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Operando laboratory XAS of Ni nanoparticles in CO_2 methanation using a plug-flow fixed-bed cell with von Hámos spectrometer

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A plug-flow fixed-bed cell for *operando* laboratory X-ray absorption spectroscopy (XAS) using a von Hámos spectrometer is presented for heterogeneous catalysis studies. The cell operates up to 1000 °C and 10 bar with controlled gas atmospheres provided by three mass flow controllers and rapid infrared heating. The performance of the setup is demonstrated across a broad usable energy range of the spectrometer, and as a proof of principle, *operando* Ni K-edge XAS was used to monitor the activation of a 20 wt% NiO/COK-12 catalyst under CO_2 methanation conditions ($CO_2 : H_2 = 1 : 4$, 350 °C). Time-resolved spectra acquired on a 5 min timescale reveal the reduction of NiO nanoparticles to metallic Ni during activation, directly correlating with increasing catalytic activity quantified by online gas chromatography. This setup enables minute-scale, time-resolved structural analysis of working catalysts under industrially relevant conditions, providing a practical laboratory-based alternative complementary to synchrotron studies.

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1 Introduction

Operando X-ray absorption spectroscopy (XAS) is a key tool for correlating oxidation state and local structure of heterogeneous catalysts with their activity under working conditions.[1–3] While such studies are routinely performed at synchrotron facilities, there is growing interest in laboratory-based XAS spectrometers that enable time-resolved measurements with reduced dependence on large-scale infrastructure.[4–6]

Recent developments in von Hámos spectrometers using optimized X-ray sources and HAPG optics have demonstrated *ex situ* and *in situ* XANES and partial EXAFS capabilities with acquisition times of 5–15 min per spectrum, sufficient to follow catalyst activation and deactivation processes.[6–8]

In this work, we demonstrate *operando* Ni K-edge laboratory XAS using a plug-flow fixed-bed reactor cell adapted from Bischoff *et al.*[9] for CO_2 methanation on 20 wt% NiO/COK-12 (COK-12 is an ordered mesoporous SiO_2 support).[10,11] We track NiO reduction to metallic Ni during activation and correlate the observed oxidation state changes with the onset of catalytic activity quantified by online GC. The focus is on the practical capabilities and limitations of this combination of cell and specific laboratory spectrometer scheme.

2 Experimental section

All XAS measurements were performed with a laboratory von Hámos spectrometer described in detail elsewhere.[5,12,13] In brief, a micro-focus X-ray tube (MCBI 50B-70 Mo, rtw Röntgen-Technik Dr Warrikhoff), cylindrically bent HAPG mosaic crystal (Optigraph) and EIGER2 R 500K (DECTRIS) detector provide wavelength-dispersive Ni K-edge XANES/partial EXAFS in transmission geometry. The sample is positioned close to the source and the beam path is evacuated to maximise flux. The modified von Hámos alignment enables Ni K-edge spectra in 5–15 min with sufficient SNR for *operando* studies. Artefacts from non-flat samples are discussed in previous work.[14]

Operando measurements used a quartz capillary reactor heated by an IR tube furnace based on Bischoff *et al.*,[9] adapted to the spectrometer (see Fig. 1 and SI). A SiC tube with 4 × 1 mm slits surrounds the 1.0/0.8 mm capillary containing ~1 mg catalyst, quartz wool plugs and downstream thermocouple. Slit heights match the capillary to probe only the catalyst bed. Full details are in the SI and Bischoff *et al.*[9]

The reactor was fed by three mass flow controllers (H_2, CO_2 and N_2/compressed air) for fast atmosphere switching. Outlet

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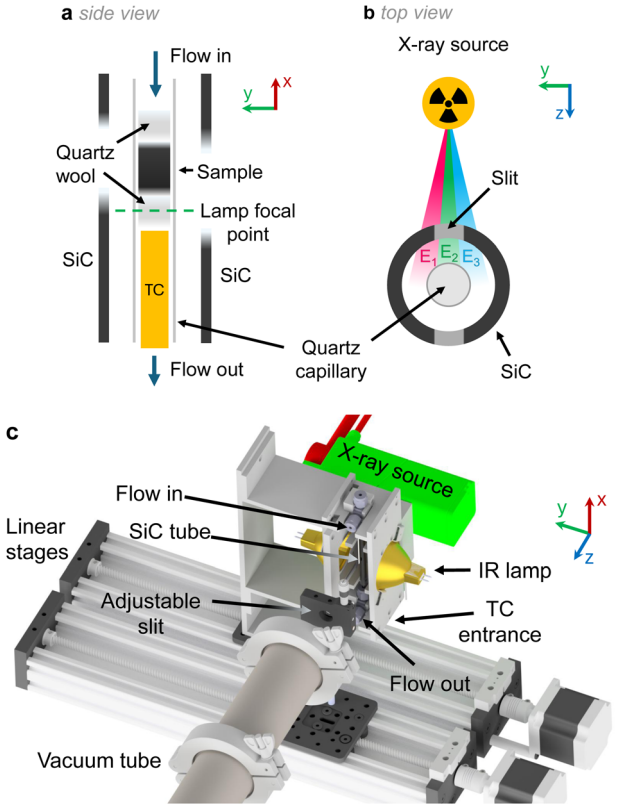

