

Tracking the metal-support interaction of size selected Co_3O_4 nanoparticles as model catalysts for Fischer-Tropsch synthesis by *in-situ* XAS



Catalyst Research for Sustainable Kerosene

GEFÖRDERT VOM



Bundesministerium
für Bildung
und Forschung

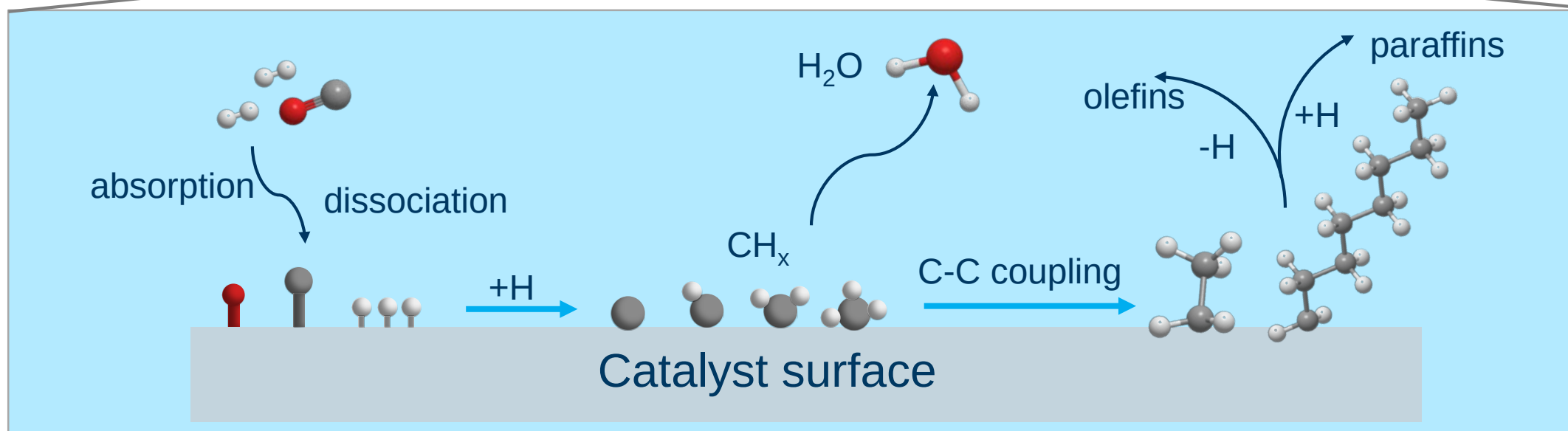
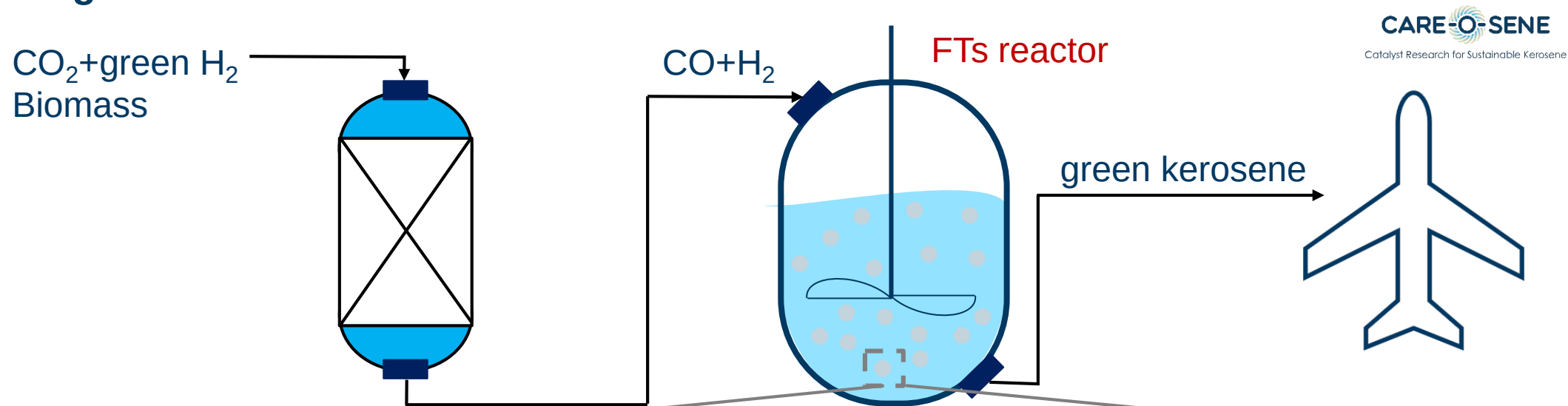
Dan Zhao, Rabia Elbuga-Ilica, Cherie Hsu, Revana Chanerika, Mohamed I. Fadlalla, Michael Claeys, Erisa Saraçi, Felix Studt, Moritz Wolf, Anna Zimina*, Jan-Dierk Grunwaldt*



13TH NATURAL GAS CONVERSION SYMPOSIUM

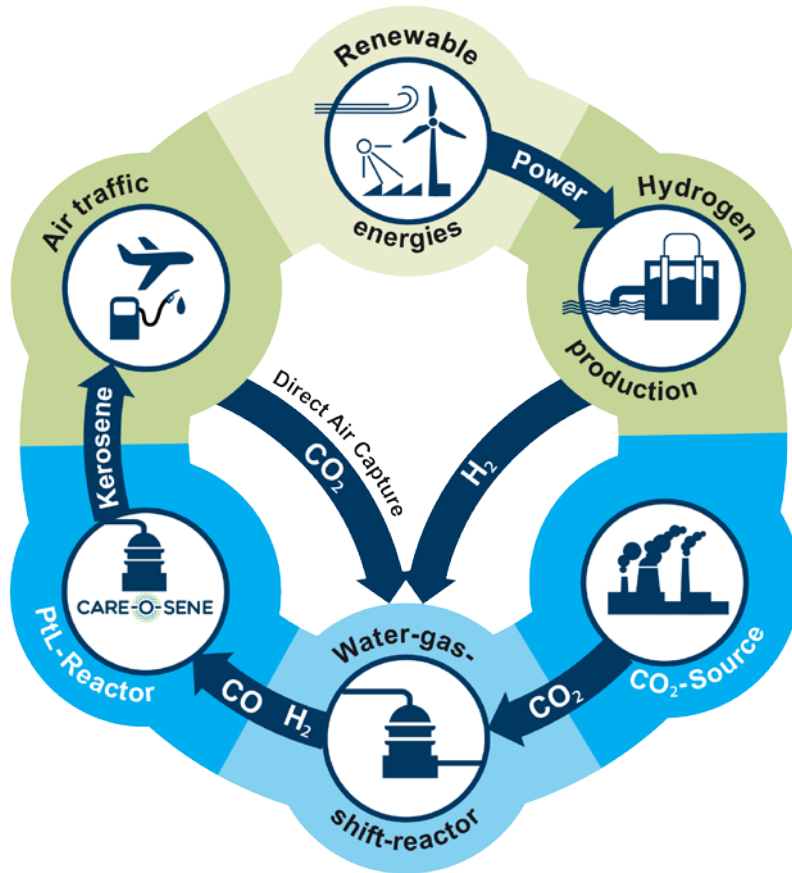
2024 APRIL 21-25

Background



Denzil Moodley et al. *Catalysis for a Sustainable Environment: Reactions, Processes and Applied Technologies*, ISBN:9781119870524, 2024

