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Imaging Reaction Dynamics on Inverse Model Catalyst Surfaces by *In Situ* Environmental SEM

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To improve the efficiency of catalytic materials, a better understanding of the catalytic processes is required from both the kinetic and material viewpoints. This can be achieved by using *in situ* imaging techniques allowing for the observation of catalytic processes under realistic conditions. Additionally, catalysts are composed of dispersed active elements and it is necessary to study the coupling between them at relevant scales. Finally, since applied formulations of catalysts use supported particles, the role and influence of the support on the catalytic activity/selectivity has to be gleaned. One convenient way to do so is to use so-called 'inverse catalysts' where the support is dispersed on a metallic surface, allowing to increase the metal/support interface and to observe the dynamic at this interface. In this frame, *in situ* environmental SEM allows the study of catalytic materials with various morphologies, under a wide pressure range (from 10^{-4} to 10^{3} Pa) and at temperatures up to 1500°C. The growth of single layers of graphene has been observed during *in situ* CVD processes, demonstrating the high sensitivity of the SE signal to variations in the surface coverage and work function of the metal catalysts [1]. More recently, it was shown that the study of gas/solid interactions was possible through the imaging of nonlinear dynamics during the NO_2+H_2 reaction on Pt surfaces [2]. This proves that ESEM is sensitive enough to differentiate work function changes due to gas adsorption and surface reaction. In this work, we use graphene dispersed on Pt as model C/Pt inverse catalyst for NO_2 hydrogenation.

In situ ESEM experiments were performed in a modified commercial ESEM (*FEI Quanta 200*) equipped with gas feeding system, heating stage, and mass spectrometry for analysis of the gas phase. Pt foils used as catalysts were first cleaned *ex situ*, and then annealed under H_2 environment before any exposure to reactive gases. Graphene was grown under a mixture of C_2H_4 and H_2 atmospheres, and reactive behaviour under NO_2+H_2 gas in the 10^{-3}-10^{-2} Pa pressure range.

A clean Pt foil (**Figure 1.a**) is first exposed to NO_2 and H_2 gas mixture to ensure the reactivity of the catalyst (**Figure 1.b**). Afterwards, a layer of graphene is grown under C_2H_4 and H_2 atmosphere (**Figure 1.c**), and then partially etched to obtain the inverse C/Pt catalyst with graphene domains of different sizes and isolated Pt regions, a useful feature to study the spatial coupling between separated Pt regions, but also to understand the influence of the C/Pt interface. When NO_2 is injected into the system, an inversion of contrast can be observed, the graphene domains switching from the darker regions to the brighter regions (**Figure 2.a-c**). This is due to the strong effect of NO_2 on the work function of Pt.
Reactive behaviors in the form of nonlinear dynamics can be observed, but only on bare Pt regions. The effect of the C/Pt interface on the propagation of chemical waves, and subsequently the surface coupling, is size-dependent: reactions front will be stopped if the C-domain is large (**Figure 2.d-e**), but small C-domains, (with a size lower than the wavelength of the reaction front) do not interfere with the propagation of chemical waves. Further analysis is required to verify the presence of intercalation between Pt and graphene. Interestingly, the emergence of reactive behavior is also size-dependent

(**Figure 2.e**). The fact that small Pt regions (< 20µm) are not reactive if isolated but becomes reactive if linked to greater regions via a channel (≈1-2 µm) (**Figure 2.e-f**) proves the coupling via surface diffusion and the absence of gas-phase coupling under these experimental conditions.

As a conclusion, the reaction on inverse catalysts can be imaged by *in situ* ESEM, allowing to study the influence of the metal/support interface on the catalytic reaction, but also the coupling between active elements, and the size-dependence in the emergence of reactive behaviors [3].

