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Composite particles as active catalysts for the SO_3 dissociation reaction of the thermochemical storage scheme based on elemental sulphur

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Our project partners

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baltic ceramics

PROCESSI INNOVATIVI

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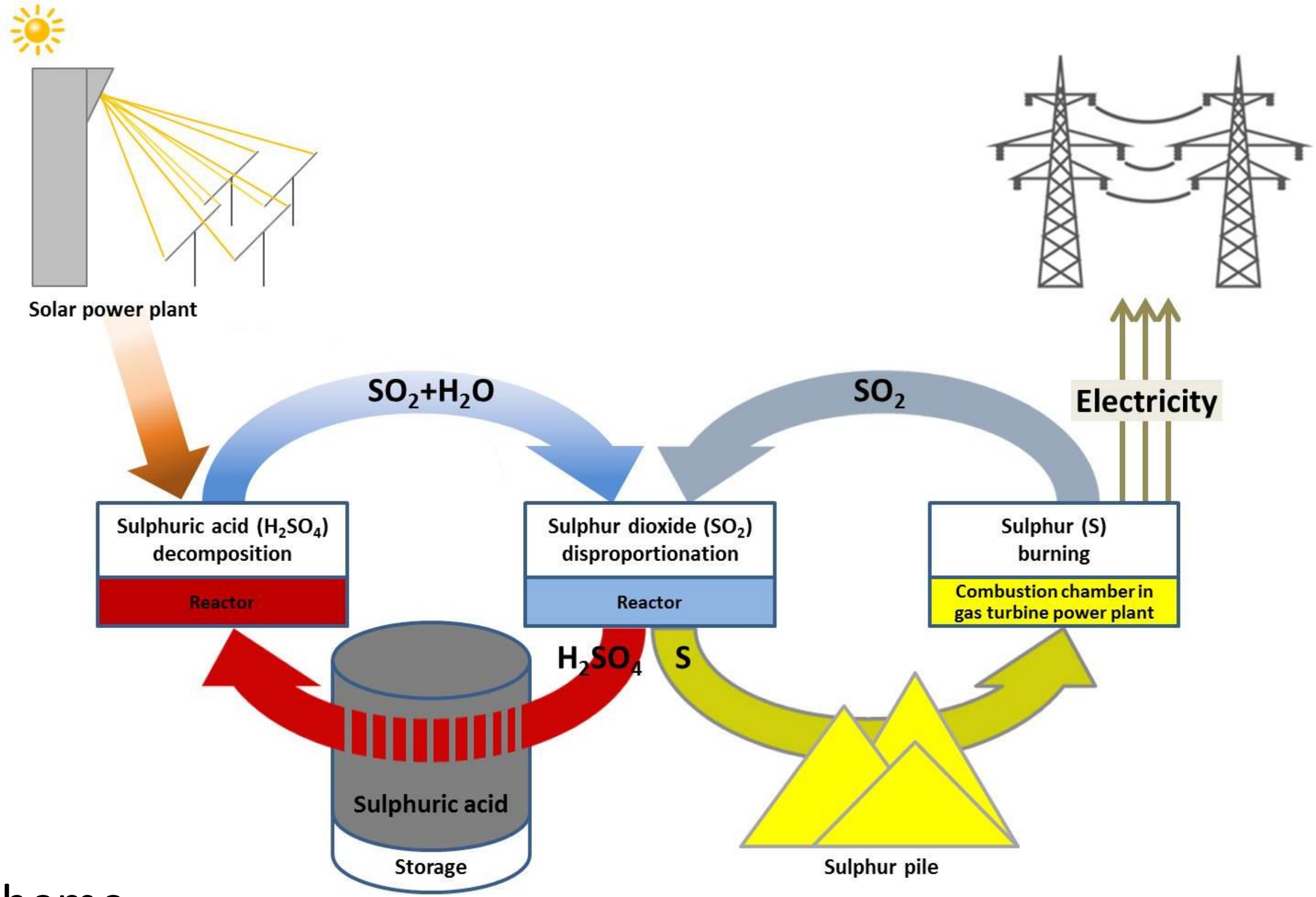
Outline

- Thermochemical storage system based on elemental sulphur
- Oxide-based materials
  - Non-modified proppants synthesized by Baltic Ceramics (BCR)
  - Particles synthesized by APTL
- Physico-chemical characterization
- Setup for catalytic activity measurements
- Results on catalytic activity
- Conclusions and next steps

