Fabrication of Hollow Spheres of Copper-Cerium Composite Oxide for Catalytic Decomposition of Nitrous Oxide

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This work investigated fabrication of hollow spheres of copper-cerium composite oxide for catalytic decomposition of nitrous oxide. The hollow spheres were obtained via coating of copper-cerium composite oxide shell on spherical silica templates, followed by leaching process in aqueous sodium hydroxide solution to remove the templates. The obtained hollow spheres with various copper contents consisted of spherical particles with a diameter of c.a. 130-150 nm and the internal cavity of c.a. 100 nm, which reflected the size of silica templates. The catalytic activity of the hollow spheres with high copper content for decomposition of nitrous oxide significantly improved with increasing reaction temperature and the conversion of nitrous oxide reached 78% at 773 K. From XPS spectra of the samples before and after the catalytic reaction, the peak assigned as Ce 4+ species in Ce 3d region shifted toward higher binding energy, and the degree the peak shift was lower in the spectra of the sample with higher copper contents. The results of the activity tests and XPS spectra suggested that the hollow spheres without significant change of valence state of Ce species showed higher activity for catalytic decomposition of nitrous oxide.

Key Words
Hollow spheres, Copper-cerium composite oxide, Catalytic decomposition of nitrous oxide, Surface oxygen

1. Introduction
Nitrous oxide (N$_2$O) possesses about 310 times higher global warming potential (GWP) than carbon dioxide, and then, has been reported as a powerful greenhouse gases. Moreover, it can cause the destruction of the ozone layer. Therefore, technology for removing N$_2$O efficiently have been expected to develop. Among methods contributing to decreasing N$_2$O emissions, its catalytic decomposition is one of the most promising method because of its high efficiency and the low costs. It can be applied for the removal of N$_2$O in the tail-gas caused by the nitric acid production, adipic acid production, fossil fuels’ combustion and fluidized-bed combustors. For these processes, noble metals, metal oxides and ion-exchanged zeolites have been reported, however, the noble metals have costly restricted their practical applications. Therefore, the development of metal oxide catalyst has attracted attention for the catalytic decomposition of N$_2$O due to the low cost and abundant resources. Cu-based catalysts have been regarded as the potential alternatives to noble metals. The catalysts supported on and mixed with CeO$_2$ has been reported as one of highly active catalysts. The

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reports indicated that some factors such as the number of small CuO clusters 13, reducibility and redox property of the catalyst 14-17 are responsible for high activity. In these factors, the arrangement of CeO2 with active copper metal is a key factor to generate oxygen ion vacancies which form interfacial active centers. The formation energy of the oxygen ion vacancies can be related to its morphological, structural, and chemical properties 21-23.

The objective of the current work is to fabricate the hollow CuO-CeO2 mixed oxide catalyst, and then elucidate its activity for the decomposition of N2O. In our previous study, homogeneity of the hollow CuO-CeO2 mixed oxide was controlled by adjusting the amount of additives to form CuO-CeO2 mixed oxide shell, and amount of active surface copper species and formation of oxygen ion vacancy in the mixed oxide can be related with the homogeneity of the hollow spheres and the activity for oxidation of carbon monoxide 24. In the present study, we investigated influence of preparation conditions on catalytic activity of hollow CuO-CeO2 mixed oxide for decomposition of N2O and relation between the catalytic activity and oxygen ion species in the hollow spheres.

2. Materials and Methods

2.1 Preparation of spherical silica templates

Spherical silica templates were prepared according to the method previously reported 25. L(+)-arginine (C6H14N4O2, Kanto Chem. Co., > 99.0 %) was dissolved in 20.7 mL of distilled water, and then, 1.108 mL of tetraethoxysilane (TEOS, (C2H5O)4Si, Wako Pure Chem. Co., >99.0%) was added into the solution. The resulting seeds were dispersed for 24 h for formation of silica template seeds, followed by filtration and drying. The resulting seeds were dispersed in solution including aqueous L(+)-arginine solution (0.1310 g of L(+)-arginine in 20.7 mL of distilled water) and ethyl alcohol (84.67 mL), and then, 5.540 mL of TEOS was introduced into the mixed solution. The mixed solution was stirred at 343 K for 24 h for formation of silica template seeds, followed by filtration and drying. The resulting seeds were dispersed in solution including aqueous L(+)-arginine solution (0.1310 g of L(+)-arginine in 20.7 mL of distilled water) and ethyl alcohol (84.67 mL), and then, 5.540 mL of TEOS was introduced into the mixed solution. The mixed solution was stirred at 343 K for 24 h, and the precursor of the silica templates was obtained after filtration and drying. The powder precursor was calcined at 873 K to obtain the silica template.

