

Pattern Formation in Catalyzed Surface Reactions Studied by *In Situ* SEM

Cédric Barroo^{1,2,3}, Zhu-Jun Wang³ and Marc Georg Willinger^{3,4}

¹ Chemical Physics of Materials and Catalysis, Université libre de Bruxelles, Belgium.

² Interdisciplinary Center for Nonlinear Phenomena and Complex Systems (CENOLI), Université libre de Bruxelles, Belgium.

³ Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Germany.

⁴ Scientific Center for Optical and Electron Microscopy (ScopeM), ETH Zurich, Switzerland.

Working catalysts correspond to systems that are operated far from thermodynamic equilibrium. The state of the active catalyst therefore differs from what is observed *ex situ*. Structure-function relationships should thus be studied under relevant reaction conditions. While *in situ* TEM enables observation of atomistic details under conditions of slow kinetics, *in situ* SEM delivers complementary information about catalyst dynamics at reduced lateral resolution. It provides insight about collective phenomena that are controlled by heat and mass transport and enables a multi-scale approach for the study of complex systems under gas pressures ranging from 10^{-4} to 10^3 Pa and temperatures up to 1500°C .

Recently, direct observation of graphene growth by chemical vapor deposition inside the chamber of an environmental SEM (ESEM) demonstrated the high sensitivity of the secondary electron signal to changes in the surface coverage and work function of metal catalysts. [1,2] The ability to directly visualize the formation of monolayers of carbon on a 1000°C hot surface suggested that the system might be sensitive enough to differentiate work function changes due to gas adsorption. In order to test this, we imaged Pt surfaces during the reaction of NO_2 with H_2 by *in situ* SEM.

Nitrogen oxides (NO_x) are produced during the combustion of fuels in lean-burn vehicles. Selective Catalytic Reduction (SCR) of NO_x is one of the options to reduce NO_x emissions. Currently, ammonia injection is considered the method of choice to meet legislative target levels. An alternative would be to use hydrogen, which could be produced through on-board reforming. One of the advantages of H_2 -SCR would be the relatively low operating temperatures so as to improve the vehicle cold start behavior. Platinum-Group-Metals (PGM's) may be anticipated to act as suitable catalysts for high NO_x conversion in H_2 -SCR. However, little is known about the elemental mechanisms and microkinetics of this reaction. Our research aims at filling this gap in knowledge and to establish reliable structure-function relationships.

In situ experiments were performed in a modified commercial ESEM (*FEI Quanta 200*) equipped with a heating stage, gas feeding system and mass spectrometry for analysis of the gas composition and detection of reaction products. Pt foils were cleaned *ex situ*, and then annealed under hydrogen prior to exposure to reactive mixtures of NO_2 and H_2 at pressures ranging from 10^{-3} to 20 Pa. Previously performed experiments on a single nanoparticle of Pt by field emission techniques served as a guideline for the interpretation of work function changes during the reaction. [3,4]

The introduction of pure NO_2 in the ESEM chamber reduces the brightness due to the increasing work function of Pt in presence of NO_2 (Figure 1). After addition of H_2 , nonlinear behaviors in the form of dynamic reaction diffusion processes and spiral patterns can be observed (Figure 2) for specific reaction conditions. A brightness analysis of the reaction pattern allows to distinguish 3 different brightness levels on a single propagating wave. This is not only the proof that ESEM is indeed a surface-sensitive technique that can be used to probe gas-surface interactions, but also that ESEM can differentiate different adsorbates species as a function of their effect on the work function. Furthermore, it is possible to directly compare the reactivity of differently oriented Pt grains and the structure sensitivity of the reaction, the spillover between different facets, and how the presence of

boundaries and defects affect the reactivity. *In situ* SEM can thus be considered as surface science method with surface sensitivities comparable to photoemission electron microscopy (PEEM), but with less restrictions regarding the structure of the sample and the advantage of a higher lateral resolution and the ability to observe surface dynamics over a large pressure range. [5]

References:

- [1] Z-J Wang *et al*, Nat Comm **7** (2016), 13256.
 [2] MG Willinger *et al*, Microsc Microanal **22** (Suppl 3) (2016), 784.
 [3] C Barroo *et al*, Appl Surf Sci **304** (2014), 2.
 [4] C Barroo *et al*, Phys Rev Lett **117** (2016), 144501.
 [5] CB thanks the Fonds de la Recherche Scientifique (F.R.S.-FNRS) and the Wallonie-Bruxelles International (Excellence grant WBI.WORLD) for financial support.

