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Catalytic Reduction of NO₂ with Hydrogen on Pt Field Emitter Tips: Kinetic Instabilities on the Nanoscale[†]

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The catalytic reduction of NO_2 with hydrogen on a Pt field emitter tip is investigated using both field electron microscopy (FEM) and field ion microscopy (FIM). A rich variety of nonlinear behavior and unusually high catalytic activity around the {012} facets are observed. Our FEM investigations reveal that the correlation function exhibits damped oscillations with a decaying envelope, showing that molecular noise will influence the dynamics of the oscillations. The dependence of the oscillatory period on the $P_{\rm H_2}/P_{\rm NO_2}$ pressure ratios is analyzed. Similar patterns are reported under FIM conditions. Corresponding density functional theory (DFT) calculations for the adsorption of NO2 on Pt{012} in the presence of an external electric field are performed in order to gain an atomistic understanding of the underlying nonlinear phenomena.

1. Introduction

The size and shape of nanoparticles can be adjusted by colloidal preparation techniques so as to control the reaction sensitivity in heterogeneous catalysis by metals. This has been demonstrated in a number of impressive studies by Gabor Somorjai and his group over the past few years.^{1–3} To provide an example, the increase in the size of Pt nanoparticles from 1 to 10 nm favors the hydrogenation of cyclohexene to cyclohexane whereas the dehydrogenation of cyclohexene to benzene is disfavored at the same time. In the studies with larger particles, 12 to 14 nm, cuboctahedral Pt, exposing mainly Pt{111} planes, favors the hydrogenation of benzene to cyclohexane and cyclohexene with maximum turnover frequencies at around 380 K.⁴ However, cubic Pt, mainly exposing {001} planes, favors exclusive hydrogenation to cyclohexane in the same range of temperature.⁵⁻⁷ In view of the significant progress made in developing tailored nanoparticle structures, it would be most desirable to probe the reaction kinetics facet by facet on individual nanoparticles. The application of field emission techniques provides this possibility.⁸⁻¹⁰ In studies with a field

(3) Jacoby, M. Chem. Eng. News 2008, 86, 15.

emitter tip, which closely resembles a single nanosized metal particle, the shape transformation due to adsorbed atoms and molecules can be made visible with atomic resolution. Moreover, the reaction behavior can be imaged and probed chemically by short field pulses during the ongoing reaction.¹⁰

In this article, which is dedicated to Gabor Somorjai, one of the true pioneers in the molecular approach to heterogeneous catalysis, we shall present data on the NO₂ reduction with hydrogen on a single Pt nanoparticle. The interest in this reaction is marked by its importance in the removal of NO_x from exhaust gases.¹¹ From a fundamental point of view, such systems also exhibit stunning nonlinear behavior.^{12,13} However, although such systems have also been considered extensively on 2D single-crystal surfaces,¹⁴ the morphological complexity as encountered in a catalytic converter is rarely dealt with. We shall demonstrate, for the case of NO₂ reduction to NO, that field emission imaging combined with video techniques and chemical probing presents a unique tool for investigating the cooperative effects and concerted behavior in a nonlinear chemical reaction. Despite the presence of a large number of nanosized facets simultaneously exposed on the surface of the nanosized particle (the "tip"), concerted reaction behavior may result, as previously investigated in detail by our group.^{15–17}

Previous work on the NO₂ reduction has shown chemical wave propagation to occur under the conditions of field ion imaging.^{13,18} However, under FEM conditions, the occurrence of regular oscillations and reaction-diffusion fronts were reported.^{12,19}

(15) McEwen, J.-S.; Gaspard, P.; Visart de Bocarmé, T.; Kruse, N. Proc. Natl. Acad. Sci. U.S.A. 2009, 106, 3006.

(19) Visart de Bocarmé, T.; Kruse, N. Chaos 2002, 12, 118.

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⁽¹⁾ Yin, Y.; Rioux, R. M.; Erdonmez, C. K.; Hugues, S.; Somorjai, G. A.; Alivisatos, A. P. Science 2004, 304, 711.

⁽²⁾ Somorjai, G. A.; Contreras, A. M.; Montano, M.; Rioux, R. M. Proc. Natl. Acad. Sci. U.S.A. 2006, 103, 10577.

⁽⁴⁾ Bratlie, K. M.; Lee, H.; Komvopoulos, K.; Yang, P.; Somorjai, G. A. *Nano Lett.* **2007**, *7*, 3097.

⁽⁵⁾ Somorjai, G. A.; Park, J. Y. Top. Catal. 2008, 49, 126.

⁽⁶⁾ Lee, H.; Habas, S. E.; Kweskin, S.; Butcher, D.; Somorjai, G. A. Angew. Chem., Int. Ed. 2006, 45, 7824.

⁽⁷⁾ Rioux, R. M.; Song, H.; Habas, S.; Grass, M.; Niesz, K.; Hoefelmeyer, J. D.; Yang, P.; Somorjai, G. A. Top. Catal. 2006, 39, 167.
(8) Müller, E. W.; Tsong, T. T. Field Ion Microscopy: Principles and Applica-

tions; Elsevier: New York, 1969.

⁽⁹⁾ Miller, M. K.; Cerezo, A.; Hetherington, M. G.; Smith, G. D. W. Atom Probe Field Ion Microscopy; Monographs on the Physics and Chemistry of Materials; Clarendon Press: Oxford, England, 1996.

⁽¹⁰⁾ Kruse, N.; Visart de Bocarmé, T. Heterogeneous Catalysis and High Electric Fields. In Handbook of Heterogeneous Catalysis; Ertl, G., Knözinger, H., Weitkamp, J., Schüth, F., Eds.; Wiley-VCH: Weinheim, Germany, 2008.

⁽¹¹⁾ Schneider, W. F. Fundamental Concepts in Molecular Simulation of NO_x Catalysis. In Environmental Catalysis; Grassian, V. H., Ed.; Taylor & Francis: Boca Raton, FL, 2005; p 233

 ⁽¹²⁾ Voss, C.; Kruse, N. Appl. Surf. Sci. 1996, 94/95, 186.
 (13) Voss, C.; Kruse, N. Ultramiscroscopy 1998, 73, 211.

⁽¹⁴⁾ Imbihl, R.; Ertl, G. Chem. Rev. 1995, 95, 697.

⁽¹⁶⁾ McEwen, J.-S.; Gaspard, P.; Visart de Bocarmé, T.; Kruse, N. J. Phys. Chem. C 2009, 113, 17045.

⁽¹⁷⁾ McEwen, J.-S.; Gaspard, P.; Visart de Bocarmé, T.; Kruse, N. Surf. Sci. 2010, 604, 1353.

⁽¹⁸⁾ Visart de Bocarmé, T.; Kruse, N. Top. Catal. 2001, 14, 35.

Here we will present some new results concerning these assessed behaviors. In particular, the regularity of the catalytic activity will be scrutinized under the conditions of field ion imaging at 515 K and under the conditions of field electron imaging at 390 K.

