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Supercritical CO_2-assisted introduction of Cu into Zr-MOFs

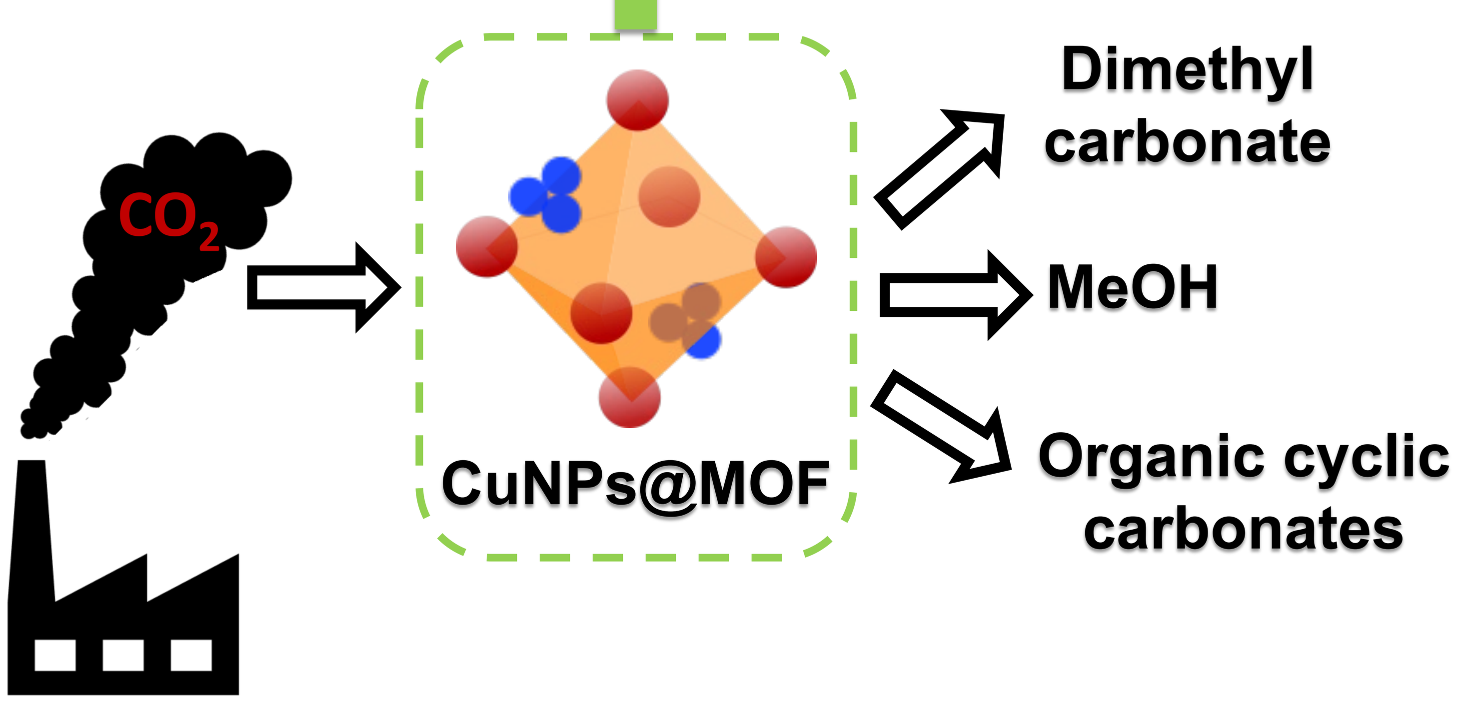
Maciej Róziewicz[a], Joanna Oczeretko[a], Janusz Trawczyński[a], Agata Łamacz[a]

[a]Department of Engineering and Technology of Chemical Processes, Faculty of Chemistry, Wroclaw University of Science and Technology, Wroclaw, Poland

Introduction:

