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Significance of β-Dehydrogenation in Ethanol Electro-Oxidation on Platinum Doped with Ru, Rh, Pd, Os and Ir

Tian Sheng, Wen-Feng Lin\*, Christopher Hardacre and P. Hu\*

School of Chemistry and Chemical Engineering, The Queen's University of Belfast, Belfast BT9 5AG, U.K.

# Abstract

In the exploration of highly efficient direct ethanol fuel cells (DEFC), how to promote the  $CO_2$  selectivity is a key issue which remains to be solved. Some advances have been made, for example, using bimetallic electrocatalysts, Rh has been found to be an efficient additive to platinum to obtain high  $CO_2$  selectivity experimentally. In this work, the mechanism of ethanol electrooxidation is investigated using first principles method. It is found that  $CH_3CHOH^*$  is the key intermediate during ethanol electrooxidation and the activity of  $\beta$ -dehydrogenation is the rate determining factor that affects the completeness of ethanol oxidation. In addition, a series of transition metals (Ru, Rh, Pd, Os and Ir) are alloyed on the top layer of Pt(111) in order to analyze their effects. The elementary steps,  $\alpha$ -,  $\beta$ -C-H bond and C-C bond dissociations are calculated on these bimetallic M/Pt(111) surfaces and the formation potential of OH\* from water dissociation is also calculated. We find that the active metals increase the activity of  $\beta$ -dehydrogenation but lower the OH\* formation potential resulting in the active site being blocked. By considering both  $\beta$ -dehydrogenation and OH\* formation, Ru, Os and Ir are identified to be unsuitable for the promotion of  $CO_2$  selectivity and only Rh is able to increase the selectivity of  $CO_2$  in DEFC.

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\*Corresponding authors.

*E-mail*: p.hu@qub.ac.uk; w.lin@qub.ac.uk.

Professor Peijun Hu, Elected Member of Royal Irish Academy

Chair of Physical and Theoretical Chemistry

Queen's University Belfast

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#### 1. Introduction

The direct ethanol fuel cell (DEFC) is a promising future energy solution instead of traditional technologies using fossil fuels by converting the chemical energy of alcohol into electricity. Ethanol exhibits a high energy density and is easier to be stored and transported than hydrogen as a source of fuel. Ethanol is also sustainable as it can be produced from biomass. However, the full electroactivity of ethanol has not been reached and there are still some challenges which slow its widespread application commercially. The main problems are the slow alcohol oxidative kinetics and the formation of intermediates which act as catalyst poisons. In addition, the DEFC often works under strongly basic or acidic conditions and, thus, the corrosion of the electrode materials is problematic and the usage of novel metals like Pt or Pd is inevitable. In the ethanol electrooxidation, the ideal anodic reaction is the complete oxidation of ethanol to  $CO_2$  (in acid condition) or  $CO_3^{2-}$  (in alkaline condition) with the transfer of 12 electrons (reaction 1). However, in reality the predominant products are acetaldehyde and acetic acid (in acid condition) or acetate (in alkaline condition) with the transfer of 2, 4 or 5 electrons only (reaction 2, for example) in most systems reported.<sup>1-9</sup> The production of CO<sub>2</sub> is confirmed in the region of 0.5%~7.5% on platinum catalysts, which is far lower than the selectivity needed for economic implementation of the technology. Since the total fuel cell efficiency is inevitably linked with the CO<sub>2</sub> selectivity, how to resolve the selectivity of CO<sub>2</sub> remains the major challenge.<sup>10-16</sup>

Complete oxidation:  $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$  (1)

Partial oxidation: 
$$C_2H_5OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-$$
 (2)

To this end, many works have been devoted to more efficient fuel cell technology. Since the pure Pt electrode is not efficient enough, the modification of Pt electrodes by other metals such as Ru, Rh, Sn, Pd, and Os has been investigated extensively.<sup>17-29</sup> In general, bimetallic catalysts are able to combine the advantage of each component and make the catalysts more efficient. Recent works have significantly improved both the activity and the selectivity using these systems.<sup>1-29</sup> Binary PtSn and PtRu systems have been found to be the most effective

