Stability of $Fe_2O_3/MgAl_2O_4$ for CO_2 utilization in super-dry reforming of CH_4

Lukas Buelens[1], A. Dharanipragada[1], V.V. Galvita[1], H. Poelman[1], G.B. Marin[1]

[1]Laboratory for Chemical Technology

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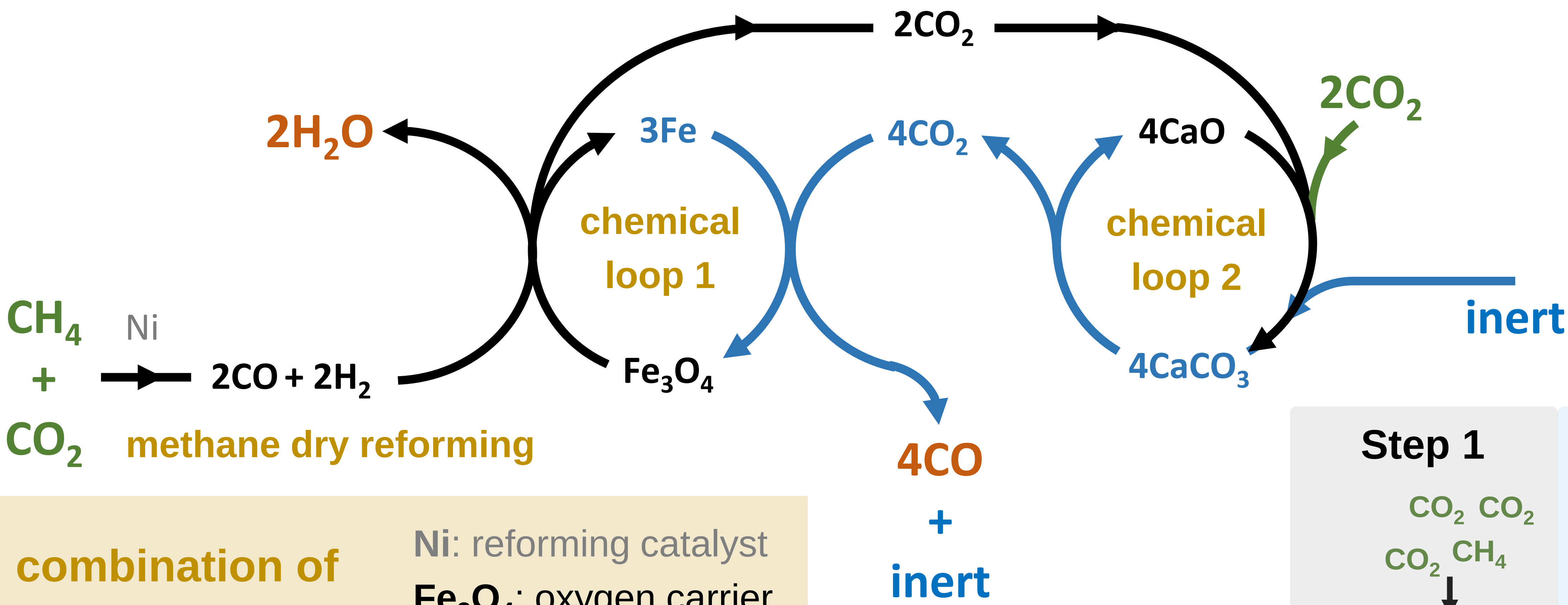
Introduction: super-dry reforming of CH_4



combination of 3 processes

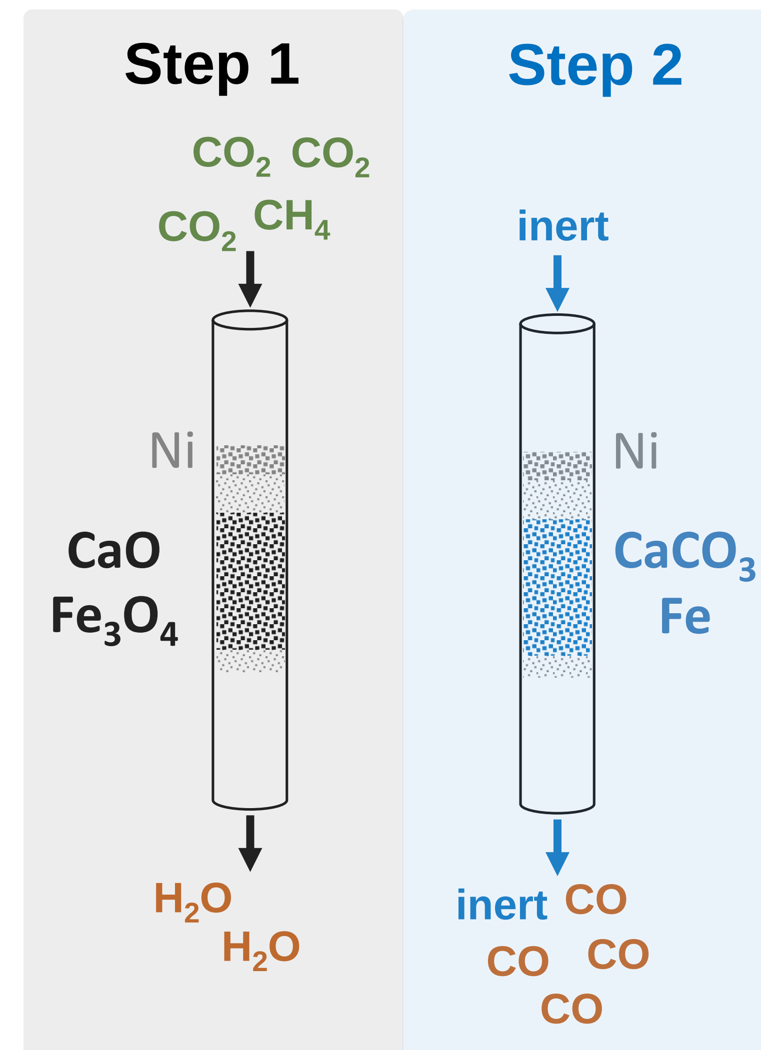
Ni: reforming catalyst
Fe_3O_4: oxygen carrier
CaO: CO_2 sorbent

Step 1: $CH_4 + 3CO_2 + Fe_3O_4 + 4CaO \rightleftarrows 2H_2O + 3Fe + 4CaCO_3$

$\Delta_r H^\circ_{1023K} = -103\ kJ\ mol^{-1}_{CO_2}$ $\Delta_r G^\circ_{1023K} = -32.4\ kJ\ mol^{-1}_{CO_2}$

