Transition metal doping of Pd(111) for the NO + CO reaction

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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. At the same time, the anti-bonding states are shifted above the Fermi level, which further strengthens the adsorption of N and O. A Brensted-Evans-Polanyi relation for NO dissociation on TM-doped Pd(111) surfaces is identified. The complete reaction pathway for N2, N2O and CO2 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 NOx into N2 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, NH3, H2 or CxHy [18,19]. In the context of TWC, NO reduction with CO or H2 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 ZrO2 during NO reduction by H2 [22]. Liu et al. reported that NO dissociation by H2 on Pd(111) and their results indicated that the N–O bond...
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 H2. 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 N2 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 x 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 x 3 unit cell. The energy difference of computed activation barriers between the 2 x 2 and 3 x 3 unit cells was negligible (i.e., less than 0.01 eV/atom). To avoid spurious interactions of adsorbates between neighboring super cells, a vacuum thickness of 12 Å was used. A Monkhorst-Pack mesh with a k-point sampling of 5 x 5 x 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 PdTl alloy with a controllable bimetalllic ratio was able to 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 Ueff = 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

\[ E_{\text{ads}} = E_{\text{m ads}} - (E_{\text{surf}} + E_{\text{n}}) \]

where \( E_{\text{m ads}}, E_{\text{surf}} \), and \( E_{\text{n}} \) 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 catayltic 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:

\[ k = \frac{k_b T Q^{TS} \rho}{h Q} e^{-\frac{\Delta E_{TS}}{k_b T}} \]

Herein \( k \) is the reaction rate constant, \( k_b \) and \( h \) the Boltzmann and Planck's constants, respectively, \( T \) the temperature (in K), and \( E_z \) the electronic activation energy (in J). \( Q^{TS} \) 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 \( ~10^{13} \text{s}^{-1} \).

For desorption 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:

\[ k_{\text{ads}} = \frac{PA^2}{\sqrt{2\pi mk_b T}} S \]

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]

\[ k_{\text{des}} = \frac{k_b T^3 A (2\pi m k_b) \sigma}{h} e^{-\frac{\Delta E_{\text{des}}}{k_b T}} \]

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.
here for clarity. For all surface reaction intermediates, the differential equations were constructed by using the rate constants of the elementary reaction steps. For each of the \( M \) components involved in the reaction network, a single differential equation is written as:

\[
    r_i = \sum_{j=1}^{N} k_j v_j \prod_{k=1}^{M} c_k^{v_k} 
\]

where \( k_j \) is the elementary reaction rate constant, \( v_j \) refers to the stoichiometric coefficient of component \( i \) in elementary reaction step \( k \) and \( c_k \) is the concentration of component \( k \) on the reaction surface.

To identify the elementary steps that control the overall reaction rate of the NO + CO reaction, Campbell’s degree of rate control (DRC) analysis \([48–50]\) was used. For a specific elementary step \( i \), the degree of rate control coefficient \( \nu_{RC}^i \) is determined by

\[
    \nu_{RC}^i = \left( \frac{\partial \ln r}{\partial \ln k_i} \right)_{k_j=1} = \left( \frac{\partial \ln r}{\partial \ln k_i} \right)_{k_j=1} 
\]

In the above equation, \( r \) indicates the overall reaction rate and \( k_i \) and \( K_i \) represent the forward rate and the equilibrium constants for step \( i \), respectively.

The DFT-based microkinetics calculations were performed using the MKMCXX program \([51]\). The overall conversion rates of the NO + CO reaction, steady-state coverages and product distribution were computed as a function of temperature by integrating the ordinary differential equations with respect to time using the backward differentiation formula method \([52–54]\).

