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Formulating the Bonding Contribution Equation in Heterogeneous Catalysis: A Quantitative Description between Surface Structure and Adsorption Energy

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ABSTRACT

The relation between surface structure and adsorption energy of adsorbate is of great importance in heterogeneous catalysis. Based on density functional theory calculations, we propose an explicit equation with three chemically meaningful terms, namely the bonding contribution equation, to quantitatively account the surface structures and the adsorption energies. Successful predictions of oxygen adsorption energies on complex alloy surfaces containing up to 4 components are demonstrated, and the generality of this equation is also tested using different surface sizes and other adsorbates. This work not only may offer a powerful tool to understand the structure-adsorption relation, but also may be used to inversely design novel catalysts.

Keywords:

Density functional theory calculations, Alloys, Adsorption, Heterogeneous catalysis, Structure-bonding relationships

1. Introduction

Understanding the relation between structure and chemical interaction is one of the most fundamental topics in chemistry. In particular, in heterogeneous catalysis it is of paramount importance to understand how the catalyst structure affects the adsorption energies of adsorbates. This is because the pivotal parameter in most of fundamental theories in heterogeneous catalysis, such as Brønsted-Evans-Polanyi (BEP) relation¹⁻⁵ and volcano curve⁶⁻⁸, is the adsorption energy; these theories unravel the activity of a catalyst as a function of adsorption property on the catalyst, and make it possible to predict the activity using the adsorption energy. However, the basic property that can be directly controlled experimentally in heterogeneous catalysis is the surface structure which results in the other properties, such as the adsorption energy and catalytic activity. If the relation between the catalyst structure and the adsorption energy is accessible, the activity of the catalyst can be directly linked to the catalyst structure and such a relation can not only significantly enhance the understanding of catalytic activity, but also make it possible to inversely design⁹ the most active catalyst. In this work, we develop a framework to quantitatively describe the relation between the surface structure and the adsorption energy. Our model is very simple and yet robust, which may have far-reaching implications in heterogeneous catalysis not only from the fundamental point of view but also from the applied perspective.

Despite its importance, only a few studies on the subject were reported. Nørskov and co-workers suggested that the adsorption energy on a surface is related to the d-band center of the surface¹⁰. Recently, Sautet and co-workers^{11, 12} proposed the generalized coordination number, which can be used to predict the adsorption properties of pure metal nanoparticles¹¹ and different facets¹². However, the former requires the calculation of density of state from DFT results, which is computationally expensive to be implemented in catalyst design; while the latter is currently applied to pure metal systems. In this work, alloy surfaces were chosen because alloy catalysts are one of the most important types of catalysts widely used in heterogeneous catalysis and electrochemistry. The great number of possibilities of alloy surfaces make it possible to design catalysts with almost any adsorption energies. In previous work, surface alloys were used to achieve excellent catalytic activity by tuning the adsorption properties. Stamenkovic *et. al.*^{13, 14} reported that manipulating Pt surfaces

by doping 3d transition metals could greatly enhance the electrocatalytic activity for oxygen reduction reaction (ORR). By tuning the oxygen adsorption strength, Pt₃Ni(111) alloy surface was found to be 10-folds more active for the ORR than the pure Pt(111) surface¹³. Goodman and co-workers showed that the promotional effect of gold in Pd-Au alloys for the acetoxylation of ethylene to vinyl acetate is mainly derived from the adsorption energies of monomer Pd on the alloy surface¹⁵. Using the adsorption strength as a descriptor, Nørskov and co-workers discovered many novel alloy catalysts for hydrogen evolution¹⁶, hydrogenation of acetylene¹⁷, ORR¹⁸ and steam reforming¹⁹ through the computational high-throughput screening. Despite of the importance of the adsorption properties on alloy surfaces for designing new materials²⁰, most alloy catalysts were discovered by trial-and-error approaches²¹.

Some investigations have been carried out to provide insight into the relation between the surface structure and adsorption energies on alloy surfaces. Nørskov and co-workers performed some pioneering work to understand the adsorption property of alloys^{22, 23}. Using DFT calculations, they identified the two significant effects in surface alloying, namely the ligand and ensemble effects²². They found that the ligand effects can be evaluated using the shifts of d-band centres of surface atoms, while the ensemble effects can be described by a simple linear interpolation model²². These findings provided a deep understanding of the adsorption energies on alloy surfaces. However, to the best of our knowledge, a quantitative approach to fast predict the adsorption energy of alloys is still missing.

