



Theoretical Study of Direct Carbon Dioxide Conversion to Formic Acid on Transition Metal-doped Subnanometer Palladium Clusters

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Highlights:

- Transition metal-doped subnanometer palladium clusters were used as catalyst for direct CO₂ hydrogenation to formic acid without the presence of base additives.
- The transition metal-doped subnanometer palladium clusters were more selective toward CO₂ hydrogenation to formic acid than the reverse water gas shift reaction.
- The nickel doped palladium cluster system had the best turnover frequency for formic acid formation.

Abstract. We studied the direct conversion of CO₂ to HCOOH through hydrogenation reaction without the presence of base additives on the transition metal-doped subnanometer palladium (Pd₇) cluster (Pd_xM: M = Cu, Ni, Rh) by using a combination of density functional theory and microkinetic calculations. It was shown that the CO₂ hydrogenation on Pd₇ and Pd₆M clusters are more selective towards the formate pathway to produce HCOOH than the reverse water gas shift pathway to produce CO. Inclusion of Ni and Rh doping in the subnanometer Pd₇ cluster could successfully enhance the turnover frequency (TOF) for CO₂ hydrogenation to formic acid at low temperature. The order of TOF for formic acid formation is as follows: Pd₆Ni > Pd₆Rh > Pd₇ > Pd₆Cu. This order can be explained by the trend of the activation energy of CO₂ hydrogenation to formate (HCOO*). The Pd₆Ni cluster has the highest TOF value because it has the lowest activation energy for the formate formation reaction. The Pd₆Ni system also has a superior TOF profile for HCOOH formation compared to several metal surfaces in low and high-temperature regions. This finding suggests that the subnanometer Pd_xNi cluster is a promising catalyst candidate for direct CO₂ hydrogenation to formic acid.

Keywords: CO₂ hydrogenation; density functional theory; formic acid; microkinetic; subnanometer Pd cluster; transition metal doping.

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1 Introduction

The conversion of carbon dioxide (CO₂) to valuable chemicals is one of humanity's grand schemes to battle the threat of global warming [1-4]. Among these schemes is the direct CO₂ conversion to formic acid (HCOOH) through a series of hydrogenation reactions [4]. This scheme is important owing to the potential applications of formic acid. It can be employed as chemical feed for producing more complex chemical structures, reversible hydrogen storage, and also as input for fuel cells to generate electricity [4].

The process of CO₂ hydrogenation to HCOOH on a heterogeneous catalyst system possesses many benefits as compared to a homogeneous catalyst, including simple product separation, good catalyst stability, easy handling, and easy usability [4,5]. Unfortunately, the catalytic activity of heterogeneous catalysts for this process is currently still limited. Some of the factors causing the low catalytic activity are the endergonic profile of the conversion process, the inertness of the CO₂ molecules, and the existence of high activation energies for the hydrogenation reactions. To improve the catalytic activity, the presence of additional base solutions is required to make the reaction exergonic [4,5].

In recent years, supported palladium-based nanoparticles on metal-oxide and carbon-based materials have been reported to give excellent catalytic activities toward CO₂ hydrogenation to HCOOH in the presence of base additives [4,6-11]. While the presence of bases is important, the possibility of omitting them is quite intriguing since it allows for the elimination of the additional product purification step and the product can also be separated with simple filtration [12]. The work of Nguyen *et al.* was the first to experimentally show that CO₂ hydrogenation to HCOOH in the absence of base additives can actually be realized at relatively low pressure by using supported Pd-Ni alloy nanoparticles on CNT-graphene composite, even though the catalytic activity is still relatively low [12]. More efforts are needed to enhance the ability of Pd-based nanoparticles to directly convert CO₂ to HCOOH without the presence of base additives. This enhancement may be achieved if we can find a catalyst that can easily activate CO₂ molecules and improve the reaction profiles for the elementary hydrogenation reactions.

In our previous study [13], we compared the ability of a small subnanometer Pd cluster (Pd_x) and supported large-Pd nanoparticles on metal oxide to catalyze the CO₂ hydrogenation to methanol. We found that a large-Pd island can only act as an H₂ dissociation center when the oxide surface acts as the CO₂ hydrogenation center. On the other hand, the Pd_x clusters can act not only as an H₂ dissociation center but also as a CO₂ hydrogenation center. One of the reasons is that the Pd_x clusters can easily activate inert CO₂ molecules by donating some charges to the

anti-bonding orbital of the CO₂ molecules, which enhances the repulsion inside the molecules. To minimize this repulsion, the CO₂ molecules break their linear O-C-O angle, which results in a bidentate adsorption configuration. The bidentate adsorption configuration weakens the C-O bonds inside the adsorbed CO₂ molecules and makes the molecules more reactive. All of these features indicate that a small subnanometer Pd_x cluster may be used as the foundation for designing a new catalyst for direct CO₂ hydrogenation to HCOOH.

