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An examination of active sites on Au-Ag bimetallic catalysts based on CO oxidation over Au/Ag₂O and a comparison to Ag-contaminated Au powder

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ABSTRACT

There are two theories regarding the origin of the remarkable synergistic effect observed in Au-Ag bimetallic catalysts when applied to various oxidative reactions. One is based on the importance of the contact interfaces between AgO_x regions and the surface of the bulk Au as active working sites, while the other holds that charge transfer from Ag to Au in a surface Au-Ag alloy causes the catalytic activity. One key point in examining these theories and determining the origin of the synergy involves determining whether or not Ag exists as an oxide or as a metallic alloy on the Au surface. To confirm that enhanced activity results from contact between Ag₂O and Au nanoparticles (NPs), a comparative study of catalytic CO oxidation over Au/Ag₂O and Ag₂O was performed in the present work, using a closed recirculation reaction system. A reaction mixture consisting of a stoichiometric composition of CO and O₂ (CO/O₂ = 2/1) was supplied to both catalysts and the resulting pressure decrease rates were tracked, from which the amounts of gas consumed as well as the quantity of CO₂ produced were determined. The steady state reactions of both Au/Ag₂O and Ag₂O did not lead to any meaningful difference in the rate of pressure decrease during the oxidation. The pressure decrease over both catalysts was attributed to the reduction of surface lattice O on Ag₂O by CO. The results obtained for Au/Ag₂O are in good agreement with previous data resulting from the use of Ag-contaminated Au powder (Ag/Au-b) having an oxidized surfaces. This finding suggests that the perimeters between AgO_x zones and the bulk Au surface may not function as active sites during CO oxidation. A review of previous results obtained with Ag/Au-b specimens having so-called steady state surfaces indicates that AgO_x species in such materials are reduced to the 0 state to form a Ag-Au alloy that provides the active sites.

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1. Introduction

Recently, Au-Ag bimetallic catalysts have attracted growing attention because of the remarkable synergistic effects exhib-

ited by these material during various oxidative reactions, such as CO oxidation over a Au-Ag alloy catalyst supported on mesoporous aluminosilicate [1–4], the liquid phase aerobic oxidation of glucose by PVP-protected Ag_{core}/Au_{shell} bimetallic nano-

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particles (NPs) [5], and the oxidative coupling of CH_3OH or CO oxidation by nanoporous gold synthesized by the selective leaching of silver from a Au-Ag alloy in HNO_3 [6–9].

Zhang et al. [5] has proposed that the synergistic effect demonstrated by Au-Ag bimetallic catalysts can be attributed to charge transfer from Ag to Au, similar to that which occurs between Pd and Au in Au-Pd bimetallic nanoparticles having a “crown jewel” structure that are highly active during the aerobic oxidation of glucose [10]. Conversely, Liu et al. [11] have suggested that, because Ag interacts much more strongly with O_2 than with Au, the boundaries between Au and AgO_x zones (generated during pretreatment with O_2 or under oxidative reaction conditions) play a key role in promoting the oxidative catalytic activity. Evidence for this theory is found in the case of $\text{TiO}_2/\text{Au}(111)$ [12], $\text{Fe}_2\text{O}_3/\text{Au}(111)$ [13] and $\text{CeO}_{2-x}/\text{Au}$ films [14]. From these discussions, it is evident that determining whether Ag exists as an oxide or in the form of a metallic alloy on the surface of the Au may be the key to obtaining additional insights into the origin of the synergistic effect in Au-Ag bimetallic catalysts.

Iizuka et al. [15] previously measured the activity for CO oxidation of seven samples of unsupported Au powder synthesized by evaporating high purity metallic Au (> 99.99%) under an inert gas. The surfaces of these samples had been purposely contaminated with various trace amounts of Ag (such that these specimens are hereafter referred to Ag/Au powder) using a closed recirculation reaction system. They calculated the k_{CO_2} values (that is, the rate constant for CO oxidation per unit surface area) of these samples and plotted these values against the surface atomic concentrations of Ag to determine the extent to which surface Ag atoms take part in the oxidation. A strong correlation between k_{CO_2} and the Ag surface concentration was found [15]. Since these Ag/Au powders were processed under 1 atm of circulating oxygen at temperatures between 423 and 453 K before exhibiting any activity for CO oxidation, it is believed that their catalytic activity resulted from the so-called “contact interface effect” between Au and AgO_x in the surface layer [15].

Thereafter, Iizuka et al. [16] studied the CO oxidation mechanism, using a representative active sample of Ag/Au powder: Ag/Au-b, with a BET specific surface area of $1.89 \text{ m}^2/\text{g}$, a bulk Ag content determined by inductively coupled plasma (ICP) of 0.110 wt%, and a surface Ag content determined by X-ray photoelectron spectroscopy (XPS) of 10.8 atomic%. Kinetic measurements, including catalytic CO oxidation over Ag/Au-b and the reduction and/or the oxidation of the sample surface by CO and/or O_2 were also performed at low pressures. Prior to these low pressure reaction rate measurements, the Ag/Au-b was subjected to one of two pretreatments, as follows.

