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# Decomposition pathways of methanol on the PtAu(111) bimetallic surface: A first-principles study

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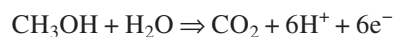
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Systematic density functional studies revealed that PtAu(111) significantly alters the reaction kinetics of methanol oxidation from that on Pt(111). PtAu(111) facilitates the reaction path that starts from cleavage of the OH bond. Furthermore, it prevents CH<sub>2</sub>O from immediate decomposition as on the clean Pt(111) surface. This indicates that proper arrangement of Au and Pt sites offers great opportunities for non-CO<sub>ad</sub> paths for high H productivity in fuel cells. © 2008 American Institute of Physics. [DOI: 10.1063/1.2835545]

Direct methanol fuel cells are ideal power sources for small devices such as cellular phones and laptops since they have low operating temperature, 50–120 °C, and no requirement for a fuel reformer. The oxidation of methanol to hydrogen ions and carbon dioxide on anodes



requires highly efficient catalysts.<sup>1–3</sup> One important consideration for the design of new catalyst is how to rapidly reduce the population of CO<sub>ad</sub>, the product of methanol dehydrogenation, so as to maintain the activity of reaction cycle.<sup>4,5</sup> This can be achieved through direct oxidation of CH<sub>2</sub>O and CHO,<sup>6</sup> which are intermediates if methanol dehydrogenation starts from cleavage of the OH bond as CH<sub>3</sub>OH → CH<sub>3</sub>O → CH<sub>2</sub>O → CHO → CO. On Pt catalysts, however, these intermediates decompose rapidly, as illustrated by Kandoi *et al.* through microscopic model simulations with activation energies calculated with density functional approaches.<sup>7</sup> Furthermore, it was found that the other reaction pathway, CH<sub>3</sub>OH → CH<sub>2</sub>OH → CHOH → COH → CO, is predominant on Pt(111). To facilitate the oxidation of methanol through the non-CO<sub>ad</sub> pathway, one may use bimetallic catalysts for the modification of reaction kinetics. It was observed that the CO poisoning quandary can be somewhat eased by adding Ru, Rh, or other elements to platinum.<sup>8,9</sup> Carbon-supported AuPt nanoparticle catalysts have also been extensively explored for their excellent properties for fuel cells, particularly fuel cells using methanol as the fuel.<sup>10</sup> As known, the activity and selectivity of bimetallic catalysts not only depend on the “ligand effects” that encompass influences of bonding, charge transfer, and strain but also strongly on the “ensemble effects” that describe the synergistic behavior of different constituents in specific arrangements.<sup>11,12</sup> It was proposed that methanol electro-oxidation requires ensembles with at least three Pt atoms together.<sup>13,14</sup> For rational design of novel catalyst for fuel

cell applications, it is imperative to study structure-related catalytic properties of bimetallic surfaces.

This article is centered on the decomposition of methanol on the PtAu(111) bimetallic surface, through systematic density functional studies. The detailed reaction processes were investigated with two different pathways of H scission. Significantly, we found two major differences for methanol oxidation on PtAu(111) and pure Pt(111). While CH<sub>3</sub>OH → CH<sub>3</sub>O → CH<sub>2</sub>O → CHO → CO has only one major barrier to overcome, CH<sub>3</sub>OH → CH<sub>2</sub>OH → CHOH → COH → CO has three sizable barriers in the process. Furthermore, the decomposition of formaldehyde (CH<sub>2</sub>O) on the PtAu(111) model surface has a meaningful energy barrier. The production of CO for methanol dehydrogenation can be avoided through direct oxidation on the PtAu(111) bimetallic surface.

The calculations were performed in the framework of density functional theory (DFT), using the generalized gradient approximation for the description of exchange-correlation interaction<sup>15</sup> with the PW91 functional. The effects of ionic cores were represented by ultrasoft pseudopotentials,<sup>16</sup> as implemented in the Vienna *ab initio* simulation package (VASP).<sup>17</sup> The energy cutoff for the wave function expansion was 350 eV, for a balance between quality and feasibility of calculations. Since large molecules are involved, we used a 3 × 3 supercell in the lateral plane to mimic adsorption and reaction of individual methanol molecule. Along the surface normal, a slab geometry with four layers of Au and 15 Å vacuum was adopted. The lattice constant in the lateral plane was fixed at 8.87 Å, according to the theoretically optimized lattice size of the bulk fcc Au, 4.18 Å. Integrals in the reciprocal space were evaluated through summations over 5 × 5 × 1 sampling *k* points. Positions of all atoms except those in the two bottommost Au layers were fully relaxed under the guidance of atomic forces. Finally, the minimum energy paths for dehydrogenation of methanol were obtained using the climbing image nudged elastic band (NEB) technique<sup>18–21</sup> with eight or ten images.

