

# Deactivation of supported Ru catalysts during the Selective CO Methanation (SelMeth): Separating structural and adlayer effects

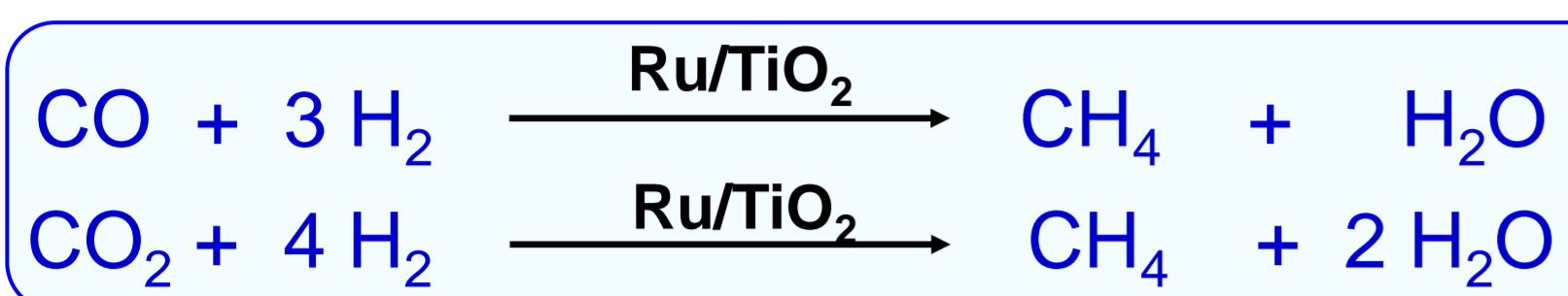
Ali M. Abdel-Mageed<sup>1</sup>, D. Widmann<sup>1</sup>, Sine E. Olesen<sup>2</sup>, I. Chorkendorff<sup>2</sup> and R. J. Behm<sup>1</sup>

<sup>1</sup>Institute of Surface Chemistry and Catalysis, Ulm University, D- 89081 Ulm, Germany

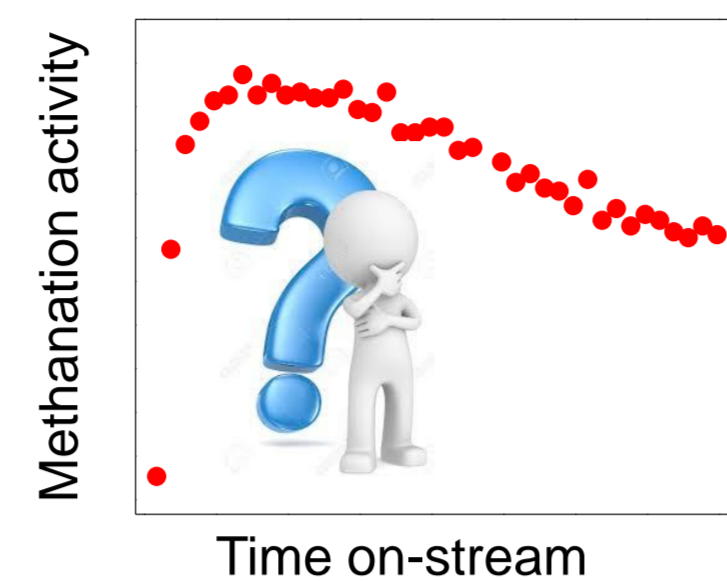
<sup>2</sup>Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark



## Motivation



- Electronic changes (oxidation state Ru)? [1]
- Geometric changes (Ru particle size / shape)?
- Surface poisoning (e.g., formates, carbonates)?



