OXIDATION OF CARBON MONOXIDE OVER NANOPARTICLES OF COBALT OXIDES

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Abstract. Nanoparticles of CoO_x and Au/CoO_x (*x* is an atomic ratio between 1.00 and 1.33) were prepared to study their catalytic activity towards the CO oxidation. The oxidation state of cobalt ions in the prepared samples was characterized with TPR (the temperature programmed reduction) technique. Their catalytic activities towards the CO oxidation were further tested in a fixed bed flow reactor. The measured activity generally increased with ratio *x* in CoO_x and Au/CoO_x. Observed variation in activity was interpreted with a mechanism of competitive CO oxidation by two kinds of oxygen species, i.e., the oxygen molecularly adsorbed on CoO_x surface and the oxygen ions on the surface of Co_3O_4 spinel structure. A deposition of Au crystallites onto the surface of CoO_x not only promoted the catalytic activity but also altered the kinetic order of CO.

1. INTRODUCTION

Carbon monoxide is a toxic gas that can effective convert a large fraction of hemoglobin in human blood to carboxyhemoglobin if the level of CO in atmosphere is around 100 ppm. The conversion generally causes a symptom of asphyxiation. The fatal damage can be prevented by an oxidation of CO pollutant in the atmosphere into CO_2,

$$CO + 1/2O_2 \rightarrow CO_2, \ \Delta G_{298\,K} = -257.1 \ kJ \cdot mol^{-1}. \quad (1)$$
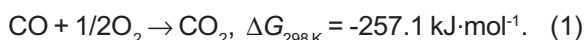
Many catalysts have been developed in literature for catalyzing reaction 1. Hopcalite ($CuMn_2O_3$) was a commercial catalyst used in early days. Haruta *et al.* discovered that supported Au catalysts were very active at sub-ambient temperature when the gold was dispersed into crystallites of tiny diameter (d_{Au} < 5 nm) [1]. However, the activity of gold catalysts significantly varies with the support used. Gold crystallites dispersed on n-type semiconductors (Co_3O_4, Fe_2O_3, TiO_2) generally displayed a higher activity than those dispersed on insulators (Al_2O_3 and SiO_2) [2].

Supported gold catalysts are active toward catalyzing many partial and deep oxidation reactions. Good catalytic activity was generally found when gold was dispersed on cobalt oxides [3]. Cobalt oxides themselves also exhibited a decent activity towards reaction 1 at moderate temperatures. Observed catalytic activity of cobalt oxides, however, increased significantly with their oxidation state of cobalt [4]. Conceivably, oxide supports in dispersed gold catalysts may participate in the mechanism of reaction 1. CoO_x and Au/CoO_x catalysts with different ratio *x* were therefore prepared in this study to pursue effects of the oxide support on the detailed mechanism and on the catalytic activity toward reaction 1.

2. EXPERIMENTAL

Catalysts of powdered CoO_x and supported Au/CoO_x with different O/Co ratios (1.00 < *x* < 1.33) were prepared in the laboratory. Powdered samples of Co_3O_4 and CoO were prepared from decomposition of $CoCO_3$ (Wako) at 673K in atmospheres of air and in nitrogen [4,5], respectively:

$$6CoCO_3 + O_2 \rightarrow 2Co_3O_4 + 6CO_2 , \quad (2)$$

$$CoCO_3 \rightarrow CoO + CO_2 . \quad (3)$$
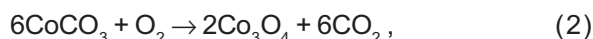
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Table 1. Properties characterized for samples prepared in this study.

Sample	T_m, K	Crystal phase	S.A., $m^2 \cdot g^{-1}$	$T_{1/2}$, K	m	E_a, kJ·mol^{-1}
$CoO_{1.33}$	–	Spinel	44	365	1	18±0
$CoO_{1.21}$	510	Spinel	–	379	1	24±2
$CoO_{1.07}$	550	Spinel	–	385	1	30±2
$CoO_{1.00}$	–	Table salt	42	401	1	38±3
$Au/CoO_{1.33}$	–	Spinel	44	222	0	19±0
$Au/CoO_{1.21}$	510	–	–	241	0	34±3
$Au/CoO_{1.06}$	550	–	–	249	0	38±4
$Au/CoO_{1.00}$	590	–	–	259	0	41±3

