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Non-linear change in oxidation state of Cu during Co oxidation on supported copper catalysts measured by the forced-oscillating reaction method

Yukiyoshi Ono [b,*], Masashi Shibata [a], Tomoyuki Inui [a]

[a] *Department of Energy and Hydrocarbon Chemistry Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan*
[b] *Human Environmental Research Laboratory, Matsushita Electric Industrial, 3-1-1, Yagumo-nakamachi, Moriguchi, Osaka 570, Japan*

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Abstract

In order to investigate the redox processes of the catalyst during the reaction, CO oxidation test on Cu-containing zeolite A (Cu-A), Cu ion-exchanged zeolite A (Cu/A), and Cu supported on silica gel (Cu/SiO_2) was carried out by using the forced-oscillating reaction method (FORM). The test was conducted under four different conditions, reductive reaction condition with large excess of CO, stoichiometry reaction condition with slight excess of CO, stoichiometry reaction condition with slight excess of O_2, and oxidative reaction condition with large excess of O_2. The order of activity for the CO oxidation was Cu-A > Cu/A, Cu/SiO_2. The highest activity of Cu-A was ascribed to the more stable and lower oxidation state of Cu than that in Cu/A and Cu/SiO_2. It was confirmed that the FORM was useful to investigate the changes of oxidation state and the property of catalyst in the CO oxidation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Forced-oscillating reaction method; CO oxidation; Oxidation state; Cu; Zeolite A

1. Introduction

Catalytic combustion systems have already been applied to the purification of exhaust gases from gasoline engines in automobiles [1] and vapors of solvents and bad odors which come from various facilities in factories [2,3]. Besides such large scale usages, application of catalytic combustion is increasing recently, in various kinds of small scale appliances for home-use, such as gas heater [4], gas oven [4], electric heater for space warmer [5], refrigerator [5], and lavatory [5]. Moreover, most recently, the catalytic combustion is aimed to apply to the combustion of fuels diluted in gas turbine to lower NO_x emission [6–8]. However, in general, the catalytic combustion of fuels explosively consumes oxygen adsorbed on the catalyst surface, and consequently, the adsorption of oxygen from gas phase cannot overtake the consumption on the surface. Moreover, for the purpose of the gas turbine, the diluted fuel component in the feed gas must be completely converted to carbon dioxide and water at a high catalytic reac-

* Corresponding author. Tel.: +81-6-6906-4829; fax: +81-6-6904-5163; E-mail: ono3@ctmo.mei.co.jp

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tion rate. Thus, the catalyst surface is apt to lack the supply of the fuel component. This also causes the disturbance in the reaction rate, and especially under the excess of O_2 condition, the catalyst metallic phase inclines more to the oxidative one, resulting in marked decrease in the reaction rate. These non-steady behaviors often cause a self-oscillation in the reaction rate [9–12]. Essentially, therefore, the self-oscillating reaction is accompanied by the repeated change of the oxidation states of a metallic catalyst between the reductive one and the oxidative one. Such a repeated change in the catalyst surface easily brings a serious deterioration owing to the sintering by the concentrated heat of oxidation and reduction on to the active catalyst surface.

Oxidation–reduction cycles on the active catalytic sites are always repeated during the oxidative reactions; however, only under very limited conditions, such as a low heat capacity of the catalyst and use of very sensitive detector for the change in oxidation state of catalyst, can the distinct, periodic, and systematic oscillation in the reaction rate be observed. In the case of the ordinary solid catalysts, even if the oscillating behaviors occur on those catalysts, the changes in the catalyst-surface temperature and the product composition are averaged, and one can only observe the simple unchanged aspects of them.

In order to observe the nature of the oxidation–reduction states of the catalysts, irrespective of the shapes and their heat capacities, Inui et al. [13] established the forced-oscillating reaction method (FORM), in which catalyst temperature is elevated at a constant heating rate, and after attaining the total conversion level, the temperature is then lowered at the same constant rate. The hysteresis in the temperature dependence of the conversion reflects the oxidation states of the catalyst surface during the reaction.

In the present study, supported Cu catalysts and CO oxidation were chosen as probes of the catalyst and the reaction, respectively. Through the observation of transient behaviors corresponding to the forced-oscillating reaction test and the change in characteristics observed by temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO), and X-ray photoelectron spectroscopy (XPS), the state of the copper surface and its change during the oxidation reaction were discussed.

2. Experimental

2.1. Catalyst preparation

A copper catalyst supported on a silica gel (Cu/SiO_2) was prepared by an ordinary impregnation method. Silica gel (Merck) calcined at 500°C for 2 h was impregnated with an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (Wako), was dried at 110°C overnight, and calcined at 500°C for 2 h. It was then reduced by heating in 10% H_2 from room temperature to 500°C at a constant heating rate of 10°C/min, and maintained at that temperature for 30 min. The content of Cu was 8.6 wt.%. This catalyst is designated as Cat. 1.