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catalysts in DEFC, increasing the peak current density and lower the onset potential significantly.<sup>17-26</sup> However, the dominant products were identified to be acetic acid and acetaldehyde and the CO<sub>2</sub> selectivity was lower than that on pure Pt. The roles of Sn and Ru were proposed to activate water on surface Sn or Ru sites at low potentials but were not effective for C-C bond dissociation.<sup>17-26</sup> Rh was discovered as an effective additive on Pt to facilitate the C-C bond splitting.<sup>27-30</sup> An exceptional ternary PtRhSnO<sub>2</sub> catalyst prepared by Adzic and co-workers was found to be considerably more effective in splitting the C-C bond, leading to a predominant CO<sub>2</sub> at room temperature under acidic conditions.<sup>31</sup>

The mechanism of ethanol electrooxidation is complicated. There are more than 40 possible intermediates and four typical chemical bonds, C-C, C-O, O-H and α-, β-C-H bonds are involved. In the investigation of ethanol oxidative process, in situ infrared reflectance absorption spectroscopy provided significant insights into the ethanol oxidation and a series of surface species, such as CH<sub>3</sub>COOH, CH<sub>3</sub>CHO, CH<sub>3</sub>CO, CO and CH<sub>x</sub>, were detected on Pt electrodes.<sup>13-19</sup> Recently, density functional theory (DFT) calculations have been widely used to understand electrochemical catalytic reactions at the atomic level.<sup>33</sup> Several studies of ethanol electrooxidation or ethanol reforming with similar elementary steps have been carried out on many transition metals, such as Pt, Pd, Rh and Ni, using DFT calculations or other theoretical approaches.<sup>34-51</sup> Alcala et al. identified that the CHCO species may be the precursor for C-C bond breaking on Pt(111).<sup>34,35</sup> Wang and Liu mapped out the whole reaction network of ethanol oxidation and structure selectivity on closed-packed Pt(111), open Pt(100) and stepped Pt(211) surfaces. They pointed out that ethanol partial oxidation prefers to occur on Pt(111) and ethanol could be fully oxidized on Pt(100).<sup>36,37</sup> Our previous work suggested that C-C bond dissociation was readily blocked by surface oxidants (adsorbed OH or O) on Pt step.43 Although the binary catalysts have extensively been used experimentally, studies on how bimetallic systems affect the selectivity in ethanol electrooxidation are still rare. Xu et al. studied the  $\alpha$ -dehydrogenation of ethanol on Pt<sub>3</sub>M cluster (M = Ru, Sn, Re, Rh, and Pd) and suggested that  $Pt_3Sn$  is the best for ethanol  $\alpha$ -dehydrogenation.<sup>46,47</sup> To data, only the additive Sn and Ru have widely been accepted for activating water at low potentials. However, the roles of some other additive metals, in

particular Rh are still not well understood.<sup>5-7</sup> Therefore, the binary catalysts in DEFC, which have lead to the discovery of highly active and selective systems need further theoretical investigation.

In the current work, we address the following problems: (i) What are the key steps of complete oxidative (to form  $CO_2$  or  $CO_3^{2-}$ ) and partial oxidative (to form acetic acid or acetate) pathways? (ii) How do the bimetallic surfaces, M/Pt(111), M = Ru, Rh, Pd, Os and Ir, affect the  $\alpha$ - or  $\beta$ -C-H bond and C-C bond dissociations? (iii) Why is only Rh found experimentally to be a good additive for the enhancement of  $CO_2$  selectivity? We will reveal the roles of the additive metals in ethanol electrooxidation and illustrate the significance of  $\beta$ -dehydrogenation in the formation of  $CO_2$ . The calculated results, including the mechanisms in ethanol oxidation,  $\alpha$ - or  $\beta$ -C-H bond and C-C bond dissociations, and the origin of the facilitation of Rh on  $CO_2$  selectivity are reported and discussed in detail.

