

Design of nano-structured Cu loaded CeO₂ catalyst for CO Oxidation

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Abstract. The catalytic activity for CO oxidation over Cu-modified cerium dioxide (CeO₂) powder was investigated using flow tube-reactor system. The nano-sized CeO₂ powders were prepared using ammonium carbonate co-precipitation method. The nano-tubes of copper oxide (CuO) on the nano-sized CeO₂ particles were fabricated by low temperature calcination. Also, nano-size Cu metal particles were included into the CuO nano-tube. The detail structure of CuO nano-tubes loaded CeO₂ catalyst was characterized by means of Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD). This characterization suggests that CuO nano-tube including nano-size Cu metal was developed on the surface of CeO₂. In addition, the temperature at 50% CO₂ yield in CO oxidation reaction was lowered by this system. This temperature would be lowered by the design of nano-structure and optimization of composition of Cu nano-tube loaded CeO₂ catalyst. It is expected that the nano-structured CuO nano-tube loaded CeO₂ will be one of promising environmental friendly catalysts for energy and environmental applications.

Key words: copper oxide nano-tube, nano-size copper metal, ceria, CO oxidation, environmental friendly catalyst

1. INTRODUCTION

It is known that cerium dioxide (CeO₂) is an important catalyst in many chemical reactions, e.g. the NO reduction under oxidation conditions or CO oxidation under reducing conditions in automotive exhaust catalysts [1]. Several studies indicate that the chemical state of ceria is a critical factor dominating the catalytic behaviour.

Noble metal catalysts have been found to be active for number of chemical reactions in the lower temperature such as 300 °C. CO oxidation over Cu metal particle-CeO₂ catalyst has been demonstrated by Flytzani-Stephanopoulos [2, 3]. The remarkable redox ability of CuO-CeO₂ at the lower temperature was found to play an essential role in CO oxidation reaction. It was shown the catalytic behavior of CuO-CeO₂ greatly depends on the preparation routes [4]. The catalysts for fundamental studies are prepared by various conventional techniques such as impregnation, ion exchange, anchoring/grafting, spreading and wetting, hydrolysis, and homogeneous deposition-precipitation [5]. Presently, it is a new trend regarding novel chemical techniques of synthesis that can lead to ultra fine, high-surface-area catalysts for heterogeneous catalysis [6].

In the present study, CuO nano-tube loaded CeO₂ catalyst was fabricated using soft chemical approach.

The nano-structural feature and catalysis of obtained nano-structured catalyst were examined.

2. EXPERIMENTAL DETAILS

2.1 Preparation of catalysts

Nano-sized CeO₂ precursor precipitations were prepared by (NH₄)₂CO₃ co-precipitation method. The precipitation was dried after filtration and rinsing. The dried powders were calcined at 400 °C to 800 °C in oxygen gas flow.

Cu loaded CeO₂ was prepared by impregnation method. The starting materials we used were Cu (II) acetate monohydrate ((C₂H₃O₂)₂·H₂O, Purity: 99.99+%, Sigma Aldrich Company, USA) and calcined nano-size CeO₂ powders. The copper acetate and CeO₂ were mixed with toluene in a magnetic stirrer for about 28 hours and dried in a flow of nitrogen. Then Cu-CeO₂ was calcined in a flow of oxygen at 300 °C for 2 hours.

2.2 Evaluation of catalytic activity

The activity of CO oxidation was examined using a flow tube-reactor. The sample powder was placed between two pieces of quartz wool in the quartz glass tube with U shape, which was placed inside the heater. The temperature was measured by thermocouple in a direct contact with the tube.

During reaction experiments, the sample was heated from room temperature up to 350 °C. In the present experiments, the mixture gas of helium (He), carbon monoxide (CO) and oxygen (O₂) was used for the measurement of activity. The inlets of gases were controlled by digital flow meters and mixed before entering the U shape tube. The flow rates were; He: 15.3 ml.min⁻¹, CO: 1.7 ml.min⁻¹ and O₂: 5 ml.min⁻¹. The total flow rate was 22 ml.min⁻¹. The outlet gas was analyzed by a Quadrupole Mass Spectrometer. Heating rate during reaction experiments was about 3 °C.min⁻¹.

2.3 Observation of microstructure

Particle morphology and nanostructure of obtained powders were observed by field emission SEM (S-5000, Hitachi, Japan) and high resolution TEM equipped with electron energy-loss spectroscopy (EELS) detector (Technai F30 FEG, Philips). Prior to SEM observation, powder specimens were dispersed into ethanol ultrasonically, with the suspensions on to a thin layer of aluminium foil. A small portion of the foil with the finest particles on it was cut, fitted onto a sample plate and then coated with tungsten. In the case of TEM observation, aforementioned suspensions dropped on the grid with amorphous carbon film. To minimize the contamination, the uncoated powder specimens were observed for element analysis at atom level. SEM and TEM observations were performed with gun voltages of 10keV and 300keV, respectively. Also, the element mapping was performed by EELS of TEM.

