Green synthesis of multifunctional MIL-100 for CO_2 cycloaddition to epoxides

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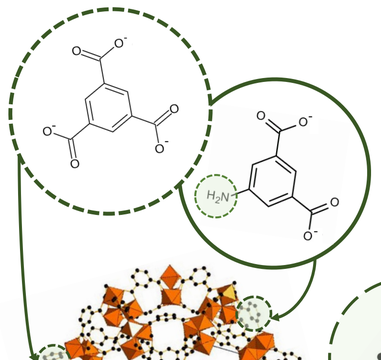
INTRODUCTION

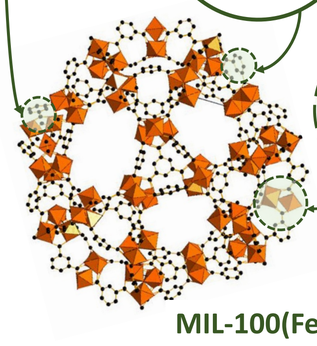
Linkers containing Lewis basic sites ($–NH_2$)



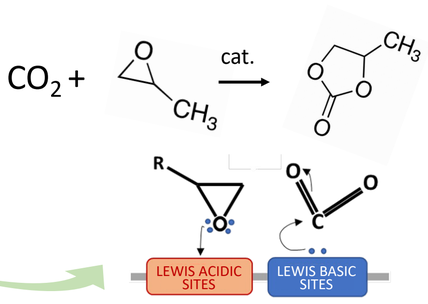
Metal-Organic Frameworks (MOFs) are porous materials consisting of metal ions or metal clusters and organic linkers. Owing to developed surface area and the possibility of modification, MOFs find application, e.g., in catalysis.

MIL-100(Fe) can be used as a catalyst for **CO_2 cycloaddition to epoxides** (reaction occurs over Lewis acidic and basic sites).

Lewis acidic sites (Fe^{3+}) in metal clusters



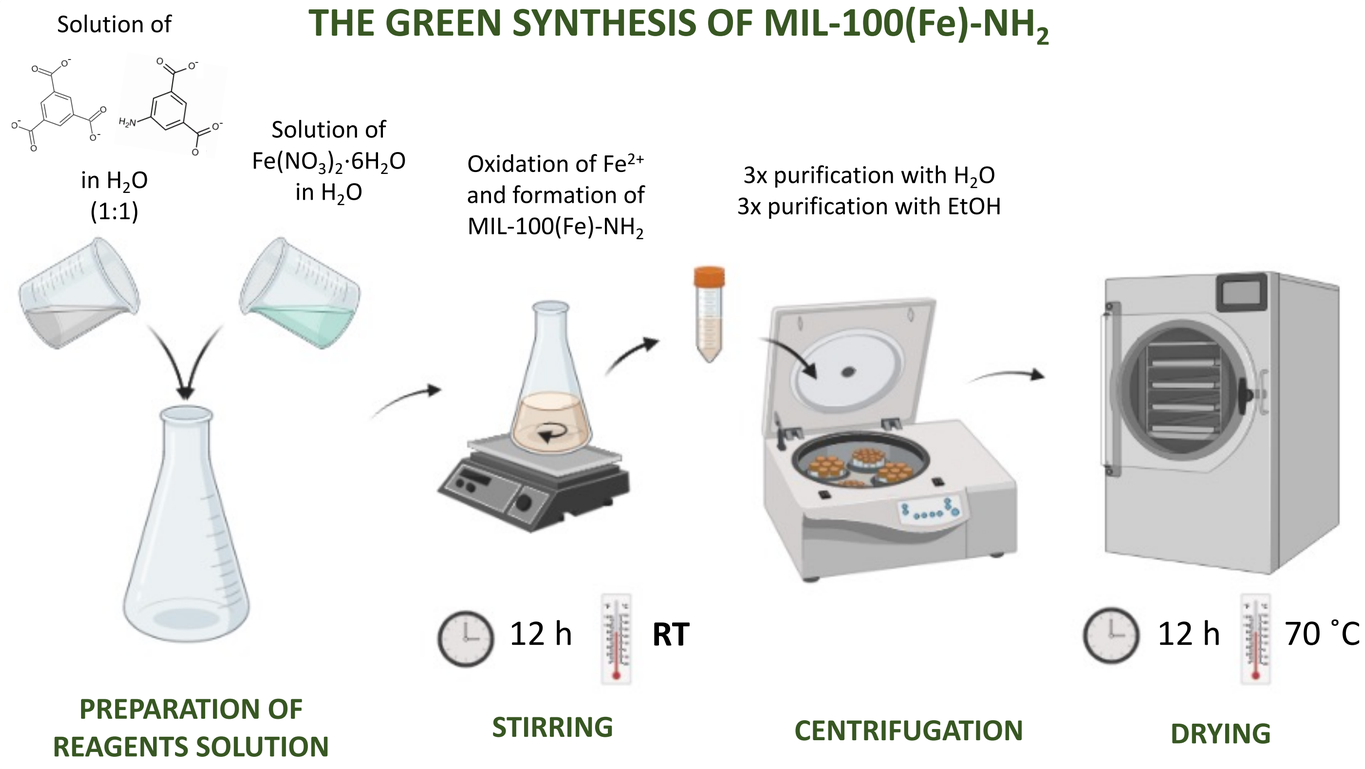
MIL-100(Fe)



