Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/catalysis

Comparison of the coupling of ethylene with acetate species and ethylene dehydrogenation on Pd-Au(100): a density functional study

Yanping Huang[ab], Xiuqin Dong[a], Qiufeng Hao[a], Yingzhe Yu[a,*1], Minhua Zhang[a,*2]

[a]Key Laboratory for Green Chemical Technology of Ministry of Education,

R＆D Center for Petrochemical Technology, Tianjin University, P R China

[b]Collaborative Innovation Center of Chemical Science and Engineering (Tianjin)

Tianjin 300072, P R China

[*1] Corresponding author. Tel.: +86-22-27405972; fax: +86-22-27406119.

E-mail address: yzhyu@tju.edu.cn (Yingzhe Yu)

[*2] Corresponding author. Tel.: +86-22-27406119; fax: +86-22-27406119.

E-mail address: mhzhangtj@163.com (Minhua Zhang)

Abstract

In this work, two key reactions in Vinyl Acetate monomer (VAM) synthesis, i.e., the coupling of ethylene with acetate species and ethylene dehydrogenation, on three different Pd-Au(100) surface configurations-the second nearest neighbors (noted as PdsnAu), the first nearest neighbors (noted as PdfnAu), and the four nearest-neighbor palladium island (noted as PdislAu)-were calculated. The energy barriers of the transition state of ethylene dehydrogenation to vinyl and the coupling of ethylene with acetate species on three different Pd-Au (100) surfaces were calculated. The influence of the surface properties of Pd-Au(100) on the reaction performance was analyzed and discussed on the microscope level. The results found that on PdsnAu surface and PdfnAu surface where the coverage of the surface Pd atoms is relatively low, it is more likely for the coupling of ethylene with acetate species to occur, while on PdislAu surface where the coverage of the surface Pd atoms is relatively high, it is more likely for ethylene dehydrogenation to happen. This work will improve the comprehension of the catalytic mechanism of Pd-Au (100) on the molecular level and electronic level and provide theoretical guidance for further application and development of efficient commercial catalysts, and the control of the reaction.

Keywords: Vinyl Acetate monomer; Dehydrogenation; Coupling reaction; Activation energy

1. Introduction

Vinyl Acetate monomer (VAM) is an important chemical intermediate for polyvinyl alcohol and poly vinyl acetate, which are widespread polymers applied as paints, adhesives, coatings and fibers. Acetoxylation of ethylene on supported Pd-Au catalysts is a well-established commercial route for the VAM synthesis[1,2], according to the following reaction:

$$CH_3COOH+C_2H_4+1/2O_2 \rightarrow CH_3COOCHCH_2+H_2O \quad (1)$$

It is known that alloying Pd catalyst with gold leads to a significant improvement in catalytic activity and selectivity[3] for the VAM synthesis. Neurock et al.[4] studied the influence of the coverage of the reactants and products on the surface on the reaction pathways and the selectivity. They found that higher coverage of Au eliminates the larger Pd emsembles that facilitates the decomposition of VAM and ethylene, thus increasing the reaction selectivity and weakening the adsorption of ethylene and acetate. However, higher coverage of Au also inhibits the activation of O_2, which decreases the rate of acid deprotonation, thus resulting in optimal Pd-Au compositions.

VAM synthesis from ethylene is based on Langmuir-Hinshelwood coadsorption reaction process[5,6,7]. 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. [8] found that O_2 can facilitate dehydrogenation of acetic acid on the catalyst surface to yield acetate species. Based on whether ethylene dehydrogenation happens before ethylene couples with acetic acid, researchers proposed two possible reaction pathways (shown in Figure 1): (1) Samanos et al. [9] 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. [10, 11] argued that ethylene adsorbed on the surface first undergoes dehydrogenation to form vinyl (-CH-CH_2) species, and then couples with the acetate species adsorbed on the surface to yield VAM. This reaction pathway is named as M-mechanism. Calaza et al.[12] studied the reaction between gas-phase ethylene and adsorbed acetate species on Pd(100) surface with infrared spectroscopy, which found that hydrogen is involved in the rate-limiting step.

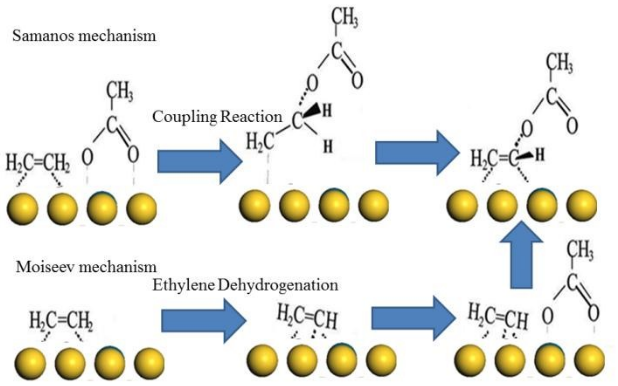


Figure 1 two possible pathways of VAM synthesis

As the surface properties of the catalyst and the adsorption properties of reactants are two fundamental factors for comprehension of the catalytic mechanism and rational design of robust Pd-Au cataslysts, further detailed theoretical investigations are needed.

Studies have suggested that the influence of alloying on surface adsorption properties can be described either in terms of the electronic effect or the geometric effect[13]. With Temperature-programmed desorption (TPD) and RAIRS, Calaza et al. systematically studied the interaction of ethylene[14], acetic acid and acetate species [15,16] on Pd-Au alloys with different surface ratios of Pd-Au, which found that the adsorption geometries and adsorption energies are closely related to the surface gold coverage. Theoretically, a redistribution of electrons among surface Pd and Au atoms can affect the bond strength of Pd-adsorbate; however, in many cases, it is challenging to distinguish the change between electronic effect and geometric effect since the formation of a geometrically favorable binding site is accompanied by an electronic effect. Rivalta et al. [17] intensively investigated the adsorption properties of the reactants, employing DFT methods but considering only a second-nearest neighbor Pd monomer pair. Since Chen et al.[18] found the VAM formation rate strongly depends on the local structure, and introduced geometric effect to explain the significant enhancement of the VAM formation rate on Pd-Au(100) with the surface Pd coverage of 0.10 ML. Han et al.[19] used ultrahigh vacuum (UHV) scanning tunneling microscopy (STM) and low-energy ion scattering spectroscopy (LEISS) to characterize the active Pd-Au(100) surface. They found that there are three primary kinds of configurations: Pd monomer, the first nearest neighbors (noted as PdfnAu) and the second nearest neighbors (noted as PdsnAu), while few higher-coordinated surface configurations (such as the Pd trimer and multiple continuous Pd) exist. Since VA synthesis follows Langmuir−Hinshelwood mechanism, the possibility that the Pd monomer acts as the active site can be excluded. However, whether PdfnAu can act as the active site still can’t be determined. Thus, in this study, PdislAu was chosen for comparison to systematical study the surface properties of PdfnAu and PdsnAu .

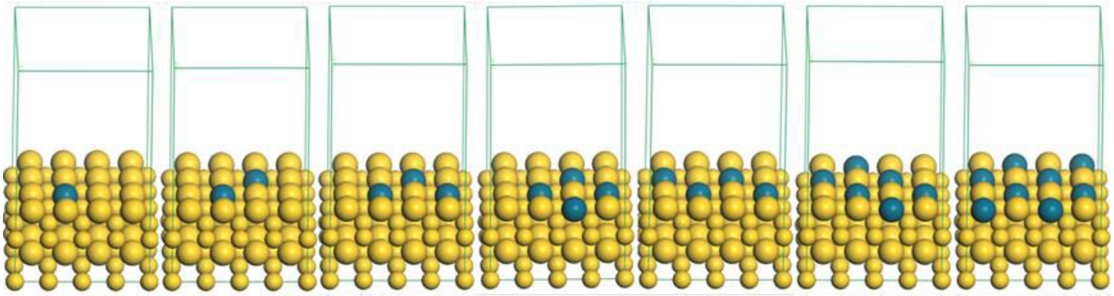
Since the difference of S-mechanism and M-mechanism lies in whether ethylene directly forms vinyl species through dehydrogenation or ethylene directly couples with acetate species to generate Vinyl Acetate-like intermediate (acetoxyethyl-palladium), in this work, two key reactions in VAM synthesis i.e., the coupling of ethylene with acetate species and ethylene dehydrogenation, on Pd-Au(100) surface were calculated. All the transition states had a single imaginary frequency. The energy barriers of the transition state of the coupling of ethylene with acetate species and ethylene dehydrogenation to vinyl on the surfaces of three different Pd-Au surface configurations were calculated. The influence of the surface properties of Pd-Au(100) on the reaction performance was analyzed and discussed at the microscope level. This work will improve the comprehension of the catalytic mechanism of Pd-Au (100) on the molecular and electronic level and provide theoretical guidance for further application and development of efficient commercial catalysts, and the control of the reaction.

2. Theoretical Methods

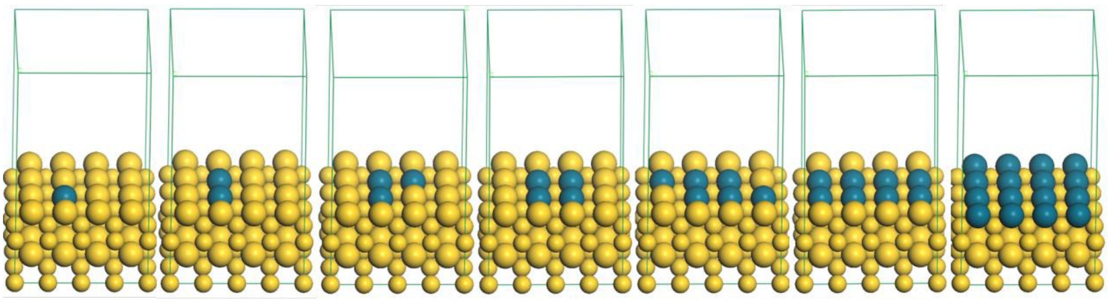
2.1. Computational model

Two groups of Pd-Au surface configurations have been built, as is shown in Figure 2. In group a (successively noted as Pd_1Au, PdsnAu, Pd_3snAu, Pd_4snAu1,

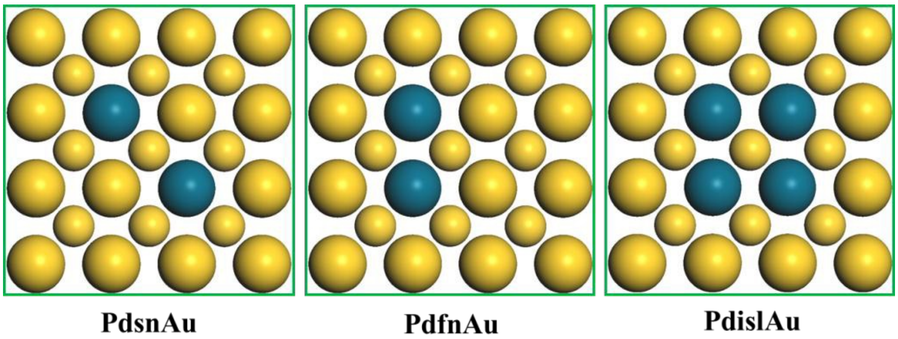
Pd_4snAu_2, Pd_6snAu and Pd_8snAu), Pd atoms are noncontinuous, while in group b (successively noted as Pd_1Au, PdfnAu, Pd_3fnAu, Pd_4fnAu, Pd_6fnAu, Pd_8fnAu and PdmlAu), Pd atoms are continuous.



a. Non-continuous Pd



b. Continuous Pd



c. Chosen ensembles on Pd-Au(100) surfaces

Figure 2 different ensembles on Pd-Au(100) surfaces (Yellow balls represent Au, and blue ones are Pd; the large and small balls represent different surface layers)

The surface formation energy of Pd atom, ΔE_{Pd}, can determine which kind of alloy surface is more likely to form at different surface coverages. The formation energy can be defined in Formula 1[20,21].

$$\Delta E_{\mathrm{Pd}} = [E_{\mathrm{Pd\text{-}Au}} - E_{\mathrm{Au\text{-}surf}} + N_{\mathrm{Pd}}\,(E_{\mathrm{Au\text{-}bulk}} - E_{\mathrm{Pdatom}})] / N_{\mathrm{Pd}} \qquad \text{Formula 1}$$

where $E_{\mathrm{Pd\text{-}Au}}$, $E_{\mathrm{Au\text{-}surf}}$, $E_{\mathrm{Au\text{-}bulk}}$ and E_{Pdatom} represent the total energy of Pd-Au alloy surface, pure Au(100) surface, bulk Au atoms, and single Pd atom, respectively; N_{Pd} represents the number of Pd atoms on the surface; E_{Pdatom} can be estimated by building a cubic cell with a single Pd atom with the vacuum slab of 10 Å in all directions.