A supported catalyst of Au/Co_3O_4 was prepared by deposition-precipitation of $AuCl_3(aq)$ (Aldrich) onto Co_3O_4 powders at pH = 7 [6]. Powdered samples of CoO_x with $1.00 < x < 1.33$ and supported catalysts of Au/CoO_x with the same x range were prepared from controlled reductions of Co_3O_4 and Au/Co_3O_4, respectively, in a temperature programmed reduction (TPR) stream (10% H_2/N_2):

$$Co_3O_4 + (4 - 3x)H_2 \rightarrow 3CoO_x + (4 - 3x)H_2O. \quad (4)$$

Table 1 summarizes all of the catalysts prepared for this study and their maximum temperature (T_m) of the TPR reduction on their preparation. Evidently from 2nd column, a high T_m temperature rendered a high extent of reduction and thus a low ratio of x in CoO_x. The x ratio in the prepared catalysts of CoO_x and Au/CoO_x was determined in the same TPR system. Surface areas of freshly prepared samples were determined from BET plots of N_2 physisorption. The crystallite phase of cobalt oxides in fresh and aged catalysts was characterized by XRD (the third column in Table 1). The loading (around 0.8 wt%) and the size of Au crystallites ($d_{Au} \sim 2$ nm) dispersed on Au/CoO_x were analyzed by ICP-AES and TEM, respectively.

The catalytic activity of prepared samples towards reaction 1 was studied in a fixed bed reactor. A 33 ml min^{-1} stream of reactant gas (with $P_{CO}:P_{O_2}:P_{He} = 1:2:97$) was catalyzed with 100 mg of freshly prepared catalysts. The reactor temperature was raised stepwise from a low temperature (300 and 200K for catalysts of CoO_x and Au/CoO_x, respectively). Temperature profiles of CO conversion were measured by a TCD-GC.

3. RESULTS AND DISCUSSION

Reduction of CoO_x. TEM photographs revealed that prepared CoO and Co_3O_4 were in a form of aggregates with a size of $d \sim 40$ nm. The surface area of these aggregates is ~ 40 $m^2 g^{-1}$. TG-DTA (from Seiko 5000) result indicated that CoO (a p-type oxide) was oxidized by air to Co_3O_4 while raising the temperature over 550K and that the formed Co_3O_4 (a n-type oxide) was subsequently decomposed back to CoO at 1200K:

$$6CoO + O_2 \Leftrightarrow 2Co_3O_4. \quad (5)$$

Obviously, CoO and Co_3O_4 are stoichiometric oxides of cobalt that are stable in ambient air at low temperatures. Co_3O_4 prefers at $550K < T < 1200K$ while CoO dominates at $T > 1200K$.

The ratio of x in the CoO_x catalysts was quantitatively determined from the consumption of hydrogen in TPR traces (Fig. 1). CoO powders ($x = 1.00$, a sample specially prepared from reaction 3) showed a single peak at $T_r = 680K$. This peak was therefore assigned to the reduction of CoO:

$$CoO + H_2 \rightarrow Co + H_2O. \quad (6).$$

A shoulder peak at $T_r = 570K$ was noticed besides a major peak at $T_r = 650K$ in profiles of CoO_x samples with $x > 1.00$. Conceivably, the reduction of these CoO_x samples in TPR proceeded in two consecutive steps. CoO_x was initially reduced to a metastable intermediate CoO (reaction 7, $T_r = 570$ K):

$$CoO_x + (x-1)H_2 \rightarrow CoO + (x-1)H_2O. \quad (7)$$
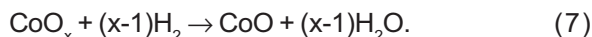
The intermediate was subsequently reduced to metallic cobalt (reaction 6) at $T_r = 650K$. Deconvoluted peaks indicates that the area ratio of the shoulder peak to the major peak indeed increases monotonously with the x ratio in CoO_x.
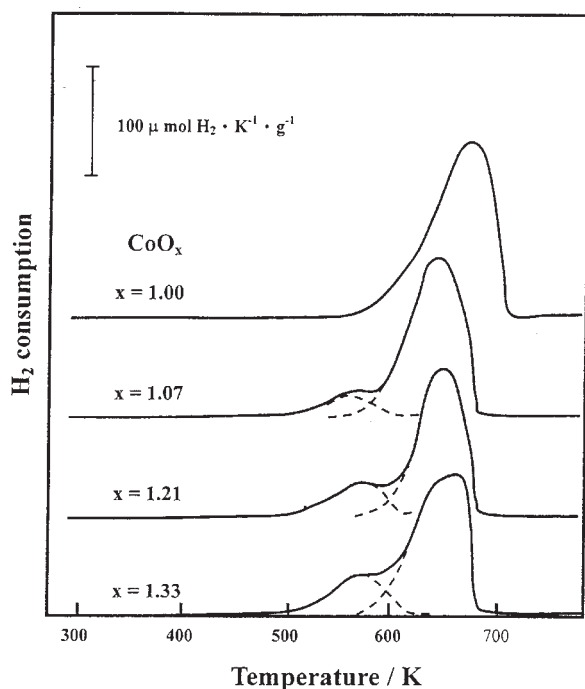
Fig. 1. TPR profiles of different CoO_x samples freshly prepared from controlled reduction of Co_3O_4.

