Continuous Synthesis of Surface-Modified Metal Oxide Nanoparticles Using Supercritical Methanol for Highly Stabilized Nanofluids

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Received June 29, 2008
Revised Manuscript Received September 9, 2008

Nanofluids, nanosize metal or metal oxide particles suspended in liquid media, have received much attention in recent years because of their superior heat transfer capacities.[1−3] Various nanoparticles including Al_2O_3, SiO_2, TiO_2, CuO, Cu, Ag, Au, and carbon nanotubes have been suspended in traditional heat transfer fluids such as water, ethylene glycol, and transformer oils. Nanofluids can be used to improve energy efficiency of thermal transfer systems in various areas including chemical plants, transportation, microelectronics, nuclear power stations, transformer cooling, and heating, ventilating, and air-conditioning (HVAC).

A major challenge of nanofluids in commercialization is to produce well-dispersed, stable nanofluids in a large-scale with an economically viable method.[3] Nanoparticles tends to form agglomerates due to strong interparticle interactions, often leading to precipitation of the particles in the fluid phase. This results in reduction of thermal conductivity and in clogging of channels in heat tranfer systems. Various methods have been developed to prepare stable nanofluids. In a one-step method, physically evaporated metal vapors are directly condensed into the base fluids in a vacuum chamber.[4−6] Although highly stable, highly efficient nanofluid can be prepared, the one-step method suffers from high production cost and low production rate associated with the batch-wise running mode. In a two-step method, nanoparticles are first synthesized with conventional techniques such as gas-phase and sol−gel methods, and then the nanoparticles are dispersed in the base fluids. A major drawback of the two-step method is the particle agglomeration. Various efforts including ultrasonication,[7−9] changing pH,[10−12] using dispersants/surfactants,[12−14] and chemical surface modification[15,16] have been extensively made to enhance stability of the suspension. However, it is still challenging to produce nonagglomerated nanofluids with the two-step method.[3] In addition, the two-step method is often time-consuming associated with the multistep, batch-wise running mode and suffers from low production rate, use of a large quantity of toxic reagent and solvents, and high production cost. Therefore, there are considerable efforts underway to develop more reliable and less-expensive techniques that can produce well-dispersed nanofluids in a continuous mode.

Nanosize metal oxide nanoparticles including CeO_2, AlOOH, Fe_2O_3, TiO_2, CuO, ZnO, and complex metal oxides have been widely prepared continuously using supercritical water (scH_2O).[17−23] High diffusivity of reactants in the supercritical medium, fast reaction rate, and high degree of supersaturation due to low solubility of starting materials results in high quality, ultrafine nanoparticles at a high rate (~10 s). More recently, surface-modified metal oxide nanoparticles have been synthesized with the supercritical hydrothermal synthesis in a batch mode.[24−29] By introducing organic ligands that are soluble in scH_2O in the hydrothermal synthesis, crystal growth can be inhibited, and surface hydroxyl groups can be replaced with the organic ligands. This results in highly dispersable, nonagglomerated metal

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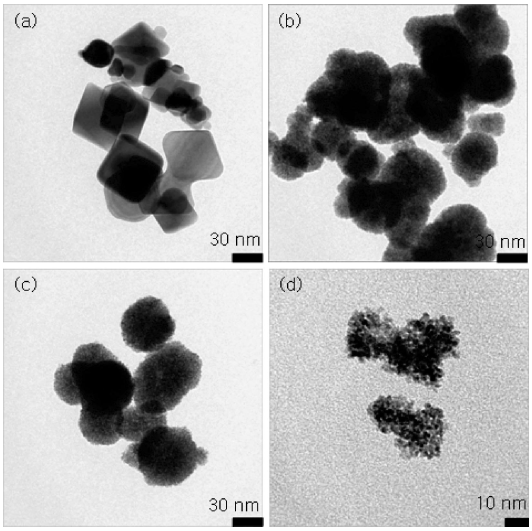

Figure 1. TEM image of ceria nanoparticles synthesized using (a) scH_2O, (b) scMeOH, (c) scMeOH with 0.03 M decanoic acid, and (d) scMeOH with 0.3 M decanoic acid. $Ce(NO_3)_3$ concentration was 0.05 M. Nanoparticle synthesis conditions were 300 bar, 400 °C, and a residence time of ~40 s.

oxide nanoparticles in organic media. However, continuous synthesis of surface-modified metal oxide nanoparticles in supercritical media has not been reported yet.

This communication describes the first use of supercritical methanol (scMeOH) for synthesis of surface-modified metal oxide nanoparticles in a continuous mode to prepare highly dispersable nanofluids. Instead of using scH_2O, we use scMeOH as a reaction medium in the continuous synthesis of surface-modified nanoparticles because (1) homogeneous metal salt solution and organic surface modifier solution can be introduced into a flow type reactor continuously and (2) line and filter clogging problems by unreacted, precipitated surface modifier in water at ambient condition can be avoided.

