Effects of pH on Au-deposited TiO_2 for catalytic photoreduction of CO_2 with H_2O

Yasuko Y. Maruo,[a,*] **Yuta Nakagawa,**[a] **Tsubasa Kondoh,**[a]
[a]*Tohoku Institute of Technology, Sendai-Miyagi, 982-8577, Japan*
**Corresponding author: Fax +81223053901, E-mail: y-y-maruo@tohtech.ac.jp*

Abstract: The photoreduction of CO_2 to hydrocarbons is a sustainable energy technology and Au/TiO_2 is used as a photoreduction catalyst. In this study, Au nanoparticles were deposited on anatase TiO_2 using various pH controlled Au ion solutions (from pH=6 to 9). CH_4 was mainly detected as the CO_2 reduction product and the pH of the solution strongly influenced the amount of CH_4 produced. The highest production efficiency was obtained when the pH of the solution was 9. We performed transmission electron microscopy and found that Au particle size at pH 9 was smaller than that at pH 6.
Keywords: CO_2 photoreduction, Au nanoparticle, TiO_2

1. Introduction

The greenhouse gases' increasing is the primary cause of global warming and climate change. The reduction of CO_2 by photocatalysts is the more preferable way to recycle CO_2 as a useful compound with energy input from cheap and abundant source (e.g. solar energy) at room temperature and ambient pressure. A variety of photocatalytic semiconductors have been studied, and among them, Au/TiO_2 is considered the one of candidates[1-3)]. Tatsuma et al. reported that Au electrons in Au/TiO_2 structure were excited by the light in UV-vis range, and the electron move from Au to TiO_2[4)]. In this report, we focused on the pH condition of the solution that used in the Au nanoparticle deposition, and consider the relationship between pH values and Au particle sizes. Further more, we carried out photoreduction measurement of CO_2 into hydrocarbon and considered the relationship between the photoreduction catalytic efficiencies and solution's pH.

2. Experimental

Hydrogen tetrachloroaurate (III) tetrahydrate was dissolved into water and NaOH solution was added into the solution until intended pH was obtained. The anatase TiO_2 particles were added into the pH controlled Au(III) ion solution and stirred for 1 hour. The obtained thin violet powder was dried and sintered at 400 °C for 2 hours. The violet powder was obtained. The catalyst of Au nanoparticle deposited on the TiO_2 was loaded as a thin film on a glass fiber filter (2cm×2cm) when it was used in photocatalytic reaction. Surface image of the samples were obtained using a scanning electron microscope (SEM) (SU1510, Hitachi) and transmission electron microscope (TEM) (JEM-2100F, JEOL). The Au/TiO_2 coated on glass fiber filter was installed in the gas reactor. A high pressure Hg lamp (Ushio-denki Co., Japan) was irradiated source. The CO_2 gas with 50 % R.H. was then introduced to the gas reactor with BaF_2 windows at the both side. The concentrations of produced gases (e.g. CO, CH_4, CH_3OH) from the photoreduction reaction were measured by a FT-IR (iS-10, Thermo) every hour. The experimental system was batch system, and not a flow one.

3. Results and discussion

We measured the XRD patterns of the Au/TiO_2 catalysts produced from pH=6 to PH=9 solutions. All patterns clearly show anatase phases of TiO_2 and Au diffraction patterns could not be measured. Figure 1 shows the SEM image of the three kinds of Au/TiO_2 catalysts and anatase TiO_2. It shows that the deposition of Au did not affect the crystalline structure of TiO_2. We also carried out TEM measurement as shown in Fig. 2, and Au particles were observed from the TEM images. We selected five number of Au particles for each images, and measured average diameters of Au particles. Table 1 showed the measured diameters of Au particles, and it was found that Au particle size at pH 9 was smaller than that at pH 6. The diffuse diffraction UV-vis spectra of the catalysts were shown in Fig. 3. The catalysts absorb light below 400 nm, corresponding to a band-gap approximately 3.0 eV. The 600 nm absorbance was caused by Au nanoparticles, because the color of the Au nanoparticles was violet causing by surface plasmon resonance[5)]. There was no significant difference between the spectra of Au/TO$_2$(pH=6) and Au/TiO$_2$(pH=7), indicating almost same concentration of Au. However, the lower absorbance at 600 nm of Au/TiO$_2$(pH=9) was indicating the lower concentration of Au than the other two kinds of Au/TiO$_2$. The effect of irradiation time on the formation of CO_2 photocatalytic reduction products was investigated over a period of 0-5 hours. Two main products (CO and CH_4) were determined in the gas phases. Methanol, formic acid and formaldehyde in a gas phase were under detectable. Comparison of CH_4 yields over three kinds of Au/TiO$_2$ was shown in Fig. 4. The yields of CH_4 increased up to several hours and after that increasing ratio gradually decreased. It was reported that the Au/TiO$_2$ surface effectively adsorbs CO molecules, therefore gradually decrease of CH_4 amounts would be caused by adsorption on the Au/TiO$_2$, because our experimental system was non-flow one. The highest yield of methane was obtained for Au/TiO$_2$ (pH=9) sample, and the production yields become greater, when the pH become higher. Therefore small particle size of Au deposited on TiO$_2$ for Au/TiO$_2$ (pH=9) would work well for CO_2 photoreduction reaction into CH_4.

