Supporting Information

Achieving Rational Design of Alloy Catalysts Using a Descriptor Based on the Quantitative Structureenergy Equation

Yunxuan Ding,^a Yarong Xu,^{a,b} Yu Mao, ^a Ziyun Wang ^a and P. Hu*^a

a. School of Chemistry and Chemical Engineering, The Queen's University of Belfast, Belfast, BT9 5AG, UK. b. Rasearch Institute of Ummai Patroching Chemical Company, China

b. Research Institute of Urumqi Petrochina Chemical Company, China Email: p.hu@qub.ac.uk

S1. Computational Methods

All the DFT calculations in the work were carried out with a periodic slab model using the Vienna *ab initio* simulation program (VASP)^{1, 2}. The projector-augmented wave (PAW) method^{2, 3} was utilized to describe the electron–ion interactions, and the cut-off energy of plane-wave basis expansion was set to be 450 eV. For the exchange and correlation functional, the generalized gradient approximation (GGA) was used with Perdew–Burke–Ernzerhof (PBE)⁴. The surfaces were modeled by using a periodic slab consisting of 4-layers of metal atoms with the 2 lower layers fixed and the 2 upper layers relaxed. A p (2 × 2) supercell was chosen with 4 ×4 ×1 Monkhorst–Pack *k*-point mesh sampling for Brillouin-zone integration. A ~12 Å vacuum layer was placed on all the surfaces. In the spin-polarized calculations, the free molecules of O₂ and NO were placed in a (10 × 10 × 10) Å³ cubic box to minimize the interaction of neighboring molecules. The optimized structures were reached when the force on the relaxed atoms became less than 0.05 eV/Å. HSE06 was also used to calculate the reaction barrier of NO oxidation on Pt(111) as a comparison (see S4).

In this work, the relative adsorption energies of an adsorbate (ΔE_{ad}) are calculated with respect to the adsorption energy of this adsorbate on the pure metal close-packed surface ($E_{ad-base}$), as follows:

$$\Delta E_{ad} = E_{adsorbate+surface} - E_{adsorbate} - E_{surface} - E_{ad-base}$$
(S1)

The transition states (TSs) were located with a constrained minimization technique⁵⁻⁷. In order to calculate the free energies of the surface species, zero-point-energy (ZPE), thermal energy and entropy derived from partition function were introduced to obtain the corrections^{8, 9}. As for gaseous species, the thermodynamic corrections were calculated using the Gaussian 03 software package with the ideal gas approximation. Taking the NO oxidation as an example, the temperature of NO oxidation was set to be 600 K; 0.10 bar, 3×10^{-4} bar and 1.7×10^{-4} bar were used for the partial pressures of O₂, NO and NO₂, respectively¹⁰. The high temperature resulted in a low coverage on the surface; thus, the influence of the coverage can be neglected. To simplify the procedure, the coverage effect was ignored. In the micro-kinetic modeling, three elementary steps (NO adsorption, O₂ dissociation and NO oxidation) were considered:

$$NO(g) + * \leftrightarrow NO^{2}$$

$$O_2(g) + 2^* \leftrightarrow 2O^*$$

$$NO^* + O^* \iff NO_2(g) + 2^*$$

All the thermodynamic corrections were taken into account and full micro-kinetic modeling^{11, 12} was carried out to calculate the turn-over frequency (TOF) and generate the volcano curve surface. The micro-kinetics modeling was performed using the code developed by our group¹³.

S2. Derivation for the Quantitative Structure-Energy Equation

The Bonding Contribution Equation

On the purpose of easier comparison, the bonding contribution equation is illustrated below with the same symbol definitions in this work:

$$\Delta E_{ad} = \sum_{i=1}^{n} g \times a_i \times \Delta E_M \tag{S2}$$

where g is the generalized parameter, a_i is the bond-counting contribution factor of different substitution type *i* and ΔE_M is the difference between the adsorption energy of the pure metal M and the adsorption energy of the pure base metal¹⁴.