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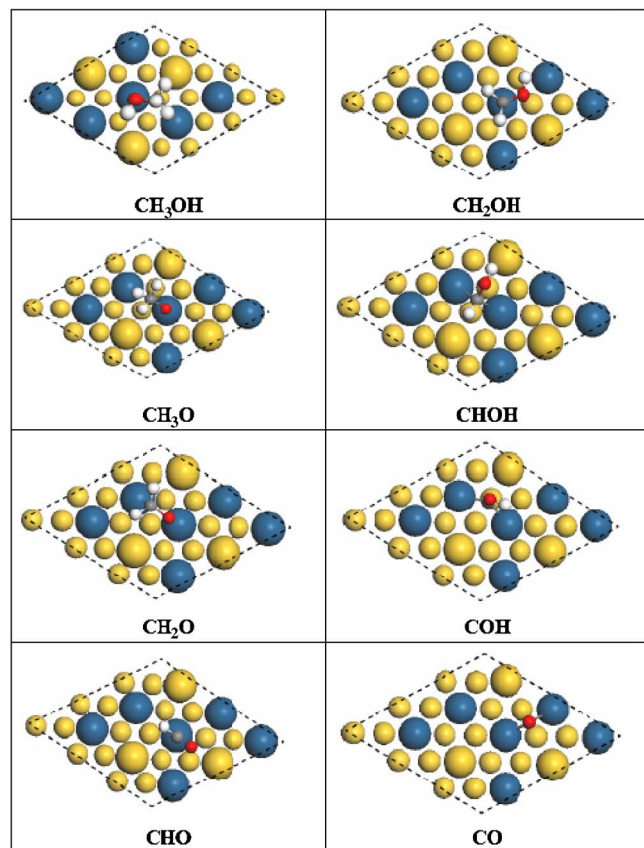


FIG. 1. (Color online) The optimized adsorption geometry of different molecules on the PtAu(111) bimetallic surface. Small spheres are for Au atoms in the subsurface layer while the large yellow and gray balls are for Au and Pt atoms in the surface layer.

For computational feasibility, we focused on the catalytic properties of a Pt ensemble with three Pt atoms forming an ordered  $3 \times 3$  pattern in the surface layer, in which each Pt has three first Pt neighbors and the neighboring Pt atoms form a chevron with  $120^\circ$  angle. This ensemble has no three-fold Pt hollow site, and hence should capture the major difference between the PtAu(111) bimetallic surface and the pure Pt(111) surface toward methanol oxidation. Through studies on the cyanide-modified Pt(111) surface, Cuesta found that ensembles with two adjacent platinum atoms inhabit the CO formation but are still effective for the oxidation of methanol to  $\text{CO}_2$  through the non-CO pathway.<sup>5</sup> Surfaces without Pt first neighbors, likely on samples prepared through high temperature annealing,<sup>11,12,22,23</sup> are expected to be inactive for methanol dehydrogenation, as we found recently for ethylene on PdAu(001).<sup>24</sup>

In order to understand the reaction mechanism of methanol decomposition, we first need to investigate the adsorption problems of reaction intermediates. The optimized geometries and adsorption energies are presented in Fig. 1 as well as in Table I. As seen in Fig. 1, methanol molecule weakly binds to Pt on the top site through its O atom. The adsorption energy, determined from total energies of different systems as  $E_{\text{ad}} = -(E_{\text{adsorbate/substrate}} - E_{\text{substrate}} - E_{\text{adsorbate}})$ , is only 0.29 eV. This is slightly smaller than that on the pure Pt(111) surface,<sup>2</sup> 0.33 eV. Since the use of the PW91 functional typically leads to overestimation in binding energies by

TABLE I. The adsorption energies ( $E_{\text{ad}}$ , in eV per molecule or atom) and the key bond lengths ( $L$ , in Å).

