Molecular dynamics study on nucleation process for supersaturated ZnO solutions in hydrothermal conditions

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Abstract

Molecular dynamics simulations were performed to investigate homogeneous nucleation mechanism of zinc oxide in ambient and hydrothermal conditions. Water model used in this work was the three-site flexible-SPC model proposed by Honma et al. Atomic models for zinc and oxygen ions were constructed with Lennard-Jones and Coulomb potentials. Nucleus sizes calculated by the geometric friend-of-friend method shows the existence of zinc and oxygen ions were found up to 353 K, because the crystal nucleus grows with incorporating ions. On the other hand, only an even number of clusters were found above 423 K. It suggests that rapid formation of ZnO particle and it incorporates into a large-size cluster.

Keywords

Hydrothermal conditions, Molecular simulation, Nucleation

1. Introduction

The physical properties of water are drastically changed from ambient to hydrothermal conditions. For example, the solubility of ionic species can be decreased by manipulating temperature and pressure. Thus, a continuous hydrothermal synthesis is an attractive method for producing functional nanoparticles of variable particle size, morphology, and crystal structure. However, prediction models for the properties or particle growing of nanoparticle was process-dependent, and empirical, a reconstruction of prediction model was required while the development of commercial process. To construct a robust prediction model, it is necessary to understand a fundamental knowledge of particle formation in hydrothermal condition.

Molecular-based analysis such as classical molecular dynamics simulation can obtain an atomic-level and a nanosecond-level information, and it is suitable to investigate the nucleation process of nanoparticles in hydrothermal conditions. In this study, molecular dynamics simulations on zinc oxide aqueous solutions were performed to investigate ZnO clusters, which have been formed rapidly produced via hydrothermal conditions. However, despite hydrothermal synthesis of ZnO nanoparticle was produced via zinc hydroxide, we neglected dehydration reaction of zinc hydroxide into zinc oxide, because of classical consideration of this study.

2. Computational Details

Molecular models used in this work were 3-sites flexible model proposed by Honma et al. for water[1]. The intramolecular potential was the sum of Morse potential for O-H bond and harmonic potentials for H-O-H angle as described in equations (1) and (2).

$$\mathrm{U_{OH}} = \mathrm{D_{OH}}\{1 - \exp(-\rho\Delta r_{OH})\}^2 \tag{1}$$

$$\mathrm{U_{HOH}} = \frac{1}{2}K_\theta(r_{OH}\Delta\theta)^2 + K_{r\theta}(r_{OH}\Delta\theta)(\Delta r_1 + \Delta r_2) + K_{rr'}(\Delta r_1 \Delta r_2) \tag{2}$$

The intermolecular potential is the sum of Lennard-Jones and Coulomb potentials.

$$\mathrm{U_{ij}} = 4\varepsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{r_{ij}} \tag{3}$$

The water model used in this work can represent phase behavior of water at ambient and subcritical conditions. Potential functions for zinc and oxygen ions as zinc oxide was also used as the sum of Lennard-Jones and Coulomb potentials. Lennard-Jones parameters for different atoms were calculated by using Lorentz-Berthelot combination rule.

MD simulations were performed with *NVT* ensembles containing 1372 and 8788 water molecules and 5 to 320 zinc oxide molecules (from 0.2 M to 2.0 M). Time steps were 1 fs for intermolecular motion and 0.2 fs for intramolecular motion. The total simulation time was 3 ns. The simulation temperature was maintained with Nose-Hoover thermostat. The cutoff distance

for potential forces was 10 Å. Long-range electrostatic interactions were handled using the particle-particle-particle-mesh (PPPM) method, with an accuracy criterion of 0.1%. Initial configuration of system was generated using Packmol software [2]. All of molecular dynamics simulations were performed by LAMMPS software [3], and visualizations were used VMD [4].

