A DFT Study on the Catalytic CO Oxidative Coupling to Dimethyl **Oxalate on Al-Doped Core-Shell Pd Clusters**

Xue Feng,[†] Lixia Ling,^{*,†,‡} Yueting Cao,[†] Riguang Zhang,[§] Maohong Fan,[‡] and Baojun Wang^{*,§}

[†]College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan, Shanxi 030024, People's Republic of China

[‡]Department of Chemical and Petroleum Engineering, University of Wyoming, 1000 E. University Avenue, Laramie, Wyoming 82071. United States

⁸Key Laboratory of Coal Science and Technology, Taiyuan University of Technology, Ministry of Education and Shanxi Province, Taiyuan, Shanxi 030024, People's Republic of China

Supporting Information

ABSTRACT: A series of core-shell catalysts aiming at CO oxidative coupling to dimethyl oxalate (DMO) were constructed, and effects of the second metal doping and surface structures on the reaction activity and favorable reaction path were investigated by using the density functional theory (DFT) method. Pd₁₃, Al@Pd₁₂, and Ag@Pd₁₂ were first studied to find the proper doping metal. Our results showed that the activity of CO oxidative coupling to DMO follows the order of $Al@Pd_{12} > Pd_{13} > Ag@Pd_{12}$, and the same result was also obtained via the electronic analysis. In addition, Al6@Pd32 and Al13@Pd42 catalysts with higher doping ratio and lower cost than that of Al@Pd₁₂ were selected to examine the influence of surface structure on the reaction activity. It showed that CO + CH₃O \rightarrow COOCH₃ + CO \rightarrow $OCCOOCH_3 + CH_3O \rightarrow DMO$ is the favorable pathway on the (100) surface of Al₆@Pd₃₂ catalyst, while CO + CH₃O \rightarrow CO + CH₃O (COOCH₃) \rightarrow COOCH₃ + COOCH₃ \rightarrow DMO is the optimal pathway on the (111)



surface of Al@Pd12 and Al13@Pd42, which indicated that the surface structure of catalysts affected the preferable pathway of DMO formation. Moreover, activities of CO oxidative coupling to DMO on AlPd core-shell catalysts followed the order of Al@ $Pd_{12} > Al_{13}@Pd_{42} > Al_6@Pd_{32}$. In addition, $Al_{13}@Pd_{42}$ also exhibited a good selectivity between DMO and DMC. Thus, $Al_{13}@Pd_{42} = Al_{43}@Pd_{42} = Al_{43}@Pd_{43} = Al_{43}@Pd_{43}@Pd_{43} = Al_{43}@Pd_{43}@Pd_{43}@Pd_{43} = Al_{43}@Pd_{43}@Pd_{43} = Al_{43}@Pd_{43}@Pd_{43} = Al_{43}@Pd_{43}@Pd_{43}@Pd_{43} = Al_{43}@Pd_{43}@Pd_{43}@Pd_{43}@Pd_{43} = Al_{43}@Pd_{43}@Pd_{43}@Pd_{43}@Pd_{43} = Al_{43}@Pd_{43}@Pd_{43}@Pd_{43}@Pd_{43} = Al_{43}@Pd_{43}\Pd_{43}@Pd_{43}\Pd_{43}@Pd_{43}\Pd_{43}\Pd_{43}\Pd_{43}\Pd_{43}\Pd_{43}\Pd_{43}\Pd_{43}\Pd_{43}\Pd_{43}\Pd_{43}\Pd_{43}\Pd$ Pd₄₂ is a proper catalyst with high activity, high selectivity, and low cost because of high Al:Pd ratio.

1. INTRODUCTION

Coal has played an important role in the development of the Chinese national economy; however, utilization of large amounts of coal at low efficiency results in serious environmental pollution. Thus, utilizing coal resources efficiently and cleanly has become a pressing task.^{1,2} Ethylene glycol (EG) is one of the crucial chemical raw materials with a global demand of about 25 million tons each year, while about half of the market demand is in China. Coal to ethylene glycol (CTEG)which has many advantages including moderate reaction condition, high efficiency, green, atom economy, and nonoil route-has drawn considerable attention.³ Moreover, it is also considered as one of the most important applications in C1 chemistry.^{4,5} The coupling of CO with nitrite esters to oxalates is the first step for the preparation of EG, which can be seen as a key step to realize the conversion of inorganic C1 to organic C2.^{6,7}

