

Promoted Effect of UV Irradiation on the Oxidation of CO in the Presence of H₂ over Au Catalyst Supported on the Non-photoexcited Al₂O₃

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Catalytic oxidation of CO into CO₂ has long been of considerable technical interest for the purification of the air as well as the removal of CO impurities from H₂ streams in fuel cells.^{1–5} Oxide-supported Au nanoparticles exhibits a good performance for CO oxidation at a low temperature,⁶ but the supported Au catalyst presents a lower stability for CO oxidation. Moreover, the Au catalyst has also been studied for the CO oxidation in the presence of H₂.^{7–13} Although the presence of H₂ enhances the activity and stability of CO oxidation, the selectivity of CO oxidation in a H₂-rich stream is not high because of the oxidation of H₂ itself.^{14,15} Photocatalytic oxidation over TiO₂, as an alternative method to removing CO, has been concerned in the past decade.^{16,17} However, with a comparison to the thermocatalytic activity of the Au catalyst, this photocatalytic activity of TiO₂ is too low to be applied in many cases.

In our previous work, we have found adding UV irradiation over Au/TiO₂ (with a thermocatalytic activity) cannot only enhance the oxidation of CO but also promote the

preferential oxidation of CO in the presence of H₂ at a low temperature.^{18,19} We proposed that the increase of the electron density of the Au surface caused by the optical absorption of TiO₂ promotes the chemisorption of CO but suppresses that of H₂ at the Au surface, resulting in the promotion of preferential oxidation of CO in a H₂-rich stream. However, the selectivity of CO oxidation in the presence of H₂ over Au/TiO₂ under UV irradiation is still low.¹⁹ This is because the formation of surface oxygen vacancy sites (SOVs) at the TiO₂ surface (a reducible oxide) induced by UV irradiation also benefits the chemisorption of O₂ at the TiO₂ surface and then the oxidation of H₂ (especially in the absence of CO) over Au/TiO₂. As a comparison to the TiO₂ support, a non-reducible oxide support (non-photoexcited oxide, e.g., Al₂O₃) maybe decreases the adsorption of O₂ because of no change of the valence state of its metal ions. With the introduction of UV irradiation, some of the adsorbed O₂ at the surface of the non-photoexcited oxide only re-desorbs by accepting extra photo-energy, similar to the thermodesorption behavior of an adsorbed species with the increase of the temperature. This maybe leads to the decrease of the adsorption of O₂ at the support and then suppresses the oxidation of H₂. Herein, adding UV irradiation over a gold catalyst supported on a non-reducible support maybe promotes the preferential oxidation of CO in the presence of H₂.

In this present work, a Au/Al₂O₃ catalyst was prepared by the deposition–precipitation method (as seen in the Supporting Information 1). In this catalyst, 5–10 nm Au nanoparticles (2.0 wt %) with the dominant (111) surface plane were dispersed on the surface of γ -Al₂O₃ (as seen in parts a and b of the Supporting Information 2). However, this deposit of Au nanoparticles does not cause the apparent change of the textural properties (pore radius, pore volume, and specific surface area) of the Al₂O₃ support (as seen in part c of the Supporting Information 2). Catalytic oxidation of CO was conducted in a fixed-bed flow reaction system at atmospheric pressure using 200 mg of catalyst at a total flow rate of 100 mL min^{–1}. The Au/Al₂O₃ catalyst was loaded in the quartz-glass tube, which was surrounded by three fluorescent lamps (4 W, a broadband light with the main wavelength at 365 nm and a visible region). To test the activity of the catalyst under dark, the quartz-glass tube was enclosed with Al foils to shut down light irradiation. A more detailed testing procedure can be seen in the Supporting Information 3.

Table 1 shows the catalytic performances of Au/Al₂O₃ for oxidizing CO in different conditions. In the case of no UV irradiation, the oxidation of CO is increased with the increase

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Table 1. Catalytic Performances of Au/Al₂O₃ at 50 °C with or without UV Irradiation

H ₂ content (vol %) ^d	TOF of CO oxidation (h ⁻¹) ^a		TOF of H ₂ oxidation (h ⁻¹) ^b		selectivity of CO oxidation (%) ^c	
	no light	light	no light	light	no light	light
0	24.60	32.92				
0.5	30.41	39.72	2.26	2.10	93.1	94.9
1.0	33.67	40.54	3.70	3.64	90.1	91.8
2.0	36.00	42.30	10.00	8.66	78.2	86.0
85.0	38.12	38.94	30.28	28.03	55.7	58.1

^a TOF of CO oxidation is defined as the molecule number of CO to CO₂ over per Au atom per 1 h. ^b TOF of H₂ oxidation is defined as the molecule number of H₂ to H₂O over per Au atom per 1 h. ^c Selectivity of CO oxidation is defined as the ratio of O₂ consumption for the CO oxidation to the total O₂ consumption. ^d In all of the cases, the respective concentration of CO and O₂ is kept at 0.5 vol % in a balance He.