A reaction scheme that will be based on the experimental investigations on platinum single-crystal surfaces when exposed to NO₂ and H₂ will also be proposed. As a matter of fact, a number of experimental studies have been done concerning the adsorption of NO₂ on single-crystal surfaces, namely on $Pt\{111\}$,^{20–22} $Pt\{011\}$,^{23,24} and $Pt\{001\}$ ²⁵ as well as on polycrystalline platinum.²⁶ The surface coverage effects on the dissociation kinetics of NO₂, such as in the presence of oxygen, have also been examined.^{27–29} As for the adsorption of H₂ on platinum single-crystal surfaces, Somorjai was the first to report on the unique chemisorption and catalytic activity of H₂ at Pt surface irregularities such as steps and kinks using low-energy electron diffraction (LEED).³⁰ The H₂ adsorption on Pt{001}, Pt{011}, Pt{111}, and Pt{112} has also been characterized using temperature-programmed desorption (TPD) experiments allowing the comparison of adsorption rates on different surfaces.³¹

From a theoretical point of view, the literature concerning the adsorption of NO₂ on single-crystal surfaces is not as rich as the corresponding experimental studies. They have mainly focused on Pt $\{111\}$, showing that an adsorbed NO₂ molecule is thermodynamically nearly as stable as coadsorbed NO and O under certain experimental conditions.^{32,33} Moreover, recent evidence indicates that the rate of NO oxidation on low Miller indexed surfaces is larger than on high-indexed ones.³⁴ Thus, the Pt{111} surface would be interesting for pollution emission control concerns because the catalytic oxidation of NO to NO₂

$$NO(gas) + \frac{1}{2}O_2(gas) \rightarrow NO_2(gas)$$
 (1)

is a common element in NO_x removal strategies that are based on NO_x storage and reduction catalysts. However, in an industrial catalyst or, as argued above, on a field emitter tip, the {111} surfaces are not the only planes that are exposed at the metal's surface. In fact, more open surfaces, such as $Pt\{012\}$ and $Pt\{001\}$, are active in NO₂ decomposition.^{12,13,35} We have therefore investigated the adsorption of NO₂ on Pt{012} in the presence and in the absence of an external electric field in order to understand better the patterns that are observed in the corresponding FIM/FEM experiments. The aim here is to give reasons, from an atomistic point of view, for what controls the activity/inactivity regimes, as observed in FIM, in order to reduce environmentally harmful gases such as NO and NO₂ selectively. In addition, we will argue that an

- (21) Bartram, M. E.; Windham, R. G.; Koel, B. E. Surf. Sci. 1987, 184, 57.
- (22) Burns, A. R.; Jennison, D. R.; Stechel, E. B. Phys. Rev. B 1989, 40, 9485. (23) Huang, W.; Jiang, Z.; Jiao, J.; Tan, D.; Zhai, R.; Bao, X. Surf. Sci. 2002,
- 506, L287.
- (24) Jiang, Z.; Huang, W.; Tan, D.; Zhai, R.; Bao, X. Surf. Sci. 2006, 600, 4860. (25) Schwalke, U.; Niehus, H.; Comsa, G. Surf. Sci. 1985, 152/153, 596. (26) Wickham, D. T.; Banse, B. A.; Koel, B. E. Surf. Sci. 1989, 223, 82.
- (27) Orlando, T. M.; Burns, A. R.; Jennison, D. R.; Stechel, E. B. Phys. Rev. B
- 1992, 45, 8679. (28) Smeltz, A. D.; Getman, R. B.; Ribeiro, F. H.; Schneider, W. F. Catal. Today
- 2008, 136, 84. (29) Getman, R. B.; Schneider, W. F.; Smeltz, A. D.; Delgass, W. N.; Ribeiro, F. H. Phys. Rev. Lett. 2009, 102, 076101.
- (30) Lang, B.; Joyner, R. W.; Somorjai, G. A. Surf. Sci. 1972, 30, 454.
- (31) Lu, K. E.; Rye, R. R. Surf. Sci. 1974, 45, 677
- (32) Burch, R.; Daniells, S. T.; Hu, P. J. Chem. Phys. 2002, 117, 2902.
- (33) Getman, R. B.; Schneider, W. F. J. Phys. Chem. C 2007, 111, 389.
- (34) Mulla, S. S.; Chen, N.; Cumaranatunge, L.; Delgass, W. N.; Epling, W. S.; Ribeiro, F. H. Catal. Today 2006, 114, 57.
- (35) Gaussmann, A.; Kruse, N. Catal. Lett. 1991, 10, 305.

understanding of the interaction of NO₂ with a Pt surface is key to understanding the nonlinear behavior as observed in FEM or FIM. This will be done in sections 4.4 and 4.5.

2. Experimental Setups

We very briefly review the two different setups that were used in the experimental studies as reported in this article. Detailed descriptions can be found elsewhere.^{12,13,35} In the first setup, a field emission microscope was used either in the field electron mode (FEM) or the field ion mode (FIM) to monitor the ongoing catalytic reaction between NO₂ and hydrogen. In both cases, the microscope was used as a flow reactor at selected reactant pressures and temperatures. In FIM, the resolution is higher and approaches 2 to 3 Å as compared to \sim 20 Å in FEM. Thus, single atoms of the metal surface can be imaged by FIM in the absence of reactive overlayers at cryogenic temperatures using high fields (~35 V/ nm).^{8,9} The electric field in FIM is on the order of 10 V/nm during reactive imaging, which is higher by an order of magnitude as compared to that in FEM. Note also that the field over the surface of the tip changes its sign from positive in FIM to negative in FEM.

The atom-resolving capabilities of the FIM technique in the presence of a noble gas are demonstrated in Figure 1 along with a ball model. Layer edges are atomically resolved, and small (mainly high Miller index) layer planes are likewise visible. To condition the field emitter tip for catalytic studies, field evaporation, thermal treatment, and cycles of ion sputtering with Ne $(P_{\rm Ne} = 10^{-3} \,\mathrm{Pa} \,\mathrm{and} \,T = 100 \,\mathrm{K})$ are usually applied. To establish the occurrence of ion sputtering, the total current is monitored through the tip sample. In this case, an increase in the current is an indication of tip sharpening.³⁶ Following the introduction of reactive gases into the microscope, the image patterns and brightness in both FEM and FIM change as compared to the original clean state of the surface. The electron emission in FEM can, in principle, be quantitatively described by the Fowler-Nordheim equation. The brightness of the images can also be analyzed as a function of time, locally as well as globally, using a video camera.

In a second setup, pulsed field desorption mass spectrometry (PDFMS) allows the chemical identification of the surface while imaging the catalytic reaction by FIM. To do so, field pulses $(\sim 100 \text{ ns width})$ with a certain repetition frequency are applied to a counter electrode (with a hole) in front of an emitter tip. Pulses rupture the adsorbed molecules as ions that pass the probe hole of the microscope screen and enter a time-of-flight mass spectrometer for chemical identification. Pulse amplitudes may vary and can be adjusted such that the dynamics of a catalytic reaction are not visibly influenced.10,37

3. Theory

To gain an atomistic understanding of the underlying reaction mechanisms, DFT calculations were performed with the Vienna ab initio simulation package (VASP), a plane wave DFT program based on the projector-augmented wave method38-40 using the generalized gradient approximation (GGA) according to Perdew et al.41 We have selected the Pt{012} surface to study the adsorption of NO₂. To do so, a cutoff energy for the expansion of the plane waves of 340 eV was found to be sufficient for an accurate description of the adsorption energies and bond lengths, unless mentioned otherwise. The surface was modeled with a (1×2) unit cell using a 21-layer slab in which the upper 11 layers

⁽²⁰⁾ Dahlgren, D.; Hemminger, J. C. Surf. Sci. 1982, 123, L739.

