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# NO<sub>x</sub> Reduction at Near Ambient Temperatures and Under Lean-Burn Conditions on Modified Pd Surfaces

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Palladium surfaces that are modified with O atoms in the subsurface broaden the NO reduction temperature regime up to 325 K with O<sub>2</sub>-rich NO+H<sub>2</sub>+O<sub>2</sub> compositions. Compared to virgin Pd surfaces, up to 150% higher deNO<sub>x</sub> catalytic activity was observed with modified Pd surfaces at the reaction maximum. Molecular beam instrument and ambient-pressure photoelectron spectroscopy were employed to follow the kinetic and surface changes. These results open up a possibility to realize the cold-start reduction of  $NO_x$  (de $NO_x$ ). De $NO_x$  activity reported in the literature with supported Pd catalysts after a simple calcination in air compares well with our present observations. Surface modification is likely to demonstrate a high potential for other catalytic reactions at relatively low temperatures.

#### Introduction

The aim of the three-way catalytic (TWC) converter used in automobiles is to convert pollutants (NO<sub>xr</sub> CO, hydrocarbon (HC)) to benign gases, such as N<sub>2</sub> and H<sub>2</sub>O. Modern internal combustion engines works at a high air/fuel ratio, which is significantly higher than the stoichiometric value (14.6).<sup>[1,2]</sup> The predominant challenge is the reduction of NO<sub>x</sub> (deNO<sub>x</sub>) under leanburn (O<sub>2</sub>-rich or fuel-lean) conditions. Recently, H<sub>2</sub>-selective catalytic reduction (SCR) has become of interest for deNO<sub>x</sub>. H<sub>2</sub>-SCR is a green method, as it generates only N<sub>2</sub> and H<sub>2</sub>O, and it has technological potential, as H<sub>2</sub> is available in many post-combustion methods. H<sub>2</sub> can be generated in diesel engines by the autothermal reforming of diesel.<sup>[3]</sup> The above points encourage H<sub>2</sub>-SCR for on-board deNO<sub>x</sub> in automotive engines and for static applications.

Rh is better known than Pd for NO reduction to N<sub>2</sub>; however, Rh forms irreversible oxides under net oxidizing conditions, whereas Pd shows more O<sub>2</sub> tolerance. This promotes Pd-based TWC converters over Rh/Pt-based versions.<sup>[4]</sup> Indeed, the kinetics and mechanism of NO reduction reactions on Pd single crystals have been investigated by a surface science approach,<sup>[5–7]</sup> and typical heterogeneous catalysis on supported Pd catalysts lead to better deNO<sub>x</sub>.<sup>[8–13]</sup>

The most critical step in NO reduction is the dissociation of NO. Molecular NO adsorption was observed up to 400 K, above which NO dissociates into N and O atoms on Pd-based

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catalyst.<sup>[6,7]</sup> Dhainaut et al.<sup>[8]</sup> demonstrate that in the absence of O<sub>2</sub>, the dissociation of NO<sub>ads</sub> species is assisted by chemisorbed H atoms on Pd/Al<sub>2</sub>O<sub>3</sub>; however, NO decomposition is not favored in the presence of O<sub>2</sub> as H atoms are preferentially consumed by O atoms. Between the two reaction pathways, NO+H<sub>2</sub> and H<sub>2</sub>+O<sub>2</sub>, the latter being faster,<sup>[9]</sup> the effect of oxygen is detrimental on the overall NO+H<sub>2</sub>+O<sub>2</sub> reaction. Pd/ W/ZrO<sub>2</sub> shows a high efficiency with 96% N<sub>2</sub> selectivity but only between 393-453 K.<sup>[13]</sup> However, Wen<sup>[11]</sup> has shown that the inhibition of O<sub>2</sub> on NO reduction at 373 K on Pd/MFI is not significant, and shows activity onset from 350 K. Apparently, there are two NO conversion maxima observed over Pd/TiO<sub>2</sub> at 390 and 510 K.<sup>[9,10]</sup> It is clear that the chemical and electronic nature of the active catalyst together with the nature of the support decide the reaction pattern/mechanism. A careful look at the literature<sup>[8-13]</sup> reveals that, in general, two different pretreatments were performed. Calcination in air at 773 K, as pretreatment, leads to two maxima for NO reduction at 390 and 510 K on Pd/TiO<sub>2</sub><sup>[9,10]</sup> or activity onset from 350 K on Pd/ Al<sub>2</sub>O<sub>3</sub>,<sup>[11,12]</sup> whereas pre-reduced catalysts show an activity onset around 380 K.<sup>[8]</sup> In particular, it is essential to isolate the role of the active Pd species to understand the fundamental aspects and to develop a better catalyst. To the best of our knowledge, there is no report available on the  $NO+H_2+O_2$  reaction on Pd(111) surfaces. We address NO reduction in the presence of  $H_2+O_2$  under net oxidizing conditions on Pd(111) and modified Pd(111) surfaces, which represent Pd<sup>0</sup> and mildly oxidized Pd (Pd<sup> $\delta+$ </sup>), respectively, to simulate the pretreatment conditions employed for supported catalysts by many researchers.<sup>[8-13]</sup>

