

Sample Environment for Operando Hard X-Ray Tomography—An Enabling Technology for Multimodal Characterization in Heterogeneous Catalysis

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1. Mass spectrometry data and calculation of CO₂ conversion

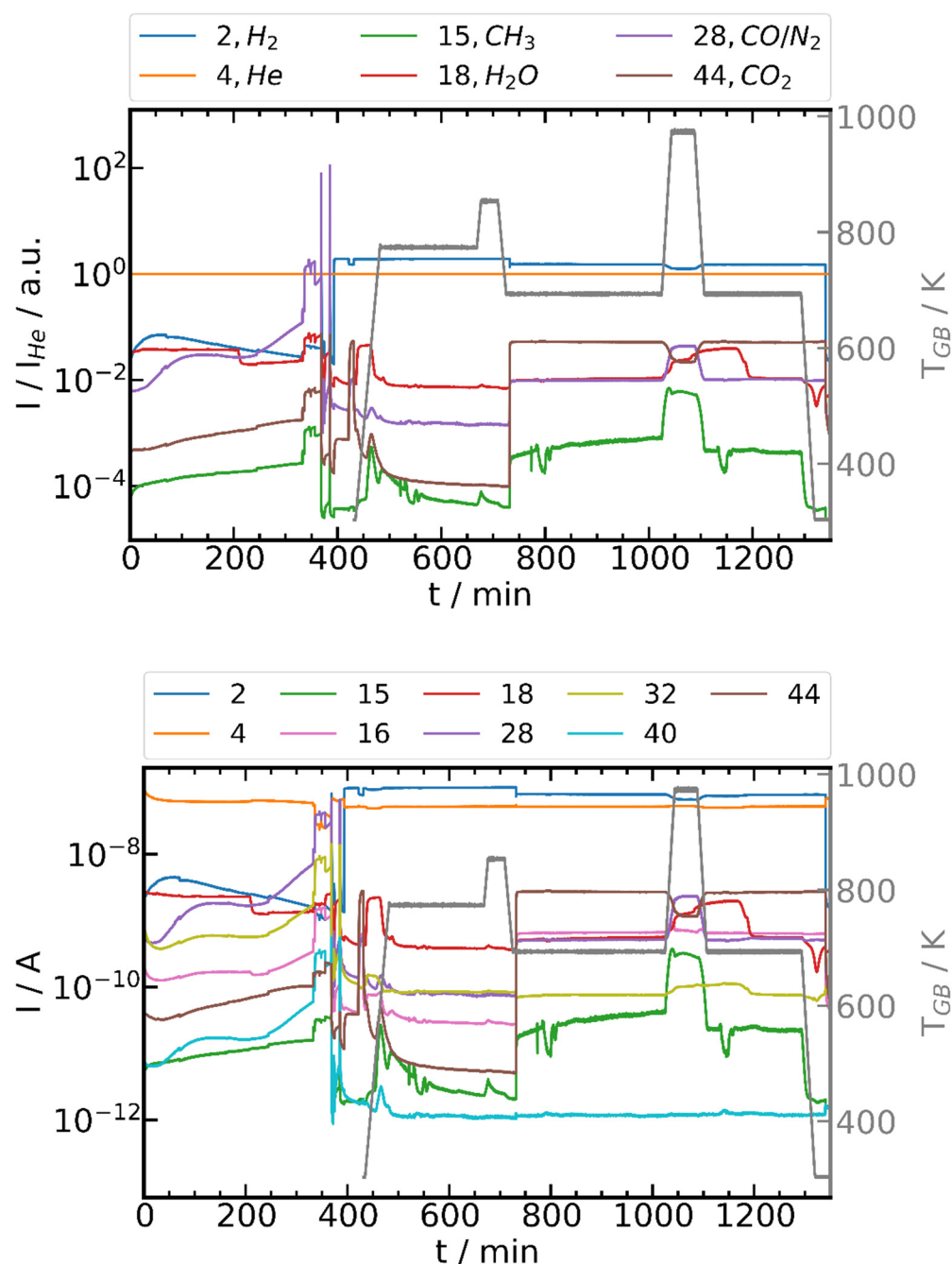


Figure S1. (a) Mass spectrometry data of the major reactants and products during CO₂ methanation studies as a function of temperature together with the relevant m/z ratio of each trace—normalised to the signal for He (m/z = 4) as inert carrier and internal standard. (b) Raw ion current signal including Ar (m/z = 40) as an indicator of potential leaks and abnormalities in the gas flow. Note logarithmic scale. T_{GB} = gas blower temperature.