⁽³⁶⁾ Miller, M. K.; Smith, G. D. W. Atom Probe Microanalysis: Principles and Applications to Materials Problems; Material Research Society: Pittsburgh, PA, 1989

⁽³⁷⁾ Kruse, N.; Abend, G.; Block, J. H. J. Chem. Phys. 1988, 88, 1307.

⁽³⁸⁾ Kresse, G.; Furthmüller, J. Phys. Rev. B 1996, 54, 11169.

⁽³⁹⁾ Kresse, G.; Furthmüller, J. Comput. Mater. Sci. 1996, 6, 15.

⁽⁴⁰⁾ http://cms.mpi.univie.ac.at/vasp/.
(41) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Phys. Rev. B 1992, 46, 6671.



Figure 1. Field ion micrograph (a) of a clean (001)-oriented Pt tip imaged by Ne at $F \approx 35$ V/nm. (b) Corresponding ball model.

were fully relaxed. This resulted, as previously reported,⁴² in a significant deviation away from their bulk positions. The remaining layers were fixed at their bulk positions at a theoretical lattice constant of a = 3.985 Å.

To estimate the error based on finite k-point sampling and fast Fourier transformation grids on a Pt{012} surface, we calculated (identical) structures using an $(8 \times 4 \times 1)$ and an $(8 \times 8 \times 1)$ k-point Monkhorst–Pack grid. The corresponding adsorption energies were found to differ by less than 10 meV. Thus, a $(8 \times 4 \times 1)$ k-point grid was used, unless stated otherwise.

For comparison with the clean Pt{012} surface, we have also performed some calculations on Pt{111} using the GGA functional according to Perdew et al.⁴¹ Here a cut off energy for the expansion of the plane waves of 400 eV was used, and the surface was modeled with a $p(3 \times 3)$ unit cell. The surface was sampled by a $(6 \times 6 \times 1)$ **k**-point Monkhorst–Pack grid using a four-layer

slab in which the upper two layers were fully relaxed and the other layers were fixed at a theoretical lattice constant of a = 3.986 Å.

4. Results

4.1. FEM Experiments. As mentioned in the Introduction, the NO₂ reduction with hydrogen was previously observed to exhibit a strong nonlinear behavior. In particular, fast local ignition phenomena were observed, followed by chemical wave propagation along certain zone lines of the nanosized particle surface. At 465 K, a front was seen to propagate anisotropically across the field emitter surface under FEM condi-tions.^{12,19} At first, four bright spots appeared around the planes of {012} symmetry. The reaction front then proceeded along the (001) zone lines toward the (001) pole. However, the surface explosions initiating these collective phenomena were not regular in time. This is in contrast to the very regular oscillations observed at 390 K. In Figure 2, a series of FEM micrographs are shown during one oscillatory period at this temperature. Interestingly, the {111} and {113} facets in Figure 2 remain dark. A high oxygen coverage on the {111} and {113} facets is therefore thought to cause a large increase in the work function and consequently to reduce the FEM current from these planes. As for the (001), {012}, and {011} facets, they exhibit a significant catalytic activity, which is a good indication of their activity in the reaction of oxygen with hydrogen to water. In Figure 2f, we depict the average intensity around the (001) facet for several oscillatory periods, where one oscillatory cycle lasts about 0.9 s and presents a double-peaked structure.

Using a different platinum field emitter tip than that used in Figure 2, self-sustained oscillations can again be observed at 390 K but at a higher hydrogen-to-nitrogen dioxide pressure ratio. The corresponding period is about 7 s now. The oscillations that appear around the $\{011\}$ and $\{012\}$ facets are found to be synchronized, as confirmed by an analysis of the time series around the four quadrants indicated in Figure 3b. Although the patterns are similar to those in Figure 2, one noticeable difference is that the (001) pole is inactive in Figure 3. We remark that the tip sample depicted in Figure 3 occasionally also showed (synchronized) regular oscillations around the (001) pole, but only when the tip had been used for some time.

We now turn to a more detailed inspection of the oscillatory behavior associated with Figures 2 and 3. Starting with the latter, although the periods of the different local oscillations on the tip are constant, their amplitude can vary substantially from one facet to the other. (See, for example, the brightness intensities around the four quadrants in Figure 3e.) To quantify the robustness of the oscillatory evolution, we carried out several simple tests. In particular, we performed interval-dependent normalized correlation analyses of the local brightness

$$C(t-t_0) = \frac{\langle I(t)I(t_0)\rangle - \langle I(t)\rangle\langle I(t_0)\rangle}{\langle I(t_0)^2 \rangle - \langle I(t_0)\rangle^2}$$
(2)

where *I* is the intensity (local brightness) and $t - t_0$ is the interval (in seconds) and where the average is taken over a time t_0 . These functions show damped oscillations with a decaying envelope (Figure 3f). This is quantitatively in accordance with theoretical predictions on the behavior of "noisy" chemical oscillators, such as the Brusselator model,^{43,44} for which such correlation functions

⁽⁴²⁾ Sun, Y. Y.; Hu, X.; Feng, Y.; Huan, A. C. H.; Wee, A. T. S. Surf. Sci. 2004, 548, 309.

⁽⁴³⁾ Baras, F.; Malek Mansour, M.; Van den Broeck, C. J. Stat. Phys. 1982, 28, 577.
(44) Gaspard, P. J. Chem. Phys. 2002, 117, 8905.



Figure 2. Self-sustained oscillations under FEM experimental conditions with $P_{H_2} = 1.5 \times 10^{-3}$ Pa, $P_{NO_2} = 5.0 \times 10^{-4}$ Pa ($P_{H_2}/P_{NO_2} = 3$), and T = 390 K with $F \approx -4$ V/nm. (a) The field emitter tip just before the brightness intensity peak of the oscillatory cycle where the {012} facets are catalytically active. (b) The reaction then propagates to the (101) and (011) facets as well as toward the (001) facet. (c, d) All of the {011} facets are now illuminated, followed by a significant decrease in brightness in image e. The tip then stays in a catalytically less active state for about 900 ms before the cycle starts anew with the field ion micrograph as given in panel a. (f) The mean brightness around the (001) facet for several oscillatory cycles with a period of 910 ms.

are damped by phase diffusion.^{45,46} Interestingly, the signal cannot be entirely reproduced by the simple product of a decreasing exponential and a periodic function. Nevertheless, the correlation function in Figure 3f further confirms that the periodic aspect of the phenomenon is a robust property of the reaction system. In

this regard, we note that the half-life, $t_{1/2}$, of the decreasing envelope is longer than the period itself ($t_{1/2} = 12.2 \pm 1.3$ s and a period of 7 s).

In our previous work on the oxidation of hydrogen on Rh,^{15–17} we showed that the origin of the observed nanopatterns lies in the different catalytic properties of the various nanofacets that are simultaneously exposed at the tip's surface. This seems to be the case here as well because the initial sticking probabilities for H₂ and

⁽⁴⁵⁾ Tomita, K.; Ohta, T.; Tomita, H. Prog. Theor. Phys. 1974, 52, 1744.
(46) Kuramoto, Y.; Tsuzuki, T. Prog. Theor. Phys. 1975, 54, 60.