### **Results and Discussion**

All kinetic experiments reported here for  $NO+H_2+O_2/Pd(111)$  surfaces were performed in a manner identical to that reported in our earlier publications.<sup>[14,15]</sup> Kinetic measurements were per-

formed between 325 and 700 K on virgin and O<sub>2</sub>-pretreated Pd(111) surfaces by using a home-built molecular beam instrument (MBI). Control experiments were measured with a combination of labeled reactants (<sup>15</sup>NO, <sup>18</sup>O<sub>2</sub>, D<sub>2</sub>) to measure the contribution from different overlapping mass species, such as NH<sub>3</sub> (<sup>15</sup>ND<sub>3</sub>, ND<sub>3</sub>, <sup>15</sup>NH<sub>3</sub>, and NH<sub>3</sub>). Nevertheless, all the reactions are mentioned as NO + H<sub>2</sub> + O<sub>2</sub>, and the reactant ratio is denoted as *x*:*y*:*z* in the same order. Ambient-pressure photoelectron spectroscopy (APPES)<sup>[16]</sup> was employed to show the changes in the surface characteristics as a result of O<sub>2</sub> dosing on Pd surfaces.



**Figure 1.** a) Kinetic data for NO+2H<sub>2</sub>+O<sub>2</sub>/Pd(111) as a function of temperature and b) time evolution of different mass signals (28, 32, 36, 44, 46, and 48 amu) after dosing <sup>18</sup>O<sub>2</sub> on Pd(111) surfaces at 900 K for 20 min followed by H<sub>2</sub> titration at 525 K and then the H<sub>2</sub>+<sup>16</sup>O<sub>2</sub> (1:1) reaction at 500 K. Shutter close and open operations are shown by upward and downward arrows, respectively. TPD was performed after the reaction was completed. The N<sub>2</sub> and H<sub>2</sub>O, and NH<sub>3</sub> and N<sub>2</sub>O signals in panel a were multiplied by two and four, respectively. c) The surface modification procedure is depicted schematically to show the diffusion of <sup>18</sup>O (red solid circles) in subsurface layers; virgin and surface modification is indicated by yellow and dark grey to denote the Pd<sup>0</sup> and oxidized Pd<sup>0+</sup>, respectively. H<sub>2</sub> oxidation was performed with <sup>16</sup>O<sub>2</sub> to produce H<sub>2</sub>O exclusively without any <sup>18</sup>O; this demonstrates that the subsurface layers.

As an example of the results obtained, Figure 1 a shows the raw data for the  $NO + H_2 + O_2$  (1:2:1) beam composition reaction on a Pd(111) surface. The initial reaction temperature was set at 400 K, and the reaction rate was measured in the steady state, which is normally reached in 60 s. Subsequently, the temperature was increased by 50 K, and the rate was measured; this step was repeated up to 700 K. The steady-state rate was measured by closing/opening the shutter deliberately. As a result of this oscillation, a definite increase (decrease) in

the  $H_2^{18}O$  (20 amu) signal showed no change in intensity. This directly demonstrates that the subsurface oxygen does not diffuse out during the reaction, at least below 900 K. However,  ${}^{18}O_2$  desorbs at 1050–1200 K, and a small amount of  ${}^{18}O$ -containing species ( $H_2^{18}O$  and  $C^{18}O$  (not shown)) desorb between 900 and 1000 K in the temperature-programmed desorption (TPD) experiment. A minor amount of CO is a result of the interaction of carbon impurities that segregate from the bulk to

the reactants (products) partial pressure occurs, which gives the rate of reaction after calibration with pure gas components.<sup>[14,15]</sup> A marginal increase in product formation at 450 K indicates the reaction onset, and no activity was observed below 450 K. Details on the MBI and APPES are available in the Supporting Information, and the experimental procedure and rate calculation are given in the Experimental Section.

