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CO oxidation behavior of copper and copper oxides

Ta-Jen Huang* and De-Hao Tsai

Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan 300, ROC

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Carbon monoxide oxidation activities over Cu, Cu_2O, and CuO were studied to seek insight into the role of the copper species in the oxidation reaction. The activity of copper oxide species can be elucidated in terms of species transformation and change in the number of surface lattice oxygen ions. The propensity of Cu_2O toward valence variations and thus its ability to seize or release surface lattice oxygen more readily enables Cu_2O to exhibit higher activities than the other two copper species. The non-stoichiometric metastable copper oxide species formed during reduction are very active in the course of CO oxidation because of its excellent ability to transport surface lattice oxygen. Consequently, the metastable cluster of CuO is more active than CuO, and the activity will be significantly enhanced when non-stoichiometric copper oxides are formed. In addition, the light-off behaviors were observed over both Cu and Cu_2O powders. CO oxidation over metallic Cu powders was lighted-off because of a synergistic effect of temperature rises due to heat generation from Cu oxidation as well as CO oxidation over the partially oxidized copper species.

KEY WORDS: CO oxidation; copper; copper oxides; surface lattice oxygen.

1. Introduction

In automotive exhaust emission control, to meet increasingly stringent environmental regulations in an economical way, the complete oxidation of carbon monoxide is of prime importance. Precious metals have long been used as the most efficient CO oxidation catalysts with high activity and stability. Due to the cost and limited availability of precious metals, considerable attention has been paid to transition metals and their oxides as substitute catalysts. Among the base metals, copper has been explored as a possible substitute for precious metals for its high activity toward CO oxidation [1,2].

Many works have been devoted to the study of carbon monoxide oxidation over copper catalysts because of its significance in understanding a number of major industrial applications, in addition to exhaust emission control. It is known that the oxidation state of copper changes thermodynamically among the three copper species, *i.e.*, Cu, Cu_2O, and CuO, as the reaction temperature and prevailing oxygen atmosphere are varied [3]. Jernigan and Somorjai [4] demonstrated that over a thin film of copper CO oxidation is catalyzed by every oxidation state of copper and the rate of the reaction varies as a function of copper oxidation state. Sadykov and Tikhov [5] pointed out that the thin film model of Jernigan and Somorjai [4] cannot be extrapolated to bulk phases, where the oxygen defect phase occurs as a metastable state and influences the catalytic activity. Nagase *et al.* [6] have proposed that the occurrence of a metastable cluster, including an oxygen vacancy, is the active site in the reaction. Pierron *et al.* [7] reported that CO reduction of cupric oxide resulted in the generation of reduced copper phases and the formation of lattice heterogeneities. In spite of these and many other significant works on carbon monoxide oxidation over copper catalysts in the literature, there have been very few studies concerning the involvement of the surface lattice oxygen in the reaction.

The purpose of this work is to elucidate the participation of surface lattice oxygen of the copper species during CO oxidation. For this purpose, activity tests were carried out to study of the properties of Cu, Cu_2O, and CuO. In addition, the temperature effect on the activity behavior was studied. It was found, for the first time as far as the authors know, that CO oxidation over metallic Cu powders could be lighted-off. The lighting-off of CO oxidation over Cu powders is proposed, in this work, to be due to a synergistic effect of temperature rises due to heat generation from Cu oxidation as well as CO oxidation over the partially oxidized copper species which are able to donate the above-described surface lattice oxygen.

2. Experimental

2.1. Catalyst samples

Powdered samples of Cu (99% purity, Aldrich), Cu_2O (99.5%, SHOWA), and CuO (98.5%, SHOWA) were ground and used as catalysts.