The surface formation energy and coverage of Pd on different Pd-Au(100)surface configurations in group a and group b were calculated from Formula 1 as is shown in Table 1.

Table 1 The formation energy and coverage of Pd on different Pd-Au(100) surface configurations

Group	Surface	Coverage /ML	Formation energy /eV
a	Pd_1Au	0.063	-2.764
	Pd_2snAu	0.125	-2.771
	Pd_3snAu	0.188	-2.766
	Pd_4snAu_2	0.250	-2.764
	Pd_4snAu_1	0.250	-2.764
	Pd_6snAu	0.375	-2.757
	Pd_8snAu	0.500	-2.756
b	Pd_1Au	0.063	-2.764
	Pd_2fnAu	0.125	-2.739
	Pd_3fnAu	0.188	-2.732
	Pd_4fnAu	0.250	-2.714
	Pd_6fnAu_2	0.375	-2.701
	Pd_8fnAu	0.500	-2.677
	PdmlAu	1.000	-2.656

From Table 1, when the coverage of Pd remains unchanged, the absolute values of the formation energy in group a are obviously higher than those in group b, suggesting non-continuous Pd atoms separated by Au atoms are more likely to form. Besides, the absolute value of formation energy of Pd_2snAu, or PdsnAu, is the largest, suggesting that Pd_2snAu is the most stable surface configuration.

Previous studies[4,22,23] have found that as for VAM synthesis, Pd-Au(100) surface is far more active than Pd-Au(111) surface. Thus, in this study, Pd-Au(100) surface was chosen as the study object. Chen[18] et al. systematically studied the VAM synthesis reaction on Pd-Au surfaces with different Pd coverages. They found that TOF of VAM is the highest when the coverage of Pd on Pd-Au(100) is about 0.1 ML. Since the Pd coverage of Pd_2snAu (i.e., PdsnAu) on Pd-Au(100) surface is 0.125 ML, close to the optimum of 0.1 ML. Therefore, in this study, PdsnAu on Pd-Au(100) surface was chosen as the study model. Pd_2fnAu (i.e., PdfnAu) and Pd_4fnAu (i.e., PdislAu) were chosen for comparison.

In this study, the stable co-adsorption configurations of ethylene and acetate species on PdsnAu, PdfnAu and PdislAu on Pd-Au(100) surface (shown in Figure 2) were selected as the reactants (Initial State, IS) of the coupling of ethylene with acetate species. Based on such configurations, the product of the coupling reaction, the Vinyl Acetate-like intermediate (Transition State, TS), acetoxyethyl-palladium (Final State, FS), was built. Also, the stable adsorption configurations of ethylene on the PdsnAu, PdfnAu and PdislAu were selected as the initial reactants of ethylene dehydrogenation. Based on such configurations, the co-adsorption configurations of the ethylene dehydrogenation products, vinyl and H, were built. Then, the transition-state search was conducted.

2.2. Computational method

The calculations were conducted on the basis of spin unrestricted density functional theory (DFT) calculations with DMol^3 in Materials Studio, using the generalized gradient approximation (GGA) with RPBE[24] as the exchange-correlation functional. To maintain the balance between the computational efficiency and accuracy, the core treatment was set to DFT Semi-core Pseudo-potential (DSPP). The convergence standard of the electron density was 1.0×10^{-5} eV and the geometry was optimized until the force on each atom was less than 0.004 Ha/Å by using smearing of 0.005 Ha. The Pd-Au(100) surface was modeled, using a 4×4 unit cell consisting of four layers of atoms with 15 Å of vacuum. The bulk Au lattice constant was optimized, yielding a value of 4.24 Å, which is close to the experimental bulk Au lattice constant of 4.08 Å. The k-point sampling consists of 2×2×1 Monkhorst–Packpoints[25]. 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 different Pd-Au(100) alloy surfaces is defined as:

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

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

The transition state was identified through the following method. Firstly, complete LST/QST[26] 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. The convergence criterion is the same as that of geometry optimization.

3. Results and Discussion

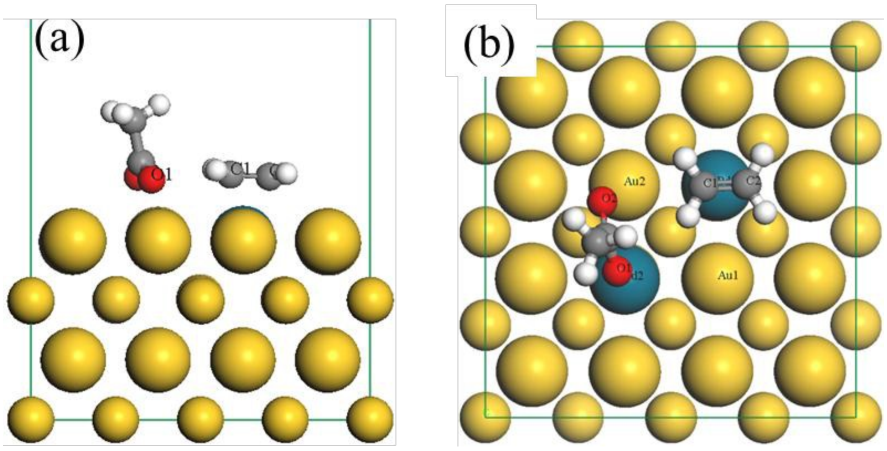
3.1. The coupling of ethylene with acetate species

The coupling of ethylene with acetate species on Pd-Au(100) surface is considered as the rate-limiting step of S-mechanism[9]. Thus, further study of the rate-limiting step of S-mechanism is of great guidance significance for the comprehension of the relation between structural information and reactivity.

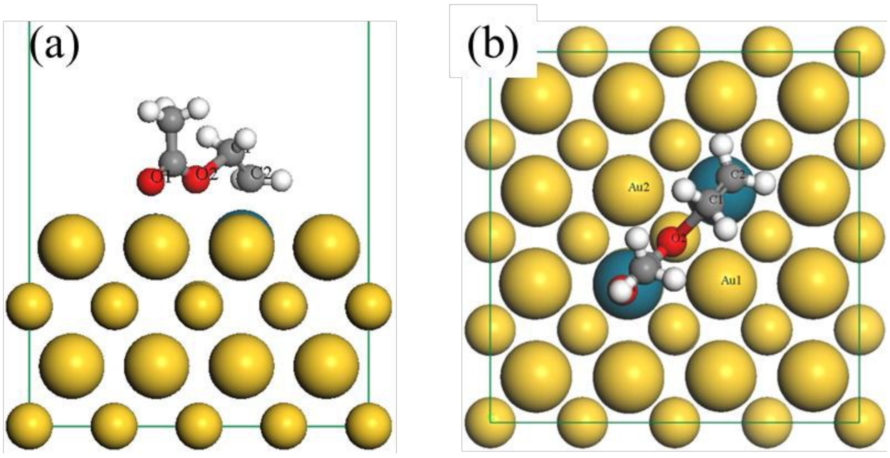
The difference of surface structure and electronic properties of PdsnAu, PdfnAu and PdislAu leads to the different energy barriers of the coupling of ethylene with acetate species.

The configurations of the initial state, transition state and final state on PdsnAu surface are shown in Figure 3.

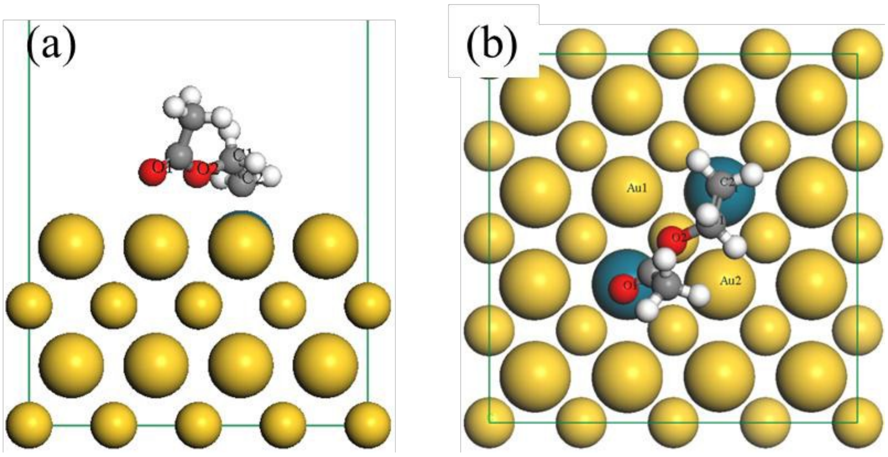
From Figure 3, the activation energy, *Ea*, of the coupling of ethylene with acetate species on PdsnAu surface is 1.10 eV. The stretching vibration of the imaginary frequency occurs between the hydroxyl O of acetate species and the ethylene's double bond C (C_1) near acetate species. The distance between O_2 and C_1 gradually becomes shorter. The distance between O_2 and C_1 of the initial state is 3.31 Å, that of the transition state becomes 1.99 Å and that of the final product, VAH, is 1.47 Å, suggesting that O_2-C_1 forms, which agrees with the study results of Plata[25] and Mazzone [27].