Cu ion-exchanged zeolite A (Cu/A) was prepared by an ordinary ion-exchange method using zeolite A in sodium form (NaA) and aqueous solution of copper nitrate. NaA was synthesized by the following procedures. Sodium aluminate, water glass, and sodium hydroxide of Wako, guaranteed grade were used as raw materials, and set at ratios of $SiO_2/Al_2O_3 = 1$, and $Na_2O/Al_2O_3 = 5$. An aqueous solution of sodium aluminate was mixed with a sodium hydroxide solution, and added to a water glass solution while being vigorously stirred by an ultra disperser immersed in an ice bath. Formed gel was further milled by a motor-driven mortar. The mixture was transferred to a closed glass bottle, and heated at 85°C for 6 h. The obtained solid materials were washed with distilled water until its pH became 7, followed by drying overnight

at 110°C. Finally, the crystals were calcined at 550°C for 2 h in an air flow. Crystal structure of the product was identified by X-ray diffraction patterns. Cu ion-exchange was carried out in an aqueous solution at 80°C for 1 h. Cu/A was calcined at 350°C for 1 h. Content of Cu determined by atomic adsorption analysis was 9.0 wt.%. This catalyst is designated as Cat. 2.

Cu-containing zeolite A (Cu-A) [14] was synthesized by the same method as NaA synthesis described above. As the source of copper $Cu(NO_3)_2 \cdot 3H_2O$ (Wako) was used. An aqueous solution of raw materials was set at ratios of $SiO_2/Al_2O_3 = 1$, $Na_2O/Al_2O_3 = 5$, and $CuO/Al_2O_3 = 0.5$. The copper nitrate solution was added to the water glass solution dropwise while being vigorously stirred. The crystal structure of the product and the content of Cu were identified by X-ray diffraction patterns and atomic adsorption analysis, respectively. Content of Cu was 8.6 wt.%. It was designated as Cat. 3.

2.2. Characterization and catalytic reaction

A differential thermal gravimetric analyzer (DTG), Shimadzu thermal analyzer DGC-30, was used as the reactor as shown in Fig. 1. Reaction behaviors in CO oxidation on Cats. 1–3 by FORM and weight change of the catalysts during the oxidation reaction were investigated simultaneously. A 50 mg portion of the sample was placed in a sample pan of 6.0 mm inner diameter and 2.0 mm depth, which was set in a quartz glass tube of 17 mm inner diameter.

