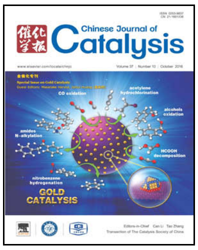
Chinese Journal of Catalysis 37 (2016) 1651–1655

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/chnjc



Communication (Special Issue on Gold Catalysis)

Correlation between catalytic activity of supported gold catalysts for carbon monoxide oxidation and metal–oxygen binding energy of the support metal oxides

Takashi Fujita, Masanori Horikawa, Takashi Takei, Toru Murayama, Masatake Haruta *

Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

A R T I C L E I N F O

Article history:
Received 20 May 2016
Accepted 4 August 2016
Published 5 October 2016

Keywords:
Metal oxide-supported gold nanoparticle catalyst
Support effects
Carbon monoxide oxidation
Volcano-like correlation
Metal–oxygen binding energy

A B S T R A C T

The effect of a wide variety of metal oxide (MO_x) supports has been discussed for CO oxidation on nanoparticulate gold catalysts. By using typical co-precipitation and deposition–precipitation methods and under identical calcination conditions, supported gold catalysts were prepared on a wide variety of MO_x supports, and the temperature for 50% conversion was measured to qualitatively evaluate the catalytic activities of these simple MO_x and supported Au catalysts. Furthermore, the difference in these temperatures for the simple MO_x compared to the supported Au catalysts is plotted against the metal–oxygen binding energies of the support MO_x. A clear volcano-like correlation between the temperature difference and the metal–oxygen binding energies is observed. This correlation suggests that the use of MO_x with appropriate metal–oxygen binding energies (300–500 kJ/atom O) greatly improves the catalytic activity of MO_x by the deposition of Au NPs.

Metal oxide (MO_x)-supported Au nanoparticle (NP) catalysts (Au/MO_x) have great potential for environmental purification and green sustainable chemical processes because a lot of Au/MO_x are active at room temperature, unlike supported palladium or platinum catalysts [1,2]. However, the origin of the unique catalytic activity of Au/MO_x remains unclear because of the complexity of the various physicochemical parameters affecting its catalytic activity. This lack of understanding limits the applications prospects of this promising catalyst.

To simplify this complexity, many researchers have used CO oxidation as a model reaction because of simple reaction stoichiometry. According to their reports, the physicochemical parameters affecting the catalytic activity are the size of the Au NPs, the interaction between the Au NPs and MO_x, and the nature of MO_x. Among these parameters, the size of the Au NPs [3,4] and the Au NPs–MO_x interaction [5,6] have been relatively well-discussed because they can be tuned by the choice of preparation method and calcination conditions. Specifically, to achieve high CO oxidation activity, the Au NPs should be smaller than 5 nm and strongly attached to the appropriate MO_x. In contrast, the effect of the MO_x support on the catalytic activity of Au/MO_x is not yet inadequately understood because of the difficulty in systematically comparing a wide variety of MO_x. This difficulty can be attributed to two causes. First, in previous studies, a variety of different preparation procedures have been used to obtain Au/MO_x catalysts to compare. Because the preparation procedures strongly affect the catalytic activity, this hampers a simple comparison of the contributions of MO_x to each Au/MO_x catalyst. Therefore, to enable a systematic comparison, Au catalysts supported on a wide variety of MO_x should be prepared using the same preparation method under the same calcination conditions. Co-precipitation and deposi-

---

* Corresponding author. Tel/Fax: +81-42-677-2852; E-mail: haruta-masatake@tmu.ac.jp

DOI: 10.1016/S1872-2067(16)62521-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 0, October 2016

tion–precipitation [7] are good candidates because both methods are very common and can easily provide the above mentioned highly active Au/MO$_x$ catalysts in most cases.

Second, there is limited understanding of the parameters of MO$_x$ that affect the catalytic activity of Au/MO$_x$. Some researchers have explored the relevance of various parameters of MO$_x$ such as its reducibility [8,9] and oxygen storage capacity [10]. However, there is no general consensus about which parameters affect the catalytic activity, hindering systematic comparisons between different MO$_x$ supports. Therefore, a new parameter of MO$_x$ should be proposed to allow us to conduct such a comparison.

Previously, we proposed that oxygen molecules are activated at the perimeter interface between Au NPs and MO$_x$ and that the formation of active sites may be related to the presence of oxygen vacancies in the perimeter region [1]. This proposition is strongly supported by several studies investigating Au/TiO$_2$. First, Widmann et al. [11] reported that lattice oxygen at the perimeter interface of Au/TiO$_2$ is easily desorbed in CO atmosphere. Maeda et al. [12] observed oxygen vacancies at the Au/TiO$_2$ interface during CO oxidation. Based on these findings, it is reasonable to suggest that the onset of catalytic activity in Au/MO$_x$ depends critically on the desorption of the lattice oxygen at the perimeter interface induced by the deposition of Au NPs on MO$_x$. On the other hand, Saavedra et al. [13] have reported the results of theoretical calculations that oxygen vacancies are not involved in CO oxidation.

In this communication, we aim to provide new insight into the nature of MO$_x$ in Au/MO$_x$ systems and to improve their application capability. We prepared Au catalysts supported on a wide variety of MO$_x$ by using co-precipitation and deposition–precipitation techniques under the same calcination conditions. To isolate the contribution of MO$_x$, we measured and compared the catalytic activities of MO$_x$ and Au/MO$_x$ for CO oxidation and then discussed the catalytic improvement effect by depositing Au NPs on MO$_x$. To enable a systematic comparison, we introduced the metal–oxygen bonding energy of MO$_x$ ($E_{\text{M–O}}$) as an indicator of the ease of lattice oxygen desorption, assuming that $E_{\text{M–O}}$ is related to the catalytic activity enhancement induced by the deposition of Au NPs on MO$_x$. This hypothesis was inspired by Balandin volcano plots which reflect the Sabatier principle, which states the reaction kinetics can be correlated with thermodynamic properties of heterogeneous catalysts [14].

