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Multimodal Operando Electron Microscopy Approach to Study Pt Catalyst During CO Oxidation Reaction

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The recent development of more robust MEMS devices and nanoreactors gives rise to new opportunities for *in situ*/operando transmission electron microscopy (TEM) studies of heterogeneous catalysts [1,2]. These MEMS-based nanoreactors allow characterization of catalysts' active state under relevant conditions, at pressures up to 15 bar and temperatures up to 1000 °C [3-5]. The first visualization of time-resolved reactions inside the MEMS-based nanoreactor system with simultaneous acquisition of the reaction conversion data by mass spectrometry (MS) has been reported on by Vendelbo *et al.* [6].

Here we report for the first time on a multimodal operando electron microscopy approach to study catalysts at work. Using home-built gas-feeding setups of an environmental scanning electron microscope (ESEM) and a conventional TEM with commercially available gas-flow TEM holders we combined both with a mass spectrometer for real-time *in situ* experiments inside the chamber. Both setups are complementary in terms of obtainable resolution, to gain information on local and global dynamics, as well as applicable pressure ranges. Our multimodal operando approach can therefore provide new insights into the fundamental understanding of how heteregenous catalysts work in reaction conditions, providing information about surface and subsurface interactions in different gas environments. To test the setups, we used CO oxidation over Pt nanoparticles and polycrystalline Pt foil as a model reaction. We were able to correlate structural and morphological changes of the Pt catalysts with activity at different spatial resolution from 1Å to several mm, at pressures from 0.01 to 1000 mbar and at temperatures between 25-1000 °C (Figure 1). Our preliminary results suggest that CO oxidation does not involve the Pt surface only, but that the reactivity is also influenced by an interplay of surface, subsurface and bulk ordering (Figure 1d and 1e). This shows that the direct correlation of structural changes over several length scales with the catalytic conversion generates new insights into the activation and deactivation mechanisms that will ultimately allow us to better understand the structure-reactivity relationships in heterogeneous catalysis.

In summary, we show that our multimodal operando electron microscopy approach using *in situ* TEM and ESEM can deliver new insights into the fundamental understanding of how heteregenous catalysts work under relevant reaction conditions by providing access to crucial information on surface, subsurface and bulk interactions in different gasous environment [7].

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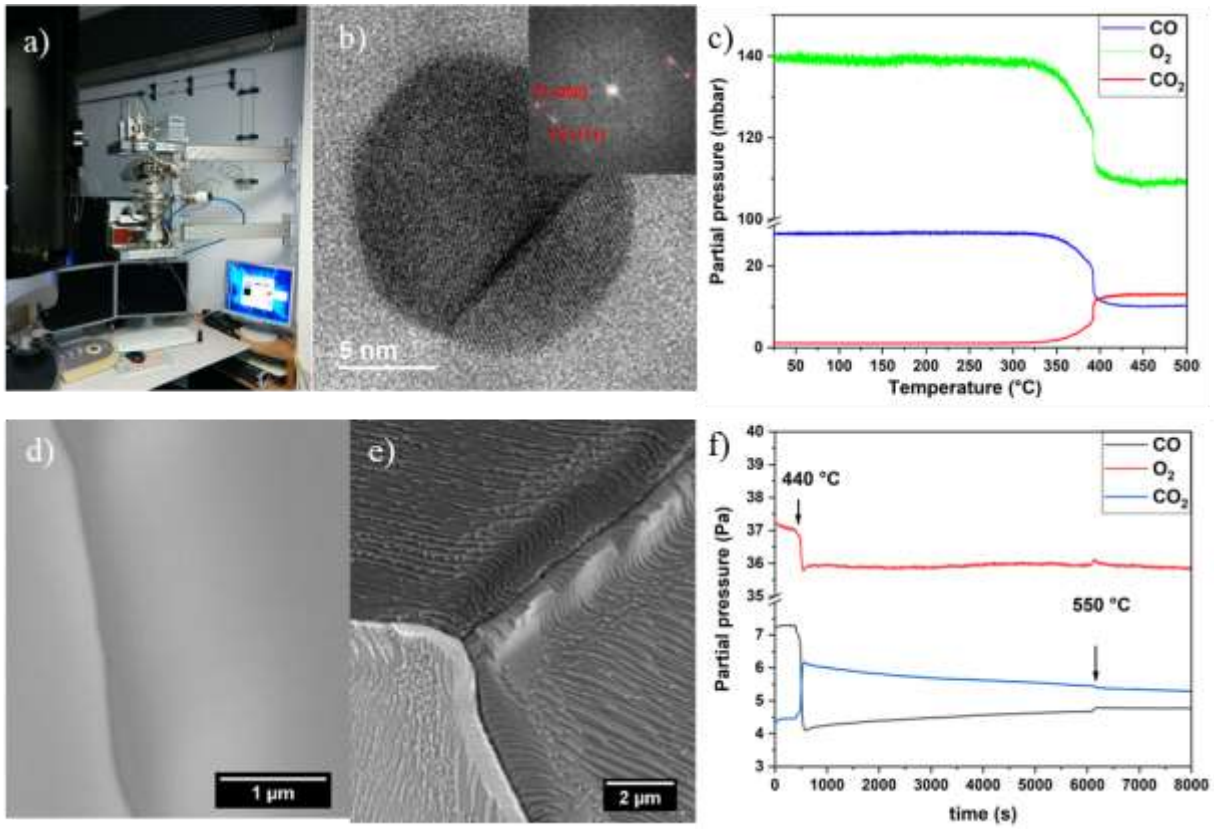

Figure 1. a) Experimental setup of the operando TEM. b) High-resolution TEM image of an individual Pt nanoparticle in $CO:O_2$=1:5 gas feed at 700 mbar and 200 °C. c) Graph showing MS data during the temperature ramp 1 °C/min from RT to 500 °C in $CO:O_2$=1:5 gas feed with a flow of 20 µl/min at 700 mbar. ESEM image of the polycrystalline surface of the Pt foil d) before and e) during CO oxidation. f) Corresponding MS data during CO oxidation reaction in the ESEM at 0.52 mbar, at 440 °C and 550 °C in $CO:O_2$=1:5 gas feed.

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