



Investigation into the catalytic reduction of NO_x at copper–ceria interface active sites



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ABSTRACT

The stoichiometric NO–CO reaction was studied over Cu/CeO₂ catalysts prepared with different Cu loadings and specific surface areas of CeO₂ to investigate the relationship between catalytic activity and the copper–ceria interaction. XRD, ESR and H₂-TPR results revealed that CuO species interacted with CeO₂ in three structurally different forms: isolated Cu²⁺, a highly dispersed CuO film, and large CuO particles. The CuO film showed a higher NO–CO reaction activity than the other species. An *Operando* XAFS study revealed that the reduction of the CuO film during the NO–CO reaction occurred at the Cu–O–Ce interface. Thus, we concluded that the most suitable CuO structure to effectively exploit Cu–O–Ce interface sites in the NO–CO reaction is a two-dimensionally dispersed CuO film.

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1. Introduction

Three-way catalysts (TWCs), which reduce the NO to N₂ in the presence of two reductants CO and HC, with the final production of CO₂ (from CO oxidation and HC combustion) and H₂O (from HC combustion), are widely used to reduce harmful automotive emissions [1,2]. The platinum group metals (PGMs) Pt, Pd, and Rh are the most essential components in TWCs because PGM metal catalysts promote extremely high reaction rates under stoichiometric conditions. However, the limited availability and high cost of these precious metals limits their use as a means of emission regulation. Therefore, the development of TWCs using non-noble metals is an attractive prospect, both commercially and environmentally.

Cu/CeO₂ catalysts are known to exhibit remarkably high activity in CO oxidation [3,4] and the water gas shift reaction [5,6]. The synergistic redox activity produced by a strong interaction between the copper and ceria is thought to have a significant enhancement effect on the activity of these catalysts [7–9]. The Cu–O–Ce interface is thought to allow the release of oxygen from the ceria and oxide surface of CuO, thus enhancing the catalytic activity in NO reduction. There are several studies that focus on the NO treatment activity of Cu/CeO₂. Bera et al. [10] reported NO reduction by NH₃, CO, and HCs using 5 wt% Cu/CeO₂ catalysts, and showed that highly

dispersed Cu²⁺ species are more active than CuO particles. Chen et al. [7] investigated the influence of ceria on the NO–CO reaction catalyzed by Cu/CeO₂, and reported that the NO dissociates at two sites; oxygen vacancies in the CeO₂ and metallic Cu sites. Djéga-Mariadassou group reported the NO–CO reaction mechanism in the case of Rh/CeO₂, oxygen vacancies between Rh^{x+} and CeO₂ interface. They suggest that 2 NO dissociate over 2 adjacent surface “Rh^{x+}-Oxygen vacancy” active sites, leaving 2 adsorbed oxygen species which have to be subsequently scavenged by CO to give 2CO₂ with simultaneously the formation of 2 new oxygen vacancies [11,12]. Recently, the NO–CO reaction at the metal–ceria interface in an Fe/CeO₂ system is also reported [13]. However, there are relatively few reports concerning the properties of Cu–ceria materials in which the influence of the Cu–O–Ce interface structures, and different CuO species, have been systematically investigated. Nor are there many papers in which the relationship between the number of Cu–O–Ce interface sites and NO_x conversion rates are discussed.

In this paper, we have investigated the catalytic activity of Cu/CeO₂ and the influence of different Cu–O–Ce interface structures on its NO_x reduction performance. We prepared Cu/CeO₂ catalysts with various conformations of CeO₂-supported CuO species and amounts of interface sites by employing different Cu loadings and using CeO₂ supports with different specific surface areas. We then measured their catalytic activity and the oxidation states of the Cu and Ce under the catalytic reaction conditions.

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2. Experimental

2.1. Catalyst preparation

CeO₂ powders were provided by the Anan Kasei Co., Ltd. (99.9% purity). CeO₂ powders with different surface areas were prepared by annealing in air for 4 h at specific temperatures between 500 and 750 °C. The specific surface area of the CeO₂ was determined by the one-point Brunauer–Emmett–Teller (BET) method using nitrogen adsorption (Table 1). Cu/CeO₂ catalysts were prepared by impregnation method. Cu(CH₃COO)₂·H₂O (Kanto Chemical Co., Inc.; 99.0% purity) was dissolved in an appropriate amount of deionized water in the presence of pre-sintered CeO₂ supports. The obtained slurry was stirred with a hot stirrer at 180 °C until excess water was evaporated, followed by drying at 110 °C for 5 h, and calcination in air at 500 °C for 4 h. Table 2 shows the Cu content and specific surface area of CeO₂ of each Cu/CeO₂ catalyst. The upper portion of the table shows the variation of Cu density with different Cu loadings on CeO₂ samples with the same specific surface area. The lower portion shows the variation of Cu density with 4 wt% and 0.5 wt% Cu loaded onto CeO₂ samples with different specific surface areas. In this paper, catalysts are denoted as Cu(*x*)/CeO₂(*y*), where *x* is Cu content (wt%) and *y* is the specific surface area of the CeO₂ (m²/g). This work covers a wide Cu atom density range from an extra low 0.23 Cu-atom/nm², a comparison of Cu atom density of Cu/CeO₂ between this work and others is shown in Supplementary information (Table S1).

