Ensemble effects on ethylene dehydrogenation on PdAu(001) surfaces investigated with first-principles calculations and nudged-elastic-band simulations

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The ensemble effects on adsorption and dehydrogenation of ethylene on PdAu(001) bimetallic surfaces are systematically investigated through first-principles calculations and nudged-elastic-band simulations. Significantly, we find that ethylene dehydrogenation is inhabited under ambient reaction temperature on the most popular second-neighbor Pd ensembles, because of the insufficient attraction of Au and Pd-Au bridge sites toward vinyl and the eliminated hydrogen in the transition state. This finding is essential for understanding the mechanism of complex reactions on such bimetallic catalysts and the synthesis of vinyl acetate. Linear correlations are found among the activation energies, reaction energies, and adsorption energies, but no obvious relationship exists between the surface activity and the Pd *d*-band center.

Bimetallic surfaces with tunable chemical properties show an ample potential for electrocatalysis and heterogeneous catalysis applications and, therefore, have attracted broad attention in recent years.[1] For instance, PdAu bimetallic catalysts are highly effective in promoting a variety of reactions such as CO oxidation,[2,3] H_2 oxidation to H_2O_2,[4] alcohol oxidation,[5] and vinyl acetate (VA) synthesis.[6] The local chemical properties of constituents are strongly altered from their parent metals by the "ligand effects," which generally describe influences of charge transfer, orbital rehybridization, and lattice strain.[7,8] Extensive experimental and theoretical studies have established clear correlations between the chemical activity of bimetallic surfaces and their electronic features such as core level shift and position of *d*-band center with respect to the Fermi level.[7,9,10] On the other hand, the "ensemble effects" associated with particular arrangements of the active constituents have received much less attention, even though they are equally or, in some cases, more important toward the reactivity and selectivity of bimetallic catalysts. Chem *et al.* found that the presence of "Pd monomer pairs" is the primary reason for the remarkable enhancements in vinyl acetate formation rates on PdAu(001).[6] Therefore, it is crucial to attain comprehensive understandings of the ensemble effects for the rational design of robust catalysts. From measurements with scanning tunneling microscope, temperature programed desorption (TPD), and infrared-absorption spectroscopy, Maroun *et al.*[11] and Luo *et al.*[12] found that the population of the Pd first neighborhoods is extremely small on PdAu(001) and PdAu(111) bimetallic surfaces annealed up to 800 K. This observation was explained in our recent density-functional studies, and, furthermore, we pointed out the energy preference of forming various Pd second neighborhoods on these bimetallic surfaces.[13]

In this Brief Report, we address the consequence of the lack of first Pd neighborhoods on adsorption and dehydrogenation of ethylene on PdAu(001). Many chemical reactions involve the dehydrogenation of ethylene but the mechanism of this reaction is still elusive. Complete dehydrogenation of ethylene occurs easily on pure Pd surfaces, which results in the formations of Pd carbides during VA synthesis on Pd

surfaces or large Pd clusters.[14] Although it was reported that the alloying of Au with Pd effectively prevents PdC_x formation,[15] it is unclear if ethylene molecules partially decompose on PdAu. Clear understanding of ethylene dehydrogenation is imperative for appreciating complex reactions such as VA synthesis.[16] The key results of our systematic density-functional calculations is that (1) the adsorption geometry and adsorption energy are strongly ensemble dependent, (2) ethylene does not dehydrogenate on PdAu(001) which has negligible amount of Pd first neighborhoods, and (3) the reaction energy and activation energy are correlated to adsorption energy. This clearly demonstrates the particular importance of the ensemble effects on adsorption and reaction on complex surfaces.

The calculations are performed using the plane-wave based Vienna *ab initio* simulation package,[17] in the level of generalized gradient approximation with the PW91 functional.[18] The effects of nuclei and core electrons are represented by ultrasoft pseudopotential.[19] To ensure the numerical convergence, the plane-wave expansion has a large energy cutoff of 350 eV, while the reciprocal space is sampled by $5 \times 5 \times 1$ *k* points in the Monkhorst-Pack[20] grids. The Au(001) surfaces are modeled with a four-layer slab and a 15 Å vacuum. In the lateral plane, we use a $c(4 \times 4)$ supercell, as shown in Fig. 1, so as to reduce the interaction between adjacent adsorbates. Representative Pd distribution patterns in the outmost layer include isolated Pd monomers as well as Pd second and first neighborhoods. We begin with adsorption studies of ethylene, vinyl, and hydrogen on different ensembles. The positions of all atoms except those in the two bottommost Au layers are fully relaxed according to the calculated atomic forces. The preferential adsorption sites of ethylene on different ensembles are sketched in Fig. 1 for geometries with its C–C bond aligned along the [100] and [110] axes. The minimum-energy paths (MEPs) and activation energies for C–H bond breaking are obtained with the climbing image Nudged-Elastic-Band (CI-NEB) approach.[21–24]

