The Effect of UV Irradiation on the Reduction of Au(III) Ions Adsorbed on Manganese Dioxide

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The effect of UV (ultraviolet) irradiation on the adsorption of Au(III) ions on manganese dioxide and their reduction to Au(0) (gold with 0 valence state) was investigated using XPS (X-ray photoelectron spectroscopy) and ¹⁹⁷Au Mössbauer spectroscopy. The UV irradiation accelerated the adsorption and the reduction. From the fact that the proportion of Au(0) estimated from Au 4f XPS spectra for surface analysis was significantly smaller than that from ¹⁹⁷Au Mössbauer spectra for bulk analysis, we deduced that Au(0) was interpenetrated to the inside of manganese dioxide (into deeper places than about 30 Å) where XPS is impossible to detect. The content of surface hydroxyl groups on manganese dioxide also increased due to the UV irradiation. The relationship between the change in the content of hydroxyl groups and the interpenetration of Au(0) is discussed.

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Introduction

It is well known that gold supported on various metal oxides shows unique catalytic properties.¹⁻³ Among the examples, gold supported on manganese dioxide is a superior catalyst to convert CO to CO₂ at low temperatures.⁴⁻⁷ Catalytic activity depends on gold particle size. The precursor of the catalyst is usually prepared by adding a mixed aqueous solution of H[AuCl₄] and Mn(NO₃)₂ into an aqueous Na₂CO₃ solution. The precursor (coprecipitate of Au(III) ions with MnO_x) is calcined in air above 250°C to completely oxidize MnO_x to MnO₂ and to reduce Au(III) ion to atomic gold due to thermal decomposition that forms gold particles by their aggregation. However, the size is significantly affected by the calcination condition and it is not easy to control the size. It is difficult to support uniform gold particles with nanometer diameters on MnO₂ because of the formation of gold particles with various sizes.

In a previous paper,⁸ we showed that the adsorption capacity of Au(III) ions by manganese dioxide was high compared with that of some metal oxides. We found that a part of the Au(III) ions adsorbed was spontaneously reduced to Au(0) (gold of 0 valence state); the material includes gold from atomic gold clusters to particles that are μm in size. If gold particles that are nm in size are formed by adsorption of Au(III) ions on the surface of manganese dioxide, this could be a useful preparation method for gold-supported manganese dioxide. To develop this method to a practical industry, one must investigate the reduction of the Au(III) ions adsorbed on manganese dioxide.

Seino *et al.*⁹ reported that gold-supported Fe(III) oxide particles were formed by irradiation of γ-rays to a suspended solution containing Fe(III) oxide and Au(III) ions. The irradiation of electromagnetic waves including γ-rays or ultraviolet (UV) rays is considered to be a useful method for the reduction of Au(III) ions without specific reagents.

In the present study we investigated the effect of UV irradiation on the reduction of Au(III) ions during their adsorption on manganese dioxide because of its simplicity.

Experimental

Reagents and sample solutions

All chemicals used were of analytical grade (Wako Pure Chemical Industry). All the solutions were prepared with pure water (Milli-Q SP system, Millipore). A gold stock solution (5000 ppm Au) was prepared by dissolving H[AuCl₄]·4H₂O in pure water. Gold sample solutions (250 ppm Au, 200 or 500 cm³) were prepared by diluting this stock solution immediately before each adsorption experiment.

Manganese dioxide (CMD 200, specific surface area: 203 m² g⁻¹) as an adsorbent of Au(III) ions was supplied from Chuo Denki Kogyo Co., Ltd. The manganese dioxide was X-ray amorphous.

Adsorption experiments

The adsorption experiments were conducted in the batch method at room temperature. Manganese dioxide (100 or 250 mg) was added into gold sample solutions (200 or 500 cm³, 250 ppm Au) with 0.12 mol dm⁻³ NaCl and then the solutions were adjusted to pH 6. In the irradiation experiment UV light was

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Fig. 1 Proportional variations (%) of adsorption over time at various initial concentrations of Au(III). Initial concentration: ▲, 50 ppm; ●, 100 ppm; ▼, 250 ppm; ■, 500 ppm.

