# Comparative study on catalytic properties for low-temperature CO oxidation of Cu/$CeO_2$ and CuO/$CeO_2$ prepared *via* solvated metal atom impregnation and conventional impregnation

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Cu/$CeO_2$ and CuO/$CeO_2$ catalysts were prepared by solvated metal atom impregnation (SMAI) and conventional impregnation (CI) and used for carbon monoxide oxidation in CO and air. The catalysts were characterized by means of XRD, XPS, AES and $H_2$-TPR techniques. The Cu/$CeO_2$ catalyst prepared *via* SMAI exhibits higher catalytic activity in CO oxidation than that prepared *via* CI with the same Cu content due to the smaller Cu particles. The CuO/$CeO_2$ catalyst prepared *via* SMAI also shows higher catalytic activity than that prepared *via* CI because the CuO particles of the former are smaller than the latter and can be reduced by CO more easily. The Cu/$CeO_2$ catalysts display higher catalytic activities than CuO/$CeO_2$ catalysts with the same Cu content and prepared by the same method. The TPR profile for CuO/$CeO_2$ catalyst prepared *via* SMAI has a single peak, indicating a one-step reduction, whereas the TPR profile for CuO/$CeO_2$ catalyst prepared *via* CI has two peaks, indicating a two-step reduction due to the existence of two kinds of CuO species.

**KEY WORDS:** CO oxidation; copper; copper oxide; cerium oxide; solvated metal atom impregnation.

## 1. Introduction

Carbon monoxide is an air pollutant emitted by many sources. Total oxidation of carbon monoxide to carbon dioxide is employed to meet environmental regulations in an economic way. Precious metals (Pt, Au, Pd) are well-known oxidation catalysts with high activity and stability, and are widely used for exhaust gas emission control [1–3]. However, the high cost of precious metals and their sensitivity to sulfur poisoning have long motivated the search for substitute catalysts. It has been reported [4–6] that high activity and resistance to poisoning catalysts for CO oxidation were achieved by doping some oxides (such as ceria, zirconia, and thoria) with transition metals (such as copper, cobalt, or nickel). Cerium oxide is widely used as a promoter in the so-called "three-way catalysts" for the elimination of toxic exhaust gases in automobiles because of the enhancement of the metal dispersion and the stabilization of the support toward thermal sintering, as well as its direct participation in chemical processes [7,8]. The catalysts for fundamental studies are prepared by various conventional techniques, such as impregnation, ion exchange, anchoring/grafting, spreading and wetting, hydrolysis, homogenous deposition precipitation, and solution combustion [9,10]. Currently, novel methods of preparation are being examined. The solvated metal atom impregnation (SMAI) method had been found to be unique for obtaining highly dispersed metallic catalysts. In this article we report the first study on CO oxidation over Cu/$CeO_2$ and CuO/$CeO_2$ catalysts prepared by SMAI. By comparative study with the Cu/$CeO_2$ and CuO/$CeO_2$ catalysts prepared by conventional impregnation (CI), we obtain some important information about the effects of oxidation states and particle sizes of copper on the catalytic activities of catalysts, which may be useful for the development of copper catalysts to replace noble metal catalysts for low-temperature CO oxidation.

## 2. Experimental

### 2.1. Preparation of catalysts

The procedures for preparing Cu/$CeO_2$ and CuO/$CeO_2$ catalysts by SMAI are as shown in scheme 1.

The support $CeO_2$ was dehydrated under vacuum ($1.3 \times 10^{-2}$ Pa) at 400 °C for 8 h. Toluene used as the solvating medium was carefully dehydrated and degassed by the "freeze–thaw" process. The design of the static metal atom reactor for the preparation of the precursor solution of bis(toluene) copper(0) has been described elsewhere [11,12]. In a typical experiment, approximately 1 g of copper chop (99.9%) was evaporated and co-condensed with 130 ml of toluene at $-196$ °C under a dynamic vacuum of less than $1.33 \times 10^{-2}$ Pa over a period of about 1 h. After finishing the co-condensation, the co-condensate was warmed up to $-78$ °C and melted down to the bottom of the reactor. The bis(toluene) copper(0) complex