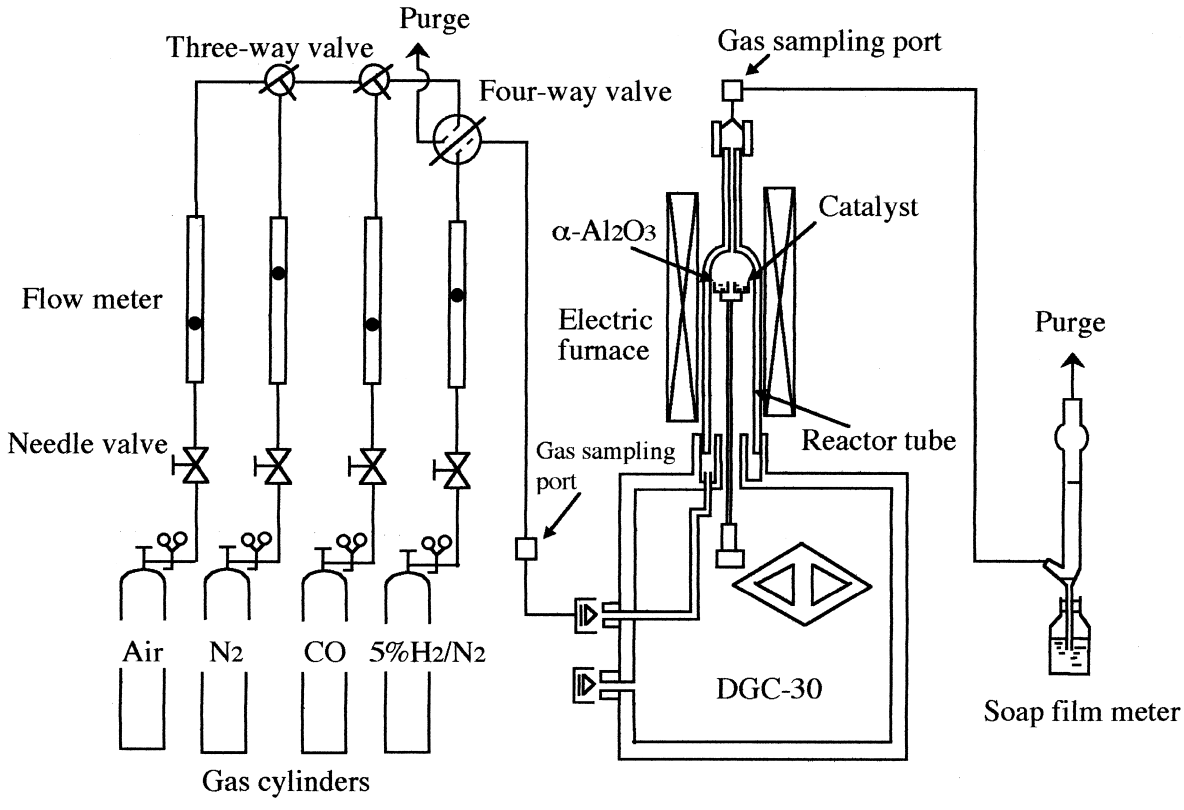

Fig. 1. Schematic diagram of the reactor and thermogravimetric analyzer for measuring the hysteresis in forced-oscillating reaction and weight change of a catalyst during the reaction.

The following four kinds of reaction gases were allowed to flow there at a flow rate of 350 ml/h.

(a) A gas mixture composed of 10% CO, 18.9% O_2, and 71.1% N_2 was used as the reaction gas; oxidative reaction condition (ORC).

(b) A gas mixture composed of 9.6% CO and 5.0% O_2, and 85.4% N_2; approximately stoichiometric reaction condition with slight excess of O_2 (SRC 1).

(c) A gas mixture composed of 13.1% CO, 4.5% O_2, and 82.4% N_2; approximately stoichiometric reaction condition with slight excess of CO (SRC 2).

(d) A gas mixture composed of 76.2% CO, 5.0% O_2, and 18.8% N_2; reductive reaction condition (RRC).

The reaction test by FORM was conducted on a catalyst in the reactor tube by temperature elevation, followed by cooling at a constant heating and cooling rate of 1°C/min. The cycle was continuously repeated several times. During the cycles the reacted gas was analyzed by a gas chromatograph (Shimadzu GC 8A) with a column of MS-5A for the analyses of CO and O_2. Since a part of the reaction gas was allowed to pass through the reactor tube without contact with the catalyst, the part of the gas was eliminated from the calculation to evaluate the performance of the catalyst.

The catalysts used were also characterized by TPR and TPO using a TG-DTA Shimadzu thermal analyzer DTG-50 [15]. For the measurement of the TPR, a 20-mg portion of the sample was placed in a sample pan and was heated in a stream of 16.8% O_2 diluted with N_2 from room temperature to 450°C at a constant heating rate of 10°C/min, and maintained at that temperature for 30 min. After cooling down, it was heated again in a stream of 4% H_2 diluted with N_2 the same way. The method for TPO was the same as that for TPR. It was pretreated in 4% H_2 diluted with N_2 at 450°C for 30 min, and heated again in a stream of 16.8% O_2 diluted with N_2. The amount of H_2 and O_2 consumption was calculated from a weight change of a catalyst during TPR and TPO, respectively.

An XPS analysis of Cu in the catalysts was done to investigate the state of Cu by ULVAC-PHI Model 5500 ESCA/MC/SIMS using MgKα X-ray at 1253.6 eV as the excitation source. The anode operated at 15 kV and 400 W, and sputter for depth profiling was performed under a condition of Xe^+ and energy 3 eV.

3. Results and discussion

3.1. Performance and state of the catalyst in Co oxidation observed by the forced-oscillating reaction method

3.1.1. Cu/SiO_2 (Cat. 1)

In Fig. 2, change in CO conversion in CO oxidation on Cat. 1 under the oxidative reaction condition (ORC) by FORM is shown. CO was oxidized above 130°C, and the CO conversion increased gradually with an increase in temperature, and reached 100% conversion at around 310°C. Almost no hysteresis in CO conversion was observed in FORM. However, the oxidation state of catalyst which can be measured by weight change showed some unique feature. When the reaction gas was allowed to flow at room temperature, the weight was increased by oxygen uptake. With an increase of temperature, it decreased maybe due to the reduction of oxidized copper by CO. However, above ca. 100°C, with an increase of the CO conversion, the weight of catalyst increased gradually again due to the oxidation of copper, and reached nearly complete oxidation of copper. During the descending temperature period until down to ca. 50°C, very slight weight decrease was observed, and below that temperature, the weight increased more than that the initial stage of the reaction at lower temperature range. At room temperature, the weight increase was beyond the level at which copper in catalyst is completely oxidized to CuO; therefore, the weight

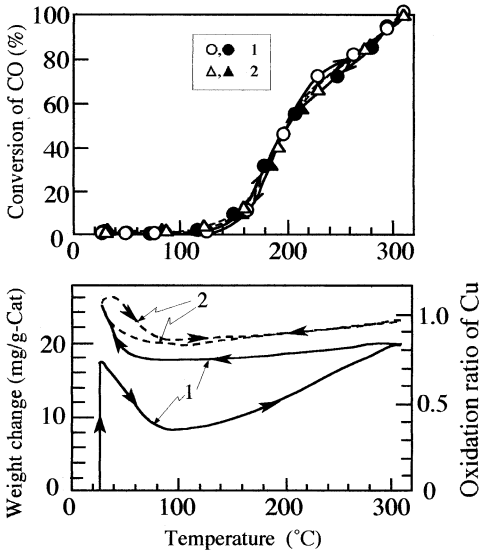

Fig. 2. Hysteresis shown during CO oxidation on 8.6 wt.% Cu/SiO_2 (Cat. 1) under the oxidative reaction condition (ORC). Numerals show the order of FORM test. Arrows show the directions of temperature change. Open symbol and closed symbol are ascending and descending temperature, respectively, in FORM measurement.

increase at lower temperature range below 50°C must be caused by adsorption of the reactants [16].

