Surface Reactions Investigated at the Nanoscale by Field Emission Techniques: Nonlinear Dynamics of the Catalytic Hydrogenation of NO and NO₂ Over Platinum Crystallites

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Introduction Methods

Methods	2
Principle of the Techniques	2
Sample Preparation and Procedures	3
Case Studies	3
NO Hydrogenation Studied by FIM	3
NO ₂ Hydrogenation Studied by Field Emission Microscopy (FEM)	6
Conclusions	8
Acknowledgments	8
References	8

Glossary

Bifurcation diagram Diagram showing the sudden change of a dynamical property (like the amplitude or frequency of oscillations) as a function of a control parameter. **Excitability** Dynamical phenomenon in which, after a small perturbation, a system will first diverge from its initial state but will eventually (for long times) come back to it. **Field electron microscopy (FEM)** Microscopy based on field emission of electrons from the extremity of a sharp tip so as to image the tip apex with nanoscale resolution under vacuum and reactive conditions. Field ion microscopy (FIM) Microscopy based on field ionization of gas species at the surface of a tip image surface structures with atomic resolution at low temperature, and surface reactions with nanoscale resolution at elevated temperatures.

Kinetic phase diagram Diagram plotting the zone of existence of different dynamical states (steady state, oscillations, etc.) as a function of the different control parameters.

Temporal autocorrelation function Function giving a measure of the degree of statistical correlation between two points, as a function of their temporal distance.

Introduction

In the context of automotive pollution control, platinum group metals are widely used as catalysts to reduce the emission of toxic gas species such as carbon monoxide (CO), unburned hydrocarbons (C_xH_y) , and nitrogen oxides (NO_x) .¹ Surface science studies of these systems can provide a foundational understanding of the reaction behavior on a microscopic scale so as to define guidelines for improving catalysts and catalytic processes under realistic conditions of automotive pollution control. Active materials in the catalytic converter contain metallic nanoparticles of a few tens of nanometers, dispersed on a support of high porosity.

A major problem under lean driving conditions is the emission of nitric oxides, NO_x . To provide a remedy, selective catalytic reduction, originally developed for NO_x abatement from stationary power plants, is being applied on a large-scale basis using ammonia, NH_3 , as a reductant. The quest for low-temperature NO_x reduction has stimulated the search for alternative methods. The use of hydrogen, which could be produced by on-board reforming, may be one such method. The present paper will provide basic insight into the fairly complex reduction kinetics of both NO and NO_2 by hydrogen using field emission techniques under "operando-type" surface science conditions. The unique capabilities of video-field electron microscopy (FEM) and field ion microscopy (FIM) to image catalytic action with nanoscale resolution, or even better, will be demonstrated. One of the advantages of these techniques, from the materials point of view, is the use of samples conditioned as sharp tips, the extremity of which resembling a quasi-hemispherical shape with typical sizes of a few tens of nanometers and mimicking a single catalyst nanoparticle. Such tips are neatly divided up into a large number of facets with different crystallographic orientation so that their communication behavior in catalytic reactions can be imaged in real time and they can be sorted for their catalytic activity.

Field emission research in the past has dealt with the occurrence of adsorbate- and reaction-induced reconstructions,^{2–6} planeto-plane variations of nonlinear reaction dynamics^{7–10} or determination of kinetic parameters.^{11–13} In this contribution, we will focus on the study of the inherently nonlinear kinetics of the catalytic NO_x reduction. The outstanding imaging capabilities of

1

video-field emission techniques will be demonstrated for the $NO+H_2/Pt$ and NO_2+H_2/Pt systems using FIM and FEM, respectively.