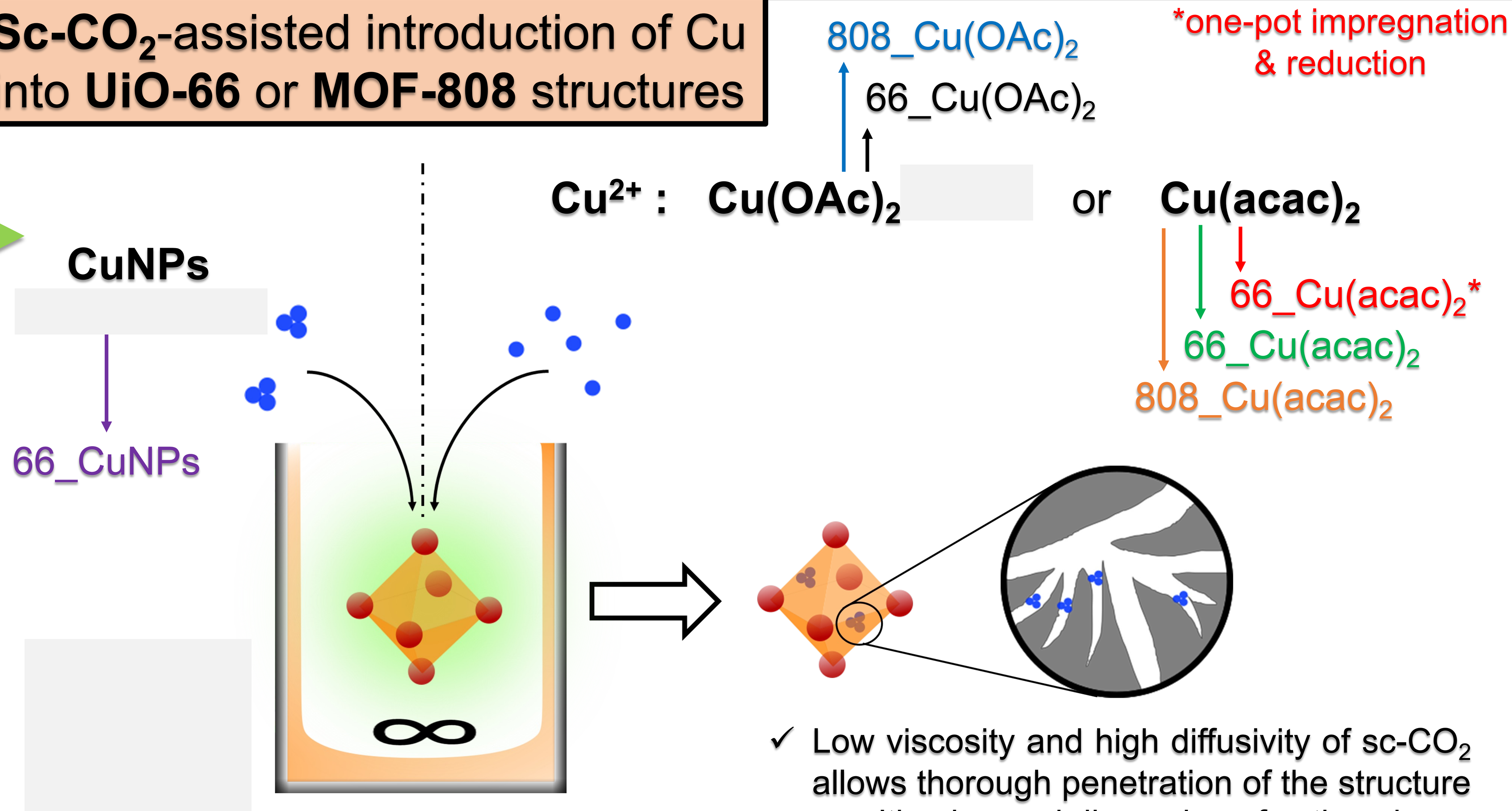
Development of MOF-based catalysts for CO_2 conversion

Target: development of method for obtaining materials with well dispersed and accessible active sites.



Method:

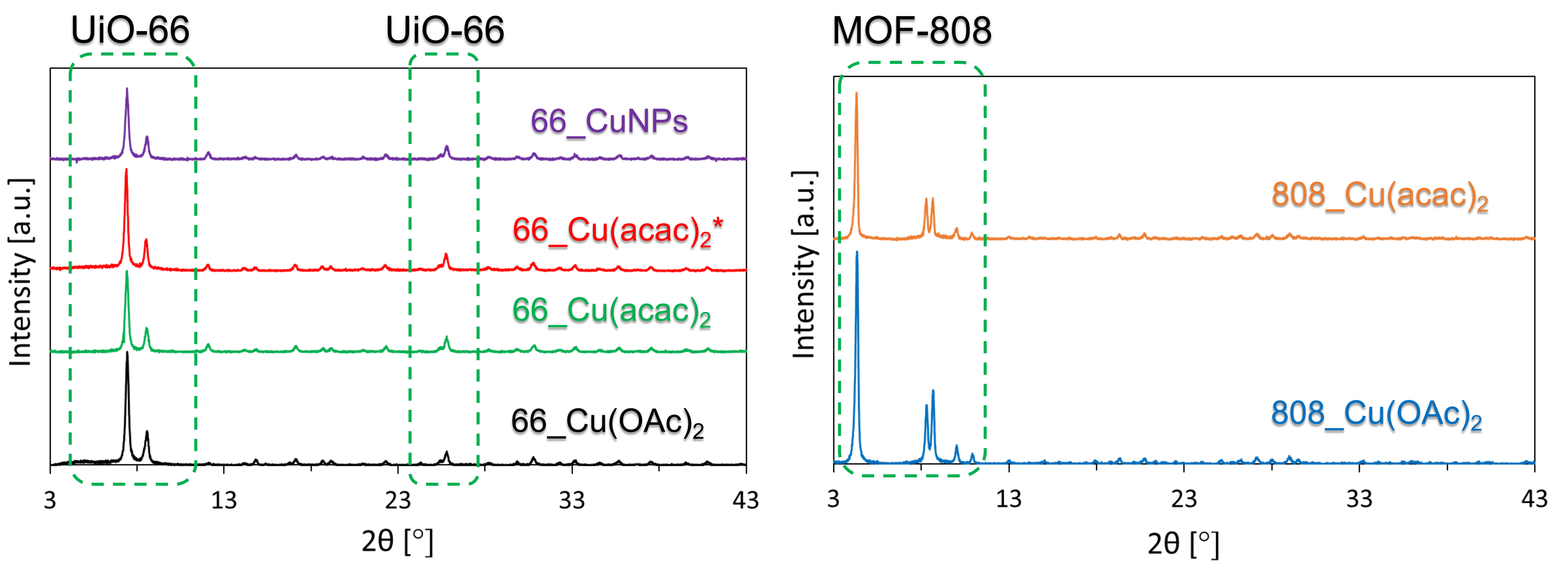
Sc-CO_2-assisted introduction of Cu into UiO-66 or MOF-808 structures



✓ Low viscosity and high diffusivity of sc-CO_2 allows thorough penetration of the structure resulting in good dispersion of active phase

Results and discussion:

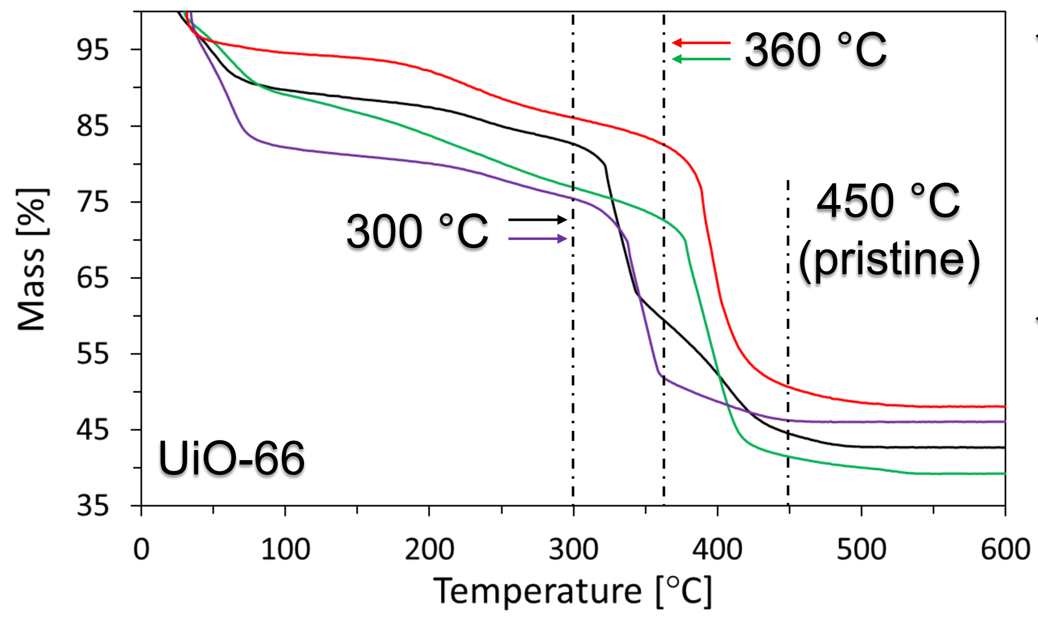
Crystalline structure – XRD



✓ Composites maintained crystalline structure after the Cu introduction process.