The raw and normalised mass spectrometry datasets obtained during tomography studies are shown in **Error! Reference source not found.**. The period from 0 to 400 min includes initial setup of the instrument and the aRCTIC setup prior to the reduction (activation phase). The reduction step began at ca. 420 min, operando reaction conditions at ca. 730 min, high temperature ageing at ca. 1030 min, and a second period of operando reaction conditions at ca. 1110 min. Tomography data was acquired during the reduction

period, and during both operando reaction periods. The absence of the Ar trace ($m/z = 40$) indicates a gas-tight condition was achieved, since this trace is naturally present in the ambient atmosphere of our planet. The He trace ($m/z = 4$) was used as an internal standard to account for drift in the detected signals, which can naturally occur in MS over extended operation periods. The He composition in the flow, and the total flow rate of gas, were kept constant starting from the reducing phase (ca. 420 min).

CO₂ conversion was calculated based on the signal observed during the thermal ageing condition, according to the following formula:

$$X_{\text{CO}_2} = \frac{\frac{I_{\text{CO}_2}}{I_{\text{He}}}, \text{ageing}}{\frac{I_{\text{CO}_2}}{I_{\text{He}}}, \text{baseline}} \quad (\text{S1})$$

where 'X_{CO₂}' indicates the conversion of CO₂, 'I_z' indicates the raw current detected for trace 'z', and 'baseline' indicates a measurement performed when there is zero expected conversion of CO₂, e.g. at room temperature. This is illustrated for the normalised CO₂ signal in **Error! Reference source not found.** The reason for determining conversion during the thermal ageing step, rather than under normal operando reaction conditions, was due to the low overall activity of the catalyst. While CH₄ was detected as a product during the operando reaction conditions, this appeared to be a relatively small amount since the concurrent change in the reactant CO₂ and H₂ signals was also relatively small. For this reason CO₂ conversion was calculated when a noticeable difference could be observed compared to the baseline condition, i.e. under thermal ageing. The catalyst used in this study is a model system selected for its structural simplicity, in order to demonstrate the use of the aRTIC setup. The catalyst is not representative of an industrial standard catalyst. Low conversion of the chosen system does not affect the validity of the setup and the experimental procedure.

