

# CO oxidation and NO reduction on metal surfaces: density functional theory investigations

Zhi-Pan Liu and P. Hu\*

*School of Chemistry, Queen's University of Belfast, BT9 5AG UK*

This article reviews the accumulated theoretical results, in particular density functional theory calculations, on two catalytic processes, CO oxidation and NO reduction on metal surfaces. Owing to their importance in automotive emission control, these two reactions have generated a lot of interest in the last 20 years. Here the pathways and energetics of the involved elementary reactions under different catalytic conditions are described in detail and the understanding of the reactions is generalized. It is concluded that density functional theory calculations can be applied to catalysis to elucidate mechanisms of complex surface reactions and to understand the electronic structure of chemical processes in general. The achieved molecular knowledge of chemical reactions is certainly beneficial to new catalyst design.

**KEY WORDS:** density functional theory; CO oxidation; NO reduction; heterogeneous catalysis; review

## 1. Introduction

The last 10 years have seen an explosion in the application of first-principles computational modelling in chemistry thanks to the ever-increasing computational resources and substantial theoretical/algorithmic improvements. Amongst the most challenging and exciting of fields into which first-principles theory is currently expanding must rank the study of chemical reactions on surfaces, the central issue in heterogeneous catalysis [1–4]. Here the quantum theory describing the molecule–surface interaction and the classical dynamics of molecular movement come into play to determine the mechanisms of catalytic processes. The output from the theoretical modelling including structures, bonding energies, reaction pathways and reaction energetics, in companion with experimental observations, can provide detailed atomic-level pictures of surface reactions [1–4]. This review is intended to summarize the accumulated theoretical results, in particular density functional theory (DFT) calculations, on two important catalytic reactions: CO oxidation and NO reduction on metal surfaces, two of the key reactions encountered in the control of vehicle emissions.

Not only are they of huge importance, but, in addition, CO oxidation and NO reduction are surface reactions of fundamental significance. The oxidation of CO on metal surfaces is a textbook example of a catalytic reaction and has been extensively investigated. The reduction of NO on metals is an interesting process since NO can be either reduced (e.g., N<sub>2</sub>, N<sub>2</sub>O) or oxidized (e.g., NO<sub>2</sub>). Both the activity and the selectivity of metal catalysts are crucial in NO reduction. Microscopically, these two reactions consist of several elementary steps, such as adsorption

(CO, NO adsorption); O<sub>2</sub> dissociation; CO oxidation (CO + O → CO<sub>2</sub> reaction); NO dissociation (NO → N + O); N<sub>2</sub> formation (N + N → N<sub>2</sub>) and the relevant side-reactions (e.g. NO<sub>2</sub> and N<sub>2</sub>O formation). These elementary reactions are cross linked to many other catalytic processes and the understanding of them can provide general insight into heterogeneous catalysis. Here we will focus on the elementary surface reactions of CO oxidation and NO reduction (the CO and NO adsorptions have been reviewed previously, see for example Ref. [2,5]). The paper is organized as follows. DFT methods used to study surface reactions are briefly introduced in section 2. In sections 3 and 4, the current theoretical progress in CO oxidation and NO reduction will be summarized, respectively. Concluding remarks are outlined in section 5.

## 2. Density functional theory approach to catalytic reactions on surfaces

A fundamental understanding of heterogeneous catalytic reactions relies on a reliable description of molecule–surface interactions. The modelling of surfaces using first principles methods was a formidable task for many years [6]. DFT calculations for surfaces have been performed since the early 1970s. But it only became mature and together with the dramatically increased computing power in the late 1980s that enable the breakthrough in the quantitative description of molecule–surface bonding. DFT provides a methodology which is both viable for systems with relatively large numbers of atoms and reliable often to quantitative accuracy. For the detailed formalisms of DFT, interested readers may refer to the monograph of Parr and Yang [7]. In general, DFT starts with a consideration of the entire electron density of the system based on the

\* To whom correspondence should be addressed.

E-mail: p.hu@qub.ac.uk

foundation work of Hohenberg and Kohn [8,9], in which the ground state total electronic energy is proved to be a function of the electron density. In the framework of DFT, the non-classical part of electron–electron interaction energy, namely electron–electron exchange and correlation, can be expressed as a unified function of a single variable, i.e., the total electron density, which is much simpler compared to the traditional Hartree–Fock approach. Although the exact form of the exchange–correlation functional is yet unknown, many approximate functionals have been proposed in practice, such as local density approximation (LDA) and its derived versions of generalized gradient correction (GGA) [10,11]. It has been demonstrated that GGA results can generally reproduce good structures up to the experimental accuracy, and bond energies within an error of a few percent compared to experimental results. Current GGA calculations provide a rather robust basis for a systematic comparison with experimental results [2].

