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Examination of the Key Issues in Microkinetics: CO Oxidation on Rh(111)

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ABSTRACT

Microkinetic modelling plays the key role to bridge first principles calculations at the atomic level to experimental data at macroscopic scales. Currently, some significant differences between the microkinetic modelling results and experimental ones still exist. In this work, CO oxidation on Rh(111) is selected as a model system for its simplicity as well as its importance, and an in-depth study of microkinetic modelling on the reaction is performed. A self-consistent microkinetic modelling iterating with respect to coverages is developed. It is found that a good accuracy of the microkinetic modelling using density functional theory energies can be obtained if adsorbate-adsorbate interactions including the coverage effect on the transition states are rigorously calculated. The calculated kinetic results including the turnover frequency (TOF), which are very close to experimental ones, can be achieved if corrections of the over-estimation of chemisorption energies of density functional theory and van der Waals forces are also included.

1. Introduction

Catalytic reactions have always been a focus in chemistry and in particular, catalytic reactions on gas-solid interfaces [1,2] have been extensively investigated both experimentally [3,4] and theoretically [5-8]: Experimentally, the techniques have been considerably improved in the last 50 years or so [3,9]. Theoretically, the microkinetic modeling [10,11] has been a unique bridge between the first principles calculations, such as density functional theory (DFT) calculations to obtain energetics of catalytic reactions at the atomic level [12,13], and the real experimental measurements, thus becoming one of the most important methods for simulating activity and selectivity for catalytic reactions. However, it was found that there are considerable differences between the calculated kinetic results and the experimental ones [14-16].

It is well known that the coverage is one of the most basic properties of surface reactions. The effect of adsorbate-adsorbate interactions was considered in previous

work [5,6,17-19] and it was found that the neglect of these interactions results in failures of microkinetic calculations; the kinetical calculations were quantitatively far away from experimental results or even showed incorrect trends for catalytic reactions if the adsorbate-adsorbate interactions were ignored [20,21].

In almost all the studies on the coverage effect, the self-interactions between adsorbates, i.e. the interactions between the same kind of species, were taken into account, while the interactions between different species including the interactions between different adsorbates and the coverage effect on the transition states, the so-called cross-interactions between adsorbates, were approximated. Several studies showed that chemisorption energies of surface species (more strictly speaking, the averaged chemisorption energies) remain almost constant below a critical coverage, typically 0.33 ML on (111) surfaces, and decreases with the increasing coverage once the surfaces are beyond the critical coverage [15,16]. In the microkinetic modelling, the differential chemisorption energies rather than the averaged chemisorption energies should be used. In the literature, for the self-interactions between adsorbates, the differential chemisorption energies were considered to be constant below the critical coverage and the changes of differential chemisorption energies of a specific adsorbate above the critical coverages were approximated by a linear function of the coverage of the specific species [15]. The slope of the linear curve was a measure of the strength of the coverage effect. For the cross-interactions, the energy correction was usually

estimated from the self-interactions. In particular, the coverage-dependent transition states were roughly estimated using the Brønsted-Evans-Polanyi (BEP) relations [22-24], where the BEP relations were obtained at a low coverage. It is expected, therefore, that the error using these approximations may not be negligible, which may lead to the theoretical results being incomparable with the experiment data.

In addition, the effect of van der Waals forces may be of importance, which was usually omitted in the kinetic calculations. In particular, when the coverage is high, often leading to the differential chemisorption energies of adsorbates to be close to zero, the effect of van der Waals forces between adsorbates is expected to be significant and thus may not be ignored. The vibrational motion of adsorbate may also be quite different at low coverage from the surfaces with high coverages. The thermodynamic corrections of adsorbates, which are used to convert the chemisorption energy in terms of the total energy to the free energy [25,26], should be primarily dependent on the vibrational motions of adsorbates and may be coverage-dependent. Furthermore, as a deficiency of DFT calculations, stronger chemisorption energies were often obtained comparing with the experimental data, especially for CO on metal surfaces [27]. This is also expected to directly influence the rate of desorption and adsorption. How these corrections impact quantitatively the kinetic results is not known.

In this work, we choose CO oxidation on Rh(111) as a model system for several reasons: Firstly, it is a model reaction; as one of the most extensively studied reactions both experimentally and theoretically [28,29], there are a substantial amount of data available for comparison. The kinetics of CO oxidation on Rh has been studied at low pressure using temperature programmed desorption (TPD), and the activity of CO oxidation on Rh(111) was reported to have the turnover frequency (TOF) of around 10^2 - 10^3 s⁻¹ at 600 K [4,30,31]. The pressures in the gas phase were also tested [3,32], which were observed to affect the activity insignificantly. Secondly, there are still some unsolved issues in the system. Compared to the experimental work, different activity was observed from theoretical work: the TOF was around 10^{-1} s⁻¹ using micro-kinetic modeling without adsorbate-adsorbate interactions and around 10^5 s⁻¹ with a simple correction of adsorbate-adsorbate interactions [33]. These results indicated that the inclusion of adsorbate-adsorbate interactions does considerably affect the activity of catalytic reactions. However, the interactions between adsorbates have not yet been thoroughly examined and some corrections mentioned above, such as the effect of van der Waals forces, have not been investigated in detail.

