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Nanostructured Ceria−Silver Synthesized in a One-Pot Redox Reaction Catalyzes Carbon Oxidation

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Abstract: We introduce a new concept for a nanomaterial in terms of both synthesis and properties. The nanomaterial, aggregates of ceria particles around central silver metal (CeO_2−Ag), was fabricated by a one-pot selective redox reaction using cerium(III) and silver(I) autocatalyzed by silver metal without the need for surfactants or organic compounds. This unique nanostructure is suitable as a catalyst, in contrast to core−shell materials wherein the shell deactivates the catalyst metal. The material was developed to be intimately related to catalytic carbon oxidation.

Carbonaceous soot can be oxidized, though just barely, below 300 °C by a catalyst containing silver and ceria,[1] even though the oxidation rate is inadequate and deterioration due to sintering of silver needs to be further suppressed. Soot oxidation is supposed to be efficiently promoted by maximizing the silver−ceria interface to activate oxygen species, increasing the contact between ceria and soot to facilitate spillover of active oxygen onto the soot at large distances,[2,3] and covering silver with ceria particles to prevent silver sintering. The desired configuration is an aggregate of ceria particles with silver metal at the center, termed the "rice ball" configuration. All efforts to date to fabricate such a nanomaterial have merely resulted in a core−shell or similarly structured material.[4−6] Hence, ease of fabrication and an inexpensive synthesis strategy are necessary for nanofabrication. In this communication, we report a novel approach to nanofabrication based on precipitation from an aqueous solution of nitrate and ammonia, which is widely utilized in industrial processes, by aggregation of precipitation-derived cerium(III) hydroxide through a redox reaction with silver(I). This approach is completely different from conventional methods for preparing supported catalysts by coprecipitation[7] or deposition−precipitation,[8] and the resulting nanomaterial is different from encapsulated materials with a core−shell configuration in which nanometal (silver, gold, or platinum) is surrounded by polymerized silica,[4] titania,[5] or ceria.[6]

To form the CeO_2−Ag material, a mixed aqueous solution of cerium(III) nitrate and silver(I) nitrate (cerium/silver molar ratio = 2:3) was coprecipitated by addition of the nitrate solution to stirred aqueous ammonia (same molar ratio as the nitrate). It was important to coprecipitate from a nitrate solution containing excess silver over cerium under near-neutral conditions. The black precipitate obtained was heated, resulting in a change to a gold-tinged brown color. The substance after calcination at 500 °C was a subtly gold-tinged black material containing exactly equal molar amounts of cerium and silver.

The scanning electron microscopy (SEM) image in Figure 1a shows that CeO_2−Ag consists of numerous spherical "balls" having diameters of ∼100 nm. One of the balls was singled out, and a thin slice from it was prepared using a focused ion beam. This slice was analyzed by transmission electron microscopy (TEM). The cross-sectional image of the ball (Figure 1b) shows that the center silver metal is surrounded by fine ceria particles. These results indicate that the configuration of CeO_2−Ag as an aggregate of ceria particles with silver at the center (Figure 1c,d) is similar to that of a rice ball, a popular Japanese food with pressed rice grains around a central filling called "onigiri". The X-ray diffraction (XRD) pattern of the aggregate displays peaks assigned to ceria and silver. The particle sizes of CeO_2 (14 nm) and Ag (28 nm) calculated from the XRD data are consistent with the TEM image. The rice-ball nanostructure is completely different from the core−shell or similar structure, wherein the shell is composed of polymerized oxide.[4−6]