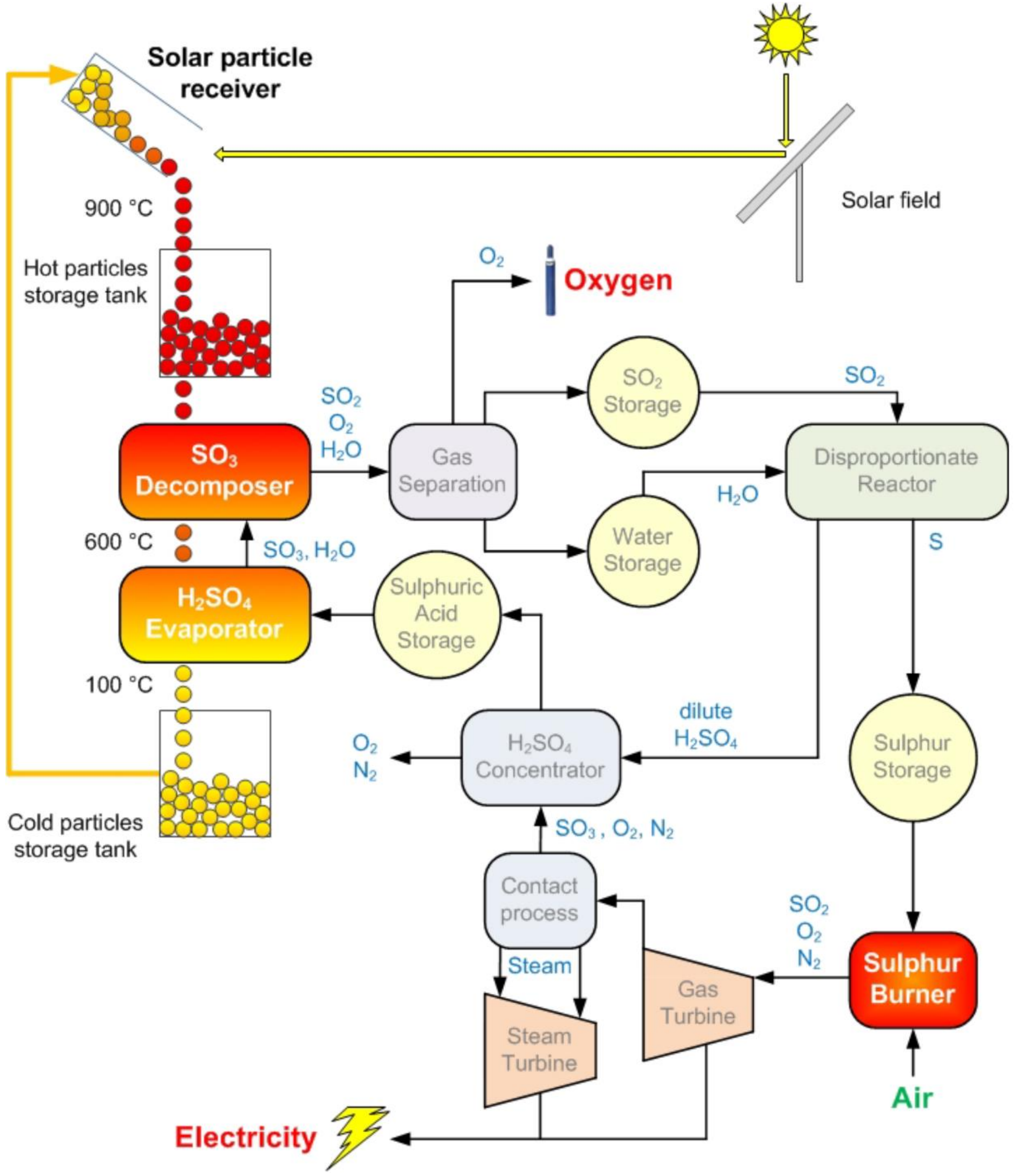
Process concept scheme

- The concept combines:
  - Solid particles as heat transfer fluid, also used for direct thermal (sensible) energy storage
  - Solid sulphur used for indirect thermo-chemical storage of solar energy



- Advantages of the sulphur energy storage scheme
  - ✓ *Very high energy density: approx. 12,500 kJ/kg cf. 300 kJ/kg for molten salts*
  - ✓ *Cost-effective material (<60 €/tn cf. ~400 €/tn for molten salts) and cheaply stored in piles under ambient conditions*
  - ✓ *Constant temperature heat recovery and possibility for higher temperature stored energy retrieval cf. original heat input*

Process diagram



➢ Sulphuric acid splitting/decomposition

	Reaction set	Temperature (ºC)	ΔH (kJ/mol)
i)	$2H_2SO_{4(aq)} \rightarrow 2SO_{3(g)} + 2H_2O_{(g)}$	450-500	560
ii)	$2SO_{3(g)} \rightarrow 2SO_{2(g)} + O_{2(g)}$	800-900	

- *CSP exploitation step*
- *Energy intensive (endothermic) step*
- *Reaction set: i) non-catalytic, 100% splitting; ii) requires **catalyst***
- *Solar receiver design requires particles as catalyst*

SO_3 decomposition catalysts state of the art

600ºC

- $CuO\text{-}V_2O_5/SiO_2$, $Ce\text{-}V/SiO_2$
- CuV/SiO_2

- Pt/Al_2O_3

- Fe_2O_3-based, Cu-Fe-Al, Fe-Cr

1000ºC

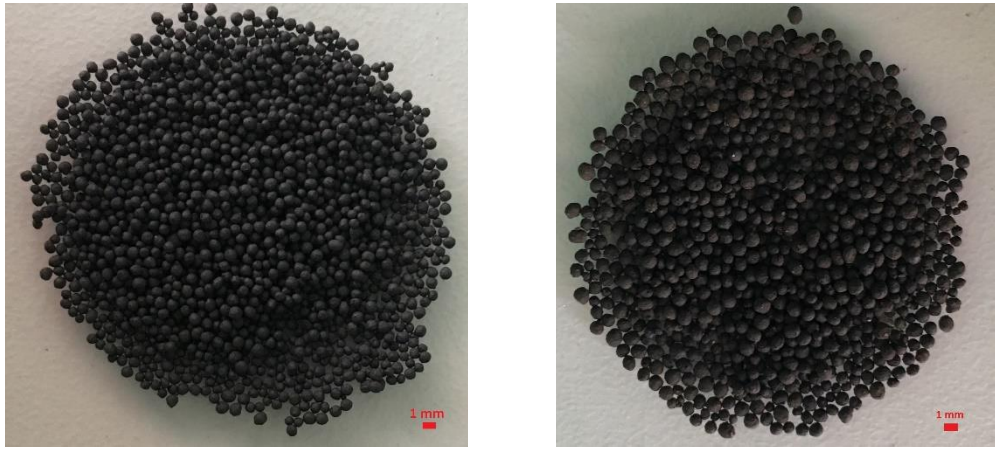
- Kawada, T. et al., 2014, Hydrothermal synthesis of CuV_2O_6 supported on mesoporous SiO_2 as SO_3 decomposition catalysts for solar thermochemical hydrogen production, Int. J. Hydrogen Energy 39, 20646-20651
- Kawada, T. et al., 2015, Structure and SO_3 decomposition activity of $nCuO\text{-}V_2O_5/SiO_2$ (n=0,1,2 and 5) catalysts for solar thermochemical water splitting cycles, Catal. Today 242, 268-273
- Kawada, T. et al., 2015, Structure and SO_3 decomposition activity of $CeVO_4/SiO_2$ catalysts for solar thermochemical water splitting cycles, Int. J. Hydrogen Energy 40, 10726-10733

- Karagiannakis, G. et al., 2011, Hydrogen production via sulfur-based thermochemical cycles: Part 1: Synthesis and evaluation of metal oxide-based candidate catalyst powders for the sulfuric acid decomposition step, Int. J. Hydrogen Energy 36, 2831-2844
- Giaconia, A. et al., 2011, Hydrogen production via sulfur-based thermochemical cycles: Part 2: Performance evaluation of Fe_2O_3-based catalysts for the sulfuric acid decomposition step, Int. J. Hydrogen Energy 36, 6496-6509