Fig. 1 (a) Schematic view of sample, quartz wool and TC position inside the capillary surrounded by the SiC tube. (b) Top view of the capillary in the SiC tube showing the X-ray beam path. (c) CAD model to the orientation of the IR tube furnace in the von Hámos set up.

gas was analysed online by micro-GC to quantifying H_2, CO_2, CH_4 and CO. Conversions/selectivities were calculated from outlet concentrations (see SI).

The 20 wt% NiO/COK-12 catalyst was prepared by incipient wetness impregnation followed by calcination.[2,15] Pellets served for *ex situ* XAS; NiO powder and Ni foil were reference standards. Synthesis details and the Mn model system are in the SI.

3 Results

All data processing (normalization, background subtraction) was carried out with the Demeter/ATHENA software package.[16] Terminology follows the IUPAC recommendations of Peterson *et al.*, distinguishing between *in situ* (controlled environment without direct activity readout) and *operando* (under working conditions with simultaneous activity measurement).[17]

To assess the performance of the setup across its usable energy window, K-edge XAS spectra were recorded for several systems spanning almost the entire range of the spectrometer: Mn (5% Ni/MnO), Ni (20-NiO/COK-12), Se (SnSe) and Zr (ZrO_2). Fig. 2 shows representative spectra obtained in capillaries as well as pellets of the same materials (see Fig. S5–S8 in the SI for undistorted and normalized data).

At lower energies (Mn K-edge, 1.0/0.8 mm capillary, 300 s acquisition), the accessible spectral window is restricted to the XANES region due to a pronounced high-energy cut-off, resulting in a modest but sufficient signal-to-noise ratio (SNR) to resolve oxidation-state changes. For the Ni K-edge under otherwise identical conditions, higher tube output and reduced absorption improve SNR and extend the usable post-edge range, although a residual rounded spectral shape is observed, arising from the cylindrical sample geometry. At intermediate energies (Se K-edge), these distortions are weak, while at the upper end of the current range (Zr K-edge, 1.5/1.0 mm capillary, 120 s acquisition) nearly undistorted XANES with high SNR is obtained, demonstrating the suitability of thicker capillaries for higher-energy measurements.

The 20-NiO/COK-12 catalyst was first tested under CO_2 methanation conditions at 350 °C (no activity detected), then reduced/activated in 5% H_2/Ar at 600 °C, and finally re-tested under methanation conditions. Ni K-edge spectra were acquired every 5 min and analyzed by linear combination fitting (LCF) using 20-NiO/COK-12 pellet and Ni foil references.

Fig. 3 shows the spectral evolution (a) and LCF quantification (b) during the reduction step. The edge shifts progressively towards metallic Ni and the white-line intensity decreases as the temperature exceeds *ca.* 450–500 °C. After ~20 min at 600 °C the spectrum closely resembles the Ni foil, with LCF indicating