The interaction of  $O_2$  with Pd(111) under conditions that varied widely suggested the formation of different phases of oxide (oxide on the surface and subsurface, metastable oxides, and bulk oxides).<sup>[17-20]</sup> Earlier reports from our group<sup>[19]</sup> have

shown kinetic evidence of subsurface oxygen in Pd(111), which influences CO oxidation. The effect of subsurface oxygen is interesting because it changes the electronic nature of the surface, which in turn changes the charge-transfer features and hence the adsorption characteristics.<sup>[17-20]</sup> A simple heat treatment to 1200 K desorbs the subsurface oxygen to bring back the original surface.[18, 19] To understand the effect of subsurface oxygen, we performed the  $NO+H_2+O_2$  reaction on Pd(111) after populating oxygen in the Pd(111) subsurface (referred to as M-Pd(111)). The Pd(111) subsurface was populated with oxygen by dosing <sup>18</sup>O<sub>2</sub> at 900 K for 1200 s (Figure 1b). This was followed by H<sub>2</sub> titration at 525 K, and then the  $H_2 + {}^{16}O_2$  (1:1) reaction was measured at 500 K. There is a clear uptake of <sup>18</sup>O<sub>2</sub> at 900 K indicated by a decrease in the partial pressure at the initial shutter opening at t = 15 s. After the <sup>18</sup>O<sub>2</sub> dosage, no H<sub>2</sub>O production was observed during H<sub>2</sub> titration, which rules out the possibility of any surface-chemisorbed <sup>18</sup>O. In the subsequent  $H_2 + {}^{16}O_2$ reaction the on M-Pd(111) surface, only H<sub>2</sub>O (18 amu) was observed, whereas

surface, and some hydrogen diffusion into the subsurface desorbs as water.

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The surface modification changes observed in Figure 1 b are represented schematically in Figure 1 c. Oxygen in the subsurface is retained within and does not participate directly in the reaction. However, it influences the electronic state of the surface layers to give partially oxidized  $Pd^{\delta+}$  from the initial zerovalent  $Pd^0$  state. The chemisorption of various reactants is influenced significantly by the partially oxidized surfaces. These modified surfaces have been utilized to perform deNO<sub>x</sub> reactions to demonstrate the influence of surface modification. Below 1000 K, subsurface oxygen stays within the subsurface layers and influences the electronic nature of the surface without taking part in the catalysis reaction. Notably, the surface-chemisorbed oxygen desorbs at around 750 K, and O<sub>2</sub> uptake at 900 K testifies the diffusion of atomic oxygen into subsurface layers of Pd.<sup>[18-20]</sup>

We explored NO reduction as a function of temperature and the NO+ $H_2$ + $O_2$  ratio on Pd(111) and M-Pd(111) surfaces, and the results are shown in Figure 2 for a virgin Pd(111) surface



**Figure 2.** A comparison of NO+H<sub>2</sub>+O<sub>2</sub> reactions performed on a) virgin Pd(111) and b–d) surface-modified Pd(111) between 700 and 325 K. Surface modification was performed by the first part of the oxygen-dosing experiment shown in Figure 1 b, which induces low-temperature activity closer to ambient temperatures. Reactions were preformed from low to high temperature and vice versa, and no significant difference or hysteresis was observed between them. Indeed, the results shown in panel a were obtained by performing the modification from low to high temperature, but the plot is reversed for comparison. The *y* axis is the same in all panels.

