Available online at www.sciencedirect.com
ScienceDirect
Catalysis Today 122 (2007) 222–225
CATALYSIS TODAY
www.elsevier.com/locate/cattod

In situ measurements under flow condition of the CO oxidation over supported gold nanoparticles

M. Daté [a,*], H. Imai [a,1], S. Tsubota [a,2], M. Haruta [b]

[a] *Research Institute for Innovation in Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8569, Japan*
[b] *Faculty of Urban Environmental Sciences, Tokyo Metropolitan University, Hachioji 192-0397, Japan*

Abstract

In situ FT-IR measurements for Au/TiO_2 and Au/Al_2O_3 have been carried out under the flow condition of CO oxidation at atmospheric pressure. It has been found that the Au particles remain neutral (Au^0) in the presence of oxygen, while negatively charged particles ($Au^{\delta-}$) is formed in the absence of oxygen, as a result of the charge transfer from the oxygen vacancies. Moisture did not significantly affect the adsorption states of CO over Au/TiO_2 and Au/Al_2O_3. Enhancement of the CO_2 production by moisture was observed over Au/Al_2O_3, which is accompanied by the decomposition of carbonate-like species by moisture.

Keywords: Gold catalysts; Carbon monoxide oxidation; Infrared spectroscopy; *In situ* measurements; Oxide supports

1. Introduction

Low-temperature CO oxidation has been most intensively studied among the reactions catalysed by gold nanoparticles [1,2]. Importance of the reaction is not restricted to the practical usage of the gold catalysts, e.g., water-gas shift reaction, oxidative removal of CO in H_2 (PROX) [3], but also stimulates a number of fundamental studies [4,5]. In order to elucidate the mechanisms for the unique catalytic reaction, CO adsorption has been investigated both experimentally and theoretically [4,5]. There have been, however, few studies of measurements under the actual flow reaction conditions at atmospheric pressure. Here we report on the *in situ* measurements of CO oxidation over supported gold nanoparticles, paying attention to moisture effect in the reactant gas.

2. Experimental

Gold nanoparticles were supported on TiO_2 (P-25, provided by a courtesy of Nippon Aerosil, Co., Ltd.) and Al_2O_3 (reference catalyst JRC-ALO-7, The Catalysis Society of Japan) by the deposition–precipitation method [6]. Samples were calcined in air at 673 K for 4 h. Gold concentration in the starting solution of $HAuCl_4$ was 3.0 wt.%, whereas the actual Au loadings over TiO_2 and Al_2O_3 were determined to be 1.6 and 1.0 wt.%, respectively, by inductively coupled plasma (ICP). Mean diameters of Au calculated from the transmission electron micrographs (TEM) were 3.7 and 3.5 nm for Au/TiO_2 and Au/Al_2O_3, respectively.

In situ Fourier transform infrared (FT-IR) spectra were taken at room temperature by using Avatar 370 (Thermo Nicolet). All the spectra were taken at 300 K with the resolution of 4 cm^{-1} and averaged over 64 scans. Powder samples were set in a diffuse-reflection cell equipped with a gas flow system and heated at 523 K for 30 min in the mixture of O_2 and He prior to each measurement. Intensities in the spectra are represented by $-\log R$, where $R = R(\text{sample})/R(\text{standard})$ denotes the relative diffuse reflectance. After R(standard) was obtained by using KBr powder, catalyst samples were measured without any dilution. The reactant gas was $CO{:}O_2{:}He = 1.0{:}6.3{:}26.0$ or

---

* Corresponding author. Tel.: +81 29 861 8482; fax: +81 29 861 8482.
E-mail address: m-date@aist.go.jp (M. Daté).

[1] Present address: Graduate School of Environmental Science, Hokkaido University, Sapporo 060-0810, Japan.

[2] Present address: Collaboration Department, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda 563-8577, Japan.

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.01.032

CO:He = 1.0:32.3 ml/min, corresponding to 3 vol.% CO in 33 ml/min in the total flow, at atmospheric pressure. The sample cell was purged with O_2/He or He before the introduction of CO/O_2 or CO, respectively. Moisture was added into the reactant gas by using a water bubbler at 273 K, which gives the H_2O concentration of ~6000 ppm (0.6 vol.%).