Fig. 2 Comparison of adsorption behavior of Au(III) ions under non-irradiated and UV-irradiated conditions. ●, Non-irradiation; ■, UV-irradiation.

continuously irradiated using a black light (15 W) to a solution suspended from the side of the reaction vessel (pyrex glass). The distance between the black light and the reaction vessel was 3 cm. The pH was continuously monitored with a pH meter and maintained within 6.0 ± 0.1 using HCl and NaOH solutions. The suspensions were magnetically stirred. At adequate intervals, aliquots of the suspension were taken out with a glass pipette and filtered with 0.45 μm membrane filter. The gold concentration in the filtrate was determined by atomic absorption spectrometry (AAS). The amount of gold adsorbed on manganese dioxide was estimated by the decrease in gold concentration from the initial concentration. Manganese dioxide, which had adsorbed gold that remained on the filter (solid sample) was dried in a desiccator in a dark room at room temperature.

Determination of Au(III) ions

The HCl concentration of gold solutions and filtrates was adjusted to 0.1 mol dm^{-3} to convert $[\text{AuCl}_{4-n}(\text{OH})_n]^-$ to $[\text{AuCl}_4]^-$, which shows UV absorption, and the absorbance of this solution was measured spectrophotometrically at 320 nm to determine the Au(III) ions.

Scanning electron microscopy (SEM)

The size and morphology of gold particles on manganese dioxide were observed using a Shimadzu SS-550S scanning electron microscope. For the SEM imaging, the powder of the solid sample was dispersed on adhesive carbon tape. Elemental composition of the sample was determined *in situ* using a Genesis 2000AY energy-dispersive X-ray spectrometer (EDX).

X-ray photoelectron spectroscopy (XPS)

The chemical states of Au, Mn and O in the solid samples were analyzed by XPS (Shimadzu KRATOS AXIS-165). Powder samples that adhered on the carbon tape were placed in an evacuated sample chamber (10^{-10} torr). The XPS spectra were acquired using a monochromatic Al K_{α} X-ray source (1486.49 eV) operated at 30 W (15 kV, 2 mA). Survey spectra were collected over the range 0 – 1400 eV with a pass energy of 80 eV. High resolution XPS spectra were acquired for C 1s, O 1s, Mn 2p and Au 4f using a pass energy equal to 40 eV. In all cases, the photoelectron take-off angle was 45° . The XPS spectra were collected internally using C 1s (284.6 eV), because the sample charging can shift the peak location in the XPS

spectra. The spectra were obtained under conditions of 0.1 eV step and 298 ms/point. The binding energies for Au(0) state and Au(III) state were obtained from a gold plate and from $\text{K}[\text{AuCl}_4] \cdot n\text{H}_2\text{O}$ as the standard materials. The Shirley method was used to correct the background of all spectra. After the corrections, the spectra were analyzed using XPSPEAK 4.1 computer software.

^{197}Au Mössbauer spectroscopy

The chemical state of gold in selected solid samples was measured by ^{197}Au Mössbauer spectroscopy. The ^{197}Pt isotope ($T_{1/2} = 18.3$ h), γ -ray source feeding the 77 keV Mössbauer transition of ^{197}Au was prepared by neutron irradiation of isotopically enriched ^{196}Pt metal from the Kyoto University Reactor. The absorbers were particle specimens. The source and the specimens were cooled with a helium refrigerator. The temperature of the specimens was in the range of 13 – 14 K. The zero velocity point of the spectra was the peak point of pure bulk gold. The spectra of all samples were fitted with single Lorentzian lines.

Results and Discussion

Variation of proportion of adsorption

For gold supported manganese dioxide catalysts, Hoflund *et al.*¹⁰ suggested that the content of gold supported on manganese dioxide should be about 20 wt% to obtain effective catalytic activity. On the other hand, our preliminary XPS experiment showed that several percent of the gold content is at least required to detect peaks assigned to Au 4f in the XPS spectra. From viewpoints of the catalytic activity and the detection limit, it is essential to examine preliminarily the relationship between the initial gold concentration and the percent of adsorption of Au(III) ions on manganese dioxide.

Figure 1 shows the relationship between initial Au(III) ion concentration and percent of Au(III) ions adsorbed on manganese dioxide. The detailed experiment conditions are shown in the figure caption. When the initial concentration of Au(III) ion was 50 or 100 ppm, most of the Au(III) ion was adsorbed. At 250 and 500 ppm, however, the percent of adsorption was about 80 and 45% against the initial concentration. In both cases, the gold content of the manganese dioxide was about 20 wt% in the dried solid samples, enough

Fig. 3 An SEM image of gold particles formed on manganese dioxide for a non-irradiated sample collected after 48 h in adsorption experiments shown in Fig. 2.

content for XPS measurements of Au 4f region. Therefore, the adsorption experiments were conducted in solutions with 250 ppm Au hereafter.