Deactivation of Ru/TiO<sub>2</sub>

## Experimental

### Catalyst

Ru/TiO<sub>2</sub>, wetness impregnation, 121 m<sup>2</sup> g<sup>-1</sup>; 2.2 wt.% Ru [2]

### Kinetics

Flow micro-reactor, 1.0 atm @ 190 °C, space velocity 5000 h<sup>-1</sup>

### EXAFS

XAFS beamline-Elettra Synchrotrone: Ru K-edge (22117eV) [3]

### HR-TEM

Philips CM 20 microscope (200 kV), ≥ 700 Ru NPs analyzed [2]

### DRIFTS

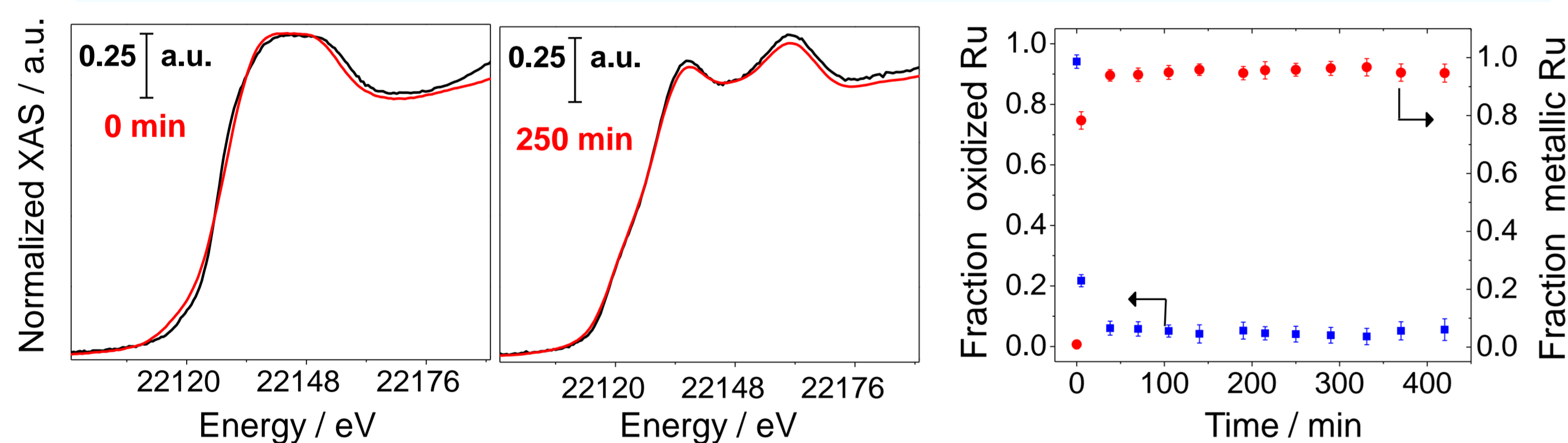
In situ reaction cell (Harricks, HV-DR2), Magna 6700 spectrometer [2]

Reaction reformates	Reaction gas ( 41.6 Nml min <sup>-1</sup> )		
	CO / ppm	CO <sub>2</sub> / %	N <sub>2</sub> / %
SR-ref 6000	6000	15.5	3.0, balance H <sub>2</sub>
ID-ref 6000	6000	0.0	3.0, balance H <sub>2</sub>