(1) Reaction with a stoichiometric mixture of CO and O_2 at an initial pressure of 5.3 kPa at 313 K for 1 h, followed by exposure to a vacuum of approximately 1.3×10^{-3} Pa, denoted as Ag/Au having steady state surfaces.

(2) Oxidation of the above Ag/Au in circulating O_2 at 13.3 kPa and 393 K for 2 h, followed by cooling to room temperature and subsequent exposure to a vacuum of approximately 1.3×10^{-3} Pa at 313 K, denoted as Ag/Au having oxidized surfaces.

In these trials, the reactor was loaded with 1.89 g of Ag/Au-b and the amount of surface Ag estimated from the BET surface area and the XPS Ag atomic content, assuming that the Ag atoms were present solely on the upper surface layer, was $8.92 \mu\text{mol}$. This amount corresponds to $198 \mu\text{L}$ of an ideal gas at standard temperature and pressure, and to a pressure of 25.5 Pa based on the pressure of CO in the reactor. During each test, the pressure decrease accompanying the catalytic CO oxidation or the reduction and/or oxidation of the catalyst surface was compared with the amount of CO_2 produced [16]. The kinetic behavior of the Ag/Au-b with the steady state surface indicated that the CO oxidation proceeded via the coadsorption of CO and O_2 to form $(\text{CO}_3)^*$ followed by the decomposition of this species, promoted by interactions with CO and O_2 , to produce CO_2 at the contact interface between surface Ag and the Au support [16].

In trials in which 17 Pa CO was introduced to the Ag/Au-b having oxidized surfaces at 313 K for 60 min, the CO pressure decreased rapidly over the initial 7 min while the pressure dropped below 4 Pa. Following this phase, the CO pressure fell more slowly for the remaining 53 min of the trial while the pressure continued to decrease to 1.5 Pa. The initial pressure decrease of 13 Pa corresponded to one half of the amount of the surface Ag of the sample ($4.5 \mu\text{mol}$). In this same test, $5.4 \mu\text{mol}$ of CO were consumed and $5.6 \mu\text{mol}$ of CO_2 were produced. The initial rapid decrease in the CO pressure and the production of CO_2 corresponding to the amount of CO consumed suggested the presence of reactive O species on the surfaces of the Ag/Au-b having oxidized surfaces prior to CO exposure. The fact that the amount of CO_2 produced was close to half the quantity of surface Ag further indicated that reactive O species may be adsorbed on the surface Ag atoms at a ratio of about 1 to 2 [16].

In other experiments, a reaction mixture of CO and O_2 with the composition $\text{CO}/\text{O}_2 = 2/1$ at an initial pressure of approximately 11 Pa was introduced twice in succession to a sample of Ag/Au-b having oxidized surfaces. In this case, only the reduction of reactive adsorbed O with the CO in the reaction mixture to produce CO_2 proceeded during the first dose of the reaction mixture, without incorporation of the O_2 in the gas phase. The participation of the O_2 in the CO_2 production process, as well as its incorporation into the catalyst surface, was found to begin gradually as the reduction of reactive adsorbed O on the Ag proceeded during exposure to the second dose [16]. This result indicated that AgO_x species tended not to be present as Ag_2O in the reaction mixture on the surface of Au [16].

On the basis of the above work, the present study prepared a material composed of a Au catalyst supported on Ag_2O to confirm the activity enhancement as a result of the contact between Ag_2O and the Au surface, using a deposition-precipitation method. This paper describes the CO oxidation activity of this Au/ Ag_2O catalyst as determined using a closed recirculation reaction system, and compares this activity to that of Ag_2O . In the second part of this report, the kinetic behavior of Au/ Ag_2O for CO oxidation is compared with that of the above-mentioned Ag/Au-b having oxidized surfaces. Finally, the kinetic behavior of Ag/Au-b having steady state surfaces

during CO oxidation as well as the structure and composition of active sites that tend to enhance the catalytic activity of this material are discussed [17].

2. Experimental

2.1. Catalyst preparation

Silver oxide (Ag_2O , Wako special grade, 99.9% purity, 0.93 m^2/g) purchased from Wako Pure Chemicals Industries, Ltd. was used both as a catalyst and as a support for Au NPs. $\text{Au}/\text{Ag}_2\text{O}$ was prepared using a deposition-precipitation method in which the Ag_2O powder is suspended in a HAuCl_4 solution adjusted to pH = 8 and heated at 343 K. The nominal Au loading in these specimens was 0.90 wt%. Changes in the Au concentration in the suspension were followed by colorimetry, employing a SnCl_2 solution as a reducing reagent to form a Au colloid. Soon after adding the support, the concentration of Au was confirmed to drop to below the detection limit of the colorimetric assay, after which the suspension was stirred for 1 h at the same temperature. The mixture was subsequently decanted to separate the precipitate from the supernatant and the precipitate was washed with deionized water several times then heated in air overnight at 393 K. The $\text{Ag}/\text{Au-b}$ powder reexamined in the present work was synthesized by evaporating high purity metallic Au (> 99.99%) in an inert gas, as described in previous publications [15,16].

