Sonochemical Preparation of Zirconia/Noble Metals Composite Nanopowders

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The possibility of preparation of Pt/3Y–TZP, Au/3Y–TZP, and Pt(Au)/3Y–TZP nano-composites by sonochemical technique was studied. The sonochemically synthesized Pt, and Au nanoparticle (~2 nm) were directly impregnated into the zirconia nano-aggregates (20–45 nm). The morphology manipulation technique allowed production of the composite zirconia-based aggregates in which a significant fraction of the Pt and Au crystallites was embedded into the zirconia aggregates. The catalytic properties of composite nanopowders were studied and described.

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1. Introduction

Nanometer-scaled clusters are very interesting in that their properties are between those of the condensed matter and atoms.1,3,7–9 These clusters also provide excellent models for the study and understanding of surfaces and catalysis.1,7,8 The specific advantages of nanocrystalline materials are superior phase homogeneity and possible low-temperature sinterability.1,3,7–7 Nanoparticle production techniques are needed for engineering high-quality powders with required composition, homogeneity and morphology. These characteristics significantly determine the later-stage processing and properties of the ceramic (or metal/ceramic composite).1,10–14,16 The addition of a metal to the ceramic matrix often produces a composite with more desirable properties than the individual components.1,2,3,7–11,17–21

The chemical effects induced by ultrasound (20 kHz to 10 MHz) do not come from the direct interaction of sound with the molecule species. In the liquid phase, the wavelength of the sonic wave is in the range of a centimeter to micrometers, which is not a molecular dimension. The origin of the sonochemical reactions is the cavitation, which occurs due to the stress induced by passing of the sound waves through the liquid.15,17 The sound waves consist of compression and decompression cycles. The pressure during the decompression is low enough for the liquid to be torn apart and leave bubbles, which grow during the decompression cycles, and implode during the compression cycles. The bubbles are filled with vapor gases, and produce radicals during the implosion. Implooding bubble is a kind of microreactor with a very high temperature and pressure inside. The concentration of energy during the multi-bubble collapse is enormous and the interior bubble temperature reaches thousands of degrees during collapse.12 The reaction rates are usually enhanced because of the formation of highly reactive radical species thus their reduction is facilitated.13–15 In the sonicated system, three kinds of reducing species may be generated from the direct sonolyses of solvent water of solute sodium dodecyl sulfate (SDS) or polystyrene glycol monostearate (PEG–MS) in the interfacial region of collapsed bubbles/neighborings of volume of liquid, and the subsequent reaction between these radicals and SDS (or PEG–MS respectively),14,15,21

The possibilities of engineering of Pt/3Y–TZP, Au/3Y–TZP and Pt(Au)/3Y–TZP nano-composites in the presence of SDS and PEG–MS surfactants were studied in this investigation. We reported that Pt (II) and Au (III) ions were sonochemically reduced from aqueous solutions of their salts onto the surface of the aggregated zirconia crystallites to form platinum nanoparticles impregnated into the zirconia (3Y–TZP) nano-aggregates.

2. Experimental procedure

The preparation conditions of the 3 mol% Y2O3 doped 97 mol% ZrO2 (3Y–TZP) nanopowder have been well described in previous publications.3,4 The temperatures of 450 (1), 600 (2) and 750°C (3) with 1 h holds were chosen for the final calcination. 3Y–TZP nanopowders with three different morphologies of nano-aggregates i.e.: opened arrangement of the primary crystallites (1), uniformly shaped secondary aggregates (2), and finally, dense nano-aggregates (3) were produced.4 Reagent-grade potassium tetrachloroplatinate (K2PtCl6); sodium tetrachloroaurate (III) dihydrate (Na(4AuCl)2·2H2O); sodium dodecyl sulfate (CH3(CH2)11OSO3Na) (SDS) and polyethylene glycol monostearate (HO(CH2CH2O)n(OCC7H15) (PEG–MS) as a surfactants (all produced by Wako Pure Chemicals Co., Osaka, Japan) were used as received without further purification. K2PtCl6 and Na(4AuCl)2·2H2O stock aqueous solutions with SDS were initially prepared and aged for 12 hours at 20°C. Stock aqueous solution of Na(4AuCl)2·2H2O with PEG–MS was prepared under the similar conditions. The initial amount of Pt and Au compounds varied according to the final concentration of metal in the metal-ceramic composites between 1.5 and 5 mass%. The concentrations of 8 M of SDS per 1 M of K2PtCl6 and 0.5 M of PEG–MS per 1 M of Na(4AuCl)2·2H2O were chosen.

