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Modulated Synthesis of Cr-MOF (MIL 101) for Hydrogen Storage Applications

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HySA Infrastructure
Hydrogen South Africa

CSIR
our future through science

NORTH-WEST UNIVERSITY
YUNIBESITI YA BOKONE-BOPHIRIMA
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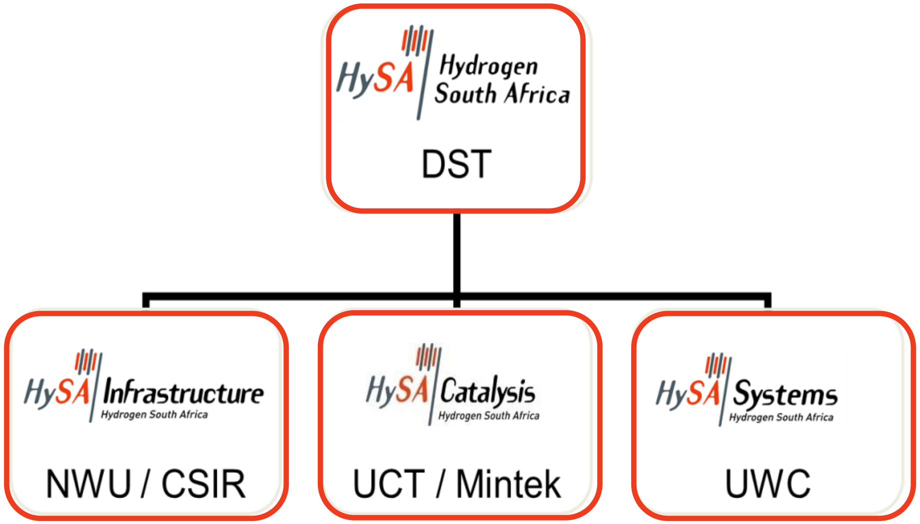
Introduction

- ❑ **Hydrogen South Africa (HySA)**



www.hysainfrastructure.org

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- ❑ Council for Scientific and Industrial Research (CSIR)

www.csir.co.za

Objectives

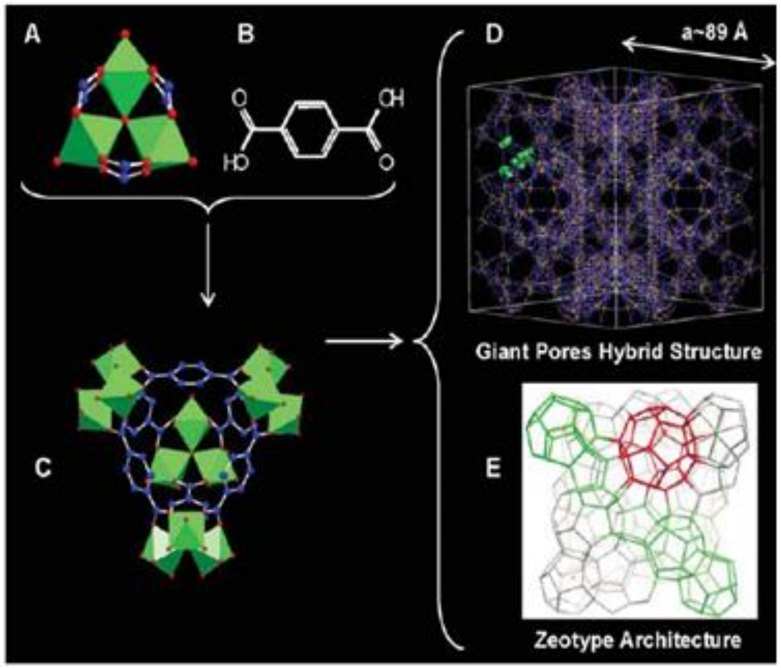
- Prepare Cr-MOF with safe synthetic method
- Maximise the H_2 adsorption of the synthesised Cr-MOFs
- Maximise safety in the synthesises procedure to enable large scale production