Methods

Principle of the Techniques

Field emission techniques allow imaging, in direct space, of a conductive sample prepared as a tip by applying electric fields.¹⁴⁻¹⁶ To do so, the tip is either negatively (FEM) or positively (FIM) polarized with respect to a detector screen consisting of a multichannel plate and a phosphor screen. A schematic view of the microscope is presented in Fig. 1A. Both techniques involve quantum mechanical tunneling processes. In FEM, electrons tunnel through a surface potential barrier before traveling toward the detector. Typical electric fields at the tip surface are of 2–5 V nm⁻¹. The intensity of the electron emission varies with the local work function, which depends on the crystallographic orientation of the exposed facet, on the temperature and the local electric field (at atomic protrusions, for example). Field emission is ruled by the Fowler-Nordheim equation.^{17,18} The resolution of the FEM pattern usually reaches 1.5–2 nm. A typical FEM pattern of a Pt sample is shown in Fig. 1B. FEM can not only be used under ultrahigh vacuum conditions so as to study the emission properties of clean field emitter tips, but can also be operated in the presence of gas species in the microscope, including reactive gases at temperatures where surface reactions occur. In the presence of adsorbed species, the electron emission varies because the local work functions change upon adsorption. These phenomena appear as variations in the brightness of the FEM patterns. The occurrence of brightness variations under isothermal conditions of coadsorbing reactive gases reflects changes in the chemical composition of the probed area, assuming that the local electric field is kept constant. It may happen, however, that the brightness signal is a convolution of compositional and morphological changes as encountered during reconstruction processes. Furthermore, subsurface diffusion may occur and alter the local emission current. In this case, a careful variation of reaction times, temperature, or gas pressures may help deconvolute and sort the different processes.



Fig. 1 (A) Principle scheme of the FEM/FIM technique; (B) field emission microscopy (FEM) pattern of a typical Pt sample (conditions: temperature T=60 K, electric field $F\approx 2.5$ V nm⁻¹); (C) field ion microscopy (FIM) of the same sample allowing atomic resolution to be achieved (conditions: T=60 K, partial Ne pressure $P_{\text{Ne}}=2\times 10^{-3}$ Pa, $F\approx 37$ V nm⁻¹); (D) ball model of a fcc metal where every ball represents an atom; the ball model correlates with the FIM micrograph in (C).

FIM uses the same setup as FEM but is based on the ionization of an imaging gas at the surface by polarizing the tip positively. A field of some 10-50 V nm⁻¹ is necessary for image gas ionization. Extracted electrons tunnel through the potential barrier into energy levels at or above the Fermi level of the metal tip, while the resulting cations are accelerated along the electric field lines toward the detector screen, Fig. 1C provides a typical example of a field ion micrograph. The resulting FIM pattern represents a map of the ionization probability of the imaging gas across the tip surface. This probability depends on the local electric field, which is enhanced at the most protruding sites of the tip sample, that is, steps, kinks, or adatoms of low coordination number. At cryogenic temperature (\approx 50 K), atomic resolution can be achieved (\approx 0.2 nm), with a magnification of about 10⁶. The comparison with a ball model, where every single ball represents an atom (Fig. 1D) and white balls correspond to step and kink sites, visualizes the high resolution attainable with this technique. The 2D representation of the 3D quasi-hemispherical tip is close to a stereographic projection.¹⁵ At temperatures of interest for catalytic reactions, usually above 300 K, the atomic resolution power is lost but remains subnanometric. Using video-FIM under catalytic reaction conditions at overall low gas pressures (below 10^{-3} mbar) then allows imaging of catalytically active sites using adsorbed species for imaging, that is, reactants, intermediates, or products. The FIM pattern brightness depends on the applied imaging field and ionization potential of the adsorbates. We also mention that the FIM instrument can be combined with a time-of-flight mass spectrometer. The combined setup is known as the 1-dimensional atom probe (1DAP) or pulsed field desorption mass spectrometry.¹⁹ By applying field pulses of varying amplitude and frequency the adsorbate layer can be field desorbed after well-defined reaction times down to the µs time-scale. Thus, reactive layer compositions varying as a function of time can be followed and provide valuable mechanistic insight into the catalytic process under study or to determine, as in the present paper, the nature of the imaging species in FIM.

