

Supporting Information

Utilization of the Three-Dimensional Volcano Surface to Understand the Chemistry of Multi-phase Systems in Heterogeneous Catalysis

Jun Cheng and P. Hu*

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

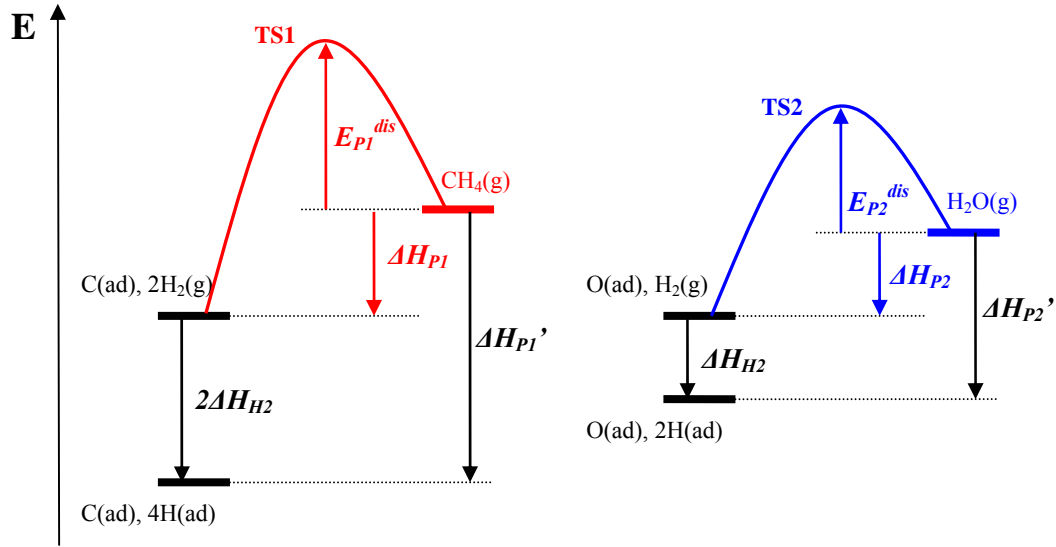
1. The derivation of Eqs. (4)-(6) in the main text

In our previous work,¹ the C and O hydrogenation reactions, $C(ad)+4H(ad)\rightarrow CH_4(g)$ and $O(ad)+2H(ad)\rightarrow H_2O(g)$, follow the BEP relations:

$$E_{P1}^{dis} = 0.27\Delta H_{P1}' + 0.52 \quad (S1)$$

$$E_{P2}^{dis} = 0.27\Delta H_{P2}' + 0.52 \quad (S2)$$

where $\Delta H_{P1}'$ is the enthalpy difference between C+4H adsorbed on the surface and CH₄ in the gas phase, and $\Delta H_{P2}'$ is the enthalpy difference between O+2H adsorbed on the surface and H₂O in the gas phase. It should be noted that $\Delta H_{P1}'$ and $\Delta H_{P2}'$ are referenced to H adsorbed on the surface in the previous work while ΔH_{P1} and ΔH_{P2} are referenced to H₂ in the gas phase in the present work. The difference is the dissociative adsorption energy of H₂ (ΔH_{H2}), which is illustrated in S-Figure 1.



S-Figure 1 Energy profile of hydrogenation of C and O atoms. ΔH_{H_2} is the dissociative adsorption energy of H₂. $\Delta H_{P1}'$ is the enthalpy difference between C+4H adsorbed on the surface and CH₄ in the gas phase, and $\Delta H_{P2}'$ is the enthalpy difference between O+2H adsorbed on the surface and H₂O in the gas phase. The other definitions can be found in the caption of Figure 1 in the main text.

From S-Figure 1, we can have:

$$\Delta H_{P1}' = \Delta H_{P1} + 2\Delta H_{H_2} \quad (S3)$$

$$\Delta H_{P2}' = \Delta H_{P2} + \Delta H_{H_2} \quad (S4)$$

Substituting Eqs. (S3) and (S4) into Eqs. (S1) and (S2), and the following relations can be obtained:

$$E_{P1}^{dis} = 0.27\Delta H_{P1} + 0.54\Delta H_{H_2} + 0.52 = 0.27\Delta H_{P1} - 0.18 \quad (S5)$$

$$E_{P2}^{dis} = 0.27\Delta H_{P2} + 0.27\Delta H_{H_2} + 0.52 = 0.27\Delta H_{P2} + 0.17 \quad (S6)$$

where the average ΔH_{H_2} of -1.30 eV is chosen from our DFT calculations because ΔH_{H_2} does not considerably change on transition metal surfaces. Combining Eqs. (2) and (3) in the main text with Eqs. (S5) and (S6), Eqs. (5) and (6) can be derived.

