



Full Length Article

Investigation of ethanol oxidation over aluminum nanoparticle using ReaxFF molecular dynamics simulation

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ABSTRACT

Aluminum nanoparticles are an effective and economical additive for producing energetic fuels. In the present study, the state of the art ReaxFF molecular dynamics (MD) simulation has been used to uncover the detailed mechanisms of ethanol oxidation over aluminum nanoparticles with different oxidation states. The MD results reveal the dynamics process of ethanol oxidation reactions at nanoscales. The presence of aluminum nanoparticles is found to reduce the initial temperature of ethanol oxidation to 324 K. It is also found that compared to ethanol, oxygen molecules are more easily adsorbed on aluminum surfaces. Moreover, different oxidation states of aluminum nanoparticles influence the initial ethanol reactions on the nanoparticles' surfaces. OH-abstraction is more commonly observed on pure aluminum nanoparticles while H-abstraction prevails on aluminum nanoparticles with oxide. The separated H atom from hydroxyl forms bonds with Al and O atom on aluminum nanoparticles surrounded by thin and thick oxide layers, respectively. Adsorptive dissociation of ethanol is hindered by the oxide layer surrounding the aluminum nanoparticle. Gas products like H₂O and CO resulting from ethanol oxidation on aluminum nanoparticles with the thick oxide layer are observed while almost all the C, H and O atoms in ethanol diffuse into the nanoparticles without or with the thin oxide layer. For ethanol dissociation, a higher temperature is required than adsorption. In addition, the rate of ethanol dissociation increases with rising reaction temperatures. The activation energy for ethanol adsorptive dissociation is found to be 4.58 kcal/mol on the aluminum nanoparticle with the thin oxide layer, which is consistent with results from much more expensive DFT calculations.

1. Introduction

Metals have high energy density and are effective energetic additives in fuels and propellants [1–3]. Nano-sized metal particles show decreased ignition delay and increased burning rates compared to micro-sized particles [4–8]. Aluminum nanoparticles, in particular, can be adopted as an energetic additive to enhance energy density and reduce the consumption of liquid fuels because of ready availability and low cost. Recently, considerable efforts have been made to study the effects of added aluminum nanoparticles on liquid fuel ignition and combustion characteristics. Allen et al. [9] studied the ignition properties of ethanol fuels with addition of 2%-wt aluminum nanoparticles in a shock tube experiment. The results showed a significant reduction of the ignition delay time as compared to pure ethanol fuels. Tyagi et al. [10] found that aluminum and alumina additives to diesel fuels

enhance ignition probability significantly. Gan et al. [11] found substantial enhancement in burning rates of ethanol due to the addition of 80 nm aluminum particles. A plausible explanation for this effect is the enhanced thermal conductivity due to nanoparticle additives [12]. However, this explanation cannot explain a contrary observation that adding aluminum nanoparticles did not influence the burning rate of JP-8 [13]. The above findings suggest that reactions between aluminum additives and the base fuel should be taken into consideration, as aluminum nanoparticles may function as catalysts. Aluminum nanoparticles are not known as a good catalyst, but its catalytic effect may improve because of high specific surface areas.

Understanding of ethanol oxidation over aluminum nanoparticles or aluminum oxide nanoparticles is limited. The size, oxidation state and morphology of the aluminum nanoparticles all affect the ethanol oxidation process. According to the DFT studies [14,15], the cleavage of

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the hydroxyl group of ethanol on Al_2O_3 (0 0 0 1) is the main reaction pathway for ethanol dissociation, and further decomposition of ethoxy has a much higher energy barrier. Results from Alexander [16] show that in the system of AlO and ethanol, the H-abstraction pathway leading to formation of AlOH and $\text{C}_2\text{H}_5\text{O}$ dominates. One problem with the quantum mechanics (QM) method is that the computational cost is prohibitively high so that QM simulations are still limited to small systems (~ 100 atoms) and small timescales (fs-ps).

All the above indicate the fundamental mechanisms of ethanol combustion with aluminum nanoparticle additives are still unclear, due to the complicated nature and a lack of effective research tools for atomic scale problems. An appealing alternative method is the reactive molecular dynamics (MD) using ReaxFF force field, which can reproduce DFT reaction energies and barriers with a significantly reduced computational cost and describe chemical reactions in a much wider range of scales than DFT [17,18]. The ReaxFF MD method has been applied to many systems, such as aluminum oxidation, hydrocarbon combustion and catalysis [19].

In this research, we use ReaxFF MD simulations to study the mechanisms of ethanol oxidation with aluminum nanoparticle additives with different oxidation states on ethanol oxidation, and the fundamental heterogeneous reaction mechanisms in general. The systems of the $\text{C}_2\text{H}_5\text{OH}/\text{O}_2$ mixture reacting over aluminum nanoparticles with different oxidation states are considered. Using ReaxFF MD, we are able to look into both the physical and chemical processes of ethanol oxidation over aluminum nanoparticles at the atomic scales. The insight gained fills an important knowledge gap and helps the preparation of aluminum nanoparticles for practical use. Reaction rates and activation energies of ethanol dissociation over the aluminum nanoparticles are determined from simulation results quantitatively.

