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

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ABSTRACT

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.

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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-

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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/TiO₂. First, Widmann et al. [11] reported that lattice oxygen at the perimeter interface of Au/TiO₂ is easily desorbed in CO atmosphere. Maeda et al. [12] observed oxygen vacancies at the Au/TiO₂ 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_{M-O}) as an indicator of the ease of lattice oxygen desorption, assuming that E_{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 chosen. This series, which includes most MO_x, excludes SiO₂, VO_x, MoO_x, and WO_x. SiO₂ 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/Ag₂O and Au/Bi₂O₃, 200 mL of a HAuCl₄ (1 mmol) aqueous solution was first added to an aqueous solution of

M(NO₃)_x or MCl_x (19 mmol) and stirred at 343 K. In the preparation of Au/Ag₂O, Au(OH)₃ (1 mmol) was used as a Au precursor instead of HAuCl₄, and in the preparation of Au/Bi₂O₃, Bi(NO₃)₃·5H₂O was dissolved in an aqueous solution of nitric acid (pH = 1) to avoid hydrolysis to form basic salt such as Bi(OH)₂NO₃ or (BiO)₂(OH)NO₃. Next, each mixture was poured into an aqueous solution of Na₂CO₃ (0.12 mol/L, 200 mL) under vigorous stirring at 343 K, except in the case of Au/Bi₂O₃. For Au/Bi₂O₃, the Na₂CO₃ 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% O₂ in N₂; oxidative atmosphere). The MO_x catalysts without gold were also prepared by the same procedure without the addition of the Au precursors.

Au/Nb₂O₅ was prepared by hydrothermal synthesis [15] at a Au/Nb atomic ratio of 1/19. NH₄(NbO(C₂O₄)₂(H₂O)₂)(H₂O)₃ (Nb: 6 mmol) and Au(en)₂Cl₃ (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/Nb₂O₅ was also prepared by deposition–precipitation [7], and calcined at 573 K for 4 h in air. Au(en)₂Cl₃ was used as a Au precursor. The gold loading of this catalyst was 1 wt%. Nb₂O₅ 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%. TiO₂ (Degussa, P25) and MnO₂ 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_{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 ($-\Delta H_f^\circ$). $T_{1/2}$ was measured in a stream of 1 vol% CO in air un-

Fig. 1. (a) Correlation between the CO oxidation activities of MO_x and $-\Delta H_f^\circ$ per atom oxygen. $T_{1/2}$ is the temperature for 50% conversion of CO. *The temperature required for 7% CO conversion on Nb_2O_5 is depicted. (b) Correlation between the CO oxidation activities of Au/MO_x and $-\Delta H_f^\circ$ per atom oxygen. Black triangles: prepared by co-precipitation. Au/M atomic ratios were 1/19 (Au loading: 6–12 wt%). Blue triangles: prepared by deposition-precipitation. Au loading: 1 wt%. The catalysts were calcined at 573 K for 4 h in air and then pretreated at 523 K for 1 h in a stream of 20% O_2 in N_2 before catalytic activity measurements. Inset: magnification of the plot for $T_{1/2}$ values from 200 to 450 K. Reaction conditions: catalyst 150 mg, reactant gas 1 vol% CO in air, flow rate 50 mL/min, SV 20000 h^{-1} mL g^{-1} , moisture content 50–200 ppm.

der a space velocity of 20000 h^{-1} mL g^{-1} . This parameter enables us to compare the catalytic activities of MO_x with widely varying reaction rates. $-\Delta H_f^\circ$ is often used to represent $E_{\text{M-O}}$ [16]. Because the $T_{1/2}$ of Nb_2O_5 could not be measured in this experiment due to its low catalytic activity, the temperature required for 7% CO conversion on Nb_2O_5 is depicted in Fig. 1(a). MO_x with $-\Delta H_f^\circ$ values below 220 kJ/atom O exhibited relatively high catalytic activities, except for Bi_2O_3 , and there was no clear dependence of $T_{1/2}$ on $-\Delta H_f^\circ$. Conversely, beyond 220 kJ, a V-shaped correlation between $T_{1/2}$ and $-\Delta H_f^\circ$ was observed. The catalytic activities decreased with increasing $-\Delta H_f^\circ$ from 220 to 470 kJ/atom O and increased with an increase in $-\Delta H_f^\circ$ above 470 kJ/atom O.