## 2. Computational Methods

All the electronic structure calculations were performed using the Vienna Ab-initio Simulation Package (VASP) with the exchange-correlation functional of Perdew-Burke-Ernzerh (PBE). The projector-augmented-wave (PAW) pseudopotentials were utilized to describe the core electron interaction. Geometry optimization was carried out by the BFGS algorithm.<sup>52-60</sup> The close-packed Pt(111) surface was modeled by p(3x3) unit cell with 4 layers and the bottom two layers were fixed in the slab while the top two layers were relaxed during all the optimization process. The vacuum region was  $\sim 12$  Å to ensure that there is little interaction between slabs. The cut-off energy was 400 eV and a 3x3x1 Monkhorst-Pack k-point sampling was used. The transition states were located with a constrained optimization approach with the force converge criteria below 0.05 eV/Å in modified VASP.<sup>61-63</sup> For M/Pt(111), where M = Ru, Rh, Pd, Os and Ir, the doped surfaces were modeled by the substitution of surface Pt atom by M atom at a coverage of 1/9 ML, and then a full structural optimization was carried out. It may be worth noting that such models have been commonly used in DFT calculations for understanding catalytic structures.<sup>64,65</sup> In

this paper, the adsorption energy was defined as:  $E_{ad} = E(adsorbate/surface) - E(adsorbate) - E(surface)$ , where E(adsorbate/surface), E(adsorbate), and E(surface) are the total energies of the adsorbate binding with metal surface, gaseous adsorbate and clean surface, respectively.

For the calculation of the OH\* formation potential,<sup>66-69</sup> the reaction free energy change ( $\Delta G$ ) in OH\* formation was calculated using the following chemical reaction:

$$H_2O \rightarrow OH^* + H^+ + e^-$$
 (3)

The free energy of species was obtained from G = E + ZPE + TS, where E is the total energy of species, S is the entropy and ZPE is the zero point energy at room temperature. Therefore, the free energy change of reaction 3 was derived as  $\Delta G = G(OH^*) + G(H^+ + e^-) - G(H_2O)$ . At the electrode potential of 0 V, pH = 0 ([H<sup>+</sup>] = 1M), at 298 K, due to the equilibrium of  $H^+ + e^- \rightarrow \frac{1}{2} H_2$ , we can use the free energy of  $\frac{1}{2} H_2$  in the gas phase to replace that of  $H^+ + e^- \frac{66-69}{12}$  Two correction terms were necessary to be added: the pH of aqueous solution (-pH*kT*ln10) and the electrode potential (eU) referring to standard hydrogen electrode (SHE), resulting in  $G(H^+ + e^-) = G(\frac{1}{2} H_2) - pHkTln10 + eU$ . When  $\Delta G = 0$ , reaction 3 is in equilibrium and the OH\* formation potential can be obtained.

### 3. Results

#### **3.1 Significance of β-dehydrogenation**

Firstly, we calculated the mechanism of ethanol electrooxidation on Pt(111). The adsorption energy of ethanol is -0.25 eV at the top site and the distance of O-Pt bond is 1.87 Å. The dehydrogenation of ethanol initially breaks the  $\alpha$ -C-H bond, forming adsorbed CH<sub>3</sub>CHOH (CH<sub>3</sub>CHOH\*) with a barrier of 0.79 eV and the C-H bond length is 1.61 Å at the transition state. Thereafter,  $\alpha$ -dehydrogenation of CH<sub>3</sub>CHOH\* was examined:

$$CH_3CHOH^* \rightarrow CH_3COH^* + H^*$$
 (4)

$$CH_3COH^* \rightarrow CH_3CO^* + H^*$$
 (5)

The CH<sub>3</sub>COH\* formed adsorbs at the top site with an H-down (OH group) configuration with a barrier of 0.81 eV for breaking C-H bond at CH<sub>3</sub>CHOH\* in reaction 4. CH<sub>3</sub>COH\* is found to be unstable since the dissociative barrier of O-H bond is only 0.19 eV in reaction 5 to form acetyl (CH<sub>3</sub>CO\*) at the top site. When all the  $\alpha$ -C-H bonds are broken in ethanol, then  $\beta$ -dehydrogenation starts to take place as reaction 6. CH<sub>3</sub>CO\* is quite stable, resulting in a high barrier for the formation of CH<sub>2</sub>CO\* from  $\beta$ -C-H bond breaking on Pt(111). In this case, the dissociative barrier is calculated to be 1.06 eV due to the high stability of methyl (CH<sub>3</sub>) group in CH<sub>3</sub>CO\*.

$$CH_3CO^* \rightarrow CH_2CO^* + H^*$$
 (6)