Adsorbates	$E_{\text{ad}}$	$L_{\text{C-O}}$	$L_{\text{O-Pt}}$	$L_{\text{C-Pt}}$
$\text{CH}_3\text{OH}$	0.29	1.45	2.40	
$\text{CH}_3\text{O}$	1.55	1.41	2.00	
$\text{CH}_2\text{O}$	0.54	1.34	2.06	2.14
CHO	2.49	1.20		1.92
$\text{CH}_2\text{OH}$	2.07	1.38		2.10
CHOH	3.41	1.35		2.05/2.08
COH	4.41	1.33		1.96/1.97
CO	1.97	1.19		2.02
H	2.90/2.66			

0.2–0.4 eV,<sup>25</sup> we would expect that methanol molecule in the gas phase desorbs from Pt and PtAu surfaces at very low temperature. The O–Pt and C–O bond lengths remain very close to those on a pure Pt(111) surface, 2.40 and 1.45 Å, respectively.

As presented in the left column in Fig. 1, the dehydrogenation of methanol may start from breaking the OH bond and produces intermediates as methoxy ( $\text{CH}_3\text{O}$ ), formaldehyde ( $\text{CH}_2\text{O}$ ), formyl (CHO), and CO. Although the adsorption geometry of methoxy ( $\text{CH}_3\text{O}$ ) is not much different from that of methanol, also with its oxygen atom pointing toward the Pt, the adsorption energy is much larger, 1.55 eV, due to one H abstraction. The O–Pt bond is also much shorter, to 2.00 Å. Moreover, the C–O bond of  $\text{CH}_3\text{O}$  aligns along the Pt–Pt direction with an angle of  $122.3^\circ$  between C–O–Pt bonds.

For formaldehyde, the  $\text{CH}_2$  radical points down toward the Pt atoms, and binds to the PtAu(111) surface with a top-bridge-top adsorption geometry. The close-shell configuration of formaldehyde results in a relatively weak adsorption energy, e.g., 0.54 eV. Therefore, formaldehyde molecules are highly mobile and easy to be oxidized on PtAu(111). The C–O, O–Pt, and C–Pt bond lengths are 1.34, 2.06, and 2.14 Å, respectively. The calculated values of  $E_{\text{ad}}$  for CHO and CO are very large, 2.49 and 1.97 eV, respectively. On the pure Pt(111) surface, the adsorption energies of  $\text{CH}_3\text{O}$ ,  $\text{CH}_2\text{O}$ , CHO, and CO are 1.54, 0.50, 2.36, and 1.82 eV, respectively.

The other dehydrogenation pathway starts from scission of the C–H bonds and therefore produces different intermediates. As listed in Table I, the values of  $E_{\text{ad}}$  for these intermediates are much larger than those for the other pathway discussed above. Hydroxymethyl ( $\text{CH}_2\text{OH}$ ) binds to the Pt top site through its C atom, and the adsorption energy is 2.07 eV. The C–Pt and C–O bond lengths are 2.10 and 1.38 Å, respectively. Hydroxymethylene (CHOH) has a close-shell electronic configuration, but its C end is still active. As a result, the adsorption energy is as large as 3.41 eV and the C atom takes the Pt–Pt bridge site. For hydroxymethyldiene (COH), the C atom has no H neighbors and hence the C–Pt interaction is even stronger, with an adsorption energy of 4.41 eV. It appears that the removal of each H atom from the  $\text{CH}_x$  end enhances the C–Pt binding energy by