The effect of UV irradiation on the adsorption of Au(III) ions

In Au(III) solutions, a decrease in the Au(III) concentration from the initial concentration indicates its reduction. If one converts $[\text{AuCl}_{4-n}(\text{OH})_n]^-$ (major species around neutral pH) to $[\text{AuCl}_4]^-$ (stable species in more than $0.1 \text{ mol dm}^{-3} \text{ HCl}$), the Au(III) concentration can be determined by spectrophotometry. Before adsorption experiments, whether Au(III) ions in solution (pH 6, 250 ppm) are reduced or not by UV irradiation was examined. No reduction was detected for 48 h, indicating that Au(III) ions were not reduced in solution during the adsorption experiments.

Figure 2 shows the comparison of adsorption behavior of Au(III) ions on manganese dioxide when UV was irradiated and when there was no irradiation. The adsorption rate was almost the same in spite of the UV irradiation within 5 h; however, the percent of adsorption under the UV irradiation was higher than that under non-irradiation after 5 h. This fact suggests that the UV irradiation accelerated the adsorption of gold. These irradiated and non-irradiated solid samples obtained after 48 h were characterized by SEM, XPS and ^{197}Au Mössbauer spectroscopy to elucidate the chemical state of gold adsorbed on manganese dioxide.

SEM observation

The UV irradiated and non-irradiated solid samples were observed by SEM. Figure 3 shows an SEM image for the non-irradiated sample. The image shows the presence of small white spherical particles on the surfaces of dark large particles. According to the analysis by EDX, the former particles consisted of gold and the latter particles consisted of manganese, suggesting that gold particles several μm in size might be formed due to reduction of Au(III) ions adsorbed on manganese dioxide. The images for the UV-irradiated samples were similar to that in Fig. 3.

Fig. 4 Peak fitting analysis of Au 4f XPS spectra for non-irradiated sample (a) and UV-irradiated sample (b) collected after 48 h in adsorption experiments shown in Fig. 2.

Au 4f XPS spectra

The present authors⁸ reported that a part of the Au(III) ions adsorbed on the surface of manganese dioxide was spontaneously reduced to Au(0). Therefore, the effect of UV irradiation on the reduction of Au(III) ions adsorbed was examined by XPS. Figure 4 shows the high resolution XPS spectra of Au 4f for non-irradiated sample (a) and for the UV-irradiated sample (b) after 48 h. As the peak assigned to Au 4f was much stronger due to high Au content than that of Mn 3s, we estimated peak intensities of Au(III) and Au(0).⁸ Both spectra were divided into two doublets, assigned to two different gold species having characteristic binding energies of Au(III) and Au(0) states,¹¹ as shown in Fig. 4. The assignment was referred to the peak position of standard materials for Au(III) and Au(0) described in the experimental section. The relative peak intensities are summarized in Table 1. The relative peak intensity assigned to Au(0) for the irradiated sample was significantly higher than that for the non-irradiated sample, clearly indicating that the reduction of Au(III) ions adsorbed on the surface of manganese dioxide is accelerated by the UV irradiation.

^{197}Au Mössbauer spectra

In contrast with XPS for surface analysis, Mössbauer spectroscopy is a method of bulk analysis. To confirm whether the reduction degree of Au(III) ions in the solid samples is different between the surface and the bulk, ^{197}Au Mössbauer spectra were measured. Figure 5 shows ^{197}Au Mössbauer spectra for the non-irradiated sample (a) and the UV-irradiated sample (b). The both spectra can be divided into one singlet having nearly zero isomer shift and two doublets having positive isomer shifts. The singlet (component 1) is due to the atomic Au(0) because the isomer shift of this component is

Table 1 Peak intensities of Au(0) and Au(III) for Au 4f XPS spectra

	Peak intensity, %	
	Non-irradiation	UV-irradiation
Au(0)	20	28
Au(III)	80	72

Table 2 ^{197}Au Mössbauer parameters for three components and peak intensity of each component

Component	Non-irradiation			UV-irradiation		
	IS/ mm s^{-1}	QS/ mm s^{-1}	S, %	IS/ mm s^{-1}	QS/ mm s^{-1}	S, %
1	0.09	—	32	0.05	—	40
2	3.18	2.06	35	3.03	2.15	29
3	3.60	3.38	33	3.69	3.29	31

IS, Isomer shift; QS, quadrupole splitting; S, peak intensity.

close to that of elemental gold. One of the doublets has a smaller positive isomer shift and smaller quadrupole splitting (component 2) than those of the third component (component 3). Both doublets can be reasonably assigned to Au(III) although their chemical state has been uncertain. Mössbauer parameters and relative peak intensities are summarized in Table 2. Comparing these two ^{197}Au Mössbauer spectra, we see that the peak intensity due to Au(0) for the irradiated sample is significantly stronger than that for the non-irradiated sample, reconfirming the acceleration of the reduction of adsorbed Au(III) ions by UV irradiation.

