Bridging the gaps: imaging reaction dynamics by environmental microscopies

Cédric Barroo[1,2,3], Zhu-Jun Wang[3], Yannick De Decker[2,4], Thierry Visart de Bocarmé[1,2], Marc-Georg Willinger[3,5]

[1]*Chemical Physics of Materials and Catalysis, CP 243, Université libre de Bruxelles, Belgium*
[2]*Interdisciplinary Center for Nonlinear Phenomena and Complex Systems (CENOLI), CP 231, Université libre de Bruxelles, Belgium*
[3]*Electron Microscopy Group, Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Germany*
[4]*Non Linear Physical Chemistry Unit, CP 231, Université libre de Bruxelles, Belgium*
[5]*Scientific Center for Optical and Electron Microscopy (ScopeM), ETH Zurich, Switzerland*
cbarroo@ulb.ac.be

Non-equilibrium reactions are observed in a variety of reactive systems, including those at the surface of catalytic materials. Probing such reactions and their dynamics during the ongoing processes remains challenging, due to the scarcity of high-resolution techniques allowing for *in situ* experiments. This study reports on the observation and analysis of nonlinear behaviours during the catalytic hydrogenation of NO_2 on Pt catalysts using field emission microscopy (FEM) and environmental scanning electron microscopy (E-SEM), two techniques sensitive to the variations of work function due to the presence of adsorbates.

On one hand, FEM enables the study of catalytic reactions taking place at the surface of a nanosized metal tip which acts as a single nanoparticle of catalyst: the reaction can be probed down to 10 nm^2 and at pressures in the 10^{-4} – 10^{-2} Pa range. Different nonlinear behaviours were observed, such as self-sustained periodic oscillations and the propagation of chemical waves as target patterns [1,2]. On the other hand, the E-SEM instrument allows the study of samples with various morphologies, allowing to approach the complexity of materials encountered in industrial applications. E-SEM can also be used with gas pressures up to tens of Pa [3,4]. Experiments during the NO_2 hydrogenation were performed on Pt single crystals and on Pt foils, and nonlinear behaviours were observed, mainly in the form of spiral patterns. Three different brightness levels can be distinguished on a single propagating wave. These patterns were observed on regions as large as 100 µm and over a wide range of pressures: from 10^{-3} to 20 Pa, over four orders of magnitude.

The combination of FEM and E-SEM can be used to observe similar phenomena over different pressure conditions, allowing to bridge the pressure-gap, from 10^{-4} to 20 Pa; but also the materials-gap by analysing the same reaction on a tip-sample, single crystal and foils: it is then possible to study the various reaction behaviors, the structure sensitivity of the reaction, the spillover between different facets, and how the presence of boundaries affects the reactivity.

References:
[1] C. Barroo *et al.*, Appl. Surf. Sci. **304**, 2 (2014).
[2] C. Barroo *et al.*, Phys. Rev. Lett. **117**, 144501 (2016).
[3] Z.-J. Wang *et al.*, Nat. Comm. **7**, 13256 (2016).
[4] M. G. Willinger *et al.*, Microsc. Microanal. **22** (Suppl 3), 784 (2016).