Step 2: inert + $4CaCO_3 + 3Fe \rightleftarrows 4CaO + Fe_3O_4 + 4CO$ + inert

$\Delta_r H^\circ_{1023K} = +212\ kJ\ mol^{-1}_{CO_2}$ $\Delta_r G^\circ_{1023K} = +23.8\ kJ\ mol^{-1}_{CO_2}$



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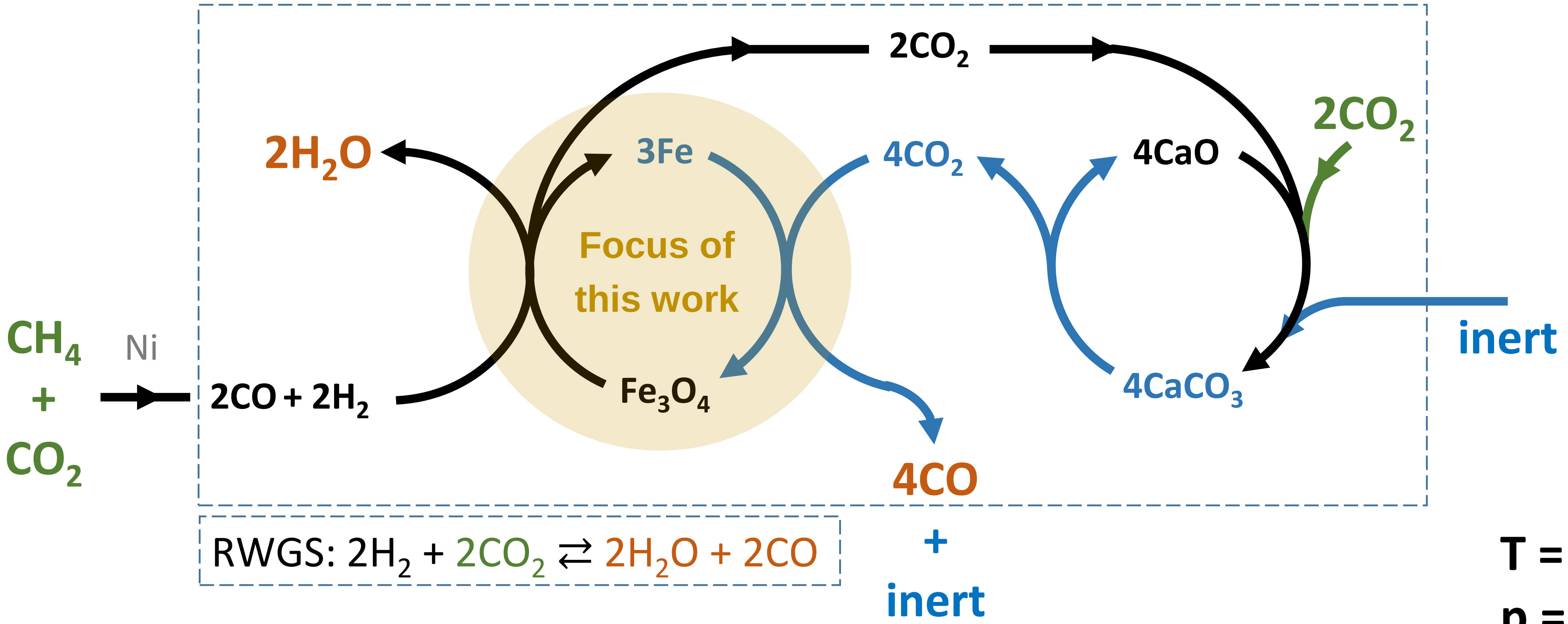
Science (2016), **354**: 449-452.

T = 1023 K

Introduction: super-dry reforming of CH_4



T = 1023 K
p = 1 atm

$CH_4 + 3CO_2$ + inert ⇄ $4CO + 2H_2O$ + inert

$$\Delta_r H^\circ_{1023K} = +109\ kJ\ mol^{-1}_{CO_2}$$
$$\Delta_r G^\circ_{1023K} = -8.6\ kJ\ mol^{-1}_{CO_2}$$

→ **Method for valorization of C_1 feedstocks (CH_4 and CO_2) through CO production**

→ **Isothermal combination of catalytic methane dry reforming and chemical looping**

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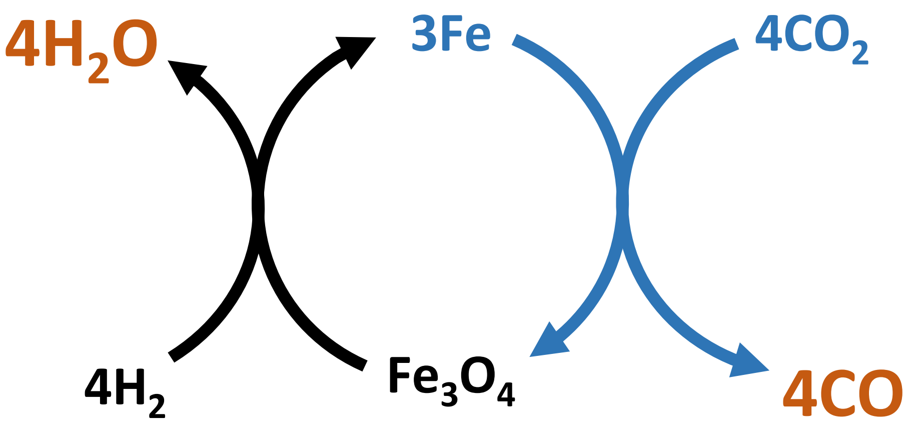
Science (2016), **354**: 449-452.

Introduction: oxygen carrier



Iron oxide as oxygen carrier

- High capacity for CO_2 conversion into CO
- Abundantly available (low cost)
- Environmentally sound

However…

➢ Rapid deactivation through sintering

→ addition of textural promoter such as Al_2O_3 (MgO)

➢ Formation of $FeAl_2O_4$ ($MgFe_2O_4$) leads to continuous deactivation

→ use of $MgAl_2O_4$ promoter

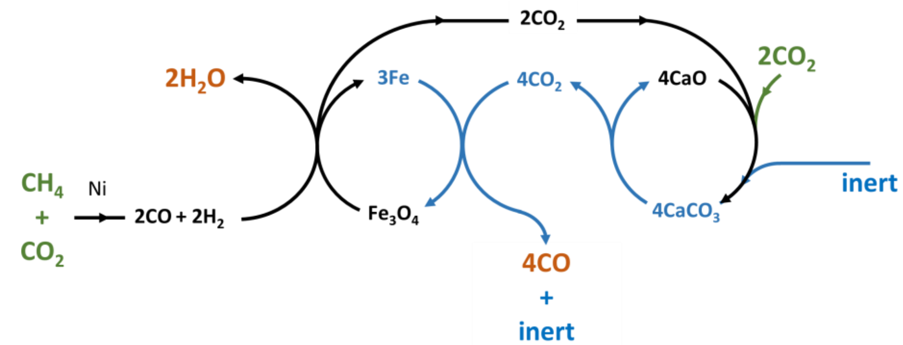
Incorporation of Fe in the $MgAl_2O_4$ spinel

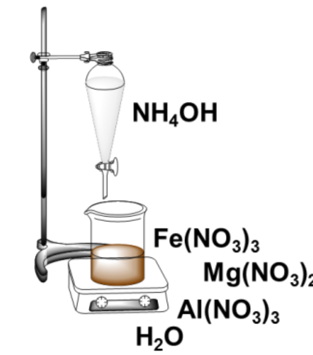
➢ Stability and performance of $Fe_2O_3/MgAl_2O_4$ over several days?

