Ab Initio Molecular Dynamics Simulations of Furfural at the Liquid-Solid Interface

Sanwu Wang, Hongli Dang, Wenhua Xue, Darwin Shields, Xin Liu, Friederike C. Jentoft, and Daniel E. Resasco

Abstract—The bonding configuration and the heat of adsorption of a furfural molecule on the Pd(111) surface were determined by *ab initio* density-functional-theory calculations. The dynamics of pure liquid water, the liquid-solid interface formed by liquid water and the Pd(111) surface, as well as furfural at the water-Pd interface, were investigated by *ab initio* molecular dynamics simulations at finite temperatures. Calculations and simulations suggest that the bonding configurations at the water-Pd interface promote decarbonylation of furfural.

Keywords—*Ab initio* molecular dynamics simulations, bio-fuels, density functional theory, liquid-solid interfaces.

I. INTRODUCTION

BIOMASS pyrolysis and other relevant catalytic reactions often occur at the liquid-solid interface. It is therefore of great importance to investigate the interfacial structure and other properties in order to achieve a deep understanding about the catalytic reactions for biomass conversion. Furfural conversion over metal catalysts, with or without the presence of liquid water, plays an important role in the studies of biomass-derived feed stocks [1], [2]. Furfural is one of the oxygenated compounds commonly found in bio-oil. It is also an important intermediate in various approaches for biofuel production. For example, furfurals are present in bio-oil obtained from the fast pyrolysis of biomass. Furfural is also produced by the acid-catalyzed dehydration of xylose, one of the constituents of biomass. The experimental and theoretical studies of furfural conversion over different metal catalysts could be helpful for improving bio-oil's storage stability, boiling point range, water solubility, and octane number.

Experimentally, it was observed that decarbonylation reaction, in which the single C-C bond of the furfural molecule is broken, dominates when palladium (Pd) was used as the metal catalyst [1], [2].

However, theoretical simulations for the dynamics of furfural on the catalytic Pd surfaces, with and without the presence of liquid water, are still lacking.

We used *ab initio* molecular dynamics (MD) simulations to study the interfaces formed by liquid water and the palladium surface. Such interfaces are involved in many catalytic reactions for biomass conversion. We also performed *ab initio* molecular dynamics simulations at finite temperatures for the dynamics of furfural at the water-Pd interface. In particular, we found that, during the dynamic process, the furan ring of furfural prefers to be parallel to the Pd surface and the aldehyde group tends to be away from the Pd surface, promoting the decarbonylation process of furfural at the water-Pd interface.

II. METHOD AND MODEL

The Pd (111) surface was modeled by repeated slabs with four metal layers separated by a vacuum region (for calculations of furfural on the surface without water) or a liquid region (when simulations involved liquid water). Each metal layer in the supercell contained 16 Pd atoms (a 4×4 surface unit cell). For furfural on the surface or at the liquid-solid interface, a single furfural molecule was placed on the top of the Pd slab. All the Pd atoms were initially located at their bulk positions, with the equilibrium lattice constant (3.96 Å) of the bulk determined by our calculations.

The calculations and simulations were performed within density functional theory (DFT), using the pseudopotential method and a plane-wave basis set [3]–[8]. The results reported in this paper were obtained using the Vienna *ab initio* simulation package (VASP) [4]–[6]. The exchange-correlation effects were treated with the generalized gradient-corrected exchange-correlation functionals given by Perdew and co-workers [9], [10]. We adopted the Vanderbilt ultrasoft pseudopotentials supplied by Kresse and co-workers [11], [12]. A plane-wave energy cutoff of 400eV and three special k points in the irreducible part of the two-dimensional Brillouin zone of the 4×4 surface cell were used for all the calculations and simulations involving the surface and the interface.

For the relaxation of configurations at the temperature of absolute zero, optimization of the atomic structure was performed for each supercell via a conjugate-gradient technique using the total energy and the Hellmann-Feynman forces on the atoms [3]. For both optimization calculations and *ab initio* MD simulations, the Pd atoms of the bottom two layers were fixed while the Pd atoms of the top two layers were allowed to move. The *ab initio* molecular dynamics simulations at finite temperatures were performed in canonical ensembles [4]–[6], [13], [14]. The time step was set to 0.5fs.

III. RESULTS AND DISCUSSIONS

We first consider of adsorption of furfural at the gas phase, without the presence of liquid water, on the Pd (111) surface.

Sanwu Wang is with the Department of Physics and Engineering Physics, The University of Tulsa, Tulsa, OK 74104 USA (phone: 918-631-3022; fax: 918-631-2995; e-mail: sanwu-wang@utulsa.edu).

Hongli Dang, Wenhua Xue, Darwin Shields, Xin Liu, Friederike C. Jentoft and Daniel E. Resascos are with the Department of Physics and Engineering Physics, The University of Tulsa, Tulsa, OK 74104 USA.