2.2. Catalyst pretreatment and activity measurements

A closed recirculation reaction system constructed of glass (base pressure of 1.3×10^{-3} Pa) previously used for the kinetic study of CO oxidation over $\text{Ag}/\text{Au-b}$ powder was also used in the present investigation of CO oxidation over $\text{Au}/\text{Ag}_2\text{O}$ and Ag_2O [16]. The details of this system and the associated experimental procedures are described elsewhere [16]. The pretreatment conditions and the procedures used in the present kinetics measurements for $\text{Au}/\text{Ag}_2\text{O}$ and Ag_2O were also the same as those employed for the kinetic study performed with $\text{Ag}/\text{Au-b}$ powder. Briefly, the sample in the reactor was heated under vacuum at 453 K for 1 h and then pretreated under 1 atm of circulating O_2 for 3 h, then cooled to room temperature.

After removing O_2 from the reaction vessel, already at the reaction temperature, a reaction mixture of CO and O_2 ($\text{CO}/\text{O}_2 = 2/1$) at an initial pressure of approximately 4.0 kPa was introduced into the circulation line (the volume of which was known) and the resulting CO_2 was condensed in a trap cooled by liquid nitrogen. In this manner, the reaction rate was derived from the decrease in the total pressure. A typical reaction rate trial ran for 60 min, following which the remaining reaction mixture was completely removed from the circulation lines. The amount of reaction mixture consumed was calculated from the pressure decrease and the CO_2 collected in the trap was evaporated at 195 K to determine the amount volumetrically.

When low pressure rate measurements were performed in the case of $\text{Ag}/\text{Au-b}$, the reaction system was changed from

circulatory to static. The pressure changes accompanying catalytic CO oxidation over $\text{Ag}/\text{Au-b}$ or the reduction and/or the oxidation of $\text{Ag}/\text{Au-b}$ with CO and/or O_2 were followed using a capacitance type manometer (MKS Instrument Inc., Baratron 627B) [16].

2.3. Characterization

After completing the kinetics trials with the recirculation apparatus, the $\text{Au}/\text{Ag}_2\text{O}$ was subjected to a series of characterizations, with the results listed in Table 1. The specific surface areas of the catalyst samples were determined in a static adsorption apparatus constructed of glass, using the BET method with N_2 as the adsorbate at liquid nitrogen temperature. The bulk Au content of the $\text{Au}/\text{Ag}_2\text{O}$ was determined by spectrochemical emission analysis combined with ICP (Shimadzu Techno-Research, Inc., ICPS-8000). The mean particle diameters of the Au NPs were found to be 4.4 ± 2.9 nm based on the analysis of 24 particles in a transmission electron microscope (TEM) image of Au NPs supported on Ag_2O (JEOL, JEM-2010/SP). The chemical state of the Au on the surface of the $\text{Au}/\text{Ag}_2\text{O}$ was ascertained by XPS (JEOL, JPS-9010MC/SP), using the $\text{Mg } K_{\alpha}$ line at 1365 eV as the X-ray source. The Au $4f_{7/2}$ binding energy was determined to be 84.1 eV after calibration relative to the C 1s peak at 284 eV. Comparing this value with those reported in the literature [18,19], we concluded that the Au had been reduced to Au^0 on the Ag_2O support.

The results of a series of characterizations of the $\text{Ag}/\text{Au-b}$ powder and some physico-chemical properties calculated based on the results of these data are summarized in Table 1 of ref. [16].

3. Results and discussion

3.1. The pressure decrease of a stoichiometric reaction mixture of CO and O_2 over $\text{Au}/\text{Ag}_2\text{O}$ and Ag_2O

Fig. 1 presents first order plots of the pressure decrease of the reaction mixture of CO and O_2 introduced over $\text{Au}/\text{Ag}_2\text{O}$ or Ag_2O at room temperature. Both catalysts were pretreated under 1 atm of circulating oxygen at 423 K prior to acquiring these data. The plot for Ag_2O is seen to be relatively linear, while the $\text{Au}/\text{Ag}_2\text{O}$ data exhibit a higher slope compared with that of Ag_2O over the initial 20 min, followed by a break to a lower slope approximately equal to that of the Ag_2O . The initial higher slope of the $\text{Au}/\text{Ag}_2\text{O}$ data is attributed to the Au NPs

Table 1
(a) Characterization of $\text{Au}/\text{Ag}_2\text{O}$.

BET specific surface area (m^2/g)	Au loading (wt%)	Mean particle size of Au NPs (nm)	Au $4f_{7/2}$ binding energy (eV)
0.93	0.66	4.4	84.1

(b) Binding energy (eV) of Au $4f_{7/2}$ according to Refs.