Sample Preparation and Procedures

Samples for FEM or FIM imaging are prepared by electrochemically etching a wire of the metal of interest.^{14–16} The nature of the electrolyte and the etching technique depend on the choice of the metal. In the case of Pt, a molten salt mixture of NaCl/NaNO₃ (1:4 w/w) at 520°C is used to produce sharp tips. For the purpose of catalysis studies, the samples must be heated to temperatures of interest and the latter must be measured and controlled. For these reasons, the sample is mounted on a sample holder allowing the sample to be resistively heated while measuring the temperature with a thermocouple attached to the basis of the tip. After introducing the tip into the microscope, cycles of annealing, Ne⁺ ion sputtering, and low temperature field evaporation are applied to provide an atomically smooth and clean surface. The sample is then characterized at low temperature, that is, 50–60 K, in FIM mode. To observe catalytic reaction behavior, different procedures can be used: (1) a reactive gas mixture with well-defined partial pressures is leaked into the steadily pumped chamber and the temperature is increased until variations in the FIM/FEM pattern are observed, or (2) the temperature is increased up to a predefined value, then one of the reactants is leaked into the chamber at constant pressure before a second gas is added up to pressures seen to modify the FIM/FEM patterns. Procedures 1 and 2 may be modified, though. For example, in some cases it is advantageous to increase the viewing field after reactive gases have been introduced into the chamber either simultaneously or successively. High-resolution FIM images are acquired with a high-resolution CCD camera and dynamical behaviors are recorded using a high-sensitivity camera with a frame rate ranging from 25 fps (frames per second) to 10.000 fps, depending on the required temporal resolution.

Case Studies

NO Hydrogenation Studied by FIM

The hydrogenation of nitric oxide (NO) on Pt has been mainly investigated in FIM mode. Strongly nonlinear reaction kinetics were observed, including fast autocatalytic ignition (surface explosions), propagating chemical waves or even oscillatory-type behaviors.^{20–25} These behaviors were generally sensitive to small variations of the temperature and/or the electric field.²⁰

Fig.2A corresponds to a clean Pt tip sample characterized by low-temperature FIM using with Ne as imaging gas. Due to the sharpness of the tip only a few facets are clearly developed besides the (001) central pole and the large {111} peripheral planes.



Fig. 2 (A) Pt tip imaged by FIM before any exposure to reactive gas (conditions: T=70 K, $P_{Ne}=2 \times 10^{-3}$ Pa, $F \approx 37$ V nm⁻¹); FIM pattern during the N0+H₂ "surface explosion" at: T=525 K, $P_{NO}=2.5 \times 10^{-3}$ Pa, $P_{H_2}=2.5 \times 10^{-3}$ Pa, $F \approx 35$ V nm⁻¹); (B) before ignition; (C) at the ignition (time t=0 ms); (D) 200 ms after ignition; (E) 400 ms after ignition.



Fig. 3 Kinetic phase diagram obtained for the N0+H₂ reaction with a base pressure $P_{N0} = 10^{-3}$ Pa, and a constant imaging field $F \approx 9$ V nm⁻¹). This phase diagram presents three domains: I—domain of low reactivity (N0-side); II—domain of low reactivity (H₂-side); III—domain of kinetic instabilities.

Note that there are small {012} and {113} facets, not indexed in Fig. 2A, along zone lines between (001)-{011} and (001)-{111}, respectively. The tip morphology, compared to that in Fig. 1A, is closer to a truncated pyramid^{26,27} than a hemisphere.

The results in Fig. 2 have been obtained at 525 K using an imaging electric field of $F \approx 8.5$ V nm⁻¹. Individual FIM snapshots (2B–E) demonstrate the time evolution of a reactive surface explosion. Obviously, {011} facets and layer edges along the <100> zone lines suddenly turn bright (Fig. 2C). The brightness then propagates toward the central (001) pole (Fig. 2D and E) before fading so as to recover a pattern similar to the initial one of Fig. 2B.^{24,25} Importantly, a very similar pattern of evolution can be observed using Pt tips of larger radius of curvature. Again, facets along the <100> zone prove to be the most active ones. For a Pt hemispherical tip with a radius of ~33 nm, {012} facets have been observed to ignite in a concerted manner within 20 ms. We notice that the unit cell of this facet is spanned by kink sites. The results obtained for Pt tips of varying size therefore suggest any ensemble of atoms located along the <100> zone, that is, any ensemble of atoms in the half-crystal position, can trigger fast ignition and play the role of a pacemaker in repetitive events of quasi-oscillatory behavior.^{24,25}