Pd-based catalysts are widely used in experiments as high activity and selectivity for the CO oxidative coupling to oxalates with nitrite esters.⁸⁻¹¹ Nevertheless, the shortage of noblemetal resources is more and more rigorous in the world, and the high price of noble-metal Pd hinders its large-scale application in industry.¹² In the previous studies, several approaches were explored to decrease the amount of Pd, including improving the degree of dispersion and alloyed Pd with non-noble transition metals.^{5,8,13–15} A series of Pd-based bimetallic catalysts were prepared, such as Ni-Pd,¹⁶ Fe-Pd,¹⁷ Ag-Pd,¹⁸ and Cu-Pd,¹⁹ and they all presented better activity and stability than corresponding monometallic Pd catalysts for electrocatalysis reactions, owing to the synergistic action between bimetallic catalysts. The selectivity of ethylene was significantly improved when Cu and Ag were added into Pd catalyst for acetylene hydrogenation. 20 Manzoor and coworkers²¹ explored the structural and catalytic properties of Al-, Hf-, and Ge-doped Au₂₀ clusters, and revealed that doping a second metal can not only change the reaction activity and catalytic behavior of gold clusters but also enhance the stability of Au based catalysts. It is worth noting that Al-doped catalysts have attracted widespread interest due to their special

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Figure 1. Optimized structures for Pd_{13} , $Al@Pd_{12}$, $Ag@Pd_{12}$, $Al_6@Pd_{32}$, $Al_{13}@Pd_{42}$, as well as possible adsorption sites. Blue, pink, and gray balls denote Pd, Al, and Ag atoms, respectively.

electronic properties, compared with doping transition metals into catalysts.^{22,23}

Core-shell bimetallic catalysts have received widespread attention recently,²⁴⁻²⁶ and previous experiments²⁷⁻²⁹ have shown that core-shell noble-metal nanoparticles can be prepared by hydrothermal synthesis, opening an avenue to design structures of noble-metal nanoparticles. For the methanol oxidation³⁰ and the C-C coupling reaction,³¹ Ni@ Pd core-shell nanoparticles showed higher catalytic activity and stability than PdNi and Pd nanoparticles. Besides, Cu@Pd core-shell catalysts also possessed higher stability and reaction activity than pure Pd catalysts for formic acid oxidation due to the synergetic effect of Cu and Pd,³² and Ag@Pd core-shell catalyst promoted hydrogen production from formic acid decomposition as strong electron feedback between core metal Ag and shell metal Pd.³³ More importantly, the effective Pd generally occupies outer shells, and the cheap metals are located in the center core in Cu@Pd, Ni@Pd and Ag@Pd core-shell catalysts. It not only increases the catalytic activity by the synergistic effect but also reduces the cost of catalysts. Recently, Al-modified catalysts have attracted more attention; for example, Al13@Pt42 core-shell exhibited better stability and activity than Pt(111) because of the strong orbital hybridization

of the p band of Al_{13} core and the d band of Pt_{42} shell for oxygen reduction reaction.³⁴ Thus, Al atom offers a new possibility as a doping element in noble-metal catalysts. However, up to now, few studies about the reaction of CO oxidative coupling to dimethyl oxalate (DMO) on Al@Pd catalysts are done, and the reaction activity and selectivity of the Al-doped catalyst is still unclear.

Previous results showed that the Pd(111) surface was more active for CO oxidative coupling reaction than the Pd(100) surface,³⁵ and the Pd(111) surface also exhibited excellent selectivity by DFT calculation.³⁶ Therefore, structure sensitivity is reflected in CO oxidative coupling reaction over Pd-based catalysts.^{37,38} Metal clusters with different sizes exhibited different surface structures and symmetry, and they often have been selected as promising catalysts because of high symmetry, high specific surface area, low dimension, and high surface atom ligand saturation.^{39–41} As we all know, the stability of metal clusters is a key factor for catalysts, and magic clusters^{42,43} show excellent stability by theoretical methods.^{44–46} Among Pd clusters, Pd₁₃, Pd₃₈, and Pd₅₅ are magic clusters and also have been studied widely in theoretical studies.^{43,47} Moreover, all three clusters possess the spherical shell and the central atom, which can be seen as stable core– shell structures.^{40,48} A cluster with 13 atoms is the smallest core–shell structure, and a cluster with 55 atoms could be formed via adding an icosahedral shell over the 13-atom cluster.⁴⁹ They are highly symmetrical icosahedron structures and mainly expose the (111) surface.^{50–54} Previous results^{55,56} indicated that the Au₅₅ cluster acted as an especially effective oxidation catalyst for oxidizing CO because of the unique electronic structure of the closed-shell cluster. In addition, Pd₃₈, as a magic cluster, has also been studied in our past studies. The cluster with 38 atoms is a truncated octahedral structure with stiff fcc-like symmetry,^{57,58} and constitutes low-index (111) and (100) surfaces.⁵³ Therefore, it is interesting to study the effects of size and exposed surface on the catalytic activity and selectivity for the CO oxidative coupling reaction.