Au^0	Au^+	Au^{3+}	Ref.
83.8	85.6	87.5	[18]
83.9	86.3	87.7	[19]

Fig. 1. First order plots of the pressure decreases of reaction mixtures ($\text{CO}/\text{O}_2 = 2/1$) over $\text{Au}/\text{Ag}_2\text{O}$ (1.51 g) or Ag_2O (2.00 g) at room temperature. The Ag_2O data has been normalized to the mass of $\text{Au}/\text{Ag}_2\text{O}$.

dispersed on the Ag_2O .

The amounts of reaction mixture consumed and CO_2 produced after exposure of the reaction mixture to the $\text{Au}/\text{Ag}_2\text{O}$ and Ag_2O for 1 h are presented in Table 2 together with the expected amounts of CO_2 calculated on the assumption that the mixture was consumed according to the reaction $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$.

These data show that the amounts of CO_2 generated by both the $\text{Au}/\text{Ag}_2\text{O}$ and Ag_2O are in good agreement with the amounts of reaction mixture consumed but do not agree as well with the expected CO_2 quantities calculated according to the catalyzed oxidation reaction equation. This result clearly indicates that the pressure decreases observed in Fig. 1 was not a result of catalytic oxidation but rather the reduction of Ag_2O by CO in the reaction mixture, over both the $\text{Au}/\text{Ag}_2\text{O}$ and Ag_2O . That is, oxidation to restore the reduced Ag_2O via the incorporation of O_2 did not proceed under the O_2 pressure in the mixture of CO and O_2 having a stoichiometric composition. It is worth noting that the initial higher slopes seen in the first order plots of the $\text{Au}/\text{Ag}_2\text{O}$ data could be reproduced only when the catalyst was reprocessed under 1 atm of circulating oxygen at room temperature.

We subsequently exposed both $\text{Au}/\text{Ag}_2\text{O}$ and Ag_2O to pure

Fig. 2. First order plots of the pressure decreases of pure CO and of a reaction mixture with the composition $\text{CO}/\text{O}_2 = 2/1$ over $\text{Au}/\text{Ag}_2\text{O}$ (1.74 g) or Ag_2O (1.54 g) at room temperature. The Ag_2O data has been normalized to the mass of $\text{Au}/\text{Ag}_2\text{O}$.

CO using almost the same initial pressure to that of the reaction mixture, and compared the resulting CO decrease rates with that of CO in the reaction mixture. The results are shown in Fig. 2, and Table 2 also presents the amounts of CO consumed and CO_2 produced in these trials. The quantities of CO consumed are in good agreement with the CO_2 generation over both the $\text{Au}/\text{Ag}_2\text{O}$ and Ag_2O . It is notable that, in Fig. 2, the slope of the first order plot for the decrease in CO pressure over $\text{Au}/\text{Ag}_2\text{O}$ is much higher than that generated by Ag_2O . That is, the reduction rate of the $\text{Au}/\text{Ag}_2\text{O}$ in contact with pure CO was almost six times that of the Ag_2O , at least over the initial 20 min. This clearly shows the remarkable ability of the Au NPs to promote the reduction of the surface of the Ag_2O support. It is likely that CO molecules adsorbed on the Au NPs migrate to the Ag_2O support surface and then create oxygen vacancies according to the Eq. (1).

A similar promotional effect of Au NPs on the reduction of the lattice O of a support oxide has also been reported for the catalytic oxidation of CO over Au/TiO_2 based on assessments using *in situ* electrical conductance measurement [20].

Fig. 2 demonstrates that the rates of reduction over both

Table 2

The amounts of reaction mixture consumed, and theoretical and actual quantities of CO_2 generated over $\text{Au}/\text{Ag}_2\text{O}$, Ag_2O , $\text{Ag}/\text{Au-b}$ having oxidized surfaces and $\text{Ag}/\text{Au-b}$ having steady state surfaces.

Sample	Reacting gas ^a	Amount of the reaction mixture consumed (μmol)	Calculated amount of CO_2 ^b (μmol)	Amount of CO_2 produced (μmol)	Pretreatment conditions
$\text{Au}/\text{Ag}_2\text{O}$	$\text{CO}/\text{O}_2 = 2/1$	92.8	61.9	90.3	423 K, O_2 , 1 h
	CO	558	—	554	423 K, O_2 , 1 h
Ag_2O	$\text{CO}/\text{O}_2 = 2/1$	79.6	53.1	74.8	423 K, O_2 , 1 h
	CO	490	—	505	423 K, O_2 , 1 h
$\text{Ag}/\text{Au-b}$ having the oxidized surfaces ^c	CO	5.4	—	5.6	393 K, O_2 , 1 h
	$\text{CO}/\text{O}_2 = 2/1$	2.23	1.49	2.56	393 K, O_2 , 1 h
	$\text{CO}/\text{O}_2 = 2/1$	2.44	1.63	2.19	313 K, $\text{CO}/\text{O}_2 = 2/1$, 1 h
$\text{Ag}/\text{Au-b}$ having the steady state surfaces ^c	CO	0.54	—	0.79	313 K, $\text{CO}/\text{O}_2 = 2/1$, 1 h
	O_2	0.0	—	0.21	313 K, $\text{CO}/\text{O}_2 = 2/1$, 1 h

^a Reaction times were 1 h, not including the 2 h reduction of Ag_2O by CO.

