Optimising methanol production from steel manufacture off-gases

Richard Porter, Ryan Wang, Qiming Wang, Haroun Mahgerefteh,

Department of Chemical Engineering, University College London

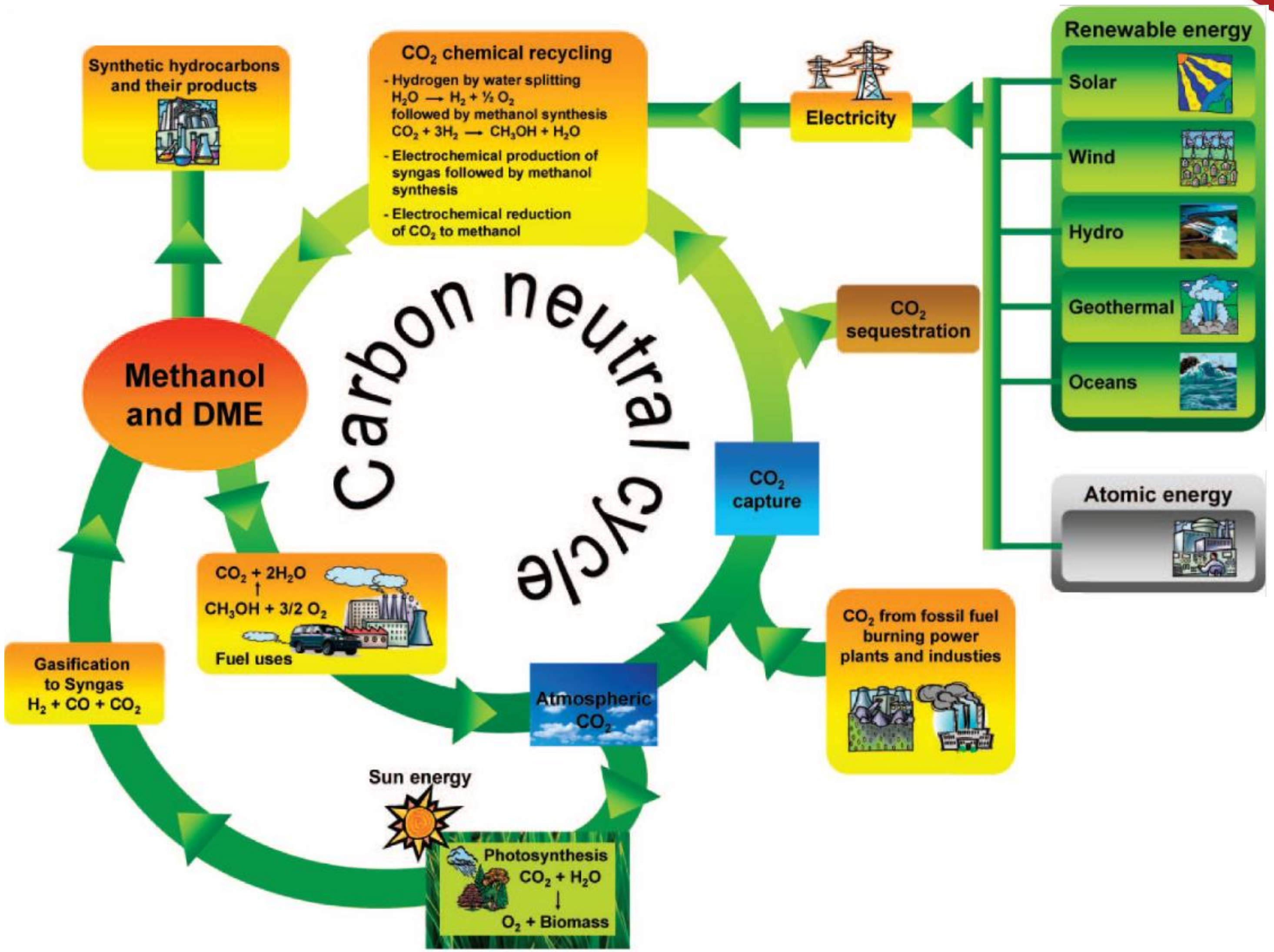
UKCCSRC Autumn Webinar Series

15th September 2020

Introduction

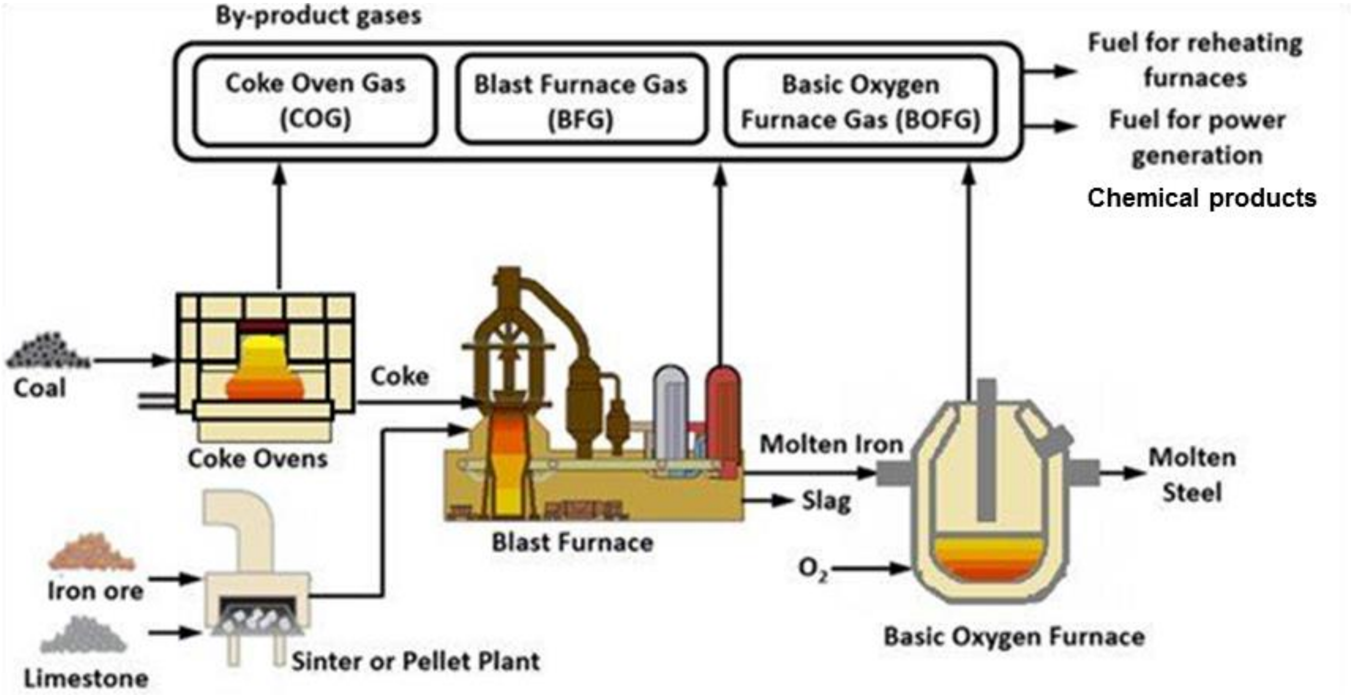
- The iron and steel industry represents the largest energy consuming manufacturing sector in the world
- Average specific emissions are 1.83 tonnes of CO_2 per tonne of steel and global crude steel production reaching 1.8 Gt for the year 2018, up by 4.6% compared to 2017
- CCUS technologies offer the opportunity to substantially reduce the CO_2 footprint of steel mills, which accounts for 5 – 7 % of anthropogenic CO_2 emission.
- Global methanol production in 2016 was around 85 million tonnes
- Methanol is currently primarily from fossil fuel sources - mostly from natural gas but in China up to 67 % from coal
- The demand for methanol is expected to increase as the world shifts away from fossil fuel consumption.

Future methanol economy



G.A. Olah. Beyond Oil and Gas: The Methanol Economy. *Angew. Chem. Int. Ed.* 2005, *44,* 2636~2639.

Off-gases from iron and steel making



Steelworks off-gases properties

	mol%		
Component	**COG**	**BFG**	**BOFG**
CO	6	20	58
CO_2	2	24	20
H_2	63	3	4
N_2	4	53	18
C_2H_6	3	0	0
CH_4	22	0	0
LHV (MJ/Nm^3)	17.5	2.85	7.6
Representative flowrate (kNm^3/hr)	40	366	28

(W. Uribe-Soto *et al.* Renew. Sust. Energ. Rev. 74 (2017) 809-823)

(J. Lundgren *et al.* Appl. Energy Rev. 112 (2013) 431-439)

Methanol from steelworks off-gases: current status

China

Commissioned 2006, Qujing City, Yunnan Province, 80 kt/yr pure methanol.

- As of 2019, ~17% of the Chinese methanol capacity is based on Coke Oven Gas

(IHS Markit. Methanol from coke-oven gas. PEP. Review 2019)

Germany

2018: Thyssenkrupp pilot-scale production of methanol from steelworks gases and electrolysis derived hydrogen in Carbon2Chem project

Main catalytic reactions of methanol synthesis

Hydrogenation of carbon monoxide

1. $CO + 2H_2 \rightleftharpoons CH_3OH$ $\Delta H_R = -90.55$ kJ/mol

Hydrogenation of carbon dioxide

2. $CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$ $\Delta H_R = -49.43$ kJ/mol

