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# Experimental and computational studies of formic acid dehydrogenation over PdAu: influence of ensemble and ligand effects on catalysis<sup>†</sup>

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The critical role of the ligand effect and ensemble effect in enhancing formic acid (FA) dehydrogenation over PdAu catalysts was highlighted by both experimental and theoretical studies. FA dehydrogenation energy was calculated by DFT on PdAu model catalysts of different surface atomic arrangements. The Pd<sub>3</sub>Au<sub>1</sub> surface exhibited the lowest reaction energy and kinetic barrier for FA dehydrogenation among four different PdAu surfaces. The Pd trimer played a critical role in stabilizing reaction intermediates. The experimental FA dehydrogenation activity of three different PdAu catalysts supported the theoretical results. In addition, the electronic interaction between the surface and subsurface layers also proved to contribute to the improved catalytic activity of PdAu catalysts *via* modification of Pd d states.

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## Introduction

Owing to the negative impacts of carbon-based fuels on the environment, the need for benign and sustainable energy sources has drastically increased. Hydrogen has long been recognized as an alternative because it has a high gravimetric energy density of 120 MJ kg<sup>-1</sup>, which is three times greater than that of gasoline (44 MJ kg<sup>-1</sup>) with essentially no carbon dioxide emission.<sup>1</sup> Additionally, hydrogen can serve as a promising medium for large scale energy storage, as it solves the 'intermittency problem' of renewable energy sources.<sup>2–4</sup> However, its direct use is limited due to the lack of safe and reversible hydrogen storage technologies.

To address the issue, the development of potentially reversible hydrogen storage systems with high hydrogen storage capacities is critical. Formic acid (FA) has garnered significant attention as a chemical hydrogen storage material because it is a stable, nontoxic liquid which has a high volumetric hydrogen storage density of 53 g L<sup>-1</sup>, much higher than compressed hydrogen gas (40 g L<sup>-1</sup> for 700 bar H<sub>2</sub>), and can be readily produced from biomass.<sup>5,6</sup> Moreover, FA can easily be

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transported using the existing infrastructure at a low cost. FA can also release hydrogen in the presence of appropriate catalysts at room temperature without CO formation which is toxic to polymer electrolyte membrane fuel cells (PEMFCs).

For FA to be employed as a viable hydrogen energy carrier, efficient catalysts that enable the generation of  $H_2$  from FA with high activity and selectivity are needed. In this context, several homogeneous<sup>7-10</sup> and heterogeneous<sup>11-21</sup> catalysts have been designed for hydrogen production from FA over the last few years. In particular, Pd-based catalysts are the most active heterogeneous catalysts for FA dehydrogenation. For example, Pd-based alloys<sup>11-14,20,21</sup> or core–shells<sup>15</sup> produced by structural modifications exhibit enhanced catalytic activity, and among them, PdAu alloys showed excellent activity and selectivity for the desired reaction.<sup>11,13,14,16,22</sup>

Despite the recent enhancement in activity and selectivity for FA dehydrogenation on the PdAu nanocatalyst, the role of Au in the hydrogen production rate and selectivity has not been profoundly understood; only a few studies<sup>11,14,23</sup> were conducted to elucidate the influence of PdAu alloys on FA dehydrogenation with mechanistic consideration. The ensemble effect, the geometric effect induced by distinct surface atomic arrangements, and the ligand effect, the electronic effect induced by bonding interaction between metals which results in the modification of the electronic structure, are important factors that affect the performance of bimetallic catalysts. The effect of the PdAu alloy on FA dehydrogenation, however, has been explained only by the ensemble effect. For example, Yuan et al.23 reported the effects of a PdAu supported Au(111) monolayer structure on FA dehydrogenation by density functional theory (DFT) calculations. Furthermore, Mullins et al.11 verified that

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distinct PdAu surface alloy ensembles on the Au(111) subsurface could affect both the reactivity and selectivity for FA dehydrogenation. Despite these model catalysts demonstrating the importance of PdAu ensembles in a highly systematic manner, the influence of PdAu sublayers in the PdAu alloy on catalytic activity (ligand effect) has not been well studied. Since the ligand effect could potentially play a pivotal role in H<sub>2</sub>release from FA as well, it is necessary to scrutinize the effect. Elucidation of both ensemble and ligand effects on catalytic activity under practical catalytic conditions is also essential to minimize the gap between actual catalytic reactions and model reactions conducted in an ultra-high vacuum system.<sup>24</sup>

We report here on experimental and theoretical evidence that accounts for the enhanced activity for FA dehydrogenation over PdAu with a distinct surface structure under practical reaction conditions, demonstrating that both ensemble and ligand effects played synergistic roles in facilitating FA dehydrogenation.