The surface-modified ceria (CeO_2) nanoparticles were prepared by introducing a solution of ceria(III) nitrate ($Ce(NO_3)_3$) and decanoic acid (as a surface modifier) in methanol to a continuous flow reactor system (see Supporting Information for detailed synthesis procedure). $Ce(NO_3)_3$ was completely soluble in methanol at the feed concentration (0.05 M). The nanoparticle production rate of the current experimental system was 3 g/h. It is noted that the production rate can be simply increased by increasing the reactor volume and flow rate to make the continuous synthesis amenable to large-scale production. Supercritical water and supercritical methanol without using decanoic acid were also used to synthesize ceria nanoparticles. Figure 1 shows the representative transmission electron microscopy (TEM) images of the ceria nanoparticles synthesized at 300 bar, 400 °C, residence time of ~40 s, and 0.05 M $Ce(NO_3)_3$. When scH_2O was used, tetrahedron shape particles with a clear facet was obtained. The particle size was in the range of 20−60 nm (Figure 1a). This result agrees well with the previously reported work.[30] When scMeOH was used, spherically shape particles with 40−80 nm diameter were obtained (Figure 1b). When a small amount of decanoic acid (0.03 M) was used with scMeOH as the reaction medium, the particle size and particle morphology did not change much compared to those of the particles synthesized without decanoic acid. (Figure 1c). Significant changes of particle morphology were observed with the use of a large amount of decanoic acid (0.3 M) (Figure 1d). Primary particles with 2−3 nm diameter were loosely aggregated and formed secondary particles with size of 30−40 nm. Similar particle morphology resulted when 0.01 $Ce(NO_3)_3$ and 0.3 M decanoic acid were used (Figure S2 in the Supporting Information). Thus, the presence of the organic modifier significantly affected the particle shape and morphology. X-ray diffraction (XRD) analysis revealed that the surface-modified nanoparticles had CeO_2 crystalline structure (see Figure S3 in the Supporting Information).

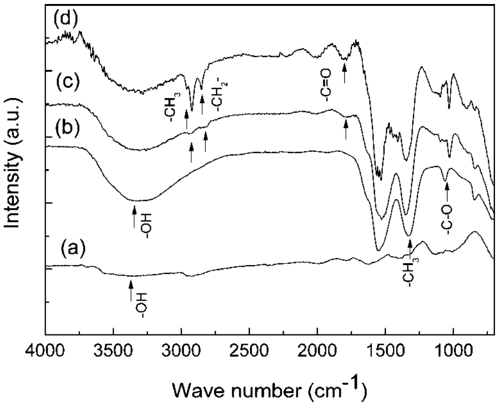

Figure 2. FT-IR spectra of ceria nanoparticles synthesized using (a) scH_2O, (b) scMeOH, (c) scMeOH with 0.03 M decanoic acid, and (d) scMeOH with 0.3 M decanoic acid.

Fourier transform infrared (FT-IR) analysis was conducted to investigate surface characteristics of the nanoparticles. Figure 2 shows FT-IR spectra of the ceria nanoparticles synthesized using (a) scH_2O, (b) scMeOH, (c) scMeOH with 0.03 M decanoic acid, and (d) scMeOH with 0.3 M decanoic acid. Weak and broad −OH stretch peaks at 3000−3750 cm^{-1} were observed in the particles synthesized using scH_2O (Figure 2a). In contrast, the spectrum of the ceria nanoparticle synthesized using scMeOH shows −C−O stretch peak at 1050 cm^{-1}, $-CH_3$ bend peak at 1330 cm^{-1}, and broad −OH stretch peak at 3000−3750 cm^{-1} (Figure 2b). Thermal gravimetric analysis (TGA) showed that the weight of the particles synthesized using scH_2O did not change much while the weight of the particles synthesized using scMeOH decreased to ~88% at a temperature above 800 °C (see Figure S4 in the Supporting Information). This indicates that the surface of the ceria nanoparticles synthesized using scMeOH are modified with CH_3O- functional groups. The ceria nanoparticles synthesized using scMeOH with 0.03 or 0.3 M decanoic acid have −C=O stretch peak at 1780 cm^{-1}, $-CH_2-$ stretching peak at 2850 cm^{-1}, and $-CH_3$ stretching peak at 2920 cm^{-1}, along with the characteristic peaks of C−O (1030 cm^{-1}), $-CH_3$ (1330 cm^{-1}), and OH (3000−3750 cm^{-1}) (Figure 2 c,d). The weight of the particles decreased to ~88% when temperature increased to 800 °C (see Figure