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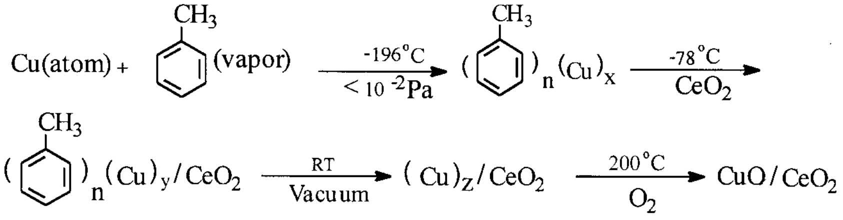

(x, y and z represent the number of Cu atoms)

Scheme 1.

prepared in this way is extremely air-sensitive and thermally unstable, and decomposes into copper(0) and toluene at about −100 °C. The precursor solution was transferred to the precooled (−78 °C) $CeO_2$ through a stainless steel tube. The $CeO_2$ (20 g) was impregnated with solvated Cu atom (cluster) solution for 5 h at −78 °C under stirring. Then the Cu–toluene/$CeO_2$ slurry was gradually warmed to room temperature. The colourless excess toluene was removed by a syringe and the Cu/$CeO_2$ catalyst was dried under vacuum at room temperature for several hours. The dry sample was stored and handled in a nitrogen-filled glovebox. CuO/$CeO_2$ catalyst was produced by oxidizing the Cu/$CeO_2$ catalyst in the reaction cell in oxygen at 200 °C for 3 h. The catalysts prepared were denoted Cu/$CeO_2$ (SMAI) or CuO/$CeO_2$ (SMAI) and the copper loading in the catalysts was determined by ICP.

The CuO/$CeO_2$ catalyst *via* CI was prepared by impregnation of the $CeO_2$ support using an aqueous solution of $Cu(NO_3)_2$ (to give a copper loading the same as the sample prepared *via* SMAI). The resulting material was dried overnight at 120 °C and subsequently calcined in air at 600 °C for 3 h. Cu/$CeO_2$ catalyst was produced by reducing the above CuO/$CeO_2$ catalyst in the reaction cell in hydrogen at 500 °C for 3 h. The catalysts prepared by CI were denoted Cu/$CeO_2$ (CI) or CuO/$CeO_2$ (CI).

### 2.2. XRD

X-ray diffraction of the supported copper particles was performed on a D/MAX-IIIA X-ray diffraction spectrometer. Diffraction patterns were recorded with Cu $K_\alpha$ radiation and a graphite monochrometer over a $2\theta$ range of 20° to 70°. The working voltage and current of the X-ray tube were 45 kV and 170 mA.

### 2.3. XPS

The X-ray photoelectron spectra were taken before each catalytic run. XPS were recorded on a PHI-5300 spectrometer using Al $K_\alpha$ radiation (1486.6 eV). The instrument was operated at a pressure below $1 \times 10^{-8}$ Pa. Samples were mounted on the holder using double-sided tape. The XPS binding energies were referenced to the graphite C 1s peak at 184.2 eV and the system was occasionally checked using the Fe $2p_{3/2}$ peak at 706.8 eV of a sputtered cleaned pure iron foil.

### 2.4. $H_2$-TPR

TPR measurements were carried out in a flow system. 10 mg of catalyst was pretreated in vacuum at 200 °C and placed in a TPR cell at 20 °C into which $H_2{:}N_2$ (5:95) mixed gas was introduced. The temperature of the sample was programmed to rise at a constant rate of 10 °C/min and the amount of $H_2$ uptake during the reaction was measured by a thermal conductivity detector (TCD).

### 2.5. Activity measurements

A steady-state catalytic test was carried out in a fixed-bed flow microreactor. The catalyst powder was embedded between glass wool plugs in an 8 mm i.d. glass reactor tube. Experiments were performed in the temperature range 273–393 K and at atmospheric pressure. For each experiment 200 mg catalyst was used which was transferred into the reactor under the protection of $N_2$ gas flow. The reaction gases contain 1.0% CO balanced with air, purified through a molecular sieve column and passed through the catalyst bed at a flow rate of 67 ml/min ($sv = 20\,000\ \mathrm{ml\,h\,g^{-1}}$). Kinetic data were taken after 10 or 20 min on stream at specified conditions. The products were analysed by an SP-501 gas chromatograph.

