Phase Sensitive Detection Analysis on Modulation Excitation PDF Data of Ni Based Catalysts

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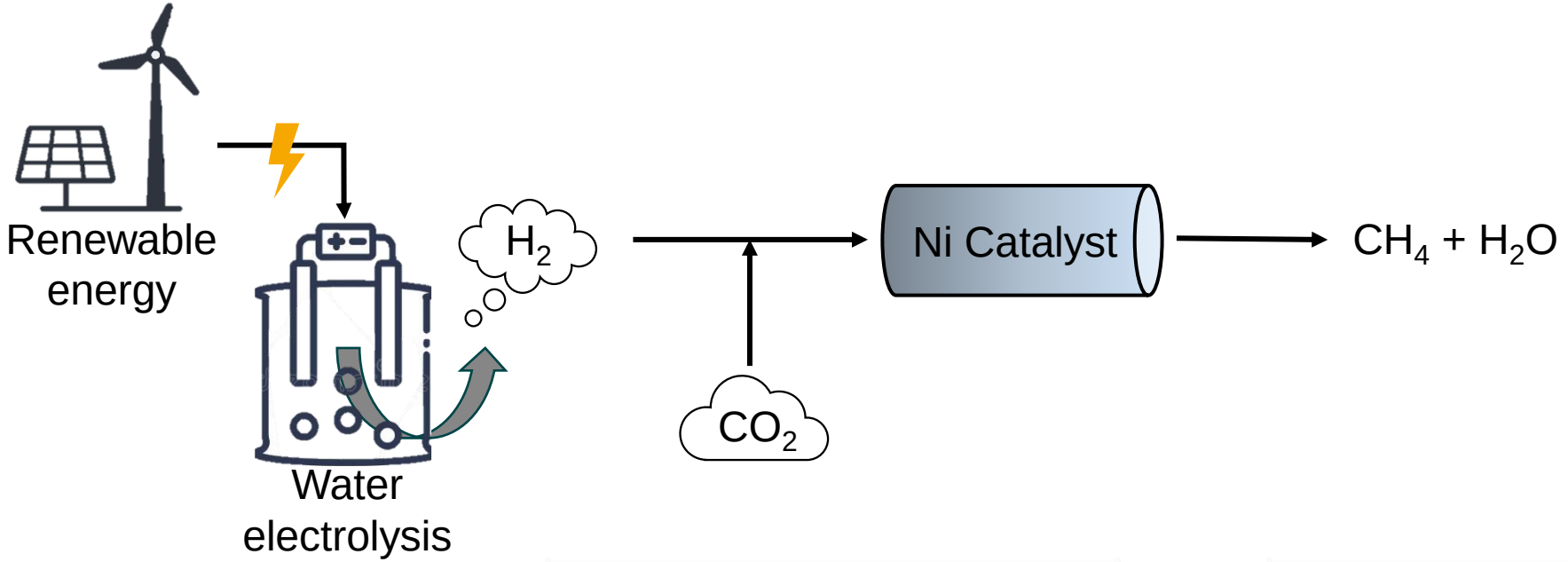
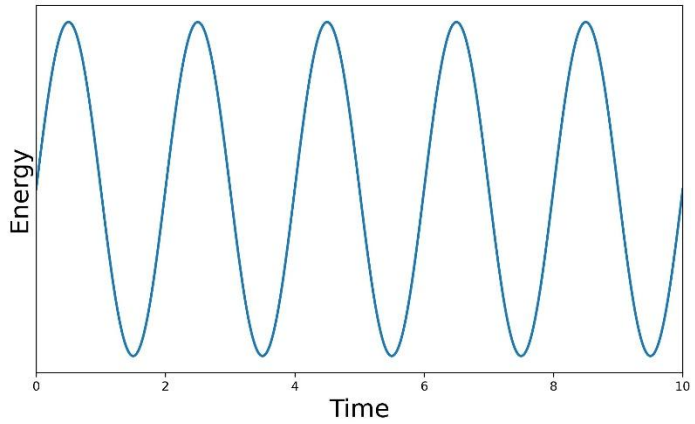
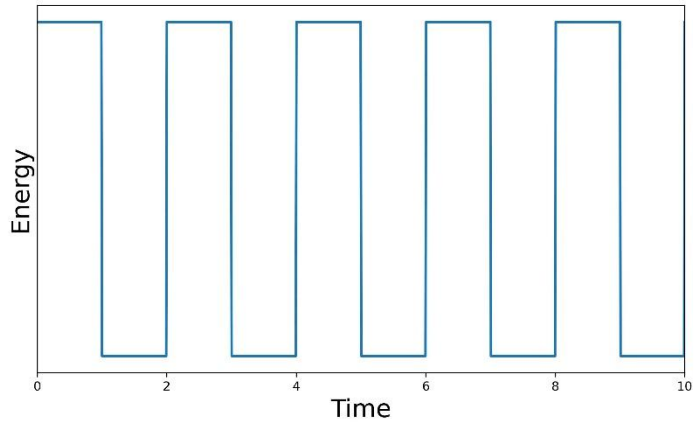
Grenoble

