J. Phys. Chem. C **2008,** *112,* 1539−1543

Origin of High Activity and Selectivity of PdAu(001) Bimetallic Surfaces toward Vinyl Acetate Synthesis

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Received: August 27, 2007; In Final Form: October 31, 2007

We perform systematic density functional studies to elucidate the mechanism of vinyl acetate (VA) synthesis on Pd/Au(001). Atomic geometries, activation energies, and reaction energies are determined for three separate reaction stages: coupling of ethylene and acetate; β-H elimination; and VA desorption. Significantly, we find that the Pd "monomer" pair is much more robust in all three reaction stages than large Pd ensembles such as Pd monolayers, mainly due to high mobility of reactants on surrounding Au sites. The remarkably high activity and selectivity of VA reaction on PdAu bimetallic surfaces observed by Goodman et al. are exclusively attributed to the ensemble effects.

1. Introduction

PdAu bimetallic surfaces have attracted extensive attention recently due to their peculiar reactivity and selectivity toward various chemical reactions such as the synthesis of vinyl acetate (VA).[1,2] It is interesting to note that VA formation rates are strongly dependent on Pd coverage and that the turnover frequency reaches its maximum when the Pd/Au ratio is 10% at the surface.[3] Goodman et al. pointed out that the presence of Pd monomer pairs is the chief factor that facilitates coupling between ethylene species and acetate on Pd-based catalysts. Depending whether ethylene dehydrogenates before or after it combines with acetate, two possible reaction pathways were proposed for the VA synthesis: (i) ethylene is first dehydrogenated to vinyl species, which then couples with a coadsorbed acetate species;[4] and (ii) ethylene inserts directly with acetate nucleophile to form an ethyl acetate-like intermediate that undergoes a β-H elimination afterward.[5] Systematic theoretical investigations are essential toward providing comprehensive information for the elucidation of the complex reaction mechanism and, furthermore, to establish connections between the catalytic properties of PdAu bimetallic surfaces and their electronic features.

Experiments[6,7] and calculations[8] show that Pd substituents prefer not to have first neighborhoods but rather form second neighborhoods on either Au(111) and Au(001) after heat treatments. One of the most important consequences is that PdAu surfaces become inactive toward promoting ethylene dehydrogenation,[3] primarily due to an inability to provide sufficient attraction to both vinyl and the eliminated H during the transition state.[9] Therefore, one may only focus on the second pathway in the forthcoming studies of formation of VA on PdAu(001). Now it is crucial to identify with both experimental and theoretical studies: (1) Is the reaction promoted essentially by two Pd atoms (denoted as $Pd_{2,SN}$ below) or, as proposed by Neurock et al.,[10] more Pd atoms? (2) Why are Pd second neighborhoods more active for VA synthesis than Pd first neighborhoods, e.g., a Pd monolayer (denoted as Pd_{ML} below)? (3) What are the most important factors in different steps of VA synthesis?

In this article, we strive to provide answers to these questions through systematic density functional simulations. Along with experimental findings of Goodman et al., we established that a Pd monomer pair is highly efficient in catalyzing the formation of ethyl acetate-like intermediate and also in the elimination of β-H without (or with) the assistance of O atoms nearby. First of all, the activation energies are modest: 1.17 eV for the formation of ethyl acetate-like intermediate and 0.56 eV (or 0.14 eV with the assistance of O) for the elimination of β-H on $Pd_{2,SN}$. Moreover, VA molecules may easily take off from the surface with weak adsorption energy, 0.52 eV. In contrast, large Pd ensembles such as Pd_{ML} are unfavorable for VA production because they are excessively attractive toward reactants and products and usually cause dissociations and catalyst poisoning. After descriptions for the computational details in section 2, key results will be discussed consecutively in sections 3−5.