Reverse water-gas shift

3. $CO_2 + H_2 \rightleftharpoons CO + H_2O$ $\Delta H_R = +41.12$ kJ/mol

Project objectives

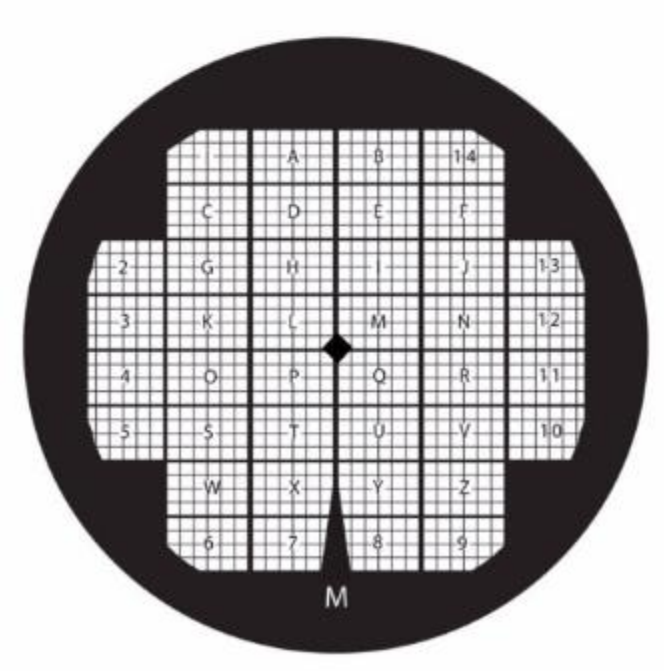
1. To investigate the effect of feed gas $CO/CO_2/H_2$ ratio and stream impurities relevant to residual steel gases including N_2, Ar, CH_4 NH_3 & H_2O on the methanol production process using selected catalysts
2. To study catalyst degradation, including morphology and composition following exposure to the BFG reaction environment using a range of analytical techniques
3. To construct and validate a catalytic reaction mechanism describing methanol synthesis from BFG
4. To assess the impact of catalyst and chemical reactor selection on methanol synthesis from BFG
5. To perform techno-economic simulations for assessing the cost of methanol production from BFG

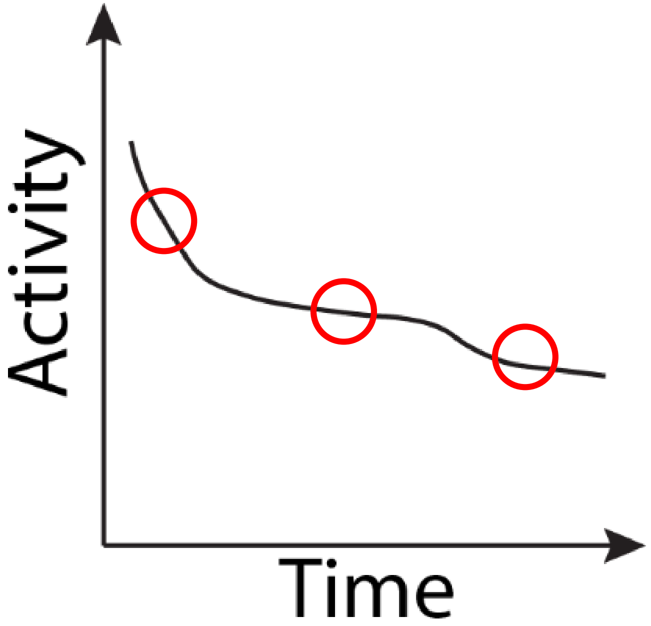
Revealing Cu/ZnO catalysts deactivation *via* identical location imaging (Preliminary result)

Feng Ryan Wang

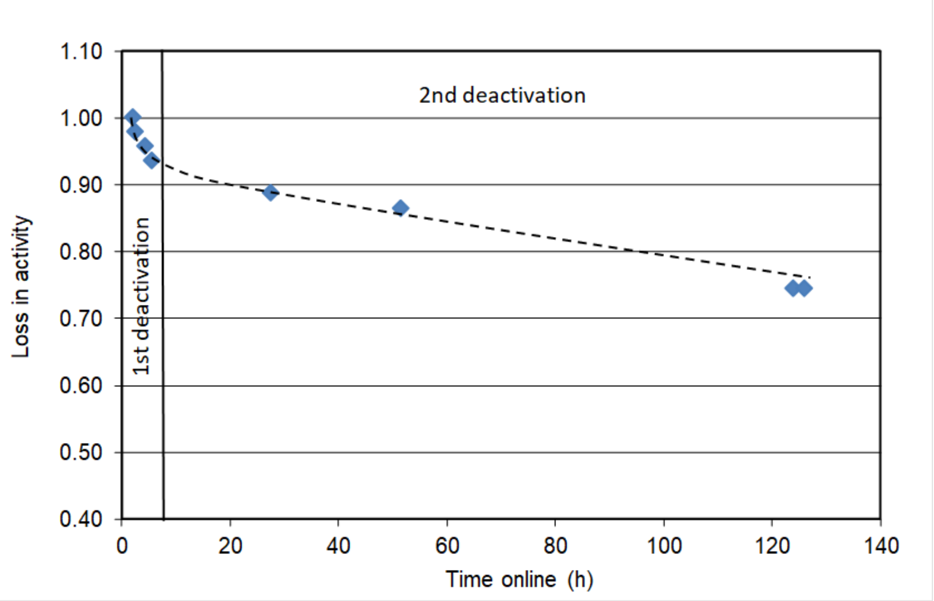
University College London

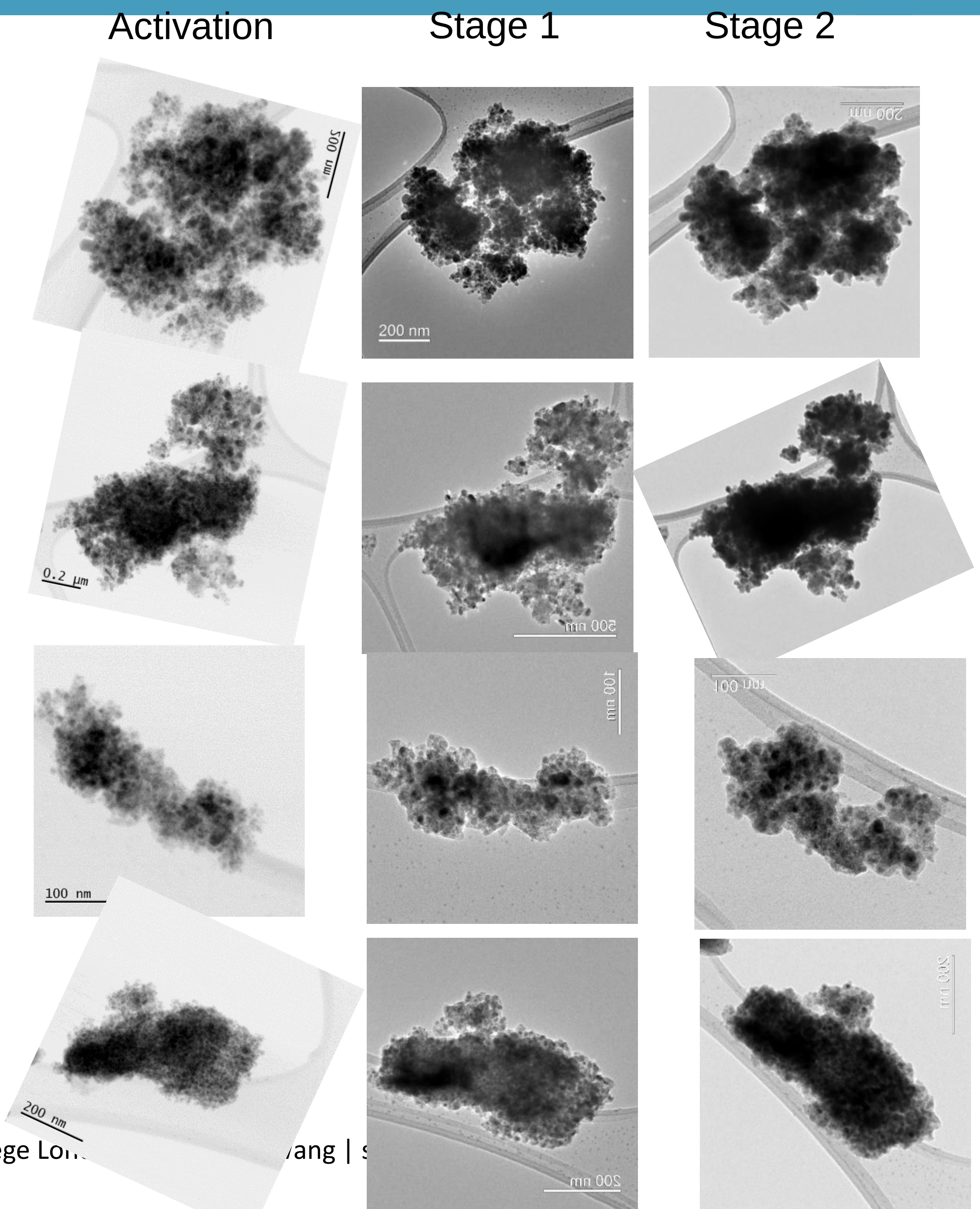
Degradation of catalysts: the Identical location study





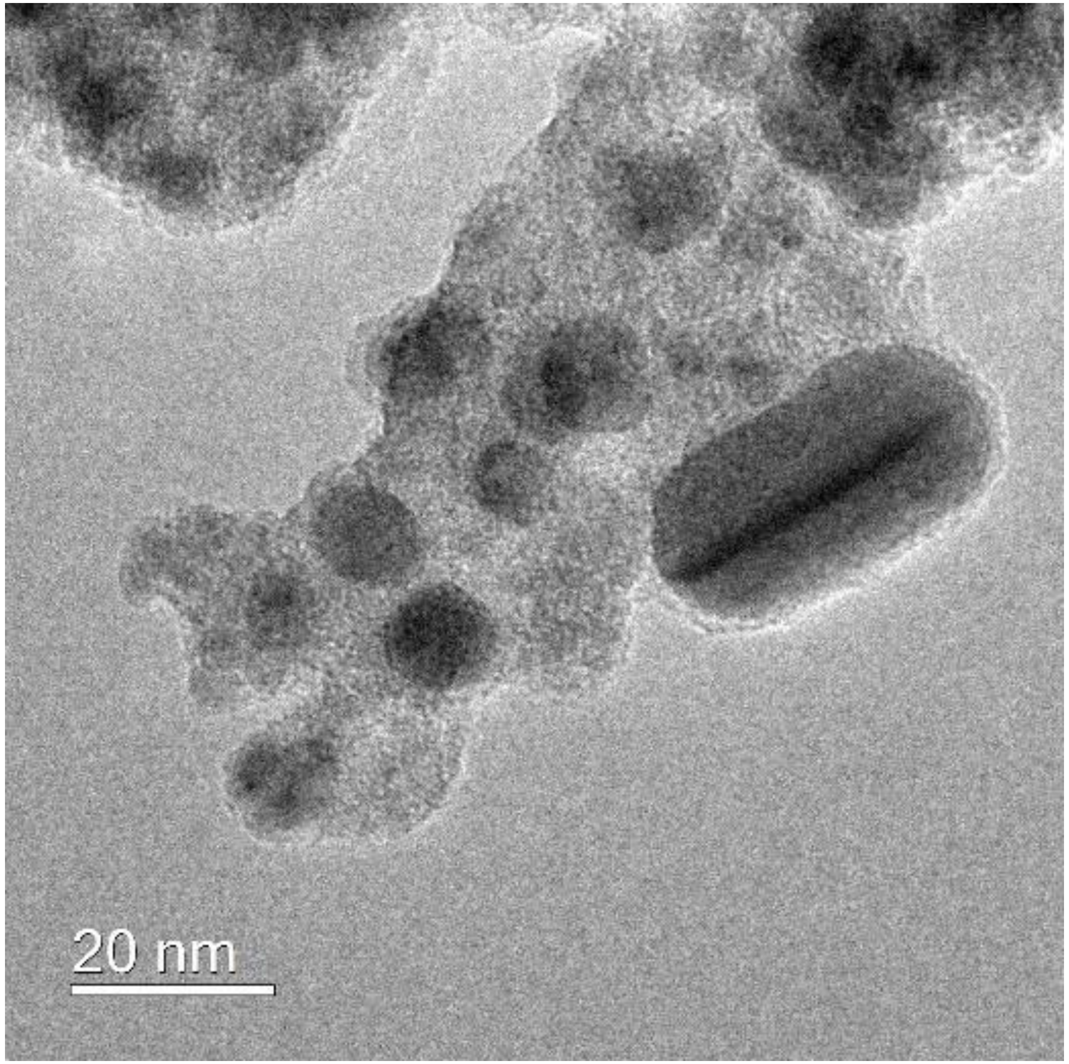
All the particles are in the original location



