In-Situ FT-IR Study on the Mechanism of CO₂ Reduction with Water over Metal (Ag or Au) Loaded Ga₂O₃ Photocatalysts*

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(Received 9 January 2014; Accepted 9 April 2014; Published 28 June 2014)

Ag loaded Ga₂O₃ (Ag/Ga₂O₃) has exhibited photocatalytic activity for CO₂ reduction with water to produce CO as well as for water splitting to H₂ and O₂. In-situ FT-IR measurements have shown CO₃ stretching vibration bands assignable to carbonate and bicarbonate species when CO₂ molecules chemisorbed on the catalyst surface. These species change to bidentate formate species under photoirradiation. It subsequently converts to CO by interacting with water molecules, not chemisorbed OH on the catalyst surface. This result suggests that formate species is an intermediate of the photocatalytic CO₂ reduction. On the other hand, Au loaded Ga₂O₃ (Au/Ga₂O₃) has produced H₂ predominantly with a very small amount of CO formation, since the less amount of CO₂ molecules chemisorb on Au/Ga₂O₃. FT-IR measurements of the Ag/Ga₂O₃ with high Ag loading have shown carbonate species due to the adsorption of atmospheric CO₂ on hydroxyl group. The carbonate species is too unstable under photoradiation to convert into formate species, but is stabilized as COO⁻ species by the reaction with water. XANES analysis has revealed that atomically dispersed Ag metal species may be effective for the adsorption of CO₂ and the subsequent conversion into formate species to promote the photocatalytic CO₂ reduction.

[DOI: 10.1380/ejssnt.2014.299]

Keywords: Infrared absorption spectroscopy; X-ray absorption near edge structure (XANES); Surface chemical reaction; Photocatalysis; Carbon dioxide; Water

I. INTRODUCTION

CO₂ reduction is important not only for the energy storage as usable and value-added products but for the abatement of CO₂ as a greenhouse gas. Especially, photocatalytic reduction of CO₂ with water is environmentally friendly and attractive as the artificial photosynthesis.

In the reduction of CO₂ over a photocatalyst, the adsorption and activation of CO₂ on the catalyst surface are required, but the processes do not occur readily, since CO₂ is one of the most stable and inert molecules among carbon compounds. Therefore, the adsorption behaviors of CO₂ as a reaction substrate as well as the conformations of adsorbed CO₂ should provide essential information about the reduction mechanism of CO₂.

It has been reported that Ga₂O₃ shows photocatalytic activity for CO₂ reduction with water to produce CO as well as for water splitting to H₂ and O₂ and Ag loading on Ga₂O₃ (Ag/Ga₂O₃) promotes the CO₂ reduction. However, the dynamic reaction processes such as the change in chemical states of adsorbates at each reaction stage, and the generation process of intermediate are not well known. It is also unclear how the loaded Ag species contribute to the CO₂ reduction and which chemical state and local structure are effective for CO production.

In the present study, we investigate the adsorbed species on Ag/Ga₂O₃ by FT-IR spectroscopy to propose the reaction mechanism of photocatalytic reduction of CO₂ over Ag/Ga₂O₃. FT-IR spectra of the adsorbed species on bare Ga₂O₃ and Au loaded Ga₂O₃ (Au/Ga₂O₃) are also measured to clarify the effects characteristic of Ag loading. Similar FT-IR analysis is performed for Ag/Ga₂O₃ with higher Ag loading to see how the amount of Ag loading affects the chemical state of CO₂ adsorbates.

II. EXPERIMENTAL

A. Catalysts preparation

Metal loaded Ga₂O₃ were prepared by impregnation method. The mixture of Ga₂O₃ powder (Kojindo Chem-

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This paper was presented at 9th International Symposium on Atomic Level Characterizations for New Materials and Devices, Sheraton Kona, Hawaii, U. S. A., December 2-6, 2013.

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TABLE I: The results of photocatalytic reduction of CO$_2$ with water over Ga$_2$O$_3$ and metal loaded Ga$_2$O$_3$ catalysts.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Amount of CO ($\mu$mol/h)</th>
<th>Amount of H$_2$ ($\mu$mol/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga$_2$O$_3$</td>
<td>0.2</td>
<td>2.5</td>
</tr>
<tr>
<td>0.1 wt% Ag/Ga$_2$O$_3$</td>
<td>2.1</td>
<td>5.2</td>
</tr>
<tr>
<td>0.1 wt% Au/Ga$_2$O$_3$</td>
<td>0.1</td>
<td>16.8</td>
</tr>
<tr>
<td>1 wt% Ag/Ga$_2$O$_3$</td>
<td>1.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>