Fig. 2. Temperature profiles of CO conversion obtained from activity tests over CoO_x catalysts.

Kinetic studies over prepared catalysts. Fig. 2 compares the CO conversion obtained from different CoO_x catalysts in activity tests towards reaction 1. With a constant contact time of 2 s, CO conversion over each fresh catalyst generally increased with the reaction temperature. To compare the relative activity of these catalysts, a temperature required for 50% CO conversion ($T_{1/2}$) was listed in column 5 of Table 1. Observed $T_{1/2}$ increased with a decrease of the ratio x in CoO_x. Conceivably, activity of CoO_x powders increases significantly with ratio x.

The catalytic activity of CoO_x in reaction 1 may vary with the reaction time. At a temperature of 400K, the conversion remained at 100% at the initial stage but decreased to and stayed at 40% after a reaction time of 2 h. A subsequent TPR characteri-zation for the aged catalyst indicated that it had been partially reduced and converted into $CoO_{1.13}$. Observed conversion change may therefore be resulted from a partial reduction of Co_3O_4 by CO.

Fig. 3 compares temperature profiles of CO conversion obtained from supported catalysts of Au/CoO_x. The conversion over these catalysts also increases with the reaction temperature and the ratio x in CoO_x supports. The deposition of gold particles onto CoO_x, however, significantly increases their catalytic activity. A decrease of 150K in $T_{1/2}$ was generally found, in the fifth column of Table 1, due to the gold deposition.
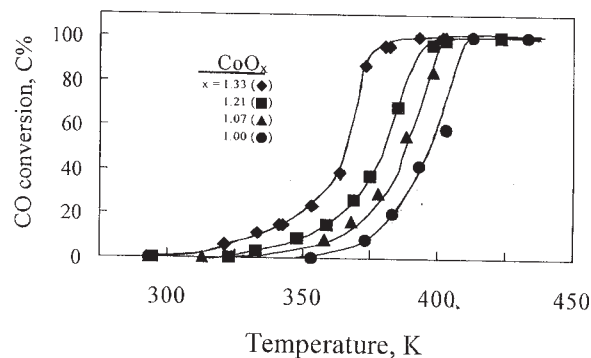
A partial pressure ratio (2.0) of oxygen (P_O^0) to carbon monoxide (P_{CO}^0) used in the reactant flow is in excess comparing to the stoichiometry (0.5) in reaction 1. The partial pressure of oxygen may therefore be regarded as constant ($P_O = P_O^0$) at low conversions. Under this condition, the rate of this reaction may be described with an empirical equation of:

$$-\frac{dP}{dt} = k(P)^m = A_m (P)^m \exp\left(-\frac{E_a}{RT}\right). \qquad (I)$$

Where m and P denote the pseudo kinetic order of CO in reaction 1 and the partial pressure of CO remained in reaction stream upon a contact time of 't', respectively. A_m and E_a presents the pre-exponential factor and the activation energy of the rate constant k.

The CO conversions (C) plotted in Figs. 2 and 3 may be related to P in Eq. I through a relation of

$$C = 1 - \frac{P}{P_{CO}^0}. \qquad (II)$$

In a case of m = 1, the conversion of CO should change with the reaction temperature according to

