# NO<sub>2</sub> Hydrogenation on Rh Catalysts: Bifurcations and Oscillations at the Nanoscale

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**ABSTRACT:** In this work, we report complex kinetic phenomena observed during the reduction of NO<sub>2</sub> on rhodium model catalysts followed by field emission microscopy (FEM). This technique uses samples prepared as sharp tips, mimicking the size and shape of one catalytic nanoparticle. The method enables one to study catalytic reactions in real time down to the nanoscale. Running the NO<sub>2</sub> + H<sub>2</sub> reaction on Rh at 450 K and in the 10<sup>-5</sup> Pa range, we observe nonlinear behaviors on the facets corresponding to {011} and {012} crystallographic orientations. The emergence of nonlinearities is studied as a function of the control parameters, and the particular case of self-sustained periodic oscillations is analyzed in detail. The corresponding bifurcation diagram shows that the oscillations appear via a supercritical Hopf bifurcation. It is moreover possible to reconstruct the underlying dynamical attractor—here, the limit cycle—using the time-delay embedding method. Different possible mechanisms of reaction leading to these oscillations are discussed.



# 1. INTRODUCTION

In the applied formulation of catalysts, platinum group metals are often used to abate toxic gas species such as CO, unburned hydrocarbons, and  $NO_x$ .<sup>1</sup> Surface science techniques have been widely used to reach a better understanding of the molecular mechanisms behind such processes.<sup>2</sup> CO oxidation is certainly the most studied catalytic reaction by surface science approaches.<sup>3–7</sup> DeNOx reactions, especially the study of nonlinear behaviors occurring during the reaction, were studied to a much lesser extent, and only a few works have focused on the analysis of these reactions, in spite of the important role that they play in environmental-related concerns, and in particular in automobile pollution control by catalysis.

In order to better understand how the DeNOx reactions proceed at the nanoscale, field emission techniques, which comprise field emission microcopy (FEM) and field ion microscopy (FIM), are of particular interest. These techniques employ sharp metallic needles, the apex of which has a size and shape which is similar to those of metallic particles found in applied catalytic formulations. By applying a voltage between a tip-sample and a phosphor screen, this apex can be imaged with atomic lateral resolution at cryogenic temperatures. At temperatures suitable for catalytic reactions, surface processes can be imaged with nanometric resolution in real time during the ongoing processes.8 One of the advantages of the FIM/ FEM technique is that the tip exposes several facets of different crystallographic orientations on the same sample, which allows one to image in real time and in a simultaneous way coupled surface processes on a collection of different facets.

Nonlinear behaviors are to be expected for the NO<sub>2</sub> + H<sub>2</sub>/Rh system by analogy with similar systems. The NO hydrogenation has, for example, been studied on Pt,<sup>9,10</sup> Rh,<sup>11,12</sup> as well as Pt–Rh alloys of various compositions.<sup>13</sup> In the case of Rh catalysts, the reaction has been studied by FEM and showed a variety of nonlinear kinetics. For NO(g) pressure in the 5  $\times$  $10^{-2}$  Pa range and H<sub>2</sub>(g) in the 6 ×  $10^{-3}$  Pa range, aperiodic behaviors were reported at 470 K, surface explosions at 465 K, local oscillations (oscillations occurring only on some parts of the sample) at 450 K, and eventually regular global oscillations, with a period of  $\sim 20$  s, for temperatures between 430 and 445 K.<sup>11,12</sup> Reactive fronts were also shown to propagate over the sample, except for the {012}, {013}, and {113} facets. This has been interpreted as being due to the formation of a strong Rh-N bond on these particular facets, which inhibits the reaction.<sup>14</sup> The same reaction studied by FIM has shown the presence of chemical waves at 350 K.<sup>15</sup> Further studies by PEEM and LEED techniques over extended facets of Rh(533) and Rh(111) demonstrated the existence of nonlinear behaviors. In the first case,<sup>16</sup> at 494 K and for a base pressure of  $8 \times 10^{-5}$  Pa in NO(g) and a H<sub>2</sub>/NO pressure ratio of 14, periodic oscillations of a period of about 25 s were observed. Mass spectrometry measurements revealed the presence of  $\rm NH_3(g),~\rm NO(g),~\rm and~\rm N_2(g)$  species. For reactions on  $\rm Rh(111),^{17}$  periodic oscillations in the production of water with a period of approximately 60 s were observed at 466 K.