Geometric Effect

After systematically study the adsorbate on the alloy surface, there are four possible substitution types (Fig. S1). To quantify the geometric effect of the base metal replaced by one solute atom, we take the lattice constant for the original bulk to be a variable with the surface structure relaxed to be optimized. Using the calculated lattice constants (deg) for bulk Pt(111), Rh(111) and Ni(111) as the equilibrium lattice constants, which are 2.805 Å, 2.704 Å and 2.487 Å, respectively, the bond distance (d) between the base atom and solute atom can be compared with deg as shown in Table S1: The maximum value of the relative lattice constant $((d-d_{eq})/d_{eq})$ is around 1.5%, except Ni-Ag alloy, which is nearly 3%. However, the calculated surface segregation energy for Ag atom at the close-packed Ni(111) surface was -0.80 eV/atom, which displayed a very strong segregation, indicating that the prediction for Ni-Ag alloy components was completely invalidated¹⁵. Thus, type I for Ag solute is removed from Ni-base alloy. All the lattice constants vary from -1.5% to 1.5% in this work. As can be seen from Table S1, most of the transition metal solutes substituted in the pure bases only have a small effect on the lattice constants. However, when noble metals (Ag and Au) are added into the system, this geometric effect is significant.

To quantitatively determine the influence of the lattice constants on the adsorption energies, the relative lattice constants of the pure metal bulks are changed from -1.5% to 1.5%, and the chemisorption energies were calculated as a function of the relative lattice constants. As shown in Fig. S2, the adsorption energy of each transition metal as a function of the relative lattice constant has its own slope. The adsorption energies become weak when the lattice constants are compressed; while the lattice constants are stretched, the interaction between adsorbate and surface is stronger, leading to the negative slopes.



Fig. S1 Four possible substitution types of the one solute Pt-based alloys. In the alloy structures of (a) type I, (b) type II, (c) type III, and (d) type IV, the O, Pt and Ag are in red, dark blue and silver, respectively.

Solute	d Pt-M	$(d-d_{eq})/d_{eq}\%$	d _{Rh-M}	$(d-d_{eq})/d_{eq}\%$	d Ni-M	$(d-d_{eq})/d_{eq}\%$
Со	2.809	0.14	2.705	0.04	2.487	0.00
Ni	2.808	0.11	2.705	0.04	2.487	0.00
Cu	2.805	0.00	2.705	0.04	2.490	0.12
Ru	2.809	0.14	2.705	0.04	2.488	0.04
Rh	2.807	0.07	2.704	0.00	2.488	0.04
Pd	2.807	0.07	2.707	0.11	2.496	0.36
Ag	2.830	0.89	2.745	1.52	2.563	3.06
Re	2.814	0.32	2.706	0.07	2.490	0.12
Os	2.813	0.29	2.706	0.07	2.488	0.04
Ir	2.810	0.18	2.705	0.04	2.487	0.00
Pt	2.805	0.00	2.705	0.04	2.488	0.04
Au	2.817	0.43	2.720	0.59	2.522	1.41

Table S1 The lattice constants for different alloy surfaces (Pt, Rh and Ni) substituted with one solute metal (Co, Ni, Cu, Ru, Rh, Pd, Ag, Re, Os, Ir, Pt and Au) are described by the bond distance between the base metal atom and solute atom (d_{Base-M}). The relative lattice constants are defined as the percentage of the difference between the alloy bond distance and the pure base bond distance.



Fig. S2 Graphs to show how the relative lattice constants affect the adsorption energies of an oxygen atom adsorbed on Co(0001), Ni(111), Cu(111), Ru(0001), Rh(111), Pd(111), Ag(111), Re(0001), Os(0001), Ir(111), Pt(111) and Au(111).