IS configuration on PdsnAu surface



TS configuration on PdsnAu surface



FS configuration on PdsnAu surface

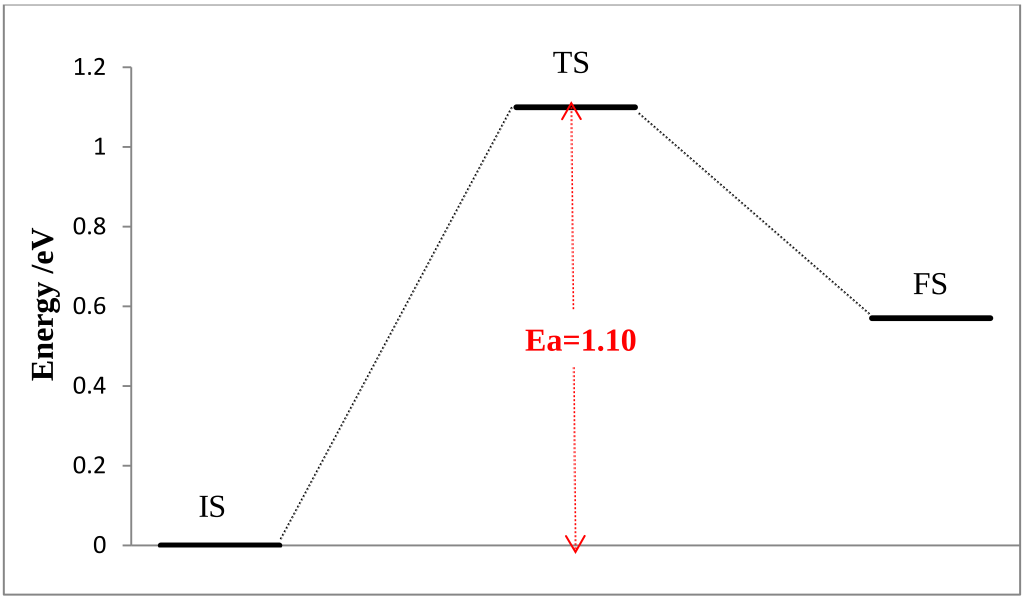
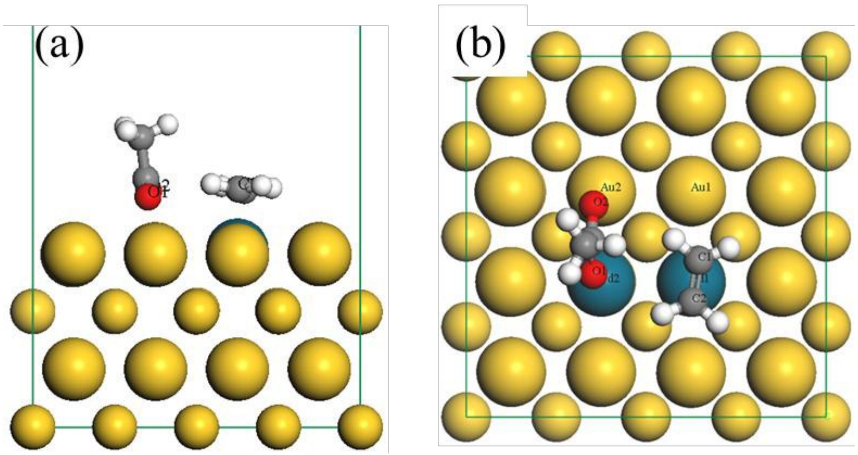
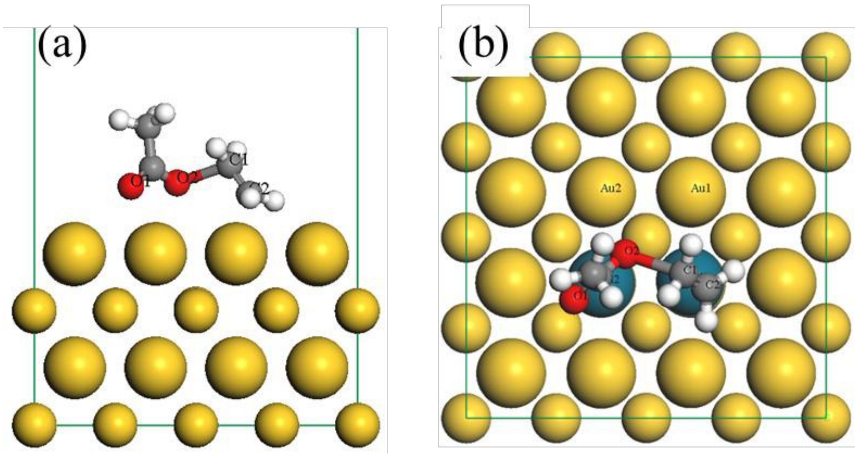


Figure 3 Energy profiles for the coupling of ethylene with acetate species on PdsnAu surface

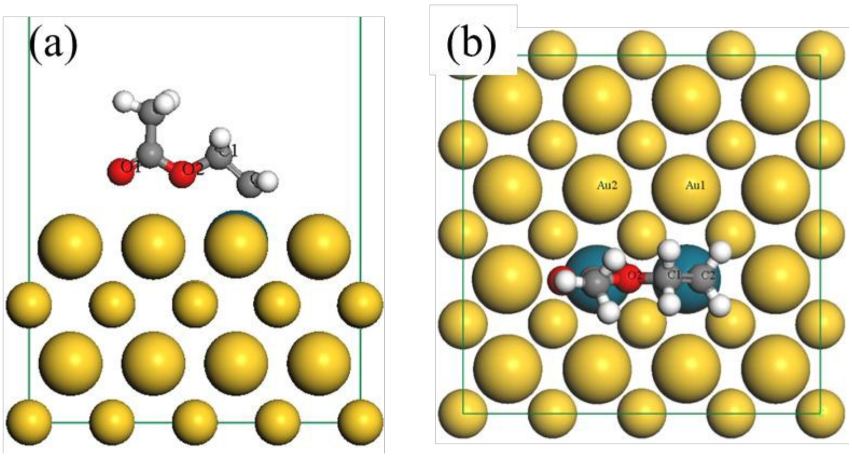
The configurations of the initial state, transition state and final state on PdfnAu are shown in Figure 4. From Figure 4, the activation energy, *Ea*, of the coupling of ethylene with acetate species on PdfnAu surface is 1.19 eV. The stretching vibration of the imaginary frequency occurs between the hydroxyl O of acetate and the ethylene's double bond C (C_1) near acetate species.



IS configuration on PdfnAu surface



TS configuration on PdfnAu surface



FS configuration on PdfnAu surface

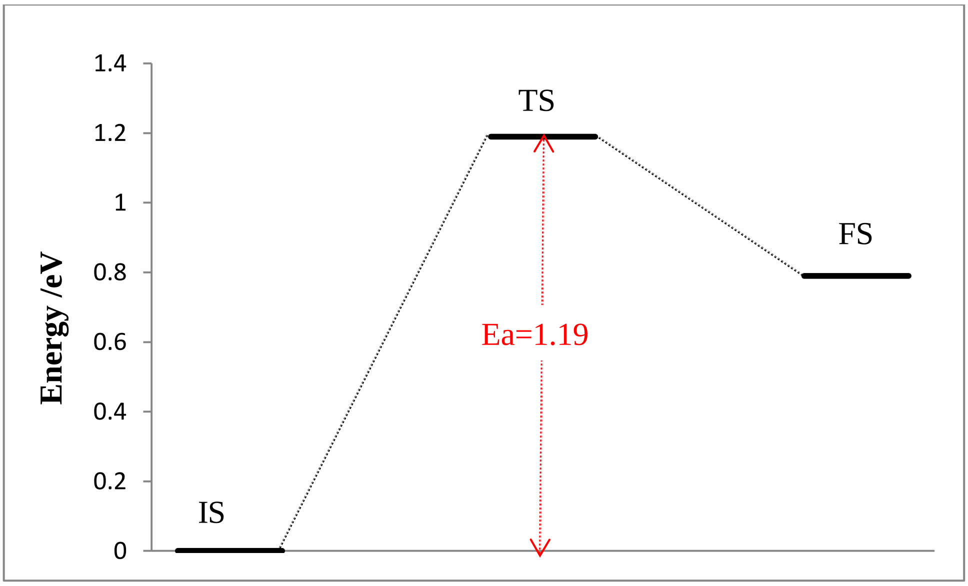


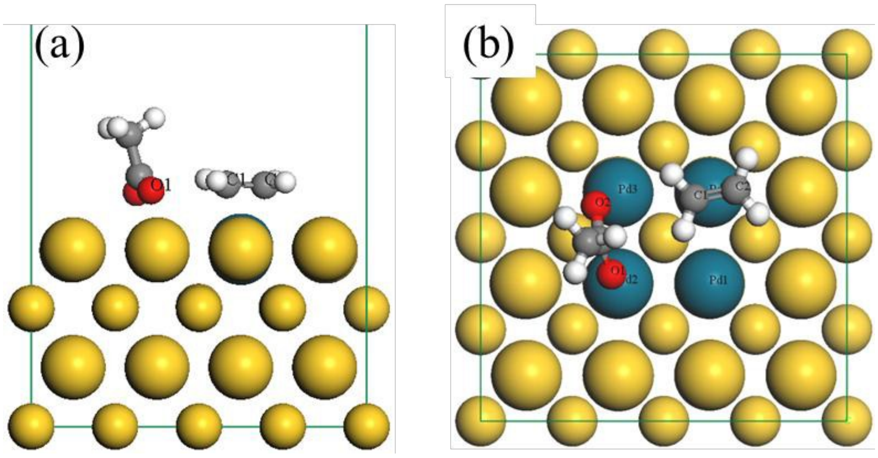
Figure 4 Energy profiles for the coupling of ethylene with acetate species on PdfnAu surface

The distance between O_2 and C_1 gradually becomes shorter. The distance between O_2 and C_1 of the initial state is 3.95 Å, that of the transition state becomes 2.16 Å and that of the final product, VAH, is 1.49 Å, suggesting that O_2-C_1 forms.

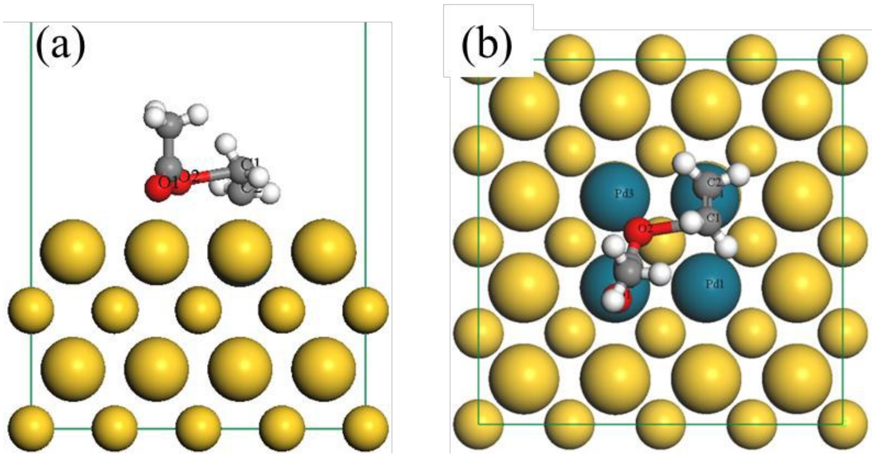
Since both ethylene and acetate species can be adsorbed on the bridge site of two neighboring Pd atoms on the surface, two stable co-adsorption configurations (co-PdislAu$_1$ and co-PdislAu$_2$) can be obtained on PdislAu surface. Calculations found that the adsorption energies of the configurations of the two products based on the two co-adsorption configurations are the same, with the value of -1.75 eV. The configurations of the initial state, transition state and final state on co-PdislAu$_1$ and co-PdislAu$_2$ are shown in Figure 5.

Beginning with the two initial configurations, the energy profiles obtained through transition-state search are shown in Figure 5. From Figure 5, the activation energies, *Ea*, of the coupling of ethylene with acetate species on PdislAu$_1$ and PdislAu$_2$ are 1.37 eV and 1.67 eV, respectively. It can be seen that on PdislAu surface, the activation energies of the coupling of ethylene with acetate species significantly become greater. The corresponding stretching vibrations of the two imaginary frequencies both occur between the hydroxyl O (O_2) of acetate and the ethylene’s double bond C (C_1) near acetate species. The distance between O_2 and C_1 gradually becomes shorter. As for co-PdislAu$_1$, the distance between O_2 and C_1 of the initial state is 3.23 Å, that of the transition state becomes 2.32 Å and that of the final product, VAH, is 1.48 Å, suggesting that O_2-C_1 forms. As for co-PdislAu$_2$, the distance between O_2 and C_1 of the initial state is 3.58 Å, that of the transition state becomes

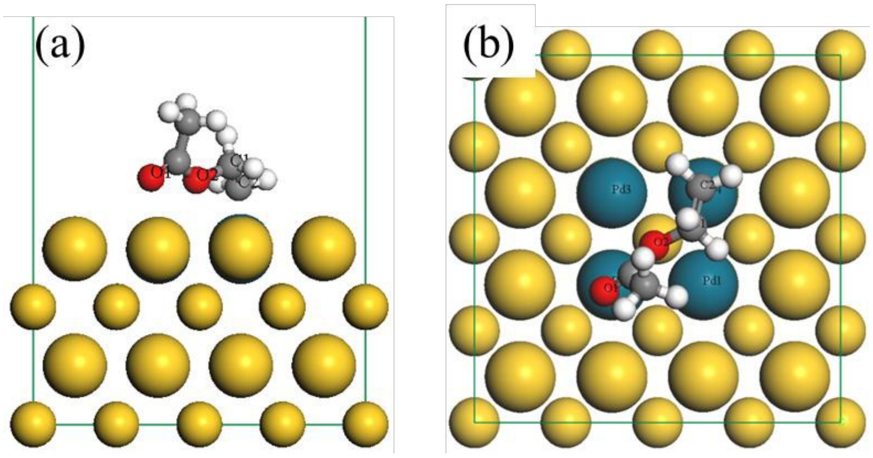
2.38 Å and that of the final product, VAH, is 1.47 Å, suggesting that O_2-C_1 forms.