We started from investigating the adsorption of ethylene on various ensembles of the PdAu(001) bimetallic surfaces.
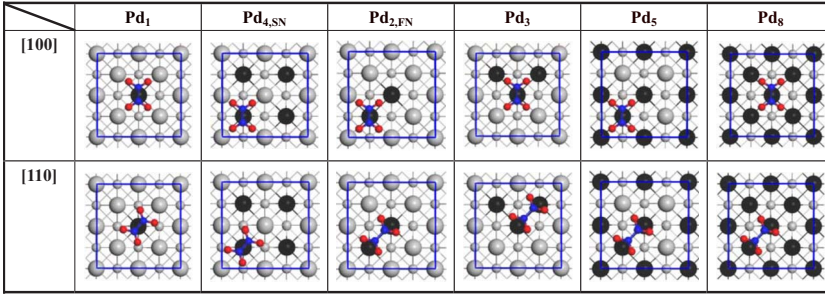
FIG. 1. (Color online) The unit cells and structures of different Pd ensembles on PdAu(001), along with stable adsorption geometries of an ethylene molecule. The large and small gray balls represent surface and subsurface Au atoms. The black balls are Pd atoms, and small blue and red balls are for C and H atoms, respectively.

Their chemical activities toward ethylene can be characterized by adsorption energies

$$E_{\text{ad,ethylene}} = -(E_{\text{ethylene/PdAu}} - E_{\text{PdAu}} - E_{\text{ethylene}}), \quad (1)$$

where the quantities in parentheses are the total energies of different systems. As known, ethylene takes two stable adsorption geometries on the pure Pd(001) surface, illustrated by different orientations of its C–C bond along either the [100] (π-bonded-type) or the [110] (di-σ-bonded) axis. As listed in Table I, our calculations indicate that the di-σ-bonded geometry is more favorable on all ensembles except Pd$_5$. For comparison, the calculated $E_{\text{ad,ethylene}}^{[100]}$ and $E_{\text{ad,ethylene}}^{[110]}$ on the clean Pd(001) surface are 0.82 and 0.94 eV, respectively. These data are very close to the results of other density-functional calculations.[25] It is apparent that ethylene adsorbs stably on all the ensembles of PdAu(001) at room temperature, as was observed experimentally.[12] On an isolated Pd monomer (Pd$_1$) and second neighborhoods (Pd$_{2,\text{SN}}$ and Pd$_{4,\text{SN}}$), the ethylene molecule takes the top site over Pd and the change in orientations of the C–C bond hardly affects adsorption energies. Unlike CO, which mostly probes the properties of a single Pd site,[13] C$_2$H$_4$ becomes aware of the presence of the second-neighbor Pd as manifested by the noticeable increase in $E_{\text{ad,ethylene}}$ on the Pd$_1$, Pd$_{2,\text{SN}}$, and Pd$_{4,\text{SN}}$ ensembles.

The interaction between ethylene and metal surfaces is described in the framework of the Dewar-Chatt-Duncanson model:[26,27] the filled π_{CC} orbital of ethylene highest occupied molecular orbital donates charge to the empty d orbitals of metal substrates, while the occupied d orbitals of metal back donate charge to the antibonding π_{CC}^* orbital of ethylene lowest unoccupied molecular orbital. Similar to what occurs on Pd(001), ethylene prefers the di-σ-bonded geometry over the Pd-Pd bridge site on Pd first neighborhoods. Overall,

$E_{\text{ad,ethylene}}$ increases monotonically as the number of Pd atoms in the ensemble grows. Particularly, $E_{\text{ad,ethylene}}$ on the Pd$_8$ (a complete Pd monolayer) are larger than those on the clean Pd(001) surface, owing to both strain and chemical effects. From the projected density of states (PDOS) of ethylene and Pd d states of clean and adsorbed PdAu surfaces in Fig. 2, it is obvious that both π_{CC} and π_{CC}^* states are broadened into a wide energy range. Accordingly, the Pd d states are shifted to the low-energy region, compared to the PDOS of the clean PdAu(001) surfaces. Although the Pd d band shift is more appreciable on larger Pd ensembles, the mechanism of ethylene-Pd interaction appears to be the same as manifested by the similarity between PDOS curves for ethylene in different panels of Fig. 2.