As an attempt to overcome the challenge of excluding base additives, in this study we tried to use small (subnanometer) Pd_x clusters doped by transition metals (Pd_xM; M = Cu, Ni, and Rh) as catalyst candidate for CO₂ hydrogenation to HCOOH. We previously found that the addition of these transition metal dopings to a subnanometer Pd₇ cluster can intensify its interaction with the CO₂ molecules and also allows the molecules to be bent and adsorbed with a bidentate adsorption configuration [14]. This strong interaction may have a positive effect on the ability of the cluster to catalyze the CO₂ hydrogenation to HCOOH.

We performed systematic density functional theory (DFT) calculations to simulate the elementary reactions of CO₂ hydrogenation to HCOOH on the Pd_xM clusters. The calculated adsorption energies, reaction energies, and activation energies of the elementary reactions from the DFT calculations were utilized to perform microkinetic simulations to obtain the turn-over frequencies (TOFs) of the CO₂ hydrogenation reaction on the Pd_xM clusters as a measure of their reactivity.

2 Computational Details

2.1 Cluster Models

We chose the Pd₇ cluster structure from our previous study as the basic model to represent small subnanometer Pd_x clusters [13]. The size of this cluster is large enough to accommodate the co-adsorption of CO₂ hydrogenation-related reactants and products. This cluster model has also been successfully used to study the HCOOH decomposition reaction [15]. In a more realistic catalyst model, the subnanometer Pd_x cluster should be placed on a support material. However, our previous study showed that the Pd₇ cluster maintained its original structure when it was deposited on a metal oxide surface, even though insignificant geometrical reconstructions were induced by the corrugated nature of the metal oxide surface [13]. Moreover, we also showed that the adsorption properties of the CO₂ molecules on this cluster did not change in the presence of a support material. Therefore, for the sake of simplicity, here we used an unsupported subnanometer Pd₇ cluster for modeling the CO₂ hydrogenation reactions.

We constructed a transition metal doped Pd₇ model by substituting one of the Pd atoms in the cluster with a transition metal atom M (Pd₆M). We then compared the total energies for all of the seven possible substitution sites. The configuration that gave the lowest total energy was chosen as the model for the Pd₆M cluster. This procedure was repeated for all of the M atoms (M = Cu, Ni, and Rh). The most stable structure of the Pd₇ and Pd₆M clusters were taken from reference [14], as presented in Figure 1.

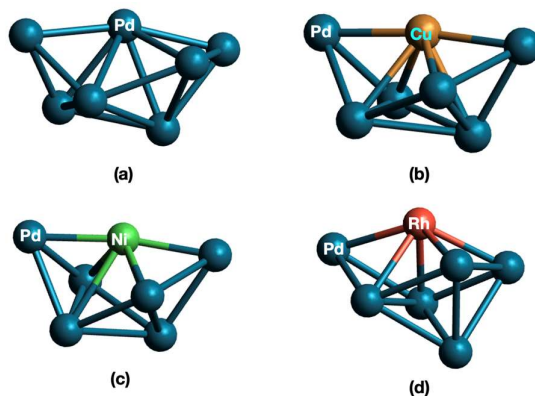


Figure 1 The most stable structures of (a) Pd₇, (b) Pd₆Cu, (c) Pd₆Ni, and (d) Pd₆Rh clusters.

2.2 DFT Calculations and Microkinetic Modeling

We utilized density functional theory (DFT) calculations to study the CO₂ hydrogenation to HCOOH on the Pd₇ and Pd₆M clusters. The DFT calculations were performed using the Gaussian09 software package. We used the same calculation parameters as in our previous study about CO₂ conversion to methanol on small Pd_x clusters. The B3LYP functional was used as the exchange-correlation potential. We used the 6-311++G** basis sets for light atoms (H, C, and O), and the LANL2DZ basis sets with effective core potentials for the transition metal atoms (Pd, Cu, Ni, and Rh).

