In situ UV-vis Characterization & Activity Testing of Flat Model Catalysts in Custom Built Micro Reactors

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Syngaschem BV

ECOSS 34, Aarhus, 2018

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Model Catalyst vs Real Catalyst

Academic science
Catalyst manufacturers

- Improved understanding
- Developing new concepts
- Compare individual components of a catalyst

- Develop an active, durable and cheap catalyst

Catalyst manufacturers,
Chemical producers

- Screening of catalysts
- Develop an active, durable and cheap catalyst

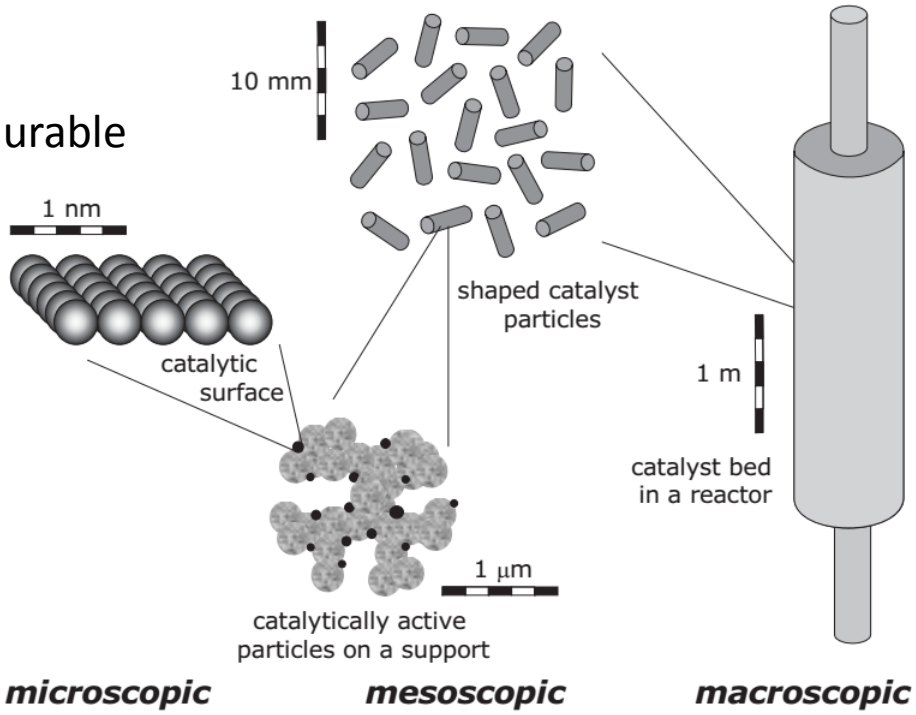
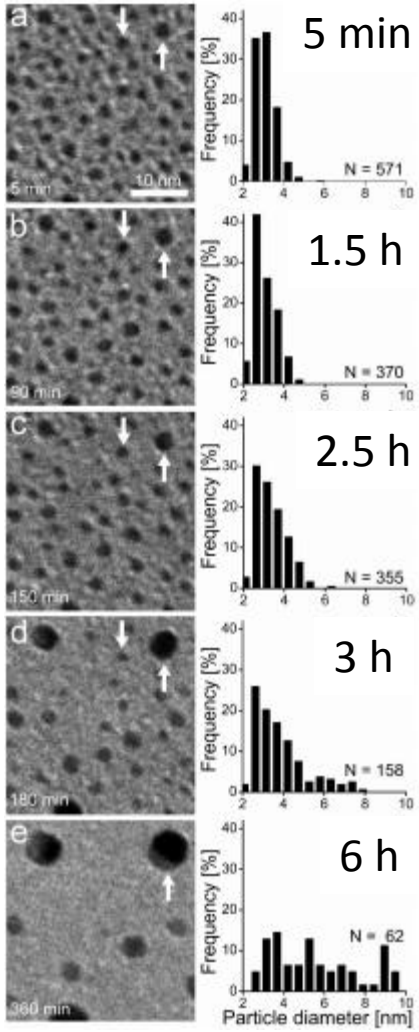


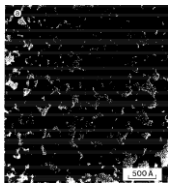
Figure from Concepts of Modern Catalysis and Kinetics, Chorkendorff & Niemantsverdriet, Wiley-VHC (2017)

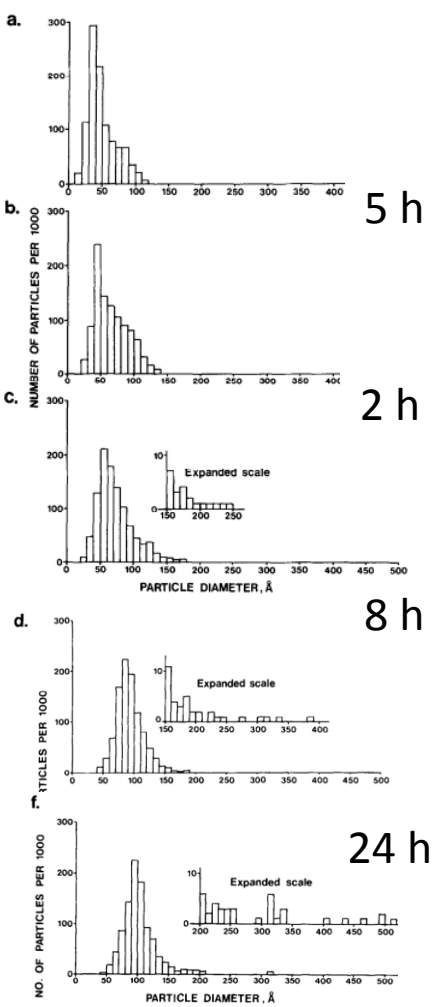
Model Catalyst vs Real Catalyst
Precision

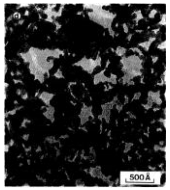
Model catalyst



Commercial catalyst







TEM - Sintering of Pt in air

√ Sample preparation X

√ TEM measurements X

√ Image analysis X

X Relevance √

X Catalyst preparation √

[1] S.B. Simonsen, I. Chorkendorff, S. Dahl, M. Skoglundh, J. Sehersted, S. Helveg, J. Am. Chem. Soc. 132 (2010) 7968–7975

[2] P.J.F. Harris, E.D. Boyes, J.A. Cairns, J. Catal. 82 (1983) 127–146

Model Catalyst vs Real Catalyst Interpretation - CO-oxidation on CuO_x

Thin film, (G.G. Jernigan,G. A. Somorjai, J. Catal. 147 (1994) 567–577)

We find that the reaction rate of CO oxidation is fastest on metallic copper, and at 300°C the rate decreases with increasing copper oxidation state: Cu (0) > Cu (+1) > Cu (+2). The apparent activation energies for the reaction

Cu(111) single crystal, (B. Eren, C. Heine, H. Bluhm, G.A. Somorjai, M. Salmeron, J. Am. Chem. Soc. 137 (2015) 11186–11190)

Under oxygen-lean conditions, the surface is not fully oxidized to Cu_2O. However, the surface is more reactive once a partial surface Cu_2O layer forms.