Figure 3. Self-sustained oscillations under FEM experimental conditions with $P_{H_2} = 2.3 \times 10^{-2}$ Pa, $P_{NO_2} = 5.4 \times 10^{-4}$ Pa ($P_{H_2}/P_{NO_2} = 43$), and T = 390 K with $F \approx -4$ V/nm. (a) The field emitter tip just before the brightness intensity peak of the oscillatory cycle where a scale bar is provided as a rough indication of the length scale that was estimated from the radius of curvature of the tip. (b) The reaction ignites in all four quadrants around the {012} facets. (c-e) The intensity of all four quadrants decreases. (f) The time dependence of the normalized correlation function within the circle of the third quadrant as indicated in panel b.

 $S_0^{H_2}$ were measured to follow the order $S_0^{H_2}(011) > S_0^{H_2}(112) > S_0^{H_2}(001) > S_0^{H_2}(111)$.³¹ Indeed, a larger initial sticking coefficient can lead to larger sticking at finite coverage if the lateral interactions between the adatoms are similar from one facet to another.⁴⁷ As a result, such a large initial sticking coefficient for H₂ on Pt{011} could be at the origin of the significant catalytic activity around the {011} facets at 390 K, as seen in the FEM.

Furthermore, one would also expect a higher hydrogen coverage as one lowers the temperature. After examining the TPD spectra of H_2 on various single-crystal platinum facets,³¹ it becomes clear that considerable coverage differences are to be expected when increasing the temperature from 390 and 465 K. Accordingly, the relatively low hydrogen coverage at 465 K, with respect to the situation at 390 K, will result in the low catalytic activity of the {011} planes.

The period of this oscillatory cycle will depend in a fundamental way on the pressure ratio of hydrogen to nitrogen dioxide,

⁽⁴⁷⁾ Kreuzer, H. J. J. Chem. Phys. 1996, 104, 9593.



Figure 4. Dependence of the oscillatory period on the pressure ratio $P_{\text{H}_2}/P_{\text{NO}_2}$ at T = 390 K under FEM conditions at T = 390 K through a Fourier transform of the oscillatory signal. If one decreases the $P_{\text{H}_2}/P_{\text{NO}_2}$ ratio, then the oscillatory period increases.

 $P_{\rm H_2}/P_{\rm NO_2}$. This is illustrated in Figure 4 where the resulting Fourier spectrum of the oscillations, such as those observed in Figure 2, is calculated over a time interval of 160 s under various pressure ratios. In the upper panel of Figure 4, we depict the Fourier spectrum when $P_{\rm H_2}/P_{\rm NO_2} = 3$, where we observe a dominant frequency of about 1.1 Hz as well as several harmonics. If we decrease the pressure ratio $P_{\rm H_2}/P_{\rm NO_2}$ to a value of 2 (middle panel of Figure 4), then the fundamental frequency is more easily obtained and is now at a lower value of 0.85 Hz. If we decrease the ratio even further to 1.4, a weak maximum can be seen around 0.6 Hz (bottom panel of Figure 4). For even smaller ratios, no maximum appears in the Fourier analysis of the corresponding time series, which could be the result of an infinite period or a Hopf bifurcation.

4.2. FIM Experiments. As mentioned in section 2, the field changes its sign from negative in FEM to positive in FIM. This sign change is not insignificant because the resulting nonlinear behavior under FIM conditions is not as regular as under FEM conditions. In Figure 5, we show the evolution of the pattern formation under FIM conditions at $P_{H_2} = 2.0 \times 10^{-3}$ Pa, $P_{NO_2} = 2.0 \times 10^{-3}$ Pa, and $F \approx 9$ V/nm. We remark that the NO₂ pressure is about 4 times as large as the oscillatory conditions given in Figures 2 and 3. The temperature is higher here as well (515 K as compared to 390 K under FEM imaging conditions). Such patterns are observed only after certain delay times (i.e., usually several minutes elapsed between the introduction of





Figure 5. Pattern formation during the NO₂/H₂ reaction on a pyramidal Pt tip with $P_{\text{H}_2} = 2.0 \times 10^{-3}$ Pa and $P_{\text{NO}_2} = 2.0 \times 10^{-3}$ Pa at T = 515 K at two different times at $F \approx 9$ V/nm.

the reacting species into the FIM chamber and visible reaction phenomena). Previously, it was demonstrated that the Pt field emitter tip underwent a morphological change from nearly hemispherical to pyramidal during this time frame.^{13,18} The resulting stunning anisotropy and the 1D propagation of reaction fronts are shown in Figure 5, where the catalytic activity is almost exclusively at the {012} planes. Once ignited on the (012) plane, the reaction spreads into the neighboring areas along the $\langle 211 \rangle$ zone lines with various timescales, as reported elsewhere.¹³

The catalytic cycles associated with Figure 5 were 5-7 s in duration each. However, the reoccurrence of these patterns is not regular in time. Indeed, after fading away, the catalytic reignition of the {012} planes (not necessarily the (012) plane seen in Figure 5) occurs irregularly in time. Interestingly, at 418 K the propagation fronts are more regular in time. As a result, the regularity of the oscillating phenomena seems more prone to

occur around 400 K than around 500 K in the FIM case (as in the FEM case).

4.3. Reaction Network. *4.3.1. Hydrogen.* The inclusion of H_2 into the gas phase allows several reaction pathways to occur. In the absence of oxygen in the gas phase, the system is completely described by the following reaction scheme:

$$H(ad) + \mathcal{O}(ad) \stackrel{k_{diff}^{H}}{\longrightarrow} \mathcal{O}(ad) + H(ad)$$
(4)

For hydrogen on rhodium under our experimental conditions (a temperature of around 390 K), hydrogen diffusion (k_{diff}) is dominant with respect to the associative desorption (k_{des}) and dissociative adsorption (k_{ads}) of hydrogen on rhodium. Indeed, the activation barrier for hydrogen diffusion is very low on plati-num single-crystal surfaces.^{48,49} Moreover, here we assume that hydrogen can diffuse only into neighboring empty sites so that the coadsorption of NO2 hinders its diffusion through a site blocking effect. However, in our previous modeling on rhodium, ^{15–17} we did not take into account the precursor state of hydrogen. This was justified by the fact that, at the experimental temperatures and pressures considered, the hydrogen coverage would be low. However, on rhodium we were interested in the modeling of oscillations at 550 K, whereas on platinum the oscillating phenomena occur at 390 K, which is in the temperature range of hydrogen desorption from platinum.³¹ As a consequence, the hydrogen coverage will be significantly higher on platinum than on rhodium and the precursor state and the influence of lateral interactions may need to be taken into account.

4.3.2. Nitrogen Dioxide. A preliminary analysis of the atomprobe mass spectrum over an area comprising the (113) plane was performed under conditions similar to those described in section 4.2. The analysis of this spectrum clearly reveals that a catalytic cycle involves NO₂ dissociation and the subsequent formation of water from adsorbed oxygen and hydrogen. Other possible ionized products of the reaction, NH₃⁺ and N₂O⁺, were not observed under the reaction conditions used. Indeed, if these products were formed, then mass spectrometric evidence in terms of NH_x⁺ ($x \le 3$) and N₂O⁺ detection would have been expected.^{18,19} This, however, is not the case. We are currently planning additional pulsed field mass spectrometry experiments to determine under what experimental conditions these reaction products can be made to appear.