The adsorption energy (E_{ads}) of a molecule on a Pd₆M cluster was calculated using Eq. (1):

$$E_{ads} = E_{system} - (E_{Pd_6M} + E_{mol}) + \Delta ZPE, \quad (1)$$

where E_{system} corresponds to the total energy of the adsorption system, E_{Pd_6M} corresponds to the total energy of the isolated Pd₆M cluster, and E_{mol} corresponds to the total energy of the isolated molecule. ΔZPE corresponds to the difference in the zero-point energy correction for the total system and the isolated systems.

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The corresponding spin configurations for the calculation of E_{system} , E_{Pd6M} and E_{mol} are set in their respective spin ground state configurations.

The activation energy for an elementary reaction (E_{act}) was calculated using Eq. (2):

$$E_{act} = E_{ts} - E_{is}, \quad (2)$$

where E_{ts} and E_{is} correspond to the total energy of the initial state and the transition state of the elementary reaction. The structure and the energy of the transition state were calculated using the synchronous transit-guided quasi-newton (STQN) method. We affirm that the obtained transition state structure only has one imaginary frequency.

The obtained energetical data from the DFT calculations were used as inputs for microkinetic simulations to obtain the turnover frequencies (TOFs) of CO₂ hydrogenation reactions. We used Eqs. (3) and (4) to address the adsorption and desorption reactions:

$$k_{ads} = \frac{A}{\sqrt{2\pi mk_B T}} \exp\left(-\frac{E_{ads}}{k_B T}\right) \quad (3)$$

$$k_{des} = \frac{k_B T^3}{h^3} \frac{A(2\pi mk_B)}{\sigma \Theta_{rot}} \exp\left(-\frac{E_{des}}{k_B T}\right) \quad (4)$$

where A is the active site catalytic surface, m is the molecular mass of the gas, σ is the symmetry number of the molecule, and Θ_{rot} is the characteristic rotational temperature of the molecule. E_{ads} and E_{des} represent the adsorption and desorption energy, respectively. The rate for surface reactions was treated using Eq. (5):

$$k = \frac{k_B T}{h} \exp\left(-\frac{E_a}{k_B T}\right) \quad (5)$$

where E_a is the reaction activation energy. We ignored the partition function ratio due to negligible entropy change.

The overall rate of each elementary step can be written as the difference between the forward and backward reaction rates:

$$r_i = k_{f,i} \prod_{j \in IS} P_j \theta_j - k_{b,i} \prod_{j \in FS} P_j \theta_j \quad (6)$$

where r_i is the rate of elementary step i , P_j is the partial gas pressure of species j , and θ_j is the fractional coverage of species j . The rate of change of all coverages can be expressed using Eq. (7):

$$\frac{d\theta_j}{dt} = \sum_{i \in FS} n_i r_i - \sum_{i \in IS} n_i r_i \quad (7)$$

where n_i is the number of adsorbate j being produced (left term) or consumed (right term) in elementary step i . The sum of all coverages has to be conserved. This condition is expressed using Eq. (8):

$$\sum_j \theta_j = 1 \quad (8)$$

Details of the microkinetic model derivation for typical hydrogenation reaction can be found in our recent works [13,16-18].

To estimate the contribution of each step to the overall reaction rate, we used Campbell's degree of rate control (XRC) [19,20], which can be defined using Eq. (9):

$$XRC_i = \left(\frac{\partial \ln r}{\partial \ln k_i} \right)_{K_i, k_{i \neq j}} \quad (9)$$

where the calculation holds the equilibrium constant of step i (K_i) and the rate constant of step j (where $i \neq j$) to be unvarying.

3 Results and Discussions

3.1 HCOOH vs CO Formations

The initial CO₂ hydrogenation step (CO₂* + H*) may result in two different reaction pathways. The first possibility is the formation of an adsorbed formate (HCOO*), which leads to the formation of HCOOH, the desired product of this study. This reaction pathway is known as the formate pathway. The second possibility is the formation of an adsorbed hydrocarboxyl (HOCO*), which leads to the formation of carbon monoxide (CO) and water (H₂O) molecules. The second pathway is known as the reverse water gas shift reaction (RWGS). The energetical data for CO₂ hydrogenation through the formate and RWGS pathways is presented in Table 1.