2.2. Characterization

2.2.1. X-ray diffraction (XRD) measurement

The XRD patterns of as-prepared Cu/CeO₂ catalysts and pure CeO₂ were recorded by an Ultima IV (Rigaku) diffractometer with scan speed of 10°/min and scan range of 20–80° using Cu Kα radiation (λ = 1.5406 Å) as an X-ray source. The identification of the phase was made by comparison to Joint Committee on Powder Diffraction Standards (JCPDS) cards. The average crystallite size of CeO₂ particles was estimated from the line width of the CeO₂(1 1 1) peak using Scherrer's equation with the Gaussian line shape approximation.

2.2.2. Electron spin resonance (ESR)

ESR spectra were recorded with an X-band ESR spectrometer, ESR300E (BRUKER). Technical parameters of ESR were as follows, microwave frequency 9.47 GHz, modulation amplitude of 5 Gauss, microwave power of 4 mW, and time constant of 163.84 ms. 40 mg of the catalysts were heated at 400 °C for 20 min under a 30 mL/min air flow in an ESR tube. After thermal treatment, the catalysts were evacuated for 5 min and replaced to N₂ atmosphere. The amount of ESR active Cu²⁺ was estimated from double integration value. CuSO₄·5H₂O was used to calibrate the *g* factor and the population of ESR active Cu²⁺.

2.2.3. Temperature programmed reduction by hydrogen (H₂-TPR)

200 mg of as-prepared catalysts were mounted on loosely packed quartz wool in a quartz U-tube reactor. The temperature

Table 1
Specific surface area of annealed CeO₂ supports.

Calcination temperature (°C)	500	550	600	650	700	750
CeO ₂ SSA ^a (m ² /g)	165	146	119	83	51	26

^a BET specific surface area.

was raised from 20 °C to 700 °C at a rate of 20 °C/min. The flow of Ar balanced 5% H₂ gas was kept at 30 mL/min using a mass flow controller. The amount of H₂ consumption was measured by a Q-Mass spectrometer (ULVAC, MMC-200).

2.2.4. Activity test

Catalytic activity was measured using a fixed-bed flow reactor system (Best-Sokki, CATA-4000). Catalysts with particle sizes of 500–1000 μm were loaded into a quartz tube reactor without any pretreatment. The amount of catalyst was controlled so that 0.04 g of CuO was contained in the reactor. The reaction gas, which comprised 0.3% NO, 0.3% CO, 10% CO₂, and 3% H₂O in N₂, was introduced to the reactor at a flow rate of 10 L/min. Catalysts were activated by heating from 20 °C to 600 °C at a rate of 20 °C/min. The CO and NO_x concentrations in the outlet gas during the heating process were quantified by a non-dispersive infrared CO analyzer and chemiluminescence NO_x analyzer.

2.2.5. Operando X-ray absorption fine structure (XAFS)

Cu K-edge (8.98 keV) and Ce K-edge (40.45 keV) X-ray absorption measurements were conducted on BL33XU (TOYOTA beamline) at SPring-8 synchrotron radiation facility, Japan [14]. A servo-motor-driven Si(1 1 1) channel-cut monochromator was used to monochromatize the incident X-ray light source. XAFS spectra were obtained in transmission mode using ionization chambers. An additional ionization chamber was used for calibration of absorption edge energy using Cu foil and CeO₂ disk standard samples. 17 mg of Cu/CeO₂ (or pure CeO₂) and 50 mg boron nitride were pressed into 10 mm diameter disks and loaded into the heating cell. The NO–CO reaction in *operando* measurement was performed with a 0.4% NO and 0.4% CO gas mixture in He introduced at a flow rate of 100 mL/min. The catalysts were heated from 50 °C to 600 °C at a rate of 20 °C/min. The outlet gas was analyzed using a quadrupole mass spectrometer. The XAFS spectra of the catalysts and on-line mass spectra of the gas species were measured simultaneously.

3. Results and discussions

3.1. Characterization of Cu/CeO₂ catalysts

3.1.1. Dispersion of CuO species in Cu/CeO₂

Fig. 1 shows XRD patterns of Cu/CeO₂ catalysts with loading from 0.5 wt% to 12 wt% Cu on 165 m²/g CeO₂. All the catalysts exhibit typical diffraction patterns of cubic fluorite CeO₂ (JCPDS card No. 00-043-1002). Diffraction patterns derived from CuO species are not observed in the patterns of Cu/CeO₂ catalysts with Cu loadings from 0.5 wt% to 8 wt%. The absence of CuO diffraction patterns below 8 wt% indicates that CuO species are highly dispersed on the CeO₂ surfaces and too small to detect by XRD.

Table 2
Cu loading, specific surface area of CeO₂, and Cu atom density of Cu/CeO₂ catalysts.

Cu loading (wt%)	0.5	1	2	3	4	6	8	10	12
CeO ₂ SSA (m ² /g)	165	165	165	165	165	165	165	165	165
Cu atom density (Cu atoms/nm ²) ^a	0.23	0.45	0.91	1.37	1.83	2.74	3.66	4.57	5.49
Cu loading (wt%)	4	4	4	4	4	0.5	0.5	0.5	0.5
CeO ₂ SSA (m ² /g)	26	51	83	119	146	26	51	83	119
Cu atom density (Cu atoms/nm ²) ^a	11.6	5.91	3.64	2.54	2.07	1.45	0.74	0.45	0.32

^a Cu atom density was calculated using BET specific surface area of CeO₂ and Cu loading.

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