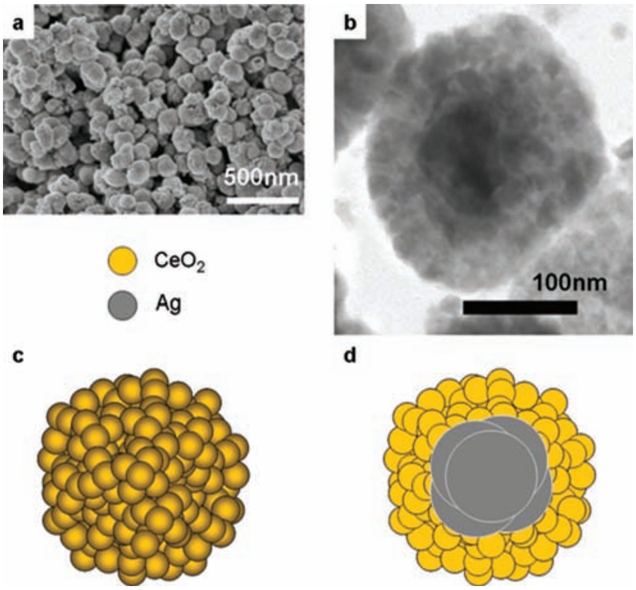

Figure 1. Micrographs of CeO_2−Ag: (a) SEM; (b) TEM. Schematic illustrations of CeO_2−Ag: (c) overview; (d) cross section.

CeO_2−Ag consists of exactly equal molar amounts of ceria and silver, regardless of the excess of silver over cerium in the ingredient nitrate aqueous solution. This indicates that the redox reaction between equal molar amounts of cerium and silver is crucial for formation of the rice-ball nanostructure. This suggests the following possible synthesis mechanism: Coprecipitation by addition of cerium(III) nitrate and silver(I) nitrate aqueous solution to stirred aqueous ammonia (equimolar to nitrate) yields $Ce(OH)_3$ and Ag_2O (the probable cause for the black precipitate) along with some $[Ag(NH_3)_2]^+$ resulting from conversion of a portion of the Ag_2O to $[Ag(NH_3)_2]^+$ due to the presence of excess ammonia immediately after the beginning of coprecipitation. The key to obtaining the rice-ball configuration of the nanostructure is the redox reaction between $Ce(OH)_3$ and $[Ag(NH_3)_2]^+$, which produces $Ce(OH)_4$ [progressively dehydrated to CeO_2 (ref 9)] and Ag accompanied by generation of

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NH_3, which reacts with Ag_2O to further produce $[Ag(NH_3)_2]^+$. Moreover, the redox reaction is selectively autocatalyzed by silver metal because a nonselective redox reaction results in a homogeneously supported catalyst, as shown in the literature.[10] Silver is selectively deposited on silver metal particles surrounded by as much of the reducing agent [$Ce(OH)_3$ particles] as possible. Consequently, the spherical rice ball, the aggregate of ceria particles with silver at the center, could be the most stable configuration to minimize the average distance between the silver metal and $Ce(OH)_3$ particles as well as the interfacial energy between the $Ce(OH)_3$ particles and the water solvent. Thus, the redox reaction between $Ce(OH)_3$ and $[Ag(NH_3)_2]^+$ proceeds until $Ce(OH)_3$ is entirely oxidized, neatly accounting for the precise equivalent composition of cerium and silver. For self-assembly of the rice-ball nanostructure, it is essential to control the reaction rate through the redox potential, which is probably well-balanced under near-neutral conditions.

Evaluation of carbonaceous soot oxidation was carried out by thermogravimetric analysis of the catalyst in contact with the carbonaceous soot[2,3] by a mortar under fixed conditions. Soot oxidation rates in 10% O_2 at each temperature were calculated from the decrease in weight, which was attributable to carbon oxidation as confirmed by mass spectrometry. Figure 2a shows that $CeO_2{-}Ag$ oxidizes soot much more efficiently below 300 °C than CeO_2 and Ag/CeO_2 (a conventional supported catalyst consisting of equimolar silver and ceria), which oxidize soot mainly above 300 °C. These results show that catalysts containing silver and ceria lower the temperature of soot oxidation, although oxidation by the catalyst without the rice-ball nanostructure is inefficient at low temperatures below 300 °C. Thus, the rice-ball nanostructure is an innovative catalyst concept with a configuration that is inverted relative to that of a conventional supported catalyst, which has a "sushi"-type structure.