Energy Materials Under Fluctuating Conditions



Energy Fluctuation Conditions





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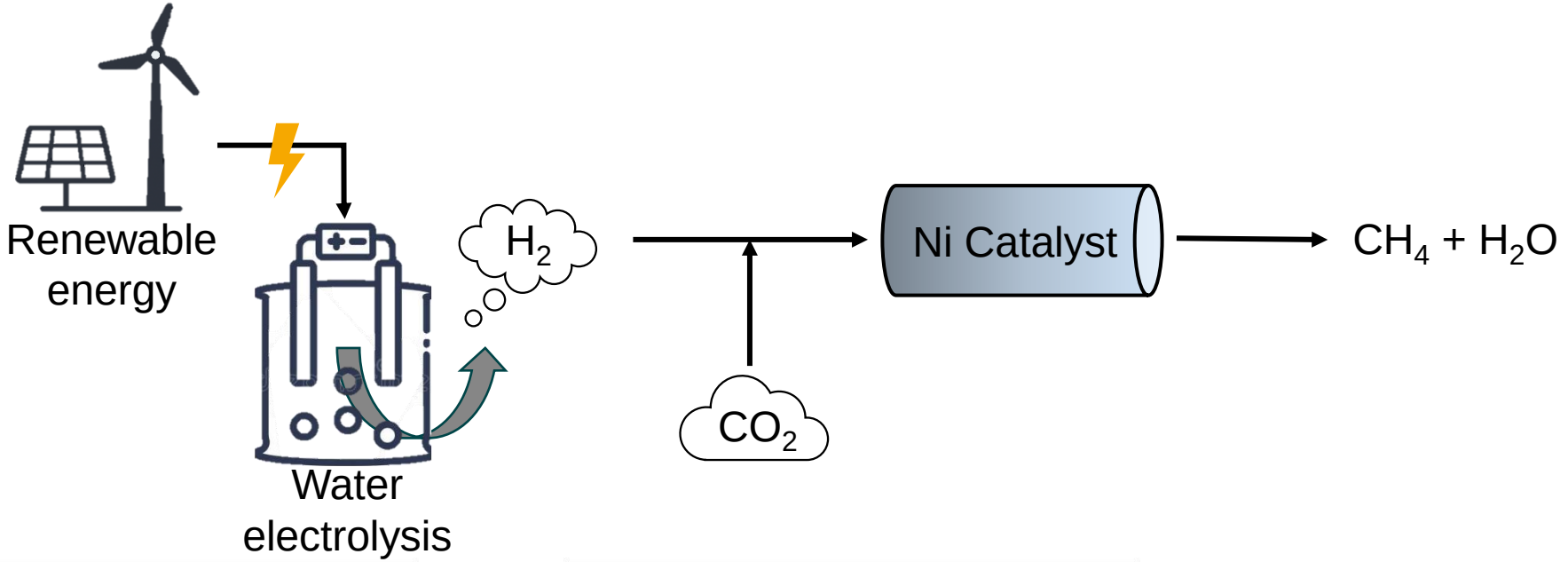
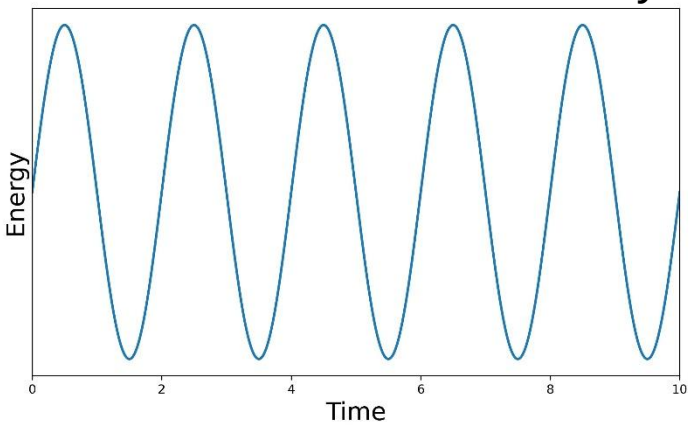
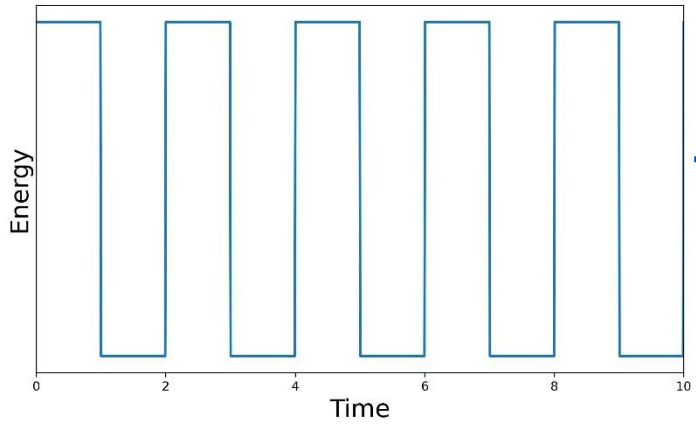
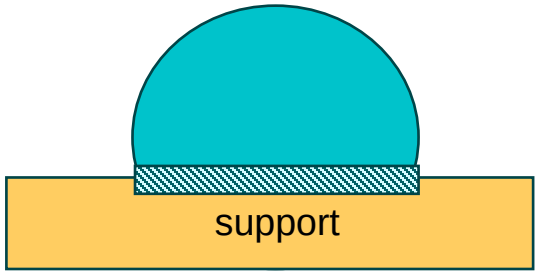






Subtle Structural Changes

Energy Materials Under Fluctuating Conditions

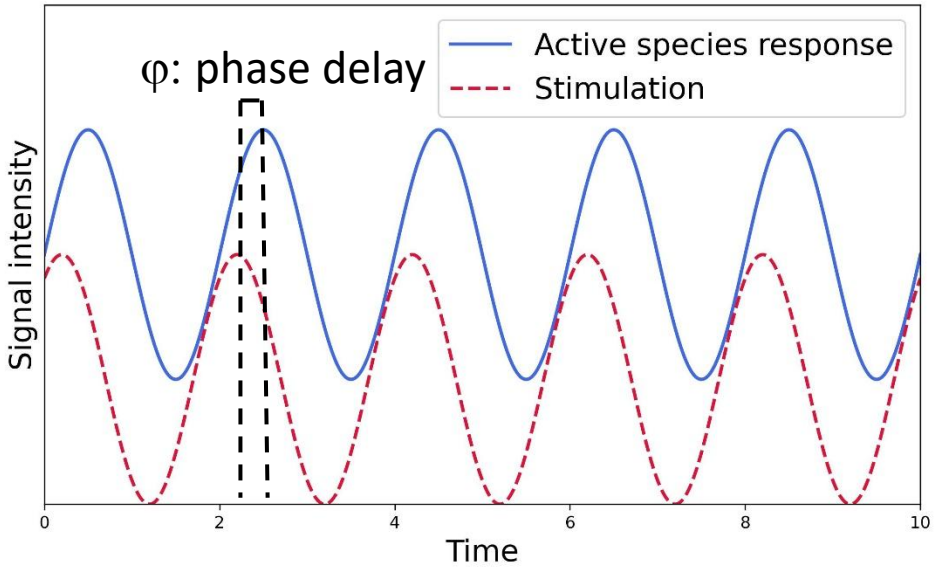


Phase change

Deactivation

Sintering

Oxidation/reduction



➡ Modulation Excitation (ME) experiments

- IR spectroscopy [1]
- X-Ray Absorption Spectroscopy [2]
- X-Ray Diffraction [3]

Phase Sensitive Detection Analysis (PSD) [4]

$$A_k\left(\phi_k^{PSD}\right) = \frac{2}{T}\int_0^T A(t)\sin\left(k\omega t + \phi_k^{PSD}\right)dt$$

- Higher signal-to-noise ratio
- Signals only from active species
- Applicable to square wave modulations

T = length of period;
k = demodulation index
ω = stimulation frequency;
ϕ_k^{PSD} = demodulation phase angle.