with 1:1:1 composition and on M-Pd(111) surfaces with 1:1:1, 1:1:2, and 1:1:3 ratios. The following points summarize the important findings from these results: 1) virgin Pd(111) surfaces show a NO decomposition onset at 450 K (as shown in Figure 1a) and N<sub>2</sub> and N-containing product formation activity at and above 500 K. A small amount of water production was observed under steady-state conditions above 400 K (Figure 2a). 2) A 1:1:1 ratio on M-Pd(111) surfaces shows an extended activity with a characteristic change in the product pattern and

for cold deNO<sub>x</sub> conditions. Highlights of the results are as follows: (a) Although the steady-state rate of N<sub>2</sub> production is low  $\leq$  375 K, highly selective N<sub>2</sub> formation is observed on M-Pd(111) surfaces. This observation is interesting as it demonstrates the NO dissociation closer to ambient temperatures and without any NH<sub>3</sub> production in the presence of excess oxygen. It is very likely that NO molecules compete more strongly for adsorption sites than oxygen, and the surface may be effectively dominated by NO+H<sub>2</sub> (vide infra, Figure 5).

enhanced activity. N<sub>2</sub> and N<sub>2</sub>O were observed under steadystate conditions at and above 400 K. Only a marginal amount of NH<sub>3</sub> was observed. A small amount of water formation was observed under steady-state conditions up to 325 K. The enhancement in the overall rate of reaction is evident from the formation of a large quantity of products. However, the reaction maximum has shifted to 500-550 K (Figure 2b) from 550-600 K on virgin Pd(111) surfaces (Figure 2a). 3) The 1:1:2 and 1:1:3 ratios on M-Pd(111) surfaces show the maximum  $N_2$  formation at 450 and 375–425 K, respectively. Further  $\mathsf{N}_2$  and  $\mathsf{H}_2\mathsf{O}$ production is extended up to 325 K in the latter case. In spite of a decreasing flux of NO ( $F_{NO}$ ) from 33.3 (1:1:1) to 20% (1:1:3) with a concurrent increase in  $F_{0,}$  to 60% at a 1:1:3 composition, a sustainable NO reduction observed close to ambient temperatures is appealing. A concurrent increase in the partial pressure of H<sub>2</sub>O and N<sub>2</sub> well above the steady-state pressure values at the point of shutter opening at 350 and 325 K (shown in the dashed box) demonstrates sustainable NO dissociation. Notably, the high-temperature activity at 700 K is re-

duced significantly in both cases compared to virgin Pd(111)

surfaces (Figure 2a). In spite of the decreasing  $F_{NO}$ ,  $N_2O$  formation was observed, but NH<sub>3</sub> production remains at marginal levels. In general, the selectivity of  $N_2$ ,  $N_2O$ , and  $NH_3$  is 76±5,  $16\pm5$ , and  $5\pm5\%$ , respectively, at the reaction maximum. N2 produced exclusively was  $\leq$  375 K on M-Pd(111) with an O<sub>2</sub>-rich mixture. These catalytic runs were repeated at least fifty times to demonstrate the true influence of the modified Pd surface for NO decomposition at ambient temperatures. These observations also support our conclusions that subsurface oxygen does not participate in the reaction directly, which would otherwise make the lowtemperature activity disappear.

The steady-state rate values reported in Figure 3 follow the above trend for different compositions. Rate values, especially, those observed at low temperatures (Figure 3), are very relevant

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production shows a similar trend as that of N2. It is also known that supported catalysts show a decrease in NO dissociation activity if CO<sub>2</sub> or water is added to the reactants.<sup>[2,21]</sup> We simulated this condition by adding 2% CO<sub>2</sub>, and the results show hardly any effect on NO dissociation (Figure S1). It is likely that the support and metal-support interaction play a significant role to influence the NO dissociation activity in the presence of CO<sub>2</sub>/ H<sub>2</sub>O; however, this aspect is beyond the scope of this study.

To investigate the influence of precalcination or preoxidation treatments of Pd, the oxidation state of Pd was measured by





**Figure 4.** Pd 3d core-level photoelectron spectra recorded at different partial pressures of O<sub>2</sub> by using the APPES system. The intensity of the Pd  $3d_{5/2}$  core level is normalized to that of the clean Pd surface. The inset shows the deconvolution that shows the presence of Pd<sup>0</sup>, Pd with subsurface oxygen (Pd<sub>x</sub>O<sub>y</sub>), and PdO. Peak fitting parameters are given in the Supporting Information.