### 3. Results and discussion

#### 3.1. Atomic and molecular species adsorption on Pd(111) and Ti-Pd(111)

We investigated the adsorption properties of all relevant intermediates in the NO + CO reaction for Pd(111) and Ti-Pd(111) surface models. Table 1 summarizes the adsorption energies and geometries of the relevant reaction intermediates. For Pd(111), NO will bind at fcc and hcp sites (at the N-terminus) with adsorption energies of \(-2.19\) eV and \(-2.17\) eV, respectively. The Pd–N bond length is 2.04 Å for both surfaces. The vibrational frequency of adsorbed NO molecule is 1584 cm\(^{-1}\) at the fcc site with an N–O bond length of 1.21 Å. These values are in good agreement with literature data \([23,55]\). NO adsorption on Ti-Pd(111) was slightly less favourable with values of \(-2.03\) eV and \(-1.95\) eV on fcc and hcp sites, respectively. Correspondingly, the Ti-N bond lengths are somewhat longer: 2.22 Å for the fcc site and 2.12 Å for the hcp site. The corresponding stretching frequency for the NO molecule is around 1533 cm\(^{-1}\) at the fcc site of Ti-Pd(111). Clearly, doping the Pd(111) surface with Ti results in a red-shift of the N–O stretching frequency, indicative of a weakening of the N–O bond with respect to NO adsorbed on Pd(111) and consistent with the

| Reaction species | Configurations | Bond lengths (Å) | \( E_{ads} \) (eV) | \( r \) | \( \partial \ln r \) | \( \partial \ln k_i \) |
|-----------------|----------------|-----------------|-----------------|-------|----------------|----------------|
| NO              | fcc (N-end)    | d(Pd–N) = 2.04  | d(Ti–N) = 2.22  | -2.19 | -2.03          |
| NO1             | hcp (N-end)    | d(Pd–N) = 2.04  | d(Ti–N) = 2.12  | -2.17 | -1.95          |
| \( \text{N}_2 \) | Bridge         | d(Pd–N) = 2.12  | d(Ti–N) = 2.16  | -0.08 | -0.23          |
| \( \text{N}_2 \) | Bridge         | d(Pd–N) = 2.07  | d(Ti–N) = 2.06  | -0.19 | -0.07          |
| N               | fcc            | d(Pd–N) = 1.90  | d(Ti–N) = 1.91  | -4.73 | -4.75          |
| N1              | hcp            | d(Pd–N) = 1.91  | d(Ti–N) = 1.90  | -4.63 | -4.67          |
| O               | fcc            | d(Pd–O) = 2.00  | d(Ti–O) = 1.85  | -4.55 | -5.73          |
| O1              | hcp            | d(Pd–O) = 2.00  | d(Ti–O) = 1.85  | -4.35 | -5.65          |
| CO              | fcc            | d(Pd–C) = 2.12  | d(Pd–C) = 2.05  | -1.63 | -1.57          |
| CO2             | fcc            | d(Pd–C) = 2.13  | d(Pd–C) = 2.06  | -0.03 | -0.71          |

\[ dy/dt = \sum_{i=1}^{N} r_i \]

\[ \nu_{RC}^i = \left( \frac{\partial \ln r}{\partial \ln k_i} \right)_{k_j=1} = \left( \frac{\partial \ln r}{\partial \ln k_i} \right)_{k_j=1} \]

Fig. 1. Potential energy diagram and associated structures for the direct dissociation of NO on Pd(111) and Ti-Pd(111).
increased N–O bond length of 1.22 Å. This result suggests that Ti doping will result in a more facile NO bond dissociation. N₂ binds weakly at the bridge site of Pd(111) (E_ads = −0.08 eV), which is in agreement with previous studies of Huai et al., who calculated an adsorption energy of −0.17 eV [23]. Similar to N₂ adsorption, the N₂O molecule has a small adsorption energy of −0.19 eV. Our calculated adsorption energy is very close to the previous work of Wei and co-workers, who reported an adsorption energy of −0.14 eV [56]. CO prefers to adsorb at an fcc site on oxygen pre-covered Pd(111) and Ti-Pd(111). The adsorption energies are −1.63 eV and −1.57 eV, respectively. The Pd–C bond is 2.12 Å on the Pd (111) surface, which is slightly longer than Ti-Pd(111) (2.05 Å).