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Since the NO<sub>2</sub> hydrogenation undoubtedly involves reaction between H(ads) and O(ads) atoms, O<sub>2</sub> hydrogenation on Rh also needs to be considered for a better understanding of the possible mechanisms governing the NO<sub>2</sub>-H<sub>2</sub>/Rh system. The O<sub>2</sub>-H<sub>2</sub> reaction on Rh has been studied on Rh by field emission techniques. From a dynamical point of view, the main results are as follows. FEM experiments performed at 280 K in the presence of an oxygen precovered surface allowed for the observation of propagating fronts for a H<sub>2</sub> pressure of  $2.6 \times 10^{-5}$  Pa.<sup>18</sup> In FIM mode, the system revealed the presence of self-sustained periodic oscillations (period: 40 s) at 550 K, as well as bistability at 450 K.<sup>19,20</sup> The origin of the oscillations has then been attributed to the presence of subsurface oxygen.<sup>21</sup>

In this work, we present and analyze the dynamics of the much less understood reduction of NO<sub>2</sub> by H<sub>2</sub>. This reaction has been previously studied on Pt using field emission techniques.<sup>22,23</sup> The main dynamical features of the NO<sub>2</sub> + H<sub>2</sub>/Pt system at 390 K include nonlinear behaviors such as periodic oscillations,<sup>24,25</sup> bimodal oscillations,<sup>26</sup> noisy oscillations,<sup>27</sup> and propagation of chemical waves.<sup>28</sup> The emergence of oscillations could be traced back to the presence of an infinite period bifurcation,<sup>29</sup> which appears in the kinetic phase diagrams of these systems. This reaction has been recently studied on Pt-17.4 at.% R where periodic oscillations have been observed at 425 K.<sup>30</sup>

In this paper, we perform analyses to unravel the dynamical origin of periodic oscillations occurring on Rh samples. In section 2, we discuss the experimental method and the characterization of the tip–sample by FIM and FEM. Section 3 is devoted to a summary of the available information concerning the interaction of  $H_2$  and  $NO_2$  gases with Rh samples. A detailed description of the nonlinear behaviors is given in section 4, in which we present among others the reconstruction of the dynamical attractor with time-delayed embedding techniques and the analysis of the bifurcation diagram. In section 5, we discuss the possible mechanisms of reaction as compared with the  $NO_2 + H_2/Pt$  system. Conclusions and potential extensions of the present work are presented in section 6.

#### 2. METHODS

**2.1. Experimental Setup.** Experiments are carried out in a stainless steel field ion/emission microscope. Details of the setup as well as basic principles of the technique can be found elsewhere.<sup>31</sup> The rhodium field emitter tips used as samples are prepared by electrochemical etching in a molten salt mixture of NaCl/NaNO<sub>3</sub> (1:4 w/w), they are subsequently cleaned with distilled water, and their shape and size are assessed by optical microscopy. After introduction of the tip in the UHV chamber of the microscope, the sample is cleaned *in situ* by different procedures: heating, field evaporation, annealing, and ion sputtering.

The tip is first characterized with atomic resolution at low temperature by FIM (Figure 1a), and then by FEM with a lower spatial resolution of  $\sim 2$  nm (Figure 1b). The brightness pattern obtained in FEM is our main source of data about the system's state, and it is thus important to discuss image formation. FEM is based on the emission of electrons from the metallic sample toward a revealing screen. The intensity of the emission is expected to be ruled by the Fowler–Nordheim equation,<sup>32</sup> following which the intensity depends on the local electric field, on temperature, and on the work function of the



**Figure 1.** (a) Characterization of a Rh tip by FIM, with neon as imaging gas, at low temperature showing the atomic resolution of the technique. The FIM pattern translates lateral variations of the ionization probability of image gas atoms at the apex of the tip. Most protruding atoms (i.e., step and kink sites) appear as white dots (conditions of acquisition: T = 60 K,  $P_{\rm Ne} = 2 \times 10^{-3}$  Pa, electric field  $F \sim 35$  V nm<sup>-1</sup>). The radius of curvature corresponds to ~15 nm and the field of view to ~30–35 nm. (b) Same sample imaged in FEM mode. The lateral resolution is ~10 times lower than that in FIM mode, but the magnification remains unchanged. Correspondence between the two patterns is found by superimposition (conditions of acquisition: T = 60 K, ultrahigh vacuum,  $F \sim 4$  V nm<sup>-1</sup>). The red circle corresponds to the probed ROI on a (011)-type facet (see text).

sample ( $\Phi \sim 4.8 \text{ eV}$  for Rh tips<sup>33</sup>). Consequently, at constant voltage, sample morphology, and temperature, the intensity varies as a function of the crystallographic orientation of the different facets,<sup>34</sup> as seen in Figure 1b.