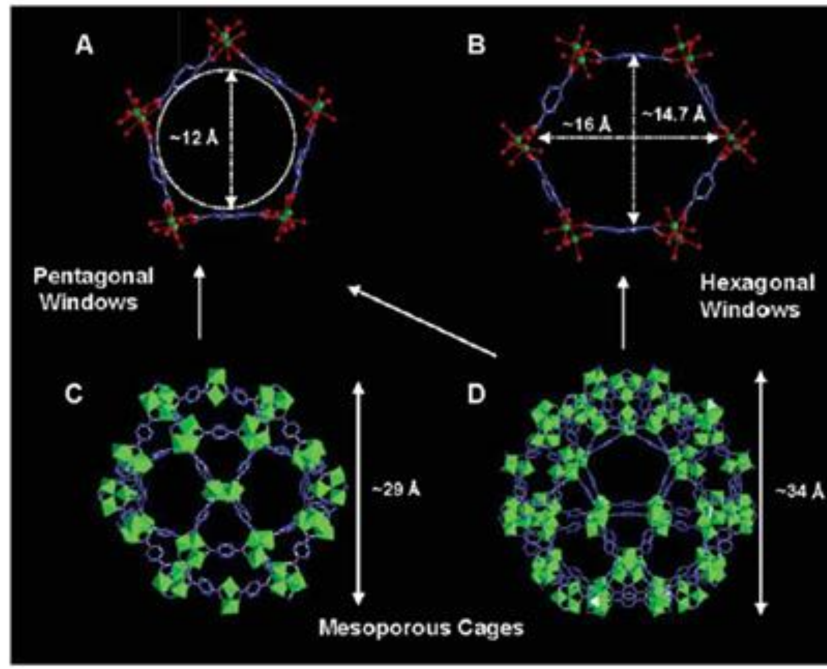
Unique Facts about Cr-MOF

- Large pores that can be used for gas storage
- Open metal sites
- Relative large surface area
- Hydrogen storage potential
- H_2O as solvent
- Draw back is the use of HF as a modulator

Chromium-based MOF (MIL-101)

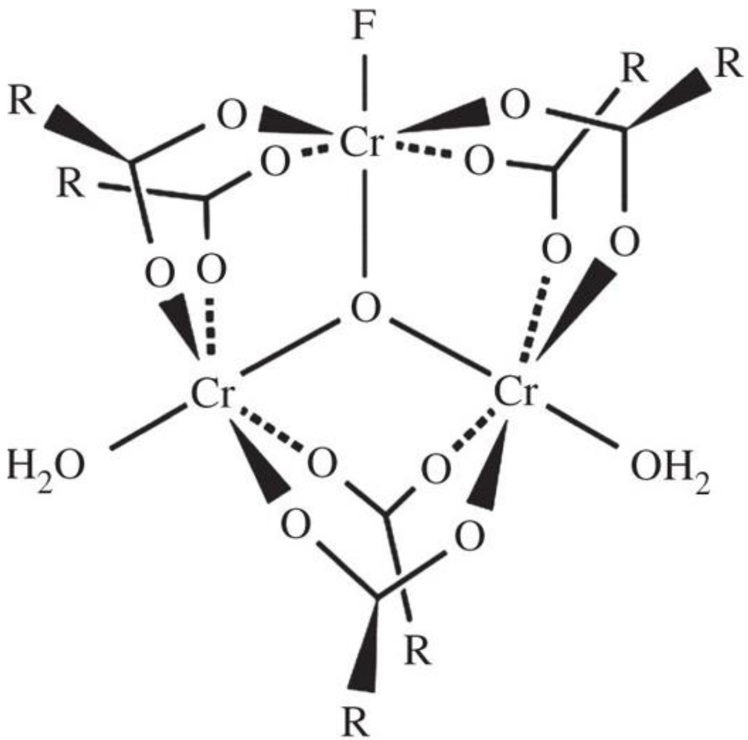
(MIL= Matériaux de l'Institut Lavoisier)





Two types of mesoporous cages: 29Å and 34Å

MIL-101 Structure



- Hydrothermal synthesis in an autoclave
- Chromium salt (usually $Cr(NO_3)_3 \cdot 9H_2O$), H_2BDC and H_2O
- 200–220 °C
- 8–20 h
- Formula: $Cr_3F(H_2O)_2O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3.nH_2O$ (where n is ~25)

Hydro Fluoric acid

- HF acid is very reactive
- Special storage and apparatus
- Very toxic and harmful to the environment
- Safe use of HF in large scale results in more expenses and increased danger for all involved as well as the environment