However, our calculations show that CH<sub>3</sub>CHOH\* is a selective intermediate in that it is not only able to break  $\alpha$ -C-H bond but also capable of breaking  $\beta$ -C-H bond. The  $\beta$ -dehydrogenation barrier of CH<sub>3</sub>CHOH\* was calculated to be 0.86 eV to form CH<sub>2</sub>CHOH\* and the C-H bond is lengthened to 1.53 Å at the transition state. From this intermediate, the C-H bond breaking barrier is 0.73 eV to yield CH<sub>2</sub>COH\* with the C-H bond length of 1.44 Å at the transition state. Once CH<sub>2</sub>COH\* is formed, the dissociation of O-H bond is easy with a barrier of 0.54 eV leading to the formation of CH<sub>2</sub>CO\*. The reactions in the  $\beta$ -dehydrogenation pathway can be written as follows:

> $CH_{3}CHOH^{*} \rightarrow CH_{2}CHOH^{*} + H^{*}$ (7)  $CH_{2}CHOH^{*} \rightarrow CH_{2}COH^{*} + H^{*}$ (8)  $CH_{2}COH^{*} \rightarrow CH_{2}CO^{*} + H^{*}$ (9)

Compared with the above two pathways, the effective barrier of  $\beta$ -dehydrogenation pathway is only 0.86 eV which is much lower than that found in the  $\alpha$ -dehydrogenation pathway of 1.06 eV. The  $\beta$ -dehydrogenation pathway is obviously more facile than the traditional  $\alpha$ -dehydrogenation pathway in the formation of CH<sub>2</sub>CO\* as the common intermediate from ethanol and the formation of CO\* does not involve the acetyl (CH<sub>3</sub>CO\*) which would be oxidized to produce acetic acid (CH<sub>3</sub>COOH\*) in the presence of surface oxidants. The C-H bond breaking in CH<sub>3</sub> group is likely to occur at the initial stage of ethanol oxidation. Therefore, it is suggested that the  $\beta$ -dehydrogenation plays an important role in the complete electrooxidation of ethanol to CO<sub>2</sub>.

The C-C bond splitting in CH<sub>2</sub>CO\* to directly forms CH<sub>2</sub>\* and CO\* is difficult because the barrier is high ( $E_a = 1.00 \text{ eV}$ ). Thus, further dehydrogenation may be necessary to form CHCO\* (reaction 10). The calculated barrier in reaction 10 is 0.78 eV. CHCO\* is a good precursor for the formation of CO\*, in which that the barrier of C-C bond breaking is decreased to 0.84 eV (reaction 11), indicating that the CO\* is formed mainly as a result of C-C bond breaking in CHCO\*.<sup>34,35</sup>

 $CH_2CO^* \rightarrow CHCO^* + H^*$  (10)  $CHCO^* \rightarrow CH^* + CO^*$  (11)

In the presence of surface oxidants (OH\* or O\*), the formation of CO<sub>2</sub> can readily occur with a small barrier of 0.23 eV in CO\* + OH\*  $\rightarrow$  COOH\*. The energy profiles from CH<sub>3</sub>CH<sub>2</sub>OH to CO including two pathways are shown in Figure 1 and all the optimized structures of intermediates and transition states are illustrated in Figure 2.



Figure 1. Energy profiles of ethanol electrooxidation on Pt(111). The blue line is the energy profile of the  $\alpha$ -dehydrogenation pathway and the red line is from the  $\beta$ -dehydrogenation pathway.



**Figure 2**. Optimized structures of the intermediates and transition states in ethanol electrooxidation involved in the two dehydrogenation pathways shown in Figure 1. Blue: Pt, red: O, grey: C, white, H. TS1 is the transition state of  $CH_3CH_2OH^* \rightarrow CH_3CHOH^*$ ; TS2:  $CH_3CHOH^* \rightarrow CH_2CHOH^*$ ; TS3:  $CH_2CHOH^* \rightarrow CH_2COH^*$ ; TS4:  $CH_2COH^* \rightarrow CH_2COH^*$ ; TS5:  $CH_2CO^* \rightarrow CHCO^*$ ; TS6:  $CHCO^* \rightarrow CH^*+CO^*$ ; TS7:  $CH_3CHOH^* \rightarrow CH_3COH^*$ ; TS8:  $CH_3COH^* \rightarrow CH_3CO^*$ ; TS9:  $CH_3CO^* \rightarrow CH_2CO^*$ .