We then apply conditions for which surface chemical reactions take place. The sample is heated up to 450 K and a field of  $\sim$ 4–5 V nm<sup>-1</sup> is applied to the tip in the FEM mode, which is sufficient for an image to appear on the screen of the microscope. Finally, NO2 and H2 gases are injected in the reaction chamber and the state of the surface is monitored in real time. Adsorbed atoms and molecules are known to modify the work function, and thus, local changes of the brightness can be attributed to changes of composition (see section 3 for a more detailed discussion). Once nonlinear behaviors appear on the catalyst, the brightness signal is probed on a specific region of interest (ROI) corresponding to a (011) facet, as indicated by a red circle in Figure 1b. Time series were acquired at 50 fps (frames per second). Details regarding the physicochemical treatments and the acquisition of time series of the brightness in the ROI have been given previously.<sup>26</sup>

2.2. Data Treatment. The acquired brightness signal (image brightness as a function of time) is analyzed with different procedures so as to define which type of dynamic behavior is taking place. We typically start by extracting the Fourier power spectrum from the time series, and then determine the robustness of the oscillations with correlation function analyses. We also reconstruct the underlying dynamical attractor by using time delay embedding methods. This data analysis technique is based on the construction of a collection of time-delayed time series, which necessitates the determination of an optimal delay. We calculated to this end the average mutual information (AMI).<sup>35</sup> The AMI is a measure of the degree of correlation between measurements taken at different times. Consequently, the first minimum of the AMI as a function of the time difference often provides a good choice for the delay, which can then be used to estimate the dimension of the phase space in which the dynamics can be embedded. To determine this dimensionality, we decided to



**Figure 2.** (a) Brightness signal representing self-sustained periodic oscillations on Rh during the NO<sub>2</sub> + H<sub>2</sub> reaction (conditions: T = 450 K, electric field  $F \approx 3.7$  V nm<sup>-1</sup>,  $P_{NO_2} = 2.29 \times 10^{-5}$  Pa,  $P_{H_2} = 9.60 \times 10^{-5}$  Pa). The mean period of oscillation is 42.1 s, as determined by Fourier power spectrum analysis (see Figure 3). (b) Enlargement on three peaks of oscillations representing relaxation-type oscillations. The brightness signal is probed on a (011) facet, as depicted in Figure 1b.

opt for a method known as the false nearest neighbors method (FNN).<sup>36</sup> This method is often less sensitive to fluctuations and is less prone to finite-size induced artifacts than, say, approaches based on the correlation dimension. The AMI and FNN analyses were performed with the TISEAN 3.0.1 package for nonlinear time series analyses.<sup>37</sup> More details on the use of these techniques for the analysis of nanoscale systems can be found in ref 38.

# 3. INTERACTION OF NO<sub>2</sub> AND H<sub>2</sub> WITH Rh: STATE OF THE ART

The interaction of hydrogen gas with rhodium leads to a dissociative adsorption of  $H_2(g)$ . For an adsorption performed at 196 K, the desorption of hydrogen species occurs at approximately 370 K for a dosing of 0.6 L and at 320 K for a dosing of 5 L (where 1 Langmuir (1 L) equals  $1.33 \times 10^{-4}$  Pa·s). Adsorption at 470 K induces the presence of a desorption peak of molecular hydrogen at 500 K, as well as a second peak in the temperature range 600–800 K attributed to subsurface hydrogen.<sup>39</sup> An increase in the work function is observed as the hydrogen coverage increases, and a maximum of  $\Delta \Phi = +0.36$  eV is reached at 196 K and  $\Delta \Phi = +0.30$  eV at 300 K.<sup>39</sup> On a Rh(110) extended facet, there is no work function variation at 300 K.<sup>40</sup> Since the ROI corresponds to such a facet, we can safely admit that adsorbed H atoms do not modify the measured brightness.

