Engineering of Noble Metals – Zirconia Nano-Composites

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Abstract

Yttria-stabilized zirconia nano-powder, which only contains extremely small uniform aggregates, was prepared using hydrothermal synthesis, nonizothermal calcinations and ultrasonic powder deagglomeration techniques.
The possibility of engineering of Pt–3Y-TZP, Pd–3Y-TZP and Au–3Y-TZP nano-composites by sonochemical technique was studied. The sonochemically synthesized Pt, Pd and Au nano-particles (~2 nm) were directly embedded on the zirconia nano-powders of different origin. The TZ-3Y (Tosoh Co.) powder and 3Y-TZP nano-powder with different primary crystallite size and different aggregate size and morphology, were used as a support for the Pt, Pd and Au nanocrystallites impregnation. The catalytic properties of composite nanopowders were studied and described.

Keywords: sonochemistry, metal-ceramic nano-composites, noble metals, morphology manipulation

1. INTRODUCTION

Nanometer-scaled clusters are very interesting in that their properties are between those of the condensed matter and atoms.[1-7] These clusters also provide excellent models for the study and understanding of surfaces and catalysis.[1, 7, 8] The specific advantages of nanocrystalline materials is a superior phase homogeneity.[1]

The processing of nanostructured materials is a part of an emerging and rapidly growing field referred to as Nanotechnology. Studying in this field emphasizes the generation of materials with controlled structural characteristics, research on their processing into bulk materials with engineering properties and technological functions.[1]

Nanopowder 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, metal or metal/ceramic composites.[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, 8-11]

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.[12, 13] 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. Imploding 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 polyethylene glycol monostearate (PEG-MS) in the interfacial region of collapsed bubbles/neighboring volumes of liquid, and the subsequent reaction between these radicals and SDS (or PEG-MS respectively).[14-15]

The possibilities of engineering of Pt/3Y-TZP, Pd/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), Pd(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 and palladium nanoparticles impregnated into the zirconia (3Y-TZP) nano-aggregates.

2. EXPERIMENTAL PROCEDURE

The starting reagents were zirconium oxychloride hydrous ($ZrOCl_2 \cdot 10H_2O$ (98% pure)), urea (NH_2CONH_2 (99% pure)), yttrium oxide (Y_2O_3 (>99.5% pure)) (High Purity Chemicals Co., Saitama, Japan), HCl (Kanto Chemical Co, Tokyo, Japan). All water used in the study was doubly distilled and deionized. Yttrium chloride preparation technique was described earlier.[6-8] Stock aqueous solutions of concentration 0.1 M of

Zr^{4+} + 3 mol% of $2Y^{3+}$ were produced.[6-11] The mixed urea-contained sol with an initial pH =1.2 was filled in a Teflon vessel and hydrothermaly treated at 155 °C for 10h. The urea decomposed into NH_3 and CO_2 through reaction with H_2O and the sol's pH changed to ~ 8.5. The homogeneous precipitate formed was hydrous yttria-doped ZrO_2, which crystallized under hydrothermal conditions to tetragonal form.[7,8]

The resulting products were washed with distilled water and each wash cycle, was followed with re-dispersion using an ultrasonic horn (Model USP-600, Shimadzu, Kyoto, Japan).

The temperatures of 450 (1), 600 (2) and 750 °C (3) with 1 h holds were chosen for the 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 tetrachloropaladate (K_2PdCl_4) (produced by Kanto Chemical Co., Tokyo, Japan); potashium tetrachloroplatinate (K_2PtCl_4); sodium tetrachloroaurate (III) dihydrate ($Na(AuCl_4)\cdot2H_2O$); sodium dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$) (SDS) and polyethylene glycol monostearate (PEG-MS) ($HO(CH_2CH_2O)_nOCC_{17}H_{35}$) as a surfactants (all produced by Wako Pure Chemicals Co., Osaka, Japan) were used as received without further purification.

K_2PtCl_4, K_2PdCl_4, and $Na(AuCl_4)\cdot2H_2O$ stock aqueous solutions with SDS were initially prepared and aged for 12 hours at 20 °C. Stock aqueous solution of $Na(AuCl_4)\cdot2H_2O$ with PEG-MS was prepared under the similar conditions. The initial amount of Pt, Pd 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 K_2PtCl_4 (or K_2PdCl_4), and 0.5 M of PEG-MS per 1 M of $Na(AuCl_4)\cdot2H_2O$ were chosen.

The aqueous suspensions of zirconia powder were impregnated with an aqueous solutions of K_2PtCl_4, K_2PdCl_4, and with $Na(AuCl_4)\cdot2H_2O$. The following sonochemical reduction of Pt, Pd or Au ions to metal platinum was applied. In the case of Pt(Au)/3Y-TZP preparation K_2PtCl_4 aqueous solution was added into the suspension after first 30 min of ultrasonic treatment.