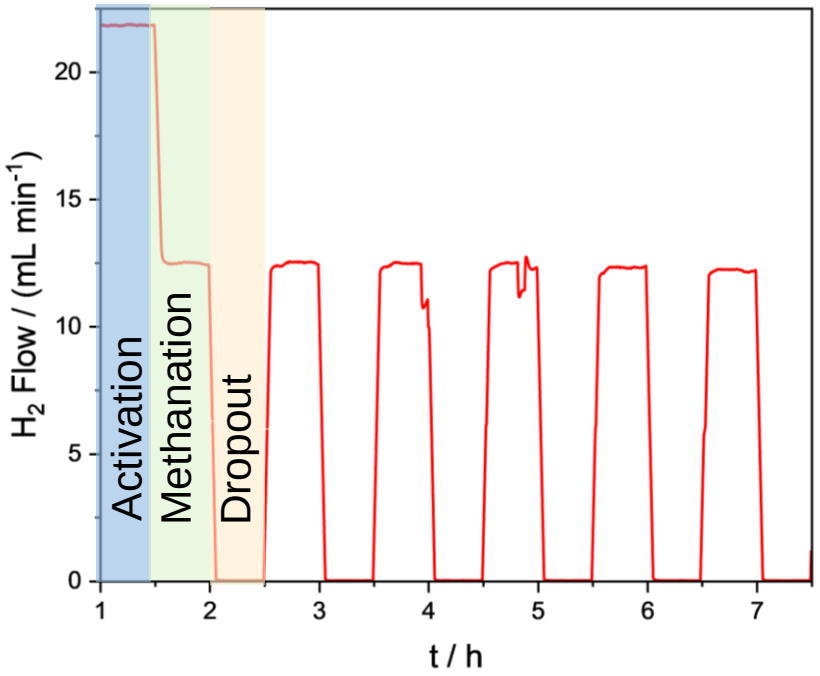
[1] D. Baurecht et al. *Rev. Sci. Instrum.,* 2001, 72, 3782–3792
[2] D. Ferri et al. *Angew. Chem*., 2014, 126, 9036–9040
[3] D. Ferri et al. *Phys. Chem. Phys*., 2013, 15, 8629-8639
[4] A. Urakawa et al. *Chemical Engineering Science*, 2008, 63, 4902-4909

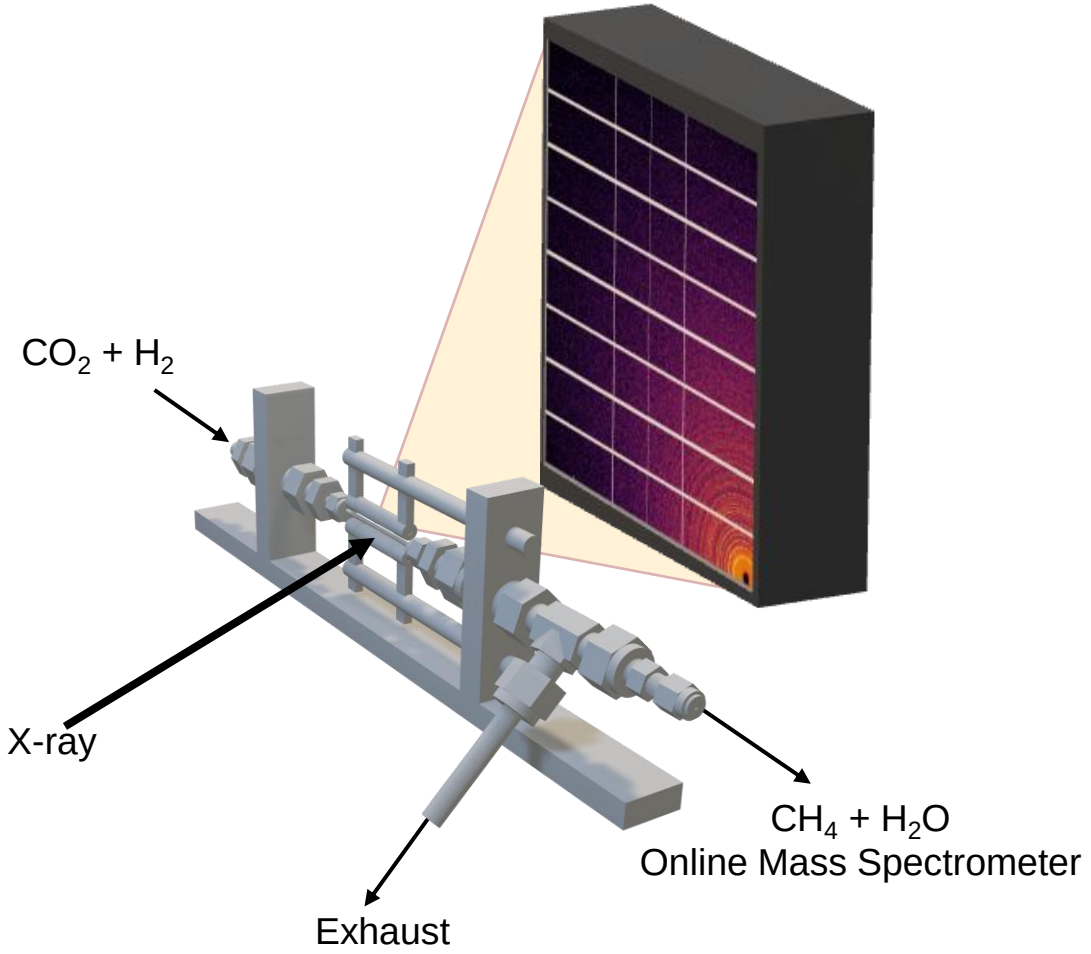
Methanation reaction on Ni@γ-Al_2O_3 model system

***In situ* methanation process of Ni@Al_2O_3 catalyst**

Two different samples:

- 10% Ni on γ–Al_2O_3
- Reference industrial catalyst (Ni on γ–Al_2O_3)