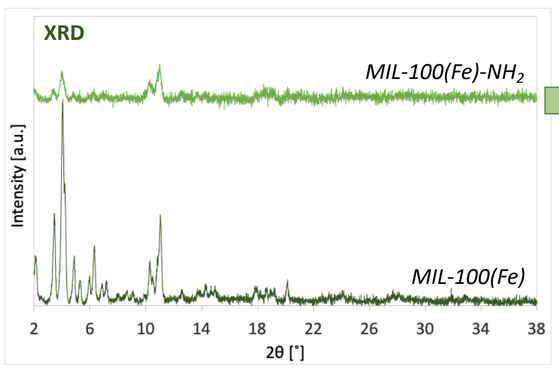
THE AIM OF THE RESEARCH

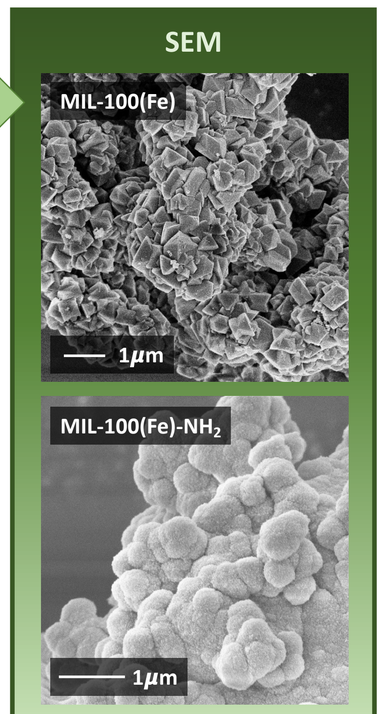
Green synthesis of MOFs with MIL-100 topology containing Fe^{3+} and linkers with NH_2 groups for CO_2 cycloaddition to epoxides.

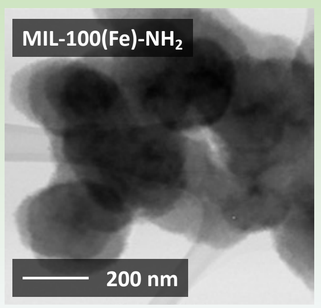
THE GREEN SYNTHESIS OF MIL-100(Fe)-NH_2



STRUCTURE AND MORPHOLOGY



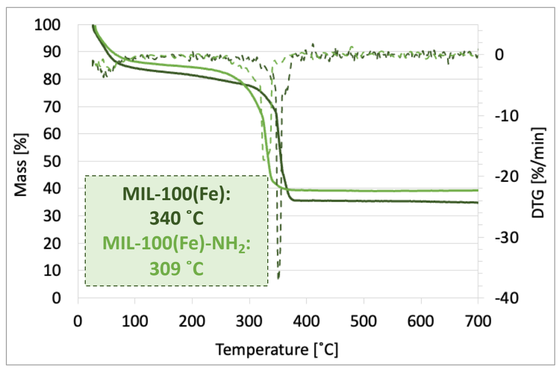




MIL-100(Fe)-NH_2:

- ✓ has a crystal structure typical for MIL-100,
- ✓ compared to MIL-100 exhibits reduced crystallinity owing to introduction of the defective linker,
- ✓ crystallizes in the form of octahedral particles (200 nm) and having rounded edges (unlike for MIL-100).

