Roles of Silver Co-catalyst on Gallium Oxide for Photocatalytic CO$_2$ Reduction to CO

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It is well known that Ag loaded Gallium oxide (Ag/Ga$_2$O$_3$) promotes photocatalytic CO$_2$ reduction to CO. However, the role of the Ag co-catalyst in the CO$_2$ reduction has not been clarified. We have intended to find the relationship between the state of Ag loaded on Ga$_2$O$_3$ and their activity for the photocatalytic CO$_2$ reduction. To achieve this, we have tried to control and stabilize the loading state of Ag on Ga$_2$O$_3$ during their use for the photocatalytic CO$_2$ reduction by adding methanol as a reducing agent.

It is confirmed that methanol stabilizes the particle sizes of Ag nanoparticles (Ag-NPs) loaded on Ga$_2$O$_3$ under the photocatalytic CO$_2$ reduction condition and is hardly decomposed to produce CO. Using Ga$_2$O$_3$ loaded with size-controlled Ag-NPs as a photocatalyst for the CO$_2$ reduction, it is found that Ag-NPs with their sizes within 10−30 nm are active sites for the photocatalytic CO$_2$ reduction and the catalytic activity linearly increases with the increase of the number density of Ag-NPs. However, a higher Ag loading amount over 1.0 wt% promotes aggregation of Ag to be larger metal particles over 70 nm which are not active for the CO$_2$ reduction.

**Keywords** CO$_2$ reduction; Ga$_2$O$_3$ photocatalyst; Silver nanoparticle; Ag co-catalyst

I. INTRODUCTION

Recently, depletion of fossil resources and global warming have been serious problems on a world scale [1−3]. As one of the solutions for these problems, photocatalytic reduction of CO$_2$ to carbon monoxide (CO) using semiconductor photocatalysts has been extensively studied [4−7]. Because this reaction can achieve the reduction of CO$_2$, one of the greenhouse gases, and the production of CO as a chemical energy source simultaneously [8, 9]. After the finding that the Ag co-catalyst can improve the photocatalytic activity for CO$_2$ reduction to CO [10], many studies have been conducted to improve the photocatalytic CO$_2$ reduction activity using the Ag co-catalyst [11−17]. However, the chemical and physical nature of Ag loaded as the co-catalyst were not well characterized to understand their roles on the photocatalytic CO$_2$ reduction and to optimize the loading amount of Ag. Furthermore, their physical and chemical states likely change during the photocatalytic CO$_2$ reduction under UV light irradiation [18]. Most probably, Ag is initially loaded as the oxidized state, reduced to the metallic state, dissolved into water as ionic state and re-photodeposited as Ag clusters and they grew to larger particles. Until now few studies have been done to examine the relationship between the photocatalytic activity of Ag loaded Gallium oxide (Ag/Ga$_2$O$_3$) photocatalyst for CO$_2$ reduction and the chemical and physical state of Ag during and after its use in the photocatalytic CO$_2$ reduction. Hence, we have tried to investigate the role of Ag loaded on Ga$_2$O$_3$ as the co-catalyst for the photocatalytic CO$_2$ reduction to CO. At first, we have tried to stabilize the Ag co-catalyst during the photocatalytic reduction by adding methanol to water as a reducing agent. Generally, methanol is often used in the photocatalytic water splitting as a sacrificial agent to consume the photo-generated holes [19−26]. However, it was not used for the photocatalytic CO$_2$ reduction from the...
concern of CO production by its photocatalytic decomposition. Nevertheless, in this study, we have used methanol for the stabilization of Ag nanoparticles on Ga2O3. Because methanol is known to work as a reducing agent for the synthesis of metal nanoparticles [27] and as a sacrificial agent as mentioned above. However, as reported in [26, 28, 29], the main products of photocatalytic decomposition of methanol are HCHO, HCOOH, and CO2, but CO is not likely produced.

Therefore, we have carefully examined the roles of methanol on both the stabilization of Ag nanoparticles on Ga2O3 and the sacrificial agent for the photocatalytic CO2 reduction. First, we have examined the influence of methanol addition on the state of Ag loaded on Ga2O3 referring to ultraviolet-visible (UV-vis) diffuse reflectance spectra. With this experiment, we have succeeded to control the size and number density of Ag loaded on Ga2O3. Next, we have investigated the effect of methanol addition on the photocatalytic CO2 reduction using Ag/Ga2O3. In this investigation, we have confirmed that the contribution of methanol on CO production in the photocatalytic CO2 reduction with its aqueous solution is quite small.