CO oxidation on certain simple MO_x supports at elevated temperature is often explained by the Mars–van Krevelen mechanism [17]. According to this mechanism, lattice oxygens in the MO_x are consumed in the oxidation reaction. Therefore, we assume that the $-\Delta H_f^\circ$ values of MO_x are related to the catalytic activities of the simple MO_x for CO oxidation. According to the Sabatier principle [14], volcano dependency is often obtained when plotting the catalytic activity for CO oxidation on simple MO_x versus ΔH_f° . From this view point, the $-\Delta H_f^\circ$ dependency shown in Fig. 1 can be regarded as a volcano curve as a top of Co_3O_4 , although Al_2O_3 , CeO_2 , and La_2O_3 deviate upward from this curve. In the left side of Co_3O_4 , incorporation of oxygen was dominant compared to release of oxygen. Therefore, a lot of oxygen vacancies may be formed under reaction condition in the lower $-\Delta H_f^\circ$ region, although we cannot show a direct evidence for amount of oxygen vacancies. Because oxygen vacancies play an important role for oxygen activation [1,10,11], we considered that these MO_x showed relatively higher catalytic activity. On the other hand, in the right side of Co_3O_4 , release of oxygen was dominant compared to incorporation of oxygen. In this condition, oxygen vacancies may be not formed very much compared to the MO_x with lower $-\Delta H_f^\circ$.

From this reason, we considered that the catalytic activities were decreased with an increase in $-\Delta H_f^\circ$. However, only this consideration cannot explain why Al_2O_3 , CeO_2 , and La_2O_3 deviate from the curve.

Fig. 1(b) shows the correlation between $T_{1/2}$ and $-\Delta H_f^\circ$ for Au/MO_x . These Au/MO_x catalysts were prepared by three different preparation methods: co-precipitation (CP, black triangles), deposition-precipitation (DP, blue triangles), and hydrothermal synthesis (HT, black triangles for $\text{Au}/\text{Nb}_2\text{O}_5$). All Au/MO_x were calcined at 573 K, which is the same calcination condition used for simple MO_x . The Au/MO_x prepared by CP (Au loading: 6–12 wt%) were characterized by XRD, and we confirmed that the Au species were deposited as NPs ranging from 4.2 to 10 nm in diameter on MO_x using the Scherrer equation from a XRD peak attributable to Au crystal plane (200), except for Au/PtO_2 (the peak was not observed) and $\text{Au}/\text{Nb}_2\text{O}_5$ (66 nm). The Au/MO_x prepared by DP (Au loading: 1 wt%) has been characterized before receipt, and the Au species were deposited as NPs ranging from 1.8 to 4.5 nm in diameter on MO_x using a transmission electron microscope (TEM). In these experiments, the difference in the $T_{1/2}$ values between the two preparation methods (CP and DP) was 100 K at a maximum. Fujitani et al. [18] revealed that the reaction rate on Au/TiO_2 was proportional to the perimeter length (below 320 K) between Au NPs and MO_x or surface area of Au NPs (above 320 K). We estimated the total perimeter lengths of Au/MO_x prepared by both CP and DP ($\text{Au}/\text{Fe}_2\text{O}_3$ and Au/CeO_2) from loading amount of Au and mean diameter of Au NPs. As a result, the total perimeter lengths of these catalysts were comparable. Thus, we can conclude that the preparation methods do not strongly affect the correlation between $T_{1/2}$ and $-\Delta H_f^\circ$, and comparison of the CP and DP results is reasonable under these experimental conditions. Moreover, we also estimated the total perimeter lengths of some Au/MO_x (M: CuO , Co_3O_4 , Fe_2O_3 , ZnO , and CeO_2). Although total perimeter lengths of Au/CeO_2 were

about quarter as long as that of other Au/MO_x, the total perimeter lengths of these catalysts were almost comparable. Therefore, we considered that the result roughly reflects support effects of MO_x.