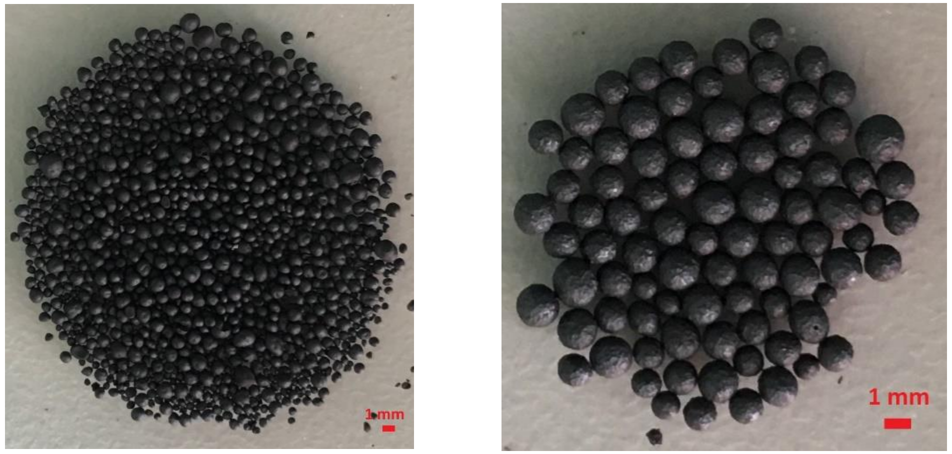
➢ Reaction thermodynamics require temperatures >600ºC, especially at high SO_3 content

Oxide-based solid particles

- Materials synthesized by both BCR and APTL
- APTL synthesized oxides rich in Fe_2O_3, the rest mainly aluminosilicates (Al-Si)
  - ✓ Dry (or slurry) mechanical mixing of oxides → wetting → shaping by applying rotary forces → drying → calcination
- Near spherical with size range 425 - 1700 μm (BCR), 700 - 1400 μm (APTL)
- Density: ~2 g/ml
- Demand for high thermo-mechanical strength & resistance to chemically harsh environment
- Particles color black or blackish
  - ✓ Achievement of high solar-irradiation absorption



BCR proppants



APTL particles

List of evaluated solid particles

Sample	Main	Secondary
BCR-1	Bauxite	Manganese oxide, Iron oxide
BCR-2/BCR-3		
BCR-4		
BCR-5/BCR-6		
BCR-7	Bauxite	Iron oxide, Manganese oxide

Samples	Main	Secondary
APTL-1/APTL-2	Commercial Iron oxide	
APTL-3/APTL-4	Commercial Iron oxide	Aluminosilicate
APTL-5/APTL-6	Iron oxide-rich steel industry byproduct	Aluminosilicate residuals

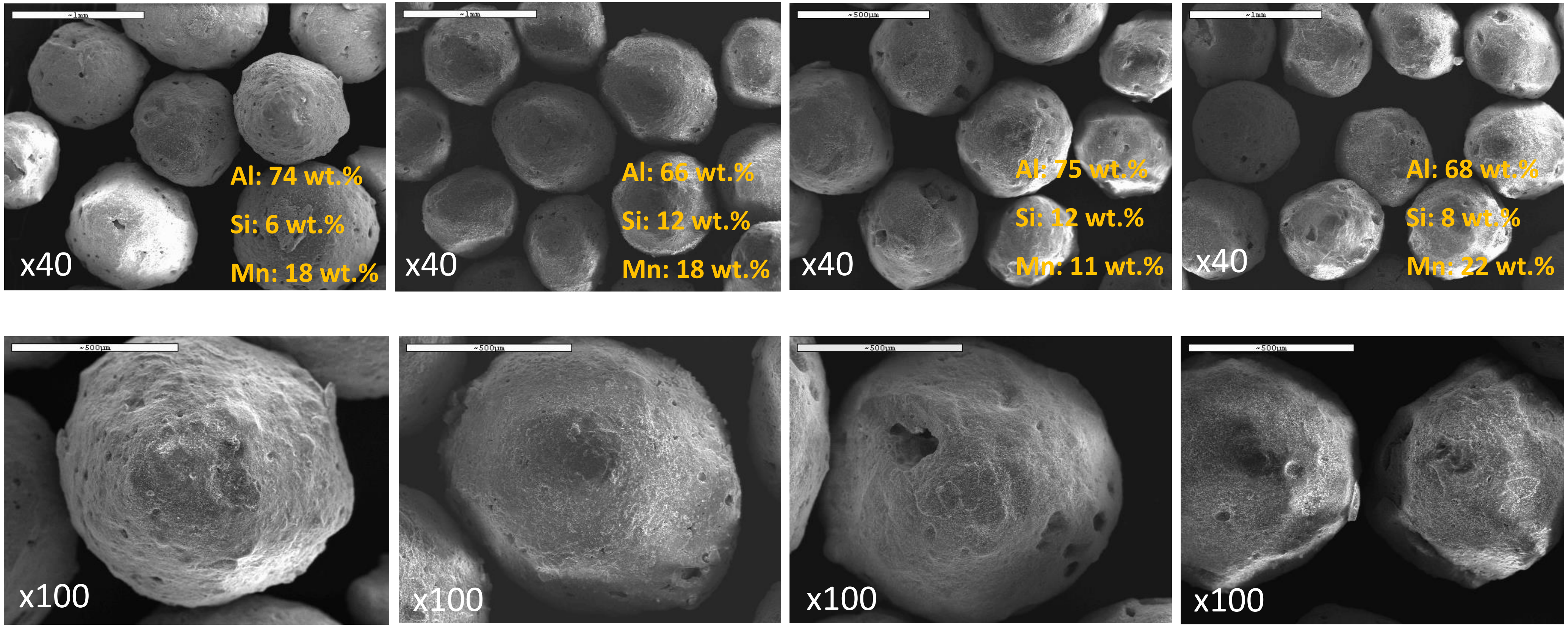
- Grouped samples
  - BCR: Same compositions, different particle sizes
    - ✓ BCR-2, BCR-5, BCR-7 → bigger p.s.
  - APTL: Same compositions, different calcination temperatures
    - ✓ APTL-1, APTL-3, APTL-5 → low calcination temperature
    - ✓ APTL-2, APTL-4, APTL-6 → high calcination temperature