X-Ray energy : 76,69 keV (λ = 0.16167 Å)
Beamline I15-1 Diamond Light Source, UK

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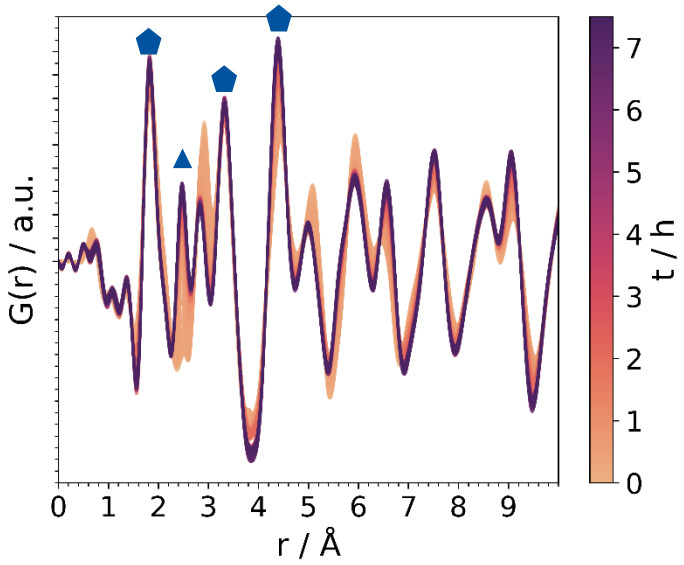
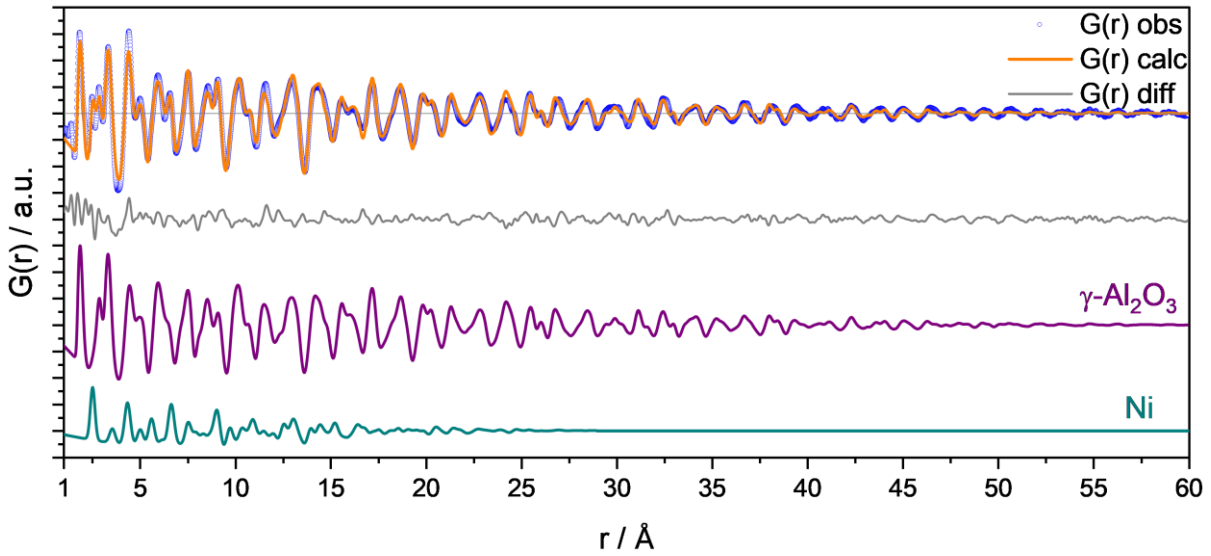
Methanation Reaction on Ni@γ-Al_2O_3 Catalysts

▲ = Ni_{fcc}
⬟ = Al_2O_3





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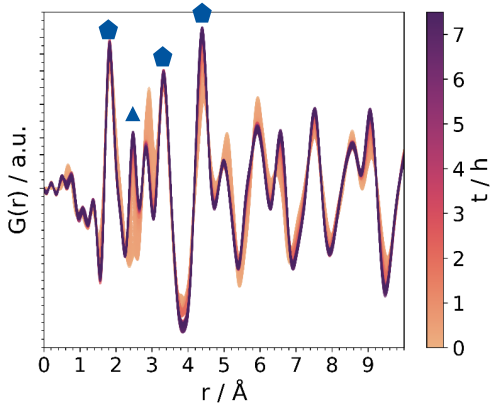

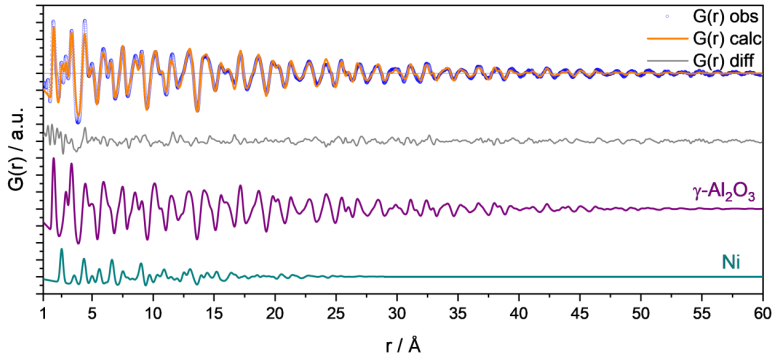

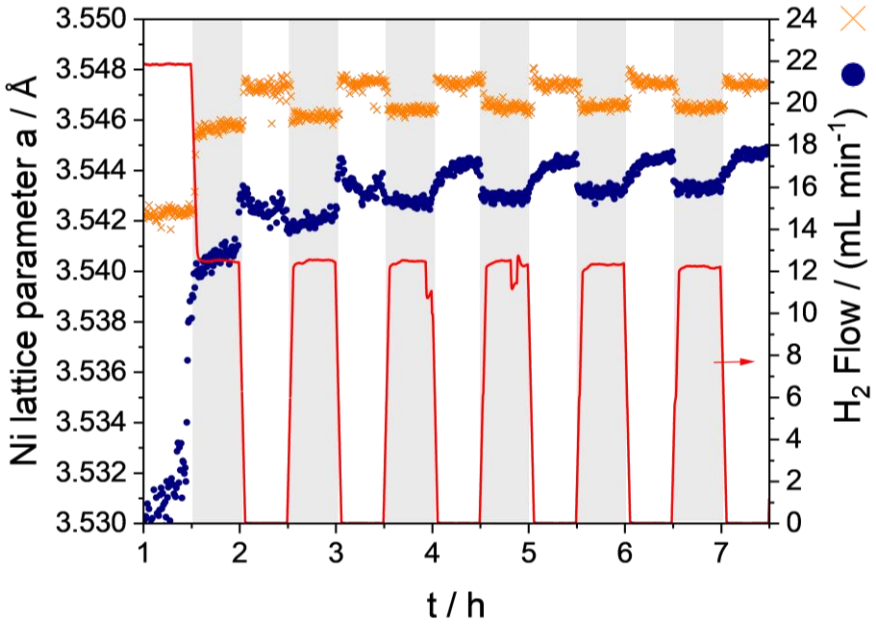

Ref cat
Ni@Al_2O_3

- Breathing behaviour → *a* increase during dropout
- Quick increase in *a* for the Ref. Cat.
- Slower increase for Ni@Al_2O_3