To model extended surface systems a so-called supercell approach is currently used, in which the structure of the surface is repeated both vertically and laterally [12]. The lateral periodicity implies that the surface is modelled as an infinite *slab* of finite thickness. To produce acceptable results, a sufficient number of surface layers and a sufficiently large vacuum region between slabs are required. Not limited to the periodical systems, the supercell approach can be also used to study aperiodical systems [12], such as surface defects and isolated molecules, as long as the modelled supercell is large enough so that the lateral interaction between the aperiodical elements is screened. Other methods such as one employing the PW-PP formalism periodic boundary conditions extensively used by Landman and co-workers are also widely utilized [13].

Using DFT, the forces on atoms can be calculated based on the Hellmann–Feynman theorem. With the forces acting on atoms being known, the structure-optimization techniques, such as BFGS method [13], molecular dynamics [12,13], and transition state (TS) search techniques can determine the various states along a surface reaction pathway (e.g., the initial state (IS), TS and the final state (FS)). The calculated pathways and energetics provide important information about the reaction mechanism. Among all the geometry-optimization techniques, to locate the TS is of particular importance as it determines the height of reaction barriers. In recent years, two different methods have been successfully used: (1) Constrained minimization method [14], (2) Nudged elastic band method [15].

### 3. CO oxidation

Experimentally, CO oxidation has been mostly studied on the late 4d and 5d transition metals, such as Ru, Rh, Pt and Pd. Among them, Pt is known to be one of

the most active catalysts, while Ru is the poorest one at low pressures of O<sub>2</sub> and CO, being only active at high O<sub>2</sub> partial pressures [16]. Recent STM experiments [17] further suggest that on other transition metals, such as Pt and Pd, the formation of oxide may largely improve the catalytic ability. Neither 3d transition metals, such as Fe, Co, Ni, nor the early transition metals, such as W, Zr are good catalysts for CO oxidation, presumably because these metals bond O atoms too strongly and they are not stable enough in the oxidative conditions. For recent years another new class of catalysts for CO oxidation, namely, oxide supported Au catalysts has attracted much attention [18,19]. Au-based catalysts have a superior high catalytic ability at low temperatures (e.g., below 300 K) compared to transition metal catalysts.

#### 3.1. CO oxidation on transition metals

It was generally believed that CO oxidation on transition metals followed a Langmuir–Hinshelwood mechanism. Because O<sub>2</sub> can readily dissociate on all transition metals at room temperatures, three elementary steps have been proposed during the CO oxidation: (i) CO adsorption on surfaces (ii) O<sub>2</sub> dissociation into O adatoms on surfaces; and (iii) CO + O → CO<sub>2</sub> reaction on surface. This straightforward mechanism is able to explain most of the experimental findings. However, when the reaction conditions vary, the mechanism may be changed. At low temperatures, say, below the O<sub>2</sub> dissociation temperature on transition metals, other alternative reaction channels may be dominant. DFT calculations by Gong *et al.* [20] showed that adsorbed H<sub>2</sub>O can significantly promote CO oxidation on Pt{1 1 1} at low temperatures (~200 K), which confirmed the earlier experimental finding by Bergeld *et al.* [21]. The other low-temperature mechanism, suggested by Eichler and Hafner [22], involves adsorbed O<sub>2</sub> directly reacting with CO to form a CO<sub>2</sub>. At high temperatures and high pressures, because transition metals may be oxidized, CO oxidation may happen on transition metal oxides and the mechanism is still under investigation. We summarize the DFT results for CO oxidation in table 1, and they are elaborated in the following.

*Close-packed transition metal surfaces.* CO oxidation on Pt{1 1 1} is a classical example of heterogeneous catalysis. The first attempt to reveal the surface reaction pathway of CO oxidation on Pt{1 1 1} was performed by Alavi *et al.* [14], and similar results were also obtained later by Eichler and Hafner [22]. The calculated reaction pathways of the CO + O → CO<sub>2</sub> on Pt{1 1 1} is shown in figure 1. At the IS 1/4 ML coverage, the CO sits on the top site and the O sits on the fcc hollow site. It should be mentioned that for pure CO chemisorption, the hollow site is favoured at the CO coverage of 1/4 ML from DFT calculations. However,