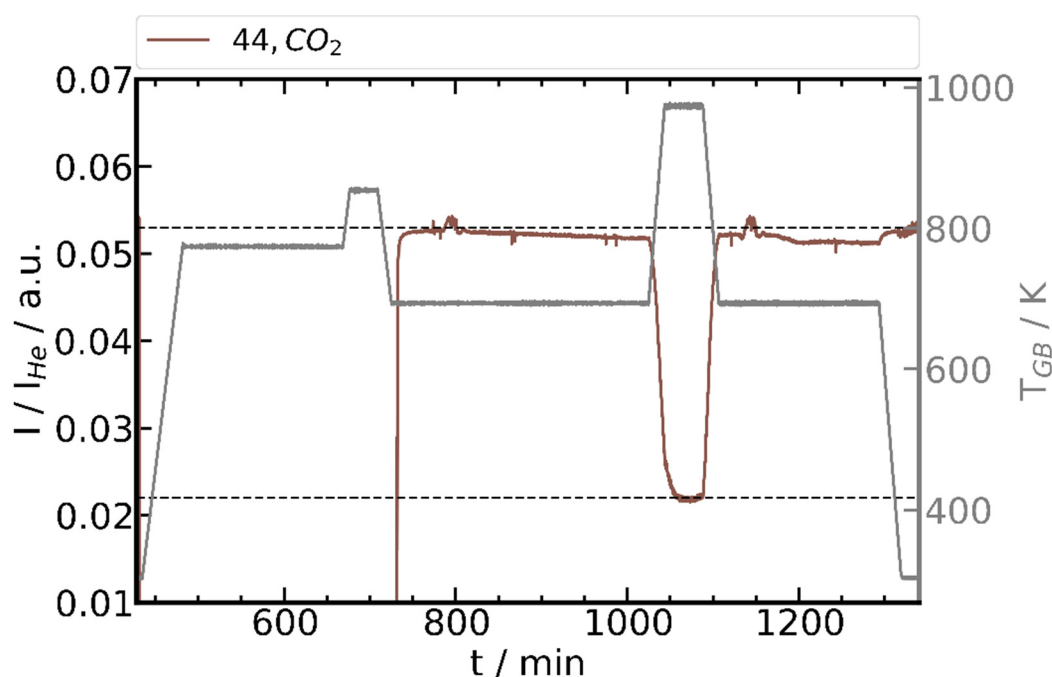


Figure S1. Calculation of CO₂ conversion during methanation studies from normalised MS trace of CO₂ ($m/z = 44$). Zero CO₂ in the feed (e.g. $t = 600$ min) was taken as 100% conversion point. CO₂ in the feed at room temperature (e.g. $t = 1325$ min) was taken as 0% conversion point or baseline measurement.

2. Hot air blower temperature calibration

The calibration made for the measured and programmed temperature of the hot air blower setup is shown in **Error! Reference source not found.**. The temperature was measured using a portable type K thermocouple at several point close to the surface and around the circumference of the capillary.

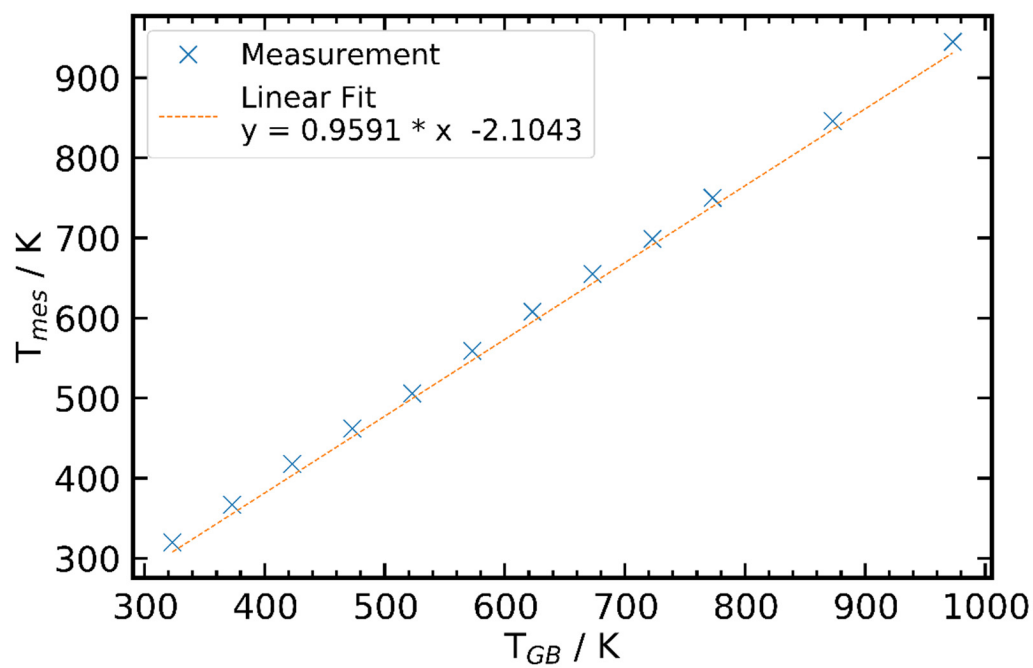


Figure S3. Hot air blower calibration curve measured before the tomography experiments. The temperature T_{mes} was measured using a portable thermometer with a Type K thermocouple depending on a certain readout temperature T_{GB} of the internal thermocouple in the hot air blowers.

3. Diagram of the aRCTIC setup

A diagram of the rotating capillary for in situ/operando tomography (aRCTIC) setup is shown in **Error! Reference source not found.**, indicating the positioning of the rotation stage, linear stages, goniometer, and sample holder. Not shown are the stainless-steel gas connections or the capillary containing the sample. In order to perform operando tomography, a gas dosing system, temperature control system, and a product analysis instrument are additionally required.

