Novel approach of advanced characterization, dedicated synthesis and theoretical modelling on commercially relevant Fischer-Tropsch catalysts for production of sustainable fuels & chemicals: Bridging industry and academia

CARE-O-SENE
Catalyst Research for Sustainable Kerosene

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Bundesministerium für Bildung und Forschung

Anna Zimina
Rabia Elbuga-Ilica
Dan Zhao
Cherie Hsu
Enrico Sireci
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Power to Liquids process:
production of sustainable aviation fuels (SAF)

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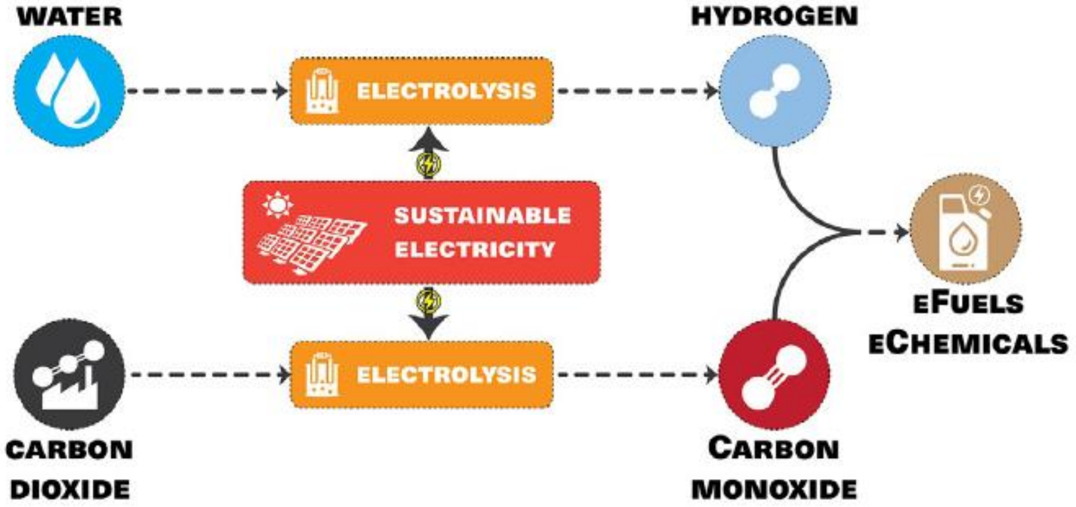
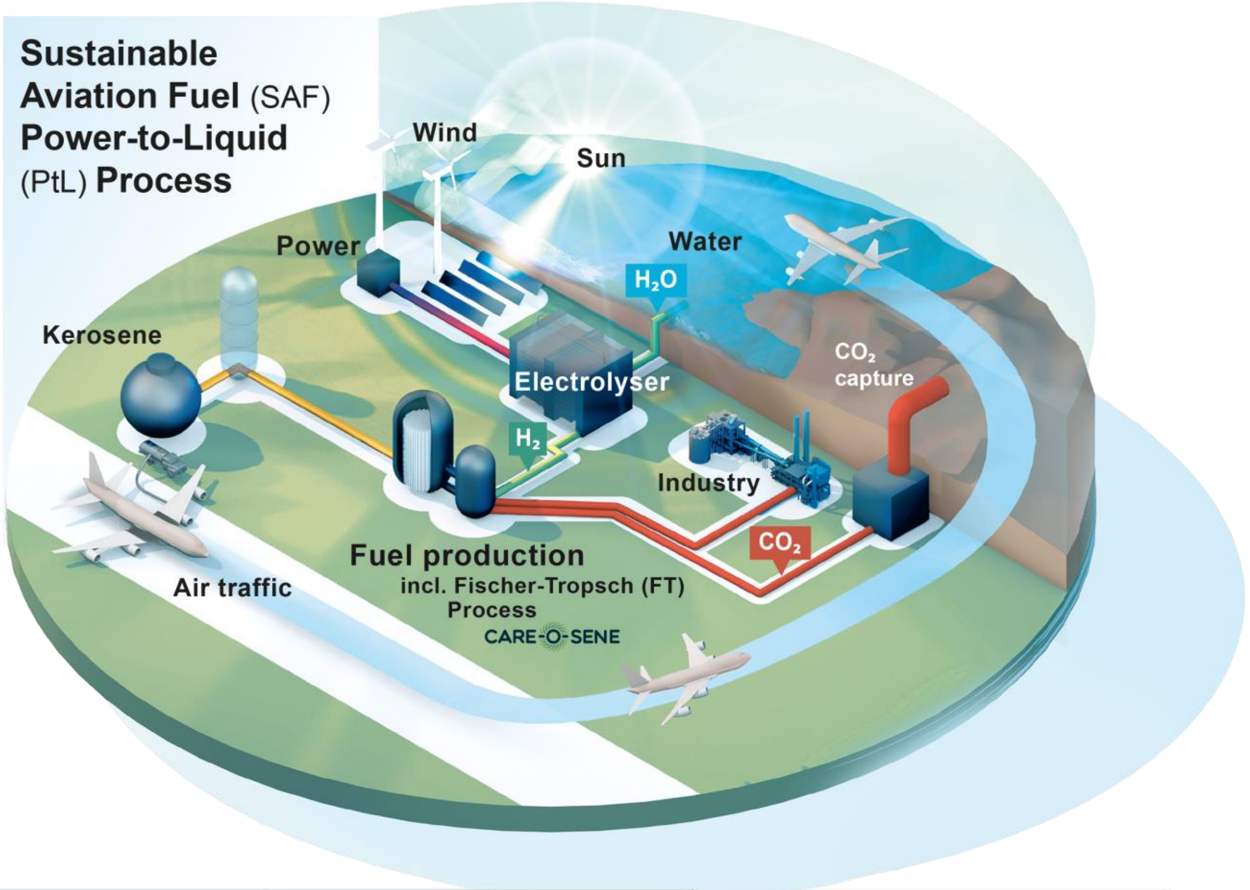


Paul B. Webb, Ivo A.W. Filot, Promoted Fischer-Tropsch catalysts in Comprehensive Inorganic Chemistry III (Third Edition), Editor(s): Jan Reedijk, Kenneth R. Poeppelmeier, Elsevier, 2023



Power from renewable sources → Production of green hydrogen → Carbon dioxide e.g. from industrial processes or direct air capture → CARE-O-SENE Fischer-Tropsch-Synthesis → synthetic sustainable aviation fuels (SAF)

CARE-O-SENE: Work Packages & Partner Involvement

WP1

CATALYST SYNTHESIS

Lab scale synthesis and testing

WP2

CHARACTERISATION AND MODELLING

Advanced Structural characterisation and modelling

WP4

IMPACT ANALYSIS

Assessment of the benefits of the FT catalyst

WP3

SCALE-UP AND DEMONSTRATION

FT catalyst production at larger scale and testing

Why do we need *in-situ* studies?

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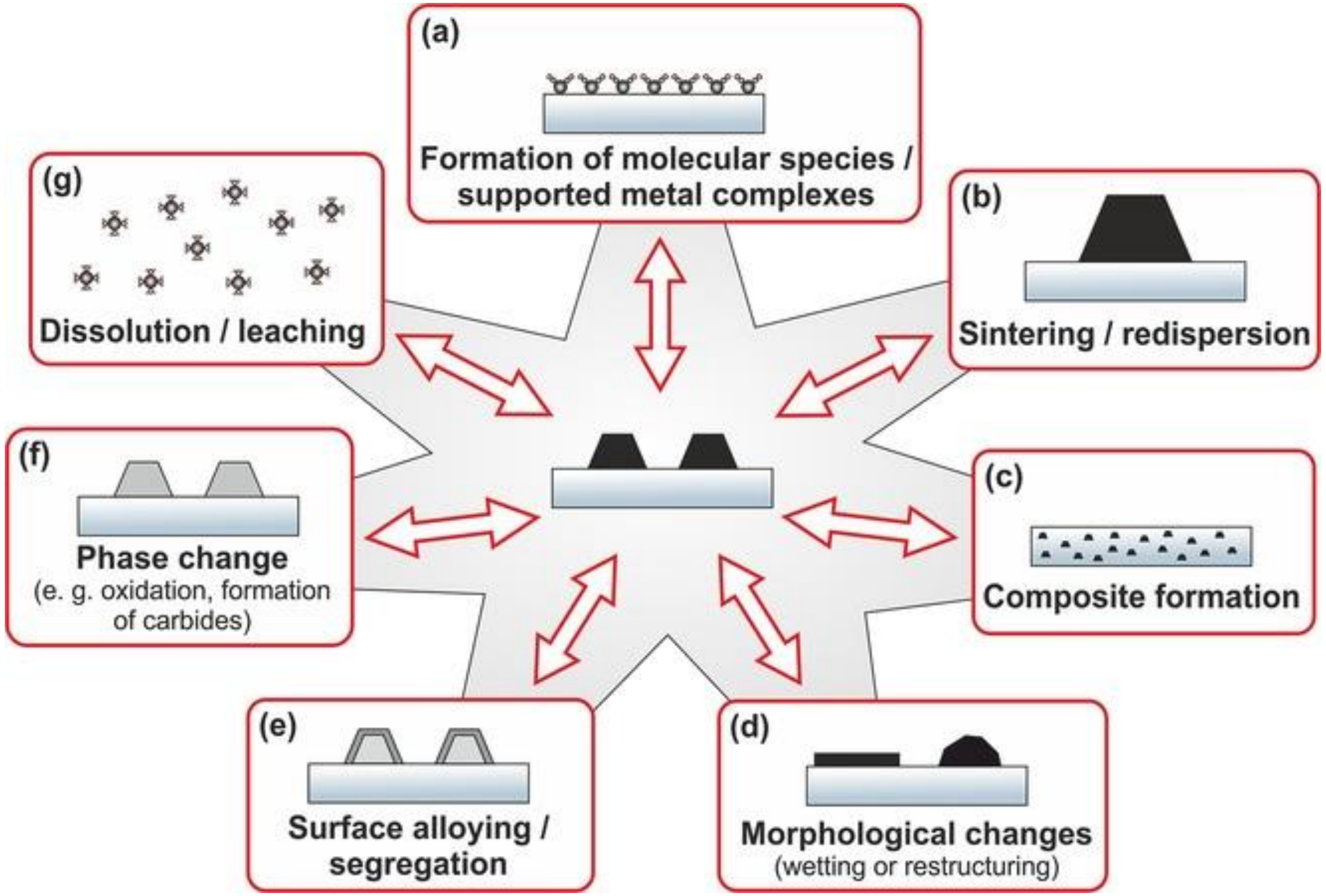
- Oxidation and reduction
- Identification of the promoter structure
- Carbide formation
- Morphological changes