Background



WP1
CATALYST SYNTHESIS
Lab scale synthesis and testing

WP4
IMPACT ANALYSIS
Assessment of the benefits of the FT catalyst



WP2
CHARACTERISATION AND MODELLING
Advanced Structural characterisation and modelling

WP3
SCALE-UP AND DEMONSTRATION
FT catalyst production at larger scale and testing

WP2:



The life cycle of a catalyst

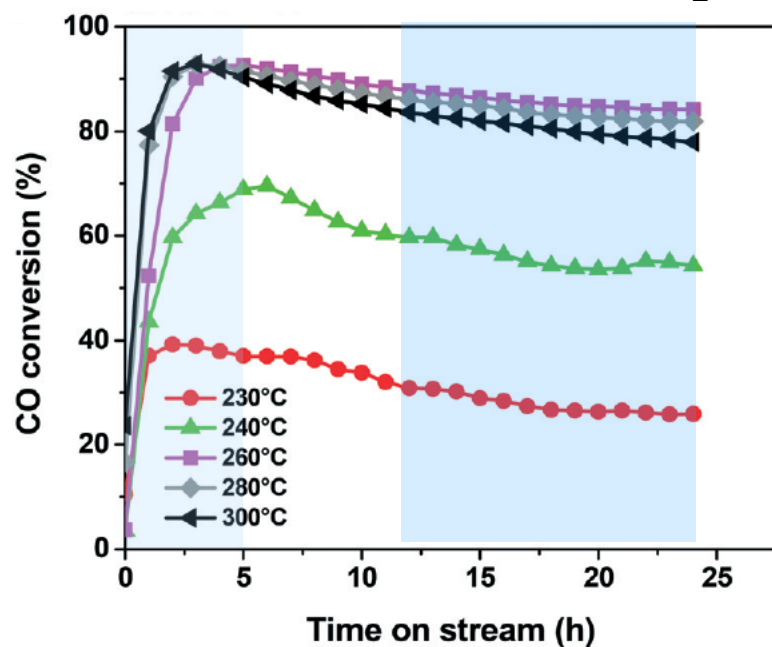
Pretreatment

Reaction

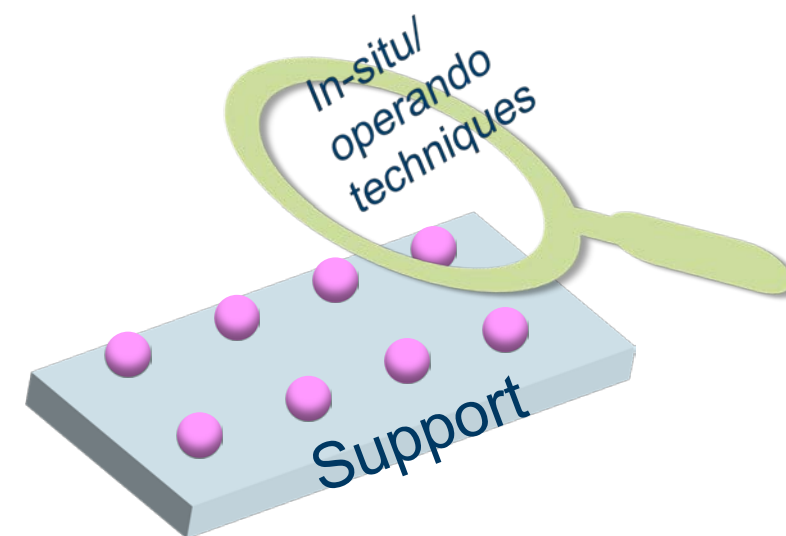
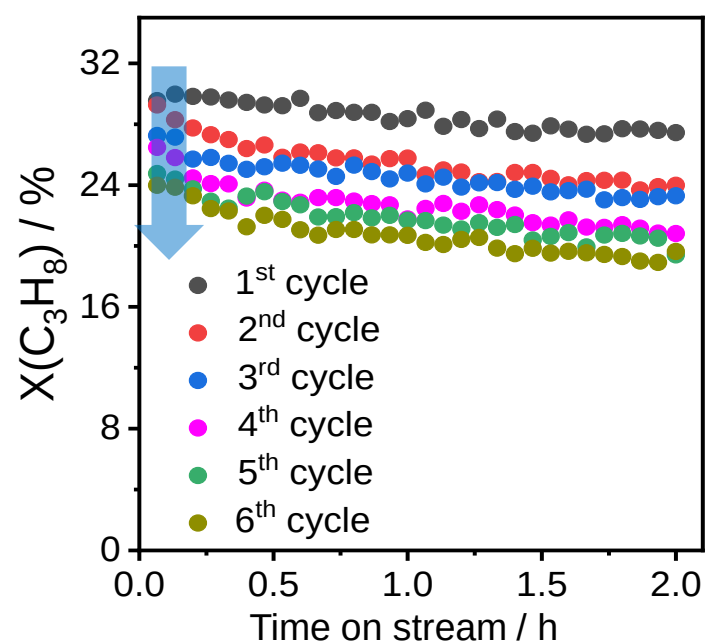
Deactivation