Main risk:
CORROSIVE Class 8

Sub risk:
TOXIC Class 6.1

Fluorine Substitution

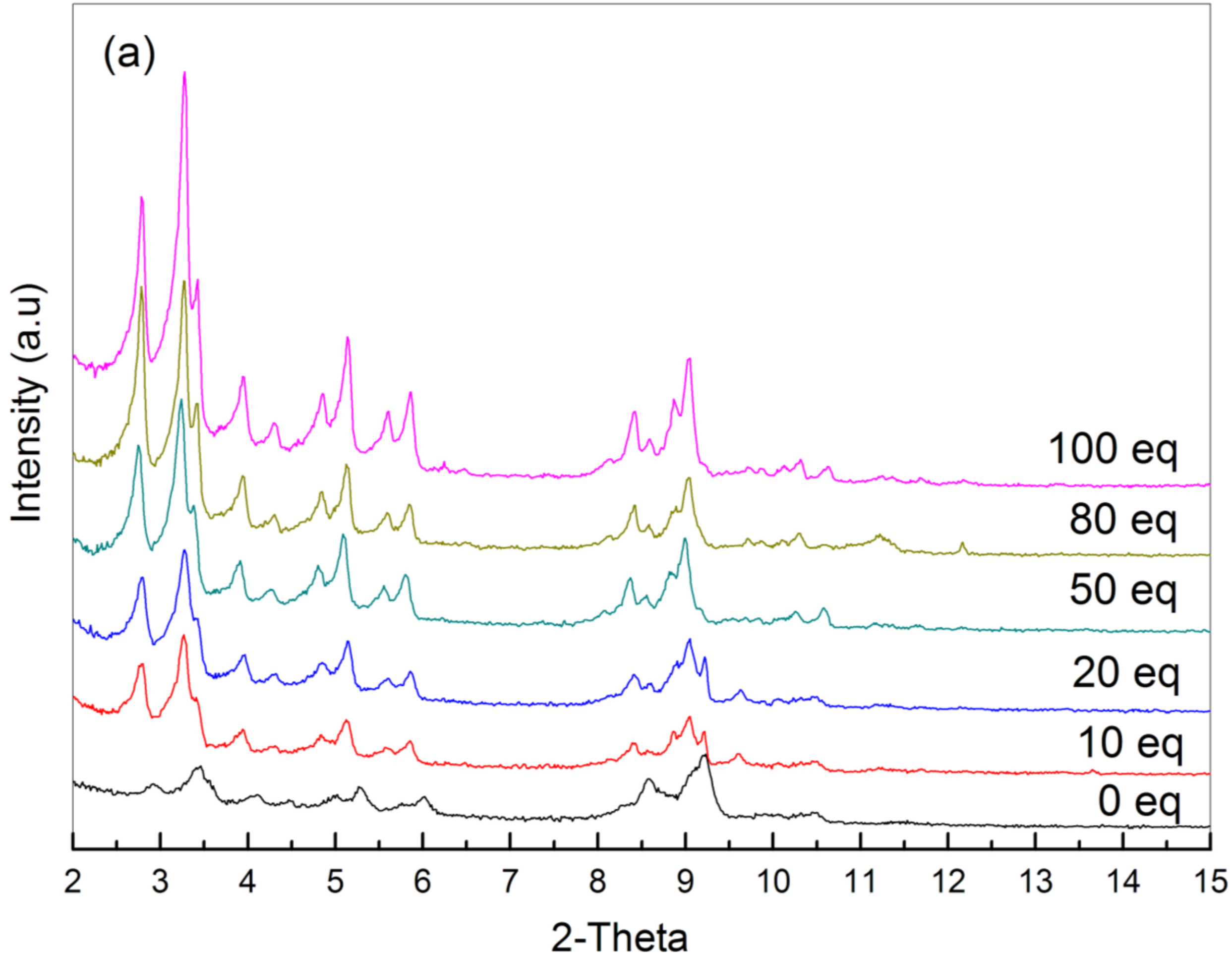
Property	Fluorine	Sulphur	Chlorine
Atomic no.	9	16	17
Std. Atomic weight	18.99	32.06	35.45
Atom group	Halogen	Chalcogen	Halogen
Electron config.	[He] 2s2 2p5	[Ne] 3s2 3p	[Ne] 3s2 3p5
Electronegativity	3.98	2.58	3.16
Oxidation state	-1 (Fluoride ion)	+6 (in H2SO4)	-1 (chloride ion)
Van de Waals Radii	135 pm	180pm	175 pm

- Chlorine is hence the best option
- Can be added via HCl or Salts ($CrCl_3 \cdot 6H_2O$)