atical Laboratory Co. Ltd. purity 99.99%) and aqueous solution of AgNO$_3$ (Kishida Chemical Co. Ltd. purity 99.8%) or HAuCl$_4$·$4$H$_2$O (Kishida Chemical Co. Ltd. purity 99.6%) was evaporated on a magnetic stirrer, followed by calcination at 673 K for 2 h, then the Ag/Ga$_2$O$_3$ and the Au/Ga$_2$O$_3$ were obtained. The total weight of each sample is 2 g and the loading amounts of silver are 0.1 and 1 wt% and that of gold is 0.1 wt%.

B. Reaction tests

The reaction tests were carried out with a fixed-bed flow reactor. Photocatalysts (mass: 0.2 g) were put into the reactor cell under flowing CO$_2$ gas. When we exposed this reactor cell to UV light for 1 h, a NaHCO$_3$ aqueous solution was added to this reactor cell in dark condition. After an hour, UV light irradiation was started. Analysis of products was performed using a thermal conductivity detector gas chromatography (TCD-GC, Shimadzu GC-8A).

C. TEM measurements

In TEM measurements, samples were dispersed in an ethanol solution, and a drop of the suspension was mounted on a holey carbon covered copper mesh. TEM images of samples were observed with an H-800 electron microscopy (Hitachi) operated at 200 kV at the High Voltage Electron Microscope Laboratory in Nagoya University.

D. FT-IR spectroscopy

FT-IR spectra were recorded with a FT/IR-6100 (JASCO Co.) in a transmission mode at room temperature. Sample (ca.15 mg) was pressed into a disk (diameter: 10 mm) at 50 MPa and placed in an in-situ IR cell equipped with CaF$_2$ windows. The cell allowed us to perform heating, introduction of photoirradiation, and measurement of spectra in-situ. Before the measurement, the sample was evacuated at 673 K for 1 h. For each spectrum, the data from 6 scans were accumulated at a resolution of 4 cm$^{-1}$.

E. XAFS spectroscopy

X-ray absorption fine structure (XAFS) measurements were carried out at the beam line 6N1 at Aichi Synchrotron Radiation Center using a two-crystal Ge(111) monochromator. Ag L$_3$-edge XANES spectra of the samples were measured at room temperature in an atmospheric chamber with He gas. The data were recorded in the fluorescent X-ray yield mode with a silicon drift detector (Vortex Electronics).
FIG. 2: Difference FT-IR spectra of 0.1 wt% Ag/Ga$_2$O$_3$ (a) after introduction of CO$_2$ and (b) after the photoirradiation for 1 h, followed by evacuation.

FIG. 4: Difference FT-IR spectra of chemisorbed species after introduction of CO$_2$ on (a) 0.1 wt% Ag/Ga$_2$O$_3$, (b) Ga$_2$O$_3$ and (c) 0.1 wt% Au/Ga$_2$O$_3$.

III. RESULTS AND DISCUSSION

The results of photocatalytic reduction of CO$_2$ with water are summarized in Table I. All samples exhibited photocatalytic activity for CO$_2$ reduction to produce CO, H$_2$ and O$_2$. The amount of CO production over 0.1 wt% Ag/Ga$_2$O$_3$ is larger than that over bare Ga$_2$O$_3$, while 0.1 wt% Au/Ga$_2$O$_3$ produces large amount of H$_2$ rather than CO. It is confirmed that the Ag loading promotes CO$_2$ reduction and the Au loading enhances photocatalytic activity for water splitting.

Figure 1 shows TEM images of 0.1, 1 wt% Ag/Ga$_2$O$_3$ and 0.1 wt% Au/Ga$_2$O$_3$ samples. Metal nano-particles less than 10 nm are predominantly observed. These metal particles are highly dispersed on Ga$_2$O$_3$ supports.

We measured FT-IR spectra of 0.1 wt% Ag/Ga$_2$O$_3$ and the absorbed species in the CO$_2$ photocatalytic reduction processes. In this paper, the difference IR spectrum of each sample is obtained by subtracting that of the pretreated sample. Figure 2(a) illustrates the difference FT-IR spectra of chemisorbed species on 0.1 wt% Ag/Ga$_2$O$_3$ after introduction of CO$_2$, followed by evacuation. The bands at 1635 and 1419 cm$^{-1}$ are assigned to asymmetric CO$_3$ stretching vibration [$\nu_{as}$(CO$_3$)] and symmetric CO$_3$ stretching vibration [$\nu_{s}$(CO$_3$)], respectively, of monodentate bicarbonate species [1–4]. The bands at 1580 and 1344 cm$^{-1}$ are ascribed to $\nu_{as}$(CO$_3$) and $\nu_{s}$(CO$_3$), respectively, of bidentate carbonate species [1–4]. CO$_2$ molecules probably react with surface hydroxyl groups on Ga$_2$O$_3$ to form monodentate bicarbonate and bidentate carbonate species.