The absence of NH_x^+ and N_2O^+ would strongly suggests that the dissociation of NO (after stripping the first oxygen atom upon NO₂ initial chemisorption) on the surface is negligible. This is a reasonable suggestion in view of the high NO₂ dissociative sticking probability, leading to large amounts of oxygen and, consequently, to the hindrance of subsequent NO decomposition. Moreover, even in the absence of oxygen, the NO dissociation barrier is too large to overcome at 390 K on the various facets that are simultaneously exposed at the surface of the field emitter tip.⁵⁰⁻⁵⁴ Concomitantly, the NO coverage on the surface should be significantly smaller than the coverage of oxygen. Indeed, in our recent work,⁵⁵ we have correlated the formation of N₂O with the presence of high NO coverages building up from NO adsorption at room temperature. In particular, it was shown that $(NO)_2$ dimers could potentially form under such circumstances.⁵⁵

With regard to the formation of NO₂ from adsorbed NO and O, very recent work of Schneider et al.⁵⁶ also indicates that certain coverage ranges of O and NO species are necessary to render this process feasible. However, the same authors report that the dissociation of NO₂ on Pt{111} and Pt{123} is favored when the oxygen coverage on the surface is low. This is in agreement with our observations. Poisoning by oxygen upon the decomposition of NO_x species was also suggested for oriented Ir surfaces such as Ir{012}, Ir{011}, and Ir{113}.⁵⁴ Clearly, the poisoning is due to the strong chemisorption of oxygen on the Pt emitter surface. In fact, the temperature of the experiments (390 K) is much lower than the desorption temperature range (600–1000 K) for oxygen on Pt field single-crystal surfaces when dosed with NO₂.^{20–22,26} Note that oxygen chemisorption is also part of the recent analysis that we provided for the catalytic production of water on rhodium.^{15–17}

Finally, the diffusion of O and NO on the surface must be taken into account with some care. Indeed, although at 390 K the oxygen atoms may be considered to be immobile, ^{57–60} the barrier for NO diffusion is considerably smaller than that for O.^{60–62} On the other hand, the barrier for the hopping of NO on Pt is much larger than that for hydrogen so that its diffusion is slower. The above observations result in the following reaction network for NO₂ in the absence of hydrogen

$$NO_2(gas) + \nu \mathcal{O}(ad) \frac{k_a^{NO_2}}{k_d^{NO_2}} NO_2(ad)$$
(5)

$$NO(ad) \underbrace{\stackrel{k_{as}}{\underbrace{\overset{NO}}{\overset{}}}}_{k_{ad}^{NO}} NO(gas) + \mathcal{O}(ad)$$
(7)

$$NO(ad) + \mathcal{O}(ad) \stackrel{k_{diff}^{NO}}{\Longrightarrow} \mathcal{O}(ad) + NO(ad)$$
(8)

where v = 0 if an NO₂ molecule adsorbs into a precursor state while v = 1 or 2 if it adsorbs onto one or two adsorption sites, respectively.

4.3.3. Water Formation. Under the conditions of the experiment, 12,13,18,19 the gas phase above the platinum surface is composed of NO₂ and H₂ but the partial pressure of water can be taken as vanishing for the purpose of our modeling. As a result, the water molecules may be assumed to be immediately desorbed once they are formed because the lowest temperatures considered in the FEM or FIM experiments (390 K) are considerably higher than the desorption temperature of water on platinum, even in the presence of coadsorbed oxygen.⁶³ Moreover, because there is a vanishing probability to return back to the surface, the system is in a fully irreversible nonequilibrium regime.

⁽⁴⁸⁾ Graham, A. P.; Menzel, A.; Toennies, J. P. J. Chem. Phys. 1999, 111, 1676.

⁽⁴⁹⁾ Uecker, H. Phys. Rev. E 2005, 71, 016207.

⁽⁵⁰⁾ Gorte, R. J.; Schmidt, L. D.; Gland, J. L. Surf. Sci. 1981, 109, 367.

⁽⁵¹⁾ Banholzer, W. F.; Masel, R. I. J. Catal. 1983, 85, 127.

⁽⁵²⁾ Gohndrone, J. M.; Park, Y. O.; Masel, R. I. J. Catal. 1985, 95, 244.

⁽⁵³⁾ Ge, Q.; Neurock, M. J. Am. Chem. Soc. 2004, 126, 1551.

⁽⁵⁴⁾ Chen, W.; Stottlemyer, A. L.; Chen, J. G.; Kaghazchi, P.; Jacob, T.; Madey, T.; Bartynski, R. A. *Surf. Sci.* **2009**, *603*, 3136.

⁽⁵⁵⁾ McEwen, J.-S.; Garcia Cantu Ros, A.; Visart de Bocarmé, T.; Kruse, N. Catal. Today 2010, 154, 75.

⁽⁵⁶⁾ Getman, R. B.; Bray, J.; Schneider, W. F. Private communication.

⁽⁵⁷⁾ Bogicevic, A.; Hass, K. C. Surf. Sci. 2002, 506, L237.

⁽⁵⁸⁾ von Oertzen, A.; Rotermund, H.; Nettesheim, S. Surf. Sci. 1994, 311, 322.

⁽⁵⁹⁾ Zhdanov, V. P. Chem. Phys. Lett. 2004, 390, 301.

⁽⁶⁰⁾ Tammaro, M.; Evans, J. W. J. Chem. Phys. 1998, 108, 7795.

⁽⁶¹⁾ Croci, M.; Félix, C.; Vandoni, G.; Harbich, W.; Monot, R. Surf. Sci. 1994, 307, 460.

⁽⁶²⁾ Brown, W. A.; Ge, Q.; Sharma, R. K.; King, D. A. Chem. Phys. Lett. 1999, 299, 253.

⁽⁶³⁾ Karlberg, G. S.; Wahnstöm, G.; Clay, C.; Zimbitas, G.; Hodgson, A. J. Chem. Phys. 2006, 124, 204712.

Table 1. Adsorption Energies of NO₂ on a Pt{012} Surface at 1/2 ML Compared to the Adsorption of NO₂ on a Pt{111} Surface

surface	method	$E_{\rm cut} ({\rm eV})$	<i>a</i> (Å)	$\theta_{\rm NO_2}(\rm ML)$	geometry	$E_{\rm ads} ({\rm eV})$	$\Delta E_{\rm ads} ({\rm eV})$
012^{a}	GGA	340	3.985	1/2	µ-N,O-nitrito	1.94	-0.016 F
012^{a}	GGA	340	3.985	1/2	O,O'-nitrito	1.75	-0.042 F
012^{a}	GGA	340	3.985	1/2	nitro	1.63	-0.041 F
012^{a}	GGA	400	3.986	1/2	µ-N,O-nitrito	1.90	
111^{b}	GGA	400	3.986	1/4	<i>µ</i> -N,O-nitrito	1.29	
012^{a}	RPBE	400	3.993	1/2	µ-N,O-nitrito	1.42	
^{<i>a</i>} This wor	rk. ^{<i>b</i>} Schneider et a	1. ³³		,	•		

Water synthesis occurs by a sequence of successive reactions involving the intermediate OH species:

$$H(ad) + O(ad) \frac{\kappa_{r_{1-}}}{\kappa_{r_{1-}}} OH(ad) + \mathcal{O}(ad)$$
(9)

$$H(ad) + OH(ad) \underbrace{\stackrel{k_{r_{2+}}}{\underset{k_{r_{2-}}}{\longrightarrow}}} H_2O(ad) + \mathcal{O}(ad)$$
(10)

$$2OH(ad) \underbrace{\overset{k_{r3+}}{\xleftarrow}}_{k_{r3-}} H_2O(ad) + O(ad)$$
(11)

$$H_2O(ad) \xrightarrow{k_{dw}} \varnothing(ad) + H_2O(gas)$$
 (12)