The aqueous suspensions of zirconia powder were impregnated with an aqueous solutions of K2PtCl6 and with Na(4AuCl)2·2H2O. The following sonochemical reduction of Pt or Au ions to metal platinum was applied. In the case of Pt(Au)/3Y–TZP preparation K2PtCl6 aqueous solution was added into the suspension after first 30 min of ultrasonic treatment.

A multiwave ultrasound generator (Model Kajo 4021, Tokyo, Japan) with a 65 mm diameter barium titanate oscillator was used for the ultrasonication. The generator operated at 200 kHz with an input power of 200 W. 100 ml of every sample solution was placed in a cylindrical glass vessel with a 50 mm inside diameter and total volume of 150 ml, than purged with an argon gas stream. The vessel was mounted at a constant position relative to the nodal plane of the sound wave (3.75 mm, i.e., the half length of the ultrasound wave from
the oscillator). The vessel was fixed at exactly the same position and closed during the irradiation. To maintain the constant temperature of 20°C, the ultrasonic treatment was carried out in a temperature controlled water bath.

After the ultrasonic treatment, the suspensions were mixed using a magnetic stirrer at 150°C (except Au/3Y–TZP, and Pt(Au)/3Y–TZP preparation) for a prescribed time. Subsequently, the powders were separated from the supernatant by centrifuging (10000 rpm for 15–20 min). The composite powders were then washed several times with distilled and deionized water to remove the chloride ions and the products of the SDS decomposition. Washing with water was followed by ethanol (C2H5OH, 99.5% reagent grade, Kanto Chemicals, Japan) washing with subsequent centrifuging, redispersing (using an ultrasonic horn (Model USP–600, Shimadzu, Kyoto, Japan)) in fresh ethanol and then a final slow evaporation of the ethanol (T = 60°C) using a drying oven.

Observation via TEM (Model JEM–2000–EX, JEOL, Tokyo, Japan) operated at 200 kV was used to determine the powder morphology. Phase identification of the metal-oxide composite powders was determined by nano-area energy dispersion X-ray spectroscopy analyser (TEM–EDX).

3. Results and discussion

A TEM micrograph of the 3 mol% Y2O3 97 mol% ZrO2 (3Y–TZP) nano-powder produced by hydrolysis (155°C, 10 h hold) and calcinations at the temperature of 600°C for 1 h is shown in Fig. 1. The primary crystallites with an average size of ~5 nm are aggregated into uniformly shaped secondary nano-aggregates with a mean aggregate size of 20–50 nm. The aqueous suspension of the above 3Y–TZP powder was mixed with K2PtCl4 and the SDS surfactant aqueous solution. Subsequent sonochemical reduction of Pt ions was applied. The color of the mixed suspensions of the 3Y–TZP nano-powder with an aqueous solution of K2PtCl4 mixed with SDS changed from yellow-white (initial color of the aqueous solution of Pt complexes is a bright yellow, color of zirconia suspension is a milky white) to light gray in the progress of the sonochemical reduction of the metallic ions. A significant amount of Pt was uniformly embedded on the surface and into the pores of zirconia nano-aggregates (Fig. 2).

The TEM–EDX spectra (Fig. 3) of the representative nano-aggregate A from Fig. 2 shows the existence of uniformly distributed platinum on the surface and inside the zirconia nano-aggregate. We can conclude from figures 2 and 3 and that the sonochemical reduction of the K2PtCl4 allowed the production of uniformly shaped zirconia-based metal-ceramic nano-aggregates impregnated with platinum.

Fig. 4 shows a transmission electron micrograph of the

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**Fig. 1.** Transmission electron micrograph of 3 mol% Y2O3–doped ZrO2 nanopowder produced by hydrolysis (155°C, 10 h hold) and calcination (600°C, 1 h).

**Fig. 2.** Transmission electron micrograph of 3 mol% yttria-doped zirconia nano-aggregates impregnated with 5 mass% of platinum.