Fig. 3 shows the result obtained under the condition of SRC 1. CO was oxidized at the same temperature as the ORC shown in Fig. 2. However, in higher temperature range, the temperature dependence of the CO conversion is somewhat lower than that under ORC. No hysteresis is observed in each FORM cycle, but the second cycle is shifted to the higher temperature side to some extent. The weight changes during the first and second FORM measurements are very similar to that of ORC shown in Fig. 2, but the oxidation state of Cu decreases around $CuO_{0.7}$. This result indicates that under the stoichiometric reaction condition, but slightly oxygen-rich condition, the reaction can advance similarly to that under ORC; however, the oxidation state of Cu under SRC 1 is considerably in a lower state between CuO and Cu_2O than that under ORC.

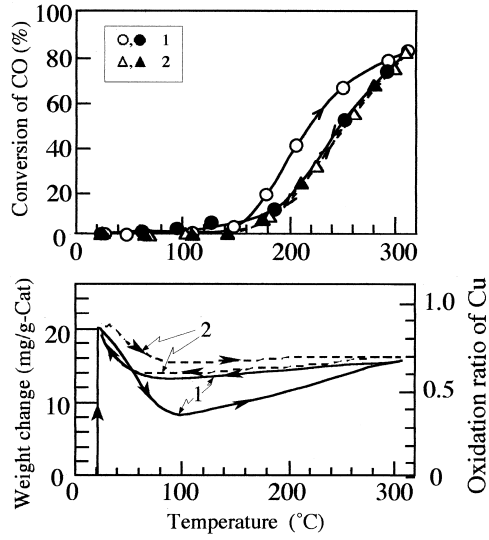

Fig. 3. Hysteresis shown during CO oxidation on 8.6 wt.% Cu/SiO_2 (Cat. 1) under the stoichiometric reaction condition with slight excess of O_2 (SRC 1). Captions are the same as shown in Fig. 2.

In Fig. 4, the results obtained under the reductive reaction condition (RRC) is shown. The results are markedly different from those in ORC and SRC 1. Since CO exists in the reac-

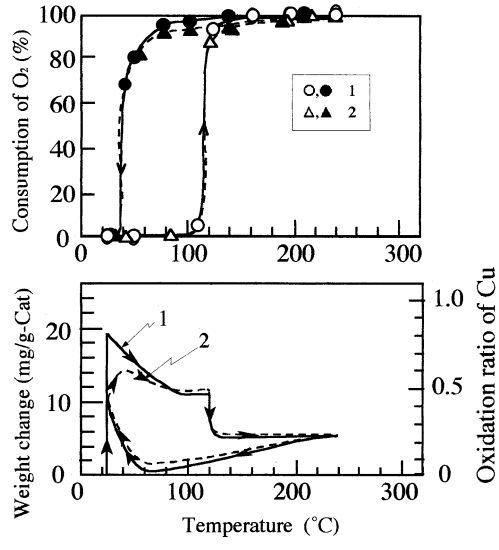

Fig. 4. Hysteresis shown during CO oxidation on 8.6 wt.% Cu/SiO_2 (Cat. 1) under the reductive reaction condition (RRC). Captions are the same as shown in Fig. 2.

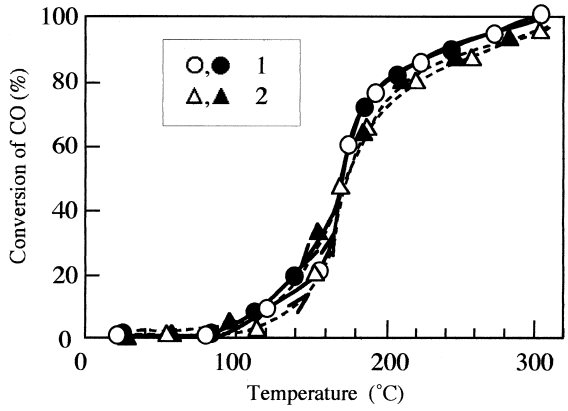

Fig. 5. Hysteresis shown during CO oxidation on 9.0 wt.% Cu/A (Cat. 2) under the oxidative reaction condition (ORC). Captions are the same as shown in Fig. 2.