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* To whom correspondence should be addressed.
E-mail: tjhuang@che.nthu.edu.tw

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2.2. Activity measurement

The time-on-stream activity tests of the catalysts were conducted for 360 min under atmospheric pressure in a continuous-flow reactor charged with 0.3 g of catalyst. The reactor was an 8 mm i.d. Pyrex U-tube embedded in a silica-oil circulating tank (Mandarin Scientific Co.). Two K-type thermocouples were employed. One was placed in the silica-oil bath to monitor and control the bath temperature (called the surrounding temperature), while the other was inserted into the catalyst bed to measure the reaction temperature in the bed (called the bed temperature). Two surrounding temperatures, *i.e.*, 140 and 205 °C, were used in this work and the resulting bed temperatures during the reaction were recorded. The catalytic activities were presented as the percentage CO conversion as a function of time on stream.

Two reaction atmospheres were adopted in this work. The oxygen-rich atmosphere was a gas mixture composed of 1.80% CO plus 2.95% O_2 in argon, and the oxygen-lean atmosphere was that of 1.85% CO, 0.56% O_2, and the balance argon, both at a total flow rate of 300 ml/min. The flow rates of the reactant gases, *i.e.*, CO (99.9% purity, Air Products), O_2 (99.995%), and Ar (99.9995%), were regulated by mass flow controllers (Hastings, Model HFC-202). The reactor outflow was analyzed on-line by a CO-NDIR (Beckman 880), a gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector, and an oxygen analyzer (Beckman 755A). Both the signals of the CO-NDIR and the temperatures of the catalyst bed were transmitted to a *Y–t* recorder (Yokogawa, LR-4110).

3. Results and discussion

3.1. Activity behaviors of copper and copper oxides

The variations of CO oxidation activities with time on stream in the oxygen-rich environment are shown in figures 1 and 2 for the surrounding temperatures of 140 and 205 °C, respectively. Note that the temperature of the catalyst bed is usually different from the surrounding temperature and the temperature effect is discussed in section 3.3. Among the three copper species (Cu, Cu_2O, CuO) tested, Cu_2O was the only one that was active at 140 °C, as shown in figure 1, and showed a feature of light-off, which was even more significant at 205 °C, as shown in figure 2. It is interesting to note that Cu was practically inert during the 140 °C run but showed a light-off behavior with a surrounding temperature of 205 °C. Also note that the light-off behavior over metallic Cu powders was observed for the first time as far as the authors know. As a result, the activity of Cu even exceeded that of Cu_2O after 180 min on stream. Nevertheless, progressive declines of activity were witnessed for both Cu_2O and Cu as reactions proceeded.

Figures 3 and 4 display the activities of the copper species when the reaction atmosphere was oxygen lean for the surrounding temperatures of 140 and 205 °C, respectively. As shown in figure 3, at 140 °C Cu_2O was still the only copper species that showed considerable activity, which increased in the initial 20 min and then decreased slightly to a relatively steady one. Compared with the 140 °C run, the rise and fall of Cu_2O activity was more significant as the surrounding temperature was raised to 205 °C, as shown in figure 4. Although no