## Results

### (1) Electronic changes

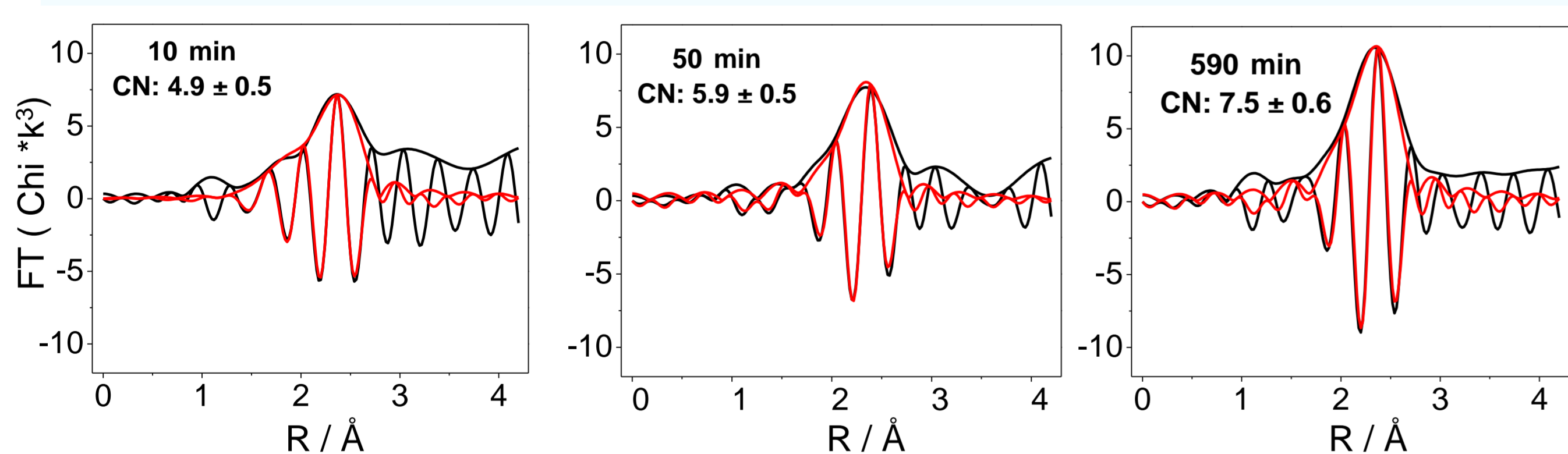
Linear combination analysis (LCA: red line) of XANES spectra (black line) with RuO<sub>2</sub> and Ru foil during reaction in ID-ref 6000 at 190°C



- RuO<sub>2</sub> decreased to < 5% in 70 min: metallic Ru dominant during reaction
- ⇒ Ru oxidation state not related to deactivation of Ru/TiO<sub>2</sub>

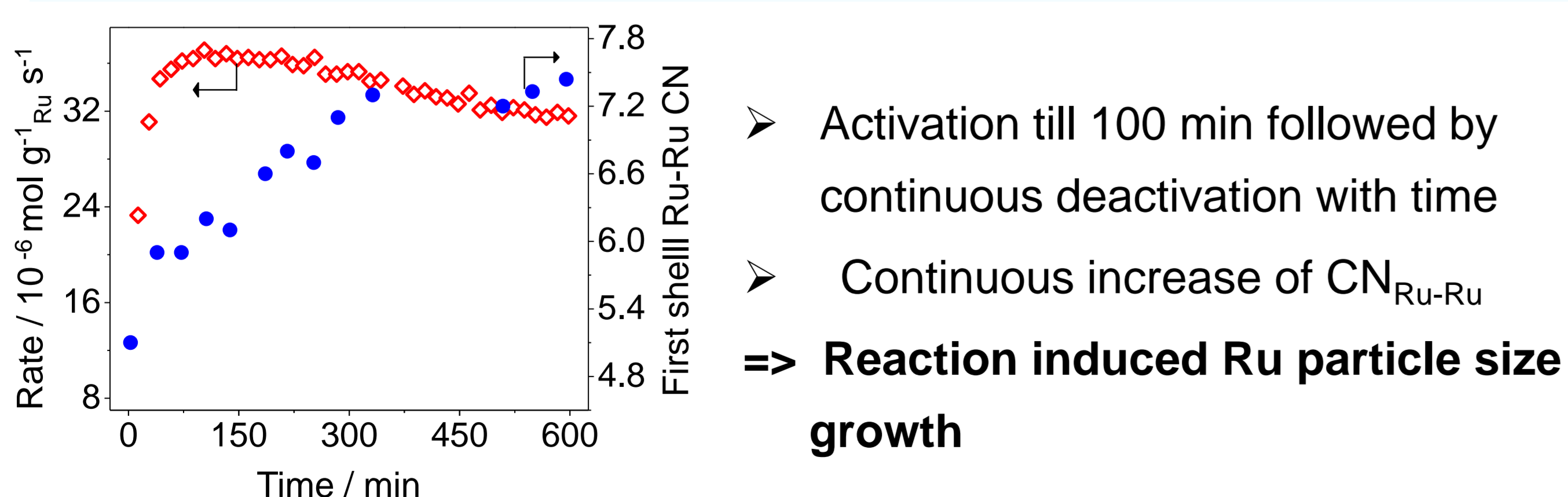
### (2) Geometric changes and deactivation

