Preparation of SiO$_2$-CuO-CeO$_2$ Composite Powders and Its Thin Film Templated with Oxalic Acid

Boyoung Son and Miewon Jung
School of Biological Sciences and Chemistry / Institute of Basic Science, Sungshin Women’s University, Seoul 142-732, Korea

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Abstract
Silica-based ceramic-matrix composites have shown promise as advanced materials for many applications such as chemical catalysts, ceramics, pharmaceuticals, and electronics. SiO$_2$-CuO-CeO$_2$ multi-component powders and their thin film, using an oxalic acid template as a chelating agent, have larger surface areas and more uniform pore size distribution than those of inorganic acid catalysts. SiO$_2$-CuO-CeO$_2$ composite powders were synthesized using tetraethylorthosilicate, copper (II) nitrate hemi (pentahydrate), and cerium (III) nitrate hexahydrate with oxalic acid as a template or pore-forming agent. The process of thermal evolution, the phase composition, and the surface morphology of these powders were monitored by thermogravimetry-differential thermal analysis (TG-DTA), X-ray diffractometry (XRD), field-emission scanning electron microscopy (FE-SEM), and energy dispersive X-ray spectrometry (EDXS). The mesoporous property of the powders was observed by Brunner-Emmett-Teller surface (BET) analysis. The improved surface area of this powder template with oxalic acid was 371.4 m$^2$/g. This multi-component thin film on stainless-steel was prepared by sol-gel dip coating with no cracks.

Key words SiO$_2$-CuO-CeO$_2$, oxalic acid, dip-coating.

1. Introduction
Silica-based ceramic-matrix composites have shown promise as advanced materials for many applications such as chemical catalysts, ceramics, pharmaceuticals, and electronics.$^{1,2}$ Mesoporous silica having stable structure with high specific surface area is widely used to enhance activity and selectivity in the fields of catalysis and optically active materials. To fabricate multi-component powders and its thin film, the sol-gel process is the efficient method because of good homogeneity, ease of composition control, low synthetic temperature with large area coating.$^3$ Chemical synthesis of these composites is the best way to control these characteristics, especially modified sol-gel process by using a template, which offers products with a homogeneous distribution, and nano-sized particles with good stoichiometry. It should be controlled on the characteristics among several synthetic factors to obtain mesoporous dense materials with specific multi-composites. Densification ability depends on powders specifications like grain size, pore size distribution, and grain morphology in early stage of thermal-treatment.$^{3,4}$

An acid catalyst is usually used to control the rate of the hydrolysis and condensation reactions. Inorganic acid catalyst, such as HNO$_3$, HCl, and H$_2$SO$_4$ is the common reagents for this synthesis, even though these are costly and environmentally contaminate. Organic acid, especially oxalic acid is more effective and eco-friendly because of its acid strength, complex and/or chelating ability as template and iron-contaminate removal reagent.$^5$ This acid has the ability to increase the pore size and specific surface area generating mesoporous materials with high metallic oxide dispersion or doping at grain boundary of the support. The chelating agent as a template with the role of acid catalyst has used to obtain the mixed oxide composites with having a different size/shape and also to improve the surface area. Morphology and textual property of the multi-composite and thin film relate to the used template due to the different types of cluster formation in the inorganic network at the initial stage.$^6$-$^7$

In this paper, SiO$_2$-CuO-CeO$_2$ composite powders and thin film, having with a relatively high doping level of CuO and CeO$_2$ in a silica matrix, were prepared using two types of oxalic acid or HNO$_3$ catalysts in a single step. The oxalic acid was used for effects as template and decreasing amounts of HNO$_3$. The structure change, morphology, and textual property of these multi-composite powders were compared. This multi-component thin film on the stainless-steel was prepared by sol-gel dip coating and characterized using XRD and FE-SEM analysis.

2. Experimental Procedure

2.1 Preparation of SiO$_2$-CuO-CeO$_2$ powders
Tetraethylorthosilicate(TEOS), (98%Si(OC$_2$H$_5$)$_4$) (CAS...
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NO. 78-10-4, Aldrich) was dissolved in distilled water and ethanol solvent with molar ratio of 5:1. Ce(NO$_3$)$_3$·6H$_2$O and Cu(NO$_3$)$_2$·6H$_2$O were added into this solution. The molar composition of the TEOS : Ce(NO$_3$)$_3$·6H$_2$O : Cu (NO$_3$)$_2$·6H$_2$O was 8:1:1. For keeping on pH = 2, 16 mol of oxalic acid or 0.16 mol of HNO$_3$ was added. Each of these solutions were stirred and made into clear sol with refluxing for 24h. Then, it was cooled down and quenched. After evaporation of solvents, gel was obtained. To remove the excess reactants, the gel was washed with ethanol and water. The powders were obtained by drying at 120°C for 24h. This powders were heat-treated every 200°C from 500 to 1100°C for 2h.

2.2 Dip-coating

The substrate STS 316 plate was polished with HCl and cleaned with solvents before deposition process. After drying process, it was dipped into the 20 ml of above sol-gel solution at a constant dipping speed of 0.1 mm/s and kept inside the solution for 60s. At this point, the viscosity of solution was 21.5cP. Then, the dip-coated substrates were kept for drying on air at room temperature for 20 min. After repeating this process for three times, it was heat-treated for 2h from 500 to 1100°C.