The adsorption of  $NO_2(g)$  on metallic surfaces has not been studied in great detail.<sup>41</sup> Previous studies on Rh(111) have shown that the adsorption of  $NO_2(g)$  is dissociative at 150 K and leads to NO(ads) and O(ads). Temperature-programmed desorption (TPD) measurements indicate: (i) the desorption of molecular NO<sub>2</sub> at 200 K, (ii) the absence of NO(ads) species above 400 K because of its desorption and/or dissociation, and (iii) the presence of N(ads) and subsurface O(sub) species at 400 K and higher temperatures. The presence of subsurface oxygen is in agreement with other studies on oxygen adsorption on Rh.<sup>42,43</sup> Regarding the work function, we observed during our experiments a noticeable decrease of the brightness after introduction of  $NO_2(g)$  in the system, so that we expect this species to lead to an increase of  $\Phi$ . This seems to be consistent with reported increases of the work function  $\Delta \Phi = 0.9$  eV at 280 K after adsorption of O<sub>2</sub> on Rh FEM tips, <sup>39,44</sup> and  $\Delta \Phi = 0.2$  eV at 300 K on the (001) facet after adsorption of NO(g).45

Regarding the deNOx reaction, the main difference between Pt and Rh lies in the ability of Rh to easily dissociate NO(ads) species. Accordingly, N(ads) should be expected to be found on the surface in addition to the previously mentioned species. Both H<sub>2</sub>O and NH<sub>r</sub> could moreover be formed during the processes, and these species are known to induce a decrease in the work function on Rh surfaces.<sup>46–48</sup> From those facts, it can be concluded that, on Rh samples exposed to a gas mixture of NO<sub>2</sub> and H<sub>2</sub> with a pressure of  $\sim 10^{-3}$  Pa at 450 K, the most probable adsorbed species are H(ads), O(ads) and O(sub), N(ads), NO(ads), as well as the products of reaction,  $H_2O$ and/or NH,. Because of the mentioned changes of work function, one can moreover conclude that a (110) facet covered in reactants appears darker than a facet without adsorbates and/ or covered with products. Note that all our considerations on the connection between brightness and surface composition are based on the hypothesis that the local electric field remains constant during the experiments, which implies that morphological changes such as surface reconstructions do not play an important role.

# 4. RESULTS AND DISCUSSION

**4.1. Initiation of Nonlinear Behaviors.** In order to initiate the reaction at the surface of the Rh tip, a constant pressure of  $NO_2(g)$  is first established in the reaction chamber of the microscope. As expected, a decrease of the FEM brightness pattern can be observed due to the dissociative adsorption of  $NO_2$ . Hydrogen gas is then introduced, in such a way that the total pressure remains constant.

Since we maintain both the temperature and the voltage constant, local changes of the brightness can be attributed to local changes of the work function due to a modification of the chemical composition at the surface. These changes in the brightness signal are monitored by probing the brightness signal on the detector screen. We observe that the brightness signal can vary substantially in time under constant reactant pressures on the  $\{011\}$  facets and on their close neighbors,  $\{012\}$ - and  $\{113\}$ -type facets. The  $\{111\}$  facets as well as the (001) central pole remain dark during the reaction and thus cannot be used to probe changes of the surface composition.

The H<sub>2</sub>(g) pressure is used as a control parameter, and its variation allows defining three different dynamical regimes. At low  $P_{\rm H_2}/P_{\rm NO_2}$  pressure ratios, the brightness of the sample is low and fluctuates around a constant value. Adsorbed oxygen



Figure 3. (a) Power spectrum of the brightness signal presented in Figure 2, showing a well-defined frequency of 0.024 Hz (41.26 s). (b) Intervaldependent normalized correlation function showing damped oscillations. The decay is characterized by a correlation time of 123 s ( $\sim$ 3 periods of oscillation). The red line corresponds to 1/e.

species released by  $NO_2(g)$  dissociation are most probably responsible for the high work function of the sample under such conditions, since hydrogen pressure is too low to remove substantial amounts of O(ads) from the surface. We will consequently refer to this situation as the nonreactive state. The second regime is characterized by a high level of brightness and is observed for higher  $P_{\rm H_2}/P_{\rm NO_2}$  pressure ratios. This regime could either correspond to a nonreactive regime where the surface is clean or mostly covered by H(ads) species or to a reactive regime characterized by a constant conversion of the reactants into products. Finally, a third regime can also be observed at intermediate pressure ratios. It is characterized by transitions between the aforementioned extreme levels of brightness. We will call this state the nonlinear regime. Once nonlinear behaviors are initiated, the pressures of both H<sub>2</sub> and NO<sub>2</sub> are maintained constant. This procedure often results in the emergence of regular oscillations of brightness, the characteristics of which are discussed below.

