Chemical dynamics in single particle catalysis: observing reactions by correlative *in situ* microscopy

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Operando spectroscopy of catalytic reactions has been very successful in mechanistic studies.[1] However, as spectroscopy typically examines large areas/volumes, this averaging "smoothens out" local variations that may be critical to understand how a reaction proceeds. Dynamics in catalyst structure, composition and adsorbate coverage may also go unnoticed by averaged spectral data. A way overcoming these limitations is to use correlative surface microsopy to directly "watch" ongoing catalytic reactions, i.e. to apply several microscopic and spectro-microscopic techniques to the same catalysts locations under identical reaction conditions.[2] Most of the methods herein not only image catalyst structure or composition, but also the adsorbed reactants, so that active and inactive states can be discerned (*kinetics by imaging),* active regions identified and mechanisms elucidated.[3]

Examples of real-time *in situ* imaging of H_2 oxidation include meso-scale polycrystalline Rh surfaces and Rh nanotips (as small as 30 nm, enabling *single particle catalysis*). For planar catalysts, UV- and X-ray photoemission electron microscopy (UV- and X-PEEM), low energy electron microscopy (LEEM) and scanning photoelectron microscopy (SPEM) were used with resolution up to 3 nm. For nanotips, field emission microscopy (FEM) and field ion microscopy (FIM) were applied with up to atomic resolution.

The direct, real-time and locally-resolved observation of H_2 oxidation on Rh-based catalysts revealed:
(i) the transition from inactive to active states via catalytic ignition and spreading of chemical waves,[4]
(ii) the mechanism of oscillatory H_2 oxidation involving subsurface oxygen,[4]
(iii) how particle size, support and surface composition (decoration, SMSI) affect the local activity,[5]
(iv) whether different facets on a single Rh nanoparticle communicate via hydrogen diffusion or not (coupled monofrequential vs. (uncloupled) multifrequential oscillations),[6]
(v) detecting active sites on a single particle via imaging water molecules,[6]
(vi) that chaos even exists at the nanoscale,[7] and
(vii) how La modifies the reaction dynamics on a Rh nanotip.[8]

Microkinetic modelling and density functional theory (DFT) rationalized the experimental observations. The novel nanoscale insights in the dynamics of reactants and surfaces, including the identification of active regions, may stimulate new ways of catalyst design and operation.

References:

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