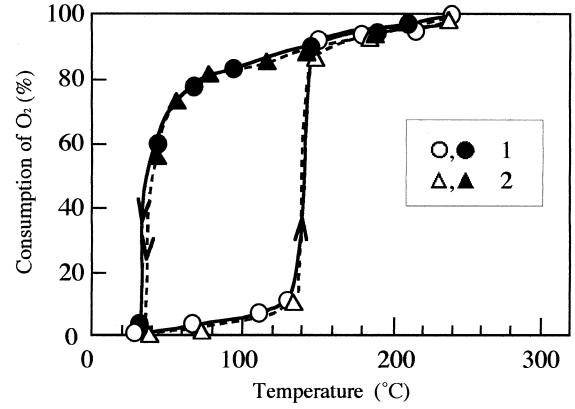

Fig. 7. Hysteresis shown during CO oxidation on 9.0 wt.% Cu/A (Cat. 2) under the reductive reaction condition (RRC). Captions are the same as shown in Fig. 2.

tion gas in an excess amount, in this case conversion is expressed by O_2 consumption. The CO oxidation occurs and increases suddenly at around 110°C, and correspondingly to this change at which temperature oxidation ratio decrease from ca. 0.5 (i.e., Cu_2O) to 0.25. A marked hysteresis is observed by FORM and the total conversion extends to lower temperature range around 70–60°C, and at this temperature range the oxidation state of Cu decreases and reaches almost 0 (i.e., reduced Cu) at around 60°C. At lower temperature than 60°C, the oxidation rate of Cu increased steeply and the CO oxidation decreases suddenly. First and second cycles of FORM were observed repeatedly.

Thus, the oxidation reaction deeply depended on the oxidation state of catalyst during the reaction.

3.1.2. Cu / A (Cat. 2)

State of Cu in Cat. 2 was estimated as an ionic state different from Cat. 1. In Fig. 5, change in CO conversion on Cat. 2 under the oxidative reaction condition (ORC) by FORM is shown. CO is oxidized above 100°C, which is 30°C lower than that on Cat. 1, and the CO

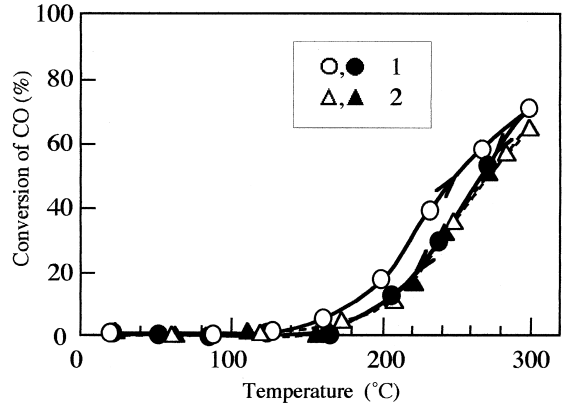

Fig. 6. Hysteresis shown during CO oxidation on 9.0 wt.% Cu/A (Cat. 2) under the stoichiometric reaction condition with slight excess of O_2 (SRC 1). Captions are the same as shown in Fig. 2.

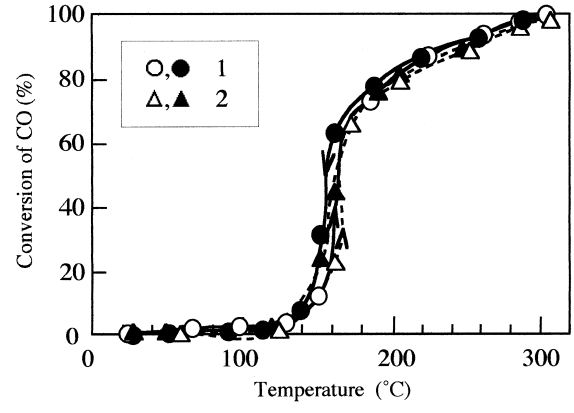

Fig. 8. Hysteresis shown during CO oxidation on 8.6 wt.% Cu-A (Cat. 3) under the oxidative reaction condition (ORC). Captions are the same as shown in Fig. 2.

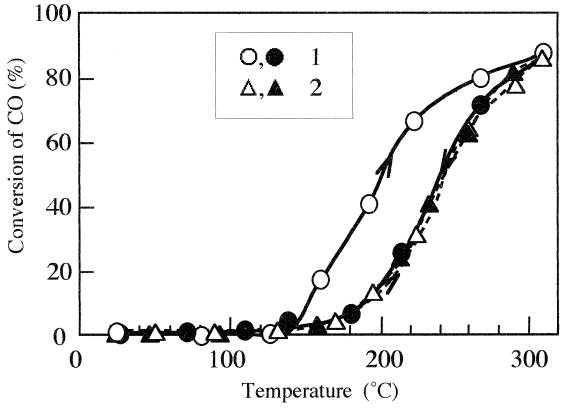

Fig. 9. Hysteresis shown during CO oxidation on 8.6 wt.% Cu-A (Cat. 3) under the stoichiometric reaction condition with slight excess of O_2 (SRC 1). Captions are the same as shown in Fig. 2.

conversion reaches 100% at around 310°C. Almost no hysteresis in CO conversion is observed in FORM. A weight change caused by redox of Cu is smaller than that of the catalyst caused by the adsorption of the reaction products, and trace amount of water included in the reaction gas into the zeolite. Therefore, the change in oxidation state of the catalyst could not be measured, but no difference between the weights before and after FORM cycle. It suggests that oxidation state of Cu in the catalyst does not change under ORC.