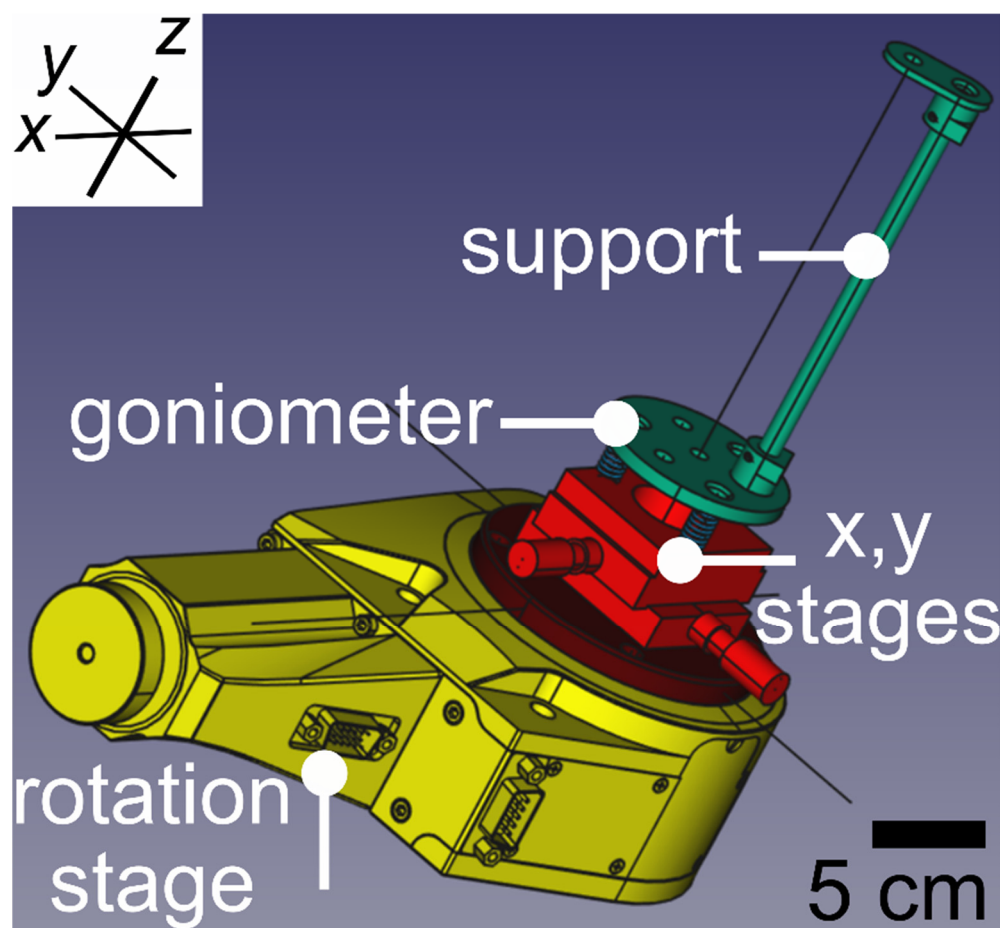


Figure S4. Schematic of the aRCTIC setup, showing required components for operando tomography experiments. The rotation stage (yellow) can be substituted for alternative models, considering the required minimum size and weight allowance. The manual x,y linear stages (red) for centre of rotation alignment can be substituted by automated stages as required. Of the sample holder itself (green), only the base plate, support and fittings are shown.

4. Tomography data treatment

4.1. Removal of the stabilising rod

Use of the aRTIC setup introduces a special consideration during data treatment. Over a specific angular range, depending on the exact layout of components, the incident X-ray beam will be eclipsed by the support when performing a 180° rotation. This is evident in the broad horizontal stripe across the sinograms shown in **Error! Reference source not found.**