- Electronic structure of active species
- Electronic structure of promoter
- Influence of support

- Understanding dynamic changes
  - deactivation



K.F. Kalz, R. Kraehnert, M. Dvoyashkin, R. Dittmeyer, R. Gläser, U. Krewer, K. Reuter, J.-D. Grunwaldt, *ChemCatChem* **2017**, *9*, 17.

Or in other words: Spectroscopy while the process is running…

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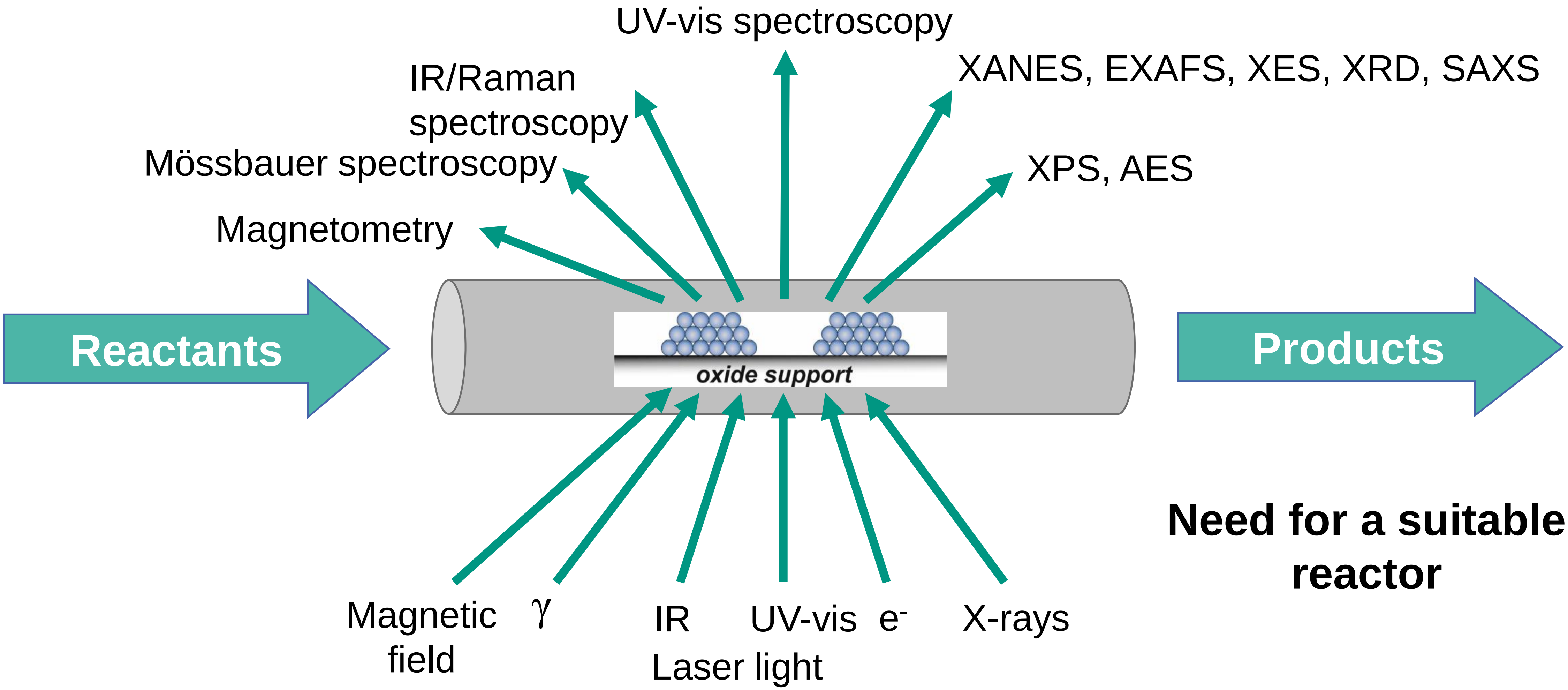
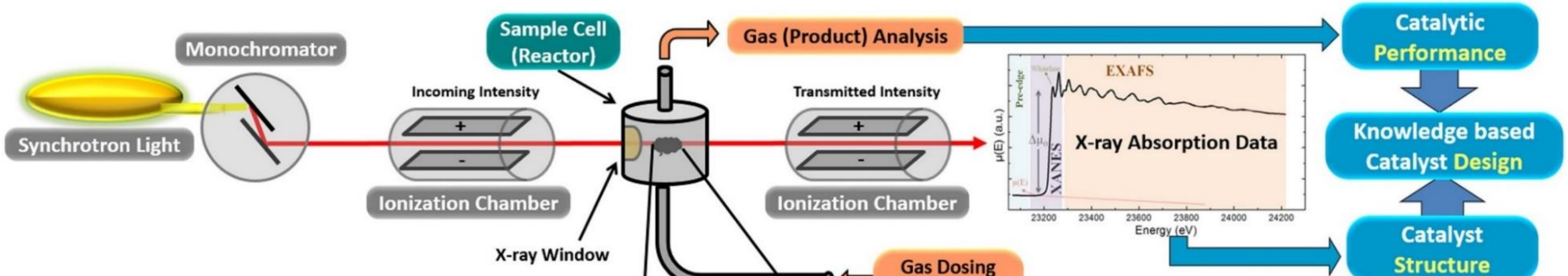


Need for a suitable reactor

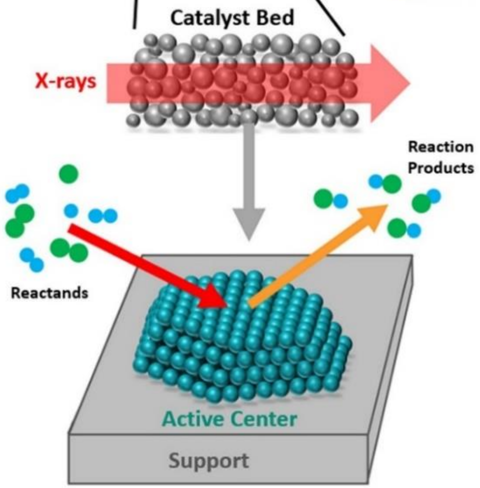
Operando X-ray Absorption Spectroscopy at CATACT

Shining a light through catalysts in closed reactors



CAT ACT beamline optics

- Superconductive wiggler: 10^{13} photons/s, 4 - 60 keV
- 2 monochromators
- slit system, monochromator stabilization system → high data quality



XAS set-up

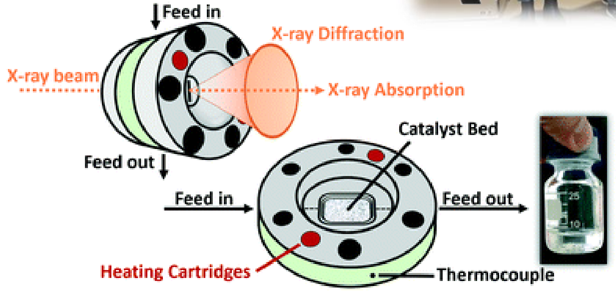
- Equipped for *in-situ and operando* studies (incl. high pressure, high temperature, liquid and gas phases)

In-situ infrastructure

- Several *in-situ* sample cells implemented
- Reactive gas supply installed
- Gas dosing units and devices for on-line gas analysis (mass spectrometry, gas chromatography)