**4.2. Self-Sustained Periodic Oscillations.** A representative time series of such oscillations is given in Figure 2a, which also plots the detail of the shape of three peaks (Figure 2b). The oscillations are characterized by a rather wide distribution of amplitude; the amplitude of a single oscillation can here vary between 40 and 120 units of brightness. The range of variation of the amplitude can thus be as large as the mean amplitude itself. It must also be noted that the oscillation peaks presented in Figure 2b are asymmetric, and that this asymmetry is preserved along the whole time series. A single oscillation is typically comprised of three different stages:

- A sharp increase of brightness occurring on a short time scale (less than a second). We will refer to this behavior as a "surface explosion", corresponding to the catalytic light-off.
- A slower decrease (here lasting approximately 10–20 s), after which the brightness reaches the value it had before the sharp increase. We notice that the signal tends to fluctuate a lot during this part of the oscillation.
- A transient period of low brightness (~25 s in Figure 2) that lasts until the next sharp peak.

These features are characteristic of relaxation-type oscillations.<sup>49</sup>

The periodicity of the time series is confirmed with Fourier power spectra (Figure 3a) that show a well-defined main frequency (0.024 Hz, i.e., a period of 41 s for the chosen

example). The period of oscillation in the different experiments is always comprised between 40 and 55 s, which is approximately 1 order of magnitude slower than the oscillations observed for the same reaction on Pt<sup>26</sup> but in the same range as those observed during the  $O_2$  +  $H_2$  reaction on Rh field emitter tips.<sup>21</sup> As we will see in more detail in the section devoted to the bifurcation analysis (section 4.2.b), the mean amplitude of the peaks is affected by the value of the  $P_{\rm H_2}/P_{\rm NO_2}$  pressure ratio. The overall robustness of the oscillations can be quantified through the autocorrelation function such as the one presented in Figure 3b. The autocorrelation function shows oscillations of decreasing amplitude due to the presence of fluctuations in the system.<sup>24,50,51</sup> The dampening of these oscillations is characterized by a correlation time  $\tau_{\rm c}$  defined as the time after which the autocorrelation function has decreased from 1 to 1/e. For the example shown in Figure 3b, the correlation time is 123 s, which corresponds more or less to three periods. Such a value of the correlation time is in agreement with theoretical predictions on fluctuation-perturbed oscillations in nanosystems.<sup>52,53</sup> These oscillations are however less regular than those observed on Pt with the same technique,<sup>29,30</sup> for which the correlation time was seen to extend over dozens of periods.

4.2.a. Reconstruction of the Dynamical Attractor. Periodic behaviors related to chemical reactions can be traced back to the existence of specific objects in the space spanned by the values of the concentrations of the different species involved. More precisely, oscillations are supposed to be associated with limit cycles, which are closed cycles attracting nearby trajectories in this so-called phase space. An interesting way to illustrate that our observations correspond to such a type of self-sustained oscillations would be to reconstruct the trajectories in phase space and verify that they indeed define an underlying limit cycle.

Since the instantaneous values of all of the concentrations are not available, we cannot access the "real" phase space or the "real" attractor. However, it was shown that the most important topological properties of attractors are conserved when using a collection of delayed time series of a single measurement (here, the brightness) instead of the original, unavailable variables.<sup>54,55</sup> We thus define such a collection of vectors by using B(t),  $B(t + \tau)$ ,  $B(t + 2\tau)$ , ..., where B stands for the brightness of the signal and  $\tau$  is the delay. For this, we work with the raw signals probed on the defined ROI.

There are several ways to choose an optimal delay for the reconstruction. As mentioned earlier, we choose to work with the AMI method, and for the time series depicted in Figures 2 and 3, the optimal delay  $\tau$  corresponds to ~2.8 s. With these delayed time series, the embedding dimension  $d_{\rm E}$  can be obtained. This parameter is a measure of the dimensionality that the phase space must have so as to embed the dynamical attractor (for more details, see ref 49). The optimal embedding dimension can be estimated with several different techniques. Here, we work with the FNN method, which is less sensitive to the length of the time series than other approaches.<sup>56</sup> We obtain a value of  $d_{\rm E}$  comprised between 3 and 4 (these results were so to say independent of the choice for the Theiler window; we also note that the embedding dimension estimated with the correlation dimension  $D_2$  is of the order of  $d_{\rm F} \approx 4-5$ for the same time series) (with  $d_{\rm E}$  = 4 for the example shown in Figure 2), which suggests that the dimension of the attractor is smaller than or equal to 3. It should be noted that noise is known to often increase the embedding dimension with respect to deterministic systems.

