Selective photocatalytic oxidation of aromatic alcohols to aldehydes over Ag-Au/TiO_2, Au/TiO_2 and Cu-Au/TiO_2 under irradiation of visible light

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Abstract: Au particles supported on SnO_2 (Au/SnO_2) were modified with Cu and Ag by the multistep photodeposition method. Absorption around λ= 550 nm, attributed to surface plasmon resonance (SPR) of Au, gradually shifted to longer wavelengths on modification with Cu and finally reached λ= 620 nm. On the other hand, the absorption shifted to shorter wavelength with increasing amount of Ag and reached λ= 450 nm. Cu-Au/SnO_2, Ag-Au/SnO_2 and Au/SnO_2 were used for selective oxidation of aromatic alcohols under irradiation of visible light. The reaction rates for the oxidation of benzyl alcohol over these materials depend on the wavelength of light.

Keywords: Surface plasmon resonance, Selective oxidation, visible light-responding photocatalyst.

1. Introduction

Nanoparticles of metals such as gold (Au), silver (Ag), and copper (Cu) have been studied extensively because of their unique properties, which are associated with their strong photoabsorption in the visible light region, due to surface plasmon resonance (SPR). The photoabsorption peaks due to SPR of Au, Ag, and Cu nanoparticles are generally observed around 550, 450, and 600 nm, respectively. Recently, we found that action spectra in photocatalytic reactions over Au/TiO_2[1], Au/CeO_2[2] and Au/WO_3[3] were in good agreement with their absorption spectra, which suggested that photocatalytic reactions were induced by photoabsorption due to SPR of the supported Au nanoparticles. In contrast to reports on supported Au nanoparticles, there have been few reports on chemical reactions induced by SPR of Ag and Cu nanoparticles, probably due to their instability under working conditions. In this study, we examined control of absorption due to SPR by modification of Au nanoparticles supported on SnO_2 with Ag and Cu. Herein, we report photocatalytic oxidation of organic compounds in aqueous suspensions of Au/SnO_2, Ag-Au/SnO_2, and Cu-Au/SnO_2 under irradiation with visible light[4].

2. Experimental (or Theoretical)

Multistep photodeposition (MSPD) was also used for preparation of Ag-Au/SnO_2 and Cu-Au/SnO_2 by modification of Au/SnO_2 with Ag and Cu. An aqueous solution of silver sulfate or copper sulfate was injected into an aqueous methanolic suspension of Au/SnO_2 and the mixture was photoirradiated with a mercury arc lamp. The resultant powder was washed repeatedly with distilled water and then dried in air at 310 K overnight.

The dried Au/SnO_2, Ag-Au/SnO_2, or Cu-Au/SnO_2 powder (50 mg) was suspended in distilled water (5 cm^3), and the suspension bubbled with O_2 and sealed with a rubber septum. Alcohols were injected into the suspensions, which were then irradiated with visible light from blue, green, and red LEDs. The amounts of alcohols and carbonyl compounds in the liquid phase were determined with a Shimadzu GC-14B gas chromatograph equipped with a DB-1 capillary column.

3. Results and discussion

Figure 1 shows absorption spectra of Au(0.2)/SnO_2, Ag(0.8)-Au(0.2)/SnO_2, Au(1.0)/SnO_2, and Cu(0.8)-Au(0.2)/SnO_2. In the spectra of Au(0.2)/SnO_2 and Au(1.0)/SnO_2, photoabsorption was observed

around λ=550 nm (Figure 1d, b), which was attributed to SPR of the supported Au particles, and more intense photoabsorption was achieved by increasing the Au contents of Au/SnO_2.

Both a shift of photoabsorption and an increase in intensity were achieved by introduction of Ag and Cu into Au(0.2)/SnO_2 (Figure 1a, c). The photoabsorption at 550 nm of Ag(0.8)-Au(0.2)/SnO_2 and that of Cu(0.8)-Au(0.2)/SnO_2 were less intense than that of the Au(0.2)/SnO_2 mother material before modification. These results suggest that the SPR properties of Ag(0.8)-Au(0.2)/SnO_2 and Cu(0.8)-Au(0.2)/SnO_2 are not inherited from Au(0.2)/SnO_2 and originate from the properties of Ag and Cu themselves. It is known that Cu nanoparticles are easily oxidized and lose their SPR gradually under ambient conditions. Therefore, Au particles are clearly indispensable for preparation of stable Cu-based particles supported on SnO_2 exhibiting intense photoabsorption at 630 nm due to SPR. The Au particles probably function as a kind of template and stabilizer for Cu and Ag metals.