Table 1  
DFT-slab calculations for the  $\text{CO} + \text{O} \rightarrow \text{CO}_2$  reaction on different metal surfaces

	Substrate	Coverage (ML)	Reaction barriers (eV)	Reference
Close-packed surface	Ru{0 0 0 1}	1/4	1.4, 1.45, 1.45	23, 24, 25
	Rh{1 1 1}	1/4	0.99, 0.91, 1.03	25–27
	Pd{1 1 1}	1/4	0.93, 0.78, 1.06	27–29
		1/6	1.49, 1.40, 1.4, 1.36	27–30
	Ir{1 1 1}	1/4	1.35	31
	Pt{1 1 1}	1/4	1.00, 0.85, 0.80, 0.74	14, 25, 27, 32
	Cu <sub>3</sub> Pt{1 1 1}	1/4	0.80	32
Open surface	Pd{1 0 0}	1/4	0.78, 0.67, 0.7	27, 28, 30
		1/6	1.05, 1.05	27, 28
	Rh{1 0 0}	1/4	1.03	27
	Pt{1 0 0}	1/4	0.87	27
Stepped surface	Pd{2 1 1}	1/6	1.0	30
	Ir{2 1 1}	1/6	1.70	31
	Au{2 2 1}	1/8	0.25	33

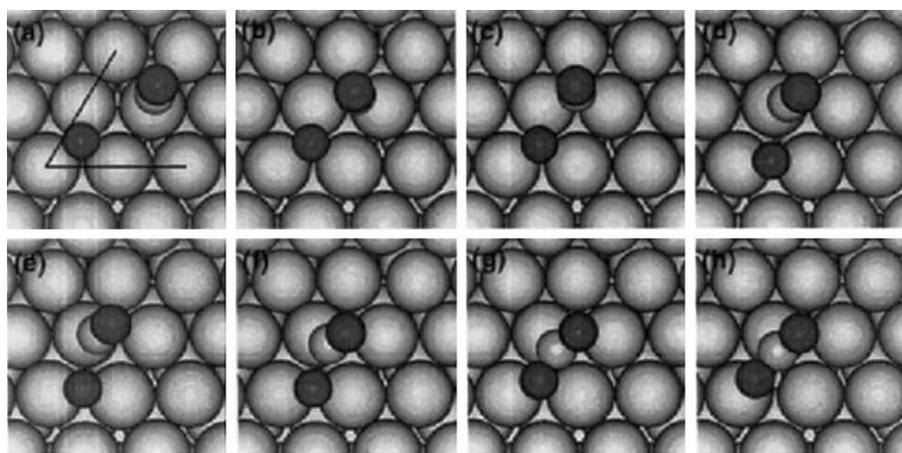


Figure 1. Snapshots of the reaction pathway from the initial state [top left, (a)] to the final state [bottom right, (h)]. The lattice vectors are indicated in (a). For clarity, the periodic images of the molecules are not shown, and the view is slightly tilted from the vertical. The Pt atoms are the largest spheres, the O atoms are the darkest spheres, and the small grey spheres are the C atoms. The transition state is (e). In (h), the molecular geometry of the  $\text{CO}_2$  molecule has bond lengths  $\text{C}-\text{O}(a) = 1.29 \text{ \AA}$  and  $\text{C}-\text{O}(b) = 1.21 \text{ \AA}$  and bond angle  $131^\circ$ . The gas-phase molecule is linear with a bond length of  $1.16 \text{ \AA}$ . From Ref. [14].

the energy difference between the top site and the hollow site is small ( $\sim 0.2 \text{ eV}$  or smaller). At the TS, the CO sits on an off-top site being close to the O, while the O is at a bridge site. At the FS, the nascent  $\text{CO}_2$  sits on the top site of Pt{1 1 1}, weakly bonded on the surface. In addition, CO oxidation on other closed-packed metal surfaces, Ru{0 0 0 1}, Rh{1 1 1}, Pd{1 1 1}, Ir{1 1 1} and an alloy surface  $\text{Cu}_3\text{Pt}\{1 1 1\}$  have been performed [22–32,34]. It appears that the reaction pathways on the close-packed metal surfaces are very similar [23], which can be generalized as three common features. (i) *Activation of the O adatom*. The O atom is activated from the initial hollow site to the bridge site in order to achieve the TS. (ii) *Early TS*. At the TS the O—CO distance is long stretched, from  $1.7\text{--}2.1 \text{ \AA}$  depending on metals, compared to the gas phase C—O distance ( $1.2 \text{ \AA}$ ) in  $\text{CO}_2$ . The early TS of CO oxidation implies that the electronic structure of the TS is similar to that

of the individual adsorbed CO and O on surfaces. (iii) *No bonding competition TS geometry* [35]. This is because at the TS no surface atom bonds simultaneously with both the CO and O (see figure 1d).

