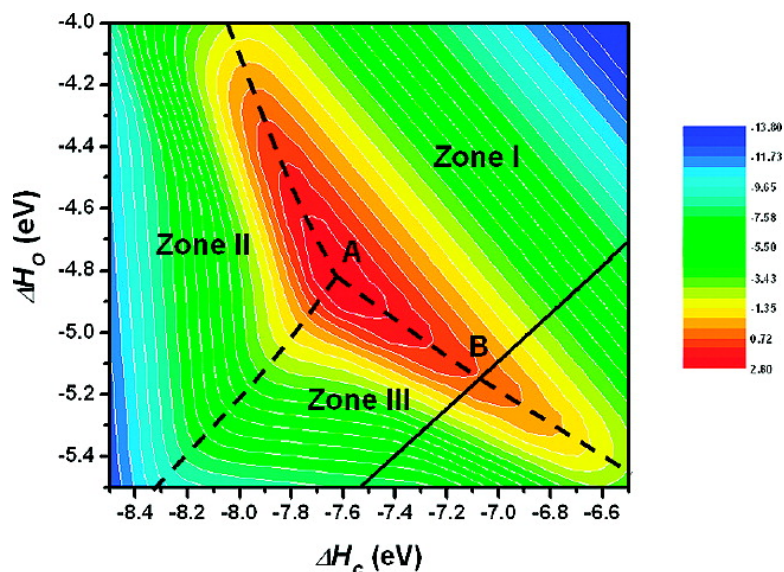


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## Utilization of the Three-Dimensional Volcano Surface To Understand the Chemistry of Multiphase Systems in Heterogeneous Catalysis

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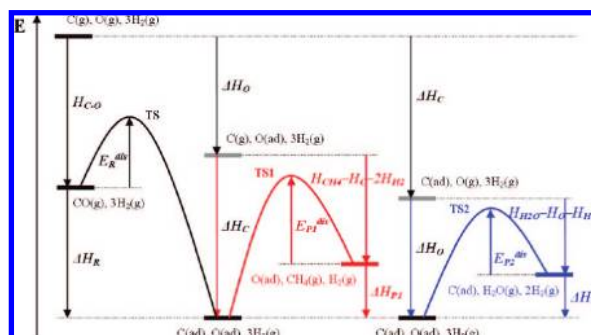
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It is well-known that most heterogeneous catalysts contain several phases. Despite the fact that the overall activity of most catalysts is often a result of multiphase effects, the understanding of the chemical role of multiphase systems is poor. In this paper, we present a simple, yet general model to provide insight into the systems with active multiphases in heterogeneous catalysis.

It is worth mentioning three major progresses related to this study in the field. First, when the activity (e.g., the turnover frequency (TOF)) is plotted against the chemisorption energy of a key surface species, a two-dimensional volcano curve is often obtained.<sup>1</sup> This is one of the most important results in heterogeneous catalysis regarding the understanding of the subject.<sup>2,3</sup> It is also extremely useful for industries: To achieve the maximum activity, one should search for catalysts with the optimal chemisorption energy.<sup>4</sup> A good example is the ammonia synthesis: Nørskov and co-workers used the N chemisorption energy as a parameter to screen many metals, and they were able to identify a very good catalyst for ammonia synthesis.<sup>5</sup> Second, several groups found that there is a linear relationship between the dissociation barrier and the enthalpy change of dissociative adsorption, the so-called Brønsted–Evans–Polanyi (BEP) relation.<sup>6–10</sup> This provides a feasible way to estimate reaction barriers from thermodynamic properties. Third, we showed recently that (i) many surface reaction steps, such as  $C + 4H \rightarrow CH + 3H \rightarrow CH_2 + 2H \rightarrow CH_3 + H \rightarrow CH_4$ , can be approximately combined to a hypothetical single step<sup>11</sup> and (ii) the barrier of the single step is a linear function of the overall reaction energy ( $\Delta H$  of  $C + 4H \rightarrow CH_4$ ).<sup>12</sup>

However, as mentioned above most catalysts consist of multiphases. There have been several fundamental questions to be answered: (i) Why are multiphases important chemically? (ii) Can we generalize them into a simple model? (iii) For what kind of reactions is the multiphase catalyst essential in order to achieve the maximum activity? In this work, we attempt to answer these questions, aiming to shed light on searching for new catalysts. In this study, we choose CO hydrogenation ( $CO + 3H_2 \rightarrow CH_4 + H_2O$ ) to tackle these issues for the following reasons: First, this is a simple but very typical system in heterogeneous catalysis, and the product formation occurs via a multistep surface reaction mechanism. Second, one of the products is  $CH_4$ , and the understanding of such a system should provide insight into other hydrocarbon formation<sup>13</sup> in heterogeneous catalysis.