Regeneration

FTs over 20Co5Mn/SiO₂



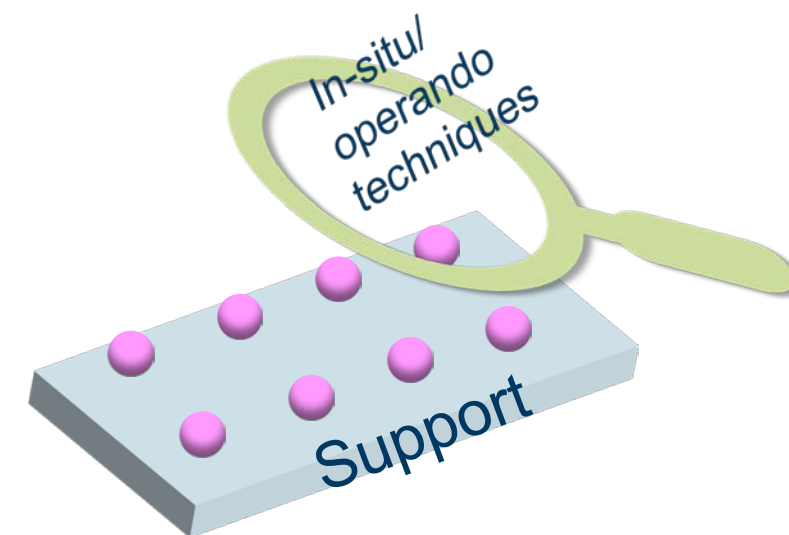
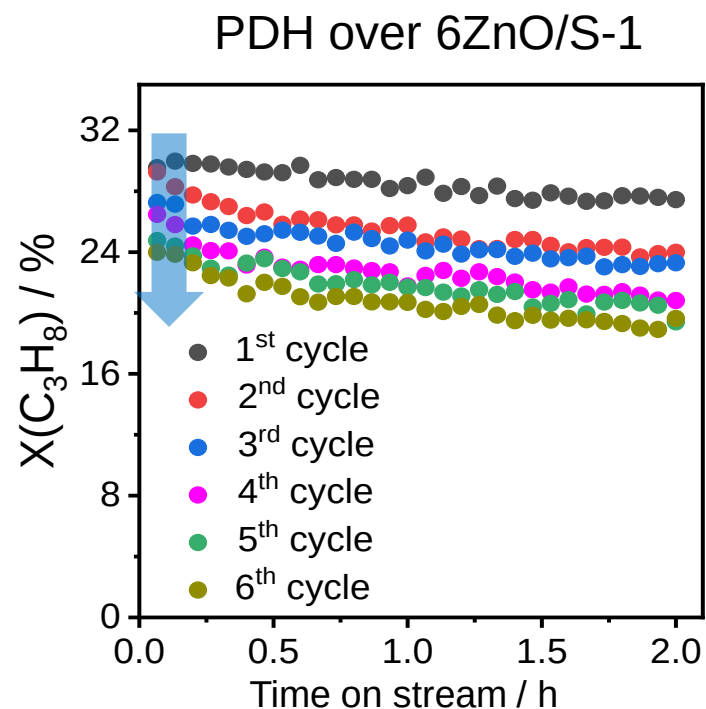
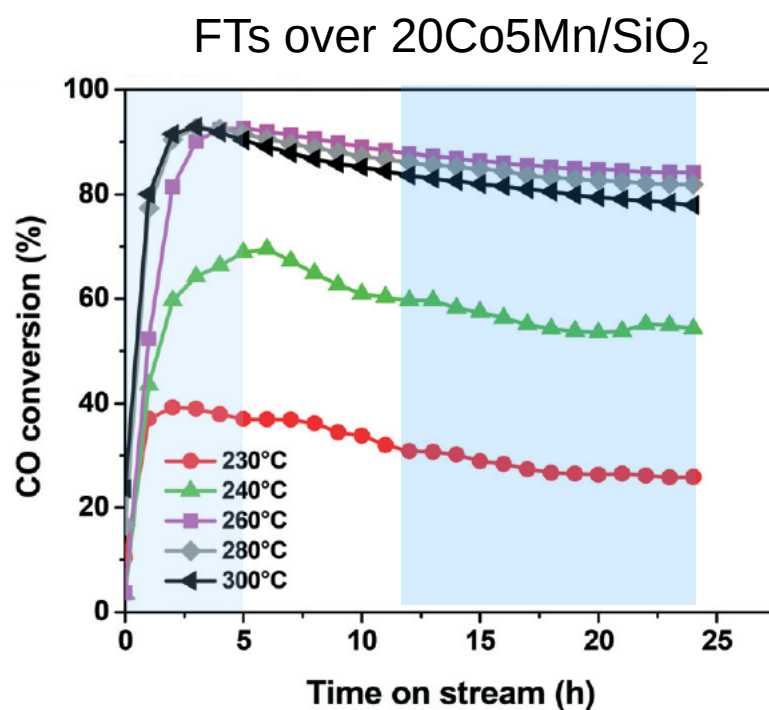
PDH over 6ZnO/S-1



X. Liu et al., *Catal. Sci. Technol.*, 2019, 9, 3238–3258

D. Zhao et al., *ACS Catal.* 2022, 12, 4608–4617

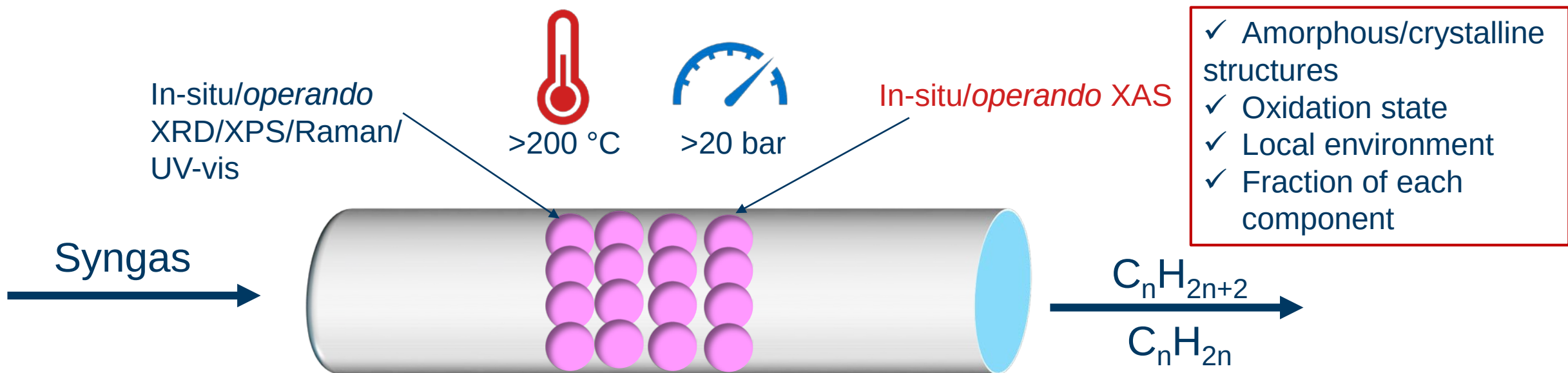
The life cycle of a catalyst



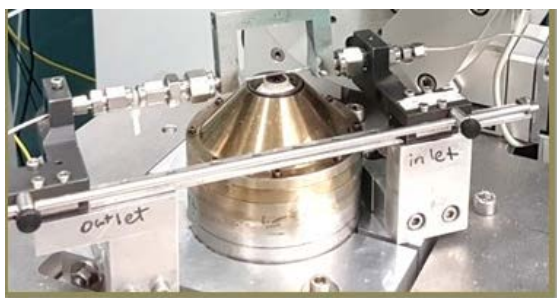
X. Liu et al., *Catal. Sci. Technol.*, 2019, 9, 3238–3258