In this study, the same size clusters with different core atoms, Pd₁₃, Al@Pd₁₂, and Ag@Pd₁₂ nanoparticles, were selected to study the relationship between the second doped metal and the reaction activity, expecting to find a suitable doped non-noble metal. Then, larger size clusters were constructed to reduce the amount of Pd, and the catalytic activity and selectivity for CO oxidative coupling reaction was also studied. The excellent catalyst with low cost, high catalytic activity, and selectivity for CO oxidative coupling to DMO was obtained.

2. COMPUTATIONAL DETAILS

2.1. Calculation Methods. All calculations were performed according to the density functional theory (DFT) approach using the Dmol³ software package.⁵⁹ The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was employed to describe the exchange and correlation term.^{60,61} In this work, the double numerical atomic orbital augmented by a polarization p-function (DNP) was chosen as the basis set. 62 The numerical basis sets can minimize the basis set superposition error. An all-electron basis set was performed for all small molecules, and clusters were treated using the effective core potential. The spin-unrestricted method was used for all calculations. A smearing of 0.005 Ha to the orbital occupation was applied to achieve accurate electronic convergence. The k-points were Gamma point for core-shell structures. The orbital cutoff values were 4.8 Å for all calculations. Thus, the value satisfied the accuracy required. The tolerances of the energy, force, and displacement convergence were 2.0 \times 10⁻⁵ Ha, 4 \times 10⁻³ Ha/ Å and 5 \times 10^{-3} Å, respectively. Transition states (TS) were located using complete linear synchronous transit/quadratic synchronous transit (LST/QST) methods.⁶³ Moreover, the accuracy of the transition state was confirmed by TS confirmation.

The adsorption energy (E_{ads}) of the adsorption species on these clusters were defined by the following equation:

$$E_{\rm ads} = E_{\rm total} - E_{\rm species} - E_{\rm cluster} \tag{1}$$

where E_{total} , E_{species} , and E_{cluster} were total energies of total adsorbed systems, isolated adsorption species and clusters, respectively.

The average binding energy (E_b) had been considered for the structural stability of core–shell bimetallic clusters, E_b was calculated⁶⁴ according to eq 2:

$$E_{\rm b} = (E_{\rm M@Pd12} - E_{\rm M} - 12E_{\rm Pd})/13$$
⁽²⁾

where $E_{M@Pd_{12}}$, E_{Pd} , and E_M were total energies of M@Pd₁₂ (M = Pd, Al and Ag), Pd atom and core atom, respectively.

The core–shell interaction energy E_{cs} was defined³⁴ as follows:

$$E_{\rm cs} = (E_{\rm M@Pd12} - E_{\rm M} - E_{\rm Pd12})/13 \tag{3}$$

where $E_{M@Pd12}$, E_M , and E_{Pd12} represented total energies of M@ Pd₁₂ (M = Pd, Al and Ag), core atom, and Pd₁₂ shell, respectively.

2.2. Models. A series of core-shell bimetallic nanoparticles were formed by replacing the centers group of three clusters with different sizes (Pd₁₃, Pd₃₈ and Pd₅₅), including M@Pd₁₂ (M = Pd, Ag, Al), Al₆@Pd₃₂ and Al₁₃@Pd₄₂ core-shell structures. The most stable configurations of clusters were shown in Figure 1.

 Pd_{13} cluster is with 12 atoms in outer shell and 1 atom in the center, which is the icosahedron structure including 20 smallest (111) surfaces. It is similar to the Pt_{13} cluster.⁴¹ There are three possible adsorption sites: top (T), bridge (B), and 3-fold hollow (Hcp). On this basis, $Al@Pd_{12}$ and $Ag@Pd_{12}$ core—shell bimetallic clusters were constructed by substituting the central Pd atom for Al and Ag atoms to change its catalytic activity and reduce the amount of noble-metal Pd. And they possess the same adsorption sites as Pd_{13} cluster.

Similarly, $Al_6@Pd_{32}$ and $Al_{13}@Pd_{42}$ core-shell bimetallic clusters were constructed by replacing Pd atoms in core of Pd_{38} and Pd_{55} with Al atoms. $Al_6@Pd_{32}$ is composed of an octahedral structure with 6 Al atoms in the center, 24 identical Pd atoms lying at the vertexes of six (100) surfaces, and 8 Pd atoms lying at the center of eight (111) surfaces in the outer shell. The corresponding diameter is 7.671 Å, and the Al:Pd ratio is about 1:5. There are eight possible adsorption sites on $Al_6@Pd_{32}$ surface: two different top sites (T1 and T2), three bridge sites (B1, B2 and B3), two different 3-fold hollow sites (Fcc and Hcp), and 4-fold hollow site (H).