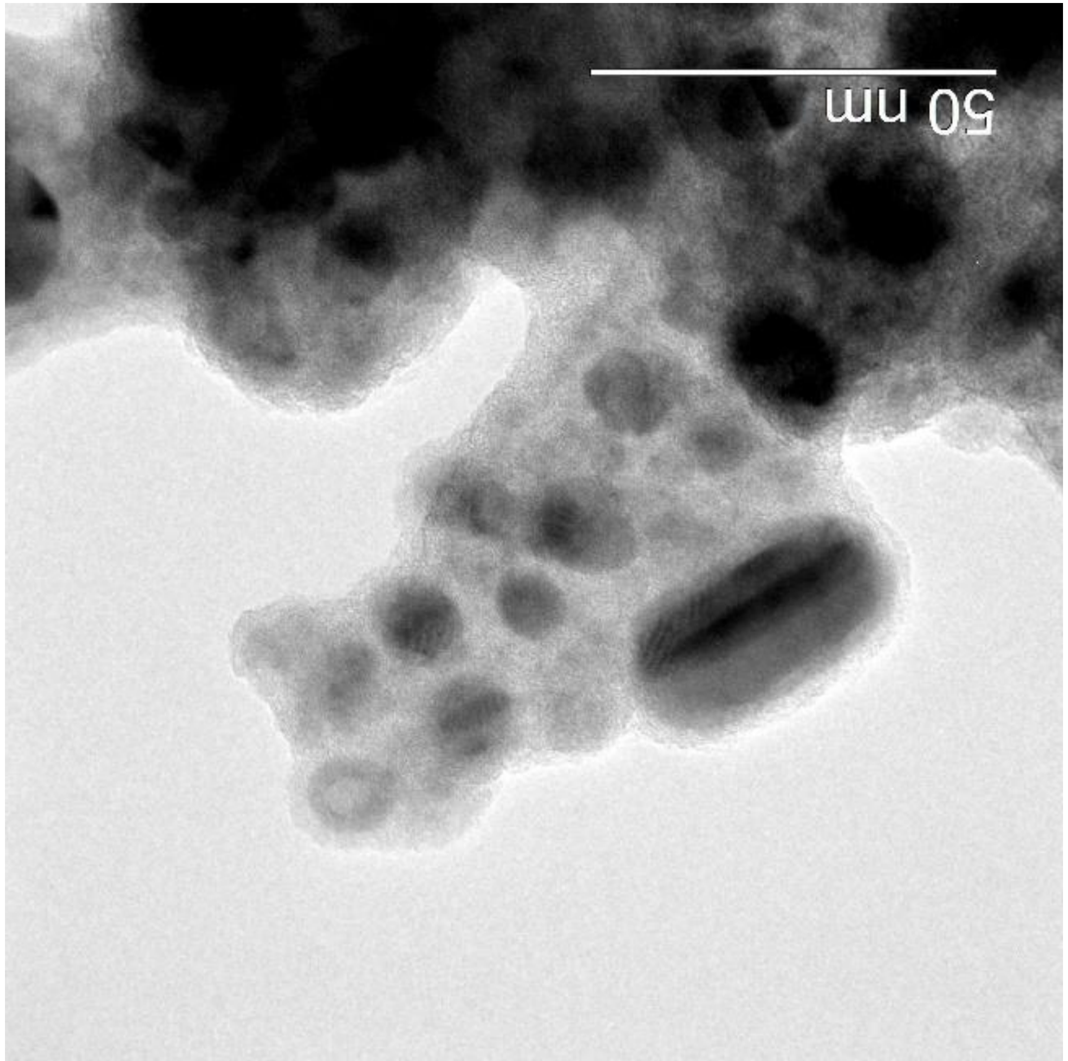


Formation of a thin layer of ZnO

Stage 1

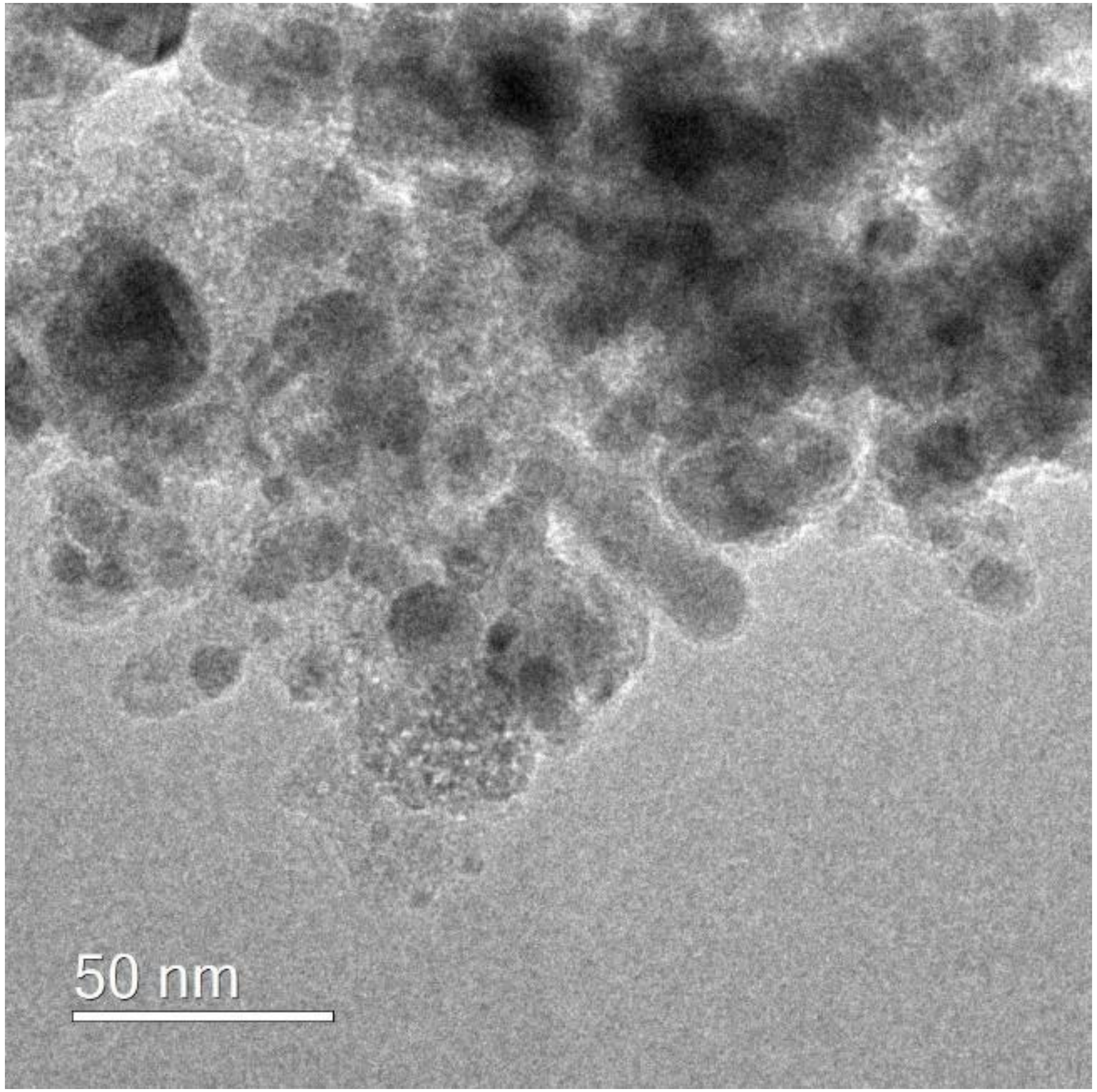


Stage 2

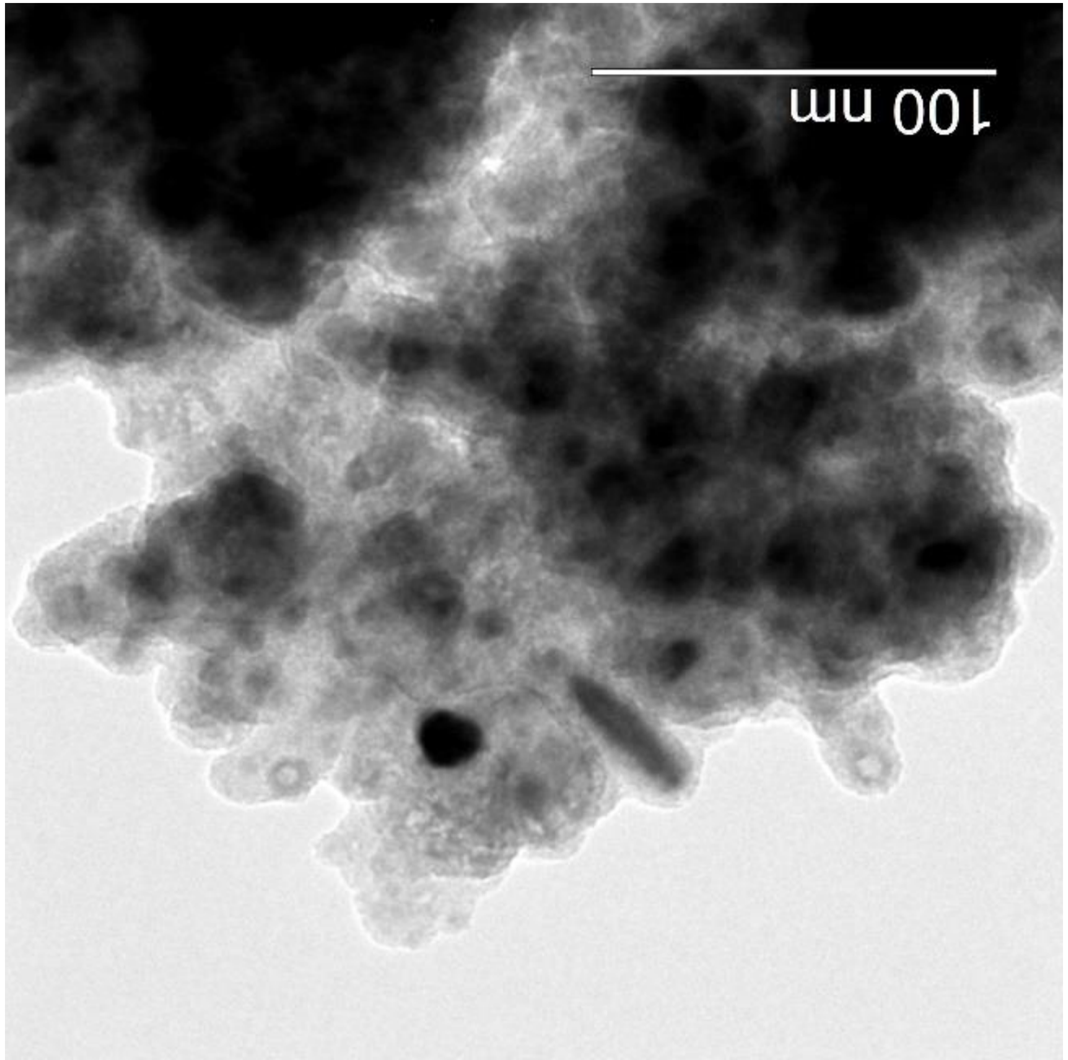


Formation of a thin layer of ZnO

Stage 1

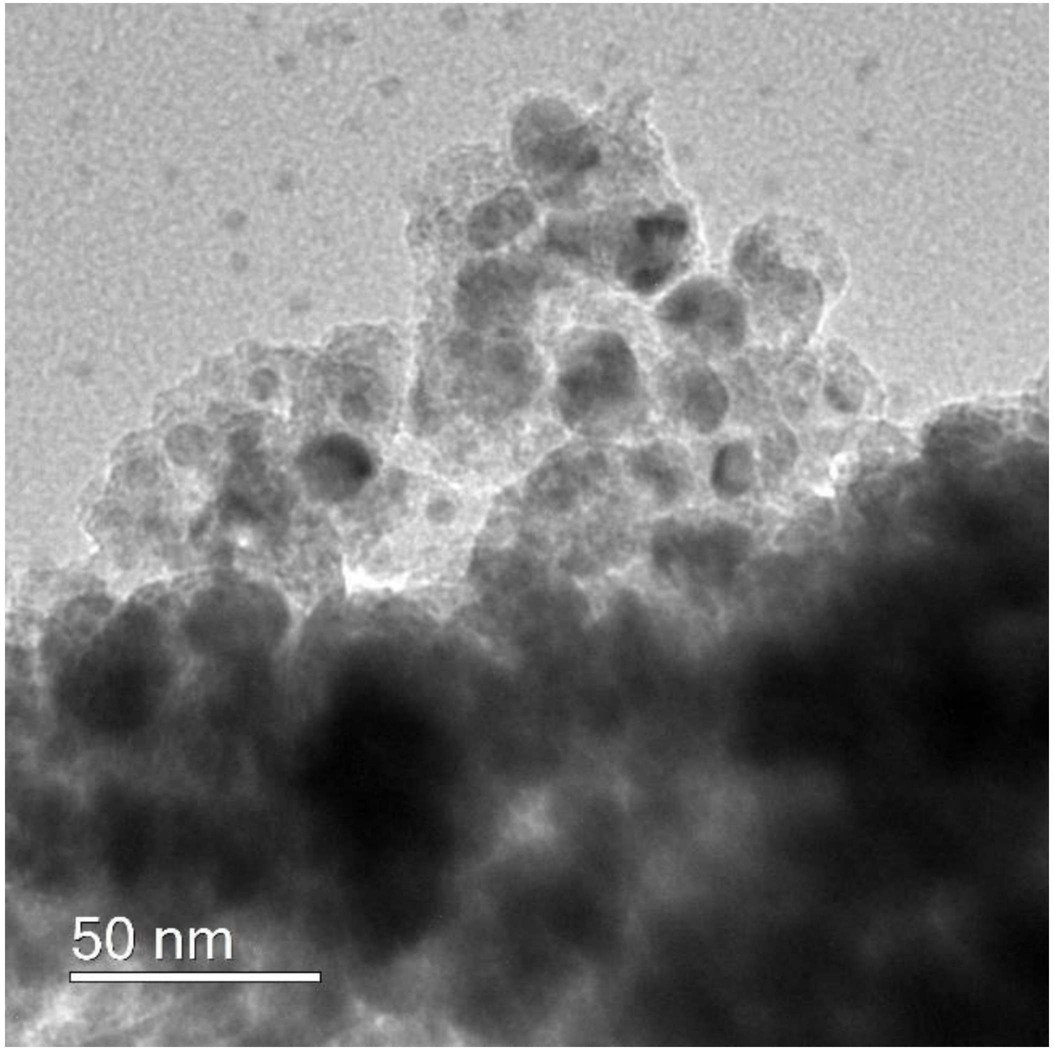


Stage 2