In order to unravel the relation between the structure and the adsorption energy, we systematically investigated the trend of adsorption energies on a series of Pt alloys. Pt was chosen as the host metal mainly for two reasons: Firstly, it is arguably the most common catalyst, and secondly, the segregation energies of most transition-metal impurities on the close-packed Pt surface are positive²⁴, suggesting that the close-packed Pt surface is favourable to form mixed alloy surfaces with most transition metals. In our work, three metals in the same period as Pt were chosen as alloying solutes, namely Re, Os and Ir. Due to the similar adsorption properties, we also considered Pd as a solute. In the current work, we first calculated the adsorption of oxygen atoms on all the possible Pt(111)-based alloy surfaces with one solute metals. We found that the effect of one substitution on the adsorption energy is related to

three chemically meaningful terms, including the intrinsic bonding ability of solute metal, the contribution factor and the generalized parameters. With these three terms, we proposed an explicit equation to predict the adsorption energies of alloy surfaces, and the generality of this equation was also tested using alloy surfaces of different sizes and different adsorbates.

2. Computational details

All the DFT calculations were carried out with a periodic slab model using the Vienna ab initio simulation program (VASP)²⁵⁻²⁸. The generalized gradient approximation (GGA) was used with Perdew-Burke-Ernzerhof (PBE)²⁹ exchange-correlation functional. It is worth mentioning that there are some approximations in the PBE functional which may cause errors in the adsorption energies. Other methods, such as hybrid DFT³⁰ and random phase approximation³¹ may provide more accurate data. However, we believe the trend of adsorption energies on alloy surfaces using PBE functional should be reliable. Projector-augmented wave (PAW) method^{32, 33} was utilized to describe the electron-ion interactions and the plane-wave basis expansion cut-off was set to 450 eV. $4 \times 4 \times 1$ and $3 \times 3 \times 1$ Monkhorst-Pack k-point mesh samplings were used for Brillouin zone integrations of the Pt(111)- $p(2 \times 2)$ and Pt(111)- $p(3 \times 3)$ alloy surfaces, respectively. All the adsorption geometries were optimized using a force-based conjugate gradient algorithm. 4-layer models were used for both the Pt(111)- $p(2 \times 2)$ and Pt(111)- $p(3 \times 3)$ alloy surface with 2 lower layers fixed and 2 upper layers relaxed. A ~ 10 Å vacuum region was placed on all the models mentioned above. In this work, the adsorption energy (ΔE_{ad}) was calculated with respect to the adsorption energy on the close-packed pure Pt surface ($E_{ads}(\text{Pt})$) as follows:

$$\Delta E_{ad} = E_{adsorb+surf} - E_{adsorb} - E_{surf} - E_{ads}(\text{Pt}). \quad (1)$$

With this definition^{34, 35}, a negative value of adsorption energy suggests that the adsorption is stronger than that on the pure Pt surface, while a positive value stands for a weaker bonding.

In this work, all the randomly generated alloy surface structures containing n solute metals were obtained with the following process: Firstly, n numbers of

substitution positions, including all the surface and subsurface atoms, are chosen randomly using the pseudo-random number generator implemented in Python Standard Library³⁶. Secondly, for each chosen substitution position, a solute metal will be randomly selected from all the solute metals considered in this work, using the same method mentioned above. Thirdly, the surface atoms are substituted at the chosen positions with the selected solute metals, and on these alloy surfaces the adsorption energies of oxygen atom are calculated. Only the hollow sites adsorptions are considered in this work, because oxygen atoms on bridge or top sites are normally considered unstable, and beyond the investigations of this work. 50 two-atom substitution and 50 three-atom substitution alloy surfaces were generated in this work using the method mentioned above, and details in substitution positions, solute metals, predicted adsorption energies, calculated adsorption energies and adsorption sites are shown in Table S1 for two-atom substitutions and Figure S2 for three-atom substitutions, respectively.