Based on these findings, photocatalytic CO2 reduction tests were conducted varying the amount of Ag on Ga2O3 keeping the state of Ag being steady to find the relationship between the state of Ag loaded on Ga2O3 and their activity of the photocatalytic CO2 reduction.

II. EXPERIMENTAL SECTION

A. Preparation of Ag loaded Ga2O3

Ag loaded Ga2O3 (Ag/Ga2O3) samples were prepared by an impregnation method of which detail was reported elsewhere [14]. A mixture of Ga2O3 powders (Kojundo Chemical Laboratory Co.; purity 99.99%) and AgNO3 powders (Kishida Chemical Co.; purity 99.8%) were dispersed into distilled water and magnetically stirred and dried up. Then, the dried mixture was calcined at 723 K for 2 h. Samples prepared in this way are referred to as xx wt% Ag/Ga2O3, where xx corresponds to the mass fraction of Ag loaded on the samples.

B. Photocatalytic CO2 reduction tests

Photocatalytic CO2 reduction test was conducted in a specially designed three-phases (gas, liquid, and solid) quartz reactor cell. An Ag/Ga2O3 sample with its mass of 0.1 g was put into the reactor cell under flowing CO2 gas with its flow rate of 3.0 mL min\(^{-1}\). After fully replacing residual gases in the reactor cell with CO2 gas, 10 mL of 0.5 mol L\(^{-1}\) NaHCO3 aqueous solution or 0.5 M NaHCO3 + 20 vol% methanol aqueous solution was added into the reactor cell and magnetically stirred. Then, the mixture was dried at 723 K for 2 h. Samples prepared in this way are referred to as xx wt% Ag/Ga2O3, where xx corresponds to the mass fraction of Ag loaded on the samples.

C. Characterizations

UV-vis diffuse reflectance (DR) spectra for Ag/Ga2O3 samples were recorded at room temperature using a JASCO V-670 equipped with an integrating sphere covered with BaSO4, which was used as the reference. High-angle annular dark field scanning transmission electron microscope (HAADF-STEM) observations were carried out with a Cs-corrected STEM (JEOL, JEM-ARM 200F Cold) equipped with a thermal field-emission gun and operated at 200 kV. In the HAADF-STEM observations, a sample was mounted directly on a carbon covered copper mesh. Scanning electron microscope (SEM) observations with a back-scattering mode were carried out with a field emission-SEM (JEOL, JSM-6500F) and operated at 15 kV.

III. RESULTS AND DISCUSSION

A. Stabilization of Ag loaded on Ga2O3 by adding methanol

In order to investigate the effect of methanol addition on the Ag loading state under the same condition employed for photocatalytic CO2 reduction tests, changes of UV-vis DR spectra with the light irradiation time were monitored and the results with and without methanol addition were compared (Figure 1). In this section, the loading amount of Ag was fixed at 0.5 wt%. The absorption derived from the bandgap transition of Ga2O3 appeared at < 290 nm. An intense peak around 430 nm is corresponding to the absorption of localized surface plasmon resonance (LSPR) of Ag nanoparticles (Ag-NPs). It is well known that the peak position and intensity of the LSPR absorption of Ag-NPs change depending on their size, shape and dielectric property of the surrounding medium [30, 31]. Therefore, the loading state of Ag-NPs can be estimated from the peak position and intensity of the LSPR peak. Broad absorption in wavelength longer than 600 nm is caused by Ag in a metallic state.

As seen in Figure 1, just after the preparation by the impregnation method, no LSPR peak appeared. An LSPR peak appeared when the UV light irradiation was started and the peak intensity increased with the light irradiation time. This indicates that Ag loaded on Ga2O3 by the impregnation method was initially in the oxidized state or forming Ag-Ga composite oxides [18], and reduced by the light irradiation to be deposited as Ag-NPs on Ga2O3 surface.