Change in surface structure of manganese dioxide and accumulation of Au(0)

Comparing both Au 4f XPS spectrum and ^{197}Au Mössbauer spectrum for a non-irradiated sample, we see that the proportion of Au(0) in the ^{197}Au Mössbauer spectrum is significantly larger than that in the XPS spectrum. The XPS spectrum gives information about only the gold on the surface of the sample (the depth of analysis is in the range of 30 Å),¹² whereas the ^{197}Au Mössbauer spectrum gives information about all the gold in the sample. Consequently, it can be concluded that a significant amount of Au(0) exists in places deep below the surface of the non-irradiated sample where XPS is impossible to detect. As shown in Fig. 3, only gold particles larger than 1 μm could be detected by SEM; however, Au(0) is probably present as particles and/or clusters with various sizes (from atom to μm scale) in the samples.

It has been confirmed from observations by high-resolution TEM that manganese dioxide particles have tunnel structures in which various cations with suitable charges and sizes and water molecule can move.^{13,14} The original size of the tunnels is in the range 7–10 Å and this is expanded by insertion of dodecylamine molecules to 26 Å.^{15,16} Cations can enter in the tunnel structure by cation exchange reaction after adsorption on the surface of manganese dioxide, while oxo anions such as molybdate and vanadate can only adsorb on the surface due to negative charge.¹⁷ Consequently, $[\text{AuCl}_{4-n}(\text{OH})_n]^-$ is considered unable to enter in the tunnel structure of the manganese dioxide by the same reason as the oxo anions. However, $[\text{AuCl}_{4-n}(\text{OH})_n]^-$ ions are reduced to Au atoms after adsorption

Fig. 5 Peak fitting analysis of ^{197}Au Mössbauer spectra for non-irradiated sample (a) and UV-irradiated sample (b) collected after 48 h in adsorption experiments shown in Fig. 2.

on the surface of manganese oxide particles. If Au atoms can transfer from the surface to deeper places through the tunnel structure due to their small size and electric neutrality, accumulation of Au(0) in the inside of manganese dioxide particles can be explained as follows.

Figures 6 and 7 show XPS spectra of Mn 2p and O 1s for manganese dioxide as an adsorbent, the UV-irradiated sample and the non-irradiated sample. For Mn 2p spectra, although a slight chemical shift occurred due to adsorption of Au(III) ions and UV irradiation, no remarkable change was observed. The O 1s spectra of manganese dioxide generally consist of three components: O^{2-} , OH^- (surface hydroxyl group) and H_2O . Although the peak intensity due to O^{2-} for the non-irradiated sample rather decreased compared with that for manganese dioxide, both spectra were similar, suggesting that OH^- content did not change even by adsorption of Au(III) ions. On the other hand, the peak intensity due to OH^- for the irradiated sample abruptly increased. According to the literature,^{12,18} the XPS relative peak intensity due to OH^- of manganese dioxide varies easily by dissolution and reaction with reagents. Consequently, the OH^- content was possible to increase by UV irradiation. In other words, the surface structure of manganese dioxide was probably changed by the UV irradiation. In Figs. 4 and 5, comparing both Au 4f XPS spectrum and ^{197}Au Mössbauer spectrum for the UV irradiated sample, the proportion of Au(0) in the ^{197}Au Mössbauer spectrum is considerably larger than that in the XPS spectrum (see Tables 1 and 2). This fact suggests that Au atoms may interpenetrate easily from the surface to deeper places through the tunnel structure due to the change in surface structure of manganese dioxide by UV irradiation. Due to the movement of Au atoms, Au(III) ions may be effectively reduced on the surface of manganese dioxide. As a result, the accumulation of Au(0) at deeper location inside of manganese dioxide might be promoted by the UV irradiation.

Fig. 6 Mn 2p XPS spectra for manganese dioxide (a), non-irradiated sample (b) and UV-irradiated sample (c).

Fig. 7 O 1s XPS spectra for manganese dioxide (a), non-irradiated sample (b) and UV-irradiated sample (c).

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