In our previous work on rhodium,^{15–17} a stationary state or slow enough oscillations were assumed that allowed us to simplify this reaction network greatly. In particular, we argued that the addition of the first H atom to chemisorbed oxygen is the slow step whereas the addition of a second hydrogen atom leading to H₂O is fast. This gave a relatively short mean lifetime of $\tau \approx$ 10^{-10} s at 550 K, which allowed us to neglect the intermediate OH adspecies. On platinum, the barrier for the addition of the second hydrogen atom has been reported to be 0.21 eV,^{64,65} which is even smaller than the corresponding barrier on rhodium (0.3 eV^{66}) . As a consequence, the mean lifetime of the OH species on Pt, assuming a prefactor of 10^{12} s⁻¹, is still $\tau \approx 10^{-10}$ s even at 390 K. The neglect of the intermediate OH species leads to a great simplification of our reaction network in the formation of water:

$$2H(ad) + O(ad) \stackrel{\kappa_r}{\longrightarrow} 3\emptyset(ad) + H_2O(gas)$$
 (13)

Because the oscillations occur on a comparable timescale on Pt (\sim 1 or 7 s) as on Rh (\sim 40 s), the above approximation also applies to platinum.

4.4. NO₂/Pt{012}. The kinetic scheme described in the previous subsection suggests a feedback mechanism for the observed oscillations on a Pt field emitter tip when exposed to NO₂ and H₂, which is in agreement with the corresponding PDFMS results. In particular, steps 5 and 6 play a key role in the overall reaction. Indeed, when the coverage of oxygen is low, there is no obstruction to the dissociative adsorption of NO₂(gas) to NO(ad) and O(ad). However, beyond a certain critical coverage (e.g., at $\theta_{\rm O}$ = 0.5 ML on $Pt\{123\}$ as shown in recent work⁵⁶), the reverse reaction becomes important, which has the effect of slowing down the forward reaction. The conditions are then favorable for the surface to be cleaned by adsorbed hydrogen, allowing the cycle to repeat itself. Another key point for the oscillatory mechanism is the interaction of NO_2 and H with Pt{012} because



Figure 6. Three adsorption conformations of NO₂ on a $Pt{012}$ surface as determined through DFT calculations in the absence of a field: the μ -N,O-nitrito (two top panels), nitro (two middle panels), and O,O'-nitrito isomers (two bottom panels). The small blue spheres are the nitrogen atoms, the small yellow spheres are the oxygen atoms, and the large gray spheres are the platinum atoms. The corresponding adsorption energies are given in Table 1.

this surface has dominant catalytic activity. In Table 1, we have calculated the adsorption energies for NO_2 on $Pt\{012\}$ at $\theta_{\rm NO_2} = 1/2$ ML,

$$E_{\rm ads} = -\left[\frac{E_{\rm tot} - E_{\rm Pt\{012\}} - N_{\rm NO_2} E_{\rm NO_2}}{N_{\rm NO_2}}\right]$$
(14)

where N_{NO_2} is the number of adsorbed NO₂ molecules, E_{tot} is the total energy of the calculated cell for NO2 in different geometries as depicted in Figure 6, $E_{Pt\{012\}}$ is the energy of a clean Pt{012} surface, and E_{NO_2} is the energy of an isolated NO₂ molecule in its ${}^{2}\Pi$ ground state in a symmetry-broken calculation. We also show in Table 1 the adsorption energies of NO₂ on Pt{111} at 1/4 ML for comparison because the unit cell area, A(hkl), on a Pt{012} surface is larger than on a Pt{111} surface.¹⁷ As a result, a coverage of 1/2 ML on Pt{012} corresponds to a surface density of $\sigma(012) = \theta_{\rm NO_2}/A(012) = (5)^{1/2}/5a^2$, which is closer to $\sigma(111) =$ $(3)^{1/2}/3a^2$ at 1/4 ML than the corresponding value of $\sigma(111)$ at 1/2 ML.

⁽⁶⁴⁾ Michaelides, A.; Hu, P. J. Chem. Phys. 2001, 114, 513.

⁽⁶⁵⁾ Michaelides, A.; Hu, P. J. Am. Chem. Soc. 2001, 123, 4235.

⁽⁶⁶⁾ Wike, S.; Natoli, V.; Cohen, M. H. J. Chem. Phys. 2000, 112, 9986.



Figure 7. (a) Plane-averaged electrostatic potential energy on a bare Pt{012} slab (solid line) and on a Pt{012} slab with 0.5 ML of NO₂ adsorbed as in Figure 6a on one side of the slab (---) with respect to the Fermi level in the absence of an external electric field. The solid vertical lines mark the positions of the Pt layers in the slab. The first vertical dashed line marks the position of the NO bond parallel to the surface, and the second vertical dashed line at a greater value of *z* marks the position of the O atom. (b) Electrostatic potential energy difference between a field of 6 V/nm and in the absence of a external field in the presence (-) and the absence of NO (---). (c) Corresponding electron-density change induced by the electrostatic field. The surface is sampled by an (8 × 8 × 1) **k**-point grid, where the periodicity perpendicular to the slab is 31.2 Å. Inside the slab, Friedel-like oscillations can be seen.

Table 1 shows that NO₂ binds to $Pt{012}$ in a remarkably stronger way than to Pt{111}. However, we find that NO₂ binds more favorably in a μ -N,O-nitrito conformation as compared to the O.O'-nitrito and nitro isomers, as was found to be the case on Pt{111}.³³ However, we also remark that, in comparison with experiment, the PW91 functional overestimates the binding of NO2 to Pt{111} because Bartram et al. obtained an adsorption energy of 0.82 eV^{21} whereas 1.35 eV is calculated theoretically at $1/16 \text{ ML.}^{33}$ Thus, although the adsorption energy of NO₂ on Pt $\{012\}$ has never been measured, it is likely to be overestimated using the PW91 functional on $Pt\{012\}$ as well. We have therefore calculated the adsorption energy of NO_2 on Pt{012} using the RPBE functional, which yields a considerably smaller adsorption energy of 1.42 eV (instead of 1.90 eV, see Table 1) and is likely to be closer to the experimental value. We also remark that NO₂ binds more strongly to $Pt{012}$ than to Pt{001} because an Arrhenius analysis of the TPD spectra of NO₂ on Pt{001} gives an adsorption energy of 0.89 eV if a prefactor of $1 \times 10^{15} \text{ s}^{-1}$ is assumed.⁶⁷

4.5. Pt $\{012\}$ and NO₂/Pt $\{012\}$ in High Electric Fields. In the previous subsections, we showed that the Pt $\{012\}$ surfaces

Table 2. Comparison of Multilayer Relaxations of Pt{012} and Pt{111} in the Presence and in the Absence of an Electric Field of 6 V/nm

			,		
	$Pt{012}^{a}$	$\begin{array}{c} \operatorname{Pt}\{012\}\\ {(F)}^a \end{array}$	$\begin{array}{c} \operatorname{Pt}\{012\}\\ (\operatorname{LEED})^b \end{array}$	$Pt{111}^{a}$	$\begin{array}{c} \operatorname{Pt}\{111\}\\ (\mathrm{F})^a \end{array}$
$\begin{array}{c} \Delta d_{12} (\%) \\ \Delta d_{23} (\%) \\ \Delta d_{34} (\%) \\ \Delta d_{45} (\%) \end{array}$	-29.3 -3.4 +16.5 -8.2	-28.1 -3.9 +16.4 -7.6	$-23 \\ -12 \\ +4 \\ -3$	+0.2	+0.3
^a This w	ork. ^b Somo	rjai et al. ⁷¹			

exhibit significant catalytic activity. In this subsection, we look at $Pt\{012\}$ and $NO_2/Pt\{012\}$ in the presence of an external field, as is the case under FEM or FIM conditions. Indeed, a field of up to 9 V/nm was applied under the FIM conditions given in Figure 5 and must be taken into account in our modeling of the experimental data.

