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# The influence of surface oxygen and hydroxyl groups on the dehydrogenation of ethylene, acetic acid and hydrogenated vinyl acetate on pure Pd(1 0 0): A DFT study

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## ABSTRACT

On the basis of a Langmuir–Hinshelwood-type mechanism, the dehydrogenation of ethylene, acetic acid and hydrogenated vinyl acetate (VAH) on pure Pd(1 0 0) with surface oxygen atoms (Os) and hydroxyl groups (OHs) was studied with density functional theory (DFT) method. Our calculation results show that both Os and OHs can consistently reduce the activation energies of dehydrogenation of ethylene, acetic acid and VAH to some degree with only one exception that OHs somehow increase the activation energy of VAH. Based on Langmuir–Hinshelwood mechanism, the three dehydrogenation reactions in presence of surface Os and OHs are almost consistently favored, compared with the corresponding processes on clean Pd(1 0 0) surfaces, and thus a Langmuir–Hinshelwood-type mechanism may not be excluded beforehand when investigating the microscopic performance of the oxygen-assisted vinyl acetate synthesis on Pd(1 0 0) catalysts.

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## 1. Introduction

Vinyl Acetate monomer (VAM) is an important chemical intermediate for polyvinyl alcohol and poly vinyl acetate [1], which are widely applied in the manufacture of emulsion-based paints, adhesives, coatings and fibers. The industrial production of VAM began in the 1960s [2]. The synthesis of vinyl acetate monomer (VAM) from the reaction of ethylene, acetic acid and oxygen is catalyzed by palladium-based catalyst with the selectivity of about 80%, according to the following reaction [3,4]:



Kumar et al. [5–7] have found that Pd(1 1 1), Pd(1 0 0), Au/Pd(1 1 1) and Au/Pd(1 0 0) single crystals all can catalyze the reaction; however, Au/Pd(1 0 0) is the most active [5–7], which arouses the exploration of the chemistry of VAM on Pd(1 0 0). VAM synthesis from ethylene is based on Langmuir–Hinshelwood coadsorption reaction process [8–10]. This reaction process holds that ethylene, oxygen and acetic acid are adsorbed on the catalyst surface and interact with each other, resulting in co-adsorbed

ethylene coupling with acetic acid to generate VAM. The H atoms from ethylene and acetic acid react with O atom to form water molecule. Hansen et al. [11] found that O<sub>2</sub> can facilitate dehydrogenation of acetic acid on the catalyst surface to yield acetate species. Li et al. [12] pointed out that on Pd(1 0 0) the surface oxygen plays a vital role in the formation of active acetate species for VAM synthesis while this role doesn't necessarily exist on Pd(1 1 1). Based on whether ethylene dehydrogenation happens before ethylene couples with acetic acid, researchers proposed two possible reaction pathways (shown in Fig. 1): (1) Samanos et al. [13,14] proposed that ethylene adsorbed on the surface directly couples with acetic acid, a nucleophilic species, to generate the Vinyl Acetate-like intermediate (acetoxyethyl-palladium) and then β-H elimination occurs, forming the product, VAM. This reaction pathway is termed as S-mechanism. (2) Moiseev et al. [2,15] argued that ethylene adsorbed on the surface first undergoes dehydrogenation to form vinyl (–CH=CH<sub>2</sub>) species, and then couples with the acetate species adsorbed on the surface to yield VAM. This reaction pathway is named as M-mechanism.

Rivalta et al. [10] carried out the dehydrogenation of ethylene on Pd second-neighboring ensembles of both Pd/Au(1 0 0) and Pd/Au(1 1 1) surface alloys in presence of surface oxygen atoms and hydroxyl groups with the density functional theory method. They found that the calculated activation barriers for ethylene dehydrogenation to form vinyl on oxygen atoms and hydroxyl groups

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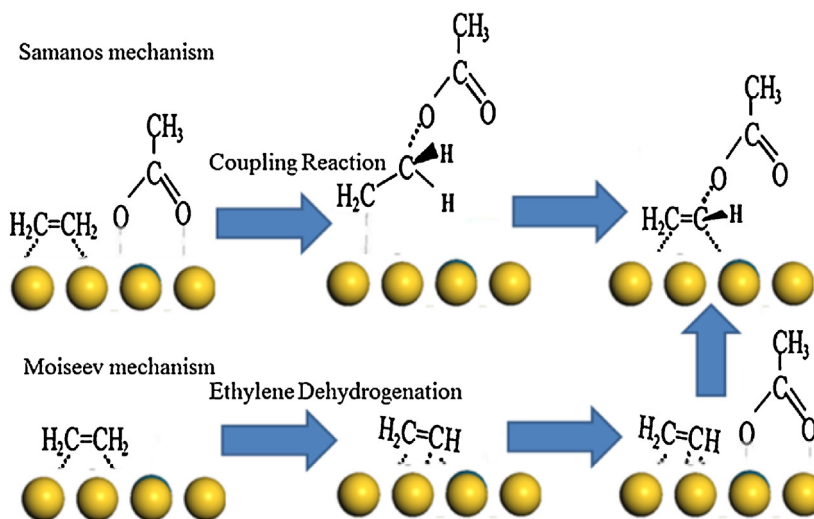