It is clear, therefore, that there are still issues that need to be addressed. More specifically, the following questions remain to be answered: What is the key issue that needs to be considered in order to improve the accuracy? Can the calculated activity of CO oxidation based on DFT energetics be corrected to be comparable to the

experimental one? In this work, we are addressing these issues/questions by calculating CO oxidation on Rh(111) using the DFT calculations and microkinetic modelling.

2. Computational Method

All DFT calculations were carried out using the Perdew–Burke–Ernzerhof (PBE) functional [34,35] through the Vienna ab initio simulation package (VASP) [36,37]. The projector-augmented wave (PAW) method was performed with a cut-off energy of 400 eV. Thermodynamic corrections of gas phase molecules were conducted using Gaussian software. The van der Waals forces were considered in some of the calculations in this work (see discussions below) using the DFT-D3 [38,39] method in the VASP code. A Monkhorst-Pack k-point 6×6×6 was used for optimizing the Rh unit cell and 3×3×1 for the surface optimization calculations with a p(3×3) supercell including 15 Å vacuum layer and 5-layer metal atoms. The convergence of force was set to be 0.01 eV·Å⁻¹. The transition states were located using the constrained optimizations [40] and all the transition states were checked by vibrational frequency calculations.

Table 1 Elementary steps and the corresponding rate equations in our model-kinetic modelling for CO oxidation on Rh(111), where * represents a free site on the surface.

Step	Elementary Step	Rate Equations
1	$\text{CO} + * \rightarrow \text{CO}^*$	$r_1 = k_1 P_{\text{CO}} \theta_* - k_{-1} \theta_{\text{CO}}$

A good model in microkinetic modelling should contain many kinetic details, considering all the elementary reactions, different active sites, adsorption energies and reaction barriers. In this work, three elementary reactions listed in **Table 1** were included for CO oxidation on Rh(111). Both self and cross adsorbate-adsorbate interactions were calculated for both the adsorbates and transition states. The energy of each elementary step at different coverages was calculated with a different number of adsorbates in p(3×3) supercell. Two adsorbates, namely CO* and O*, were studied with both self and cross-interactions (CO*/CO_{sur}, CO*/O_{sur}, O*/CO_{sur}, O*/O_{sur}, where A*/B_{sur} describes adsorbed A on a surface with adsorbed B at a certain coverage of B). The transition state energies were also calculated under different coverages (CO-O*/CO_{sur}, CO-O*/O_{sur}, O-O*/CO_{sur}, O-O*/O_{sur}) (for the structures see the **Supporting Information**).

The interactions between adsorbates are divided into two classes as the self-interactions and the cross-interactions, which were approximately described using a two-line model in the literature [15]. In this work, we developed a modified two-line model, in which

two linear lines to describe the low and high coverages, respectively (see more details of our two-line model in the **Supporting Information**). The low coverage range is defined when all the first neighbor sites for each adsorbate are free (see the **Supporting Information**, O^*/O_{sur} 0.11 - 0.33 ML). In the high coverage region, the effect of adsorbate-adsorbate interactions shows a significant increase with more adsorbed species on the surface. In this case, at least one first neighbor site will be occupied when the coverage is larger than 0.33 ML (see, for example, O^*/O_{sur} 0.44 - 0.99 ML in the **Supporting Information**,). Thus, the critical point separating the low coverages from the high coverages is found to be 1/3 ML. The chemisorption energy of a surface species at 1/9 ML was set to be a reference point as the average chemisorption energy is the same as the differential chemisorption energy at such low coverage. The influence of adsorbate-adsorbate interactions at different coverages can be considered as the difference between the differential energy at the specific coverage and the reference differential energy (E_{i0} in Equation (1)). Therefore, we can write as follows:

$$E_i(\theta) = E_{i0} + E_{\text{correction}}(\theta) \quad (1)$$

$$E_{\text{correction}}(\theta) = \sum_j (a_{i/j} \times \theta + b_{i/j}) \times \frac{\theta_i}{\theta} \quad (2)$$

where θ , θ_i , i , j , a and b represent the total coverage, the coverage of species i , adsorbate A, adsorbate B, and the two parameters (slopes and intercept) of the linear lines, respectively. It should be noted that the linear model applied in this work provides only one kind of reasonable description of the effect from adsorbate-adsorbate interactions.

For example, attractive interactions of adsorbate-adsorbate have been found in previous studies [41-43], where stronger adsorption energies were obtained with the increase of surface coverage. Thus, we suggest to calculate adsorbate-adsorbate interactions in detail, from which a good model to describe the interactions can be obtained and then used in microkinetic simulations.

Figure 1 (a) Flow chart of the coverage-dependent microkinetic modeling, where X and τ represent the convergence and mixing weight of coverages, respectively. (b) Tests of the accuracy of reaction rates described by the relationship between the TOF and the convergence of coverages. The convergence of coverages (X) refers to the coverage difference between INPUT and OUTPUT coverages in one iteration of microkinetic calculations. (c) The mixing weight tests with the iteration steps reaching different convergence of coverages in the iterations of microkinetic modeling.

The self-consistent kinetic calculations are illustrated in the scheme in Figure 1: An iterative approach with respect to the coverage is used and the convergence is controlled by the difference between the input coverage and output one (see **Figure 1(b)**). The converged TOF is achieved when the convergence of coverages reaches the level that is smaller enough ($-\log(X) < 3$). The mixing weight τ is applied to select a suitable input coverage in each iteration, where a significant decrease of iteration steps can be obtained if τ is appropriate (see **Figure 1(c)**). In addition, random initial settings of surface coverages before the iterations were tested, giving rise to the same converged results.