For this investigation, a variety of MO$_x$ (M: Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Ru, Rh, Pd, Ag, In, La, Ce, Ir, Pt, and Bi) was choosen. This series, which includes most MO$_x$, excludes SiO$_2$, VO$_x$, MoO$_x$, and WO$_x$. SiO$_2$ was excluded because its catalytic activity is too low to be measured, while VO$_x$, MoO$_x$, and WO$_x$ were excluded because of the technical difficulties faced when attempting to deposit Au NPs.

First, Au NPs supported on various MO$_x$ (Au/MO$_x$, M: Al, Cr, Fe, Co, Ni, Cu, Zn, Zr, Ru, Rh, Pd, Ag, In, La, Ce, Ir, Pt, and Bi) with Au/M atomic ratios of 1/19 (Au loading: 6–12 wt%) were prepared by co-precipitation [7]. To prepare every Au/MO$_x$ except for Au/Ag$_2$O and Au/Bi$_2$O$_3$, 200 mL of a HAuCl$_4$ (1 mmol) aqueous solution was first added to an aqueous solution of M(NO$_3$)$_x$ or MCl$_x$ (19 mmol) and stirred at 343 K. In the preparation of Au/Ag$_2$O, Au(OH)$_3$ (1 mmol) was used as a Au precursor instead of HAuCl$_4$, and in the preparation of Au/Bi$_2$O$_3$, Bi(NO$_3$)$_3$·5H$_2$O was dissolved in an aqueous solution of nitric acid (pH = 1) to avoid hydrolysis to form basic salt such as Bi(OH)$_2$·NO$_3$ or (BiO)$_2$(OH)NO$_3$. Next, each mixture was poured into an aqueous solution of Na$_2$CO$_3$ (0.12 mol/L, 200 mL) under vigorous stirring at 343 K, except in the case of Au/Bi$_2$O$_3$. For Au/Bi$_2$O$_3$, the Na$_2$CO$_3$ aqueous solution was substituted by a NaOH aqueous solution (1 mol/L), and the NaOH aqueous solution was then added until the precipitate was completely formed. All of the precipitates were aged at 343 K for 1 h and then washed with distilled water (313 K) until the pH of a supernatant stabilized. The filtrated precipitates were dried at 353 K overnight and then calcined at 573 K for 4 h in air (20 vol% O$_2$ in N$_2$; oxidative atmosphere). The MO$_x$ catalysts without gold were also prepared by the same procedure without the addition of the Au precursors.

Au/Nb$_2$O$_5$ was prepared by hydrothermal synthesis [15] at a Au/Nb atomic ratio of 1/19. NH$_4$(NbO(C$_2$O$_4$)$_2$(H$_2$O)$_2$)(H$_2$O)$_3$ (Nb: 6 mmol) and Au(en)$_2$Cl$_3$ (Au: 6/19 mmol) were added to 40 mL of water under stirring. The mixture was placed in a Teflon-lined cylindrical autoclave and then heated at 448 K for 24 h in air. The solid residue was filtered, washed with water, dried at 353 K, and then calcined at 573 K for 4 h in air. Au/Nb$_2$O$_5$ was also prepared by deposition-precipitation [7], and calcined at 573 K for 4 h in air. Au(en)$_2$Cl$_3$ was used as a Au precursor. The gold loading of this catalyst was 1 wt%. Nb$_2$O$_5$ was prepared by the same procedure without the addition of the Au precursor.

Some supported Au catalysts (Au/MO$_x$, M: Al, Ti, Mn, Fe, Zr, and Ce) were provided by Haruta Gold Inc. These catalysts were prepared by deposition–precipitation and had been calcined at 573 K for 4 h in air before receipt. The gold loadings of these catalysts were 1 wt%. TiO$_2$ (Degussa, P25) and MnO$_2$ were purchased from Nippon Aerosil and Chuo Denki, respectively. All the catalysts (prepared and provided) were passed through 120-mesh sieves and pretreated at 523 K for 1 h in air before catalytic activity measurements and characterization.

Catalytic activity measurements for CO oxidation were carried out using a U-shaped glass fixed-bed flow reactor. The mass of the catalyst was 150 mg, and the reaction temperature ranged from 173 to 700 K. The reactant gas (1% CO in air) was passed through the catalytic bed at a rate of 50 mL/min using a mass flow controller (hourly space velocity of 20000 h^{-1} mL g$_{\text{cat}}^{-1}$). The compositions of the effluent gases were determined by gas chromatography (Ohkura Riken model-802 and Shimadzu GC-8A). The moisture content of the reactant gas was monitored by a dew-point meter (Air Liquid DPO-6) and was controlled in the range from 50 to 200 ppm. X-ray diffraction (XRD) patterns were recorded with a diffractometer (Rigaku RINT-TTR III) using a Cu K_α radiation operating at 50 kV and 300 mA over the 2θ range of 10° to 70°.

Fig. 1(a) shows the correlation between the $T_{1/2}$ values (the temperature for 50% conversion of CO in CO oxidation) of simple MO$_x$ and its standard heat of formation per oxygen atom ($-\Delta H_f^0$). $T_{1/2}$ was measured in a stream of 1 vol% CO in air un-