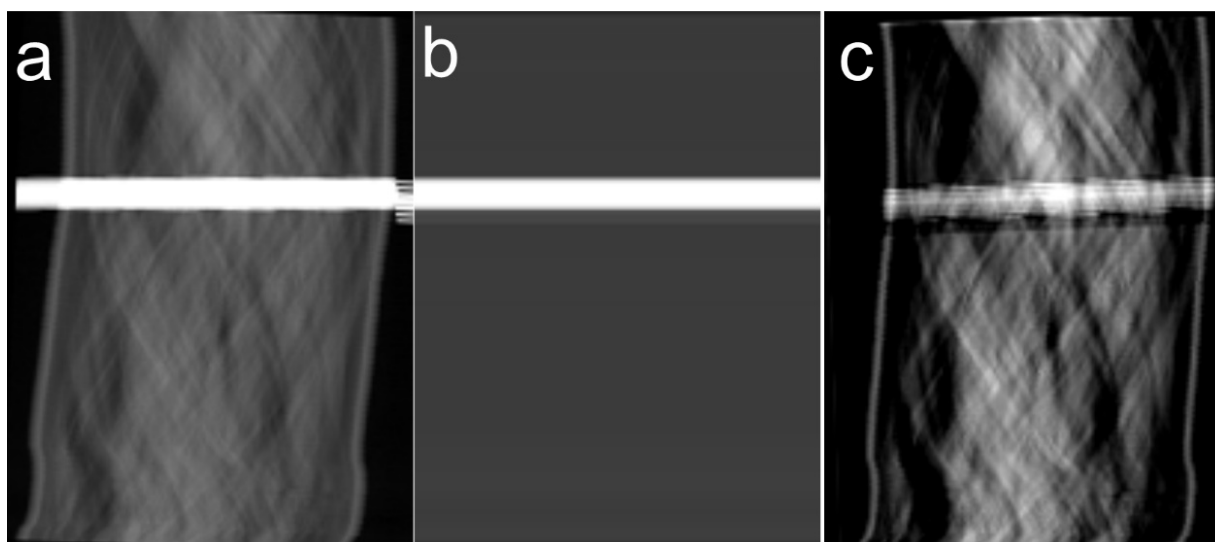


Figure S5. Removal of the support from the recorded sinograms during CO₂ methanation studies: (a) raw sinogram at one given 2θ value; (b) extracted rod and background intensity; (c) adjusted sinogram resulting from subtracting (b) from (a). Data from angles where the incident beam is eclipsed by the support can clearly be recovered, as shown by the features in (c) where the rod was formerly present.

Depending on the incident energy of the beam, and on the contrast mode used, this artefact can either be disregarded, or manually removed from the sinograms before tomographic reconstruction. The requirement to perform this step therefore depends strongly on the system of interest, the required data quality, and the tolerance for artefacts. Rod removal can be considered on a case-by-case basis. For example, during the XRD tomography studies performed here, the glassy carbon support rod contributed to a significant scattering signal across the entire angular range measured. This can be considered as background scattering not related to the catalyst sample, and furthermore can be regarded as a uniform background due to the circular nature of the rod. This background signal can be removed by: (i) extracting the scattered signal from the air region on either side of the sample attributed purely to the rod and a negligible amount of background scattering from air; (ii) extrapolating this background within the confines of the recorded sinogram, and aligning the resulting background image with the original sinogram; (iii) subtracting the scattered background from the original image to recover the interior sample features covered by the support rod. Although this method is not entirely free of artefacts, in cases such as this one, an appreciable signal may be recovered. A further example where the may rod may be ignored or disregarded, is in the case of X-ray absorption spectroscopic tomography at higher energies. Here the relative attenuation of the pure carbon support rod may be relatively small. A second example of the rod removal procedure following data acquisition at Pt L₃ edge is shown in **Error! Reference source not found.**