The geometric effect should be affected by the base metal and the solute metal, which indicates that the lattice constant of the base and solute metals should both involve in the equation. To quantify the geometric effect, the averaged bond distance of the pure solute and base metals is used. By comparing the averaged bond distance and the bond

distance of the pure solute metal, we can easily obtain the difference between the adsorption energy of the alloy and the pure metal from Fig. S2, which can be calculated by the equation below.

$$E_{Base-M}^{geo} = \lambda_M \times \left[\left(d_M + d_{Base} \right) / 2 - d_M \right] / d_M$$
(S3)

where λ_M is the gradient of the relative lattice constant affecting the adsorption energy, while d_M and d_{Base} are the bond distances of the solute metal and the base metal, respectively.

Electronic Effect

Not only has the geometry of the surface changed, but also the electronic environment of the slab has changed by other metals introduced. Thomson and co-workers¹⁶ found that the binding ability between the adsorbate and the alloy will increased, when the proportion of Pt alloys contained more Au (PtAu₂ > Pt₂Au > Pt₃ > Au₃). Au is inert for adsorbates comparing with Pt, and thus the binding affinity of Pt alloy can be intrinsically affected by the Au solute. This indicates that the solute metal can influence the intrinsic bonding energy of the base metal. The difference between the bonding energy before and after adding the solute metal should not be ignored. The bonding energy is obtained from Eq. S4:

$$E_{bond} = E_M - E_{M-vacancy} - E_{M-atom}$$
(S4)

where E_M , $E_{M-vacancy}$ and E_{M-atom} are the optimization energies of the system, the system with an atom removed and the atom, respectively. The system with an atom removed is illustrated in Fig. S3.



Fig. S3 Taking Ag as an example, the total energy is from (a) Ag(111) p (2 × 2) surface, while the vacancy energy is from (b) the surface with one Ag atom removed. Silver and yellow atoms refer to Ag and the removed atom, respectively.

The difference of the bonding energy between the base metal and the solute metal can be calculated by Eq. S5, which is named as the electronic effect.

$$\Delta E_{Base-M}^{ele} = (E_{Base} - E_{Base-vacancy} - \frac{E_{Base-bulk}}{n}) - (E_M - E_{M-vacancy} - \frac{E_{M-bulk}}{n})$$
(S5)

where E_{Base} is the total energy for the base metal surface, $E_{Base-vacancy}$ and $E_{M-vacancy}$ are the total energies with one atom removed from the pure base metal and pure solute metal, respectively. $\frac{E_{Base-bulk}}{n}$ and $\frac{E_{M-bulk}}{n}$ stand for the energies of the base metal and the solute metal per atom, respectively¹⁷. E_{bulk} is the energy of each unit-cell.

Quantitative Structure-Energy Equation

Combining the bonding, geometric and electronic effects, we can finally obtain the quantitative structure-energy equation (Eq. 1 in the main text). a_i is the coefficient of the bonding effect of type i, which are 7/27, -6/27, -2/27 and -3/27 for type I, II, III and IV, respectively¹⁴. ΔE_M , ΔE_{Base-M}^{ele} and E_{Base-M}^{geo} are the intrinsic activity of the pure solute metal, the difference of the bonding energy between the pure base metal and the solute metal, and the geometric effect caused by introducing the solute metals. The value of **b** is fitted to be 1.3 for the three base metals. The adsorption energies of all one atom substitution alloys are used to fit c_i coefficients, which are 0, -4.5, 1 and 0 for type I, II, III and IV, respectively. The bonding effect for type I can be substantial for the adsorbate directly binding with the solute metal; while for type III and type IV, the contributions of the geometric effect are small for the solute metal in the subsurface. This is due to the neighboring base metal atoms forming a highly stable shell-like structure around the solute atom. For NO molecule, the experimental work¹⁸ showed that NO adsorbed on Pt and Rh metals at the top site. Therefore, we placed NO at the

top site¹⁹. Thus, a_i for all types I, II, III and IV are 1, -2/9, -1/9, 1/10, respectively⁴.