References:
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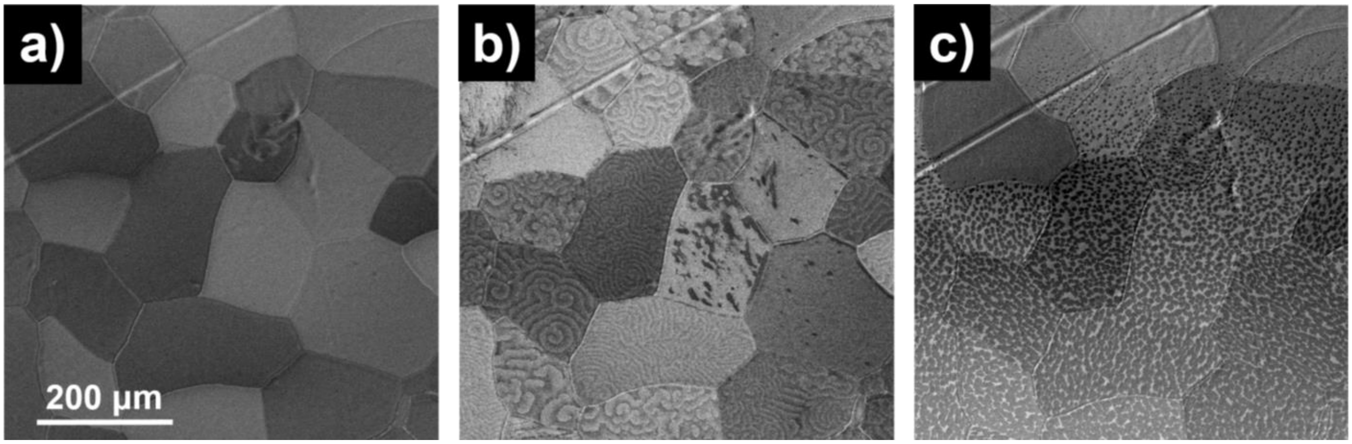

Figure 1. Pt foil: **a.** after H_2 cleaning; **b.** during the NO_2+H_2 reaction exhibiting nonlinear behaviors (T = 453°K, P_{tot}≈10^{-2} Pa); **c.** during graphene growth under C_2H_4 and H_2 gas exposure (T = 1300°K).

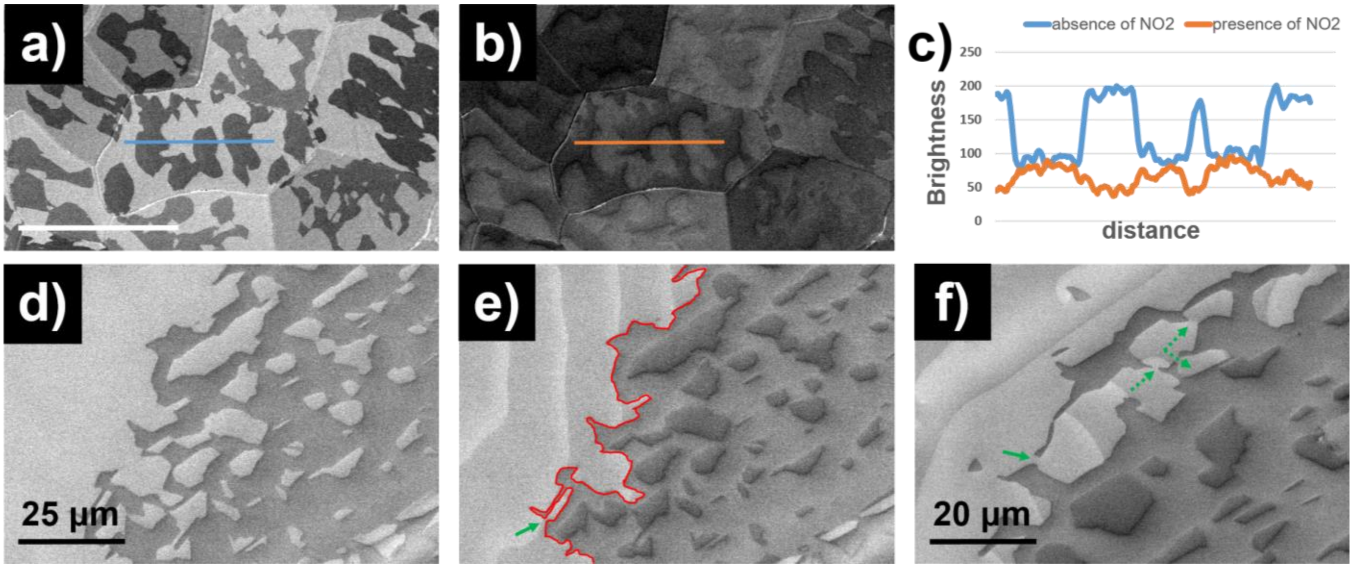

Figure 2. a. graphene/Pt inverse catalyst (graphene appears as darker regions) (scale bar: 200 µm); and **b.** during NO_2 exposure (graphene appears as brighter regions); **c.** Brightness signal probed along the lines in **a.** and **b.** showing the contrast inversion. Size-dependence of the emergence of reactive behavior: graphene/Pt **d.** before; and **e.** during NO_2+H_2 exposure, the red line delimits the reactive/non-reactive region; **f.** coupling via surface diffusion (imaging conditions: T = 445-465 K, 7.5 kV).