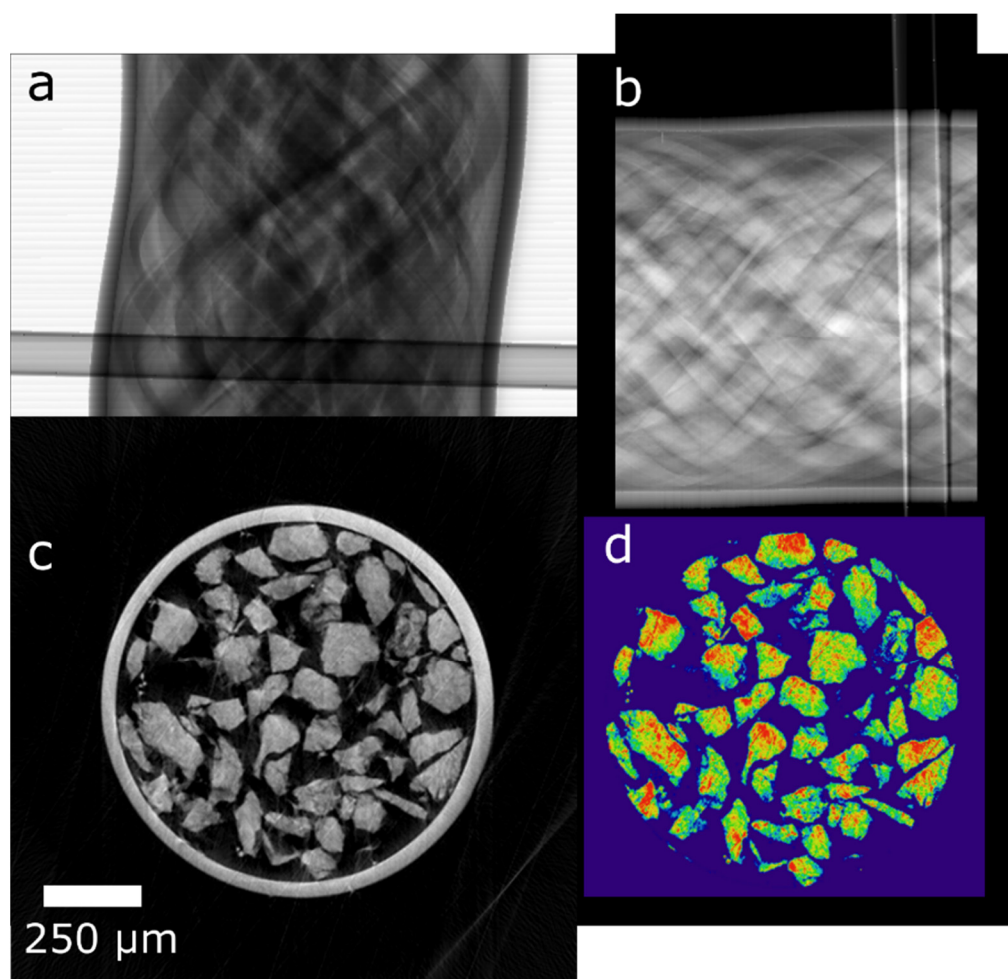


Figure S6. Summary of tomography reconstruction steps, methane CPO studies: (a) raw sinogram of one slice of the sample at a single energy point; (b) background and I0 corrected sinogram; (c) reconstructed sample with visible quartz capillary and catalyst particles; (d) reconstructed particles without the capillary, the colour coding depicts concentration of Pt in the sample.

Another possibility for data reconstruction is to simply exclude a portion of the sinogram from the reconstruction, therefore performing so-called missing wedge tomography. The specific approach chosen will depend on the sample system of interest and the measurement itself. In any case, this potential data treatment step does not impact the validity of the aRTIC setup and the experimental procedure for operando tomography.

4.2. Determining spatial resolution of tomography data

An example of sharp edge fitting is shown in **Error! Reference source not found.** Sharp edge fitting is an empirical method of determining spatial resolution in image data. Two neighbouring features are chosen with an obvious difference in intensity, in this example (XRD tomography) representing different abundance of a specific crystalline phase in neighbouring regions of the sample. The number of pixels over which the intensity gradient can be observed provides an indication of the spatial resolution, in this case chosen as the physical difference between 90% and 10% signal of the feature with higher intensity. In scanning tomography with a focused beam as performed here, the pixel size of the resulting images can be approximated to the horizontal step size of the motor during tomography data acquisition, in this case 10 μm .

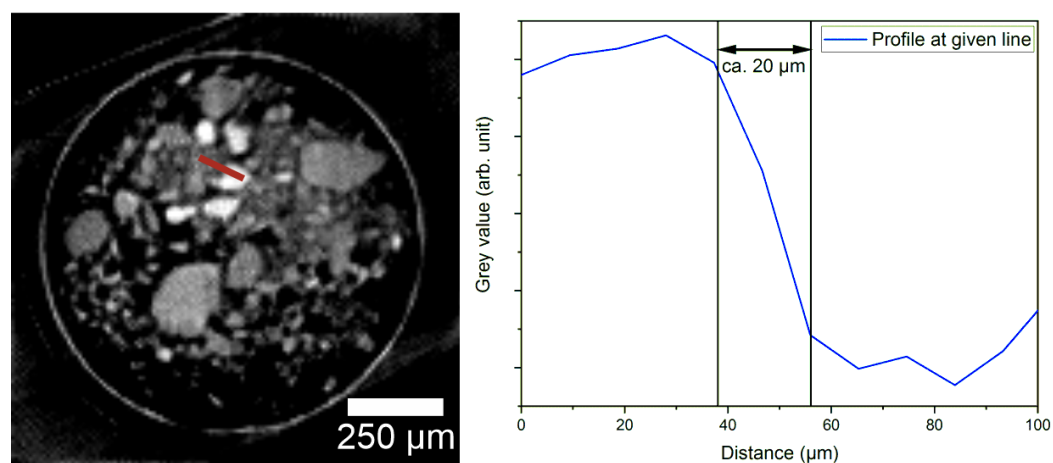


Figure S7. Sharp edge fitting of a line between two particles in the ex-situ sample to define the reachable resolution: (left) reconstruction of the sample with line at which position the profile as measured; (right) the profile with estimated resolution.

