NENE 2020 – September 7th-10th, 2020

Capture of gaseous radionuclides in porous Metal-Organic Frameworks

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Context

Severe nuclear accidents
- → Three Mile Island , USA (1974)
- → Chernobyl, Ukraine (1986)
- → Fukushima , Japan (2011)

Very recent
- → Mayak, Russia (2017)
  Recycling of nuclear waste

Gaseous fission products :

^{76}Kr, ^{79}Kr, ^{85}Kr, ^{103}Ru, ^{106}Ru, ^{129}I, ^{131}I, ^{133}Xe, ^{135}Xe…

https://www.irsn.fr/FR/Pages/Home.aspx

Ruthenium

- ➢ Production > 100 kg (900 MWe reactor)
- ➢ 2 main radioactive isotopes (^{103}Ru (39 d) and ^{106}Ru (372 d))
- ➢ Hard radiotoxicity suspected
- ➢ Gaseous RuO_4 stable at RT

Iodine

- ➢ Production > 12 kg (900 MWe reactor)
- ➢ 2 main radioactive isotopes (^{129}I (15 My) and ^{131}I (8 d))
- ➢ Causes thyroid cancer

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How to capture gaseous species ?

Research about RuO_4 capture :

Natural zeolites

Clinoptilolite
Ø pores : 3 – 10 Å
Ss < 900 $m^2.g^{-1}$
Good adsorption at 150°C - irreversible
Less at 50 °C - reversible

F. Kepak, *et al.*, J. Radioanal. Nucl. Chem. **1992,** *159*, 317–334.

Sand

Ss < 10 $m^2.g^{-1}$
Degradation into RuO_2 at 120°C
No adsorption at 50 °C

P. Nerisson, *et al.*, J. Radioanal. Nucl. Chem. **2019,** *321*, 591–598.

Research about I_2 capture :

Academic studies under investigation

Activated carbons

Ø pores : 4- 60 Å
Specific surface < 4000 $m^2.g^{-1}$
Cheap
Doping (amine)
Competition with water
Fire risk

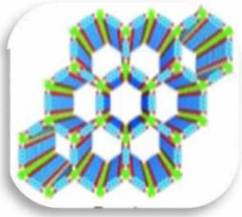
Silver zeolites

Ø pores : 3 – 10 Å
Ss < 900 $m^2.g^{-1}$
Strong bond Ag-I
Limited porosity
Competition with water

Mesoporous silicas

Ø pores : 3 – 10 Å
Ss < 1000 $m^2.g^{-1}$
Doping silver
Strong bond Ag-I

Porous polymers



Ø pores : 2 - 33 Å
Ss < 2000 $m^2.g^{-1}$
Large pores
Chemisorption

J. Huve, *et al.*, *RSC Adv.* **2018**, *8*, 29248–29273.
H. Sun, P , *et al.*, *J. Mater. Sci.* **2015**, *50*, 7326–7332.

N. Mnasri, *et al.*, Microporous Mesoporous Mater. **2014**, *196*, 305–313.
N. Huang, *et al.*, Angew. Chemie Int. Ed. **2015**, *54*, 8704–8707.

New hybrid porous materials :

Metal-Organic Frameworks (MOFs)

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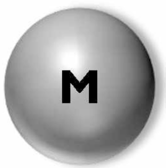
What is MOF ?

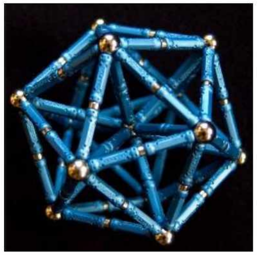


Metallic cluster

+

Organic ligand

Δ → Solvent

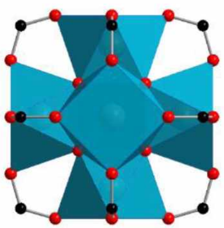


3D structure

Features :

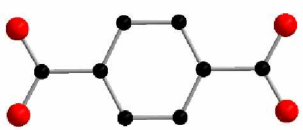
- World wide record specific surface (until 7000 $m^2.g^{-1}$)
- Framework functionalization
- High varieties of topologies
- Cristallized

Example



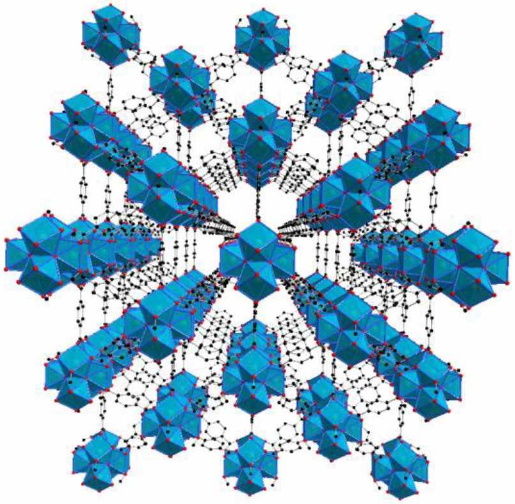
Zirconium cluster

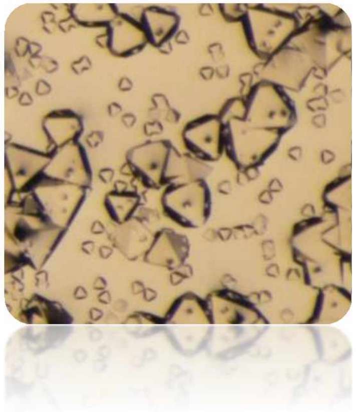
+



Benzene dicarboxylate

Δ → Solvent



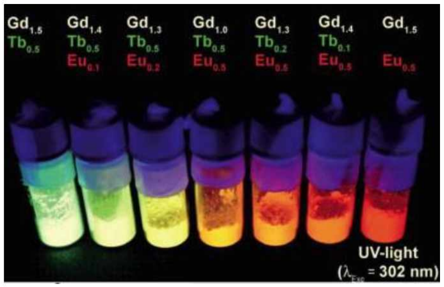


UiO-66-(Zr)