3. Results and Discussion

3.1 Kinetic Calculations without the Coverage Effect

The reaction kinetics of CO oxidation on Rh(111) was first investigated using traditional microkinetic approach based on the energies from DFT calculations at a low coverage (1/9ML). The chemisorption energies of surface species and the barriers of elementary steps were calculated on a p(3×3) supercell (**Table 2**). The thermodynamic corrections were included to obtain the free energy changes for CO oxidation at a temperature of 600 K and the pressures of 0.01 bar (8 Torr) for both CO and O₂, and

the kinetic results were obtained, which can be compared with the experimental data (see **Table 2**).

Comparing the calculated results and the experimental ones, interestingly several differences can be found. Firstly, the TOF of the reaction was found to be around $5.6 \times 10^2 \text{ s}^{-1}$ ($\log(\text{TOF}) = 2.75$) in the experiment [3] whereas it was calculated to be $3.6 \times 10^{-1} \text{ s}^{-1}$ ($\log(\text{TOF}) = -0.40$) from the microkinetic modelling with the DFT energetics: A large discrepancy between the experimental work and the calculated TOF without the consideration of adsorbate-adsorbate interactions can be seen. The under-estimation of the TOF was mainly caused by the over-estimation of adsorption energies, which were calculated at the low coverage of 1/9 ML, leading to a higher surface coverage at the steady state where the surface reactions are blocked by the strongly adsorbed species. Secondly, the dissociation of O_2 was experimentally found³ to be the rate-determining step for CO oxidation on Rh(111); however, the microkinetic modelling using the DFT energetics without the adsorbate-adsorbate interactions shows that the high free energy barrier of CO-O coupling ($\text{CO} + \text{O} \rightarrow \text{CO}_2$) appears to be the rate-determining step.

Table 2 Energies from DFT calculations with thermodynamic corrections at the coverage of 1/9 ML and kinetic results from micro-kinetic modelling for CO oxidation on Rh(111).

Elementary Steps	Energies		Kinetic Results
	Forward Free Energy Barrier (eV)	Reaction Free Energy (eV)	Surface Coverage

$\text{CO} + * \rightarrow \text{CO}^*$	0.10*	-0.74	CO	0.01
$\text{O}_2 + 2* \rightarrow 2\text{O}^*$	-0.06	-2.74	O	0.99
$\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2 + 2*$	1.38	-0.53	TOF (s ⁻¹)**	3.57×10^{-1}

* Adsorption barrier for CO on Rh(111) was considered as a constant to be 0.1 eV, which was calculated using the umbrella sampling in our previous work [44].

** The activity of CO oxidation on Rh(111) is presented by the TOF of the CO consumption rate.

3.2 Cross-interactions between Adsorbates

It was mentioned in the introduction that some coverage-dependent kinetic calculations were carried out in previous work [15,16], in which only the self-interactions of adsorbates were calculated rigorously, and both the cross-interactions of different adsorbates and the cross-interactions between the adsorbates and the transition states were treated using some approximations. However, the cross-interactions may be pivotal to the accuracy of kinetic calculations.

Figure 2 Effects from adsorbate-adsorbate interactions for adsorbed O and CO with different surface coverages including both self-interactions and cross-interactions. The points in the figure show the surface coverages at the steady state from self-consistent kinetic calculations for CO oxidation on Rh(111) considering only self-interactions (geometric mean method for the cross-interactions [13]) and both rigorously calculated self-/cross-interactions.

In this work, more rigorously calculated adsorption energies with the adsorbate-adsorbate interactions (both the self- and cross-interactions) were obtained with different coverages of adsorbed CO and O (see **Figure 2**). In the previous researches [15], the differential adsorption energies that were obtained from the averaged chemisorption energies were considered to be constant when the total coverages were below 0.33 ML on the (111) surfaces. However, the differences between our more rigorously calculated differential chemisorption energies and those obtained from the approximated method for O and CO at the coverages below 0.33 ML are found to reach 0.6 eV and 0.4 eV, respectively. This will obviously affect the kinetics in the system considerably.

As mentioned before, beyond 0.33 ML on the (111) surfaces, the chemisorption energies decrease significantly with the increase of surface coverages. To take this into account, the linear approximations were used (introduced in the section of computational method) to determine the energy changes as a function of high surface coverages [15,16]. In this work, for the surface coverages above 0.33 ML, the cross-

interactions between different adsorbates were calculated using Equation 2, and the slopes were obtained to be 2.11 and 2.45 for $\text{CO}^*/\text{O}_{\text{sur}}$ and $\text{O}^*/\text{CO}_{\text{sur}}$, respectively. Interestingly, if the geometric mean approximation in the literature was used, the slopes of 2.22 were obtained for both $\text{CO}^*/\text{O}_{\text{sur}}$ and $\text{O}^*/\text{CO}_{\text{sur}}$; a difference of 0.15 eV for the energy correction between the more rigorously calculated one and the geometric mean method can be seen, which may not be negligible in the reaction kinetics.