A two-dimensional projection of the reconstructed trajectories is represented in Figure 4. In Figure 4a, we show (as a thick line) the average oscillation obtained by performing a periodic averaging of the original time series, which are depicted as faint blue lines. The cyclic character of the trajectories is obvious. More precisely, each occurrence of the oscillations can be related to the three distinct phases mentioned earlier. The (0,0)



**Figure 4.** (a) Reconstructed dynamical attractor from the time series presented in Figure 2, with a time delay of 2.8 s. The bold line is a periodic average of the signal, and the other curves are the original trajectories. (b) This figure plots the mean trajectory superimposed on a color map showing the probability to find a trajectory point in phase space. We used here a value of dB = 1 luma. Note that we additionally performed a graphical spline interpolation of the color map for better legibility of the graph. The brightness is expressed in units spanning over the grayscale defined by the 8 bits coding each pixel, i.e., 256 levels of brightness expressed as luma.

point corresponds to the baseline of oscillations. Starting from this point, the system first undergoes a rapid increase of brightness, which here takes the form of a vertical line, since  $B(t + \tau)$  increases rapidly while B(t) remains so to say constant. This is followed by a period where  $B(t + \tau)$  slowly decreases as B(t) goes through the large-amplitude explosion, which results in a horizontal line. Finally, both measures of the brightness decrease together and end up again close to the (0,0) point. We observe that the trajectories tend to concentrate around the average path, except during the second phase of oscillation. Since the amplitude of the explosions is widely distributed, the length of both the vertical and horizontal transients strongly varies from one realization of the oscillation to another, which results in a dispersion of trajectories.

An alternative way of showing this is given in Figure 4b. There, we plot the probability to find the system in a given interval of brightness along with the averaged trajectory. These probabilities are calculated by first coarse-graining the 2D phase space into boxes of size  $dB^2$ , and then counting the relative number of trajectory points in each phase-space box. The linear size of these coarse-grained boxes is determined by using the  $\sqrt{n}$  rule for the number of bins in a histogram, where *n* is the number of data points. We observe that most of the probability mass is concentrated close to the (0,0) point where the system spends a lot of time. Along two of the branches of the attractor, the probability remains close to the average, while the upper boundary of the cycle is much more diffuse. This means that, in probability space, the cycle defines a stochastic "crater" whose rim would correspond to the averaged oscillation and whose slopes would be extremely stiff along two directions and much shallower during the second phase of the cycle. A similar observation was made for the NO2 + H2/Pt system studied with the same technique,<sup>38</sup> with the difference that the dispersion of the trajectories is much more important for Rh. The shape we observe is more probably characteristic of relaxation-type oscillations, since we expect the amplitudes to be highly dispersed in that class of systems.

4.2.b. Bifurcation Diagram. The next step in the characterization of the system is to unravel the class of dynamical instability leading to the emergence of periodic oscillations, in other words to determine the type of bifurcation leading to the limit cycle. To do so, we varied the pressure of dihydrogen while maintaining the other control parameters constant and we measured both the amplitude and frequency of oscillations. As explained in the previous section, the initiation of oscillations only occurs while the  $H_2(g)$  pressure is decreased from high to low values. We can detect in this way two different bifurcations, as explained below.

Bifurcation diagrams corresponding to a NO<sub>2</sub> pressure  $P_{\rm NO_2} = 2.93 \times 10^{-5}$  Pa and a temperature T = 450 K are presented in Figure 5a and b, which show the frequency and the amplitude of oscillations, respectively. Two bifurcations are observed as  $P_{\rm H_2}$  is decreased. The first one (at  $P_{\rm H_2} = 8.3 \times 10^{-3}$  Pa) corresponds to a transition from a stable regime of high brightness to periodic oscillations. The second one (at  $P_{\rm H_2} = 5.0 \times 10^{-4}$  Pa) is a transition between oscillations and a stable regime of low brightness, which is found only at very low  $P_{\rm H_2}$ .