J. Mater. Chem. A (2015), **3**: 16251-16262.

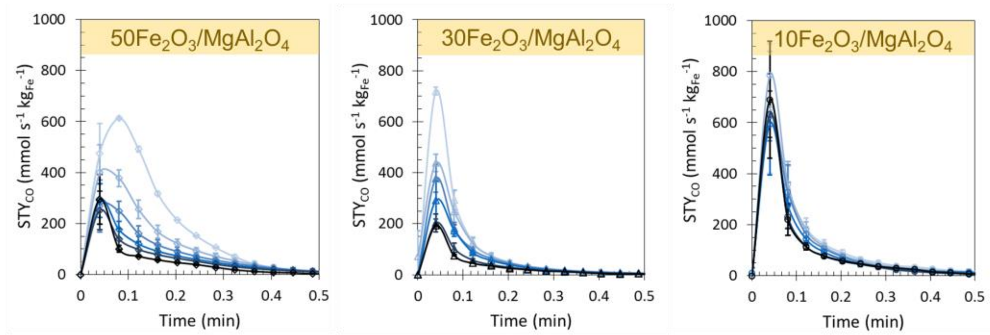
Outline

Introduction

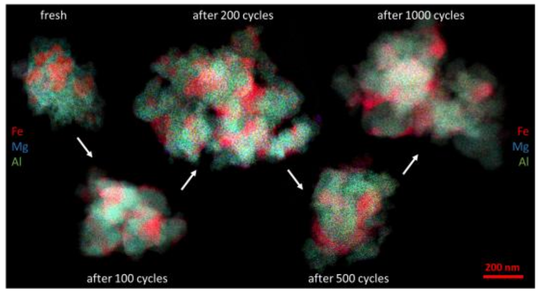




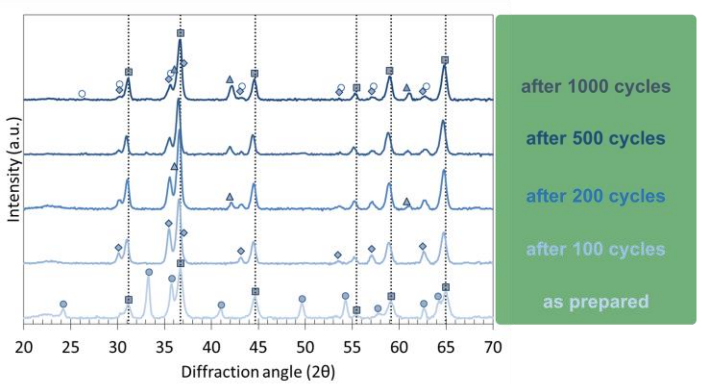
Material synthesis



Activity tests



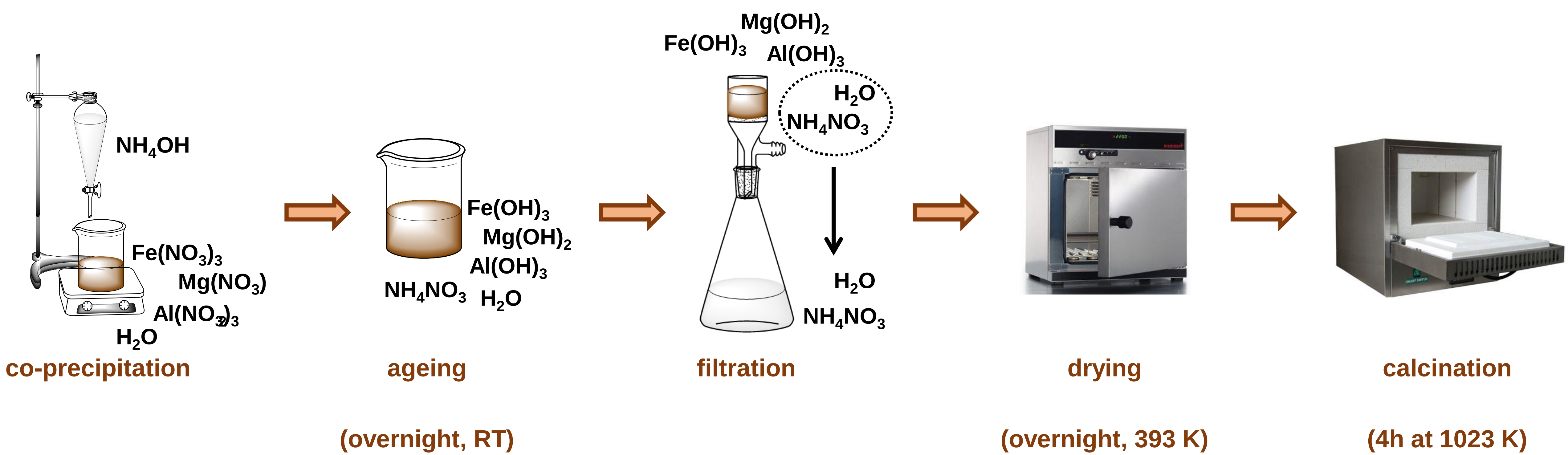
Characterization



Conclusions

Material synthesis

- One-pot co-precipitation of $Fe(NO_3)_3$, $Mg(NO_3)_2$ and $Al(NO_3)_3$ using NH_4OH
- 3 different materials: X-$Fe_2O_3/MgAl_2O_4$ (with X = 10, 30, 50 w%)
- Denoted as 10FMA, 30FMA and 50FMA