Fig. 6 shows the result obtained under the condition of SRC 1. CO was oxidized at above 160°C, which is 60°C higher than that under ORC. The CO conversion increases with an increase in temperature, but it was lower than that under ORC at every temperature. The lower CO conversion might be caused by lower O_2 concentration in the reaction gas after the first cycle, no hysteresis is observed in successive cycles.

In Fig. 7, the results obtained under the condition of RRC is shown. The CO oxidation occurs and increases suddenly at around 130°C with rapid decrease of the weight, which corresponds to 0.50 atom of oxygen per 1.0 atom of Cu in the catalyst. This rapid decrease in the weight is observed repeatedly in the first and second cycles of FORM. A hysteresis of CO conversion as similar as that on Cat. 1 for RRC was observed similar to the case of Cat. 1.

3.1.3. Cu-A (Cat. 3)

In Figs. 8 and 9, changes in the CO conversion under the conditions of ORC and SRC 1 are shown, respectively. The feature of CO oxidation on Cat. 3 is almost the same as that on Cat. 2 under the corresponding condition. It is reconfirmed that the oxidation state of Cu in

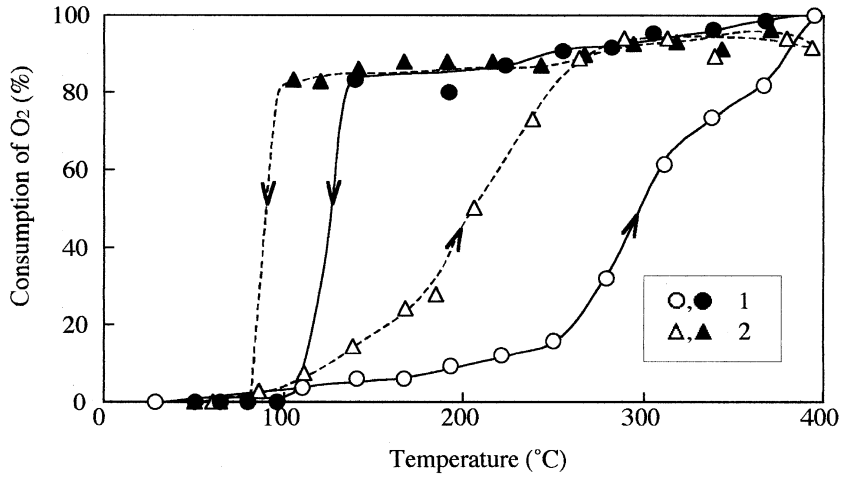

Fig. 10. Hysteresis shown during CO oxidation on 8.6 wt.% Cu-A (Cat. 3) under the stoichiometric reaction condition with slight excess of CO (SRC 2). Captions are the same as shown in Fig. 2.

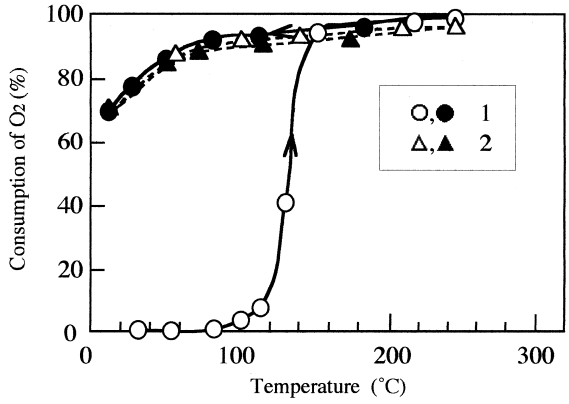

Fig. 11. Hysteresis shown during CO oxidation on 8.6 wt.% Cu-A (Cat. 3) under the reductive reaction condition (RRC). Captions are the same as shown in Fig. 2.

the catalyst does not change under the excess of O_2 condition. On the other hand, the result obtained under the condition of SRC 2 shows very large hysteresis as shown in Fig. 10. The CO oxidation is drastically changed by change of reaction condition from oxidative to reductive. A marked hysteresis is observed in each FORM cycle, and the second cycle is shifted to the lower temperature side to a large extent, as large as 80°C. In Fig. 11, the results under RRC with large excess of CO is shown. The CO oxidation occurs and O_2 consumption increased suddenly at around 120°C with rapid decrease of the weight, which corresponds to 0.73 atom of oxygen per 1.0 atom of Cu in the catalyst. The rapid decrease in the weight indicates that the copper oxide is reduced to a more reduced state. The O_2 consumption decreased gradually with decrease in temperature below 80°C, and even at 5°C it was still at 67%. The temperature down to 0% conversion is largely shifted to the lower temperature side than that of Cats. 1 and 2. In the second FORM cycle, the O_2 consumption is higher than 67% at every temperature, and hysteresis and the rapid weight change of the catalyst are not observed.