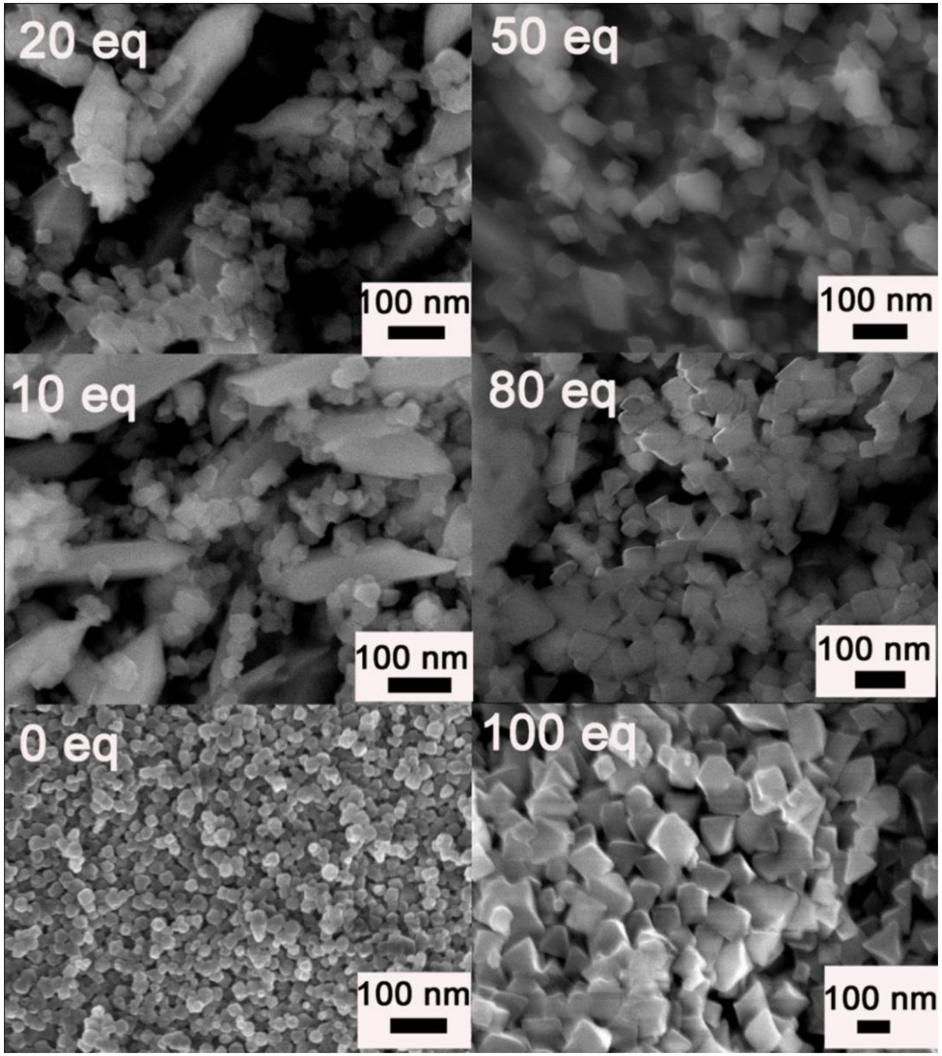
Formic acid Modulation

- Initial experiments gave small sized crystals
- To improve hydrogen storage, we had to obtain bigger sized crystals
- An acid with a similar functional group to that of H_2BDC was needed to slow down the reaction to allow for bigger crystal growth