3. Results and discussion

FT-IR spectra for Au/TiO_2 in the region of CO and CO_2 are shown in Fig. 1. Under the mixture flow of CO and O_2, a strong band for the gas-phase CO_2 was observed at 2349 cm^{-1} as a consequence of CO oxidation. CO_2 intensity was almost constant independent of the reaction time. CO band was observed at 2110 cm^{-1} (Fig. 1(a) and (c)) incorporated in the broad envelope of gas-phase CO, which is attributed to the adsorption on the neutral Au^0 [7,8]. In the absence of oxygen, CO_2 production was negligible and the band for CO adsorbed on Au^0 slightly red-shifted to 2100 cm^{-1}, as reported in the literature [9]. The band was dominant just after the introduction of CO, but gradually substituted by a new band at 2075 cm^{-1} as well as a broad band around ~2000 cm^{-1} (Fig. 1(b) and (d)). No band arising from the adsorbed CO was observed above 2150 cm^{-1} and the shoulder at 2120 cm^{-1} in Fig. 1(c) may be due to the P branch of gas-phase CO that has not been completely subtracted from the original spectrum.

It is said that the CO stretching band shifts to lower frequencies for the negatively charged Au clusters ($Au^{\delta-}$), whereas positively charged Au clusters ($Au^{\delta+}$) give higher frequencies [7]. Such changes in the frequency are explained by the back donation from Au clusters to the 2π* antibonding orbital of CO. For example, charge transfer from the colour centres (oxygen vacancies) of the MgO surface to the Au clusters enhanced the back donation, resulting in weakening of the C–O bond [7,10]. Therefore, it is considered that continuous exposure to CO gives rise to oxygen vacancies on the TiO_2 surface, which might cause the gradual charge transfer to the Au particles. Actually CO bands in the range of 1950–2050 cm^{-1} were observed for Au nanopartilcles supported on TiO_2 and Fe_2O_3, when the samples were reduced [8]. Complex feature below 2100 cm^{-1} in Fig. 1(b) and (d) indicates various charging of the $Au^{\delta-}$ particles, since the band shift reflects the magnitude in the charge transfer [10].

Yoon et al. [10] demonstrated that the activity for CO oxidation over Au_8 clusters on MgO is correlated not to Au^0 but to $Au^{\delta-}$. Under our experimental conditions, the CO species adsorbed on $Au^{\delta-}$ was observed only in the absence of oxygen and immediately disappeared by the introduction of O_2. This could suggest that CO–$Au^{\delta-}$ might be the intermediate species for CO oxidation over TiO_2. However, it took a few minutes to replace CO–Au^0 by CO–Au^- even after pretreatment of the sample in the pure He flow, which indicates that the CO–$Au^{\delta-}$ species cannot be produced during the CO oxidation but gradually formed on the reduced surface. Recently Henao et al. [9] showed that the CO species observed at 2090 cm^{-1} is responsible to CO oxidation and that the species at 2112 cm^{-1} is rather unreactive. We also observed similar behaviour of these species as reported in the literature: quick change in the frequency (within 1 min) from ~2100 to ~2110 cm^{-1}, when O_2 was added to the mixture of CO and He, and *vice versa*.

When moisture was added to the reactant gas, little change was recognised for CO_2 production as shown in Fig. 2(a). No substantial change in the CO_2 band was observed by adding moisture into CO/He. Although intensity of the bands for CO adsorption was decreased by the addition of moisture, neither new band nor drastic change was observed in the carbonyl region regardless of the presence of oxygen (Fig. 2(a) and (b)). This indicates that moisture does not significantly modify the