2.2 Preparation of hollow copper-ceria composite spheres

Hollow copper-ceria composite spheres were prepared according to the method previously reported 25. L(+)-arginine (C6H14N4O2, Kanto Chem. Co., > 98.0%) was dissolved in 1746 mL of distilled water, and then, 1.108 mL of tetraethoxysilane (TEOS, (C2H5O)4Si, Wako Pure Chem. Co., >99.0%) was added into the solution. The solution was stirred at 343 K for 24 h for formation of silica template seeds, followed by filtration and drying. The resulting seeds were dispersed in solution including aqueous L(+)-arginine solution (0.1310 g of L(+)-arginine in 20.7 mL of distilled water) and ethyl alcohol (84.67 mL), and then, 5.540 mL of TEOS was introduced into the mixed solution. The mixed solution was stirred at 343 K for 24 h, and the precursor of the silica templates was obtained after filtration and drying. The powder precursor was calcined at 873 K to obtain the silica template.

2.3 Characterizations

The morphologies of the samples were observed using a Hitachi FE2000 transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV. The BET surface areas of the catalysts were measured by nitrogen sorption at 77 K using Micromeritics Gemini VII 2390 Surface Area Analyzer. The crystalline phase was determined by X-ray powder diffraction (XRD) using a Rigaku MultiFlex X-ray diffractometer. X-ray photoelectron spectra (XPS) were acquired with an ESCA-3400 spectrometer (Shimadzu Co. Ltd) equipped with a Mg Ka X-ray exciting source (1253.6 eV) operating at 10 kV and 10 mA. The binding energies (BE) referred to the C 1s peak at 2850 eV.

2.4 Activity tests for decomposition nitrous oxide

Catalytic decomposition of nitrous oxide was performed in a tubular quartz microreactor using 0.05 g of the catalyst. The feed gas consisted of 0.5 % N2O in Ar with a total flow rate of 50 mL (NTP) min⁻¹. First, the catalyst was exposed to pure He gas for 1 h at 773 K. After cooling to 473 K, the gas was switched to the reaction feed gas, and then, the reaction was started. The reaction temperature was monitored by a thermocouple placed in the middle of the catalyst bed, and the activity was monitored at each reaction temperature (473-773 K) for 1 h. According to the reaction formula described below:

\[ \text{N}_2\text{O} \rightarrow \text{N}_2 + 1/2\text{O}_2 \]  

(1)

catalytic activity was assessed from the conversion of N2O. The N2O concentration in the reactor effluent was analyzed using a GC-2014 gas chromatograph (Shimadzu Co. Ltd) equipped with a thermal conductivity detector (TCD) attached to an SHINCARBON ST column. The conversion was calculated as \( \left( \frac{[\text{N}_2\text{O}]_{\text{in}} - [\text{N}_2\text{O}]_{\text{out}}}{[\text{N}_2\text{O}]_{\text{in}}} \right) \times 100\% \), where
[N\textsubscript{2}O\textsubscript{in}] refers to the peak area at room temperature, and [N\textsubscript{2}O\textsubscript{out}] refers to the peak area at an elevated temperature.