The self-consistent microkinetic modelling was performed to calculate the TOF based on both DFT calculated cross-interactions and those obtained from the method in the literature, which give rise to $1.2 \times 10^4 \text{ s}^{-1}$ ($\log(\text{TOF}) = 4.09$) and $2.2 \times 10^5 \text{ s}^{-1}$ ($\log(\text{TOF}) = 5.34$), respectively. Obviously, a significant difference exists from these two approaches. Although similar total surface coverages (0.42 ML) were obtained from the two approaches, different specific adsorbate coverages were discovered; the surface was almost purely occupied by adsorbed O at the steady state if the geometric mean approximation was used for the cross-interactions among adsorbates, while 0.33 ML and 0.09 ML were calculated for adsorbed CO and O, respectively, if the cross-interactions were more rigorously taken into account (see **Figure 2**). It is clear that a sizable difference can be seen from the results.

3.3 Cross-interactions between the Adsorbates and the Transition States

It is clear that the TOF ($1.2 \times 10^4 \text{ s}^{-1}$) from the kinetic calculations including the cross-interactions between adsorbates still possess errors compared with the experiments ($5.6 \times 10^2 \text{ s}^{-1}$). Another important correction that is the cross-interactions between the adsorbates and the transition states is needed to be checked. Several approximations were developed in previous work to calculate the effect of adsorbate interactions on the reaction barriers [33]. Then, how large is the error of the kinetic result between the approximations and more rigorous DFT calculations for adsorbate interactions on the barriers?

Figure 3 (a) Different TOF values were calculated with different considerations of cross-interactions for adsorbates/transition-states. Parameters used in the calculations: ① the rigorously calculated TS energies in this work; ② the use of BEP relations (see the **Supporting Information**); ③ $x = y = 0.5$ in the Equation in (b); ④ $x = 1, y = 0$; ⑤ $x = 0, y = 1$; ⑥ $x = 0, y = 1$ for the O-O TS; $x = 1, y = 0$ for the CO-O TS; and ⑦ $x =$

1, $y = 0$ for the O-O TS; $x = 0$, $y = 1$ for the CO-O TS. **(b)** Illustration of the equation used for considering the coverage-dependent activation barriers. **(c)** Comparison of the transition state for the CO-O coupling with/without the coverage effect. **(d)** Comparison of the transition state for the O-O bond breaking with/without the coverage effect.

In this work, the coverage effects on the transition states were rigorously calculated. The transition states O-O dissociation as well as the O-CO bond formation were searched at different coverages of CO and O. It is found that the distance between the two reacting species increases with the increase of surface coverage, which affects the energies of the transition states: The distance of O-CO increases from 1.813 Å at low coverage to 1.933 Å on the surface that reaches the steady state (see **Figure 3(c)**). A similar trend is observed for the transition states of O-O dissociation (the O-O distance from 1.696 Å to 1.804 Å, see the **Figure (d)**). The TOF of CO oxidation on Rh(111) was calculated to be $3.2 \times 10^3 \text{ s}^{-1}$ ($\log(\text{TOF}) = 3.50$), which is closer to the experimental results (see **Figure 3(a)**).

The TOF of CO oxidation were also calculated using several approximations to include the effect of adsorbate-adsorbate interactions on the transition states for comparison. The transition state energy was corrected using the equation in **Figure 3(b)**, where x and y are the parameters describing the structure differences between the transition state and initial and final states, respectively. Parameter x approaches to 1 when the structure of the transition state resembles the initial state and vice versa. Obviously, different

results can be obtained using different parameters x and y , and it is difficult to determine how the transition state is close to the initial state or the final state. It is found that the model of $x/y = 0.5/0.5$ give rise to the closest result to our rigorously calculated one for this system. Moreover, the reaction barriers were also obtained using the BEP relations, which was built basing upon the DFT calculations on different metal surfaces with low coverages (see the **Supporting Information**). The TOF was calculated to be $4.7 \times 10^4 \text{ s}^{-1}$ ($\log(\text{TOF}) = 4.67$) at the steady state (**Figure 3(a)**, column 2), which differs by one order of magnitude from the more rigorously calculated one.

3.4 Additional Corrections for the Coverage-dependent Micro-kinetic Modelling

Figure 4. Activities ($\log(\text{TOF})$) for CO oxidation on Rh(111) at 600 K with different combinations of the corrections (the dash line shows the experimental result). Three different kinds of corrections were considered: (A) the correction from rigorously calculated adsorbate-adsorbate interaction; (B) the correction of coverage-dependent thermodynamic corrections; (C) the correction of over-estimation bonding energies; and (D) the correction of Van der Waals forces. Different combinations were tested as

(i) A; (ii) A + B; (iii) A + C; (iv) A + D; (v) A + B + C; (vi) A + B + D; (vii) A + C + D; and (viii) A + B + C + D.

With the increase of surface coverage, the surface becomes more crowded; some additional issues should, therefore, be considered. Firstly, the vibrational motions of adsorbates will be affected, which will decrease the entropy for each of the adsorbates due to the crowded nature of the structure. As a basic correction to convert the total energy to the free energy, the zero-point energy (ZPE) is also related to the vibrational frequencies. Thus, the coverage-dependent vibrational frequencies were calculated and included in the micro-kinetic modelling in this work. Secondly, it is well known that the PBE functional over-estimates the chemisorption energies on transition metals especially for CO [45]. Moreover, the Gibbs free energies of gas phase reactions calculated from the VASP code using the PBE functional possess errors. Therefore, in this work, the reaction energies in the gas phase and the over-bonding of PBE functional were corrected by those calculated by Gaussian software (see the **Supporting Information**). Finally, the van der Waals forces were considered in the micro-kinetic modelling. The DFT-D3 method in the VASP code was used in this work to include the effect of van der Waals forces. **Figure 4** illustrates the TOF of CO oxidation under these corrections, which are discussed below.