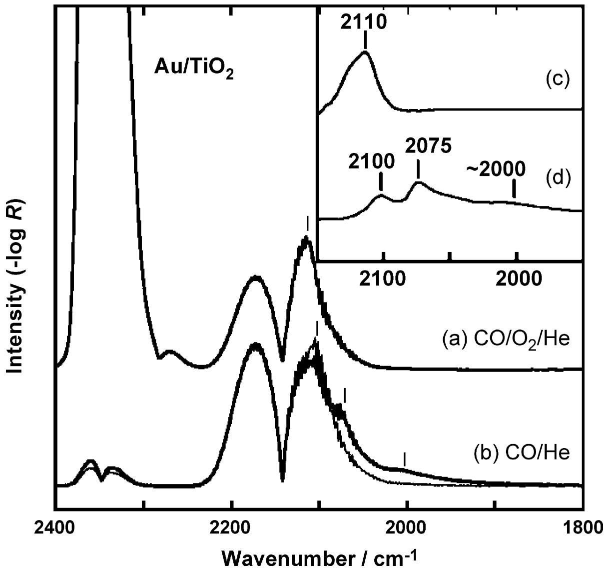

Fig. 1. FT-IR spectra for Au/TiO_2 under the flow of (a) CO/O_2/He and (b) CO/He. Spectra were taken after 20 min of flow, except for the thin line in spectra (b) (after 1 min). Insets (c) and (d): bands for gas-phase CO are subtracted from the spectra (a) and (b) (thick lines), respectively.

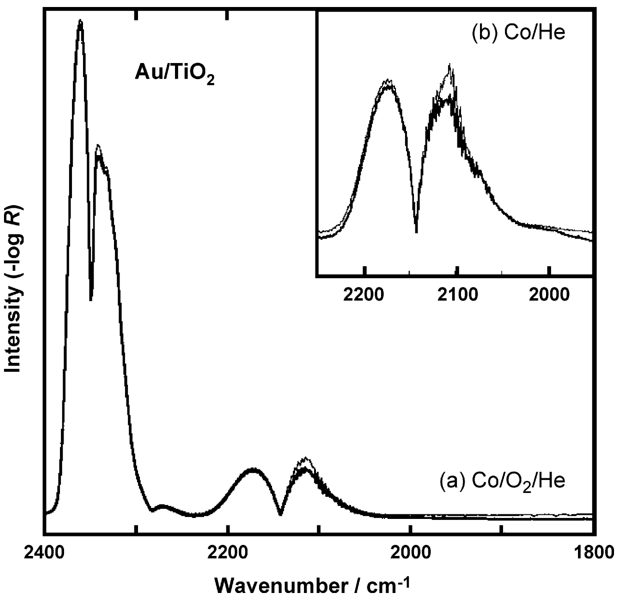

Fig. 2. FT-IR spectra for Au/TiO_2 under the flow of (a) CO/O_2/He and (b) CO/He. Spectra were taken after 10 min of flow without moisture (thin lines), then after additional 10 min of flow with moisture (thick lines).

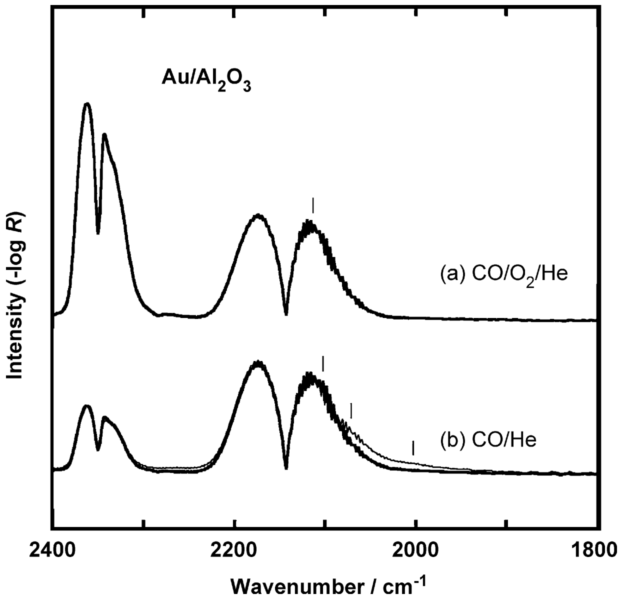

Fig. 3. FT-IR spectra for Au/Al_2O_3 under the flow of (a) $CO/O_2/He$ and (b) CO/He. Spectra were taken after 20 min of flow, except for the thin line in spectra (b) (after 60 min).