Regarding CO dissociation, our previous work¹ showed the BEP relation is:

$$E_R^{dis} = 0.93\Delta H_R + 1.14 \quad (S7)$$

Combining Eq. (1) in the main text with Eq. (S7), we can obtain Eq. (4).

2. Plotting detail of three-dimensional volcano surface

To obtain the reaction rate, the De Donder relation^{2,3} is utilized. The reversibility of the elementary step i , z_i , is defined as:

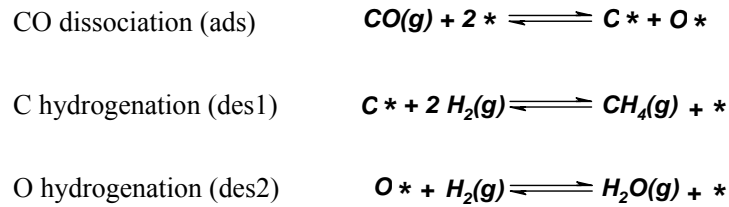
$$z_i = \frac{\prod_j a_j^{v_{ij}}}{K_{ieq}} \quad (S8)$$

where v_{ij} is the stoichiometric coefficient for the j reactant (or product) of step i , a_j is the activity of the j reactant (or product) of the step i and K_{ieq} is the standard equilibrium constant. The value of z_i is between 0 to 1 if step i proceeds in the forward direction. When the value of z_i approaches zero, step i is irreversible; as it approaches one, step i reaches quasi-equilibrium. The net reaction rate of step i , r_i , can be expressed by using the reversibility:

$$r_i = r_{+i} - r_{-i} = r_{+i}(1 - z_i) \quad (S9)$$

where r_{+i} and r_{-i} are the forward and backward reaction rates of step i , respectively.

CO hydrogenation is divided into three steps, as shown in S-Figure 2. The schematic energy profile is shown in Figure 1 in the main text, and the notation definitions in derivation are summarised in S-Table 1.



S-Figure 2 Reaction scheme of CO hydrogenation. CO dissociation, C hydrogenation and O hydrogenation are abbreviated as ads, des1 and des2, respectively.

Reactions	Enthapy change	Barriers	Rate constant	Equilibrium constant	Rate	Reversibility
CO dissociation (ads)	ΔH_R	E_R^{dis}	k_{ads}	K_{ads}	r_{ads}	z_{ads}
C hydrogenation (des1)	ΔH_{P1}	E_{P1}^{dis}	k_{des1}	K_{des1}	r_{des1}	z_{des1}
O hydrogenation (des2)	ΔH_{P2}	E_{P2}^{dis}	k_{des2}	K_{des2}	r_{des2}	z_{des2}

S-Table 1 Summary of notation definitions.

According to the De Donder relation, the reaction rates and reversibilities of the three steps can be written as follows:

$$r_{ads} = k_{ads} p_{CO} \theta_*^2 (1 - z_{ads}) \quad (S10)$$

$$z_{ads} = \frac{\theta_C \theta_O}{p_{CO} \theta_*^2 K_{ads}} \quad (S11)$$

$$r_{des1} = k_{des1} p_{H_2}^2 \theta_C \theta_* (1 - z_{des1}) \quad (S12)$$

$$z_{des1} = \frac{p_{CH_4} \theta_*}{p_{H_2}^2 \theta_C K_{des1}} \quad (S13)$$

$$r_{des2} = k_{des2} p_{H_2} \theta_O \theta_* (1 - z_{des2}) \quad (S14)$$

$$z_{des2} = \frac{p_{H_2O} \theta_*}{p_{H_2} \theta_O K_{des2}} \quad (S15)$$

where p is the partial pressure and θ is the surface coverage.