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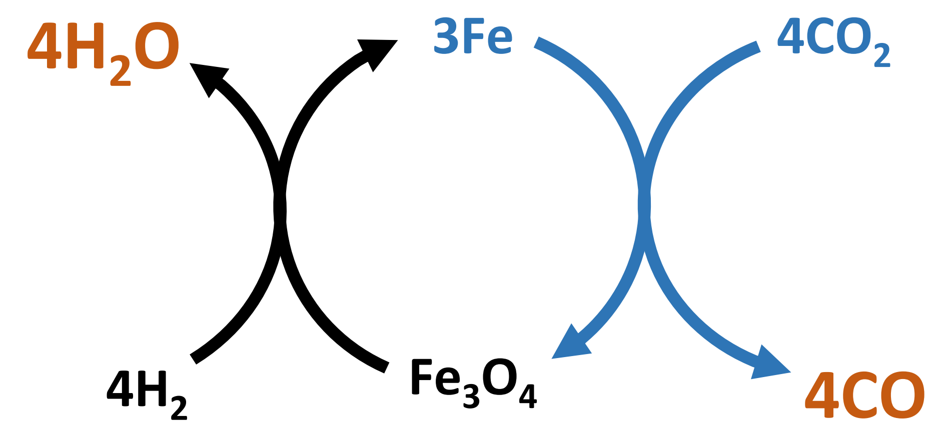
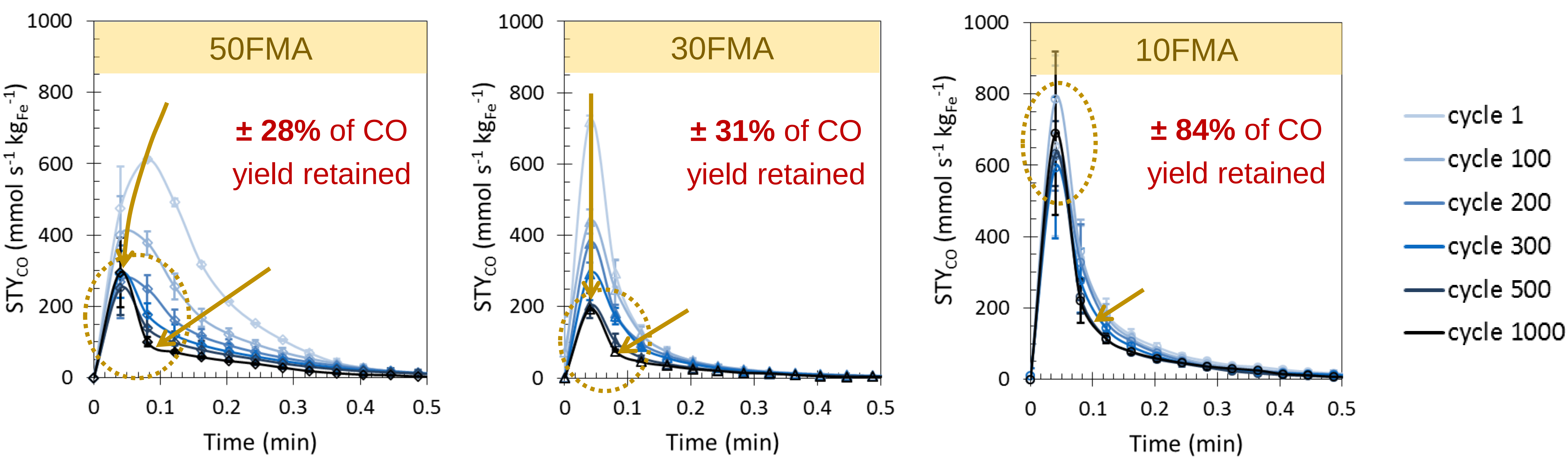
Activity tests: 1000 redox cycles

Redox cycle (1023 K, 1 atm)

