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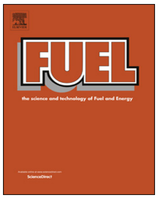

Full Length Article

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 H_2O 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 C_2H_5O 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 C_2H_5OH/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).

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{val}} + E_{\text{tors}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} \tag{1}$$

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 (${BO_{ij}}^{\sigma}$), pi-bonds (${BO_{ij}}^{\pi}$) and double pi bonds (${BO_{ij}}^{\pi\pi}$). Here we use E_{bond} as an example to illustrate how the bonded interaction is calculated:

$$E_{bond} = -{D^{\sigma}}_{e}\cdot {BO_{ij}}^{\sigma}\cdot \exp[\mathrm{p_{bel}}(1-(\mathrm{BO_{ij}}^{\sigma})^{\mathrm{P_{be2}}})]-\mathrm{D_e}^{\pi}\cdot {BO_{ij}}^{\pi}-{D_e}^{\pi\pi}{BO_{ij}}^{\pi\pi} \tag{2}$$

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 C_2H_5OH/O_2 mixture reactions on Al nanoparticles. Simulations were performed on four different systems in a box size of equal measurements, which were 50 × 50 × 50Å. 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

AnAl 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 × 50 × 50Å.

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 led 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 C_2H_5OH/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: $KE = \dim \times NKT/2$