Physico-chemical characterization

- Applied techniques:
  - Scanning Electron Microscopy (SEM)
  - X-Ray Diffraction (XRD)
  - Hg porosimetry
  - Surface area (BET) by liquid N_2 adsorption
  - Crushing strength measurements

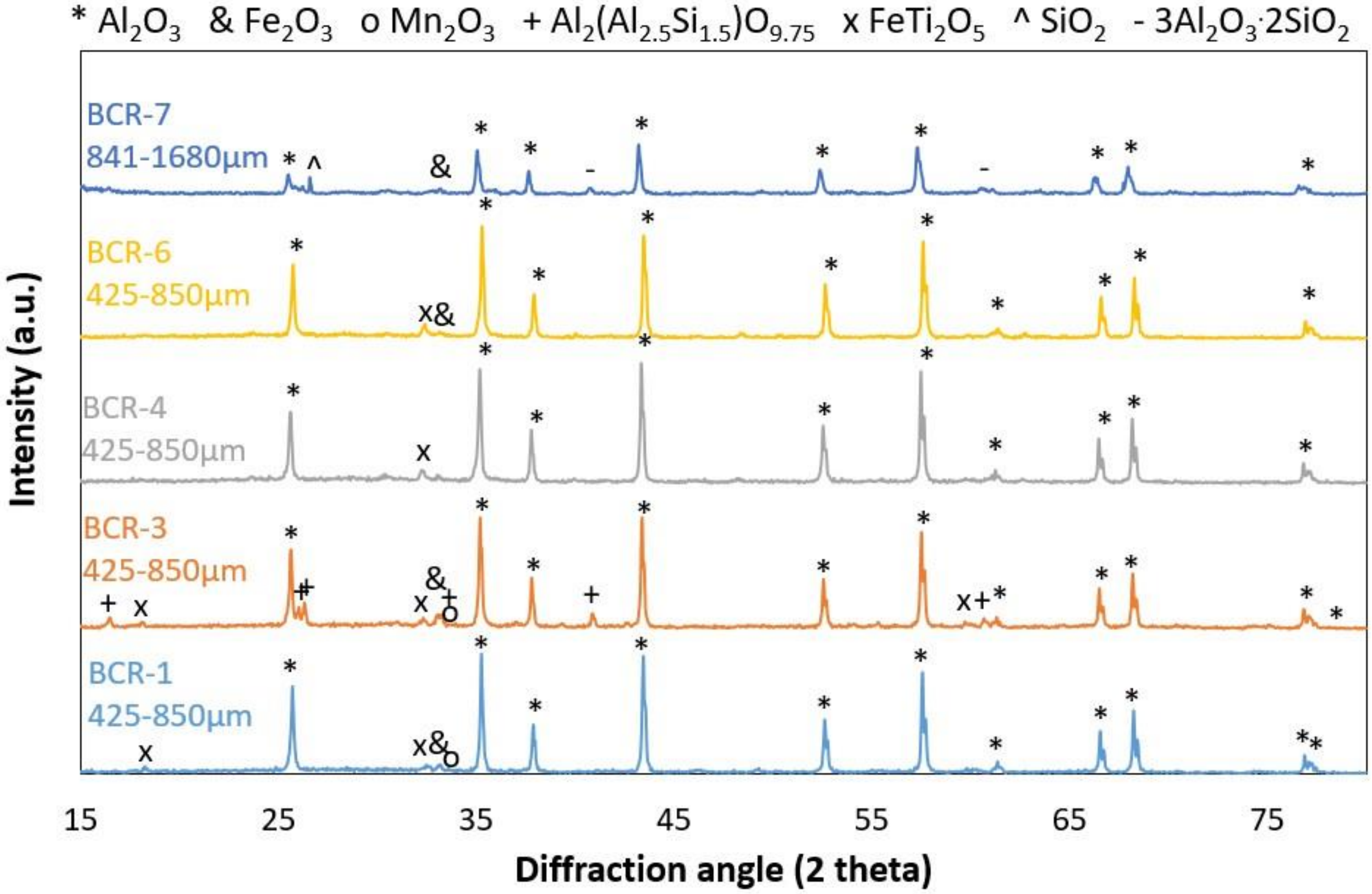
BCR samples - SEM analysis

BCR-1 425-850µm | BCR-3 425-850µm | BCR-4 425-850µm | BCR-6 425-850µm



- Results very similar for all 425-850 µm samples
- Major elements identified by EDS: Al, Mn, Si, O. Also present: Ca, Ti & Fe