2. Methodology

ReaxFF-based reactive molecular dynamics is a powerful tool for simulating heterogeneous reactions. ReaxFF is a general bond-order based force field, in which the connectivity of atoms is determined by bond orders calculated from interatomic distances that are updated at every MD step. The bond order between a pair of atoms can be obtained directly from interatomic distance. In calculating the bond orders, ReaxFF distinguished between contributions from sigma bonds, pi-bonds and double pi bonds. The force field is parameterized against quantum mechanics based training sets and able to describe the bond formation and breaking which cannot be achieved by other non-reactive force fields [20]. Compared to QM calculations, ReaxFF MD allows simulations of reaction for longer physical time and larger systems. The overall system energy expression is shown in Eq. (1).

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{val}} + E_{\text{tors}} + E_{\text{vdW}} + E_{\text{Coulomb}} \quad (1)$$

The total energy E_{system} includes connectivity dependent terms such as the bond energy (E_{bond}), overcoordination energy (E_{over}), undercoordination energy (E_{under}), lone-pair energy (E_{lp}), valence angle energy (E_{val}) and torsion angle energy (E_{tors}) [21]. The bond order (BO) between a pair of atoms can be obtained directly from interatomic distance. In calculating the bond orders, ReaxFF distinguished between contributions from sigma bonds (BO_{ij}^{σ}), pi-bonds (BO_{ij}^{π}) and double pi bonds ($BO_{ij}^{\pi\pi}$). Here we use E_{bond} as an example to illustrate how the bonded interaction is calculated:

$$E_{\text{bond}} = -D^{\sigma} e^{-BO_{ij}^{\sigma}} \cdot \exp[p_{\text{bel}}(1 - (BO_{ij}^{\sigma})^{p_{\text{be}2}})] - D_e^{\pi} \cdot BO_{ij}^{\pi} - D_e^{\pi\pi} BO_{ij}^{\pi\pi} \quad (2)$$

where the first part is the sigma bonds energy, the second part is the pi-bonds energy and the third part is the double pi bonds part. Furthermore, ReaxFF describes non-bonded interactions such as van der Waals and Coulomb interactions between all atoms, irrespective of connectivity [21]. Shielding terms have been used to avoid extremely short-range interactions. The ReaxFF also takes into account

polarization effects by using a geometry-dependent charge distribution derived from an electronegativity equalization method. Further information about the ReaxFF formalism is available in previous studies [22]. The Al/C/H/O ReaxFF force field we used in our study has been developed by Hong [24]. It has been successfully trained to high temperature reactions and applied to aluminum oxidation, aluminum carbon coating and other Al containing systems [23–25].

ReaxFF MD simulations are conducted using canonical ensemble (NVT) [26,27] to prepare Al nanoparticles with oxide and to study the $\text{C}_2\text{H}_5\text{OH}/\text{O}_2$ mixture reactions on Al nanoparticles. Simulations were performed on four different systems in a box size of equal measurements, which were $50 \times 50 \times 50 \text{ \AA}$. Periodic boundary conditions were implemented in all three directions. The ReaxFF MD simulations are carried out with the REAXC package in the LAMMPS platform [28]. Visual Molecular Dynamics (VMD) [29] and OVITO [30] are used to display simulation results and the system configurations.

3. Results and discussion

3.1. Aluminum nanoparticle preparation

An Al nanoparticle of a diameter 2.8 nm containing 856 atoms is firstly prepared. The selection of this diameter is based on the objective of investigating aluminum melting temperature, oxidation process and carbon coating process by ReaxFF molecular dynamics without excessive computational cost. The prepared aluminum nanoparticle is then placed in a simulation box that is measured $50 \times 50 \times 50 \text{ \AA}$.

Two NVT MD simulations with temperature of 298 K are performed to prepare aluminum nanoparticles with different oxide before investigating ethanol oxidation reactions. 300 and 600 oxygen molecules were distributed randomly around the aluminum nanoparticle in the simulation box. The initial system configurations are displayed in Fig. 1. The velocities and positions are updated by the Velocity-Verlet method. A time step of 0.2 fs for 2×10^6 iterations (up to 0.4 ns) was assigned because 0.2 fs describes the reactions of oxygen molecules on aluminum nanoparticles efficiently [25]. The changes in potential energy and oxygen consumption over time are illustrated in Fig. 1. After 0.3 ns, it is observed that the potential energy is stable and there is no more oxygen consumption, which means the oxidation process is equilibrated and the aluminum nanoparticle is inert. A single aluminum nanoparticle with oxide can be produced by removing oxygen molecules in environmental gas. The oxide layer thicknesses are 0.76 nm and 1.03 nm for the aluminum nanoparticles surrounded by 300 and 600 oxygen molecules, respectively. The oxide layer thickness in our simulation is consistent with previous studies [23]. Here, we denote the pure aluminum nanoparticle AP, the aluminum nanoparticle with 300 oxygen molecules APO300 and the aluminum nanoparticle with 600 oxygen molecules APO600. The nanoparticles that were produced in these simulations will be used in the later ethanol oxidation reactions.