Except for the case of Au/Bi₂O₃, the $T_{1/2}$ values of Au/MO_x were within the range of 200 to 450 K. In this range (Fig. 1(b), inset), a volcano-like tendency with the Au/Co₃O₄ at the top was observed, except in the cases of Au/Cr₂O₃ and Au/Nb₂O₅. The results of Au/Cr₂O₃, Au/Nb₂O₅, and Au/Bi₂O₃ deviate from this volcano-like tendency. Notably, Cr₂O₃, Nb₂O₅, and Bi₂O₃ are acidic MO_x, and the deposition of Au NPs on acidic MO_x using a wet process is very difficult technically. Therefore, these catalysts may include very large Au NPs, or the interaction between Au NPs and MO_x may be very weak. In the future, optimization of the preparation methods for these acidic MO_x is necessary.

Comparison of Fig. 1(a) with Fig. 1(b) indicates that the catalytic activities of Au NPs supported on noble MO_x are similar to those of noble MO_x alone. In contrast, the deposition of gold on base MO_x markedly enhanced CO oxidation. Gold catalysts supported on base metal oxides exhibit high catalytic activities for CO oxidation. Our result is thus in good agreement with previous reports. These results suggest that the catalytic improvement induced by deposition of Au NPs is strongly dependent on the type of MO_x used.

To discuss the catalytic improvement, we focus on the difference ($\Delta T_{1/2}$) between $T_{1/2}$ (MO_x) and $T_{1/2}$ (Au/MO_x) as an index of the effect. Fig. 2 shows the correlation between $\Delta T_{1/2}$ and $-\Delta H_f^\circ$. The $\Delta T_{1/2}$ values of noble MO_x were almost zero, whereas those of base MO_x were positive. This result indicates that catalytically inert simple MO_x were dramatically improved by deposition of Au NPs. Moreover, these values of base MO_x showed a clear volcano-like tendency, with TiO₂ having the highest $\Delta T_{1/2}$. According to the above-mentioned discussion about Fig. 1(a), this improvement may be due to formation of oxygen vacancies by deposition of Au NPs.

Fig. 2. Correlation between $\Delta T_{1/2}$ and M–O bond energy per molar oxygen atom. $\Delta T_{1/2}$ is the difference between the $T_{1/2}$ values of Au/MO_x and MO_x. Black triangles: Au/MO_x were prepared by co-precipitation. Blue triangles: Au/MO_x were prepared by deposition-precipitation. *The temperatures required for 7% CO conversion on Nb₂O₅ were used instead of $T_{1/2}$ values of Nb₂O₅.

Based on these results, the MO_x can be preliminary classified by $-\Delta H_f^\circ$ as follows. First, the MO_x with lower $-\Delta H_f^\circ$ values are listed ($-\Delta H_f^\circ < 150$ kJ/atom O): Ag₂O, PtO₂, PdO, Rh₂O₃, IrO₂, and RuO₂. These MO_x do not effectively improve the catalytic activity for CO oxidation by Au NPs deposition, because these noble MO_x have very low E_{M-O} . This result may be due to the slow incorporation of oxygen from the gas phase to oxygen vacancies. Moreover, we considered that formation of oxygen vacancies by Au NPs deposition may be not effective because lattice oxygens in noble MO_x intrinsically can desorb easily. Second, the MO_x with middle $-\Delta H_f^\circ$ values are listed ($-\Delta H_f^\circ = 150$ –500 kJ/atom O): CuO, Co₃O₄, NiO, MnO₂, Fe₂O₃, In₂O₃, ZnO, Cr₂O₃, Nb₂O₅ and TiO₂. These MO_x are effective supports for Au/MO_x, and their effectiveness increases linearly with $-\Delta H_f^\circ$. Consequently, TiO₂ is the most effective for improving the catalytic activity for CO oxidation by Au NPs deposition. This may mean oxygen vacancies effectively form in these MO_x by Au NPs deposition. Moreover, ZnO, Cr₂O₃, and Nb₂O₅ may have great potential for improving the catalytic activity by optimization of the preparation method and pretreatment conditions. Third, the MO_x with higher $-\Delta H_f^\circ$ values are listed ($-\Delta H_f^\circ > 500$ kJ/atom O): CeO₂, ZrO₂, Al₂O₃, and La₂O₃. These MO_x are also effective, but their effectiveness decreases linearly with increasing $-\Delta H_f^\circ$. Bi₂O₃ cannot be classified by $-\Delta H_f^\circ$ because of its low $\Delta T_{1/2}$ value (–10 K).