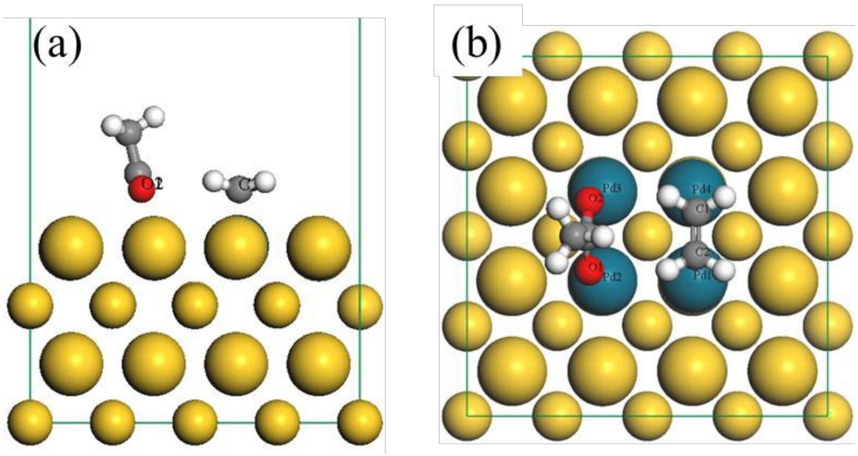
IS configuration on PdislAu$_1$ surface



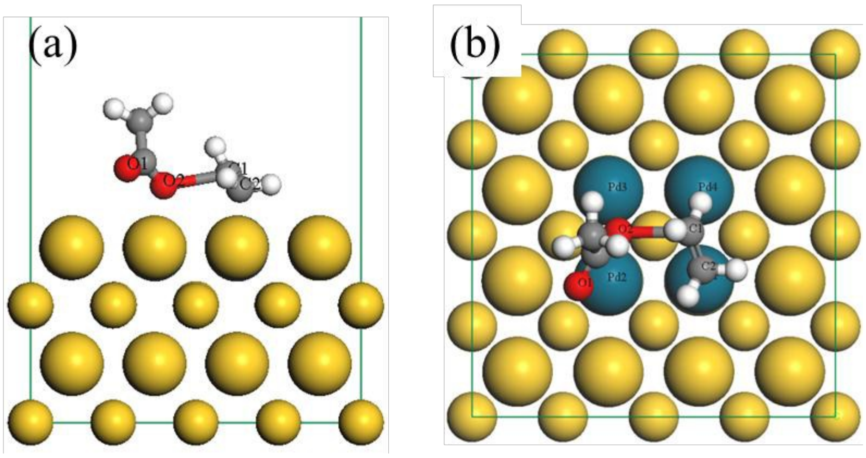
TS configuration on PdislAu$_1$ surface



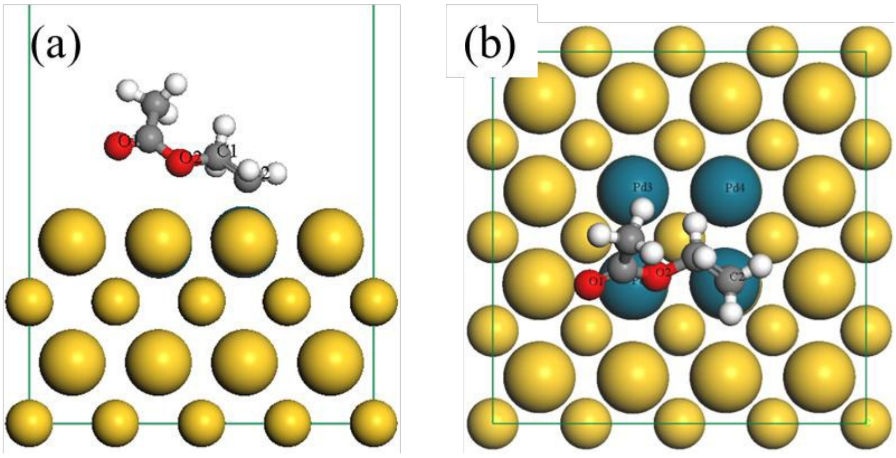
FS configuration on PdislAu$_1$ surface



IS configuration on PdislAu$_2$ surface



TS configuration on PdislAu$_2$ surface



FS configuration on PdislAu$_2$ surface

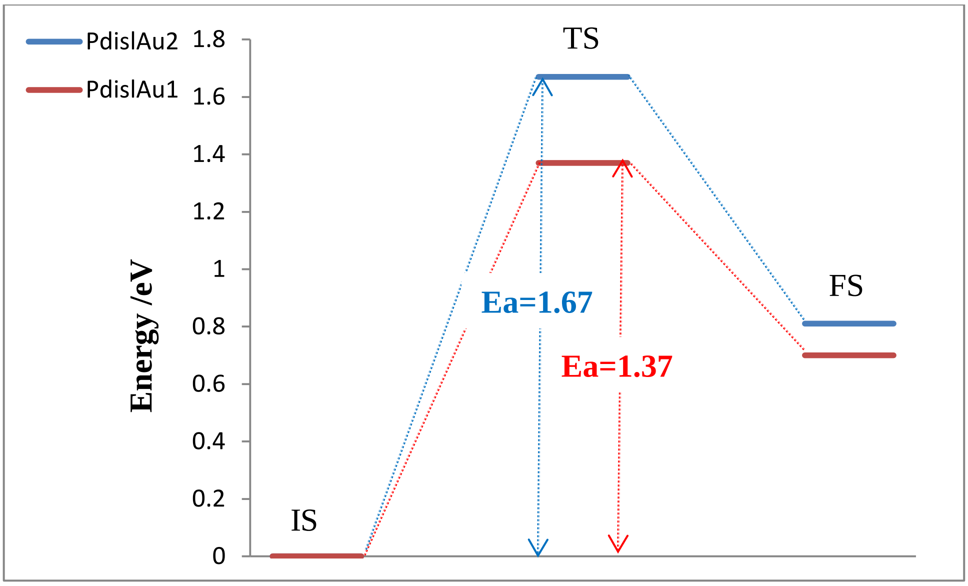


Figure 5 Energy profiles for the coupling of ethylene with acetate species on PdislAu surface

From the configurations of three transition states on Pd-Au(100) surface, the hydroxyl O (O_2) of acetate species bonds with the double bond C (C_1) of ethylene. The distance between O_2 and C_1 gradually becomes shorter until a new bond forms, generating the intermediate, acetoxyethyl-palladium.

Figure 6 compares the energy barriers of the transition states of the coupling of ethylene with acetate species on the three surface models. It can be seen that the activation energy barrier of PdsnAu is the lowest, with the value of 1.10 eV. With the number of surface neighboring Pd atoms increasing, the activation energy barrier gradually becomes greater. It can be inferred that under the same reaction conditions, the incidence of the coupling of ethylene with acetate species becomes smaller, with the number of surface neighboring Pd atoms increasing. PdislAu surface has two possible stable co-adsorption configurations, and two possible reaction pathways, (1) and (2), were obtained through transition-state search. When co-PdislAu$_2$ was taken as the initial reactant, the activation energy barrier was the highest, with the value of 1.67 eV. And the corresponding incidence of the reaction is the lowest.

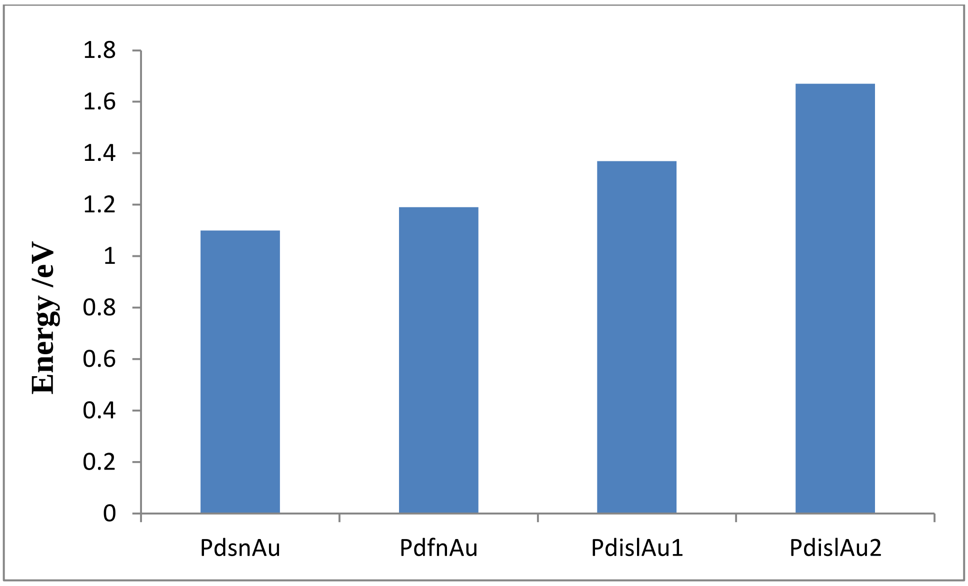


Figure 6 Energy barriers of the coupling of ethylene with acetate species on different Pd-Au(100) surfaces

From the study of the surface electronic properties, and adsorption and co-adsorption properties of Zhang[28], it can be inferred that with the number of surface neighboring Pd atoms increasing, the adsorption of ethylene and acetate species on PdsnAu, PdfnAu and PdislAu gradually becomes stronger. From the adsorption energy of the rate-limiting step, relatively strong chemisorption may be not conducive to the coupling of ethylene with acetate species. The addition of Au can not only make the active component (Pd atoms) dispersed, but also moderate the electronic properties of d band of the surface Pd atoms. Both aspects can play a crucial role in modifying the activity of the catalyst.

3.2. Ethylene dehydrogenation

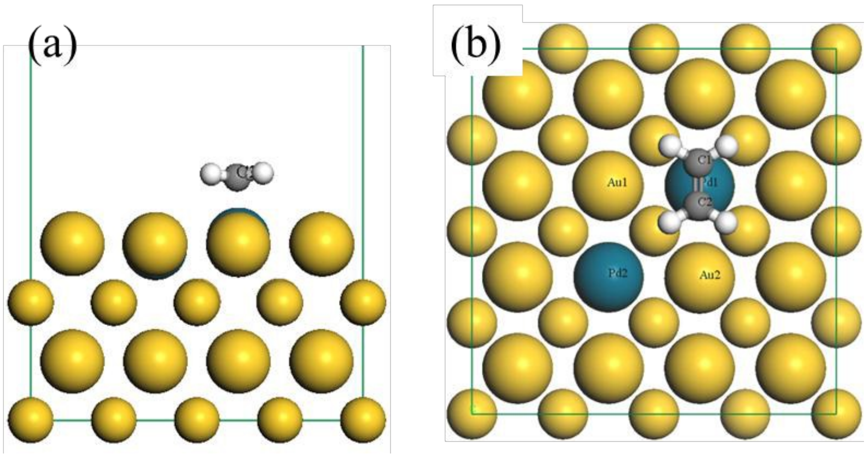
Nakamura et al.[11] studied the mechanism of VAM synthesis with in situ X-ray photoelectron spectroscopy and in situ infrared spectroscopy, and found that Oxygen was necessary for dissociation of acetic acid to acetate species on the catalyst surface. When only the vapor of acetic acid and ethylene gas were on the catalyst surface, no VAM was generated. However, when ethylene gas was added directly onto the palladium-acetate ($Pd(OCOCH_3)_2$) surface, VAM could also be obtained. Thus, when ethylene reacted with acetate species, oxygen was not necessary for the activation of ethylene[29].

The difference of Samanos mechanism and Moiseev mechanism lies in whether ethylene dehydrogenation occurs before ethylene participates in the coupling reaction, i.e., whether ethylene is dehydrogenated to vinyl first or ethylene directly couples with acetate species to form Vinyl Acetate-like intermediate (acetoxyethyl-palladium). In response to this difference, this work focuses on the influence of different Pd-Au(100) surface configurations on ethylene dehydrogenation in order to obtain more comprehensive understanding of VAM synthesis mechanism on Pd-Au(100) surface.