The key event in CO oxidation on close-packed metal surfaces is the O activation from the hollow site to the bridge site. By comparing the local density state of the O on the hollow and the bridge site, Zhang and Hu [28] explained why the O needs to be activated. At the hollow site, the O bonds with three metal atoms and its  $p$  orbitals are largely saturated. As the O adatom is activated to the bridge site, one of its  $p$  orbitals that originally bonds with a metal atom is freed and can further bond with the incoming CO.

The DFT calculated reaction barriers are in general very consistent with experimental findings. As shown in table 1, CO oxidation on Pt{1 1 1} has the lowest barrier ( $\sim 0.7\text{--}0.8 \text{ eV}$ ), and on Ru{0 0 0 1} has the

highest barrier ( $\sim 1.5$  eV); CO oxidation on Pd{1 1 1} is sensitive to the CO coverage: at a high CO coverage the barrier can be much lower ( $\sim 0.9$  eV) compared to the  $\sim 1.4$  eV at a low CO coverage (this is due to the change of initial CO position on the surface at different CO coverages [27–29]). It should be noted that due to the usage of different calculation setups and various DFT packages, the value of barriers in the same system can be different by around 0.25 eV, which is close to the accuracy of DFT.

One of the fundamental questions in CO oxidation is what controls the reactivity change from metal to metal. It was initially suggested by several authors that the barrier to CO oxidation may be determined by the activation of the O. This comes from the fact that on going from the IS to the TS, the O loses one bond with a surface metal atom (O activation) and this energy cost may contribute greatly to the barrier and is the reason for the reactivity difference among metals [14,24]. However, this argument was found to be too simplistic by Liu and Hu [25], and they pointed out that the activation of CO is also crucial. Based on a barrier decomposition analysis, they correlated the barriers with the total initial adsorption energies of the CO and O atom on the surfaces, as shown in figure 2. The higher the energy with which the surface can bond CO and O, the higher is the barrier. The reason behind this is that there is little interaction between the CO and O at the TS, and the barrier is largely due to the coactivation of CO and O from a local minimum to the TS structure. Using the framework of extended Huckel theory Glassey and Hoffman [36] also found that the dominant part of the reaction barrier comes from the surface-mediated co-activation of adsorbed CO and an O atom, although during the CO oxidation, the interaction of the  $2\pi$  orbital of CO with the O  $2p$  orbitals is the principle driving force for the  $\text{CO}_2$  formation.

*Open and stepped metal surfaces.* In addition to the close-packed metal surfaces, CO oxidation on more

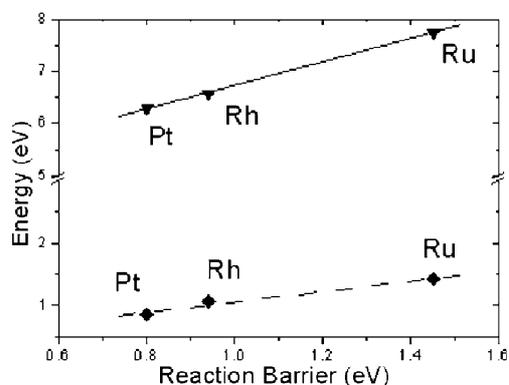


Figure 2. Illustration of the CO oxidation barrier as a linear function of the total reactant-activation energy ( $\Delta E_{\text{O}} + \Delta E_{\text{CO}}$ ) (dashed line) and the total chemisorption energy at the IS (solid line) on Ru, Rh and Pt. As can be seen,  $E_a \approx \Delta E_{\text{O}} + E_{\text{CO}} \propto \sum_X E_X^{\text{IS}}$ . From Ref. [25].

open surfaces, such as the {1 0 0} surface for fcc metals, and the monatomic steps has also been examined by DFT. In different contexts, CO oxidation on Pd{1 0 0} has been studied by three individual groups: Zhang and Hu [28], Eichler [27], and Hammer [30]. Eichler [27] also calculated systematically the reaction rate of CO oxidation on Rh{1 0 0}, Pd{1 0 0} and Pt{1 0 0} based on transition state theory<sup>1</sup>, and compared them with the results on the corresponding close-packed flat surfaces. For the stepped surfaces, Hammer [30] studied CO oxidation on Pd{2 1 1} (stepped surface) and edge, missing-row reconstructed Pd{3 1 1}; Liu *et al.* [31] studied CO oxidation on Ir{2 1 1}. These results are compiled in table 1. Typical TS structures of CO oxidation on {1 0 0} and {2 1 1} surfaces are shown in figure 3a and b, respectively.