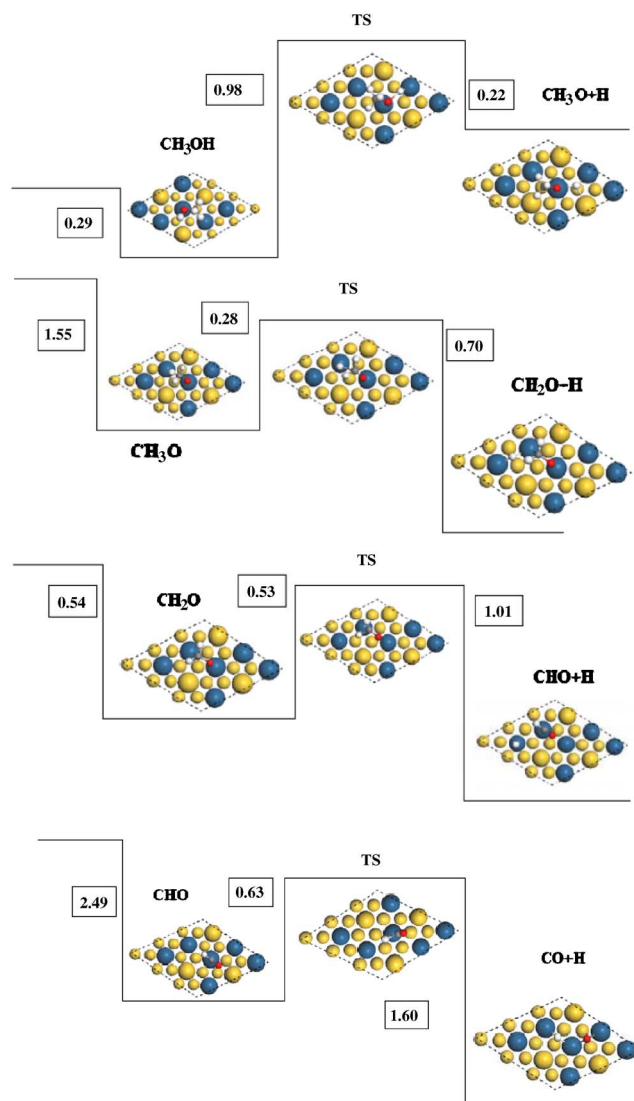


FIG. 2. (Color online) The energetics of the methanol dehydrogenation process along the pathway  $\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} \rightarrow \text{CHO} \rightarrow \text{CO}$ . Insets show adsorption geometries in different stages.

1.0–1.5 eV. In comparison, the adsorption energies are 1.98 eV ( $\text{CH}_2\text{OH}$ ), 3.24 eV ( $\text{CHOH}$ ), and 4.45 eV ( $\text{COH}$ ) on the Pt(111) surface, respectively. Due to the unavailability of Pt first neighboring trimer, COH and CO bind to the Pt–Pt bridge sites on the PtAu bimetallic surface instead of to the threefold hollow site as on the clean Pt(111) surface.

From the adsorption geometries, we can set up simulations for the dehydrogenation processes with the NEB approach. As mentioned before, methanol decomposition may start from either O–H or C–H bond scission, and each path needs several steps to accomplish. It is crucial to identify the rate-limiting step and study the effect of Au for the reactions on the PtAu bimetallic surfaces. On the clean Pt(111) surface, abstraction of the first H atom from methanol was found to be the rate-limiting step<sup>2,3</sup> and formaldehyde can decompose to CHO simultaneously without a barrier to overcome.<sup>2</sup> In Fig. 2, we present the energetics for reactions  $\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} \rightarrow \text{CHO} \rightarrow \text{CO}$  on the PtAu(111) bimetallic surface. It is clear that the most difficult step is still to break the OH bond in methanol. The activation energy

for this step on the PtAu bimetallic surface, 0.98 eV, is larger than that on the Pt(111) surface, 0.81 eV. Also the reaction is endothermic with a reaction energy of 0.76 eV and the barrier for reversed process is low, 0.22 eV. Nevertheless, the C–H scission from methoxy is very easy, with the activation energy as small as 0.28 eV. Moreover, this reaction is exothermic with a reaction energy of 0.42 eV. Therefore,  $\text{CH}_3\text{O}$  should decompose rapidly to  $\text{CH}_2\text{O}$  on PtAu(111) and the reverse reaction  $\text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH}$  is unlikely to occur. The two forthcoming reactions,  $\text{CH}_2\text{O} \rightarrow \text{CHO} \rightarrow \text{CO}$ , have energy barriers of 0.53 and 0.63 eV, respectively. For comparison, the activation energies for  $\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} \rightarrow \text{CH}_2\text{O} \rightarrow \text{CHO} \rightarrow \text{CO}$  reaction steps are 0.81, 0.25, <0.10, and 0.23 eV on the clean Pt(111) surface. These energy barriers are much lower than those on the PtAu(111) bimetallic surface, primarily because of the availability of the threefold Pt hollow site.