The adsorption geometries displayed in Fig. 1 can be viewed as the initial states (IS) for the dehydrogenation process. In the final states (FS), we have vinyl (or CH$_2$CH), a univalent chemical radical, and the eliminated hydrogen atom on the PdAu(100) bimetallic surface. Since both of them need to be accommodated in a small region, the ensemble effect is expected to play a more significant role in the final states. We found that both H and CH$_2$CH take the Pd-Pd or Pd-Au bridge sites in the final state, as sketched in Fig. 3. To identify the easiness of dehydrogenation, we calculated both the reaction energy ($\Delta E = E_{\text{FS}} - E_{\text{IS}}$) and the activation energy (E_a) for C–H bond breaking through total energy and CI-NEB simulations. The CI-NEB approach has been successfully applied in theoretical studies of various chemical reactions, including dehydrogenation of ethylene on Pd(111) and Pd/Au(111).[28,29] As benchmarks, the calculated values of ΔE and E_a are 0.54 and 1.04 eV on the clean Pd(001) surface, where ethylene can be easily dehydrogenated. As list in Table I, ΔE and E_a on large first-neighbor Pd ensembles (Pd$_3$, Pd$_5$, and Pd$_8$) are comparable to those on the Pd(001) surface, whereas they are twice larger on Pd mono-

TABLE I. The adsorption energies for ethylene ($E_{\text{ad,ethylene}}^{[100]}$ and $E_{\text{ad,ethylene}}^{[110]}$), the reaction energies (ΔE), and activation energies (E_a) for breaking a C–H bond of ethylene, and the positions of the Pd d band centers with respect to the Fermi levels ($E_{\text{Pd}\,d}$) on different ensembles of the PdAu(001) bimetallic surface as well as on the clean Pd(001) surfaces. All energies are given in eV.

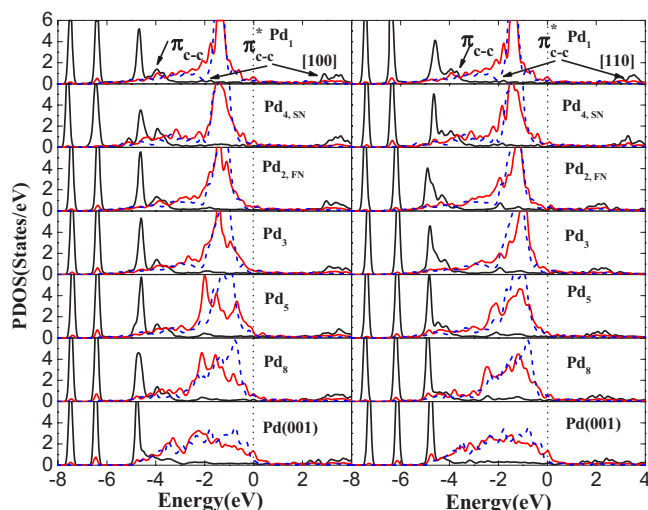|	Pd$_1$	Pd$_{2,\text{SN}}$	Pd$_{4,\text{SN}}$	Pd$_{2,\text{FN}}$	Pd$_3$	Pd$_5$	Pd$_8$	Pd(100)
$E_{\text{ad,ethylene}}^{[100]}$	0.54	0.63	0.65	0.68	0.76	0.91	0.87	0.82
$E_{\text{ad,ethylene}}^{[110]}$	0.56	0.66	0.69	0.74	0.83	0.90	0.98	0.94
ΔE	1.34	1.19	1.08	1.01	0.88	0.66	0.50	0.54
E_a	1.83	1.82	1.68	1.26	1.13	0.95	0.83	1.04
$E_{\text{Pd}\,d}$	−1.47	−1.41	−1.38	−1.37	−1.32	−1.35	−1.28	−1.58

FIG. 2. (Color online) The PDOS of ethylene (black lines) and Pd d states (red lines) for C_2H_4/PdAu(100). Pd d states of the clean PdAu(001) surface are plotted with the blue dashed line.

mers and second neighborhoods. Since the reaction probability scales exponentially with E_a, it is obvious that Pd monomers and second neighborhoods on PdAu(001) are incapable in facilitating C–H bond breaking for ethylene.