## Experimental

#### Synthesis of catalysts

The PdAu/Al<sub>2</sub>O<sub>3</sub> catalyst (5 wt%, Pd : Au = 1 : 1) was prepared by conventional incipient wetness impregnation.<sup>25,26</sup> An impregnating solution containing Pd and Au was prepared by dissolving HAuCl<sub>4</sub> · xH<sub>2</sub>O (17 mg mL<sub>H<sub>2</sub>O<sup>-1</sup></sub>, STREM Chemical) and PdCl<sub>2</sub> (7.7 mg mL<sub>H<sub>2</sub>O<sup>-1</sup></sub>, Sigma Aldrich) in distilled water with gentle heating.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder (Alfa Aesar, BET = 220 m<sup>2</sup> g<sup>-1</sup>) was then added to the brownish aqueous solution (0.4 mL<sub>solution</sub> g<sub>\gamma-Al<sub>2</sub>O<sub>3</sub><sup>-1</sup>). The obtained solids were ground and dried at 100 °C to remove residual H<sub>2</sub>O. The resulting powders were finally calcined at 400 °C for 4 h to ensure the formation of the PdAu alloy and then reduced under 10% H<sub>2</sub> gas at 250 °C for 4 h to give PdAu/Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub> (2). Modification of surface PdAu arrangements was achieved by a heat treatment of 2 at 250 °C for 4 h either under N<sub>2</sub> to give PdAu/Al<sub>2</sub>O<sub>3</sub>-N<sub>2</sub> (3) or 7% CO to afford PdAu/Al<sub>2</sub>O<sub>3</sub>-CO (1).</sub>

#### Characterization of catalysts

The particle size distribution of the PdAu catalysts was analyzed by scanning transmission electron microscopy (STEM) using a FEI Tecnai F20 at 200 kV. The surface distributions of Pd and Au in the PdAu nanoparticles were measured by energy dispersive spectroscopy (EDS) at 200 kV. Due to the drift of the small sizednanoparticles under a high energy electron beam, we first prepared larger nanoparticles with a size of 10 nm by the calcination of the original PdAu materials at 800 °C. The enlarged nanoparticles were then heat-treated using H<sub>2</sub>, CO or N<sub>2</sub> at 250 °C. To monitor the formation of PdAu alloys, X-ray photoelectron spectroscopy (XPS) was recorded on a PHI 50000 Versa Probe from Al K $\alpha$ -ray (1486.6 eV) at 6.7  $\times$  10<sup>-8</sup> Pa. The enlarged PdAu nanoparticles were further characterized using high-angle annular dark field (HAADF) microscopy (Talos F200X) coupled with scanning transmission electron microscopy (HAADF-STEM) and energy dispersive spectroscopy (EDS) with elemental mapping at 200 kV.

Relative quantities of Pd on the PdAu surface were determined by CO-temperature programmed desorption (CO-TPD) using BELCAT-M (Bel Japan Inc.). Five samples were evaluated: Al<sub>2</sub>O<sub>3</sub> (for the blank), PdAu/Al<sub>2</sub>O<sub>3</sub>-CO (1), PdAu/Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub> (2), PdAu/Al<sub>2</sub>O<sub>3</sub>-N<sub>2</sub> (3), and Pd/Al<sub>2</sub>O<sub>3</sub> (4). A catalyst was placed in a measurement tube and purged with He for 1 h at 25 °C to stabilize the background signal. CO was adsorbed on the catalysts by supplying 7% CO diluted with He into the sample tube for 30 min. The temperature of the tube was then increased to 400 °C with a heating rate of 5 °C min<sup>-1</sup> under the flow of He. To obtain the amounts of adsorbed CO purely on the metallic surface, all the data were calibrated by subtracting relevant CO-TPD data obtained from Al<sub>2</sub>O<sub>3</sub> as the blank sample.