These results under RRC suggest that reduced Cu in Cu/SiO_2 (Cat. 1) and Cu/A (Cat. 2) in CO oxidation is re-oxidized easily in descending reaction temperature, and they lose activity for CO oxidation, but reduced Cu in Cu-A (Cat. 3) is stable against the re-oxidation even at the low temperature range.

3.2. Oxidation state of copper in the catalysts

In Fig. 12, Cu-2p XPS profiles for the copper located on the outer surface of the catalyst particles before FORM test are shown. The profile of Fig. 12(1) for Cu/SiO_2 (Cat. 1)

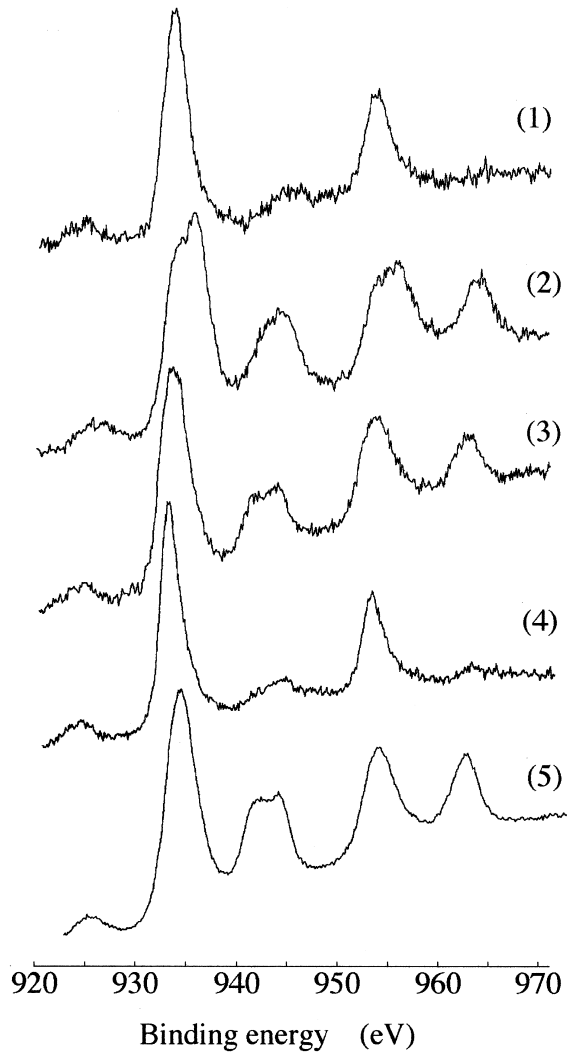

Fig. 12. Oxidation states of copper analyzed by XPS for different kinds of catalysts before the use for the reaction. (1) Cu/SiO_2 (reduced), (2) Cu/A, (3) Cu-A, (4) Cu-A after the sputter, (5) pure CuO.

coincided with Cu^0 [17] due to the pretreatment with 10% H_2. As shown in Fig. 12(2), besides the peaks of Cu^0 shown in Fig. 12(1), two obvious satellite peaks which belong to Cu-2p in two ranges of 940.0–949.0 and 960.0–967.0 eV are observed for Cu/A (Cat. 2) which was calcined in air at 550°C. A ratio of the area of the satellite peak in a range of 940.0–949.0 eV to that of Cu-$2p_{3/2}$ at 935.6 eV ($Cu_{satellite}/Cu_{2p}$) [18] is almost the same as that of a pure CuO (provided by Wako), as can be seen in Fig. 12(5). These satellite peaks are also observed in Fig. 12(3) for Cu-A (Cat. 3) which was calcined in air at 550°C. But $Cu_{satellite}/Cu_{2p}$ is lower than that of the pure CuO. The result suggests that lower valent Cu than Cu^{2+} existed stably in Cat. 3 even after the calcination in air. The amount of Cu^{2+} that was roughly estimated from the ratio of $Cu_{satellite}/Cu_{2p}$ is 73% of total Cu in the surface. The intensity of the satellite peaks after the sputter for 2.0 min is weaker than that for the surface, as shown in Fig. 12(4), and its auger parameter of 1850.0 eV indicates increase in Cu^+ species as the main Cu species in the bulk [19].