J. H. Cavka, *et al*,. *J. Am. Chem. Soc.* **2008**, *130*, 13850–13851.

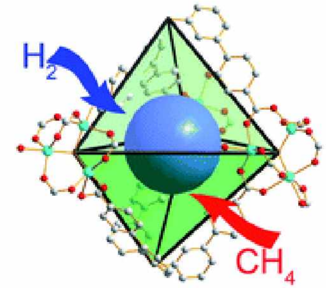
Examples of applications of MOFs

Luminescence

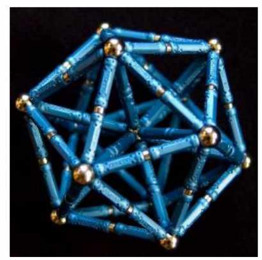


Müller, *et al.*, **j.micromeso.2015**.*03*.036

Hydrogen and methane storage



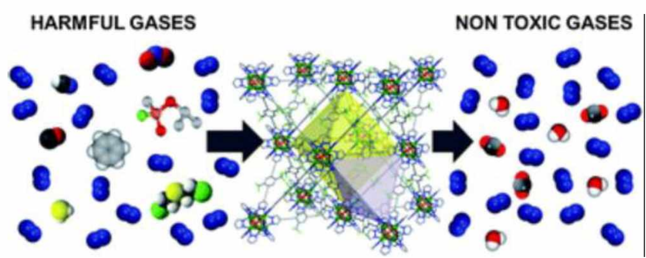
Liu, *et al.*, **Chem. Sci.**, **2012**,*3*, 3032-3037



Heterogeneous catalysis

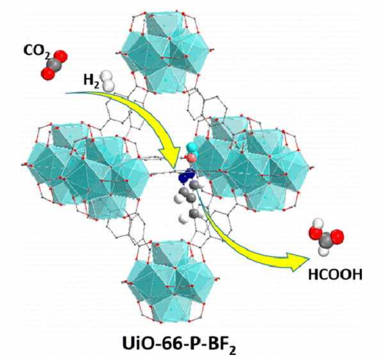
Ma, *et al.*, **J. Mater. Chem. A**, **2015**,*3*, 23136

Removal of harmful and toxic chemicals



Barea, *et al.*, **Chem. Soc. Rev.**, **2014**,*43*, 5419-5430

CO_2 capture



Ye, *et al.*, ***ACS Catal.*** **2015**, *5*, *5*, 2921–2928

P. Silva, *et al.*, *Chem. Soc. Rev.* **2015**, *44*, 6774–6803.

Industrial productions and applications

novoMOF

CSIRO

MOF WORX

NuMat TECHNOLOGIES

ION-X

STREM CHEMICALS, INC.

