Utilization of La$_2$O$_3$ as a Support of Ga$_2$O$_3$ Photocatalyst to Enhance Activity on CO$_2$ Reduction with Water

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We have prepared La$_2$O$_3$ supported Ga$_2$O$_3$ (Ga$_2$O$_3$/La$_2$O$_3$) photocatalyst to improve the photocatalytic activity of Ga$_2$O$_3$ for CO$_2$ reduction with water under ultraviolet light irradiation without a noble metal cocatalyst. Significant improvement on both CO$_2$ reduction and water splitting was attained compared with those for non-supported Ga$_2$O$_3$ and La$_2$O$_3$. The improvement is attributed to the transformation of the La$_2$O$_3$ surface to NaLa(CO$_3$)$_2$ during the photocatalytic reduction tests in aqueous solution of NaHCO$_3$. NaLa(CO$_3$)$_2$ was preferentially formed on the surface of La$_2$O$_3$ without changing Ga$_2$O$_3$ resulting in the structure of Ga$_2$O$_3$ supported by NaLa(CO$_3$)$_2$. Once NaLa(CO$_3$)$_2$ fully covered the surface of La$_2$O$_3$, the high catalytic activity was kept long.

Keywords La$_2$O$_3$ supported Ga$_2$O$_3$; High activity and stability; Carbonate species; Structural change before and after reaction

I. INTRODUCTION

Nowadays, global warming and lack of energy fuel are serious concerns. Artificial photosynthesis is attracting much attention as one of the methods to mitigate these problems. Photocatalytic CO$_2$ reduction has been examined for conversion of CO$_2$ to useful chemicals such as CO, HCOOH, and CH$_4$ [1–5]. Semiconductor oxides have been extensively studied as the photocatalyst for water splitting and/or CO$_2$ reduction [4–18].

To improve the photocatalytic activity of the semiconductor oxides on CO$_2$ reduction to CO, Ag is often employed as a cocatalyst. Following Kudo et al., who have reported that Ag cocatalyst loaded on ALa$_2$Ta$_2$O$_7$ (A = Ca, Sr, and Ba) promotes the photocatalytic CO$_2$ reduction [6], several groups have shown the promotion of the photocatalytic CO$_2$ reduction by the Ag cocatalysts loaded on composite oxides, such as BaLa$_2$Ta$_2$O$_7$, KCaSrTa$_3$O$_{15}$ [7, 8], CaTiO$_3$ [9], La$_2$Ti$_2$O$_7$ [10], and SrO-modified Ta$_2$O$_5$ [11].

Although photocatalytic CO$_2$ reduction using Ga$_2$O$_3$ related oxides with the Ag cocatalyst has been studied by Yamamoto et al. for Ga$_2$O$_3$ [14–16] and Teramura et al. for Zn doped Ga$_2$O$_3$ and Yb modified Ga$_2$O$_3$ [17–19], the role of the Ag cocatalyst on the photocatalytic CO$_2$ reductions is not well understood yet. In addition, Ag loaded on Ga$_2$O$_3$ was sometimes unstable in reaction environments, oxidized or reduced resulting in the deterioration of the photocatalytic activity.

Since Ga$_2$O$_3$ shows polymorphs, correlation of the crystalline structure of synthesized Ga$_2$O$_3$ and its photocatalytic activity has been examined [14–23]. For example, Ga$_2$O$_3$ consisting of different two phases shows high photocatalytic activity on the CO$_2$ reduction with water without the Ag
catalyst [20–22]. We have succeeded to improve the photocatalytic activity of Ga2O3 for water splitting and CO2 reduction without the Ag catalyst but employing Al2O3 as a support of Ga2O3 [24, 25]. Ga2O3 supported by Al2O3 was consisted of two phases (α and γ) and their particle size was changed depending on the amount of Ga2O3 loaded on the Al2O3 support. Thus, the control of the crystal phase and the particle size of Ga2O3 is likely a key factor for the improvement of its photocatalytic activity. In a separate work [26], we have examined various metal oxides as the support of the Ga2O3 photocatalyst. Among all examined oxides, La2O3 supported Ga2O3 (Ga2O3/La2O3) showed the highest photocatalytic activity.