3. Results and discussion

There are a great number of possibilities of the alloy surfaces, even if only a few solute metals were taken into account. For example, for a Pt(111)- $p(2\times 2)$ surface with four solute metals, in total there are 390625 (5^8) possibilities if only the surface and subsurface atoms are allowed to be substituted, expecting that the relation between the surface structure and the adsorption energy is extremely complicated. To start with, we investigated all the Pt alloy surfaces with only one solute metal (defined as one-atom substitution). We chose the adsorption of oxygen atom on the Pt(111)- $p(2\times 2)$ alloy surfaces, because the adsorption of oxygen atom is found to be important in many reactions catalysed by Pt-based catalysts such as ORR¹⁴ and CO oxidation³⁷. The most favourable adsorption site for oxygen atom is the fcc hollow site³⁸, and considering the symmetry, there are four different types of substitution positions as shown in Figure 1: The first type (type I) of substitution positions involve the three atoms of hollow site (Figure 1(a)), which are the nearest neighbour atoms to the adsorbed oxygen. The position of type II is the substitution shown in Figure 1(b), which is a second nearest neighbour atom to the adsorbed oxygen. The positions of type III and type IV refer the subsurface atoms as illustrated in Figure 1(c) and Figure 1(d), respectively. These atoms are also the second nearest neighbour atoms.

We calculated the O adsorption energies on all the possible one-atom substituted alloy surfaces by replacing each type of atoms with the solute metals mentioned above, and the results are shown in Table 1. From the table, it can be seen that the effects of different solute metals on the adsorption energies are in the same order as all the solute metals, namely $\text{Re} > \text{Os} > \text{Ir} > \text{Pd}$. Interestingly, these metals are listed from the left to the right in the periodic table, suggesting that the influences of solute metals are related to their intrinsic bonding abilities, which can be evaluated using the O adsorption energies on these pure close-packed surfaces. If we plot the intrinsic bonding abilities of solute metals against the calculated adsorption energies on the one-atom substituted surfaces, several interesting features can be found (Figure 2): Firstly, for all the types of substitution positions, the calculated adsorption energies correlate linearly with the intrinsic bonding abilities of solute metals (Figures 2(a), (b), (c) and (d) for type I, type II, type III and type IV, respectively), suggesting that the O adsorption energies on the close-packed surfaces are good descriptors for the intrinsic bonding abilities. Secondly, for the substitution of the nearest neighbor atoms (type I), the intrinsic bonding abilities and calculated adsorption energies are positively correlated, while negative correlations are found for all the second nearest neighbor substitutions (type II, type III and type IV). Thirdly, for all the linear relations of different substitution positions (Figure 2), the slopes of these lines are quite different, indicating that for the same solute metal, different substitution positions have different inferences on the adsorption energies. The absolute values of the slopes are in the following order: type I > type II > type IV > type III. It is obvious that the substitution of type I possesses the most significant effect on the adsorption energy. This can be understood as follows: the atom at the position of type I bonds directly to the adsorbed O, leading to the great effect of this type of substitutions on the adsorption. However, the rest orders seem to be puzzling: These three types of positions are all the second nearest neighbor atoms, but the influences of these substitutions on the adsorption energies are highly different, namely the slope ratios of these substitutions in Figure 2, slope (type II): slope (type IV): slope (type III), being 3.1 : 1.7 : 1. More puzzlingly, we can see from Figure 1 that the distances between O and the positions of type IV are much longer than those of type III and thus the inference of substitution of type IV might be lower. However, our results show clearly that the substitution of type IV has almost twice effects on the adsorption

energy compared to that of type III. How can we rationalize these peculiar results? Can we find some simple and yet robust property to describe the contributions of different substitution sites?

To answer the questions above, we propose a bond-counting contribution factor (BCCF) for each type of substitutions, which is defined as follows: Taking the substitution of type I as an example, as shown in Figure 1(a), O bonds directly with three surface atoms, and thus each of the nearest neighbor atoms is counted as 1/3. Furthermore, the following can be seen from Figure 1(a): On one hand, due to the periodic boundary condition the substitution of type I also changes a second nearest neighbor atom to O. On the other hand, each of the rest two nearest neighbor Pt atoms is separately bonded with one solute metal in the nearby periodic unit cell (Figure 1(a)), suggesting that 1/9 (9 is the coordinate number of a surface Pt atom) of the neighbor atoms of adsorption sites is affected by the periodic neighbor substitution. Thus, the contribution of each second neighbor substitution is counted as $-1/3 \times 1/9$, where the negative sign accounts for the negative adsorption influence of the second neighbor substitution mentioned above (the reason for the negative influence can be found in SI). Therefore, the BCCF of type I is:

$$c(\text{type I}) = \frac{1}{3} - \frac{1}{3} \times \frac{1}{9} \times 2 = \frac{7}{27} \quad (2)$$