### 3.2 Breaking of C-H bond and C-C bond on Bimetallic M/Pt(111)

As stated above,  $\beta$ -dehydrogenation is significant in the formation of CO/CO<sub>2</sub>. One may expect that doped Pt surfaces by a second metal may be helpful to promote  $\beta$ -dehydrogenation. To test this idea, the top layer of Pt(111) was doped with a series of transition metals (Ru, Rh, Pd, Os and Ir) at a coverage of 1/9 ML to identify whether they could promote  $\alpha$  and  $\beta$  dehydrogenation and C-C bond splitting. The calculated barriers, the reaction energies and the bond lengths at the located transition states are listed in Table 1. For  $\alpha$ -dehydrogenation it can be seen that from CH<sub>3</sub>CHOH\* to CH<sub>3</sub>COH\* (reaction 4), the barriers are not significantly affected by the doped metals. The highest barrier is observed on Os/Pt(111) (E<sub>a</sub> = 0.85 eV) and the lowest is 0.76 eV on Pd/Pt(111) with the difference only found to be 0.09 eV. Furthermore, the C-H bond distances at the transition states are around ~1.45 Å. However, the barriers of the  $\beta$ -dehydrogenation reactions are sensitive to the presence of the second metal.

On Ru/Pt(111), Os/Pt(111), Rh/Pt(111) and Ir/Pt(111),  $\beta$ -dehydrogenation is more facile than Pt(111), in general. From CH<sub>3</sub>CHOH\* to CH<sub>2</sub>CHOH\* (reaction 5), the barrier on Pt(111) is 0.86 eV. However, it is only 0.40 eV on Os/Pt(111) which is highly active for  $\beta$ -dehydrogenation, while Ir/Pt(111), Ru/Pt(111) and Rh/Pt(111) are slightly less active than Os/Pt(111), on which the barriers are 0.42 eV, 0.48 eV and 0.58 eV, respectively. It is clear that Ru/Pt(111), Os/Pt(111), Rh/Pt(111) and Ir/Pt(111) can accelerate  $\beta$ -dehydrogenation, leading to the C-C bond breaking. In contrast, Pd/Pt(111) is found to be less inactive than

pure Pt(111) for  $\beta$ -dehydrogenation due to an increased barrier (E<sub>a</sub> = 1.06 eV), which is 0.20 eV higher than that on pure Pt. The same trend is also obtained in reaction 6, another reaction involved  $\beta$ -dehydrogenation: On Pt(111), the  $\beta$ -dehydrogenation barrier from CH<sub>3</sub>CO\* to CH<sub>2</sub>CO\* is 1.06 eV. However, on Os/Pt(111) the barrier is decreased to 0.58 eV. On Ru/Pt(111), Ir/Pt(111) and Rh/Pt(111), the barriers are 0.65 eV, 0.60 eV and 0.74 eV, respectively. Why do  $\alpha$  and  $\beta$  dehydrogenation reactions show remarkably different sensitivities on the various bimetallic surfaces? We suggest that it is determined by the way that the doped metal is involved in the dehydrogenation. The  $\alpha$ -C-H bond breaking is catalyzed by one single platinum site (Figure 3a), therefore, the effect of a neighbouring second metal is limited as no adsorption needs to take place on this site. However, the  $\beta$ -C-H bond dissociation requires two adjacent metal sites and one of them is the additional metal atom resulting in the formation of a metal-C bond, which is shown in Figure 3b. One may expect that the strength of metal-C bond would affect the  $\beta$ -dehydrogenation barrier considerably, which is shown in Table 2 in which the strength of metal-C bond is measured by the adsorption energy of CH<sub>3</sub>\* on the metal top site. It can be seen that the more active the surface towards  $\beta$ -dehydrogenation is, the higher the adsorption energy of CH<sub>3</sub>\* is. The adsorption energy of CH<sub>3</sub>\* on Pd top site is the lowest (-1.62 eV) among the doped metals, resulting in the  $\beta$ -dehydrogenation barrier being the highest (1.06 eV). However, on Os and Ir sites the CH<sub>3</sub>\* adsorption energies are -2.07 eV and -2.08 eV, respectively, leading to the barriers of  $\beta$ -dehydrogenation being low (0.42 eV and 0.40 eV, respectively). Therefore, the modification of the neighbour site by doping other elements is likely to affect β-dehydrogenation.