A multiwave ultrasound generator (Model Kaijo 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 (10 000 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 (C_2H_5OH, 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).

Hydrogenation of 4-pentenoic acid was performed for evaluation of the catalytic activity of the sonochemically prepared Pt/3Y-TZP nano-composites. The hydrogenation reaction was carried out in a conventional vacuum line equipped with a diaphragm manometer (total volume: 240 ml). The round glass vessel was used for the reaction, which had a silicon rubber septum for sample injection. An aqueous solution (30 ml) containing 0.1 g of the composite particles or commercially available palladium black was pretreated under 760 Torr (~0.1 MPa) of hydrogen for 1 hour at room temperature. After the sample solution was evacuated, 4-pentenoic acid (0.678 mmol of $C_5H_8O_2$) and hydrogen were introduced into the reaction system. Hydrogenation was carried out at 20 °C under stirring at 0.1 MPa of hydrogen, and the rate of hydrogenation was evaluated by measuring the uptake of hydrogen.

3. RESULTS AND DISCUSSION

3.1. Sonochemical preparation of ceramic/noble-metals nano-composites

A TEM micrograph of the 3mol% Y_2O_3 97 mol% ZrO_2 (3Y-TZP) nano-powder produced by hydrolysis (155 °C, 10 h hold) and non-isothermal calcination (to the final temperature of 600 °C with 1 h hold) 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.

30nm

Fig. 1. TEM micrograph 3Y-TZP nanoaggregates.

The aqueous suspension of the above 3Y-TZP powder was mixed with K_2PtCl_4 or K_2PdCl_4 and the SDS surfactant aqueous solution. Subsequent sonochemical reduction of Pt or Pd ions was applied. The color of the mixed suspensions of the 3Y-TZP nano-powder with an aqueous solution of K_2PtCl_4 (or K_2PdCl_4) mixed with SDS changed from yellow-white (initial color of the

aqueous solution of Pt and Pd 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 (Pd) was uniformly embedded on the surface and into the pores of zirconia nano-aggregates (Fig. 2).
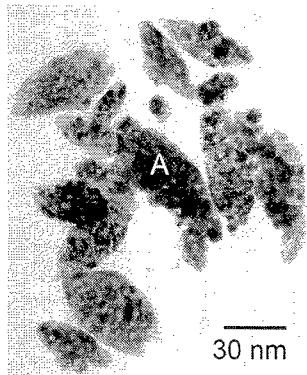

Fig.2. Transmission electron micrograph of 3mol% yttria-doped zirconia nano-aggregates impregnated with 5 mass% of platinum.
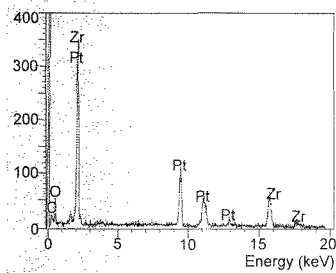

Fig. 3. TEM-EDX of nano-aggregate A on Fig. 1.

The TEM-EDX spectra (Fig. 3) of the representative nano-aggregate A from Fig. 1 shows the existence of uniformly distributed platinum on the surface and inside the zirconia nano-aggregate. We can conclude from figures 1 and 2 and that the sonochemical reduction of the K_2PtCl_4 allowed the production of uniformly shaped zirconia-based metal-ceramic nano-aggregates impregnated with platinum. The sonochemical reduction technique of the Pd from K_2PdCl_4 in the presence of SDS is similar to the reduction of platinum.
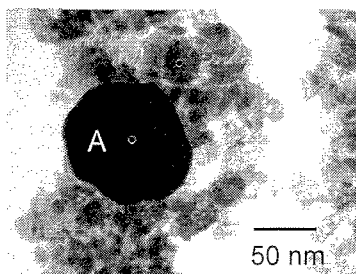

Fig. 4. Transmission electron micrograph of 3mol% Y_2O_3-doped ZrO_2 powder embedded with 1.5 mass% of Au in the presence of SDS as a surfactant.

Fig. 4 shows a transmission electron micrograph of the 3mol% 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 and Pd/3Y-TZP preparation conditions, however, the longer-time 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. 3.
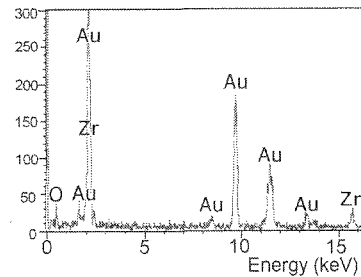

Fig. 5. TEM-EDX of particle A of Fig. 4.

