



# Transition metal doping of Pd(1 1 1) for the NO + CO reaction

Long Zhang, Ivo A.W. Filot, Ya-Qiong Su, Jin-Xun Liu, Emiel J.M. Hensen\*

Laboratory of Inorganic Materials Chemistry, Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands



## ARTICLE INFO

### Article history:

Received 4 March 2018  
Revised 19 April 2018  
Accepted 21 April 2018

### Keywords:

DFT calculation  
NO + CO reaction  
Transition metal doping  
Pd(111)

## ABSTRACT

The replacement of platinum group metals by non-noble metals has attracted significant attention in the field of three-way catalysis. Here, we use DFT calculations to comprehensively study NO reduction by CO and CO oxidation on Pd(111) and transition metal doped Pd(111). Whilst direct NO dissociation is very difficult on metallic Pd(111), doping with transition metals can substantially lower the reaction barrier for NO dissociation. The lowest barrier is predicted for Ti-doped Pd(111). An electronic structure analysis shows that the low barrier is due to the strong adsorption of N and O on surface sites involving Ti atoms. It relates to strong hybridization of the N and O orbitals with the half-filled *d*-band of the metallic surface. At the same time, the anti-bonding states are shifted above the Fermi level, which further strengthens the adsorption of N and O. A Brønsted-Evans-Polanyi relation for NO dissociation on TM-doped Pd(111) surfaces is identified. The complete reaction pathway for N<sub>2</sub>, N<sub>2</sub>O and CO<sub>2</sub> formation on Pd(111) and Ti-doped Pd(111) was considered. Besides more facile NO dissociation, the energy barrier for CO oxidation is decreased for the Ti-doped surface. Microkinetics simulations confirm that the activity and selectivity for NO reduction and CO oxidation are drastically improved after Ti doping. Our findings indicate that doping of Pd with non-noble metal can further improve the performance of three-way catalysts.

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## 1. Introduction

Nitric oxide (NO), carbon monoxide (CO) and unburnt hydrocarbons are major pollutants emitted from automobile exhaust. These toxic gases are harmful to human health and the environment. Therefore, the catalytic removal of these exhaust gases has become an important technology [1,2]. Current three-way catalysts (TWCs) consist of typical platinum-group metals, such as Pt, Pd and Rh, which promote NO reduction and CO and hydrocarbon oxidation reactions [3]. Previous reports showed that the activity of these metals for the NO dissociation differs significantly. In general, Rh and Pt nanoparticles are the more active components for NO reduction in TWCs. Especially Rh-based catalysts can convert NO<sub>x</sub> into N<sub>2</sub> with high activity and selectivity at relatively low temperature [4,5]. Early DFT computations showed that the energy barriers of NO dissociation on Rh(100) and Rh(111) are 0.48 eV and 1.53 eV, respectively. These barriers are much lower than the barrier of 2.44 eV reported for Pd(111) [6]. Eichler and Hafner predicted a barrier of 1.21 eV for NO dissociation on Pt(100) as the rate-limiting step in the NO + CO reaction [7].

While for a long time the combination of Pt and Rh has been utilized to simultaneously reduce NO and oxidize CO [8–11], the high

price of these noble metals has driven research to employ cheaper transition metals (TM). The lower price has been a driver to replace Pt by Pd in TWCs, although recently Pt and Pd prices are comparable Pd-based catalysts have gained wider spread interest from the academic community in recent years [12–15]. The possibility of alloying a noble metal like Pd with cheaper TMs has also been explored. Lopez and Nørskov investigated synergetic effects in CO adsorption on Cu-doped Pd(111) alloys and found that differences in adsorption energies can be correlated to changes in the electronic structure [16]. Yang and co-workers studied NO adsorption and dissociation on neutral and charged TM-doped Pd clusters [17]. Sautet's group investigated the structure sensitivity of NO dissociation on Pd surfaces and computed NO dissociation barriers of 2.44 eV and 1.63 eV for Pd(111) and Pd(100), respectively. NO dissociation on the stepped Pd(511) surface also involved a relatively high barrier of 1.54 eV [6]. The higher barriers for Pd compared to Rh are consistent with the preference to use Rh for achieving good NO reduction activity in practical TWCs.