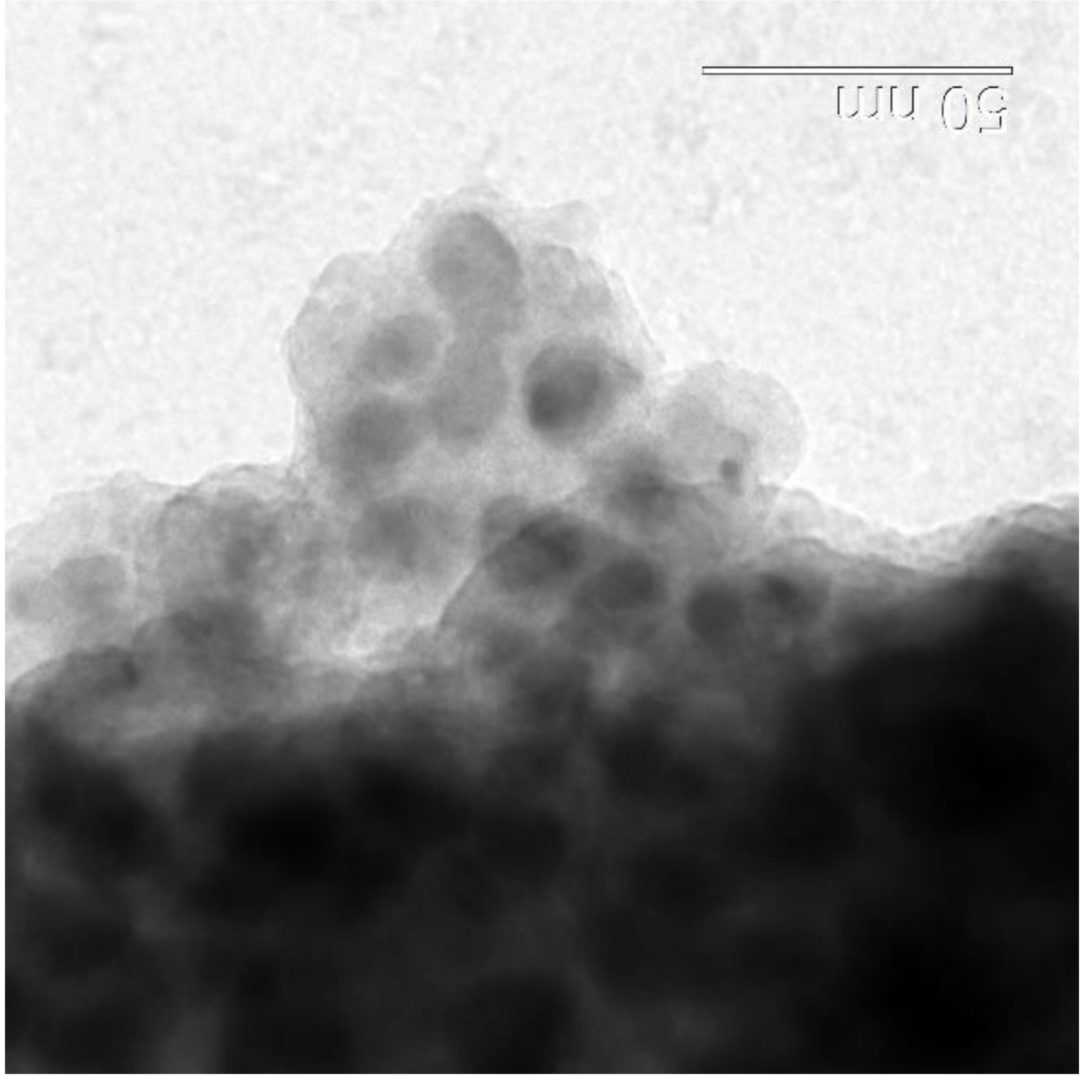


Formation of a thin layer of ZnO

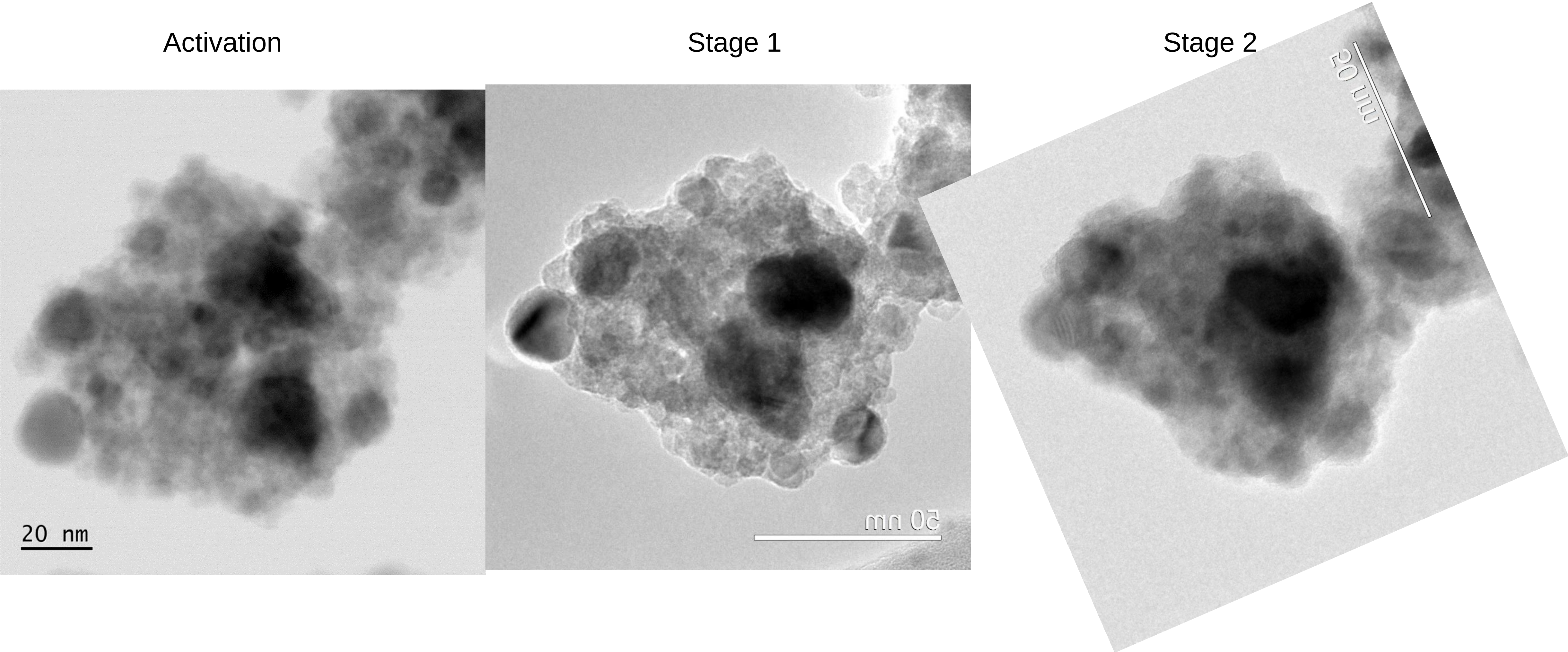
Stage 1



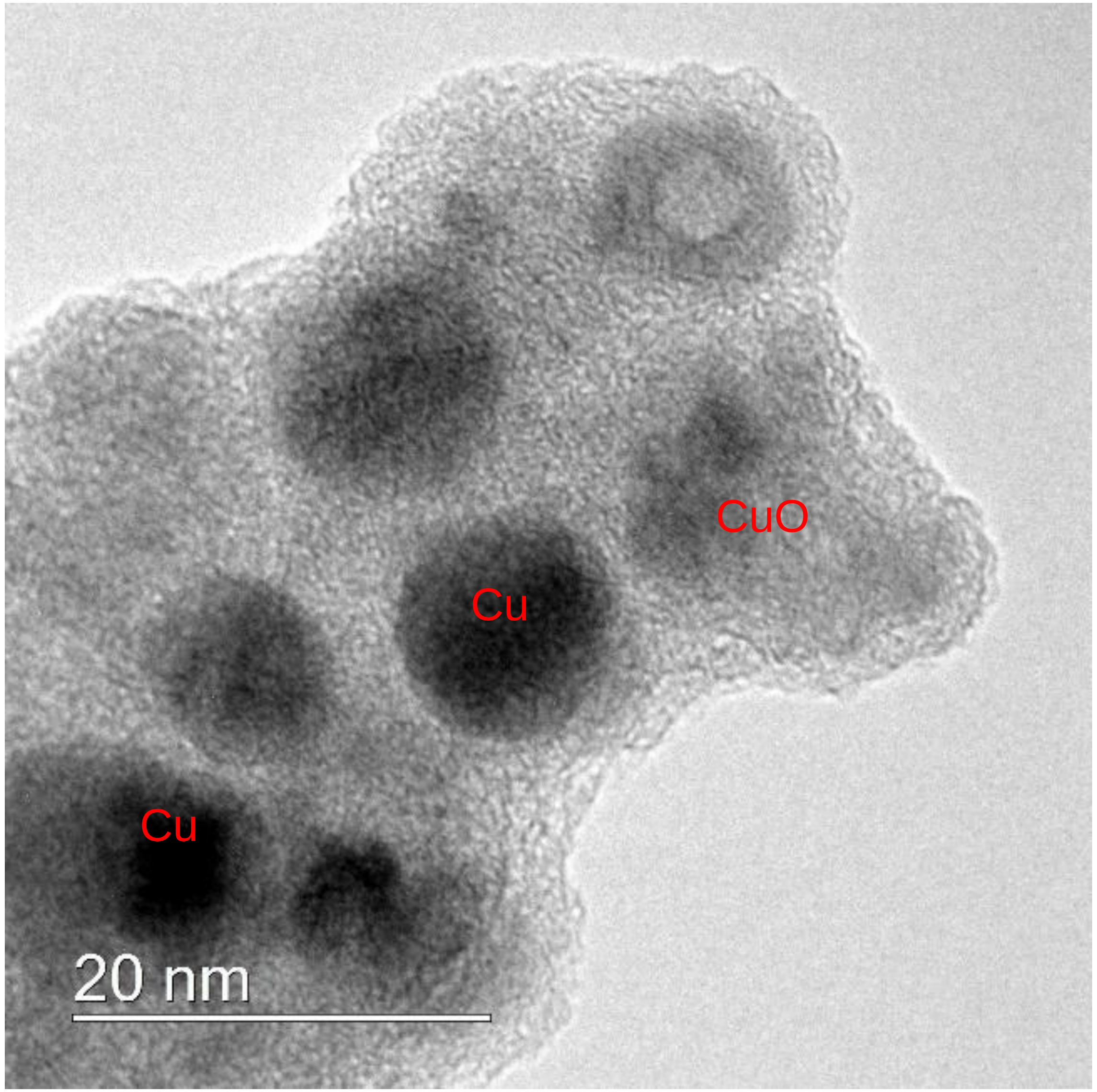
Stage 2

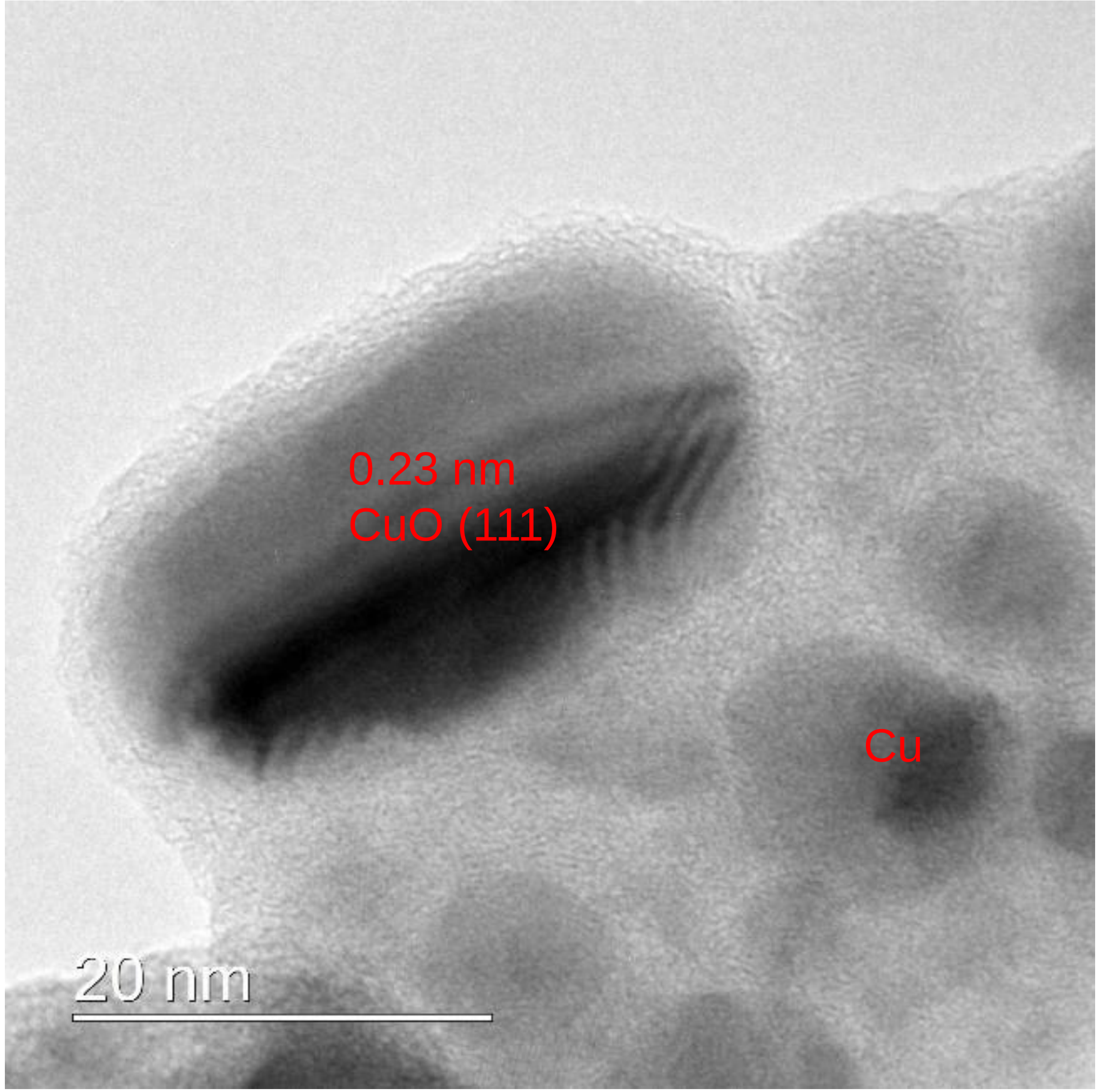


Tendency of aggregation

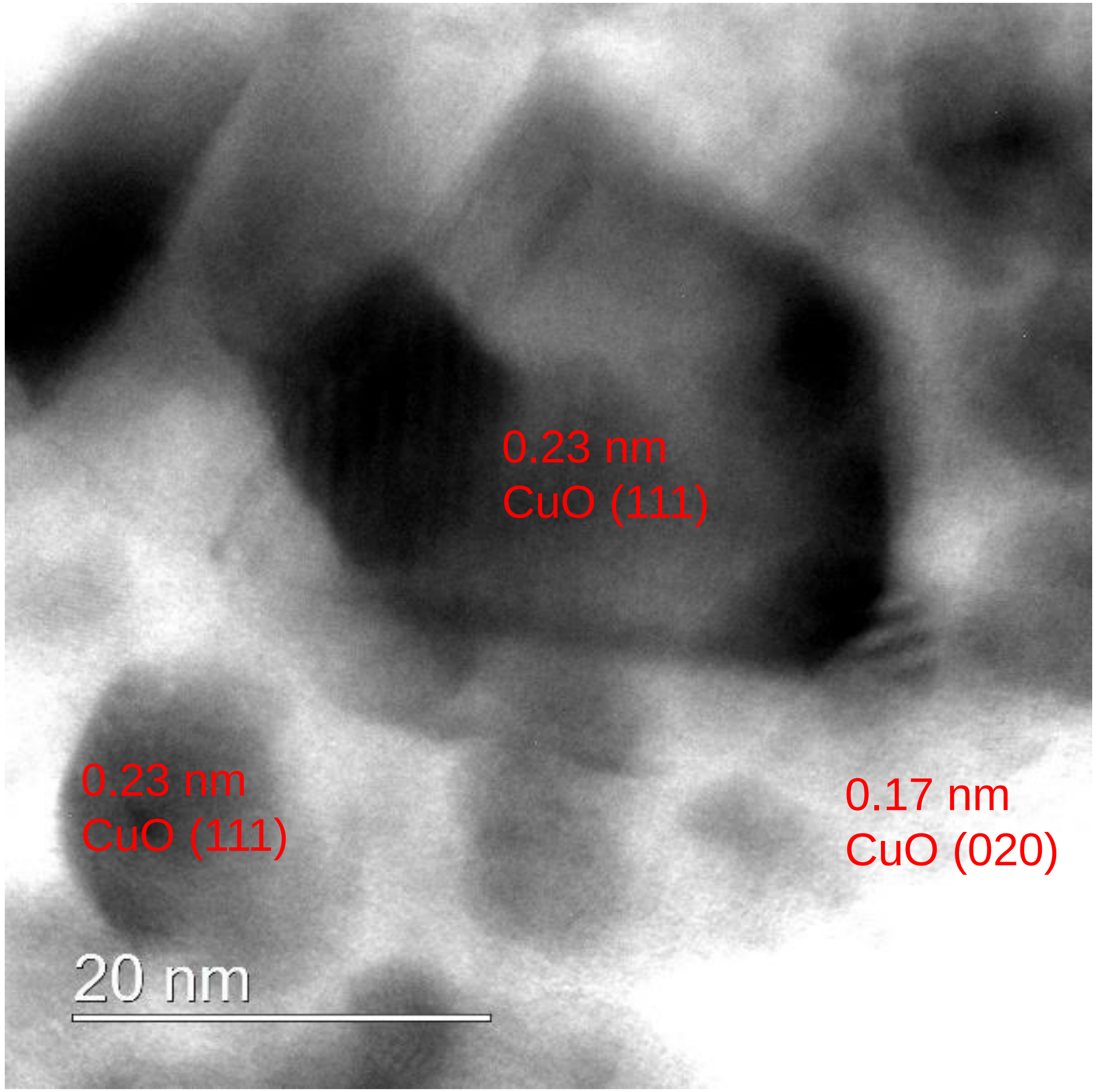


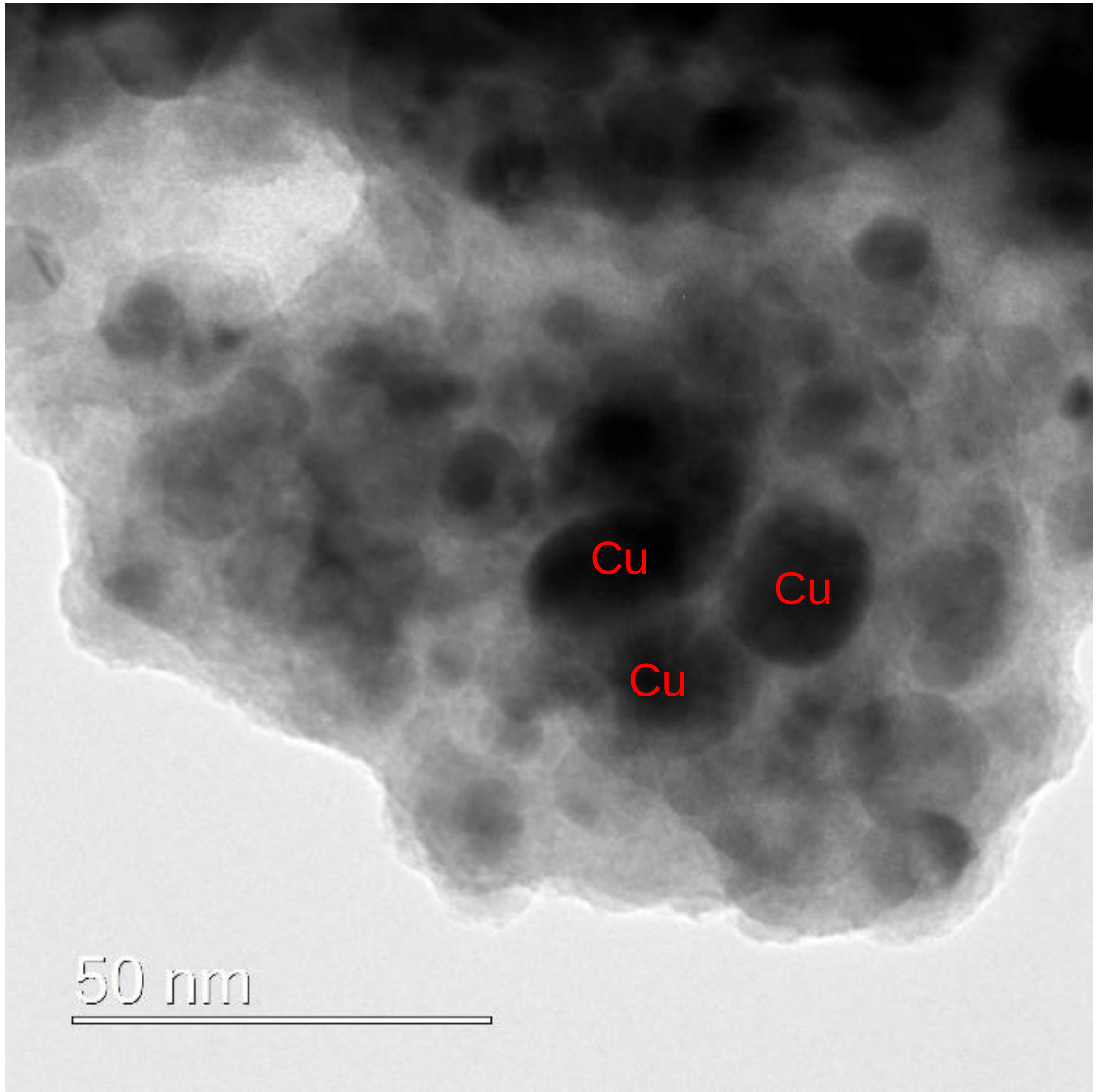