Firstly, linear relationships between the thermodynamic corrections and the coverages are found from the coverage-dependent vibrational motions: The thermodynamic corrections were plotted against the total coverage and the correction values are found to be constant below the total coverage of 0.33 ML; above the total coverage of 0.33 ML, the corrections are observed to increase linearly. Thus, a two-line model was utilized to obtain the corrections. The largest difference of adsorbate-adsorbate interactions from vibrational motions is around 0.1 eV between the total coverages of 0.11 ML and 1 ML. However, both the transition state and the initial state suffer from these adsorbate-adsorbate interactions and the effect on the barriers is therefore seen to be cancelled considerably. Thus, the corrections of adsorbate-adsorbate interactions on the vibrational motions show almost no influence on the TOF for our system, as shown in **Figures 4(i)** and **4(ii)**.

On the other hand, the corrections from either the over-estimated chemisorption energies or the van der Waals forces possess much more significant impacts on the TOF of CO oxidation. The TOF of CO oxidation was decreased when the correction of over-estimated chemisorption energy was included, as shown in **Figures 4(i)** and **4(iii)**. The results from the self-consistent microkinetic modelling indicate that a higher dissociation barrier of O₂ is found at the steady state (see the **Supporting Information**), which was calculated to be 1.21 eV with the corrections from the over-estimated chemisorption energies compared to 0.88 eV without the corrections. The reduction of

calculated TOF can also be obtained by taking the correction of the van der Waals forces into account (see **Figures 4(i)** and **4(iv)**), where a higher dissociation barrier of O₂ (1.17 eV) was obtained at the steady state. Interestingly, an excellent agreement between the calculated TOF and that measured by the experiment is found by including all the corrections (**Figure 4 (viii)**).

3.5 General Discussion

In this work, some important approximations in the literature for reaction kinetics calculations were tested against more rigorously calculated kinetics for CO oxidation on Rh(111) at 600 K. The main results can be put together in **Figure 5**. It illustrates that the methods based on self and cross-interactions of adsorbates (0.5/0.5 model for coverage-dependent transition states) can be used to correct the under-estimation of activity from no coverage effect calculations (point B, **Figure 5**). It is clear from **Figure 5** that to include the cross-interactions properly for adsorbate/transition-state is pivotal to the accuracy of TOF calculations; the TOF can be changed by several orders of magnitude to be closer to the correct value. Additionally, with the consideration of coverage-dependent thermodynamic corrections, over-estimations of chemisorption and the van der Waals forces, the TOF of CO oxidation was finally calculated to be $8.2 \times 10^2 \text{ s}^{-1}$ ($\log(\text{TOF}) = 2.92$), very close to the experimental result ($5.6 \times 10^2 \text{ s}^{-1}$). On the other hand, it is also important to benchmark the accuracy of microkinetic modelling

using the distribution of surface coverage at the steady state [46]. Our results show that a reasonable surface coverage at the steady state can be obtained (0.43 ML) with these corrections rather than a fully covered surface obtained from no corrections used. Nevertheless, an in-depth investigation is required in the future for the improvement of microkinetic modelling with more accurate prediction of surface coverage compared with experiments.

Figure 5 Activity and surface coverage results for CO oxidation on Rh(111) at 600 K with different correction on adsorbate-adsorbate interactions (A: coverage-independent; B: including adsorbate-adsorbate self-interactions and cross-interactions and 0.5/0.5 model for coverage-dependent transition states; C: including rigorously calculated cross-interactions for adsorbates-adsorbates and adsorbates-transition states; D: including coverage-dependent thermodynamic corrections, over-estimation of adsorption energies and van der Waals forces in addition to the corrections in C).

Figure 6 Energy profiles of CO oxidation on Rh(111) at 600 K with (red line) and without (blue line) coverage corrections. Both energies were corrected to free energies with the standard thermodynamic corrections, and the corrections from van der Waals forces and over-estimated chemisorption energies were also considered (the energies are listed in **Table 3**).

Table 3 Elementary reaction energies of CO oxidation with/without the consideration of coverage effect. All energies were corrected to free energies with the standard thermodynamic corrections, and the corrections from van der Waals forces and over-estimated chemisorption energies were also considered.

Elementary reactions	Coverage-independent		Coverage-dependent	
	Activation barrier (eV)	Reaction energy (eV)	Activation barrier (eV)	Reaction energy (eV)
$\text{CO(g)} + * \rightarrow \text{CO}^*$	-	-0.61	-	0.05
$\text{O}_2(\text{g}) + 2* \rightarrow 2\text{O}^*$	-0.32	-2.98	0.93	-0.94
$\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2(\text{g}) + 2*$	1.42	-0.35	0.85	-2.03

Interestingly, the kinetic characteristics of the system is also changed significantly by including adsorbate-adsorbate interactions. The free energy profiles of the whole reaction with (the red curve) and without (the blue curve) the coverage effect are shown in **Figure 6**, from which we can see the following features: Firstly, the free energy

barrier of O₂ dissociation is increased by including the coverage effect; it was calculated to be higher than that of CO-O coupling at the coverage of 0.54 ML (the steady state). Secondly, the free energy barrier of CO-O coupling is decreased when the kinetic modelling was performed with the consideration of adsorbate interactions. As a result, the rate-determining step was swapped from the CO-O coupling step without the coverage effect to the O₂ dissociation with the coverage effect at the steady state (0.54 ML).