Fig. 1 shows the most stable configuration at the temperature of absolute zero for adsorption of a single furfural molecule on the Pd(111) surface, determined by our *ab initio* DFT calculations. The molecular plane, while no longer exact two-dimensional, is almost parallel to the Pd surface. The binding energy (the heat of adsorption) is approximately 0.75eV, a considerable amount indicating a chemical bonding. The bonding of carbon atoms in furfural with the Pd surface decreases the bonding strengths between the carbon atoms within furfural, promoting decarbonylation of furfural in which the C-C single bond in furfural is broken.
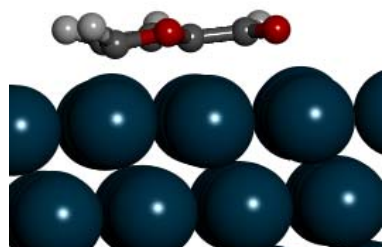
(a) Side view
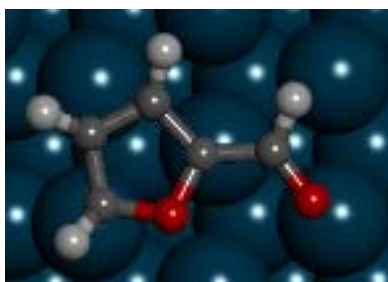
(b) Top view

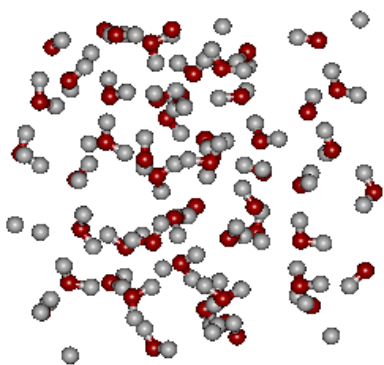Fig. 1 The most stable configuration for adsorption of a single furfural molecule on Pd (111)

Fig. 2 A snapshot equilibrium configuration of liquid water obtained from *ab initio* MD simulations (T = 300K). Periodic boundary condition is applied
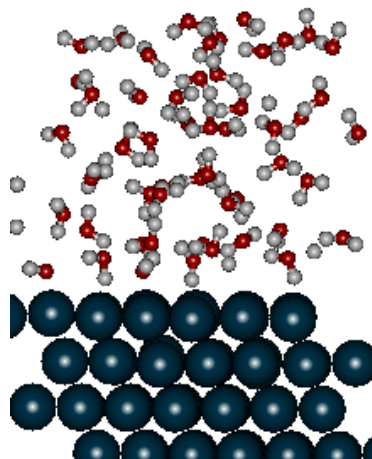

Fig. 3 A snapshot equilibrium configuration of the liquid-solid interface obtained from *ab initio* MD simulations (T = 373K)

Since catalytic reactions of biomass often involve liquid water or other liquid, and the reactions usually occur at the interface formed by liquid and the solid catalyst (the liquid-solid interface), we investigated the liquid-solid interface formed by water and the Pd (111) surface. Pure water in the liquid phase was also studied with *ab initio* MD simulations at two different temperatures (300K and 373K).

Fig. 2 shows a snapshot equilibrium configuration of bulk liquid water, obtained from our *ab initio* MD simulations at the room temperature. We used a supercell containing 54 water molecules and we run simulations for a time period of 3 ps. We found the hydrogen-bond (H-bond) network of liquid water is well represented by our model and the equilibrium configurations obtained from our *ab initio* simulations. Similarly, we carried out *ab initio* MD simulations for the interface formed by liquid water and the Pd (111) surface (also at two different temperatures of 300K and 373K. The supercell contains 54 water molecules and a slab of 4 Pd layers (64 Pd atoms).
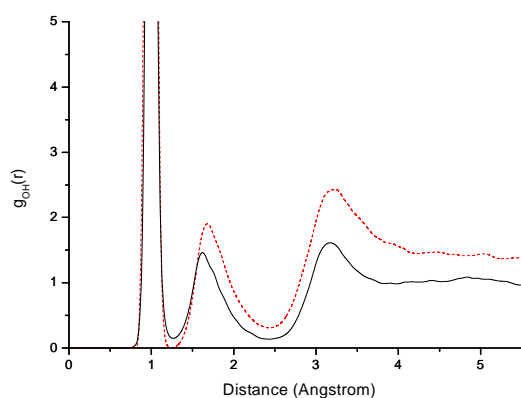

Fig. 4 Equilibrium radial distribution function (the solid line) for the O-H distances of the interface at a temperature of 373K. Also shown is the corresponding RDF of the pure water (the dotted line)
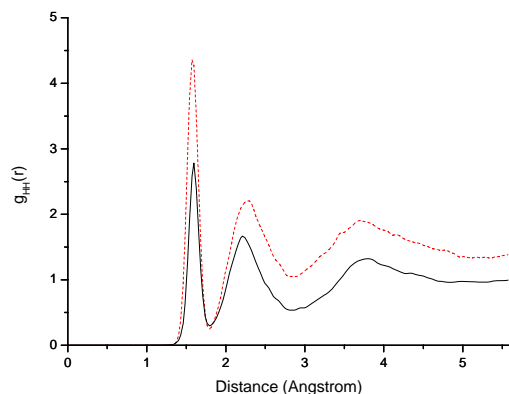
Fig. 5 Equilibrium radial distribution function (the solid line) for the H-H distances of the interface at a temperature of 373K. Also shown is the corresponding RDF of the pure water (the dotted line)

Fig. 3 shows a snapshot equilibrium configuration when the temperature is 373K. We observe that the hydrogen atoms in most of the water molecules near the surface have H-bonds with the surface (with bond lengths of 2.2–2.7Å) while the oxygen atom of one water molecules is also bonded with the surface with a bond length of 2.13Å (Fig. 3).