Figure 2(b) shows the difference IR spectrum of adsorbed species on the same sample after the photoirradiation for 1 h, followed by evacuation. The bands derived from carbonate and bicarbonate species decrease and new bands appear at 1577, 1388 and 1353 cm$^{-1}$. These bands are assigned to $\nu_{as}$(CO$_2$), CH deformation vibration [$\delta$(CH)] and $\nu_{s}$(CO$_2$), respectively, of bidentate formate species [1–5]. Therefore, it is clear that carbonate and/or bicarbonate species change to formate species as the intermediate product under photoirradiation. The bands originated from formate species become broad after introduction of water vapors [Fig. 3(a)]. The broadening of the bands exhibits the interaction of the chemisorbed formate species with H$_2$O molecules. After evacuation, the broad bands return to original sharp bands and an additional OH deformation vibration band [$\delta$(OH)] of chemisorbed H$_2$O appears in 1636 cm$^{-1}$ [Fig. 3(b)] [6–8].

The bands assigned to formate species decrease after photoirradiation in an atmosphere of water [Fig. 3(c)]. On the other hand, they remained unchanged under photoirradiation to chemisorbed formate species and H$_2$O molecules (OH species) on the sample surface. We can conclude that formate species as an intermediate product converts to CO by interacting with water molecules, not chemisorbed OH on the surface under photoirradiation.

Figure 4 provides the comparison of difference FT-IR spectra of chemisorbed species after introduction of CO$_2$ among 0.1 wt% Ag/Ga$_2$O$_3$, 0.1 wt% Au/Ga$_2$O$_3$ and Ga$_2$O$_3$. The bands due to monodentate bicarbonate and/or bidentate carbonate species become larger.
FIG. 5: Difference FT-IR spectra of chemisorbed species after photoirradiation on (a) 0.1 wt% Ag/Ga₂O₃, (b) Ga₂O₃ and (c) 0.1 wt% Au/Ga₂O₃.

FIG. 6: Reaction mechanism for the photocatalytic reduction of CO₂ with water.

in the following order; 0.1 wt% Au/Ga₂O₃, Ga₂O₃ and 0.1 wt% the Ag/Ga₂O₃. The amount of the adsorbed CO₂ molecules was found to increase in this order.

After photoirradiation, the bands ascribed to formate species arise at 1577, 1388 and 1353 cm⁻¹ in all the IR spectra [Fig. 5]. Note that the bands observed in 0.1 wt% Ag/Ga₂O₃ are remarkably intense whereas those in 0.1 wt% Au/Ga₂O₃ are small. As mentioned above, Ag loading on Ga₂O₃ was confirmed to generate the active sites effective for the CO₂ adsorption and the subsequent conversion into formate species. On the contrary, Au loading would inhibit the CO₂ adsorption on Ga₂O₃, resulting in the decrease of CO production.

Accordingly, we propose the mechanism for the photocatalytic reduction of CO₂ with water as shown in Fig. 6. The FT-IR spectrum showed that carbonate and bicarbonate species are formed in the presence of CO₂ on the catalyst surfaces. These species change to formate species under photoirradiation. Formate species was found to interact with H₂O molecules to produce CO under photoirradiation.

FIG. 7: Difference FT-IR spectra of adsorbed species on 1 wt% Ag/Ga₂O₃ (a) after the introduction of CO₂ followed by evacuation, (b) under photoirradiation for 1 h in vacuo, and (c) under photoirradiation for 1 h in the presence of CO₂ and water vapor.

Figure 7 shows the difference FT-IR spectra of adsorbed species on 1 wt% Ag/Ga₂O₃ (a) after the introduction of CO₂ followed by evacuation, (b) under photoirradiation for 1 h in vacuo, and (c) under photoirradiation for 1 h in the presence of CO₂ and water vapor.

FIG. 8: Ag L₃-edge XANES spectra of (a) 0.1 wt% Ag/Ga₂O₃, (b) 1 wt% Ag/Ga₂O₃, (c) Ag foil and (d) Ag₂O.