2. Computational Details

The calculations were performed in the framework of density functional theory (DFT), using the generalized gradient approximation (GGA) for the description of exchange−correlation interaction.[11] The effects of ionic cores were represented by ultrasoft pseudopotentials,[12] as implemented in the Vienna ab initio simulation package (VASP).[13] The energy cutoff for the wave function expansion was 350 eV, for balance between quality and feasibility of computation. Since large molecules are involved, we used a 5 × 5 supercell in the lateral plane to minimize interaction between reactants in adjacent cells. Along the surface normal, a slab geometry with 4 layers of Au and 15 Å vacuum was adopted. The lattice constant in the lateral plane was fixed at 10.22 Å, according to the theoretically optimized lattice size of the bulk face-centered cubic Au, 4.18 Å. Positions of all atoms except those in the two bottom-most Au layers were fully relaxed under the guidance of atomic forces. Structural optimizations were performed through calculations

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10.1021/jp076831+ CCC: $40.75

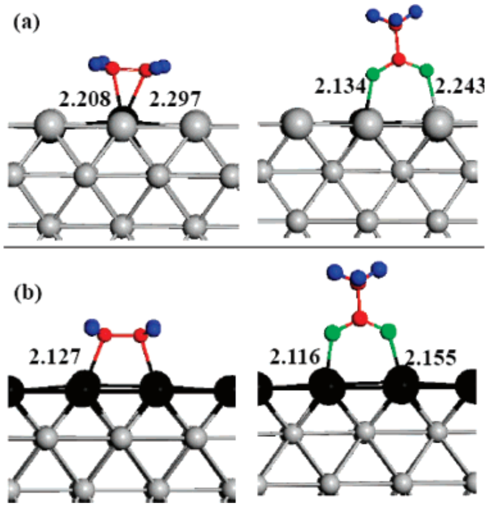

Figure 1. The adsorption geometries of ethylene and acetate on the $Pd_{2,SN}$ and Pd_{ML} ensembles on PdAu(001). The lengths of Pd−C, Pd−O, and Au−O bonds are given in unit of angstroms.

with the Γ-point while 3 × 3 × 1 k-points were used for the determination of total energies and electronic properties. Since forces remained negligible in calculations with large numbers of k-points, the use of Γ-point for structural optimization should be sufficient for the outsized unit cell adopted here. Finally, the MEPs (minimum energy paths) for chemical reactions were obtained using the climbing image nudged elastic band (CI-NEB) technique.[14−17]

3. Adsorption of Ethylene and Acetate

To explore MEPs for VA synthesis on PdAu surfaces, it is crucial to have well-optimized adsorption geometries for both reactants and products. We start by discussing the adsorptions of ethylene and acetate on the $Pd_{2,SN}$ ensemble. In separate calculations, we study the adsorption and dehydrogenation of ethylene on PdAu(001) considering the isolate Pd to as well as first neighborhood ensembles.[9] As illustrated in Figure 1, ethylene binds with Pd monomers with the π-bond geometry, and its C−C bond aligns along the [110] direction. The adsorption energy, determined from total energies of different systems as $-(E_{\text{ethylene/substrate}} - E_{\text{substrate}} - E_{\text{ethylene}})$, is 0.66 eV per molecule. In comparison, ethylene prefers the di-σ geometry on Pd_{ML} supported on the Au(001) surface and the adsorption energy increases to 1.01 eV, which is somewhat larger than that of 0.94 eV on Pd(001) surface due to the ligand effect. According to the calculated activation energies, ethylene is more likely decomposed on Pd_{ML} or other first neighborhoods but should remain unchanged on Pd second neighborhoods because of the insufficient attraction of Au and Pd−Au bridge sites toward vinyl and the hydrogen atom eliminated in the transition state, and the barriers are 0.83 and 1.82 eV on Pd_{ML} and $Pd_{2,SN}$, respectively. Therefore, ethylene and vinyl molecules may decompose too rapidly on $Pd_{ML}$to combine with acetate for VA syntheses.