Crystal phases of obtained specimens were analyzed by XRD (RINT 2500 HF, Rigaku X-ray diffractometer, operated condition: 40 kV, 300 mA, and Cu-K α radiation). The crystallite size was calculated using Sherrer's formula, defined as follows:

$$D = (K\lambda) / (B\cos\theta) \quad (1)$$

where D is the crystallite size, K is the constant depended on crystallite shape (0.9), λ is the wavelength of the incident X-rays (0.15406 nm), B is full width of half maximum (FWHM) of integral breadth and θ is the diffraction angle.

3. RESULTS AND DISCUSSION

3.1 Crystallite size and crystal phases

Figure 1 shows XRD patterns of CeO₂ calcined at 400 °C for 4 hours, at 800 °C for 2 hours and Cu loaded CeO₂ calcined at 300°C for 2 hours. For preparation of Cu loaded CeO₂, the calcined CeO₂ powders at 400°C was used. The calcined CeO₂ consisted of simple fluorite structure. Both of CeO₂ and Cu loaded CeO₂ were well crystallized powders.

From the Sherrer's formula (1) and FWHM of (111), (200), (220), (311) and (400) peaks, we determined the crystallite size of calcined CeO₂. The calculated particle size of CeO₂ calcined at 400°C and 800°C were 50 and 60nm, respectively. This is consistent with the SEM observations. The XRD pattern of Cu loaded CeO₂ consisted of CuO peaks and fluorite peaks. The calculated particle size was approximately 20 nm.

3.2 Particle morphology

To characterize obtained specimens, the particle morphologies were observed using SEM. Two kinds of SEM images recorded from calcined CeO₂ and Cu

loaded CeO₂ sample were displayed in figures 2 and 3, respectively.

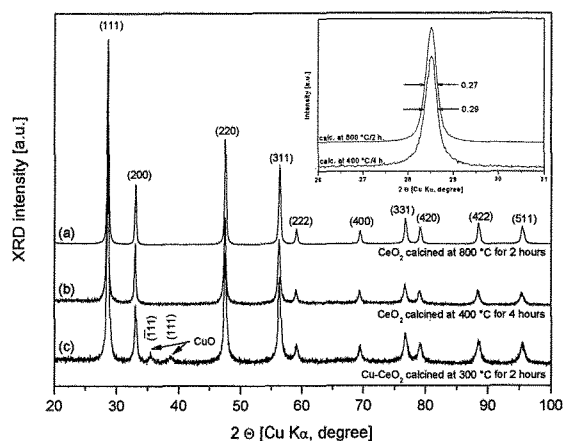


Fig. 1 X-ray diffraction patterns of CeO₂ and Cu-CeO₂ calcined in different calcination conditions; calcination condition: (a) 400°C for 4 hours, (b) 800°C for 2 hours and (c) Cu-CeO₂ calcined at 300 °C for 2 hours.

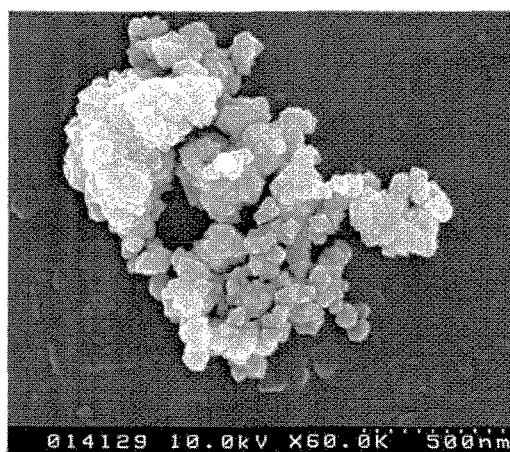


Fig. 2 SEM image of CeO₂ calcined at 400°C for 4 hours.

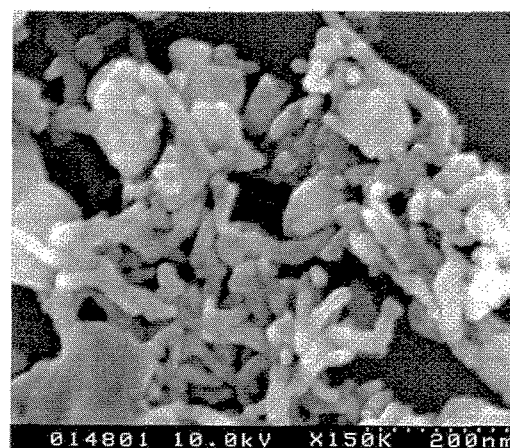


Fig. 3 SEM image of Cu-CeO₂ calcined at 300°C for 2 hours.