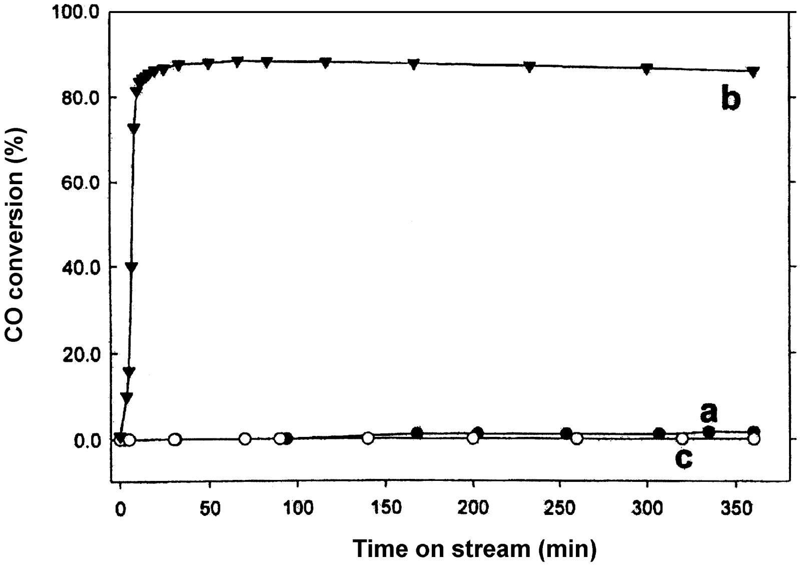

Figure 1. CO oxidation activities of Cu, Cu_2O, and CuO under oxygen-rich conditions. Surrounding temperature: 140 °C. (a) Cu: ●, (b) Cu_2O: ▼, (c) CuO: ○.

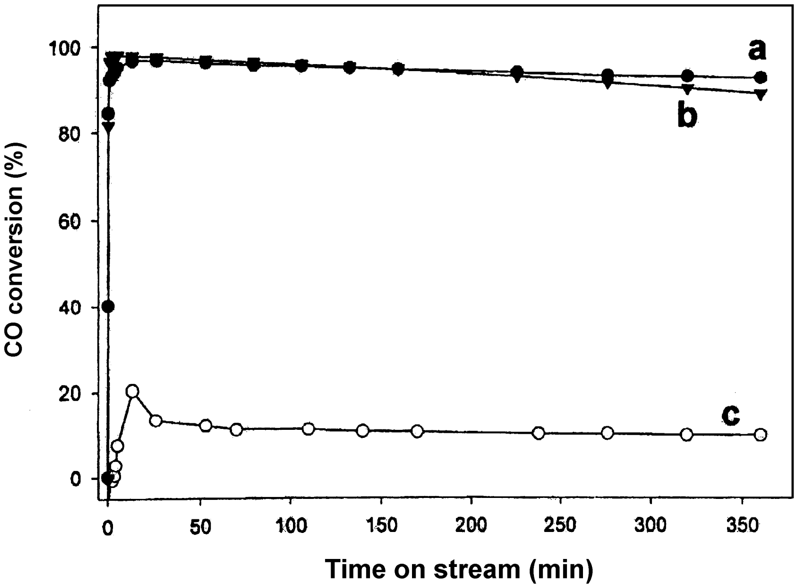

Figure 2. CO oxidation activities of Cu, Cu_2O, and CuO under oxygen-rich conditions. Surrounding temperature: 205 °C. (a) Cu: ●, (b) Cu_2O: ▼, (c) CuO: ○.

detectable activity was noted for both Cu and CuO during the 140 °C run, a drastic increase and sharp decrease of CO conversion to a steady value of about 2% were observed for Cu when it was reacted with a surrounding temperature of 205 °C. In addition, unlike Cu_2O and Cu, CuO exhibited a sustained increase in activity after a short induction period.

In figure 2 the negligible activity of CuO at 205 °C in the first 4 min may be considered as an induction period, which is due to strong adsorption of oxygen on copper under oxygen-rich conditions. This phenomenon has also been found by Severino and Laine [8] over unsupported CuO and agrees with the results of inert supported metallic copper [9,10]. However, under oxygen-lean conditions at 205 °C the induction period of CuO, as shown in figure 4, was negligible because of lower prevailing oxygen concentrations. Under oxygen-rich conditions at 205 °C the activity of CuO increased rapidly following the induction period and then, after 20 min on stream, declined to an ultimate steady activity which is due to thermodynamic favoring of CuO [11,12]. On the other hand, the progressive increase of CuO activity in the oxygen-lean atmosphere is ascribed to the formation of Cu_2O due to kinetic favoring [10,11]. In contrast to CuO, Cu_2O, with no observable induction period, exhibited considerable activity at the low surrounding temperature of 140 °C where metallic Cu and CuO were not active. Therefore, substantial kinetic differences should exist between CuO, Cu_2O, and Cu, and are addressed in this regard in the following.