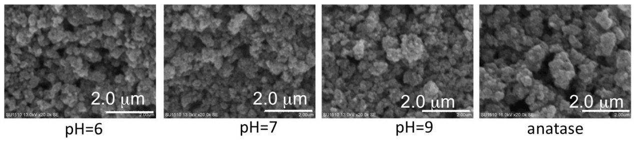

Figure 1. SEM images of Au nanoparticle deposited TiO$_2$ using several pH solutions.

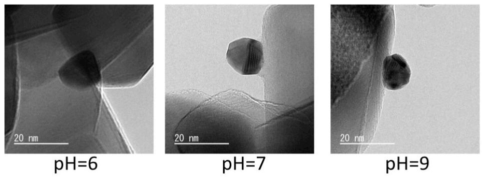

Figure 2. TEM images of Au nanoparticle deposited TiO$_2$ using several pH solutions.

Table 1. Particle size of deposited Au at several pH conditions

pH	6	7	9
size(nm)	15±2	15±2	10±1

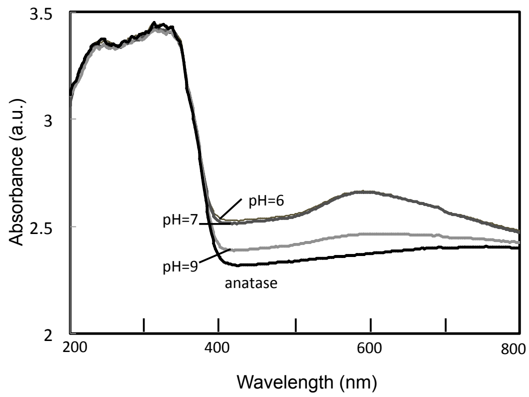

Figure 3. Diffuse diffraction UV-vis spectra of Au nanoparticle deposited TiO$_2$ using several pH solutions.

4. Conclusions

Several kinds of Au nanoparticle deposited TiO$_2$ were synthesized using pH controlled solutions. We considered the photoreduction properties of Au/TiO$_2$ for CO_2 with 50% H_2O. The main products was CH_4 and the greatest efficiency was obtained when Au/TiO$_2$ was formed from pH=9 solution. Considering TEM results, the smaller particle size of Au nanoparticles was deposited when the alkali condition, and this works well for CO_2 photoreduction into CH_4.

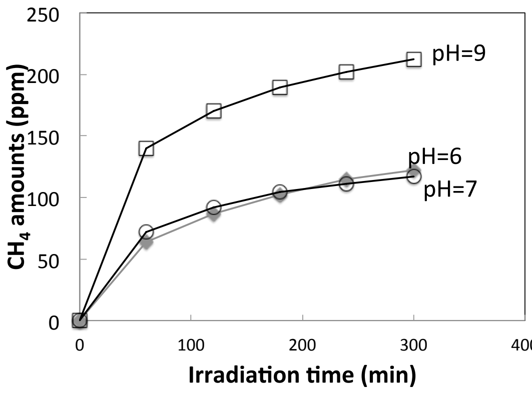

Figure 4. Time dependence of produced CH_4 amounts for Au nanoparticle deposited TiO$_2$ using several pH solutions.

References

1. W.-N. Wang, W.-J. An, D. M. Niedzwiedzki, P. Biswas, B. Ramalingam, S. Mukherjee, S. Gangopadhyay, J. Am. Chem. Soc., 134 (2012)11276.
2. D. Kong, J. Z. Y. Tan, F. Yang, J. Zeng, X. Zhang, Appl. Surf. Sci., 277 (2013)105.
3. O. Ishitani, C. Inoue, Y. Suzuki, T. Ibusuki, J. Photochem. Photobiol. A, 72 (1993)269.
4. Y. Tian, T. Tatsuma, J. Am. Chem. Soc., 127 (2005)7632.
5. S. K. Ghosh and T. Pal, From Theory to Applications, Chem. Rev., 107 (11), 2017, p. 4797.