^b The amounts of CO_2 were calculated on the assumption that the reaction mixture was consumed according to $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$.

^c The reaction was performed at 313 K for 1 h.

Au/Ag₂O and Ag₂O under pure CO are much faster than those obtained when exposed to the CO in the reaction mixture. One possibility is that the reduction of the surface lattice O of the Ag₂O by CO is significantly hindered by the presence of O₂ in the gas phase, such that the promotional effect of the Au NPs on the reduction of Au/Ag₂O is counteracted. In this case, O₂ molecules interfere with the reduction of surface lattice O by CO, as expressed by Eq. (1).

Next the reduction process of Ag₂O in both the Au/Ag₂O and pure Ag₂O samples by CO in the reaction mixture was investigated by oxidizing samples in circulating oxygen at 1 atm and 423 K to restore them to their initial oxidized states. The reaction mixture was subsequently introduced to the Au/Ag₂O or Ag₂O at temperatures between 253 and 313 K to examine the effect of temperature on the rate of reduction by CO in the reaction mixture. The rate constants for the reduction of Au/Ag₂O and Ag₂O by CO in the reaction mixture, k_{CO} , were calculated from the rates of pressure decrease. In the case of the Au/Ag₂O, the rate was determined after the slope break (Fig. 1). Fig. 3 presents Arrhenius plots of k_{CO} , in which the plots of the Au/Ag₂O and Ag₂O data are seen to coincide and to have almost the same slope. Since the Au NPs supported on the Ag₂O do not affect the value of k_{CO} nor the slope of the Arrhenius plot, the reduction of the surface lattice O of these materials by CO in the presence of gaseous O₂ presumably occurs on the Ag₂O surface apart from the interface with the Au NPs, and must be controlled by some process in which O₂ molecules retard the creation of O vacancies.

It is worth noting here some results that were obtained by simple calculations employing the experimental results presented in Fig. 1. These calculations were based on a model in which hemispherical Au NPs with a mean particle diameter of 4.4 nm are dispersed on the Ag₂O surface. These results were as follows.

- (1) A total of 2.4 μmol of oxide ions were present at the interfaces between Au NPs and Ag₂O.
- (2) A total of 36.5 μmol of lattice oxide ions were present on the surface monolayer of the Au/Ag₂O.
- (3) A total of 48.6 μmol of lattice oxide ions were present on

the surface monolayer of the Ag₂O.

- (4) A total of 62 μmol of the reaction mixture (equivalent to the amount of CO) was consumed before the inflection in the Au/Ag₂O plot.

From the above, we can make the following conclusions.

- (1) The reduction of lattice O on the Au/Ag₂O by the CO in the reaction mixture prior to the inflection point far exceeded the amount available at the interfaces around Au NPs and evidently proceeded to the second subsurface layer.
- (2) Au NPs appear to promote the reduction of Au/Ag₂O by CO in the reaction mixture only in the case of oxide ions on or very near to the upper surface layer and do not affect the reduction of subsurface layers.

The reduction of Ag₂O by CO in the reaction mixture proceeded at the same rate observed in the case of the Au/Ag₂O after the inflection point seen in Fig. 1. The results presented in Table 2 show that O vacancies were generated in proportion to the progress of the reduction and remained on or near the upper surface layer of the Ag₂O. In the absence of O₂, both the reduction rate of the Ag₂O and the amount of CO₂ generated were approximately 8.4 times greater than those obtained when using CO in the reaction mixture, as can be seen from the results for the reduction of Ag₂O by pure CO in Fig. 2 and Table 2. It is clear that the presence of O₂ in the reaction mixture retards the rate at which O vacancies are produced by the reduction of lattice oxide ions by CO on or near the upper surface layer of the Ag₂O where the O vacancies remain.

Catalytic CO oxidation over many reducible metal oxides can be explained by the Mars-van Krevelen mechanism, in which lattice oxide ions are reduced by CO to produce CO₂ molecules, and the O vacancies thus formed are replenished by the dissociative adsorption of O₂. In other versions, the adsorption of O₂ occurs at O vacancies adjacent to lattice oxide ions. In the case of Ag₂O, however, adsorbed O₂ cannot dissociate and oxidize O vacancies. The fact that the presence of O₂ remarkably retards the rate of the production of O vacancies indicates that the adsorption of O₂ at O vacancies is much stronger than the adsorption of CO on adjacent lattice oxide ions, and inhibits the reduction of the oxide ions by CO to produce CO₂ and oxygen vacancies [21].

