Control of Morphology and Reaction Activity of CeO_2–TiO_2 Composite Nanostructures by Changing the Mole Ratio of Cerium to Titanium Alkoxides

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Crystallized CeO_2–TiO_2 composite nanostructures were prepared by surfactant-assisted method using mixed solution of alkoxides at 353 K. The morphology and crystalline structure of CeO_2–TiO_2 composite were varied with changing the mole ratio of cerium *n*-butoxide/tetraisopropyl orthotitanate. These nanostructured materials after calcinations showed reaction activity to oxidize I^- to I_2 owing to Lewis acid sites without irradiation of light.

Ceria-based materials have been extensively studied and employed in various applications.[1–3] Ultrafine nanoparticles have been receiving much attention recently owing to the physical and chemical properties that are significantly different from those of bulk materials. Various aqueous-solution-based methods for synthesizing nanocrystalline CeO_2 powders have been investigated, and some of the properties such as dispersibility of the particles and catalytic properties have also been studied. CeO_2 and CeO_2-based mixed oxides are the effective catalysts for the reactions of oxidation.[3,4] The mixing of two different oxides adds unique parameter because they are liable to form new stable compounds that may lead to totally different physicochemical properties and catalytic behavior.[5] These properties of nanosize materials strongly depend on the morphology and crystalline structure of particles. Thus the control of the morphology and crystalline structure of nanosize materials is very important. We have already reported the formation of nanostructured materials of TiO_2 and CeO_2.[6,7] Here we present morphology control of CeO_2–TiO_2 composite nanostructures by changing the mole ratio of cerium *n*-butoxide/tetraisopropyl orthotitanate. In addition, the dependency of reaction activity on compositions of composite materials and conditions of calcinations are also presented.

Typical synthesis of CeO_2–TiO_2 composite nanostructures is as follows: first laurylamine hydrochloride (LAHC) was dissolved in distilled water. Cerium *n*-butoxide (CeBu) and tetraisopropyl orthotitanate (TIPT) were then mixed with acetylacetone (ACA) in a glass and immediately added to aq LAHC solution of pH 4.6. The mole ratio of metal alkoxides to ACA and metal alkoxides to LAHC were 1 and 4, respectively. The mole ratio of CeBu to TIPT (CeBu/TIPT) was changed to 100/0, 75/25, 25/75, and 0/100. When the two solutions were mixed, precipitation occurred immediately. After stirring at room temperature for 1 h, the reaction temperature was then changed to 353 K. After 1 week, the solution became purple-precipitates with transparent liquid layer. After both freeze-drying and vacuum drying, the obtained products were calcined in air at different conditions.

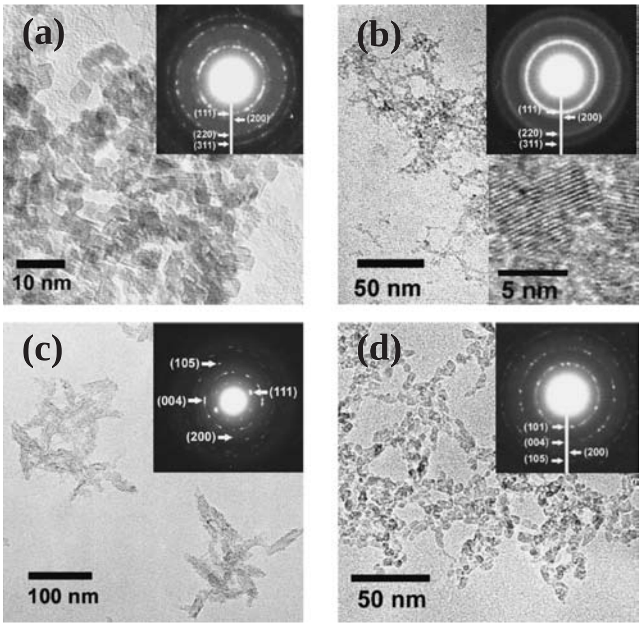

Figure 1. TEM images of CeO_2–TiO_2 composite nanostructures after reaction at 353 K for 1 week, (a) CeBu/TIPT = 100/0, inset: SAED patterns (b) CeBu/TIPT = 75/25, inset: SAED patterns and HRTEM image (c) CeBu/TIPT = 25/75, inset: SAED patterns (d) CeBu/TIPT = 0/100, inset: SAED patterns.

Figure 1 shows the transmission electron microscope (TEM; JEOL JEM-200CX) images and the selected area electron-diffraction (SAED) patterns of the gel samples at the different mole ratio of CeBu/TIPT after reaction at 353 K for 1 week. When CeBu/TIPT was 100/0, CeO_2 nanoparticles of cubic shape whose particle size was about 3–6 nm were observed as shown in Figure 1a and had very high monodispersity, which was achieved by adsorption of LAHC to the surface of nanoparticles. SAED pattern shows the Debye–Scherrer rings, which can be indexed as those of CeO_2 with the cubic fluorite structure. Lattice image of (111) plane of cubic fluorite structure could be clearly observed for most particles. Thus, CeO_2 nanoparticles had high crystallinity.