Powder, (T.J. Huang, D.H. Tsai, CO oxidation behavior of copper and copper oxides, Catal. Letters. 87 (2003) 173–178)

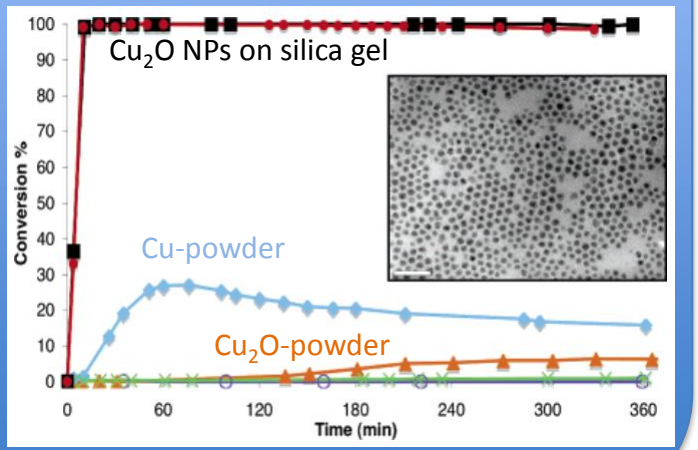
Among the three copper species (Cu, Cu_2O, CuO) tested, Cu_2O was the only one that was active at 140°C

Cu^0, Cu^+ and Cu^{2+}, all suggested as active species

Supported nanoparticles

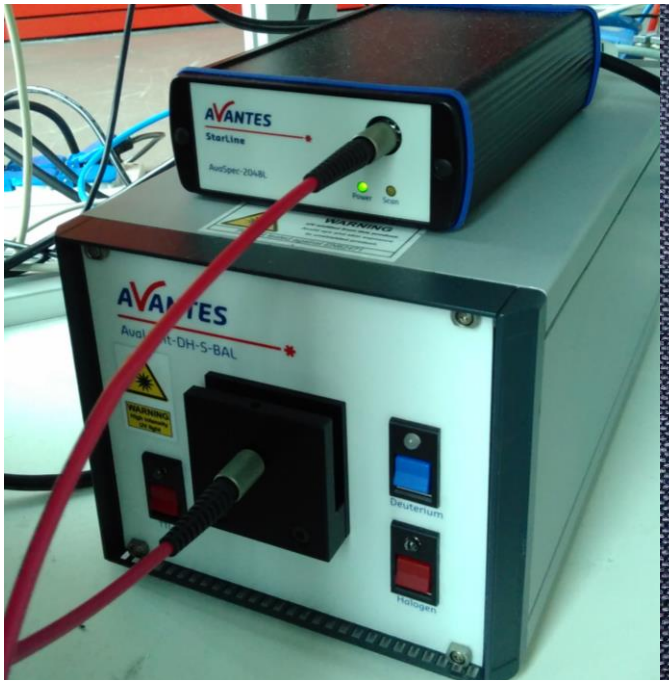
(B. White, M. Yin, A. Hall, D. Le, S. Stolbov, T. Rahman, N. Turro, S. O'Brien, Nano Lett. 6 (2006) 2095–2098)

Cu_2O most active for CO-oxidation



Model Catalyst Testing

UV-vis fiber spectrometer



Quartz tube reactor

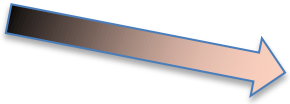
Mass spectrometer

Model Catalyst Testing - Activity on Powders

Quartz tube reactor

Mass spectrometer

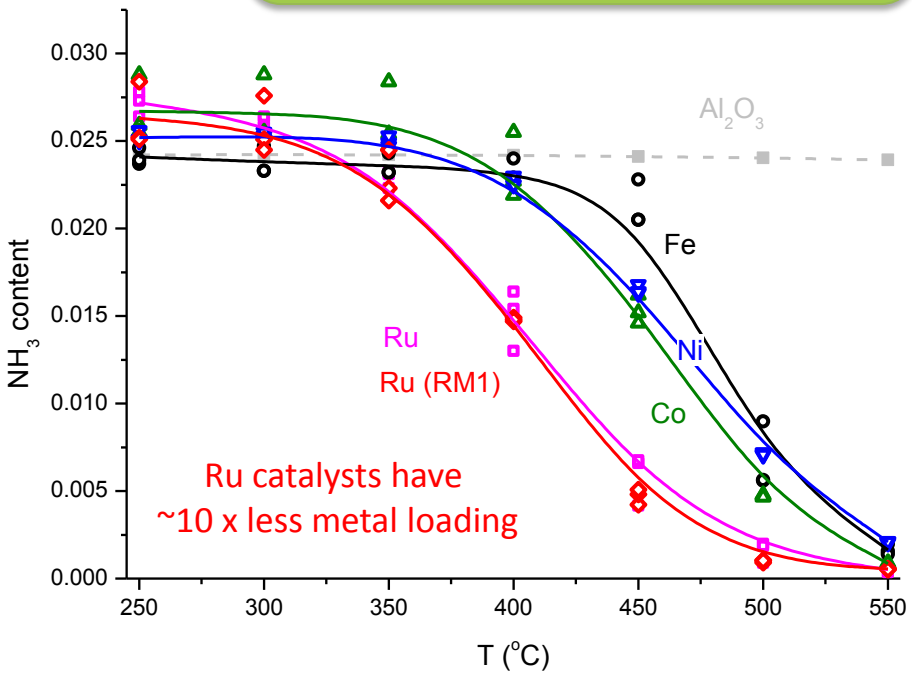
Powder catalysts – Quartz tube reactor



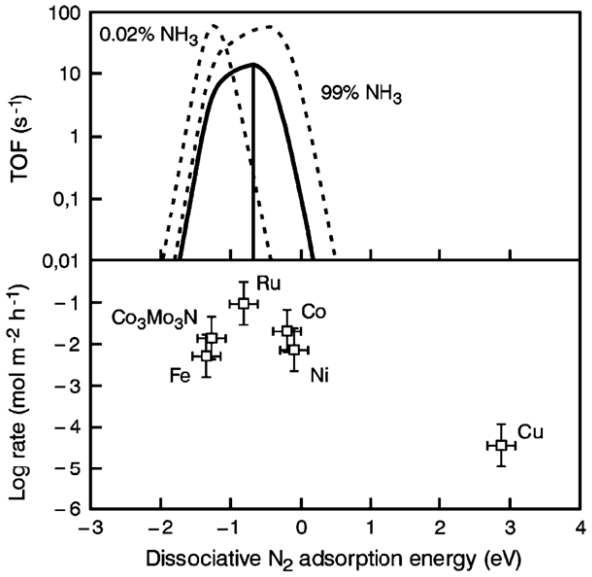
+ Small catalyst mass (~10 mg)
+ Small gas volume
- Small surface area

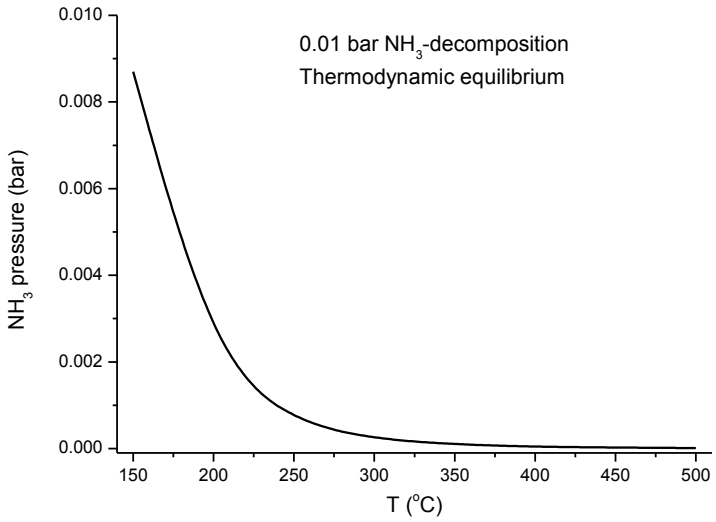
NH_3 decomposition – Bench mark measurements