3. Results and discussions

2.1. Size Effects during Nucleation

To evaluate size effect of nucleation process, MD simulations with small (1372 water molecules) and large (8788 water molecules) systems were employed at 573 K and 0.2 M and 1.6 M of zinc oxide concentrations. Figure 1 shows radial distribution function (RDF) for zinc oxide at 573 K and 0.2 M. The central atom was set to zinc ion (Zn^{2+}) and accumulated counter ions were zinc and oxygen ions to study nucleation behavior. Large first and second peaks at 1.65 Å and 2.35 Å indicates the formation of contact ion pair for ZnO or $(ZnO)_2$ particles. RDF peaks at large interatomic distance such as 2.95 Å, 3.35 Å, and 3.75 Å was disappeared on small system due to the lack of zinc oxide molecules. However, peak positions and heights at first and second peaks up to 2.6 Å were almost identical.

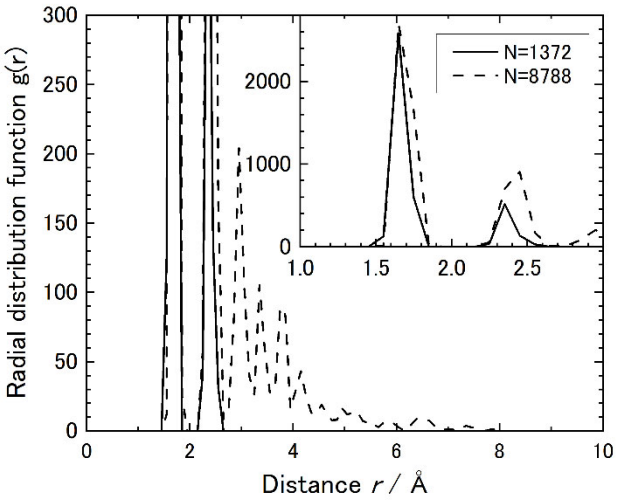

Fig. 1. Radial distribution function of zinc oxide around zinc atom at 573 K, 0.2 mol/kg-water. Solid line: 1372 water system (5 molecules of zinc oxide). Dashed line: 8788 water system (32 molecules of zinc oxide).

Figure 2 shows radial distribution function (RDF) for zinc oxide at 573 K and 1.6 mol/kg-water for large and small systems. Identical peak positions and heights may be acceptable for the nucleation behavior with the small system. Three peaks located at 1.65 Å, 2.35 Å, and 2.95 Å indicates the formation of larger nuclei, however, radial distribution function

far from 6 Å for the small system was lower than that for large system, because less zinc oxide molecule exist in the simulation boxes.

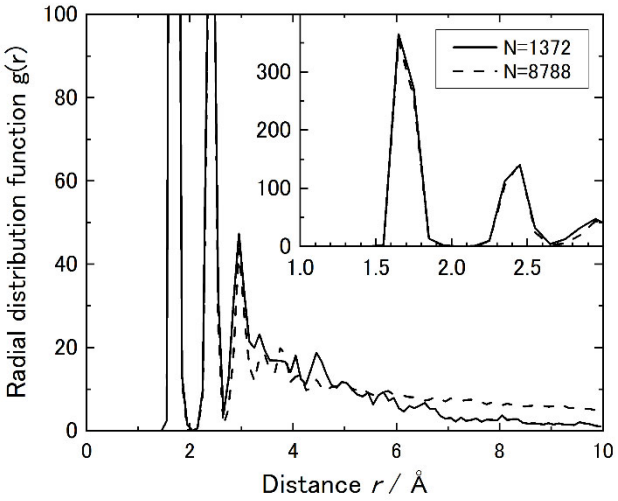

Fig. 2. Radial distribution function of zinc oxide around zinc atom at 573 K, 1.6 mol/kg-water. Solid line: 1372 water system (40 molecules of zinc oxide). Dashed line: 8788 water system (256 molecules of zinc oxide).