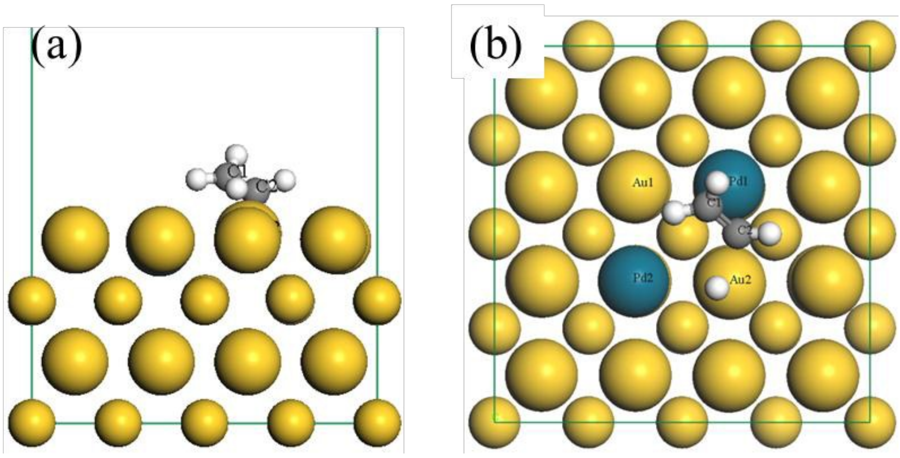
The configurations of the initial state, transition state and final state on PdsnAu surface are shown in Figure 7.

The distance of C_1 in initial state and its corresponding H is 1.09 Å, and it becomes 1.86 Å in transition state. In final state, both vinyl and H are adsorbed on the bridge sites of Pd-Au (seen in Figure 7). The distance of C_1 and its corresponding H becomes 2.84, suggesting that C_1-H breaks.

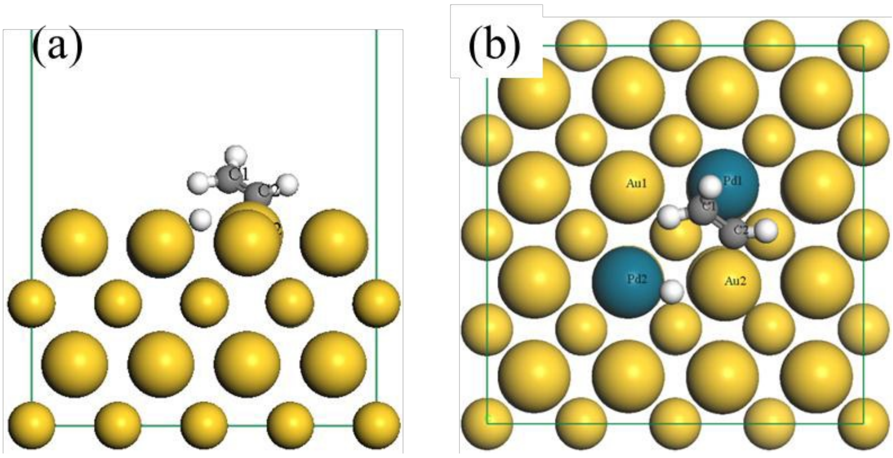
From Figure 7, the activation energy, *Ea*, of ethylene dehydrogenation on PdsnAu surface is 1.81 eV.



IS configuration on PdsnAu surface



TS configuration on PdsnAu surface



FS configuration on PdsnAu surface

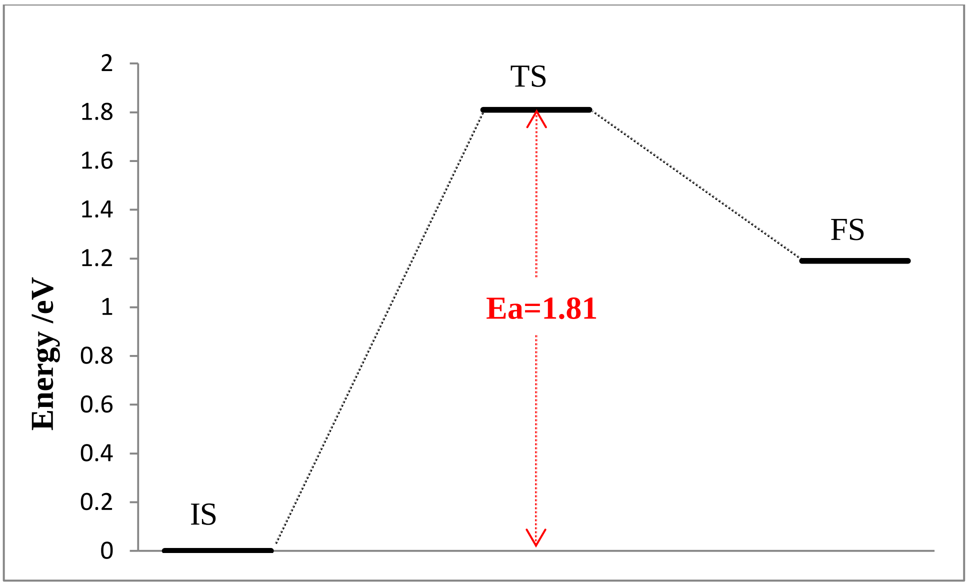


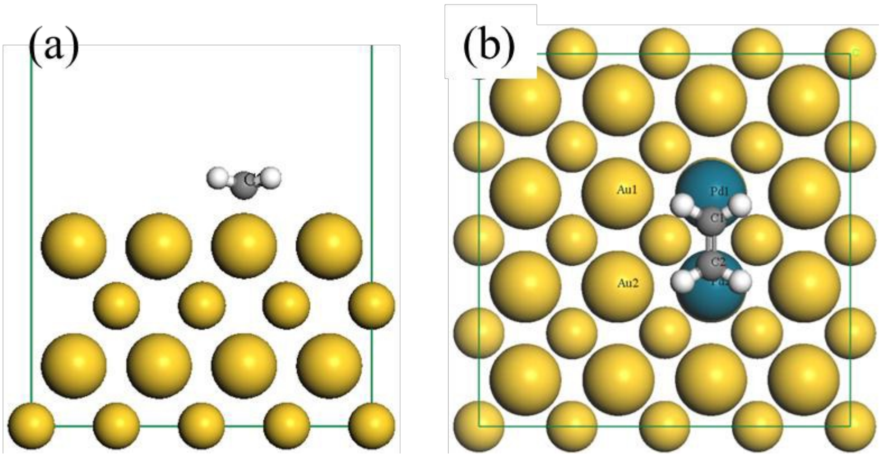
Figure 7 Energy profiles for ethylene dehydrogenation on PdsnAu surface

It was found that ethylene has two kinds of stable adsorption configurations on both PdfnAu and PdislAu, i.e., π- and di-σ configurations. And the adsorption energy difference of the two stable adsorption configurations is small. Therefore, on the two kinds of Pd-Au surfaces, the two kinds of adsorption configurations should be considered as the initial reactants of ethylene dehydrogenation.

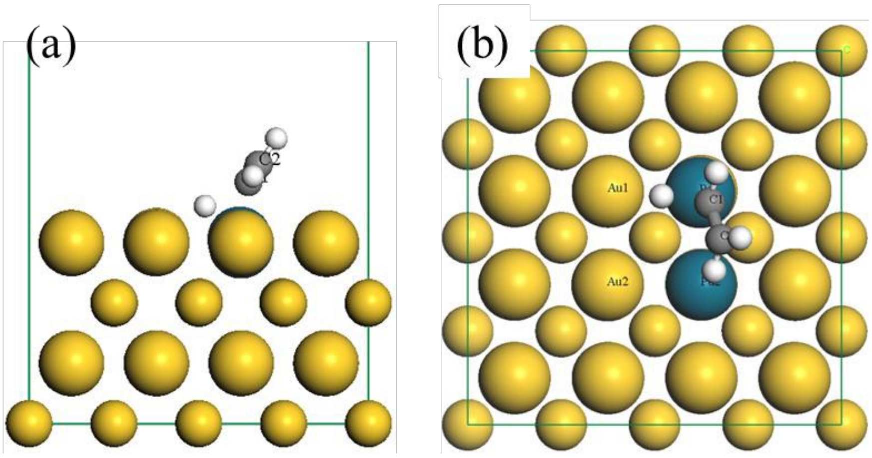
When ethylene is adsorbed on PdfnAu surface through di-σ configuration and π-configuration, the configurations of the initial state, transition state, and final state of ethylene dehydrogenation are shown in Figure 8.

The distances of C_1 and its corresponding H in initial di-σ configuration and initial π- configuration are 1.10 Å and 1.09 Å, respectively, and become 1.77 Å and 1.68 Å in the transition states. Vinyl species of the final state are adsorbed on the Pd-Pd bridge sites, with H adsorbed on the neighboring Pd-Au bridge sites. The distances of C_1 and its corresponding H become 2.37 Å and 2.48 Å, suggesting that C_1-H breaks.

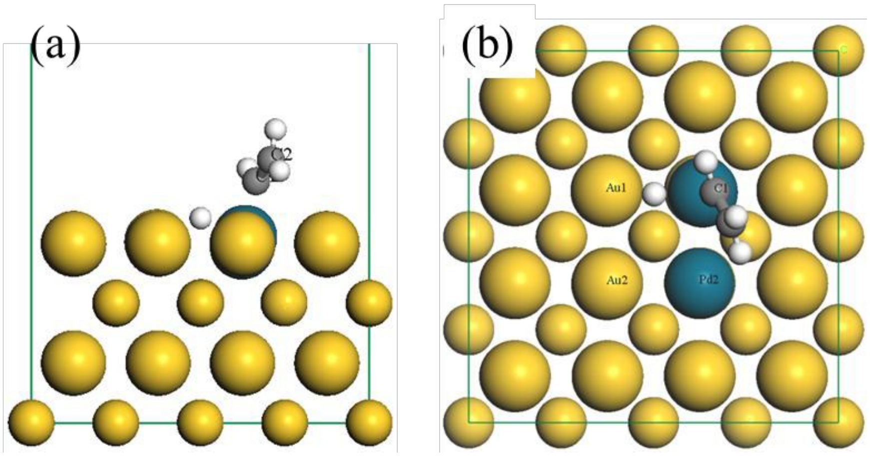
From Figure 8, the activation energy, *Ea*, of ethylene dehydrogenation on PdfnAu surface with di-σ configuration as the initial reactant is 1.28 eV, while that with π- configuration as the initial reactant is 1.31 eV. The stretching vibrations occur from the reactants to products.