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). 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% Y_2O_3)). From figures 3-5 we can conclude that the above powder is actually not a composite powder, but a mix of two separated nanopowders.
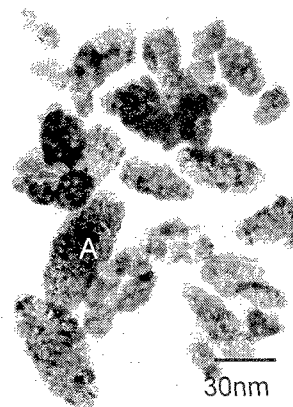

Fig.6. Transmission electron micrograph of 3mol% Y_2O_3-doped ZrO_2 nano-aggregates embedded with 1.5 mass% of Au (in the presence of PEG-MS) and subsequently covered with 5 mass% of Pt.

The transmission electron micrograph of 3mol% Y_2O_3-doped ZrO_2 nano-aggregates embedded with 1.5 mass% of Au and subsequently covered with 5 mass% of Pt is shown on Fig. 6. For the preparation of this composite the initial aqueous solution of $Na(AuCl_4)\cdot2H_2O$ 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 K_2PtCl_4 was added into the glass reactor. Within the following 20 min. the reddish 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 (1 000 rpm for 10 min.) gave the dark gray sediment and a translucent supernatant. After washing and drying the powder was characterized by TEM (Fig. 6) and TEM-EDX. The TEM-EDX spectra of the representative nano-aggregate A from Fig. 6 is shown on Fig. 7.
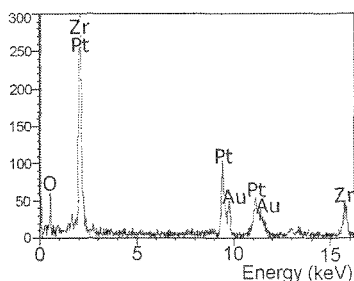
Fig. 7. TEM-EDX of nano-aggregate A on Fig. 6.

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 on this case gold was uniformly distributed within the zirconia nano-aggregates, and 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.

3.2. Evaluation of the catalytic activity of the Pt/3Y-TZP nano-composites

3Y-TZP nanopowders with three different morphologies of nano-aggregates i.e.: open arrangement of the primary crystallites (1), uniformly shaped, porous secondary aggregates of crystallites (2), and dense nano-aggregates (3) were produced from the same initial precursor hydrous zirconia powder. With this matter three calcinations temperatures were chosen. 3 mol% yttria-doped 97 mol% zirconia powders were calcined for with 1 h holds at the temperatures of: 450 °C (1), 600 °C (2) and 750 °C (3). The following sonochemical impregnation of 5 mass% Pt onto the surface of 3Y-TZP powders was performed in the same way as described earlier.
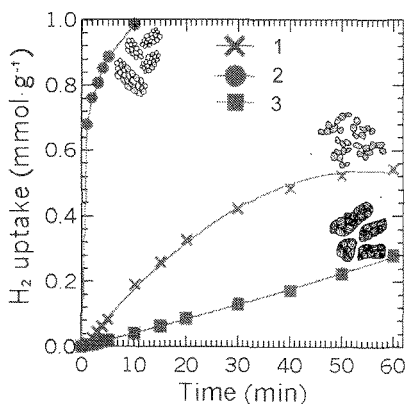
Fig. 8. Influence of the morphology of 5 mass% Pt – 3Y-TZP nano-composite on the rates of catalytic hydrogenation of 4-pentenoic acid.

The influence of the morphology of 5 mass% Pt – 3Y-TZP nano-composite powders on the rates of catalytic hydrogenation of 4-pentenoic acid is shown on Fig. 8. The highest rate of catalytic hydrogenation of 4pentenoic acid over the Pt – 3Y-TZP catalysts was detected for the composite (2). This composite consists of the uniformly aggregated zirconia crystallites covered with platinum. For this nano-composite hydrogen uptake of 1.8 $mmol·g^{-1}$ was detected during only 10 minutes. Hydrogen uptake of only 0.52 $mmol·g^{-1}$ and 0.27 $mmol·g^{-1}$ were detected for the composites (1) and (3) respectively.

4. CONCLUSION

Platinum, palladium 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 (20–50nm). The Pt/Au – 3Y-TZP nano-composite was also produced.

The catalytic hydrogenation of 4-pentenoic acid over the platinum-zirconia nano-composite powders with different morphologies was studied and described. The best catalyst was found to be 5 wt% Pt – 3Y-TZP nano-composite with a uniformly aggregated zirconia zirconia primary crystallites.

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