## 3. Results and discussion

### 3.1. XRD

Figures 1 and 2 show the XRD patterns for Cu/$CeO_2$ and CuO/$CeO_2$ catalysts prepared by both SMAI and CI. There are no Cu diffraction peaks in figure 1 (Cu(III), $2\theta = 43°$) to be observed on a 5 wt% Cu/$CeO_2$ sample prepared by SMAI. This is because the Cu particles in the sample are so small that they go beyond the limit of the instrument sensitivity (~2.5 nm). It can be clearly seen that there are Cu(III) peaks for 5 wt% Cu/$CeO_2$ (CI) and 15 wt% Cu/$CeO_2$ (SMAI) and a little sharper Cu(III) peak for 15 wt%

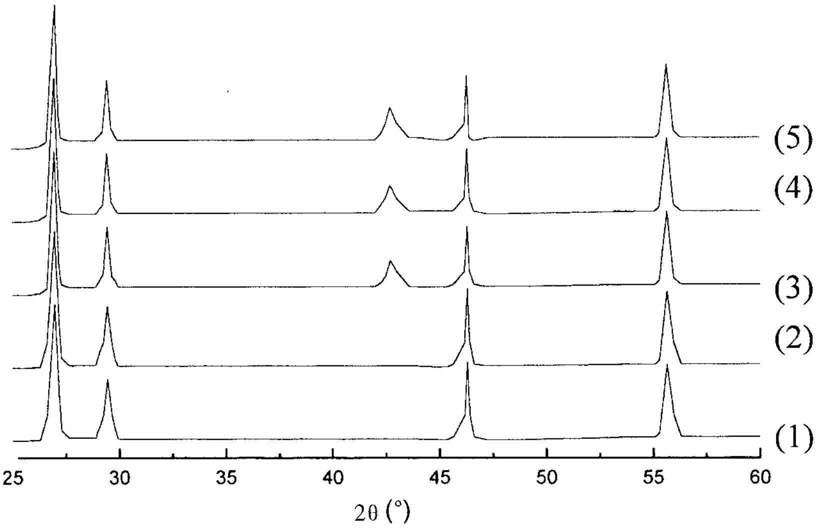

Figure 1. XRD patterns of Cu/CeO$_2$ catalysts and CeO$_2$. (1) Support CeO$_2$; (2) 5 wt% CuO/CeO$_2$ (SMAI); (3) 5 wt% CuO/CeO$_2$ (CI); (4) 15 wt% CuO/CeO$_2$ (SMAI); (5) 15 wt% CuO/CeO$_2$ (CI).

Cu/CeO$_2$ (CI) in figure 1. The copper particle sizes calculated from peak broadening using Scherrer's equation are 8, 11 and 48 nm for 15 wt% Cu/CeO$_2$ (SMAI), 5 wt% Cu/CeO$_2$ (CI) and 15 wt% Cu/CeO$_2$ (CI), respectively. For CuO/CeO$_2$ catalysts, no CuO peaks were found by XRD except for 18 wt% CuO/CeO$_2$ prepared by CI (figure 2(4)) in which CuO appeared in smaller and broader peaks. The major peaks were due to the CeO$_2$ crystal phase. No Cu$_2$O phase was found by XRD.

### 3.2. XPS

The Cu 2p3/2 XPS binding energies and Cu LMM Auger kinetic energy of Cu/CeO$_2$ and CuO/CeO$_2$ catalysts are summarized in table 1. Figures 3 and 4 show the XPS spectra of Cu 2p$_{3/2}$ and CuL3M4.5M4.5 Auger lines for these catalysts respectively. The shake-up peak and higher Cu 2p$_{3/2}$ binding energy are two major XPS characteristics of CuO, while the lower Cu 2p$_{3/2}$ binding energy and absence of the shake-up peak are characteristic of reduced copper species [13]. From table 1, figure 3 and figure 4, it can be seen that the Cu 2p$_{3/2}$ binding energies and peak shapes for Cu/CeO$_2$ catalysts are different from that of CuO/CeO$_2$ catalysts. In the Cu 2p$_{3/2}$ XP spectra of CuO/CeO$_2$ catalysts, there were shake-up peaks and the Cu 2p$_{3/2}$ binding energies were higher (934.4–934.1 eV), which suggested the presence of Cu(II) species (CuO). The lower Cu 2p$_{3/2}$ binding energies (933.0–933.1 eV), and lack of any shake-up satellite structure of Cu/CeO$_2$ catalysts, indicated the absence of any CuO or other Cu(II) species.