Since the C-C bond breaking is a crucial step in the production of CO/CO<sub>2</sub>, we calculated the barriers on M/Pt(111) (reaction 11), which are listed in Table 1. It can be seen from the table that the barriers of C-C bond splitting are not sensitive to the presence of the additional metals. The barriers are all around 0.80 eV and the C-C bond distance are ~1.90 Å at the transition states. Os/Pt(111) is found to be active towards the C-C bond dissociation with the lowest barrier ( $E_a = 0.73 \text{ eV}$ ). In all the other cases, lower barriers are found compared with the pure Pt system ( $E_a = 0.84 \text{ eV}$ ), namely, on Ru/Pt(111), Rh/Pt(111) and Ir/Pt(111), the dissociative barrier are 0.80 eV and on Pd/Pt(111) the barrier is 0.79 eV.





**Figure 3**. Illustration of transition states of (a)  $\alpha$ -dehydrogenation and (b)  $\beta$ -dehydrogenation of CH<sub>3</sub>CHOH\* on M/Pt(111) (M = Ru, Os, Rh, Ir and Pd). Blue: Pt, red: O, grey: C, white, H, green: M. They show that the  $\alpha$ -dehydrogenation occurs on a single metal atom while the  $\beta$ -dehydrogenation takes place over two metal atoms.

Table 1. Calculated reaction barriers (E<sub>a</sub>, eV), reaction energy ( $\Delta$ E, eV) and bond lengths (Å) at the transition states for reactions 4, 7, 5 and 11: CH<sub>3</sub>CHOH\*  $\rightarrow$  CH<sub>3</sub>COH\* + H\*, CH<sub>3</sub>CHOH\*  $\rightarrow$  CH<sub>2</sub>CHOH\* + H\*, CH<sub>3</sub>CO\*  $\rightarrow$  CH<sub>2</sub>CO\* + H\*, CHCO\*  $\rightarrow$  CH\* + CO\* on Pt(111) and M/Pt(111), where M = Ru, Rh, Pd, Os and Ir.

	Ru/Pt(111)	Rh/Pt(111)	Pd/Pt(111)	Os/Pt(111)	Ir/Pt(111)	Pt(111)
$\rm CH_3CHOH* \rightarrow$	Ru/Pt(111)      Rh/Pt(111) $CH_3CHOH^* \rightarrow CH_3COH^* + H^*$ Ea      0.82      0.80        d(C-H)      1.454      1.449      1.449 $\Delta E$ -0.34      -0.33      -0.33 $CH_3CHOH^* \rightarrow CH_2CHOH^* + H^*$ Ea      0.48      0.58					
$\mathbf{E}_{\mathbf{a}}$	0.82	0.80	0.78	0.85	0.83	0.81
d(C-H)	1.454	1.449	1.457	1.462	1.466	1.474
ΔΕ	-0.34	-0.33	-0.33	-0.33	-0.33	-0.32
$CH_{3}CHOH^{*} \rightarrow CH_{2}CHOH^{*} + H^{*}$						
$\mathbf{E}_{\mathbf{a}}$	0.48	0.58	1.06	0.40	0.42	0.86
d(C-H)	1.573	1.533	1.591	1.515	1.466	1.529
ΔΕ	0.01	0.02	0.21	-0.16	-0.18	-0.03
$CH_3CO^* \rightarrow CH_2CO^* + H^*$						
$\mathbf{E}_{\mathbf{a}}$	0.65	0.74	1.26	0.58	0.60	1.06

d(C-H)	1.512	1.503	1.582	1.448	1.404	1.492		
ΔΕ	0.14	0.16	0.41	-0.07	-0.08	0.10		
$CHCO^* \rightarrow CH^* + CO^*$								
E <sub>a</sub>	0.80	0.80	0.79	0.73	0.80	0.84		
d(C-C)	1.887	1.921	1.889	1.905	1.911	1.936		
ΔE	-0.65	-0.63	-0.64	-0.66	-0.58	-0.54		

Table 2. Relation between the  $\beta$ -dehydrogenation barrier (E<sub>a</sub>, eV) of the reaction: CH<sub>3</sub>CHOH\*  $\rightarrow$  CH<sub>2</sub>CHOH\* + H\*, and the adsorption energy (E<sub>ad</sub>) of CH<sub>3</sub>\* on Pt(111) and M/Pt(111), where M = Ru, Rh, Pd, Os and Ir.