The sequence of elementary reactions for the formation of HCOOH through the formate pathway follows reactions R1-R5, while the formation of CO through the RWGS pathway follows reactions R1-R2 and R6-R10. The optimized geometries for important adsorbates are presented in Figure 2. We will compare the turnover frequencies (TOFs) for these two reaction pathways on the Pd₇ and Pd₆M clusters to understand the selectivity of the clusters toward HCOOH production.

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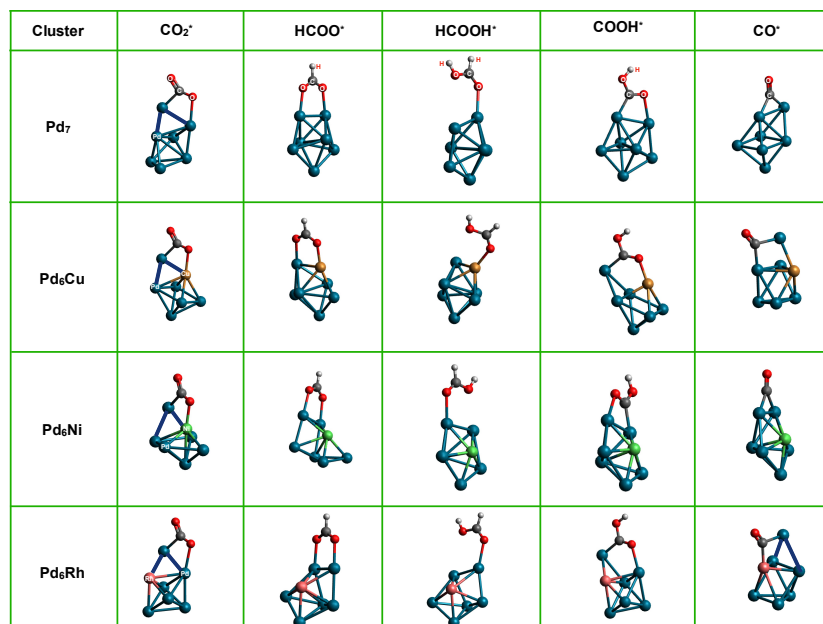


Figure 2 Optimized geometries for CO₂, HCOO, HCOOH, COOH, and CO adsorptions on the Pd₇ and Pd₆M clusters.

Table 1 Activation energies (E_{act}) and reaction energies (ΔE) for elementary reactions involved in the CO₂ hydrogenation to HCOOH and CO. All values are in eV. * and *X corresponds to the free adsorption site and adsorbed X species.

Elementary Reaction	Pd ₇ [13]		Pd ₆ Cu		Pd ₆ Ni		Pd ₆ Rh	
	E_{act}	ΔE	E_{act}	ΔE	E_{act}	ΔE	ΔE	E_{act}
R1 H _{2(g)} + * + * → H* + H*	-	-0.73	-	-0.64	-	-0.58	-	-0.73
R2 CO _{2(g)} + * → CO ₂ *	-	-0.21	-	-0.45	-	-0.40	-	-0.24
R3 CO ₂ * + H* → HCOO* + *	0.93	-0.21	1.06	-0.31	0.87	-0.22	0.94	-0.19
R4 HCOO* + H* → HCOOH* + *	1.16	0.94	1.05	1.05	1.05	0.72	1.19	1.02
R5 HCOOH* → HCOOH _(l) + *	-	0.50	-	0.55	-	0.43	-	0.31
R6 CO ₂ * + H* → HOCO* + *	1.90	0.39	1.92	0.48	0.80	0.27	1.71	0.22
R7 HOCO* + * → CO* + OH*	0.44	-1.05	0.83	-0.88	1.04	-0.85	0.63	-0.51
R8 CO* + OH* + H* → CO* + H ₂ O* + *	1.26	-0.17	1.12	-0.22	0.71	-0.47	0.84	-0.28
R9 CO* + H ₂ O* → CO* + H ₂ O _(l) + *	-	0.51	-	1.16	-	0.44	-	0.35
R10 CO* → CO _(g) + *	-	1.88	-	1.24	-	1.86	-	1.28