**Fig. 3.** TEM–EDX of nano-aggregate A on Fig. 2.

**Fig. 4.** Transmission electron micrograph of 3 mol% Y2O3–doped ZrO2 powder embedded with 1.5 mass% of Au in the presence of SDS as a surfactant.
3 mol% yttria 97 mol% zirconia powder sonochemically covered with 1.5 mass% of Au in the presence of SDS surfactant. The preparation conditions of the precursors, and the sonication conditions were similar to the Pt/3Y–TZP preparation conditions, however, the longer-sonication treatment (4 hours) was necessary to change the color of the mixed suspension to reddish-violet (color of colloidal gold). A quite different morphology of the composite powder (in comparison with Fig. 2) can be seen in Fig. 4. The agglomerated (because of a long-time sonication) zirconia nano-aggregates adjoin relatively large (~70 nm) particles of gold. The TEM–EDX spectra of the region A on Fig. 4 is shown on Fig. 5. We can conclude from the EDX analysis that the darker particle on Fig. 4 is a nano-particle of gold, or, at least, gold is prevailing in this region (two slight pikes of zirconium were also detected on this region). The TEM–EDX of region B from Fig. 4 is shown on Fig. 6. Only yttria-doped zirconia was detected on the regions neighboring to the gold particle (lines of zirconium, oxygen, and a slight line of yttrium (3 mol% Y₂O₃)). From figures 4–6 we can conclude that the above powder is actually not a composite powder, but a mix of two separated nanopowders.

The morphology of this two nanopowders (zirconia particles and gold particles) is very different. As we can assume on the basis of our previous studies, the single zirconia nanoparticle consists of two different microstructural units: primary nano-crystallites (1) and secondary aggregates of crystallites (2). Actually the particle of yttria-doped zirconia is nano-aggregate assembled during chemical synthesis from finest nano-crystallites (Fig. 1). In contrast with zirconia nanoparticls, the nanoparticles of gold (produced by sonochemical reduction of sodium tetrachloroaurate (III) dihydrate in the presence of SDS surfactant) was found to be the single, relatively large (50–80 nm) nanoparticles. This means that SDS, which also decomposes during imploiding of bubbles, doesn’t stabilize the size of as-synthesized gold nanoparticles. As a result, it was impossible to receive the uniform distribution of gold onto the surface of ceramic nano-particles.

We can assume that using of sodium dodecyl sulfate as a stabilizer of as-prepared finest gold nanoparticles don’t allow uniformly impregnate gold nanoparticles on the surface of zirconia nano-aggregates as it was in the case of Pt/3Y–TZP.

The transmission electron micrograph of 3 mol% Y₂O₃–doped ZrO₂ nano-aggregates embedded with 1.5 mass% of Au and subsequently covered with 5 mass% of Pt is shown on Fig. 7. For the preparation of this composite the initial aqueous solution of Na[AuCl₄]·2H₂O with PEG–MS (instead of SDS) was prepared, aged, mixed with zirconia aqueous suspension and subsequently sonicated under the similar conditions as before. Only 30 minutes sonication was enough for changing the color of the suspension to redish violet (for complete reduction of gold). After 30 min. the aqueous solution of K₂PtCl₆ was added into the glass reactor. Within the following 20 min. the redish violet color of the suspension was changed to dark gray, that indicate the completion of the platinum reduction. The sonication was stopped. The centrifuging of the suspension (1000 rpm for 10 min.) gave the dark gray sediment and a translucent supernatant. After washing and drying the powder was characterized by TEM and TEM–EDX. The TEM–EDX spectra of the representative nano-aggregate A from Fig. 7 is shown on Fig. 8. The nano-area energy dispersion X-ray spectroscopy analyses showed the strong lines of zirconium, platinum, gold and oxygen. From this figure, coupled with Fig. 7, we can conclude, that in presence of PEG–MS (as a particles size stabilizer of gold) gold nanoparticles were uniformly distributed within the zirconia nano-aggregates. Reduced from the sodium tetrachloroaurate gold nanoparticles were stabilized in size with polyethylene glycol monostearate possibly because much shorter period was necessary for reduction of gold in this case. As a result of reaction time shortening (i.e. shortening of ultrasonic treatment) the PEG–MS surfactant, which was not decomposed completely (as in the case of long-time sonication in the presence of SDS) covered the as-synthesized gold particles and prevents its further growing. Subsequently
the Au/3Y-TZP composite was embedded with platinum. The resulting 5 mass% Pt–1.5 mass% Au-3Y-TZP nano-composite was obtained.

4. Conclusions
Platinum and gold nano-particles produced by sonochemical reduction of its salts in aqueous media in presence of the SDS (PEG–MS for Au reduction) surfactant were directly embedded onto zirconia (3Y-TZP) nano-aggregates (20-50 nm). The Pt/Au-3Y-TZP nano-composite was also produced.

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References