Fig. 1. two possible pathways of VAM synthesis.

covered Pd/Au surfaces are significantly lower than those on clean surface alloys. Jiang et al. [16] used DFT together with periodic slab models to systematically study the adsorption and dehydrogenation mechanisms of methane on clean and oxygen-covered Pd (100) surfaces. They found that the effect of co-adsorbed oxygen atom tends to weaken the adsorbate–substrate interaction on the Pd (100) surface. The surface chemistry of acetic acid has been investigated on clean Pd(100), Pd(100)-p(2 × 2)-O and Pd(100)-c(2 × 2)-O surfaces and it is found that acetate species predominantly form on the oxygen-covered surfaces and are stable up to about 380 K on Pd(100)-p(2 × 2)-O and about 375 K on Pd(100)-c(2 × 2)-O [17,18].

Stacchiola et al. [19] conducted an experimental study on VAM synthesis on Pd(111) clean surface and found that the reaction proceeds via the Samanos mechanism. Besides, they suggested that the presence of coadsorbed oxygen does not significantly affect the reaction kinetics. He also pointed out that the surface oxygen plays a vital part in the vinyl acetate synthesis reaction on Pd(100) surface [12]. Nevertheless, which mechanism is preferable on Pd(100) surface has not been clearly indicated in the literature.

In this work, with density functional theory method, all the dehydrogenation reactions in both Samanos mechanism and Moiseev mechanism on Pd(100) surface, the dehydrogenation of ethylene, acetic acid and hydrogenated vinyl acetate, were taken into consideration to examine the influence of surface oxygen atoms and hydroxyl groups on the three dehydrogenation reactions. Also, the corresponding adsorption of the aforementioned three species was investigated. Both aspects will provide mechanistic insights into VAM synthesis reaction.

## 2. Computational models and methods

### 2.1. Computational surface models

On the basis of the optimized Pd bulk structure, the five-layered Pd(100) surface model was built. The calculated value of the lattice constant of Pd bulk was 3.96 Å, which is almost the same as the result of Li [20] and which is close to the experimental value of 3.89 Å.

### 2.2. Computational details

The calculations were conducted on the basis of spin unrestricted DFT calculations with CASTEP Module in Materials Studio, using the generalized gradient approximation (GGA) with the revised

Perdew–Burke–Ernzerhoff (rPBE) functional [21] as the exchange–correlation functional. The energy cutoff was set to 345.0 eV. The Pd(100) surface was modeled, using a 4 × 4 unit cell consisting of five layers of atoms with 15 Å of vacuum. The k-point sampling consists of 2 × 2 × 1 Monkhorst–Packpoints [22]. The two upmost surface layers and the adsorbates have been optimized, while the lowest layers are kept fixed.

The adsorption energy of different reactants on Pd(100) surfaces is defined as:

$$E_{\text{ads}(A)} = E_{A^*-\text{slab}} - E_{\text{slab}} - E_A^{\text{gas}}$$

where  $E_{A^*-\text{slab}}$ ,  $E_{\text{slab}}$  and  $E_A^{\text{gas}}$  are the total energies of different reactants adsorbed on the corresponding Pd surface slabs, the bare Pd surface slabs and the free reactants, respectively.

The co-adsorption energy on Pd(100) surface is defined as:

$$E_{\text{co-ads}} = E_{(A+B)/\text{slab}} - E_A^{\text{gas}} - E_B^{\text{gas}} - E_{\text{slab}}$$

where  $E_A^{\text{gas}}$ ,  $E_B^{\text{gas}}$ ,  $E_{\text{slab}}$  and  $E_{(A+B)/\text{slab}}$  are the total energy of A and B, the Pd slab with a (2 × 2) super-cell and the co-adsorbed (A + B)/Pd slab, respectively.

The transition state was identified through the following method. First, complete LST/QST [23] was used to identify the possible transition state. Then, the possible transition state was refined. Finally, whether it was the real transition state was determined by the frequency analysis. That there is only one imaginary frequency is the standard to determine whether it is the real transition state. And the imaginary frequency is the vibration between the reactants and the products.

## 3. Results and discussion

### 3.1. Adsorption of H, O, OH and H<sub>2</sub>O

For H, O, OH and H<sub>2</sub>O, three adsorption sites, including top, bridge, and hollow sites, were calculated for the Pd(100) surface. The adsorption energies of the four species were calculated. The most stable configurations of H, O, OH and H<sub>2</sub>O on Pd(100) surface were determined.

For H adsorption on the clean Pd(100), three stable configurations (top, bridge, hollow) were compared. The corresponding adsorption energies are 89.2 kcal/mol (top), 89.1 kcal/mol (bridge) and 89.3 kcal/mol (hollow), which suggests that the single H atom prefers to be adsorbed at the hollow site with the Pd–H bond length of 2.041 Å.

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