Theoretical Study of Sodium-Water Surface Reaction Mechanism*

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Abstract
Computational study of the sodium-water reaction at the gas (water) - liquid (sodium) interface has been carried out using the \textit{ab initio} (first-principle) method. A possible reaction channel has been identified for the stepwise OH bond dissociations of a single water molecule. The energetics including the binding energy of a water molecule on the sodium surface, the activation energies of the bond cleavages, and the reaction energies, have been evaluated, and the rate constants of the first and second OH bond-breakings have been compared. It was found that the estimated rate constant of the former was much larger than the latter. The results are the basis for constructing the chemical reaction model used in a multi-dimensional sodium-water reaction code, SERAPHIM, being developed by Japan Atomic Energy Agency (JAEA) toward the safety assessment of the steam generator (SG) in a sodium-cooled fast reactor (SFR).

\textbf{Key words}: Fast Reactor, Sodium Water Reaction, Reaction Path, Rate Constant

1. Introduction

In a sodium-cooled fast reactor (SFR), liquid sodium is used as heat transfer fluid to carry the energy from the reactor core to the steam generation (SG) system for power generation. If the heat transfer tube in the SG is failed, high pressurized water vapor blows into the liquid sodium and the sodium-water reaction (SWR) takes place. The extremely high-temperature reaction jet formed by the SWR, causes damage to the surface of the neighboring heat transfer tubes by thermal and chemical effects. Therefore, it is important to clearly understand the SWR for safety assessment of SG.

In the past, a lot of experiments of the SWR were performed in the former Japan Atomic Energy Agency. However, the SWR is generally complex, and the experimental measurement technologies have not been matured enough to unroll the reaction mechanism in detail. With regard to the chemical effect, it was inferred that reaction products were sodium hydroxide (NaOH), sodium oxide (Na₂O), sodium hydride (NaH) and so on from the X-ray diffraction (XRD) analysis of the residues in a dump tank after the experiments (1). However, it was difficult to even identify the major reaction products and understand the reaction mechanism during the SWR. To study the reaction mechanism is, therefore, integral part of clarification on the SWR.

Currently, the Japan Atomic Energy Agency has been developing a multi-dimensional sodium-water reaction code, SERAPHIM (Sodium-watEr Reaction Analysis PHysics of Interdisciplinary Multi-phase flow) for the analytical evaluation of this reaction (2). In
SERAPHIM code, the surface and gas-phase reactions are considered, which are illustrated in Figure 1. The water vapor encounters the liquid sodium, and the reaction occurs at their interface (surface reaction). Subsequently, the chemical reaction heat vaporizes the liquid sodium, causing the gas-phase reaction. To support the chemical reaction model, the knowledge on the microscopic phenomena such as the reaction mechanism, energetics and so on is indispensable.

Regarding the gas-phase reaction, some works have been reported from both experimental and theoretical sides.

Buck et al. (3) (4) performed the crossed molecular beam experiment to investigate the reaction of sodium atoms with water clusters. The water cluster beam was generated by the supersonic expansion and crossed an atmosphere of sodium vapor. As a result of the collisions, the hydration complexes containing a single sodium atom, Na (H₂O)_n, were produced at low sodium vapor pressure, while the Na (NaOH)_n type aggregates were observed when the sodium vapor pressure was raised. Their result strongly suggests that high density of sodium and the multiple collisions are essential even for the gas-phase reaction.

Takata et al. (2) theoretically investigated the following reactions, using the ab initio Molecular Orbital method.

\[
\begin{align*}
\text{Na} + \text{H}_2\text{O} & \rightarrow \text{NaOH} + \frac{1}{2}\text{H}_2 & (1) \\
2\text{Na} + \text{H}_2\text{O} & \rightarrow \text{Na}_2\text{O} + \text{H}_2 & (2)
\end{align*}
\]

They treated the reactions among one or two sodium atoms and a single water molecule, and found that both reactions were endothermic, which indicates that those reactions hardly occur at an early stage of the SWR. Their results also showed that the direct generation of Na₂O is unlikely to occur in the gas-phase, though this species has been suspected to accelerate the corrosive and erosive effects by the SWR.

On the other hand, the study of the surface reaction is quite scarce, due to the experimental difficulty of the real-time observation of the surface reaction which is extremely-rapid. Thus, in spite of the observation of NaOH in the residues, even the reaction path for its generation has remained unknown to date.

![Cross section of heat transfer tubes](image)

**Fig. 1** Reactions considered in SERAPHIM code
In this work, we have studied the surface reaction in the SWR by using the ab initio method. The successive OH cleavages of a water molecule on the liquid sodium surface have been focused. The possible reaction path and the related energies including the barrier heights are reported. The relative rates of the first and second OH dissociation are also discussed.