Close to (but above) the low-pressure bifurcation point, the frequency of oscillations varies only slightly when changing  $P_{H_2}$ . As shown in Figure 5a, the frequency is comprised between



**Figure 5.** (a) Bifurcation diagram plotting the frequency of oscillations as a function of hydrogen pressure for a base pressure of NO<sub>2</sub>,  $P_{\rm NO_2} = 2.93 \times 10^{-5}$  Pa. Hydrogen pressure is used as the control parameter. The frequency of oscillations remains stable on the range studied. (b) Bifurcation diagram plotting the amplitude of oscillations as a function of hydrogen pressure for a base pressure of NO<sub>2</sub>,  $P_{\rm NO_2} = 2.93 \times 10^{-5}$  Pa. Except the experimental point at  $P_{\rm H_2} = 1.56 \times 10^{-3}$  Pa, the amplitude presents a quadratic dependence characteristic of a supercritical Hopf bifurcation. The blue line corresponds to the best fit for the experimental points.

0.0245 and 0.020 Hz in this neighborhood. It then suddenly drops to zero as the bifurcation point is crossed. The average amplitude, on the other hand, increases smoothly in the same neighborhood. The scaling of both the period and the amplitude of oscillations with respect to the distance from the bifurcation point can be analyzed more precisely by introducing a rescaled (nondimensional) pressure

$$\mu = \frac{P_{\rm H_2} - P_{\rm H_2}^{\rm c}}{P_{\rm H_2}^{\rm c}}$$

where  $P_{H_2}^c$  stands for the critical H<sub>2</sub> pressure (here estimated as the midpoint of the pressures surrounding the transition point,  $P_{H_2}^c = 2.2 \times 10^{-4}$  Pa). We find that the frequency scales as  $f \propto \mu^{\alpha}$  with  $\alpha = -0.04 \pm 0.02$ , while the average amplitude increases like  $\overline{A} \propto \mu^{\beta}$  with  $\beta = 0.4 \pm 0.1$ . These laws are consistent with the bifurcation being a *supercritical Hopf point*.<sup>49</sup> A similar analysis cannot be performed for the high-pressure bifurcation point due to lack of experimental data. However, in this case, the system presents a sudden transition to oscillations with finite amplitude, which suggests that this bifurcation point could correspond to a subcritical Hopf or to an infinite-period bifurcation. It should be noted that, in the case of NO<sub>2</sub> + H<sub>2</sub>/ Pt, the transition leading to oscillations was shown to be of the infinite-period type.

#### 5. MECHANISM OF REACTION

We discuss here different possible chemical mechanisms that could explain the emergence of oscillations. We can expect to find clues on the reaction mechanism on Rh in the characteristics of the nonlinear dynamics. Different important observations need to be taken into account:

- the presence of two stable regimes, one at low and one at high levels of brightness, corresponding respectively to low and high pressures of H<sub>2</sub>
- the observation of periodic oscillations defining a limit cycle, which implies that any mean-field reaction model would require a minimum of two variables and the presence of feedback loops
- the fact that the oscillations are of the relaxation type, which means that processes with very different time scales are involved in the reaction
- the simultaneous ignition of all of the active facets (within a time resolution of 20 ms), which suggests the presence of fast transport/coupling processes.
- On this basis, the following steps can be expected:
- 1. The Dissociative Adsorption of  $H_2(g)$  and  $NO_2(g)$

$$H_2(g) + 2^* \rightleftharpoons 2H(ads)$$

$$NO_2(g) + n^* \rightleftharpoons NO(ads) + O(ads) + (n-2)^*$$

where the \* symbol stands for an empty active site on the surface.

2. The Subsequent Decomposition of NO

 $NO(ads) + m^* \rightleftharpoons N(ads) + O(ads) + (m-1)^*$ 

This process is known to be very fast at high temperatures on (110) surfaces.<sup>57</sup>

3. Surface Reactions

H(ads), O(ads), and N(ads) species are supposed to be present on the Rh surface. By comparison with the  $O_2$ + H<sub>2</sub>/Rh system studied by FIM,<sup>19,58</sup> the NO + H<sub>2</sub>/Rh system studied by FEM<sup>12,16,44,59,60</sup> and PEEM,<sup>61-63</sup> and more recent work on NO<sub>2</sub> + H<sub>2</sub>/Pt,<sup>24,26,28,30</sup> we can expect the formation of H<sub>2</sub>O or NH<sub>3</sub> species via the following global reactions:

$$O(ads) + 2H(ads) \rightleftharpoons H_2O(g) + 3^*$$

$$N(ads) + 3H(ads) \rightleftharpoons NH_3(g) + 4^*$$

The mechanism proposed in this way certainly involves more than two species and also contains different sources of feedback necessary for the emergence of oscillations in the system. The feedback could be either due to the presence of a secondary "inert" species or to the presence of subsurface oxygen in the system. Further experimental and modeling work is necessary to unravel the nature of the adsorbates and the exact mechanism of reaction.