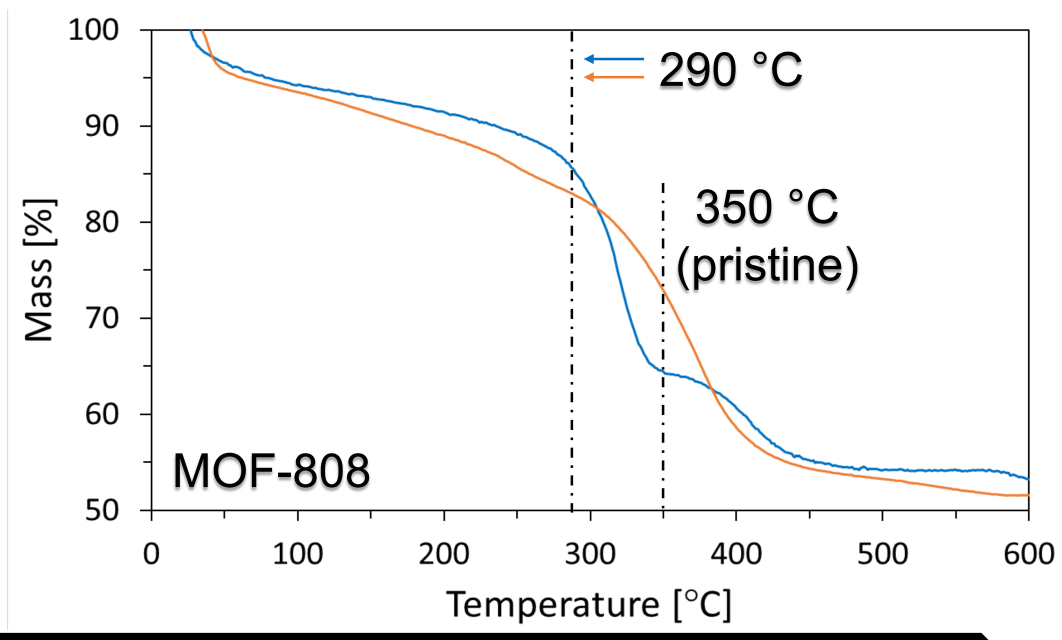
✓ No additional, undesired phases were observed.