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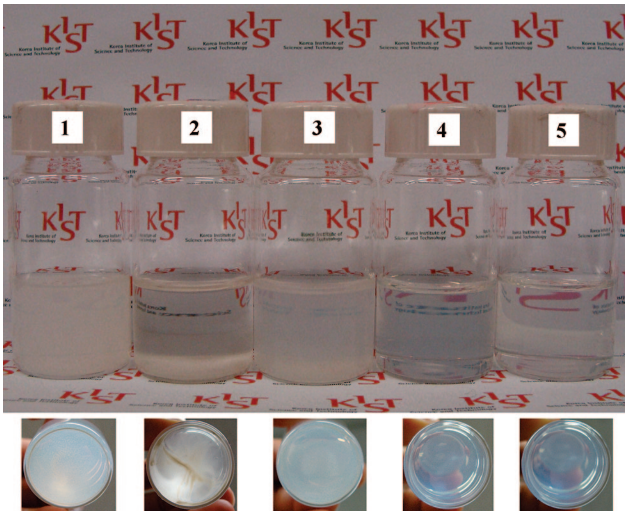

Figure 3. Dispersability of ceria nanoparticles in ethylene glycol. The ceria particles were synthesized using (1) scH_2O, (2) scMeOH, (3) scMeOH with 0.05 M $Ce(NO_3)_3$ and 0.03 M decanoic acid, (4) scMeOH with 0.05 M $Ce(NO_3)_3$ and 0.3 M decanoic acid, and (5) scMeOH with 0.01 M $Ce(NO_3)_3$ and 0.3 M decanoic acid. The bottom pictures are the bottom view of the vials.

S4 in the Supporting Information). This suggests that some portion of the particle surfaces was chemically modified with decanoic acid. The presence of C═O peak may suggest that the carboxyl groups of decanoic acid are chemically bonded on the surface of the nanoparticles.

Figure 3 shows dispersability of the ceria nanoparticles synthesized using scH_2O and scMeOH without using decanoic acid, and scMeOH using decanoic acid. Water, ethylene glycol, and transformer oil were used as the base fluids. The transformer oil consists of cycloalkanes with a low portion of *n*-alkanes. Details on the dispersability experiment procedures are given in the Supporting Information. The pictures in Figure 3 were taken after two weeks. All of the nanoparticles, synthesized using either scH_2O or scMeOH with or without using decanoic acid, aggregated and precipitated at the bottom of the vials when 0.1 wt % of the nanoparticles were dispersed in water (see Figure S5 in the Supporting Information). Similarly, when 0.1 wt % of the nanoparticles were dispersed in the transformer oil, all of the particles were precipitated (see Figure S5 in the Supporting Information). Aggregation and precipitation were observed when 1 wt % and 0.01 wt % of the nanoparticles were dispersed in water or the transformer oil. The surface-modified nanoparticles dispersed in ethylene glycol showed better stability behavior. When 0.01 wt % of the nanoparticle synthesized using scH_2O were dispersed in ethylene glycol, some portion of the particles was still dispersed and the other portion precipitated (Figure 3-1). Most of particles synthesized using scMeOH were precipitated (Figure 3-2). When the surface of the particles was modified with 0.03 M decanoic acid, the dispersability was similar to that of the nanoparticles synthesized using scH_2O (Figure 3-3). In sharp contrast, transparent, perfect dispersion was observed when the nanoparticles synthesized using scMeOH with 0.3 M decanoic acid (Figure 3-4,-5) were dispersed in ethylene glycol.

Thus, surface-modified ceria nanoparticles show much better dispersion stability in ethylene glycol. Similar dispersability behavior was observed when the 0.1 and 1 wt % of the particles were dispersed in ethylene glycol (see Figure S6 in the Supporting Information). This may be due to the unique surface property of the surface-modified nanoparticles. As discussed previously, both the hydroxyl group and the aliphatic group were present in the surface-modified nanoparticles. Thus, the hydrophilicity of the particles can be a point between hydrophilic and hydrophobic. This may result in the particle precipitation in the hydrophilic fluid (water) and the hydrophobic fluid (transformer oil) but good dispersion in the medium hydrophilic fluid (ethylene glycol).

In conclusion, surface-modified ceria nanoparticles were synthesized using scMeOH in a continuous mode. The nanoparticles showed good dispersion stability in ethylene glycol. This method should also be applicable to various surface-modified metal oxides such as CuO, Fe_2O_3, ZnO, AlOOH, and so on. This continuous method is amenable to large-scale production of nanofluids or other applications such as catalysts, cosmetics, bioimagings, and optics by scale-up from laboratory to commercial scale.

Acknowledgment. This research was supported by Nano R&D program through the Korea Science and Engineering Foundation funded by the Ministry of Education, Science and Technology (2008-02344). The authors acknowledge Energy and Environmental Research Division at Korea Institute of Science and Technology for additional support.

Supporting Information Available: Detailed experimental methods, continuous supercritical nanoparticle synthesis apparatus, TEM, TGA, XRD, and dispersion results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM8017314