3.2. Reaction of ethanol and oxygen mixture over aluminum nanoparticles

Allen et. al [9] have revealed that with addition of 2 wt% aluminum nanoparticles in ethanol fuel, a 32% reduction of ignition delay compared to pure ethanol fuel has been observed which could lead to enhancement in ignition probability. However, the experimental timescales (~ 10 ms) are beyond MD simulation timescales due to computational cost consideration [31,32]. In our simulations, 20 ethanol molecules and 60 oxygen molecules were added in the environment, which made it a stoichiometric mixture. NVT molecular dynamics simulations are employed to study $\text{C}_2\text{H}_5\text{OH}/\text{O}_2$ mixture reactions over aluminum nanoparticles with different oxidation states as shown in Fig. 2. Ethanol and oxygen molecules were initially given Gaussian velocity distribution at 298 K. The nanoparticles with different oxidation states were placed in the middle of three simulation boxes. The temperature is calculated by: $KE = \text{dim} \times NKT/2$

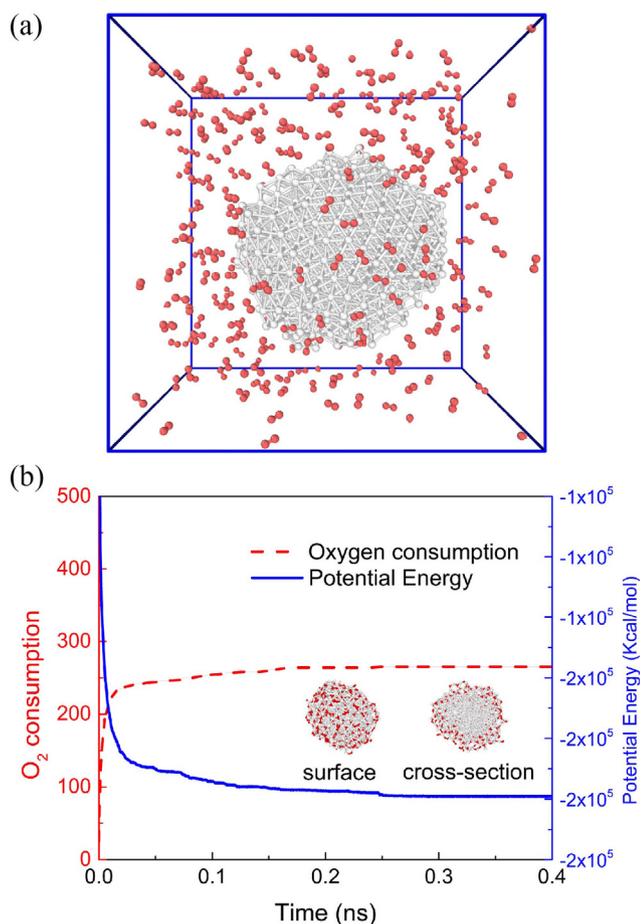


Fig. 1. (a) Initial configuration of a single aluminum nanoparticle surrounded by 300 oxygen molecules (b) Number of oxygen molecules consumed and potential energy decrease over time at 298 K.

where KE is total kinetic energy of the system, dim is the dimensionality of the simulation, N represents number of atoms in the group, k is the Boltzmann constant, and T is temperature. To compare the influence of nanoparticles, the C_2H_5OH/O_2 mixture without the presence of any aluminum nanoparticle was simulated first. For the C_2H_5OH/O_2 mixture system, the temperature was set at 298 K initially and was increased to 3000 K at a rate of 2 K/ps. The initial reaction was observed at 2610 K. The key reactions are illustrated in Fig. 3, in which ethanol molecules were decomposed into H_2O and CH_3CH radical first. Oxygen reacted with CH_3OH radical to form CH_3CHO (acetaldehyde) and O radicals. Then the O radical reacted with ethanol to produce CH_3CH_2O (ethoxy radical) and OH radical. The OH radicals also reacted with ethanol to form CH_3CH_2O (ethoxy radical) and H_2O .