Atomic N adsorbs strongly on the metal surfaces. Its adsorption energy, with respect to gaseous N, is −4.73 eV and −4.63 eV at fcc and hcp sites, respectively. The Pd–N bond length is ~1.90 Å. For Ti-Pd(111), N adsorbs even more strongly with energies of −4.75 eV and −4.67 eV, respectively for fcc and hcp sites. For O adsorption, a similar trend was found. For Pd(111), an O atom adsorbs with energies of −4.55 eV and −4.35 eV on fcc and hcp sites, respectively. For Ti-Pd(111), O adsorption is much more

Fig. 2. (a) Partial density of states (PDOS) analysis of N and O in the initial, transition and final states for the NO dissociation on Pd(111). The panels on the left represent to the PDOS of N, and the panels on the right to the PDOS of O. (b) PDOS analysis of N and O in the initial, transition and final states for the NO dissociation on Ti-Pd(111). The panels on the left represent to the PDOS of N, and the panels on the right to the PDOS of O.
exothermic with $-5.73$ eV for the fcc site and $-5.65$ eV for the hcp site. Clearly, the impact of Ti doping is greater for O adsorption than for N adsorption.

3.2. Direct NO dissociation

NO dissociation is an important elementary reaction step in car exhaust clean-up catalysis, as it is a critical step in the overall reaction to reduce NO into $N_2$. We choose NO adsorbed in its most stable adsorption mode as the initial state (IS) for direct NO dissociation, which is in a threefold coordination on a fcc site. In the transition state (TS), the N and O atoms migrate to adjacent bridge sites. In the final state (FS), the N and O atoms are bound in adjacent fcc sites of Pd(111). The reaction barrier for this process is 2.32 eV (Fig. 1) and the reaction is endothermic by 1.12 eV. This calculated energy barrier is very close to previous result [6]. Exploring the same pathway on Ti-Pd(111) resulted in an activation barrier of only 0.65 eV. It is important to mention that this barrier is much lower than previously obtained barriers for NO dissociation on open Pd(100) and stepped Pd(511) surfaces [6].

In order to understand the origin of the enhanced activity towards direct NO dissociation upon Ti doping, the electronic structure of the surfaces was analysed in more detailed by a partial density of states (PDOS) and crystal orbital Hamilton population (COHP) analysis [57,58]. Fig. 2a shows the orbital-resolved PDOS for N and O in the initial, transition and final states. The features in the PDOS were identified by comparison with the PDOS of NO placed in an empty simulation cell (Fig. S2). We will first discuss the PDOS of NO dissociation on Pd(111) and then contrast the insights with corresponding data for Ti-Pd(111).

In Fig. 2a, it can be seen that in the initial state the 5s, 1p and 4s molecular orbitals of NO are respectively located around $7.76$ eV, $8.01$ eV and $13.34$ eV with respect to the Fermi level. In free NO, the 2p orbital of NO is only partially filled, whereas in the adsorbed state it lies far below the Fermi-level (i.e., at $-2.55$ eV). This shows that there is back–donation from the filled d-orbitals of the Pd metal to the partially filled 2p molecular orbital. In the transition state, the N and O atoms are only weakly bound to each other, as can be seen from the disappearance of the 5s and 1p molecular orbitals.

Instead, two p bands appear between $-5.02$ eV and $-7.11$ eV for the N and O atom, respectively. These p bands correspond to the atomic orbitals of N and O. The PDOS for the final state closely resembles the PDOS of the transition state, indicative of a late transition state. This is also apparent from the similar geometries of the transition and final state. The late character of the transition state is further confirmed by the linear coefficient of the BEP analysis (vide infra).