Previously, we found almost quantitative oxidation of benzyl alcohols to benzaldehydes in an aqueous suspension of Au/CeO_2 under irradiation with green light from an LED.[5] Herein, Ag(0.8)-Au(0.2)/SnO_2, Au(1.0)/SnO_2, and Cu(0.8)-Au(0.2)/SnO_2 were used for oxidation of benzyl alcohol under irradiation with light from three LEDs. No oxidation of benzyl alcohol occurred over metal-free SnO_2; thus, visible light from the LEDs did not cause bandgap excitation of SnO_2. On the other hand, Ag(0.8)-Au(0.2)/SnO_2, Au(1.0)/SnO_2, and Cu(0.8)-Au(0.2)/SnO_2 were active in the oxidation of benzyl alcohol and yielded benzaldehyde with quite high selectivity (>99%) at greater than 99% conversion of benzyl alcohol after 20 h when blue, green and red LEDs were used, respectively. Since the amount of benzaldehyde increased linearly with photoirradiation time of the three materials, the formation rates were determined from slopes of the time courses of benzaldehyde formation (Figure 2). The highest reaction rates were obtained when the irradiating light overlapped well with photoabsorption due to SPR.

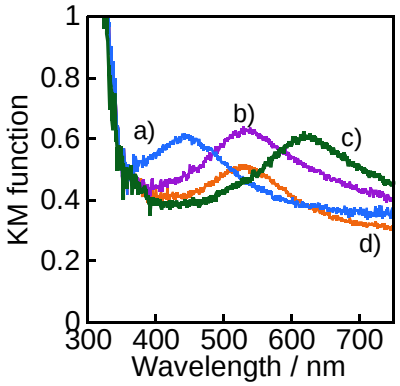

Figure 1 Absorption spectra of a) Ag-Au/SnO_2, b) Au/SnO_2, c) Cu-Au/SnO_2 and d) Au/SnO_2.

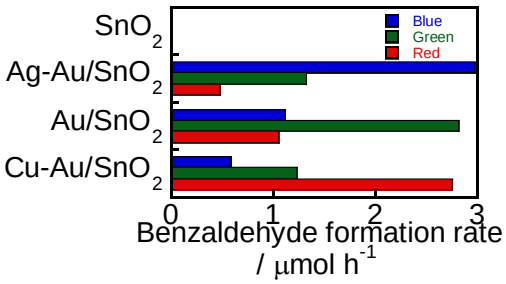

Figure 2 Rates of formation of benzaldehyde from benzyl alcohol over SnO_2, Ag-Au/SnO_2, Au/SnO_2, and Cu-Au/SnO_2 under irradiation with visible light from green, blue and red LEDs.

4. Conclusions

SnO_2-supported Au particles exhibiting strong photoabsorption due to SPR of Au were prepared by MSPD. Modification of 0.2 wt%Au/SnO_2 with Cu and Ag by MSPD resulted in formation of Cu-Au/SnO_2 and Ag-Au/SnO_2. The absorption of the Au/SnO_2 around λ= 550 nm gradually shifted to longer and shorter wavelengths with increasing contents of Cu and Ag, respectively. These samples were active for selective oxidation of alcohols to carbonyl compounds under visible-light irradiation and exhibited the best performance when irradiated by light overlapping with their SPR.

References

1. A. Tanaka, S. Sakaguchi, K. Hashimoto, H. Kominami, *ACS Catal.*, **2013**, *3*, 79.
2. A. Tanaka, K. Hashimoto, H. Kominami, *Chem. Commun.*, **2011**, *47*, 10446.
3. A. Tanaka, K. Hashimoto, H. Kominami, *J. Am. Chem. Soc.*, **2014**, *136*, 586.
4. A. Tanaka, K. Hashimoto, H. Kominami, *Chem. A: Eur. J.*, **2016**, *22*, 4592.
5. A. Tanaka, K. Hashimoto, H. Kominami, *J. Am. Chem. Soc.*, **2012**, *134*, 14526.