where 2 accounts for the two second nearest neighbor substitutions in type I due to the periodic boundary condition, and each substitution is only counted once to avoid double counting (Figure 1(a)). With the same approach, the contributions of the other substitution types are calculated as:

$$c(\text{type II}) = -\frac{1}{3} \times \frac{1}{9} \times 6 = -\frac{2}{9} \quad (3)$$

$$c(\text{type III}) = -\frac{1}{3} \times \frac{1}{9} \times 2 = -\frac{2}{27} \quad (4)$$

$$c(\text{type IV}) = -\frac{1}{3} \times \frac{1}{9} \times 3 = -\frac{3}{27} \quad (5)$$

Using these contribution factors, the unexpected results mentioned can be readily rationalized: The contribution ratios are calculated to be 3:1.5:1 for the substitutions of types II, IV and III, respectively, which are very closed to 3.1:1.7:1 from the slopes mentioned above, explaining that the contribution of type IV is higher than that of

type III. Using such a simple model, the contributions of different sites can be clearly determined with simple arithmetic calculations.

With these BCCFs, the relation between different types of substitutions can be easily obtained manually. However, the absolute effects of one-atom substitution on the adsorption energy are elusive in this definition. Namely, we need to define a generalized parameter to evaluate how much the adsorption energy will change when a metal with an intrinsic bonding ability of 1.0 eV substitutes a position with a contribution factor of 1. An example of calculating the generalized parameter can be found in SI. By averaging all the generalized parameters of the solute metals from the substitutions of type I, the generalized parameter was calculated to be 2.75. The significance of this parameter will be discussed later.

Having defined the concepts and obtained the understanding above, we are in the position to include the three terms together to explain all the adsorption energy results on the one-atom substituted alloy surfaces using a unified equation. The adsorption energy change on the one-atom substituted alloy surfaces with respect to that on Pt(111) is clearly related to the intrinsic bonding ability of the solute metal and the contribution factor of substitution positions. Thus, the O adsorption energies on all the one-atom substituted alloy surfaces can be predicted as:

$$E_{predicted} = g \times c \times a \quad (6)$$

where g is the generalized parameter, and c and a are the contribution factor and the intrinsic bonding ability of solute metal, respectively. In Figure 3(a), the actually calculated adsorption energies from DFT are plotted against the predicted adsorption energies, and an excellent correlation can be seen, suggesting that Equation 6 includes the most important terms affecting the O adsorption energy on the alloy surfaces. Because this equation contains two major terms: the intrinsic bonding ability of solute metal and the contribution factor, we name the equation as the bonding contribution equation.

In most real catalytic systems, the alloy surfaces contain more than one solute metals³⁹. How can we predict the adsorption energies on these alloys? In order to answer this question, we randomly generated 100 alloy surfaces based on Pt(111)-

$p(2\times 2)$ and calculated the O adsorption on these alloy surfaces: The typical percentage of solute metals in real Pt-based catalysts is usually $1/4^{13,14}$, and therefore only two or three of eight Pt atoms were replaced by solute metals. By analyzing the results, we found that in general, the different substitutions contribute separately to the overall adsorption energies, and thus we can rewrite the bonding contribution equation for the adsorption energies on the alloy surfaces with n solute metals as:

$$E_{ad} = \sum_{i=1}^n g \times c_i \times a_i \quad (7)$$

where c_i and a_i are the BCCF and the intrinsic bonding ability of solute metal i , respectively. The comparison between the calculated O adsorption energies and the predicted adsorption energies is shown in Figure 3(b). It is clear that our bonding contribution equation can explain the general trend of adsorption energies on the alloy surfaces, and give a good prediction of adsorption energies of oxygen.

In order to further test the generality of our bonding contribution equation, we investigated the O adsorption energies on alloy surfaces of Pt(111)- $p(3\times 3)$. In this system, the effect of periodical boundary condition on the adsorption is ignorable. Eight random substituted surfaces were generated and all the results are shown in Figure 3(c) and a good correlation can be seen, which demonstrates that our bonding contribution equation also works well for these systems. It was found that only the substitution of type I affects the adsorption energies considerably ranging from -1.65 eV to 0 (Figure 3(c)), while the adsorption energy changes due to a second nearest neighbor substitution are less than 0.5 eV.