$$\ln[-\ln(1-C)] = \ln(A_1 t) - \frac{E_a}{RT}. \qquad (III)$$

If m = 0, the conversion would vary with the temperature according to

$$\ln C = \ln(A_0 t) - \frac{E_a}{RT}. \qquad (IV)$$

Therefore, a re-plot of the experimental conversions in each profile of Figs. 2 and 3 with T^{-1} may yield a
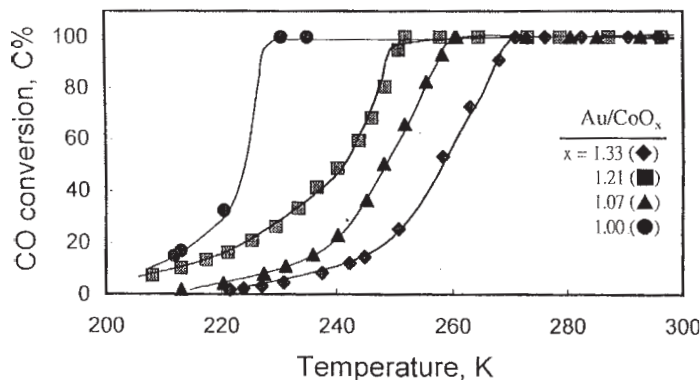
Fig. 3. Time profile of CO conversion during the life test of CO oxidation over Co_3O_4 catalyst.

straight line if an appropriate equation (III or IV) is selected.

Kinetics over CoO_x. Data of CO conversion at different temperatures in Fig. 2 were thus plotted according to Eqs. (III) and (IV) to find order m in the catalysis. A kinetic order of $m = 0$ was given up for reaction 1 over CoO_x catalysts because curved lines (omitted in this report) were always obtained from plots according to Eq. (IV). A plot of low-conversion data (high-conversion data are given up to eliminate possible reductions of CoO_x during the catalytic reaction) in Fig. 1 according to Eq. III, however, yields straight lines. Evidently, the reaction order of CO over catalysts CoO_x is $m = 1$. This reaction order suggests a weak adsorption of CO ($\theta_{CO} \rightarrow 0$) on surface of CoO_x powders under the reaction condition:

$$CO + * \Leftrightarrow CO\text{-}*, \tag{8}$$

where * denotes an adsorption site on CoO_x surface.

According to Eq. III, the slope of the lines plotted in Fig. 1 provides information on the activation energy required for reaction 1. Calculated E_a (the last column in Table 1) varies with the ratio x in CoO_x catalysts. Among them, Co_3O_4 ($CoO_{1.33}$) exhibits the least activation energy of $E_a = 18$ kJ·mol^{-1}. A gradual increase in E_a (up to 38 kJ·mol^{-1}) is found on decreasing the atomic ratio to $x = 1.0$. This variation of E_a with ratio x will be discussed in the section of reaction models.

Kinetics over Au/CoO_x. A dispersion of gold crystallites on CoO_x caused a change to the kinetic order of CO on reaction 1. We have re-plotted data of each profile in Fig. 3 according to Eq. IV. Obtained plots in low conversion regions display a straight line for each of these gold dispersed catalysts. Evi-

dently, the kinetic order of CO was shifted to $m = 0$ for CO oxidation over Au/CoO_x catalysts. The decrease of order m by the gold deposition probably reflected an enhanced adsorption of CO on the surface of gold crystallites (*$_g$ sites) [7]:

$$CO + *_g \rightarrow CO\text{-}*_g. \tag{9}$$

The last column in Table 1 lists E_a estimated from the straight lines. $E_a = 19$ kJ·mol^{-1} was calculated for catalyst Au/Co_3O_4. This activation energy is in decent agreement to that (16.3 kJ·mol^{-1}) reported in an early literature [8] over Au/Co_3O_4 catalyst. Similar to catalysis over CoO_x, calculated E_a over Au/CoO_x also increased on decreasing the ratio x in the support.

Active oxygen species on CoO_x surface. The variation of E_a with ratio x of CoO_x catalysts suggests that the structure of CoO_x plays an important role on their activity towards reaction 1. CoO and Co_3O_4 are two stoichiometric cobalt oxides synthesized in this study through decomposition of $CoCO_3$ (reactions 2 and 3). XRD study indicates that these two oxides exhibited a structure of table salt and spinel, respectively.

Powders of CoO are p-type semi-conductor with a high tendency to adsorb oxygen onto the surface [9]:

$$O_2 + * \Leftrightarrow O_2\text{-}*. \tag{10}$$

This tendency renders an application of CoO_x in the fabrication of gas sensors. The adsorbed oxygen may oxidize CO molecules weakly co-adsorbed to produce CO_2 through reaction 11, i.e.,

$$2\ CO\text{-}* + O_2\text{-}* \rightarrow 2\ CO_2 + 3\ *. \tag{11}$$
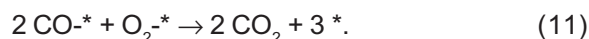
A combination of reactions 8, 10 and 11 forms the route of CO oxidation over CoO catalyst.