We first analyzed carefully all the elementary steps in CO hydrogenation. It was found that the energetics of these reactions can be simplified as follows: (i)  $H_2$  dissociative adsorption can readily occur, and it should reach quasi-equilibrium under reaction conditions. (ii) According to our recent work<sup>11,12</sup> surface hydrogenation reactions from C to  $CH_4$  and from O to  $H_2O$  can be combined to the following steps:  $C(ad) + 4H(ad) \rightarrow CH_4(g)$  and  $O(ad) + 2H(ad) \rightarrow H_2O(g)$ . By combining the results of (i) and (ii), one can write  $C(ad) + 2H_2(g) \rightarrow CH_4(g)$  and  $O(ad) + H_2(g) \rightarrow H_2O(g)$  as single steps (see Supporting Information, SI).



**Figure 1.** Energy diagram of CO hydrogenation. The black, red, and blue curves refer to  $CO(g) \rightarrow C(ad) + O(ad)$ ,  $C(ad) + 2H_2(g) \rightarrow CH_4$ , and  $O(ad) + H_2(g) \rightarrow H_2O(g)$ , respectively. TS, TS1, and TS2 are the transition states of CO dissociation,  $CH_3$  hydrogenation, and OH hydrogenation, respectively. The definitions of energy terms are given in the main text.

Therefore, the energetic diagram of CO hydrogenation can be described in Figure 1. We can see from the figure that the enthalpy changes of the CO dissociative adsorption ( $\Delta H_R$ ) and two desorption processes ( $\Delta H_{P1}$  for  $CH_4$  and  $\Delta H_{P2}$  for  $H_2O$ ) can be expressed by the chemisorption energies of C ( $\Delta H_C$ ) and O ( $\Delta H_O$ ) on surfaces:

$$\Delta H_R = \Delta H_C + \Delta H_O - H_{C-O} = \Delta H_C + \Delta H_O + 10.86 \quad (1)$$

$$\Delta H_{P1} = \Delta H_C - (H_{CH_4} - H_C - 2H_{H_2}) = \Delta H_C + 8.20 \quad (2)$$

$$\Delta H_{P2} = \Delta H_O - (H_{H_2O} - H_O - H_{H_2}) = \Delta H_O + 4.92 \quad (3)$$

where  $H_{C-O}$  is the bond energy of CO in the gas phase,  $H_{CH_4} - H_C - 2H_{H_2}$  is the enthalpy difference between  $CH_4(g)$  and  $C(g) + 2H_2(g)$ , and  $H_{H_2O} - H_O - H_{H_2}$  is the enthalpy change from  $O(g) + H_2(g)$  to  $H_2O(g)$ . Then we carried out DFT calculations with zero-point energy (ZPE) and thermal corrections<sup>14</sup> and found that these values are  $-10.86$  eV ( $H_{C-O}$ ),  $-8.20$  eV ( $H_{CH_4} - H_C - 2H_{H_2}$ ) and  $-4.92$  eV ( $H_{H_2O} - H_O - H_{H_2}$ ), respectively, as shown in eqs 1–3.

In conjunction with the BEP relations obtained in our previous work,<sup>12</sup> the reaction barriers can also be described by the chemisorption energies of C ( $\Delta H_C$ ) and O ( $\Delta H_O$ ) (see SI for derivation):

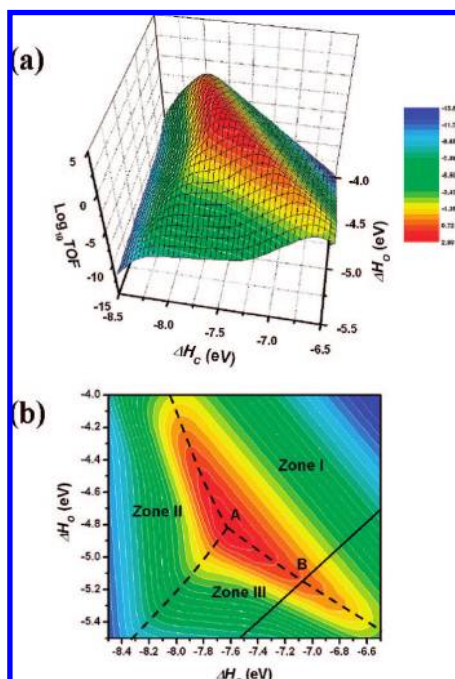
$$E_R^{dis} = 0.93(\Delta H_C + \Delta H_O) + 11.24 \quad (4)$$

$$E_{P1}^{dis} = 0.27\Delta H_C + 2.03 \quad (5)$$

$$E_{P2}^{dis} = 0.27\Delta H_O + 1.50 \quad (6)$$

where  $E_R^{dis}$ ,  $E_{P1}^{dis}$ , and  $E_{P2}^{dis}$  are the barriers defined in Figure 1.