Fourier transform of EXAFS spectra during reaction in ID-ref 6000 at 190°C



- Small contribution of Ru-O shell in FT disappeared completely after 40 min
- ⇒ Sintering of metallic Ru NPs / shape changing during reaction?

Grow of Ru NPs during selective CO methanation / deactivation in ID-ref 6000

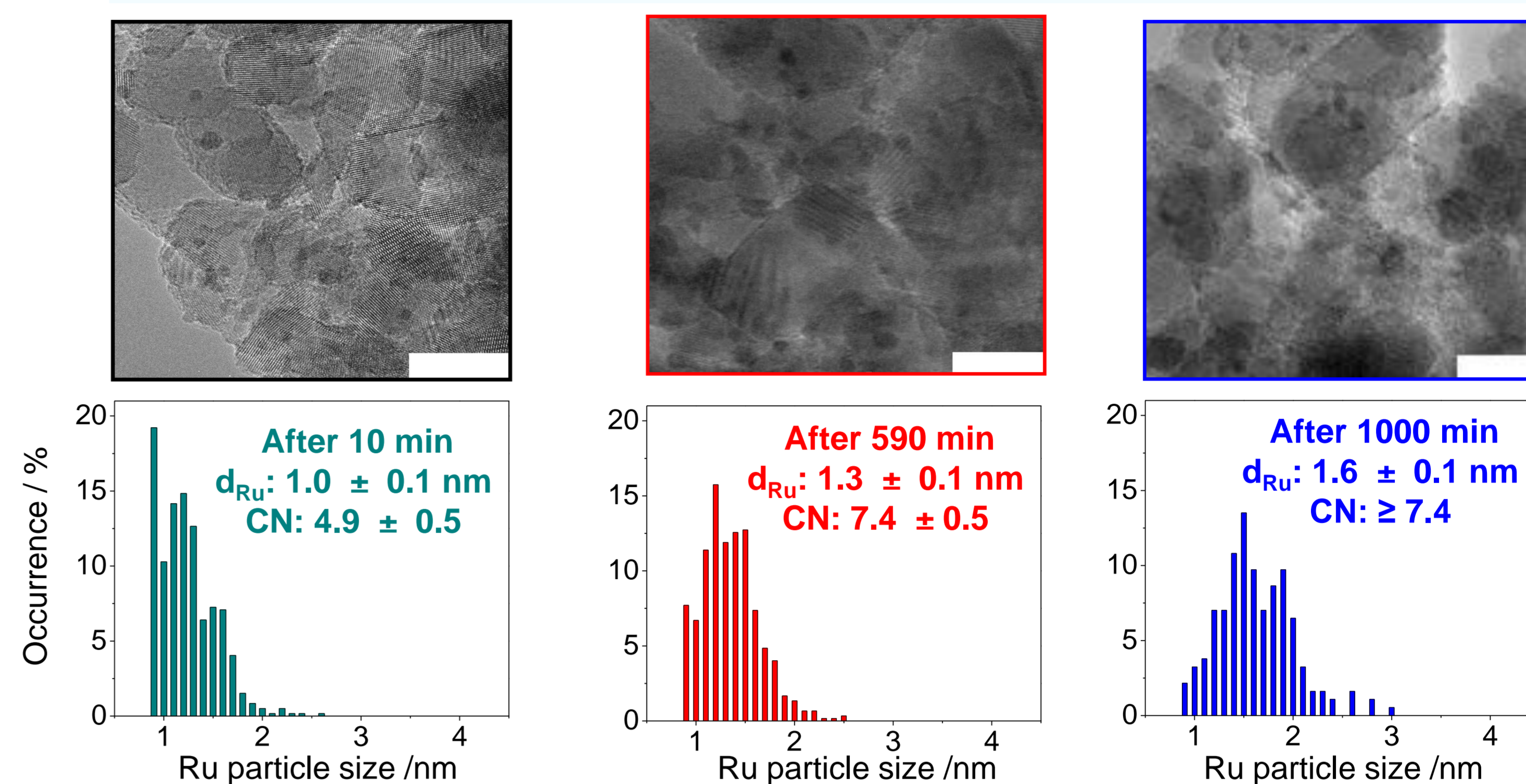


- Activation till 100 min followed by continuous deactivation with time
- Continuous increase of CN<sub>Ru-Ru</sub>
- ⇒ Reaction induced Ru particle size growth

## References

- [1] S. Tada and R. Kikuchi, *Catal. Sci. Technol.* 5 (2015) 3061.
- [2] A. Abdel-Mageed et al., *ACS Catal.*, 5 (2015) 6753.