We show in Figure 7 the plane-averaged electrostatic potential energy on a bare Pt{012} slab, its electrostatic potential energy difference in the presence of a external field of 6 V/nm as compared to when it is absent, and the corresponding electrondensity change. Because applying a positive electric field *F* adds the potential energy |e|Fz for the electrons outside the metal, one can easily estimate the corresponding field's influence on the potential energy landscape.⁶⁸ As can be seen by examining Figure 7, the electric field dies out in the metal, as expected. However, it is not as rapidly screened as compared to more dense surfaces, such as Al{111}⁶⁹ and Pt{111}.⁷⁰

This increase in the Debye length on more open surfaces correlates well with the change in the interlayer spacings from their bulk values. In Table 2, we compare the interlayer spacings on a Pt{012} surface with those on a Pt{111} surface. In the absence of the field, the change in the interlayer spacings are more significant on a Pt{012} surface than on a Pt{111} surface and are in good agreement with previously published experimental⁷¹ and theoretical values.⁴² In the presence of a positive electric field, Table 2 also shows that Δd_{12} on Pt{012} changes from -29.3 to -28.1% whereas on Pt{111} Δd_{12} changes from 0.2 to 0.3%. As a result, an external field changes the interlayer spacing quite substantially on a Pt{012} surface.

We remark that similar results with regard to the field effects on more open surfaces were previously reported using a cluster embedded in jellium model, where the field enhancement effects on stepped surfaces were examined.^{72,73} In addition, our previous work⁷⁴ has also indicated that the electric field can have a significant influence on the surface chemistry of more open surfaces. In particular, by comparing the Rh{001}, Rh{011}, and Rh{111} surfaces, we found that an electric field has a significant influence on the Rh{001} surface whereas its effect is smaller on the Rh{111} surface.

The presence of an external field will also influence the binding of NO_2 on a platinum field emitter tip. To estimate this effect, we have calculated the adsorption energy change when a field of

⁽⁶⁷⁾ Garcia Cantu Ros, A. Private communication.

⁽⁶⁸⁾ Kreuzer, H. J.; Wang, R. L. C. Philos. Mag. B 1994, 69, 945.

⁽⁶⁹⁾ Neugebauer, J.; Scheffler, M. Phys. Rev. B 1992, 46, 16067.

⁽⁷⁰⁾ Deshlahra, P.; Wolf, E. E.; Schneider, W. F. J. Phys. Chem. A 2009, 113, 4125.

⁽⁷¹⁾ Zhang, X.-G.; Van Hove, M. A.; Somorjai, G. A.; Rous, P. J.; Tobin, D.; Gonis, A.; MacLaren, J. M.; Heinz, K.; Michl, M.; Lindner, H.; Müller, K.; Ehsasi, M.; Block, J. H. *Phys. Rev. Lett.* **1991**, *67*, 1298.

⁽⁷²⁾ Suchorski, Y.; Schmidt, W. A.; Ernst, N.; Block, J. H.; Kreuzer, H. J. Prog. Surf. Sci. 1995, 48, 121.

⁽⁷³⁾ Suchorski, Y.; Ernst, N.; Schmidt, W. A.; Medvedev, V. K.; Kreuzer, H. J.; Wang, R. L. C. Prog. Surf. Sci. **1996**, 53, 135.

⁽⁷⁴⁾ McEwen, J.-S.; Gaspard, P.; Mittendorfer, F.; Visart de Bocarmé, T.; Kruse, N. Chem. Phys. Lett. 2008, 452, 133.

6 V/nm is applied, which is comparable to an experimental field value of 9 V/nm as applied in the FIM imaging mode in Figure 5. When one increases the field value from 0 to 6 V/nm, the O-N-O angle will increase by 0.6, 0.5, and 1.7° for the μ -N,O-nitrito, the O,O'-nitrito, and nitro conformations, respectively. (The fieldfree values are given in Figure 6.) As for the NO bond lengths, they remain unchanged with respect to the field-free case for the O,O'-nitrito conformation but decrease slightly from 1.24 to 1.23 Å for the nitro conformation. However, the NO bond length parallel to the surface in the μ -N,O-nitrito conformation is identical to the field-free case, whereas the other NO bond length decreases from 1.22 to 1.21 Å. As for the adsorption energy, E_{ads} , it will be altered as well. Here, E_{ads} in the presence of a field is a simple generalization of eq 14, where all three terms are fielddependent and in which the orientation of the NO₂ molecule in the gas phase with respect to the field is the same as when it is adsorbed on the surface. The field dependences of the adsorption energy are given in Table 1. As can be seen from Table 1, the adsorption energy of the μ -N,O-nitrito conformation decreases by 0.016F eV when an external field, F(in V/nm), is applied. As for the O,O'-nitrito and the nitro conformations, they have a much stronger field dependence with a decrease in the adsorption energy of 0.042FeV and 0.041FeV, respectively. This screening of the electric field in the μ -N,O-nitrito conformation as compared to those in the O,O'-nitrito and nitro conformations can be explained classically by the orientation of the dipole vector with respect to the external field. Indeed, the dipole vector is neither parallel nor antiparallel to the field in the μ -N,O-nitrito conformation. Thus, the corresponding significant influence of the field in the electrostatic potential energy and electron density, as shown in Figure 7, influences the adsorption energy of NO₂ in the O,O'-nitrito and the nitro conformations more strongly than in the μ -N,O-nitrito conformation.

5. Discussion

The above theoretical results correlate well with the observed nonlinear phenomena under FIM and FEM imaging conditions. In particular, hints are provided on why such phenomena are observed under both imaging conditions. Indeed, in our recent previous work,55 we reported that dynamic pattern formation in the NO and H₂ reaction on a Pt field emitter tip occurred only under FIM imaging conditions. Why then should one expect such a rich variety of nonlinear phenomena to be observed under both FIM and FEM imaging conditions when exposing the Pt tip to NO2 and H2? The answer to this question is, of course, related to the adsorption and dissociation behavior of NO₂ as compared to that of the NO molecule. As mentioned in the Results section, an NO2 molecule should easily dissociate on the surface whatever the facet of the Pt nanocrystal. By contrast, large plane-to-plane variations are encountered in the dissociation probability of an NO molecule. As a result, the amounts of adsorbed oxygen will vary considerably between the different Pt facets upon exposure to NO. The different reactivity of the two molecules is also well reflected at the atomistic level of our DFT calculations. Accordingly, the different orientational degrees of freedom of the two molecules must be considered to explain the different dissociation activity. For an adsorbed NO molecule, it will bend from an upright position (including a tilt angle) to attain a transition state in which both the N and the O atoms bind to the Pt surface. An alternative mechanism would be that an NO molecule reacts with another NO molecule to form an (NO)2 dimer, which would then decompose to N₂O and O.55 Such mechanisms are significantly different from the one involved for an NO₂ molecule, which is bound in a µ-N,O-nitrito conformation as considered in our DFT calculations. Until now, only adsorption energies have been calculated for this binding mode. The information gleaned from these calculations will provide clues for possible pathways of the molecule to attain a transition state suitable for dissociation. In this context, it is also quite interesting to note that the large catalytic activity around the {012} facets correlates nicely with the significantly stronger binding of NO₂ to $Pt\{012\}$ as compared to $NO_2/Pt\{001\}$ or $NO_2/Pt\{111\}$. In particular, we remark that the {001} facets are active only at 390 K in FEM, whereas under FIM conditions at 515 K they are inactive with the catalytic activity concentrated uniquely around the {012} facets. This is a clear demonstration of the occurrence of electric field effects. The electric field vector actually changes sign when switching from FEM to FIM imaging. Our DFT results, as shown in Table 1, imply that the adsorption energy of NO₂ will decrease when a positive external electric field is applied.