Once we have eqs 1–6, the TOF can be computed. It is clear that there are only two fundamental parameters: the chemisorption energies of C and O atoms on surfaces. In other words, TOF is a binary function of  $\Delta H_C$  and  $\Delta H_O$ . A 3-D surface plot<sup>15</sup> of TOF against  $\Delta H_C$  and  $\Delta H_O$  is shown in Figure 2 (see SI for plotting details).



**Figure 2.** (a) 3-D volcano plot of  $\log_{10}$  TOF as a function of  $\Delta H_C$  and  $\Delta H_O$  in CO hydrogenation. (b) Two-dimensional contour of  $\log_{10}$  TOF as a function of  $\Delta H_C$  and  $\Delta H_O$  in CO hydrogenation. The black line shows the correlation between  $\Delta H_C$  and  $\Delta H_O$ . The dashed lines indicate the ridges of the 3-D volcano, which divide the surface of  $\Delta H_C$  and  $\Delta H_O$  into three zones. Point A is the global maximum of the volcano, and point B is the maximum with the constraint between  $\Delta H_C$  and  $\Delta H_O$ .

Several striking features can be found in the figures. First, the best catalyst can be located at the top of the volcano surface with  $\Delta H_C \approx -7.6$  eV and  $\Delta H_O \approx -4.8$  eV. Second, according to the ridges of the 3-D volcano surface, the surface of  $\Delta H_C$  and  $\Delta H_O$  can be divided into three zones with different characteristics (Figure 2b): (i) in Zone I the chemisorptions of C and O are both weak, leading to CO dissociation to be rate-determining; (ii) in Zone II the C chemisorption is strong, and the C desorption via hydrogenation is the rate-determining step; and (iii) in Zone III the O chemisorption is strong, resulting in the O desorption to be rate-limiting.

In general, both chemisorption energies of C and O atoms become weaker from the left to the right across the periodic table, suggesting the existence of a linear correlation between them. The regression line of the correlation between  $\Delta H_C$  and  $\Delta H_O$  from our calculations, which is similar to the results of Nørskov and co-workers,<sup>1-16</sup> is shown as the black line in Figure 2b (see detailed results and comparison in SI). Such a correlation restricts the utilization of monophase catalysts to reach the maximum of the 3-D volcano surface: If monophase catalysts such as pure metals or uniform alloys are used, one can locate the best catalyst along the black line by tuning both  $\Delta H_C$  and  $\Delta H_O$ . Point B may be achieved in this approach, which is way off from the global maximum in the 3-D surface.

However, interfaces between two separated phases can release such a constraint between  $\Delta H_C$  and  $\Delta H_O$ . For example, if CO dissociates at the interface with the C atom on one phase and O atom on the other, then C and O atoms are hydrogenated on the two separated phases. In such a system,  $\Delta H_C$  and  $\Delta H_O$  decouple, and the global maximum of activity may be achieved. Therefore, the relaxation of the constraint between  $\Delta H_C$  and  $\Delta H_O$  can give

rise to more freedom to search for the best catalyst along the 3-D volcano surface.

Now we are in a position to discuss some implications of our finding. First, it is worth addressing the fundamental question mentioned above: Is our finding reaction-system dependent? There are some reactions for which monophase catalysts should be as good as any multiphase catalysts. For example, in ammonia synthesis the only key surface intermediate is the adsorbed N. Obviously, there is no need to have two different phases to hydrogenate N. However, for reactions with more than one key surface intermediate it is likely that multiphase catalysts may have some advantages over monophase catalysts. Second, our approach described in this work may be, in general, extended to other reaction systems. Also, our finding may be used to explain the activity of Au/oxides. For example, for a water gas shift reaction ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ) there is evidence<sup>17,18</sup> that some key elementary reactions may occur on the interface between Au and oxides, which may be optimal for the reaction to achieve the high activity.

In summary, this is, to the best of our knowledge, the first attempt to explain the chemical significance of multiphase catalysts for the overall activity of reactions in heterogeneous catalysis. In contrast to traditional approaches in which either only the barriers of elementary reactions or rate-determining steps are considered to investigate the activity, in this work both the adsorption and the subsequent surface reactions are kinetically included. Owing to the constraint between the chemisorption energies of key intermediates, monophase catalysts may not achieve the global maximum of activity. However, multiphases may be able to release the constraint. These results may possess some important implications for searching for new catalysts.

**Supporting Information Available:** Derivation of eqs 4–6 and plotting detail of Figure 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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