This motivates us to investigate the structure of Ga2O3/La2O3 and the reason for its high photocatalytic activity for CO2 reduction in detail. After confirming the high activity of Ga2O3/La2O3 synthesized here on the photocatalytic reduction of CO2 with water, Ga2O3/La2O3 was characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Ga K-edge X-ray absorption near edge structure (XANES), La L1-edge XANES, and field emission scanning electron microscope (FE-SEM), and the role of La2O3 on the photocatalytic activity was discussed.

II. EXPERIMENTAL

A. Preparation of Ga2O3/La2O3 photocatalyst

Ga2O3/La2O3 photocatalyst samples were prepared by an impregnation method. La2O3 (Kishida Chemical) was calcined at 1273 K to remove carbonate before mixing with Ga(NO3)3·8H2O (Kishida Chemical, purity: 99.0%) [27]. The amounts of them were selected to be 6 : 4 for the mass ratio of Ga2O3 and La2O3 (referred as 40 wt% Ga2O3 hereafter). It was the optimum loading amount for Ga2O3/Al2O3 in our previous work [24]. Then, they were dispersed into 200 mL of distilled water. The dispersion was stirred with a magnetic stirrer and air was bubbled through, followed by calcination at 823 K for 4 h, resulting the Ga2O3/La2O3 samples [21]. Unsupported Ga2O3 and La2O3 were also prepared in a similar way to compare their photocatalytic activities with that of Ga2O3/La2O3.

B. Characterization

Crystalline structures of all Ga2O3/La2O3 samples were examined by XRD analysis. 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 current of 15 mA. The XRD patterns were collected at 2θ angles of 20°−70°. The 2θ step size was 0.02° with the scanning rate of 2 °/min. To examine the surface composition of the samples, XPS measurements were carried out using ESCA 3400 (Shimazu). Mg Kα was used as an X-ray source with an electron acceleration voltage of 10 kV and a current of 20 mA. Ga K-edge XANES and La L1-edge XANES were measured with the transmission mode using the beam line of BL5S1 at Aichi Synchrotron Radiation Center. Morphology of the samples were observed by a FE-SEM (JSM-6500F, JEOL) with a backscattered electron mode under acceleration voltage of 15 kV.

C. Photocatalytic CO2 reduction and water splitting tests

Photocatalytic CO2 reduction with H2O under UV light irradiation was tested for 0.1 g of a sample in aqueous solution of NaHCO3 with using a fixed-bed flow reactor cell under CO2 gas flow. The reactor cell is shown in Figure S1 in Supplementary Material. The ultraviolet (UV) light intensity was 40 mW cm−2 in the range of 254 ± 10 nm. Before the test, the sample was irradiated with a 300 W Xe lamp for 1 h under CO2 gas flow with a flow rate of 20.0 mL min−1. Then, the reduction test was started by introducing 10.0 mL of the NaHCO3 aqueous solution (1.0 M) and the CO2 gas with the flow rate of 3.0 mL min−1 under the UV light irradiation. The reaction products (CO, H2, and O2) were analyzed by a gas chromatograph equipped with a thermal conductivity detector (GC-TCD). To confirm that the CO production was caused by the photocatalytic process, the CO2 reduction tests without UV light or NaHCO3 were also conducted.

III. RESULTS

A. Photocatalytic reduction tests

Figure 1 shows the time course of the production rates of H2, O2, and CO for Ga2O3/La2O3. All production rates continuously increased within 4 h and then saturated to keep nearly constant for 5 h of the reaction. After 24 h of the reaction, the CO production rate was reduced to around 2/3 of the highest rate observed at 5 h.