3. Results and discussion

TEM images showed that hollow spheres of copper-cerium composite oxide with all the copper ratios mainly consisted of spherical particles with a diameter of c.a. 130-150 nm (Fig. 1). The internal cavity of the hollow spheres was c.a. 100 nm, which reflected the size of silica templates, and the wall thicknesses was c.a. 20-40 nm, indicating that copper-cerium composite oxide shells were coated on the silica templates to form the particles with the hollow voids. From energy dispersive X-ray measurements of the samples, CuCe-5, CuCe-20, and CuCe-40 include 6.2, 13.4, and 27.1 wt.% of copper oxide, respectively. The result indicates that copper contents were lower than the introduced values in the hollow sphere with relatively high copper content probably because certain amount of copper species was dissolved in the leaching process and the dissolved amount increase with increasing the copper contents. On the other hand, all the samples possessed the specific surface area more than 100 m\textsuperscript{2} g\textsuperscript{-1}, and the surface areas of CuCe-5, CuCe-20, and CuCe-40 were 97, 177, and 159 m\textsuperscript{2} g\textsuperscript{-1}, respectively. The result suggested that certain amount of copper species of the samples with high copper contents were leached in aqueous sodium hydroxide solution, and the resulting hollow spheres showed relatively high specific surface areas. Crystalline structures of the samples were examined by XRD. Fig. 2 shows XRD profiles of the samples with various copper contents. In all profiles, no peaks could be indexed to the copper species, suggesting that copper in the samples is well-dispersed and/or amorphous. All the profiles of the samples include diffraction peaks at 28.8, 33.2, 47.6, and 56.6°, corresponding to the (111), (200), (220), and (311) planes, respectively, that can be indexed to the cubic fluorite structure of CeO\textsubscript{2} crystals (JCPDS 34-0394). The result indicates that all the samples included almost same crystalline structure.

Fig. 3 illustrates the conversion of nitrous oxide over the hollow spheres of copper-cerium composite oxide as a function of reaction temperature. The conversion over the hollow spheres increase with increasing reaction temperatures. Over 573 K, the conversion was highly improved over CuCe-20 and CuCu-40 compared with CuCe-5, and reached 78 % at 773 K over CuCe-40. In addition, the catalyst showed higher activity than the catalyst prepared without silica template (Fig. 3 (d)). The result indicates that content active copper species played an important role.
in improvement of catalytic activity for decomposition of nitrous oxide.

The Cu 2p and Ce 3d spectra confirm the surface chemical states of the copper-cerium composite oxides prepared with copper contents. Peaks around 936 and 956 eV ascribed to Cu2+ 24) are observed in the spectra of all the sample before and after the catalytic reaction, while, the peak shifts in the spectra after the catalytic reaction were not observed (Fig. 4 (A)). This result indicates that all the hollow spheres with various copper content included similar valence state of copper species. In the spectra in Ce 3d regions, observed peaks centered at around 883, 890, 902, 908, and 917 eV could be ascribed to Ce4+ 25), and the additional peaks centered around 887 and 904 eV, ascribed to Ce3+ 25), were observed in the spectra of all the samples before the catalytic reaction (Fig. 4). In the spectra of the samples after the catalytic reaction, the peaks shifted toward higher binding energy, indicating that the certain amount of cerium species was reduced to Ce3+ during the catalytic reaction because of consumption of surface oxygen atoms on cerium oxide. The degree of the peak shift decreased with increasing copper content as shown in Fig. 4. It has been reported mechanism of decomposition of nitrous oxide, N2O molecule adsorbs on Cu+ active sites 26) 27). After N-O bond cleavage accompanied by N2 molecule liberation, Cu2+-O - species are formed. Active Cu + sites can be regenerated either by a recombination step (if two oxidized copper sites are close enough to each other) or through reduction by Ce3+ species. The latter step is likely to occur because of synergetic effect and high lattice oxygen mobility between CuO and CeO2 active phases. Formed Ce4+ species can further desorb oxygen and regenerate oxygen vacancy and Ce3+ species. Valence states of copper and cerium species in the highly active CuCe-40 catalyst were similar before and after the catalytic reaction, indicating that the hollow spheres catalyst without significant change of valence state of cerium species showed high activity for decomposition of nitrous oxide.

4. Conclusions

Hollow spheres of copper-cerium composite oxide with various copper contents were fabricated using spherical silica templates, followed by removing the templates treating in aqueous sodium hydroxide solution. All the hollow spheres mainly consisted of spherical particles (particle diameter: c.a. 130-150 nm, internal cavity diameter: c.a. 100 nm, wall thickness: c.a. 20-40 nm) with their specific surface areas more than 100 m² g⁻¹. The activity for decomposition of nitrous oxide was highly improved over CuCe-20 and CuCu-40 compared with CuCe-5, and reached 78% at 773 K over CuCe-40. From the XPS spectra in Ce 3d region before and after the catalytic reaction, the peaks assigned as Ce4+ species shifted toward higher binding energy in the spectra of the samples after the catalytic reactions, and the degree of the peak shift decreased with increasing copper content.
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