Bench mark catalysts
Impregnation/porous support
1 ml NH_3/min (0.01 bar)



Literature reference





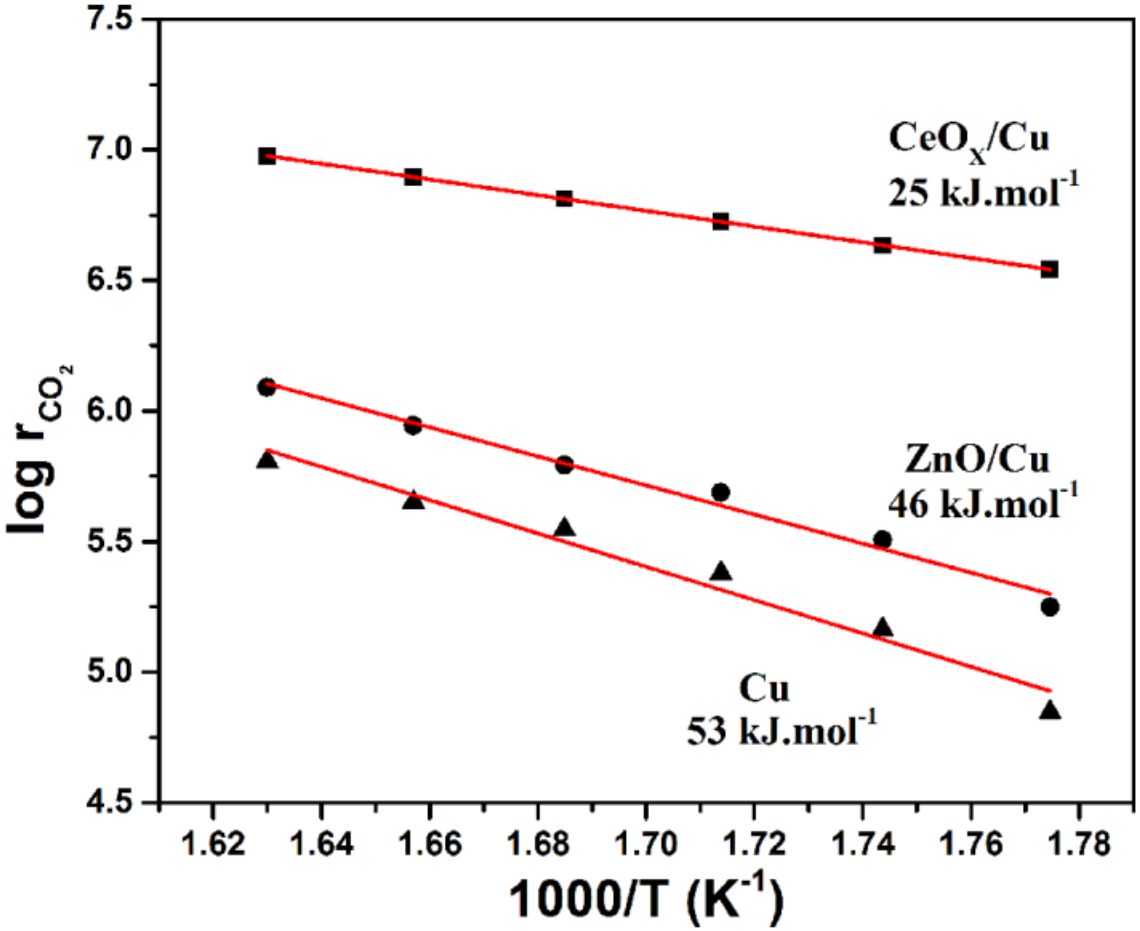
Qualitative agreement with literature/theory
Ru>>Co>Ni>Fe
Not limited by thermodynamic equilibrium

Water-gas shift – Activity measurements

Cu powder catalyst with CeO_x & ZnO promoters

Ce:Cu & Zn:Cu is 1:6

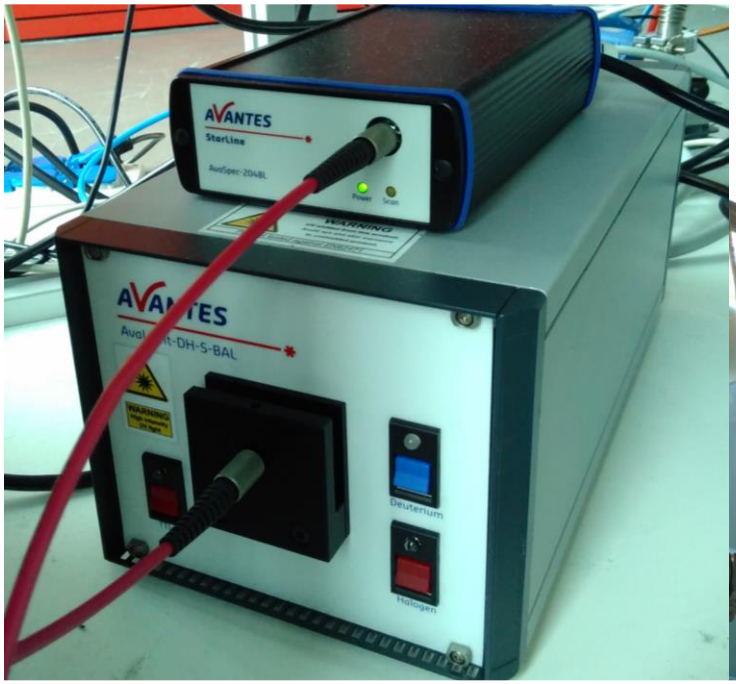
CeO_x/Cu > ZnO/Cu > Cu



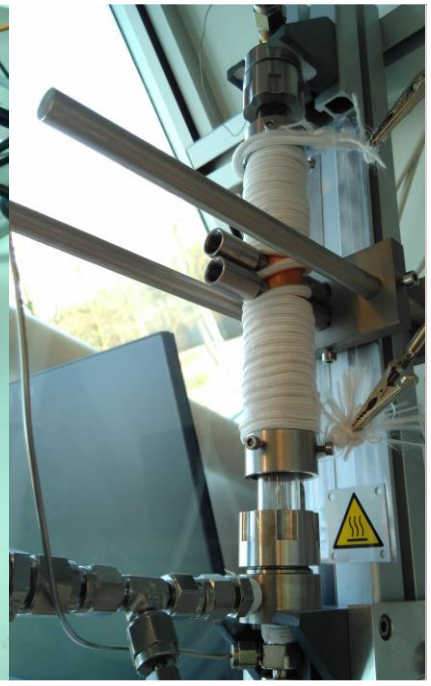
Y. Bu, C.J. Weststrate, J.W. Niemantsverdriet, H.O.A. Fredriksson, ACS Catal. 6 (2016) 7994–8003

