

Structure-activity relationship of Pt nanoparticles during the CO oxidation reaction

Christian Fink Elkjær¹, **Ph.d. Sebastian Jespersen**¹, Søren Vendelbo², Christian D. Damsgaard³, Patricia Koymann⁴, Ib Chorkendorff³, Stig Helveg³

¹Topsoe A/S, Kgs. Lyngby, Denmark, ²Technological Institute, Taastrup, Denmark, ³Technical University of Denmark, Kgs. Lyngby, Denmark, ⁴University of Cape Town, Rondebosch, South Africa

Background incl. aims

The coupling between catalytic activity and the structure of supported nanoparticles under reaction conditions has been a significant driver for the development of in situ and operando characterization techniques in catalytic research. Traditional photon-techniques provide spatially averaged structural information of nanoparticle ensembles in miniaturized reactors, with conversion of reactants measured at the reactor exit by use of e.g. Mass Spectrometry (MS). To improve the spatial resolution of local structure and catalytic function of nanoparticle ensembles it is, however, beneficial using miniaturized reactors in conjunction with Transmission Electron Microscopy (TEM) [1,2,3,4].

Methods

Herein we focus on operando electron microscopy based on a nanoreactor. The nanoreactor is a Micro Electro-Mechanical System (MEMS) device equipped with a unidirectional and micrometer-sized gas channel, including a heating element, which facilitates MS of the exhaust gas from the nanoreactor as well as reaction calorimetry. With an array of electron transparent windows, the nanoreactor permits atomic-resolution TEM imaging of the nanoparticles under ambient pressure levels at different positions along the heated reactor zone [1,2,3]. Previously, we demonstrated how this system offered unprecedented insight into the oscillatory CO oxidation reaction catalyzed by an ensemble of Pt nanoparticles at ambient pressure levels by correlating high-resolution TEM of individual nanoparticles with global MS and calorimetry data. Moreover, a time-dependent first-principal reactor model was established that suggested marked gradients in the reactants along the gas flow channel under conditions of finite conversion levels.

Results

Herein, we will examine experimentally such gradients in the reaction environments by means of Electron Energy-Loss Spectroscopy (EELS). EELS offers sensitive detection of lighter elements in the gas phase with a special resolution defined by the area of illumination with the electron beam. EELS has therefore previously been used investigate gradients in temperature of heating devices [3] and gas composition[4]. Here we employ EELS for the first time to a gas flow reactor. By recording EELS at the Carbon K ionization edge, we examine the CO conversion profile along the nanoreactor and compare with mass-flow calculations through the nanoreactor and we relate the local structure and conversion to resolve spatially dependent structure-activity relationship during the Pt-catalyzed CO oxidation reaction.

Conclusion

In perspective, this operando electron microscopy and spectroscopy approach sets apart from the vast number of operando photon-techniques by the ability to relate nanoparticle structures with their catalytic activity, selectivity, and stability. However, such analyses take the reactor and mass-flow conditions into account conditions in order to develop chemical meaningful insight.

Keywords:

TEM, EELS, in-situ, Operando, Nanoreactor

Reference:

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