On the other hand, it is known that acetic acid easily dissociates to stable adsorbate−acetate on metal surfaces, even well below room temperature. Acetate decomposes into CO_2, H_2, and C via an autocatalytic route around 300−400K on active metal surfaces, according to experimental observations.[18] However, it was found that acetate is stable in a wide temperature range on Pd surfaces modified by Au.[19] High-resolution electron energy loss spectroscopy experiments suggested that both bidentate and monodentate acetate can exist on Pd(111) below 190 K,[18] and bidenatate acetates play a key role in VA synthesis on PdAu(001).[1,20] In the present calculations, we considered two adsorption geometries for acetate adsorption on either atop or bridge sites. As a result, the di-σ geometry with two oxygen atoms bound separately on two substrate atoms is energetically favorable. The adsorption energies for acetate on $Pd_{2,SN}$ and Pd_{ML} in this bridge geometry are 2.06 and 2.41 eV, much larger than those in the atop π-bond geometry with both oxygen atoms attaching to a single Pd atom, 1.50 and 1.83 eV. It is hence reasonable to believe that the bidentate acetate adsorbed on the bridge site is the initial structure for imminent reaction with ethylene on PdAu bimetallic surfaces. The difference in adsorption energies for acetate on two ensembles, 0.33−0.35 eV, reflects the ligand effect. As known, the Pd d band for Pd monomers surrounded by Au is much lower in energy than that for Pd monolayer or Pd surfaces.[8,9]

TABLE 1: Adsorption Energies (in eV) of Ethylene (E_{ethylene}), Acetate (E_{acetate}), Ethyl Acetate-Like Intermediate ($E_{\text{intermediate}}$), and VA (E_{VA}) (ΔE and E_a Are the Reaction Energy and Activation Energy for the Coupling of Ethylene and Acetate)

	$Pd_{2,SN}$/Au	Pd_{ML}/Au
E_{ethylene}	0.66	1.04
E_{acetate}	2.06	2.41
$E_{\text{intermediate}}$	2.05	2.37
ΔE	0.67	0.89
E_a	1.17	1.30
E_{VA}	0.52	0.93

As presented in Table 1, the adsorption energies of ethylene and acetate on $Pd_{2,SN}$, are significantly lower than these on Pd_{ML}. From the analysis of the projected density of d states, we found that the single Pd ensemble has a very narrow and fully occupied d band below the Fermi level[8] and hence poor reactivity due to weak binding toward reactants. For instance, the adsorption energy of CO on Pd monomer is reduced to 1.11 eV, a value that is significantly smaller than 1.39 eV for CO on the Pd(111) surface.[8] However, moderate adsorption of both ethylene and acetate on the $Pd_{2,SN}$ ensemble may actually facilitate the formation of ethyl acetate-like intermediate, as elucidated below.

4. Formation of VA

As known, VA molecules are produced in two sequential reaction steps, i.e., the formation of ethyl acetate-like intermediates and the β-H elimination. They have different reaction mechanisms and will be discussed separately in subsections 4.1 and 4.2.

4.1. Formation of Ethyl Acetate-Like Intermediate. As mentioned above, the most probable mechanism for VA production on $Pd_{2,SN}$ is that ethylene directly inserts to acetate species, followed by the β-H elimination from the ethyl acetate-like intermediate. For computational convenience, we investigated these two steps through separate NEB simulations. For the first step, we optimized the geometry of the initial state (IS), i.e., co-adsorption of ethylene and acetate on $Pd_{2,SN}$. As shown in Figure 2, ethylene now adsorbs along the [110] direction, and acetate also adjusts its position slightly. Nevertheless, the co-adsorption energy, 2.72 eV, is very close to the sum of individual adsorption energies for ethylene and acetate. This indicates that it is almost effortless for reactants to adjust their positions on $Pd_{2,SN}$ for the readiness of forthcoming reaction. In the final state (FS), the ethyl acetate-like intermediate takes two Pd sites with the C_1 and O_2 atoms, while the O_1 atom drifts to the hollow site. The C−C bond in the ethylene section is lifted upward, with a Pd−C−C angle of 117°. Meanwhile, the