Complementary methods

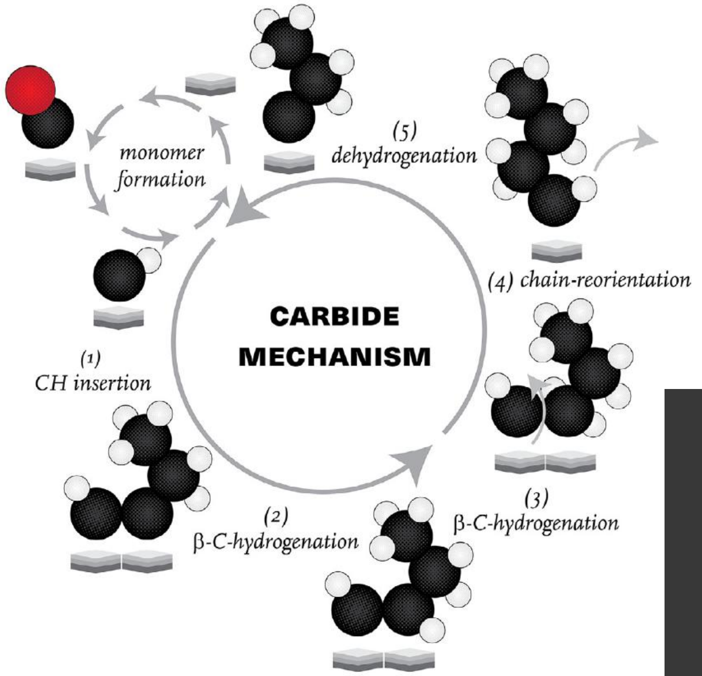
- Combined XAS-XRD, XAS-IR



A. Zimina et al., *J. Phys.: Conf. Ser.* ***712***, 012019 (2016)
A. Zimina et al., *Rev. Sci. Instrum*. ***88***, 113113 (2017)

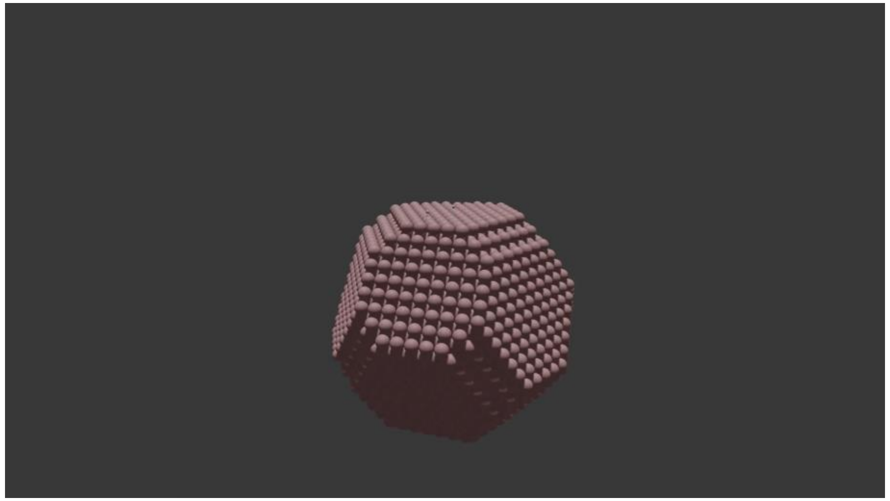
M. Loewert et al. React. Chem. Eng. **5**, 1071 (2020)
L. Pandit et al. Chem. Methods (2022).

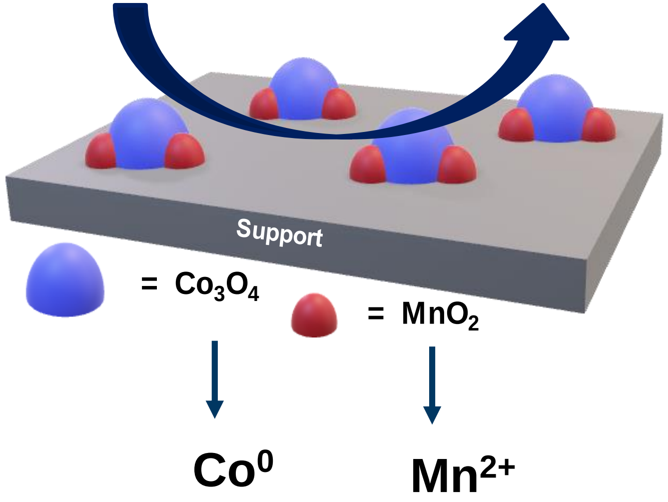
Fischer-Tropsch reaction over Mn promoted Co-based catalysts



CO and H_2 dissociation and CH_4 formation

Long chain formation





Paul B. Webb, Ivo A.W. Filot, Promoted Fischer-Tropsch catalysts in Comprehensive Inorganic Chemistry III (Third Edition), Editor(s): Jan Reedijk, Kenneth R. Poeppelmeier, Elsevier, 2023

V. Vermaak, J.H. Potgieter, E. van Steen, D.J. Moodley, M. Claeys, J.L. Visagie, R. Crous, J.M. Botha „Lift-off to sustainable aviation fuels: Optimization of Fischer-Tropsch performance with manganese promotion" CATSA 2022,13-16th November 2022, Drakensburg, South Africa

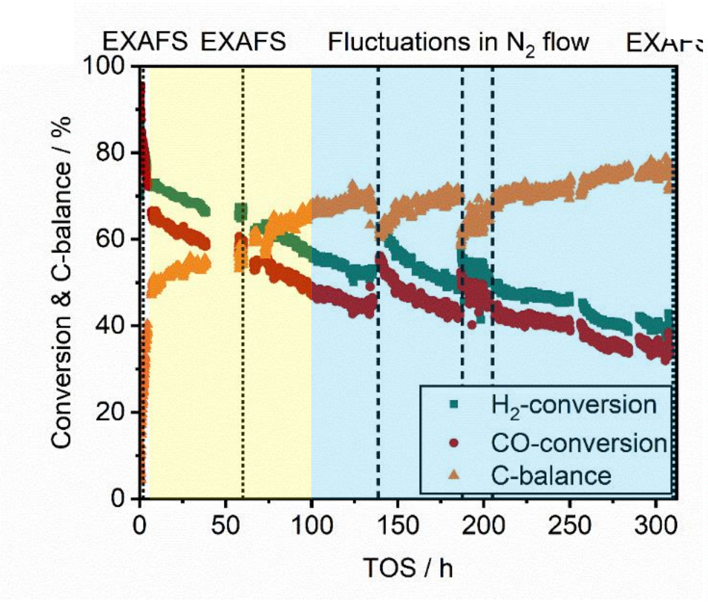
Long-term operando studies for FTS

Re-Co/γ-Al_2O_3 Catalyst

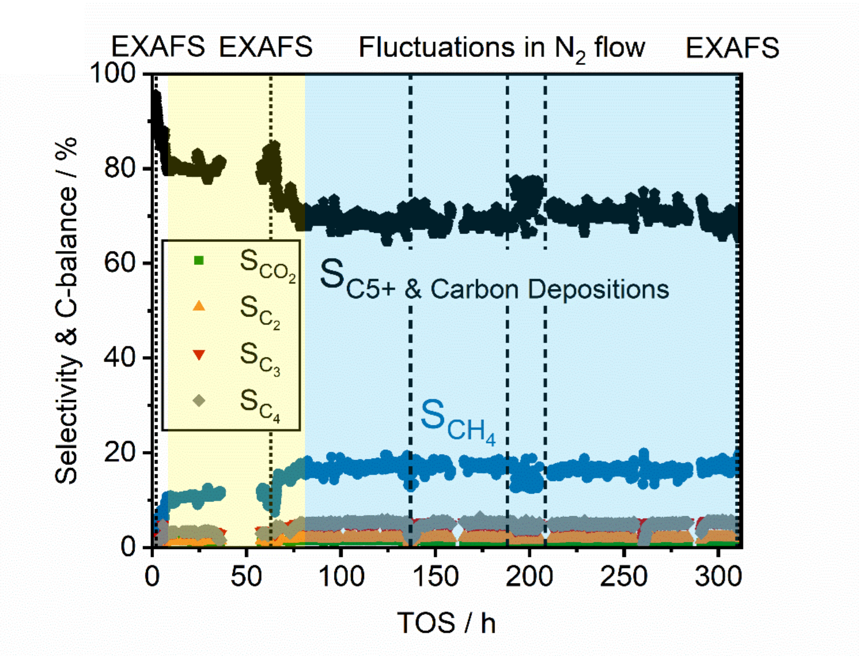
1:4 γ-Al_2O_3; 83,8 mg; 100-200 µm

M. Loewert, M.-A. Serrer, T. Carambia, M. Stehle, A. Zimina,,K. F. Kalz, H. Lichtenberg, E. Saraçi, P. Pfeifer and J.-D. Grunwaldt., React. Chem. Eng. 2020, **5**, 1071