Our results suggest that the rigorous consideration of the cross-interactions for the transition states is the key for performing accurate kinetic results, and the errors can reach several orders of magnitude if some approximations are used (see **Figure 3**). Even at the low coverages, the adsorbate-adsorbate interactions should not be omitted; the difference of differential chemisorption energies between our calculated values and those obtained from omitting the adsorbate-adsorbate interactions can reach around 0.6 eV. It is noted that the large computational costs should be expected for the rigorous consideration of all the cross-interactions between the transition states and different adsorbates, when more complex catalytic systems with many different adsorbates are studied. Here, we suggest to choose less than 3 key adsorbates, which should be the major adsorbates covered on the surface, conducting the coverage-dependent microkinetic modelling (considering the interactions between all adsorbates vs key adsorbates and transition states vs key adsorbates). The choice of major adsorbates can

be determined from a basic microkinetic modelling or previous experimental work. It is obvious that the kinetic result for a system is related to the reaction mechanism in the system. Therefore, in order to obtain reliable kinetic results, a complete mechanism is required. We suggest that obtaining elementary reactions may start from the determination of all possible intermediates, which can be derived from the reactants and products. Then, all possible elementary reactions can be obtained considering the reaction network among all the intermediate adsorbates, where the error from missing elementary steps can be decreased as low as possible. In addition, it is worth emphasizing that the accuracy of kinetic modelling can be considerably improved by including the corrections of the over-estimation of chemisorption energies and the effect from the van der Waals forces, while the coverage effect on the thermodynamic corrections may be ignored at least for our system. It should be noted that in addition to the microkinetic modelling, another kinetic approach, the kinetic Monte Carlo (kMC) simulations, is also widely used in the investigation for surface reactions in the field [47-49]. However, a large amount of computational times may be required if the coverage effects are rigorously considered [50,51]. In general, it is vital to choose a suitable method to solve kinetic issues [52, 53], and our work indicates that the coverage effect is a main issue in microkinetic modelling.

4. Conclusion

In this work, an iterative approach of self-consistent microkinetic modeling was proposed and all the major coverage effects on the reaction kinetics for CO oxidation on Rh(111) were investigated. A rigorous consideration of both self and cross interactions for adsorbates and transition states were performed. The main conclusions can be summarized as follows:

(i) The TOF of CO oxidation on Rh(111) calculated using the self-consistent microkinetic modelling based on DFT energies with rigorously simulated adsorbate-adsorbate interactions and the corrections of DFT overbonding and van der Waals forces is very close to the experimental value.

(ii) Both the cross-interactions, i.e. the interactions between adsorbates and the interactions between the adsorbates and the transition states, are pivotal for obtaining accurate kinetic results.

(iii) The thermodynamic corrections (ZPE and entropies) are found to be constant when the total surface coverage is below 0.33 ML, but be linear functions of coverage as the coverages are above 0.33 ML. However, the corrections are largely cancelled out between the initial and transition states or final states, and thus do not affect the kinetic

results in our system. In contrast, the corrections of DFT overbonding and van der Waals forces are found to affect significantly the kinetic results.

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Appendix A. Supplementary material

Supporting Information can be found at XXX

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Supporting Information

Examination of the Key Issues in Microkinetics: CO Oxidation on Rh(111)

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1. Structures of Self-Interaction and Cross-Interaction in the System of CO Oxidation on Rh(111)

The most stable adsorbed site for CO and O on Rh(111) was considered, which is the hcp hollow site for both adsorbates. Both adsorbate-adsorbate self-interactions and cross-interactions were considered for adsorbates on $p(3\times3)$ supercell and partial structures are shown below. Different coverages on the surface were studied from 0.11 ML to 0.99 ML by the step of 0.11 ML, where the total number of adsorbed sites was considered as 9. The optimized structure of adsorbed CO of 0.55 ML showed a different adsorbed site on the surface (see **Figure S1**), which was assumed as an effect from periodic lattice in this work. The same behavior was found of CO surrounded by adsorbed O at the total coverage 0.55 ML (see **Figure S3**). The O covered structures showed more average without different adsorbed sites (see **Figure S2**). The cross-interactions were considered representing one of the adsorbate in the center (see **Figure S3**). The transition states were also considered with covered CO and O for both CO oxidation and O_2 dissociation. It was considered occupying two adsorbed sites and partial structures showed below (see **Figure S4** and **Figure S5**).

Figure S1 Structures of self-interactions of CO on Rh(111) from 0.11 ML to 0.99 ML.

Figure S2 Structures of self-interactions of O on Rh(111) from 0.11 ML to 0.99 ML.

Figure S3 Partial structures of cross-interactions of CO and O on Rh(111) with different total coverage.

Figure S4 Partial structures of cross-interactions of transition state of CO-O on Rh(111) with different total coverage.

Figure S5 Partial structures of cross-interactions of transition state of O-O on Rh(111) with different total coverage.

