Surface-modified cerium oxide nanoparticles synthesized continuously in supercritical methanol: Study of dispersion stability in ethylene glycol medium

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ABSTRACT

Dispersion stability of surface-modified cerium oxide (CeO_2) nanoparticles in ethylene glycol is examined and the experimental stability results are compared with an extended DLVO model consisting of electrostatic, van der Waals, and hydrophobic/hydrophilic interactions. Unmodified, decanoic acid-modified and oleic acid-modified CeO_2 nanoparticles are synthesized continuously in supercritical methanol (scMeOH). The surface charge of the surface-modified CeO_2 particles changes from positive to negative with an increment in the medium pH while the surface charge of the unmodified CeO_2 particle does not change with varying pH. Long-term dispersion stability test (up to 100 days) shows that the oleic acid-modified nanoparticle with a concentration of 0.3 M retains most stable dispersion in ethylene glycol. The unmodified and decanoic acid-modified nanoparticles with a concentration of 0.03 M precipitate within 7–15 days. In contrast, initial short-term stability evolution reveals different stability behavior compared to the long-term stability. The unmodified and the decanoic acid-modified nanoparticles with a concentration of 0.03 M were less attractive than the oleic acid-modified nanoparticle with 0.3 M. The experimental short-term stability data is in good agreement with the computational results of energy profiles for the CeO_2 nanoparticle suspension.

1. Introduction

Recently, new types of high performance heat transfer fluids have received considerable attention in a variety of areas including microelectronics, chemical plants, transportation, nuclear power station, and HVAC (heating, ventilating, and air conditioning). The thermal conductivity of the heating or cooling fluids plays a vital role in the development of energy-efficient heat transfer equipments. Conventional heat transfer fluids such as water, ethylene glycol, and transformer oil retains poor heat transfer properties [1]. In 1995, Choi introduced a new class of heat transfer fluids, called nanofluids, that can transfer heat more efficiently than the conventional fluids [2]. Nanofluids, in which metal nanoparticles, metal oxide nanoparticles or carbon nanotubes are dispersed in the conventional heat transfer media, can enhance both the thermal conductivity and the heat convection of the base fluids up to two times [3]. Despite the high potential of the nanofluids, agglomeration and rapid settling of the nanoparticles in the base fluids, due to strong interparticle interactions, have been a major obstacle to successful application of the nanofluids [4]. This often causes problems such as severe clogging in micro-channels, corrosion on the pipe's wall, and decrease in the thermal performance of the nanofluids. Therefore, dispersion stability of the nanoparticles in the base fluids has become a primary issue in the research of the nanofluids [5–8].

Surface chemical modification of nanoparticles with appropriate organic ligands is one of the promising methods to attain well-dispersed nanoparticles in liquid media [9,10]. Typically, presynthesized nanoparticles were dispersed in a medium and the surface chemical groups of the nanoparticles reacted with the organic ligands. Recently, one-pot synthesis of surface-modified metal oxide nanoparticles in supercritical water (scH_2O) has received much attention due to high diffusivity of reactants in supercritical fluid condition, fast reaction rate, miscibility of organic ligands in scH_2O condition ($T_c = 374\,°C$ and $P_c = 22.1\,MPa$), and high reactivity condition. This leads to produce surface-modified nanoparticles in a high rate [11–13]. The hydroxyl groups present on the surface of metal oxide nanoparticles can be replaced with the organic ligands that are miscible in scH_2O condition. Various types of surface-modified nanoparticles including CeO_2, ZnO, AlOOH, Fe_2O_3, $CoAl_2O_4$ and TiO_2 were synthesized in scH_2O using a batch reactor [11,14–17]. More recently, we showed that

surface-modified cerium oxide (CeO_2) and surface-modified zinc oxide (ZnO) nanoparticles can be synthesized continuously in supercritical methanol (scMeOH, $T_c = 240\,°C$ and $P_c = 8.1$ MPa) using decanoic acid or oleic acid as the surface modifier [18–20]. Inhomogeneous reactant feeding and line/filter clogging problems associated with continuous synthesis of surface-modified nanoparticles in scH_2O can be avoided when scMeOH is used as the continuous reaction medium. The decanoic acid-modified or the oleic acid-modified CeO_2 nanoparticles with diameters in the range of 10–50 nm were synthesized. The surface-modified nanoparticles synthesized in scMeOH showed good dispersion stability in ethylene glycol [18].

Herein, dispersion stability of unmodified, decanoic acid-modified, oleic acid-modified CeO_2 nanoparticles dispersed in ethylene glycol is examined in detail by performing zeta potential measurement, contact angle measurement, long-term stability test (100 days) and short-term stability test (few minutes). The unmodified and the surface-modified CeO_2 nanoparticles were synthesized continuously in supercritical methanol. Even though there are a few reports on the synthesis and the stability of CeO_2 nanocolloids in water or in organic solvents [12,21–24], no information on dispersion stability of surface-modified CeO_2 nanoparticles in ethylene glycol has been reported. In this paper, the stability tests of the surface-modified CeO_2 nanoparticles dispersed in ethylene glycol were performed by measuring optical ultraviolet transmittance variations with time. To gain a better insight into the stability of the surface-modified CeO_2 nanoparticles in ethylene glycol, the experimental stability data were compared with theoretical prediction using an extended DLVO (Derjaguin–Landau–Verwey–Overbeek) theory. For the theoretical prediction, long-range and short-range colloidal interactions are taken into account and each interaction contribution to the overall particle–particle interaction energy is estimated.

