Biomass-assisted Hydrothermal Synthesis of Ceria Nanoparticle —A New Application of Lignin as a Bio-nanopool—

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We introduced a nanometer-sized reaction pool in the hydrothermal synthesis of ceria (CeO_2). The addition of a heat-stable biopolymer, lignosulfate, in the hydrothermal synthesis resulted in the drastic downsizing of CeO_2 particle to 5 nm. We, further, show that the lignosulfate functions as an accelerator for the CeO_2 nanoparticle synthesis.

Ceria (CeO_2) is used in various fields; catalyst,[1] ultraviolet absorbers,[2] gas sensors,[3] solid electrolytes in solid oxide fuel cell,[4] and abrasive of chemical mechanical planarization.[5,6] Physical and chemical properties of the nanoparticles are varied by changing the size and morphology; especially, the downsizing of the particles promotes catalytic activity.

Hydrothermal technique is one of the effective methods for the synthesis of highly crystalline metal oxide materials. The high crystallization leads to the formation of single crystal materials, but the downsizing below 10 nm is hardly performed because of the difficulty of controlling the crystal growth. In other wet-chemical approaches, reverse-micelle,[7] hot-soap,[8] sol–gel methods,[9] and bio-nanopool,[10,11] have been utilized for the synthesis of nanoparticle. The applied surfactants supply a nanometer-sized reaction pool or suppress the particle growth. However, the reaction pools supplied from surfactant or its assembly are not stable at the high temperature applied for conventional hydrothermal synthesis. Here, we attempted to introduce a reaction nanopool in the hydrothermal synthesis of metal oxide particles by utilizing sodium lignosulfate (weight-average molecular weight 58,000) as a surfactant polymer. Lignin is a biopolymer in which hydroxyphenylpropane units, such as *trans-p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, are connected with ether and carbon–carbon bonds in a helical structure.[12] The heat resistance of lignin in water has been reported in the field of biomass materials.[13,14]

The lignin biopolymer was introduced in the hydrothermal synthesis of CeO_2 particles. The sodium lignosulfate was added at 10 wt % of cerium in a 0.5 M $Ce(NO_3)_3$ solution, and the solution was loaded into a pressure-resistant vessel (SUS316) with 5 mL of inner volume. The reactor was heated and shaken for 10 min in an electric furnace that controlled external surface temperature of the reactors at various temperatures. The reacted products were exported from the reactor and then separated into solid particles by centrifugation. The insoluble fraction was dried in vacuum for more than 1 day at room temperature after washing with water and THF.

The hydrothermal reaction at 250 °C in the lignosulfate-containing solution led to insoluble particles. The X-ray diffraction (XRD) patterns of the particles precipitated in the lignin-containing solution showed that cerium ion was transformed to CeO_2; that is, no Ce_2O_3 and cerium hydroxide were detected (Figure 1). The TEM images were examined for the CeO_2 particles synthesized without and with lignosulfate (Figure 2). The CeO_2 particles synthesized without lignosulfate had the diameter of about 20 nm (Figure 2a), while the addition of lignosulfate resulted in the drastic downsizing to less than 5 nm (Figure 2b). This suggests that the lignosulfate controls the crystal growth of CeO_2 at the hydrothermal condition. Interestingly, the synthesized CeO_2 nanoparticles with lignosulfate were more dispersed in hexane than in water. The addition of lignosulfate also changed the surface properties of the CeO_2 partciles.

We also synthesized CeO_2 at 400 °C in the lignin-free and

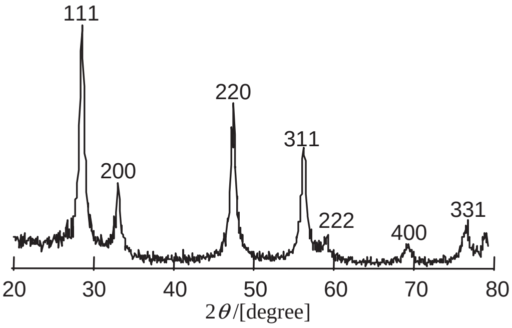

Figure 1. X-ray diffraction pattern of the precipitated particles in the lignin-containing solution. The numbers on the spectrum represents Miller indices of CeO_2.

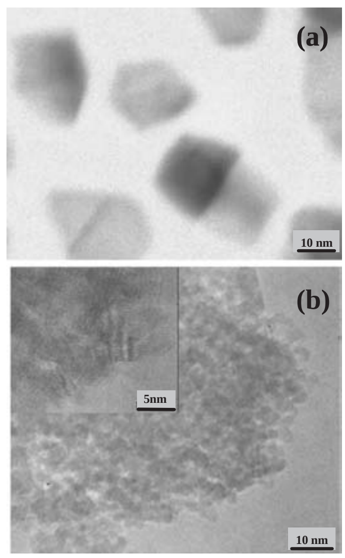

Figure 2. TEM image for the synthesized CeO_2 particle without lignosulfate (a) and with lignosulfate (b) by hydrothermal reaction at 250 °C.