Formation of Cu, Cu2O and CuO





Formation of Cu, Cu_2O and CuO





Conclusion

1. The concept of IL imaging is proven across different time and length scale at very hash chemical condition

2. Formation of a thin amorphous layer around Cu nanoparticles. According to literature they are ZnO and are responsible for the CO/CO2 activation. However, it is still not clear on their role in deactivation.

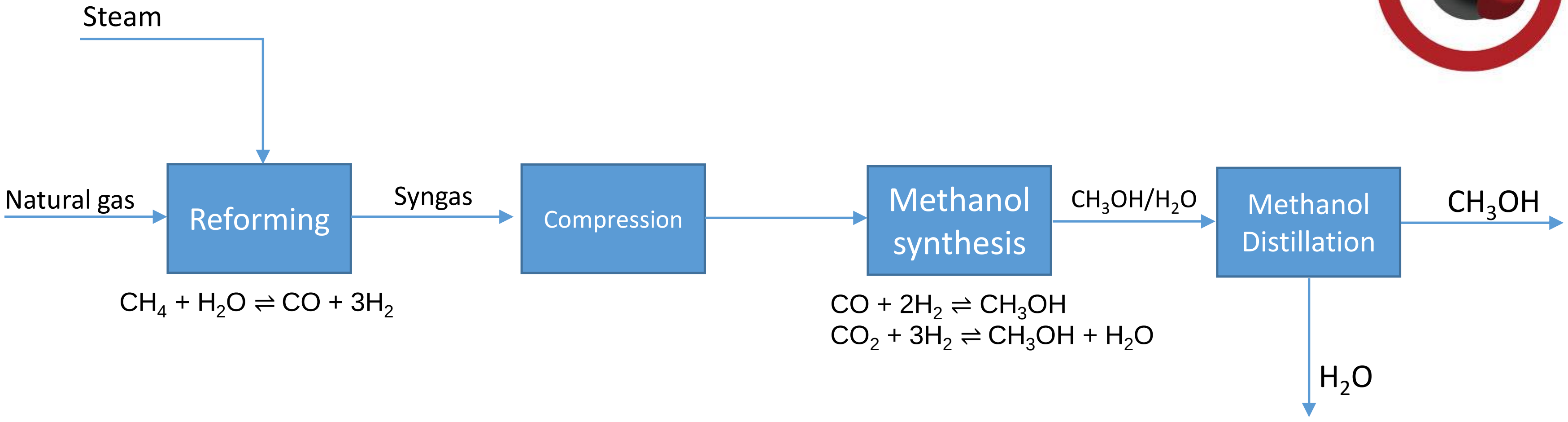
3. Cu nanoparticles are spherical with 5 nm diameter, whereas CuO nanoparticles are in irregular shapes with slight bigger size.