Fig. 2b depicts the PDOS of Ti-Pd(111). As compared to Pd (111), the 5s, 1p and 4s orbitals of molecular NO are shifted towards the Fermi level in the initial state. This is evident from the fact that Ti, a d2 metal, has fewer electrons than Pd, which is a d10 metal. The $p_x$ and $p_y$ orbitals corresponding to the 2π
molecular orbital are more delocalized, which indicates a stronger orbital overlap between NO and the \( d \)-band as well as a stronger back-donation from Ti-Pd(111) as compared to Pd(111). This can be further rationalized by the stronger ability of Ti to accept electrons from the 5\( \sigma \) molecular orbital and consequently to donate electrons in the 2\( \pi \) orbital. Similar to NO dissociation on Pd(111), the PDOS shows that the 5\( \sigma \), 1\( \pi \) and 4\( \sigma \) molecular orbitals disappear in the transition and final state.

To analyse the bonding nature of the different states, a COHP analysis was conducted. In Fig. 3, the Pd–N interaction is shown. It can be seen that there are a number of anti-bonding states close to the Fermi-level for the transition and final states for NO dissociation on Pd(111). In comparison, these states are bonding in nature for Ti-Pd(111). The COHP analysis for the interaction between the next-nearest neighbour Pd atom on the surface and adsorbed N is shown (Fig. S3). Herein, a similar trend is seen, indicating that the adsorption of N atom is strengthened by Ti doping. The same kind of analysis was conducted for the interaction of Pd with O, further confirming the observed trend (Fig. 5). For Pd(111), there are several anti-bonding states around the Fermi-level, whereas for the Ti-doped case, these Ti-O states are bonding. Again, this shows that substitution of a Pd surface atom with a Ti atom results in a stronger interaction between the metal surface and the N and O atoms and in turn this results in a lower activation barrier for NO dissociation.

In Fig. 4, the averaged PDOS of the first atomic layer of the surface is shown. For Pd(111) in the initial state, the majority of the \( d \)-states lie below the Fermi level. For the corresponding Ti-Pd(111) case, a large number of \( d \)-states are located above the Fermi level and are thus empty. These empty \( d \)-states are able to accept electrons and they will, via \( \sigma \)-donation and \( \pi \)-back-donation, weaken the N–O molecular bond. The DOS analyses are consistent with the COHP analyses. Both indicate that Ti doping can effectively modulate the electronic structure of Pd metal surface, which strengthens the back-donation effect and facilitates the NO dissociation.

![Fig. 4. Partial density of states (PDOS) analysis of the first atomic layer in the initial, transition and final states for the NO dissociation on Pd(111) (left panels) and Ti-Pd(111) (right panels).](image)

![Fig. 5. (a) Brønsted–Evans–Polanyi relation for NO dissociation on transition metal surfaces. The energy barrier is linearly related to the NO dissociation energy. (b) The energy barrier is linearly related to the sum of the N and O adsorption energies.](image)
Next, we carried out similar transition state calculations for a wider range of TM-doped Pd(111) surfaces. The activation barrier for direct NO dissociation is plotted against the NO dissociation reaction energy in Fig. 5a. It emphasizes the existence of a BEP relation for NO dissociation with a linear scaling parameter of \( \alpha = 0.86 \). This high BEP value implies that NO dissociation occurs via a late transition state, which is common dissociation reactions \[59\]. The activation barrier depends in a similar manner on the atomic adsorption energy (Fig. 5b). This result is not surprising, as NO adsorption energies are relatively independent of the transition metal dopant. Therefore, the reaction enthalpy is mainly determined by the differences in adsorption energies in the final state. The correlation in Fig. 5b can be used to explore other catalyst compositions without having to explicitly perform a transition state search.

The COHP analysis in Fig. 6 concerns the metal-N interaction, which is presented in descending order of the NO dissociation barrier. It clearly shows that with increasing energy of the anti-bonding states, the metal-atom binding strength increases and the corresponding barrier for NO dissociation decreases. In other words, the anti-bonding states are shifted above the Fermi level, which strengthens the adsorption of the atoms and decreases the reaction barriers.

