ga_2O_3 photocatalyst using the same reaction system.^{5–7} Hence, we can conclude that the synthesized $\alpha\text{-Ga}_2\text{O}_3$ samples exhibit very high photocatalytic activity for the CO_2 reduction with water.

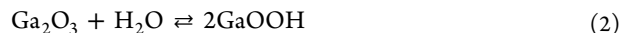
This is observed for the first time that the single phase of $\alpha\text{-Ga}_2\text{O}_3$ shows photocatalytic activity for CO_2 reduction with water and water splitting as well. Nevertheless, the selectivity of CO production compared with H_2 production remained low. Because the activity for H_2 production 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 use, except for the appearance of the traces of GaOOH in the sample calcined at 823 K. Ga_2O_3 could react with water as follows



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



so that GaOOH could be produced in water during the use of $\alpha\text{-Ga}_2\text{O}_3$ 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_2O_3 and/or GaOOH. Still, the reaction mechanism of CO_2 reduction with water over $\alpha\text{-Ga}_2\text{O}_3$ is not clear and should be investigated in the future.

3. CONCLUSIONS

We have succeeded to synthesize α -phase Ga_2O_3 with the calcination of GaOOH obtained by the water oxidation of liquid Ga metal and examined the photocatalytic activity of the synthesized α -phase Ga_2O_3 for the CO_2 reduction with water. $\alpha\text{-Ga}_2\text{O}_3$ 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 $\alpha\text{-Ga}_2\text{O}_3$ 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_2O_3 consisting of two phases, α - and β -phases or β - and γ -phases, exhibits high activity for the photocatalytic CO_2 reduction,^{5,15,16} while the present study indicates that the single phase of $\alpha\text{-Ga}_2\text{O}_3$ 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 99.99%) 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 ± 10 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 K α as a radiation source with an operating voltage of 40 kV and a current of 15 mA. The XRD patterns were collected at a 2 θ angle range of 20–70°. The 2 θ 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.

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