BASF The Chemical Company

NANOSHEL Creating Miracles in Black

ProfMOF

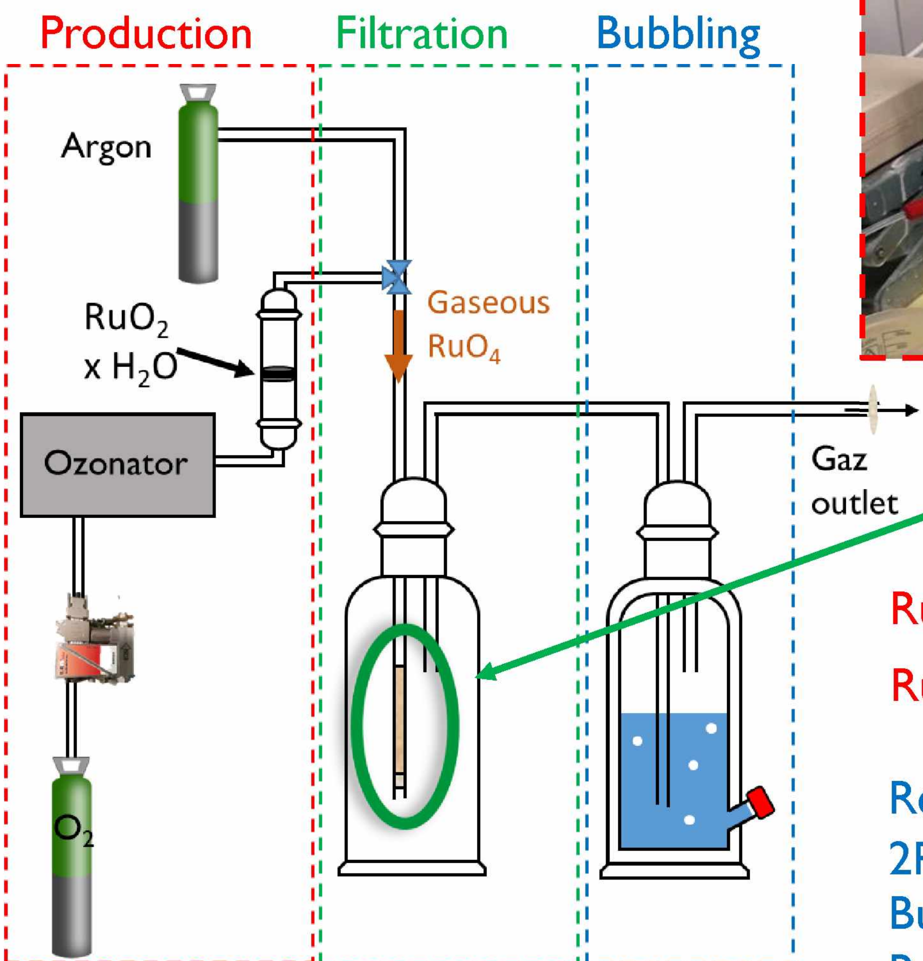
MOF Technologies™

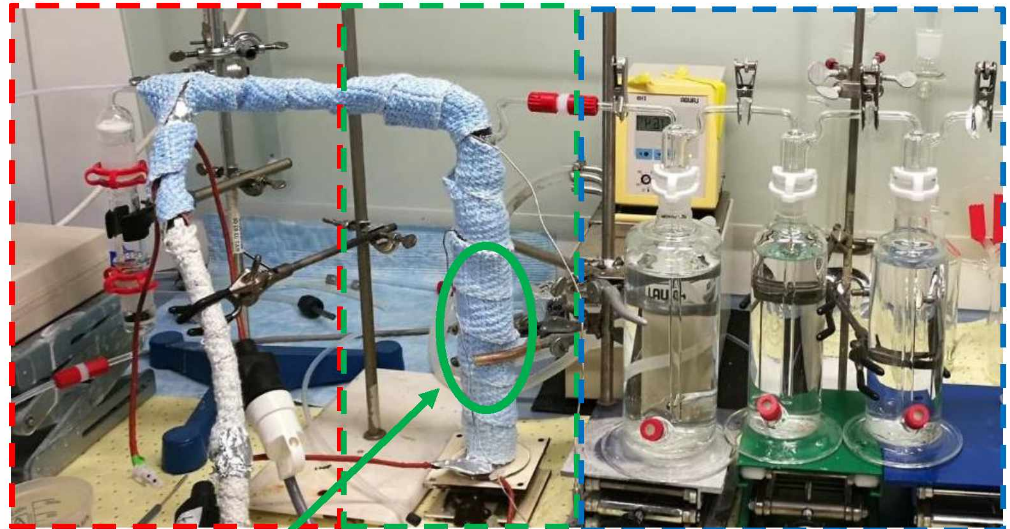
Adsorbent Nanomaterials

Ruthenium capture

Setup for the RuO_4 capture

Ruthenium capture : SAFARI installation (Measurement of the efficiency of the ruthenium filtration)





RuO_4 : Ø ≈ 6 Å

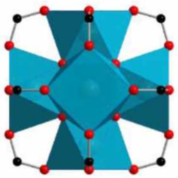
MOF
RuO_4 capture at 50 °C

RuO_4 production :

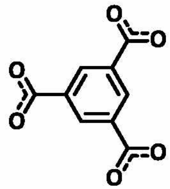
$RuO_2 + 2/3\ O_3 \longrightarrow RuO_4$

Reaction : Bubbler NaOH (1 M)
$2RuO_4 + 4NaOH \rightarrow 2Na_2RuO_4 + O_2 + 2H_2O$
Bubbler temperature RT
Ru quantify by ICP-AES

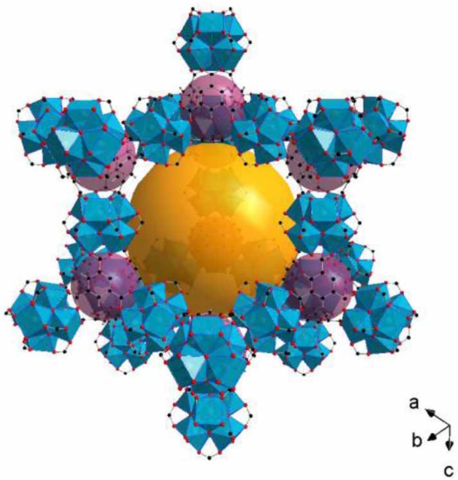
Tests : MOF-808-(Zr)



Zirconium cluster



1,3,5 -benzene tricarboxylate



Features :

2 types of cavities (Ø : 5 and 20 Å)

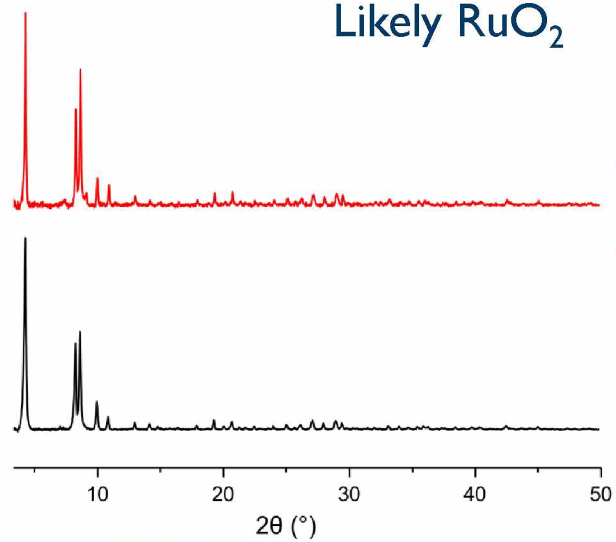
High specific surface (> 2000 $m^2.g^{-1}$)

RuO_x@MOF
Likely RuO_2

Decontamination factor :

$$DF = \frac{[RuO4]_{upstream}}{[RuO4]_{downstream}}$$

Maximum DF reach 3h
DF ≈ 192



RuO_2@MOF (50 °C, 3h)