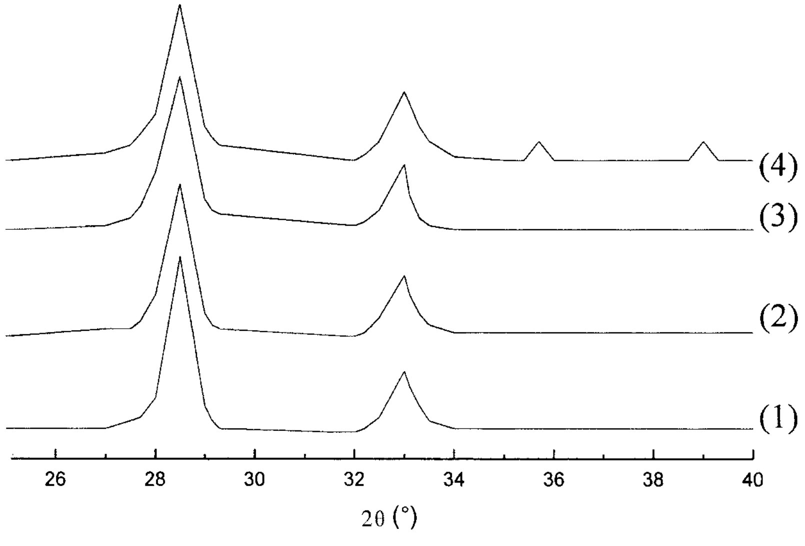

Figure 2. XRD patterns of CuO/CeO$_2$ catalysts and CeO$_2$. (1) 6% CuO/CeO$_2$ (SMAI); (2) 6% CuO/CeO$_2$ (CI); (3) 18% CuO/CeO$_2$ (SMAI); (4) 18% CuO/CeO$_2$ (CI).

Table 1
Binding and kinetic energies of $Cu/CeO_2$ and $CuO/CeO_2$ catalysts

| Sample | Cu $2p_{3/2}$ | | Cu LMM Auger | | |
|---|---|---|---|---|---|
| | $Cu^0$ or $Cu_2O$ | CuO | $Cu^0$ | $Cu_2O$ | CuO |
| 5% $Cu/CeO_2$ (SMAI) | 933.0 | – | 918.5 | – | – |
| 5% $Cu/CeO_2$ (CI) | 933.1 | – | 918.4 | – | – |
| 15% $Cu/CeO_2$ (SMAI) | 933.1 | – | 918.5 | – | – |
| 15% $Cu/CeO_2$ (CI) | 933.1 | – | 918.5 | – | – |
| 6% $CuO/CeO_2$ (SMAI) | 933.0 | 934.0 | – | 916.5 | 917.6 |
| 6% $CuO/CeO_2$ (CI) | 933.1 | 934.1 | – | 916.4 | 917.6 |
| 18% $CuO/CeO_2$ (SMAI) | 933.1 | 934.1 | – | 916.5 | 917.6 |
| 18% $CuO/CeO_2$ (CI) | 933.1 | 934.1 | – | 916.5 | 917.6 |

Such shake-up satellite peaks have been attributed to either 3d → 4s or ligand to metal (O 2p → Cu 3d) transition which are not seen for $Cu^{1+}$ compounds and metallic $Cu^0$ [14]. In addition, the full width at half maximum (FWHM) Cu $2p_{3/2}$ line of CuO is about twice that of $Cu_2O$ or Cu. This broadening is caused by the multiple splitting of Cu(II) [15]. The Cu $2p_{3/2}$ binding energies and peak shapes cannot be used to distinguish between $Cu_2O$ and $Cu^0$ because they are essentially identical. However, the Cu LMM Auger lines of $Cu_2O$ and $Cu^0$ are separated by 2.0 eV and their peak shapes are different, allowing easy distinction between the two species. Our present observation suggests both CuO and $Cu^{1+}$ species exist in these $CuO/CeO_2$ catalysts. Although we could deconvolute the Cu $2p_{3/2}$ peaks to find the relative proportion of CuO in the $CuO/CeO_2$ catalysts, it is hard to obtain a reliable value from this mathematical process because this peak did not show an apparent doublet shape. Figure 4 shows the kinetic energy spectra of the Auger LMM electron, and the doublet peaks for $CuO/CeO_2$ samples also suggest the presence of the copper species. The 918.5, 917.6 and 916.5 eV peaks in the Auger kinetic spectra correspond to $Cu^0$, CuO and $Cu^+$ species, respectively.