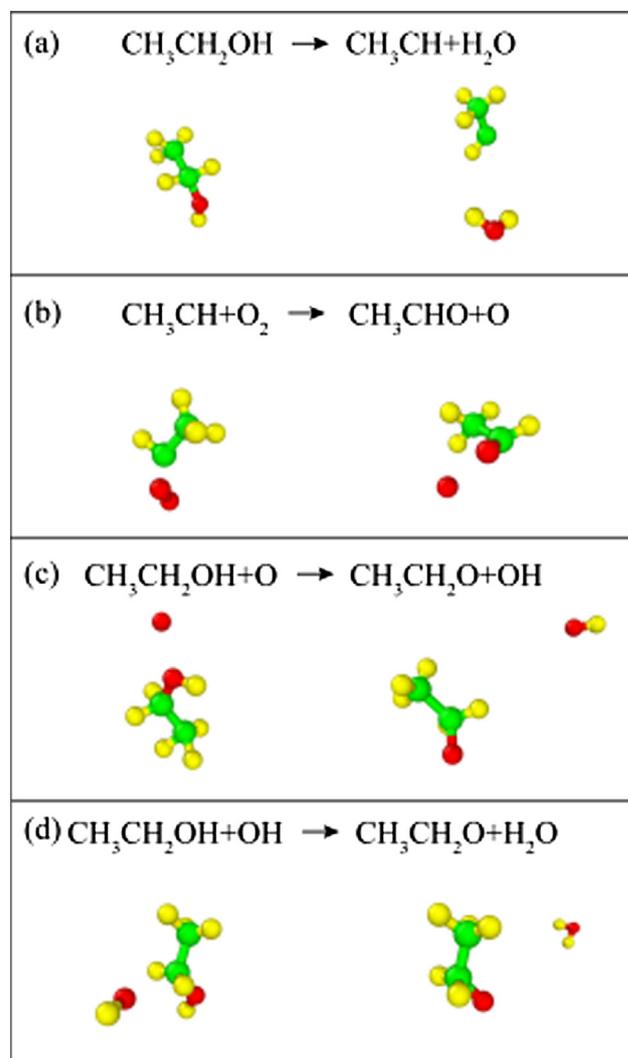


Fig. 3. Key reactions in ethanol oxidation at 3000 K.

For the aluminum nanoparticle systems, the temperature was initially set at 298 K and then increased to 500 K with the same heating rate. Fig. 4 illustrates evolutions of the temperature, relative potential energy and number of ethanol molecules for the three systems with different aluminum nanoparticles. In the pure aluminum nanoparticle system, the relative potential energy decrease and ethanol consumption rates are faster than the other two systems, which indicates a faster reaction rate in pure aluminum nanoparticle system. The ethanol oxidation reaction process for the C_2H_5OH/O_2 mixture over the aluminum nanoparticle can be summarized in two steps: ethanol and oxygen

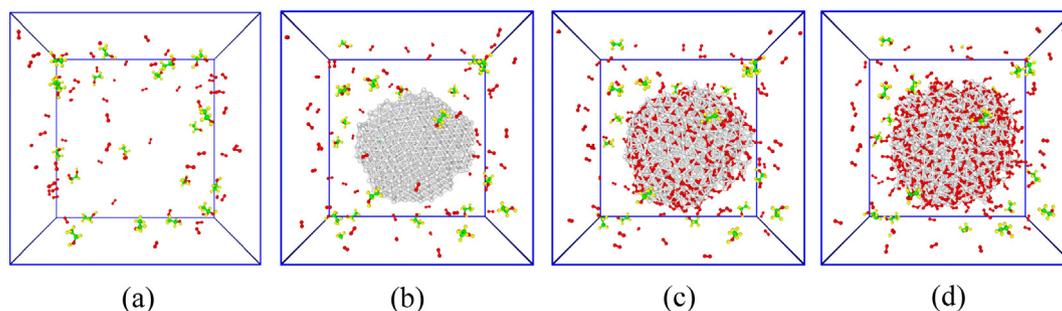


Fig. 2. Initial configurations of ethanol oxidation reaction systems (a) C_2H_5OH/O_2 mixture (b) AP surrounded by C_2H_5OH/O_2 mixture (c) APO300 surrounded by C_2H_5OH/O_2 mixture (d) APO600 surrounded by C_2H_5OH/O_2 mixture (white = aluminum, red = oxygen green = carbon, yellow = hydrogen). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

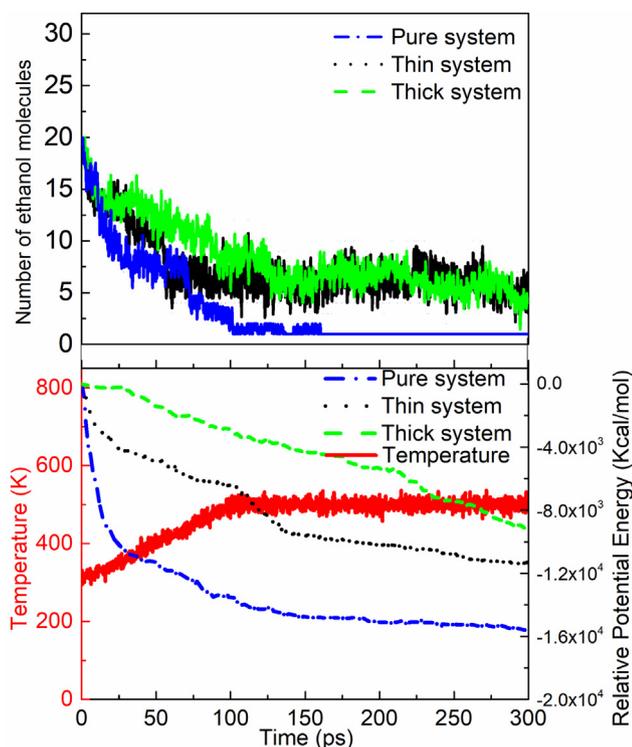


Fig. 4. Changes in relative potential energy, temperature and number of ethanol molecules as a function of time.