All the investigations above are related to the O adsorption, and one may ask whether this bonding contribution equation is generally applicable for other adsorbates. To answer this question, we examined the CO adsorption energies on the one-atom substituted Pt alloy surfaces. This system was chosen due to the following reasons: Firstly, the adsorption of CO is very important in many reactions such as CO oxidation^{37,40}, dry reforming³⁸, CO₂ reduction⁴¹, and methane oxidation⁴². Secondly, CO adsorbs on the top site of Pt(111), which can also test the generality of the BCCF. Thirdly, the oxygen atoms are intermediates in the reactions in most cases, while CO is often involved as reactants or products and also bonds with the surface much weakly compared to oxygen atoms, suggesting that it may be an important class of

surface species to be tested. The BCCF for all the types of substitution atoms are 1, 2/9, 1/9 and 1/10 for type I, type II, type III and type IV, respectively, according to our model mentioned above (see SI for more details). With these contribution factors and the intrinsic bonding abilities of CO adsorption calculated, we found that the CO adsorption energies can also be predicted using Equation 6 (Figure 3(d)) with a different generalized parameter comparing to those of oxygen mentioned above. Therefore, different adsorbates can be characterised by their corresponding generalized parameters.

Finally, it is worth mentioning the significance of the bonding contribution equation: Firstly, with this equation, the adsorption energies of alloy surfaces can be obtained from a few DFT calculation results with reasonable accuracy. For example, For the Pt(111)-*p*(2×2) alloy system with 4 types of solute metals, there are 390625 possibilities, which requires 390625 DFT calculations for slabs and adsorption states separately to obtain the adsorption properties (781250 DFT calculations in total). Using our bonding contribution equation, only 8 DFT calculations for intrinsic bonding abilities (4 for slabs and 4 for adsorption states) and 8 calculations for generalized parameters are needed to predict the adsorption properties of these alloy systems (16 calculations in total). Secondly, as mentioned in the introduction, the adsorption energy is related to the catalytic bonding of catalyst. Therefore, using this equation, the alloy surfaces with desiring catalytic activities can be inversely designed. Thirdly, there are only three terms involved in this equation. As discussed above, these three terms are chemically meaningful: The generalized parameter is system-dependent and illustrates the sensitivity of adsorption energy change due to the substitutions. The intrinsic bonding ability is used to evaluate the effects of different solute metals, while the contribution factor shows the effects of different substitution positions. Therefore, this equation offers a quantitative representation of adsorption energies on alloy surfaces, which includes not only the first neighbour atoms but also second neighbours, greatly extending the theories in the literature⁴³.

4. Conclusions

In summary, in this work we systematically investigated the adsorption energies of O and CO on many Pt-based alloys. The important terms in chemisorption which might appear intangible were found to be separable and the total effect of multiply substitutions can be treated as a summation of each contribution in the system. We proposed the bonding contribution equation to predict the adsorption energies of alloy surfaces, which is not only a huge step towards the understanding of adsorption on surfaces in general, but also make it possible to inversely design alloy catalysts.