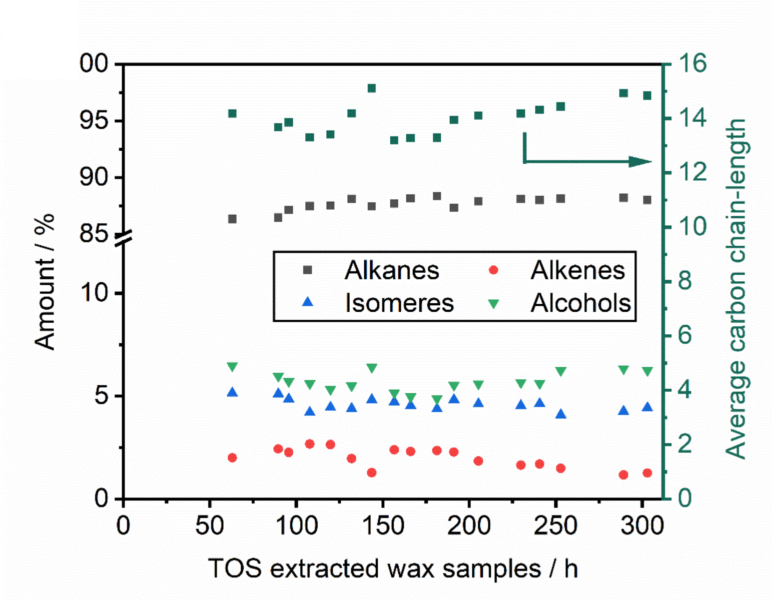
- Conversion & C-balance



- Selectivity gas-phase



- Selectivity liquid-phase



- 3 regimes of deactivation
  - 1-8 h TOS: ~85 % X_{CO} to 66 %
  - 8-100 h TOS: 66 % X_{CO} to 55 %
  - 100-310 h TOS: 55 % X_{CO} to 33 %

- 3 regimes of selectivity
  - 1-8 h TOS: ~2 % SCH4 to 7 %
  - 8-60 h TOS: 7 % SCH4 to 18 %
  - 60-310 h TOS: 18 % SCH4

- First sample obtained after 70 h TOS
- Stable product selectivity

Operando long-term FTS – 310 h TOS

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Re-Co/γ-Al_2O_3 Catalyst
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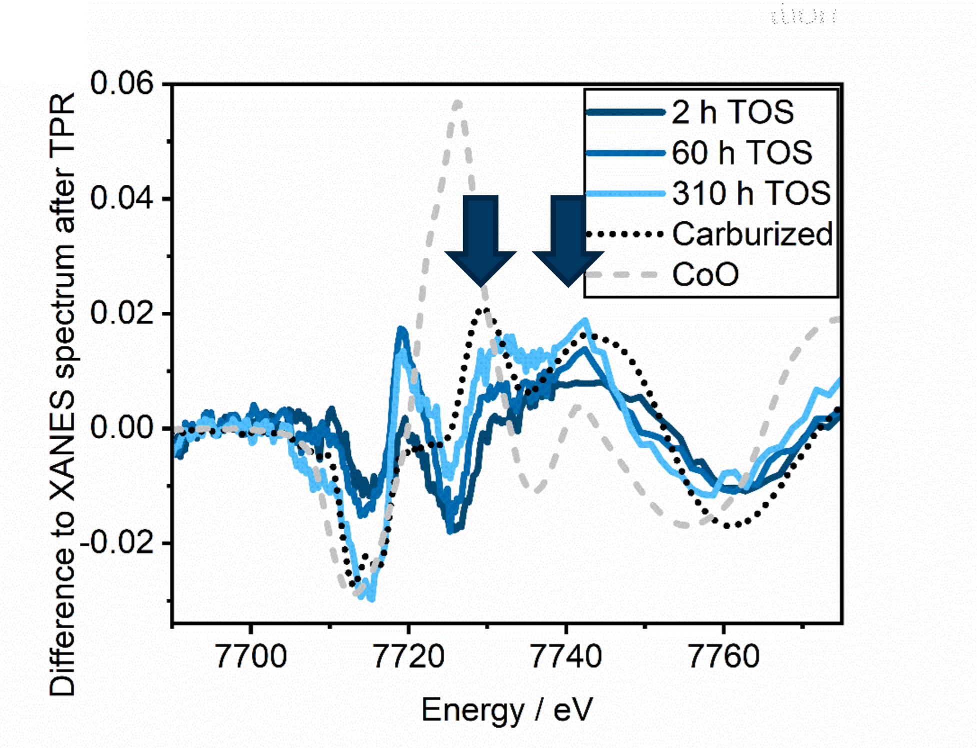
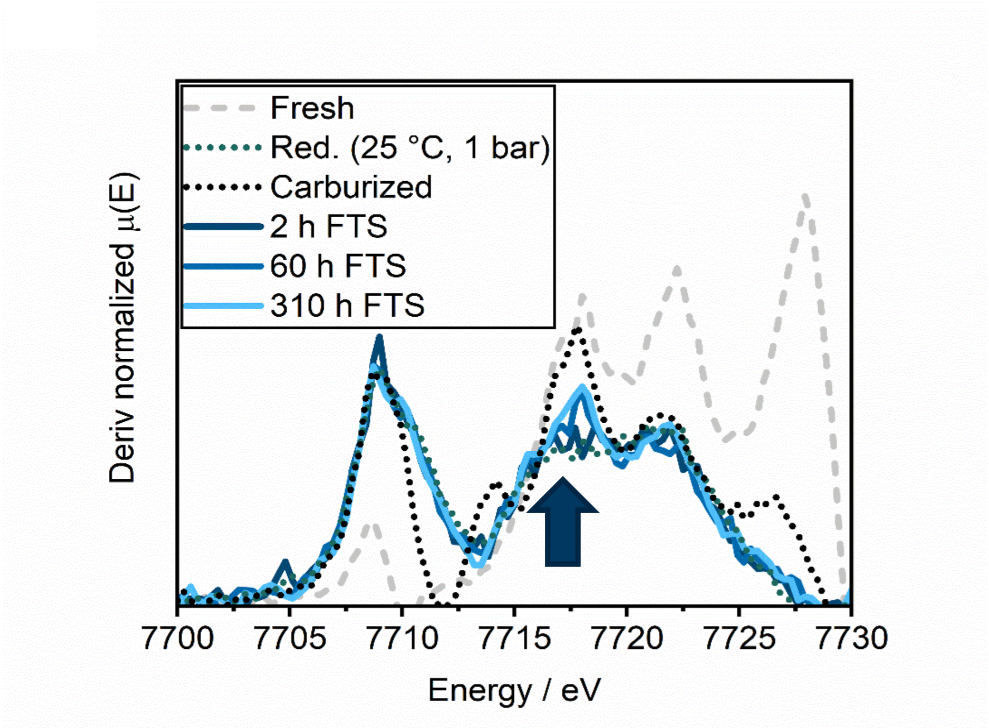
Difference Spectra

- No carburization or oxidation between 2 h TOS and 60 h TOS



First Derivative

- Peak at 7717 eV sensitive to



Comparison of yield/selectivity of Co- and Mn-Co-based FT catalyst

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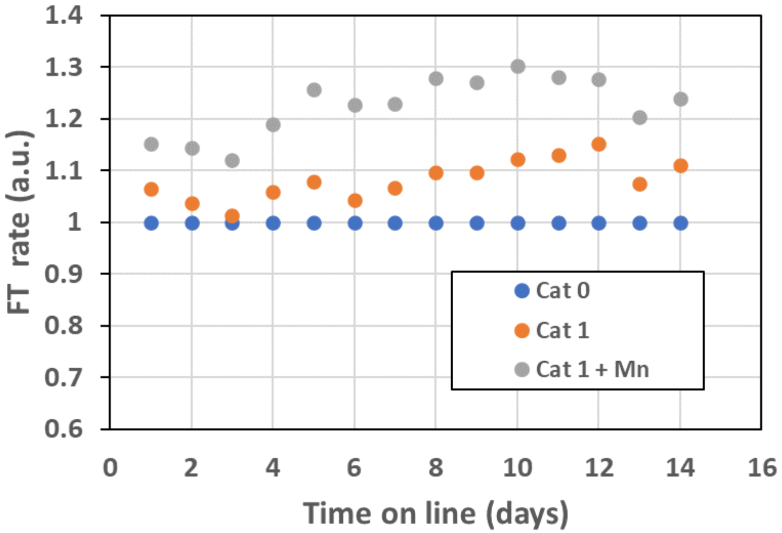
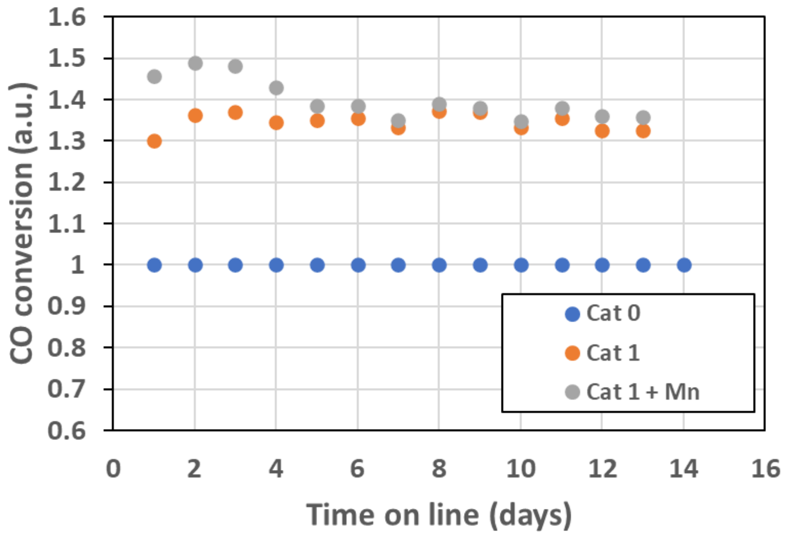
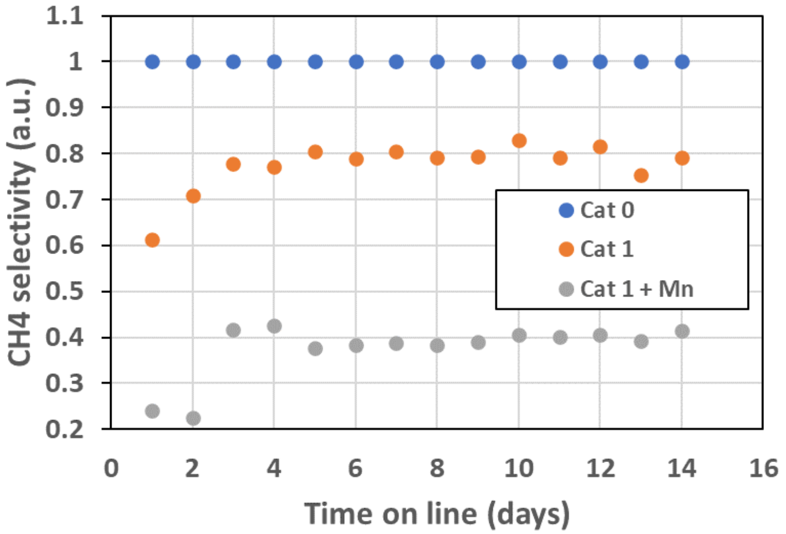