DFT calculations showed that CO oxidation on {1 0 0} surfaces has quite similar barriers to those on close-packed surfaces, whilst the barriers on the stepped surfaces are usually higher than those on the flat surfaces. For example, Zhang and Hu reported that on Pd{1 0 0} the barrier is 0.78 eV while it is 0.93 eV on Pd{1 1 1} at a  $1/4$  ML coverage [28]. Eichler showed that on Pt{1 0 0} the barrier is 0.87 eV and on Pt{1 1 1} it is 0.74 eV [27]. On Ir{2 1 1}, the CO oxidation barrier is about 0.3 eV larger than that on the flat Ir{1 1 1} [31], and a similar difference was observed for CO oxidation on Pd{2 1 1} and Pd{1 0 0} [30].

These DFT results indicate that CO oxidation is not very sensitive to surface structures. Liu and Hu have explained the reason for the structure insensitivity of CO oxidation using the barrier decomposition analysis [25,37]. Because the barrier for CO oxidation is largely determined by the total bonding energy of CO and O (not sensitive to the surface structure change), at stepped or edged surfaces where CO and O bond with the surface more strongly, the barriers are usually higher than those on the flat surfaces.

*High temperatures and high pressures.* Following the experimental observations [16,17] that at high temperatures and high pressures transition metal surfaces may be partially oxidized and CO oxidation may occur on oxides. DFT calculations of CO oxidation on transition metal oxides have been carried out recently. CO

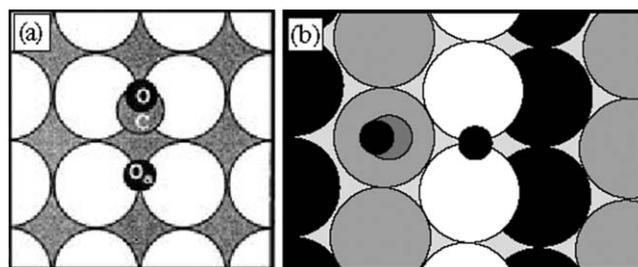


Figure 3. TSs of CO oxidation on Pd{1 0 0} (from Ref.[26]) and CO oxidation on Ir{2 1 1} (from Ref. [31]).

oxidation on  $\text{RuO}_2\{1\ 1\ 0\}$  is the case being mostly studied. The reaction was first thought to proceed through adsorbed CO reacting with a lattice O of the  $\text{RuO}_2$  oxide as suggested by the STM experiment of Over *et al.* [16]. DFT results following this mechanism showed that the barrier is around 1.2 eV (see [38–40]). It was noticed that in this mechanism the barrier is considerably lower than that on pure Ru (around 1.5 eV). However, recent DFT studies by Reuter and Scheffler [40] identified a new mechanism: on the oxide surface the adsorbed CO can react with the nearby adsorbed O to produce a  $\text{CO}_2$ , where both CO and the O atom sit atop of the surface Ru atoms. The barrier in this mechanism is lower, being only 0.9 eV. This CO + O mechanism appears to be more likely, because CO oxidation on Ru oxides have been observed around 400 K [16,39]. Very recently CO oxidations on other transition metal oxides, such as  $\text{PtO}_2\{1\ 1\ 0\}$  and  $\text{PdO}_2\{1\ 1\ 0\}$  were studied by Gong *et al.* [34]. They found that the CO + O mechanism on oxides, as suggested by Reuter and Scheffler [40], can indeed provide a lower energy pathway compared to the reaction on the corresponding pure metals.

### 3.2. CO oxidation on Au/oxide

Au/oxide catalysts, as first shown by Haruta [41] in the late 1980s, possess a surprisingly high catalytic ability at low temperatures. The activity of CO oxidation was found to be very sensitive to the size of Au particles and also to the choice of oxides. Systems with Au supported on reducible oxides (e.g.,  $\text{TiO}_2$ ,  $\text{Co}_2\text{O}_3$ ) are generally more active than the ones with Au supported on irreducible oxides (e.g.,  $\text{MgO}$ ,  $\text{SiO}_2$ ). The experimental findings about Au-based catalysts have been reviewed (see Ref. [18,19]). Despite extensive experimental studies, the mechanism of CO oxidation on Au-based catalysts is still much in debate. One of the major controversies is where and how  $\text{O}_2$  is activated on the catalysts.