4. It is not clear the aggregation is due to Cu or ZnO.

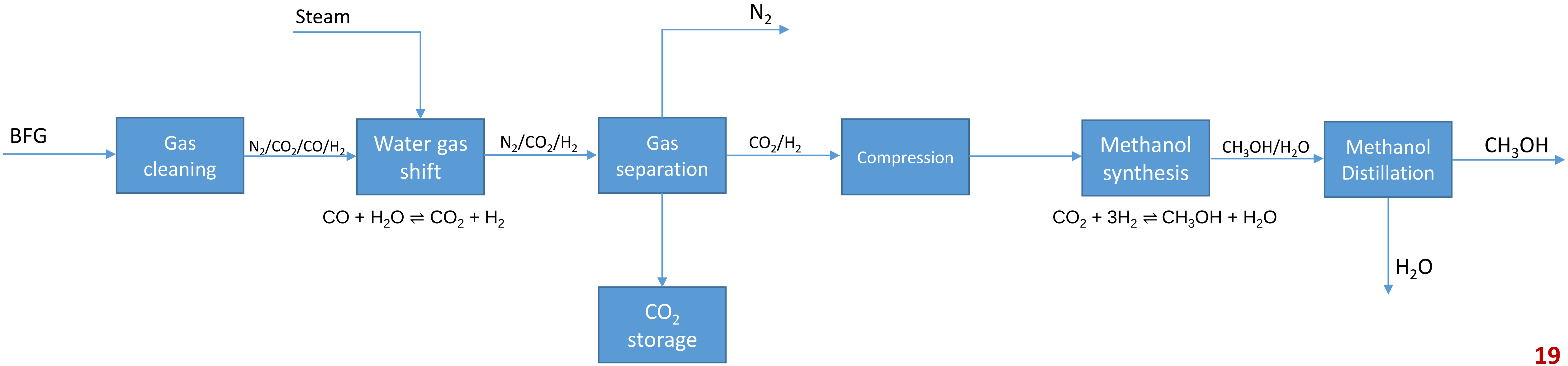
5. Quantification of Cu, Zn and their oxidation states is possible with the X-ray nanoprobe.

Design and simulation of full-scale BFG-to-methanol process

Conventional methanol production process



BFG-to-methanol process based on direct CO_2 hydrogenation



Process advantages/disadvantages of direct CO_2 hydrogenation BFG-to-methanol synthesis route

Advantages

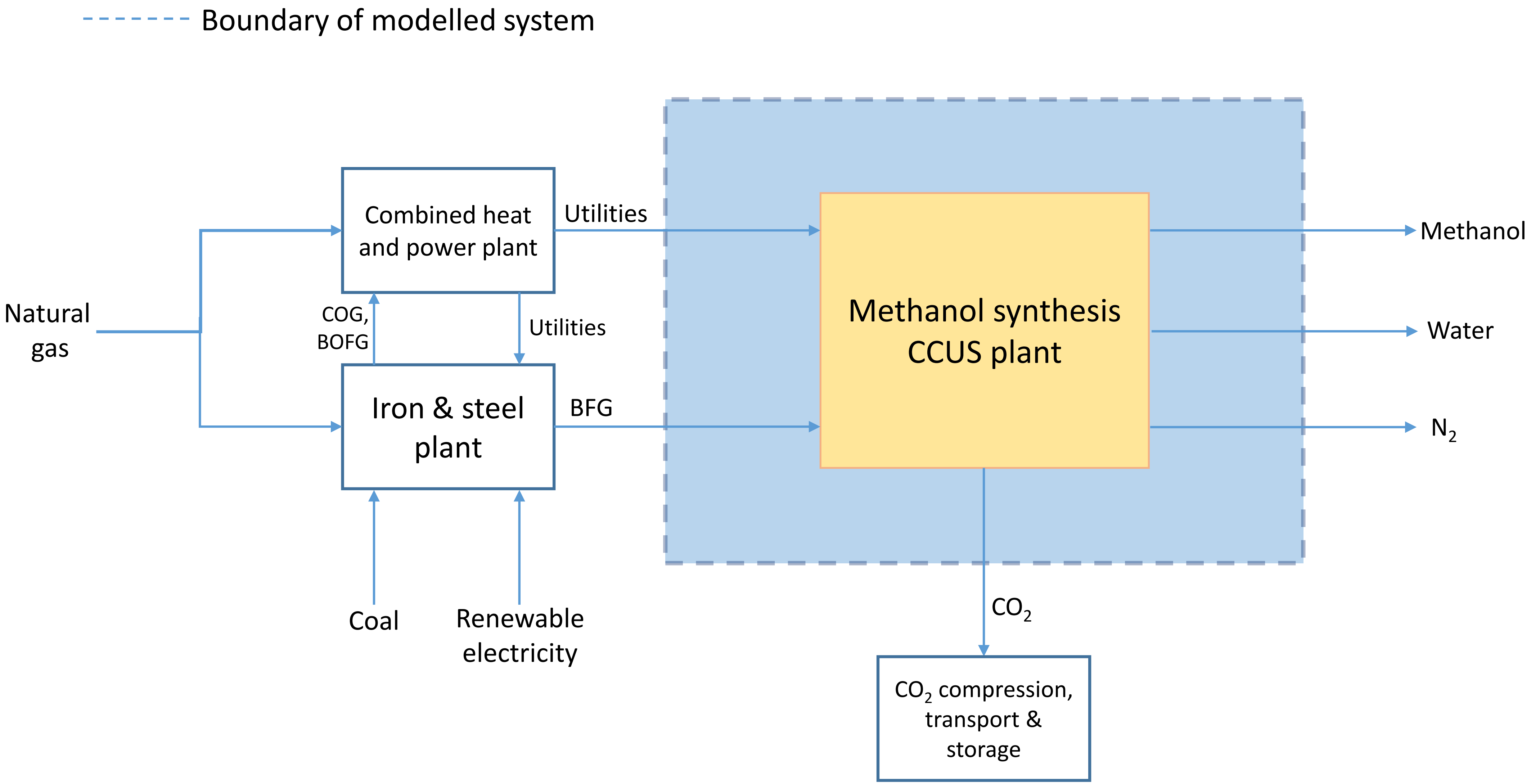
- Avoids difficult N_2 / CO separation
- Synthesis reaction impurities (typically higher alcohols, esters, ethers and ketones) are limited to water and dissolved CO_2 in crude methanol
- Allows for only a single methanol distillation unit
- Less intense exotherm compared to syngas reaction
- Allows the use of tube cooled reactor with lower cost, higher efficiency and relative simplicity of operation
- Avoids use of multiple reactors in series which may be required with adiabatic
- Improved the heat distribution with the reactor helps to prevent catalyst sintering

Disadvantages

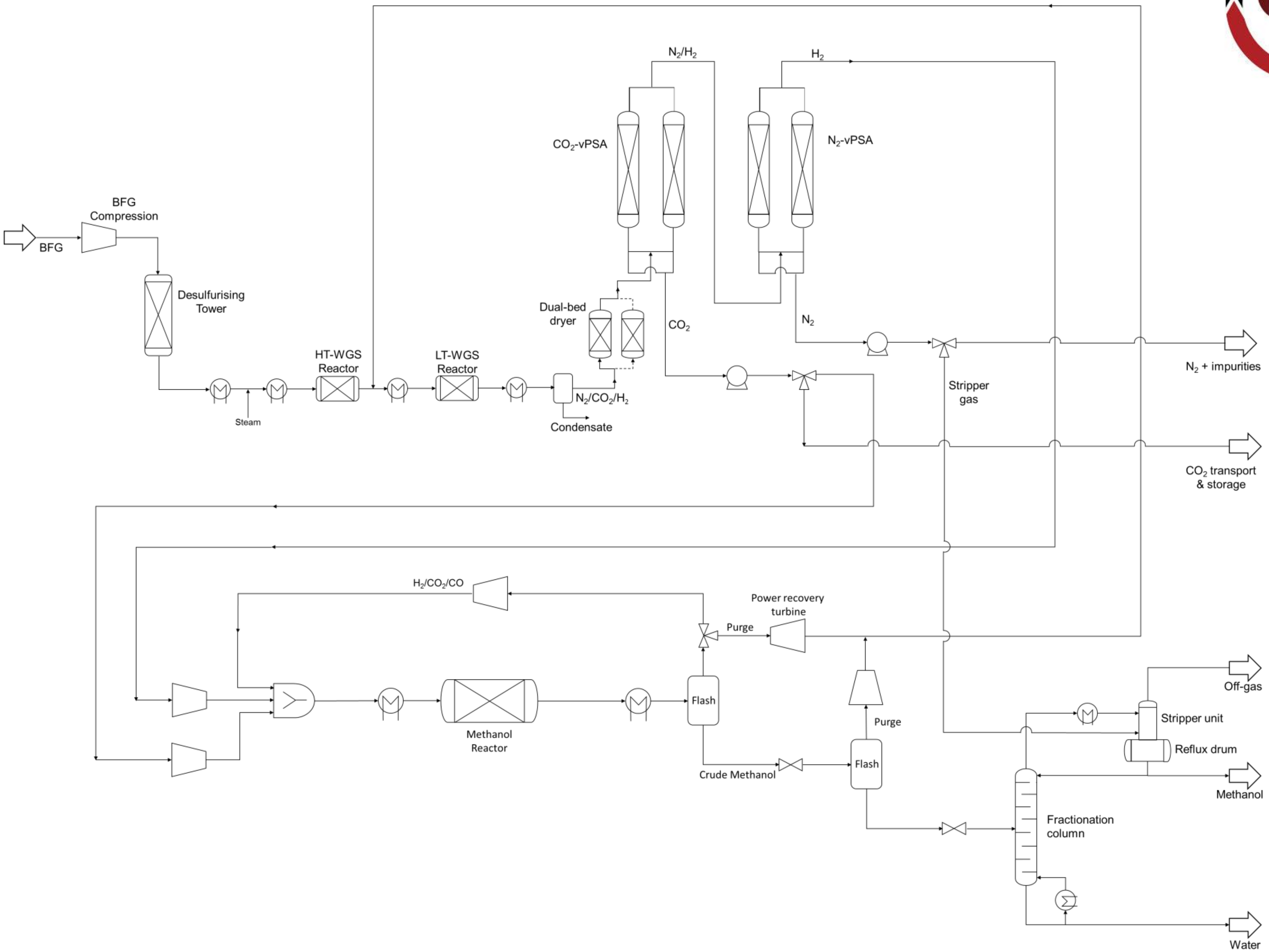
- Some heat may be lost in the water gas shift process
- CO_2-syngas is less reactive than CO-syngas which may lead to a larger reactor
- More water produced due to the reaction stoichiometry

(D.S. Marlin, E. Sarron, Ó. Sigurbjörnsson. 2018. Process Advantages of Direct CO_2 to Methanol Synthesis. Frontiers in Chemistry 6.)