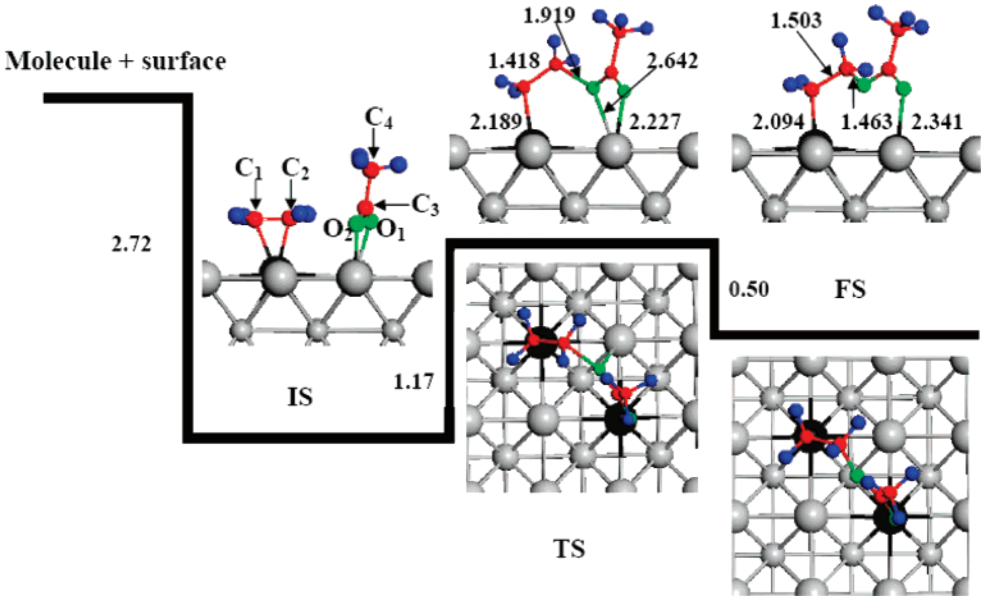

Figure 2. Energies (in eV) and geometries of initial states, TS, and FS for the coupling between ethylene and acetate on $Pd_{2,SN}$ ensemble on the Au(001) surface. The key bond lengths (in angstroms) are inserted in positions nearby.

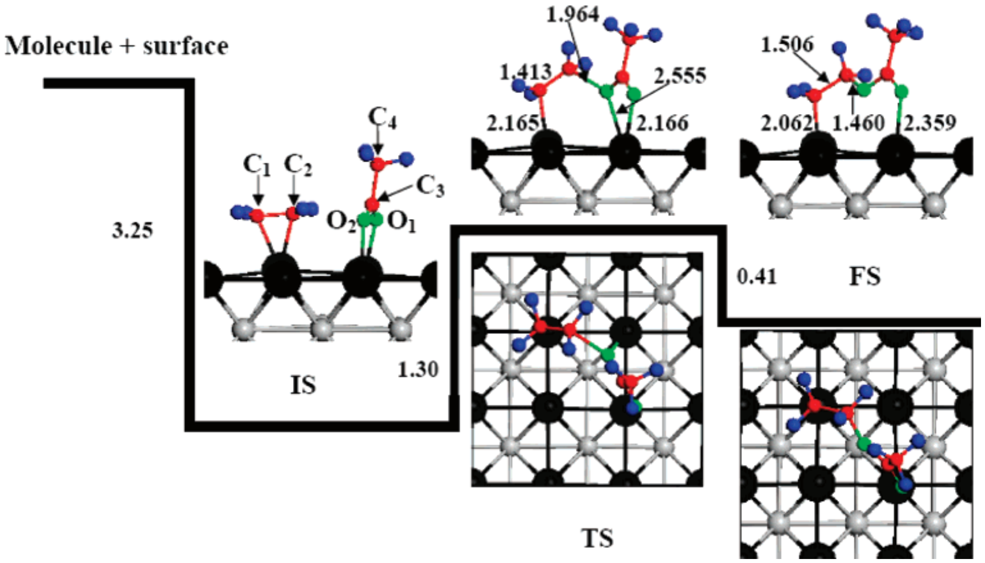

Figure 3. Energies (in eV) and geometries of initial states, TS, and FS for the coupling between ethylene and acetate on the Pd_{ML}/Au(001) surface. The key bond lengths (in angstroms) are inserted in positions nearby.