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Figures and tables

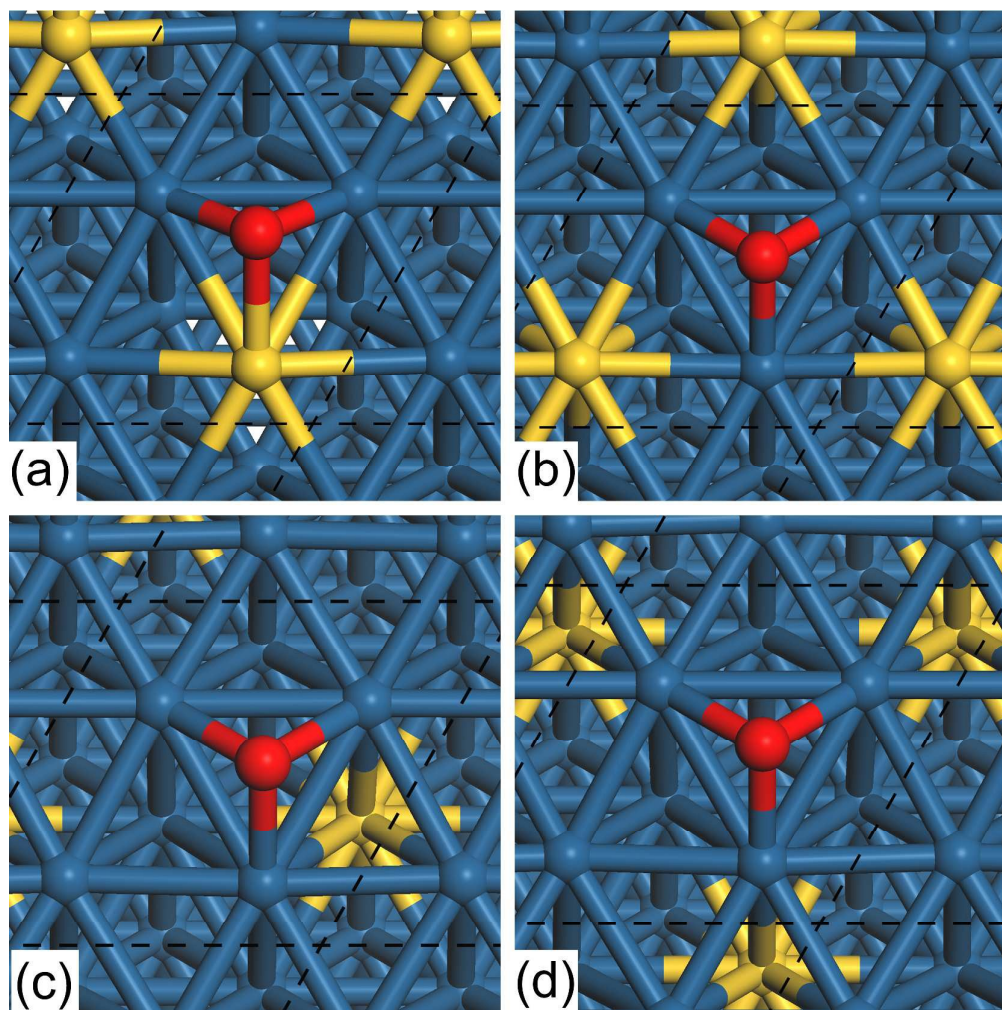


Figure 1. Four different types of substitution positions on p(2x2) Pt(111) surfaces, namely (a) type I, (b) type II, (c) type III and (d) type IV substitution positions. The atom at the substitution position is highlighted in yellow, while the Pt and O atoms are in blue and red, respectively.

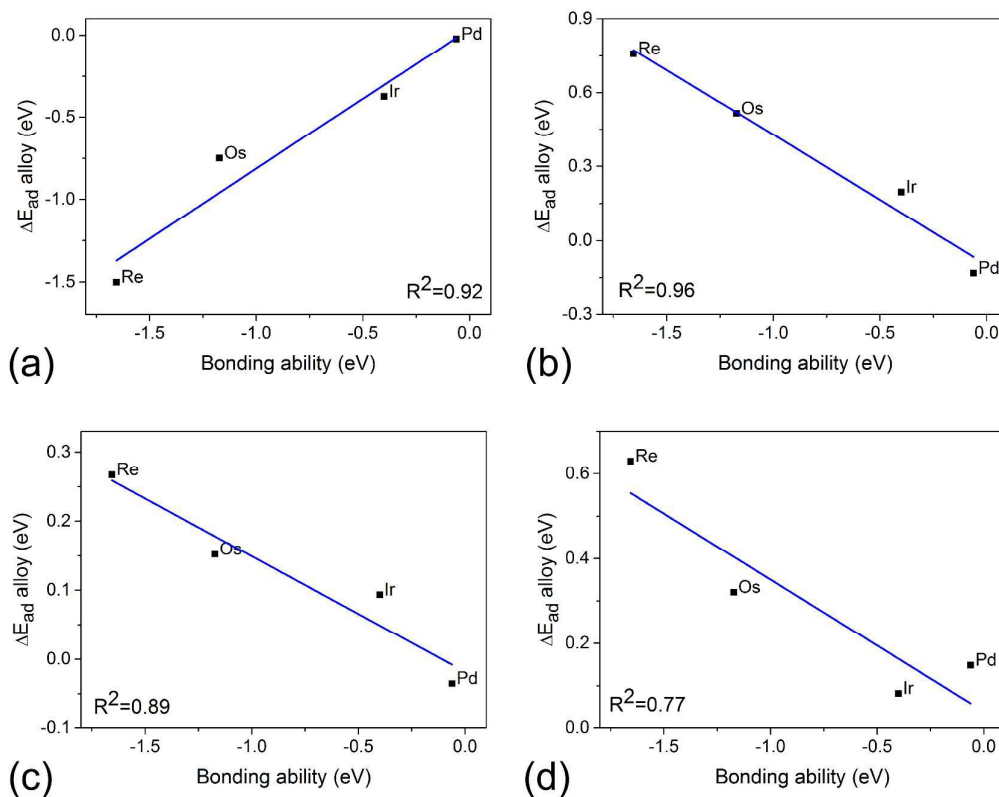


Figure 2. The relations between the bonding abilities of substitution metals and the calculated adsorption energies of the oxygen atom ($\Delta E_{ad\ alloy}$), for (a) type I, (b) type II, (c) type III, and (d) type IV substitutions.