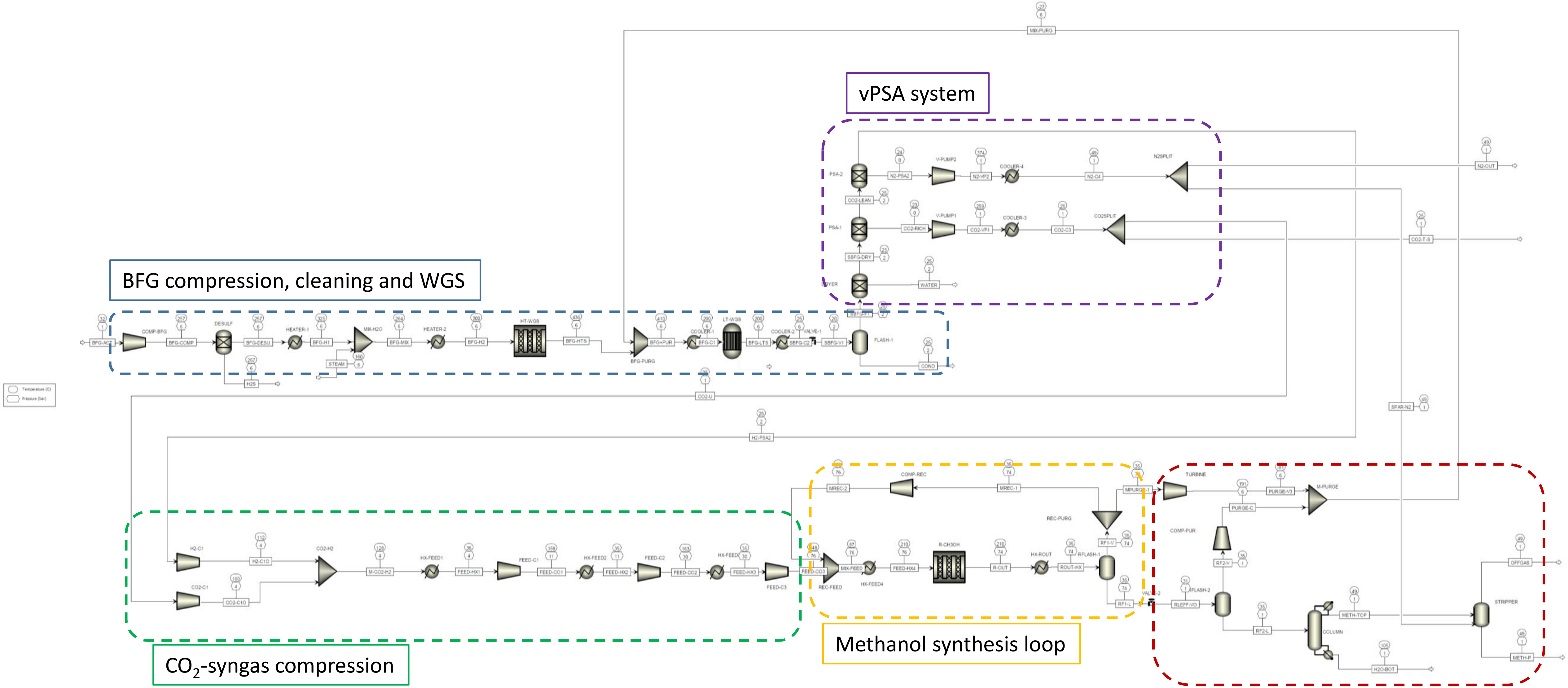
System boundary of the CCUS BFG-to-methanol plant



Process flow diagram BFG-to-methanol process



Aspen Plus flowsheet - BFG-to-methanol process



vPSA system

BFG compression, cleaning and WGS

CO_2-syngas compression

Methanol synthesis loop

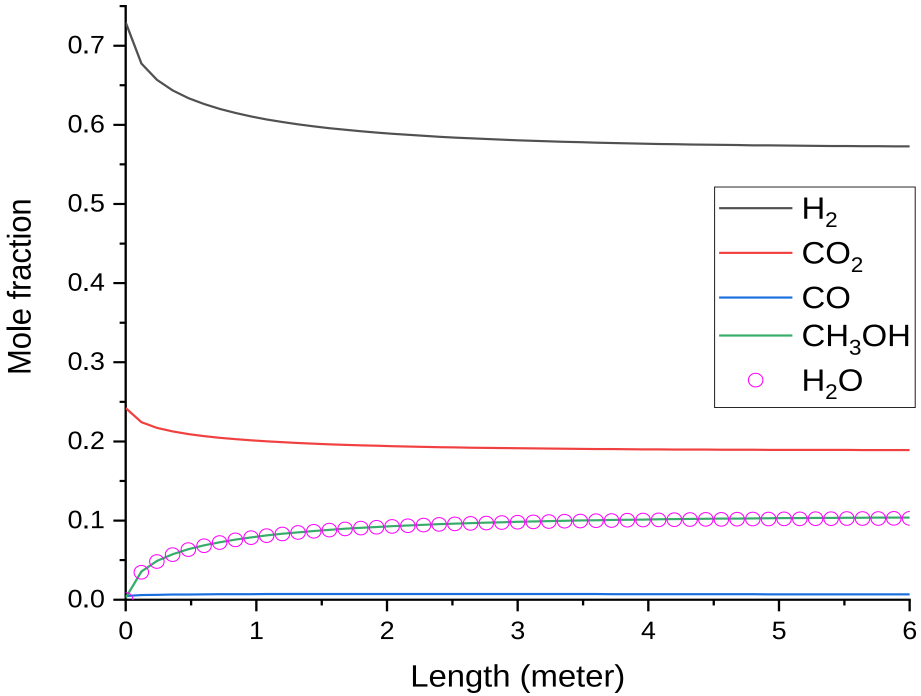
Methanol purification

Methanol reactor kinetic model

- Isothermal plug flow reactor using a Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model† is used
- Two reactions are modelled: CO_2 hydrogenation and RWGS

Methanol reactor operating conditions
Catalyst
material: $Cu/ZnO/Al_2O_3$
density: 1.3 kg/m^3
bed voidage: 0.41
catalyst loading: 20,865 kg
Reactor
bed volume: 16.05 m^3
gas hourly space velocity: 22,898 hr^{-1}
Operating conditions
temperature: 210 °C
pressure: 76 bar
mass flow: 124.2 tonne/hr

Chemical species profiles over reactor length



CO_2 conversion per pass = 36%

---

† Vanden Bussche and Froment, Journal of Catalysis 161, 1–10, 1996

Overall process mass balance

Component	BFG-in	Steam-in	Sulfur-out (tonne/hr)	Condens.-out	Dryer-out	N_2-out	CO_2_T&S-out	Offgas-out (tonne/hr)	Bottoms-out	Methanol-out
CO_2	118	-	-	6.61×10^{-3}	-	48	146	0.972	-	2.51×10^{-2}
CO	72.4	-	-	-	-	0.7	1.14×10^{-2}	1.03×10^{-2}	-	7.39×10^{-6}
N_2	145	-	-	4.10×10^{-6}	-	141	2.30	2.07	-	1.36×10^{-3}
H_2	0.947	-	-	-	-	1.09	0.118	1.60×10^{-2}	-	5.71×10^{-6}
H_2O	-	107	-	57.7	3.19	-	-	-	14.6	1.32×10^{-3}
CH_3OH	-	-	-	3.52×10^{-2}	-	-	0.118	2.79	2.55×10^{-3}	22.7
H_2S	3.72×10^{-3}	-	3.72×10^{-3}	-	-	-	-	-	-	-
CH_4	4.21×10^{-3}	-	-	-	-	4.08×10^{-2}	6.66×10^{-4}	5.99×10^{-4}	-	1.75×10^{-6}
O_2	0.629	-	-	-	-	0.61	9.96×10^{-3}	8.96×10^{-3}	-	1.82×10^{-5}
HE	4.37×10^{-4}	-	-	-	-	4.24×10^{-4}	6.92×10^{-6}	6.24×10^{-6}	-	-
AR	2.71	-	-	1.79×10^{-6}	-	2.62	4.28×10^{-2}	3.85×10^{-2}	-	7.67×10^{-5}

Total ~340 tonnes/hr

96% purity
85% overall capture
~75% of post-shift CO_2 to storage

99.9% purity
~200,000 tonnes/yr

Overall process energy balance

Process units	Energy consumption (MW)
Compressors	77.9
Energy recovery turbine	-0.89
Heaters	23.8
Coolers	-188.0
Methanol reactor	-13.6
Distillation column:	
Condenser	-12.0
Reboiler	12.8

Summary

- CCUS processes will play an important role in CO_2 mitigation by capturing the emitted CO_2 and using it to make chemical products that otherwise would be made from fossil fuels.
- Hydrogen produced from BFG where a large part of CO_2 is captured and geologically stored may be considered ‘carbon free’
- The analysis presented here considers a promising CCUS technology for the iron & steel industry: BFG-to-CH_3OH based on direct hydrogenation of CO_2
- A full-scale conceptual design has been simulated in Aspen Plus in order to obtain the needed mass and energy balances to evaluate the technological, economic and environmental criteria

Acknowledgements

This work was supported by the UK CCS Research Centre through the 2018 Flexible Funding Call.

In-kind contributions from Tata Steel UK, Swerim AB and Johnson Matthey are gratefully acknowledged.