

Hydrolysis of Cellulose in Supercritical Water: Quantum Simulation

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Abstract – Among several fabrication processes of cellulose nanofibers (CNF), we focus on the hydrolysis of cellulose in supercritical water. In order to analyse the detailed chemical reaction, a series of quantum molecular dynamics simulation were performed based on the density functional theory coupled with the tight binding model (DFTB). After locating the vapor-liquid critical point of the DFTB water system, we explored the hydrolysis reaction of cellulose using a simplified system consisting of a cellobiose and 100 water molecules. We observed cleavage of a β -glycosidic bond at a high temperature (1000 K). The charge analysis suggests that the oxygen atom at the cleavage site gives an electron to a water molecule approaching with sufficiently large velocity.

Keywords: cellulose nanofiber, hydrolysis, supercritical water, MD simulation, DFTB

1. Introduction

Cellulose nanofiber (CNF) is fairly new nanomaterial made from various type of cellulose. They have recently attracted much attention in many fields [1], such as electronic device, medical material, and food additives. One of the significant features is its high aspect ratio; a typical width is 4-100 nm while the length is often more than 5 μm . It is so light and tough that many applications as structural material are proposed, such as automobile bodies. Cellulose is a renewable resource since it is mainly made from wood pulp.

To fabricate CNF from conventional cellulose resources (e.g., wood pulp and grass), some treatment is required to smash macromolecules of cellulose. Currently two methods are major: (i) Chemical treatment [2], which uses hydrolysis reaction with strong acid or catalysts. This is not environment-friendly nor cost-effective. (ii) Mechanical approach [3], in which the pulp is mechanically smashed or ground under to high shear force. It generally gives large dispersion of fiber size. Less popular treatment is the hydrolysis using supercritical water [4], which is environment-friendly and has a possibility of precise size control, but its detailed mechanism is not fully understood.

In this study, we focus on the cellulose hydrolysis in supercritical water. To analyse the chemical reaction in atomic scale, we executed a series of molecular dynamics (MD) simulations with quantum effects taken into account as the density functional tight binding (DFTB) model.

2. Methods

To investigate the chemical reaction (hydrolysis), we have utilized the DFTB+ software [5] to perform MD simulations. A self-consistent charge (SCC) DFTB calculations are adopted with the third order correction [6]. The 3ob-3-1 parameter set is used [7], which is known to be well applicable to a wide range of organic and bio molecules. Use of appropriate hydrogen bond correction is relevant to our investigation, and we adopted a damping method for modification of short range potential energy U [6], as

$$U = \frac{1}{2} \sum \Delta q_a \Delta q_b \gamma_{ab} \quad (1)$$

$$\gamma_{ab} = \frac{1}{r_{ab}} - S(r_{ab}, U_a, U_b) \times \exp \left[- \left(\frac{U_a + U_b}{2} \right)^\zeta r_{ab}^2 \right] \quad (2)$$

where r_{ab} is the distance between atom a and b , Δq_i is the electric charge on atom i , U_i is the Hubbard parameter of atom i , and S is a short-ranged damping function [6]. The time step for the MD calculation is 0.25 fs.

3. Evaluation of Critical Point

Before starting the main simulations, we have to determine the critical point of the model water. Using 100 water molecules confined in a cubic simulation cell of various size with periodic boundary conditions, we performed the DFTB MD simulations under constant temperature condition (Fig. 1); three temperature conditions were chosen, 400, 650 and 800 K.

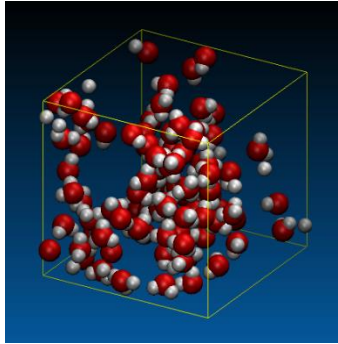


Fig. 1: Example of snapshot for pure water system with density 0.513 g/cm^3 ($18 \times 18 \times 18 \text{ \AA}^3$).

After equilibrating the system, the mean pressure was evaluated. The obtained p - V curve is shown in Fig. 2, which suggests that the liquid-vapor critical point of this model water exists around $(T_c, V_c) = (650 \text{ K}, 80 \text{ \AA}^3)$; 80 \AA^3 per molecule corresponds to the density $\rho_c \cong 0.374 \text{ g/cm}^3$. A reported experimental value for water is $(647 \text{ K}, 0.322 \text{ g/cm}^3, 22.1 \text{ MPa})$ [8], and the agreement is reasonable.

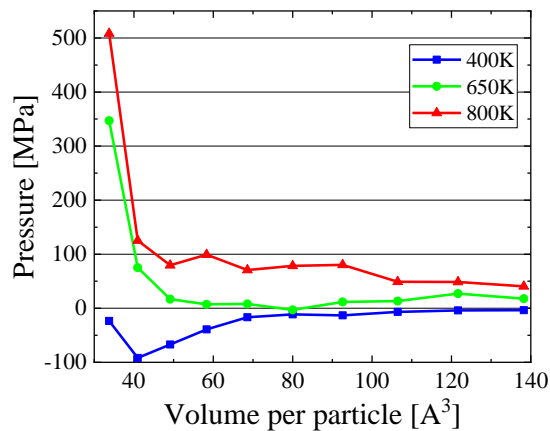


Fig. 2: p - V relation for the pure water system.