→ Different NP-Support interaction

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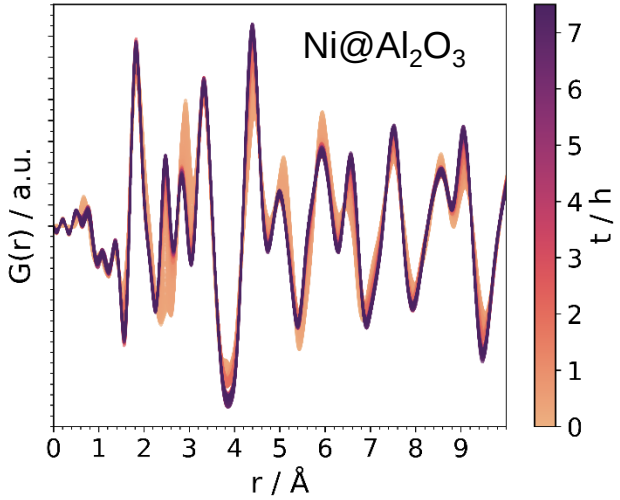
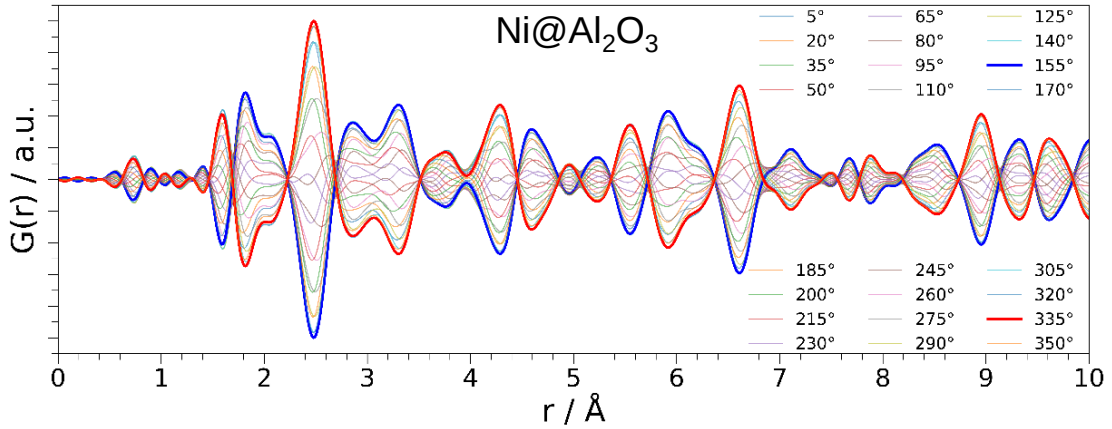
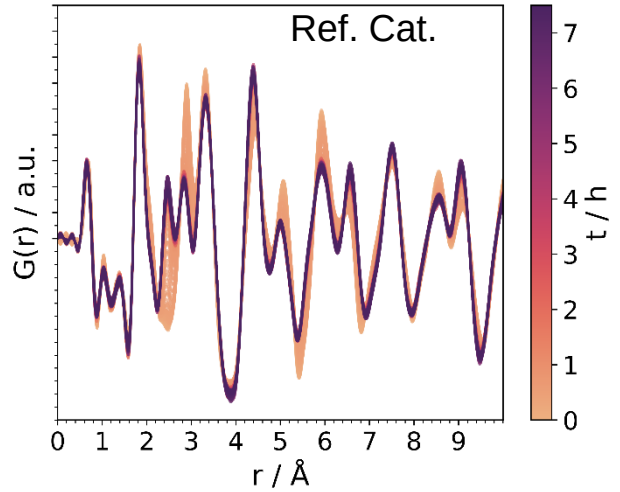
Phase Resolved ME-PDF



PSD





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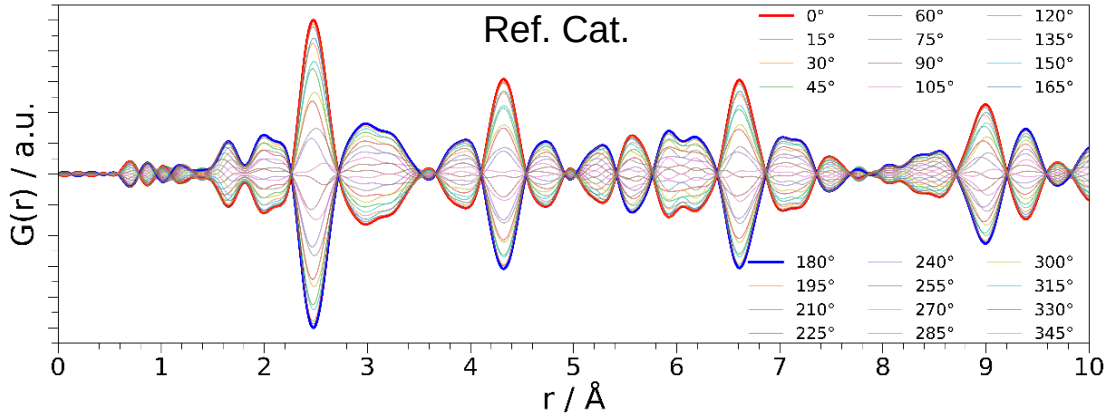

[1] F. Manzoni et Al., “Modulation Excitation Pair Distribution Function Experiments in Catalysis to Increase Phase Sensitivity”, Nanoscale 17 (32), 18766-18776.

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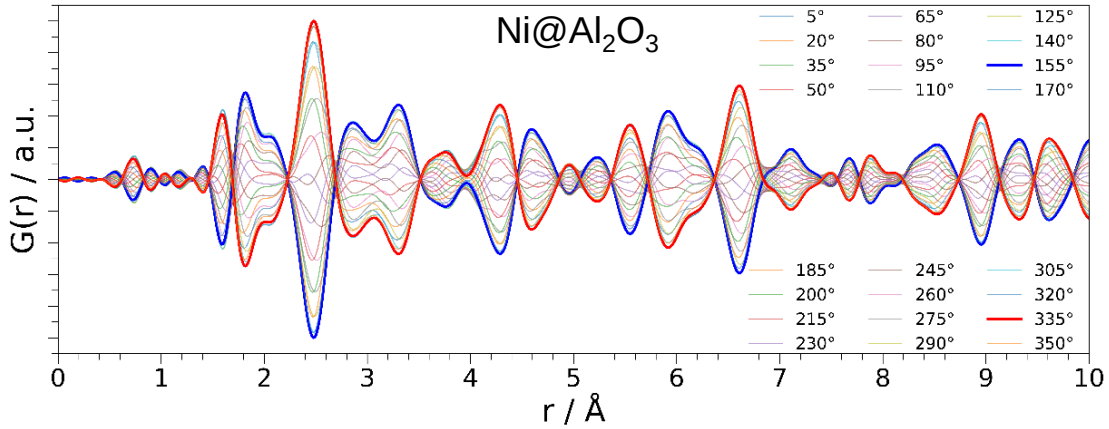