Moreover, some MO_x have unique characteristics. For example, TiO₂, ZnO, and ZrO₂ have relatively high oxygen storage capacities. Widmann et al. [9] proposed that the oxygen storage capacity of MO_x was correlated with the catalytic activity of Au/MO_x for CO oxidation, demonstrating this correlation for four MO_x: Au/TiO₂>Au/ZrO₂>Au/ZnO>Au/Al₂O₃. This ordering is also evident in our results for the improvement effect (Fig. 2). In addition, Cr₂O₃, Nb₂O₅, and Bi₂O₃ are classified in acidic MO_x, whereas La₂O₃ is classified as basic MO_x. The acid–base properties of MO_x may be related to their catalytic activities. However, it is difficult to make this comparison in this study due to the lack of basic MO_x among the investigated catalysts.

To the best of our knowledge, our work provides the first nearly comprehensive comparison of Au/MO_x catalysts featuring a wide variety of MO_x. To perform a systematic comparison, we attempted to standardize the preparation procedure for Au/MO_x as much as possible and introduced E_{M-O} (represented by $-\Delta H_f^\circ$) as a parameter of MO_x. A clear volcano-like correlation was observed between $\Delta T_{1/2}$ and $-\Delta H_f^\circ$, which suggests that the selection of MO_x with appropriate $-\Delta H_f^\circ$ (300–500 kJ/atom O) greatly improves the catalytic activity induced by the deposition of Au NPs. Furthermore, this clear correlation implies that E_{M-O} is a good candidate in terms of MO_x parameters that affect the catalytic activity of Au/MO_x, and such thermodynamic parameters are useful for a primary selection of catalyst candidates. The results of this study are expected to improve the application prospects of these catalysts, and we hope that the present systematic comparison will become a technique of choice in future investigations of MO_x in Au/MO_x catalysts. Moreover, this systematic work is expected to give a useful policy to design appropriate mixed metal oxides as new support materials for dispersed Au NPs.

Graphical Abstract

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

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The effects of a wide variety of metal oxide supports in Au catalysts on CO oxidation were evaluated. Clear volcano-like correlation between the effectiveness and the metal–oxygen binding energies was observed.

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负载金催化剂上CO氧化反应活性与金属氧化物载体中金属-氧结合能之间的关系

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摘要: 讨论了金属氧化物载体(MO_x)对其负载纳米金催化剂(Au/MO_x)上CO氧化反应的影响。采用典型的共沉淀法和沉积-沉淀法在完全相同的焙烧条件下制备了一系列MO_x负载金催化剂, 以CO氧化转化50%时的反应温度(T_{1/2})定量评价了MO_x载体和Au/MO_x催化剂的催化活性。进一步将MO_x载体与相应Au/MO_x催化剂的T_{1/2}值之差对MO_x载体的金属-氧结合能做曲线进行关联, 发现二者呈明显的火山型关系。这一结果表明, 采用具有适当金属-氧结合能(300–500 atom O)的MO_x可大大提高沉积于其上的Au纳米颗粒的催化活性。

关键词: 金属氧化物负载金纳米粒子催化剂; 载体效应; 一氧化碳氧化; 火山型关系; 金属-氧结合能

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