The calcined CeO_2 specimens were uniformly size and squared shaped particles. The average particle size was approximately 50 nm. On the other hand, the Cu loaded CeO_2 has quite different morphology, as shown in Fig.3. Copper loaded CeO_2 consists of the mixture of elongated particles and squared shaped particles. The size of elongated particles was 20-25 nm in diameter and 200 nm or less in length. The uncalcined Cu loaded CeO_2 is composed of squared shaped particles only. This indicates that the small elongated particles were prepared during low temperature calcination process (i.e. 300 °C for 2 hours). It is concluded that the size and content of these small particles is controllable by selection of optimum preparation conditions (i.e. calcination temperature, calcination time, and flow rate of oxygen gas).

3.3 Characterization of nano-size elongated particles in Cu loaded CeO_2

Figure 4 presents a bright field (BF) TEM image and energy filtering TEM image for analysis of Ce, Cu, and O atoms recorded from calcined Cu- CeO_2 particles. The energy filtering images can clarify the distribution of Ce, Cu and oxygen atoms in Cu- CeO_2 particles. In the BF image, the transparent elongated particles can be observed. This suggests that elongated particles consist of nano-size tube structure. Also, the EELS analysis indicates that Cu-loaded CeO_2 specimen contained a lot of copper oxide (CuO) nano-tube particles. Nano-size Cu metal particle could be inside CuO nano-tube.

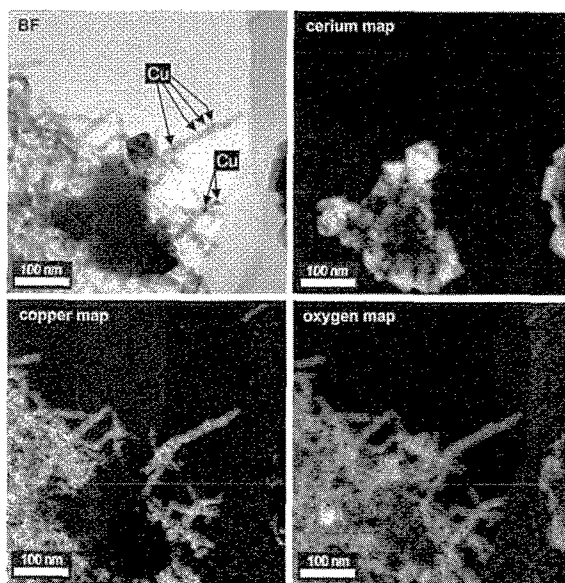


Fig. 4 Bright field image and element maps of Cu- CeO_2 catalyst analyzed by EELS detector.

To characterize the inside of CuO nano-tubes, high magnification BF image and element maps of Ce, Cu and oxygen atoms recorded from Cu loaded CeO_2 particle were displayed in Fig. 5. Some much brighter areas can be observed in Cu map, even though the contrast of oxygen atom is uniform in oxygen map. This indicates that quite small Cu metal particles (Cu metal size: 2-4 nm) could be inside CuO nano-tube. The interface of nano-size Cu metal and CuO nano-tube

would have a lot of defects and oxygen vacancy. It is possible this defect sites are an active site for low temperature CO oxidation reaction.

In Fig. 6 there is presented high-resolution TEM (HRTEM) image and element maps of Ce and Cu recorded from Cu loaded CeO_2 particle. The coherent interface between CeO_2 and CuO nano-tube can be observed in this figure. This suggests that CuO nano-tube developed on the surface of nano-sized CeO_2 . The growth of CuO nano-tube would be influenced by

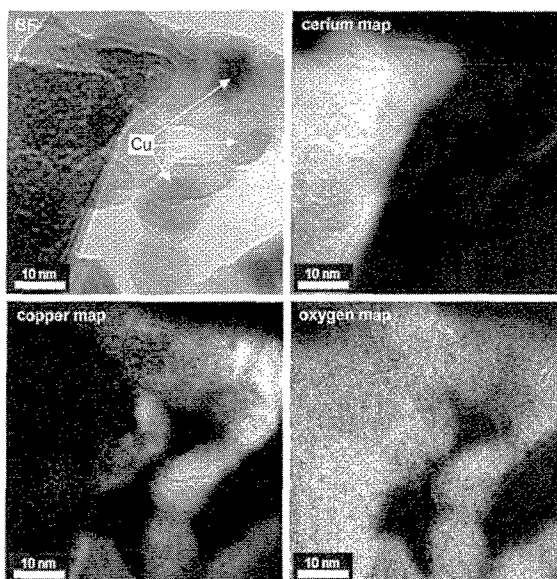


Fig. 5 Bright field image and element maps of Cu- CeO_2 catalyst analyzed by EELS detector at high magnification (x 470,000 times).

the surface defect structure of CeO_2 . The growth of CuO nano-tube would be controllable on the model surface of oxide. Therefore, it is expected that two dimensional ordered CuO nano-tubes on CeO_2 oxide thin film will be able to develop for a lowering of CO oxidation temperature. This concept can be used to develop a new nano-structured device for energy and environmental applications.