2.3 Characterization

Thermal degradation of the composite powders was measured by means of thermogravimetry(TG) and differential thermal analysis(DTA) using a NETZSCHSTA 490PC from room temperature to 1100°C with a heating rate of 3 K/min under air atmosphere. The structure change and phase transformation of the SiO$_2$-CuO-CeO$_2$ powders and thin film with HNO$_3$ or oxalic acid was characterized by X-ray diffraction measurements(XRD, Bruker D8 Focus, 40 kV, 40 mA, 0.2°/min, 10-80°) using CuKα radiation(λ = 1.5406 Å). The morphology and microstructure of these powders and thin film heat-treated at 700°C were analyzed by field-emission scanning electron microscopy(FE-SEM, JEOL-JMS 7500F, 0.5~30 kV) and energy dispersive X-ray spectrometer(EDXS, Oxford model 7585 EDXS system, 4Be to 92U) for the case of powders. The specific surface area and pore size of these powders heat-treated at 700°C were measured by brunauer-emmett-teller surface analyzer (BET, BELSORP-mini).

3. Results and Discussion

Thermal analysis data of synthesized powders with HNO$_3$ and oxalic acid are shown in Fig. 1(a) and (b), respectively. The major weight loss of about 70%, observed from RT to 300°C in (a) and (b) curves, are due to the vaporization of water, the liberation of ethyl alcohol and organic groups produced from the reactions. They are corresponded to endothermic peaks between 100°C and 300°C on the DTA curves. The two exothermic peaks around 700°C and 1100°C are due to the crystallization of CeO$_2$, CuO and SiO$_2$ arisen from different temperatures.

Fig. 2 shows XRD patterns of the SiO$_2$-CuO-CeO$_2$ powders synthesized with HNO$_3$ or oxalic acid. All of peaks in a sample with oxalic acid are more remarkable, implying an improvement in crystalline formation, than with HNO$_3$ at low temperatures. The CeO$_2$ peaks(JCPDS file No. 03-065-2975, Cubic, SG = Fm-3m) are first shown up at 500°C, while the CuO peaks(JCPDS file No. 01-089-5895, monoclinic, SG = C2/c) begin to show up at 700°C. Both peaks are gradually sharpened with the increase of temperature. The stable peaks of SiO$_2$(JCPDS file No. 04-0379, tetragonal, SG = P41212) appear at 1100°C in all samples. From the analysis of all of peaks, those peaks with oxalic acid were more shape and clear, especially

![Fig. 1. TG-DTA curves of SCC powders with (a) HNO$_3$ and (b) oxalic acid.](image-url)
temperature at 700°C, because oxalic acid provides the local heat for the formation of crystal during the decomposition.\(^5\) Heat produced in the gel combustion process makes the nucleation and crystallization process complete at the early stage. Thus, the SiO\(_2\), CeO\(_2\) and CuO could be remained as independent phases in the powders and form a three phase composite system.

The FE-SEM images and specific surface area of the SiO\(_2\)-CuO-CeO\(_2\) powders were described in Fig. 3. The morphologies of particle in Fig. 3(b) look smooth and dense. These particles were aggregated to each other to make clusters in the powders with oxalic acid. Also, the surface area with adding oxalic acid is larger than with

![Fig. 2. XRD patterns of SCC powders with (a) HNO\(_3\) and (b) oxalic acid.](image)

![Fig. 3. FE-SEM micrographs of SCC powders with (a) HNO\(_3\) and (b) oxalic acid heat-treated at 700°C (× 50000). *EDXS of the SCC powders are shown on inset diagram.](image)

![Fig. 4. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distributions of the SCC powders with HNO\(_3\) and oxalic acid heat-treated at 700°C.](image)
The surface area added with chelating agent or pore-directing agent was slightly larger than powders without it due to the coordination effect of the mixed composites with this agent.

Fig. 4(a) shows the nitrogen adsorption-desorption isotherms after calcinations at 700°C. According to International Union of Pure and Applied Chemistry (IUPAC) classification, all isotherms show a typical type IV model and have a H1 hysteresis loop that is representative of the porosity of the particles having mesopore structure. The (b) indicate the pore size distribution of composite powders by Barrett-Joyner-Halenda method (BJH) and both samples show the primary mesoporous size distribution. Adding with oxalic acid as a chelating agent, the total pore volume and the pore diameter of powders were larger than with HNO₃. The shape of pore is slit type with having pore volume, ~0.80 m³/g, as well as pore diameter, 4.40 nm for powders with oxalic acid and bottle neck type with pore volume, ~0.50 m³/g, with the pore diameter, 3.02 nm for powders with HNO₃. Oxalic acid has the ability to increase pore size and specific surface area generating a uniform distribution of mesoporous materials. The presence of this agent contributes to efficient CuO and CeO₂ dispersion by aggregation as shown in inset diagram of EDX analysis.

Fig. 5(A) shows the XRD diffraction patterns of the STS 316 substrate surface covered by SiO₂-CuO-CeO₂ dip-coating solution modified with oxalic acid. The peak of CeCuSi (JCPDS file No. 01-089-2063, hexagonal), which didn’t show up in the XRD result of composite powders, is observed with the cubic CeO₂ peaks at 900°C. The three peaks including cubic SiO₂ are clearly shown at 1100°C. Fig. 5(B) shows the FE-SEM images of this thin film and the morphological features of the surface treated with varying temperatures are not smooth and uniform. As temperature increase, the particle size is continued to grow and the surface of the film shifted into the agglomerated state with intercrystallite pores.
4. Conclusion

The SiO$_2$-CuO-CeO$_2$ multi-component powders and its thin film using oxalic acid template as chelating agent have the larger surface area and uniform pore size distribution than from the inorganic acid catalyst. Besides of the ability of oxalic acid to crystallize at low temperature (700°C) and to increase in surface area of the multi-component composites, it contributes to disperse more in silica-matrix. Because the crystalline phase transition temperature and the morphology of the final product depends on a catalyst used in the sol preparation, this modified method could apply to fabricate the multi-component thin films.

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References