sasol



D. Moodley, JM Botha, J. Potgieter et al., SASOL

Micro-slurry reactor (10-20g catalyst) at industrially relevant conditions

How is the structure during reduction & under reaction conditions? – X-ray absorption spectroscopy

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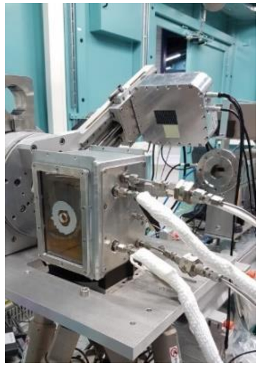

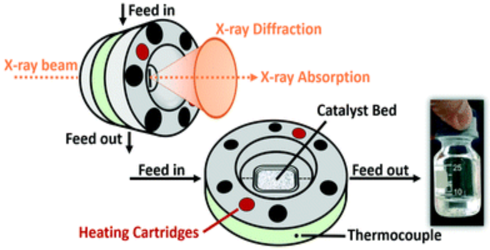

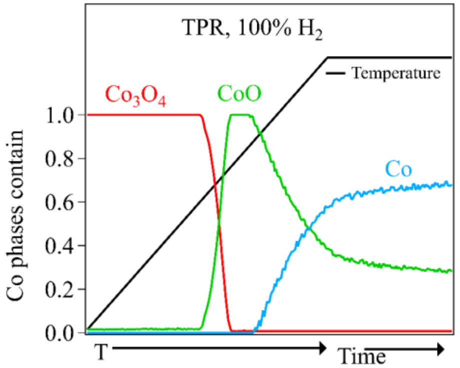

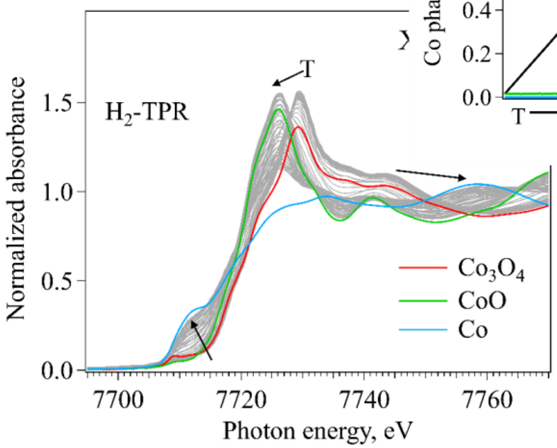

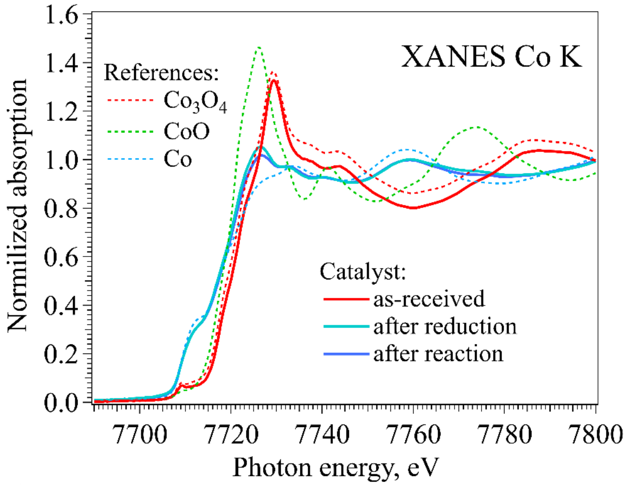

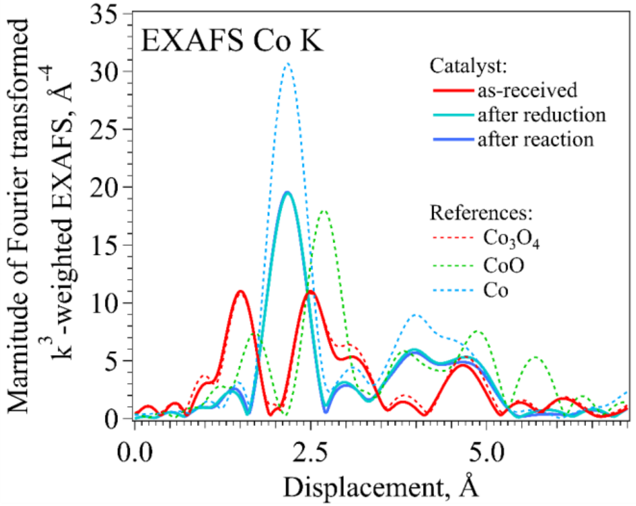

Active state: metallic cobalt

Different supports: variation in Co(II)

Promoter structure: mainly Mn^{2+}, non-stoichiometric

Reduction behavior: support dependent, reduction of cobalt oxide starts earlier in presence of Mn, but formation of metallic Co is retarded.

Further reduction **upon time-on-stream** (note: short reaction time), metallic Co NP growth.

In-situ magnetometry on Co/Co-Mn Fischer Tropsch catalysts

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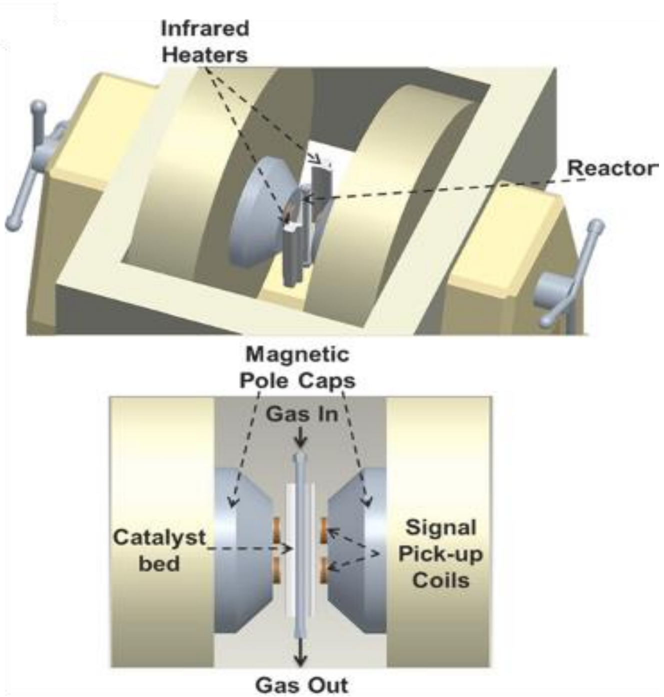
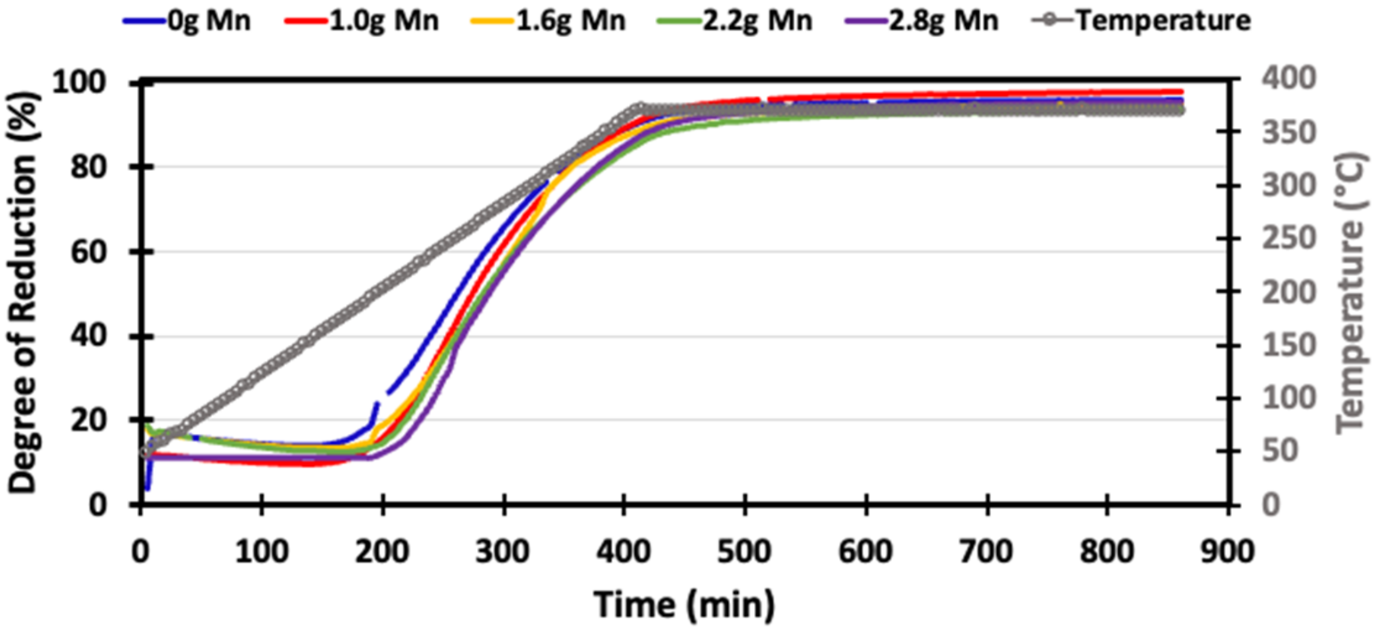