10% in He	100% He	40% in He	100% He
H_2	inert	CO_2	inert
1 min	2 min	1 min	2 min





stabilization after 300 redox cycles

stabilization after 500 redox cycles

most stable

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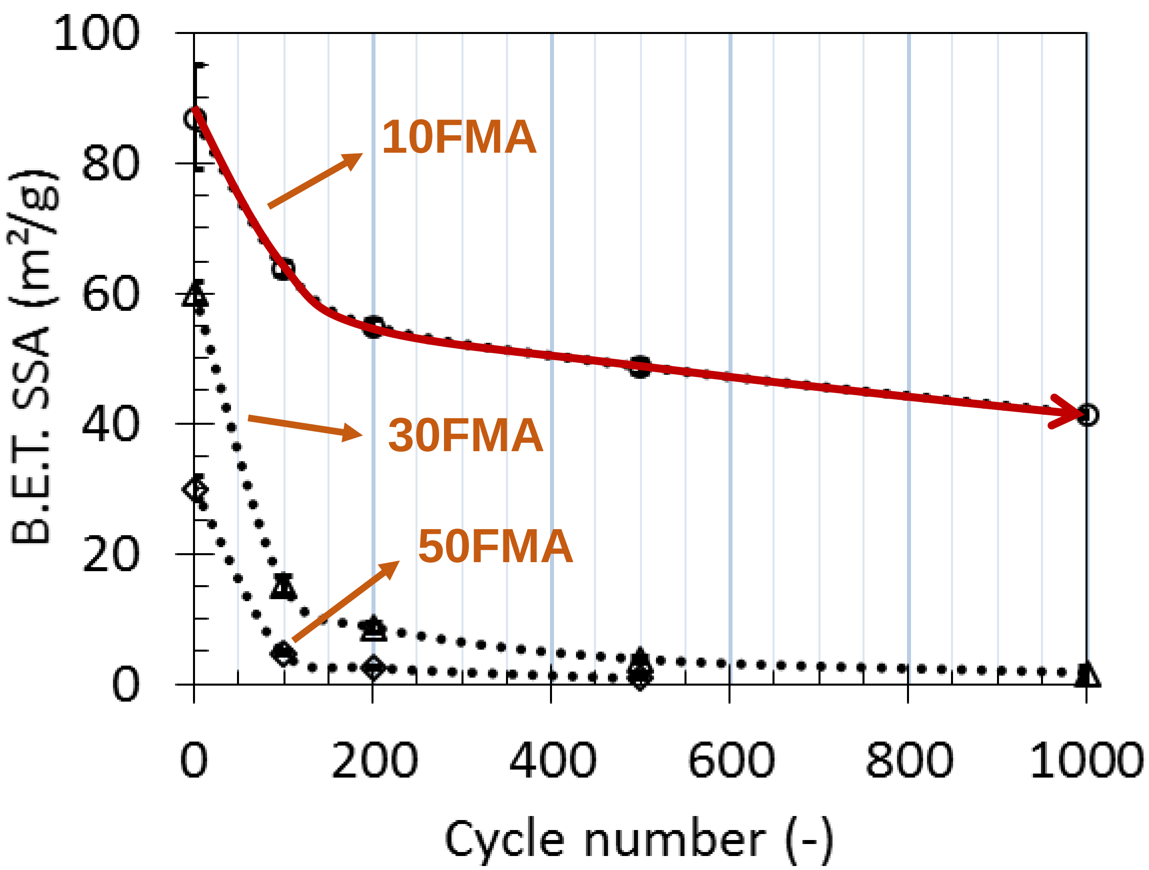
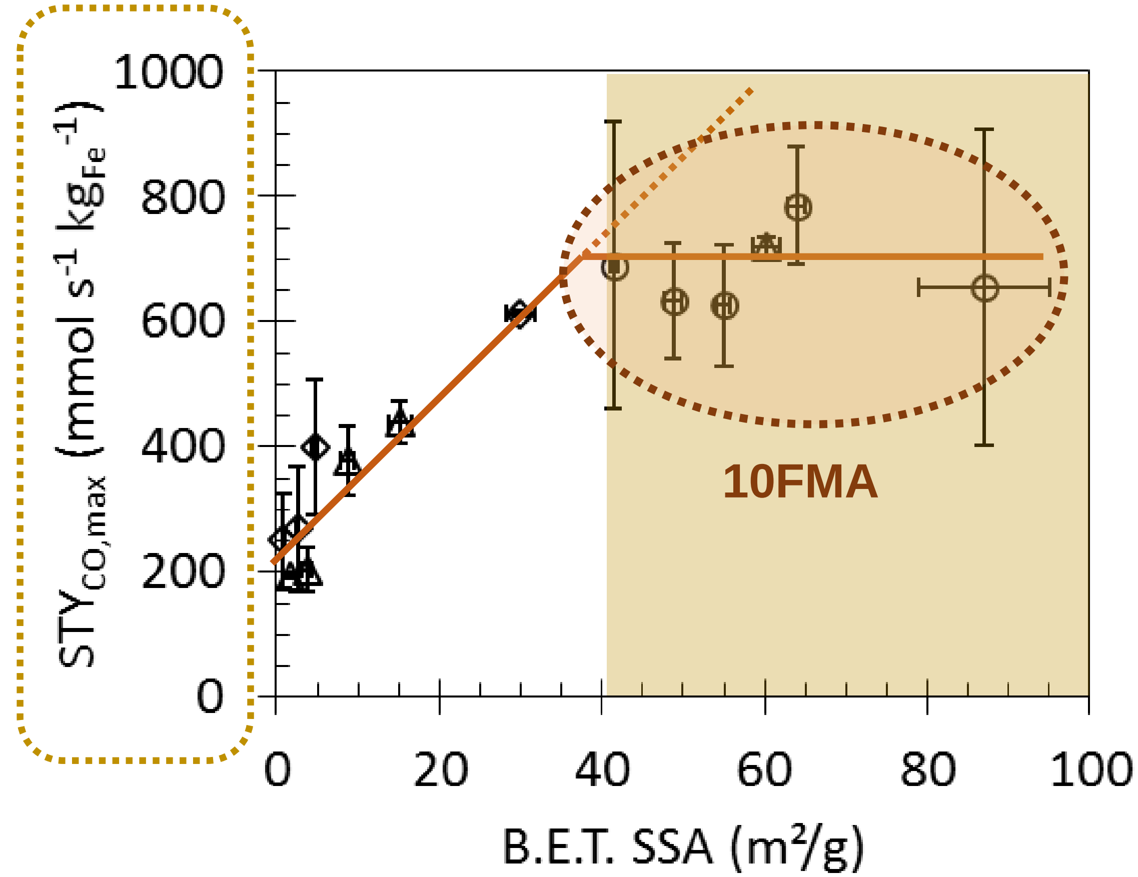
Step response: 100, 200, 500 and 1000 redox cycles (1 min 10% H_2 in He; 2 min purging in 100% He; 1 min 40% CO_2 in He; 2 min purging in 100% He) were performed using $50Fe_2O_3/MgAl_2O_4$, $30Fe_2O_3/MgAl_2O_4$ and $10Fe_2O_3/MgAl_2O_4$ at p = 1.013 bara, T=1023 K, F_{tot} = 2.35 10^{-4} mol s^{-1}