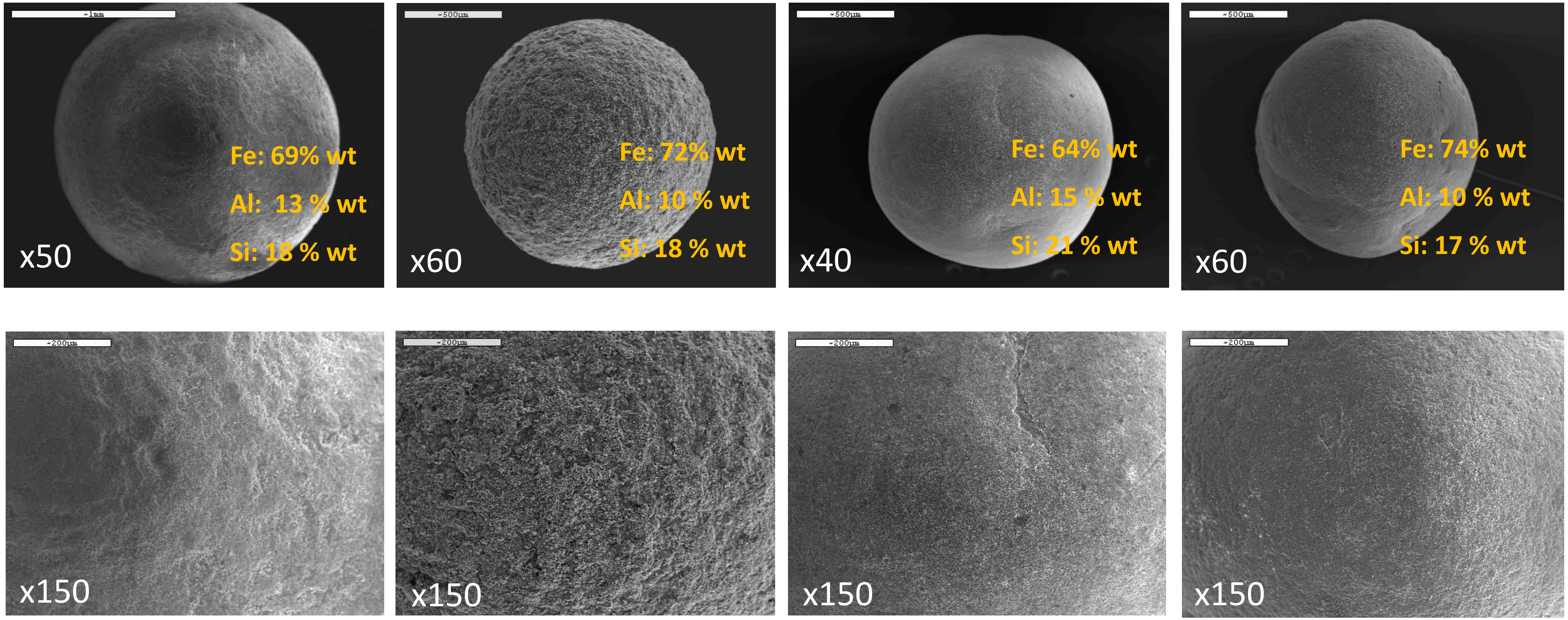
BCR samples - XRD analysis



- Main phases: alumina & aluminosilicates. Small amounts of Fe_2O_3, Mn_2O_3 & $FeTi_2O_5$

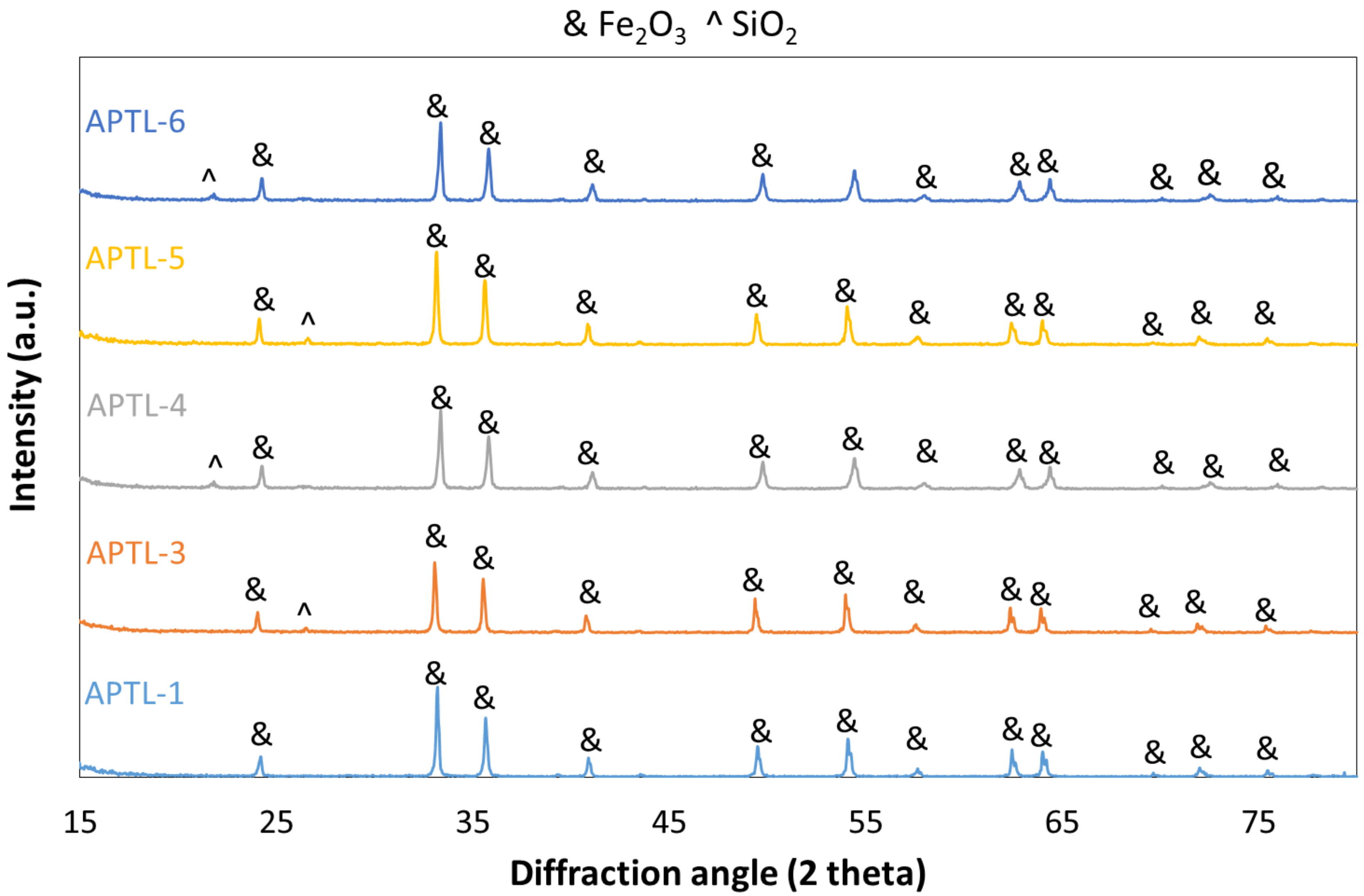
APTL samples - SEM analysis

APTL-3 APTL-4 APTL-5 APTL-6



- ➢ Results similar for all samples
  - APTL-3/APTL-4 & APTL-5/APTL-6 have the same compositions but different calcination temperature
  - Higher calcination temperature → more sintered structures
- ➢ Major elements (EDS): Fe, Al, Si