Under the UV light irradiation, Ag in the oxide state is reduced to be Ag ion (Ag+) in the aqueous solution and Ag+ precipitated as Ag-NPs on Ga2O3 surface. Without methanol addition [Figure 1(a)], the LSPR peak intensity turned to a decrease for further UV light irradiation. In contrast, the
broad absorption over 600 nm continuously increased or its peak position shifted to longer wavelength. With methanol addition [Figure 1(b)], the LSPR peak continued to grow and nearly saturated after 5 h of the UV light irradiation, while the broad absorption reached a maximum at 1 h and then decreased. This is a clear indication that the addition of methanol enhances the formation of Ag-NPs keeping their state and suppresses the growth of Ag-NPs to large Ag particles or to a metallic state.

Since such stabilization of Ag-NPs by methanol is very likely caused by its reducing power, three different kinds of reducing agents (alcohols) were tested under the same procedure as for methanol. Table 1 summarizes the characteristics of the reducing agents such as their number of α-hydrogen (α-H), alcohol oxidation potential, molecular weight, and observed photocatalytic activities after the photocatalytic CO2 reduction test. Comparing the UV-vis DR spectra measured after 5-h light irradiation, the sharp LSPR absorption peak appeared regardless of the kind of the reducing agents (Figure 2). This indicates that as long as a solvent having the reducing power, Ag-NPs are stabilized without re-dissolving or aggregating to be metallic Ag particles.

In the present photocatalytic CO2 reduction test, NaHCO3 is added to enhance the dissolution of CO2. However, NaHCO3 could be decomposed to produce CO2. In addition, methanol added as a reducing agent should be oxidized to form HCHO, HCOOH, and CO2. Thus, there remains a possibility to produce CO in the photocatalytic CO2 reduc-

tion with the aqueous solution of NaHCO3 and methanol.

Therefore, to clarify the role of NaHCO3 and methanol on the photocatalytic CO2 reduction, some supplementary works were conducted as indicated in Table 2. The table gives both experimental conditions and resultant production rates of CO and H2 together with CO selectivity after the 5-h reaction. The results were also compared in Figure 3. Entry (a) in Table 2 is a standard condition for comparison. As clearly seen in Figure 3, when introducing gas was changed from CO2 to He [entry (b)], the CO production rate was less than 1/10 of the standard condition. Without the catalyst [entry (c)], CO was hardly observed. Furthermore, the CO production rate hardly changed even for reducing the

![Figure 1](image1.png)

**Figure 1:** Time sequences of UV-vis DR spectra of 0.5 wt% Ag/Ga2O3 during the light irradiation (a) without methanol (b) with methanol.

![Figure 2](image2.png)

**Figure 2:** UV-vis DR spectra of 0.5 wt% Ag/Ga2O3 after the reaction with various reducing agents.

<table>
<thead>
<tr>
<th>Number of α-H</th>
<th>Alcohol oxidation potential (V)</th>
<th>Molecular weight</th>
<th>CO (μmol h⁻¹)</th>
<th>H2 (μmol h⁻¹)</th>
<th>CO selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>5</td>
<td>0.004</td>
<td>92.09</td>
<td>33.1</td>
<td>0</td>
</tr>
<tr>
<td>Methanol</td>
<td>3</td>
<td>0.016</td>
<td>32.04</td>
<td>58.8</td>
<td>35.2</td>
</tr>
<tr>
<td>Propanol</td>
<td>2</td>
<td>0.097</td>
<td>60.09</td>
<td>63.3</td>
<td>59.4</td>
</tr>
<tr>
<td>2-Popanol</td>
<td>1</td>
<td>0.088</td>
<td>60.01</td>
<td>71.4</td>
<td>101.7</td>
</tr>
</tbody>
</table>

Table 1: Summarized physical properties and photocatalytic activities of the alcohol reduction agents (sample: 0.5 wt% Ag/Ga2O3).
concentration of methanol from 20 to 5% [entry (d)].