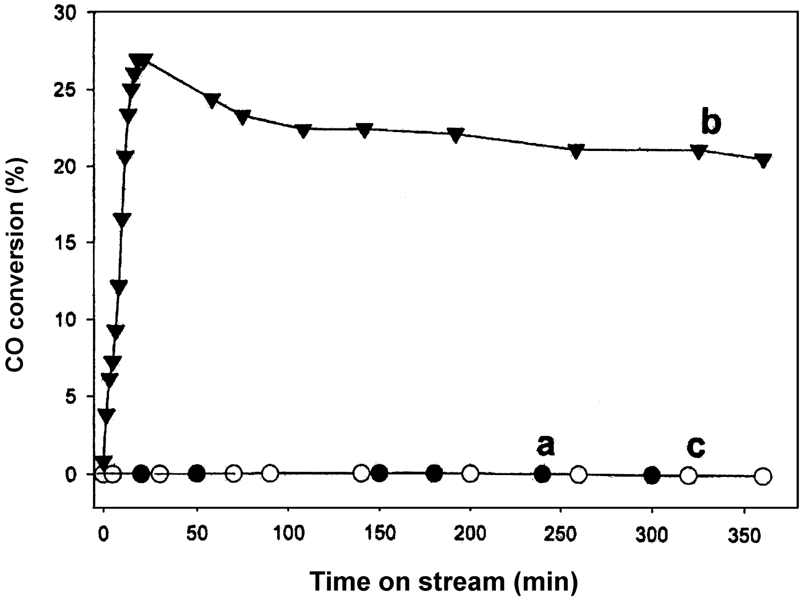

Figure 3. CO oxidation activities of Cu, Cu_2O, and CuO under oxygen-lean conditions. Surrounding temperature: 140 °C. (a) Cu: ●, (b) Cu_2O: ▼, (c) CuO: ○.

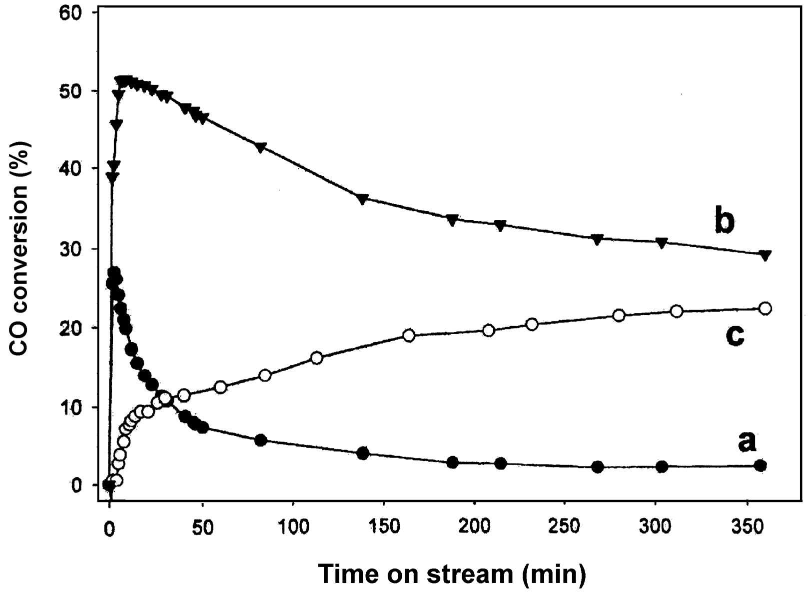

Figure 4. CO oxidation activities of Cu, Cu_2O, and CuO under oxygen-lean conditions. Surrounding temperature: 205 °C. (a) Cu: ●, (b) Cu_2O: ▼, (c) CuO: ○.