$-CH_3$ ligand in the acetate section becomes slightly tilted. The C_2-O_1 bond length is 1.463 Å, very close to the counterpart 1.459 Å in the gas-phase compound formed from ethylene and acetate. The adsorption energy of the ethyl acetate-like intermediate on the $Pd_{2,SN}$ ensemble decreases to 2.05 eV, primarily because of the shift of O_1. The formation of a new C_2-O_1 bond also weakens the C−C bond of ethylene, as manifested by a large expansion in its length from 1.33 Å in the gas-phase ethylene to 1.50 Å in the ethyl acetate-like intermediate. The reaction energy, defined as $\Delta E = E_{FS} - E_{IS}$, is +0.67 eV per product molecule (or 15.4 kcal/mol), indicating that forming an acetate-like intermediate from coadsorbed ethylene and acetate molecules is endothermic.

By use of the NEB method, we found an activation energy (E_a) of 1.17 eV, moderate for reactions around 400−500 K. Hence, the rate for ethylene−acetate combination on $Pd_{2,SN}$ is rather high.[1,3] In the transition state (TS), the C_2-O_1 bond length is 1.919 Å, and the $Au-O_1$ bond is elongated to 2.642 Å. It is obvious that the major change during the reaction lies in the acetate adsorption geometry, which turns from the [110] direction toward the [001] direction about the O−Pd bond for coupling with the adjacent ethylene molecule. Obviously, no more than two Pd atoms are crucial to anchor ethylene and acetate for this reaction, in contrast to what was found in ref 10.

To further confirm these results and also examine the ensemble effects, we also investigate the coupling of ethylene and acetate on Pd_{ML} on Au(001) with similar IS and FS. Surprisingly, both activation energy and reaction energy shown in Figure 3 (1.30 and 0.89 eV, respectively) are somewhat higher than their counterparts in Figure 2 (1.17 and 0.67 eV, respectively). This mainly stems from the fact that ethylene and acetate bind to Pd_{ML} more strongly, and therefore, it is more difficult to adjust their orientations from the initial state to transition state. Specifically, on $Pd_{2,SN}$, one Au−O bond is broken due to the rotation of acetate, but one Pd−O bond breaking occurs on Pd_{ML}. The presence of continuous Pd ensemble somewhat reduces the reaction probability of forming VA on the PdAu bimetallic surfaces. In addition, the activation energy for dissociation of ethyl acetate-like intermediate (inverse reaction)