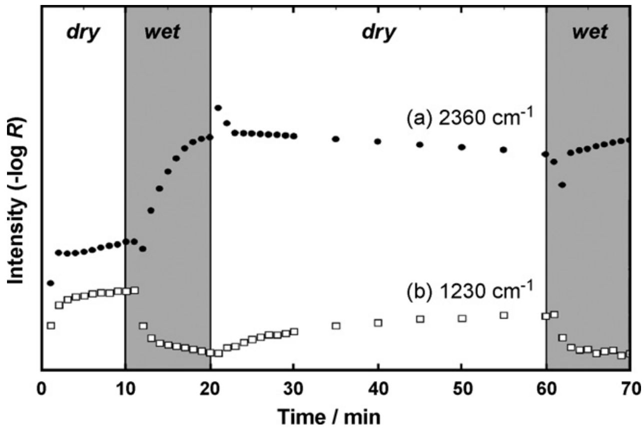

Fig. 5. Time dependence of the bands at (a) 2360 cm^{-1} and (b) 1230 cm^{-1} observed for Au/Al_2O_3 under the flow of $CO/O_2/He$. Moisture was added between 10 and 20 min, as well as 60–70 min. Intensities at 2360 and 1230 cm^{-1} were measured from the backgrounds at 2400 and 1240 cm^{-1}, respectively. The latter intensity was multiplied by 20. Because of non-flat background in the spectra, zero point of the *y*-axis in the graph does not corresponds to the zero intensity.

adsorption state of CO. Activity of the Au/TiO_2 catalyst, which exhibits full conversion to CO_2 below 273 K, may be too high to see the effect of moisture at 300 K.

In the carbonate region, Henao et al. reported the band at 1242 cm^{-1} and assigned to the possible intermediate hydroxycarbonyl [9]. We observed the band at 1250 cm^{-1} under the steady flow of $CO/O_2/He$, as well as just after the exposure to CO/He (data not shown). Absence of the band on TiO_2 under the flow of CO_2 indicates that this species is not directly formed from the produced CO_2 over Au/TiO_2. The band, however, disappeared by the addition of moisture.

Fig. 3 shows the spectra for the CO adsorption over Au/Al_2O_3. Similar bands as for Au/TiO_2 were observed, but the band intensities for Au/Al_2O_3 were lower than those for Au/TiO_2. It took longer for the transition of CO band at 2100 cm^{-1} to those at 2075 and ~2000 cm^{-1} (Fig. 3(b)). CO_2 production was smaller than that over Au/TiO_2 and gradually decreased by the reaction time, which is consistent with our previous results obtained with a fixed-bed flow reactor [11].

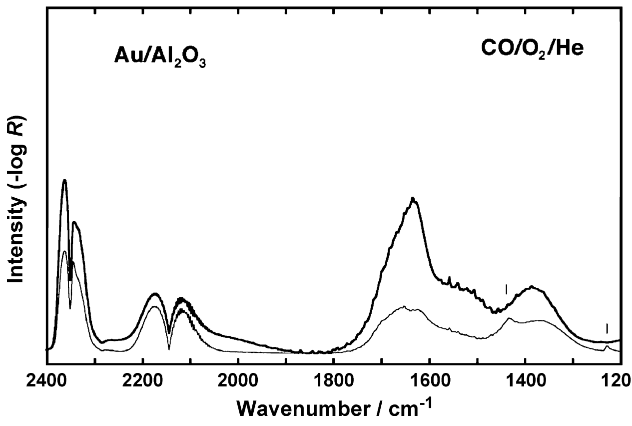

Fig. 4. FT-IR spectra for Au/Al_2O_3 under the flow of $CO/O_2/He$. Spectra were taken after 10 min of flow without moisture (thin line), then after additional 10 min of flow with moisture (thick line).