Surface ensembles of PdAu catalysts were further monitored by CO vibrational frequencies using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy (Nicolet iS10, Thermo Scientific) equipped with a mercury cadmium telluride (MCT) detector. In a typical experiment, a catalyst was loaded in the DRIFT cell in powder form and purged with N<sub>2</sub> to remove moisture and oxygen inside the IR chamber. A background spectrum was initially recorded under a N<sub>2</sub> atmosphere. Then, 1% CO gas diluted with N<sub>2</sub> was supplied for 30 min at room temperature to adsorb CO onto the catalyst surface. The desired CO absorption spectra were obtained after the removal of gaseous CO residues by purging the cell with N<sub>2</sub> gas for 20 min.

#### Catalytic activity test for FA dehydrogenation

An aqueous FA solution (*ca.* 1.0 M) containing distilled water (9.7 mL) and FA (370  $\mu$ L, 10 mmol) was added to a reaction tube with a catalyst (50 mg, 1, 2, 3, or 4) and stirred at 300 rpm with a magnetic stirrer. The quantities of gaseous products during dehydrogenation at 50 °C were measured using a gas burette connected to a real time recording system. The amount of H<sub>2</sub> produced after 5 min was calculated as follows.

Moles of H<sub>2</sub> produced in 5 min (n) = 
$$\frac{PV}{RT}$$
  
=  $\left(\frac{1 \times V_{\text{gas}} \text{ in 5 min}}{0.08206 \times \text{temperature}}\right) \times \frac{1}{2}$ 

#### Theoretical details

The calculations reported herein were performed on the basis of spin polarized density functional theory (DFT) within the generalized gradient approximation (GGA-PW91),27 as implemented in the Vienna Ab-initio Simulation Package (VASP).28 The projector augmented wave (PAW) method<sup>29</sup> with a planewave basis set was employed to describe the interaction between core and valence electrons. An energy cutoff of 350 eV was applied for the planewave expansion of the electronic eigen functions. For the Brillouin zone integration,<sup>30</sup> we used a  $5 \times 5 \times 1$  Monkhorst– Pack mesh of k points to calculate geometries and total energies. Reaction pathways and barriers were determined using the climbing image nudged elastic band method (CI-NEBM)<sup>31</sup> for each elementary step. For the Pd<sub>2</sub>Au<sub>2</sub>(111) model surfaces, as shown in Fig. S1,† we constructed a five atomic-layer slab, each of which contains four atoms. The slab is separated from its periodic images in the vertical direction by a vacuum space corresponding to seven atomic layers. While the bottom two layers of the five-layered slab are fixed at corresponding bulk positions,

the upper three layers are fully relaxed using the conjugate gradient method until residual forces on all the constituent atoms become smaller than  $5 \times 10^{-2}$  eV A<sup>-1</sup>. The lattice constant for bulk Pd is predicted to be 3.95 Å which is virtually identical to the previous calculations and also in good agreement with the experimental value of 3.89 Å.<sup>32</sup>

## **Results and discussion**

To investigate the effects of bimetallic PdAu structure on FA dehydrogenation activity, spin-polarized density functional theory (DFT) calculations were performed. First, we scrutinized how the FA dehydrogenation kinetics were affected by surface arrangements (ensembles) of Pd atoms on four different PdAu(111) model alloys (I-IV) which had varying surfaces and subsurface PdAu arrangements (Fig. 1a). The first surface layers of model PdAu catalysts consisted of pure Pd (I), triangular shaped Pd (II), linear shaped Pd (III), and mono Pd (IV), respectively. Fig. 1b shows changes in the total energy and activation barriers for FA dehydrogenation based on two sequential reactions: (i) HCOOH\*  $\rightarrow$  HCOO\* + H\* (D1) and (ii)  $HCOO^* \rightarrow CO_2^* + H^*$  (D2). Among all surface models, II showed the most favorable reaction energies ( $\Delta E = -0.18$  eV for D1; -0.70 eV for D2) and lowest kinetic barriers ( $E_a = 0.60$  eV for D1; 0.87 eV for D2) (Table S1<sup>†</sup>), suggesting that the triangular shaped Pd atoms on the PdAu alloy surface played an important role in the catalysis, which originates from the strong attractive force between Pd and the reaction intermediates in the transition states. For instance, FA requires three adjacent metal atoms for the coordination of two oxygens and one bridging hydrogen in the first transition state (TS1, Fig. S1<sup>†</sup>). The kinetic