APTL samples - XRD analysis

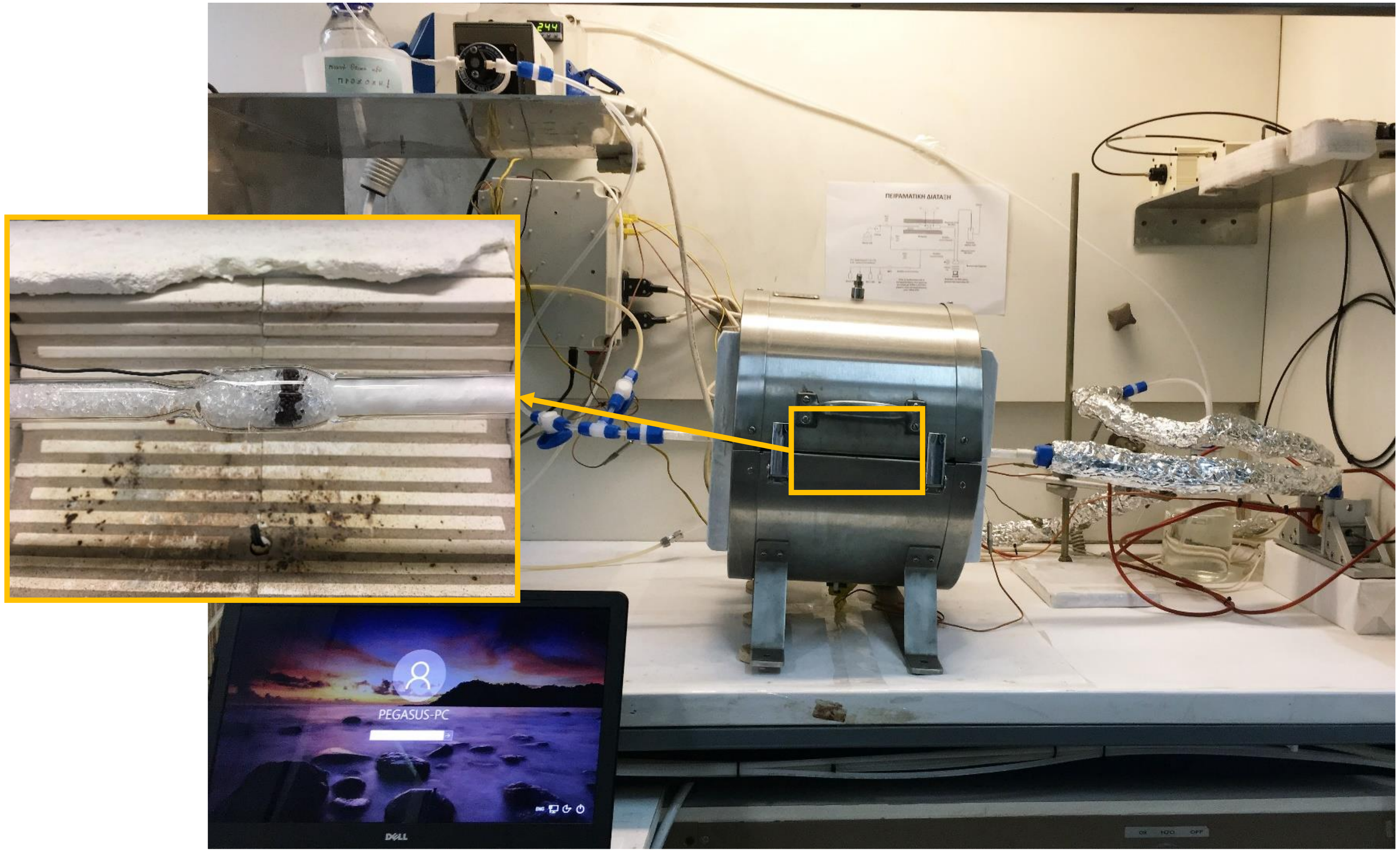


- Main phase: Fe_2O_3. Small amounts of SiO_2 in all but APTL-1 (pure iron oxide)
- Relatively low crystallinity & absence of clear Al_2O_3 & Al-Si-O peaks

Hg porosimetry & BET Surface Area measurements (BCR and APTL)

- No specific surface area (BET measurements) for BCR proppants
- Low specific area in APTL samples (~0 for high calcination temperatures, ~5 m^2/g for lower)
- No appreciable porosity by Hg-porosimetry in BCR proppants (if any, < 5%)

Setup for catalytic activity measurements



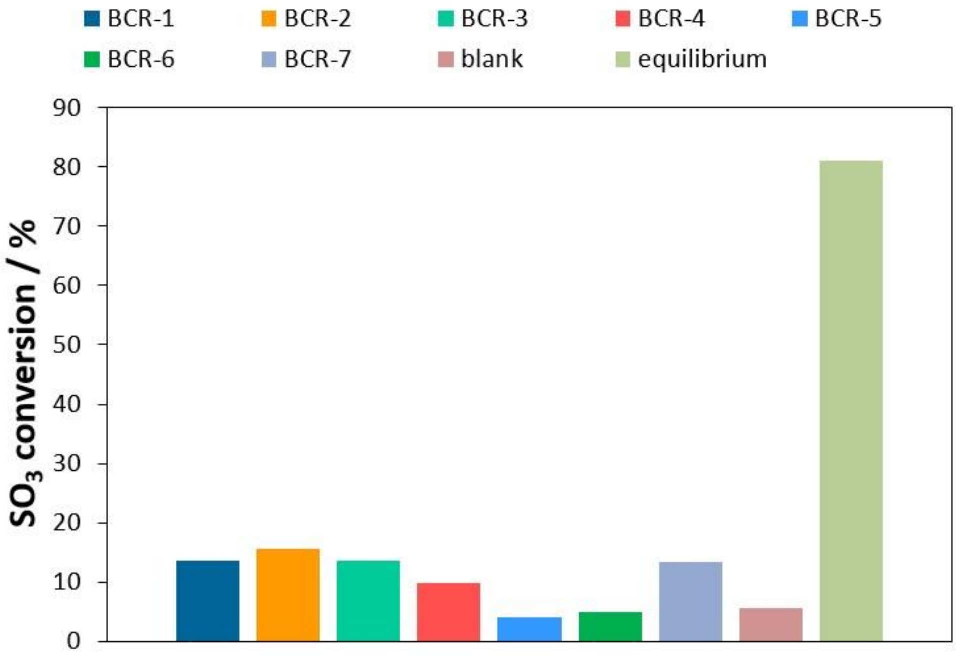
- Quartz tube reactor filled with quartz beads (left side) and quartz wool (right side). Particles in fixed bed formulation
- SO_2 analysis in a heated (210^{o}C) quartz cuvette by UV-Vis spectrometry