These bands decrease drastically in intensity under photoirradiation, and simultaneously, the band at 1577 cm⁻¹ attributed to formate species comes out [Fig. 7(a)]. However, the observed band is significantly small compared with that in 0.1 wt% Ag/Ga₂O₃. Thus, atmospheric CO₂ adsorbed on hydroxyl groups is unstable under photoirradiation, and hardly changes to formate species.

Under photoirradiation in the presence of CO₂ and water, the band at 1388 cm⁻¹ ascribed to CO₂⁻ species appears together with the 1638 cm⁻¹ band due to adsorbed H₂O molecules [Fig. 7(c)] [10, 11]. This result

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indicates that adsorbed CO$_2$ molecules are stabilized as CO$_2^-$ species on the surface of 1 wt% Ag/Ga$_2$O$_3$ by reacting with water.

Figure 8 shows Ag L$_3$-edge XANES spectra of silver-loaded gallium oxide samples (Ag/Ga$_2$O$_3$) together with those of Ag and Ag$_2$O reference samples. The spectrum feature in the post-edge region reflects the local structure around the target Ag atom, that is, the coordination symmetry and electronic state of the Ag atom. The XANES spectrum of 1 wt% Ag/Ga$_2$O$_3$ [Fig. 8(b)] exhibits a sharp absorption (whiteline) at 3354 eV due to the oxidized Ag as well as the fine resonance peaks at 3380, 3399 eV characteristic of the metallic Ag. This result suggests that Ag metal particles are partially oxidized in 1 wt% Ag/Ga$_2$O$_3$. Note that the absorption peaks due to the Ag metal and oxides are weak in the spectrum of 0.1 wt% Ag/Ga$_2$O$_3$ and indistinct broad feature is observed. It seems that the Ag particles are atomically dispersed by connecting directly to Ga$_2$O$_3$.

Figure 9 demonstrates the first derivative spectra of XANES in Fig. 8. In the spectra, the energy position of the peak maximum corresponds to that of the absorption edge, therefore we can estimate the edge position precisely by differentiating each XANES spectrum. We found that the edge position of Ag L$_3$-edge XANES shifts to lower energy side by oxidation of Ag species. The energy position of the edge is estimated at 3353 eV in (a) 0.1 wt% Ag/Ga$_2$O$_3$, (b) 1 wt% Ag/Ga$_2$O$_3$, and (c) Ag foil, in the meanwhile at 3351 eV in (d) Ag$_2$O. Although the XANES spectra of the Ag loaded samples show the absorption assigned to the Ag oxide, the energy position of the absorption edge is not the same between Ag loaded samples and the Ag$_2$O reference. The valence of the oxidized silver species in Ag loaded samples would be lower than that of Ag$_2$O [Ag(I)], suggesting the interaction of Ag metal particles with the Ga$_2$O$_3$ support.

Thus, XANES analysis revealed that Ag metal and Ag oxide species coexist in the Ag loaded samples and the Ag metal species are atomically dispersed in 0.1 wt% Ag/Ga$_2$O$_3$. Such highly dispersed Ag species may be effective for the adsorption of CO$_2$ and the subsequent conversion into formate species, and promote the photocatalytic reduction of CO$_2$ with water.

IV. CONCLUSIONS

Ag loaded Ga$_2$O$_3$ of 0.1 wt% loading (0.1 wt% Ag/Ga$_2$O$_3$) shows higher activity for the photocatalytic reduction of CO$_2$ with water than bare Ga$_2$O$_3$, while 0.1 wt% Au/Ga$_2$O$_3$ has lower activity. We propose the reduction mechanism of CO$_2$, based on in-situ FT-IR measurements as follows; carbonate and bicarbonate species are formed on the catalyst surfaces in the presence of CO$_2$. Under photoirradiation, these species change to formate species, and the intermediate species interact with H$_2$O molecules to produce CO.

Ag loading on Ga$_2$O$_3$ has been confirmed to generate more active sites effective for the CO$_2$ adsorption and the subsequent conversion into formate species. On the contrary, Au loading would inhibit the CO$_2$ adsorption on Ga$_2$O$_3$, resulting in the decrease of CO production.

XANES analysis has showed that Ag oxide species are coexistent with Ag metal species in the Ag loaded Ga$_2$O$_3$. In 0.1 wt% Ag/Ga$_2$O$_3$, Ag metal species are highly dispersed and the Ag species may be effective for the photocatalytic reduction of CO$_2$ with water.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research (No. 24360332 and 24656489) from the Japan Society for the Promotion of Science (JSPS).


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