### 3.3. Temperature-programmed reduction

The TPR profiles for $CuO/CeO_2$ catalysts are shown in figure 5. The reduction profile of pure CuO is characterized by a single peak at 380 °C and the reduction of pure $CeO_2$ begins at 400 °C, neither of which are shown in figure 5. A two-step reduction profile is

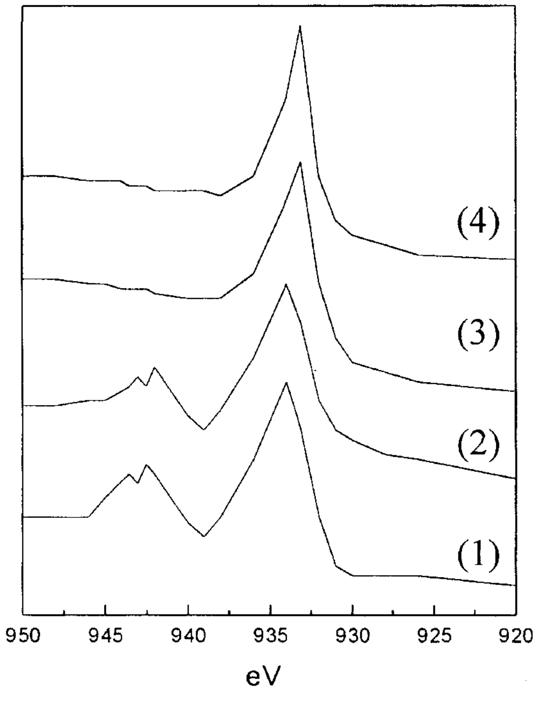

Figure 3. XP spectra of Cu $2p_{3/2}$ for $Cu/CeO_2$ and $CuO/CeO_2$ catalysts. (1) 6% $CuO/CeO_2$ (CI); (2) 6% $CuO/CeO_2$ (SMAI); (3) 5% $Cu/CeO_2$ (CI); (4) 5% $Cu/CeO_2$ (SMAI).

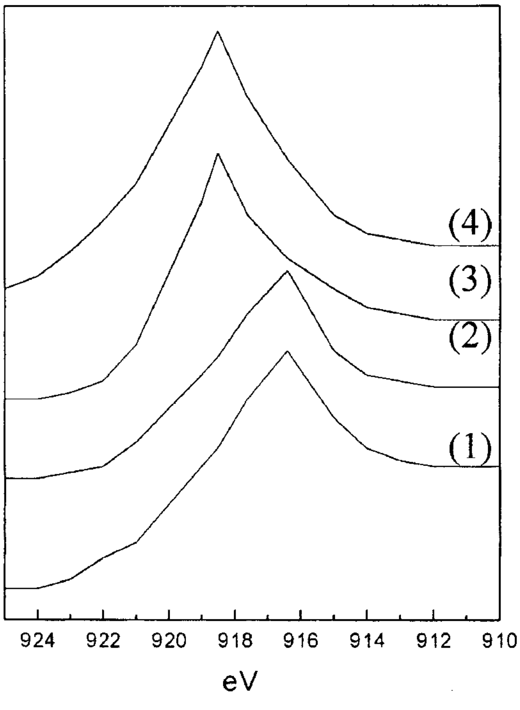

Figure 4. Kinetic energy spectra of the Cu Auger LMM for $Cu/CeO_2$ and $CuO/CeO_2$ catalyst. (1) 6% $CuO/CeO_2$ (CI); (2) 6% $CuO/CeO_2$ (SMAI); (3) 5% $Cu/CeO_2$ (CI); (4) 5% $Cu/CeO_2$ (SMAI).