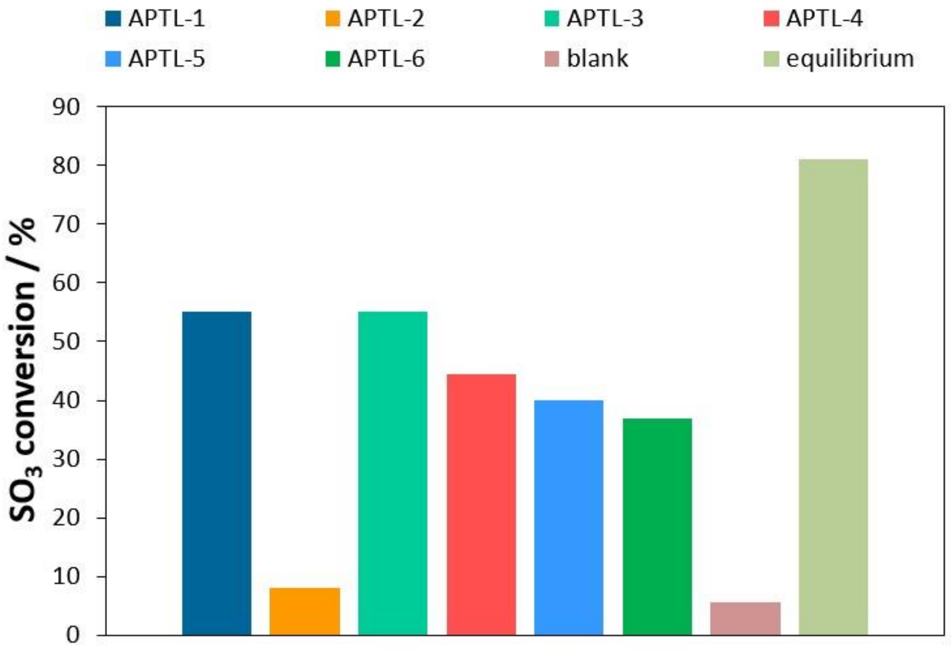
Experimental conditions

- Experimental conditions set for the preliminary tests
  - ✓ Reaction temperature: 850°C, selected samples at 800-900°C
  - ✓ Pressure: 1 bar
  - ✓ Feed: conc. sulfuric acid (98%), 0.12 ml/min
  - ✓ GHSV = ~25,000 - 50,000 h^{-1}
  - ✓ Catalyst quantity per test: 1 g, selected samples 2 g
  - ✓ Dilution of reactor outlet with N_2 flow to achieve measurable SO_2 concentration values
  - ✓ On-stream exposure per test: approx. 60 min

Evaluation results

- Decomposition reaction (SO_3 conversion to SO_2)

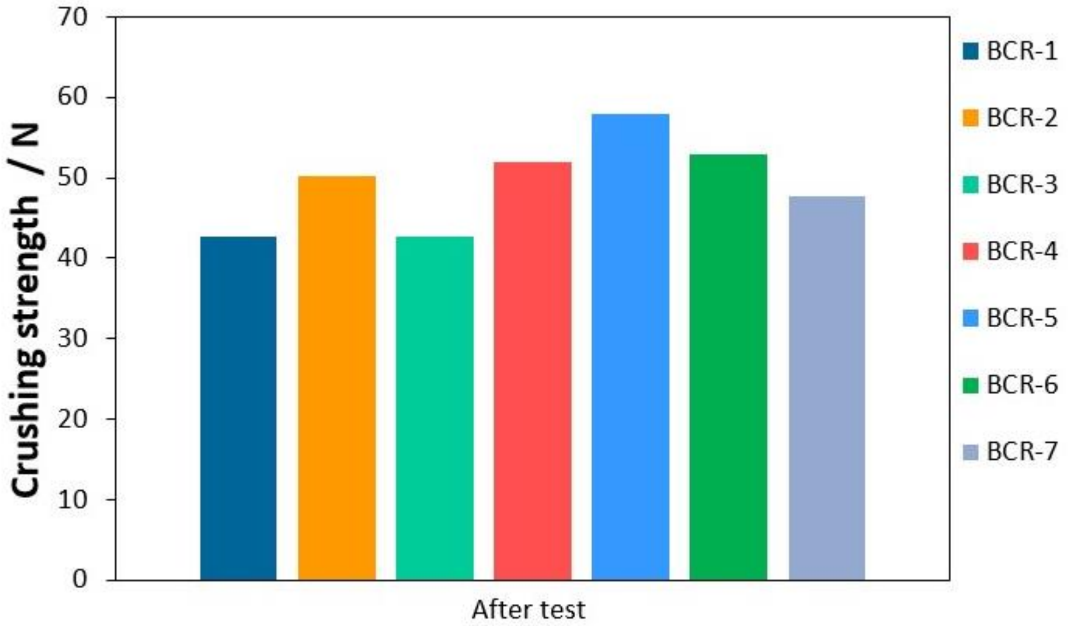




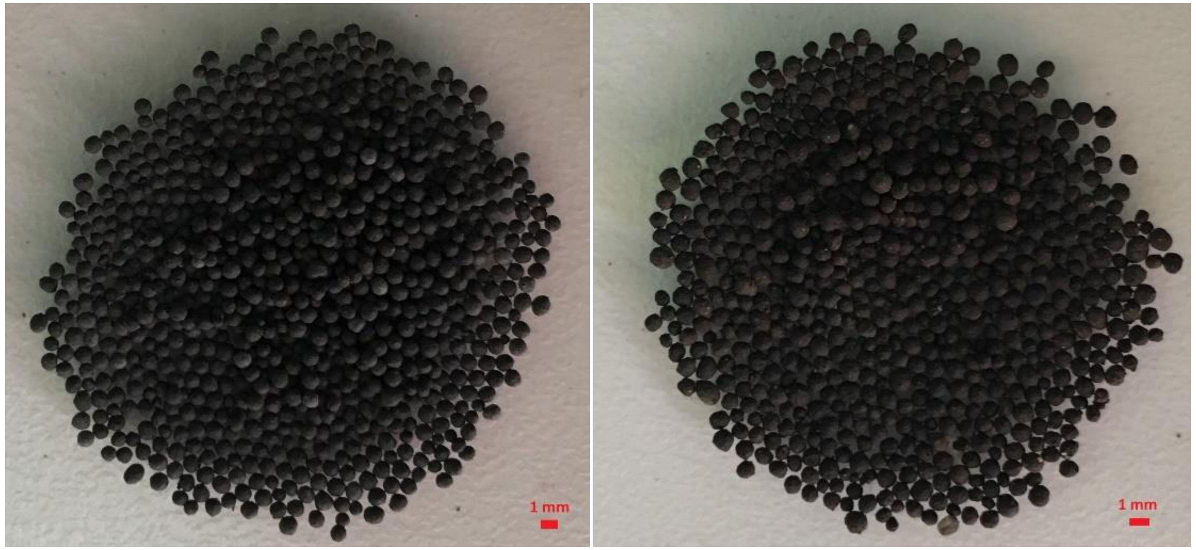
- Gas-phase SO_3 dissociation (blank) → conversion of approx. 5%
- BCR proppants → relatively low performance, no significant effect of p.s. Absence of catalytically active phases
- APTL particles (rich in Fe_2O_3) much higher efficiency
  - Samples calcined at lower temperature (APTL-1, APTL-3, APTL-5) more active cf. the ones calcined at high temperature
  - Pure Fe_2O_3 calcined at high temperature significant conversion decrease (<10%) → withstood in composite cases