3.3. Redox property of the catalysts

In Fig. 13, the results of TPR and TPO for Cats. 1–3 are shown. Uptakes of H_2 in TPR and O_2 in TPO are estimated from the weight change of the catalysts, and they are expressed as stoichiometric ratio on the basis of CuO or Cu. Before TPR and TPO tests, each catalyst was pretreated in 16.8% O_2 and 4.0% H_2 at 450°C for 30 min, respectively.

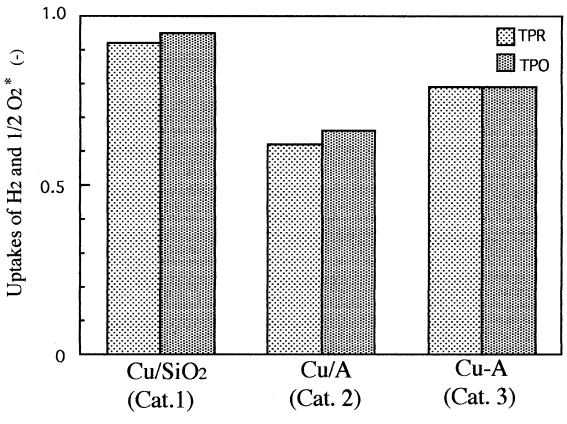

Fig. 13. Uptakes of H_2 and O_2 in TPR and TPO test for the catalysts. * Stoichiometric ratio on the basis of CuO or Cu.

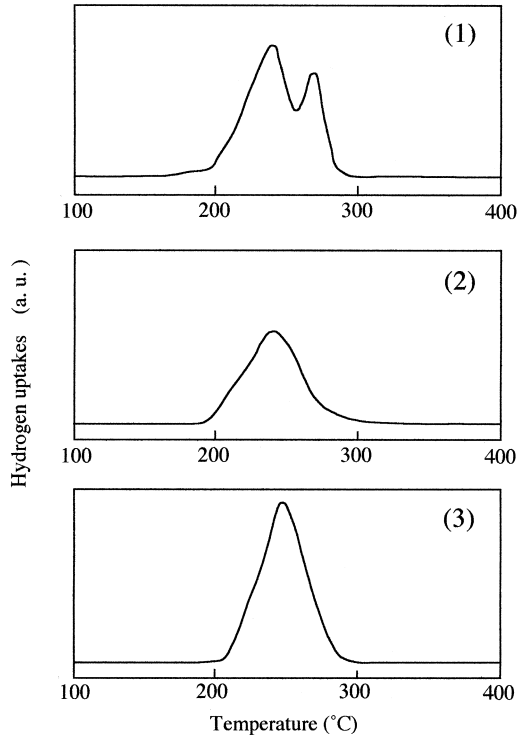

Fig. 14. TPR profiles for the catalysts. (1) Cat. 1, (2) Cat. 2, (3) Cat. 3.

Almost all of Cu oxide in Cat.1 is reduced to Cu^0 in TPR, and oxidized to Cu^{2+} in TPO. On the other hand, the amount of redox of copper in Cat. 2 is the lowest among the catalysts, and it is only ca. 65% of the stoichiometric change of $Cu^{2+} \rightarrow Cu^0$. The results of TPR, TPO, and XPS indicate that valence of Cu in Cat. 2 changes from +2 to +0.7, and not to zero [20]. In case of Cat. 3, the change of weight is ca. 80% of the stoichiometric change. It roughly accords with the rapid decrease of the weight under RRC.

In Fig. 14, TPR profiles for Cats. 1–3 pretreated in 16.8% O_2 at 450°C for 30 min are shown. H_2 uptakes were estimated from de-

crease of catalyst weight. Two peaks of reduction of copper in Cat. 1 are observed at 240 and 270°C. The result indicates a two-step reduction of copper oxide ($Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$) in the catalyst [21]. In case of Cat. 2, only one peak is observed at 240°C as the same temperature as the lower peak for Cat. 1. The single peak suggests that copper in Cat. 2 would be reduced from Cu^{2+} to Cu^{+}, but additional reduction to Cu^{0} does not occur. A single peak at 250°C is observed on Cat. 3. Reduction of copper in the catalyst to Cu^{0} would occur at that temperature. The peak temperature is lower than that of the higher peak on Cat. 1. It suggests that copper in Cat. 3 is more easily reduced to Cu^{0} than that on Cat. 1.

4. Conclusion

Performance of a catalyst for CO oxidation deeply depended on the oxidation state of the catalyst during the oxidation reaction, and the FORM was useful to investigate the changes of the oxidation state and the property of the catalyst during the reaction. The lower oxidation state of Cu in the catalyst led the higher CO oxidation rate, and change of oxidation state of catalysts during the reaction led a hysteresis in the CO conversion corresponding to the change of the reaction temperature. The order of the activity for CO oxidation was Cu-A > Cu/A, Cu/SiO_2. The highest activity of Cu-A was caused by the copper species in more stable and lower oxidation state than that in Cu/A and Cu/SiO_2 under all of the conditions tested, especially under the reductive condition.

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