Figure 1: Time course of production rates of CO, H2, and O2 for photocatalytic CO2 reduction with aqueous solution of NaHCO3 under UV light irradiation on Ga2O3/La2O3 from 1 h to 5 h and 24 h. Circles of white, gray, and black correspond to the production rates of H2, O2, and CO, respectively. The production rate of O2 after 24 h could not measure.
Figure 2 compares H₂, O₂, and CO production rates for Ga₂O₃/La₂O₃, La₂O₃, and Ga₂O₃ after 5 h of the photocatalytic reduction test. Ga₂O₃/La₂O₃ showed significantly higher activities in the production rates of CO and H₂ compared with those of Ga₂O₃ by 4.3 and 2 times, respectively. Furthermore, Ga₂O₃/La₂O₃ also showed a higher CO selectivity. Both kept stoichiometry among the products. La₂O₃ did not show the catalytic activity. Thus, the photocatalytic activity of Ga₂O₃ was significantly improved by the La₂O₃ support. Additional tests changing the reaction conditions were done as shown in Table 1. It should be noted that without the UV light or NaHCO₃ dissolution, Ga₂O₃/La₂O₃ showed no CO production.

B. XRD measurements

Figure 3 showed XRD pattern of Ga₂O₃/La₂O₃ before and after use as the photocatalyst. After use, the part of La₂O₃ in Ga₂O₃/La₂O₃ changed its structure to be carbonate which was assigned as NaLa(CO₃)₂ later. Although the XRD pattern before use was broad, no other components than α-Ga₂O₃, γ-Ga₂O₃, and La₂O₃ were found. However, after use, the carbonate assigned as NaLa(CO₃)₂ appeared and dominated [shown in Figure 3(b)] [28–30]. On the other hand, Ga₂O₃ was left unchanged in XANES measurements as shown later.

The formation of NaLa(CO₃)₂ was observed in all samples after use except entry e which was tested without NaHCO₃ as shown in Figure 4. Without NaHCO₃, as depicted in Figure 4(e), the hydrated La carbonate with a chemical form of La(CO₃)₃·8H₂O was produced. Therefore, NaLa(CO₃)₂ was formed in the reaction of NaHCO₃ with La₂O₃ of Ga₂O₃/La₂O₃. NaLa(CO₃)₂ was disappeared with annealing at 773 K in vacuum [compare (b) and (c) in Figure 3].

C. XANES spectra

Figure 5 shows La L₁-edge and Ga K-edge XANES spectra. The former are clearly different before and after use, indicating the change of a bonding nature of La from the oxide (La₂O₃) to the carbonate [NaLa(CO₃)₂] [31]. On the other hand, the Ga K-edge XANES spectra did not show an appreciable change, indicating that most of Ga remained as the oxide.

D. XPS spectra

Figure 6 shows C1s XPS spectra of Ga₂O₃/La₂O₃ before and after use. After use, the small peak appeared around 290
eV became appreciable. The main peak was caused by surface contamination of C. From the peak energy, the small peak was attributed to the carbonate [32], agreeing with the XRD analysis. The carbonate peak observed in the sample before use was probably caused by the reaction of La2O3 with CO2 in atmosphere. With a curve fitting method, peak areas of the carbonate and the main peak were determined. It was indicated that the area ratio of the carbonate peak and the main peak increased from 4.3 % before use to 13.4 % after use.

**IV. DISCUSSION**

The photocatalytic activity of Ga2O3/La2O3 was increased almost linearly with the reaction time until 4 h, and afterward they became nearly constant or saturated. Even after

**E. FE-SEM observation**

Figure 7 shows FE-SEM images of the sample before and after use taken with a back scattered electron mode, of which contrast well corresponds to the mass of consisting atoms of the sample. Before use, needle-like fine particles of Ga2O3 were on larger La2O3 particles, which confirms that Ga2O3 was supported by La2O3. After use, the sizes of the supporting La2O3 particles became large probably owing to the formation and growth of the carbonate on the surface of La2O3, while the Ga2O3 fine particles kept their original structure. Thus, Ga2O3/La2O3 turned to be Ga2O3 supported by LaNa(CO3)2.
24 h, the reaction rates almost kept the highest values, which were achieved at 5 h, as seen in Figure 1. At the same time, the crystalline structure of La2O3 changed to NaLa(CO3)2 as seen XRD (Figure 3). The full conversion from La2O3 to NaLa(CO3)2 occurred after 3–4 h as shown in Figure S2 in Supplementary Material. Accordingly, its morphology changed as seen in Figure 7. On the other hand, Ga2O3 remained mostly as prepared without some possible modification at the boundary between Ga2O3 and La2O3 as shown in Figure 5(A). Correspondingly, the catalytic activity was improved until the surface of La2O3 was fully converted with NaLa(CO3)2.