Thermal stability – TGA

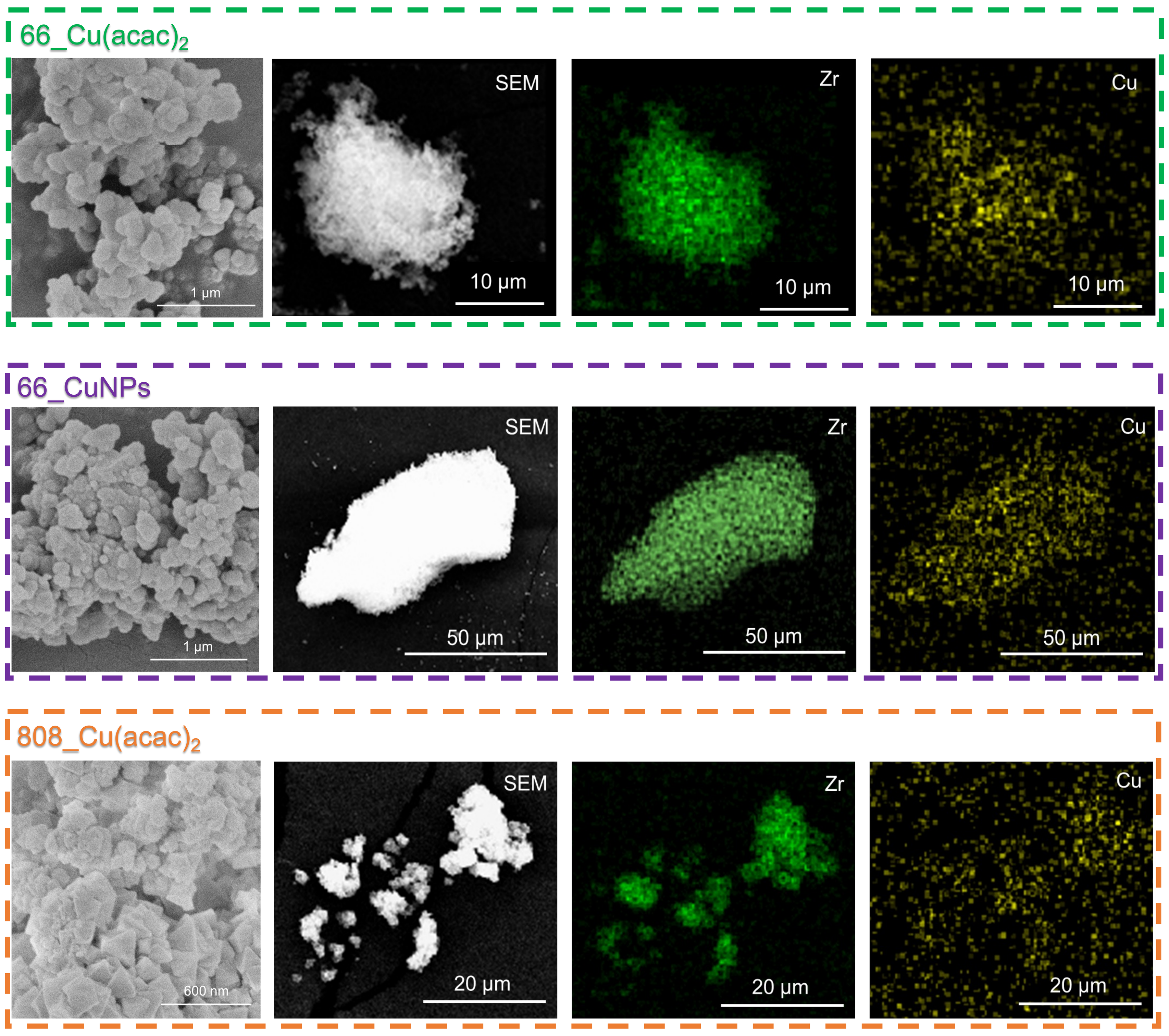


✓ Decrease of thermal stability of all materials, compared with pristine MOFs.

✓ Lower stability of samples obtained with use of co-solvent in case of UiO-66 structures.



Morphology and chemical composition – SEM & EDS



Material	Cu [wt. %]	
	EDS	nominal
66_Cu(OAc)$_2$	0,7	4,0
66_Cu(acac)$_2$	0,7	1,4
66_Cu(acac)$_2$*	2,5	1,5
66_CuNPs	5,5	4,6
808_Cu(OAc)$_2$	5,2	5,7
808_Cu(acac)$_2$	2,0	2,2

✓ Uniform distribution of copper in the MOF crystals was achieved.

✓ Introduction of Cu was especially efficient for MOF-808 materials.

Specific surface area – N_2 sorption at 77 K

Material	S_{BET} [$m^2 \cdot g^{-1}$]
UiO-66 (pristine)	**1335**
66_Cu(OAc)$_2$	1037
66_Cu(acac)$_2$	668
66_Cu(acac)$_2$*	1023
66_CuNPs	895
MOF-808 (pristine)	**1356**
808_Cu(OAc)$_2$	1131
808_Cu(acac)$_2$	1362

Conclusions:

- Supercritical CO_2-assisted introduction of Cu into UiO-66 and MOF-808 materials was successful. All composites maintained crystalline structure and morphology of the pristine metal-organic frameworks.
- Presence of uniformly distributed Cu inside the crystals was confirmed by EDS analysis.
- According to results of N_2 sorption, composite materials exhibited lower values of specific surface area due to the filling of the pores.
- Results of TGA shows that thermal stability of the composites were worsened compared with the pristine materials.
- In UiO-66 materials, use of co-solvent may have induced formation of additional structural defects, resulting in worse thermal stability than for samples processed in sole sc-CO_2.

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