5. Additional ED-XAS-CT data

5.1. ED-XAS imaging results at 673 K

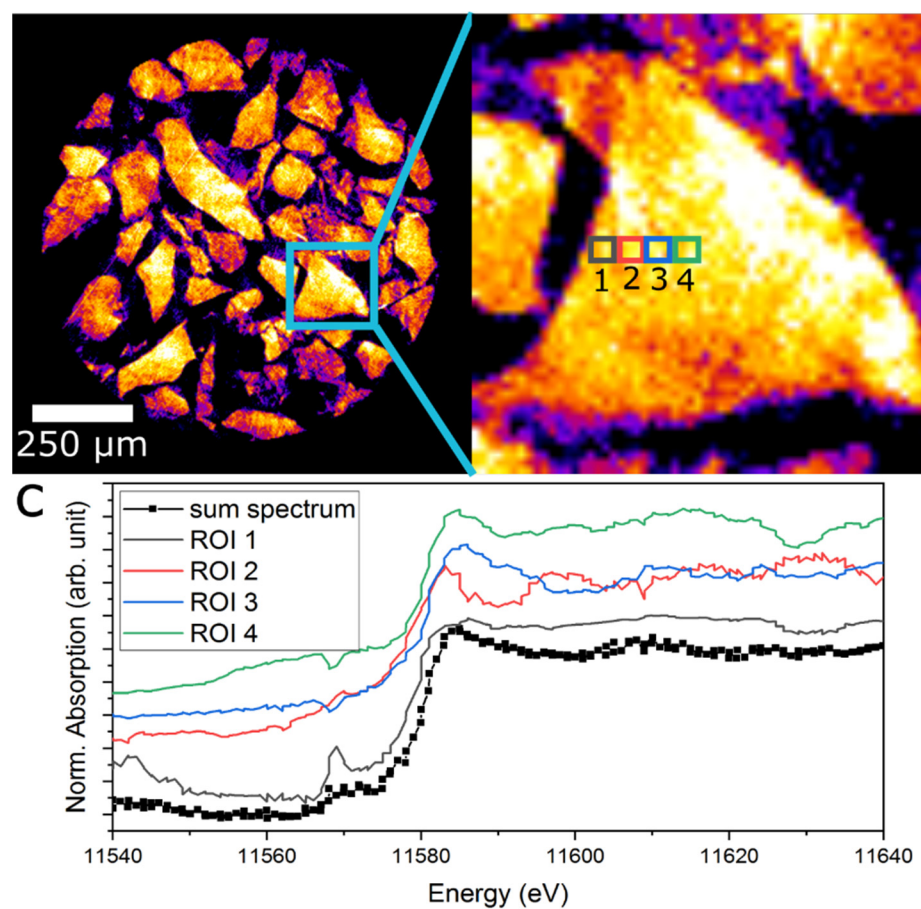


Figure S8. Overview of ED-XAS tomography data measured at 673 K; (a) reconstructed orthogonal high-resolution slice with the capillary masked out, the colour coding depicting the absorption intensity at 11585 eV; (b) extracted single particle of the same slice with marked regions of interest (ROIs) where XANES spectra were extracted; (c) XANES spectra of the four ROIs with sum spectra of the whole slice for comparison.