**Comparison with Pt.** The emergence of nonlinear behaviors during the NO<sub>2</sub> hydrogenation can be observed on both Rh and Pt field emitter tips. In the case of platinum tip samples, complex phenomena were seen with a NO<sub>2</sub>(g) pressure of  $\sim 10^{-4}$  Pa and a pressure of H<sub>2</sub>(g) ranging from  $\sim 10^{-4}$  to  $\sim 10^{-2}$  Pa.<sup>26,29</sup> Increasing the H<sub>2</sub> pressure, we could identify on Pt (i) a nonreactive regime of low brightness, (ii) a nonreactive regime of high brightness. In spite of these similarities, the reactivity on these two metals (Pt and Rh)

presents important qualitative differences, which are shortly discussed here.

- 1. Most of the nonlinearities on Pt have been observed at temperatures ranging between 390 and 515 K.<sup>18,23</sup> On Rh, the reaction is possible at 450 K, as well as 500 K, but no oscillations could be observed outside this range. The temperature range thus seems more restricted for Rh.
- 2. The NO<sub>2</sub> pressure required to initiate oscillations is 1 order of magnitude lower for Rh than for Pt. This could be explained by the higher probability to form subsurface oxygen on Rh, or by the higher dissociation rate of NO(ads), which both contribute to the formation of an O-species reservoir so that a lower pressure of NO<sub>2</sub> would be necessary to initiate the reaction on Rh.
- 3. In the case of Pt, the transitions between dynamical regimes are fully reversible: conversion from a steady state to oscillations can be obtained either by decreasing or increasing the H<sub>2</sub> pressure.<sup>26</sup> As mentioned earlier, this is not the case for Rh. This difference in reactivity could also be explained by different coverages in oxygen species at the surface of Pt and Rh, since as mentioned before Rh is more prone than Pt to form O species on the surface or as subsurface species. The hydrogen pressure required to reduce such a rich O layer is thus expected to be higher in the case of Rh. This might also explain why reactive behaviors are not observed while the hydrogen pressure is increased starting from an O-rich surface, since adsorbed oxygen species are known to "poison" the surface by blocking adsorption sites for H<sub>2</sub>. Such a poisoning effect is not present when starting from high  $P_{\rm H_2}$  values, since in this case the surface is initially almost oxygen-free.
- 4. The oscillations on Rh present more fluctuations than those on Pt.<sup>29</sup> This affects the robustness of the periodic process, as can be seen in the autocorrelation functions and in the "blurred" aspect of the underlying limit cycle.
- 5. The type of bifurcation leading to oscillations is not the same for the two metals. In the case of Rh, the oscillations appear at low  $H_2$  pressures through a supercritical Hopf bifurcation, while the transition corresponds to a homoclinic (infinite period) bifurcation for Pt.

#### 6. CONCLUSIONS

The study of NO<sub>2</sub> hydrogenation on Rh field emitter tips allows observing different dynamics. We found two monostable regimes characterized by a low level of brightness associated with an oxygen-covered surface and by a high level of brightness associated with a clean or hydrogen-covered surface, respectively. Self-sustained periodic oscillations have also been observed, in a parametric region sandwiched between these two regimes. These oscillations have a period of 40–50 s, and their autocorrelation shows that they remain coherent over approximately three periods. Time-delay embedding methods showed the presence of a limit cycle underlying this dynamics. The emergence of this cycle takes place via a supercritical Hopf bifurcation characterized by a constant period and increasing amplitude of oscillations as one goes further away from the bifurcation point.

The reaction is expected to produce either  $H_2O$  or  $NH_3$ , through an autocatalytic production of vacant sites. Other processes involving slower time scales are also probably at play here. Such mechanistic details are however not available with FEM analyses, and further experiments with complementary techniques are necessary to resolve the mechanism of reaction. Further studies will address the presence and properties of more complex and irregular dynamics, which were observed at high temperatures on Rh but were not discussed here.

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#### Notes

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