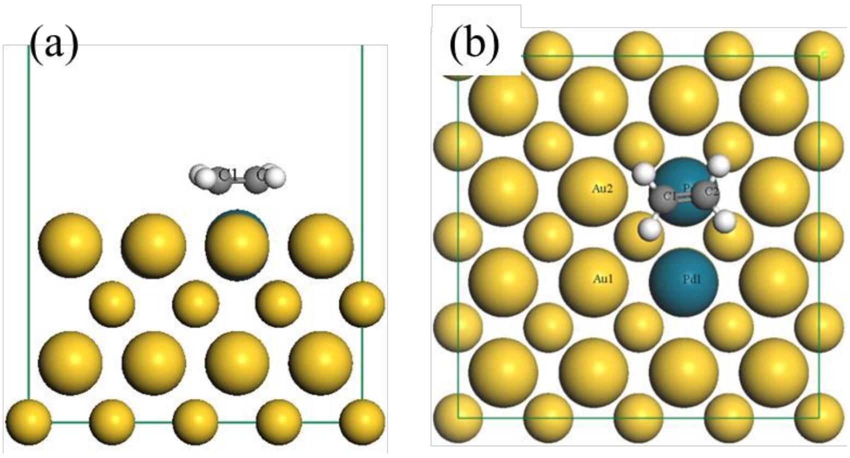
IS configuration on PdfnAu$_1$ surface



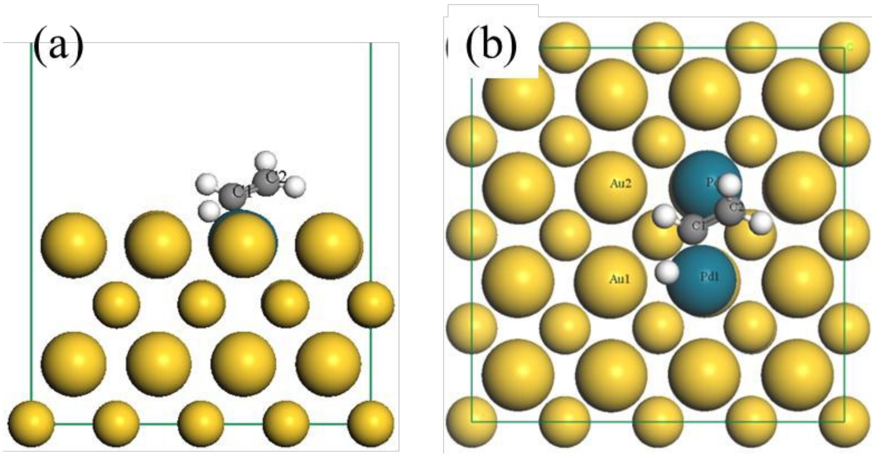
TS configuration on PdfnAu$_1$ surface



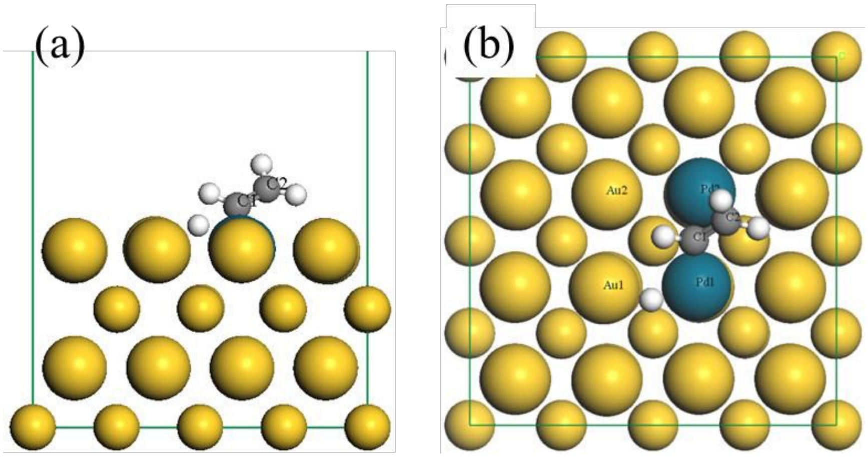
FS configuration on PdfnAu$_1$ surface



IS configuration on PdfnAu$_2$ surface



TS configuration on PdfnAu$_2$ surface



FS configuration on PdfnAu$_2$ surface

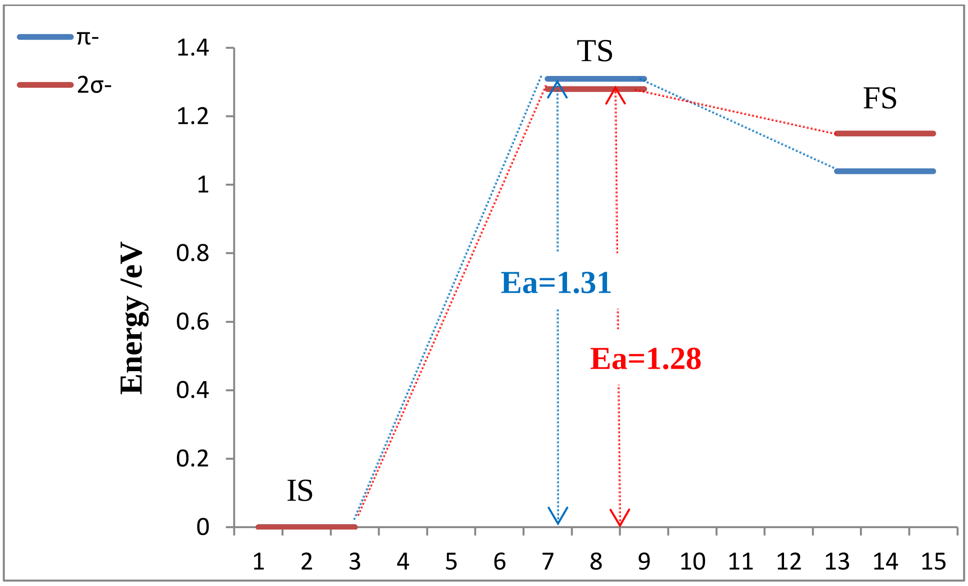
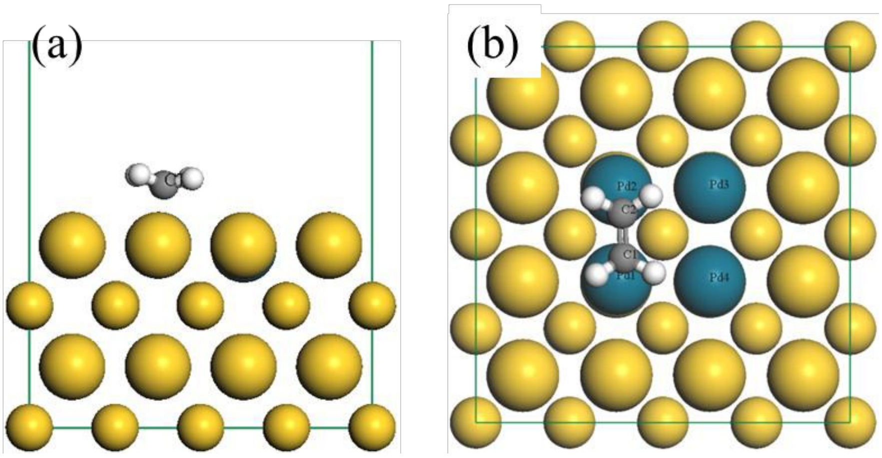


Figure 8 Energy profiles for ethylene dehydrogenation on PdfnAu surface

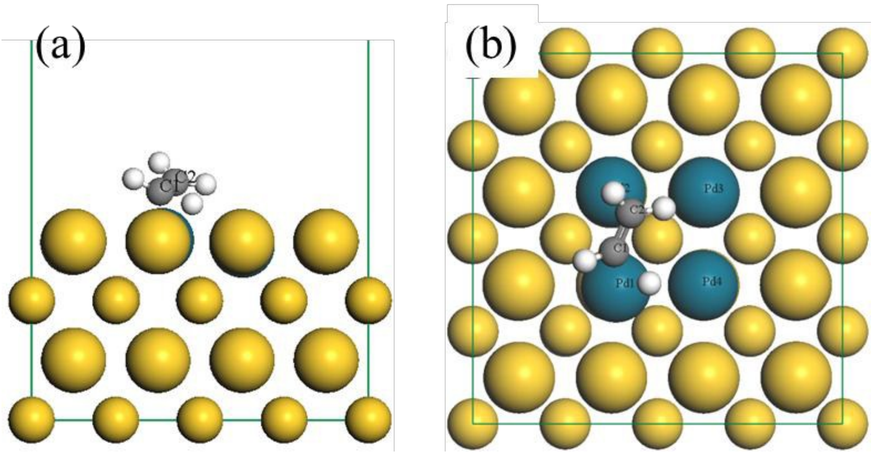
When ethylene is adsorbed on PdislAu surface through di-σ configuration and π-configuration, the configurations of the initial state, transition state, and final state of ethylene dehydrogenation are shown in Figure 9.

The distances of C_1 and its corresponding H in initial di-σconfiguration and initial π-configuration are 1.10 Å and 1.09 Å, respectively, and become 1.59 Å and 1.62 Å in the transition states. Vinyl species of the final state are adsorbed on the Pd-Pd bridge sites. The distances of C_1 and its corresponding H become 2.56 Å and 2.47 Å, suggesting that C_1-H breaks.

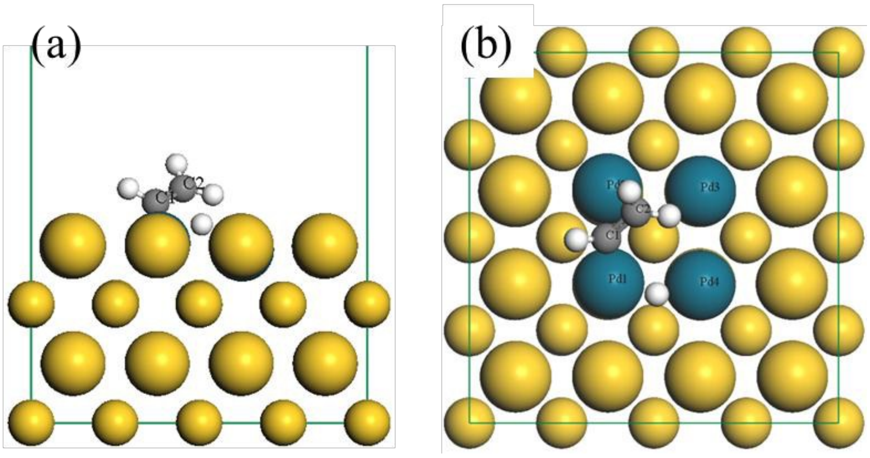
From Figure 9, the activation energy, *Ea*, of ethylene dehydrogenation on PdislAu surface with di-σ configuration as the initial reactant is 0.90 eV, while that with π-configuration as the initial reactant is 0.93 eV. The stretching vibrations occur from the reactants to products.



