Operando Studies of Catalytic Surface Reactions

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Abstract

Operando characterization of working catalysts, requiring the simultaneous measurement of catalytic performance, is crucial to identify the relevant catalyst structure/composition and how molecules interact with interfaces [1]. Three examples illustrate what can be learnt from area-averaging and locally-resolved measurements.

i) *Area-averaging operando spectroscopy*: CO oxidation on Pt/ZrO_2 prepared by atomic layer deposition (ALD) was examined by sum frequency generation (SFG) spectroscopy and near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), combined with mass spectrometry (MS) [2]. Complemented by Density Functional Theory (DFT), we show that the reaction onset is determined by a delicate balance between CO disproportionation (Boudouard reaction) and oxidation.

ii) *Spatially-resolved operando microscopy*: A combined photoemission electron microscopy (PEEM) and DFT study of supported meso-scale Pd particles demonstrates how a minute fraction of sites at the perimeter of the metal-oxide interface affects the CO oxidation performance of an entire Pd aggregate [3]. The initiation of CO-poisoning fronts is visualized at the perimeter, at a CO pressure two times higher for oxide-supported Pd aggregates than for unsupported ones. DFT calculations reveal stronger oxygen binding at the perimeter sites, explaining the higher CO-tolerance. As long as catalyst deactivation is not initiated, metal sites on oxide-supported Pd particles that are as far as several tens of μm away from the metal-oxide boundary maintain high catalytic activity even at increased CO pressure.

iii) *Single particle catalysis*: Using the apex of a Rh-nanotip as model of a single catalytic particle and field emission microscopy (FEM) as imaging tool, ongoing catalytic reactions can be visualized on the nm-scale [4]. Novel effects were revealed for H_2 oxidation, such as multifrequential oscillations on the nanoscale and limited interfacet coupling. Using ionized water as imaging species, the active sites were directly imaged by field ion microscopy (FIM). Local nano-pacemakers [5] were identified as being surface atomic configurations at the border between strongly corrugated Rh{973} regions and adjacent atomically flat terraces.

The insights by monitoring *ongoing* reactions may stimulate new ways of catalyst design.

Keywords: operando, sum frequency generation, photoelectron spectroscopy, photoemission electron microscopy, field emission microscopy

References

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