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Theoretical study on the surfactants in the mesoporous materials synthesis process

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【Introduction】

In 1992, ionic surfactant was first reported to be used in the synthesis of inorganic mesoporous materials as template molecules. Since then, surfactant-template synthesis has gathered a considerable attention because this method has been used to form a variety of mesoporous materials, which could find applications in catalysis, membrane and separation technology, and molecular engineering.

Ionic surfactants self-assemble into micelles, and organize inorganic materials into a variety of mesoporous forms through the mediation of electrostatic, hydrogen-bonding, covalent and van der Waals interactions. This process is composed of both physical and chemical interactions, which is not possible to be simulated using traditional classic molecular dynamics (MD) simulation, and also because of its large scale, the systems can not be studied using ab initio quantum chemical methods. In this study, MD program “New-Ryudo”, and macroscopic simulators, which are developed in our la boratory, were successfully used to simulate the formation of Cetylmetylammonium Bromide (CTAB) cylindrical micelle and organization of TiO_2 on the micelle surface.

【Method】

“New-Ryudo” program, a molecular dynamics simulator developed in our laboratory, was used to simulate the formation of cylindrical micelle structure of CTAB molecules and organization of TiO_2 on the micelle surface. We introduced a new function to stochastically deal with chemical reaction within the scheme of classical molecular dynamics. Equilibration and MD simulation of systems were performed using CVFF force field. We also developed macroscopic simulators based on coarse grained Monte Carlo and MD methods, and applied them to the study on synthesis process of mesoporous materials.

【Results and discussion】

Under the experimental conditions, our “New-Ryudo” program was successfully performed on the study of organization of TiO_2 on the CTAB micelle surface. Initial structure composed by micelle surface of 9 CTAB molecules, 64 water molecules, 8 TiO^{2+} and 8 SO_4^{2-} ions to represent ionic state $TiSO_4$ in water solvent. After 12.5 ps MD simulation, the system was equilibrated, as shown in Fig. 1A. The next 2.5 ps simulation was performed to simulate the reaction process in forming TiO_2 solid phase. The final structure is shown in Fig. 1B. Water molecules around TiO^{2+} and SO_4^{2-} were deprotonated into H^+ and OH^-, we defined the O atom of water molecules, SO_4^{2-} and of $Ti(OH)_2$ as different colors. It is observed that there was formation of bonds between TiO^{2+} and OH^- ions. The simulation is in good agreement with the reaction mechanism obtained from experiments, indicating that our program is certified to simulate chemical reaction in large scale systems. Furthermore, in order to simulate the real scale systems for mesoporous materials synthesis, we performed calculations using macroscopic simulators. In the calculations, a group of atoms was represented as one particle, which constructs a real scale of model system. The calculation results of these investigations will be presented at the conference.

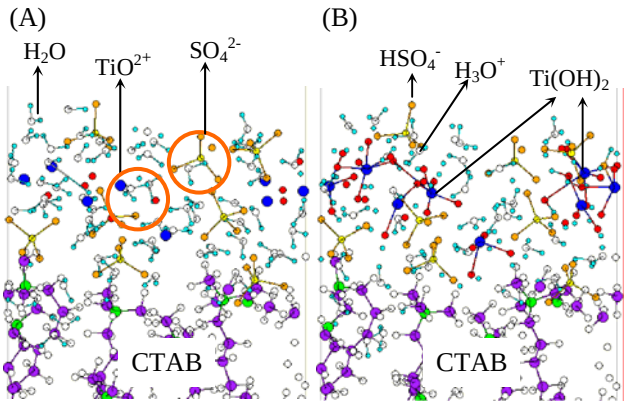

Fig. 1 MD simulation of TiO_2 organization on CTAB micelle surface. (A) equilibrated system after 12.5 ps MD simulation. (B) final structure after 15.0 ps MD reaction simulation.