DFT studies by several groups have been carried out to clarify the mechanism. Lopez and Norskov [42] studied CO oxidation on a small Au cluster (10-atom). They found that the mechanisms with or without  $\text{O}_2$  dissociation are equally likely. On the other hand, Liu *et al.*, [33] reported that  $\text{O}_2$  dissociation on pure Au, including flat, stepped Au surfaces and several Au clusters is not an easy step (barrier above 0.9 eV). They identified a reaction route involving CO reacting with molecular  $\text{O}_2$  at Au steps, which possess a barrier around 0.5 eV. This CO +  $\text{O}_2$  bimolecular mechanism was also identified by Molina and Hammer [43] in their recent study on CO oxidation over  $\text{MgO}$ -supported Au. However, Liu *et al.* showed that  $\text{O}_2$  adsorption energy is very low on Au ( $\sim 0$  eV). Similarly, Molina and Hammer reported a weak chemisorption of  $\text{O}_2$  on Au/ $\text{MgO}$  ( $\sim 0.2$  eV). These results imply that the CO +  $\text{O}_2$  reac-

tion occurs through a gas phase  $\text{O}_2$  reacting with the adsorbed CO. Naturally, the probability of this type of reaction is very low compared to the conventional surface reactions through the Langmuir–Hinshelwood mechanism. However, the low  $\text{O}_2$  adsorption problem seems to be overcome when the specific oxide support is used. For example, on  $\text{TiO}_2$  it was found by Liu *et al.* [33] that  $\text{O}_2$  can adsorb readily at the Au– $\text{TiO}_2$  interface. Another possibility to increase the  $\text{O}_2$  adsorption on Au involves the charged Au clusters instead of the neutral ones. DFT-cluster studies of  $\text{O}_2$  adsorption on small neutral and charged Au clusters, for examples see Ref. [44,45], seem to suggest an increased  $\text{O}_2$  adsorption on negatively charged Au. One important study by Landman group [46] showed that small Au clusters with negative charges, such as  $\text{Au}_8^-$ , which sit on the O-vacancy F-center of  $\text{MgO}$ , can adsorb molecular  $\text{O}_2$  strongly and catalyze CO oxidation.

## 4. NO reduction

Generally, there are two types of NO removal that are important in various after-treatment systems [46,47]. The first type is NO reduction under a reductive environment, e.g., NO reduction by CO ( $\text{CO} + \text{NO} \rightarrow 1/2\text{N}_2 + \text{CO}_2$ ),  $\text{H}_2$ , or  $\text{NH}_3$ . This type of NO reduction can be efficiently achieved by the traditional three-way catalysts, which employ various combinations of Pt, Pd and Rh for the simultaneous removal of NO, CO and unburned hydrocarbons. The second type of NO reduction is NO reduction under lean-burn conditions (excess  $\text{O}_2$  conditions), where the three-way catalysts do not work well because of the poisoning of metal catalysts by excess O. So far, there is no best solution for the NO reduction under lean-burn conditions. Noble metals, Cu, Ag, Au based catalysts, and platinum-group metal based catalysts are currently being intensively investigated experimentally for the lean-burn NO reduction [46,47]. The mechanism of NO reduction on transition metals is expected to follow the scheme shown in figure 4, while the mechanism on noble metal based catalysts is less certain since NO dissociation is believed to be unlikely on noble metals [44]. To

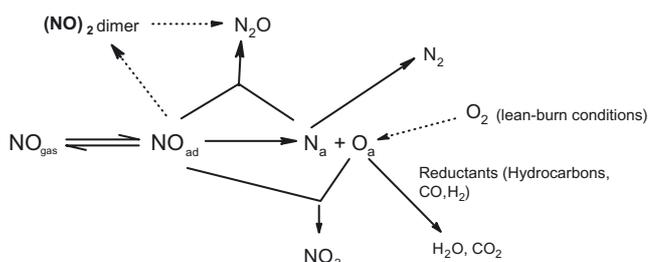


Figure 4. General mechanism of NO reduction on transition metal surfaces.

date, theoretical studies have been mostly focused on NO reduction in reductive conditions on Rh, Pt and Pd catalysts. Two systematic DFT studies on NO reduction by CO have been reported in recent years: on Pt{1 0 0} surface by Eichler and Hafner [48,49]; and on Pd surfaces by Hammer [30]. There are also a number of DFT studies on the NO dissociation process.