Pristine MOF

PXRD pattern proves the stability

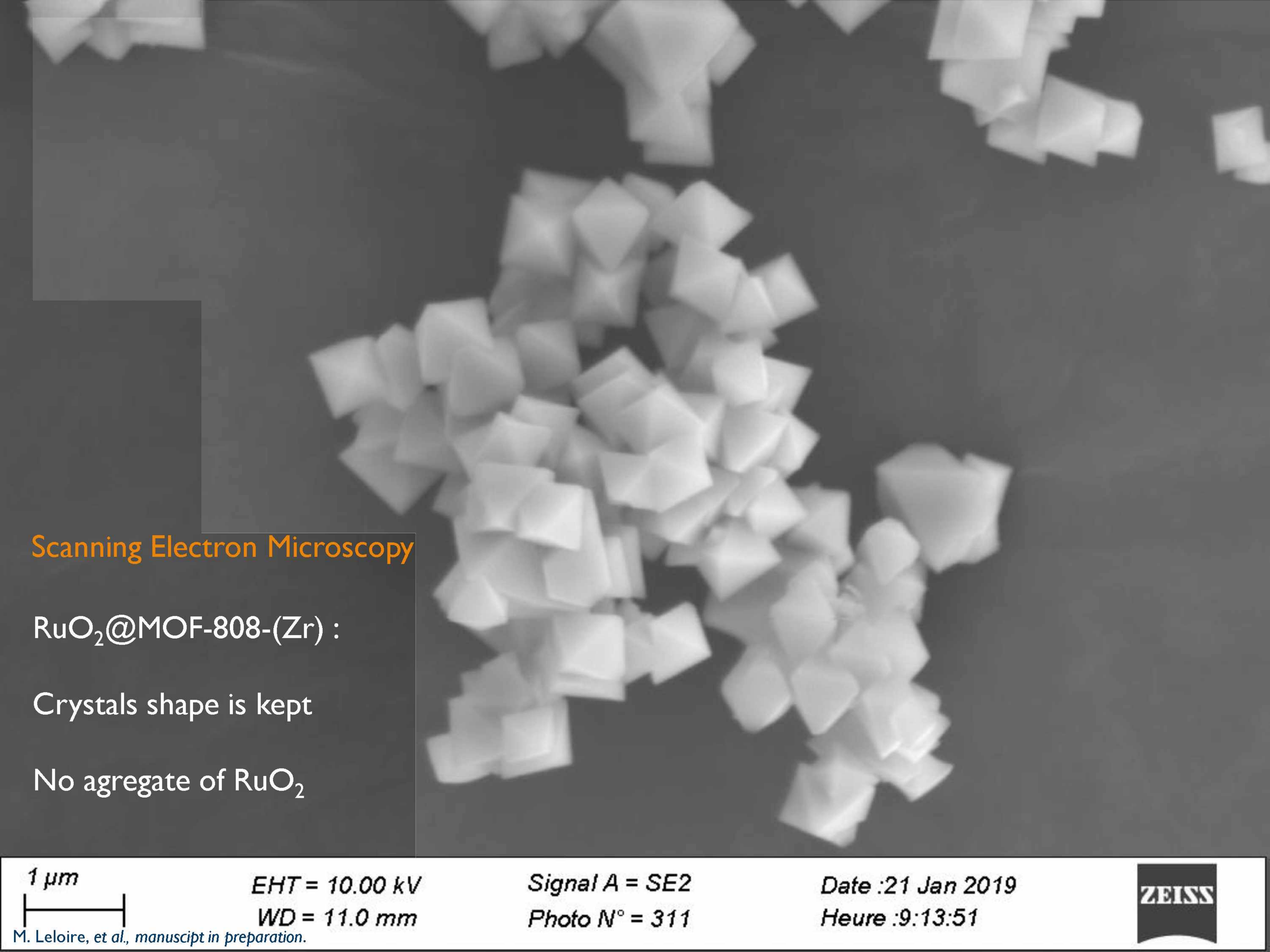
M. Leloire, *et al., manuscipt in preparation.*

Scanning Electron Microscopy

RuO_2@MOF-808-(Zr) :