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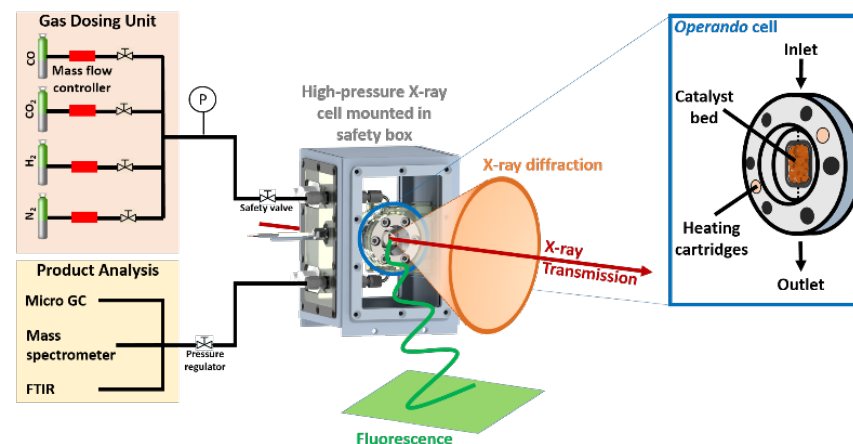
Why in-situ/operando X-ray absorption spectroscopy for FTs?



In-situ cells



- Up to
- ☐ 20 bar
 - ☐ 900 °C
 - ☐ ~10 mg of catalyst

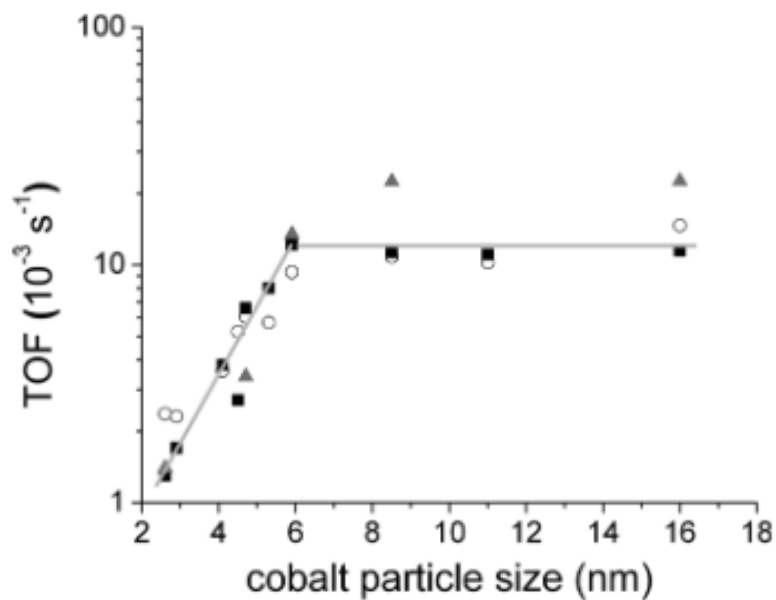


- Up to
- ☐ 80 bar
 - ☐ 450 °C
 - ☐ ~150 mg of catalyst

J-D. Grunwaldt et al. Rev. Sci. Instrum. 2017, 88, 113113

J-D. Grunwaldt et al. Chemistry-Methods, 2022,2, e202100078

Model catalysts/structures



K. P. de Jong et al., J. Am. Chem. Soc. 2009, 131, 20, 7197–7203

Model catalysts/structures

Pure Co_3O_4 NPs:

Co_3O_4 _3 nm

Co_3O_4 _5 nm

Co_3O_4 _7nm

Co_3O_4 _10nm



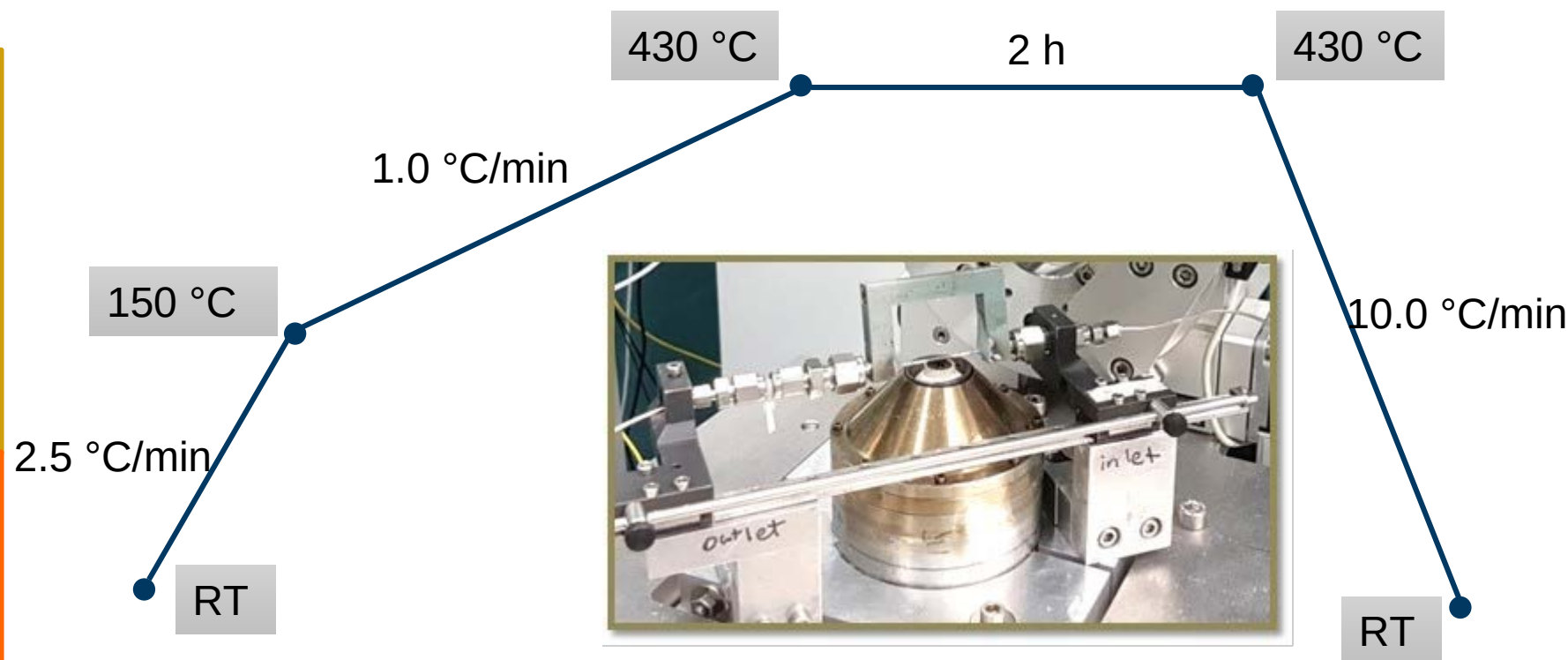
Supported Co_3O_4 NPs:

Co_3O_4 _3 nm/Al-based material

Co_3O_4 _5 nm/Al-based material

Co_3O_4 _7 nm/Al-based material

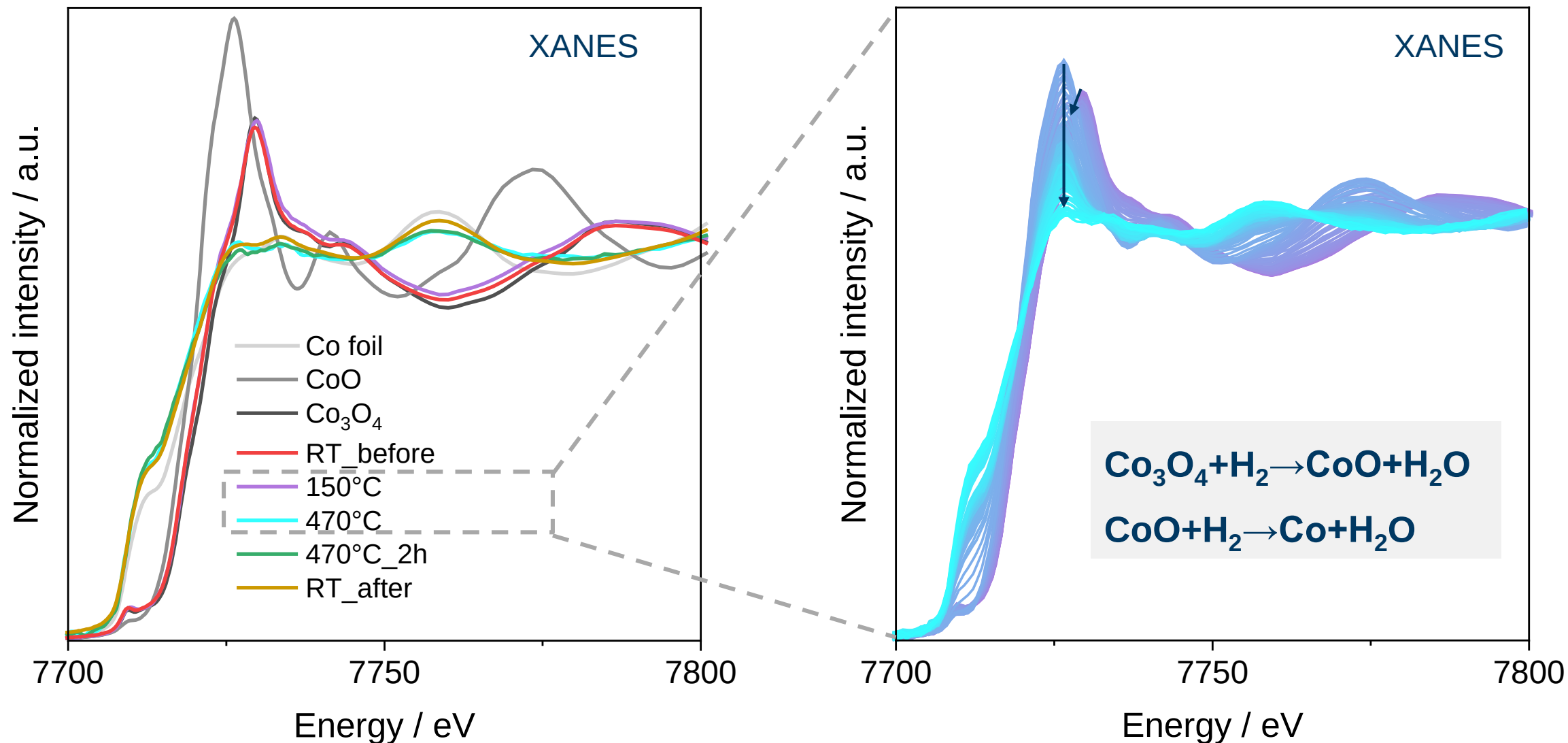
Co_3O_4 _10 nm/Al-based material



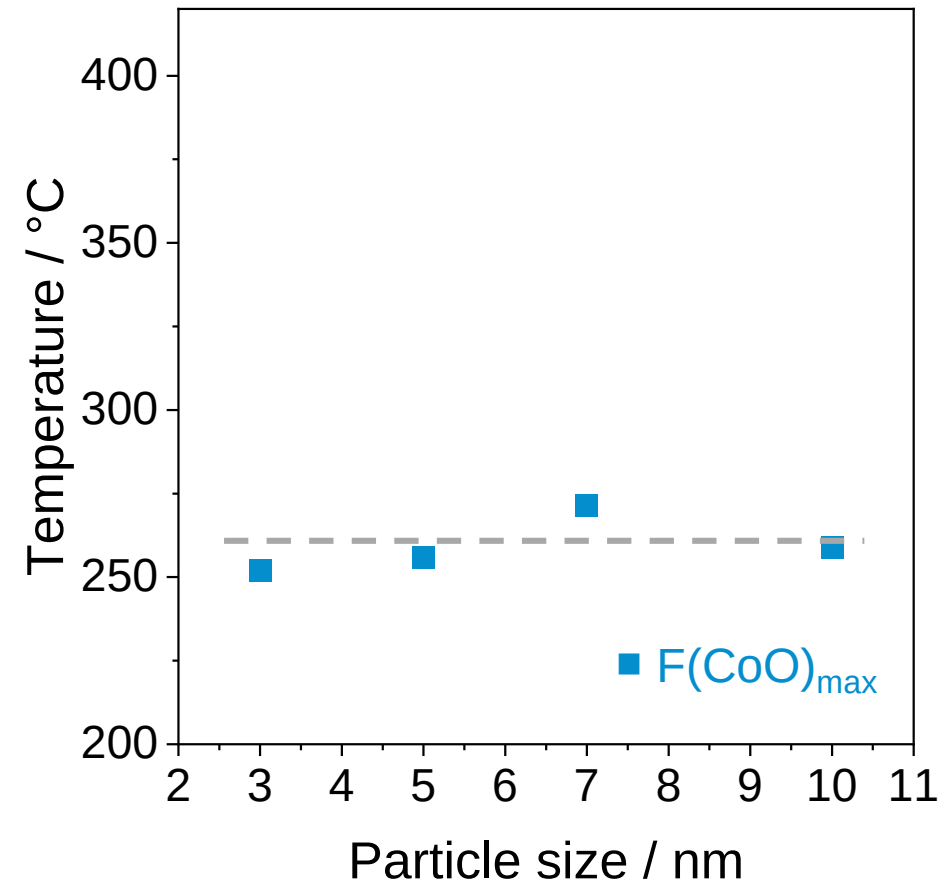
