Study on metal oxide photocatalysts for CO_2 reduction with H_2O

Yuma Kato[1], Muneaki Yamamoto[2], Akiyo Ozawa[1] and Tomoko Yoshida[3]
[1] *Graduate School of Engineering, Osaka City University Osaka, Japan*
[2] *Graduate School of Engineering, Nagoya University, Nagoya, Japan*
[3] *Advanced Research Institute for Natural Science, Osaka City University Osaka, Japan*

*E-mail:dkdklive17@gmail.com,
tyoshida@ocarina.osaka-cu.ac.jp

In artificial photosynthesis, carbon dioxide can be reduced and converted to useful chemical materials in C1 chemistry such as carbon monoxide and methane. Although the photocatalytic CO_2 reduction with hydrogen has been reported [1], there are still few studies about CO_2 reduction with water. In the present study, we examined various metal oxides whether they promote CO_2 reduction with water.

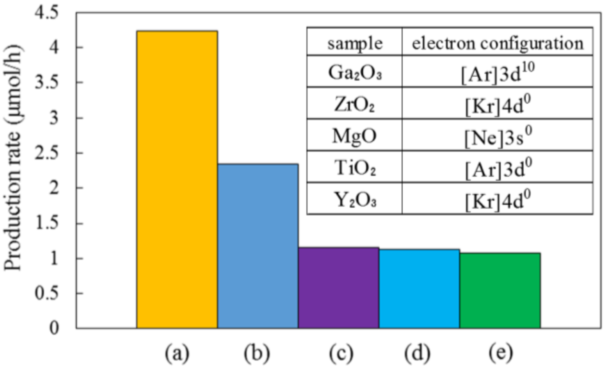
We prepared silver loaded metal oxide samples in an impregnation method using aqueous solution of silver nitrate. The loading amount of silver cocatalyst was 0.1 wt%. Photocatalytic activity for each sample was examined by the CO and H_2 production rates. To estimate the charge separation efficiency of the photo-generated electrons and holes, we have performed photoelectrochemical measurements of the samples. We also carried out in-situ FT-IR measurements of the samples at each reaction steps.

Fig.1 shows the CO production rates of the photocatalytic active samples after 5h reaction. Among the Ag loaded metal oxide samples, Ag/MgO, Ag/Ga_2O_3, Ag/Y_2O_3, Ag/ZrO_2, and Ag/TiO_2 promoted the CO_2 reduction to produce CO while Ag/La_2O_3, Ag/Yb_2O_3, Ag/NiO and Ag/Nd_2O_3 did not. We found that metal oxides involving metal ions with closed shell electronic structures such as Mg^{2+}, Ga^{3+}, Y^{3+}, Zr^{4+} and Ti^{4+} have the potential for CO_2 reduction with water. However Ag/La_2O_3 (La^{3+}) having the closed shell electronic structure did not proceed the reaction.

In the photoeletrochemical measurements of Ag/Ga_2O_3, Ag/ZrO_2, Ag/MgO, Ag/TiO_2 and Ag/Y_2O_3 exhibited higher current densities than Ag/NiO and Ag/Nd_2O_3. The closed shell electronic structures of metal ions might be effective for the charge separation of electrons and holes. However, Yb_2O_3 (Yb^{3+}) with [Xe]$4f^{13}$ electron configuration showed high current density.

To investigate why the CO_2 reduction could not proceed over Ag/La_2O_3 and Ag/Yb_2O_3, we carried out in-situ FT-IR measurements of CO_2 adsorbates on these samples. It was revealed that few amount of CO_2 molecules were adsorbed on Ag/La_2O_3 since a lot of CO_2 species were strongly chemisorbed before introduction of CO_2 molecules.

On the other hand, by introduction of CO_2 molecules to photocatalytic inactive Ag/Yb_2O_3 and active Ag/Y_2O_3, the IR bands assigned to monodentate bicarbonate species were observed for both samples. After introduction of CO_2, followed by photoirradiation for 1 h, the above bands decreased only for Ag/Y_2O_3, suggesting that monodentate bicarbonate species would convert to a reaction intermediate such as the formate species only over Ag/Y_2O_3 [2]. Therefore the amount of CO_2 adsorption as well as chemical states of CO_2 adsorbates would be one of the important factors relating to the photocatalytic activity for CO_2 reduction.



sample	electron configuration
Ga_2O_3	[Ar]$3d^{10}$
ZrO_2	[Kr]$4d^0$
MgO	[Ne]$3s^0$
TiO_2	[Ar]$3d^0$
Y_2O_3	[Kr]$4d^0$

Fig.1 CO production rates of the photocatalytic active samples after 5h reaction. (a) Ag/Ga_2O_3 (b) Ag/ZrO_2 (c) Ag/MgO (d) Ag/TiO_2 and (e) Ag/Y_2O_3.

REFERENCES

[1] K. Teramura, H. Tsuneoka, T. Shishido and T. Tanaka. Chem. Phys. Lett. 467 (2008) 191-194.
[2] M. Yamamoto, T. Yoshida, N. Yamamoto, T. Nomoto, Y. Yamamoto, S. Yagi and H. Yoshida, J. Mater. Chem. A, 3 (2015) 16810-16816.