Co_3O_4 powders, on the other hand, are n-type semiconductor and tend to lose lattice oxygen on surface (O_L) upon interaction of the adsorbed CO. Consumed O_L may be restored through adsorption of oxygen molecules on the resulted vacancy, i.e.,

$$\text{*-CO} + O_L \rightarrow CO_2 + \square, \qquad (12)$$

$$2\,\square + O_2 \rightarrow 2\,O_L . \qquad (13)$$

Where $\square$ denotes a vacancy in the lattice. A combination of steps 8, 12 and 13 therefore accounts the dominant route for reaction 1 to proceed over Co_3O_4.

Support effect on dispersed gold catalysts. Dispersed gold catalysts have been known to be active toward CO oxidation for several years [10]. A general agreement has been reached that the support of these catalysts has a function of dispersing gold into small crystallites ($d_{Au} < 5$ nm). However, a controversy remains in literature over the contribution of the chemical property of support to the activity. Early studies on catalysts prepared by liquid phase method (deposition precipitation) suggested that the nature of support played a significant role on the activity: Gold catalysts supported on oxides of n-type semi-conductor, i.e., Co_3O_4, Fe_2O_3 and TiO_2 displayed a higher activity than those of insulators, i.e., Al_2O_3, SiO_2 and ZrO_2. The advantage of n-type oxides was attributed to an enhanced ability in oxygen adsorption on their defect sites [2]. However, Haruta *et al.* recently observed a similar activity from catalysts of Au/Al_2O_3, Au/SiO_2 and Au/TiO_2 prepared by chemical vapor deposition of a gold complex [11]. They suggested that the semi-conductivity nature of support does not seriously affect the activity of gold catalysts.

The activation energy required for catalyzing reaction 1 at sub-ambient temperatures has been pursued in literature for many supported gold catalysts. An activation energy of $E_a = 35 \pm 6$ kJ·mol^{-1} was generally found for Au/TiO_2 (8, 11, 12), Au/Fe_2O_3 (8), and Au/Al_2O_3 [11]. A similar E_a was also observed from catalysts CoO and Au/CoO in the present study (Table 1). Probably, reaction 1 proceeded through a similar reaction mechanism (route b where O_2-* is the active oxygen species) over these catalysts.

In the present study, E_a required for reaction 1 over Au/CoO_x varies with the ratio x in the support. The experimental activation energy over Au/Co_3O_4 decreases to $E_a \sim 20$ kJ·mol^{-1}. The decrease in E_a on increasing the ratio x on Au/CoO_x is attributed to a shift in the active oxygen species, from O_2-* to O_L, in the reaction mechanism. Accordingly, it is proposed that CoO_x support of Au/CoO_x does participate the catalytic kinetics of reaction 1. The distinguished activity observed by Haruta *et al.* [8] from Au/Co_3O_4 over other supported gold catalysts may therefore be attributed to a participation of O_L on Co_3O_4 in the oxidation.

CONCLUSIONS

Non-stoichiometric catalysts of CoO_x and Au/CoO_x with $1.00 < x < 1.33$ were prepared by controlled reduction of Co_3O_4 and Au/Co_3O_4 in TPR system at $T_m > 500K$. Prepared catalysts are active toward CO oxidation. Following conclusions have been made from the kinetic results of this study:

1. Experimental E_a and $T_{1/2}$ of CoO_x and Au/CoO_x were decreased on increasing the ratio x of catalysts.

2. The variation of E_a and $T_{1/2}$ with the value x was attributed to a competition of two parallel Langmuir-Hinshelwood mechanisms. The rate-determining step of both mechanisms is the oxidation of adsorbed CO by surface oxygen. However, different surface oxygen (O_2-* or O_L) was used in the rate-determining step of these two mechanisms. Comparatively, O_L on Co_3O_4 phase is more active and requires less E_a (20 kJ·mol^{-1}) than O_2-* adsorbed on CoO_x (35 kJ·mol^{-1}).

3. A dispersion of gold crystallites on CoO_x increased significantly the density of CO adsorbed on catalysts. Consequently, $T_{1/2}$ required for CO oxidation was reduced from 380 to 230K and the kinetic order of CO was changed from $m = 1$ to $m = 0$.

ACKNOWLEDGMENT

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