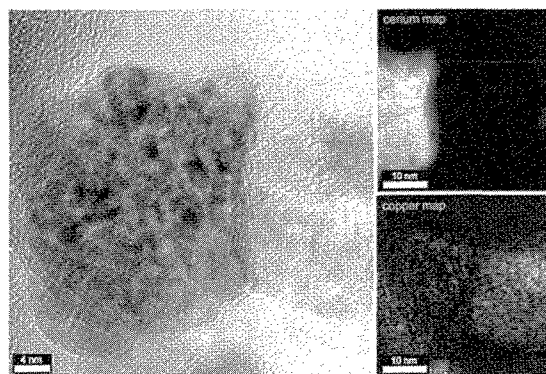


Fig. 6 HRTEM image of Cu nano-tube loaded CeO_2 particle and element maps of Ce and Cu analyzed by EELS detector.

3.4 CO oxidation reaction

We compared the catalytic activity for CO oxidation reaction over CeO₂ and CuO nano-tube loaded CeO₂ catalysts. The reaction temperature dependence of catalytic activity is demonstrated in Fig. 7. Both lines are calibrated to the partial pressure of helium. The yield of CO₂ in the CO oxidation reaction on the surface of both catalysts increased with increasing reaction temperature and reaches the maximum.

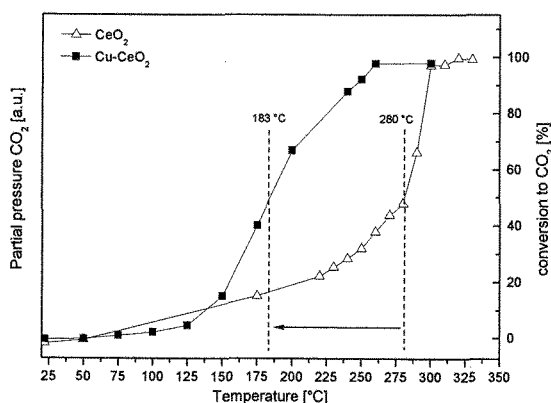


Fig. 7 The comparison of CO oxidation reaction over CeO₂ and nano-structured Cu-CeO₂ catalysts.

The reaction curves in Fig. 7 can be characterized by the reaction temperature at 50% yield of CO₂ in CO oxidation reaction. This 50% CO₂ yield temperature on CeO₂ and CuO nano-tube loaded CeO₂ were 280 °C and 183 °C, respectively. It means that the temperature of 50% CO₂ yield on CuO nano-tube loaded CeO₂ catalyst is 100 °C lower than that on pure CeO₂ catalyst. Since this temperature on CuO nano-tube loaded CeO₂ was lower than the previously reported temperature in CO oxidation reaction on Cu metal particles loaded on CeO₂ catalysts [2,3], CuO nano-tube with nano-sized Cu metal particle would contribute to a lowering of this characteristic temperature on the surface of CeO₂ catalyst. This suggests that nano-structured CuO nano-tube loaded CeO₂ catalyst is one of promising oxidation catalysts.

4. SUMMARY

The nano-sized CeO₂ and CuO nano-tube loaded CeO₂ catalysts were prepared using soft-chemical approach. The obtained specimens were characterized using XRD, TEM, SEM and reaction experiments.

The calcined CeO₂ particles consisted of squared shape and discrete particles. The average particle size of CeO₂ was approximately 50 nm. The nano-structured Cu modified CeO₂ catalysts were prepared by impregnation method. After low temperature (i.e. 300 °C) calcination process, CuO nano-tubes were developed around CeO₂ particles. In addition, nano-size Cu metal particle inside the nano-tube was observed. This indicates that unique nano-structure of Cu-CeO₂ catalyst is fabricated in the calcination process. The micro-analysis suggests that the growth of CuO nano-tube was influenced by the surface defect structure of CeO₂ particle.

To characterize obtained catalysts, CO oxidation reaction on pure CeO₂ and CuO nano-tube loaded CeO₂ was examined using flow reactor. The temperature of 50% CO₂ yield in CO oxidation reaction on CuO nano-tube loaded CeO₂ catalyst is 100 °C lower than that on pure CeO₂ catalyst. Since this characteristic temperature on the present nano-structured Cu-CeO₂ was lower than the previously reported one on Cu metal particles loaded on CeO₂ catalysts, it is concluded that the prepared CuO nano-tube with nano-sized Cu metal particle in this study is one of promising oxidation catalysts.

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