- [3] A. Abdel-Mageed, S. Eckle and R. J. Behm, *J. Am. Chem. Soc.* 137 (2015) 8672.
- [4] S. J. Tauster, *Acc. Chem. Res.* 20 (1987) 389.
- [5] A. Karim et al., *J. Am. Chem. Soc.* 137 (2009) 8672.

High resolution TEM after different periods of reaction in ID-ref 6000 at 190°C



After 10 min:

TEM: Top view spherical shape & d<sub>Ru</sub> = 1.1 nm

EXAFS: CN 4.9 → d<sub>Ru</sub> ~ 0.5 nm only for hemispherical particle shape [4]

→ d<sub>Ru</sub> > 0.5 (~1.2) nm assuming flat particle shape

⇒ Flat Ru NPs wetting TiO<sub>2</sub> prevailing at the beginning of the reaction

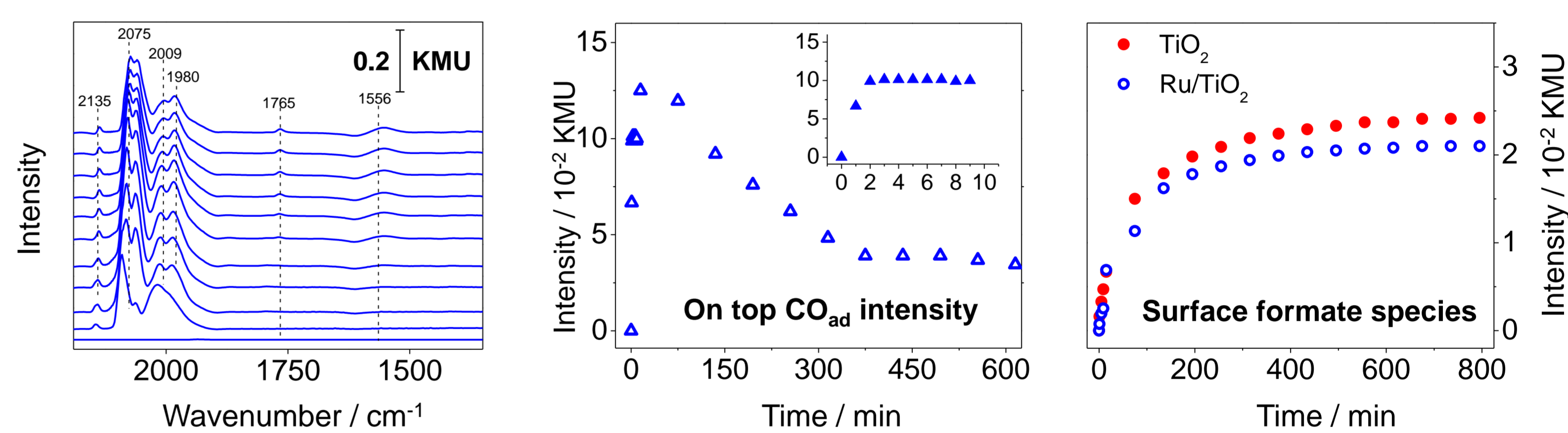
After 590 min:

d<sub>Ru</sub>-EXAFS ~1.2 nm / d<sub>Ru</sub>-TEM ~1.3 nm ⇒ hemispherical shape [5]