2. Methods

2.1 Simulation of liquid sodium

Liquid sodium was simulated by ab initio molecular dynamics (MD) method using the VASP (5). The density functional theory (DFT) was employed on a plain-waves basis, whose energy cutoff was set to 300 eV. The employed system is illustrated in Figure 2, and the conditions of the simulation are summarized in Table 1.

The NVT ensemble was considered. A total of 128 sodium atoms were included in a super cell of the size 1.84 nm × 1.84 nm × 1.84 nm (4×4×4), and the periodic boundary condition was applied to all directions. A trajectory calculation was carried out for 2000 fs with time step of 1 fs, starting from the BCC crystal structure. The temperature was kept at 1000 K, which is sufficiently higher than the melting point (371 K) and below the boiling point (1153 K) of the sodium.

![Fig. 2 Schematic illustration of the studied system](image)

<table>
<thead>
<tr>
<th>Table 1 Conditions of MD simulation (VASP)</th>
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<tbody>
<tr>
<td>Number of sodium atoms</td>
</tr>
<tr>
<td>Initial structure</td>
</tr>
<tr>
<td>Lattice constant [nm]</td>
</tr>
<tr>
<td>Number of unit cell</td>
</tr>
<tr>
<td>Algorithm</td>
</tr>
<tr>
<td>Scaling</td>
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<tr>
<td>Ensemble</td>
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<tr>
<td>Temperature [K]</td>
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<tr>
<td>Time step [fs]</td>
</tr>
<tr>
<td>Total step [fs]</td>
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<tr>
<td>Cut off [eV]</td>
</tr>
<tr>
<td>Potential</td>
</tr>
</tbody>
</table>
Pair correlation function $g(r)$, which is the probability of finding a particle at the distance $r$ from another particle, was calculated. The structures of the sodium at time $= 0$ and 2000 fs are shown in Figures 3 and 4, respectively, together with the corresponding $g(r)$ for each structure.

In Fig. 3(b), four sharp peaks are observed at 0.40, 0.46, 0.65 and 0.77 nm, each of which represents the distance between a sodium atom and the first to the fourth neighbors in the crystal.

On the other hand, the second and higher peaks almost vanish and only two can be identified at around 0.38 and ~0.70 nm, respectively, in Fig. 4(c), in good agreement with the $g(r)$ of molten sodium reported by Silverstrelli (6). Thus, we judged that the final structure of the trajectory at 2000 fs, can be regarded as a liquid state.

The geometry of a potential energy minimum was calculated by optimizing the liquid to 0K. The obtained structure and its $g(r)$ are also shown in Fig. 4(b) and (c). The $g(r)$ of the minimum is appreciably structured compared to that of the liquid with a strong peak of 0.38 nm.

![Initial structure of crystal sodium](image1)

![Pair correlation function of crystal sodium](image2)

Fig. 3 Crystal sodium (0 K, 0 fs)
(a) Structure of molten sodium

(b) Structure of optimized molten sodium

(c) Pair correlation function of molten sodium structure

Fig. 4 Molten sodium (1000 K, 2000 fs)
2.2 Calculations of reaction paths and energetics

It is practically impossible to study the SWR by the dynamics simulations, because it is too demanding to carry out even a single trajectory computation until the reaction occurs. However, the potential energy surface should provide us with the valuable information for the reaction path, which leads us to the following calculations.

Figure 5 shows schematic potential energy diagram for the reaction formulae (3) and (4) in the SWR.

\[
\text{Na}^{128+} + \text{H}_2\text{O} \rightarrow (\text{Na}^{127})(\text{NaOH})(\text{H}) \quad (3)
\]

\[
(\text{Na}^{127})(\text{NaOH})(\text{H}) \rightarrow *{(\text{Na}^{128})(\text{O})(\text{H})(\text{H})} \quad (4)
\]

The total potential energy of the isolated state was computed by summing the energies of the sodium in Fig. 4 (b) and a free water molecule.

To examine the reactant state of the reaction formula (3), R1, the super cell was expanded by 2.31 nm in a single direction, and a water molecule was included in the system from above the surface of sodium with the potential-minimum configuration shown in Fig. 2. The geometry-optimization of the sodium-water system was conducted, whose final result is illustrated in Figure 6. In this structure, one OH is directed to the sodium, while the other to the vacuum. Both OH bond lengths are about 0.10 nm, being very close to those estimated by Bacelo, 0.097-0.099 nm (7).

To locate the transition state, TS1, and the product state, P1, a series of the potential energies was calculated by fixing the O-H bond in the sodium side at several lengths from 0.10 to 0.40 nm, while optimizing all other geometric parameters in R1. We employed the Advance/PHASE (8) for the optimization, since the rotation of the water could not be taken into account with the VASP. The theoretical level was DFT as well as the case of the
calculations by VASP, but the energy cutoff of the plane waves was 340 eV in the Advance/PHASE computations. The geometry at the maximum of the potential energy plots against the OH bond lengths was regarded as a transition state, while the structure of which fixed OH was 0.40 nm, was used as a product state, because the separated H was already embedded in the sodium at this distance.