Figs. 4 and 5 show the radial distribution functions [15] (RDFs) for the interface and pure liquid water at a temperature of 373K, determined by *ab initial* MD simulations. It can be observed that the second and third peaks for the O-H distances, as well as the second peak for the H-H distances, of the liquid-solid interface shift slightly to the right when comparing to the corresponding peaks of the pure water. This is due to the fact that water molecules near the interface have bonding with the Pd surface, causing charge redistribution and hence changing slightly the strength of the hydrogen bonds (corresponding to the second peaks of the RDF curves).

When furfural was placed at the interface, the initial configuration is shown in Fig. 6. The furfural molecule was titled near the surface initially. This initial configuration is far away from the equilibrium. We performed *ab initio* MD simulations for this system at a temperature of 373K. Figs. 7 and 8 show two snapshot configurations obtained from our *ab initio* MD simulations.

At the time (t) of 0.9ps, the configuration is still away from the equilibrium. When the system reaches equilibrium (Fig. 8; t =3.0ps), the carbon atoms and one oxygen atom in furfural are boned with the Pd surface with the bond lengths ranging from 2.1Å to 2.8Å, but another oxygen in furfural is bonded with a hydrogen atom in water with a bond length of 1.8Å, indicating a hydrogen bond. On the other hand, hydrogen atoms in furfural are essentially bonded with Pd (2.3–2.5Å), and there are no H-bonds corresponding to the hydrogen atoms in furfural and any oxygen atom in water, indicating a little H-bonding of furfural with water.

During the dynamic process from non-equilibrium to equilibrium configurations, we observe that the furfural plane gradually becomes almost parallel to the Pd surface, consistent with the result obtained from furfural adsorption when there is no liquid water present. This fact is important as it suggests that the C-C single bond in furfural is weakening so that decarbonylation of furfural could occur at the interface.
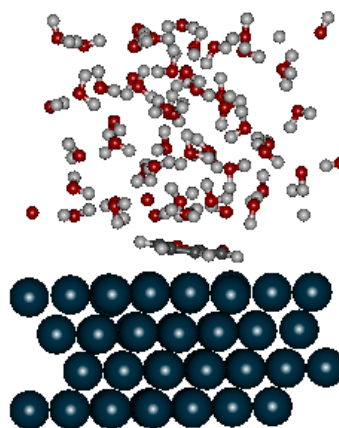

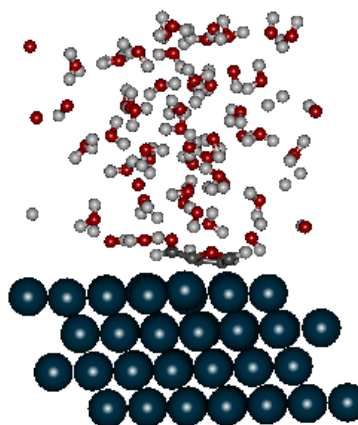Fig. 6 The initial configuration of a furfural molecule at the liquid/solid interface

Fig. 7 The snapshot configuration from *ab initio* MD simulations (t = 0.9 ps; T = 373 K)

IV. CONCLUSION

We have presented results of *ab initio* DFT calculations for the bonding configuration and the binding energy of furfural on the Pd (111) surface, as well as *ab initio* MD simulations, at finite temperatures, for furfural at the liquid-solid interface formed by liquid water and the Pd (111) surface. We have observed that the dominant equilibrium bonding structure is the parallel configuration in which the furfural plane, while slightly distorted, is parallel to the Pd (111) surface. This configuration promotes the reaction of furfural decarbonylation, consistent with the experimental measurements.
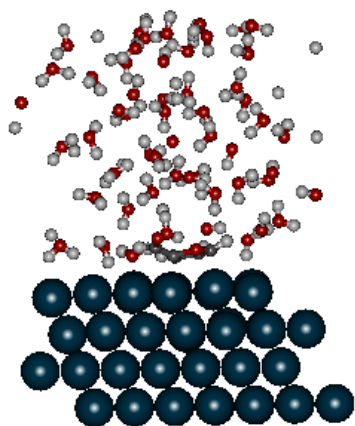
Fig. 8 The snapshot equilibrium configuration from *ab initio* MD simulations (t =3.0ps; T = 373K)

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