 Al_{13} @Pd₄₂ core-shell bimetallic cluster shows the icosahedron structure with the high symmetry, the size increases to 10.764 Å and the Al:Pd ratio is about 1:3. The outer shell contains 20 of the same triangular Pd(111) surfaces, and the center core corresponds to an icosahedron cluster with 13 Al atoms.^{34,49,65,66} The previous work also indicated that the preferable doping site was the inner metal core by Dharmaratne et al.⁶⁷ Thus, six possible adsorption sites exist: two different top sites (T1 and T2), two bridge sites (B1 and B2), two different 3-fold hollow sites (Fcc and Hcp).

3. RESULTS AND DISCUSSION

3.1. Reaction Pathways of CO Oxidative Coupling to DMO. CO oxidative coupling to DMO plays a crucial role in CTEG process.⁶⁸ CO couples with methyl nitrite (CH₃ONO) to produce DMO (eq 4) under atmospheric pressure, and CH₃ONO is regenerated by recycling NO (eq 5), which is a rapid reaction at ambient temperature without any catalysts.⁶⁹ The overall reaction is an environmentally benign process of chemical-looping with CH₃ONO as an efficient reoxidizing agent,^{70–72} as eq 6.

$$2CO + 2CH_3ONO \rightarrow (COOCH_3)_2 + 2NO$$
(4)

$$2NO + 2CH_3OH + \frac{1}{2}O_2 \rightarrow 2CH_3ONO + H_2O$$
 (5)

$$2CO + 2CH_3OH + \frac{1}{2}O_2 \rightarrow (COOCH_3)_2 + H_2O$$
 (6)

Table 1. Average Atomic Distance (d_{M-Pd}) , the Average Binding Energy (E_b) , the Core–Shell Interaction Energy (E_{cs}) and CO Adsorption Energy $E_{ads}(CO)$ for M@Pd₁₂ (M = Pd, Al, and Ag) Nanoparticles

parameters	Ag@Pd ₁₂	Pd ₁₃	Al@Pd ₁₂
M–Pd distance (Å)	2.693	2.677	2.563
Pd–Pd distance (Å)	2.787	2.783	2.728
$E_{\rm b}~(\rm kJ\cdot mol^{-1})$	-217.8	-226.0	-255.5
$E_{\rm cs}~({\rm kJ}{\cdot}{\rm mol}^{-1})$	-30.3	-36.1	-63.0
$E_{\rm ads}(\rm CO)~(kJ\cdot mol^{-1})$	-179.8 to -241.8	-183.1 to -242.0	-161.9 to -206.1

CO oxidative coupling reaction is a catalytic process over Pdbased catalysts. However, CH_3ONO is easily dissociated into CH_3O and $NO.^{71,73}$ Hence the dissociation of CH_3ONO is not discussed in following sections, CH_3O radical molecule initiates the reaction of CO oxidative coupling to form DMO.³⁶ Two possible pathways leading to DMO via the reaction of CO and CH_3O are considered and show that

Path 1:

$$\begin{array}{l} \text{CO} + \text{CH}_3\text{O} \rightarrow \text{COOCH}_3 \xrightarrow{+\text{CO}+\text{CH}_3\text{O}} \text{COOCH}_3 \xrightarrow{+\text{COOCH}_3} \text{DMO} \\ \text{Path 2:} \\ \text{CO} + \text{CH}_3\text{O} \rightarrow \text{COOCH}_3 \xrightarrow{+\text{CO}} \text{OCCOOCH}_3 \xrightarrow{+\text{CH}_3\text{O}} \text{DMO} \end{array}$$

In Path 1, the coupling reaction initiates by coadsorption of CO and CH₃O, and CH₃O oxidizes CO to form a highly stable intermediate COOCH₃. Then, the other COOCH₃ is formed via combining CO and CH₃O. Two COOCH₃ couple to each other leading to the formation of DMO, and a new C-C bond is formed in this process, which realizes the conversion of inorganic C1 to organic C2. So Path 1 is named as COOCH₃-COOCH₃ coupling path. Path 2 has the same first step as Path 1, in which CO attacks CH₃O to form a new C-O bond in COOCH₃. Subsequently, COOCH₃ intermediate couples with CO to form intermediate OCCOOCH₃. Therefore, CO-COOCH₃ coupling is named for Path 2. Finally, CH₃O attacks OCCOOCH₃ to generate DMO. Another possible path begins with CO-CO coupling to OCCO and then combines with two CH₃O at two ends of OCCO leading to the formation of DMO, namely, CO + CO \rightarrow OCCO + CH₃O \rightarrow $OCCOOCH_3 + CH_3O \rightarrow DMO$, which has also been presented by Li et al.36 However, the intermediate OCCO cannot stably exist in this catalytic reaction system, so this path will not be considered in our study.