The rate constants and equilibrium constants that appear in Eqs. (S10)-(S15) can be expressed:

$$k_{ads} = \frac{k_B T}{h} e^{-\frac{S_{CO}}{R}} e^{-\frac{E_R^{dis}}{RT}} \quad (S16)$$

$$K_{ads} = e^{-\frac{S_{CO}}{R}} e^{-\frac{\Delta H_R}{RT}} \quad (S17)$$

$$k_{des1} = \frac{k_B T}{h} e^{-\frac{2S_{H_2}}{R}} e^{-\frac{E_{P1}^{dis} - \Delta H_{P1}}{RT}} \quad (S18)$$

$$K_{des1} = e^{\frac{S_{CH_4} - 2S_{H_2}}{R}} e^{-\frac{\Delta H_{P1}}{RT}} \quad (S19)$$

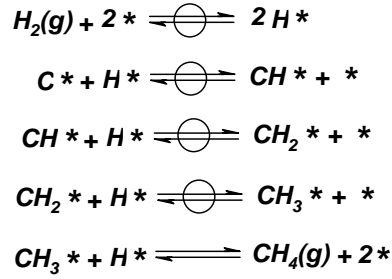
$$k_{des2} = \frac{k_B T}{h} e^{-\frac{S_{H_2}}{R}} e^{-\frac{E_{P2}^{dis} - \Delta H_{P2}}{RT}} \quad (S20)$$

$$K_{des1} = e^{\frac{S_{H_2O} - S_{H_2}}{R}} e^{\frac{\Delta H_{P2}}{RT}} \quad (S21)$$

where S is the entropy. The entropies of surface species (C(ad) and O(ad)) are usually very small and neglected. The entropies of gaseous molecules were calculated using Gaussian 03 (the setting can be found in Ref. 18 in the paper): $S_{CO}=213 \text{ J mol}^{-1}\text{K}^{-1}$, $S_{H_2}=145 \text{ J mol}^{-1}\text{K}^{-1}$, $S_{CH_4}=207 \text{ J mol}^{-1}\text{K}^{-1}$, and $S_{H_2O}=206 \text{ J mol}^{-1}\text{K}^{-1}$.

It should be noted that the C and O hydrogenation reactions in S-Figure 2 are not elementary reactions. Eqs. (S12) and (S14) can be derived from kinetics of the sequential elementary steps and quasi-equilibrium approximation as follows:

The elementary steps in the C hydrogenation reaction can be written as,



As mentioned in the main text, the H_2 dissociative adsorption reaches quasi-equilibrium under typical reaction conditions. It is also true for the surface hydrogenation steps from C to CH_3 .⁴ Thus,

$$K_{H_2} = e^{-\frac{\Delta H_{H_2} + TS_{H_2}}{RT}} = \frac{\theta_H^2}{p_{H_2} \theta_*^2} \quad (S22)$$

$$r_{des1} = \frac{k_B T}{h} e^{-\frac{E_{P1}^{dis} - \Delta H_{P1}}{RT}} \left(\frac{\theta_H}{\theta_*}\right)^3 \theta_C \theta_H - \frac{k_B T}{h} e^{-\frac{S_{CH_4}}{R}} e^{-\frac{E_{P1}^{dis}}{RT}} p_{CH_4} \theta_*^2 \quad (S23)$$

Substituting Eq. (S22) into Eq. (S23), we can have

$$\begin{aligned}
r_{des1} &= \frac{k_B T}{h} e^{-\frac{E_{P1}^{dis} - \Delta H_{P1}}{RT}} \left(\frac{\theta_H}{\theta_*}\right)^4 \theta_C \theta_* - \frac{k_B T}{h} e^{-\frac{S_{CH4}}{R}} e^{-\frac{E_{P1}^{dis}}{RT}} p_{CH4} \theta_*^2 \\
&= \frac{k_B T}{h} e^{-\frac{E_{P1}^{dis} - \Delta H_{P1} + 2\Delta H_{H2} + 2TS_{H2}}{RT}} p_{H2}^2 \theta_C \theta_* - \frac{k_B T}{h} e^{-\frac{S_{CH4}}{R}} e^{-\frac{E_{P1}^{dis}}{RT}} p_{CH4} \theta_*^2 \\
&= \frac{k_B T}{h} e^{-\frac{2S_{H2}}{R}} e^{-\frac{E_{P1}^{dis} - \Delta H_{P1}}{RT}} p_{H2}^2 \theta_C \theta_* - \frac{k_B T}{h} e^{-\frac{S_{CH4}}{R}} e^{-\frac{E_{P1}^{dis}}{RT}} p_{CH4} \theta_*^2
\end{aligned} \tag{S24}$$

which can be transformed into Eq. (S12). For the O hydrogenation reaction, Eq. (S14) can be derived in a similar way.