(b) M-Pd(111) shows a higher N<sub>2</sub> production rate values than Pd(111) surfaces and extended activity at lower temperatures (up to 375 K) with a 1:1:1 reactant composition. (c) 1:1:2 and 1:1:3 compositions exhibit N<sub>2</sub> production up to 350 and 325 K, respectively. Moreover, the NO content decreases with increasing O<sub>2</sub> content in the reaction mixture. A relatively steep decrease in N<sub>2</sub> production at  $T \ge 550$  K with a 1:1:3 composition, compared to that of other compositions, is likely because of the onset of Pd<sub>x</sub>O<sub>y</sub> formation. (d) NH<sub>3</sub> production shows a complex trend. A 1:1:3 (1:1:2) composition shows the maximum (minimum) NH<sub>3</sub> production at temperatures >425 K; a 1:1:1 composition shows a similar trend on Pd(111) and M-Pd(111), except for a shift to low temperatures with the latter. (e) N<sub>2</sub>O

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**Figure 5.** Reactant uptake under steady-state reaction conditions measured for the reaction shown in Figure 2c with a 1:1:2 composition between 500 and 325 K. The shutter close and open operations are shown by dashed and dotted lines. Sustainable NO and H<sub>2</sub> adsorption was observed at lower temperatures, whereas no O<sub>2</sub> adsorption was observed.

X-ray photoelectron spectroscopy (XPS). APPES measurements were performed on Pd(111) and polycrystalline Pd surfaces at 573 K in the presence of  $O_2$  at different pressures, and the results are shown in Figure 4. There is evidence for changes in the nature of Pd surfaces owing to their interaction with oxygen. Our results on the Pd(111) surface are in good agreement with those of Ketteler et al. and Teschner et al.<sup>[17]</sup> and hence will not be discussed further. APPES results obtained on polycrystalline Pd surfaces are directly relevant to real-world

Pd-based catalysts as both surfaces are similar in terms of the variety of defects and multiple adsorption sites and hence the results can be correlated directly rather than compared to those of a single crystal.

The spectrum obtained on clean polycrystalline Pd shows a typical metallic  $Pd3d_{5/2}$  feature at 335.0 eV. In the presence of  $O_2$  up to 0.2 mbar and 573 K, the  $Pd3d_{5/2}$  core level shows a broadening at 335.7 eV attributed to Pd<sub>x</sub>O<sub>y</sub>. However, on increasing the pressure to 0.3 mbar, a distinct shoulder appears at 336.5 eV that then grows into a full peak, which is attributed to PdO.<sup>[22]</sup> In addition to metallic Pd, both of the above features at 335.7 and 336.5 eV<sup>[17]</sup> are present, which is evident from the deconvolution shown in Figure 4 (inset). It is also clear that PdO grows at the expense of metallic Pd. A further increase in O<sub>2</sub> pressure and/or temperature increases the surface concentration of PdO. These results compare well with those of Ketteler et al.<sup>[17]</sup> on Pd(111) at 0.35 Torr and 660 K. The defects present on polycrystalline Pd surfaces enhance oxygen diffusion and hence PdO was facilitated under less severe conditions.<sup>[19]</sup> Notably, the intensity of the valley between the metallic Pd and PdO features decreases with increasing O<sub>2</sub> pressure, which demonstrates the coexistence of three surface components (Pd, Pd<sub>x</sub>O<sub>y</sub> and PdO) under the present experimental conditions. However, NO reduction reactions measured on PdO-dominated surfaces show a much lower NO conversion, which indicates the inactive nature of the surface. A simple reduction treatment of Pd surfaces in  $H_2$  at 0.1 mbar and 573 K, exposed previously to 0.6 mbar  $O_2$  at 573 K (Figure 4), reduces only the surface PdO feature to metallic Pd; indeed, the spectrum recorded after the reduction treatment is the same as that of the Pd surface treated with 0.2 mbar O<sub>2</sub> at 573 K. This highlights that the surface modification that results from subsurface oxygen is retained, even in the presence of hydrogen, under the APPES and reaction conditions in the MBI. Our results shown in Figure 1b are in full agreement with the above results and increase the reliability of the correlation.