⇒ Reaction induced changes of particle shape and size ~ deactivation

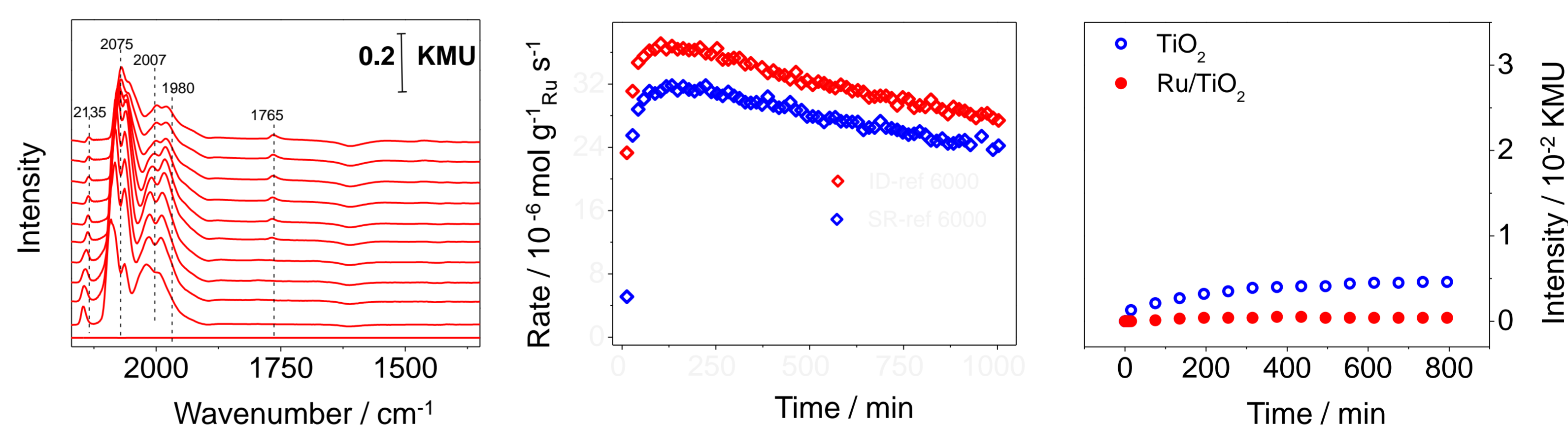
### (3) Surface poisoning and deactivation

CO adlayer and surface poisoning species during reaction in SR-ref 6000 at 190



- CO<sub>ad</sub> decreased with deactivation ~ decreasing Ru dispersion
- No surface CO<sub>3,ad</sub> but HCO<sub>ad</sub> accumulating on Ru/TiO<sub>2</sub> ~ TiO<sub>2</sub>
- ⇒ No correlation between buildup of surface formates and deactivation

Activity in absence of CO<sub>2</sub> (ID-ref 6000) and carbon containing species in deactivation



- Deactivation in presence of CO<sub>2</sub> ~ deactivation absence of CO<sub>2</sub>
- Almost no surface formate / carbonate species in absence of CO<sub>2</sub>
- ⇒ Poisoning by carbonate / formate excluded as origin of deactivation

## Conclusions

- Deactivation in the presence of CO<sub>2</sub> similar as in the absence of CO<sub>2</sub>
- Surface formate buildup on the support due to interaction with CO<sub>2</sub>
- ⇒ Deactivation not attributed to the blocking of active sites with time
- Particle changed from flat to hemispherical Ru NPs during initial activation
- Continuous increase of Ru particle size during reaction ~ catalyst deactivation
- ⇒ Reaction induced change in Ru particle size / shape responsible for deactivation