molecules were first absorbed on the surface of the nanoparticle, and then ethanol dissociated on the nanoparticle. At 500 K, the carbon-carbon bond in all the three systems did not break because the temperature is not high enough. For the pure aluminum nanoparticle system which will be referred to the “AP system”, the initial reaction was observed at 324 K, when the OH in ethanol fell apart and formed bonds with the aluminum atom. In AP system, the OH-abstraction reaction dominates. By using bond-restraint method in ReaxFF, the activation energy for O–H and C α –O bond cleavages energy barriers on Al (111) surface are 26.2 and 6.5 kcal/mol, which are in accordance to previous DFT results that OH-abstraction reaction has the lowest energy barrier for atomic Al and ethanol system. The energy required for oxygen dissociation on aluminum surface is lower than that for ethanol dissociation. As a result, for the AP system at 500 K, oxygen molecules dissociated while C₂H₅ molecules were still stuck on the aluminum surface.

For the thin oxide aluminum nanoparticle system, which will be referred to as the “APO300 system”, the initial ethanol dissociation reaction on the surface of the nanoparticle is different from the AP system. At 330 K, the H atom in the hydroxy fell apart which resulted in it bonding with the aluminum atom. For the thick oxide aluminum nanoparticle system, which will be referred to as the “APO600 system”, the first ethanol reaction was observed at 484 K, the H atom in the hydroxy fell apart but formed bonds with oxygen atoms on the surface of the nanoparticle instead of the aluminum atom. In ReaxFF, the O–H and C α –H bond cleavages reaction energy barriers on Al₂O₃ (001) surface are 12.8 and 41.2 kcal/mol, which are close to previous DFT values of 18.7 and 57.6 kcal/mol. As a result, in APO300 and APO600 systems, the O–H bond cleavage dominates. The finding that H atom in the hydroxyl fell apart confirms previous DFT studies [14]. In the DFT studies of ethanol and AlO reaction, the H-abstraction activation energy leading to ethoxyl radical formation is lower than that required for hydroxyethyl radical formation. From ReaxFF results, the adsorption energies for oxygen and ethanol molecules on Al₂O₃ (001) surface are –13.2 and –7.8 kcal/mol. As a result, the oxygen molecules are

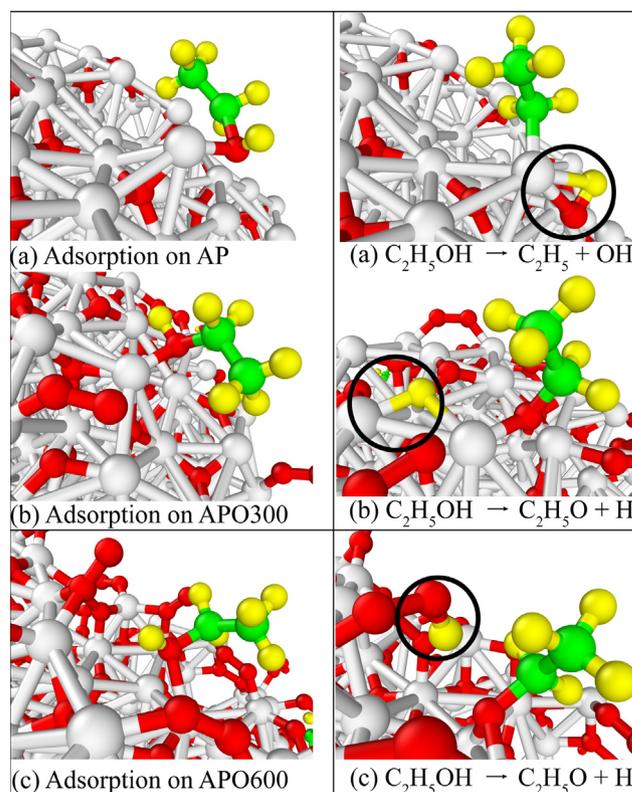


Fig. 5. Snapshots of C₂H₅OH adsorption and dissociation over (a) AP (b) APO300 (c) APO600.

favorably adsorbed on aluminum nanoparticle surface. At 500 K, based on the results of the simulations, we can conclude that with addition of aluminum nanoparticle, a significant reduction of the initial ethanol reaction temperature was observed, which could potentially advance the ethanol ignition. Additionally, for different aluminum nanoparticles with different oxidation states, the initial ethanol oxidation reaction pathways on the surface of the aluminum nanoparticle are different as shown in Fig. 5.

With the same heating rate, the temperature is increased to 2000 K for the aluminum nanoparticle systems. The reactions observed at 500 K were the OH or hydrogen separating from ethanol molecules and oxygen dissociation. At 2000 K, the initial ethanol oxidation reactions are same with 500 K. For the AP system, the ethanol absorbed and dissociated on the surface of the nanoparticle completely. All the C and H atoms in the ethanol fell apart and diffused inside the Al nanoparticle. The adsorbed C₂H₅OH decomposed to C₂H₅ and OH, with H and O diffusing inside the nanoparticle and the C₂H₅ sticking to Al. After that, the H atoms in C₂H₅ fell apart and formed bonds with aluminum atoms. Fig. 6 illustrates the evolution of the number of H and O atoms both inside and on the surface of the nanoparticle. The H and O atoms increased first and then remained constant, which means the ethanol molecules dissociated completely and the H and O atoms diffused inside nanoparticle. No product is found in the gas phase.