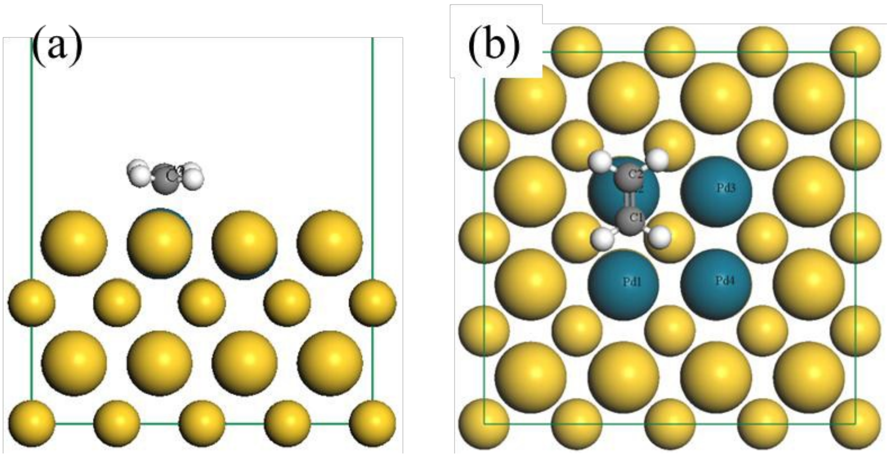
IS configuration PdislAu$_1$ surface



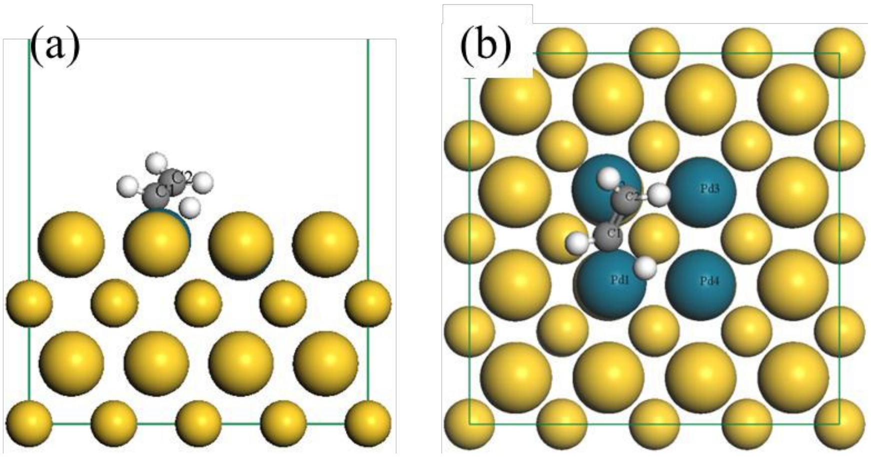
TS configuration PdislAu$_1$ surface



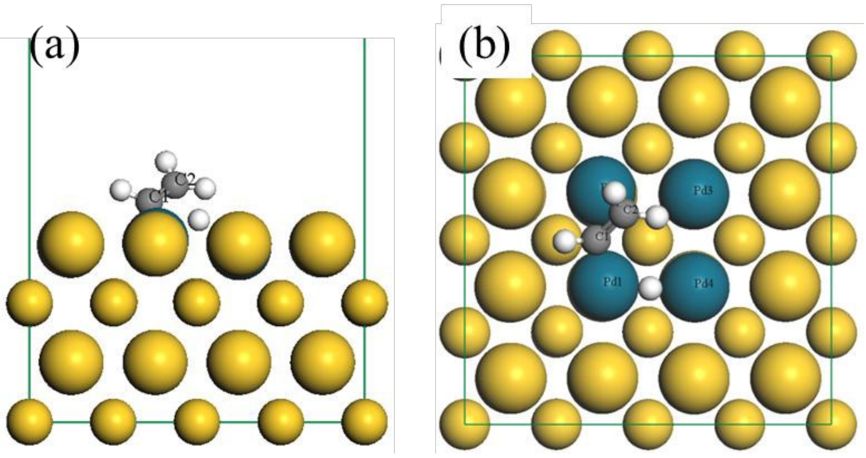
FS configuration PdislAu$_1$ surface



IS configuration on PdislAu$_2$ surface



TS configuration on PdislAu$_2$ surface



FS configuration on PdislAu$_2$ surface

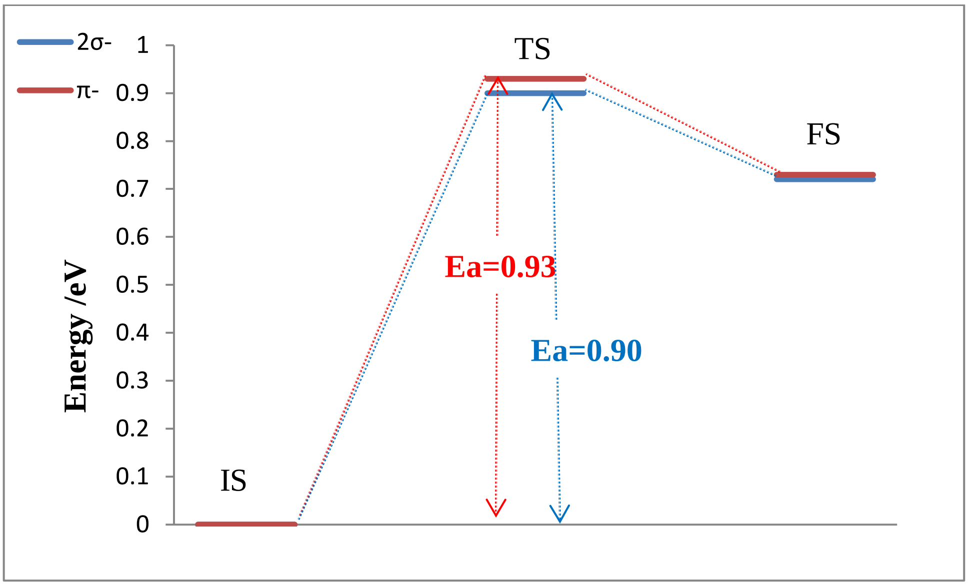


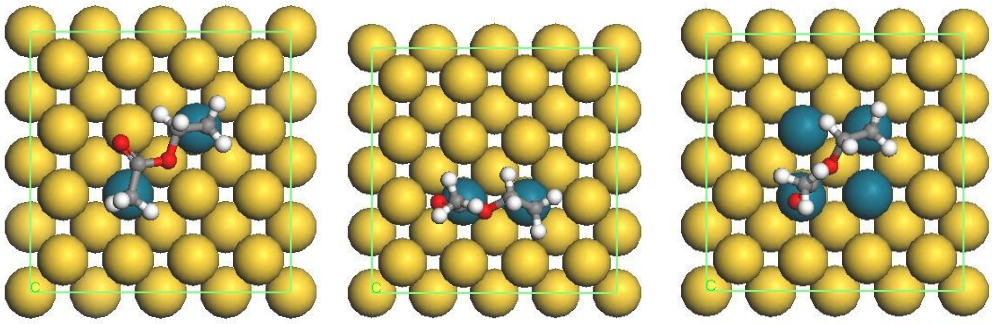
Figure 9 Energy profiles for ethylene dehydrogenation on PdislAu surface

The comparison of the elementary reactions of ethylene dehydrogenation on the three Pd-Au(100) surfaces shows that the energy barrier of transition state decreases with the number of neighboring Pd atoms increasing, suggesting that continuous Pd atoms on the surface facilitate ethylene dehydrogenation, which is in good agreement with the study results of Yuan[21], and it is mainly because PdislAu can provide the sufficient attraction of Pd and Pd-Au bridge sites toward vinyl and the eliminated hydrogen.

3.3. VAH dehydrogenation and the coupling of vinyl with acetate species

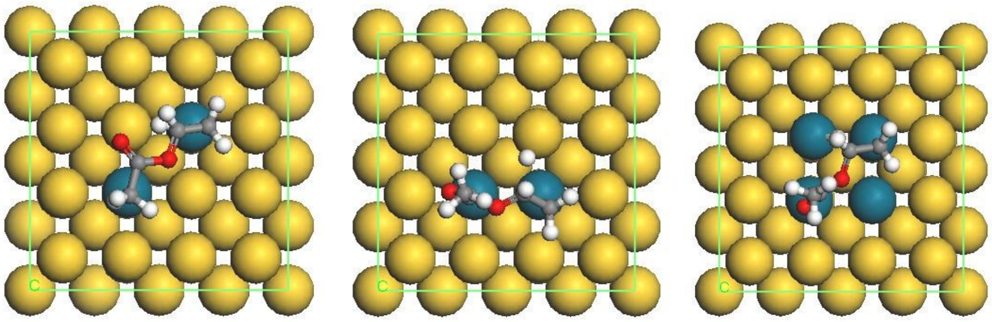
In order to confirm the role of the coupling of ethylene with acetate species and ethylene dehydrogenation in Samanos pathway and Moiseev pathway, the remaining two reactions in the two pathways, VAH dehydrogenation and the coupling of vinyl with acetate species, were also studied in this work on PdsnAu, PdfnAu and PdislAu as supplement and comparison.

The activation energy, *Ea*, of VAH dehydrogenation on PdsnAu, PdfnAu and PdislAu is 0.48 eV, 0.89 eV and 1.29 eV, respectively. The configurations of the initial state, transition state and final state of VAH dehydrogenation on PdsnAu, PdfnAu and PdislAu surfaces are shown in Figure 10.



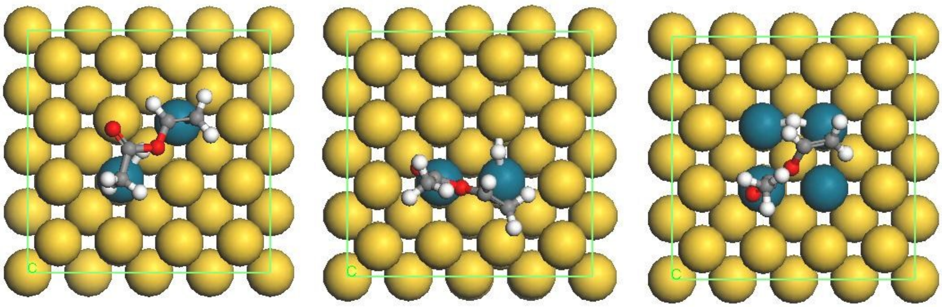
PdsnAu PdfnAu PdislAu

IS configurations



PdsnAu PdfnAu PdislAu

TS configurations

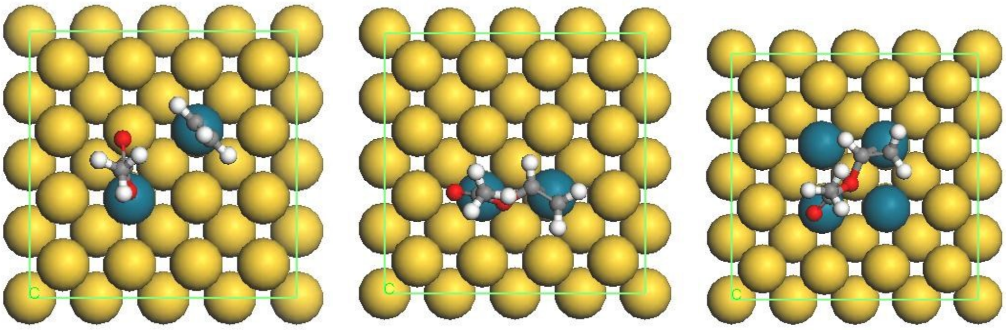


PdsnAu PdfnAu PdislAu

FS configurations

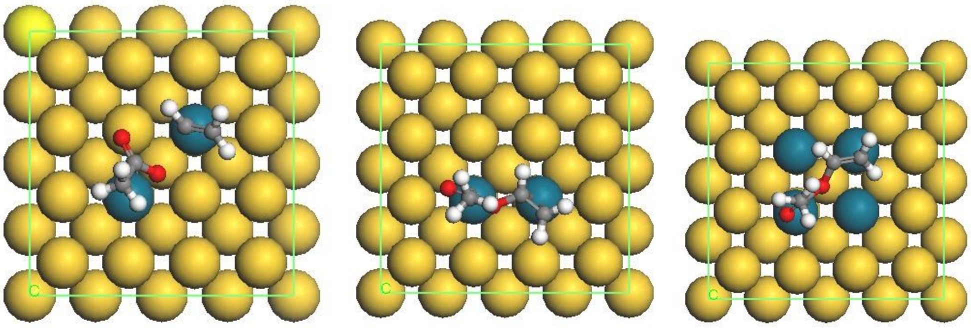
Figure 10 The configurations of the initial state, transition state and final state of VAH dehydrogenation on PdsnAu, PdfnAu and PdislAu surfaces

The activation energy, *Ea*, of the coupling of vinyl with acetate species on PdsnAu, PdfnAu and PdislAu is 1.39 eV, 0.07 eV and 0.24 eV, respectively. The configurations of the initial state, transition state and final state of the coupling of vinyl with acetate species on PdsnAu, PdfnAu and PdislAu surfaces are shown in Figure 11.



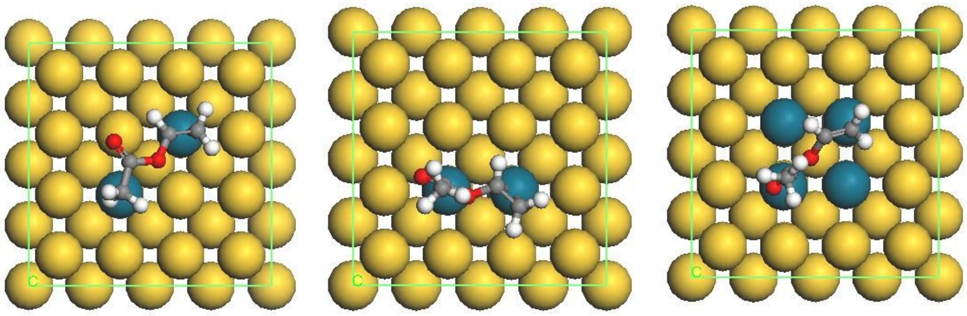
PdsnAu PdfnAu PdislAu

IS configurations



PdsnAu PdfnAu PdislAu

TS configurations



PdsnAu PdfnAu PdislAu

FS configurations

Figure 11 The configurations of the initial state, transition state and final state of the coupling of vinyl with acetate species on PdsnAu, PdfnAu and PdislAu surfaces

All the relevant activation energies are listed and compared in Table 2.