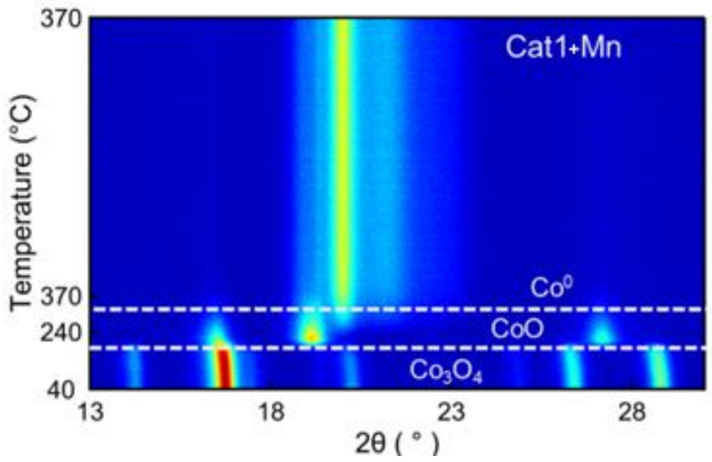
Claeys, et al, US Patent, US20110204884A1, 2009

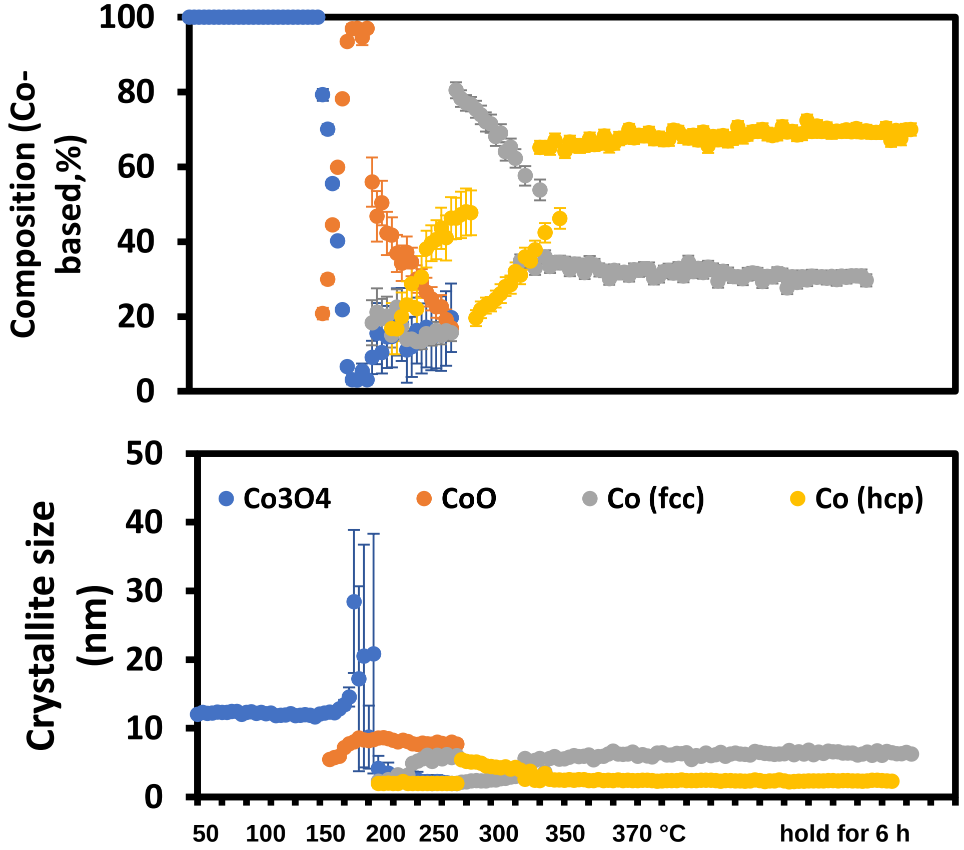
M. Claeys, D. Moodley, JM Botha, J. Potgieter, et al. (UCT/Sasol)

- Support influences the magnetization degree of cobalt (lower for Alumina-based compared to Silica-based).
- Mn addition influences the Co^0 crystallite size and retards the reduction of cobalt oxide to Co^0.

In-situ XRD on Co/Co-Mn Fischer Tropsch catalysts

Claeys and Fischer, US 8.597.598 (2013)





- Support influences the reduction temperature and degree of cobalt oxides and final crystalline phase composition of Co^0
- Mn addition influences the Co^0 crystallite size, accelerates the reduction of Co_2O_3 to Co^{2+} and retards the reduction of Co^{2+} to Co^0.

Need for model systems to understand complex nature of catalyst

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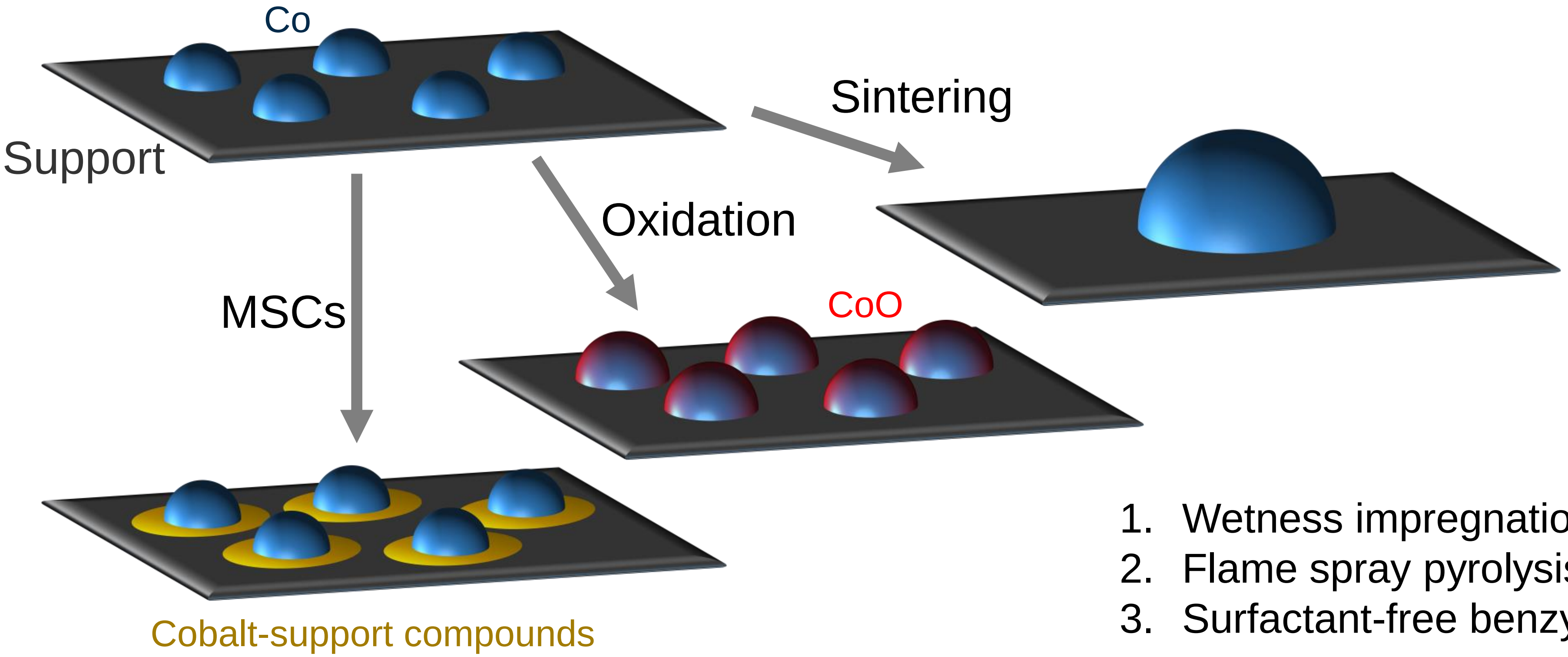
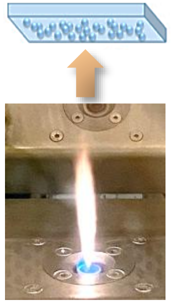
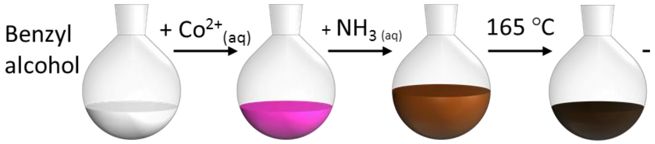