The explosive transients presented above last a few hundred milliseconds and tend to repeat in a more or less regular manner. The delay between two surface explosions is usually comprised between 10 and 40 s.^{20,24} The parameter space for which these phenomena appear defines a specific region in the corresponding kinetic phase diagram. The term "kinetic phase diagram" is used as an analogy to phase diagram, involving transitions between steady states far from thermodynamic equilibrium. To produce Fig 3, the NO pressure and the imaging field are kept constant. At a given temperature, the H₂ pressure is increased so as to observe transitions between different kinetic behaviors that can be discerned by their FIM pattern: regime I corresponds to NO-rich conditions (low reactivity); II to the H₂-side with likewise low reactivity; and III to the realm of kinetic instabilities.²⁵ This latter regime also spans the parameter values for the occurrence of "surface explosions" when all other control parameters are kept constant.

Although the surface explosions repeat themselves, the delay between any two such events may vary, meaning that the observed signal is not periodic but rather presents the typical characteristics of intermittent dynamics. This is illustrated in Fig. 4, which plots



Fig. 4 Brightness signal probed during the NO+H₂ reaction, showing the nonperiodic oscillating behavior of the system. Conditions: T=500 K, $P_{NO}=3.0 \times 10^{-3}$ Pa, $P_{H_0}=4.0 \times 10^{-3}$ Pa, $F\approx 8-9$ V nm⁻¹.



Fig. 5 Autocorrelation function of the time series from Fig. 4 presenting a nonperiodic behavior.

the brightness signal as a function of time during the catalytic reaction. Several surface explosions are presented (left-hand side) where the nonperiodic character of the dynamics becomes apparent. On the right-hand side, the signal of a single explosive transient is presented. We can clearly observe the presence of a sharp peak of increased intensity directly followed by a decrease of the brightness so that the system returns close to its initial state after less than a second.

The reported dynamical features can be further quantified using techniques dedicated to time-series analyses. Autocorrelation functions, for example, determine how strongly two measurements separated by a time delay τ are correlated to each other. In the case of periodic oscillations, the autocorrelation function should be oscillating with a period corresponding to that of the original signal. The periodicity of a time series can, however, be blurred by the presence of noise, a phenomenon that should turn the autocorrelation function into damping oscillations. One way to characterize the robustness of a periodic behavior therefore is to measure the delay for which the autocorrelation has decreased from 1 (at $\tau = 0$) to a value of 1/e (at τ_e). Fig. 5 shows the autocorrelation function of the time series presented in Fig. 4. As anticipated, there is no well-defined periodicity and the time to reach the 1/e value is very short. Thus, the kinetic instabilities are nonperiodic and very sensitive to noise.

To determine the chemical nature of the imaging species responsible for FIM pattern formation, 1DAP investigations were performed during the ongoing reaction. Selective probing of {012} and (001} facets and their vicinals (usually between a few dozen to several hundred sites are probed, depending on the size of the tip and critical distances of the probe hole—detector system) showed NO⁺ as major species in the mass spectra along with smaller amounts of H_2O^+/H_3O^+ . The ionization rate of NO was seen to increase in a burst-like manner during surface explosions, leading to the conclusion that once the surface reaction was triggered to form water, NO molecules diffusing into emptied surface areas underwent ionization with high probability; NO⁺ therefore must be considered the imaging species in Fig. 2B–E.²³ We also mention that 1DAP studies with higher field strength of the pulses revealed platinum oxide species to field evaporate as PtO_x^{n+} with x=1-3.²⁴ This result suggests the surface of the sample be oxidized rather than metallic during the reaction. It must be concluded that the electric field can cause adsorbed oxygen to penetrate the surface, which should be accounted for in the global mechanistic description of the system.