2. The Two-Line Model

Differential chemisorption energy was studied in this work describing the effect of adsorbate-adsorbate interactions. As discussed before, optimized structures with different coverages on Rh(111) was calculated based on DFT calculations and the differential chemisorption energy can be calculated as:

$$E_{ad}^{diff}(\theta) = E_{total}(n + 1) - E_{total}(n) - E_{gas} \quad (S1)$$

$$\theta = \frac{\theta_n + \theta_{n+1}}{2} \quad (S2)$$

where θ represents the coverage on surface, n represents the number of adsorbates. The chemisorption energy at the coverage of 0.11 ML was used as the reference and the two-line model was used to fit the value of the difference between differential chemisorption energy and the reference. Using the results in this work, 9 differential chemisorption energies can be calculated with different coverage. The first few points (from 0.056 ML to 0.389 ML) were used to fit the first straight line describing the adsorbate-adsorbate interactions in low coverage area and another some other points (from 0.278 ML to 0.944 ML) were used for high coverage area (see **Figure S6** for CO*/CO_{sur} and O*/CO_{sur} as examples). The two straight lines in the two-line model were not crossed at a specific point with the coverage of 0.33 ML. In this work, the critical point was set as 0.33 ML of all the corrections and the error of the cross-point was just ignored. The parameters of two-line model were showed below (see **Table S1**).

Figure S6 Two-line model correction for $\text{CO}^*/\text{CO}_{\text{sur}}$ and $\text{O}^*/\text{CO}_{\text{sur}}$.

Table S1 Parameters of the two-line model

Adsorbate-adsorbate interactions	low coverage area		high coverage area	
	slope	intercept	slope	intercept
$\text{CO}^*/\text{CO}_{\text{sur}}$	0.7740	-0.0332	2.6773	-0.6076
$\text{O}^*/\text{O}_{\text{sur}}$	2.5501	-0.1993	1.8479	0.0624
$\text{O}^*/\text{CO}_{\text{sur}}$	1.1857	-0.1271	2.4461	-0.5163
$\text{CO}^*/\text{O}_{\text{sur}}$	1.3342	-0.0671	2.1063	-0.3119
$\text{TS}(\text{CO-O})/\text{CO}_{\text{sur}}$	0.3583	-0.0428	4.8301	-1.5644

TS(CO-O)/O _{sur}	1.2310	-0.1169	4.5470	-1.3901
TS(O-O)/CO _{sur}	0.4971	-0.0504	5.2853	-1.6698
TS(O-O)/O _{sur}	1.0798	-0.0869	5.2387	-1.7033
<hr/>				
Adsorbate-adsorbate interactions	low coverage area		high coverage area	
(including Van der Waals effect)	slope	intercept	slope	intercept
<hr/>				
CO*/CO _{sur}	0.9818	-0.1251	2.1706	-0.5213
O*/O _{sur}	2.4696	-0.1906	1.7912	0.0641
O*/CO _{sur}	1.2855	-0.0975	2.2495	-0.4141
CO*/O _{sur}	1.1523	-0.0522	1.9423	-0.3012
TS(CO-O)/CO _{sur}	0.5323	-0.0567	4.4846	-1.4046
TS(CO-O)/O _{sur}	1.0899	-0.1013	3.8838	-1.0388
TS(O-O)/CO _{sur}	0.7723	-0.0773	4.6298	-1.3157
TS(O-O)/O _{sur}	0.9969	-0.0787	5.0553	-1.6618
<hr/>				

3. Thermodynamic Corrections

Thermodynamic corrections of adsorbates on surfaces and corrections of molecule in gas phase were conducted using DFT calculations, where zero-point energy (ZPE) corrections, inner energy corrections and entropy corrections were considered [1,2]. The correction of adsorbates were calculated based on vibrational frequencies. The corrections from translational and rotational motions were ignored for adsorbates, which means only vibrational motions were considered. Therefore, the thermodynamic corrections for adsorbates can be carried out by DFT calculations using VASP code. The vibrational frequencies for adsorbates were calculated, while the whole surface was fixed in the calculations. On the other hand, the translational and rotational motions must be considered in the corrections for gas phase molecules. Therefore, the thermodynamic corrections were obtained using the Gaussian [3] calculations including all the vibrational, translational and rotational motions.

The thermodynamic corrections for adsorbates with different surface coverages were also calculated in this work, where only vibrational motion was considered. Here, the vibrational frequencies of adsorbates with a specific surface coverage were calculated with one adsorbate (or the transition state) relaxed with all the co-adsorbates and the surface fixed. The relationship between different correction energies and surface coverages were established using the same method in **Figure S6**.

4. Chemisorption Energy Corrections (Energy Corrections for Gas Phase Molecules)

It is known that the energies of CO, O₂ and CO₂ using PBE functional from VASP need to be improved. For example, the over-bonding of CO on transition metals using DFT calculations based on PBE functional in VASP were found previously by many groups. The O-O over-bonding is also well known from VASP using PBE. Therefore, in this work, the energies of CO, O₂ and CO₂ in the gas phase were corrected as follows. Taking the energy of CO as an example, using Gaussian DFT calculations with B3LYP

and basis set 6-311G, where the molecular energies are known to be more reasonable, the reaction energy of $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ is obtained to be -2.85 eV (Table S2 below). From the VASP calculation using PBE functional, the energies of H_2 , CH_4 and H_2O are -6.76 eV, -24.02 eV and -14.13 eV, respectively, which are known to be reasonable and considered as the reference energies [4]. Using the reaction energy of -2.85 eV from Gaussian, the energy of CO can be derived to be -15.03 eV. Similarly, the energies of O_2 and CO_2 can also be obtained from the reactions of $\text{O}_2 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O}$ and $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$, respectively (see **Table S2**).