Fig. 1 (a) The PdAu model catalysts used for DFT calculations and (b) the calculated potential energy diagram for the FA dehydrogenation on I-IV. Yellow and gray balls represent the Au and Pd atoms, respectively.

in the energy barriers were not as significant as those in the first transition state due to the high energies of the starting intermediates on the surfaces of **III** and **IV**, **II** showed the lowest barrier among all catalysts (Fig. 1 and Table S1†). Numerous reports suggested that for bimetallic surfaces, their surface structures change upon gas adsorption due to metal segregation on the surface.<sup>6,33-37</sup> Since CO preferentially by surface

binds to Pd over Au, the Pd segregation energies in the alloy were evaluated as a function of the Pd coverage. We assessed the energetically preferred composition of Pd in the first surface layer by calculating the total energy variation ( $\Delta E$ ) as a function of surface Pd concentration. Under a CO environment, the surface composition of 75 atom% Pd [Pd<sub>3</sub>Au<sub>1</sub>/Pd<sub>1</sub>Au<sub>3</sub>/ Pd<sub>2</sub>Au<sub>2</sub>(111), **II**] was the most stable structure, followed by 50 atom% Pd [Pd<sub>2</sub>Au<sub>2</sub>/Pd<sub>2</sub>Au<sub>2</sub>(111), **III**] and 25 atom% Pd [Pd<sub>1</sub>Au<sub>3</sub>/Pd<sub>3</sub>Au<sub>1</sub>/Pd<sub>2</sub>Au<sub>2</sub>(111), **IV**] (Table 1). This indicated the higher availability of triangular shaped Pd trimers (three-fold hollow sites associated with three Pd atoms) on the PdAu surface than linear shaped Pd atoms (two-fold bridge sites associated with two Pd atoms) and Pd monomers (one-fold top sites of a single Pd atom which is completely surrounded by Au atoms) under a CO atmosphere.

energy barrier for the D1 step on the surface of II was 0.27 eV

and 0.80 eV lower than those of III and IV, respectively, because

three contiguous Pd atoms favorably stabilize the transition

state. In D2, the involvement of three metal atoms resulted in

the lowest transition state energy on II. Although the differences

We prepared several PdAu catalysts possessing different surface atomic concentrations according to the theoretical calculations and the previous reports.25-29 The PdAu alloy nanoparticles were impregnated on y-alumina according to the reported procedure<sup>25,26</sup> and the as-prepared catalysts were thermally treated at 250 °C with three distinct gases of CO, H<sub>2</sub>, and N2 to alter the surface atomic arrangements of the PdAu catalysts. The resulting catalysts were denoted as PdAu/Al<sub>2</sub>O<sub>3</sub>-CO (1), PdAu/Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub> (2), and PdAu/Al<sub>2</sub>O<sub>3</sub>-N<sub>2</sub> (3), respectively. We also prepared pure  $Pd/Al_2O_3$  (4) for comparison. The formation of PdAu alloys was verified by the shift of the Pd 3d<sub>5/2</sub> peak from 335.2 eV (pure Pd) to 335.4 eV (PdAu alloys) in the XPS spectra (Fig. S2 and Table S2<sup>†</sup>).<sup>22</sup> STEM revealed the formation of PdAu nanoparticles with the average sizes of 1.2-1.3 nm (Fig. S3<sup>†</sup>). The particle sizes were found to be nearly identical after heat treatment. To compare the surface concentrations of Pd and Au in the prepared materials, we measured EDS line profiles of 1-3. The EDS line profiles with these enlarged nanoparticles confirmed that the "surface Pd" concentration of 1 (CO treated) was found to be higher than 2 ( $H_2$  treated) and 3 ( $N_2$  treated) (Fig. S3<sup>†</sup>). The results again supported that the CO treatment can alter the surface PdAu atomic ratio.