*NO dissociation.* As the first step for NO reduction on transition metals, NO dissociation on a group of surfaces has been investigated by DFT: Pd and Rh surfaces by Loffred *et al.* [50,51]; Rh, Pd, Ru surfaces by Hammer [30,52]; Pt{1 0 0} by Eichler [48,49]; Ir and Pt surfaces by Liu *et al.* [31]. It has been shown that NO dissociation is very similar to other diatomic reactions, such as CO, N<sub>2</sub> dissociation. Two general features for NO dissociation on transition metals can be generalized from these studies.

First, the TS of NO dissociation belongs to *late TS* (FS like). As a result, the reaction barrier of NO dissociation is to a large extent determined by the stability of the FS. This feature has been observed by Hammer [30] for NO dissociation on Ru, Rh and Pd flat surfaces, by Liu and Hu [53] for CO dissociation on Ru{0 0 0 1}, Rh{1 1 1}, Pd{1 1 1}, Os{0 0 0 1}, Ir{1 1 1} and Pt{1 1 1}, and also by Logadottir *et al.* [54] for N<sub>2</sub> dissociation. This feature explains well the general consensus in experiments: from left to right across the Periodic table NO dissociation becomes more and more difficult because the N and O bonding on the metals becomes weaker. Michaleidis *et al.* [55] showed that this FS-stability dependence appears to be quite general for reactions over metal surfaces.

Second, NO dissociation is highly structure sensitive. The stepped, edged or open surfaces are generally much more active than the close-packed flat surface. For example, for NO dissociation on Ru, Hammer [52] showed that the dissociation barrier at the Ru monatomic step is more than 1 eV lower than that at the flat Ru{0 0 0 1}. The understanding of the structure-sensitivity of NO dissociation can be obtained when comparing the TS of NO dissociation on the close-packed flat surfaces and stepped surfaces, as illustrated in figure 5. At the TS on the flat surface, three (or four)

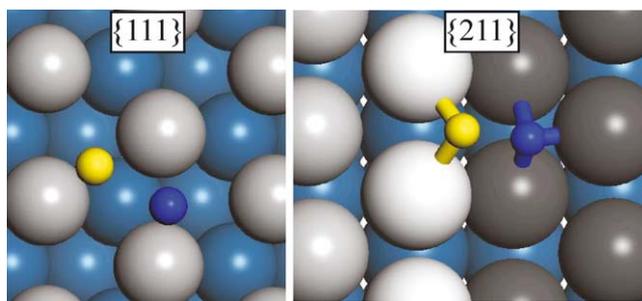


Figure 5. TS structures of NO dissociation on the close-packed {1 1 1} surface and the stepped {2 1 1} surface.

metal atoms are involved in bonding with the N—O TS complex and the N and O share bonding with one metal atom. In contrast, at the TS on the stepped surface, a total of five atoms are involved in bonding with the TS complex and no surface atom bonds simultaneously with the dissociating N and O [36,52]. This indicates that on going from the flat surface to the stepped surface the TS is more stabilized because of the enhanced coordination and non-bonding competition geometry at steps. The structure-sensitivity phenomenon of surface reactions has been put into a more general framework by Liu and Hu [37].

*NO reduction by CO.* NO reduction by CO on transition metals, specifically Rh, Pd and Pt, consists of the following main steps (also see figure. 4): CO and NO adsorption, NO dissociation, N + N → N<sub>2</sub> association, N<sub>2</sub> desorption, CO oxidation and CO<sub>2</sub> desorption. Among these steps, NO dissociation and CO oxidation have been discussed above; and the N<sub>2</sub> association reaction has the similar reaction features to those mentioned above for the NO dissociation reaction. The reactivity is strongly metal-dependent and surface-structure sensitive. On Pt{1 0 0} NO dissociation is rate limiting with an activation barrier of 1.21 eV and N<sub>2</sub> desorption through the N + N → N<sub>2</sub> reaction is an essentially barrierless process [48,49]. On Pd surfaces, both NO dissociation and N<sub>2</sub> association have a barrier more than 1 eV, i.e., 1.6, 1.3 eV on Pd steps, respectively [30]. However, the barriers for these processes on other surfaces, namely Pd{1 1 1}, Pd-edge and Pd{1 0 0} are even higher than those on Pd-steps [30].