To put the above findings into a more general perspective of fundamental deNOx research, we state that one of the distinguishing features, as compared to Rh catalysts, is that NO dissociation, an essential step of the overall process, is strongly dependent on the crystallographic orientation of the plane where adsorption occurs: adsorption of NO is molecular on {111} facets,²¹ but dissociative on {001} facets.¹³ Adsorption also preferentially takes place at step sites and induces a roughening of the surface around {012} facets when exposed at 573 K.^{6,28,29} Independent FEM studies of NO chemisorption on Pt tips³⁰ support our conclusions. In particular, and similar to our observations under dynamic conditions of the ongoing NO hydrogenation, surface diffusion of O(ads) has been observed in the 375–450 K temperature range while above 400 K, diffusion of oxygen into the bulk occurred, with a resegregation becoming active at higher temperatures.

On extended Pt(001) single crystal planes, oscillatory behavior can be observed by Auger electron spectroscopy and low energy electron diffraction in the temperature range 420–520 K^{31-34} and the reaction leads to the formation of N₂, NH₃, and N₂O, species which have not been observed in our studies. Mathematical modeling of this system obviously reproduced surface explosions and kinetic oscillations,^{35–40} for which the most important step involved the autocatalytic creation of empty sites.^{35–38}

To illustrate how autocatalytic behavior and fast ignition of the reaction can be triggered through vacant site formation, we consider the following equation

$$NO(ads) + 2H(ads) + S \rightarrow H_2O(g) + \frac{1}{2}N_2(g) + 4S$$

to be relevant for our studies,²⁴ with "S" standing for an empty surface site. This equation is the result of lumping the relevant elemental processes of NO adsorption, dissociation, and product formation along with their site requirements. The availability of a reservoir of mobile H(ads), which is a prerequisite for fast ignition to occur, has been demonstrated in FIM measurements with

varying pressures H_2 .²⁵ While the above equation neglects the possible formation of surface oxides,²⁴ simulations on the basis of a set of elementary reactions (without including such surface oxidation) have been performed^{41,42} and found to reproduce the explosive phenomena along with the bistable character of the system. An important consequence of this bistability is the occurrence of burst-like transitions through "excitation" of the system from a highly NO-covered inactive state to a less covered active surface, as observed experimentally and described in Fig. 3. The dynamics of excitation are characterized by the formation of water species, along with the formation of empty sites. Monte Carlo simulations also included the presence of fluctuations in the system inducing a wide dispersion in ignition time and explaining the aperiodic character of the system. Therefore, it may be concluded that the reaction is controlled by a vacant-site autocatalytic mechanism, leading to the emergence of fluctuations-induced intermittency related to the intrinsically excitable character of the reaction.

NO₂ Hydrogenation Studied by Field Emission Microscopy (FEM)

Nitrogen dioxide hydrogenation on Pt has been studied in FEM mode at 390 K^{5,25,43–46} and in FIM mode at temperatures up to 515 K.^{21,47} These studies revealed the presence of several complex dynamics, including self-sustained periodic oscillations.

Previous results obtained by FIM at 515 K suggest that the presence of truncated pyramid morphology is necessary to observe complex dynamical behaviors.

In the case of FEM experiments, an evolution of the reactivity was observed over time.⁵ Fig. 6A–C depict FEM micrographs during a "surface explosion" in the NO₂+H₂ system at 390 K, right after the behaviors were initiated. Mainly facets of {011} and {012} orientation appear bright while {111} and {113} remain dark suggesting these latter facets to be inactive during the catalytic process. Another important result from the FEM studies shown in Fig. 6 is that all active facets ignite simultaneously during the explosion within the temporal resolution of 40 ms defined by the camera system. After ignition, the intensity of the brightness signal fades with a longer time-scale (less than a second) to recover its initial value indicative of low catalytic activity. Previous FEM work at 465 K also showed the occurrence of fronts propagating anisotropically across the surface. The pacemakers of the reaction were identified in the {012} planes and the reaction proceeded along the <001 > zone lines toward the (001) pole.²¹

It is interesting to note that after 10–20 min, the same tip as used in Fig. 6 has been observed under very similar experimental conditions, to develop activity in the (001) center as well. The evolution of brightness in the (001) pole is most probably due to a local reconstruction the details of which are not fully understood at present. On the other hand, a surface oxidation due to following dissociative NO₂ adsorption can be safely excluded for a reaction temperature of 390 K under FEM conditions.⁴⁸

