

## Field Ion Microscopy and Pulsed Field Desorption Mass Spectrometry: Unique Tools for Surface and Subsurface Analysis

Cédric Barroo<sup>1,2,3</sup> and Thierry Visart de Bocarmé<sup>3</sup>

<sup>1</sup>. John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge MA USA

<sup>2</sup>. Department of Chemistry and Chemical Biology, Harvard University, Cambridge MA USA

<sup>3</sup>. Chemical Physics of Materials, Université Libre de Bruxelles (ULB), CP243, 1050 Brussels, Belgium

Microscopy has always been used for applications in the field of heterogeneous catalysis, and there is an abundant literature regarding the analysis of size, shape and morphology of catalysts before and after various physicochemical treatments so as to improve the design of catalytic particles. Recent developments of *in situ* instruments, such as the environmental TEM or *in situ* reaction cells, allow to study the structural and morphological changes occurring during the reaction. Unfortunately, the high working temperatures of some catalysts may prevent getting a high resolution, and it may also become difficult to analyse the composition of the sample via spectroscopic methods. There is thus a lack of techniques allowing the imaging of the surface of the catalyst during reaction, and allowing the analysis of the chemical composition of the surface and subsurface species.

Field emission techniques are particularly suited to study the behavior of a catalyst during the ongoing processes. These techniques use a sample prepared as a very sharp tip, the size and shape of which mimics a single nanoparticle of catalyst. Field Ion Microscopy (FIM) is based on the ionization of gas species at the surface of the tip, due to the application of an electrical field, providing a micrograph of the sample with atomic lateral resolution (0.2 nm). This allows studying morphological changes occurring during the reaction, as well as their influence on the local catalytic activity. As an example, we studied the interaction of O<sub>2</sub> on a Rh sample to show that the exposure of less than 10 Langmuir of O<sub>2</sub> is sufficient to induce significant morphological changes. Higher exposures lead to the formation of dissolved oxygen, known as subsurface oxygen, which can assist a morphological reconstruction upon a short heating of the sample [1]. Similar pattern is also visible at high temperature (505 K) in the presence of a reactive mixture of H<sub>2</sub> and O<sub>2</sub>.

There is however a lack of identification of the local chemical composition. This can be achieved by removing surface material from the tip extremity, as ions, by field desorption of the adsorbate layer, or by field evaporation of the catalyst. The ions are then accelerated and collected by an ion detector, and their chemical nature is determined by the presence of a mass spectrometer between the sample and the detector. Pulses are necessary to trigger the ionization and to measure the time of flight. This principle can be combined with the high-resolution of the FIM technique, and is called Pulsed Field Desorption Mass Spectrometry (PFDMS). To do so, an aperture – called the “probe hole” – is produced in the FIM screen, allowing the ions to pass through the screen and enter the mass spectrometer (**Figure 1a**). Due to the high magnification of the FIM technique, the probe hole on the screen corresponds to some 10 nm<sup>2</sup> on the sample. Analysis can thus be performed on a single nano-facet of the sample (**Figure 1b**).