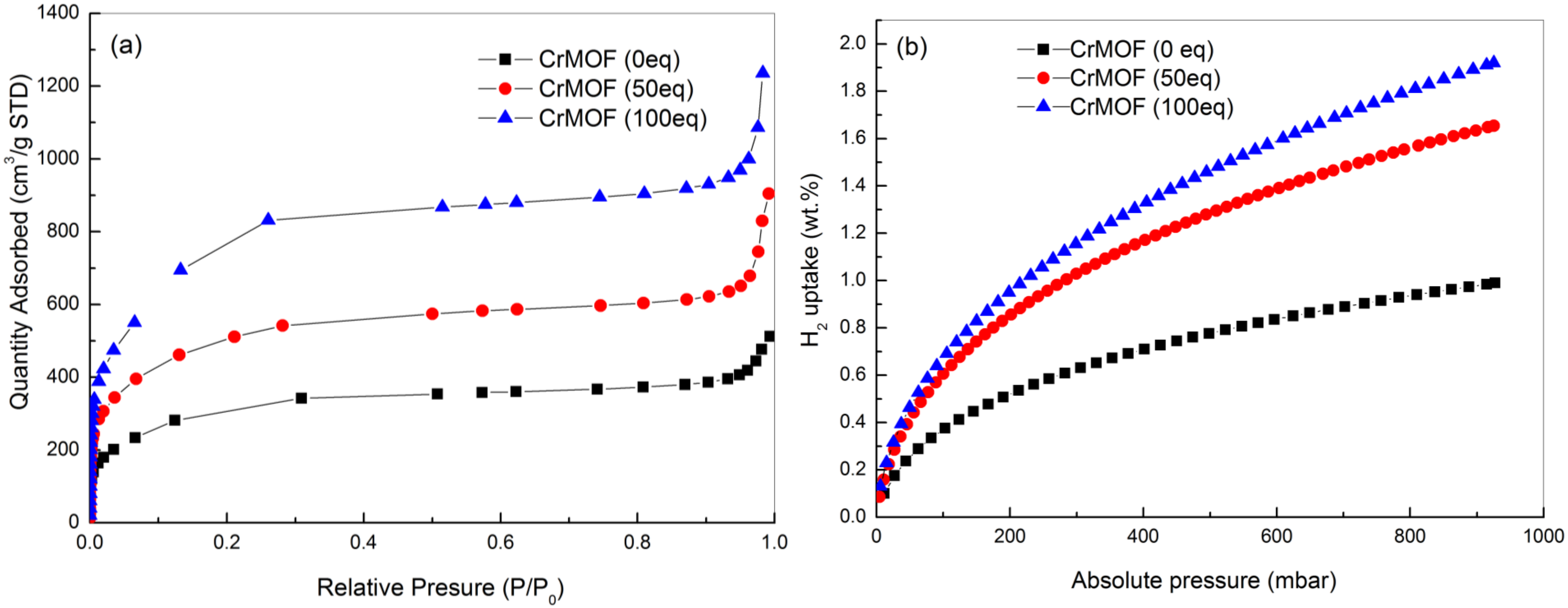
PXRD patterns of the obtained MIL-101



Effect of different ratios of formic acid/$CrCl_3$



(a) N_2 and (b) H_2 sorption isotherms at 77 K and 1 bar

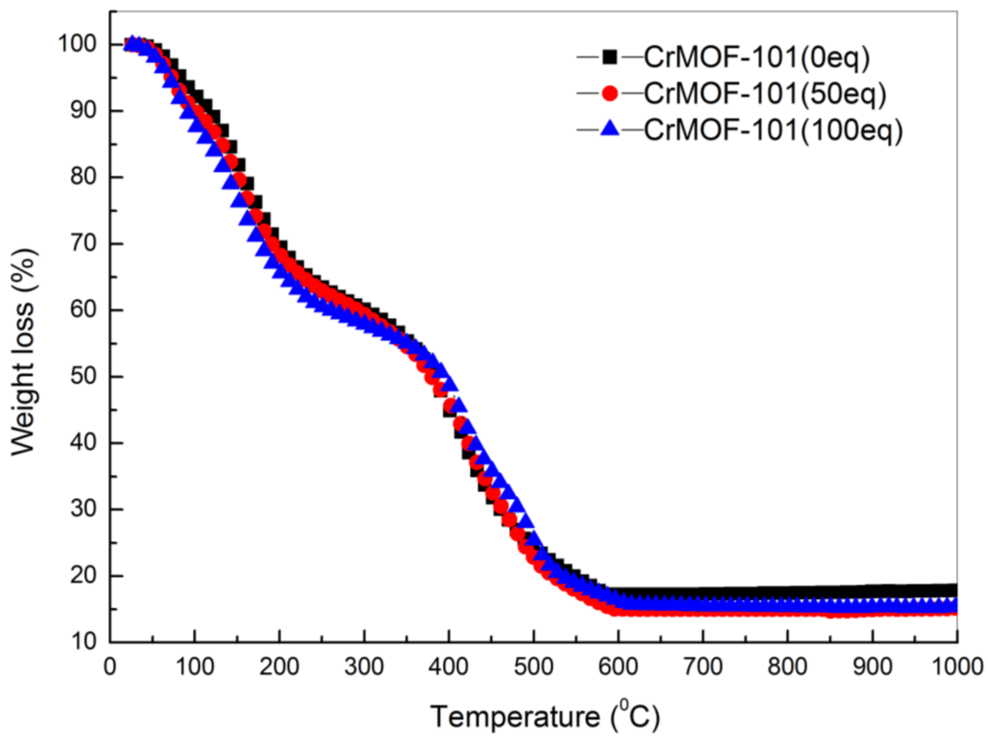


Physical properties and H_2 uptake capacities of the desolvated MIL-101(Cr)