For the APO300 system, H in hydroxyl fell apart and formed bond with aluminum atoms first, then diffused inside the nanoparticle. After that, O and other H atoms in ethanol molecules fell apart and diffused inside the nanoparticle. The C atoms were the last to diffuse inside the nanoparticle. At 2000 K, the temperature is high enough for H and O to diffuse and form OH radical. As a result, several H₂ molecules and OH radicals were observed in the gas phase as illustrated in Fig. 7. The trend of evolution in the number of H and O atoms over time in the APO300 system is similar to that in the AP system. The H and O atoms increased and then remained almost constant, which means they diffuse into the nanoparticle. The lower increase rate of H and O atoms

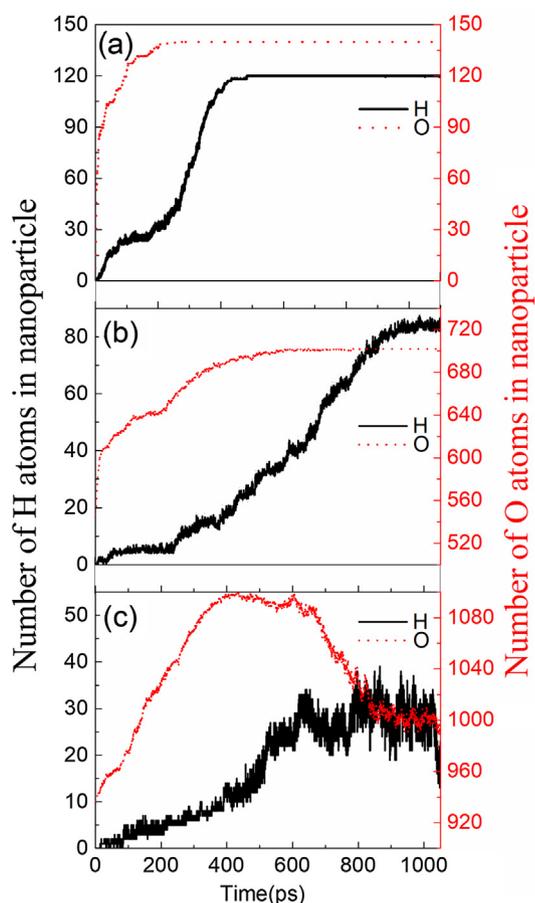


Fig. 6. The number of H and O atoms in the aluminum nanoparticle when the temperature increases from 298 K to 2000 K. (a) AP system (b) APO300 system (c) APO600 system.

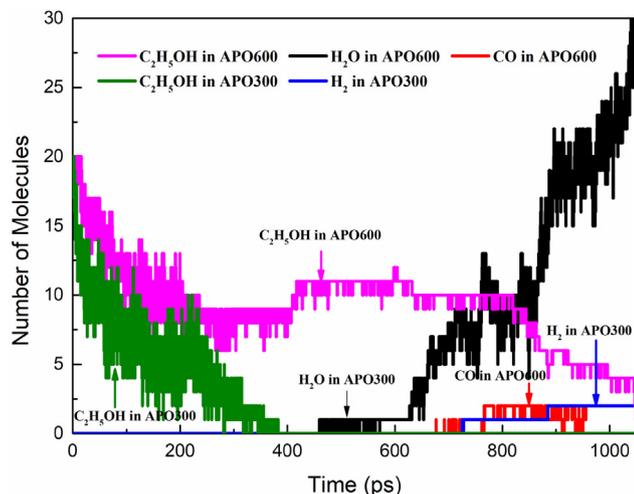


Fig. 7. Number of gas products from ethanol oxidation at 2000 K in APO300 and APO600 systems.

compared to the AP system indicates a lower reaction rate.

For the APO600 system at 2000 K, there are more O atoms on the nanoparticle surface, so reactions and products were different from the pure and thin ANP systems. The H atom fell apart and formed bonds with oxygen atoms instead of aluminum atoms. After that, at 2000 K, the H and O atoms separated from ethanol were not able to diffuse inside the nanoparticle, resulting in the formation of more gas products like H₂O and CO as shown in Fig. 7. The number of O atoms increased

at first and then decreased, which indicates that oxygen atoms came out of the aluminum nanoparticle and formed O-containing species. Compared with the AP and APO300 system, more gas products were observed in the APO600 system. The number of H atoms fluctuated more than the APO300 system. The difference confirms that the different oxidation states of the aluminum nanoparticle influence the ethanol reactions on the aluminum nanoparticle surface.

From the simulation results, we can conclude that: first, aluminum nanoparticle additives in ethanol reduce the initial reaction temperature, which consequently accelerates the ethanol ignition; and second, the different oxidation states of the aluminum nanoparticles influence the ethanol reactions and products on the surface.