2.2. Effect of Temperature on nucleation behavior

Nucleus sizes were calculated with the simple Stillinger-type cluster criterion. It also known as the friend-of-friends method. The linking length was set at 1.85 Å according to the first minimum of the radial distribution functions. Figure 3 shows temperature dependence of cluster size distribution normalized total number of clusters at 0.2 mol/kg-water. At temperatures up to 473 K, majority of clusters was two membered clusters identified as the existence of ZnO particle as expected. The formation of ZnO particle suggests rapid and first process by ion diffusion, because no ions were found above 423 K. However, zinc and oxygen ions as one membered cluster was found at temperatures up to 353 K due to slower ion diffusion with the cage effect of water hydration. The presence of odd number of clusters below 353 K suggests that the crystal nucleus grow during incorporating ions. On the contrary, only an even number of clusters exist above 423 K, ZnO was formed first and a large cluster was produced while incorporating ZnO particles.

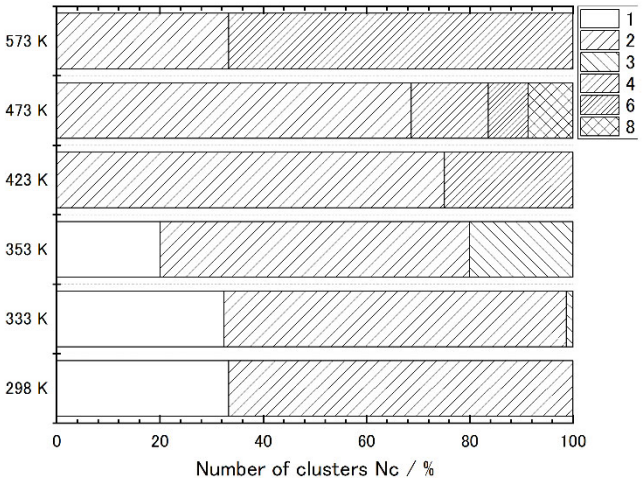

Fig. 3. Temperature dependence of the normalized cluster size distribution at 0.2 mol/kg-water of zinc oxide concentrations. Empty box: zinc or oxygen ions. Right coarse hatched box: 2 atoms. Left coarse hatched box: 3 members, Right hatched box: 4 members. Right fine hatched box: 6 members. Double hatched box: 8 members.

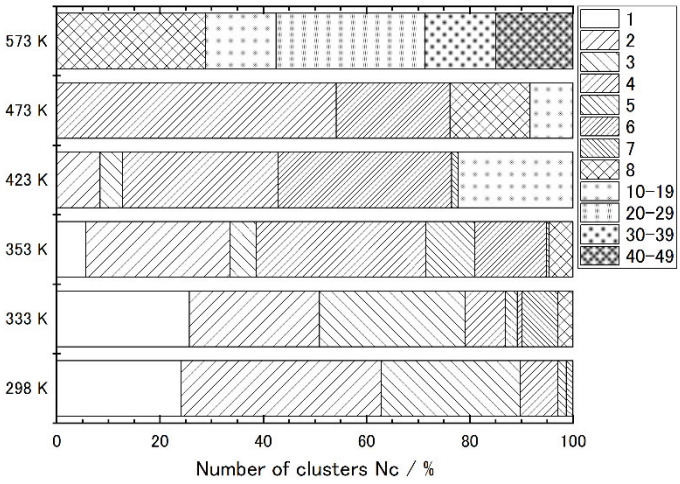

Fig. 4. Temperature dependence of the normalized cluster size distribution at 1.6 mol/kg-water of zinc oxide concentrations. Empty box: zinc or oxygen ions. Right coarse hatched box: 2 atoms. Left coarse hatched box: 3 members, Right hatched box: 4 members. Right fine hatched box: 6 members. Double hatched box: 8 members.

Figure 4 shows temperature dependence of cluster size distribution normalized total number of clusters at 1.6 mol/kg-water. At temperature up to 353 K, an odd number of clusters found. As mentioned above, the presence of odd membered clusters suggests ions participate nucleus growing mechanism, because the diffusion coefficient of clusters was greater than that of ions due to the solvation of water molecules. The nucleation behavior at temperature above 423 K shows 2, 4, 6, or 8- member or more of clusters. This behavior is similar mechanism of the case of 0.2 mol/kg-water in high temperature condition, however, larger clusters were produced due to higher zinc oxide concentration and it will increase a collision probability between growing nuclei.