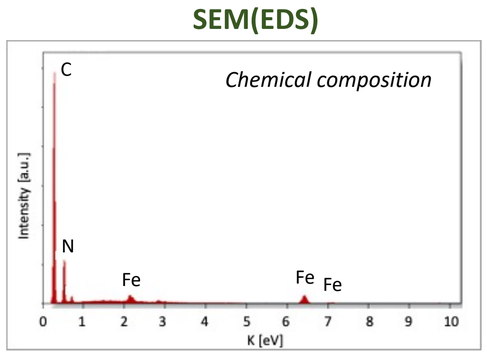
THERMAL STABILITY



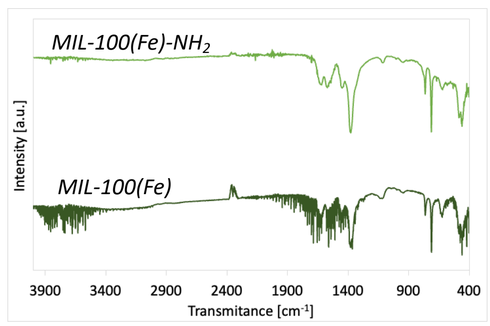
Reduced thermal stability of MIL-100(Fe)-NH_2 is caused by the presence of defective linkers.

CHEMICAL COMPOSITION OF MIL-100(Fe)-NH_2

SEM(EDS)

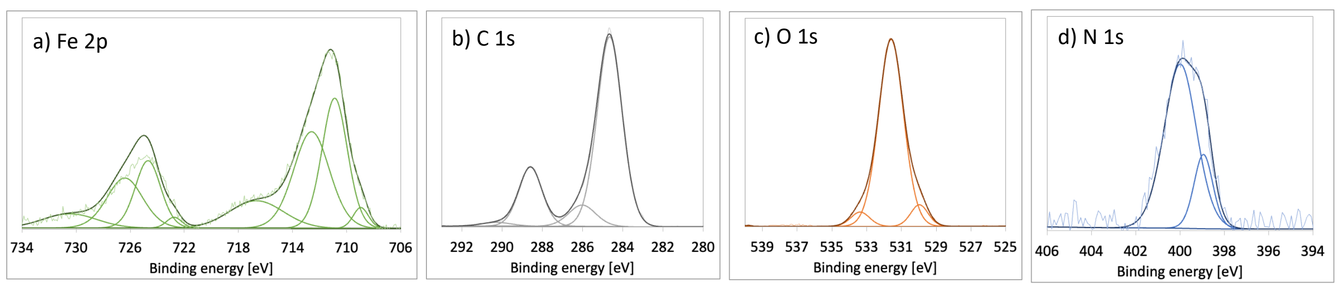


FT-IR



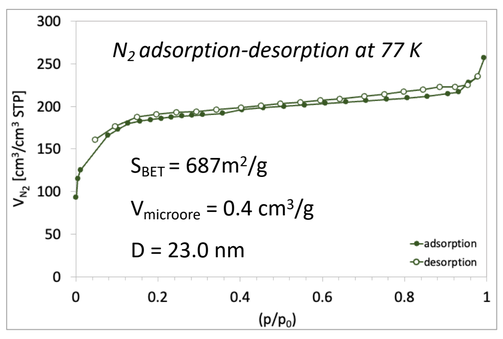
- ✓ Typical bands for C-O and Fe-O in linkers and metal nodes detected.
- ✓ Band at 1440 cm^{-1} assigned to C=O proves the presence of the uncoordinated linker molecules