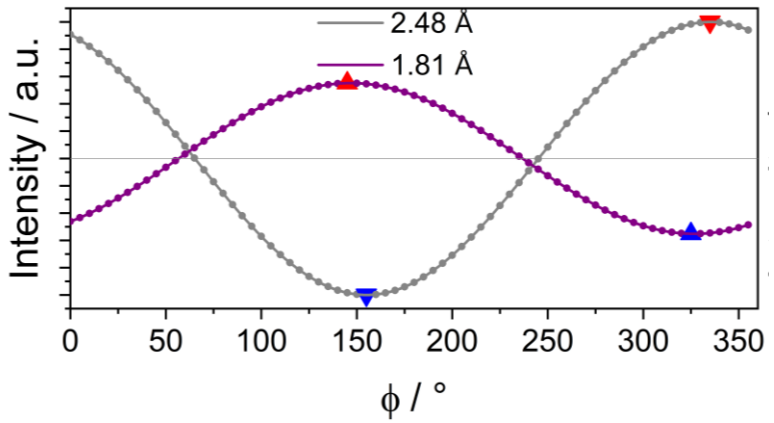

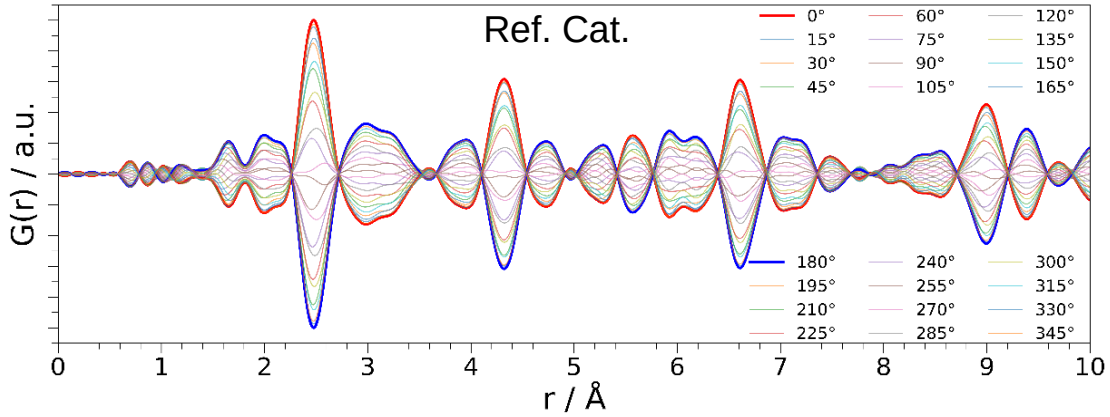

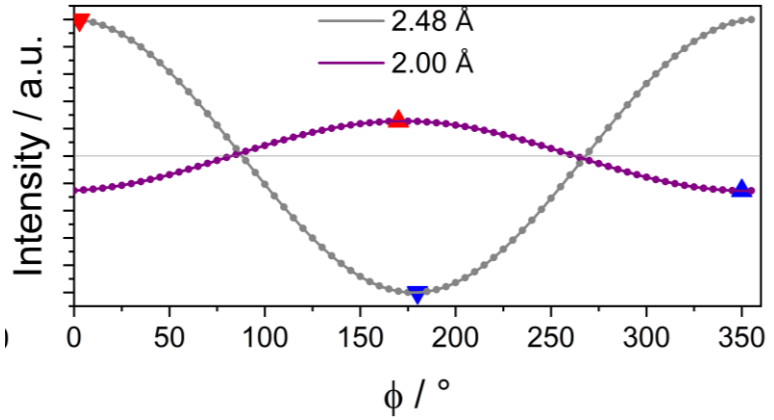

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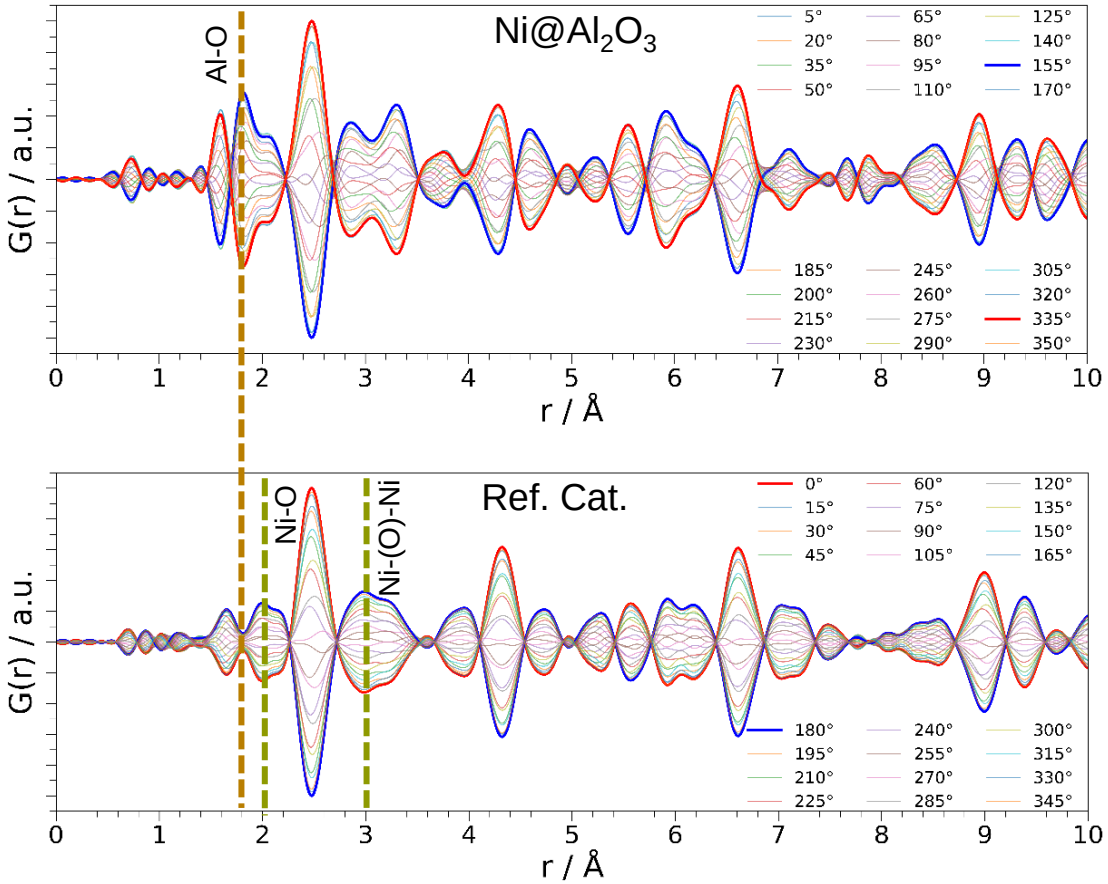


- No oxidation of Ni observed
- γ–Al_2O_3 signals in the PSD transformed data → involvement of the support in the process

$CO_2 + Ni_{surface} \rightarrow CO + NiO_{surface}$ [2]

- NiO formed during H_2 dropout;
- Methanation condition recover the surface by reducing the NiO

[1] F. Manzoni et al. *Nanoscale* 17 (32), 18766-18776.
[2] C. Heine, et al. *J. Am. Chem. Soc.*, 2016, 138, 13246–3252.