Model Catalyst Testing – In-situ UV-vis

UV-vis fiber spectrometer

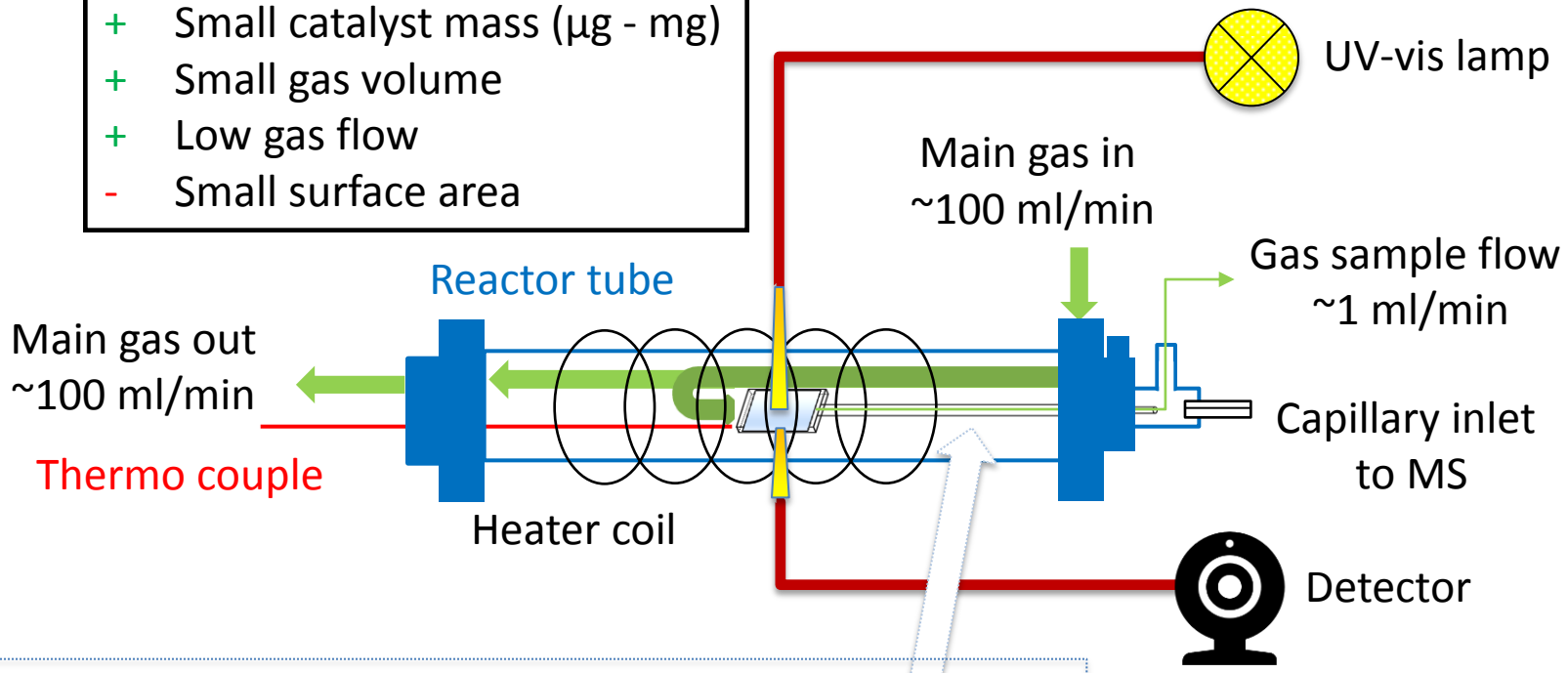


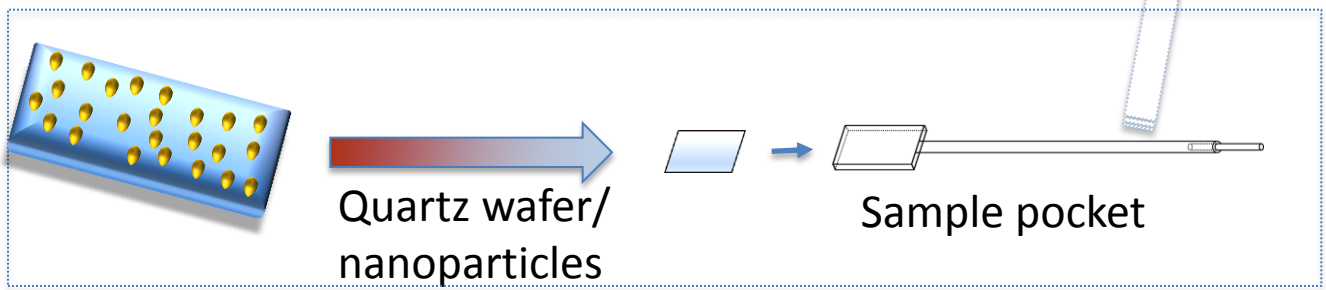
Quartz tube reactor



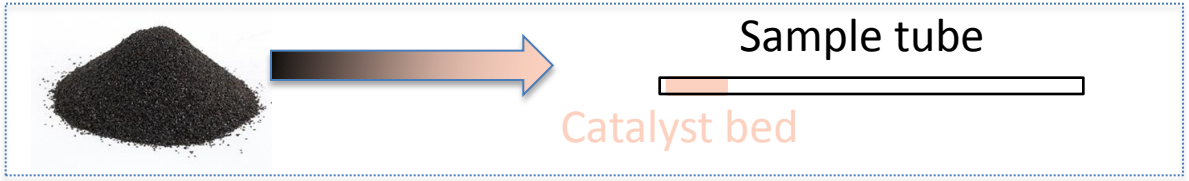
Flat model catalysts – reactor design

+ Small catalyst mass (µg - mg)
+ Small gas volume
+ Low gas flow
- Small surface area