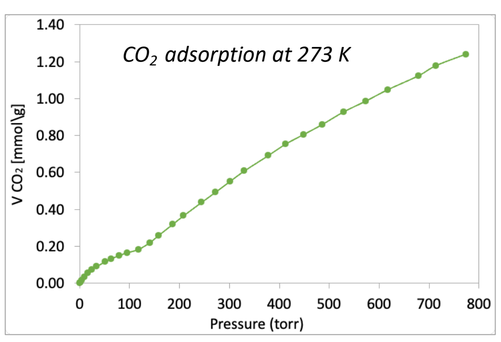
XPS



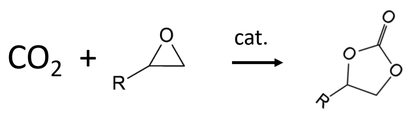
- ✓ O 1s peak at 532.0 eV confirms the presence of Fe-O-C, thus the formation of Fe-metal nodes.
- ✓ The peak at 399.2 eV confirms the presence of $–NH_2$ groups in MIL-100(Fe)-NH_2 .

TEXTURAL PROPERTIES OF MIL-100(Fe)-NH_2





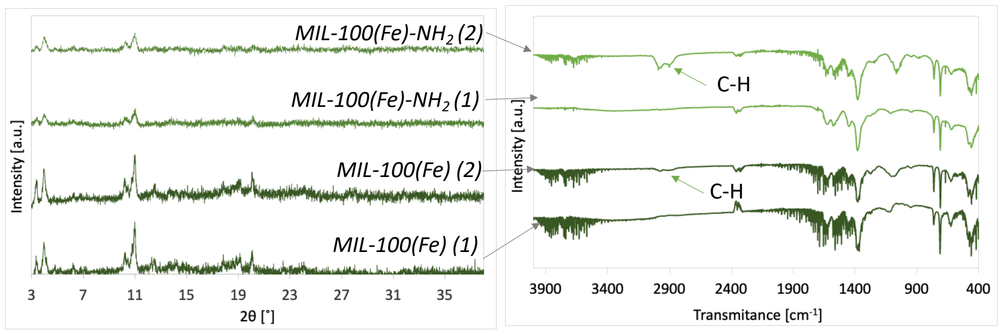
APPLICATION OF MIL-101(Fe)-NH_2 IN CYCLOADDITION CO_2 TO EPOXIDES



CYCLOADDITION CO_2 TO EPOXIDES	
CATALYST	YIELD [%]
Synthesis of propylene carbonate [PC] (1)	
MIL-100(Fe)	61
MIL-100(Fe)-NH_2	70
Synthesis of styrene carbonate [SC] (2)	
MIL-100(Fe)	87
MIL-100(Fe)-NH_2	>99

Reagent: 18 mmol, TBABr: 0,9 mmol, mass of catalyst: 50 mg; T = 60˚C, p = 3 bars, t = 5 h(1), 24h(2)

XRD and FTIR of MIL-100(Fe) and MIL-100(Fe)-NH_2 **spent** in CO_2 cycloaddition to propylene oxide.



- ✓ The presence of NH_2 moieties in the structure increases the activity in the PC and SC synthesis.
- ✓ MIL-100(Fe)-NH_2 and MIL-100(Fe) preserve their crystal structure after the catalytic reaction.
- ✓ After PC synthesis MIL-100(Fe)-NH_2 and MIL-100(Fe) are easily purified (regenerated).
- ✓ Residues of reagents are present on MIL-100(Fe)-NH_2 and MIL-100(Fe) after the synthesis o SC (detected by band assigned to C-H stretching vibrations).

CONCLUSIONS

- ✓ MIL-100(Fe)-NH_2 was successfully obtained via **the green synthesis** carried out at room temperature, atmospheric pressure and in an aqueous solution, which was confirmed using X-ray diffraction.
- ✓ MIL-100(Fe)-NH_2 crystals have octahedron shape with rounded edges.
- ✓ The MIL-100(Fe)-NH_2 material has a well-developed specific surface area and good N_2 and CO_2 sorption capacity.
- ✓ The obtained material consisted of Fe, C, O, N; the presence of the -NH_2 groups was confirmed by XPS.
- ✓ The presence of -NH_2 in the MIL-100(Fe)-NH_2 increases its catalytic activity in both PC and SC synthesis.
- ✓ After catalytic reactions, the materials preserved their crystal structure.

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