3.3. Acceleration of ethanol oxidation by phase transition of aluminum core

To investigate the effects of the nanoparticle on ethanol oxidation, we also conducted simulations in microcanonical ensemble (NVE) for APO300 and APO600 systems with an initial temperature of 298 K. As shown in Fig. 8, the potential energy decreased over time. Energy released from ethanol oxidation caused the temperature increase. The temperature of the APO300 and APO600 systems increases up to 2700 K and 2400 K, respectively. The temperature increases faster and earlier in the APO300 system compared to the APO600 system, indicating that ethanol oxidation in APO300 system has a lower energy barrier. It is worth noting that the temperature increases in a very short time period (200–250 ps), which validate that the oxidation reaction is a highly exothermic process. The results demonstrate that the presence of aluminum nanoparticle increases the heat release and accelerates ethanol oxidation, therefore decreasing the ignition delay from the atomic level. Fig. 8 shows that the nanoparticle oxide thickness increases at the same time period with temperature increase. The oxide thickness and temperature increase dramatically when the temperature is beyond 700 K, which is the melting point of aluminum cluster [23]. As a result, further diffusion occurs through the liquid aluminum and accelerates the ethanol oxidation. The temperature range over the sharp increase period is consistent with the previous finding that the micro-explosion regime of nanofuel with aluminum nanoparticle additives combustion started at 700 K [11]. The growth of the oxide layer is both inward and outward: inward because of the movement of oxygen atoms towards the interior of the nanoparticle, and outward because of the movement of aluminum atoms towards the oxide surface.

The increase of temperature and oxide thickness leads to disorder of the aluminum nanoparticle. Radical distribution function (RDF) is utilized to identify the nanoparticle structure information. RDF describes how density varies as a function of distance from a reference aluminum atom, the first highest peak in Al–Al RDF represents the nearest Al–Al bond length. The RDFs of APO300 at 500 K and 2000 K are shown in the supplemental material (Fig. S1). The first peak height at 2000 K is lower than at 500 K, which indicates the transition from ordered to disordered structure. The aluminum core could change from solid state to liquid state in the temperature increase range. The liquid state aluminum core makes it easier for the H and O atoms to diffuse inside the aluminum nanoparticle, which could provide more active reaction sites on the surface. Based on these findings, it can be concluded that the phase transition of the aluminum core accelerates the ethanol oxidation, which indicates a possible transition from a diffusively-controlled combustion process to a kinetically-controlled combustion process. These conclusions explain phenomena in ignition delays and gasification rates of nanofuel dependence on temperature.

3.4. Chemical kinetic parameters for C₂H₅OH dissociation

We use C₂H₅OH consumption rates to study the activation energy of the C₂H₅OH dissociation on aluminum nanoparticles. The systems were simulated in NVT ensemble with temperatures varying in a range from 400 K to 2000 K over the APO300. Fig. 9 represents C₂H₅OH

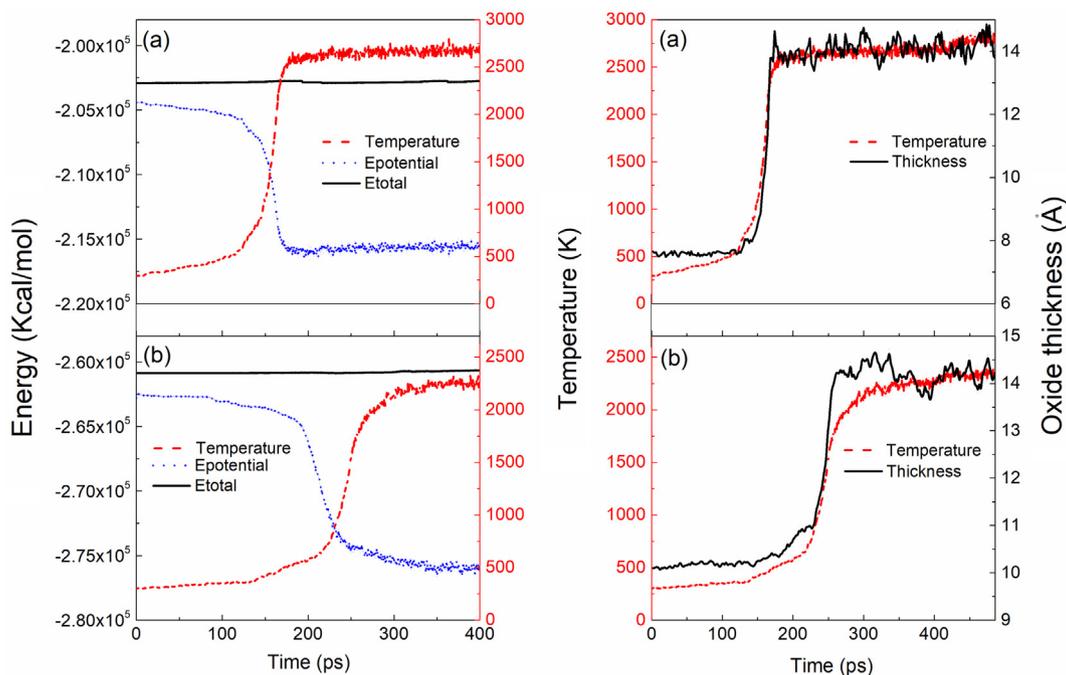


Fig. 8. Temperature, energy and oxide thickness evolutions in NVE simulations for (a) APO300 system (b) APO600 system.