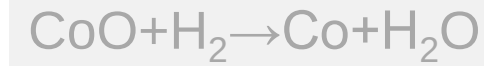
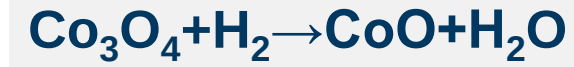
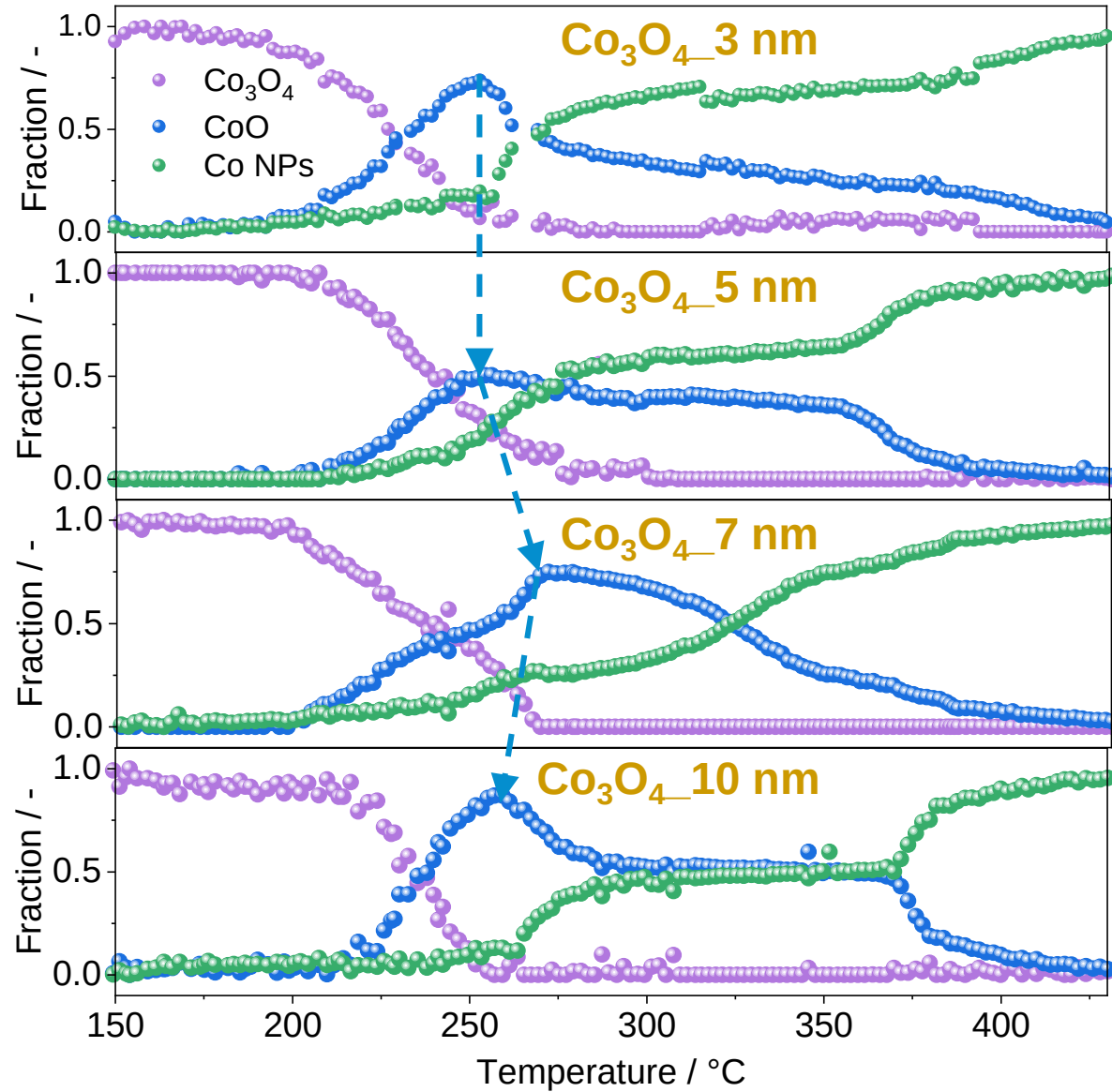
J-D. Grunwaldt et al. Rev. Sci. Instrum. 2017, 88, 113113