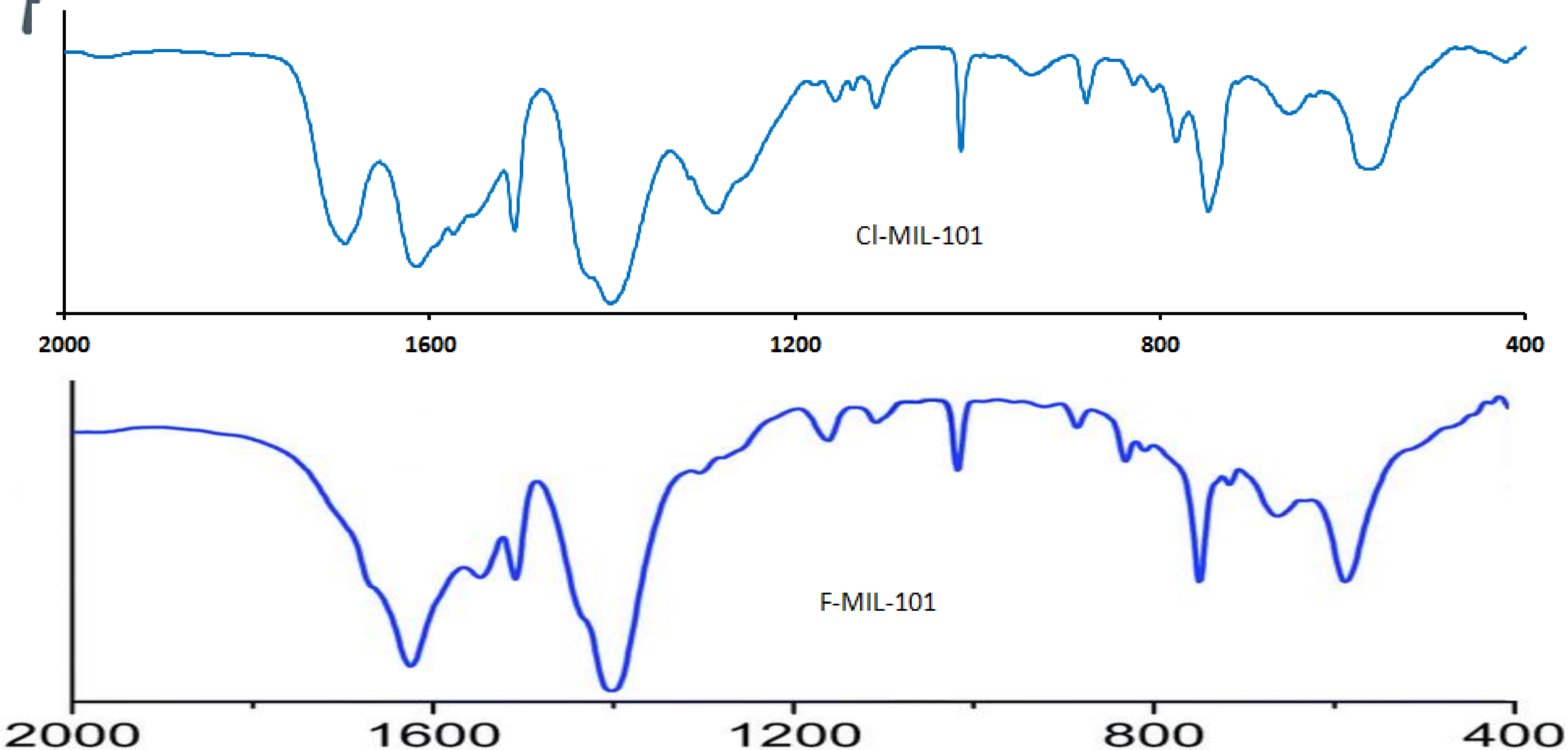
Sample	Density $(g/cm^3)^c$	S_{BET} $(m^2 \cdot g^{-1})^d$	Pore vol. $(cm^3 \cdot g^{-1})^e$	Micropore vol. $(cm^3 \cdot g^{-1})^f$	H_2 uptake $(wt.\%)^g$
MIL-101(0 eq)	1.55	1133.7	0.51	0.43	0.99
MIL-101(50 eq)	1.58	1715.7	0.91	0.78	1.65
MIL-101(100 eq)	1.60	2618.5	1.36	1.22	1.92

[a] Estimated from SEM images. [b] Calculated relative crystallinity. [c] Determined by pycnometer. [d] BET surface area. [e] From H-K analysis. [f] From H-K analysis. [g] Absorbed at 77K and 1 bar.