1. Wetness impregnation
2. Flame spray pyrolysis
3. Surfactant-free benzyl-alcohol synthesis

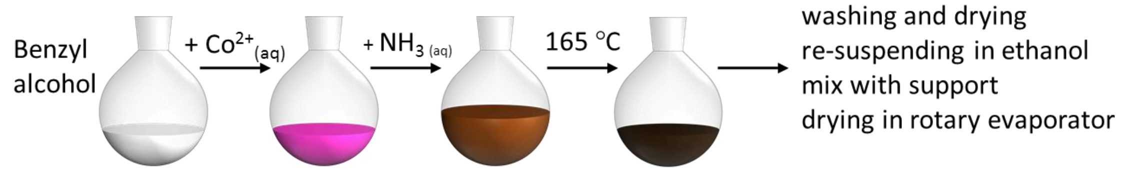




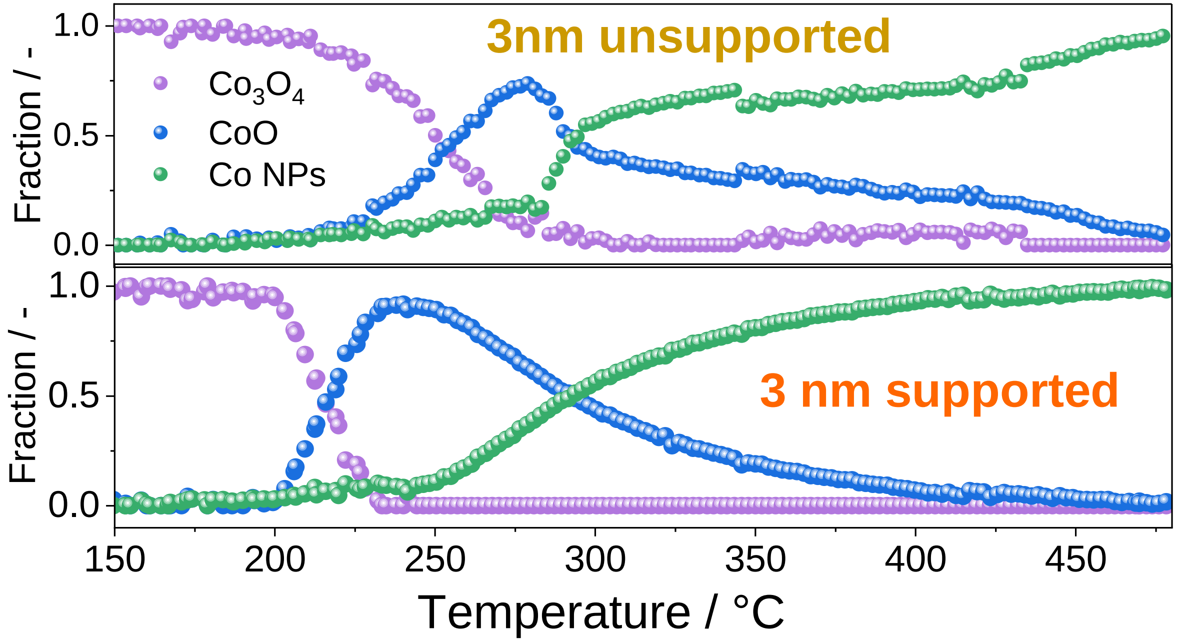
Isolation via

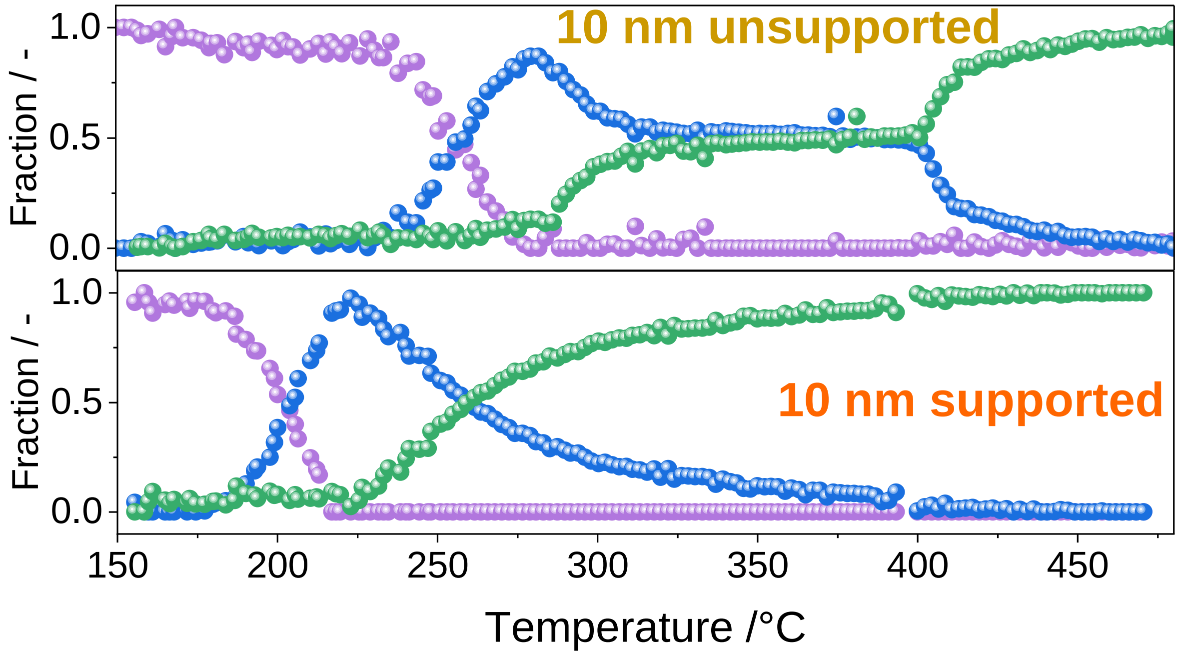
- Dedicated synthesis (model structures and model catalysts)
- Theoretical consideration (MSI, Co-promotor interaction)

Unfluence of support via dedicated synthesis

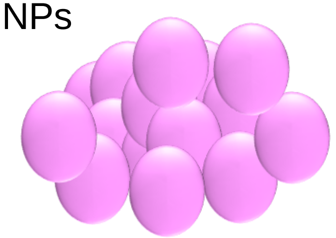


Wolf *et al.* 2018. *Mat. Chem. Phys*. 213, 305
Fischer *et al.* 2014. *Angew. Chemie Int. Ed*. 53.





Co_3O_4 NPs

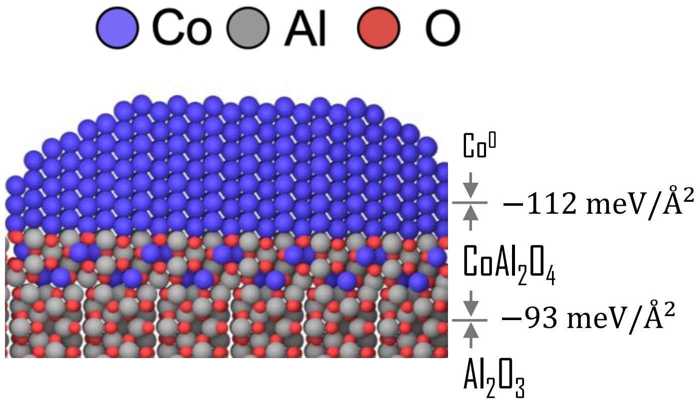


vs.