3.2. The origin of the synergistic effect of Au-Ag bimetallic catalysts during CO oxidation and a review of the study on Ag-contaminated Au powder

Here it is helpful to reconsider the origin of the synergistic effect exhibited by Au-Ag bimetallic catalysts for CO oxidation, based on the experimental results obtained with Au/Ag₂O and a review of work performed previously with Ag/Au-b [16].

3.2.1. Comparison of the experimental results for Au/Ag₂O with those for Ag/Au-b having oxidized surfaces

Some experimental results obtained with Ag/Au having oxidized surfaces have already been described briefly in the Introduction, and Table 2 summarizes these data for comparison with the results obtained from Au/Ag₂O [16].

The interaction of CO at 17 Pa, which corresponds to 67% of

Fig. 3. Arrhenius plots of k_{CO} (the rate constant for the reduction of surface lattice O by CO in a reaction mixture of CO and O₂ with a composition of CO/O₂ = 2/1) for Au/Ag₂O and Ag₂O.

the total amount of surface Ag, with Ag/Au having oxidized surfaces at 313 K for 60 min was found to result in a rapid decrease in the CO pressure over an initial period of 7 min, with a continued gradual decrease up to 60 min [16]. Likewise, in the case of the reduction of Au/Ag₂O and Ag₂O by CO, the amount of CO consumed was in good agreement with the quantity of CO₂ produced (Table 2).

The initial rapid decrease in the CO pressure ceases at approximately the point at which the pressure change corresponds to one half of the amount of surface Ag atoms. Judging from this result, it can be proposed that Ag species on the surface of the Au powder must be oxidized to be nearly all in the +1 state following the pretreatment under 1 atm circulating oxygen at 393 K for 1 h, and that almost all of these Ag species can be reduced to the 0 state by CO at an initial pressure of 17 Pa at 313 K. Judging from the experimental results showing that the reduction rate of Au/Ag₂O by CO is about six times that of Ag₂O (Fig. 2), the reduction of AgO_x species on Ag/Au having oxidized surfaces by CO is evidently greatly enhanced by the presence of the bulk Au substrate.

Table 2 also shows the amounts of reaction mixture consumed and CO₂ produced in the experiment during which a reaction mixture with an initial pressure of 11 Pa was introduced successively to Ag/Au-b having oxidized surfaces at 313 K for 60 min [16]. It can be seen that the total amount of CO contained in the reaction mixture over the two exposures (14.7 Pa) was somewhat greater than half the amount of Ag on the surface of the Au powder (13 Pa, see Introduction) [16]. During the first exposure, the pressure of the reaction mixture decreased rapidly over the initial 10 min, although this decrease ceased after 30 min [16]. The amount of CO₂ produced (2.56 μ mol) was somewhat larger than the amount of reaction mixture consumed (2.23 μ mol, Table 2). If the consumption of the reaction mixture had been solely a result of catalytic oxidation with O₂, the amount of CO₂ produced should have been 1.49 μ mol, equal to two-thirds of the reaction mixture consumed (Table 2). This result indicates clearly that only the reduction of reactive O species on the Ag/Au-b having oxidized surfaces by reaction with the CO in the reaction mixture proceeded, without any incorporation of the O₂ in the gas phase. Therefore, almost half the reactive O species on the Ag/Au-b having oxidized surfaces were removed as CO₂ in the first exposure [16].

Throughout the second exposure, the pressure of the reaction mixture decreased more slowly compared with the first exposure, and continued to decrease until 60 min [16]. Table 2 gives the amount of reaction mixture consumed in the second exposure (2.44 μ mol), which again almost coincided with the amount of CO₂ produced (2.19 μ mol). Although the amount of CO₂ generated was much greater than two-thirds of the reaction mixture consumed (1.63 μ mol), this amount was somewhat less than the quantity of reaction mixture consumed. This result differs from those obtained in the first exposure, indicating that gaseous O₂ was incorporated into the CO₂ production process due to the catalytic oxidation reaction of CO and O₂ [16]. Accordingly, a significant proportion of the CO₂ production during the second exposure was still a result of the reduction of O species in the AgO_x initially formed on the Ag/Au-b

having oxidized surfaces via reaction with CO in the reaction mixture. However, the catalytic oxidation between CO and O₂ began to contribute to the CO₂ production process at those surfaces where the majority of the reactive O species had been removed by reaction with CO [16].

Comparing the kinetic results obtained using Au/Ag₂O with those generated by the Ag/Au having oxidized surfaces described above, it can be seen that both catalysts exhibit similar behavior in conjunction with the reaction mixture. That is, only the reduction of O species by CO proceeds, without incorporation of O₂ in the gas phase to restore the active O sites. As such, the reduced AgO_x species cannot dissociate adsorbed O₂ molecules. This might be ascribed to the very weak bond strength between Ag and O, which is the lowest among all the metal oxides, including Fe₂O₃, TiO₂ and CeO₂ [22]. With regard to the origin of the synergistic effect shown by Au-Ag bimetallic catalysts, the possibility that the perimeters between AgO_x regions and the bulk Au surface function as important active sites during CO oxidation appears unlikely.