3.2. CO Oxidative Coupling on M@Pd₁₂ (M = Pd, Al, and Ag) Catalysts. 3.2.1. Structural Properties of M@Pd₁₂ (M = Pd, Al, and Ag) Nanoparticles. Pd_{13} , $Al@Pd_{12}$ and Ag@Pd₁₂ core-shell clusters have been constructed and the structural property and stability of three catalysts have also been analyzed. The atomic radius of Al atom (1.430 Å) and Ag atom (1.440 Å) are similar, which are slightly larger than that of Pd atom (1.370 Å).^{66,74} However, the average atomic distances (d) between the core atom M (M = Pd, Al, and Ag) and the shell atom Pd are 2.677, 2.563, and 2.693 Å in Pd₁₃, Al@Pd₁₂, and Ag@Pd₁₂, respectively. It is found that d_{M-Pd} is mainly affected by the interaction between M atom and Pd atom rather than by the atomic radius. The d_{M-Pd} of Al@Pd₁₂ core-shell bimetallic cluster is minimum, which indicates that Al atom strongly bonds with Pd atoms via orbital hybridization between p orbit of Al and d orbit of Pd. Therefore, Al@Pd₁₂ core-shell bimetallic cluster shows the advanced stability, which is consistent with the previous study.³⁴ However, the stability of Ag@Pd12 core-shell bimetallic cluster is weaker than that of Pd_{13} . Additionally, the average binding energy (E_b) and the

core—shell interaction energy (E_{cs}) are also calculated to further analyze the stability of $M@Pd_{12}$ (M = Pd, Al, and Ag) nanoparticles, which are presented in Table 1. The more negative E_b and E_{cs} are, the more stable the catalyst structures are. Obviously, the stability of $M@Pd_{12}$ (M = Pd, Al, and Ag) nanoparticles follows the order of $Al@Pd_{12} > Pd_{13} > Ag@Pd_{12}$. It can be seen that $Al@Pd_{12}$ is the most stable core—shell bimetallic cluster and is expected to be an excellent catalyst for CO oxidative coupling reaction.

3.2.2. DOS and Adsorption Properties. Apparently, the dband center is considered as an important parameter in measuring the distribution of solid energy levels and determining the ability of the surface bonding with adsorption species.⁷⁵ Thus, it is proved that the d-band center of ultrafine Pd nanoclusters is an effective descriptor for the reactivity. In this study, projected density of states (pDOS) and d-band analysis for M@Pd₁₂ (M = Pd, Al, and Ag) nanoparticles are calculated to understand the electronic structure of clusters. The d-band center is calculated as eq 7:⁷⁶

$$\varepsilon_{\rm d} = \frac{\int_{-\infty}^{+\infty} E \rho_d(E) dE}{\int_{-\infty}^{+\infty} \rho_d(E) dE}$$
(7)

where ρ_d represents the density of states projected onto Pd atom's d-band, and *E* is the energy with respect to the Fermi energy, and the integral limits are in the range of $-\infty$ to $+\infty$.

Previous studies have shown that the d-band center determines the energy level of the metal's d-orbitals to some extent, which plays an important role in species adsorption.⁴⁸ So, we have analyzed the relationship between the adsorption energy of CO and the electronic structure of $M @Pd_{12}$ (M = Pd, Al, and Ag), because CO acts as an important reactant in CO oxidative coupling reaction. Adsorption energies of CO on M@ Pd_{12} (M = Pd, Al, and Ag) nanoparticles are shown in Table 1, the corresponding adsorption structures can be seen in the Supporting Information. As shown in Figure 2, d-band centers of Pd₁₃, Ag@Pd₁₂ and Al@Pd₁₂ are -1.36, -1.34, and -1.51 eV, which have a similar trend with the order of the CO adsorption energy E_{ads} (CO) (as shown in Table 1). Taking the d-band center on Pd₁₃ catalyst as the reference, the d-band center of Al@Pd₁₂ moves away from the Fermi energy and CO adsorbed on Al@Pd₁₂ catalyst is the smallest adsorption energy $(-161.9 \text{ to } -206.1 \text{ kJ} \cdot \text{mol}^{-1})$, while the d-band center of Ag@ Pd₁₂ catalyst is close to the value of Pd₁₃ catalyst and CO exhibits similar adsorption capability. This result is consistent with previous studies, in which the lower d-band center shows weaker metal-adsorbate binding strength.^{77,78} As described above, different doped metal atoms lead to different d-band centers of clusters, which can be cited to explain the adsorption capability of species and can also be used to predict the catalytic activity. The catalytic activity of these clusters with different core atoms and same shell atoms will be discussed in the following section.



Figure 2. Projected density of states (pDOS) plots of the d-orbitals for the outer layer Pd atoms of $M@Pd_{12}$ (M = Pd, Al, and Ag) nanoparticles. The vertical dashed line represents the location of d-band center, and the vertical solid line indicates Fermi energy level.