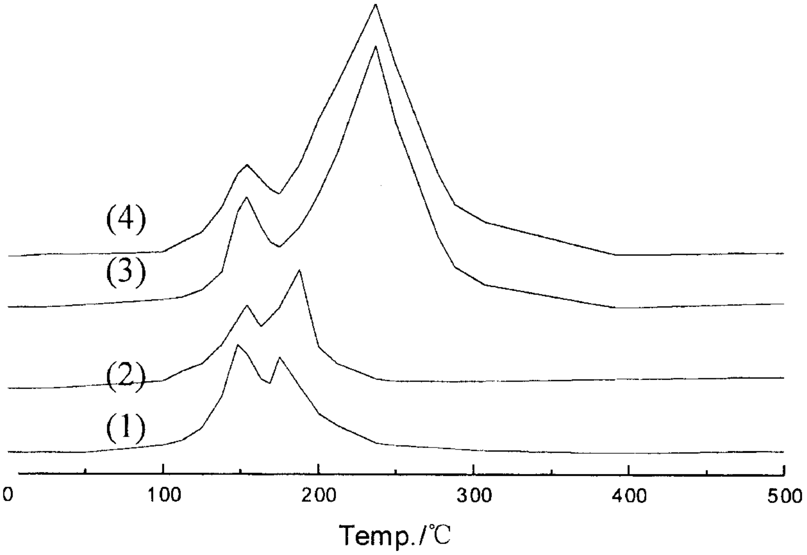

Figure 5. TPR profiles of $CuO/CeO_2$ catalysts. (1) 6% $CuO/CeO_2$ (SMAI); (2) 6% $CuO/CeO_2$ (CI); (3) 18% $CuO/CeO_2$ (SMAI); (4) 18% $CuO/CeO_2$ (CI).

observed for all $CuO/CeO_2$ catalysts, indicating the existence of two kinds of CuO species. Luo *et al.* [16] suggested that one was represented by small copper particles and reduced at lower temperature, another was represented by larger particle CuO and reduced at higher temperature. TPR peak temperature of all $CuO/CeO_2$ catalysts is much lower than that of pure CuO. The position basically remains unchanged with increasing CuO loading around 165 °C. The intensity of the peak increases with CuO loading. Compared with the $CuO/CeO_2$ catalysts prepared by CI, the position of TPR peak temperature of SMAI-prepared catalysts slightly shifts to lower temperature. Another difference of the profiles between SMAI- and CI-prepared catalysts is that the intensity of the low temperature is higher than that of the high temperature for the lower loading 6% $CuO/CeO_2$ SMAI catalyst, whereas the intensity of the high temperature is higher than that of the low temperature for the corresponding CI catalyst. This is because the content of the small Cu particle is greater than that of the larger Cu particle for 6% $CuO/CeO_2$ catalyst prepared by SMAI. By contrast, the content of the larger Cu particle is greater than that of the small Cu particle for the corresponding catalyst prepared by CI. The reduction profile of all $Cu/CeO_2$ catalysts only has a single peak around 400 °C (not shown in figure 5) which is the reduction of $CeO_2$, indicating that copper exists in a metallic state.

### 3.4. Catalytic activity for CO oxidation

Figure 6 shows the light-off curves over $Cu/CeO_2$ and $CuO/CeO_2$ catalysts prepared by both SMAI and CI. None of those catalysts were pretreated before running

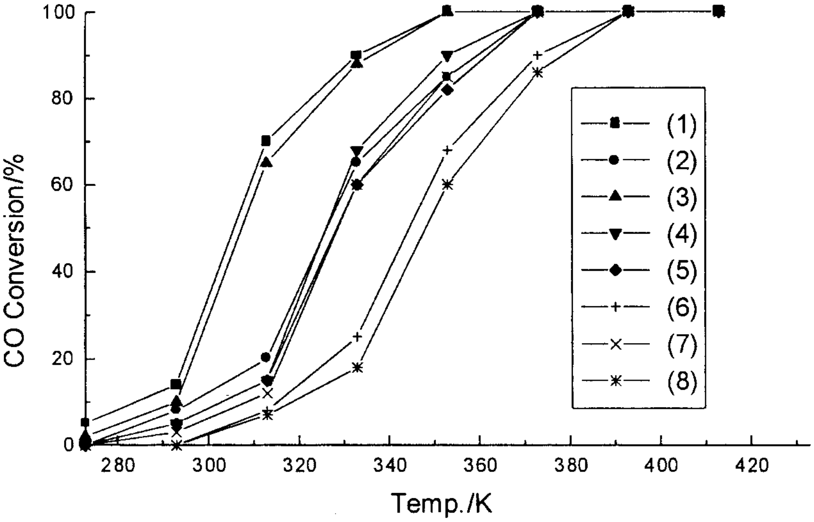

Figure 6. Catalytic activities of $Cu/CeO_2$ and $CuO/CeO_2$ catalysts in CO oxidation as a function of reaction temperature. (1) 5% $Cu/CeO_2$(SMAI); (2) 5% $Cu/CeO_2$(CI); (3) 15% $Cu/CeO_2$(SMAI); (4) 15%$Cu/CeO_2$(CI); (5) 6% $CuO/CeO_2$(SMAI); (6) 6% $CuO/CeO_2$(CI); (7) 18% $CuO/CeO_2$(SMAI); (8) 18% $CuO/CeO_2$(CI).