*Side-reactions of NO reduction.* Apart from the activity, the selectivity is also important for NO reduction. In fact, the issue of selectivity is of particular importance when dealing with NO reduction under lean-burn conditions where NO<sub>2</sub> and N<sub>2</sub>O production over transition metals is one of the leading problems. Burch *et al.* [56] studied NO + N → N<sub>2</sub>O and NO + O → NO<sub>2</sub> reactions on Pt{1 1 1} at low coverage conditions. The TSs of these two reactions have been found to be similar to those for the CO + O reaction: At the TS, the atomic reactant, N or O is activated to a bridge site and the NO is sitting off an atop site to react with N or O. Burch, Daniells and Hu [56] showed that at low NO coverages, the calculated barriers for these two reactions were 1.78 and 1.52 eV, respectively; at high NO coverages, the barriers were estimated to be around 1.2 and 0.9 eV. They also pointed out that the high barrier of the NO + N → N<sub>2</sub>O reaction is somewhat inconsistent with the experimental finding of the low-temperature N<sub>2</sub>O formation on Pt/SiO<sub>2</sub> (~50 °C) under lean-burn conditions [46]. Several plausible explanations may explain these contradictions: N<sub>2</sub>O formation may readily occur on other surface facets rather than the close-packed Pt{1 1 1}, where barriers of NO dissociation and N<sub>2</sub>O production (NO + N → N<sub>2</sub>O) are both low. Alternatively, N<sub>2</sub>O may be formed through weakly-bounded (NO)<sub>2</sub> dimer at particular sites of Pt surface.

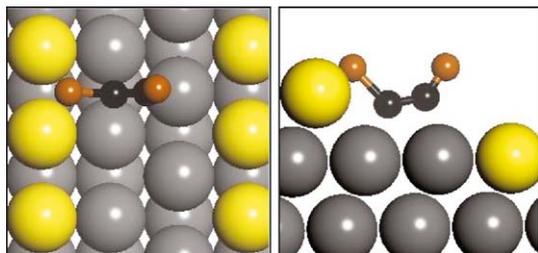


Figure 6.  $(\text{NO})_2$  dimer formation at the  $\text{Pt}\{2\ 1\ 1\}$  step. Left: top view. Right: side view. Starting from this dimer,  $\text{N}_2\text{O}$  can be readily produced with a barrier of only 0.25 eV. Small black atoms are nitrogen, and the small grey atoms are oxygen. From Ref. [57].

Very recently, Burch *et al.* [57] went one step further to investigate  $\text{N}_2\text{O}$  formation on a stepped Pt surface, i.e.  $\text{Pt}\{2\ 1\ 1\}$ . Among a variety of  $(\text{NO})_2$  dimer structures investigated, a possible pathway involving  $(\text{NO})_2$  formation at the terrace near to a Pt step is identified as the possible mechanism for low-temperature  $\text{N}_2\text{O}$  formation, as shown in figure 6. The unique feature of the dimer is that it forms bonding with both lower and upper terrace surface atoms, which gives rise to a reasonably large chemisorption energy, 1.7 eV. Starting from the dimer, it requires an activation energy of 0.25 eV to form a  $\text{N}_2\text{O}$  molecule and an adsorbed O atom at the step-edge of the upper terrace. Because the chemisorbed O will presumably block the sites for the  $\text{N}_2\text{O}$  formation, Burch *et al.* [57] also studied the removal of the step-edge O by  $\text{H}_2$ . The barriers for the O-removal process are around 0.8 eV. It was concluded that  $\text{N}_2\text{O}$  formation may be very facile at Pt surface defects but the consequent removal of O atoms requires higher activation energy. The energetics from DFT calculations appear to be consistent with the experimental observations.

## 5. Concluding remarks

The field of theoretical density functional theory studies on surface chemical reactions is rapidly expanding and developing. This short article serves to summarize current theoretical progress on two key reactions involved in the control of vehicle emissions: CO oxidation and NO reduction on metal surfaces. Because of their fundamental importance and relative simplicity compared to other large molecule surface reactions, the two reactions, in particular CO oxidation, have been extensively studied by DFT calculations.

The key points that this review has highlighted include: (i) mechanisms of CO oxidation on transition metals and the origin of the barrier to CO oxidation; (ii) mechanisms of CO oxidation on transition metal oxides and Au-based catalysts; (iii) mechanisms of NO dissociation on transition metals and NO reduction by CO on transition metals; (iv) many unique features of metal surface reactions (for instance, the early (late) TS of

surface association (dissociation) reactions; the bonding competition effect; surface structure sensitivity). Obviously, there are still many open questions related to these points and they should continue to provide opportunities for fruitful research for many years to come.

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