Characterization: N_2 adsorption

○ 10FMA
△ 30FMA
◇ 50FMA





Superior morphological stability of 10FMA

⇩

Application as redox active catalyst support

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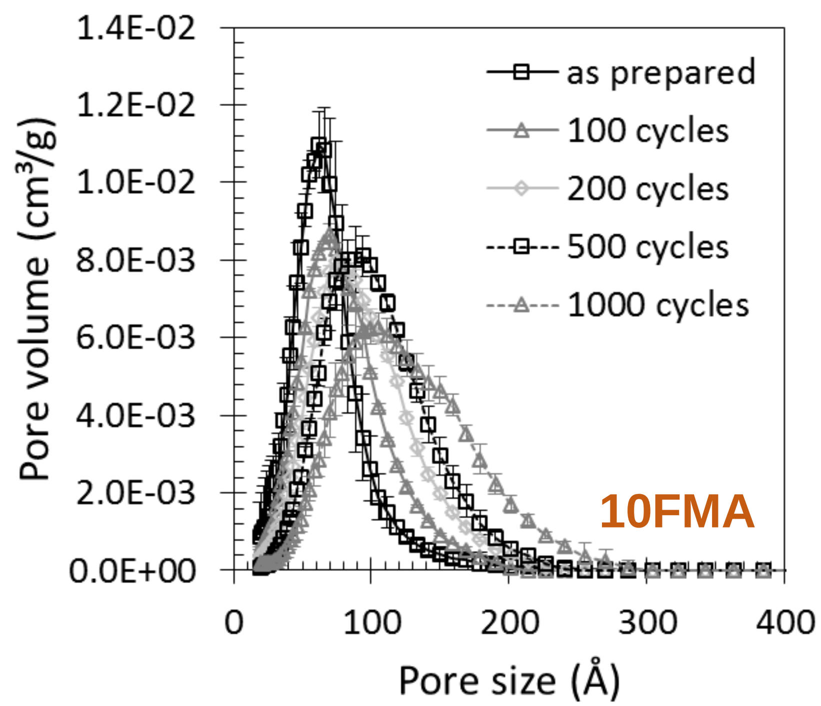
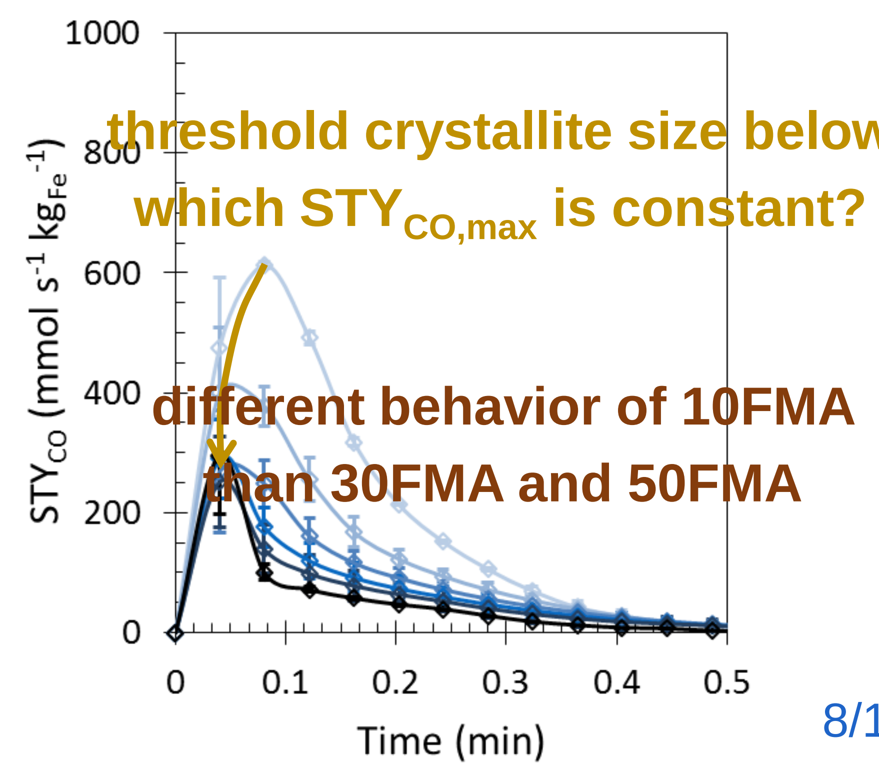
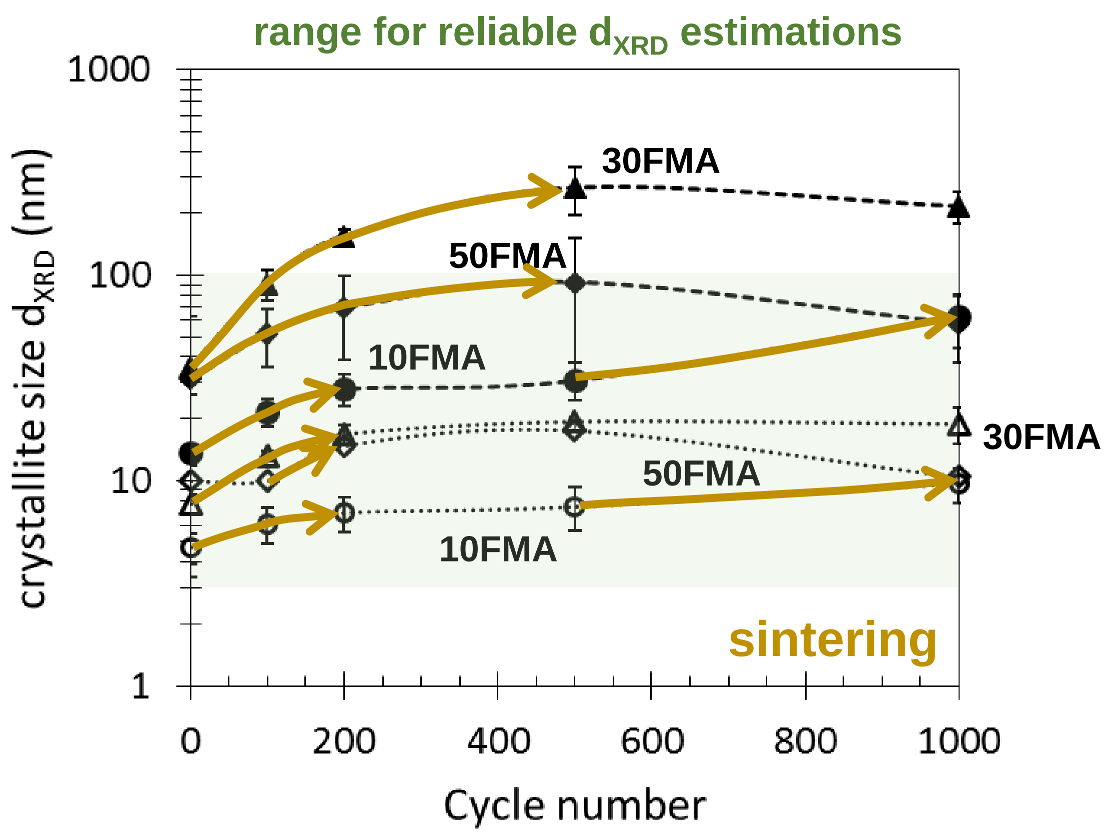




Characterization: X-ray diffraction (Mg-Fe-Al-O spinel)



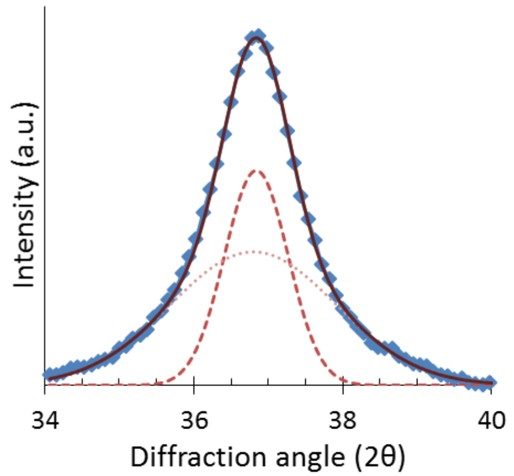
Mg-Fe-Al-O diffraction peak

→ well reproduced with bimodal crystallite size

(2 Gaussians, Scherrer's equation)