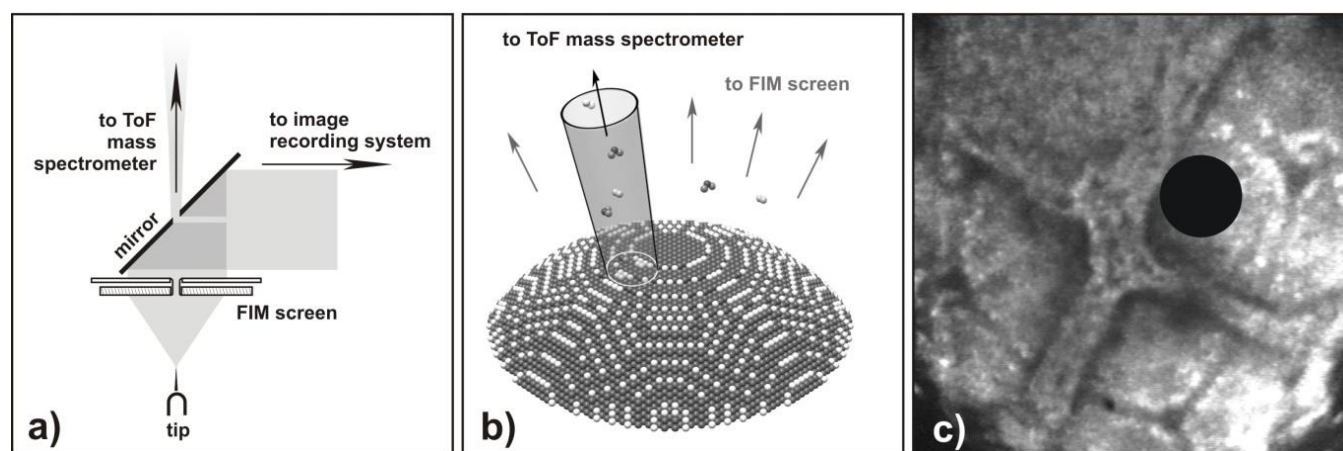
Field ion microscopy allows observing how the catalyst and the catalytic reaction behave in real time. The PFDMS technique can image the reaction *and* analyze the surface composition while imaging the reaction on the whole sample. On **Figure 1c**, the surface composition of a rhodium tip sample is

investigated during the ongoing water production in the presence of a reactive  $\text{H}_2/\text{O}_2$  gas mixture, and the dark region corresponds to the probed region analyzed by mass spectrometry [2]. Species such as  $\text{RhO}^{2+}$  and  $\text{RhO}_2^{2+}$  can be observed, further proof of the presence of subsurface oxygen, influencing both the reconstruction and the reaction.

The advantage of this technique is that we can tune the pulses amplitude and frequency. The pulse itself typically has a 100 ns width. By changing the amplitude, it is possible to desorb either only the adsorbate layer, or the adsorbate layer and the very first atomic layers. After each pulse, the surface is clean (i.e. free of adsorbates) and the adsorption and reaction process can resume. By changing the frequency of the pulses, we can give more or less time for the adsorption/reaction to occur, giving access to the evolution of the adsorbate layer and the chronology of events. With such experiments, it is possible determine kinetic parameters. Different systems are studied with this technique, among others, the catalytic  $\text{O}_2+\text{H}_2$  reaction on Rh, as well as the interaction of ethylene and acetylene with Ni tips to study the early stages formation of carbon nanotubes [4]. This technique can thus be applied to a wide variety of systems. [5]

#### References:

- [1] C. Barroo, N. Gilis, S.V. Lambrechts, F. Devred, T. Visart de Bocarmé, *Appl. Surf. Sci.* **304** (2014) 2  
 [2] N. Kruse, T. Visart de Bocarmé, in “*Handbook of Heterogeneous Catalysis*”, 2nd edition, Eds. G. Ertl, H. Knözinger, J. Weitkamp, F. Schüth, Wiley-VCH 2008, p.870  
 [3] C. Barroo, P. A. J. Bagot, G. D. W. Smith, T. Visart de Bocarmé, “Investigating Nano-structured Catalysts at the Atomic scale by Field Ion Microscopy and Atom Probe Tomography”, in *Atomically-Precise Methods for Synthesis of Solid Catalysts*; RSC Catalysis Series, 2015, pp. 248-295  
 [4] M. Moors, T. Visart de Bocarmé, N. Kruse, *Ultramicroscopy* **109** (2009) 381  
 [5] C.B. thanks the Fonds de la Recherche Scientifique (F.R.S.-FNRS) for financial support. The authors gratefully thank the Van-Buuren Foundation for a financial support for the acquisition of equipment.



**Figure 1.** a) Schematic principle of the PFDMS technique allowing the imaging of the sample by FIM and the probing of the reaction by ToF mass spectrometry - b) Scheme of the probe-hole: the hole in the screen of the microscope shown in a) selects a small area of the sample, allowing analysis of the surface composition during any surface processes - c) FIM micrograph during an ongoing catalytic reaction ( $\text{H}_2+\text{O}_2$  / Rh). The black region corresponds to the probed area which is in the  $10 \text{ nm}^2$  range. (Image reproduced from [3]).