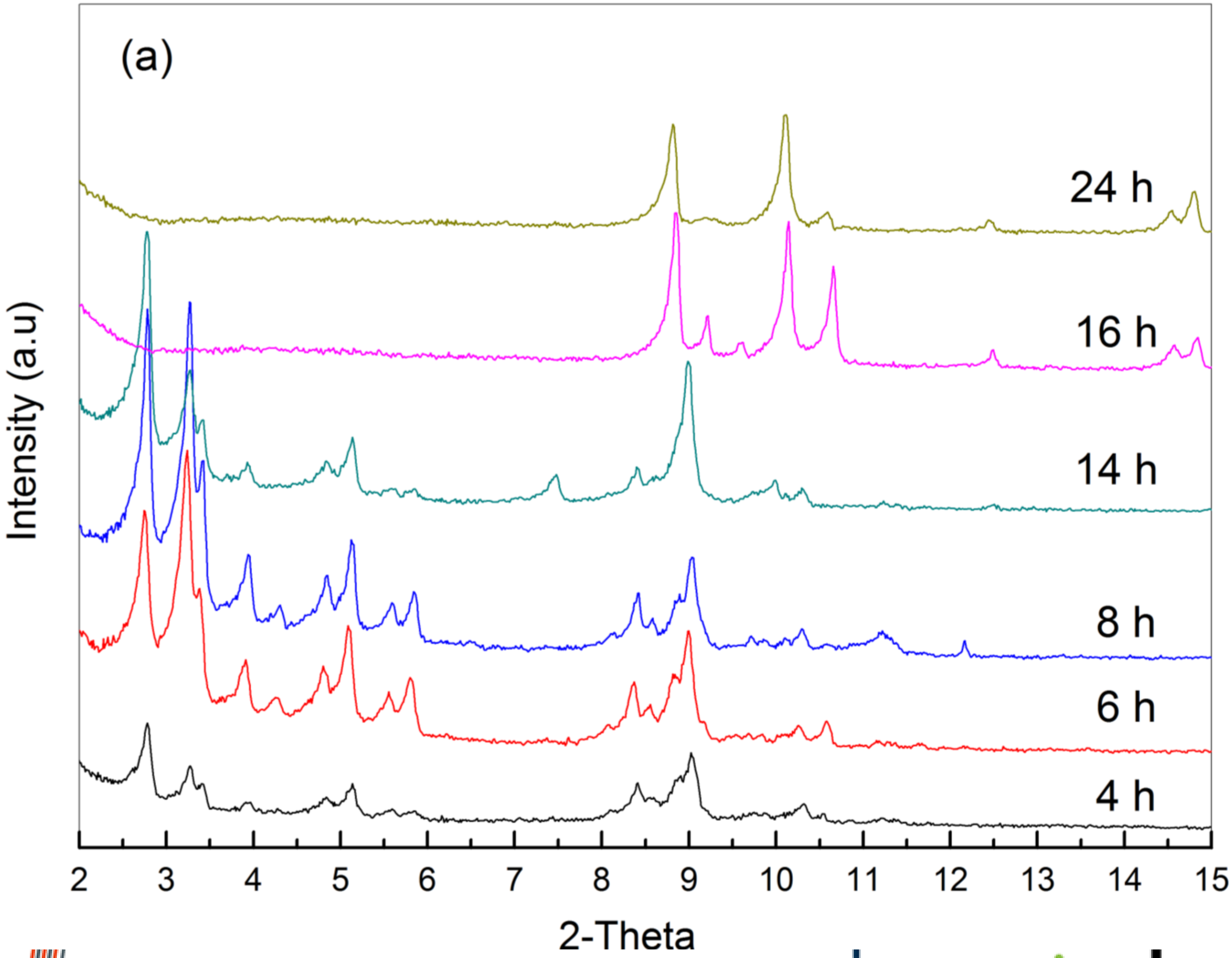
Thermo gravimetric analysis



Cl-MIL-101 and F-MIL-101 FTIR



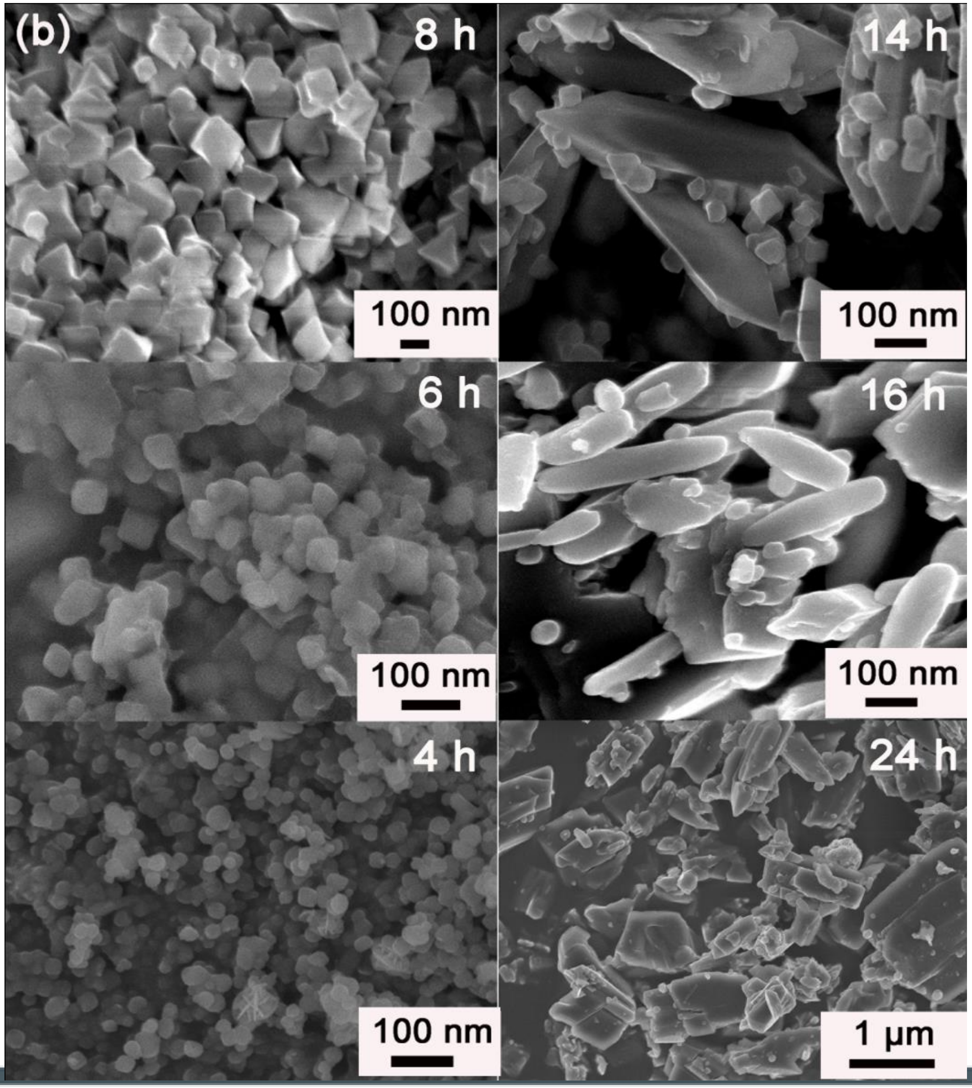
PXRD patterns of CrMOF samples obtained in 100 eq synthesis.