There remains the possibility of CO production by dissociation of NaHCO3 and/or during the formation of NaLa(CO3)2. Therefore, we have conducted four additional photocatalytic reduction tests as shown in Table 1. As given in entry b of Table 1, without the CO2 flow, CO production was quite small even with NaHCO3. This indicates that the CO production was not caused by the decomposition of NaHCO3 but by CO2 introduced into the reaction cell. Entry e shows that bare La2O3 in NaHCO3 without Ga2O3 hardly showed the photocatalytic activity but La2O3 was converted to NaLa(CO3)2. This confirms that, without Ga2O3, NaLa(CO3)2 did not show the photocatalytic activity. Without UV irradiation, no reaction occurred indicating that the CO2 reduction was caused photocatalytically but not by pyrolysis of NaLa(CO3)2. Entry e shows that without the formation NaLa(CO3)2, Ga2O3/La2O3 did not show catalytic activity. NaHCO3 is essential for the CO2 reduction reaction, because it raised pH of its aqueous solution accompanying the increase of CO2 solubility [33].

Thus, we can conclude that Ga2O3/La2O3 shows high photocatalytic activity of CO2 reduction in NaHCO3 aqueous solution owing to the conversion of La2O3 into NaLa(CO3)2. To confirm this conclusion, it is necessary to prepare Ga2O3 supported by NaLa(CO3)2 as a photocatalyst and to conduct the reduction test with using it. However, it is hardly possible to carry out such a confirmation study. This is because the preparation of the Ga2O3 catalyst supported by NaLa(CO3)2 is difficult if the catalyst would be prepared by the impregnation method, in which annealing at temperatures higher than 773 K, a decomposition temperature of NaLa(CO3)2, is necessary. Thus, confirmation of our claim remains for future works.

### V. SUMMARY AND CONCLUSION

We have succeeded to improve photocatalytic activity of Ga2O3 employing La2O3 as a supporting material for CO2 reduction with the aqueous solution of NaHCO3 under UV light irradiation. The improvement of the activity is not directly caused by the La2O3 support but caused by the conversion of La2O3 to NaLa(CO3)2 during the photocatalytic reduction in aqueous solution of NaHCO3 under the UV light. It is also confirmed that CO2 production was not caused the decomposition of NaHCO3. The conversion continued rather long time accompanying the improvement of the photocatalytic activity.

It should be noted that Ag was not used as a cocatalyst in the present work. Hence, as noted in our previous papers [24, 25], some lattice distortion in Ga2O3 should be introduced during the conversion of the La2O3 support to NaLa(CO3)2, which would provide high activity for CO2 reduction without using the Ag cocatalyst.

### Appendix

The reaction cell for CO2 reduction tests and the change of the XRD patterns of Ga2O3/La2O3 with the reaction time are available in Supplementary Material at https://doi.org/10.1380/ejssnt.2020.110.

### Note

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**Table 1**: CO production rates for photocatalytic CO2 reduction with water under various conditions. Symbols, ○ and ×, mean the presence or absence, respectively, of CO2; the UV light; and NaHCO3 during the reaction.

| Entry | Catalyst      | CO2 | UV light | NaHCO3 | CO production rate (μm h⁻¹) |
|-------|---------------|-----|----------|--------|-----------------------------|
| a     | Ga2O3/La2O3  | ○   | ○        | ○      | 7.1                          |
| b     | Ga2O3/La2O3  | He  | ○        | ○      | 0.15                         |
| c     | La2O3        | ○   | ○        | ○      | 0.04                         |
| d     | Ga2O3/La2O3  | ○   | ×        | ○      | N.D.                         |
| e     | Ga2O3/La2O3  | ○   | ○        | ×      | N.D.                         |
| f     | Ga2O3        | ○   | ○        | ○      | 1.64                         |

*Under He flow.*  

*Not detected.*
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