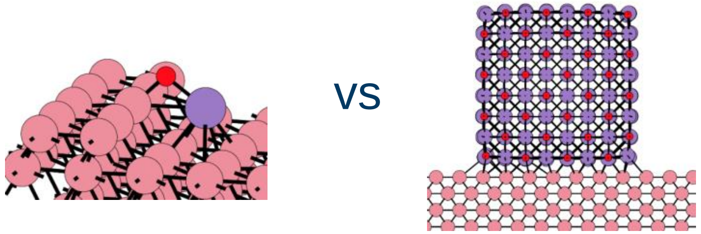
Size dependence and MSI…

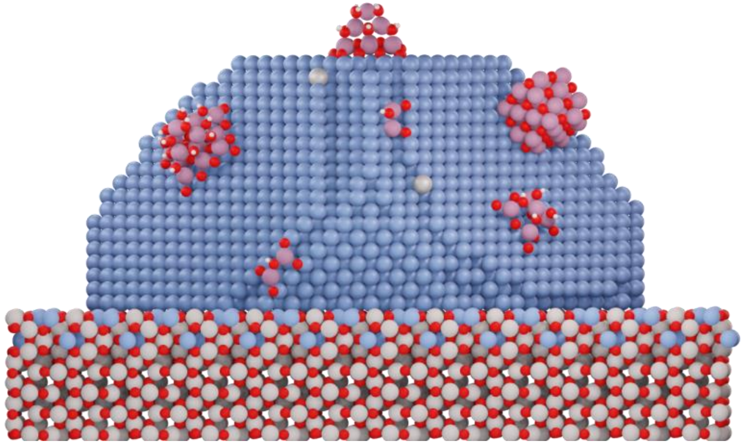
Theoretical approach towards understanding promotion and support interaction via DFT

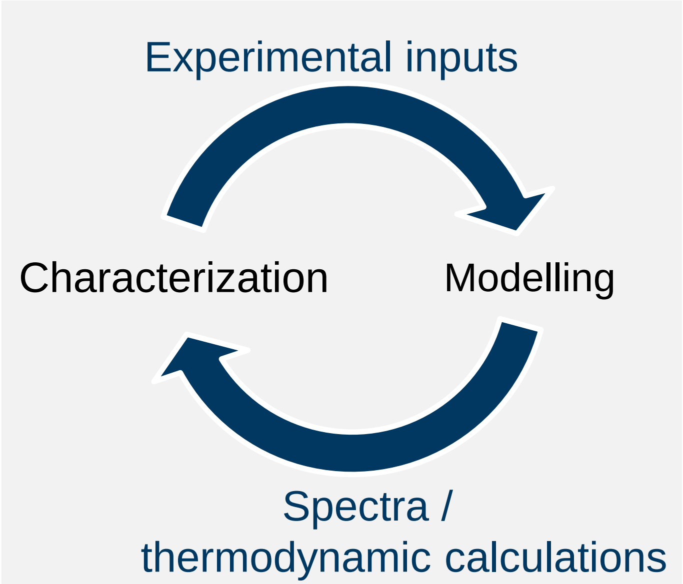
Metal-Support-Interaction:
solid phase formation



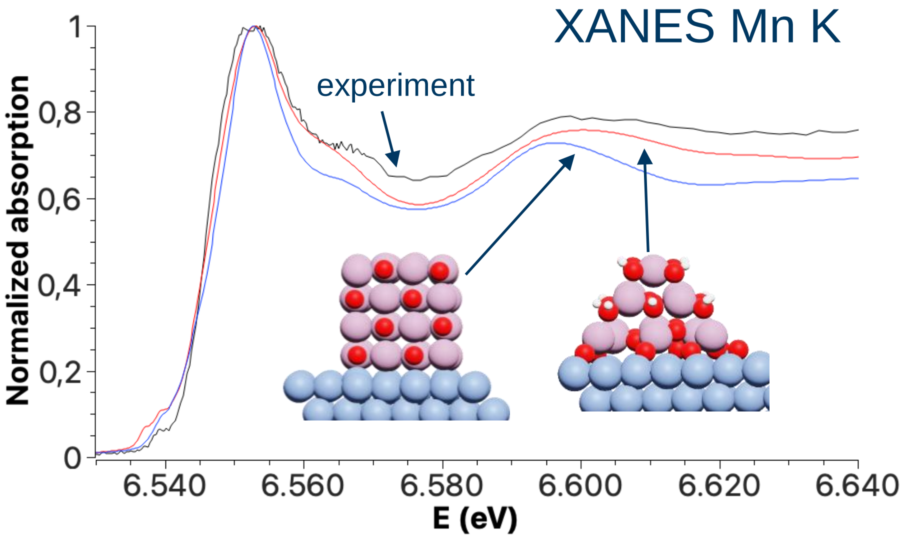
Metal-Promoter-Interaction:
Size dependence







Structure of promoter



Deactivation of Co-based Fischer-Tropsch catalysts

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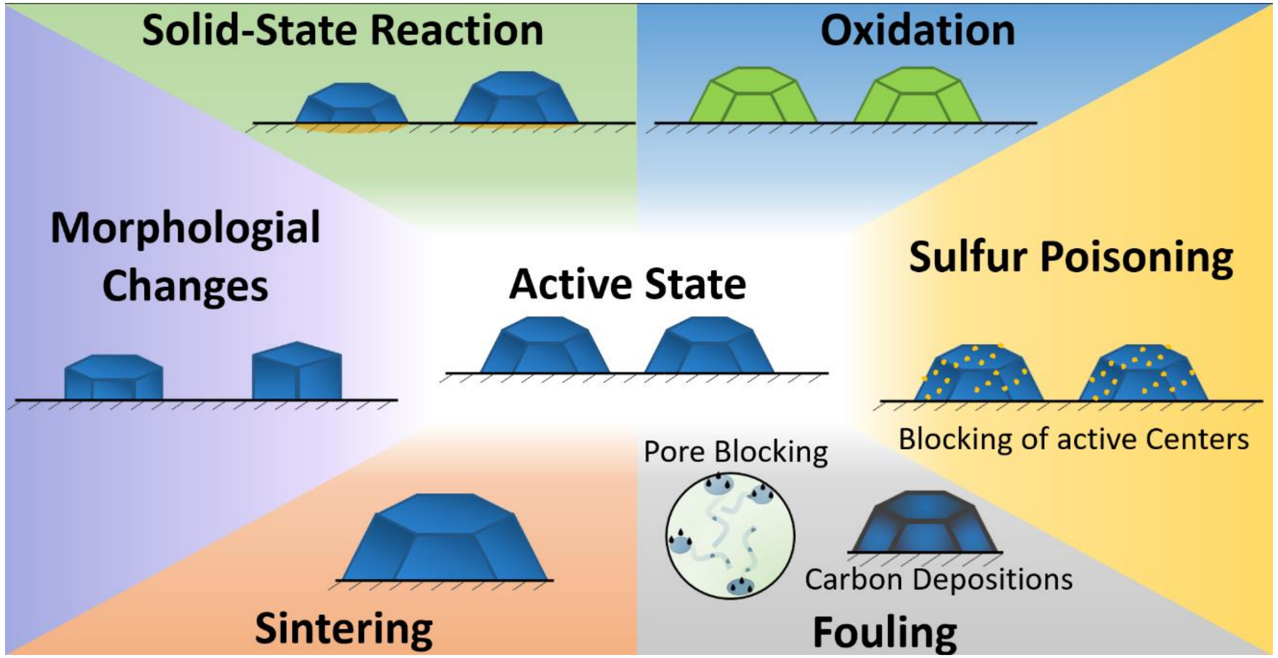
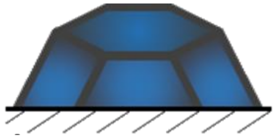


Pore blocking

Interface formation



Carbon deposition

Catalytic testing

Spectroscopic methods

Imaging methods

Conclusions and outlook

- On the way of bridging the gap between industrially applied catalysts and studies at the synchrotron
  - Characterization under industrial relevant conditions on commercial relevant materials demanding (but possible)
  - Fouling processes are critical for deactivation
  - Multimodel and multiscale approach required for characterization
  - Dedicated synthesis of defined model systems and theoretical considerations

- Know-how transfer to the CARE-O-SENE Project: interdisciplinary, institutional and international collaborative project for long term cooperation in the field of sustainable catalysis
  - Improved understanding and development of PtL catalysts for sustainable kerosene
  - XAS studies: catalyst behavior and deactivation phenomena
  - Theory: knowledge-based design of catalysts, understanding of reaction dynamics and deactivation mechanics
  - Next steps: Hard and soft XAS, extension to imaging methods

Acknowledgements

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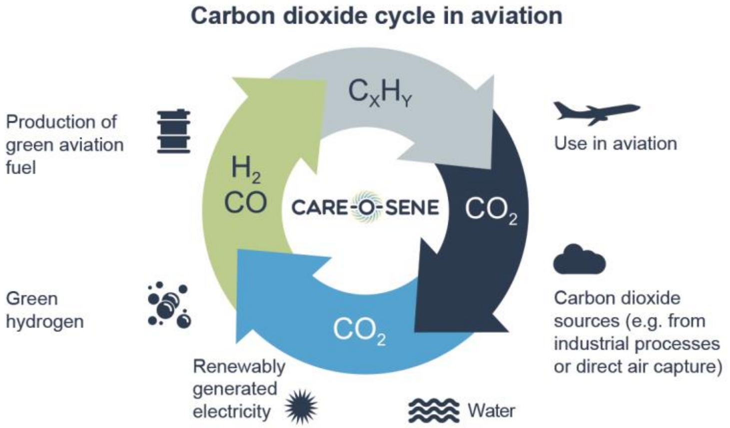

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- Prof. Eric Van Stehen

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- Dr. Dmytro Sharapa

Group Wolf @ IKFT

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Group Grunwaldt @ IKFT/ITCP

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- Dr. Erisa Saraci
- Dr. Anna Zimina
- Dr. Danielle S. Goncalves

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HZB Helmholtz Zentrum Berlin

sasol

KIT Karlsruher Institut für Technologie

Fraunhofer IKTS

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