### 3.3. N\(_2\) and N\(_2\)O formation

After NO dissociation, there are two competing pathways that lead to either N\(_2\) or N\(_2\)O. In the first pathway, two N atoms recombine to form N\(_2\). In the second one, a N atom reacts with an adsorbed NO molecule to N\(_2\)O. In the following, we compare these two reaction routes for N\(_2\) and N\(_2\)O formation on Pd(111) and Ti-Pd(111). In Fig. 7, the reaction energy diagram is shown. The barrier for N + N recombination to form N\(_2\) is 0.99 eV and the process is strongly exothermic by 2.17 eV.

Subsequently, N\(_2\) can readily desorb from the surface as its adsorption energy is only 0.08 eV. The activation barrier for N\(_2\) formation on Ti-Pd(111) is only 0.55 eV; this reaction is exothermic by 2.00 eV. It is noteworthy that this barrier is much lower than the N\(_2\) recombination barrier of 1.60 eV on Pd(100). N\(_2\) adsorsbs slightly stronger on Ti-Pd(111) (0.23 eV) than on Pd(111).

The other product of NO reduction is N\(_2\)O. In order for NO and N to react, they need to migrate to adjacent fcc sites on the surface. This migration is energetically unfavourable and the migration energy with respect to NO and N infinitely far apart is 0.90 eV and 1.09 eV for Pd(111) and Ti-Pd(111), respectively. The energy barriers for the formation of N\(_2\)O by reaction of N + NO on Pd(111) and Ti-Pd(111) are 1.00 eV and 0.77 eV, respectively (Fig. 7). N\(_2\)O desorption is facile in both cases due to its weak binding with the surface. The energy barrier for N\(_2\)O formation is very close to the energy barrier for N\(_2\) formation on Pd(111). On the other hand, the energy barrier for N\(_2\)O formation is much higher than for N\(_2\) formation on Ti-Pd(111). Thus, we infer that Ti doping of Pd will result in enhanced selectivity to N\(_2\) over N\(_2\)O.

### 3.4. CO oxidation on oxygen pre-covered surfaces

Besides N\(_2\) and N\(_2\)O formation, another important pathway is the formation of CO\(_2\). Here, we explored the effect of Ti doping on CO oxidation on oxygen pre-covered Pd(111). In our model (Fig. 8), the initial state is represented by co-adsorbed molecular CO and atomic O on Pd(111). The reaction proceeds through a
transition state with a barrier of 0.92 eV. Herein, the distance between C and O atoms decreases from 2.80 Å to 1.88 Å. In the final state, adsorbed CO2 is formed which is only weakly bound on Pd (111). For oxygen pre-covered Ti-Pd(111), the adsorption energy of CO on the surface is similar to that on Pd(111). In contrast, the bond distance of the C and O atom decreases to 1.79 Å in the transition state. Correspondingly, the energy barrier for CO oxidation is only 0.74 eV. Clearly, the C–O bond on Ti-Pd(111) is much stronger as compared to that on Pd(111). As such, not only NO reduction benefits from Ti doping in Pd, but CO oxidation is also facilitated by it.

4. Microkinetics simulations

In order to gain a detailed insight into the impact of Ti doping on the performance of Pd(111) in environmental catalysis, we carried out microkinetics simulations to compute reaction rates and product distributions. Here, we will discuss the reaction network in more detail in terms of the composition of the adsorbed layer and the degree of rate control as a function of temperature.

Fig. 9 shows that the N2, N2O and CO2 conversion rates are much higher on Ti-Pd(111) than on Pd(111) at relatively low temperatures. The reason for this is the much lower barrier for direct NO dissociation on Ti-Pd(111). Also, the activation barriers for N2, N2O and CO2 formation on Ti-Pd(111) are lower than on Pd (111).

The steady-state surface coverages as a function of temperature are shown in Fig. 10. It can be clearly seen that the Pd(111) is completely covered by NO at low temperature. As NO dissociation proceeds at intermediate temperatures, N2O is produced. At higher temperature, the fraction of free sites increases sharply until the surface is nearly completely empty. For Ti-Pd(111), NO can already dissociate at room temperature, which leads to a high atomic N coverage at relatively low temperature (Fig. 10c). With increasing temperature, N2 is the main product which leads to a decrease of the atomic N coverage at intermediate temperatures. Furthermore, a small amount of atomic O is present at intermediate temperatures. Adsorbed CO can react with atomic O to form CO2, which can easily desorb.