3.2.3. Reaction Mechanism on $M@Pd_{12}$ (M = Pd, Al, and Ag) Catalysts. All possible reaction pathways for CO oxidative coupling to DMO on $M@Pd_{12}$ (M = Pd, Al, and Ag) catalysts, including reactive species on different adsorption sites (Figures S1-S3), are considered. We investigate almost all possible of the coadsorbed conformations for each elementary reaction in order to find the optimal reaction pathway, and a series of stable configurations are obtained and used for the transition state search, finally TS confirmation is used to prove its accuracy. Potential energy diagrams for each elementary reaction on Pd₁₃ catalyst can be seen in Figures S4-S8 in the Supporting Information, potential energy diagrams for different reaction paths on Pd₁₃, Al@Pd₁₂, Ag@Pd₁₂ catalysts are shown in Figures S9-S11, and the potential energy diagram of the favorable reaction path of CO oxidative coupling to DMO on these three catalysts is shown in Figure 3.

It is found that CO oxidative coupling to DMO prefers to $COOCH_3$ - $COOCH_3$ coupling path on M@Pd₁₂ (M = Pd, Al, and Ag) catalysts. The rate-limiting step is that CO is oxidized by CH₃O to form an intermediate COOCH₃ on Pd₁₃ and Ag@ Pd₁₂ catalysts, corresponding elementary reactions are needed to overcome activation barriers of 142.0 and 276.1 kJ·mol⁻¹, respectively. However, the rate-limiting step is that CO attacks CH₃O to form the other COOCH₃ on Al@Pd₁₂ catalyst with an activation barrier of 72.7 kJ·mol⁻¹. Obviously, Al@Pd₁₂ catalyst exhibits higher activity for CO oxidative coupling to form DMO than Pd13, while Ag@Pd12 catalyst shows lower catalytic activity. In addition, the catalytic activity of Al@Pd₁₂ is even higher than that of the Pd(111) surface (72.7 vs 114.6 kJmol⁻¹).³⁶ The d-band center is also used to investigate the activity of different catalysts. The d-band center is far away from the Fermi energy; the adsorption of CO is slightly weak but still retains chemical adsorption, implying that CO is easier to move at surface. It will reduce the reaction energy barrier of CO reacting with CH₃O and facilitate the progress of the reaction. The study of Kible et al.⁷⁹ also showed that the situation leads to a maximum in catalytic activity when the ability of the Pd surface to bind adsorbates is not too weak and not too strong. Thus, we expect that Al-doping can provide a good clue for further reducing the amount of noble-metal Pd aiming at CO oxidative coupling reaction.

3.3. CO Oxidative Coupling on Al_6@Pd_{32} Catalyst. Adsorptions of all possible species during CO oxidative coupling to DMO on $Al_6@Pd_{32}$ are shown in Figure S12. The reaction starts from CO and CH₃O located at two adjacent bridge sites of the square (100) facet, and it needs to overcome a higher energy barrier of 147.5 kJ·mol⁻¹ to produce intermediate COOCH₃ undergoing TS4-1, as shown in Figure 4. It is harder to occur on $Al_6 @Pd_{32}$ than that on $Al @Pd_{12}$. For Path 1, COOCH₃ adsorbs at H-site, CO and CH₃O adsorb at two adjacent B-sites, which overcomes a higher barrier of 181.3 kJ·mol⁻¹ to form other COOCH₃. And then, two COOCH₃ locate at the opposite bridge sites on the (100) facet. Subsequently, the complex of two COOCH₃ intermediates overcomes an energy barrier of 162.2 kJ·mol⁻¹ to form DMO. For Path 2, the coadsorption configuration of CO and $COOCH_3$ occurs through C-C coupling via TS4-4 to form a stable intermediate OCCOOCH₃ at H site on the (100) facet, which is the rate-limiting step and needs to overcome a highest barrier of 152.4 kJ·mol⁻¹. This process is also the rate-limiting step on the Pd(111) surface with an energy barrier of 118.4 kJ. mol^{-1} .³⁶ Besides, we can see that the (111) surface exhibits a high reaction activity for this step compared with that on the (100) surface. Subsequently, CH₃O attacks OCCOOCH₃ via TS4-5 to form DMO, the energy barrier and reaction energy are 105.0 and -9.5 kJ·mol⁻¹. Obviously, Path 2 is the optimal pathway when we compare the activation energies of the ratelimiting steps of these two pathways (152.4 kJ·mol⁻¹ vs 181.3 kJ·mol⁻¹).