5.2. ED-XAS study—mass spectrometry data

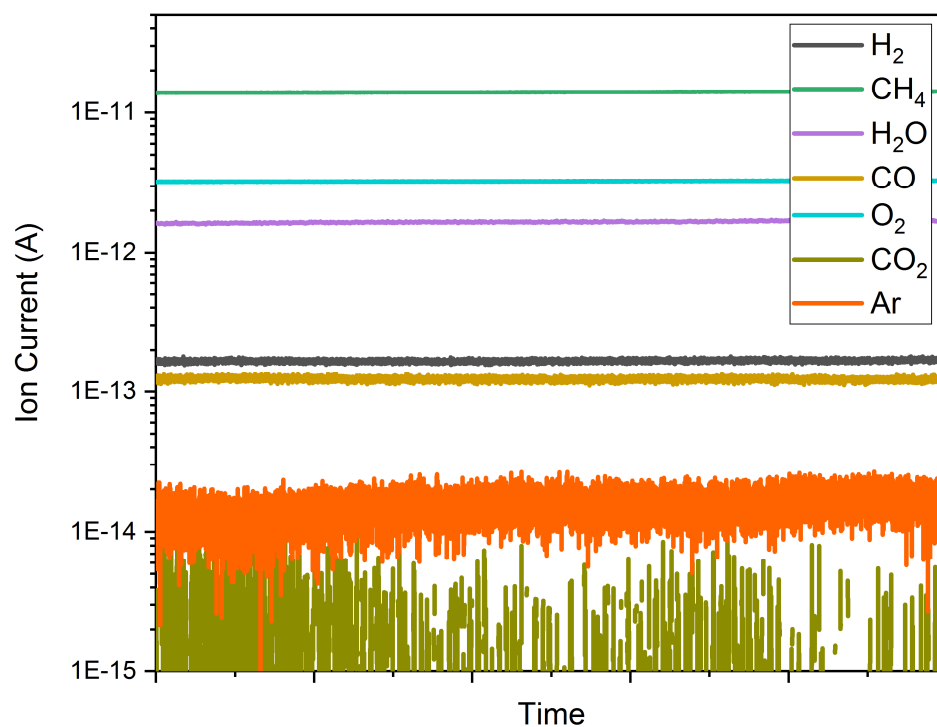


Figure S2. Overview of the MS signals from the ED-XAS-CT measurement at 523 K. The corresponding fragments for the labelled molecules are $m/z = 2$ (H_2), 15 (CH_4), 18 (H_2O), 28 (CO), 32 (O_2), 44 (CO_2), 30 (Ar).

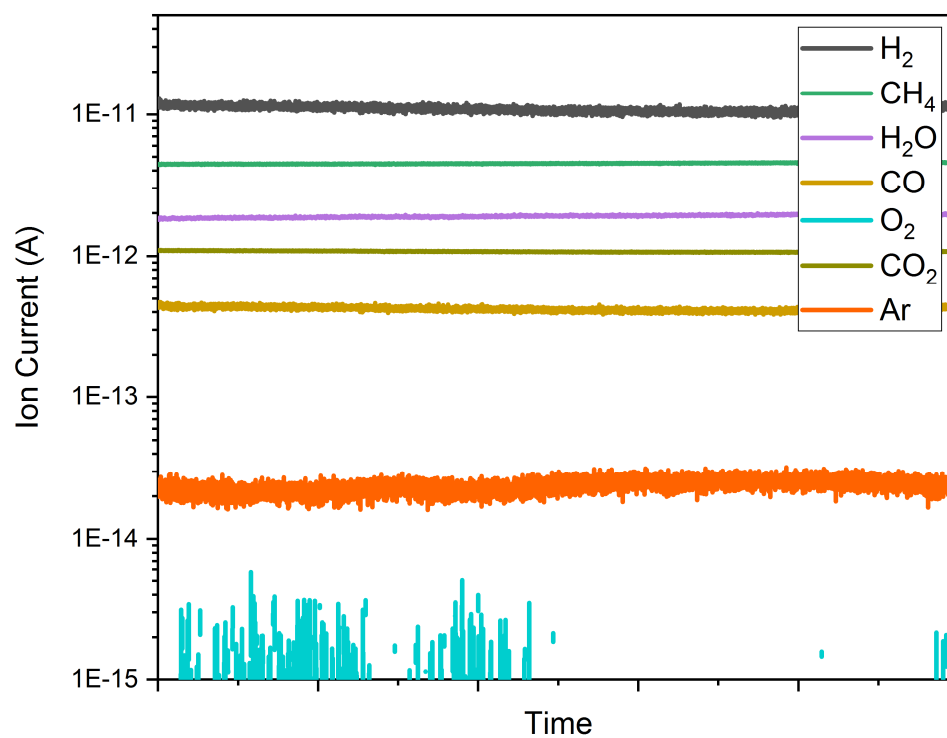


Figure S10. Overview of the MS signals from the ED-XAS-CT measurement at 673 K. The corresponding fragments for the labelled molecules are $m/z = 2$ (H_2), 15 (CH_4), 18 (H_2O), 28 (CO), 32 (O_2), 44 (CO_2), 30 (Ar).