

## NO<sub>2</sub> Hydrogenation over Pt and Rh Catalysts: a Study at The Atomic Level by Field Emission Microscopy

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This study aims at investigating the catalytic hydrogenation of nitrogen dioxide (NO<sub>2</sub>) on Pt, Rh and Pt-Rh alloy catalysts. Nitrogen oxides (NO<sub>x</sub>) are produced during the combustion of gasoline in the lean-burn regime, and their emission remains an issue especially for Diesel-type engines. Platinum-Group-Metals are used as active components of the catalytic converter. They turn toxic gases into harm less compounds, for example, NO<sub>x</sub> into nitrogen. The catalyst is dispersed in the form of metallic nanoparticles of approximately 5 to 10 nm over a support of high specific surface area. In most studies of heterogeneous catalysis, the structure of the supported catalyst is determined before and after reaction. Unfortunately, very little information is available about the possible local morphological/structural changes that might occur during the reaction. Moreover, from a dynamical point of view, the kinetic parameters only reflect the global kinetics of the reaction taking place on the surface a large ensemble of nanoparticles with specific size and shape distribution. Thus, ensemble-averaging takes place eventually hiding more complex dynamics, such as periodic oscillations. A better understanding of the ongoing catalytic reaction would lead to a better reproducibility, predictability and control of this reaction. In this view, a study of the hydrogenation of NO<sub>2</sub> gas over Pt, Rh and Pt-Rh nanocrystals is undertaken at the molecular level by means of field emission methods [1,2].

Experiments were carried out in a stainless steel field ion/electron emission microscope. Field emitter tips, used as model catalysts, were electrochemically etched, and then cleaned *in situ*. After characterization of the tips by Field Ion Microscopy (FIM), the samples were heated and a field of 5 V/nm was applied using Field Electron Microscopy (FEM). A mixture of NO<sub>2</sub> and H<sub>2</sub> was then admitted in the chamber, and the reaction was followed by recording the FEM patterns appearing dynamically on the screen of the microscope. Time series were extracted from videos (at 50 frames per second - fps) and established by probing the mean brightness over regions of interest (**Fig1a**). The dynamic of the process was analyzed by measuring the variations of grey levels with time, image by image. Transient phenomena were also monitored with an acquisition rate of 10,000 fps.

The catalytic hydrogenation of NO<sub>2</sub> was monitored in real time. On Pt at 390K, amongst several non-linear behaviors, self-sustained periodic oscillations were observed (**Fig1b**) [3,4]. Fourier transform analyses and temporal autocorrelation functions were used to characterize the dynamics and to quantify the robustness of the kinetic oscillations. NO<sub>2</sub> hydrogenation was also studied on Rh at 450K and found to present many similarities by with platinum. However, the details of the dynamics reveal significant differences, such as the emergence of oscillations via a different bifurcation, the robustness of the

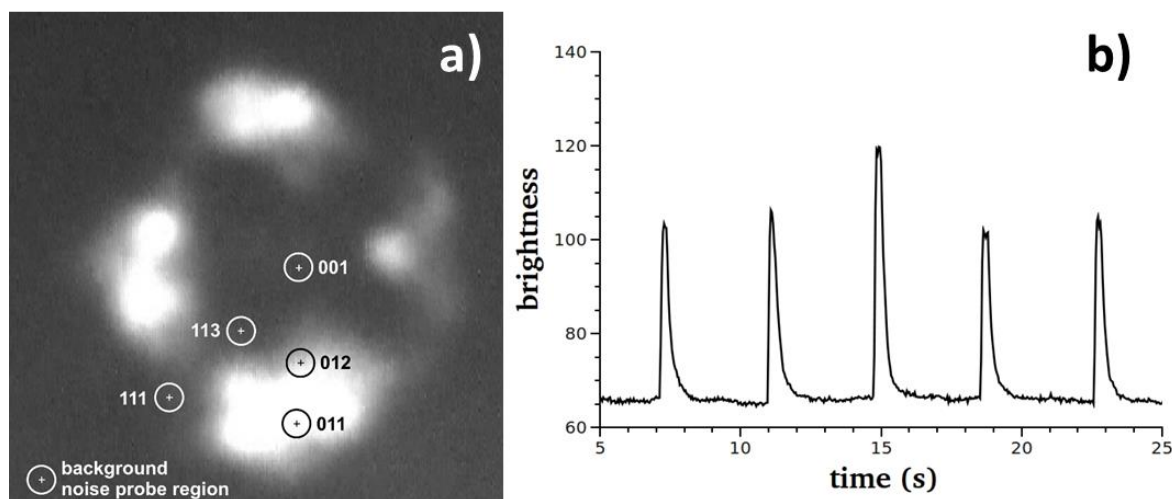
system, as well as the pressure range for the occurrence of non-linear behaviors. Finally, the  $\text{NO}_2+\text{H}_2$  reaction was studied on a Pt-17.4at.%Rh alloy catalyst of similar composition -that is used in catalytic converters. Surface explosions were observed in the temperature range of 390-515K. At 425K, periodic oscillations are observed with features lying between those observed on pure Pt and pure Rh samples. This observation implies the existence of synergistic effects between the metals.

In the case of Pt, high-speed experiments highlighted the presence of diffusing processes down to the nanoscale between active facets. The propagation of chemical waves on a single facet of the nanocrystal was also observed. This proves the robustness of dissipative, nonlinear behaviors down to the nanoscale. The velocity of the observed waves is of the order of a few  $\mu\text{m/s}$ , which is in good agreement with previous studies of catalytic reactions at the mesoscale.

Field ion microscopy and field emission microscopy are powerful techniques in materials science and chemistry. By exploiting the nanoscale resolution of the techniques, the results obtained allow for a better understanding of catalytic systems at the molecular level. The experiments prove that robust nonlinear behaviors can be observed down to the nanoscale, without a significant loss of correlation due to fluctuations inherent to small chemical systems. These results shed a new light on the conditions under which collective order can emerge at the nanoscale [5].

#### References:

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**Figure 1.** a)  $\text{NO}_2\text{-H}_2$  reaction over platinum imaged by field emission microscopy (Reproduced from C. Barroo *et al.*, *New J. Chem.* 38 (2014) 2090 with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.) – b) Experimental time series over the (012) facet during self-sustained periodic oscillations