It is worth noting an observation made by Wen:<sup>[11]</sup> a preoxidized Pd/MFI catalyst in O2 at 773 K was evaluated for NO reduction with H<sub>2</sub> at 373 K and compared with that of the same material after H<sub>2</sub> reduction at 573 K. The reduced Pd/MFI shows NO conversion from the beginning, whereas the NO conversion gradually increases with the preoxidized catalyst and shows a similar activity to that of reduced Pd/MFI after approximately 60 min. Although there is no mention of oxygen diffusion into Pd subsurfaces in Ref. [11], this is inevitable under atmospheric pressure and 773 K. Pre-reduction converts the surface PdO to Pd, which also happens under NO+H<sub>2</sub> reaction conditions on a preoxidized catalyst to result in a gradual improvement in activity. However, we believe that the high deNO<sub>x</sub> activity observed at 373 K is likely because of modified surfaces, similar to the concept proposed in this report. Nevertheless, more work on supported catalyst systems is required regarding surface modification and correlation with low-temperature deNO<sub>x</sub> activity.

The results shown in Figures 2–4 explain the importance of surface modification through oxygen diffusion as well as the contradictory results<sup>[8–13]</sup> observed for the NO+H<sub>2</sub>+O<sub>2</sub> reaction

on supported Pd catalysts. A small amount of Pd ( $\leq$  1 wt%) on any support is likely to be in the nanoparticulate form with a high defect density. Oxygen diffusion into the subsurfaces of Pd particles is easily possible at moderate temperatures around 573 K, which will modify the surface as a result of calcination in air. However, the pre-reduced catalyst exhibited a metallic Pd character, which is different from the catalysts that are pre-calcined in air or pre-oxidized. When the reactions were measured on surfaces with different oxidation states, they show different activity because of changes in the electronic structure and hence the interaction with reactants. In any case, chemisorption involves charge transfer and this is severely influenced by the surface electronic structure and hence the subsequent catalysis. A correlation between NO reduction activity and surface electronic structure reveals that the M-Pd(111) surface is partially oxidized, which decreases the surface electron density. Oxygen atoms that are diffused into the subsurface layers interact with Pd to form  $Pd_xO_y$  (x > y). A significant amount of electron density is transferred from Pd to oxygen to form Pd<sub>x</sub>O<sub>y</sub> which in turn decreases the overall electron density of surfaces. Electron-deficient M-Pd surfaces enhance NO dissociation at the cost of O<sub>2</sub> adsorption below 400 K. This is further confirmed from the analysis of reactant adsorption below 400 K. The adsorption of reactants under steady-state conditions between 500 and 325 K for the results reported in Figure 2c with a 1:1:2 composition are shown in Figure 5. The adsorption of all reactants can be seen clearly between 375 and 500 K through an increase (decrease) in the partial pressure for shutter-closed (open) operations. However, below 375 K, no O<sub>2</sub> adsorption could be observed, even though there is plenty of O<sub>2</sub> available in the gas phase; whereas sustainable NO and  $\mathrm{H}_{\mathrm{2}}$  adsorption was observed even at 325 K. Indeed, this supports a cationic M-Pd(111) surface that hinders oxygen adsorption as the electron-donating capacity of the cationic surface decreases considerably. A simple comparison of reactants adsorption at a reaction maximum (500 K) and <400 K demonstrates that only the NO+H<sub>2</sub> reaction occurs in the latter, even though oxygen makes up 50% of the reactant content in the gas phase (Figure 5).

### Conclusions

NO conversion to innocuous  $N_2$  with increasing efficiency under net oxidizing conditions will be attempted as long as gasoline/diesel-driven vehicles and power-plants exist. A potential remedy for this problem by the surface modification of Pd is suggested by minimizing oxygen adsorption under net oxidizing conditions. Indeed, fine tuning of the pretreatment of Pd-based supported catalysts in air/O<sub>2</sub> could show improved deNO<sub>x</sub> activity in an O<sub>2</sub>-rich environment under ambient conditions. This aspect needs to be evaluated carefully. A simple change in the surface modification that could broaden the catalytic activity regime, especially towards lower temperatures, has been demonstrated. Although it is demonstrated here for NO reduction, similar surface modification is very likely to broaden the catalytic activity regime,<sup>[19]</sup> especially towards ambient temperatures and it is worth exploring for different catalytic reactions.