Photocatalytic decomposition of methanol with Ag/Ga2O3 was tested in entries (e) and (f) under He gas flow and CO2 gas flow respectively. Under He gas flow, no CO2 was observed, while very small amount of CO and CH4 were detected. This indicates that methanol was photo-decomposed. However, the products such as HCHO should have remained in methanol. Under CO2 gas flow [entry (f)] a little larger amount CO was detected. Probably some of H2 produced by the decomposition of methanol was used for reduction of CO2 as observed in the reduction of H2 product in entry (f) compared with entry (e). In a separate photocatalytic CO2 reduction test without using methanol, we have observed the production of O2 with keeping stoichiometry among CO, H2, and O2 (Figure S1 in Supplementary Material), which indicates that methanol is working as a sacrificing agent to remove O2 by consuming photo-generated holes. It should be noted that without methanol, Ag-NPs were not stable.

All these observations confirm that CO production in entry (a) was dominated by the photocatalytic reduction of CO2. Thus, we can conclude that the methanol addition hardly influences the photocatalytic CO2 reduction to CO in the present experimental condition.

### Table 2: Experimental conditions and resultant production rates of CO and H2, and CO selectivity after 5-h reaction of supplementary experiments (sample: 0.5 wt% Ag/Ga2O3).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Flow gas</th>
<th>Sample</th>
<th>Methanol in water (vol%)</th>
<th>NaHCO3 (mol L⁻¹)</th>
<th>CO (μmol h⁻¹)</th>
<th>H (μmol h⁻¹)</th>
<th>Other detected products</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>CO2</td>
<td>w</td>
<td>20</td>
<td>0.5</td>
<td>60.3</td>
<td>15.6</td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td>He</td>
<td>w</td>
<td>20</td>
<td>0.5</td>
<td>6.13</td>
<td>15.2</td>
<td></td>
</tr>
<tr>
<td>(c)</td>
<td>CO2</td>
<td>w/o</td>
<td>20</td>
<td>0.5</td>
<td>0.066</td>
<td>3.14</td>
<td></td>
</tr>
<tr>
<td>(d)</td>
<td>CO2</td>
<td>w</td>
<td>5</td>
<td>0.5</td>
<td>54.4</td>
<td>15.1</td>
<td></td>
</tr>
<tr>
<td>(e)</td>
<td>He</td>
<td>w</td>
<td>100</td>
<td>-</td>
<td>0.46</td>
<td>1485</td>
<td>CH4 (1.02 μmol h⁻¹)</td>
</tr>
<tr>
<td>(f)</td>
<td>CO2</td>
<td>w</td>
<td>100</td>
<td>-</td>
<td>10.3</td>
<td>19.0</td>
<td>CH4 (0.98 μmol h⁻¹)</td>
</tr>
</tbody>
</table>

* w: with sample, w/o: without sample

B. Relationship between the Ag loading state and photocatalytic activity

Based on the above-described finding that methanol addition prevents re-dissolution and aggregation of Ag-NPs and stabilizes Ag-NPs on Ga2O3, we have tried to examine any relationships between the loading state of Ag and the activity of Ag/Ga2O3 for the photocatalytic CO2 reduction with water including methanol. We prepared samples with various Ag loading amounts (0.1, 0.3, 0.5, 1.0, and 2.0 wt%).

As described below, this change of the loading amounts...
resulted in the changes of loading density of Ag-NPs on Ga$_2$O$_3$ without significant changes in their size distribution.

Figure 4 compares UV-vis DR spectra for all samples before and after the photocatalytic CO$_2$ reduction tests with a methanol aqueous solution. No clear LSPR absorption peak was observed before the reaction tests for all samples because most of Ag loaded on Ga$_2$O$_3$ by the impregnation method were initially in the oxidized state as described above. Before the reduction tests, the broad absorption above 600 nm was appreciably large for higher Ag loaded samples. Probably excess Ag was loaded as metallic states. However, the broad peak above 600 nm significantly decreased after used for the photocatalytic reduction tests. Also, for all samples, the sharp LSPR absorption appeared with a higher intensity for a higher Ag loading amount after the reaction. These results indicate that Ag in the metallic state would be dissolved and precipitates as Ag-NPs owing to the stabilizing effect of methanol.