As for the oscillation mechanism, we remark that a complex surface reconstruction^{75,76} has been reported for a Pt(001) singlecrystal surface when exposed to NO and H₂. On a Pt field emitter tip, the (001) plane is relatively small. Actually, a large number of facets are simultaneously present and determine the overall (nano)particle morphology. Whereas the surface reconstruction of the (001) plane cannot be excluded here, it must be emphasized that, if it occurs, it is embedded in an overall change in the nanoparticle morphology from hemispherical to polyhedral under the reaction conditions. Once this shape transformation is achieved, it is not reversible without changing the chemical composition of the gaseous reactants. However, the presence of surface oxides was shown to play an important role in the oscillatory mechanism when a rhodium tip is exposed to hydrogen and oxygen. $^{15-17}$ Thus, despite the fact that Pt is less prone to oxidation than Rh, the presence of surface oxides, which would cause a "chemical" reconstruction of the surface, cannot be completely ruled out when platinum is exposed to H_2 and NO_2 . To inquire about this possibility, we plan to use a 3D atom probe, which we consider to be ideally suited to perform a layer-by-layer compositional analysis of the tip.⁷⁷ On the theoretical side, we are planning to study the stability of the {012} surface in the presence of oxygen using DFT, as was recently done for $Ir\{012\}$.⁷⁸

Finally, in the kinetic model presented in section 4.3, the oscillatory behavior is attributed to an inhibition process induced by the lateral interactions between the adsorbed O, NO, and NO_2 adspecies, which will cause strong nonlinearities in the underlying kinetic equations. Indeed, it was recently shown that the interaction of O, NO, and NO_2 will inhibit NO_2 from dissociating.⁵⁶

6. Conclusions and Outlook

In this article, we presented new experimental results concerning the observed nonlinear behavior when exposing a Pt field emitter tip to NO₂ and H₂ under FEM and FIM imaging conditions. In FEM, the field electron micrographs exhibit a high catalytic activity around the $\{012\}$ facets. They also show that very regular oscillations can occur. The regularity of these oscillations is also demonstrated by calculating the associated correlation function in a region of interest around the (102) facet. Moreover, a Fourier

⁽⁷⁵⁾ Baraldi, A.; Vesselli, E.; Bianchettin, L.; Comelli, G. J. Chem. Phys. 2007, 127, 164702.

⁽⁷⁶⁾ Slinko, M.; Fink, T.; Löher, T.; Madden, H. H.; Lombardo, S. J.; Imbihl, R.; Ertl, G. Surf. Sci. 1992, 264, 157.

⁽⁷⁷⁾ Bagot, P. A. J.; de Bocarmé, T. V.; Cerezo, A.; Smith, G. D. W. Surf. Sci. 2006, 600, 3028.

⁽⁷⁸⁾ Kaghazchi, P.; Jacob, T.; Ermanoski, I.; Chen, W.; Madey, T. E. ACS Nano 2008, 2, 1280.

analysis of the oscillations provides a better understanding of how the oscillatory period depends on the NO₂/H₂ pressure ratio. Such analyses reveal that these oscillations are damped with a characteristic half-life of $t_{1/2} = 12.2 \pm 1.3$ s, which is in accordance with theoretical predictions of the behavior of "noisy" chemical oscillators.⁴⁴ In the future, it could be interesting to analyze how $t_{1/2}$ changes as a function of the region of interest, the size of the tip, or the distance with respect to a bifurcation point in order to confirm the trends highlighted in the corresponding theoretical work.^{43–46} In FIM, a dominant catalytic activity around the {012} facets is observed but the nonlinear behavior is not found to be regular in time.

We also proposed here a reaction network to explain the observed nonlinear behavior, which is based not only on the FEM and FIM observations but also on the experiments performed on single-crystal surfaces as well as recent ab initio calculations. In particular, we correlated previous PDFMS results with a feedback mechanism involving poisoning by oxygen upon the decomposition of NO₂ on Pt field emitter tips.

From an atomistic point of view, we examined how the {012} surfaces interact with NO₂ and compared our results to other surfaces, such as Pt{111}. Our results indicate that NO₂ interacts much more strongly with Pt{012} than with Pt{111}, which correlates well with the corresponding FEM and FIM micrographs. The influence of an external field on the adsorption energy of NO₂ is also evident. The next obvious step is to examine, using DFT, how NO₂ dissociates on a Pt{012} surface and how the presence of coadsorbed oxygen and nitrogen oxide influences this dissociation process. In particular, if the dissociation mechanism is similar to what occurs on $Pt\{111\}^{29}$ then the increased length of the NO bond parallel to the Pt{012} surface from 1.22 to 1.34 Å (Figure 6) will be a precursor of this dissociation process: its bond length will increase as the NO₂ molecule decomposes. Such efforts are necessary to fix the various energy barriers and prefactors within a kinetic model so as to develop a multiscale model of the observed nonlinear phenomena. Moreover, if eqs 5 and 6 do indeed generate a feedback mechanism, then it will lie at the heart of our model of the nanometric chemical clock associated with NO₂ reduction.

The next step would be to elaborate a theoretical kinetic model that would involve such a poisoning effect by oxygen on the tip's catalytic activity to determine if self-sustained oscillations can emerge. Such a kinetic model would be more elaborate than our previously proposed model involving the catalytic production of water on Rh field emitter tips when exposed to H_2 and O_2 for two reasons:

- (i) The diffusion of NO should be treated with care. As argued in section 4.3, NO molecules cannot be considered to be immobile nor can their diffusion be treated as ultrafast, as is the case for hydrogen atoms.
- (ii) The influence of noise must be taken into account so as to be able to explain the experimentally measured time dependence of the correlation function as depicted in Figure 3.

Efforts are currently underway to address both issues within our kinetic scheme.^{79,80}

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⁽⁷⁹⁾ Garcia Cantu Ros, A.; McEwen, J.-S.; Gaspard, P.; Visart de Bocarmé, T.; Kruse, N. The effect of ultrafast diffusion on adsorption, desorption and reaction processes on heterogeneous surfaces; to be submitted for publication.

⁽⁸⁰⁾ Pineda, M.; McEwen, J.-S.; Gaspard, P.; Visart de Bocarmé, T.; Kruse, N. To be submitted for publication.