For CO oxidation over copper oxide catalysts it is generally agreed that the reaction obeys a Mars–van Krevelen redox mechanism [13]:

$$CO + O_{SL} \rightarrow CO_2 + \square_s \quad (1)$$

$$O_2 + \square_s \rightarrow 2O_{SL}, \quad (2)$$

where O_{SL} is a surface lattice oxygen and $\square_s$ is a surface oxygen vacancy on the metal oxide surface. In this mechanism, re-oxidation of the catalytic surface, *i.e.*, reaction (2), is usually rather fast and oxygen withdrawal from copper oxide, *i.e.*, reaction (1), appears to be the rate-determining step [4,14,15]. Thus, the reaction rate will be enhanced when more surface lattice oxygen is withdrawn from the metal oxide.

On the basis of the same weight, CuO possesses more lattice oxygen, or equivalently more surface lattice oxygen, than Cu_2O. Under oxygen-rich conditions there is no change in the oxidation state of CuO, but both Cu_2O and Cu are oxidized partially to increase their surface lattice oxygen. On the other hand, under oxygen-lean conditions CuO and Cu_2O are liable to be reduced to lower oxidation states resulting in the loss of surface lattice oxygen.

Metallic Cu was not active at low temperatures because of its inability to donate surface lattice oxygen. In spite of this, as the catalyst bed temperature was raised under oxygen-rich conditions, the rate of Cu oxidation increased, thereby forming more surface lattice oxygen. As a result, the CO oxidation activity increased. This, coupled with a temperature effect, may lead to a light-off behavior as is discussed in section 3.3. On the other hand, under oxygen-lean conditions, even though the temperature was high enough, the increase of surface lattice oxygen obtained from the reactants was limited due to the inadequacy of oxygen. Moreover, metallic Cu sinters and loses surface area more rapidly than its oxides at elevated temperatures, thereby reducing its surface lattice oxygen. This leads to the observation that, after a surge in activity, metallic Cu deactivates steadily and becomes the least active of the three copper species, as shown in figure 4.

3.2. Species transformation among Cu, Cu_2O, and CuO

Nagase *et al.* [6] proposed that variations in copper valence during CO oxidation over CuO and Cu_2O cycled between II and 0 for CuO, while for Cu_2O the valence changed from I to II first and then cycled between II and I. This result, coupled with the discussion above, suggests that the rate of CO oxidation over Cu_2O is quite different from that on CuO, and Cu_2O is more active than CuO. We noted earlier that, under oxygen-rich conditions at the surrounding temperature of 205 °C, CuO, owing to thermodynamic favor, reached an ultimate steady activity, as shown in figure 2, where the consumption rate of surface lattice oxygen of CuO was in equilibrium with the re-oxidation rate of Cu. The valence variation of copper is accompanied by a change in the number of surface lattice oxygen ions and species transformations of copper oxides. Under oxygen-lean conditions the significant decline of the activity of Cu_2O, as shown in figure 4, is due to the decrease of its surface lattice oxygen and to its being transformed into metallic copper. In the oxygen-rich atmosphere, only a slight progressive decline in the activity of Cu_2O was observed, as shown in figure 2, because the increase in the number of surface lattice oxygen ions compensates somewhat the adverse effects of formation of the less active copper(II) oxide.

Above all, the activity scenario of copper oxide species can be elucidated in terms of species transformation and change in the number of surface lattice oxygen ions.

Table 1
Variations of the color of copper and copper oxides after 360 min of reaction at the specified surrounding temperature

Species	Initial	O_2 rich, 140 °C	O_2 lean, 140 °C	O_2 rich, 205 °C	O_2 lean, 205 °C
CuO	Black	Black	Black	Black	Red and black
Cu_2O	Dark brown	Black	Black and red	Black	Red and black
Cu	Brown	Brown and black[a]	Brown	Black	Brown and red

[a] Only a few black spots were detected.