Results

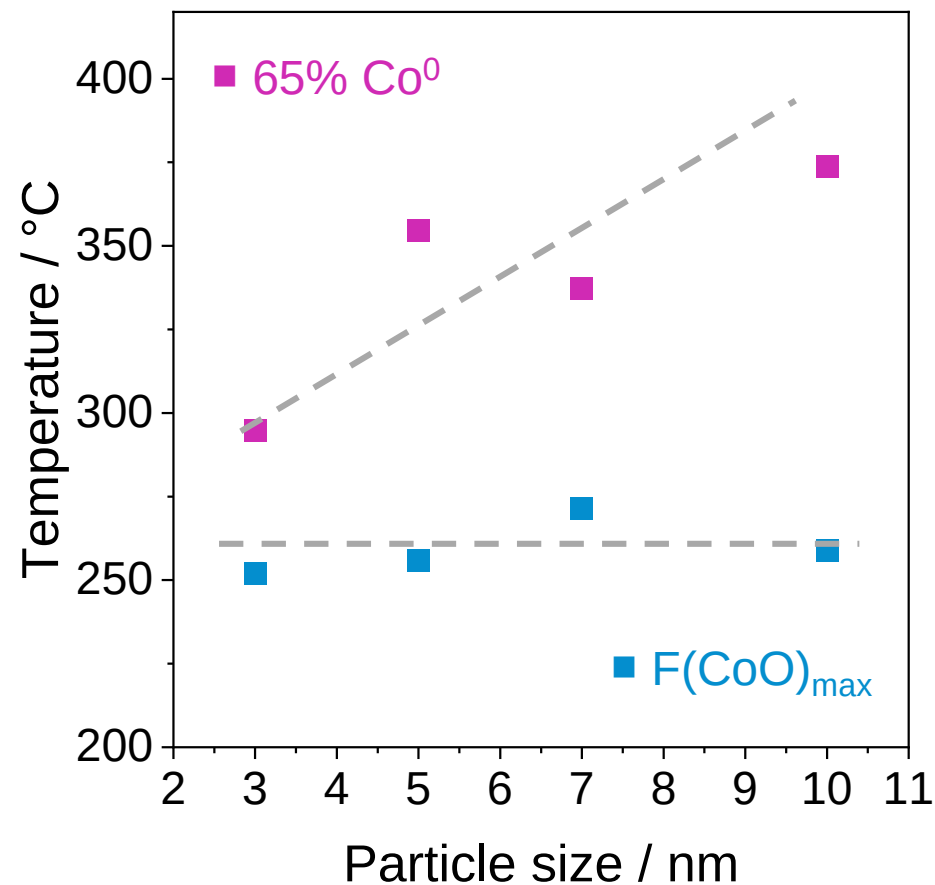
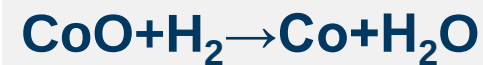
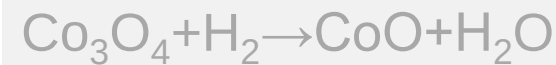
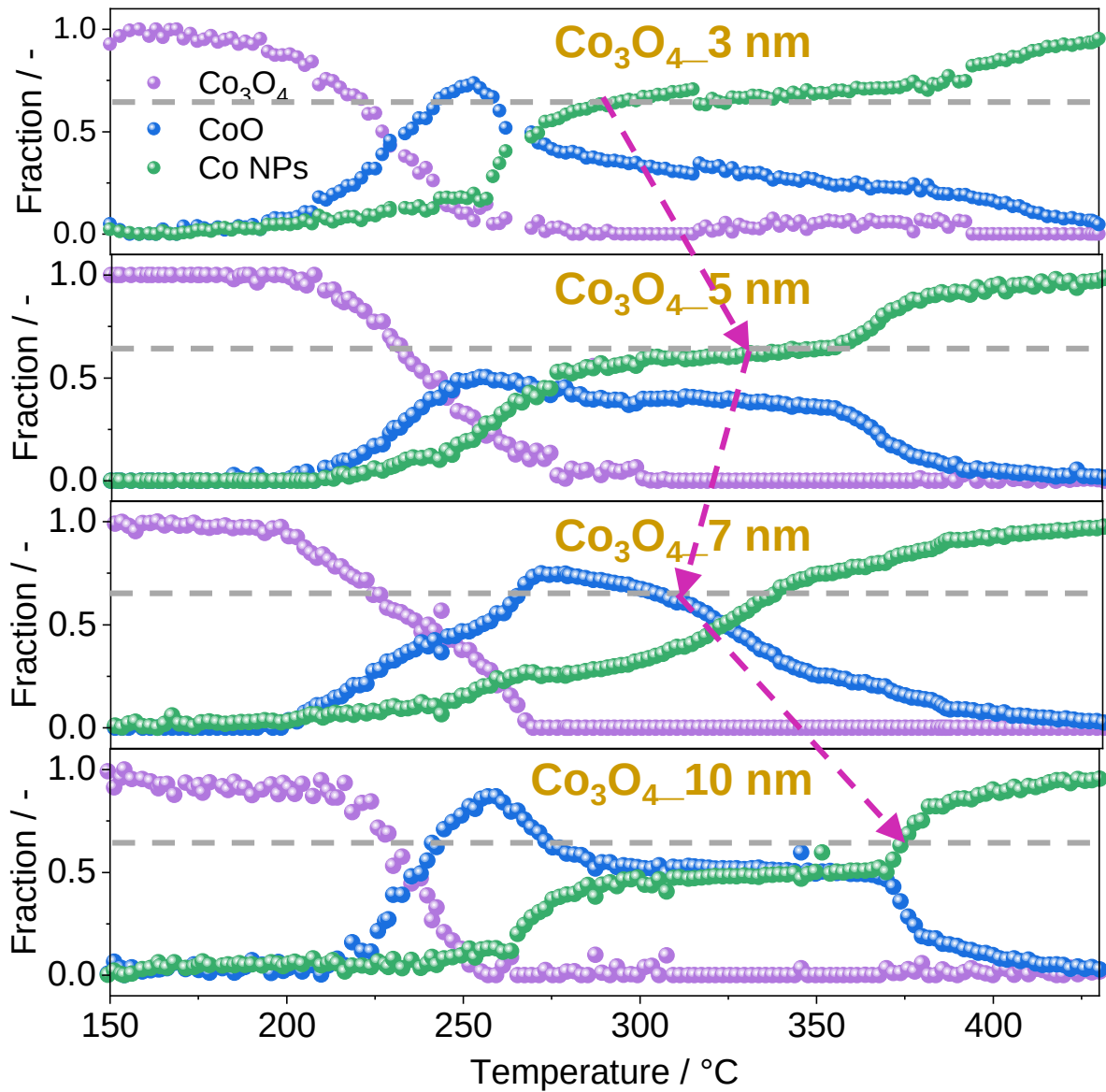
Co₃O₄_3 nm