In dynamic studies with FIM, however, a morphological reconstruction of an initially hemispherical Pt tip yet has been observed at 515 K. A pyramidal shape with truncated (001) top and large {111} oriented slopes resulted and served to demonstrate successive ignitions of the {012} facets, together with a wave propagation along <211> zone lines, bridging {012} via {113} facets.^{46,49}

The domain of existence and the frequency of explosions, as observed in Fig. 6 under FEM conditions, have been summarized in the bifurcation diagram of Fig. 7.⁴⁵ To generate this diagram, a base pressure of NO_2 was first leaked into the chamber, followed by a gradual increase of the hydrogen pressure (which plays here the role of a control parameter). A transition from a dark FEM pattern to periodic variations of the brightness has been observed. The scaling of the frequency of these oscillations as a function of the control parameter is consistent with a transition known as homoclinic bifurcation.⁵⁰ These results are also in line with our earlier investigations of the system.²¹

The brightness signal corresponding to typical periodic oscillations is presented in Fig. 8. Obviously, repetitive surface explosions can be highly regular, self-sustained, and robust against the inherently present noise in this nanosized reaction system. A single explosive event, as presented on the right-hand side of Fig. 8, begins with a low level of brightness which can be related to the presence of O(ads) and NO(ads) species resulting from the dissociative adsorption of NO_2 .⁵¹ The sharp increase in brightness then reflects the catalytic light-off. Individual peaks are usually asymmetric, which is characteristic of relaxation-type oscillations. For different H₂/NO₂ pressure ratios, the peaks can present more complex shapes (such as bimodality) whose properties can be



Fig. 6 FEM patterns during NO₂+H₂ reaction during the first minutes of the NO₂+H₂ interaction over a freshly developed Pt tip sample. (conditions: $T=390 \text{ K}, F\approx 4 \text{ Vnm}^{-1}, P_{\text{H}_2}=1.85 \times 10^{-4} \text{ Pa}, P_{\text{NO}_2}=5.4 \times 10^{-6} \text{ Pa}$); (A) 200 ms before the maximum intensity of the FEM pattern during surface explosion, (B) at the highest intensity, (C) 400 ms after the "surface explosion."



Fig. 7 Bifurcation diagram plotting the frequency of oscillations in the NO₂+H₂ reaction as a function of hydrogen pressure, which is used as the control parameter (conditions: T = 390 K, $F \approx 4$ V nm⁻¹, $P_{H_2} = 8.5 \times 10^{-3}$ Pa, $P_{NO_2} = 5.4 \times 10^{-4}$ pa). The shaded region corresponds to the zone of existence of oscillations.



Fig. 8 Brightness signal probed during the NO₂+H₂ reaction, showing the periodic oscillating behavior of the system. Conditions: T=390 K, $P_{NO_2}=3.6 \times 10^{-4}$ Pa, $P_{H_2}=1.5 \times 10^{-2}$ Pa, $F \approx 4$ V nm⁻¹.

studied with different techniques such as periodic averaging, Fourier power spectra, or interpeak interval maps.⁴⁴ It has to be noted that nonperiodic oscillations could also be observed in this system and result in asymmetric peaks as well.⁴⁶

The reaction system can be further characterized by temporal autocorrelation functions.⁴³ As can be seen in Fig. 9, the autocorrelation function is periodic in our case, with a decaying envelope which is due to the presence of fluctuations inducing what is called "phase diffusion of oscillations."^{52–54} These results are in agreement with theoretical predictions of noisy chemical oscillators, and the system can thus be defined as a chemical nanoclock.