Table 2 Comparison of the activation energies

Activation energy /eV	PdsnAu	PdfnAu	PdislAu
VAH dehydrogenation	0.48	0.89	1.29
Coupling of ethylene with acetate species	1.1	1.19	1.37/1.67
Ethylene dehydrogenation	1.81	1.28/1.31	0.90/0.93
Coupling of vinyl with acetate species	1.39	0.07	0.24

From Table 2, it is obvious that in Samanos pathway, the activation energy of the coupling of ethylene with acetate species on each alloy surface is higher than the activation energy of VAH dehydrogenation on corresponding alloy surface; similarly, in Moiseev pathway, the activation energy of ethylene dehydrogenation on each alloy surface is higher than the activation energy of the coupling of vinyl with acetate species on corresponding alloy surface. Therefore, the reaction steps studied here are energetically feasible.

3.4. Discussion

An energy barrier comparison between the coupling of ethylene with acetate species and ethylene dehydrogenation on different Pd-Au(100) surfaces is shown in Figure 12.

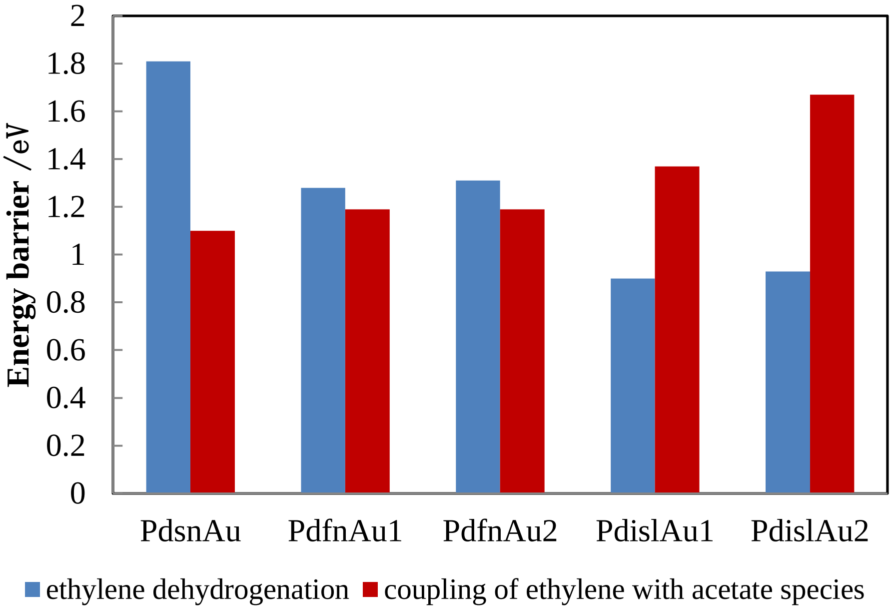


Figure 12 An Energy barrier comparison between ethylene dehydrogenation and the coupling of ethylene with acetate species on different Pd-Au(100) surfaces

From the comparison, the activation energy of ethylene dehydrogenation on PdsnAu surface is up to 1.81 eV, suggesting it is more difficult for ethylene dehydrogenation to occur on PdsnAu surface, while activation energies of ethylene dehydrogenation on PdfnAu surface and PdislAu surface which have continuous surface Pd atoms are lower than 1.30 eV, suggesting it is more likely for ethylene dehydrogenation to occur on these two kinds of surfaces. However, the experimental activation energies of ethylene dehydrogenation on PdsnAu and PdfnAu are higher than that of the coupling of ethylene with acetate species, while the activation energy on PdislAu is obviously lower than that of the coupling of ethylene with acetate species to the intermediate, acetoxyethyl-palladium.

Thus, it can be inferred that on the PdsnAu and PdfnAu surfaces (when the surface coverage of Pd atoms is relatively low), as for dehydrogenation, ethylene is more likely to directly couple with acetate species to generate VAH, while on the PdislAu surface (when the surface coverage of Pd atoms is relatively high), ethylene is more likely to undergo dehydrogenation.

Han et al.[30] found that ethylene is more likely to undergo complete dehydrogenation on pure Pd surface and form surface coke deposition during the VAM synthesis. Actually, when the surface coverage of Pd atoms is relatively high, even if ethylene first undergoes dehydrogenation, the reaction unnecessarily falls into Moiseev mechanism and the dehydrogenation product is likely to be decomposed to byproducts. Thus, the mechanisms of the main reaction and side reaction of VAM synthesis on such surface still need further investigations.

4. Conclusions

In this study, DFT method was employed to study the influence of surface properties of Pd-Au(100) on VAM synthesis from gas-phase oxidation of ethylene on molecular level and electronic level from the microscopic perspective.

The following conclusions can be drawn:

(1) On each Pd-Au(100) surface, the activation energy of the coupling of ethylene with acetate species rises with the number of neighboring Pd atoms increasing, suggesting that the possibility of the coupling of ethylene with acetate species becomes smaller. The activation energy of the coupling ethylene with acetate species on PdsnAu is the lowest, with the value of 1.10 eV, while that on PdislAu is the highest, with the value of 1.67 eV.

(2) On each Pd-Au(100) surface, the activation energy of ethylene dehydrogenation decreases with the number of neighboring Pd atoms increasing, suggesting that the possibility of ethylene dehydrogenation becomes larger. The activation energy of ethylene dehydrogenation on PdsnAu is up to 1.81 eV, while that on PdislAu is low to 0.90 eV, suggesting that under the same conditions, more continuous Pd atoms on the surface facilitate the ethylene dehydrogenation.

(3) From the discussions above, on PdsnAu and PdfnAu surfaces where the coverage of the surface Pd atoms is relatively low, it is more likely for the coupling of ethylene with acetate species to occur, while on PdislAu surface where the coverage of the surface Pd atoms is relatively high, it is more likely for ethylene dehydrogenation to happen.

References

[1] R. Abel, P. Collins, *et al.* Ocyacetylation: Vinyl Acetate from Ethylene. in: G. Ertl, H. Knozinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis,Wiley-VCH, Weinheim, Germany. 5 (1997) 2298-2301.

[2] N. Macleod, J. M. Keel, *et al.* The effects of ageing a bimetallic catalyst under industrial conditions: a study of fresh and used Pd-Au-K/silica vinyl acetate synthesis catalysts. Appl. Catal., A-Gen. 2004, 261: 37-46.

[3] M. Chen and D. W. Goodman. Promotional Effects of Au in Pd-Au Catalysts for Vinyl Acetate Synthesis. Chin. J. Catal. 2008, 29: 1178-1186.

[4] M. Neurock and W. T. Tysoe. Mechanistic Insights in the Catalytic Synthesis of Vinyl Acetate on Palladium and Gold/Palladium Alloy Surfaces. Top. Catal. 2013, 56: 1314-1332.

[5] A. Baiker, H. Blaser, *et al.* Handbook of Heterogeneous Catalysis. Weinheim: Wiley-VCH. 1997: 974-980.

[6] Y. F. Han, J. H. Wang, *et al.* A kinetic study of vinyl acetate synthesis over Pd-based catalysts: kinetics of vinyl acetate synthesis over Pd-Au/SiO2 and Pd/SiO2 catalysts. J. Catal. 2005, 232: 467-475.

[7] I. Rivalta, G. Mazzone, *et al.* The influence of surface oxygen and hydroxyl groups on the dehydrogenation of ethylene on PdAu surface alloys. A theoretical cluster model study. Chem. Phys. Lett. 2010, 493: 87-93.

[8] E. Hansen and M. Neurock. First-principles based kinetic simulations of acetic acid temperature programmed reaction on Pd(111). J. Phys. Chem. B. 2001, 105:

9218-9229.

[9] B. Samanos, P. Boutry, *et al.* The mechanism of vinyl acetate formation by gas-phase catalytic ethylene acetoxidation. J. Catal. 1971, 23: 19-30.

[10] I. Moiseev, M. Vargaftik, et al. About the mechanism of the reaction between palladium and alkenes in hydroxyl containing solvents. Dokl. Akad. Nauk SSSR: 1960, 133: 133-377.

[11] S. Nakamura and T. Yasui. The mechanism of the palladium-catalyzed synthesis of vinyl acetate from ethylene in a heterogeneous gas reaction. J. Catal. 1970, 17: 366-374.

[12] F. Calaza, Z. Li, *et al.* Reaction Between Ethylene and Acetate Species on Clean and Oxygen-Covered Pd(100): Implications for the Vinyl Acetate Monomer Formation Pathway. Catal. Lett. 2011, 141: 266-270.

[13] P. Liu and J. K. Norskov. Ligand and ensemble effects in adsorption on alloy surfaces. PCCP. 2001, 3: 3814-3818.

[14] F. Calaza, F. Gao, *et al.* The adsorption of ethylene on Au/Pd(111) alloy surfaces. Surf. Sci.. 2007, 601: 714-722.

[15] Z. Li, F. Calaza, *et al.* The adsorption of acetic acid on Au/Pd(1 1 1) alloy surfaces. Surf. Sci. 2007, 601:1351-1357.

[16] Z. J. Li and W. T. Tysoe. The adsorption of acetic acid on clean and oxygen-covered Au/Pd(100) alloy surfaces. Surf. Sci. 2012, 606: 1934-1941.

[17] I. Rivalta, G. Mazzone, *et al.* Adsorption of Ethylene, Vinyl, Acetic Acid, and Acetate Species on PdAu(111) and PdAu(100) Surface Alloys: A Cluster Model Study.

J. Chem. Theory Comput. 2009, 5: 1350-1360.

[18] M. S. Chen, D. Kumar, *et al.* The promotional effect of gold in catalysis by palladium-gold. Sci. 2005, 310: 291-293.

[19] P. Han, S. Axnanda, *et al.* Atomic-scale assembly of a heterogeneous catalytic site. J. Am. Chem. Soc. 2007, 129: 14355-14361.

[20] H. J. Gotsis, I. Rivalta, *et al.* Atomic configurations of Pd atoms in PdAu(111) and PdAu(100) surface alloys: Ab initio density functional calculations. Chem. Phys. Lett.. 2009, 468(4-6): 162-165.

[21] D. W. Yuan, X. G. Gong, *et al.* Ensemble effects on ethylene dehydrogenation on PdAu(001) surfaces investigated with first-principles calculations and nudged-elastic-band simulations. Phys. Rev. B. 2007, 75(23).

[22] F. Calaza, M. Mahapatra, *et al.* Disentangling ensemble, electronic and coverage effects on alloy catalysts: Vinyl acetate synthesis on Au/Pd(1 1 1). J. *Ca*tal. 2014, 312: 37-45.

[23] J. J. Plata, M. Garcia-Mota, et al. J. Phys. Vinyl Acetate Synthesis on Homogeneous and Heterogeneous Pd-Based Catalysts: A Theoretical Analysis on the Reaction Mechanisms.Chem. A. 2009, 113:11758-11762.

[24] B. Hammer, L. B. Hansen, *et al.* Improved adsorption energetics within density-functional theory using revised Perdew–Burke–Ernzerhof functionals. Phys. Rev. B. 1999, 59: 7413-7421.

[25] H. J. Monkhorst and J. D. Pack. Special points for Brillouin-zone integrations. Phys. Rev. B. 1976, 13: 5188-5192.

[26] N. Govind, M. Petersen, *et al.* A generalized synchronous transit method for transition state location. Computat. Mater. Sci. 2003, 28: 250-258.

[27] G. Mazzone, I. Rivalta, et al. The geometric effect in palladium-gold catalysis. Is the coupling the rate-determining step in the vinyl-acetate synthesis? Chem. Commun. 2009, (14): 1852-1854.

[28] M. Zhang, M. Gao, *et al.* DFT study on effect of CO on the system of acetoxylation of ethylene to vinyl acetate. Rsc Adv. 2014, 4(34): 17709-17716.

[29] D. Stacchiola, F. Calaza, *et al.* Elucidation of the reaction mechanism for the palladium-catalyzed synthesis of vinyl acetate. Angewandte Chemie-International Edition. 2005, 44: 4572-4574.

[30] Y. F. Han, D. Kumar, *et al.* Kinetics of ethylene combustion in the synthesis of vinyl acetate over a Pd/SiO2 catalyst. J. Catal. 2004, 224: 60-68.