Effect of excitation energy on the activity for CO_2 reduction to CO of Ag/Ga_2O_3 photocatalysts

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Abstract: The influence of excitation photon energy on the CO_2 reduction activity of Ag/Ga_2O_3 was investigated by using several optical filters. The band gap excitation of Ga_2O_3 was necessary for this reaction and the CO selectivity differed depending on the kind of filter. It was revealed that Ag nanoparticles grow during reaction and the particle size was different with each filter. CO selectivity depended on not only the size of Ag nanoparticles but also excitation photon energy. The highest CO selectivity was obtained by using photons filtered by 33U for a 230-420 nm wavelength range.

Keywords: CO_2 reduction with water, Ag loaded Ga_2O_3 photocatalysts, excitation energy dependence of photocatalytic activity

1. Introduction

Photocatalytic reduction of carbon dioxide (CO_2) to CO has been studied from the viewpoint of environmental issues and energy storage. Gallium oxide (Ga_2O_3) photocatalyst is known to promote CO_2 reduction with water to produce CO, H_2 and O_2 under UV photon irradiation. Recently, it has been reported that Ag loading on Ga_2O_3 as co-catalyst significantly improves the photocatalytic activity for CO_2 reduction to CO [1]. In this study, we have investigated the influence of photon energy on CO production as the result of photocatalytic reduction of CO_2 with water over Ag loaded Ga_2O_3.

2. Experimental

0.5 wt% Ag co-catalysts were loaded on Ga_2O_3 by an impregnation method (IMP). The Ag loaded Ga_2O_3 is referred as Ag/Ga_2O_3 hereafter. In the photocatalytic reduction tests, the prepared Ag/Ga_2O_3 (0.1 g) was dispersed into 1 M $NaHCO_3$ aqueous solution (10 mL) under CO_2 gas flow (3.0 mL/min) and irradiated with photons given by 300 W Xe lamp with energy selection using band pass filter or cut-off filter. Reaction products dominated by CO, H_2 and O_2 were analyzed by GC-TCD. Selectivity for CO among the all products was defined as follows: CO selectivity (%) = 100 × (production rate of CO) / (sum of production rates of CO and H_2). The size and aggregation states of Ag particles were investigated by TEM and Ultraviolet Visible (UV-Vis) diffuse reflectance measurements.

3. Results and discussion

Table 1 summarizes the wavelength regions of selected photons using filters of 254bp, 33U and 37L. Figure 1 shows diffuse reflectance (DR) spectra of Ag/Ga_2O_3 before and after reaction tests using energy selected photons with indication of the name of used filter. The DR spectra showed a large absorption band in the wavelength region shorter than 290 nm with a small shoulder around 300 nm and a broad band around 450 nm. They were respectively assigned to the band gap transition of the Ga_2O_3, the absorption due to small clusters and/or Ag-Ga composite oxide ($AgGaO_2$) and a localized surface plasmon resonance (LSPR) of Ag nanoparticles [2]. Therefore, using photons filtered by 37L, photocatalytic reduction test was carried out under the excitation of only LSPR of Ag nanoparticles. Subsequently photons filtered by 254bp can excite only the band gap transition of the Ga_2O_3 while those filtered by 33U can excite this band gap transition,

Table 1. Results of CO_2 reduction tests using photons selected by filters.

Irradiated photons		Catalytic activity on CO_2 reduction for 5 hours		Catalytic activity on CO_2 reduction test after irradiation photons filtered by 37L [a)]	
Filter name used for photon energy selection	Wavelength region (nm)		Growth of Ag nanoparticle size observed by plasmon resonance		CO selectivity(%)
No filter (Xe lamp)	200-	Active	Significant	Active	52.7
254bp	240-270	Active	Significant	Active	32
33U	230-420	Active	Significant	Active	100
37L	350-	No reaction (inactive)	Significant but remained as fine	-	-

a) The reaction was continuously carried out by changing the photon energy after reaction for 5 hours with a 37L filter

Ag-Ga composite oxide ($AgGaO_2$) and Ag small clusters.

In the photocatalytic reduction tests, reaction products of CO, H_2 and O_2 were observed with 254bp and 33U filtered photons, while no products with 37L. This clearly indicated that to proceed the CO_2 reduction with water, energy of photons should be above the energy required to excite electrons over band gap of Ga_2O_3. The CO selectivity also changed with the photon energy, while it did not with the photon flux. After the reduction tests, the LSPR absorption band became larger. This suggests the increase of Ag nanoparticle size. During the reduction tests, Ag atoms in the Ag nanoparticles would be oxidized by photogenerated holes and dissolved as Ag^+ cation, and then Ag^+ captured photoexcited electrons to be redeposited on the Ag particles. The process repetitively occurs to grow the Ag nanoparticle size. Besides, the shape of LSPR peak after the reduction tests differed with photon energy. The LSPR peak was especially sharp by using photons filtered by 37L, representing that some fine Ag nanoparticles are still maintained in this sample. This result was also supported by our TEM observation. In order to investigate whether the difference in the CO selectivity in each reaction derived from the size of Ag nanoparticles and/or the excitation photon energy, the reaction was continuously carried out by changing the photon energy for the Ag/Ga_2O_3 after reaction for 5 hours with a 37L filter. As shown in Table1, CO selectivity of the same Ag/Ga_2O_3 sample differed depending on the kind of filter, and the highest CO selectivity was obtained by using photons filtered by 33U for a 230 to 420 nm wavelength range.

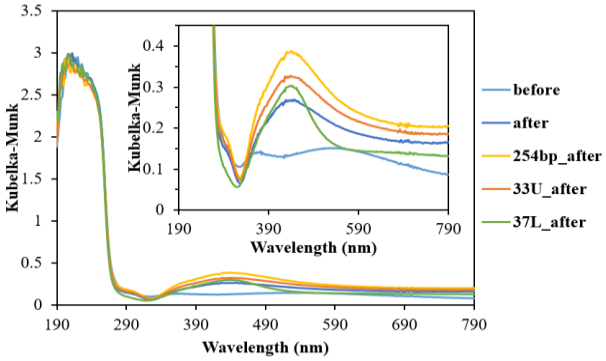

Figure 1. DR spectra of Ag/Ga_2O_3 samples before and after 5 h reaction using photons selected by the kind of the filter.

4. Conclusions

Ag loaded gallium oxide photocatalyst (Ag/Ga_2O_3) was prepared by impregnation method. We investigated the influence of photon energy (wavelength) on photocatalytic reduction of CO_2 with water over Ag/Ga_2O_3 with selection of the photon energy using band pass and cut-off filters. UV-Vis diffuse reflectance measurement suggested that Ag nanoparticles were aggregated during the reaction and the size distribution of Ag nanoparticles would be different by the kind of used filter. It was revealed that CO selectivity depends on not only the size of Ag nanoparticles loaded on Ga_2O_3 but also photon energy. The highest CO selectivity was obtained by using photons filtered by 33U for a 230 to 420 nm wavelength range.

References

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