To look at the fluid structure near the critical point, the oxygen-oxygen radial distribution function is calculated at $V = 80 \text{ \AA}^3$. Based on the results shown in Fig. 3, clustering is suggested at 400 K, while uniform gas phase is realized at 800 K. Thus the state in between (650 K) is close to the critical point. Based on these results, we performed the main simulation of hydrolysis at $T \geq 650 \text{ K}$.

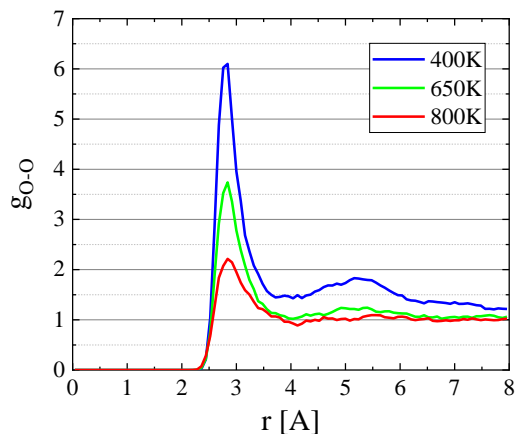


Fig. 3: O-O radial distribution function of fluid water with $V = 80 \text{ \AA}^3$ per molecule.

4. Hydrolysis of Cellobiose

We performed DFTB-MD simulations for the hydrolysis of cellulose in water at supercritical states. To reduce the computational resource, a minimum unit of cellulose, i.e., a cellobiose molecule, was targeted, which is surrounded by 100 water molecules, as shown in Fig. 4. The size of the simulation cell is $23.107 \times 23.107 \times 9.58 \text{ \AA}^3$ with periodic boundary conditions. 50 water molecules are arranged at each side of the cellobiose. Constant temperature MD simulations were carried out at 650, 800 and 1000 K.

At low temperatures of 650 and 800 K, no cleavage of β -glycosidic bond was observed during our observation (50,000 steps = 12.5 ps for each temperature condition with several different initial configurations). At 1000 K, the bond breaks after 3000 steps, as shown in Fig. 5.

The bond cleavage seems a rare event, and we need many samplings to investigate the statistical properties of the cleavage process. As a preliminary analysis, we have evaluated the electric change (Mulliken charge) on the oxygen atom in the bond. As shown in Fig. 5, the electron around the reaction site is lost before the breakage, similar to the hydrolysis in the strong acid [9].

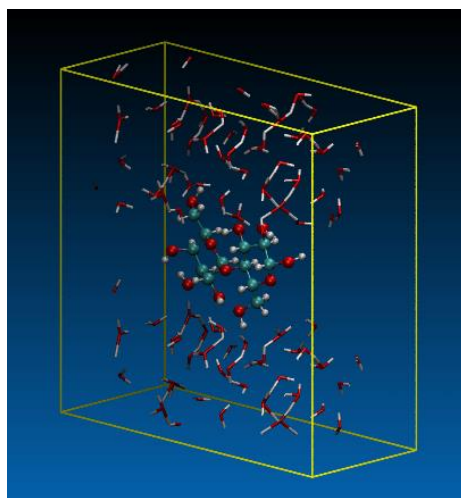


Fig. 4: Snapshot of a cellobiose surrounded by 100 water molecules.

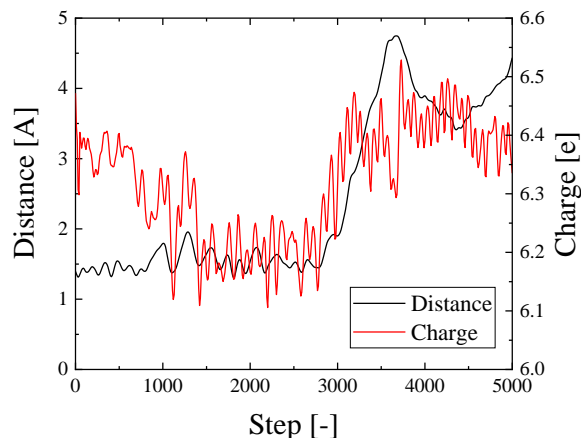


Fig. 5: Change of β -glycosidic bond length and electric charge on the bonding oxygen atom.

5. Conclusion

We examined a model cellulose in fluid water with quantum molecular dynamics simulation and found the of hydrolysis in supercritical conditions. However, the β -glycosidic bond is so strong that it requires large kinetic energy (high temperature, such as 1000 K) of water molecules. The bond cleavage is initiated by the loss of electron on the bonding oxygen atom.

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