The energetical data in Table 1 were used as inputs for the microkinetic simulation to calculate the TOFs of the formate and RWGS pathways on the Pd₇ and Pd₆M clusters. The microkinetic simulation was done at p = 50 bar with CO₂:H₂ ratio of 1:1. These parameters were used to mimic the reaction conditions of direct CO₂ hydrogenation to HCOOH on supported Pd-Ni alloy nanoparticles on CNT-graphene in the absence of base additives [12]. A comparison of the TOFs of the formate and RWGS pathways is presented in Figure 3. It can clearly

be seen that the TOFs of HCOOH formation from the formate pathway were significantly larger than the TOFs of CO formation through the RWGS pathway. One of the reasons is that the activation energies for HOCO formation are in general larger than those for the HCOO formation. Moreover, the reaction profiles for HCOO formation are in general exothermic while the reaction profiles for HOCO formation are endothermic. These two factors make the initial step of CO₂ hydrogenation energetically prefer HCOO formation. The other reason is due to the strong CO adsorption energy on the Pd₇ and Pd₆M clusters (E_{ads}^{CO} is equivalent to the $-\Delta E$ value for reaction R10). The CO adsorption energies are significantly larger than the HCOOH adsorption energies (E_{ads}^{HCOOH} is equivalent to the $-\Delta E$ value for reaction R5). The very strong CO adsorption energy prevents the molecule to be desorbed as a product and this makes the TOF of CO production on Pd₇ and Pd₆M clusters become significantly lower than that of HCOOH production. The strongly adsorbed CO molecule may be reduced to HCO with high activation energy ($E_{act} > 1.4$ eV [13]) or it may be reverted to CO₂ through the water-gas shift reaction. This result suggests that CO₂ hydrogenation on Pd₇ and Pd₆M clusters is indeed more selective towards HCOOH production than CO production.

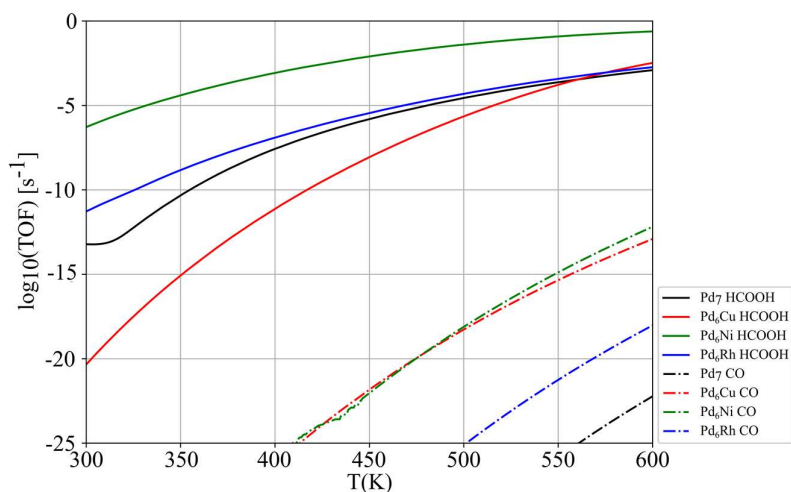


Figure 3 Comparison of TOFs for the formation of HCOOH and CO on the Pd₆M clusters at $p = 50$ bar and a CO₂:H₂ ratio of 1:1.

In general, the trend of the TOF for HCOOH formation on the Pd₆M system is the following: Pd₆Ni > Pd₆Rh > Pd₇ > Pd₆Cu. This trend shows that the inclusion of transition metal doping to the subnanometer Pd₇ cluster can really enhance the TOF for CO₂ hydrogenation to HCOOH, especially for Ni doping and Rh doping.

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The trend of TOF towards CO₂ hydrogenation to HCOOH for Pd₆M clusters is explained as follows. The rate-limiting reaction for HCOOH formation on Pd₇ and Pd₆M clusters can be identified by analyzing the profile of the degree of rate control (XRC) as a function of temperature. An XRC_{*i*} of zero indicates that the rate constant of elementary step *i* has no effect on the overall rate constant, where XRC_{*i*} = 1 implies that step *i* determines the overall reaction rate [19,20]. The XRC for the Pd₇ system is presented in Figure 4 as an example,.

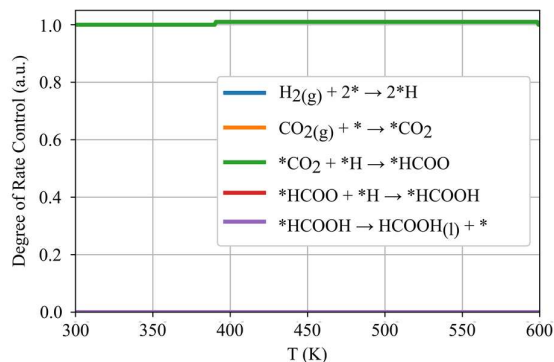


Figure 4 Degree of rate control (XRC) for CO₂ hydrogenation to HCOOH on the Pd₇ and Pd₆M clusters.

