

CO₂ adsorption states affected by Ag co-catalyst over Ga₂O₃ photocatalyst

Muneaki Yamamoto¹, Shinya Yagi², Tomoko Yoshida³

¹Graduate School of Engineering, Nagoya University, Nagoya, Japan

²Institute of Materials and Systems for Sustainability, Nagoya University, Nagoya, Japan

³The OCU Advanced Research Institute for Natural Science and Technology, Osaka City University, Osaka, Japan

*E-mail:

yamamoto.muneaki@f.mbox.nagoya-u.ac.jp

Photocatalytic CO₂ reduction with water into usable chemicals has been considered a promising method to address the problems of global warming and energy crisis. Ga₂O₃ is one of the photocatalysts to show the photocatalytic activity for the reduction of CO₂ with water into CO, H₂ and O₂. In our previous study, the photocatalytic activity for CO production was enhanced by the loading of Ag metal clusters as co-catalyst [1], and we have been studying the role of the Ag co-catalyst in the CO production mechanism. In our present study, we focused on the differences of CO₂ adsorption states caused by the states of Ag co-catalyst such as an activated Ag nanoparticle surface or an interface structure between a photocatalyst support. In the present study, we investigated the adsorption states of CO₂ on the Ag loaded Ga₂O₃ (Ag/Ga₂O₃) photocatalysts before and after the photocatalytic CO₂ reduction test by means of in situ FT-IR measurements. HRTEM and XAFS measurements of the Ag/Ga₂O₃ photocatalysts before and after the photocatalytic reaction were also performed to reveal the sizes and the chemical states of Ag co-catalysts.

Ag/Ga₂O₃ samples were prepared by an impregnation method. The loading amounts of Ag were 0.1, and 1.0 wt%. In the FT-IR measurements the difference IR spectrum of a sample was obtained by subtracting the background spectrum of the sample before the CO₂ introduction into an in-situ cell. Fig.1 shows the difference IR spectra of the

adsorbed species on the samples after the introduction of 45 Torr of CO₂. The bands at 1635, 1420, and 1225 cm⁻¹ are assigned to vibration modes of monodentate bicarbonate while the bands around 1590 and 1320 cm⁻¹ are ascribed to those of bidentate carbonate species. All the spectra showed these bands, so that all the samples adsorbed CO₂ on the bare Ga₂O₃ surface to form monodentate bicarbonate and bidentate carbonate. Two bands around 1510 and 1350 cm⁻¹ were observed only in the Ag loaded samples before the reaction (Fig.1 (b), (c)) and the bands increased with the loading amount of Ag. These bands should be assigned to vibration modes of monodentate carbonate on oxidized Ag surface. The FT-IR spectra of the samples after the reaction (Fig.1 (d~f)) were almost the same each other, and the species adsorbed only on the bare Ga₂O₃ surface were detected. HRTEM and XAFS measurements revealed that Ag species became to be metallic and larger in size after the reaction, therefore, large metallic Ag particles would not adsorb CO₂. However, these FT-IR experiments were performed in a steady state of each reaction step. Photo-adsorbed or short-lived CO₂ species on Ag co-catalyst still remains a possibility.

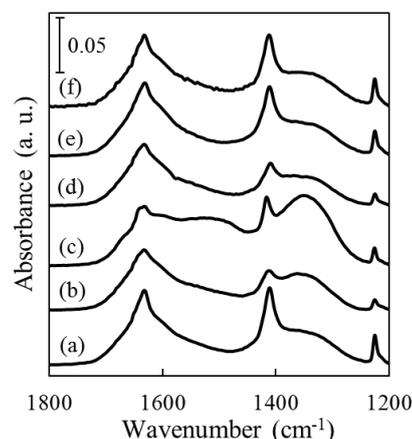


Fig.1 Difference IR spectra of the adsorbed species on the samples after the introduction of 45 Torr of CO₂. (a) Ga₂O₃, (b) 0.1 wt% Ag/Ga₂O₃ and (c) 1.0 wt% Ag/Ga₂O₃ samples before the reaction. (d) Ga₂O₃, (e) 0.1 wt% Ag/Ga₂O₃ and (f) 1.0 wt% Ag/Ga₂O₃ samples after the reaction.

REFERENCES

[1] M. Yamamoto, T. Yoshida, N. Yamamoto, T. Nomoto, Y. Yamamoto, S. Yagi and H. Yoshida, *J. Mater. Chem. A*, 3 (2015) 16810.