The carbon atom adsorbing at the hcp site^{20, 21} has the same a_i as the oxygen. The electronic effect is mainly an intrinsic property of the alloys; therefore, the values of the electronic effect are kept constant for different adsorbates for simplicity. The relative adsorption energies of C adsorbed on Pt-based alloys with one solute metal (Ni, Cu, Ru, Rh, Pd, Ag, Os, Ir, Pt and Au) have a good correlation to the DFT calculated results with R² of 0.82 (Fig. S4).



Fig. S4 Comparisons between the predicted relative adsorption energies of C on the Pt-based alloys from the quantitative structure-energy equation and those from DFT calculations.

S2. Structures and Data for the Designed Alloys



Fig. S5 Top and side (insert) views of (a) NO and (b) O adsorbed on the p (2 × 2) Pt(111) surface. Top and side (insert) views of the transition states of (c) NO oxidation and (d) O₂ dissociation. Pt atom, oxygen atom and nitrogen atom are in dark blue, red and blue, respectively. First and second layer of Pt atoms are numbered from 1 to 4 and 5 to 8.



Fig. S6 Partial structures of the alloys in Table S2. The metals are marked inside.

Table S2 The adsorption energies of O ($E_{ad}(O)$) and NO ($E_{ad}(NO)$), the reaction barriers of O₂ dissociation ($E_a(O-O)$) and NO ($E_a(O-NO)$) oxidation, and TOF from each alloy. The atoms on the first and second layers are listed, and structures are shown in Fig. S5. The units of energies and TOF are eV and s⁻¹, respectively. The activities are calculated under typical experimental conditions (T=600 K, $P_{O2}=0.10$ bar, $P_{NO}=3\times10^{-4}$ bar and $P_{NO2}=1.7\times10^{-4}$ bar).

Structure				$\mathbf{E}(0,0)$	\mathbf{E} (O NO)	TOF
First layer	Second layer	$- \mathbf{E}_{ad}(\mathbf{O})$	Ead (INO)	$E_a(\mathbf{U-U})$	$E_a(0-NO)$	IOF
PtPtPtAg	PtPtIrIr	-1.33	-1.42	0.59	0.71	$9.00 imes 10^2$
PtCuPtPt	PtNiCuPt	-1.12	-1.30	1.15	0.69	$2.05 imes 10^2$
PtPtPtAg	PtPtRhCo	-1.29	-1.24	0.60	0.63	3.14 imes 10
PtPtPtAg	PtPtRhIr	-1.31	-1.38	0.57	0.77	1.57 imes 10
CuPtPtPt	PtNiCuPt	-1.15	-1.31	1.21	0.99	1.32×10
PtPtNiPt	RePtRhPt	-1.51	-1.53	0.53	0.91	6.92
CuNiNiOs	NiNiNiCo	-1.34	-1.28	1.09	0.79	1.31
CuNiNiOs	NiNiNiRu	-1.36	-1.29	0.62	0.86	$4.86\times10^{\text{-}2}$

S3. Rationale of the Volcano Surface

In this work, O_2 adsorption and O_2 dissociation were combined, as well as NO oxidation and NO₂ desorption. Thus, the rate equations for each elementary step were illustrated below:

$$r_1 = k_1 P_{NO} \theta_* - k_{-1} \theta_{NO} \tag{S6}$$

$$r_2 = k_2 P_{O_2} \theta_*^2 - k_{-2} \theta_0^2 \tag{S7}$$

$$r_{3} = k_{3}\theta_{NO}\theta_{O} - k_{-3}P_{NO_{2}}\theta_{*}^{2}$$
(S8)

where k is the rate constant, P is the partial pressure and θ is the coverage.



Fig. S7 BEP relations (a) between the adsorption energies of O and the reaction barriers of O_2 dissociation, and (b) between the sum of adsorption energies of NO and O and the reaction barriers of NO oxidation.

S4. Comparison between PBE and HSE06 for NO Oxidation

Table S3 Comparison of the NO oxidation barrier on Pt(111) between PBE and HSE functionals.

Functional	E _a (O-NO)/eV		
PBE	0.55		
HSE06	0.51		

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