3.2.2. Active sites related to the synergistic effect based on a review of data for Ag/Au-b having steady state surfaces

Let us review here the experimental results reported for Ag/Au-b having steady state surfaces [16]. The steady state surfaces of Ag/Au-b were supplied by catalytic oxidation using a stoichiometric reaction mixture of CO and O₂ with an initial pressure of 5.3 kPa at 313 K for 1 h, followed by exposure to a vacuum of approximately 1.3×10^{-3} Pa [16]. It is worth to note that the amount of CO₂ produced while establishing the steady state surface was calculated to be 32 times greater than the number of surface Ag atoms and is in good agreement with two-thirds of the amount of the reaction mixture consumed [16]. The Ag/Au-b having steady state surfaces was subsequently exposed to CO and/or O₂ at an initial pressure of 11 Pa [16], and Table 2 presents the amounts of CO and/or O₂ consumed and of CO₂ produced during the exposure to CO and/or O₂.

In the case of CO exposure, the first order plot of the pressure decrease data tends to overlap with the data for the catalytic CO oxidation with O₂ over the initial 20 min [16]. However, the CO pressure decrease almost ceases after the slope break at 20 min. The amount of CO consumed during the initial 20 min was 0.41 μ mol, equivalent to 4.6% of the surface Ag, suggesting that only a small fraction of these surface Ag atoms participated in the catalytic oxidation of CO with O₂ [16]. The total amount of CO consumed after the exposure for 60 min was 0.54 μ mol, whereas the amount of CO₂ produced was found to be 0.79 μ mol, which is 46% greater than the amount of CO consumed (Table 2) [16]. In contrast, the O₂ pressure did not decrease at all during the 60 min trial, although 0.21 μ mol of CO₂ was produced [16]. Several observations can be made here. First, the CO pressure decreased at the same rate as that of a reaction mixture of CO and O₂ until the pressure decrease reached a value corresponding to 4.6% of the surface Ag atoms. Second, the amount of CO₂ produced during CO exposure was 46% greater than the amount of CO consumed. Last, the O₂ exposure generated a small amount of CO₂ without exhibiting a decrease

in pressure. On this basis, a mechanism has been proposed for CO oxidation with O_2 at the steady state surfaces of Ag/Au-b, in which the reaction proceeds at the interfaces between surface Ag and the Au support by repeated co-adsorption of CO and O_2 to form COO_2 , followed by decomposition due to interactions with CO and/or O_2 to yield CO_2 [16]. It should be noted that, in this mechanism, the bond dissociation of O_2 molecules is effected through the formation and decomposition of the COO_2 complex.

It is evident from the data in Table 2 that both the amounts of CO consumed and of CO_2 produced in the experiment using 11 Pa of CO and the Ag/Au-b having steady state surfaces were approximately 10% of the amounts obtained in the trial using CO at the same pressure in conjunction with Ag/Au-b having oxidized surfaces. Furthermore, according to the proposed reaction mechanism, the production of CO_2 by CO exposure over the Ag/Au-b having steady state surfaces can be assumed to have resulted from decomposition of COO_2 intermediates. Accordingly, we can state that no AgO_x species were present on the Ag/Au-b having steady state surfaces; almost all Ag atoms would have been in the 0 state.

Following the reduction of AgO_x species to Ag(0) during CO oxidation over the Ag/Au-b having steady state surfaces, it is probable that metallic Ag(0) zones formed on the Au support surface on which the catalytic CO oxidation took place [23]. To examine this possibility, unsupported Ag powder (1.03 m²/g) manufactured by evaporating high purity Ag metal in an inert gas was obtained from the Vacuum Metallurgical Co., Ltd. The catalytic activity for CO oxidation of this material was determined using the same equipment and procedure employed in the measurement of the Ag/Au-b powder [16], and the rate constant for CO oxidation per unit surface area of Ag, kCO_2 , was calculated. The value of kCO_2 over the Ag/Au-b was found to be 30 times greater than that on unsupported Ag powder at 253 K and four times that at room temperature. The apparent activation energies were 7 kJ/mol for the Ag/Au-b and 28 kJ/mol for the unsupported Ag powder. The significant reduction in the activation energy would be expected to greatly increase the kCO_2 value for Ag/Au-b below room temperature. These results indicate that the CO oxidation mechanism in the case of Ag/Au-b powder differs from that over unsupported Ag powder owing to the contribution from the Au support. As well, it appears that Ag(0) interacts chemically with the surrounding Au atoms on the support surface of the Ag/Au-b powder. In fact, recent investigations of the chemical environments of Ag atoms in Ag/Au-b using Ag K-edge extended X-ray absorption fine structure (EXAFS) have shown that the Ag atoms are dispersed atomically within two upper surface layers on the Au powder through the formation of Ag–Au bonds and by maintaining Ag–Ag bonds slightly. The EXAFS data also show the absence of a peak attributable to Ag–O bonds [17]. These results demonstrate that Ag atoms dispersed on the surface of Ag/Au-b bond not with O but with surrounding Au and Ag atoms to form a Ag–Au alloy [17].