	<b>Os/Pt(111)</b>	Ir/Pt(111)	Ru/Pt(111)	Rh/Pt(111)	Pt(111)	Pd/Pt(111)
$\mathbf{E}_{\mathbf{a}}$	0.40	0.42	0.48	0.58	0.86	1.06
Eads	-2.07	-2.09	-1.97	-1.90	-1.82	-1.62

## 3.3 Origin of High Selectivity on Rh/Pt(111)

We have shown that the selective dehydrogenation of CH<sub>3</sub>CHOH\* is crucial to the formation of CO<sub>2</sub> or acetic acid. In order to identify the effects of these alloys, we define the selectivity as the barrier difference as follows:  $\Delta E_a = E_{a,\alpha-CH} - E_{a,\beta-CH}$ , where  $E_{a,\alpha-CH}$  is the barrier of  $\alpha$ -dehydrogenation and  $E_{a,\beta-CH}$  is the barrier of  $\beta$ -dehydrogenation. Obviously, the higher  $\Delta E_a$ is, the more favoured the  $\beta$ -dehydrogenation is, and the higher possibility to form CO. Our calculations show the following order of the promoted effects of doped metals:

Os/Pt(111) > Ir/Pt(111) > Ru/Pt(111) > Rh/Pt(111) > Pt(111) > Pd/Pt(111)

However, these results are not completely consistent with experimental results: Only Rh was experimentally found to be highly selective towards CO<sub>2</sub>.<sup>27-30</sup> Ru modified Pt provides a high activity at low potentials but predominant products are still acetic acid and acetaldehyde.<sup>4-7</sup> In order to rationalise these results, realistic working conditions on electrode must be considered.

It is well known that with the increased external potential water would dissociate to OH\* accompanying the separation of proton and electron (reaction 3). In order to study the effects of the OH\* formation potential ( $U_{OH*}$ ) on M/Pt(111), we calculated the free energy diagrams ( $\Delta$ G) for the OH\* formation at varied potential (vs SHE). The results are shown in Figure 4a. OH\* adsorption on Os/Pt(111) readily occurs at the potential of -0.40 V (the lowest among the M/Pt(111) systems). The OH\* formation potentials on Ru/Pt(111) and Ir/Pt(111) shift positively to -0.04 V and 0.04 V, respectively. On Rh/Pt(111), OH\* forms at a potential of 0.36 V, which is higher than those of Os, Ru and Ir, but lower than that of Pt, on which at 0.64 V OH\* starts to form. The OH\* formation potential calculated on Pt(111) matches well the previous calculations and experimental observations, indicating the description of OH\* adsorption in our work is reasonable.<sup>11-16</sup> Pd/Pt(111) is found to be inactive; the OH\* formation potential is 0.92 V on doped Pd site.

The relationship between the selectivity ( $\Delta E_a$ ) and the OH\* formation potential (U<sub>OH\*</sub>) is plotted in Figure 4b which illustrates that the more active the metals is, the more selective the surface is towards  $\beta$ -dehydrogenation, the data is listed in Table 3. However, the typical working potential is in the range of  $0.3 \sim 0.7$  V. Under these conditions, Os/Pt(111), Ru/Pt(111) and Ir/Pt(111) would be oxidized by OH\* from water dissociation. The typical working potential is in the range of  $0.3 \sim 0.7$  V, while the OH\* formation potentials of Os/Pt(111), Ru/Pt(111) and Ir/Pt(111) from our calculations are -0.40 V, -0.04 V and 0.04 V, respectively. Thus, under the typical working potentials, Os/Pt(111), Ru/Pt(111) and Ir/Pt(111) should be less inactive than Pt(111) because of OH\* adsorbed on the doped sites of surfaces: Firstly, the surfaces will be covered by a certain amount of OH\* that will block the active sites for  $\beta$ -dehydrogenation. OH\* are likely to play a role to provide surface oxidants for the oxidation of acetyl or CO. Secondly, once OH\* forms on surfaces, the formation of acetaldehyde and yield acetic acid readily occurs resulting in the non-CO2 pathway, as shown in our previous work and observed experimentally.<sup>1,42,44,69</sup> However, the OH\* formation potential on Rh/Pt(111) is just on the edge of the typical working potential range. Hence, at the low potentials of the working potential range, OH\* formation on Rh/Pt(111) may just start and may not affect dramatically the surface chemistry, but the presence of Rh will increase the