Morphology and crystalline structure of CeO_2–TiO_2 composite nanostructures varied with changing the mole ratio of CeBu to TIPT. When CeBu/TIPT was 75/25, nano-network structure with diameter of 3–4 nm was observed and SAED pattern indicated cubic fluorite structure as shown in Figure 1b. Whereas, when CeBu/TIPT was 25/75, aggregate structures of nanorod like morphology with average diameter of 20 nm and length of

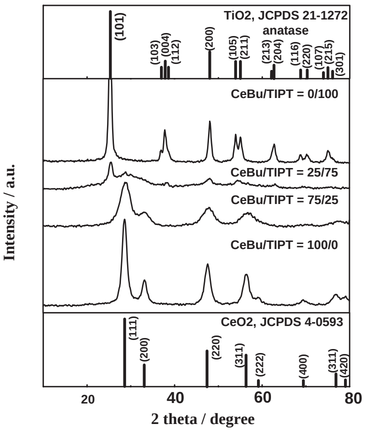

Figure 2. XRD patterns of CeO_2–TiO_2 composite nanostructures calcined at 673 K for 4 h.

80 nm were observed and SAED pattern showed several spots corresponding to lattice plane of the anatase phase of TiO_2 as shown in Figure 1c. When CeBu/TIPT was 0/100, TiO_2 nano-network structure connecting nanowires with diameter of 5–15 nm formed by oriented attachment mechanism[6] was observed and SAED pattern showed the anatase phase as shown in Figure 1d.

Figure 2 shows the X-ray diffraction (XRD; Rigaku RAD-IIC) patterns of CeO_2–TiO_2 composite calcined at 673 K for 4 h. The peaks at CeBu/TIPT = 100/0 are sharp and can be indexed to a CeO_2 cubic fluorite structure (JCPDS file No. 4-0593). The crystalline size of the sample was estimated from the Scherrer equation using X-ray line-broadening of the (111) peak was 5.7 nm at CeBu/TIPT = 100/0. This value agreed with the TEM results. When CeBu/TIPT was 75/25, XRD peaks were indexed to a CeO_2 cubic fluorite structure, although the peaks became very broad. In HRTEM image shown in the inset of Figure 1b, lattice image of (111) plane of cubic fluorite structure could be observed. These observations indicate that the crystalline structure of nano-network at CeBu/TIPT = 75/25 consists of a CeO_2 cubic fluorite structure, but is quite different from that of pure CeO_2. No TiO_2 anatase peaks were also observed. Therefore, the formed materials under CeBu/TIPT = 75/25 constitute composite materials of CeO_2 and TiO_2, i.e., the formed materials are not simple mixture of pure CeO_2 and TiO_2. As a characteristic of our reaction system, the initial solution including two metal alkoxides is well mixed uniformly in molecular scale, leading easily to formation of composite materials. Since positive partial charge of cerium alkoxide is larger than that of titanium alkoxide, it is inferred that reaction rate of CeBu is faster than TIPT. Moreover, the content of cerium is much higher than titanium. From these facts, the crystalline structure of composite materials is inferred to become a CeO_2 cubic fluorite structure, but quite different from that of pure CeO_2. The different crystal structure makes a new morphology, i.e., nano-network structure and also leads to formation of Lewis acid sites as shown later. The XRD patterns at CeBu/TIPT = 25/75 show mainly broad peaks of TiO_2 anatase phase, which coincide with the results of SAED analysis, and also show a broad peak of CeO_2 around $2\theta = 30°$. Broad peaks indicate formation of composite materials, which leads to nanorod structure. Since the content of titanium is much higher than cerium, main crystalline structure becomes TiO_2 anatase phase, but small amount of CeO_2 crystalline structure are also included, because the reaction rate of CeBu is faster than TIPT.

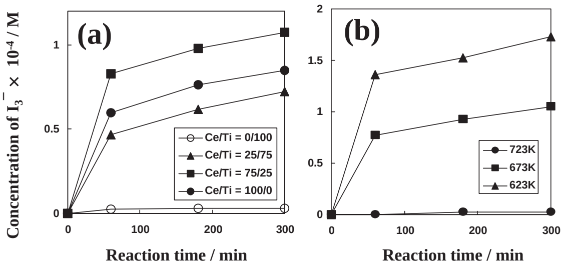

Figure 3. Reaction activity of oxidation of I^-, (a) the effects of mole ratio of CeBu/TIPT under calcinations at 673 K, (b) the effects of calcination temperature at CeBu/TIPT = 75/25.

The effects of synthesis conditions on reaction activities were investigated through the formation rate of I_3^- due to the oxidation of I^- to I_2 in excess KI aqueous solution. CeO_2–TiO_2 composite nanostructures oxidized I^- to I_2 without irradiation of light. Figures 3a and 3b show the effects of mole ratio of CeBu/TIPT calcined at 673 K and effects of temperature at CeBu/TIPT = 75/25 to the reaction activities. The activity became maximum at CeBu/TIPT = 75/25 with calcinations at 623 K. The specific surface areas of CeO_2–TiO_2 composites at CeBu/TIPT = 100/0, 75/25, 25/75, and 0/100 calcined at 673 K are 137.8, 124.9, 107.0, and 106.2 m^2/g, respectively. And those of the composites at CeBu/TIPT = 75/25 and calcined at 623 and 723 K are 127.5 and 60.1 m^2/g, respectively. These results indicate that the specific surface area is not the main factor, which controls the reaction activity, but there is another important factor, i.e., amount of Lewis acid sites.

The amount of Lewis acid sites could be changed by changing the composition ratio of CeO_2–TiO_2 composite because mixed oxide have been frequently reported to have higher catalytic activity than the pure metal oxide, e.g., SiO_2–TiO_2 composite.[8] As pointed out above, the uniformly mixed solution of the metal alkoxides led to homogeneously mixed composite oxides in atomic scale in our preparation method.

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