## **Experimental Section**

All kinetic measurements were performed by using a home-built MBI using an effusive mixed molecular beam. The detailed description of the set up can be found in the Supporting Information and in our earlier reports.<sup>[14-15]</sup> Isothermal kinetic experiments with  $NO+H_2$  and  $NO+H_2+O_2$  were conducted on clean Pd(111) surfaces between 400 and 700 K and on a modified (subsurface populated with oxygen) Pd(111) surface between 325 and 700 K with xNO:yH<sub>2</sub>:zO<sub>2</sub>; hereafter x:y:z represents the composition of the respective individual components varied from x = 1, y = 1-2, and z =0-3. Different steps involved in most of the experiments can be elaborated with reference to Figure 1a: (1) First the temperature of the crystal is set at 400 K. At t = 10 s, a molecular beam of a mixture of reactants was turned on with the shutter in the intercepting position. This leads to an immediate increase in the reactant partial pressure. As the shutter is in the intercepting position the beam cannot react directly with Pd(111), but some adsorption from the background cannot be avoided at this stage. (2) The shutter was removed at t = 15 s. The reactant beam can then directly react with Pd(111) kept at 400 K. A clear decrease in the partial pressure of the reactants (NO, H<sub>2</sub>, and O<sub>2</sub>) was observed, which indicates the adsorption of the reactants on Pd(111). An increase in the partial pressure of the products N<sub>2</sub> (28 amu), H<sub>2</sub>O (18 amu), NH<sub>3</sub> (17 amu), and N<sub>2</sub>O (44 amu) indicates their evolution. The system was allowed to evolve until a steady state was reached, which generally occurred within 60 s of unblocking the beam under the experimental conditions employed here. The period from the unblocking of the beam to when the steady state was reached is termed as the transient state (TS). (3) In the steady state, the rate of the reaction can be measured by shutter operation (deliberately blocking the shutter for  $\approx$  30 s) for the particular temperature (t =120–150 s for 400 K). (4) After the shutter operation for a given temperature was performed, the crystal was quickly heated to the next temperature, and the system was allowed to reach steadystate conditions to measure the rate at the next temperature. This procedure was repeated for several temperatures up to 700 K in this example. (5) Finally the beam was turned off at t = 900 s (Figure 1 a). After the pressure of the ultra-high vacuum (UHV) chamber reached the initial background level, the TPD of all the relevant species was recorded.

The partial pressures of the different gases were then converted into reaction rates by following a calibration procedure described in our earlier publications.<sup>[14–19]</sup> As an example of these calculations, Figure 6 displays the temporal evolution of the (calibrated) reaction rates for all the products and reactants during the steadystate part of the experiment performed at 600 K with a 1:2:1 NO + $H_2 + O_2$  beam composition. The rate of NO uptake (0.041 ML s<sup>-1</sup>) is almost equal to that of all N-containing products. Similarly, the rate of oxygen adsorption and generation from NO is equal to its consumption through water formation, within the experimental error limit. The formation of one N<sub>2</sub> molecule requires the dissociation/ conversion of two NO molecules, which also applies to N<sub>2</sub>O; hence the rate values for N<sub>2</sub> and N<sub>2</sub>O were multiplied by two to account for the NO conversion and, similarly, the H<sub>2</sub> and O<sub>2</sub> adsorption. The proportions expected from the stoichiometry of the overall reaction are maintained within the experimental error limits. This stoichiometry was found to hold for most of the reaction conditions used in our experiments, especially below 600 K.



**Figure 6.** Steady-state rate  $[MLs^{-1}]$  calculation for the data collected at 600 K shown in Figure 1 a. The rate of NO adsorption is equal to the sum of all N-containing products. Similarly, the rate of oxygen adsorption (from O<sub>2</sub> and NO) is equal to that of its consumption through water formation.

APPES<sup>[16]</sup> was employed to show the changes in surface characteristics as a result of O<sub>2</sub> dosing on Pd surfaces. A description of APPES is available in the Supporting Information as well as in our earlier publication.<sup>[16]</sup>

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