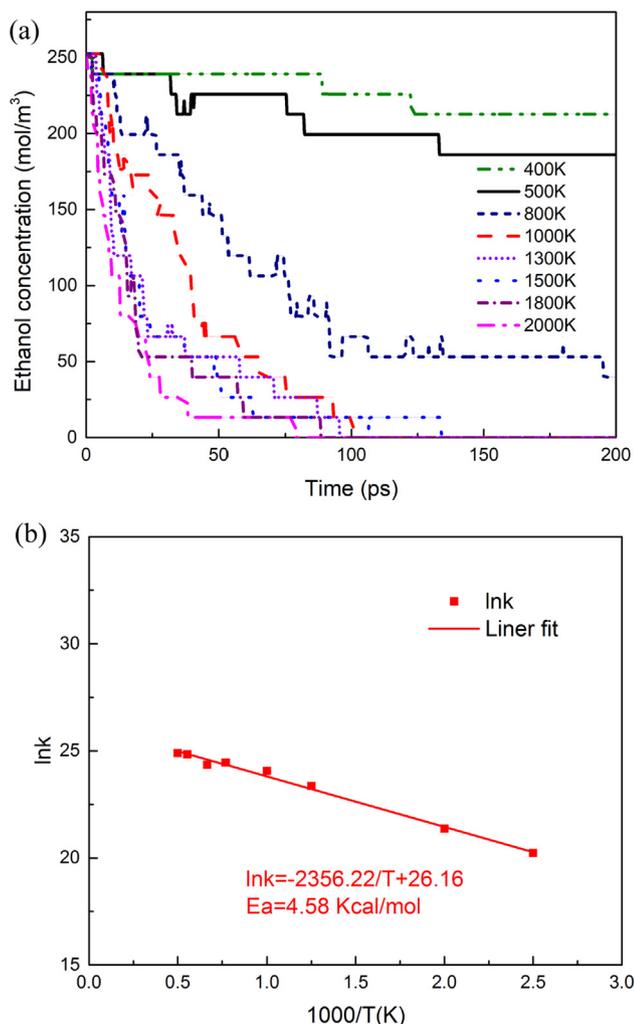


Fig. 9. (a) C_2H_5OH concentration at various temperatures over APO300 (b) Arrhenius plot for the C_2H_5OH dissociation over APO300.

concentration evolutions over time obtained from simulation at each temperature. At the initial reaction stages, the C_2H_5OH consumption rates increases with increasing temperature.

According to chemical kinetics, the first-order rate constant k can be calculated from a linear fit to $\ln[C_2H_5OH]_t/[C_2H_5OH]_0$. The $[C_2H_5OH]_0$ and $[C_2H_5OH]_t$ represent the C_2H_5OH concentration initially and at an arbitrary moment. Arrhenius parameters for ethanol dissociation on APO300 are calculated by the linear fit line from the Arrhenius plot in Fig. 9. The activation energy for ethanol dissociation on APO300 is 4.58 kcal/mol. Our ReaxFF simulation results are in accordance with quantum mechanics results, for the C_2H_5OH dissociation energy on AlO diatomic is 1.96 kcal/mol [16]. Activation energy of ethanol decomposition over Al_2O_3 (001) surface by DFT calculations is 18.68 kcal/mol [14], which is also in agreement with our results.

4. Conclusion

ReaxFF molecular dynamics simulations have been conducted to investigate ethanol oxidation over aluminum nanoparticles with different oxidation states at the atomic scale. In the C_2H_5OH/O_2 mixture and nanoparticle system, the presence of aluminum nanoparticles has reduced the initial reaction temperature to 324 K. The reaction pathways and products are different in aluminum nanoparticle systems with different oxidation states. OH-abstraction is more commonly observed on the pure aluminum nanoparticle while H-abstraction prevails on the aluminum nanoparticle with oxide. The separated H atom from hydroxyl forms bonds with Al and O atoms on aluminum nanoparticle with thin and thick oxide layers, respectively. The dissociation of the adsorbed oxygen and ethanol molecules on the oxygen-coated surface is harder than on the pure aluminum nanoparticle surface. Gas products like H_2O and CO resulting from ethanol oxidation in the APO600 system are observed. In contrast, almost all the C, H and O atoms in ethanol diffuse inside pure and thin aluminum nanoparticle systems. Moreover, the ethanol dissociation requires a higher temperature than adsorption. From the NVE simulations, we conclude that during the ethanol oxidation over the aluminum nanoparticle, the solid state aluminum core has changed to liquid state, which could make further H and O atoms diffuse inside the nanoparticle more easily. It provides more active reaction sites on the surface and therefore accelerates the

ethanol dissociation dramatically. The activation energy for C₂H₅OH adsorptive dissociation over the Al nanoparticle with a thin oxide layer is determined to be 4.58 kcal/mol, which is in agreement with results from much more expensive DFT calculations.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.fuel.2018.06.119>.

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