The surface structure of Pd was further characterized by temperature programmed desorption (TPD) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy using CO gas. As depicted in Fig. 2, the Pd coverage on the surface was significantly altered upon calcination. The sample with pure Pd showed the highest CO adsorption capacity as it has only Pd on the surface. The CO desorption temperatures and adsorbed CO quantities on the PdAu catalyst surfaces increased in the order Table 1 Variation in the total energy ( $\Delta E$  for CO adsorption) as a function of the surface Pd composition. Yellow and gray balls represent the Au and Pd atoms, respectively

Model (1st layer/2nd layer/substrate)	Surface Pd composition (%)	Top view of the Au <sub>2</sub> Pd <sub>2</sub> slab	$\Delta E (eV)$
$Pd_4/Au_4/Pd_2Au_2$ (I)	100	688°	0.28
$Pd_{3}Au_{1}/Pd_{1}Au_{3}/Pd_{2}Au_{2}$ (II)	75		-0.05
$Pd_{2}Au_{2}/Pd_{2}Au_{2}/Pd_{2}Au_{2}\left(III\right)$	50		0
$Pd_{1}Au_{3}/Pd_{3}Au_{1}/Pd_{2}Au_{2}\left(IV\right)$	25		0.17

of  $1 > 2 \ge 3$ , indicating that 1 possessed a Pd-enriched surface with numerous CO binding sites, i.e., the increased CO adsorption area of 1 originated from the increased Pd surface coverage because only negligible amounts of CO can adsorb on Au atoms at room temperature.<sup>38</sup> In addition, the increased CO desorption temperature of 1 indicated the presence of specific Pd sites that interacted strongly with CO, which is likely supported by the DFT results (vide supra). In DRIFT spectra, CO species adsorbed on Pd surfaces are known to exhibit three characteristic vibrational frequencies depending on the binding modes at distinct sites:<sup>38-41</sup> (i) *ca.* 2080 cm<sup>-1</sup> (linear, atop site), (ii) 1900-2050 cm<sup>-1</sup> (2-fold, bridge site), and (iii) 1800–1900  $\text{cm}^{-1}$  (3-fold, hollow site). Given the Pd surface coverage of the as-prepared catalysts, the number of Pd hollow sites at the surface likely increased in the order of 1 > 2 > 3. Indeed, DRIFT studies supported the TPD results; the intensity of the CO vibration of 1 increased at the Pd hollow sites (1800-1900  $\text{cm}^{-1}$ ), while 3 exhibited a negligible intensity in the same region (Fig. 3). The population of hollow sites with respect to total Pd sites for 1 and 2, calculated using fitted peak areas, was 4.3 and 2.8 times greater than that of 3, respectively

(Table S3<sup>†</sup>).<sup>40</sup> The CO intensities attributed to Pd atop sites decreased as the amount of surface Pd increased, which indicated that the atomic surface arrangements were altered by the heat treatment under different atmospheric conditions. Despite **4** having the highest number of hollow sites as it consists of a pure Pd surface, **4** exhibited a lower relative ratio for hollow sites than **1**. It implies that CO adsorption on the bridge sites is favorable over the hollow sites on the pure Pd surface at high CO coverage.<sup>41,42</sup>

The modified bimetallic PdAu catalysts likely provided different dehydrogenation activities owing to their distinct surface ensembles. To verify the influence of atomic ensembles at the PdAu surfaces, we performed dehydrogenation reactions using a 1.0 M aqueous FA solution at 50 °C. The catalytic activity increased as the surface Pd/Au ratio increased (1 > 2 > 3; Fig. 4a), which was closely correlated with the relative quantity of 3-fold hollow sites. The amount of H<sub>2</sub> produced for 5 min catalyzed by 1 (0.13 mmol) was found to be much greater than those of 2



Fig. 2 The CO-TPD profiles of the as-prepared catalysts.



Fig. 3 The DRIFT spectra of the vibrations of CO adsorbed on different surfaces.