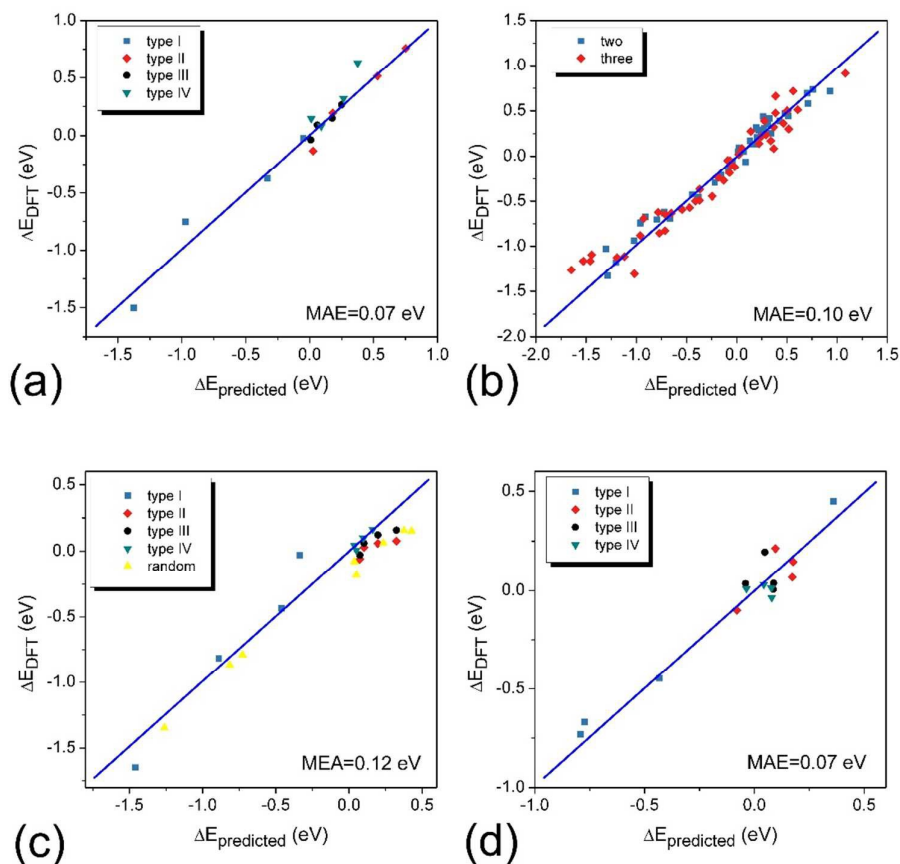


Figure 3. The comparisons between predicted adsorption energies from the bonding contribution equation and the calculated adsorption energies of (a) the oxygen atom on alloys of Pt(111) p(2×2) substituted one atom, (b) the oxygen atom on the random generated alloys of Pt(111) p(2×2) substituted two or three atoms, (c) the oxygen atom on alloys of Pt(111) p(3×3) substituted one atom, (d) CO on alloys of Pt(111) p(2×2) substituted one atom.

Table 1. The adsorption energies of oxygen atom on p(2×2) Pt(111) alloy surfaces with one solute metal (Ir, Os, Pd and Re) substituting different positions (type I, type II, type III and type IV). The adsorption energies of oxygen atom on pure close-packed surfaces of all the solute metals are also listed (ΔE_{adslab}). All the energies are in eV, and were calculated with respect to the adsorption energy of oxygen atom on Pt(111).

	type I	type II	type III	type IV	ΔE_{adslab}
Ir	-0.37	0.20	0.09	0.08	-0.40
Os	-0.75	0.51	0.15	0.32	-1.17
Pd	-0.02	-0.13	-0.04	0.15	-0.06
Re	-1.50	0.76	0.27	0.63	-1.66