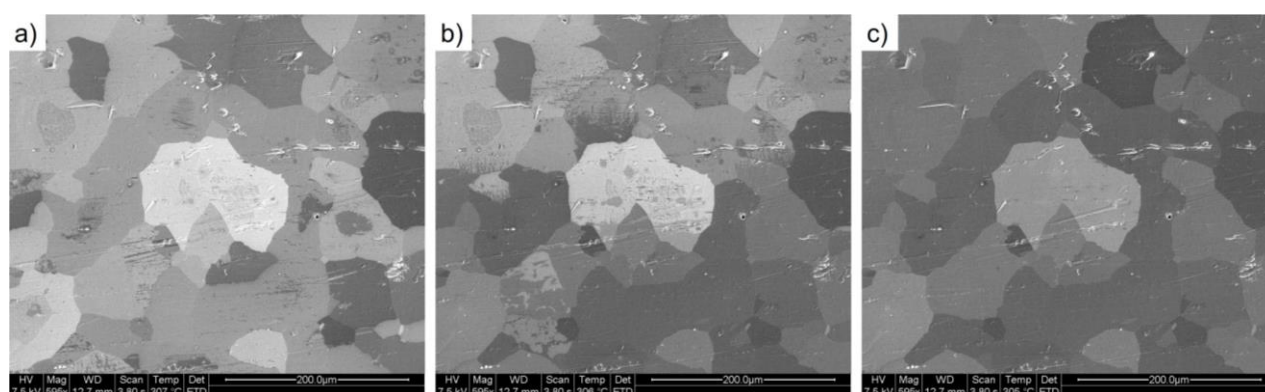


Figure 1. Changes in brightness during the adsorption of NO_2 on Pt foil at $\approx 300^\circ\text{C}$. Scale bar: 200 μm .

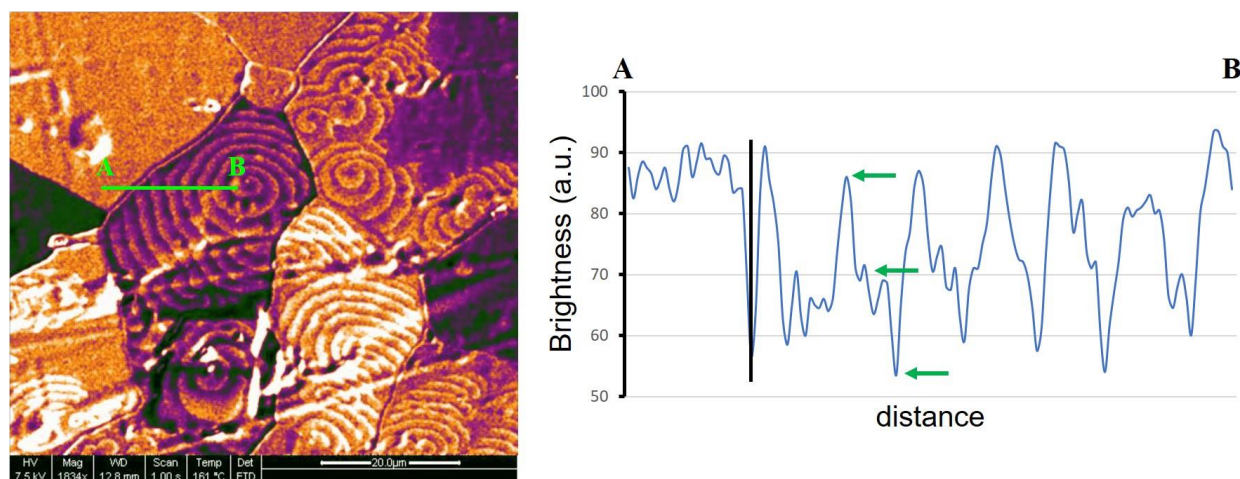


Figure 2. (left) ESEM snapshot during spiral pattern formation in the NO_2+H_2 reaction on Pt foil. (right) Brightness analysis showing three distinct brightness levels on a single propagating wave (marked as three arrows) and proving the sensitivity of the ESEM to different adsorbate-species. Scale bar: 20 μm .