The DRC analysis supports these trends. From Fig. 10b, it can be seen that NO dissociation is the rate-determining step below 750 K for Pd(111). With increasing temperature, both N2O as well as CO2 formation become rate-controlling steps with a similar DRC coefficient (χ = 0.5). For Ti-Pd(111), Fig. 10d shows that NO dissociation controls the overall NO consumption rate at very low temperatures (T < 400 K). With increasing temperature, N2 formation by atomic N recombination becomes the rate-determining step around 600 K.
This result is reflected in Fig. 9a, wherein it can be seen that the rate of $\text{N}_2$ formation is significantly higher for Ti-Pd(111) as compared with Pd(111). At the highest temperature on both surfaces, CO$_2$ formation and $\text{N}_2$ formation become rate-controlling steps as the temperature is sufficiently high that all previous elementary reaction steps pose no longer a kinetic barrier.

In terms of selectivity, $\text{N}_2$ is formed on Ti-Pd(111) at a much higher rate than $\text{N}_2\text{O}$. In other words, the pathway for NO reduction to $\text{N}_2$ is kinetically more favourable on Ti-Pd(111). This can be clearly seen in Fig. 11, wherein the selectivity as a function of temperature is depicted. At low temperature, $\text{N}_2\text{O}$ is the dominant product of NO reduction. However, the main production switches...
to N₂ at high temperatures. In Fig. S5, plots of the degree of selectivity control (DSC) for N₂ and N₂O as a function of temperatures for the Pd(111) suggest that elementary steps of N₂ and N₂O formation control the product selectivity at high temperature. For Ti-Pd(111), the DSC analysis for N₂ and N₂O formation indicates that the selectivity of N₂ is determined by NO dissociation and N atom recombination, while the reaction of N + NO controls the selectivity of N₂O at low temperatures (Fig. S6). Thus, the very high selectivity of N₂ on the Ti-doped surface can be attributed to the low energy barrier for NO dissociation and N atom recombination.

In summary, from our microkinetics simulations it is clear that under typical reaction conditions, the Ti-Pd(111) surface is much more active as well as selective towards N₂ formation as compared to pristine Pd(111). The dominant contributor to this enhanced activity is the very low NO dissociation barrier on Ti-Pd(111) as is evident from the DRC analysis. Whereas this elementary reaction step is rate-determining over a relatively large temperature range for Pd(111), it is only moderately rate-controlling for Ti-Pd(111).

5. Conclusions

We have investigated the thermodynamics and kinetics of all elementary reaction steps relevant to NO + CO reaction on pristine and Ti-doped Pd(111) using DFT calculations and used these data to predict reaction rate and product distribution in microkinetics simulations. Direct NO dissociation faces high activation barriers on Pd(100) and Pd(111). Ti-doping of Pd(111) results in a strong decrease of the NO dissociation barrier to 0.65 eV. DOS and COHP analyses show that Ti-doping changes the electronic structure such that N and O atoms binds strong, explaining the lower barrier for NO dissociation. This fact is further reflected by a BEP relation showing that the transition state is late and stabilization of dissociated N and O thus facilitates a decrease of the reaction barrier. The mechanism of N₂, N₂O and CO₂ formation is explored on Pd(111) and Ti-Pd(111). The energy barriers for the N + N and CO + O association on the Ti-doped surface are also lower than on the Pd(111) surface. Microkinetics simulations show that NO already can be dissociated at room temperature on Ti-Pd(111) which leads to much higher overall reaction rates at low temperatures. In addition, the rate-determining step for NO + CO reaction is identified. At low temperatures, the NO dissociation controls the overall reaction rate on both unpromoted and Ti-doped Pd surfaces. Importantly, our findings indicate that the activity and selectivity can be drastically improved by non-noble transition metal doping and point out a very promising way to design the Pd-based three-way catalysts.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcat.2018.04.025.

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