Selective catalytic reduction (SCR) of NO requires a reductant such as CO, NH<sub>3</sub>, H<sub>2</sub> or C<sub>x</sub>H<sub>y</sub> [18,19]. In the context of TWC, NO reduction with CO or H<sub>2</sub> has been extensively studied [9,10,20,21]. Paredis et al. explored the evolution of the structure and oxidation state of Pd nanoparticles supported on ZrO<sub>2</sub> during NO reduction by H<sub>2</sub> [22]. Liu et al. reported that NO dissociation by H<sub>2</sub> on Pd(111) and their results indicated that the N–O bond

\* Corresponding author.

E-mail address: [e.j.m.hensen@tue.nl](mailto:e.j.m.hensen@tue.nl) (E.J.M. Hensen).

scission can be facilitated via H-assisted reaction pathway, with the activation barrier of 1.58 eV. [23]. Molecular beam studies have also been used to study the NO + CO reaction on Pd(111) [24]. Goodman et al. explored the structure sensitivity of the NO + CO reaction on Pd(100) and Pd(111) [25]. They observed that Pd(111) was about five times more active than Pd(100) for NO + CO reaction. In general, it can be stated that Pd is not active enough for NO dissociation, even in the presence of H<sub>2</sub>. This relates to the weak activation of NO on Pd surface and, possibly, the poisoning effect of N and O atoms produced by NO dissociation [26]. Recent reports provide new directions to the field of TWC [27,28]. Ham and co-authors reported that small Pd ensembles in AuPd alloys facilitate CO oxidation [29]. Cheng et al. found that the activity of AuPd alloys for CO oxidation can be tuned by changing the composition [30]. These results suggest that the CO oxidation activity of Pd can be improved by TM doping. A comprehensive overview of the effect of TM doping on the NO + CO reaction is however lacking.

In this work, we use density functional theory (DFT) calculations combined with microkinetics simulations of the model TWC NO + CO reaction to investigate the influence of TM doping of Pd(111). We use the Pd(111) surface as a reference as it is the dominant surface of Pd nanoparticle catalysts [31,32]. We first investigate the adsorption of atomic and molecular species on Pd(111) and Ti-doped Pd(111), followed by a mechanistic study of direct NO dissociation on various TM-doped Pd(111). A strong Brønsted-Evans-Polanyi (BEP) correlation of the NO dissociation barrier as function of the N and O adsorption energies will be discussed. We computed the complete potential energy diagram for the NO + CO reaction on Pd(111) and Ti-doped Pd(111). The results show that Ti doping not only improves NO dissociation but also facilitates N atom recombination as well as the oxidation of CO with the O atom originating from NO dissociation. Microkinetics simulations revealed that the activity and N<sub>2</sub> selectivity of Pd in the NO + CO reaction can be drastically improved by Ti doping.

## 2. Computational methods

### 2.1. DFT calculations

We performed spin-polarized DFT calculations by using the projector augmented wave (PAW) [33] method as implemented in the Vienna Ab Initio Simulation Package (VASP) [34,35]. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [36] was used. The cut-off energy for the plane-wave basis was set to 400 eV. Partial occupancies were determined by the first-order Methfessel-Paxton scheme with a smearing width of 0.2 eV. The optimized lattice constant of bulk Pd was 3.95 Å, which agrees well with previous results [23,37]. In order to model the Pd(111) surface, we constructed a 2 × 2 unit cell with five atomic layers, giving a slab thickness of 9.15 Å. The top two layers were relaxed and the bottom three layers were frozen to the configuration of the bulk. To evaluate the influence of lateral interactions between periodic images, we calculated for some elementary reaction steps the transition states in a larger 3 × 3 unit cell. The energy difference of computed activation barriers between the 2 × 2 and 3 × 3 unit cells was negligible (*i.e.*, less than 0.01 eV/atom). To avoid spurious interactions of adsorbates between neighbouring super cells, a vacuum thickness of 12 Å was used. A Monkhorst-Pack mesh with a *k*-point sampling of 5 × 5 × 1 was used for the Brillouin zone integration. For the doped Pd(111) model, a Pd atom in the top layer was substituted by a transition metal (TM = Ti, Pt, Fe, Au, Ag, Cu, Ni), resulting in a surface doping content of 25%. The doping of Pd(111) in this way with a TM atom is indicated by TM-Pd(111). To investigate the stability of these TM-Pd(111) surfaces,