Crystals shape is kept

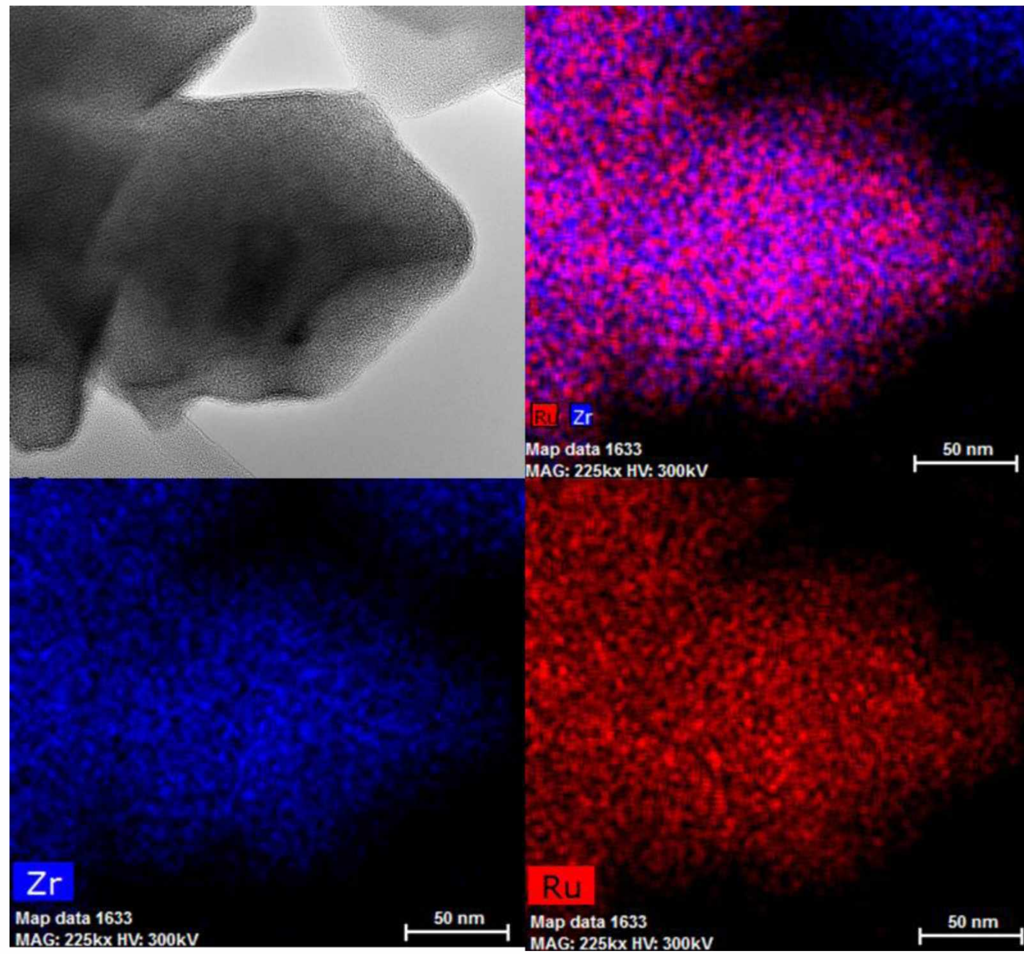
No agregate of RuO_2



M. Leloire, *et al., manuscipt in preparation.*

Quantification and localisation : Transmission Electron Microscopy

FEI Titan Themis 300



- Likely stable species : RuO_2 (X-Ray photoelectron spectrometry)

Energy-dispersive X-ray spectroscopy analysis :

- Homogenous localisation
- Ratio 2 Ru for 1 Zr

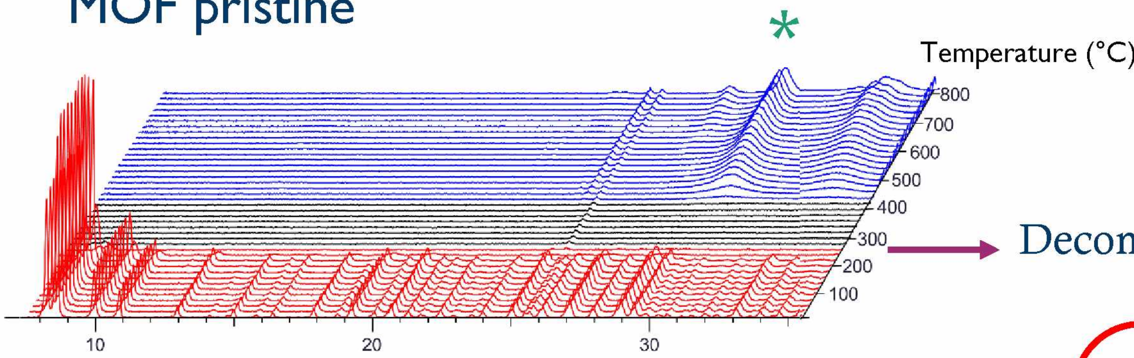
1.17 g_{RuO2} for 1g_{MOF}

$Zr_6O_5(OH)_3(BTC)_2(Formate)_6\,(H_2O)_2(RuO_2)_{12}$

M. Leloire, *et al., manuscipt in preparation.*

Strange behaviour of thermal stability : High temperature powder X-Ray diffraction