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Fig. 4 (a)  $H_2$  production from catalytic FA dehydrogenation over different catalysts. (b) Correlation between the amounts of  $H_2$ produced in 5 min and the relative quantities of Pd hollow sites existed at the catalysts.

(0.081 mmol) and 3 (0.066 mmol). These results indicated that a high Au surface concentration was detrimental because it inhibited the formation of Pd hollow sites, as supported by the results obtained by DFT methods. The importance of hollow sites was highlighted again by the close correlation between amounts of  $H_2$  production and ratios of hollow Pd sites on PdAu catalysts (Fig. 4b).

Although ensemble effects can reasonably explain the catalytic behavior of the as-prepared PdAu catalysts, ligand effects could also play an important role in accelerating the FA dehydrogenation. The presence of the ligand effect can be supported by the result of the lower H<sub>2</sub>-release activity of 4 compared to 1, despite the higher quantity of the 3-fold hollow Pd sites in 4 (Fig. 4a) *i.e.*, the enhanced dehydrogenation activity for 1 originated additionally from the electronic perturbation induced by Au-containing sublayers. To verify this hypothesis, we further optimized HCOO adsorption on **II** as well as on pure Pd(111) (as a model surface for 4) in a bridging bidentate mode (Fig. S4<sup>†</sup>). A substantial reduction in the binding energy of HCOO on surface Pd atoms in II ( $E_{\text{bind}} = -2.34 \text{ eV}$ ) was predicted as compared to pure Pd atoms ( $E_{\text{bind}} = -2.42 \text{ eV}$ ), suggesting a reduced adsorption energy of surface Pd atoms in II owing to Pd-Au interactions, which likely contributed to the FA



Fig. 5 Projected local density of states plots on the d states of surface Pd atoms for the pure Pd(111) and  $Pd_3Au_1/Pd_1Au_3/Pd_2Au_2(111)$ . The displayed vertical line at 0 eV stands for the Fermi level.

decomposition. For the Pd-Au system in particular, the ensemble effect is a primary effect where the catalytically more active component (Pd) is diluted by the less active component (Au).43 In earlier studies on late-transition metals such as Pd and Au, the importance of the d state of the surface was emphasized over the s and p states in defining chemisorption and catalytic properties.44 In the presence of a Pd-dominated surface supported by an Au dominated subsurface, such as in I and II, there is an increase in the d electron density of surface Pd atoms owing to charge transfer from the subsurface Au atoms.<sup>24,45</sup> Together with ensemble effects, the charge transfer in II leads to a reduced binding energy of HCOO compared to that in Pd(111), as there is no ensemble effect on the surface. This decreased activity toward formate chemisorption is related to the significant modification of the d states in surface Pd atoms owing to electronic interactions with subsurface Au atoms. Fig. 5 shows the local density of states (LDOS) projected on the d states of surface Pd atoms for II and pure Pd(111). A noticeable reduction in the occupied LDOS near the Fermi level  $(-0.5 \le E - E_{\rm f} \le 0)$  was found for **II** as compared to that of pure Pd(111). This explained the lower activity of Pd atoms toward HCOO chemisorption in the alloy as compared to pure Pd(111). It is worth noting that the higher the LDOS near the Fermi level, the higher the activity of surface atoms toward chemisorption.46 The calculated d-band centers for II and Pd(111) were -1.97 eV and -1.71 eV, respectively.

### Conclusions

In summary, the possible roles of PdAu alloys in the rate of FA dehydrogenation were demonstrated as independent functions of (i) surface atomic ensembles (side by side interactions) and (ii) surface charge polarization (interactions between top and second layers). Several surface compositions were prepared by varying the calcination conditions and the resulting catalytic

activities were evaluated. Triangular shaped Pd sites were proposed to play pivotal roles in facilitating FA dehydrogenation by reducing the reaction energy and kinetic barrier. In addition to Pd ensemble effects, the dehydrogenation activity was also influenced by the Pd electronic structure. Our study revealed the importance of both ensemble and ligand effects for dehydrogenation catalysis, which will provide valuable insight into the development of highly capable catalysts not only for FA dehydrogenation, but also for other Pd based alloy materials for a number of chemical transformations.

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