As for the second OH dissociation, namely, the reaction formula (4), the reactant was the same as the product state of the preceding reaction formula (3), P1. It is worth noting that the remaining OH in P1 is directed towards the sodium because of the structural optimization during the first reaction. Starting from P1 (R2), the same procedure was applied to locate the transition state, TS2, and the product state, P2, as that used for the reaction formula (3).

Fig. 6 Initial structure of water dissociation on liquid sodium surface for reaction formula (3)

3. Results and Discussion

3.1 Reaction paths

3.1.1 $\text{H}_2\text{O}$ dissociation, reaction formula (3)

The calculated potential energies of the sodium-water system relative to the isolated state are plotted against the OH bond length in Figure 7. The result obtained by the VASP is also discussed in detail later.

The intercept of the vertical axis implies the interaction energy between a single water molecule and the sodium surface: the addition of water to the sodium is exothermic by 43 kJ/mol. One can see the transition state at 0.14 nm, whose energy is ~ +5 kJ/mol. The average kinetic energy of the water molecule at the temperature $T$ can be evaluated by the following equation:

$$E_{\text{kin}} = \frac{1}{2}mv^2 = \frac{3}{2}RT \quad (5)$$

Here, $m$ and $\bar{v}$ are the molar mass and the root-mean-square velocity of the water, respectively, and $R$ is the gas constant. By substituting $T$ by 642 K, a typical temperature of water vapor in the evaporator of the SG of a SFR (10), we get the kinetic energy of ~8 kJ/mol, which is higher than the barrier. This result indicates that there exists an energetically possible channel of the $\text{H}_2\text{O}$ dissociation on the liquid sodium surface under the realistic condition caused by the failure of the steam generator.

The overall reaction energy is calculated to be 136 kJ/mol. The experimental reaction enthalpy is 155 kJ/mol at 1000 K (10). Though the calculated value cannot be compared
straightforwardly with the experimental one, the agreement is reasonably good. The
exothermic surface reaction points out the importance of the collective effect of sodium
atoms: the NaOH generation by the 1:1 reaction between a sodium atom and a water
molecule is known to be endothermic in the gas-phase.

The potential energy profile calculated by using the VASP is generally similar to that by
the Advance/PHASE, though the deviation is appreciable at 0.40 nm. Reminding that the
rotation of the water was not allowed in the calculation by the VASP, it can be said that the
reorientation of the remaining OH is important for the precise estimate of the product state,
P1, namely, the initial state of the second reaction. Thus, we used only the Advance/PHASE
for the reaction formula (4).

![Potential energy plots of reaction formula (3) against the OH bond lengths](image)

**3.1.2 OH dissociation, reaction formula (4)**

The energies of the transition state, TS2 and the product state, P2, relative to the
reactant state, R2 (P1) were +104 kJ/mol and -10 kJ/mol, respectively. The latter is
comparable with the experimental value, -13 kJ/mol at 1000K \(^{(10)}\). Figure 8 shows the
energy diagram of the reaction formulae (3) and (4). Though the activation energy of the
second OH cleavage is high, the level of the TS2 is below that of the isolated state: the
barrier can be overcome by the huge reaction energy of the reaction formula (3). The total
heat for the reaction formulae (3) and (4) is 146 kJ/mol.

![Reaction paths on H₂O and OH dissociation on liquid sodium surface](image)
3.1.3 Overall reaction

It is known from the experiment \(^{(11)}\) that Na\(_2\)O is generated when the NaOH is transported to sodium rich environments. Thus, it may be natural to regard the reaction formula (4) as the Na\(_2\)O generation preceded by the initial \(\text{H}_2\text{O}\) dissociation on the sodium surface, namely, the NaOH generation. Then the overall reaction for formulae (3) and (4) can be rewritten as follows.

\[ \text{Na}^+ \text{H}_2\text{O} \rightarrow \text{NaOH} + \frac{1}{2} \text{H}_2 \quad (6) \]

and

\[ \text{Na}^+ \text{NaOH} \rightarrow \text{Na}_2\text{O} + \frac{1}{2} \text{H}_2 \quad (7) \]

3.2 Rate constants

In general, the determination of the rate constant for the surface reaction is a difficult task and a controversial issue from both experimental and theoretical viewpoints. However, since little is known about the rate constant of the SWR, even the estimation of its order by the simple treatment is worth trying.