2.3. Effect of Zinc Oxide Concentration

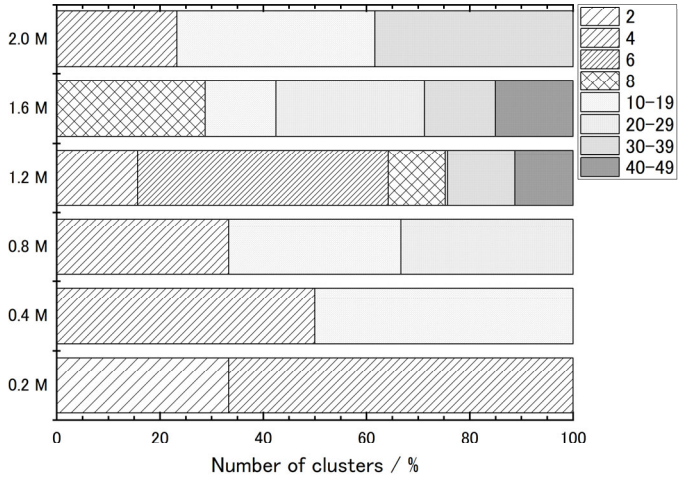

Fig. 5. Normalized cluster size distribution of zinc oxide at 573 K on the dependence of zinc oxide concentrations. Zinc oxide concentrations were set on 0.2 mol/kg-water to 2.0 mol/kg-water. Coarse hatched box: 2 atoms. Hatched box: 4 members. Fine hatched box: 6 members. Double hatched box: 8 members. Light gray box: 10 to 19 members, Gray box: 20 to 29 members, Heavy gray box: 30 to 39. Black box: 40 to 49 members.

Figure 5 shows normalized cluster size distribution against zinc oxide concentration at temperatures 573 K. Zinc oxide concentrations were selected from 0.2 to 2.0 mol/kg-water. The presence of the even numbered cluster suggests rapid ZnO formation and the nucleus growing by ZnO particle participation. A large-size cluster up to 10 members were found and the fraction of large-size clusters was increased with zinc oxide concentration. The large size clusters may be produced by incorporating 4-membered cluster, after the aggregation of ZnO monomer at

initial stage of nucleation due to higher number density of ZnO monomer. At 1.6 mol/kg-water of zinc oxide concentration, 8 membered cluster and large-size cluster were found. It is responsible for an exhaustion of ions, 2-, and 4-membered cluster promotes an aggregation between large-size clusters.

4. Conclusion

Homogeneous nucleation mechanism of zinc oxide was investigated by means of molecular dynamics simulations at 298 K to 573 K, and 0.2 to 1.6 mol/kg-water. Influences of system size, temperature, and zinc oxide concentrations on cluster structure and size were discussed by means of radial distribution function and the simple Stillinger cluster analysis. The effect of system size on the nucleation behavior shows identical radial distribution function was obtained for the simulations at 573 K, and higher zinc oxide concentrations.

In the case of lower temperature conditions, zinc and oxygen ions were found due to hydration shell of water molecule, therefore, growth mechanism of cluster was occurred by incorporating zinc or oxygen ions. On the contrary, in case of higher temperature conditions, zinc and oxygen ions were rapidly aggregated to form ZnO particle, following a particle growth by incorporating ZnO particle. This difference may be responsible for diffusion coefficient between ions and ZnO particles. Cluster size distribution on the dependence of zinc oxide concentration suggests that the large size cluster was formed with increasing zinc oxide concentration while incorporating 4-membered ZnO cluster. However, at the latter stage of nucleation, the exhaustion of the small size cluster promotes an aggregation between large-size clusters.

Acknowledgement

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