Production of CO_2 was enhanced by moisture as seen in Fig. 4. CO bands did not seem to significantly change by the addition of moisture, though they are superimposed on the broad envelope of H_2O adsorbed on the Al_2O_3 surface [12]. It is noted that two bands at 1435 and 1230 cm^{-1} in the carbonate region disappeared rapidly by the introduction of moisture, while their intensities gradually restored after the moisture supply stopped. These bands were also observed when Al_2O_3 was exposed to CO_2, indicating that they originate from the CO_2 produced by the reaction over Au/Al_2O_3. Fig. 5 shows time-on-stream change of the band intensity at 1230 cm^{-1}, together with that at 2360 cm^{-1} (CO_2 production). The correlation might be mainly explained by the accumulation of the carbonate-like species near the active sites, which can be decomposed by the addition of moisture.

In the previous article, we reported that moisture enhanced the activities of Au/TiO_2 and Au/Al_2O_3 for CO oxidation without significant change in the reaction mechanisms [11]. Based on the experimental results, a reaction mechanism model was proposed, where moisture plays two roles. One is decomposition of the carbonate species accumulated during the reaction at the perimeter interface between Au nanoparticles and oxide support. Because the carbonate species blocks the active sites, its removal results in enhancement of the steady-state activity, as well as in regeneration of the deactivated catalysts. This effect of moisture is remarkable for the gold catalysts with high initial activity, such as Au/TiO_2 and Au/Al_2O_3. The other is activation of oxygen: probably dissociation of O_2 molecules. This greatly contributes to the CO oxidation over Au/SiO_2, since the support does not have an ability to activate oxygen. It can be said that the results reported here are consistent with the model, although the activity enhancement by moisture was not observed for Au/TiO_2 in this study because of the high initial activity corresponding to the full conversion of CO.

4. Conclusions

From the results of the *in situ* FT-IR measurements for Au/TiO_2 and Au/Al_2O_3, it has been found that the adsorption state of CO on the Au nanoparticles is gradually changed from CO–Au^0 to CO–Au^δ under the flow of CO/He. This can be explained by on the oxide surface, which are produced by the exposure to CO without oxygen, to the Au nanoparticles. Addition of moisture did not significantly change the adsorption states of CO. Production of CO_2 over Au/TiO_2 was stable and not affected by moisture under the current experimental conditions, whereas that over Au/Al_2O_3 gradually decreased and recovered by moisture. Amount of the carbonate-like species accumulated during the reaction on Au/Al_2O_3 were reduced by the addition of moisture, which seemed to correlate with the enhancement of CO oxidation.

References

[1] G.C. Bond, D.T. Thompson, Gold Bull. 33 (2000) 41.
[2] H.H. Kung, M.C. Kung, C.K. Costello, J. Catal. 216 (2003) 425.
[3] C.W. Corti, R.J. Holliday, D.T. Thompson, Appl. Catal. A: Gen. 291 (2005) 253.
[4] R. Meyer, C. Lemire, Sh.K. Shaikhutdinov, H.-J. Freund, Gold Bull. 37 (2004) 72.
[5] P. Pyykkö, Angew. Chem. Int. Ed. 43 (2004) 4412.
[6] S. Tsubota, D.A.H. Cunningham, Y. Bando, M. Haruta, et al. in: G. Poncelet (Ed.), Preparation of Catalysts, vol. VI, Elsevier, Amsterdam, 1995, p. 227.
[7] M. Sterrer, M. Yulikov, E. Fischbach, M. Heyde, H.-P. Rust, G. Pacchioni, T. Risse, H.-J. Freund, Angew Chem. Int. Ed. 45 (2006) 2630.
[8] F. Boccuzzi, A. Chiorino, M. Manzoli, D. Andreeva, T. Tabakova, J. Catal. 188 (1999) 176.
[9] J.D. Henao, T. Caputo, J.H. Yang, M.C. Kung, H.H. Kung, J. Phys. Chem. B 110 (2006) 8689.
[10] B. Yoon, H. Häkkinen, U. Landman, A.S. Wörz, J.-M. Antonietti, S. Abbet, K. Judai, U. Heiz, Science 307 (2005) 403.
[11] M. Daté, M. Okumura, S. Tsubota, M. Haruta, Angew Chem. Int. Ed. 43 (2004) 2129.
[12] J.M. Roscoe, J.P.D. Abbatt, J. Phys. Chem. A 109 (2005) 9028.