2. Interaction energy of nanoparticles

To examine the stability of the unmodified and the surface-modified CeO_2 nanoparticles dispersed in ethylene glycol, the extended-DLVO model of interaction is used. In this model, the net interaction is considered as adding the short-range hydrophobic (or hydrophilic) attraction (or repulsion) into the superposition of the long-range electrostatic double-layer (EDL) repulsion and van der Waals attraction [25]. To estimate these interactions, the diffuse double-layer potential of the particles, the Hamaker constant of the particles in aqueous media, and the acid/base components of the surface free energy of the solids need to be determined. The diffuse double-layer potential can be approximated by the zeta potential from electrophoretic measurements, and the other two quantities can be obtained from contact angle measurements.

According to the previous literature [25–27], the three components of dispersion, induced dipole, and polarization are combined into the Liftshitz–van der Waals component γ^{LW}. The acid/base component γ^{AB} consists of the electrostatic and acceptor–donor interactions, hydrogen bonding, and π bonding. The total surface free energy γ of solid or liquid surface tension can be expressed as

$$\gamma = \gamma^{LW} + \gamma^{AB}. \tag{1}$$

The γ^{AB} component conforms to the equation

$$\gamma^{AB} = 2\sqrt{\gamma^+ \gamma^-} \tag{2}$$

where γ^+ and γ^- are the nonadditive parts of the surface free energy of solid or liquid surface tension resulting from electron–acceptor and electron–donor interactions, respectively.

Then, Eq. (1) yields total surface free energy of the solid and the liquid, given as

$$\gamma_S = \gamma_S^{LW} + 2\sqrt{\gamma_S^+ \gamma_S^-} \tag{3}$$

$$\gamma_L = \gamma_L^{LW} + 2\sqrt{\gamma_L^+ \gamma_L^-} \tag{4}$$

where subscripts S and L denote solid and liquid surfaces, respectively. Using Young's equation, the following relationship can be derived:

$$\gamma_L(1 + \cos\theta) = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+}\right) \tag{5}$$

where θ is the contact angle of the liquid on the solid. By measuring θ for three liquids of known γ_L components, three equations along Eq. (5) are solved in the unknowns γ_S^{LW}, γ_S^+, and γ_S^-.

In this study, the most important potential energies are the electrostatic repulsion E^{EL}, the van der Waals attraction E^{LW}, and the hydrophobic/hydrophilic interaction relating to the acid/base contribution E^{AB}, although the colloidal interactions originate from various forces. Hence, the total interaction can be estimated as follows:

$$E^{TOT}(s) = E^{EL} + E^{LW} + E^{AB} \tag{6}$$

where s means the surface-to-surface distance (i.e., $s = r - 2a$, with r being the center-to-center distance between the particles of radius a). The total interaction force is determined as $F^{TOT}(s) = -dE^{TOT}(s)/ds$.

Many researchers have studied two-particle interactions by using the Poisson–Boltzmann equation [28]. One of the well-known approaches is the Derjaguin approximation when both the EDL thickness (or Debye length) and the separation distance are small compared to the curvature of the surfaces. Taking the constant potential boundary condition at the surfaces, the Derjaguin results for electrostatic repulsion are given by

$$E^{EL}(s) = 2\pi\varepsilon a\zeta^2 \ln\left(1 + e^{-\kappa s}\right), \tag{7a}$$

$$F^{EL}(s) = \frac{2\pi\varepsilon\kappa a\zeta^2}{(1 + e^{-\kappa s})}e^{-\kappa s}. \tag{7b}$$

Here, ε is the dielectric constant given as a product of the dielectric permittivity of a vacuum ε_o ($= 8.854 \times 10^{-12}\,C^2/J\,m$) and the relative permittivity ε_r for the dispersion medium and ζ is the electrokinetic zeta potential used as estimation of the diffuse layer potential at the slip plane (or shear surface). The parameter κs corresponds to the surface separation normalized by the EDL thickness κ^{-1} (cf., $\kappa^{-1} = \sqrt{\varepsilon kT/2N_A c_b \Lambda_i^2 e^2}$, where c_b (mM) is the electrolyte ionic concentration in the bulk medium at the electroneutral state, Λ_i the valence of type i ions, e the elementary charge, kT the Boltzmann thermal energy at room temperature), and N_A the Avogadro's number.

Based on a pairwise summation method, the van der Waals attraction between two particles of radius a is quantified by

$$E^{LW}(s) = -\frac{A}{6}\left[\frac{2a^2}{s(4a + s)} + \frac{2a^2}{(2a + s)^2} + \ln\frac{s(4a + s)}{(2a + s)^2}\right], \tag{8a}$$

$$F^{LW}(s) = -\frac{A}{6}\left[\frac{4a^2(2a + s)}{(4as + s^2)^2} + \frac{4a^2}{(2a + s)} - \frac{(4a + 2s)(2a + s) - (8as + 2s^2)}{s(4a + s)(2a + s)}\right]. \tag{8b}$$

Note that Hamaker constant A can be obtained from the Liftshitz–van der Waals components of the surface free energy of solid and liquid surface tension (i.e., γ_S^{LW} and γ_L^{LW}) as follows:

$$A = 24\pi s_o^2\left(\sqrt{\gamma_S^{LW}} - \sqrt{\gamma_L^{LW}}\right)^2 \tag{9}$$

where s_o can properly be assumed as 1.58 ± 0.08 Å, which are obtained from the literature [25,28].