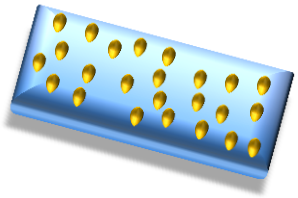


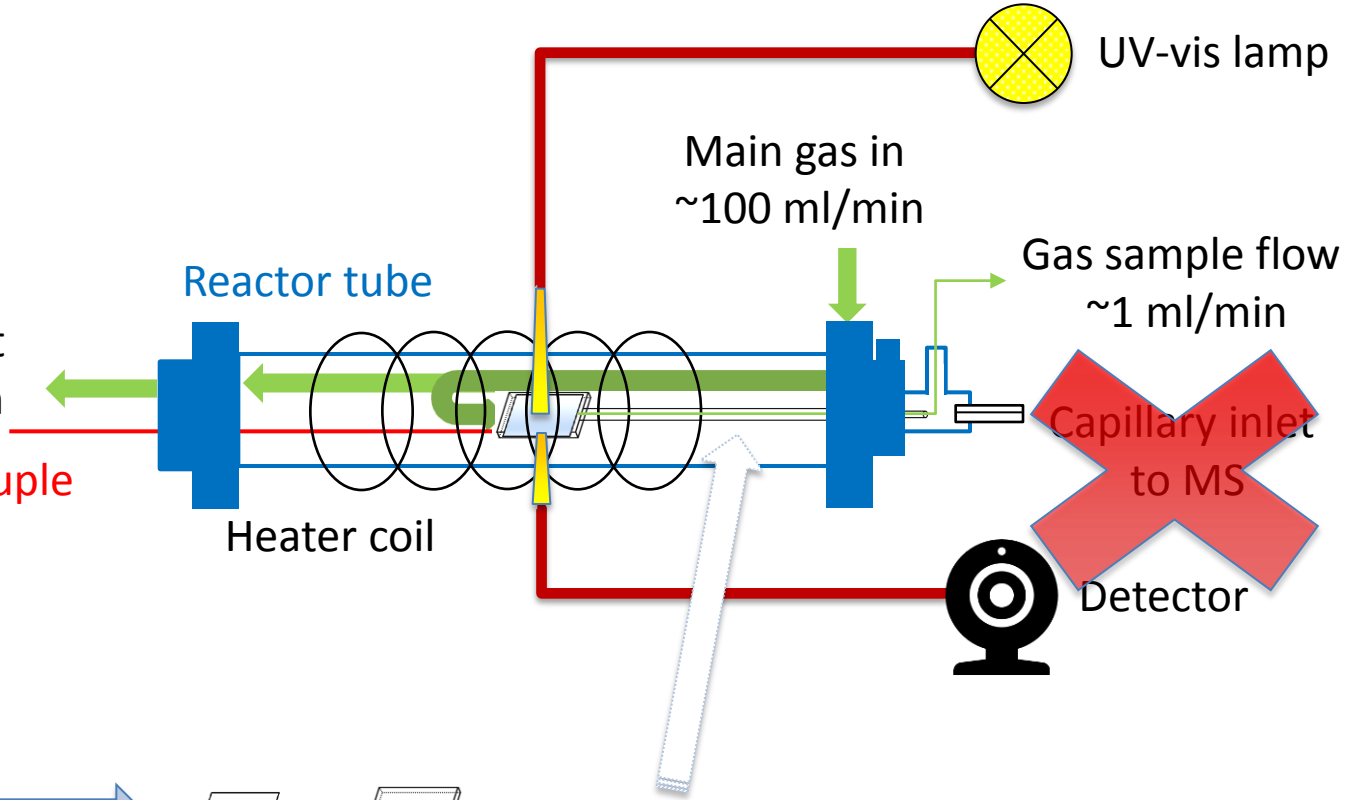
or



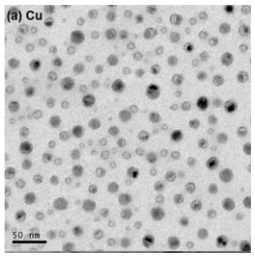
(R)WGS with in-situ UV-vis and XPS

(R)WGS is a slow reaction – mass spec. not sensitive enough

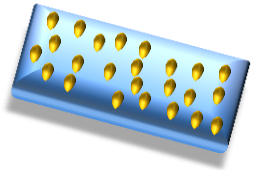




Evaporated thin film
Nanoparticles, ⌀ 15 nm



RWGS conditions - XPS



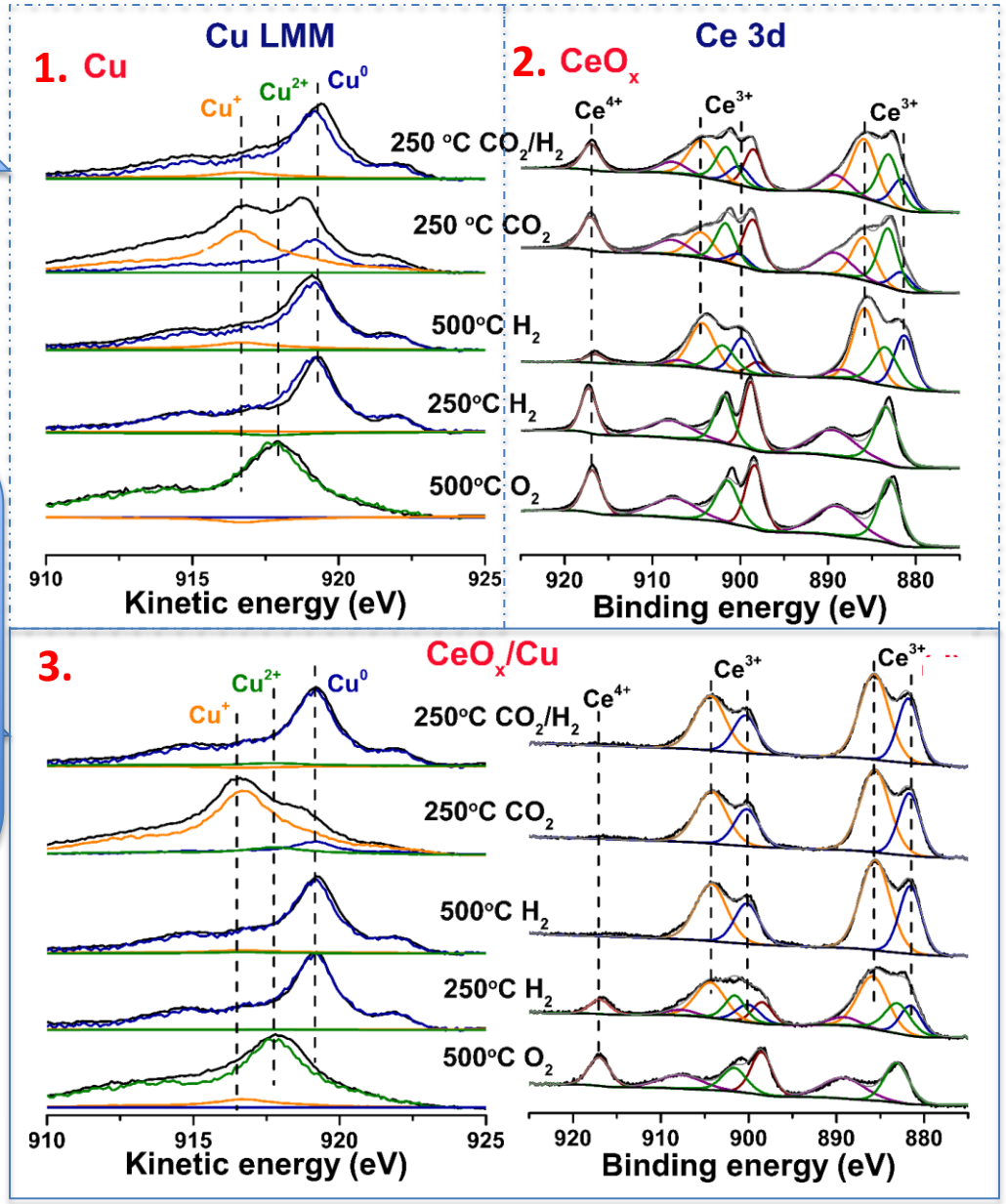
Three catalysts:

- Cu, CeO_x and Cu/CeO_x

At 250 °C, under RWGS conditions

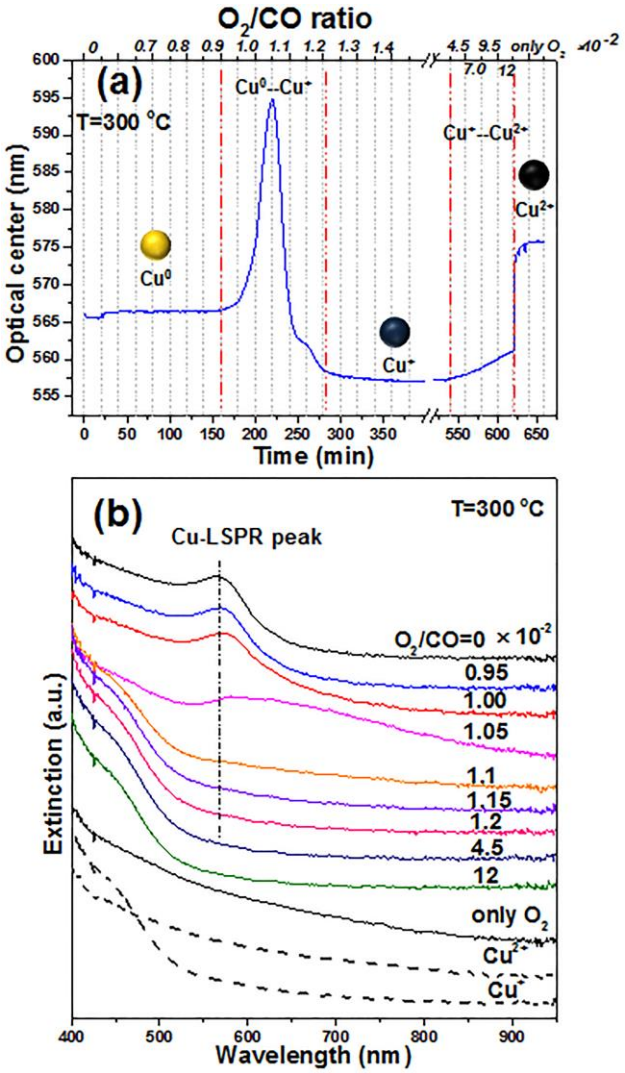
- Cu can switch between Cu^0 and Cu^{1+}
- CeO_x cannot
- CeO_x promotes Cu red-ox

- Ce^{3+} oxidized in CO_2, supressed by Cu

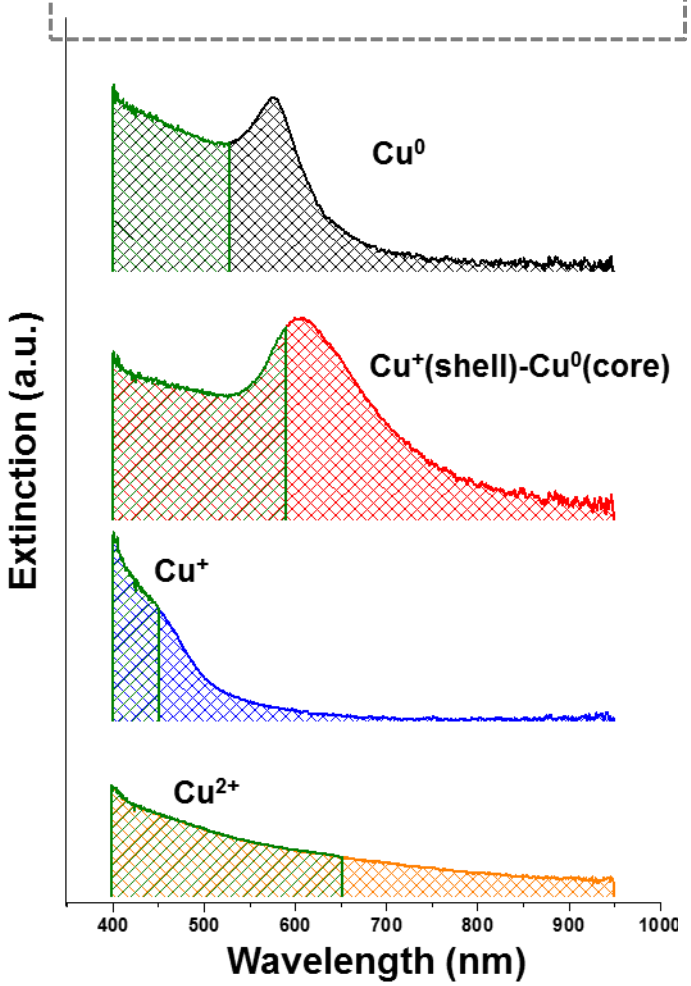


Optical center – oxidation state descriptor

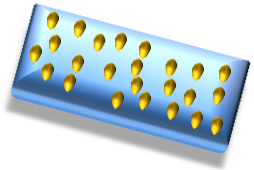
Peak shifts reveal Cu oxidation



$$\int_{\lambda min}^{\lambda} E(\lambda)d\lambda = \frac{1}{2}\int_{\lambda min}^{\lambda max} E(\lambda)d\lambda$$



Cu and Cu/CeOx red-ox – UV-vis

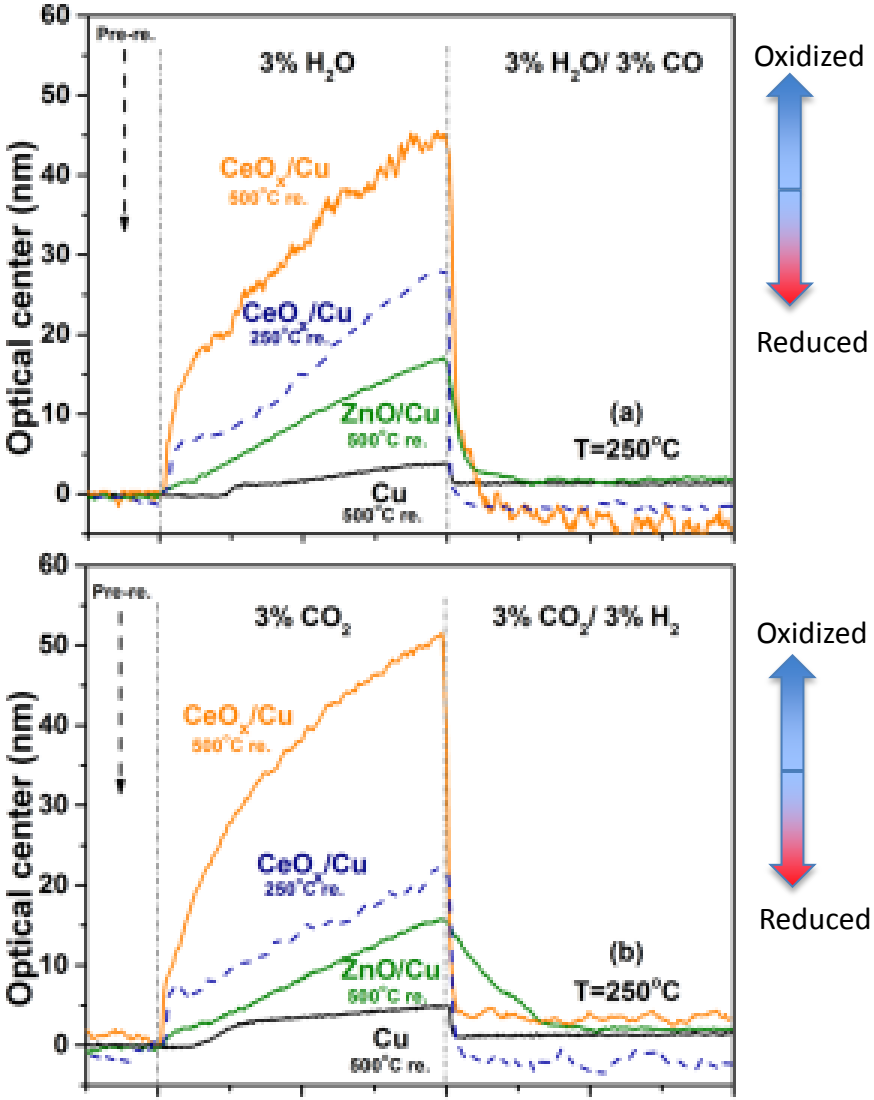


Observations:

- Ce^{3+} promotes H_2O and CO_2 dissociation
- Dissociated H_2O and CO_2 oxidize $Cu^{(0)}$ to Cu^{+}
- $Cu^{(0)}$ promotes Ce^{4+} reduction to Ce^{3+}
- Cu oxidation follows the trend
  $CeO_x/Cu > ZnO/Cu > Cu$ (same as activity)

At 250 °C, under RWGS and WGS conditions

- Cu shows red-ox behavior that is promoted by CeO_x (in the Ce^{3+} state)



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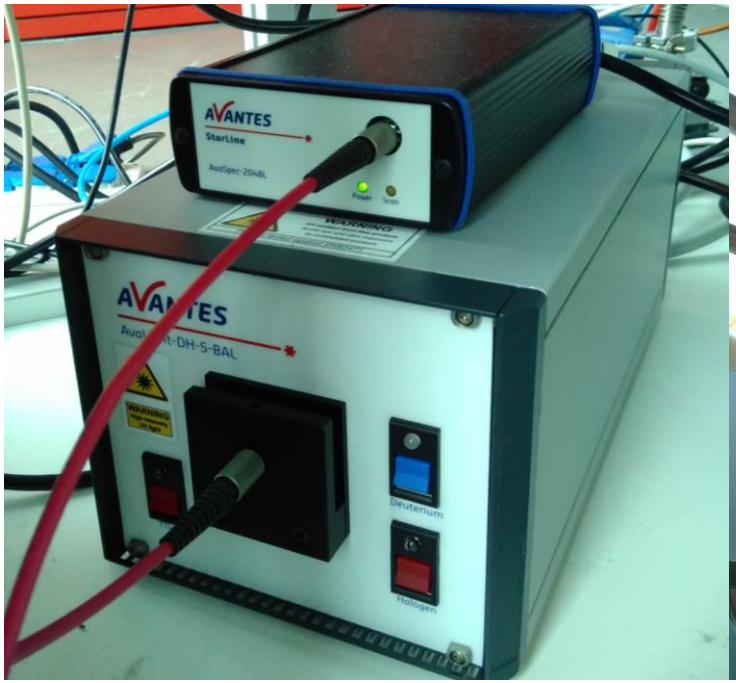
Y. Bu, C.J. Weststrate, J.W. Niemantsverdriet, H.O.A. Fredriksson, ACS Catal. 6 (2016) 7994–8003

Model Catalyst Testing

UV-vis fiber spectrometer



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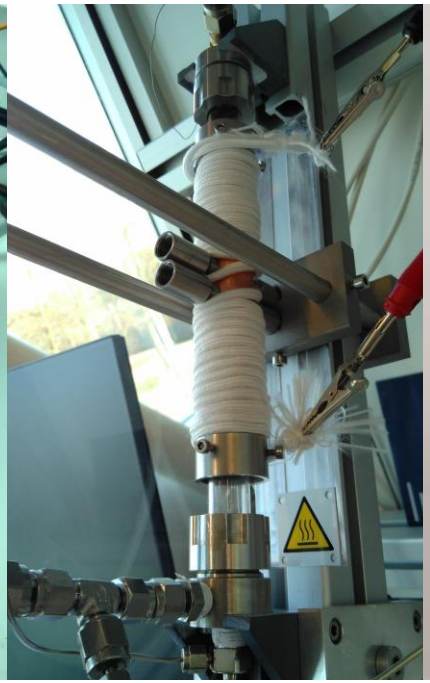
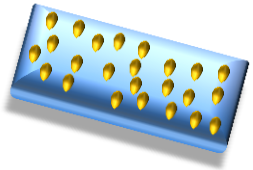


Mass spectrometer

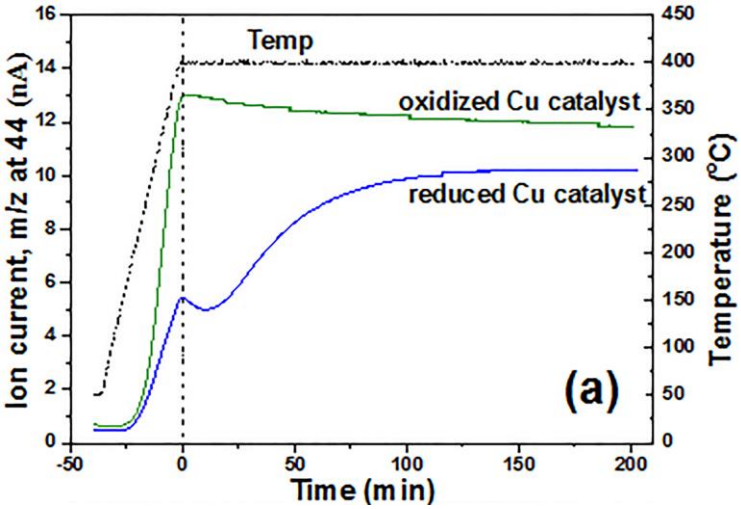
Simultaneous in-situ UV-vis and mass spectroscopy



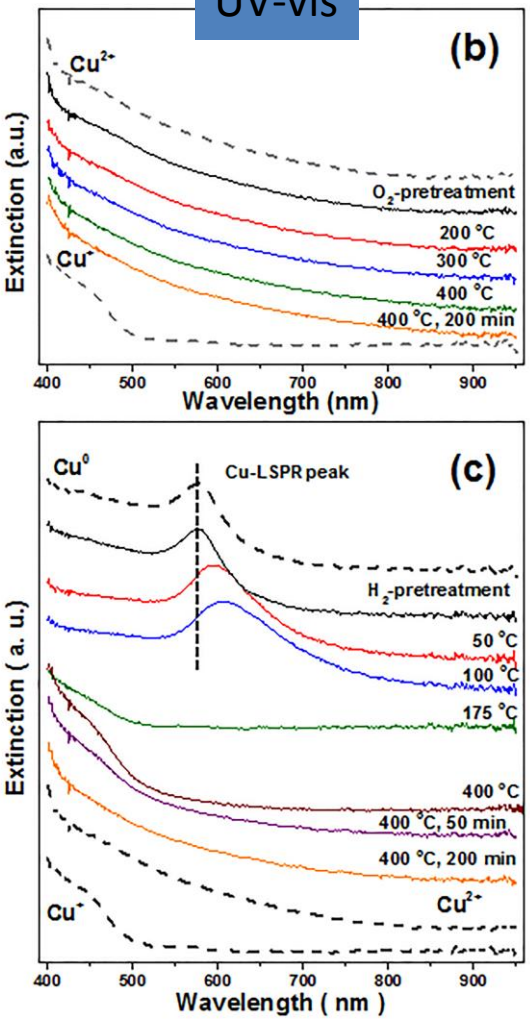
CO-oxidation on $Cu^{(0)}$ or Cu^{2+}

- 6.6 vol. % CO
- 3.3 vol. % O_2

Mass spec



UV-vis



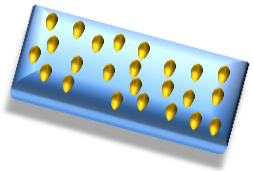
- Oxidized catalyst (Cu^{2+}) more active