On the other hand, it was revealed both experimentally and theoretically that the population of Pd first neighborhoods is very small on annealed PdAu(001). The Pd formation energy, defined as $E_{Pd}=-[E_{PdAu}-E_{Au\text{-}slab}+N_{Pd}(E_{Au\text{-}bulk}-E_{Pd\text{-}atom})]/N_{Pd}$, of ensembles comprising Pd second neighborhoods (e.g., 3.61 eV for $Pd_{2,SN}$) is remarkably larger than those of Pd first neighborhoods (e.g., 3.56 eV for $Pd_{2,FN}$). Ethylene molecules are thereby unlikely to be decomposed on the PdAu(001) bimetallic surfaces from the reason discussed in the last paragraph, a conclusion that is in good accordance with the experimental observations of Luo *et al.* in their (TPD) measurements.[12] This finding is imperative for
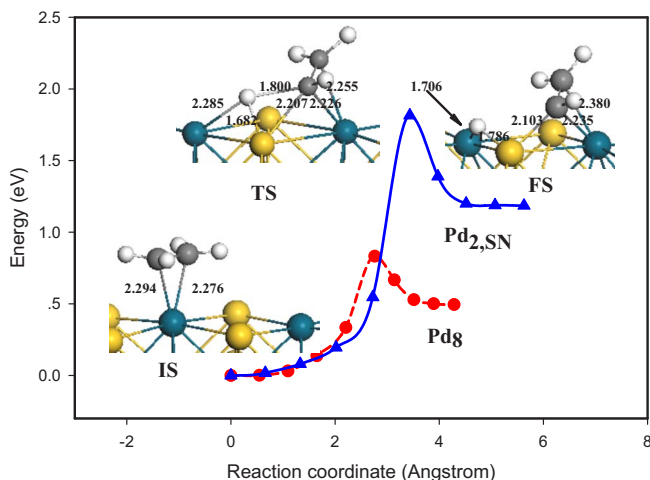

FIG. 3. (Color online) Reaction energy diagrams and atomic configurations for ethylene dehydrogenation on ensembles of $Pd_{2,SN}$ and Pd_8. Some key bond lengths are given for initial, transition, and final states on $Pd_{2,SN}$.
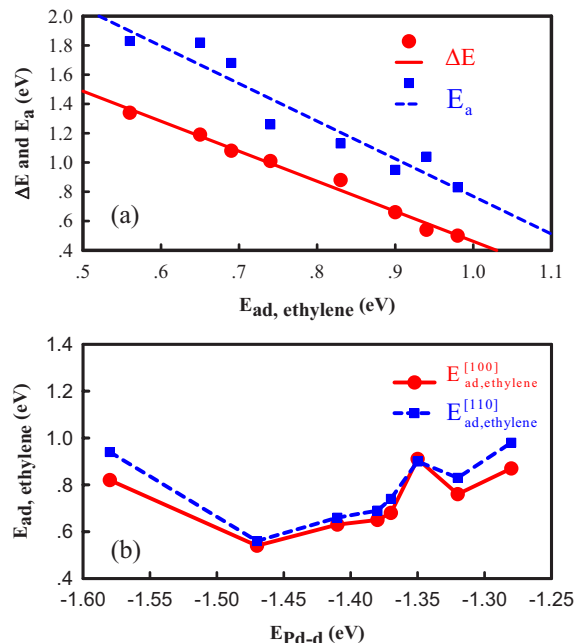

FIG. 4. (Color online) The correlations among (a) E_a, ΔE, and $E_{ad,ethylene}$, and (b) $E_{ad,ethylene}^{[100]}$, $E_{ad,ethylene}^{[110]}$, and $E_{Pd\ d}$.

understanding more complex reactions that require ethylene dehydrogenation as the precursor step.

We want to point out here that the dramatic change in E_a is primarily determined by the ensemble effect, whereas the ligand effect plays only a minor role. To elucidate the origin of the difference between activation energies on Pd first and second neighborhoods, we present in Fig. 3 the energies along the paths of eliminating one H atom from the ethylene molecule on the $Pd_{2,SN}$ and Pd_8 ensembles. For both cases, the vinyl molecule and eliminated H atom take the adjacent Pd-Pd or Pd-Au bridge site in the final states. Separate calculations revealed that the adsorption energies for hydrogen and vinyl on Pd-Pd bridge site are about 0.4 eV larger than those on the Pd-Au bridge site. Furthermore, one CH_2 fragment needs to be placed on the unfavorable Au site in the transition state of ethylene dehydrogenation on Pd monomers or second neighborhoods. As a result, E_a strongly surges on these ensembles and the dehydrogenation is expected to be inhabited.