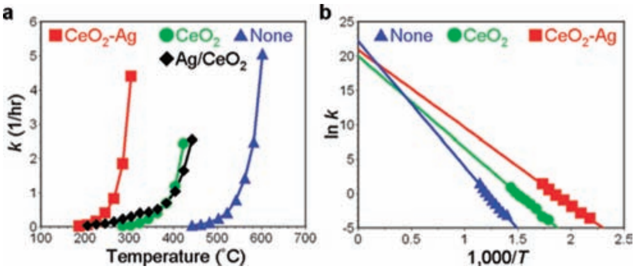

Figure 2. $CeO_2{-}Ag$ compared with conventional catalysts and the absence of a catalyst: (a) evaluations of carbonaceous soot oxidation; (b) Arrhenius plots.

From the standpoint of practical application as a diesel particulate matter (PM) catalyst, thermal durability up to 800 °C is necessary. However, $CeO_2{-}Ag$ showed drastically decreased catalytic activity upon aging at 800 °C for 5 h in air. To improve the thermal stability of the material, we redesigned the catalyst to prevent the ceria from being sintered by stabilizing it with lanthanum, which is known to improve thermal stability toward sintering,[2] while maintaining the rice-ball nanostructure. We fabricated lanthanum-stabilized $CeO_2(La){-}Ag$ in a similar way as $CeO_2{-}Ag$, except for the raw-material composition (molar ratios: Ce/La = 9:1; Ce/Ag = 2:3). SEM and TEM images showed that $CeO_2(La){-}Ag$ has the same rice-ball nanostructure as $CeO_2{-}Ag$. The XRD pattern, which contained lanthanum-stabilized ceria [$CeO_2(La)$] and silver metal peaks, indicated that the lattice constant of $CeO_2(La)$ is 5.43 Å, which is larger than that of CeO_2 (5.41 Å). $CeO_2(La){-}Ag$ is also composed of exactly equal molar amounts of cerium and silver, indicating that the rice ball was fabricated by an identical redox reaction irrespective of the presence of lanthanum. From the SEM and TEM images, $CeO_2(La){-}Ag$ aged at 800 °C for 50 h in air was seen to maintain the rice-ball nanostructure, with $CeO_2(La)$ particles that were smaller than the CeO_2 particles in the aged $CeO_2{-}Ag$. The particle sizes calculated from the XRD pattern were 29 nm for CeO_2 and 62 nm for Ag, consistent with the TEM image. Equivalent soot oxidation rates of $CeO_2(La){-}Ag$ and aged $CeO_2(La){-}Ag$ indicated that $CeO_2(La){-}Ag$ has extremely high thermal stability. Hence, $CeO_2(La){-}Ag$ fabricated using this facile self-assembly approach is an extremely practical catalyst for carbonaceous soot oxidation.

Arrhenius plots of carbonaceous soot oxidation rates (Figure 2b) indicated that the frequency factors for $CeO_2{-}Ag$ and CeO_2 are equivalent to that for the absence of a catalyst, for which the frequency factor should be a maximum because noncatalytic spontaneous oxidation of carbonaceous soot in an oxygen atmosphere takes place throughout the soot at elevated temperatures. This indicates that the spillover of "active oxygen" generated from the catalyst occurs not only at the primary soot particle level (30 nm) but also at much greater distances,[2,3] certainly farther than the distance between the centered silver and soot (~50 nm). Therefore, active oxygen spreads into every corner of the carbonaceous soot particles through the ceria particles undisturbed by the silver metal, and catalytic carbon oxidation occurs for all of the soot particles. The lower activation energy for $CeO_2{-}Ag$ (94 kJ/mol) than for the others (CeO_2, 111 kJ/mol; no catalyst, 151 kJ/mol) suggests that "extremely active oxygen" is efficiently generated on the rice-ball nanostructure.

In summary, we have fabricated a nanomaterial with a rice-ball configuration that is suitable for application as a catalyst. The synthesis mechanism of the nanomaterial can potentially be extended to other compositions because the autocatalyzed reaction, well-known as electroless deposition, is not limited to silver and also because transition metals often change valency as well as cerium.

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Supporting Information Available: Synthesis procedures, SEM and TEM micrographs, and other characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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