Table 2. TOF of H₂ Oxidation over Au/Al₂O₃ in the Absence of CO at 50 °C with or without UV Irradiation

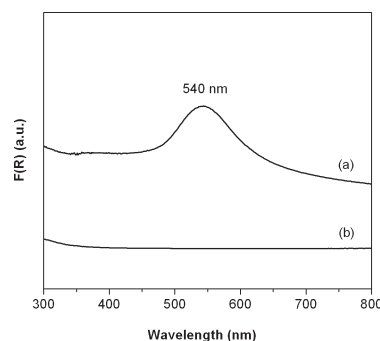
H ₂ content (vol %) ^a	TOF of H ₂ oxidation (h ⁻¹)	
	no light	light
0.5	2.50	1.85
1.0	8.12	7.42
2.0	17.42	16.41
85	72.90	71.77

^a In all of the cases, the concentration of O₂ is kept at 0.5 vol % in a balance He.

of H₂ content; e.g., the turnover frequency (TOF) of CO oxidation increases from 24.60 h⁻¹ in the absence of H₂ to 38.12 h⁻¹ in 85.0 vol % H₂ stream (the concentration of unconverted CO decreases from 3135.6 to 2111.2 ppm). This promoted oxidation of CO can be attributed to the formation of hydroxyl species induced by the oxidation of H₂.²⁰ However, the competitive oxidation of H₂ becomes stronger and stronger with the increase of the H₂ content, resulting in the decrease of the selectivity of CO oxidation over Au/Al₂O₃. Note that Au/Al₂O₃ exhibits a higher selectivity of oxidizing CO than Au/TiO₂ in the H₂-rich stream in our previous report (55.7% over Au/Al₂O₃ versus 35.6% over Au/TiO₂).¹⁹ With the introduction of UV irradiation, the oxidation of CO is promoted but that of H₂ is suppressed; i.e., UV irradiation promotes the preferential oxidation of CO in the presence of H₂ over Au/Al₂O₃. Moreover, UV irradiation also suppresses the oxidation of H₂ itself over Au/Al₂O₃ in the absence of CO (Table 2), contrary to that over Au/TiO₂ in our previous report.¹⁹

Considering the coexistence of CO, H₂, H₂O, and CO₂ during the reaction processes in the presence of H₂, a water–gas shift reaction (a feed stream containing 0.5 vol % CO and 0.2–0.5 vol % H₂O) and its reverse reaction (a feed stream containing 0.2–0.5 vol % CO₂ and 85 vol % H₂) over the prepared Au/Al₂O₃ were also tested at 50 °C with or without UV irradiation, respectively. However, no reaction is observed in all of the cases. This means that the low selectivity of CO oxidation does not arise from the reverse water–gas shift reaction in this case but is probably caused by the competition oxidation of H₂.

With respect to a low-temperature thermocatalytic oxidation of CO over Au nanoparticles deposited on metal oxides, it is generally proposed that there exists two active sites: One is CO adsorbed at Au nanoparticles, and another is O₂ (or its derivate species) adsorbed at the Au/oxide interface or oxide support.^{21,22} As for the oxidation of H₂ over Au/Al₂O₃, it is

**Figure 1.** UV–vis diffuse reflection spectra of (a) Au/Al₂O₃ and (b) Al₂O₃.

also proposed that the –OH species derived from the adsorbed oxygen reacts with the H species adsorbed at Au surface to form H₂O.²³ With this viewpoint, the promoted effect of UV irradiation on the preferential oxidation of CO may be attributed to the change of chemisorption behaviors of CO, H₂, and O₂ at Au/Al₂O₃. To demonstrate it, the chemisorption behaviors of CO, H₂, and O₂ at the Au/Al₂O₃ surface under UV irradiation were investigated via temperature-programmed desorption (TPD) testing (as seen in the Supporting Information 4). The TPD result shows that UV irradiation over Au/Al₂O₃ promotes the adsorption of CO at the Au surface but suppresses the adsorption of H₂ at the Au surface and that of O₂ at the Al₂O₃ surface. Therefore, the oxidation of CO over Au/Al₂O₃ is promoted by UV irradiation because of the increase of CO adsorption at the Au surface, while the oxidation of H₂ in the presence or absence of CO is suppressed by UV irradiation because of both the suppressed adsorption of H₂ at the Au surface and that of O₂ at the Al₂O₃ surface. However, the oxidation of H₂ in the absence of CO over Au/TiO₂ was promoted by UV irradiation because of the increased adsorption of O₂ at the TiO₂ surface in our previous study.¹⁹ This may be one reason that Au/Al₂O₃ exhibits a higher selectivity of oxidizing CO in the presence of H₂ than Au/TiO₂.

Note that the Al₂O₃ support is not photoexcited above 300 nm (Figure 1), this means that the above chemisorption change of reactants over Au/Al₂O₃ cannot be attributed to the optical absorption of the support. However, an optical absorption at 540 nm induced by the surface plasma resonance (SPR)^{24–26} of Au nanoparticles is observed in Figure 1.

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Because the SPR is a behavior of the oscillation of the conduction band of Au atoms, it can be acted as a process of electron transfer between two Au atoms ($2\text{Au} + h\nu \rightarrow \text{Au}^{\delta-} + \text{Au}^{\delta+}$) and then cause the increase of electron density at the Au surface. Considering that the adsorption of CO at the Au surface is associated with the electron density of the Au surface,^{27–30} the promoted adsorption of CO at the Au surface may be attributed to the increase of electron density of the Au surface induced by the SPR effect. However, this explanation needs to be further investigated and also needs to be confirmed by a visible light irradiation instead of UV irradiation.

This study indicates that UV light maybe promotes the preferential oxidation of CO in the presence of H₂ over a

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Au catalyst supported on the non-photoexcited oxide. A similar study about the Au nanoparticle catalysts dispersed on other non-photoexcited supports (e.g., SiO₂) is in progress. Moreover, to investigate the feasibility of UV light on the purification of H₂ steam in fuel cell systems, a further study about the behavior of UV light on the preferential oxidation of CO over Au catalysts also needs to be performed in a full reformat stream (including CO₂ and H₂O) with different reaction temperatures.

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Supporting Information Available: Preparation procedures, testing methods, and results of transmission electron microscopy (TEM), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), TPD, and catalytic performance. This material is available free of charge via the Internet at <http://pubs.acs.org>.