It should be stressed that the activation energy relies on proper placement of two segments in the transition state. Hence  $E_a$  is more sensitive to the atomic distribution in a large area, namely, the ensemble effects. In contrast, the adsorption energies for small molecules such as COH and CO only depend on the local activity, which is governed by the ligand effects.<sup>26</sup> On the clean Pt(111) and Pd(111) surfaces, the adsorption energy changes only slightly ( $\sim 0.2$  eV) for CO on the hollow and bridge sites. On the PtAu(111) bimetallic surface, Pt becomes more active owing to the ligand effects and  $E_{\text{ad}}$  for CO on the bridge site of PtAu(111) is even larger than that on the hollow site of Pt(111).

The activation and reaction energies for the other reaction pathway of methanol dehydrogenation,  $\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CHOH} \rightarrow \text{COH} \rightarrow \text{CO}$ , are shown in Fig. 3. Interestingly, the activation energies in different steps are rather close to each other and hence there is no obvious rate-limiting step for this path. Also all the reaction steps are exothermic, with reaction energies ranging from 0.02 to 0.81 eV. To break the first C–H bond, both H and C bind to the same Pt atom underneath the transition state, and the H–Pt and C–Pt bond lengths are 1.68 and 2.38 Å, respectively. The activation energy for dehydrogenation of hydroxymethyl ( $\text{CH}_2\text{OH}$ ) to hydroxymethylene ( $\text{CHOH}$ ) is the smallest among the four steps, 0.66 eV. In the transition state, hydroxymethyl binds to two Pt atoms, and the H–Pt, C–Pt, and C–H bond lengths are 1.66, 1.96, and 1.64 Å, respectively. The cleavage of H from CHOH to COH appears to be the most difficult step in this pathway, with an activation energy of 0.91 eV. Finally, the activation energy for  $\text{COH} \rightarrow \text{CO}$  is 0.81 eV. The corresponding activation energies for  $\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CHOH} \rightarrow \text{COH} \rightarrow \text{CO}$  reactions on the clean Pt(111) surface are 0.67, 0.63, 0.80, and 0.97 eV, respectively.

Overall, removal of the Pt threefold hollow sites on PtAu(111) has a stronger impact in the first reaction pathway than the second reaction pathway. It appears to be rather difficult to cleave the OH bond in the adsorbed methanol molecule. However, as discussed above, methanol molecules are usually detached from the Pt(111) or PtAu(111) surface and the first H atom is more likely knocked out in a collision. With this complexity, it is difficult to draw a conclusion on