Small crystallites: dotted lines

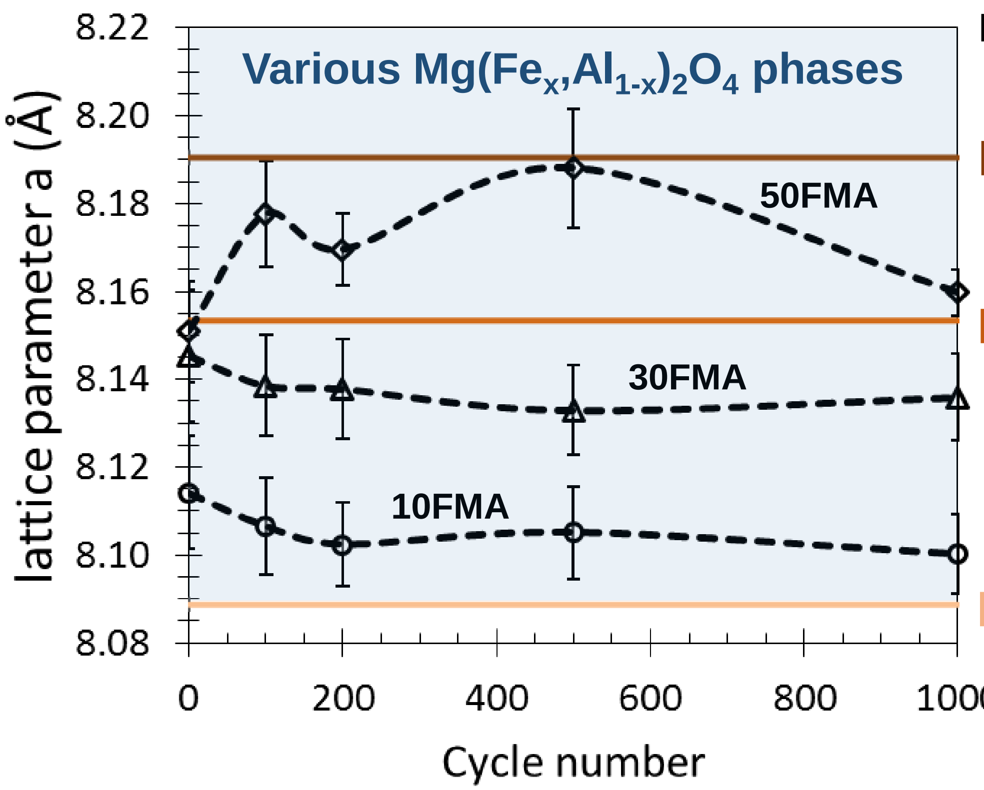
Large crystallites: dashed lines



- o 10FMA
- △ 30FMA
- ◇ 50FMA

Fe_3O_4 - 8.396Å

$MgFe_2O_4$ - 8.369Å



$Mg(Fe,Al)_2O_4$

$FeAl_2O_4$

$MgAl_2O_4$

Fe remains present in the spinel phase, even after 1000 redox cycles

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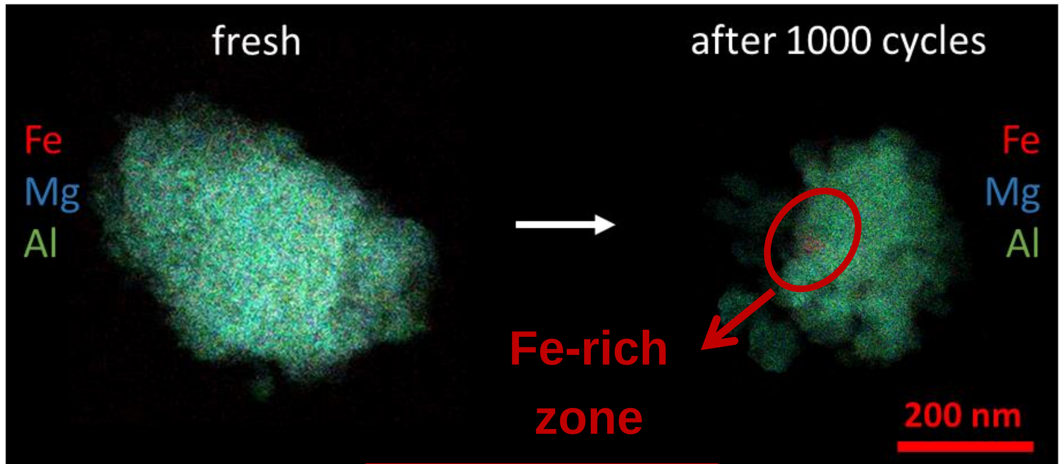
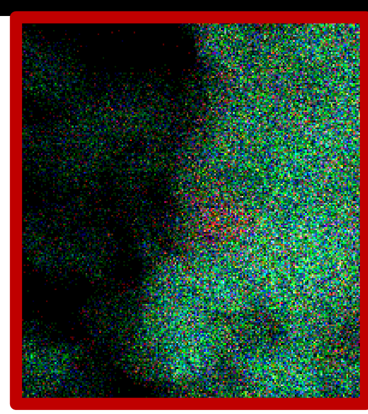
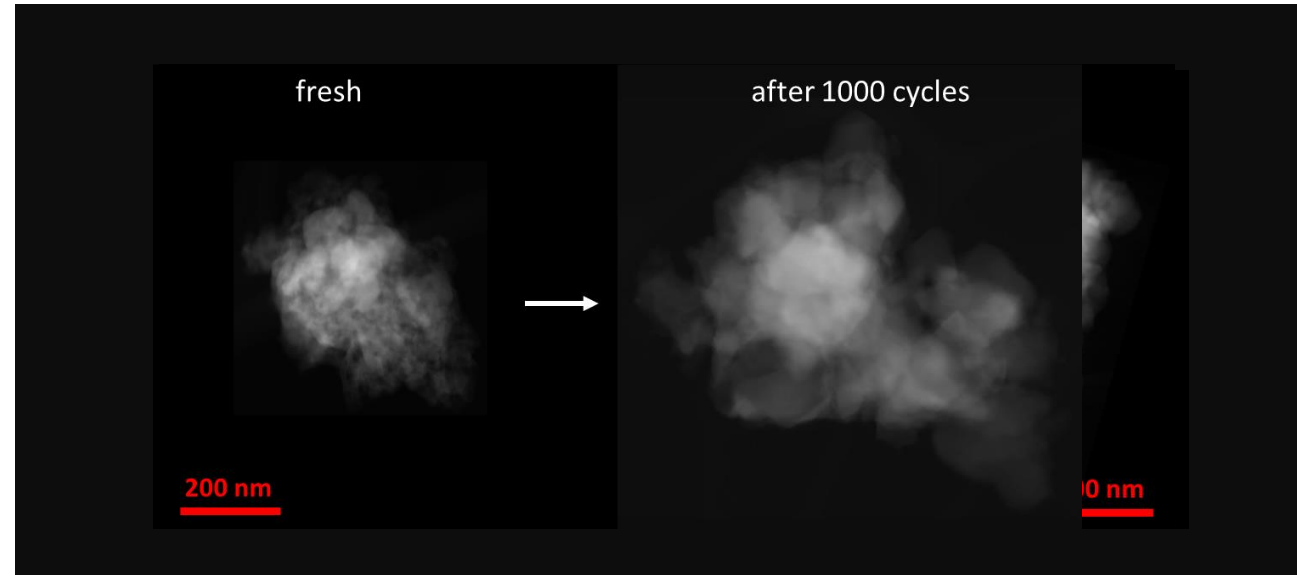
Characterization: STEM-EDX