Zhang et al. [5] reported that PVP-protected Ag_{core}/Au_{shell} bimetallic NPs exhibited enhanced catalytic activity during the liquid phase aerobic oxidation of glucose. They proposed that

the formation of Au–Ag bonds induced charge transfer from Ag to Au and ascribed the higher activity of the Ag/Au NPs for glucose oxidation to the presence of negatively charged Au atoms [5]. Chang et al. [24] performed a theoretical investigation of CO oxidation on unsupported icosahedral $Au_{25}Ag_{30}$ nanoclusters. The reaction path they proposed involves an $OOCO$ intermediate formed through the coadsorption of CO on Au sites and O_2 on Ag sites [24], which agrees with the mechanism we propose for Ag/Au-b [16]. Furthermore, they reported that the co-adsorption energy required to produce the COO_2 complex from CO and O_2 on the $Au_{25}Ag_{30}$ alloy clusters is larger than the values calculated for monometallic Au_{55} and Ag_{55} clusters [24], which should lead to a higher reactivity for CO oxidation.

The combination of Ag and Au can therefore be concluded to enhance the catalytic activity of Ag/Au-b for CO oxidation with O_2 by lowering the activation barrier to the formation and decomposition of the COO_2 and this may explain the synergistic effect seen in other Ag–Au bimetallic catalysts.

4. Conclusions

This work investigated the enhanced catalytic activity for CO oxidation exhibited by Ag-contaminated Au powder after an oxidizing pretreatment. To determine if this effect can be explained by the generation of a contact interface between AgO_x and the Au support, the catalytic activity for CO oxidation over Au/ Ag_2O was compared with that over Ag_2O . Differences between Au/ Ag_2O and Ag_2O in the rate of reaction mixture pressure decrease were absent in the steady state. In the case of both catalysts, the pressure decrease was attributed to the reduction of surface lattice O on Ag_2O by CO in the reaction mixture. The kinetic results obtained with Au/ Ag_2O were similar to those observed when working with Ag/Au having oxidized surfaces, indicating that it is unlikely that the interfaces between AgO_x regions and the bulk Au surface function as important active sites on Ag/Au-b. AgO_x species in Ag/Au-b having oxidized surfaces produced by an oxidizing pretreatment was completely reduced to the 0 state under steady state CO oxidation using a reaction mixture composed of CO and O_2 with a composition of $CO/O_2 = 2/1$. A comparison of the kCO_2 and activation energy values between Ag/Au-b and unsupported Ag powder indicated that Ag atoms on the surface layer of the Ag/Au-b powder form a Ag–Au alloy. This theory agrees with the results of recent investigations concerning the chemical environment of Ag atoms in Ag/Au-b by means of Ag K-edge EXAFS.

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Graphical Abstract

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An examination of active sites on Au-Ag bimetallic catalysts based on CO oxidation over Au/Ag₂O and a comparison to Ag-contaminated Au powder

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The synergistic effect of Au-Ag catalysts was determined to originate from the formation of AgAu alloy sites where the co-adsorption of CO and O₂ occurs, rather than from the interfaces between Au and AgO_x regions.

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Au/Ag₂O与Ag掺杂的Au粉催化剂上CO氧化反应: Au-Ag双金属催化剂活性位

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摘要: 有关用于各种氧化反应中Au-Ag双金属催化剂存在显著协同效应的来源有两种观点: (1) AgO_x块与体相Au表面的接触界面起重要作用, 体相Au的表面是催化活性位; (2) Au-Ag双金属催化剂中形成的Au-Ag合金中电荷从Ag转移到Au上, 可能对催化剂活性起作用。因此, 确定Au表面上Ag是以氧化物还是以金属合金形式存在可能是深度理解该协同效应的关键。

为了检测和验证催化剂活性的增加是由于 Ag_2O 与Au纳米粒子的紧密接触,在密闭循环反应体系中比较研究了Au/ Ag_2O 和 Ag_2O 催化剂上CO氧化反应.将CO/ O_2 摩尔比为2的混合气通入到这二个催化剂上来跟踪压力降低的速率.因而检测了气体的消耗量和 CO_2 的生成量.结果发现,在稳态下Au/ Ag_2O 和 Ag_2O 催化剂的压力降低的速率不存在差别.这两个催化剂上压力的降低是由于 Ag_2O 中表面晶格氧被混合气中CO的还原所致. Au/ Ag_2O 催化剂上得到的结果与以前研究的具有氧化表面的Ag掺杂的Au粉末(Ag/Au-b)上的一致,也表明 AgO_x 块与体相Au表面界面周边不大可能是CO氧化反应催化活性位.基于具有稳态表面的Ag/Au-b样品上的研究结果,我们认为 AgO_x 物种被还原为0价态Ag而形成的Ag-Au合金很可能是催化活性位.

关键词: 金-银双金属催化剂; 协同效应; 一氧化碳氧化; 活性位; 金-银合金

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