315c Molecular Dynamics Simulation of Titania Nanoparticles

Vishal N. Koparde and Peter T. Cummings

Nanoparticles have been the area of active research in recent years as they have novel and unique properties, which distinguish them from the bulk phase(1). Given the difficulties associated with experimental analysis at the nanoscale, these systems are good candidates for study using molecular modeling methods, particularly molecular dynamics simulation.

Titania nanoparticles have been used as white pigments in paints and paper, as photocatalyst in wastewater treatment(2), in solar cells and also as gas sensor. Titania has three polymorphs in nature, namely, anatase, rutile and brookite(3). As anatase and rutile are predominantly used in the prior mentioned applications, we concentrate our studies on these phases.

Among the available force fields for titania, we have chosen the atomistic model by Matsui and Akaogi(4), equation 1, where the first term is non-Coulombic short range repulsion followed by the dispersion attraction term and the Coulombic interaction term, respectively. The ions are treated as rigid spheres with partial charges at their centers in this force-field. The force-field successfully predicts bulk properties such as crystal structure, volume compressibility, thermal expansivities, etc. for all the polymorphs of TiO2 considered. All the simulations in the work were conducted using the molecular dynamics program, DLPOLY v2.13(5).

Constant-volume, constant-temperature simulations of various sizes of anatase and rutile nanoparticles ranging from 2 to 5 nm were conducted at a series of temperatures. The resulting data is used to determine the dependence of melting point on particle diameter, which is then compared with the empirical formula for melting point depression. The result were also analyzed to determine the variation of Ti-coordination along the radius of the particles, variation of surface charge with particle size and the ionic diffusivities and their dependence on particle size, temperature and phase.

Additional molecular dynamics simulations of the coalescence of 3nm and 4nm particles of anatase have been carried out at 573, 973 and 1473K in a constant-volume, constant-energy ensemble. The driving force for sintering of nanoparticles is the reduction in potential energy due to the decrease in surface area(6). The loss of potential energy manifests itself as an increase in the temperature of the sintering particles(7). We have tried to predict the time required for completion of sintering and the corresponding rise in temperature using a simple energy balance model.

Since titania nanoparticles in solution at hydrothermal environment is important from an applications point of view(8), molecular dynamics simulations of 3nm anatase and rutile particles were conducted. The SPC/E forcefield(9) for water and ab-initio derived parameters(10) for ion-water interactions were used in these simulations. Results indicated only one prominent hydration shell around these particles. Residence time and diffusivity of water molecules has been reported.

We acknowledge the National Science Foundation for the financial support.

(1) O. Preining, Journal of Aerosol Science 29, 481 (1998).

(2) V. Augugliaro, V. Loddo, L. Palmisano, et al., Journal of Catalysis 153, 32 (1995).

(3) H. Zhang and J. F. Banfield, Journal of Physical Chemistry B 104, 3481 (2000).

(4) M. Matsui and M. Akaogi, Molecular Simulation 6, 239 (1991).

(5) W. Smith and T. R. Forester, Journal of Molecular Graphics 14, 136 (1996).

(6) K. E. J. Lehtinen and M. R. Zachariah, Journal of Aerosol Science 33, 357 (2002).

(7) K. E. J. Lehtinen and M. R. Zachariah, Physical Review B 6320, 205402 (2001).

(8) H. Cheng, J. Ma, Z. Zhao, et al., Chemistry of Materials 7, 663 (1995).

(9) H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, Journal of Physical Chemistry 91, 6269 (1987).

(10) A. V. Bandura and J. D. Kubicki, Journal of Physical Chemistry B 107, 11072 (2003).

Equation 1,