Structural stability performance – BCR proppants

➢ Crushing Strength measurements of particles after decomposition experiments



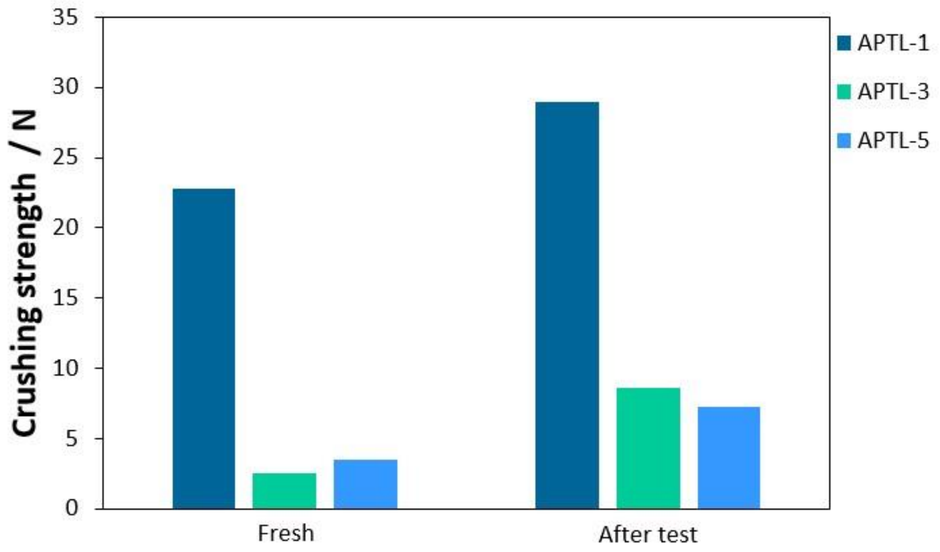
➢ Indicative post-experimental photos → samples unharmed

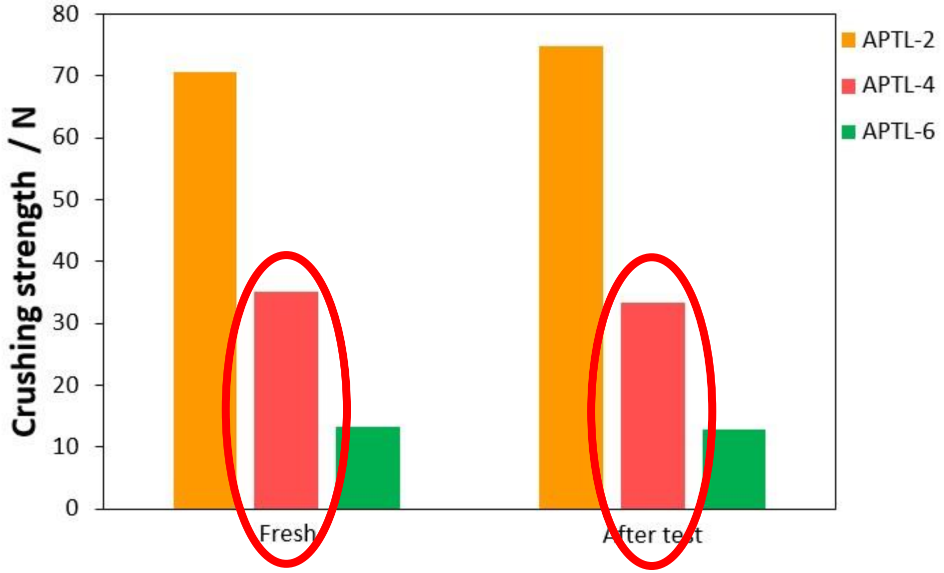


- CS for the case of BCR proppants reduced by >50% after 60 min of exposure (>>100N before test), still high
- Independent of p.s. for BCR proppants, remains approx. same

Structural stability performance – APTL particles

➢ Crushing Strength measurements of particles before & after decomposition experiments





➢ Indicative post-experimental photos → samples unharmed

- APTL particles tend to have almost unchanged CS after test, if not increased
- Due to sintering phenomena, samples calcined at high temperature (APTL-2, APTL-4, APTL-6) have higher structural stability than the same ones calcined at low temperature (APTL-1, APTL-3, APTL-5)
- **APTL-4** seems to have the in-principle most promising compromise between SO_3 conversion and CS

Conclusions & future improvements

- Extremely high mechanical integrity leads to low catalytic activity in the proppants
  - ✓ Lack of sufficient catalytically active phases
- Low to negligible surface areas → seems not to play a major role in the SO_3 conversion
- APTL-4 most promising material so far
  - ✓ Commercial Fe_2O_3/Aluminosilicate composite
  - ✓ Combines blackish color, SO_3 conversion > 40% and CS > 20 N → However, s.o.a catalysts higher conversion
- Both approaches should be combined to create modified proppants relatively rich in catalytically active phases (e.g. Fe_2O_3, **CuO** etc.)
- Need to find optimum compromise between catalytic activity and mechanical integrity
  - ✓ Challenging conditions in the solar receiver
  - ✓ Particles constantly circulated within the relevant steps of the integration process
- **Encouraging first results towards this direction**

Thank you for your attention!

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