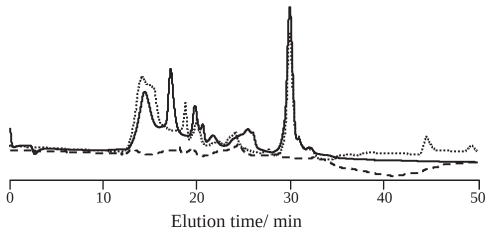

Figure 3. Size exuclusion chromatography for untreated lignosulfate (solid line), and lignosulfate heated at 250 °C (dotted line) and at 400 °C (heated line).

lignin-containing solutions; however, the synthesized CeO_2 particles had a similar large particle size of about 50–100 nm (data not shown). Lignosulfate had no effect on the size-control in the CeO_2 hydrothermal synthesis at high temperature. In order to investigate the stability of lignosulfate at hydrothermal condition, the lignosulfate was reacted in the same conditions as the hydrothermal reaction of the ceria particle synthesis. Figure 3 shows the size exclusion chromatography for lignosulfate heated at 250 and 400 °C. The chromatography for the lignosulfate heated at 250 °C showed that the molecular weight distributions are comparable with that of untreated lignosulfate (dotted line in Figure 3); however, the hydrothermal treatment at 400 °C resulted in little high molecular weight compound because of the polymerization to insoluble char or the hydration to small molecules (dashed line in Figure 3). This implies that the conservation of lignosulfate in the hydrothermal reaction is critical to synthesize a small CeO_2 nanoparticle with the diameter of 5 nm, suggesting that a reaction nanopool supplied by lignosulfate suppresses aggregation and particle growth of CeO_2 nanoparticles.

Figure 4 shows the conversion ratio from $Ce(NO_3)_3$ to CeO_2 at various reaction temperatures. The conversions were estimated from the weight of formed precipitates (open circles and squares). In the lignin-free solution, a few precipitates were observed only at 250 °C (open circles in Figure 4). In contrast, CeO_2 was formed at 200 and 250 °C in the lignin-containing solution (open squares in Figure 4). We also evaluated the conversion from the residual cerium concentration in the reacted solution using inductively coupled plasma (ICP) emission spectrometry (close squares in Figure 4). The conversion ratio evaluated from ICP spectrometry showed the similar values to those from the weight of precipitates. This indicates that little organic compounds derived from lignin are contained in the precipitates formed at 200 and 250 °C; that is, most of insoluble compounds are CeO_2.

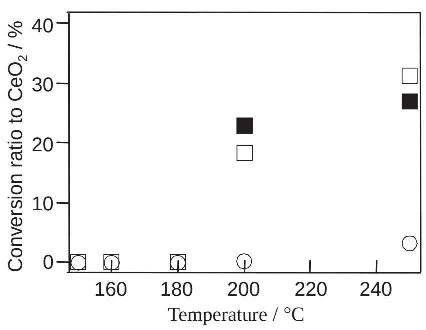

Figure 4. The conversion ratio from $Ce(NO_3)_3$ to CeO_2 in the lignin-free (open circles) and lignin-containing solutions (open and close squares). The ratios were estimated from the weight of formed precipitates (open circles and squares) or residual cerium ion (close squares).

In order to investigate the influence of polymer on the hydrothermal synthesis of CeO_2, we applied hydrophilic polymer, such as polyethylene glycol and methyl cellulose to the lignin-free solution; however, there was no difference in size and amount of synthesized CeO_2 particle. The addition of lignosulfate leads to the pH change from 3.0 to 2.3 in the $Ce(NO_3)_3$ solution. We also tried the hydrothermal synthesis of CeO_2 after the pH adjustment by adding sulfuric acid, but no difference was observed. The mechanism of an accelerating CeO_2 synthesis in the presence of lignosulfate has not yet been elucidated, but the lignosulfate might supply some hydrophobic environment in the solution to instabilize the reactants of cerium ion and cerium hydrate. The water-soluble polymer with hydrophobic environment might be necessary for accelerating the synthesis of CeO_2 nanoparticles.

Plant biomass materials are constituted of useful biomolecules; 50 wt % cellulose, 20 wt % of hemicellulose and 30 wt % of lignin, approximately.[15] Lignin is a biopolymer and massively arises as a by-product when pulpifing woods, but the biomass molecule has been utilized only as a heat source for the pulp industry. Recently, the liquefaction of lignins[13,14] and the conversion of them into low molecular compounds by hydrolysis in sub- and supercritical water,[16,17] were reported. However, the liquefied biomass has not been applied to various utilizations in comparison with cellulose. Here, we propose a new approach of fusing lignin utilization engineering and nanotechnology.

In conclusion, the addition of lignosulfate in subcritical fluid controls the size of CeO_2 nanoparticle to 5 nm and promotes its hydrothermal synthesis. Reverse micelles and macromolecules have been often applied in the nanoparticle synthesis to utilize the nanometer-sized reaction fields. We propose the utilization of lignin polymer as an accelerator for the CeO_2 nanoparticle synthesis.

This work was supported by a Scientific Research Grant from the Ministry of Education, Culture, Sports, Science and Technology of Japan (T.A.). This research was also partly supported by the HEIWA NAKAJIMA foundation (T.A.).

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Published on the web (Advance View) June 3, 2006; doi:10.1246/cl.2006.732