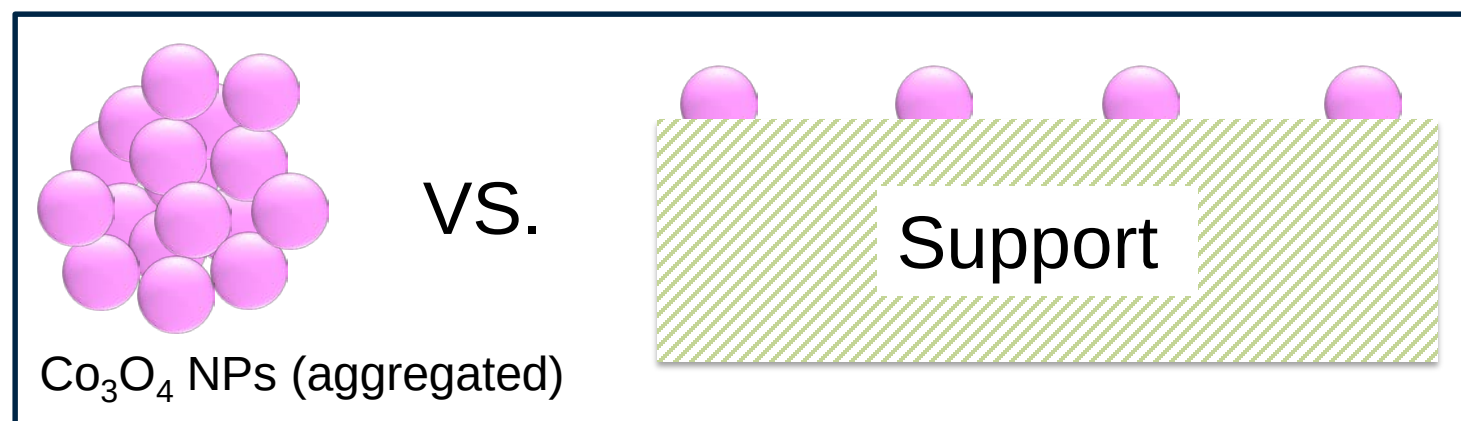
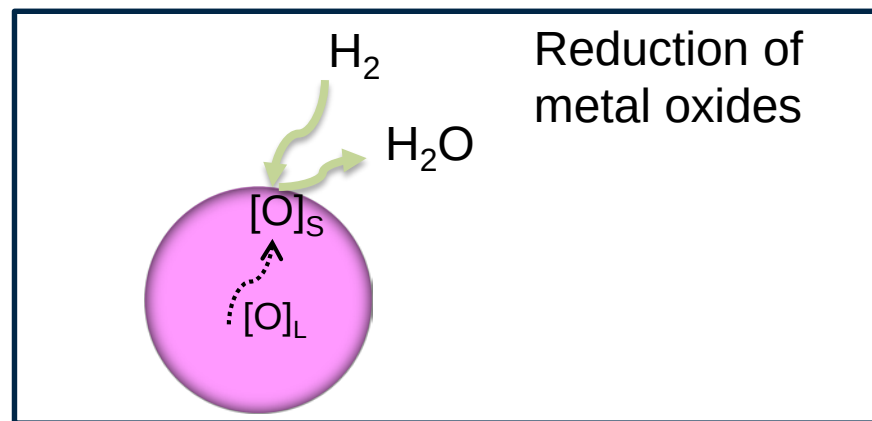
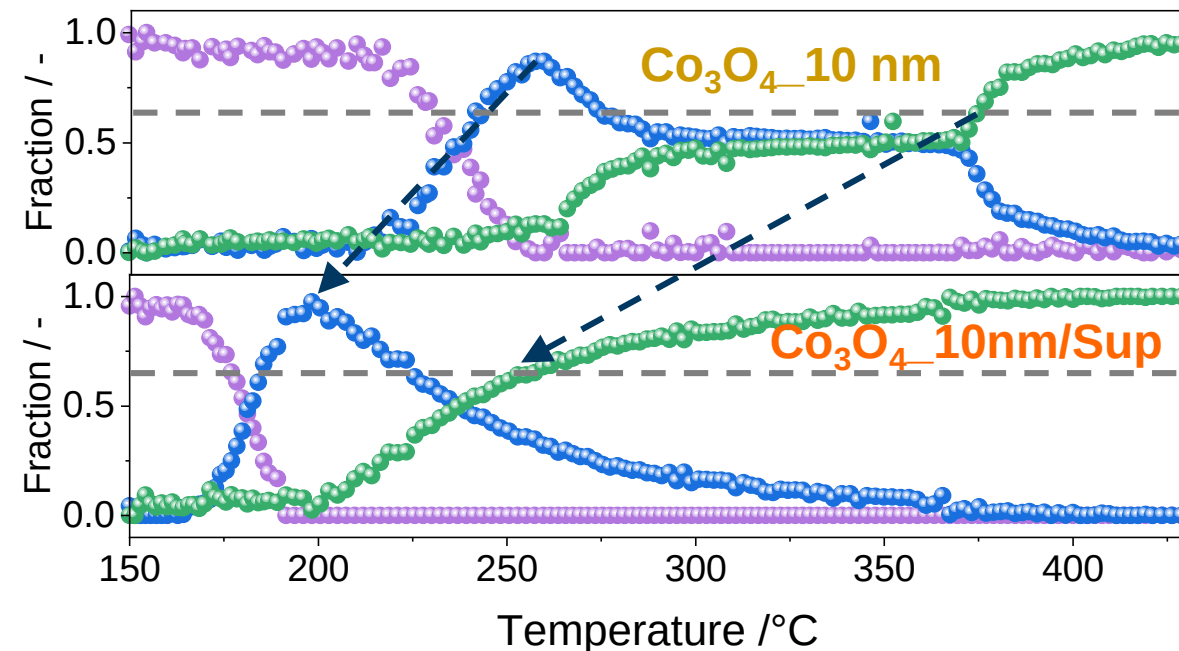
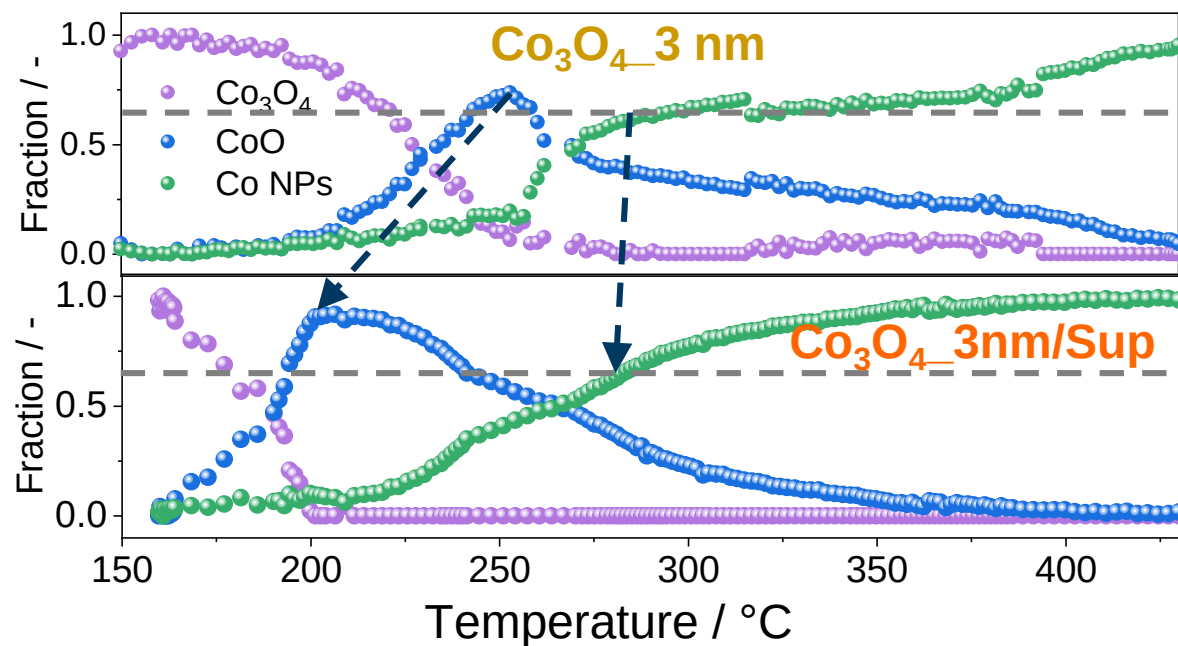
Results



Results



Results



Summary and outlook

Regardless of the particle sizes and the presence of support, two steps reduction were in general involved:
 $\text{Co}_3\text{O}_4 \rightarrow \text{CoO}$ and $\text{CoO} \rightarrow \text{Co}^0$.

The particle size of Co_3O_4 does not have a strong effect on the reduction temperature of Co_3O_4 to CoO , but on the second reduction step. The smaller the initial particle size of Co_3O_4 NPs is, the lower the temperature to obtain 65% Co^0 in the sample is.

When the support was introduced, for the Co_3O_4 3 nm, the first reduction step was enhanced significantly, while the second step was not. For the Co_3O_4 10 nm, both steps were facilitated strongly. That can be explained by the increased dispersion of Co_3O_4 .

Our results provide fundamentals for optimizing the reduction conditions of Co-based catalysts.

Acknowledgment

Grunwaldt's Group
Claeys' Group

Cat-Act beamline
IBPT/KIT light source

Funded by



Catalyst Research for Sustainable Kerosene

A large, vibrant sunset sky with streaks of orange, pink, and purple. In the foreground, there is a large, dark silhouette of a tree and a multi-story building with several lit windows. The overall scene is a peaceful urban landscape at dusk.

Thank you for your attention!



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