Since calculations for ΔE and E_a are computationally demanding, it is instructive to inspect their correlations with $E_{ad,ethylene}$ on different ensembles. Interestingly, both ΔE and E_a scales almost linearly with $E_{ad,ethylene}$ in Fig. 4(a).[30] ΔE can also be determined through adsorption energies of C_2H_4, CH_2CH, and H as

$$\Delta E = E_{ad,ethylene} - E_{ad,vinyl} - E_{ad,H} + 4.93 \text{ eV}. \quad (2)$$

Here, 4.93 eV represents the energy required for breaking a CH bond of ethylene in vacuum. Since H and vinyl take the bridge sites, both $E_{ad,vinyl}$ and $E_{ad,H}$ are *more* sensitive to the ensemble underneath than $E_{ad,ethylene}$. As a result, $\Delta E \sim E_{ad,ethylene}$ line in Fig. 4(a) shows a negative slope, -2.05 (or $E_{ad,vinyl}+E_{ad,H}=3.05E_{ad,ethylene}+2.43$ eV). The same argu-

ment can be used for understanding of the monotonic relationship between E_a and $E_{ad,ethylene}$ but the interaction between H and vinyl in the transition state is non-negligible and ensemble dependent. Therefore, the quality of linear fitting for the $E_a \sim E_{ad,ethylene}$ data is less satisfactory in Fig. 4(a) with a root-mean-square residue of about 0.13 eV. Nevertheless, it appears that one can reasonably estimate the catalytic behavior of different ensembles from adsorption energies of reactants alone. This is certainly useful in expediting the process for identifying key ensembles through theoretical calculations. Liu and Hu also found correlations between adsorption energy of reactants and reaction barriers for several oxidation and hydrogenation reactions, but the trend is opposite to what we observed here.[31] This is because the products in those reactions are formed by combining two reactants while here the reactant splits into two pieces.

It is useful to correlate $E_{ad,ethylene}$ to more fundamental electronic properties of the substrate such as Pd d band center with respect to the Fermi level, $E_{Pd\,d}$. Unfortunately, the $E_{ad,ethylene} \sim E_{Pd\,d}$ plot shown in Fig. 4(b) displays no obvious correlation between these two quantities.[32] This is understandable since $E_{ad,ethylene}$ now strongly depends on the ensemble effect, whereas $E_{Pd\,d}$ only reflects the ligand effect. From Table I, it can be found that $E_{Pd\,d}$ changes only slightly for all the ensembles, whereas $E_{ad,ethylene}$ swings in a large range. Therefore, $E_{Pd\,d}$ is no longer a good measure for the

local activity of different ensembles on bimetallic surfaces. For uniform surfaces such as Pd$_8$ and Pd(001), however, the correlation between E_{ad} and $E_{Pd\,d}$ appears to hold. For example, $E_{Pd\,d}$ of Pd$_8$ is higher by 0.30 eV compared to that of pure Pd(001) surface. Accordingly, $E_{ad,ethylene}$ on the former is larger by 0.05 eV.

To conclude, first-principles calculations indicate that the dehydrogenation of ethylene is unlikely to occur on the PdAu(100) bimetallic surfaces. This mainly stems from the inability of the popular Pd second ensembles to simultaneously provide strong attraction for vinyl and H. The ensemble effects are extremely important for the adsorption, decomposition, and chemical reaction of large molecules on bimetallic surfaces. Interestingly, we found a correlation between activation energy and adsorption energy, which allows quick estimation of reaction rates without calculations for the transition and final states. Furthermore, since the ensemble effects play a dominant role, the center of Pd d band cannot measure the surface activity.

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[30] The fitting functions for ΔE and E_a are $\Delta E = -2.05 E_{ad,ethylene} + 2.50$ and $E_a = -2.57 E_{ad,ethylene} + 3.40$, with rms residues of 0.037 and 0.128 eV, respectively.

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[32] Technically, it is difficult to obtain accurate results for $E_{Pd\,d}$ since the d shell is open and the partial d-DOS has a long tail in the unoccupied region as shown in Fig. 4. Actually, different authors reported diverse results for $E_{Pd\,d}$ for the same system, e.g., from −2.01 to −1.46 eV for the Pd(111) surface [see, Ref. 27 and R. Hirschl and J. Hafner, Surf. Sci. **498**, 21 (2002); A. Roudgar and A. Groβ, *ibid.* **559**, L180 (2004)]. In the present calculations, we terminate the upper limit of energy integrals up to 4.0 eV above the Fermi level for the determination of $E_{Pd\,d}$.