surface selectivity towards CO<sub>2</sub>. Under the high potential region of working potentials (for example ~0.7 V), OH\* will cover sufficient amount of Rh sites on Rh/Pt(111) according to our calculations. Therefore, Rh, which is less active than zero valent Ru, Os and Ir, but more active than Pt, may facilitate the  $\beta$ -dehydrogenation, particularly at low potentials. On the other hand, the  $\alpha$ -dehydrogenation of ethanol may also have possibility to occur on Rh sites of Rh/Pt(111). Therefore, we calculated the  $\alpha$ -dehydrogenation of ethanol on a Rh site, giving rise to the barrier of 0.70 eV, which is only slightly smaller than that on pure Pt(111) ( $E_a =$ 0.79 eV). In addition, we find that the water adsorption on the Rh site is stronger than that on Pt(111): the adsorption energy of  $H_2O^*$  on the Rh site is -0.45 eV while on Pt it is -0.22 eV only. Since in realistic systems water molecules are always abundant, we believe that the dehydrogenation reactions are more likely to occur on Pt sites, which is consistent with previous work.<sup>70-71</sup> In the field of ethanol elecrooxidation, a general consensus is that the additive of Rh usually facilitates the selectivity of C1 products, while Ru significantly increases the activity at lower potential compared with monometallic Pt systems<sup>1-9</sup>, which are consistent with our results. Even though Os and Ir are less well studied experimentally resulting in lack of data to be compared with our DFT results, from our calculations we find that the onset potentials on Os/Pt(111) and Ir/Pt(111) are close to Ru/Pt(111). Thus, we suggest that these three doped metals may have similar properties on this respect. It is worth mentioning that the surface models used in this work may not be the same as practical systems, our results provide some insight into understanding the roles of modification of pure Pt by doping other transition metals in ethanol electrooxidation.



**Figure 4**. (a) The free energy diagram ( $\Delta G$ ) for the formation of OH\* (reaction 3) on Pt(111) and M/Pt(111), at varied potentials (U<sub>OH\*</sub>, V vs SHE). (b) Selectivity ( $\Delta E_a$ ) on Pt(111) and M/Pt(111) plotted against OH\* formation potential, where M = Ru, Rh, Pd, Os and Ir.

**Table 3.** Calculated OH\* formation potentials ( $U_{OH*}$ , V vs SHE) and the barrier differences ( $\Delta E_a$ , eV) on Pt(111) and M/Pt(111) where M = Ru, Rh, Pd, Os and Ir.

Ru/Pt(111) Rh/Pt(111) Pd/Pt(111) Os/Pt(111) Ir/Pt(111) Pt(111)

U <sub>OH*</sub>	-0.09	0.36	0.92	-0.40	0.04	0.64
$\Delta E_a$	0.34	0.22	-0.28	0.45	0.41	-0.05

# 4. Conclusions

In this work, the reaction mechanism of ethanol electrooxidation in direct ethanol fuel cell has been investigated. CH<sub>3</sub>CHOH\* is identified to be a key intermediate affecting the selectivity from the calculations of the ethanol electrooxidation mechanism on Pt(111).  $\beta$ -dehydrogenation is found to be the determining factor that affects the selectivity to CO<sub>2</sub> (CO<sub>3</sub><sup>2-</sup>) or acetic acid (acetate). Five transition metals (Ru, Os, Rh, Ir and Pd) are doped on Pt(111) at a coverage of 1/9 ML as bimetallic models to investigate their roles. Our findings show that the modified metals have little effect on  $\alpha$ -dehydrogenation and C-C bond splitting, but  $\beta$ -dehydrogenation is sensitive to these alloyed systems. In general, Ru, Os, Rh and Ir can accelerate  $\beta$ -dehydrogenation, while Pd cannot. In order to consider realistic electrocatalytic conditions, OH\* formation potentials of M/Pt(111) have been calculated. A relationship between the selectivity and OH\* formation potential is obtained, which suggests that the more active transition metals provide the higher selectivity, but are more easily blocked by OH\*. Under typical working potentials, adding Ru, Os and Ir to Pt is not found to be effective in the promotion of CO<sub>2</sub> selectivity due to the formation of surface OH. However, Rh plays a positive role in increasing the CO<sub>2</sub> selectivity in the DEFC.

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