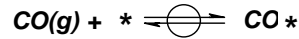
Under steady state conditions, the overall reaction rate is equal to the net reaction rates of the three steps:

$$r = r_{ads} = r_{des1} = r_{des2} \tag{S25}$$

The total surface coverage is equal to unity, thus

$$\theta_{CO} + \theta_C + \theta_O + \theta_* = 1 \tag{S26}$$

where the H surface coverage is neglected because it is usually small, while on many transition metal surfaces (e.g. Co) CO is the most abundant surface species, and hence the CO coverage is included in our consideration. It is known that CO adsorption can reach quasi-equilibrium:



Thus,

$$K_{CO} = e^{-\frac{\Delta H_{CO} + TS_{CO}}{RT}} = \frac{\theta_{CO}}{p_{CO} \theta_*} \tag{S27}$$

where the CO adsorption energy (ΔH_{CO}) of -1.20 eV is used. It should be mentioned that (i) ΔH_{CO} is different on different surfaces, but its variance is relatively small;⁵ and (ii) the value used is estimated from experimental work.⁶

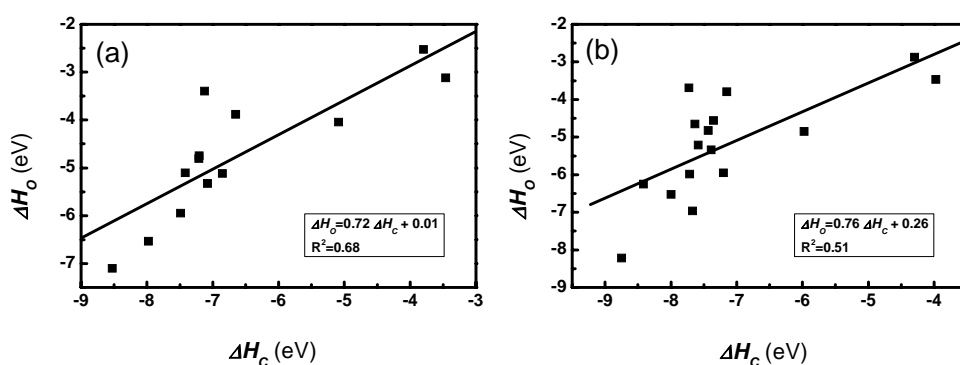
Combining Eqs. (S10)-(S21), (S25)-(S27) and Eqs. (1)-(6), we can obtain the overall reaction rate as a function of chemisorption energies of C and O (ΔH_C and ΔH_O). By solving these equations numerically, the three-dimensional volcano surface is

obtained, as shown in Figure 2 in the paper. In the calculations, the partial pressures of CO, H₂, CH₄ and H₂O are 1 bar, 3 bar, 1 bar and 1 bar, respectively, and the temperature is 500 K.

It should be mentioned that CO and H adsorption energies are assumed to be constant for simplicity in our treatment. This is because (i) CO and H₂ adsorption occur readily on metal surfaces and thus it is not very important kinetically; and (ii) the adsorption energies do not significantly change on metal surfaces.

3. Constraint between ΔH_C and ΔH_O

To obtain the correlation between ΔH_C and ΔH_O we use two sets of data calculated from the RPBE and PBE functionals. The RPBE data were obtained from the work of Nørskov and co-workers,^{5,7} and the PBE data were calculated by the SIESTA code,⁸ the setting detail of which can be found in our previous work.¹ The plots are shown in S-Figure 3. As we can see, the fitted linear equations are similar from these two sets of data although R^2 in S-Figure 3(a) is better than that in S-Figure 3(b).



S-Figure 3 Correlation between the chemisorption energies of C and O atoms (ΔH_C and ΔH_O). (a) Results of RPBE functional from Nørskov's group. (b) Our results using PBE functional.

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