We find that the XRC for HCOOH formation on Pd₆M clusters actually has a similar profile as on the Pd₇ cluster. This means that the rate-limiting reaction for HCOOH formation on all of these clusters originates from the initial CO₂ hydrogenation step to formate (R3: CO₂* + H* → HCOO*), since this reaction dominates the XRC profile. Because all of the Pd₆M clusters exhibit similar XRC profiles, we can explain the trend of TOFs towards CO₂ hydrogenation to HCOOH by using the trend of activation energy (E_{act}) towards formate formation (R3). The trend of E_{act} versus TOF at the selected temperatures is given in Figure 5. We can see in general that the TOF increased as the E_{act} decreases. The Pd₆Ni cluster had the highest TOF because this system had the lowest activation energy for the initial CO₂ hydrogenation to formate.

The formation of formate requires two steps: (1) the bending of the linear O-C-O configuration, and (2) the desorption of an adsorbed H from the catalyst to the adsorbed CO₂ molecule [13,18,21]. The first condition is already fulfilled on Pd₇ and Pd₆M clusters due to the formation of CO₂ bidentate configuration. The second condition depends on the hydrogen adsorption energy on the cluster. The Pd₆Ni cluster has the lowest activation energy for formate formation because this system has the weakest H adsorption energy, as indicated by the value of ΔE for

R1 in Table 1. Interestingly, the inclusion of Ni doping to the Pd₇ cluster not only reduces the activation energy for formate formation, but also for the subsequent hydrogenation reaction (R4: HCOO* + H* → HCOOH*) relative to the non-doped Pd₇ cluster system. These two conditions only occur in the Pd₆Ni system. This makes the Pd₆Ni system have the highest activity towards HCOOH production.

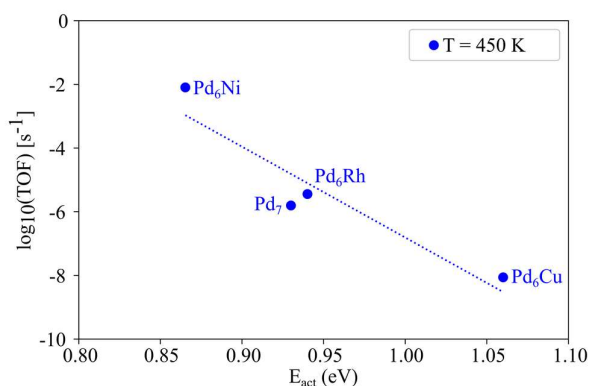


Figure 5 Comparison of activation energy (E_{act}) of formate formation (R3) versus TOF of CO₂ hydrogenation to HCOOH on the Pd₇ and Pd₆M clusters.

3.2 Trend of HCOOH Formation

In this subsection, we compare the TOF for CO₂ hydrogenation to HCOOH on the Pd₇ and Pd₆M clusters with other catalyst models. We used the energetical data available from the literature for HCOOH formation or decomposition as the inputs for microkinetic simulations to calculate the TOFs for CO₂ hydrogenation to HCOOH formation in the absence of base additives. We used the energetical data of a large Pd₅₅ cluster [22] to represent the model of Pd nanoparticles. We also use the energetical data of flat Pd(111) [23], Cu(111) [24], Ni(111) [18,25,26], and Rh(111) [26,27] surfaces to show the initial activities of the transition metal M doping. The calculated TOFs are presented in Figure 6. The comparison was done at $p = 50$ bar with CO₂:H₂ ratio of 1:1.

In general, the TOF profiles for HCOOH reaction on Pd₆M clusters were relatively better than those on their respective M(111) surfaces, except for the Pd and Cu cases. In the Pd case, the TOFs of the pure Pd₇ cluster and Pd(111) surface were slightly smaller than that of the Pd₅₅ cluster at low temperature region. However, their TOFs converged into the same value in a higher temperature region. This suggests that Pd nanoparticles in pure form are more appropriate for low-temperature direct CO₂ hydrogenation to HCOOH catalyst than the

subnanometer Pd₇ cluster and the Pd(111) surface. For the Cu case, the TOF of the Cu(111) surface in the low temperature region was much higher than that of the Pd₆Cu cluster. Interestingly, the Cu(111) surface also had the best TOF profile for HCOOH formation compared to the other flat metal surfaces in the low temperature region. The good TOF profile of the Cu(111) surface was in agreement with a recent experimental finding that showed the exceptional performance of Cu-based active sites in catalyzing CO₂ hydrogenation to HCOOH [28].