Under different oxygen atmospheres, Cu_2O gives the highest reaction rate per mole of Cu because it can seize or release surface lattice oxygen more readily than the other two. The intermediate oxidation state of copper oxide species is active because of its excellent ability to transport surface lattice oxygen. Therefore, the metastable cluster of CuO is more active than the stable species of CuO, and the activity of catalysts will be significantly enhanced when non-stoichiometric copper oxides are formed.

Color variation is an indication of the transformation of the copper species with reaction temperatures and oxygen atmospheres. Table 1 gives the color variation of copper and its oxides in different oxygen atmospheres after 360 min of reaction. Under oxygen-rich conditions after the 205 °C reaction, both the colors of copper and copper(I) oxide shaded from brown into black. The color of copper(I) oxide and copper(II) oxide developed into red and black under oxygen-lean conditions after the 205 °C reaction. The color of Cu only varied when the operating condition was oxygen rich at 205 °C, while CuO changed its color only in an oxygen-lean environment at this temperature. At the reaction temperature of 140 °C Cu_2O was the only copper species with remarkable color changes. It is thus apparent that the copper species transform among Cu, Cu_2O, and CuO with the prevailing oxygen atmospheres and reaction temperatures. As a result it is conceivable that the three copper species would exhibit diverse catalytic behavior under different oxygen atmospheres, as is manifested by figures 1–4.

3.3. *Temperature effect on light-off behaviors of Cu and Cu_2O*

As shown in figure 2, at the surrounding temperature of 205 °C both Cu and Cu_2O exhibit a light-off behavior, while at the surrounding temperature of 140 °C, as shown in figure 1, only Cu_2O exhibits a drastically increased activity close to light-off but Cu has almost no activity. These phenomena may be attributed to a temperature effect. As shown in figure 5, which depicts the variations of the catalyst bed temperatures corresponding to the activity tests of figure 2, the bed temperature of Cu in the oxygen-rich atmosphere increased drastically from below 205 °C to 242 °C and then gradually decreased to a steady one of 232 °C. Note that if no heat generation via CO oxidation occurs, *i.e.*, when there is no CO oxidation activity, the catalyst bed temperature should be lower than that of the surrounding due to the heat transfer resistance. As indicated in table 1, in the oxygen-rich atmosphere at 205 °C Cu would be oxidized to CuO.

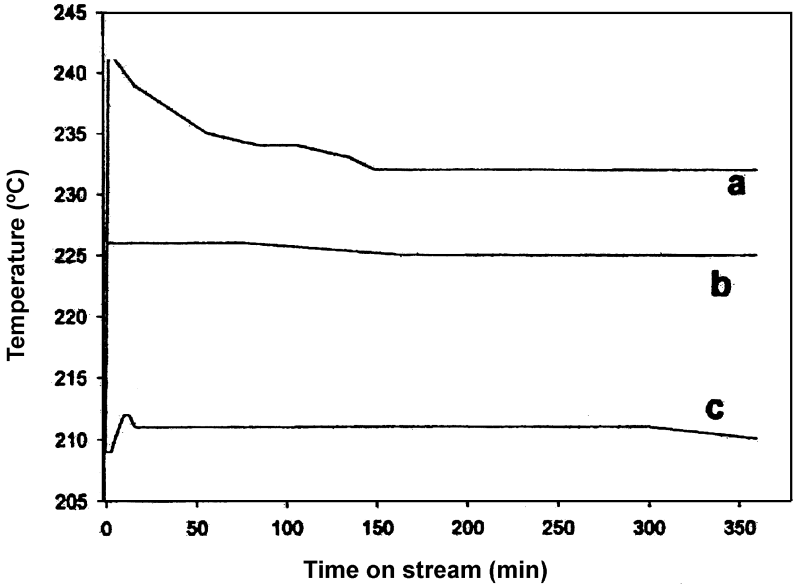

Figure 5. Catalyst bed temperature profiles of Cu, Cu_2O, and CuO for Co oxidation in the oxygen-rich atmosphere. Surrounding temperature: 205 °C. (a) Cu, (b) Cu_2O, (c) CuO.