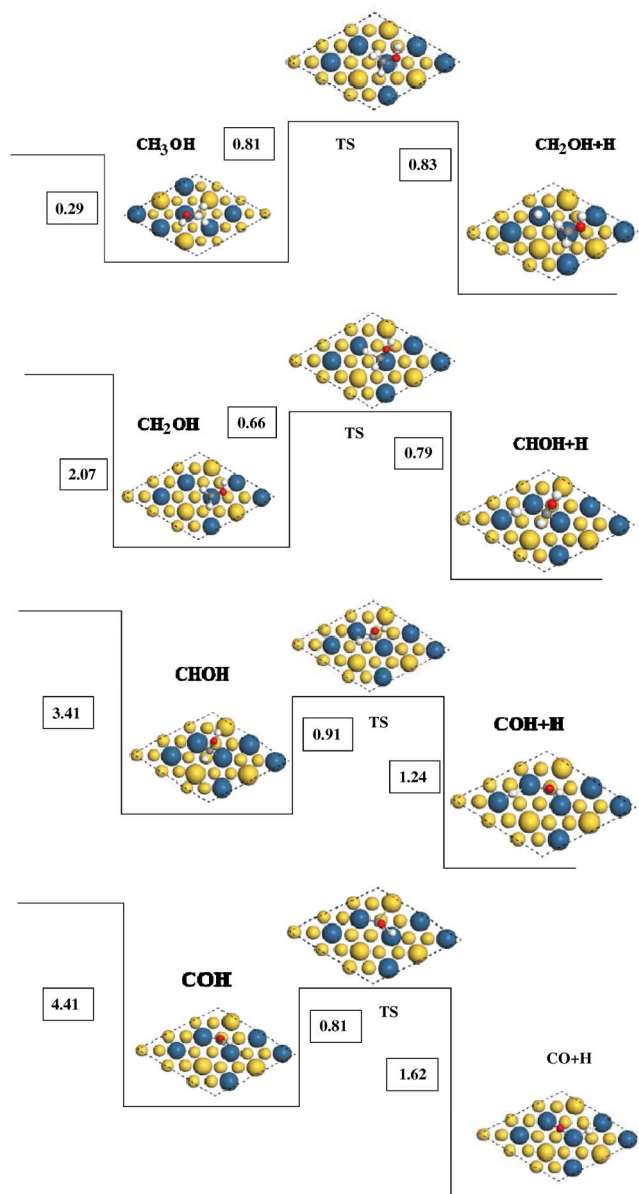


FIG. 3. (Color online) The energetics of the methanol dehydrogenation process along the pathway  $\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CHOH} \rightarrow \text{COH} \rightarrow \text{CO}$ . Insets show adsorption geometries in different stages.

which pathway is more dominant since the subsequent energy barriers for the first pathway are much lower. Another major difference from the pure Pt(111) is the existence of a sizable energy barrier for the decomposition of  $\text{CH}_2\text{O}$  on PtAu(111), 0.53 eV. This may bestow enough opportunity for direct oxidation of formaldehyde on PtAu(111) so as to avoid CO production in the first reaction pathway. Further studies on how to reduce the barrier for  $\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}$ , including the kinetics of surface collisions, and how to accelerate  $\text{CH}_2\text{O}$  oxidation will be conducted for facilitation of non- $\text{CO}_{\text{ad}}$  reaction paths.

The two reaction pathways may also cross each other in the middle stage. To estimate the chance of such crossover, we also investigated the reaction of  $\text{CH}_2\text{OH}$  dehydrogenation to  $\text{CH}_2\text{O}$ . As shown in Fig. 4, the activation energy for this reaction is 0.96 eV, much higher than that for  $\text{CH}_2\text{OH} \rightarrow \text{CHOH}$ , 0.66 eV. This energy barrier obviously increases

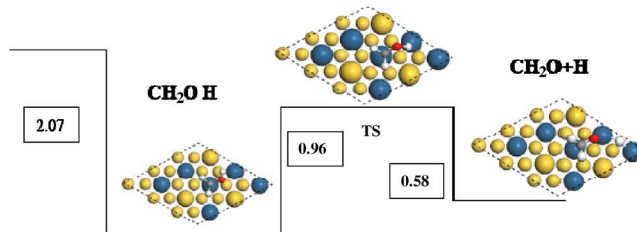


FIG. 4. (Color online) The energetics for reaction  $\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{O}$ . Insets show adsorption geometries in different stages.

from the corresponding value on Pt(111), 0.75 eV.<sup>3</sup> Moreover, the reaction  $\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{O}$  is endothermic with a reaction energy of 0.38 eV. From these factors, the chance for the two pathways to crossover at this step should be rare. In their DFT calculations for methanol dehydrogenation on Pt(111), Greeley and Mavrikadis<sup>3</sup> also considered a simultaneous removal of two hydrogen atoms, i.e.,  $\text{CHOH} \rightarrow \text{CO}_{\text{ad}} + 2\text{H}_{\text{ad}}$ , and found a shallow energy barrier, 0.43 eV. However, the probability to have two bonds broken simultaneously should be much smaller than that for procedures shown in Figs. 2–4.

In summary, we found that PtAu(111) can be as active as Pt(111) to catalyze methanol dehydrogenation through systematic density functional calculations. The most crucial consequence is the surge in activation energy for  $\text{CH}_2\text{O} \rightarrow \text{CHO}$ , from almost zero on the clean Pt(111) surface to 0.53 eV on the PtAu(111) surface. This provides a good chance for direct oxidation of  $\text{CH}_2\text{O}$  so that the production of CO can be avoided. Clearly, the drastically different activities of the Au and Pt sites offer ample potential to tune the reactivity and selectivity of catalysts through design of Pt distribution patterns. Density functional calculations are powerful for the identification of crucial ensembles for each reaction step and hence allow catalyst engineering at the atomic and electronic levels. For the search of prospective substitutes to Pt electrode for hydrogen production, more extensive studies for PtAu alloy surfaces are needed for the formation of ensembles, their thermal stability, and reactivity of oxidation processes.

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