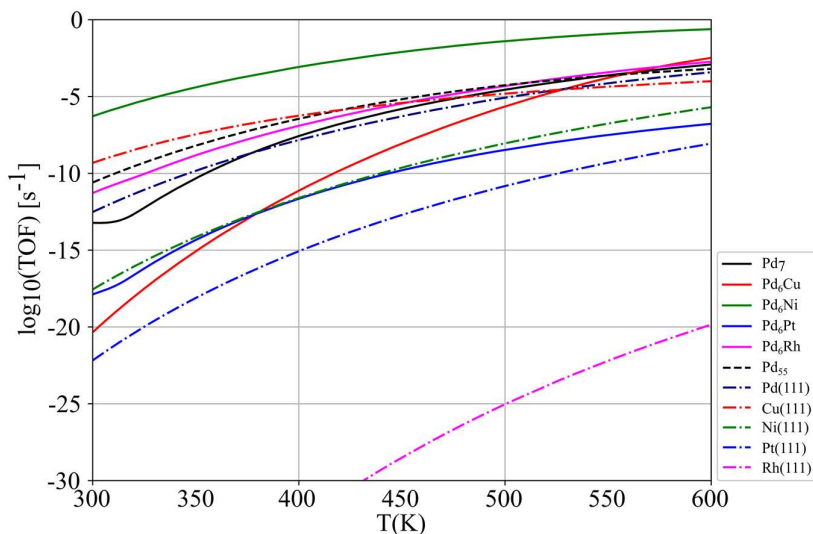


Figure 6 Comparison of turn-over frequencies (TOF) of CO₂ hydrogenation to HCOOH at $p = 50$ bar and CO₂:H₂ ratio of 1:1 for the Pd₇ and P₆M clusters with some metal surfaces.

The best TOF profile for HCOOH formation in this comparison was achieved in the Pd₆Ni cluster system. This system has superior TOF profiles in low and high temperature regions. This result suggests that the subnanometer Pd_xNi cluster may be used as a promising catalyst candidate for direct CO₂ hydrogenation to HCOOH. The activity of this catalyst can still be improved by optimizing several physical parameters. Our previous study showed that the size of the subnanometer Pd_x cluster affects the TOF for CO₂ hydrogenation to methanol [13]. The TOF increases as the size increases. However, at some point, the activity of the Pd cluster will decrease because a large size Pd island can only act as an H₂ dissociation center and not as a CO₂ hydrogenation center. Therefore, the activity of the Pd_xNi cluster towards CO₂ hydrogenation to HCOOH may be enhanced by optimizing the cluster size. The alloy composition [12] and the type of support materials [11] are known to affect the catalytic activity of Pd nanoparticles. These

two factors can also be optimized to improve the activity of the Pd_xNi cluster. These optimizations will be the main focus of our next works.

4 Conclusion

We studied direct CO₂ hydrogenation to HCOOH without the presence of base additives on the subnanometer Pd₇ cluster doped by transition metals (Pd₆M: M = Cu, Ni, Rh) by combining density functional theory calculations and microkinetic simulations. It was shown that the CO₂ hydrogenation on the Pd₇ and Pd₆M clusters are kinetically much more selective towards the formate pathway to produce HCOOH than the RWGS pathway to produce CO. We further found that inclusion of Ni and Rh doping to the subnanometer Pd₇ cluster could enhance the turnover frequency for CO₂ hydrogenation to HCOOH at low temperature. The order of TOF for HCOOH formation can be explained by the trend of the activation energy for the reaction CO₂* + H* → HCOO*. The Pd₆Ni cluster has the highest TOF because this cluster has the lowest activation energy for this formation. The Pd₆Ni system also has a superior TOF profile for HCOOH formation compared to several metal surfaces in low and high temperature regions. This finding suggests that the subnanometer Pd_xNi cluster is a promising catalyst candidate for direct CO₂ hydrogenation to HCOOH. The catalytic activity of the Pd_xNi cluster may be further improved by optimizing several parameters such as cluster size, Pd-Ni composition, and support material.

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