MOF pristine

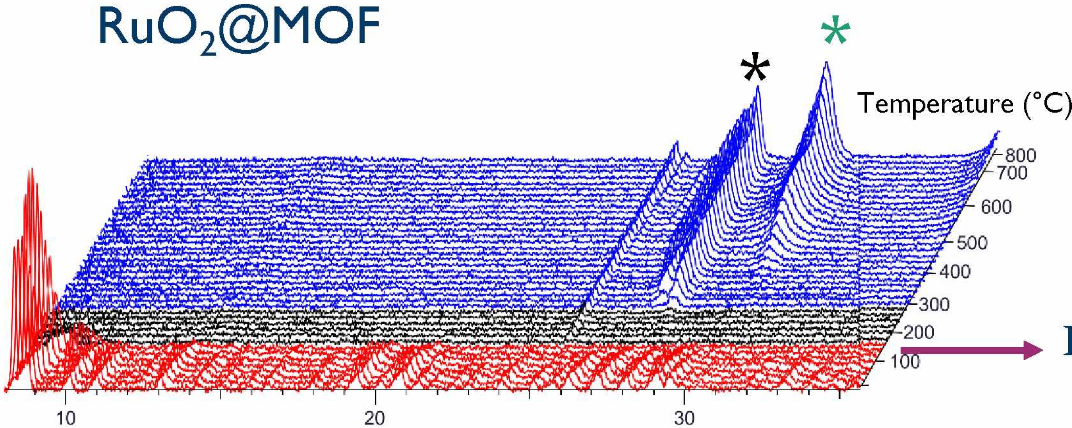


→ Decomposition at 250 °C

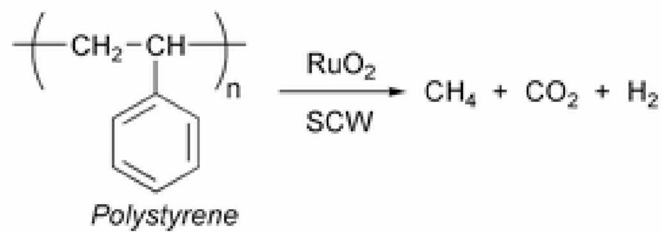
* ZrO_2

* RuO_2

RuO_2@MOF



→ Decomposition at 140 °C



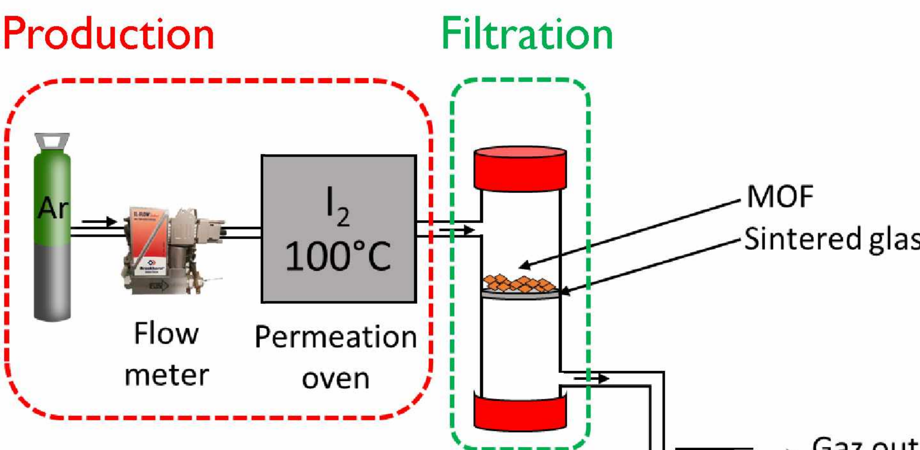
Carbon conversion: quant.
Product distribution: CH_4 (54%), CO_2 (39%), H_2 (7%)

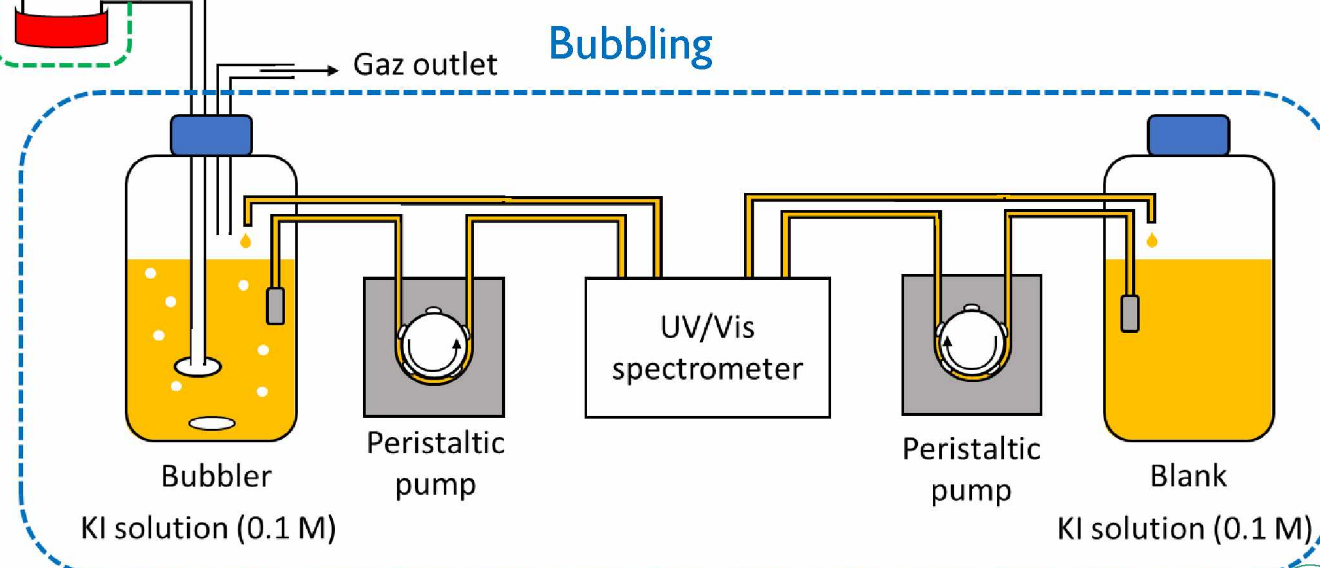
K. C. Park, H. Tomiyasu, *Chem. Commun.* **2003**, *3*, 694–695.

M. Leloire, *et al., manuscipt in preparation.*

Iodine capture

Iodine setup





Features :

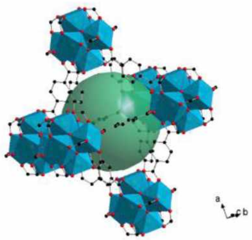
Gaseous I_2 : 0.8 $mg.h^{-1}$
I_2 capture at RT

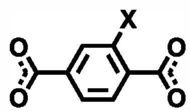
$I_2 + I^- \leftrightarrow I_3^-$

UV analysis

M. Leloire, *et al., manuscipt in preparation.*

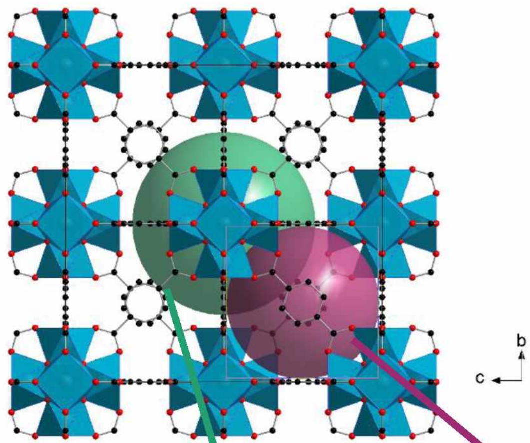
Effect of fonctionnalization





UiO-66-(X)-(Zr)