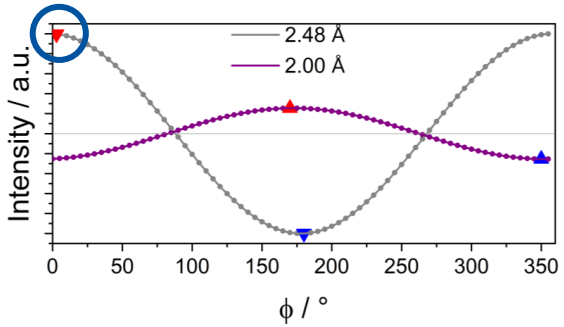
Comparison between ME-PDF and d-PDF

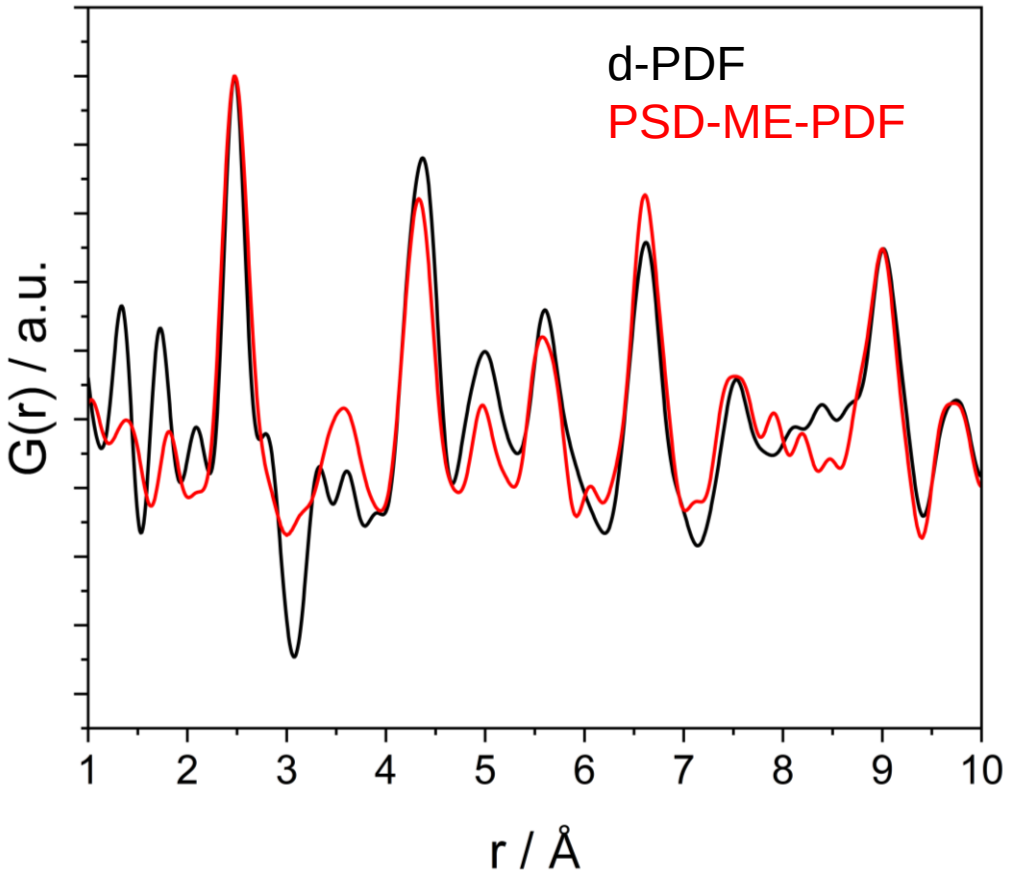
Differential PDF approach (d-PDF):

- Subtraction of the support signal from the total PDF
- More common procedure in catalysis
- Emphasize the active phase signal

Reference catalyst:

- d-PDF for t = 1.5 h (methanation conditions) after subtraction of the bare γ-Al_2O_3 support
- PSD-transformed ME-PDF G(r, ϕ^{PSD} = 0°)





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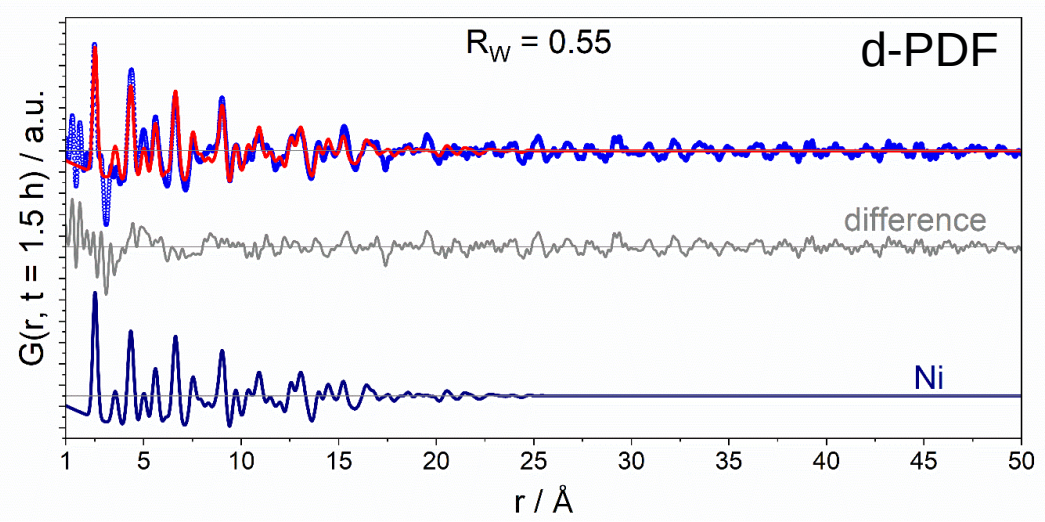

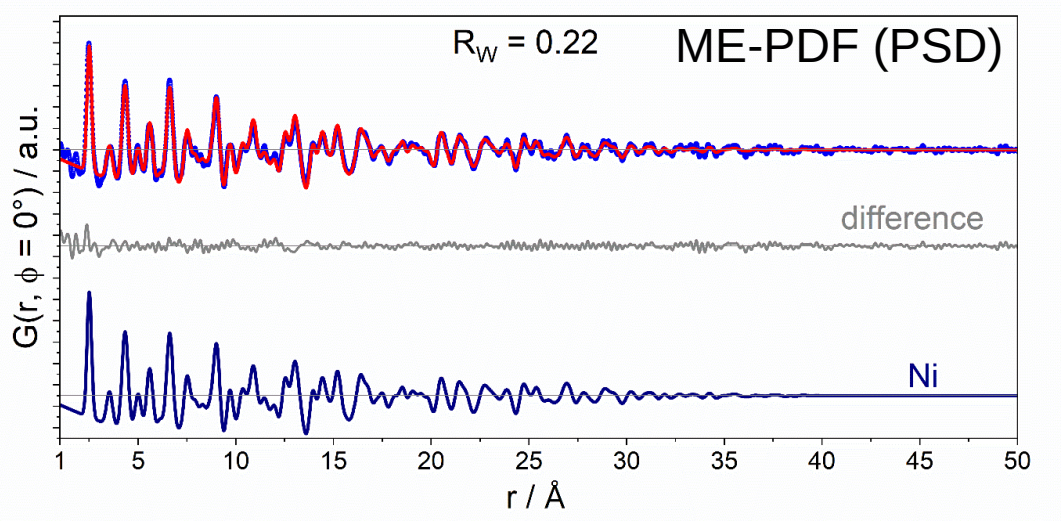

d-PDF:

- Poor fit
- High noise
- Residual of Al_2O_3 contributions
- Underestimation of NP size

ME-PDF (PSD):

- Good fit
- Low noise
- No Al_2O_3 contributions
- Reliable NP diameter

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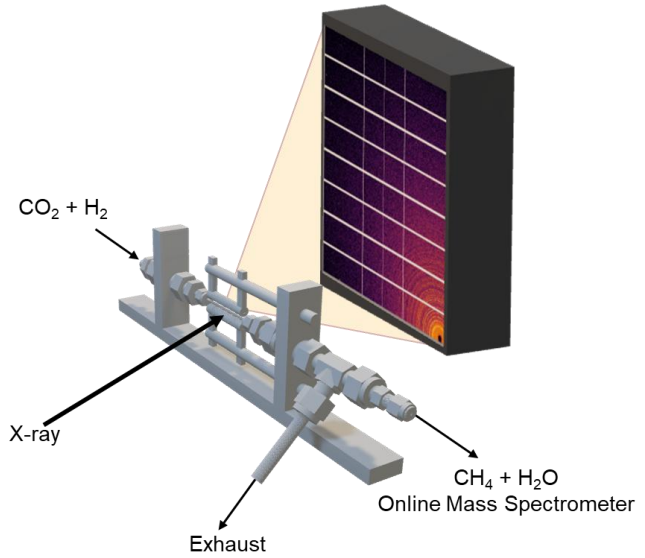
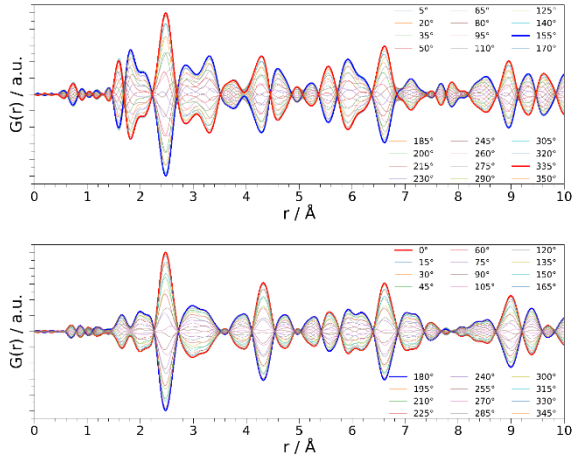
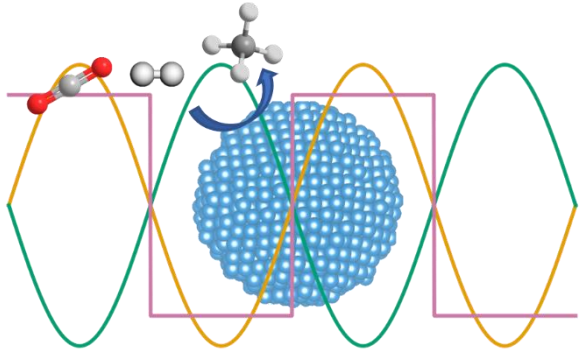
Conclusions

- For the first time PSD method was successfully applied to PDF data
- ME-PDF detects subtle structural changes:
  - Dynamic γ-Al_2O_3 restructuring
  - Ni oxidation in industrial catalyst







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Acknowledgements

Prof. Zobel's group
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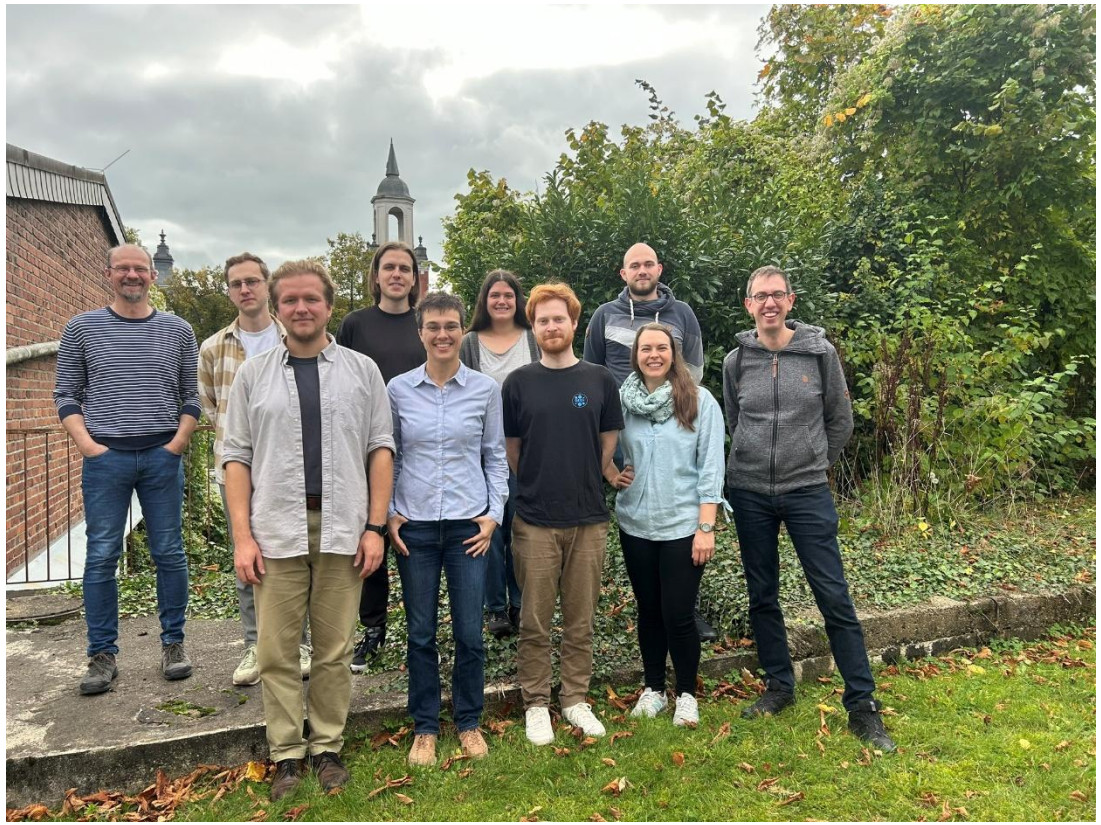

SPP 2080 DynaKat

diamond

ESRF The European Synchrotron

DESY.

Acknowledgements

THANK YOU FOR YOUR KIND ATTENTION!