3.4. DMO Formation on Al₁₃@Pd₄₂ Catalyst. Al₁₃@Pd₄₂ catalyst with a higher Al:Pd ratio of 1:3 is investigated in this section. CO and CH₃O at T2 and T1 sites are first conjoined with each other, as shown in Figure 5. It overcomes an energy barrier of 26.4 kJ·mol⁻¹ to form a new C-O bond, the produced COOCH₃ intermediate adsorbs at T2 site. However, a higher energy barrier of 34.8 kJ·mol⁻¹ is needed on the Pd(111) surface for the same step.³⁶ It is similar to the previous work that Pd(111) is an active surface for CO oxidative coupling reaction.³⁵ Subsequently, the produced COOCH₃ migrates to more stable B1 site via TS5-2 with a low energy barrier of 2.9 kJ·mol⁻¹. And then, starting from CO + CH₃O (COOCH₃), two different next steps are undergone: the process of forming the second COOCH₃ of Path 1 needs to overcome an activation energy of 119.9 kJ·mol⁻¹, and a new C–C bond is formed via TS5-5 with an energy barrier of 135.7 kJ·mol⁻¹ for Path 2. They are the rate-limiting steps of Path 1 and Path 2, respectively. In the last step, an energy barrier of 66.4 kJ·mol⁻¹ is need in two COOCH₃ coupling to each other via TS5-4 of Path 1, and CH₃O approaches OCCOOCH₃ to form DMO via TS5-6 with an energy barrier of 60.3 kJ·mol⁻¹ of Path 2. Obviously, Path 1 is more optimal than the Path 2 on Al₁₃@Pd₄₂ catalyst, which is in consistent with that on Al@Pd₁₂ catalyst, but is not in agreement with that on Al₆@Pd₃₂ catalyst. At the same time, $Al@Pd_{12}$ and $Al_{13}@Pd_{42}$ have a similar surface structure to Pd(111) surface, and Al₆@Pd₃₂ exhibits Pd(100) surface properties. Thus, we suggest that surface structures affect the favorable reaction pathway, which agrees with previous work showing that three different preferable pathways for C diffusion are on three Fe surfaces.⁸⁰

3.5. General Discussion. 3.5.1. Effect of Surface Structures on Reaction Activity for DMO Formation. Nanoclusters that have different atom coordination number from the surface, unsaturated Pd atoms with low-coordinated are the main adsorption sites for different clusters. Previous studies have shown that C_2H_2 selective hydrogenation occurs at the edge and corner sites of Cu_n cluster (n = 13, 38, and 55) because of low coordination numbers.⁸¹ Moreover, CO is at the vertex site and CH₃O is at the edge bridge site, when the



Figure 3. Potential energy profile for the most favorable formation pathway of CO oxidative coupling to DMO on $M@Pd_{12}$ (M = Pd, Al, and Ag) catalysts.

formation pathway for CH_x (x = 1-3) species occurs in Cu_{55} cluster,⁸² which is consistent with the conclusion we have obtained in this study. Even though there is a similar conclusion on the stepped surface, the Pd(211) surface is composed of a stepped surface with a coordination number of 7 and a plane with a coordination number of 9, it is found that species adsorbed on the edge atom with a coordination number of 7 for reduction of NO by H₂ on the Pd(211) surface.⁸³ However, all reaction occurs on different surfaces consisting of unsaturated Pd atoms, which show different reaction properties. The

preferable pathways of CO oxidative coupling to form DMO are different for Al@Pd₁₂, Al₆@Pd₃₂, and Al₁₃@Pd₄₂ catalysts. CO–COOCH₃ coupling path is the favorable pathway on Al₆@Pd₃₂ because of lower symmetry and which occurs on the (100) surface. However, COOCH₃–COOCH₃ coupling path becomes the optimal pathway on Al@Pd₁₂ and Al₁₃@Pd₄₂, which exhibits high activity similar to (111) surface. Simultaneously, the structure–activity relationship for gold alloy nanoclusters has been investigated by the DFT method,



Figure 4. Potential energy diagram of the reaction of CO oxidative coupling to DMO, as well as structures of initial states, transition states, and final states on Al₆@Pd₃₂ core-shell bimetallic catalyst.

and the result showed that icosahedral metal clusters exhibited special catalytic properties.⁸⁴