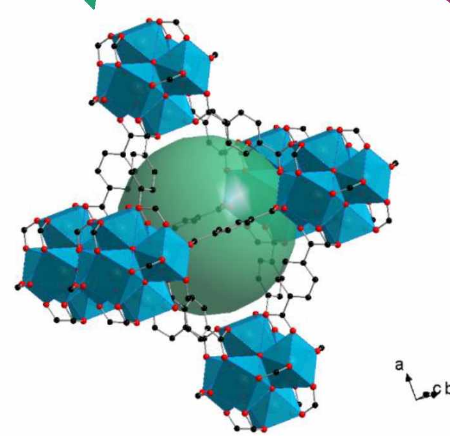
X = H, Cl, Br,
OH, CH_3, NO_2,
NH_2…



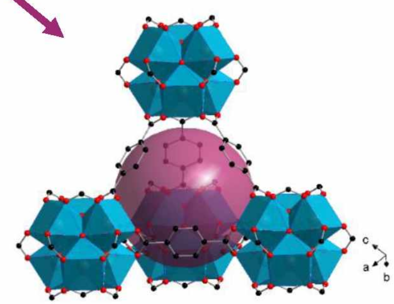
Features UiO-66-(Zr) :

- Air stable
- Steam stable
- Highly stable vs γ irradiations

C. Volkringer, *et al.*, Chem. Commun. **2016**, *52*, 12502–12505.



Diameter : 12 Å

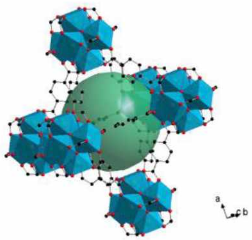


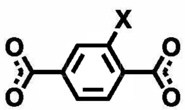
Diameter : 7 Å

Window : 5 Å

M. Leloire, *et al., manuscipt in preparation.*

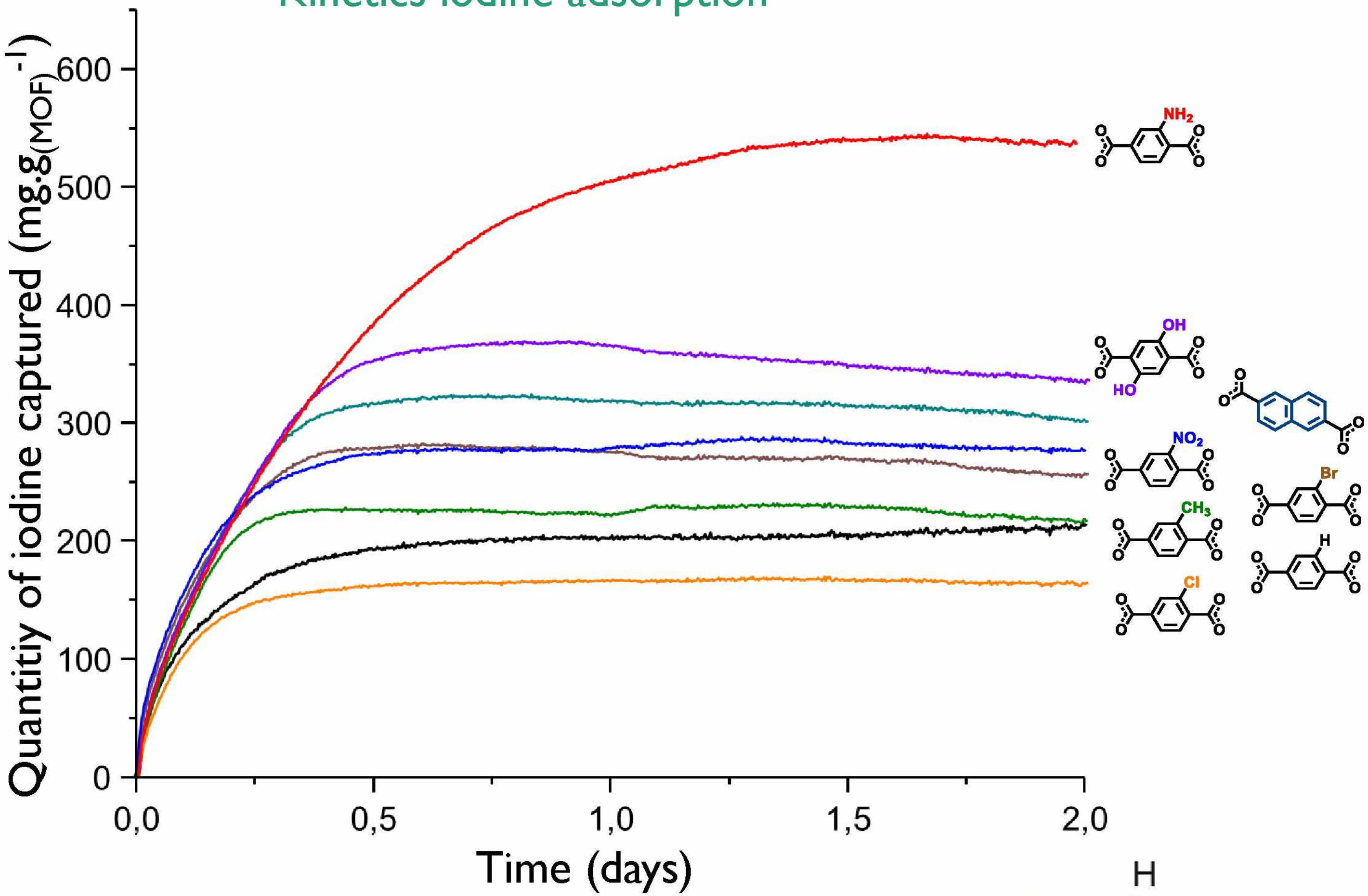
Effect of fonctionnalization : Kinetics iodine adsorption



