In situ Local Temperature Mapping in X-ray Microscopy Nano-Reactors with Luminescence Thermometry

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In situ and operando spectroscopy experiments play a crucial role in resolving the mechanisms behind catalytic processes. In order to mimic conditions used in industry, it is important to have reactors available that allow precise control over temperature and pressure during the experiment. Here, we present an in-house developed setup for in situ and operando scanning transmission X-ray microscopy (STXM) using a Microelectromechanical systems (MEMS) reactor (Figure 1a-b). [1] This setup allows STXM experiments at up to 5 bars and temperatures up to 800 °C. However, in catalytic processes deviations from the set temperature and possible temperature gradients inside the reactor can severely influence the reaction (Figure 1d). In order to precisely determine the local temperature and possible temperature gradient, the setup was tested by luminescence thermometry in combination with confocal microscopy, using microcrystalline NaYF₄:Er³⁺,Yb³⁺. [2-3] This allowed resolving the exact temperature, at ~ 7 µm spatial resolution, and its distribution inside the reactor under different conditions, i.e. under vacuum, in air and under He or H₂ gas flow. The temperature distribution over the heating spiral has been successfully mapped from room temperature up to 600 °C and compared to the read-out obtained from resistivity measurements (Figure 1e-f for vacuum and H₂ flow conditions, respectively). Under vacuum, the temperature obtained from luminescence thermometry matched well with the values from the read-out and were homogeneous. However, under ambient conditions the heat dissipation plays an important role and the maximum temperature reached in the reactor was 450 °C, compared to the set temperature of 600 °C. The temperature distribution also became heterogeneous, with a temperature gradient of 200 °C. This shows that the local temperature can be significantly different compared to the average temperature read-out.

**Figure 1** (a) In-house developed holder to use microelectromechanical systems (MEMS) reactors (b) for scanning transmission X-ray microscopy (STXM). A zoom-in of the heating spiral is shown (c), with three locations highlighted. The X-ray absorption spectra (XAS) of the Co-particles at these locations are shown (d). Depending on the location in the spiral, the particles experience a different temperature and therefore display a different behavior during reduction. To monitor the temperature distribution, luminescence thermometry using microcrystalline NaYF₄:Er³⁺,Yb³⁺, was used in combination with confocal microscopy. The results are shown in (e) and (f) for vacuum and H₂ flow conditions, respectively.