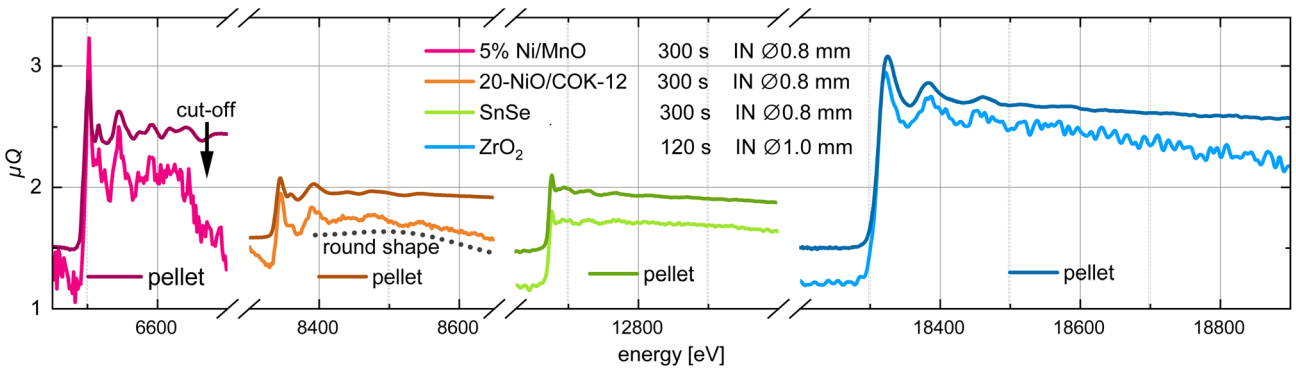

Fig. 2 K-edge XAS spectra of 5% Ni/MnO (Mn K-edge), 20-NiO/COK-12 (Ni K-edge), SnSe (Se K-edge) and ZrO_2 (Zr K-edge), measured in quartz capillaries (0.8/1.0 mm for Mn, Ni, Se; 1.0/1.5 mm for Zr). Vertical offsets were applied for clarity. The overlaid dark traces show reference spectra of the same materials measured as pellets. Full, unshifted spectra are provided in Fig. S6–S9 (SI).

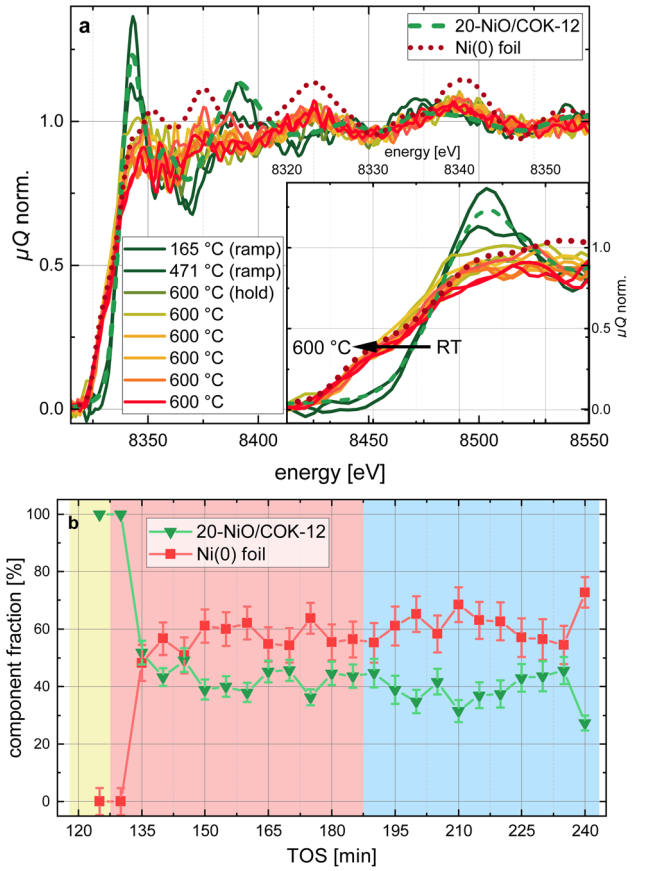

Fig. 3 *Operando* Ni K-edge XAS during reduction of 20-NiO/COK-12 in 5% H_2/Ar at 600 °C. (a) Representative spectra acquired every 5 min. (b) LCF-derived Ni(0) fractional component *vs.* time-on-stream (TOS) during reduction. Yellow: ramp, red: 600 °C, blue: cool down.

a majority Ni(0) phase. After cooling and heating to 350 °C under $CO_2:H_2$ (1 : 4) conditions, CH_4 appears in the GC with CO_2 conversions of ~10% and 100% selectivity, confirming that the reduced Ni phase is catalytically active. A comparison of pre- and post-reduction spectra with standards is shown in SI, alongside with the full *operando* series (including pre/post-reduction methanation) and additional validation experiments.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article and further information have been included as part of the supplementary information (SI). Furthermore, the raw and normalized XAS data for this article are available on Zenodo at https://doi.org/10.5281/zenodo.17063731. Supplementary information: a detailed view of the setup with the reactor cell, sample synthesis/prep, raw and normalized data from the *operando* and *in situ* measurements of 20-NiO/COK-12 and 5% Ni/MnO, and GC analyse. See DOI: https://doi.org/10.1039/d6ja00027d.