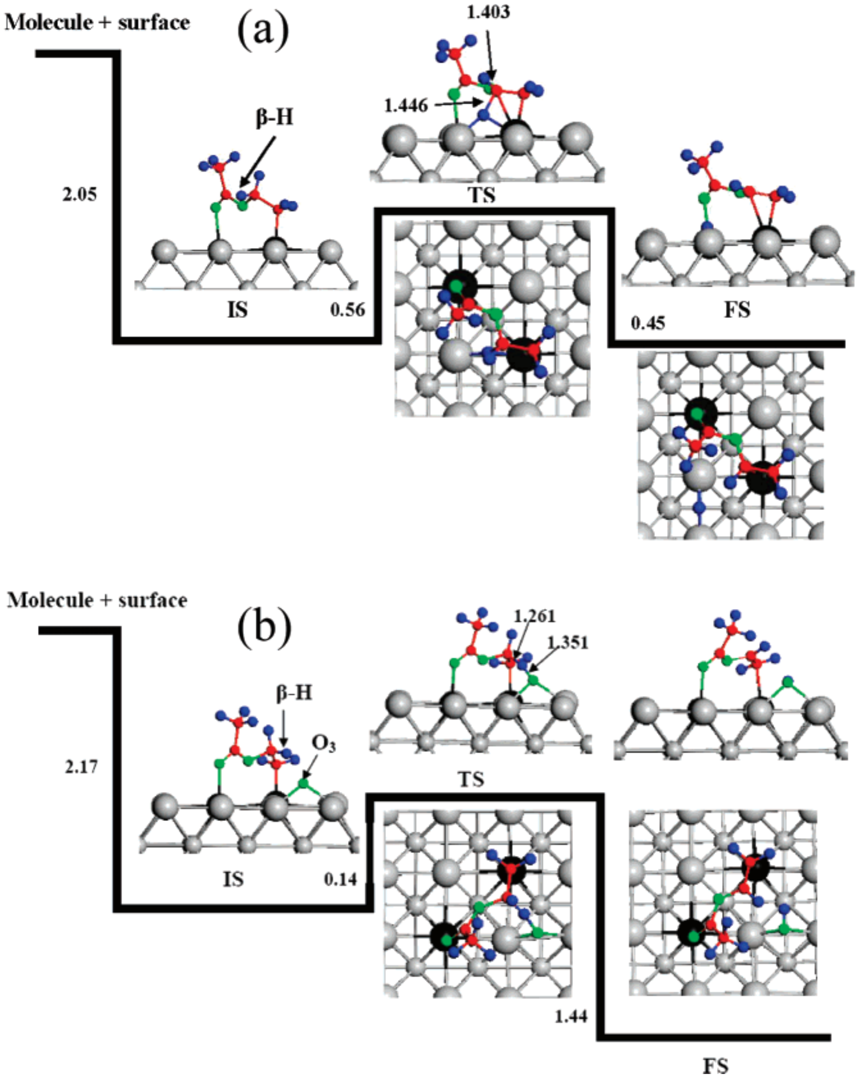

Figure 4. Energies (in eV) and geometries of initial states, TS, and FS for the β-H elimination of ethyl acetate-like intermediate (a) without or (b) with the presence of coadsorbed O on the $Pd_{2,SN}$ ensemble on the Au(001) surface. The key bond lengths (in angstroms) are inserted in positions nearby.

on Pd_{ML} is somewhat smaller than that on $Pd_{2,SN}$. Although the differences in activation energies on the two ensembles appear to be small (0.13 eV for forward reaction and −0.09 for backward reaction), one may still expect significant differences in production rates by a factor of a few tens according to the Arrhenius equation.

4.2. β-H Elimination of Ethyl Acetate-Like Intermediate on $Pd_{2,SN}$. Though the ethyl acetate-like intermediate can form on $Pd_{2,SN}$, it is unstable thermodynamically and easily decomposes into individual reactants at 500−600 K with a shallow energy barrier of 0.50 eV. To form a stable VA product, the redundant H in the ethyl acetate-like intermediate should be removed swiftly. Now we discuss the second stage of VA synthesis: β-H elimination from the ethyl acetate-like intermediate. According to previous calculations,[9] ethylene dehydrogenation is easier on Pd monolayer than on small Pd ensembles, and a very high barrier, 1.82 eV, was found for breaking a H−C bond on $Pd_{2,SN}$. The main question to answer here is whether it is possible to remove the excessive H atom from the ethyl acetate-like intermediate to form VA on $Pd_{2,SN}$.

As shown in Figure 4a, the activation energy for β-hydrogen elimination from the ethyl acetate-like intermediate on $Pd_{2,SN}$ is 0.56 eV. Therefore, this process is rather easy to occur under typical reaction conditions. The energy difference between FS and IS is +0.09 eV, and hence the reaction is slightly endothermic. In the TS, the β-hydrogen binds to the Au−Pd bridge site and still keeps a modest interaction with C with a C−(β)H bond length of 1.446 Å. Meanwhile, the C_2−O_1 bond length changes to 1.403 Å in the TS, which is close to that in the FS, 1.392 Å.

It was reported that the presence of O robustly promotes VA synthesis,[21] and we believe this may result from formation of hydroxide in the stage of β-H elimination. As shown in Figure 4b, oxygen tends to occupy the Au−Au bridge site near an ethyl acetate-like intermediate in the IS. In the FS, OH occupies the Au−Au bridge site in our limited unit cell. In reality, OH should diffuse far away because of the repulsion with VA, and the adsorption energy can be reduced further by as much as 0.26 eV with OH standing upright on the bridge site away from VA molecule. Significantly, the activation energy for β-H elimination under coexistence of O is as small as 0.14 eV, because of the energy gain from formation of strong O−H bond in the TS. Moreover, very large reaction energy of 1.30 eV is released in this process. Finally, the hydroxide can be combined with the other H (e.g., from acetic acid) into H_2O. The presence of O can thus drastically promote dehydrogenation and reduce the probability of dissociation of ethyl acetate-like intermediate back to ethylene and acetate.