Even though the adsorption- and reaction-induced changes of the work function leading to dynamic FEM pattern evolution may be complex, several qualitative statements can be made to provide a basic understanding of the elemental processes occurring. First, NO₂ adsorption is dissociative and causes oxygen coverages to build up. As a consequence, the work function increases, that is, the image brightness of the sample decreases. The reaction between O(ads) and H(ads) is supposed to form water which, different from O(ads), is known to decrease the work function. The desorption of water from the sample then generates empty sites, that is, leaves behind a clean surface with a higher brightness signal.²¹ Complimentary 1DAP measurements have been performed and confirmed dissociative NO₂ adsorption and subsequent formation of water under conditions similar to those applied in FEM.^{23,49} We also conclude that the reaction steps toward the formation of water are similar to those of the NO+H₂ reaction, with the exception of NO₂ dissociative adsorption leading to additional amounts of O(ads). The {111} facets appear dark and remain dark after NO₂ adsorption, that is, they are not active at all, indicative of insufficient amounts of coadsorbed hydrogen to initiate water formation.²¹ Due to the fast catalytic light-off in active surface planes, the process governing the water production is supposed to be identical and independent of the actual surface crystallography.²⁵ The fact that ignitions appear simultaneously suggests the presence of a strong spatial coupling. Recent experiments using a camera with a much higher temporal resolution have shown that this coupling is ensured by the rapid propagation of nanometric fronts within and between the active {011} facets.⁴⁶ The presence of periodic oscillations of increasing complexity, mainly bimodal periodic oscillations, was assigned to the formation of water



Fig. 9 Autocorrelation function of the time series from Fig. 8 presenting a periodic behavior with a decaying envelope.

following two different routes: either the addition of H(ads) to an OH(ads) intermediate species, or the combination of 2 OH(ads) to form $H_2O(ads)$ and O(ads). In both cases, the global reaction involving autocatalytic formation of empty sites remains the same,⁴⁴ just like in the NO+H₂ system.

Conclusions

Despite the catalytic reduction of NO and NO₂ having strong mechanistic similarities, quite different reaction dynamics can be observed. Water formation is believed to follow the same path in both systems and H₂ adsorption should be the same as well. The main difference between the chemistry of the two systems thus resides in the adsorption and dissociation mechanisms for NO and NO₂. NO₂ is known to have a higher sticking probability than NO.²¹ Dissociation of this species is therefore supposed to enhance the oxygen coverage, possibly inhibiting further NO dissociation.⁵⁵

In both systems, all the active facets ignite simultaneously, with $\{012\}$ facets acting as pacemakers. The apparent simultaneousness indicates a fast chemical coupling between facets in both cases, which is probably due to the high mobility of hydrogen species. A high activity is observed along the <001> zone lines, with an important reactivity of $\{012\}$ and $\{001\}$ facets (despite considerable incubation times in the case of NO₂). $\{111\}$ facets remain inactive in both cases.

Adsorbate-induced surface restructuring is possible with both reaction systems. However, deep reconstruction involving the transformation from nearly hemispherical to polyhedral morphology has been observed to occur only under FIM conditions. This transformation is most likely associated with the formation of an oxide in the near-surface region. Obviously, the presence of a high "positive" electric field promotes the subsurface diffusion of surface oxygen produced by NO or NO₂ dissociation. Such a field influence is understandable because the Pt–O^{δ -} surface dipole has an opposite orientation with respect to the electric field vector. In the "negative" FEM mode, however, this unfavorable surface dipole orientation is inexistent. In line with these considerations is also the observation that "transient" oscillatory behavior of the NO+H₂ reaction over Pt tips, using the FEM mode, has only been observed in stepped facets around the (111) pole.^{35–38} Quite generally, while both FEM and FIM have been shown successful in imaging the nonlinear dynamics of the NO-H₂ reaction, it is clear that the parameter space spanned by (*T*; *P*_{NO₂}; *P*_{H₂}; *F*) combinations is larger in the case of the NO₂+H₂ reaction.

Finally, one of the most striking differences between the two reaction systems is the robustness of the rate oscillations. While the oscillations observed for the NO+H₂ reaction on Pt are transient and rather irregular, they are highly regular for the NO₂+H₂ reaction. It seems clear that fluctuations at the nanoscale of our investigations play a major role and induce the transitions. An analysis of the fluctuations' influence, for a wide range of parameters, has proved the remarkable robustness of this system.⁴⁵

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