we calculated the exchange energy of the doped surfaces (see Fig. S1). It was thus found that the doped TM atoms are strongly bound in the Pd metal surface. It is noteworthy that PdTi alloy with a controllable bimetallic ratio was able to be fabricated via a mild dealloying process [38]. Besides, recent studies show that Pd-based alloys were stable [39,40]. For the Ti and Fe atom, a Hubbard-like term describing the on-site Coulombic interactions was introduced and set to  $U_{\text{eff}} = 4.5$  eV and 4 eV, respectively. This approach was previously reported to provide a better description of localized states for strongly correlated system [41,42]. We also tested the effect of *U* on Ti-doped and Fe-doped system and found that the *U* term has limited influence on energy difference and activation barrier. The systems were assumed to be converged when the Hellmann-Feynman forces were less than 0.05 eV/Å. To study the reaction mechanism, we calculated the location and energy of transition states by the climbing-image nudged elastic band (CI-NEB) method [43,44].

Adsorption energies are computed by

$$E_{\text{ads}} = E_{\text{m} + \text{surf}} - (E_{\text{surf}} + E_{\text{m}}) \quad (1)$$

where  $E_{\text{m} + \text{surf}}$ ,  $E_{\text{surf}}$  and  $E_{\text{m}}$  are the total energies of the adsorbed system, the empty surface and the corresponding gas phase species, respectively. Repulsion was also considered in our study, which is defined as the difference between the total energy of the co-adsorbed species and their corresponding configuration at infinite separation on the catalytic surface.

### 2.2. Microkinetics modelling

Using the stable and transition states identified for the explored reaction mechanisms, we carried out microkinetics simulations to determine the reaction rate and the product distribution. For surface reactions, the computed activation energies are used to estimate the forward and backward rate constant using the Eyring equation:

$$k = \frac{k_{\text{b}} T}{h} \frac{Q^{\text{TS}}}{Q} e^{-\frac{E_{\text{a}}}{k_{\text{b}} T}} \quad (2)$$

Herein  $k$  is the reaction rate constant,  $k_{\text{b}}$  and  $h$  the Boltzmann and Planck's constants, respectively,  $T$  the temperature (in K), and  $E_{\text{a}}$  the electronic activation energy (in J).  $Q^{\text{TS}}$  and  $Q$  refer to the partition functions of the transition state and the ground state, respectively. As an approximation, we assumed that all vibrational partition functions equal unity. This leads to a pre-factor for all surface elementary reaction steps of  $\sim 10^{13} \text{ s}^{-1}$ .

For adsorption reactions, we assumed that the molecule loses one of its translational degrees of freedom with respect to the gas phase. Therefore, the rate for molecular adsorption was defined as:

$$k_{\text{ads}} = \frac{PA'}{\sqrt{2\pi m k_{\text{b}} T}} S \quad (3)$$

where  $P$  is the partial pressure of the adsorbate in the gas phase,  $A'$  the surface area of the adsorption site, and  $m$  and  $S$  the mass of the adsorbate and its sticking coefficient, respectively.

For desorption, we assumed that the activated complex has two translational and three rotational degrees of freedom. Accordingly, the rate of molecular desorption is defined as [45]

$$k_{\text{des}} = \frac{k_{\text{b}} T^3}{h^3} \frac{A'(2\pi m k_{\text{b}})}{\sigma \theta_{\text{rot}}} e^{-\frac{E_{\text{des}}}{k_{\text{b}} T}} \quad (4)$$

where  $\sigma$  indicates the symmetry number,  $\theta$  refers to the characteristic temperature for rotation, and  $E_{\text{des}}$  is the desorption energy.

The details for the microkinetics simulations have been described in our previous work [46,47] and is briefly discussed

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