The actual sizes of Ag-NPs and their distribution on Ga$_2$O$_3$ were inspected with HAADF-STEM and SEM measurements. Figure 5 shows HAADF-STEM images focusing on the Ag particles on Ga$_2$O$_3$ and the size distribution of Ag-NPs determined from HAADF-STEM images for 0.5 and 2.0 wt% Ag/Ga$_2$O$_3$, respectively. The particle sizes of Ag-NPs were in the range of 10−30 nm even in higher Ag loaded samples, i.e., 1.0 and 2.0 wt% Ag/Ga$_2$O$_3$. This would be evidence of the stabilizing effects of methanol. In SEM images taken with back-scattering electron mode shown in Figure 6, Ag-NPs with diameters of 10−30 nm could not be observed because of its limited resolution [Figure 6(a, b)]. However, large Ag particles of 80−200 nm were clearly observed for the higher Ag loading samples [Figure 6(c, d)]. Thus, the consideration of the particle sizes and their distribution with UV-vis DR measurement and HAADF-STEM and SEM observations agreed well, i.e., Ag-NPs with the sizes of 10−30 nm were loaded on all samples and their number density increased with the Ag loading amount. In addition, larger Ag particles with the sizes of 80−200 nm were deposited on the samples with the higher Ag loading amount.

The results of the photocatalytic CO$_2$ reduction tests with a methanol aqueous solution for Ag/Ga$_2$O$_3$ which characterized above are compared in terms of the Ag loading amount (Figure 7). The figure compares production rates of CO and H$_2$ and CO selectivity for all samples. Without Ag loading, CO production was hardly observed, this indicates that loaded Ag plays a crucial role in the CO$_2$ reduction. The CO

Figure 5: HAADF-STEM images and particle size distribution of Ag/Ga$_2$O$_3$ samples after the reaction with methanol; (a) Ag 0.5 wt% and (b) Ag 2.0 wt%.

Figure 6: Backscatter SEM images of 0.5 and 2.0 wt% Ag/Ga$_2$O$_3$ samples after the reaction with methanol; (a) Ag 0.5 wt% before, (b) Ag 0.5 wt% after, (c) Ag 2.0 wt% before, and (d) Ag 2.0 wt% after.

Figure 7: Production rates of evolved CO (black), H$_2$ (white), and CO selectivity (diamond) in the photocatalytic reduction of CO$_2$ using methanol solution in various Ag loading amounts.
production rate increased with increasing the loading amount of Ag up to 0.5 wt%. Over 0.5 wt%, no significant difference appeared. It is important to note the nearly linear relationship of the LSPR intensity (i.e., the number density of small Ag-NPs from 10 to 30 nm) and the CO production rate up to 0.5 wt% as shown in Figure 8. This is the clear evidence that the Ag-NPs with the sizes of 10−30 nm are active sites for the photocatalytic CO₂ reduction. In samples of more than 1.0 wt% Ag loaded, excess Ag was aggregated as larger Ag particles or as metallic state and did not contribute to the CO₂ reduction.

IV. CONCLUSIONS

In the photocatalytic CO₂ reduction using a semiconductor photocatalyst, it is known that the Ag co-catalyst enhances the CO₂ reduction to CO. However, few studies have been done to examine the relationship between the loading state of Ag and their activity on the photocatalytic CO₂ reduction because loaded Ag is unstable under the reaction condition. In this study, we have tried to control the size and number density of Ag-NPs on Ga₂O₃ and succeeded to make the loading state of Ag-NPs stable during the photocatalytic reduction by adding methanol in water as a reducing agent. We have found that methanol works to enhance the precipitation of Ag as nanoparticles, to suppress the growth of their particle sizes, and consequently to keep the sizes of Ag-NPs on Ga₂O₃ uniform to be 10−30 nm. It is also confirmed that methanol added into the reaction solution is working as a sacrificial agent and little influence on the photocatalytic CO₂ reduction. Using Ga₂O₃ loaded with size-controlled Ag-NPs as a photocatalyst for CO₂ reduction, it was found that Ag-NPs with their sizes within 10−30 nm are active sites for the photocatalytic CO₂ reduction and the catalytic activity linearly increased with the increase of the number density of Ag-NPs. However higher Ag loading amount over 1.0 wt% promotes aggregation of Ag to be larger particles over 70 nm showing metallic character, which are not active for the CO₂ reduction.

Acknowledgments

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Appendix

The result of the photocatalytic reduction of CO₂ with water over 0.5 wt% Ag/Ga₂O₃ photocatalyst is available in Supplementary Material at https://doi.org/10.1380/ejssnt.2020.168.

Note

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