This oxidation should release heat of reaction and increase the catalyst bed temperature. Moreover, at the initial stage of this oxidation some Cu species would be oxidized to Cu_2O, which was very active toward CO oxidation, as discussed above, and thus the CO oxidation activity would be triggered and additional reaction heat other than that of Cu oxidation would be released. Thus, the catalyst bed temperature should be increased even higher and this should in turn greatly increase both the Cu oxidation and the CO oxidation. In addition, some metastable clusters of CuO may be formed during Cu oxidation and this should help in maintaining the high CO oxidation activity. As a consequence, the catalyst bed temperature jumped to 242 °C and, simultaneously, CO oxidation was lighted-off over these Cu powders, as shown in figures 5 and 2, respectively.

The gradual decrease of the catalyst bed temperature from 242 °C to a steady one of 232 °C, as shown in figure 5 for Cu, is due to the complete oxidation of Cu to CuO, at least for the surface layer as indicated in table 1. Thus, no more heat generation from Cu oxidation but only the heat generated from CO oxidation was added into the catalyst bed. Note that the surrounding temperature for each run was kept constant over the entire run and the catalyst bed temperature should increase with increased conversion of CO. However, the extent of the temperature increase is not exactly proportional to the CO oxidation activity since heat transfer to the surrounding and to the flow stream was involved. Therefore, the existence of the steady temperature of 232 °C is due to a relatively steady conversion of CO over Cu as shown in figure 2, as well as to the heat balance among heat generation and heat transfer.

From the above, it is seen that high bed temperature and high CO activity can be maintained over CuO formed via Cu oxidation. However, if the starting material was CuO, both the CO oxidation activity and the bed temperature were low, as shown in figures 2 and 5, respectively. One possible explanation for this phenomenon is that CO oxidation would not be lighted-off over CuO; however, if the bed temperature is already at a high level, the CO oxidation should be high to give a high heat generation so as to keep the high bed temperature, and thus the high CO oxidation activity and the high bed temperature are maintained simultaneously.

As also shown in figure 5, for Cu_2O the temperature jumped to 226 °C and then slightly fell to 225 °C due to a heat balance as described above. This temperature jump was due to the light-off of CO oxidation over Cu_2O powder. However, no heat generation due to the Cu_2O oxidation, as indicated in table 1 at the surrounding temperature of 205 °C in the oxygen-rich atmosphere, was observed in figure 5. This may be because the oxidation of Cu_2O was slow and thus the heat generated was easily dissipated. As a consequence, no temperature peak such as that for Cu was observed. A similar temperature profile without a peak was also observed for Cu_2O at the surrounding temperature of 140 °C in the oxygen-rich atmosphere.

On the other hand, in the oxygen-lean atmosphere of figure 4, since the CO oxidation activity was already low even for the most active Cu_2O species, the rate of heat generation was low and thus no light-off behavior could appear even for the high surrounding temperature of 205 °C.

4. Conclusions

The CO oxidation activities over varying valences of copper oxides (Cu, Cu_2O, and CuO) have been explored. The activity of copper oxide species can be elucidated in terms of species transformation and change in the number of surface lattice oxygen ions. The propensity of Cu_2O toward valence variations and thus its ability to seize or release surface lattice oxygen more readily enables Cu_2O to exhibit higher activities than the other two copper species. The non-stoichiometric metastable copper oxide species formed during reduction are very active in the course of CO oxidation because of its excellent ability to transport surface lattice oxygen. Consequently, the metastable cluster of CuO is more active than CuO, and the activity will be significantly enhanced when non-stoichiometric copper oxides are formed. In addition, the light-off behaviors were observed over both Cu and Cu_2O powders. CO oxidation over Cu was lighted-off because of a synergistic effect of temperature rises due to heat generation from Cu oxidation as well as CO oxidation over the partially oxidized copper species.

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