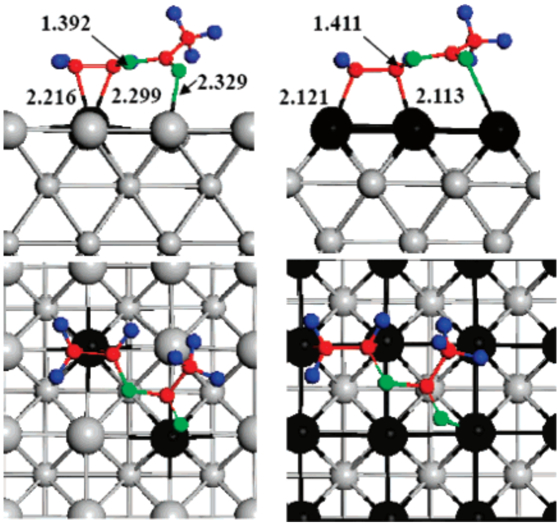

Figure 5. The adsorption configurations of VA molecule on $Pd_{2,SN}$ and Pd_{ML} on the Au(001) surface. The key bond lengths are inserted in unit of angstroms.

5. Desorption of VA

To complete the catalysis cycle, VA desorption is also an essential step to avoid catalytic poisoning. Meanwhile, VA decomposition back to vinyl and acetate can be prevented if the products rapidly depart from the catalyst surface. The optimized geometries for VA adsorption on $Pd_{2,SN}$ and Pd_{ML} shown in Figure 5 indicate that the CH_3- radical falls toward the substrate after the removal of the β-H. The ethylene−acetate interaction is much strengthened with the formation of strong C−O bond, whereas the VA−substrate interaction is weakened. As a result, the calculated adsorption energies of VA on $Pd_{2,SN}$ and Pd_{ML} are 0.52 and 0.93 eV (shown in Table 1), respectively. Clearly, VA molecules formed on $Pd_{2,SN}$ can easily leave the substrate at a reaction temperature of 400−500 K, and hence, the whole catalytic cycle remains active for VA production. From E_{VA}, the desorption rate for VA on Pd_{ML} is expected to be much smaller than that on $Pd_{2,SN}$. One may argue that desorption of VA is not the rate-limiting step since $E_{VA} < E_a$. However, VA also has a good chance to dissociate to smaller molecules on substrate according to the small activation energy for the reversed reaction.[22] Therefore, rapid desorption is beneficial for VA production by preventing both poisoning and reaction reversal. In Figure 5, it is interesting to see that VA adsorb on different sites on $Pd_{2,SN}$ and Pd_{ML}. On $Pd_{2,SN,}$ the vinyl radical takes the π-bond geometry on Pd and one O atom is anchored on top of another Pd atom. The separation between the two Pd atoms is just right for the size of VA molecule. On Pd_{ML}, the vinyl radical adopts the σ-bond geometry, and the acetate section is dragged toward the hollow site. The sizable adsorption energy of VA on Pd_{ML} originates from strong Pd−C bonding in the vinyl side.

6. Conclusions

By use of the first-principles method, we identified the most probable reaction paths for the synthesis of VA on PdAu bimetallic surfaces. Significantly, we found that the most efficient reaction processes take place on $Pd_{2,SN}$, the smallest Pd second neighbor ensemble, with several facilitating factors: (1) neither ethylene and acetate decomposes, (2) ethylene and acetate may easily adjust their alignments, (3) the two Pd atoms provide proper anchors for both reactants in the transitions state and so the activation energy is small, and (4) the product can take off at regular reaction temperature so the catalytic cycle remains active. As summarized in Table 1, the availability of excessive Pd atoms in their first neighborhoods is detrimental due to overbinding for both reactants and products. Our results indicate the usefulness of density functional calculation for studies of catalytic properties despite the fact the absolute value of energies might be still somewhat off with GGA functionals. It is clear that the ensemble effects play an essential role for properties of complex nanocatalysts and should be explored more extensively in the future.

Acknowledgment. We acknowledge simulative discussions with Dr. M. S. Chen and Prof. D. W. Goodman. Work was supported by the DOE-BES (Grant No. DE-FG02-04ER15611). Calculations are performed on supercomputers in the NERSC.

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