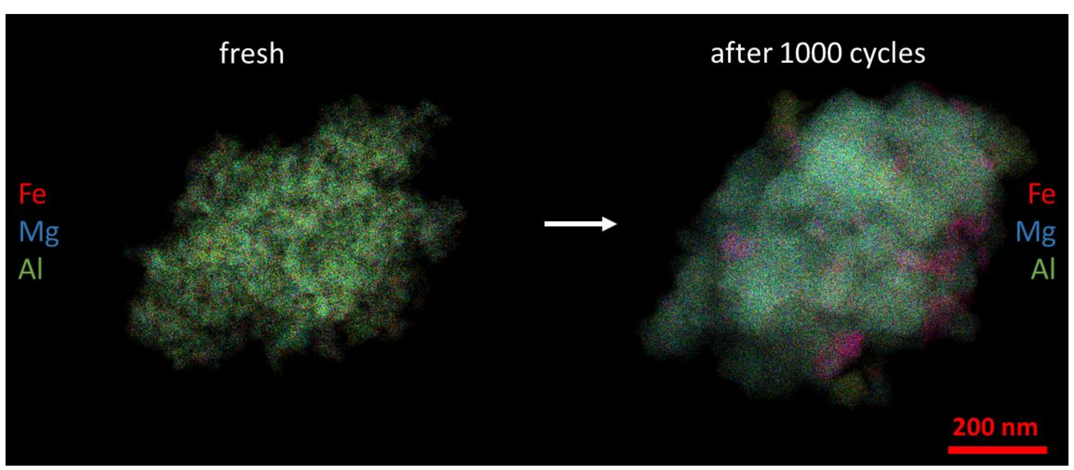
10FMA



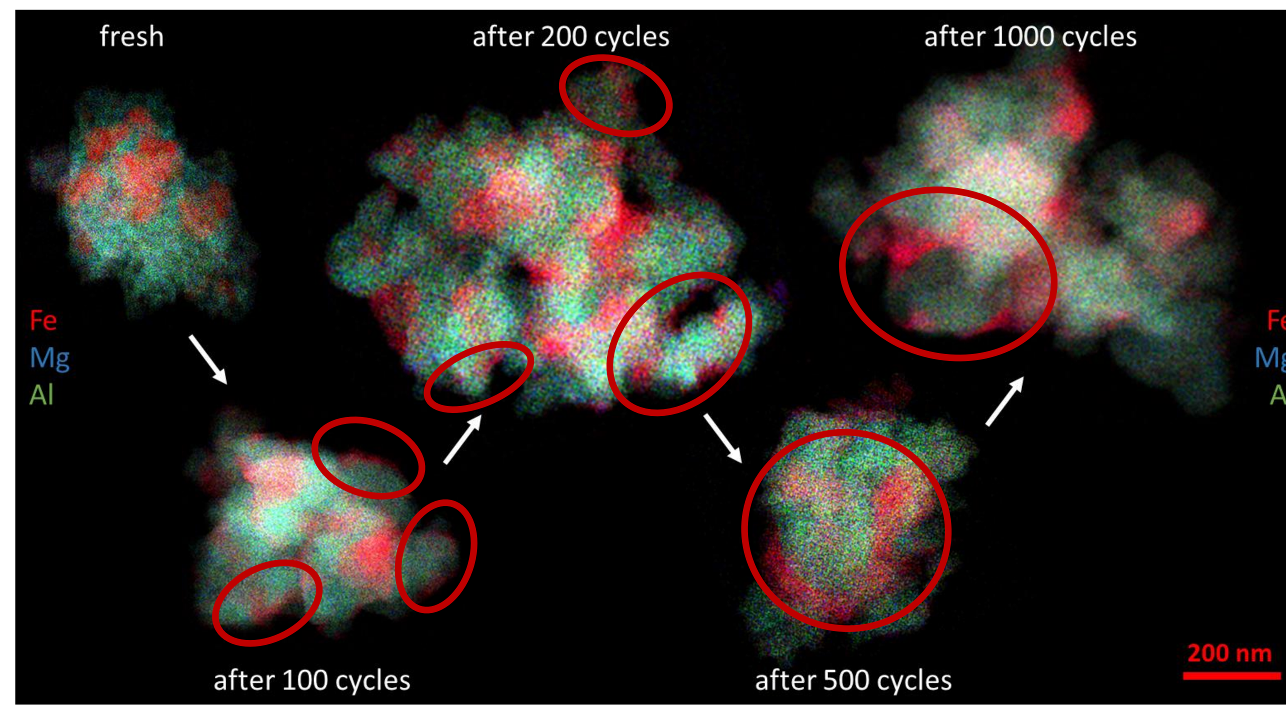




30FMA



50FMA



Enrichment of Fe along the surface of Mg-Fe-Al-O spinel

Indicates low surface tension between Fe-rich phase and Mg-Fe-Al-O spinel

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Conclusions

$10Fe_2O_3/MgAl_2O_4$

✓ Stable redox properties and morphology over 1000 redox cycles

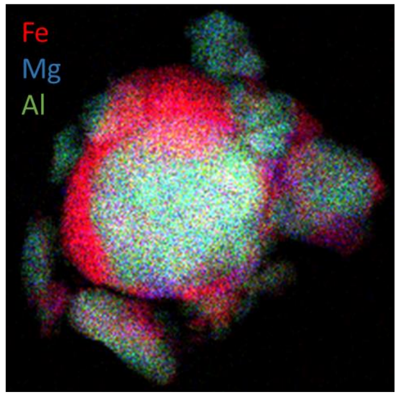
⇨ **promising oxygen carrier for CO_2 conversion or redox active catalyst support**

$50Fe_2O_3/MgAl_2O_4$

✓ Redox activity stabilizes after 300 redox cycles, despite deterioration of morphological properties

✓ STEM-EDX analysis suggests a good interaction between the Fe-rich phase and the Mg-Fe-Al-O spinel

⇨ **promising oxygen carrier for CO_2 conversion**



$X\text{-}Fe_2O_3/MgAl_2O_4$

✓ Fe remains (partially) incorporated in the spinel, even after 1000 redox cycles

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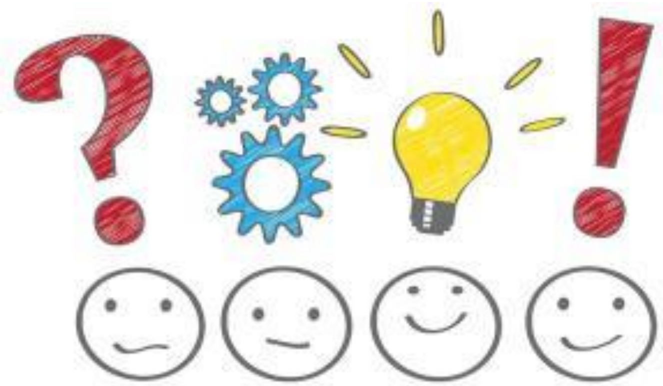
Thank you



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