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Notes and references

1 A. Bergmann and B. Roldan Cuenya, Operando Insights into Nanoparticle Transformations during Catalysis, *ACS Catal.*, 2019, **9**(11), 10020–10043, DOI: 10.1021/acscatal.9b01831.
2 A. Gili, L. Schlicker, M. F. Bekheet, O. Görke, S. Penner, M. Grünbacher, *et al.*, Surface Carbon as a Reactive Intermediate in Dry Reforming of Methane to Syngas on a 5% Ni/MnO Catalyst, *ACS Catal.*, 2018, **8**(9), 8739–8750, DOI: 10.1021/acscatal.8b01820.
3 N. Bonmassar, M. F. Bekheet, L. Schlicker, A. Gili, A. Gurlo, A. Doran, *et al.*, In Situ-Determined Catalytically Active State of LaNiO3 in Methane Dry Reforming, *ACS Catal.*, 2020, **10**(2), 1102–1112, DOI: 10.1021/acscatal.9b03687.
4 G. T. Seidler, D. R. Mortensen, A. J. Remesnik, J. I. Pacold, N. A. Ball, N. Barry, *et al.*, A laboratory-based hard x-ray monochromator for high-resolution x-ray emission spectroscopy and x-ray absorption near edge structure measurements, *Rev. Sci. Instrum.*, 2014, **85**(11), 113906, DOI: 10.1063/1.4901599.
5 C. Schlesiger, L. Anklamm, H. Stiel, W. Malzer and B. Kanngießer, XAFS spectroscopy by an X-ray tube based spectrometer using a novel type of HOPG mosaic crystal and optimized image processing, *J. Anal. At. Spectrom.*, 2015, **30**, 1080–1085, DOI: 10.1039/C4JA00303A.
6 W. Malzer, C. Schlesiger and B. Kanngießer, A century of laboratory X-ray absorption spectroscopy – A review and an optimistic outlook, *Spectrochim. Acta, Part B*, 2021, **177**, 106101, DOI: 10.1016/j.sab.2021.106101.
7 S. Praetz, D. Grötzsch, C. Schlesiger, D. Motz, M. Würth, R. Zimmermann, *et al.*, In situ heating cell for temperature dependent transmission x-ray absorption spectroscopy (XAS) measurement with a laboratory based spectrometer, *Rev. Sci. Instrum.*, 2025, **96**(3), 035120, DOI: 10.1063/5.0253653.
8 S. Praetz, M. Johansen, D. Kober, M. Tesic, C. Schlesiger, D. B. Ravnsbæk, *et al.*, Operando laboratory XAS on battery materials using the DANOISE cell in a von Hámos spectrometer, *J. Anal. At. Spectrom.*, 2025, **40**, 2447–2461, DOI: 10.1039/D5JA00155B.
9 B. Bischoff, M. F. Bekheet, E. Dal Molin, S. Praetz, B. Kanngießer, R. Schomäcker, *et al.*, *In situ/operando* plug-flow fixed-bed cell for synchrotron PXRD and XAFS investigations at high temperature, pressure, controlled gas atmosphere and ultra-fast heating, *J. Synchrotron Radiat.*, 2024, **31**(1), 77–84, DOI: 10.1107/S1600577523009591.
10 S. Rönsch, J. Schneider, S. Matthischke, M. Schlüter, M. Götz, J. Lefebvre, *et al.*, Review on methanation – From fundamentals to current projects, *Fuel*, 2016, **166**, 276–296,

available from: https://www.sciencedirect.com/science/article/pii/S0016236115011254.

11 O. E. Medina, A. A. Amell, D. López and A. Santamaría, Comprehensive review of nickel-based catalysts advancements for CO_2 methanation, *Renewable Sustainable Energy Rev.*, 2025, **207**, 114926, available from: https://www.sciencedirect.com/science/article/pii/S136403212400652X.

12 C. Schlesiger, S. Praetz, R. Gnewkow, W. Malzer and B. Kanngießer, Recent progress in the performance of HAPG based laboratory EXAFS and XANES spectrometers, *J. Anal. At. Spectrom.*, 2020, **35**, 2298–2304, DOI: 10.1039/D0JA00208A.

13 S. Praetz, C. Schlesiger, D. A. Motz, S. Klimke, M. Jahns, C. Gottschalk, *et al.*, Can laboratory-based XAFS compete with XRD and Mössbauer spectroscopy as a tool for quantitative species analysis? Critical evaluation using the example of a natural iron ore, *PLoS One*, 2025, **20**(5), e0323678, DOI: 10.1371/journal.pone.0323678.

14 C. P. Schlesiger, Röntgenabsorptionsspektroskopie im Labor, PhD thesis, Technische Universität Berlin, 2019, available from: https://depositonce.tu-berlin.de/handle/11303/9336.

15 J. Jammaer, A. Aerts, J. D'Haen, J. W. Seo and J. A. Martens, Convenient synthesis of ordered mesoporous silica at room temperature and quasi-neutral pH, *J. Mater. Chem.*, 2009, **19**, 8290–8293, DOI: 10.1039/B915273C.

16 B. Ravel and M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT, *J. Synchrotron Radiat.*, 2005, **12**, 537–541, DOI: 10.1107/S0909049505012719.

17 V. K. Peterson, M. Bianchini, K. W. Chapman, M. Elice, D. B. Hibbert, P. Roche, *et al.*, Terms of Latin origin relating to sample characterization (IUPAC Technical Report), *Pure Appl. Chem.*, 2024, **96**(11), 1531–1540, DOI: 10.1515/pac-2022-1103.