Table S2 Energies of CO, O_2 and CO_2 obtained from the reactions of $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$, $\text{O}_2 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O}$ and $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$, respectively, where the energies of H_2 , CH_4 and H_2O from VASP and the reaction energies from Gaussian were used as the reference energies. The energies marked by * were derived.

	CO	3H_2	$\rightarrow$	CH_4	H_2O	ΔE
Gaussian (eV)	-3084.39	3×-32.10		-1102.99	-2080.54	-2.85
VASP (eV)	-15.03*	3×-6.76		-24.02	-14.13	-2.85

	2H_2	O_2	$\rightarrow$	$2\text{H}_2\text{O}$	ΔE
Gaussian (eV)	2×-32.10	-4091.79		2×-2080.54	-5.10
VASP (eV)	2×-6.76	-9.64*		2×-14.13	-5.10

	2CO	O_2	$\rightarrow$	2CO_2	ΔE
Gaussian (eV)	2×-3084.39	-4091.79		2×-5133.35	-6.13
VASP (eV)	2×-15.03	-9.64		$2 \times -22.91^*$	-6.13

It is found that the energy of CO was corrected by around 0.2 eV compared with the energy from VASP directly (-14.79 eV), and O_2 and CO_2 have similar corrections. As a result, the Gibbs free energies of the reactions are corrected to be close to experimental ones.

5. The BEP relation

The BEP relation was tested in the correction of adsorbate-adsorbate interaction for the activation barrier. The relation was estimated using the DFT calculated energies on Ru(001), Pt(111), Rh(111), Ir(111) and Ag(111) clean surfaces. The reaction energy was represented using the adsorption energies, which can be corrected by a constant number from the reaction energies, to be the X axis.

Figure S7 The BEP relation between activation barriers and adsorption energies.

6. Microkinetic modeling results

Microkinetic modelling was used in this work. It was carried out by MATLAB and the code was improved by Chen, J. [5]. Three elemental reactions were considered as mentioned in main text. The pressure of CO O₂ and CO₂ were set as 0.01052 0.01052 and 0.00105 bar in order to be consistence with experimental conditions at the temperature of 600 K. All the kinetic results with surface coverage at steady state were displayed in the **Table S3**.

Table S3 Activity results with different corrections of adsorbate-adsorbate interactions

Coverage (ML)		Effective barrier (eV)				Adsorbate-adsorbate interactions		
CO	O	O ₂ dissociation	CO oxidation	TOF (s ⁻¹)	Log (TOF)	Adsorbate	Transition state	Corrections
0.00	1.00	-0.06	1.38	3.57E-01	-0.40	Coverage-independent		
0.42	0.01	0.75	0.73	4.70E+04	4.67	Self-interactions	BEP relationship	None
0.25	0.19	0.88	0.98	3.41E+03	3.53	Self/cross-interactions	Cross-interactions	None
0.00	0.54	0.93	0.85	8.22E+02	2.92	Self/cross-interactions	Cross-interactions	Vb, Gas, VdW
0.42	0.00	0.82	0.68	1.23E+04	4.09	Self-interactions	0.5/0.5 model	None
0.33	0.09	0.67	0.74	2.19E+05	5.34	Self/cross-interactions	0.5/0.5 model	None
0.25	0.19	0.88	0.98	3.41E+03	3.53	Self/cross-interactions	Cross-interactions	None
0.33	0.09	0.67	0.74	2.19E+05	5.34	Self/cross-interactions	0.5/0.5 model	None
0.00	0.63	-0.06	1.38	3.24E-03	-2.49	Self/cross-interactions	1/0 model	None
0.42	0.42	1.31	0.16	8.33E-01	-0.08	Self/cross-interactions	0/1 model	None
0.00	0.63	-0.06	-0.76	7.04E+09	9.85	Self/cross-interactions	Mixed model	None
0.39	0.04	1.34	1.38	4.49E-01	-0.35	Self/cross-interactions	Mixed model	None
0.25	0.19	0.88	0.98	3.41E+03	3.53	Self/cross-interactions	Cross-interactions	None

0.21	0.22	0.86	0.96	5.18E+03	3.71	Self/cross-interactions	Cross-interactions	Vb
0.00	0.54	1.21	0.86	3.71E+00	0.57	Self/cross-interactions	Cross-interactions	Gas
0.00	0.53	1.21	0.83	3.73E+00	0.57	Self/cross-interactions	Cross-interactions	Vb, Gas
0.55	0.00	1.17	0.77	7.46E+00	0.87	Self/cross-interactions	Cross-interactions	VdW
0.54	0.00	1.13	0.77	1.64E+01	1.21	Self/cross-interactions	Cross-interactions	Vb, VdW
0.00	0.54	0.93	0.87	8.17E+02	2.91	Self/cross-interactions	Cross-interactions	Gas, VdW
0.00	0.54	0.93	0.85	8.22E+02	2.92	Self/cross-interactions	Cross-interactions	Vb, Gas, VdW

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