We estimated the rate constant for the reaction formula (3) from R1 to P1 via TS1, and for the reaction formula (4) from R2 to P2 through TS2, respectively, according to the Arrhenius’s theory, where the rate constant of a reaction, \(k\), is given by

\[ k = A \exp \left( \frac{-\Delta E}{RT} \right) \quad (8) \]

Here \(A\), \(R\), \(\Delta E\) and \(T\) are the frequency factor, the gas constant, the activation energy, and the temperature. In the present case, the activation energies are 48 kJ/mol and 104 kJ/mol for the reaction formulae (3) and (4), respectively, as given in Fig. 8.

The approximate harmonic frequencies of the stretching vibration of the dissociating \(\text{OH}\) at the reactant states, R1 and R2, were used as the frequency factor \(A\) for each reaction. Briefly, the following equation was used.

\[ A = \frac{1}{2\pi} \sqrt{\frac{\gamma}{\mu}} \quad (9) \]

\(\gamma\) is the force constant (spring constant) of the vibrational mode, which is the second-derivative (curvature) of the potential energy function with respect to the OH stretch coordinate at the potential bottom, while \(\mu\) is the OH reduced mass. \(\gamma\) was calculated by the parabola fitting of the potential energy curve drawn against the OH bond length at R1 and R2, respectively. The calculated values of the \(A\) are \(8.6 \times 10^{13}\) s\(^{-1}\) and \(1.0 \times 10^{14}\) s\(^{-1}\), for the reaction formulae (3) and (4), respectively.

Figure 9 shows the temperature dependence of the rate constants of the reaction formulae (3) and (4). The rate constant of the former is much larger than that of the latter: there is 3 or 4 digit-difference between them for all temperature examined.

Up to date, there is limited knowledge on the rate constant of NaOH and Na\(_2\)O generation. Here, we referred to the surface reaction model of sodium-concrete reaction analysis code CONTAIN \(^{(12)}\) for NaOH generation, whose frequency factor \(A\) and activation energy \(\Delta E\) in the Equation (8) have been reported to be \(9.9 \times 10^{6}\) s\(^{-1}\) and 7.5 kJ/mol, respectively.

As for Na\(_2\)O generation, Kong et al investigated the kinetics of NaOH dissociation in liquid sodium by injecting NaOH in sodium loop \(^{(13)}\). Here, we referred to the Kong’s correlation equation for Na\(_2\)O generation, whose frequency factor \(A\) and activation energy
∆E in the Eq. (8) have been reported to be 2.1×10⁴ s⁻¹ and 51.5 kJ/mol, respectively.

Table 2 shows the temperature dependence of the rate constants of NaOH and Na₂O generation based on the experimental data.

The rate constant of NaOH generation in the surface reaction model of CONTAIN code is around 10⁶ s⁻¹ at 773 K. Kong found that NaOH dissociation in the liquid sodium is about 10⁷ s⁻¹ at 773 K. There is 5 or 6 digit-difference between rate constant of NaOH generation and that of Na₂O. It was found that the calculated results in Fig. 9 qualitatively correspond to these experimental results.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Rate constant of NaOH generation [s⁻¹]</th>
<th>Rate constant of Na₂O generation [s⁻¹]</th>
<th>Difference [s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>773 (500 deg C)</td>
<td>3.1×10⁶</td>
<td>7.1</td>
<td>2.3×10⁻⁶</td>
</tr>
<tr>
<td>1073 (800 deg C)</td>
<td>4.3×10⁶</td>
<td>6.7×10¹</td>
<td>1.6×10⁻⁵</td>
</tr>
</tbody>
</table>

4. Conclusions

In this study, we investigated the surface reaction mechanism in the SWR by ab initio method. The potential energy profiles of the dissociations of H₂O and OH were obtained. The estimated rate constant of the former was much larger than the latter.

Combined with the experimental knowledge, the present results suggest the overall reactions can be written by the formulae (6) and (7). The calculated rate constants agree qualitatively well with the available experimental data for the NaOH and Na₂O generations in the sodium-rich environment. It follows that the NaOH is produced at the initial stage and the slow Na₂O generation proceeds later during the SWR. Though the more elaborated work is necessary for the deeper understanding of the SWR and the precise estimate of the reaction rate, these results can be the basis for the surface reaction model in developing SERAPHIM code.
Nomenclature

g(r) : pair correlation function, [-]

$E_{k,0}$ : average kinetic energy of the water, [kJ/mol]

m : molar mass of water, [kg/mol]

$\bar{v}$ : root-mean-square velocity of the water, [m$^2$/s$^2$]

R : gas constant, [kJ/mol$\cdot$K]

T : temperature, [K]

K : rate constant, [s$^{-1}$]

A : frequency factor, [s$^{-1}$]

$\Delta E$ : activation energy, [kJ/mol]

$\gamma$ : force constant, [m$^{-2}$kJ/mol]

$\mu$ : OH reduced mass, [kg/mol]

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