The energy barriers of rate-limiting steps during CO oxidative coupling to DMO on Al@Pd12, Al6@Pd32, and Al_{13} @Pd₄₂, as well as Pd(111) surface are shown in Figure 6. It can be seen that the order of the energy barrier is Al₆@Pd₃₂ $(152.4 \text{ kJ} \cdot \text{mol}^{-1}) > \text{Al}_{13} @ \text{Pd}_{42} (119.9 \text{ kJ} \cdot \text{mol}^{-1}) \approx \text{Pd}(111)$ $(114.6 \text{ kJ} \cdot \text{mol}^{-1})^{36} > \text{Al} @ \text{Pd}_{12} (72.7 \text{ kJ} \cdot \text{mol}^{-1}). Obviously,$ Al₆@Pd₃₂ core-shell catalyst exhibits the lowest activity of CO oxidative coupling to DMO. The reason is that Al₆@Pd₃₂ has a similar Pd(100) surface, and all elementary reactions happen on that facet. Previous research has also proved that the Pd(100)surface shows lower activity than the Pd(111) surface.³⁵ Al@ Pd₁₂ and Al₁₃@Pd₄₂ show high activity, which is similar to the Pd (111) surface. However, the Al_{13} @Pd₄₂ catalyst can achieve a significant reduction in the amount of noble-metal Pd and maintain the relative activity of the Pd-based catalyst. Moreover, previous study showed that Al13@Pt42 catalyst can also improve the activity and reduce the amount of noble metals aiming at oxygen reduction reaction.³⁴

3.5.2. Selectivity of AI_{13} @Pd₄₂ Catalyst for DMO. In addition, a good catalyst not only possesses high activity and

low cost but also has high selectivity. In this work, $Al_{13}@Pd_{42}$ catalyst shows high activity and doped ratio of Al than other clusters; thus, it is necessary to study the selectivity to DMO on $Al_{13}@Pd_{42}$ catalyst, as shown in Figure 7. CH₃O approaches and attacks COOCH₃ intermediate will lead to the formation of Dimethyl carbonate (DMC), which is detected in experiment.^{4,35,36} The formation of DMC needs to overcome a high barrier of 215.9 kJ·mol⁻¹, which is 96.0 kJ·mol⁻¹ higher than the process of forming the second COOCH₃ in Path 1 (119.9 kJ·mol⁻¹). It indicates that the formation of DMC is very difficult to happen on $Al_{13}@Pd_{42}$ catalyst, implying a high selectivity toward DMO. A similar high selectivity of DMO has also been obtained on the Pd(111) surface by in situ DRIR spectroscopy and space-time yields.³⁶

4. CONCLUSIONS

The activities of core-shell Pd-based catalysts toward CO oxidative coupling to DMO were evaluated by the DFT calculation, and the effects of doped non-noble metal and surface structures of Pd-based catalysts on reaction activity and preferable pathway were revealed. For $M@Pd_{12}$ (M = Pd, Al, and Ag) catalysts, both energy barriers and electronic analysis



Figure 5. Potential energy diagram of the reaction of CO oxidative coupling to DMO and structures of initial states, transition states, and final states on Al_{13} @Pd₄₂ core-shell bimetallic catalyst.



Figure 6. Energy barriers of rate-limiting steps during CO oxidative coupling to DMO on $Al@Pd_{12}$, $Al_6@Pd_{32}$, $Al_{13}@Pd_{42}$, and Pd(111) surface.

showed that $Al@Pd_{12}$ exhibited the best activity for CO oxidative coupling to DMO. However, the non-noble-metal doping ratio of $Al@Pd_{12}$ was relatively low, only 1:12. Therefore, $Al_6@Pd_{32}$ and $Al_{13}@Pd_{42}$ catalysts with higher Al:Pd ratios of 1:5 and 1:3 were selected to further reduce the amount of noble-metal Pd. In addition, the preferable pathway of DMO formation changed with the change of surface structures, in which CO-COOCH₃ coupling path was the favorable pathway on the (100) surface of $Al_6@Pd_{32}$ catalyst, and the favorable pathway on the (111) surface of $Al@Pd_{12}$ and $Al_{13}@Pd_{42}$ catalysts was COOCH₃-COOCH₃ coupling path. The catalytic activity of $Al_{13}@Pd_{42}$ catalyst was higher than that



Figure 7. Comparison of the simplified potential energy profile for the pathway of DMO and DMC formation together with structures of initial states, transition states, and final states on $Al_{13}@Pd_{42}$ core-shell bimetallic catalyst.

of $Al_6@Pd_{32}$, similar to the pure Pd catalyst, while lower than that of $Al_@Pd_{12}$. In addition, $Al_{13}@Pd_{42}$ catalyst showed a good

selectivity. Thus, Al_{13} @Pd₄₂ core-shell catalyst was a good candidate for CO oxidative coupling to DMO with a low cost and relatively high activity and selectivity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b09272.

Details of adsorption energies and adsorption configurations of the relevant species during CO oxidative coupling reaction on different core-shell Pd-based catalysts, and structures of initial states, transition states, and final states of all elementary steps involving in all possible reaction pathways (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail for B.J.W.: wangbaojun@tyut.edu.cn. Tel.: +86 351 6010898. Fax: +86 351 6041237.

*E-mail for L.X.L.: linglixia@tyut.edu.cn

ORCID 0

Maohong Fan: 0000-0003-1334-7292

Baojun Wang: 0000-0002-9069-6720

Notes

The authors declare no competing financial interest.

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