but

- Reduced catalyst ($Cu^{(0)}$) changes phase during reaction

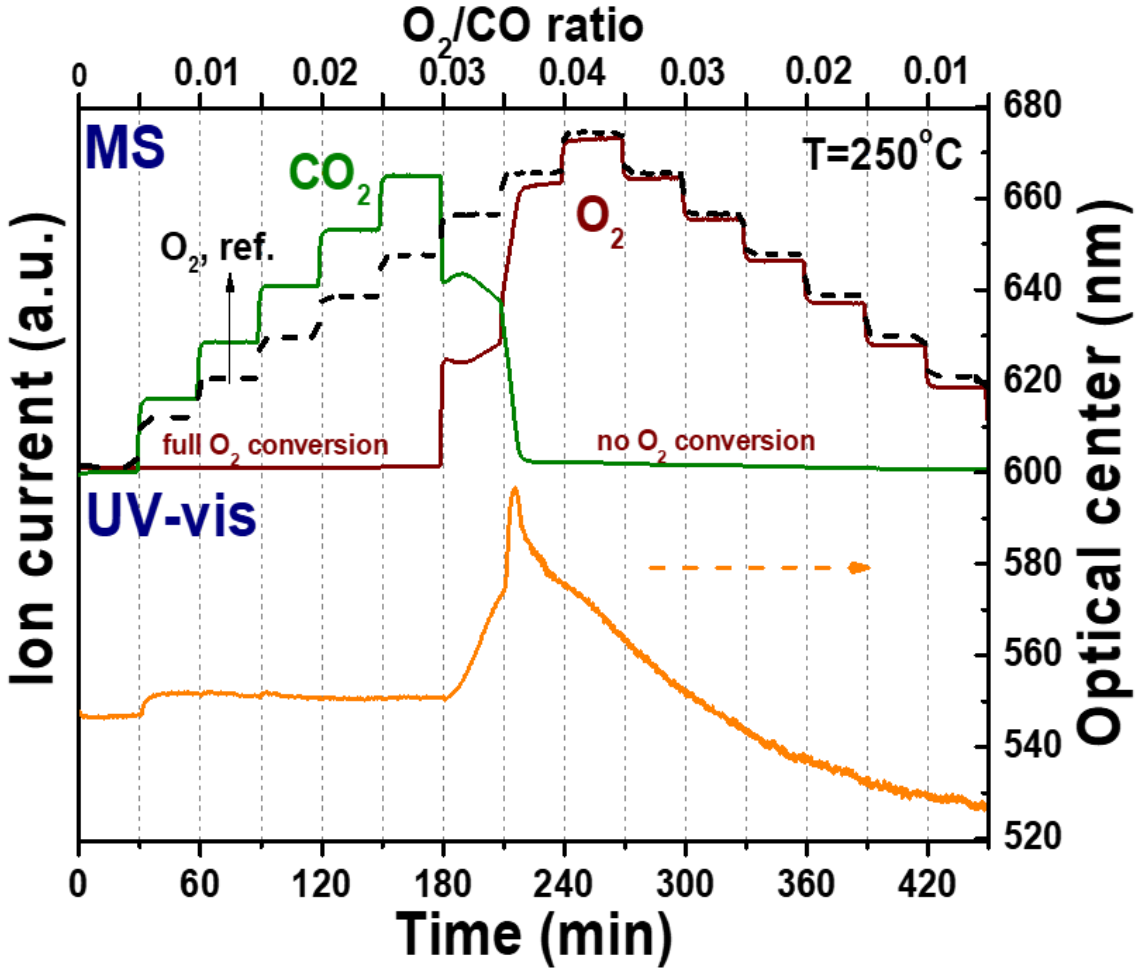
Y. Bu, J. W. (Hans) Niemantsverdriet, H. O. A. Fredriksson, ACS Catal. 2016, 6, 2867−2876

CO-oxidation on metallic copper



O_2 concentration starting at less than 0.5%

- Cu oxidation coincides with catalyst deactivation
- $Cu^{(0)}$ only maintained upon full O_2 conversion
- Activity: $Cu^{(0)} > Cu^{2+} > Cu^{+}$



Y. Bu, J. W. (Hans) Niemantsverdriet, H. O. A. Fredriksson, ACS Catal. 2016, 6, 2867−2876

Y. Bu, J. W. (Hans) Niemantsverdriet, H. O. A. Fredriksson, J. Catal., 357 (2018) 176–187

Model Catalyst vs Real Catalyst Interpretation - CO-oxidation on CuO_x

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We find that the reaction rate of CO oxidation is fastest on metallic copper, and at 300°C the rate decreases with increasing copper oxidation state: Cu (0) > Cu (+1) > Cu (+2). The apparent activation energies for the reaction

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Under oxygen-lean conditions, the surface is not fu… re…

Thin film, (**Cu Model Catalyst Dynamics and CO Oxidation Kinetics,** Y. Bu, J. W. (Hans) Niemantsverdriet, H. O. A. Fredriksson, ACS Catal. 2016, 6, 2867−2876)
(**Preferential Oxidation of CO in H_2 on Cu and Cu/CeO_x Catalysts,** *Y. Bu, J. W. (Hans)Niemantsverdriet, H. O. A. Fredriksson,* J. Catal., 357 (2018) 176–187)

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Supported nanoparticles

(B. White, M. Yin, A. Hall, D. Le, S. Stolbov, T. Rahman, N. Turro, S. O'Brien, Nano Lett. 6 …)-

P…

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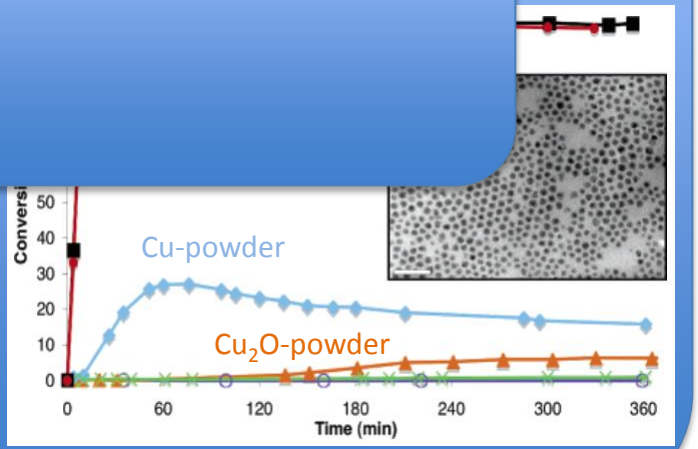

Conclusions

- ***In situ characterization of flat model catalysts – powerful combination***
- ***Oxidation state of catalyst depends on gas composition***
- ***Catalyst activity depends on oxidation state***

Reduction of Cu-Promoted Fe Model Catalysts
Studied by In Situ Indirect Nanoplasmonic Sensing and X-ray Photoelectron Spectroscopy
H. O. A. Fredriksson, E. M. Larsson Lanhammer J. W. (Hans) Niemantsverdriet, J. Phys. Chem. C, 2015, 119, 4085-4094

Cu Model Catalyst Dynamics and CO Oxidation Kinetics
Studied by Simultaneous in Situ UV–Vis and Mass Spectroscopy
Y. Bu, J. W. (Hans) Niemantsverdriet, H. O. A. Fredriksson, ACS Catal. 2016, 6, 2867−2876

Preferential Oxidation of CO in H_2 on Cu and Cu/CeO_x Catalysts
Studied by in situ UV-Vis and Mass Spectrometry and DFT
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Intrinsic Role of the Oxide Phase in Cu-based Model Catalyst Dynamics
Studied by in situ UV-vis and XPS
Y. Bu, C. J. Weststrate, J. W. (Hans) Niemantsverdriet, H. O. A. Fredriksson, ACS Catal. 2016, 6, 7994-8003

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