Fast Surface Reactions at the Nanoscale

Insights into the Emergence of Nonlinear Behaviors

The catalytic hydrogenation of NO\textsubscript{2} on platinum is studied by field emission microscopy, which allows chemical activity to be monitored on samples whose shape and size are close to those of a single nanoparticle. The high lateral resolution of field emission techniques is combined with the high temporal resolution of a high speed camera to reveal the presence of nonlinear kinetics over different spatiotemporal scales.

Introduction

Chemical reactions, when kept far enough from their equilibrium state, can induce time and space symmetry breaking of a system’s composition resulting in the emergence of complex behaviors. Such phenomena have been observed in surface science studies at the micrometer scale, but their observation at the level of nanoparticles remains challenging due to the lack of experimental techniques that allow operando studies with nanometric resolution. Furthermore, the small size of these reactive systems makes them sensitive to fluctuations, which could hinder the identification of a well-defined class of kinetic behavior. Field emission techniques, including field ion microscopy (FIM) and field emission microscopy (FEM), are especially suited for such situations: the nanosized metal tip used as sample represents a good model for a single nanoparticle, and FIM/FEM investigations can be performed during the ongoing processes. Here, we address nanoscale behaviors observed with these techniques during the catalytic hydrogenation of NO\textsubscript{2} on Pt at 390 K.

Material & Methods

Platinum samples are prepared as sharp tips by electrochemical etching followed by \textit{in situ} treatments [1] and are then characterized by field ion microscopy. FIM is based on the ionisation of a so-called imaging gas at the surface of the sample where an intense electric field is present when a high positive voltage is applied on the tip-sample. The latter points towards a detector screen, which is grounded. At cryogenic temperatures, atomic resolution can be obtained (fig. 1.a). The sample is then imaged in FEM mode (fig.1.b). FEM relies on the emission of
electrons from the tip when it is negatively charged.

The intensity of the electronic current depends on the local work function of the metal, which in turn depends on crystallographic orientation. A mixture of reactive gases is then admitted in the UHV chamber and the microscope runs as an open nanoreactor. Since the presence of adsorbates also affects the local work function, following the brightness signal in space and time amounts to obtaining information on the local surface state. In our experiments, the brightness signals are recorded with a Panasonic Moonlight high sensitivity analogic camera and digitized to a 25 fps, 8 bits uncompressed video file format. High-speed experiments are recorded with a Photron FastCam SA4 camera operating at a frame rate of 10,000 fps. A 4x4 binning was applied to increase the sensitivity of the detector (spatial resolution 128X128 after binning, with 8-bit dynamic range).

Results

Gaseous NO\textsubscript{2} is introduced in the chamber, the dissociative adsorption of which induces an increase of the work function and thus a decrease of the overall brightness pattern of the surface. For a given pressure of NO\textsubscript{2}, the brightness signal reaches in this way a constant value. The partial pressure of hydrogen is then systematically incremented up to the moment where spikes in the brightness signal appear. These spikes are signs of a sudden change of surface composition and thus of surface reactions. During these experiments several types of complex dynamical phenomena can be observed, depending on the \ce{H2}/\ce{NO2} pressure ratio. For specific values of both pressures, periodic oscillations can be observed under the form of periodic peaks of higher intensity in the brightness signal (fig. 1.c), which have been attributed to the formation of water. With the temporal resolution of one of the recording devices (40 ms - 25 fps), all the active facets appear to ignite simultaneously. These facets are located along the [010] line zones connecting the (011) facets to the (001) center. Further data analyses confirmed the robustness of those oscillations, which can then rightfully be named chemical nanoclocks [1-2].
The robustness and the synchronicity over the whole surface suggest a coupling by surface diffusion rather than a gas-phase coupling, due to the isothermal conditions and the low pressures used.

Experiments were also performed during the oscillating phenomena with a camera having a much higher temporal resolution of 0.1 ms – 10000 fps. These conditions of acquisition allow observing a desynchronization in the ignition of the active facets (fig. 1.d). The size of the tip can be estimated, and so can the distance between two active (011) facets. Therefore, with the measured delays between ignitions, a velocity of propagation of the brightness state between facets can be calculated, leading to a value of about 2 μm/s. This result is in the same range as what is found for coupling in space by reaction-diffusion processes, which further confirms the hypothesis of coupling by surface diffusion.

A careful analysis of the very first moments of the surface explosion moreover reveals an unexpected behavior: The sharp increases of brightness in the center of the {011} facets are sometimes followed by the propagation of a wave inside the facet itself (fig. 2). This wave propagates and disappears at a place that seems to correspond to the border of the facet (as depicted in fig. 3 corresponding to the upper (011) facet). After the propagation of this first wave, a second pulse of brightness can be observed in the center of the facet, which then propagates in a similar way. These features are characteristic of a class of reaction-diffusion phenomena known as target patterns, which are here observed for the first time at the nanoscale [3]. Target patterns can be observed in about 50% of the observations, which underlines the importance of fluctuations in their appearance.

The target waves appear within a single {011}-facet of a few nanometers, as opposed to the aforementioned oscillations occurring over the whole surface. The two phenomena are nevertheless connected. The waves propagate within a single {011} facet with a velocity close to that of the inter-facet coupling, i.e. at ~2 μm/s. This suggests that the nanotargets are the source of the long-range coupling, in other words that the local nonlinear kinetics in the facets play the role of pacemakers for a larger-scale oscillating reaction.

In view of the observations presented in figure 2 and figure 3, we cannot but stress the importance of high temporal resolution experiments for the study of complex kinetic behaviors in surface science. Indeed, we can see that the synchronization of the facets takes less than ~30 ms, a time scale that cannot be investigated in details with regular recording devices. The discovery of fast nonlinear behaviors at the nanoscale was made possible here by combining the high spatial resolution of the field emission techniques with the high temporal resolution of the camera.
Conclusion

As a conclusion, we have provided experimental evidence that dynamics hitherto thought to be confined to macro and microscopic scales can persist down to the nanoscale. We observed highly regular periodic oscillations and target-like propagation of waves, the latter being observed for the first time at this scale. By exploiting the nanoscale resolution of the field emission techniques, and by using a recording device with high temporal resolution, the results obtained offer an unexpected proof that very small reactive systems can present robust dynamics. This underlying feature opens the way to a new rationale for assessing the reproducibility, predictability and controllability of nanoscale chemically active entities, such as nanoreactors.

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References

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