MIL-53

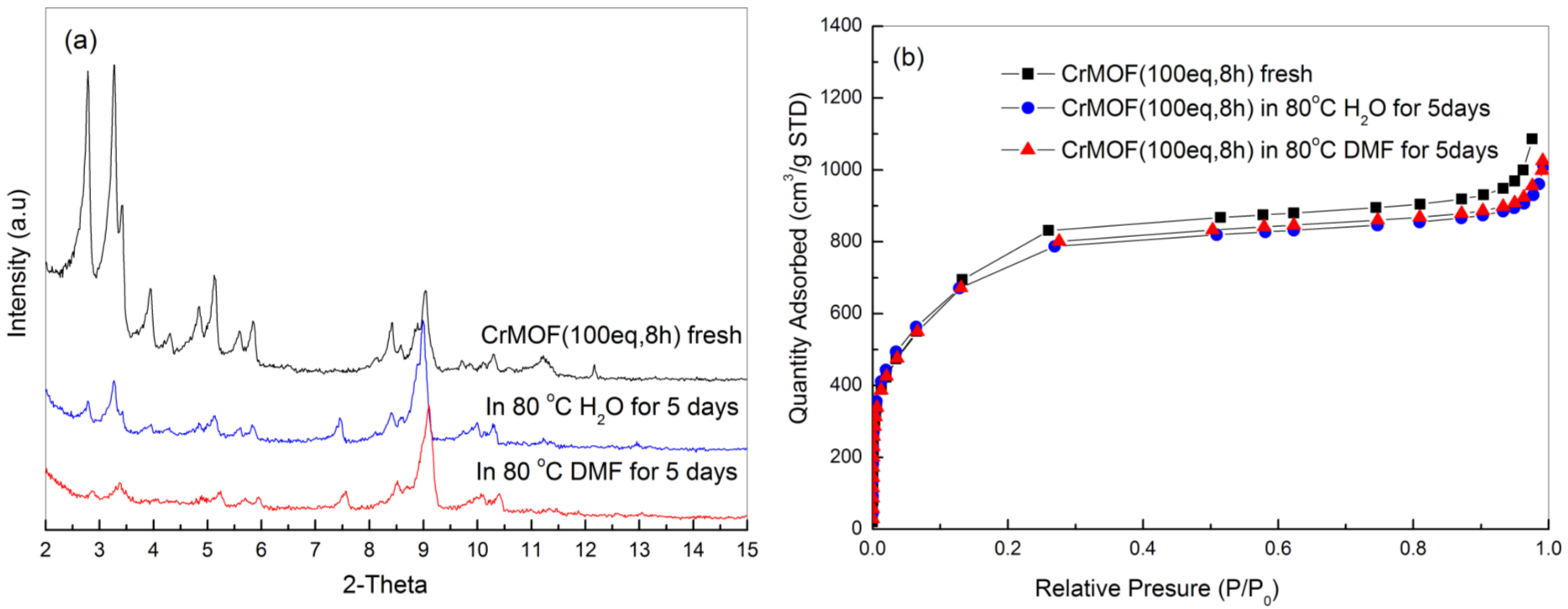
MIL-101

Time dependant reaction



Phase-transition from MIL-101 to MIL-53 observed at the longer synthesis time

Stability in H2O and DMF



(a) XRD patterns, and (b) N_2 adsorption isotherms of MIL-101 after exposure to 80 °C water and DMF for 5 days.

Confirmed synthesis

- Reagents: $CrCl_3 \cdot 6H_2O$, H_2BDC, Formic Acid, H_2O
- Reaction time: 8hrs in high pressure autoclave
- Formic acid:$CrCl_3 \cdot 6H_2O$ equivalents: 100eq

Conclusions

- Successful synthesis of Cr-MOF with no HF
- Water stability confirmed
- Economical and safe industrial production possible
- **GREEN INDUSTRIAL SYNTHESIS POSSIBLE**

Acknowledgments

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