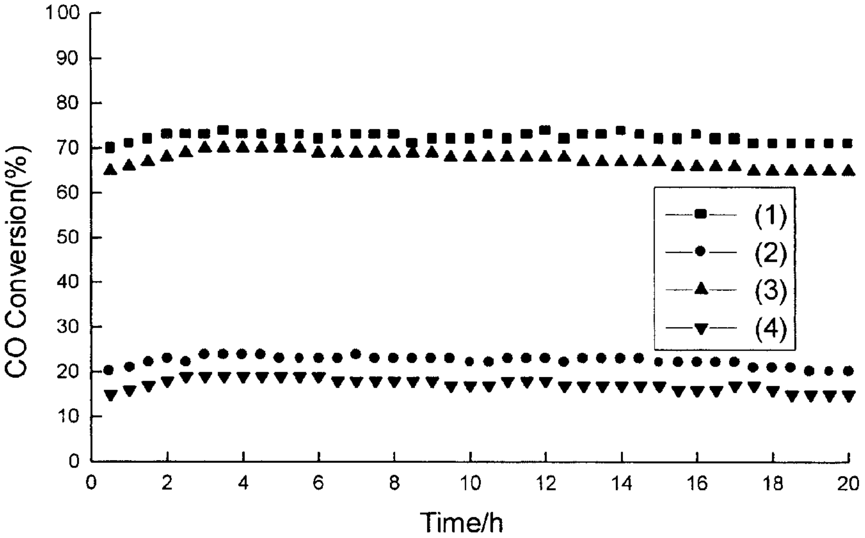

Figure 7. CO conversion over 5% $Cu/CeO_2$ and 6% $CuO/CeO_2$ catalysts as a function of reaction time at 313 K. (1) 5% $Cu/CeO_2$ (SMAI); (2) 5% $Cu/CeO_2$ (CI); (3) 6% $CuO/CeO_2$ (SMAI); (4) 6% $CuO/CeO_2$ (CI).

the reaction. At each reaction temperature, the reaction was continued for about 50 min to achieve steady-state activity. From figure 6, it can be seen that the light-off temperature of $Cu/CeO_2$ and $CuO/CeO_2$ catalysts prepared by SMAI is lower than that of the corresponding catalysts prepared by CI. This indicates that activity of the SMAI-prepared catalysts is higher than that of CI-prepared catalysts with the same composition. We think the reason is that the copper particles of catalysts prepared *via* SMAI are much smaller than that of those prepared *via* CI. Catalytic test result also indicate that CO oxidation activity of $CuO/CeO_2$ catalyst is related to the reduction temperature of CuO species. The smaller the CuO particles, the easier they are to reduce and the higher the activity exhibited by the catalysts. The kinetic data for CO oxidation on metallic copper and copper(II) oxide clearly show that the activity of finely dispersed metallic copper is higher than that of finely dispersed CuO species. This result is in good agreement with Jernigan's work [17].

The oxidation activity of 5% $Cu/CeO_2$ and 6% $CuO/CeO_2$ catalysts prepared by SMAI and CI as a function of reaction time is shown in figure 7. The activity of these catalysts apparently does not decay with reactive time. The activity of these catalysts for CO oxidation is close to finely dispersed good catalyst in the literature [18].

## 4. Conclusions

$Cu/CeO_2$ and $CuO/CeO_2$ catalysts have been prepared by two different methods and tested for low-temperature carbon monoxide oxidation. The catalysts prepared *via* SMAI exhibit higher CO oxidation activity than that of the catalysts prepared *via* CI, and the $Cu/CeO_2$ catalysts show higher activity than that of $CuO/CeO_2$ with the same copper content. Both $Cu/CeO_2$ and $CuO/CeO_2$ catalysts prepared by either SMAI or CI demonstrate fairly high CO oxidation activity and do not show deactivation of catalytic activity. The very finely dispersed Cu and CuO on $CeO_2$ are responsible for the high activity in low-temperature CO oxidation and the large Cu and CuO particles contribute little to the activity. The TPR investigation of $CuO/CeO_2$ catalysts reveals that $CeO_2$ promotes the reduction of CuO species and the smaller the CuO particles, the easier they are to reduce.

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