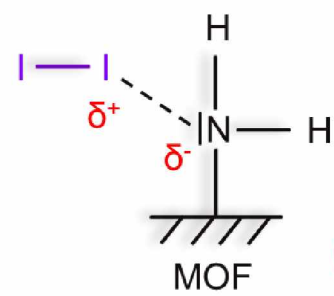


UiO-66-(X)-(Zr)

X = H, Cl, Br, OH, CH_3, NO_2, NH_2…



Amino group : best fonction for iodine capture



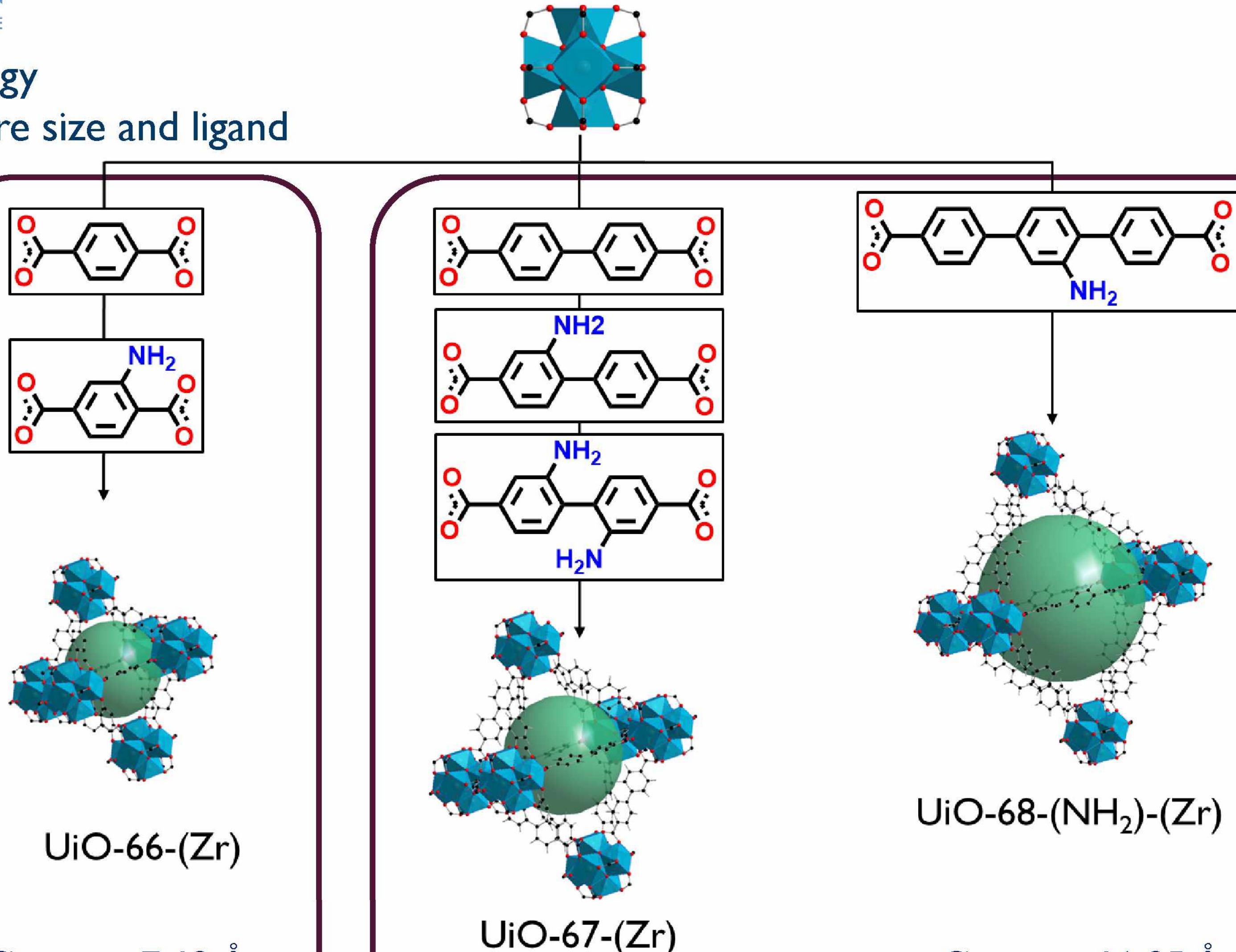
➢ Charge transfer complex (I_2-MOF)

C. Falaise, *et al.*, *Chem. Commun.* **2013**, *49*, 10320–10322.

M. Leloire, *et al., manuscipt in preparation.*

Effect of fonctionnalization and pore size

Same topology
Different pore size and ligand



Ø pores : 7-12 Å
Specific surface
< 1500 m².g⁻¹

Ø pores : 12-23 Å
Specific surface
< 2500 m².g⁻¹

Ø pores : 16-25 Å
Specific surface :
1100 m².g⁻¹

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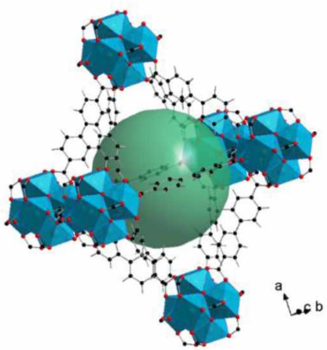
Effect of fonctionnalization and pore size
Kinetics iodine adsorption



UiO-66-(Zr)

UiO-66-(NH_2)-(Zr)

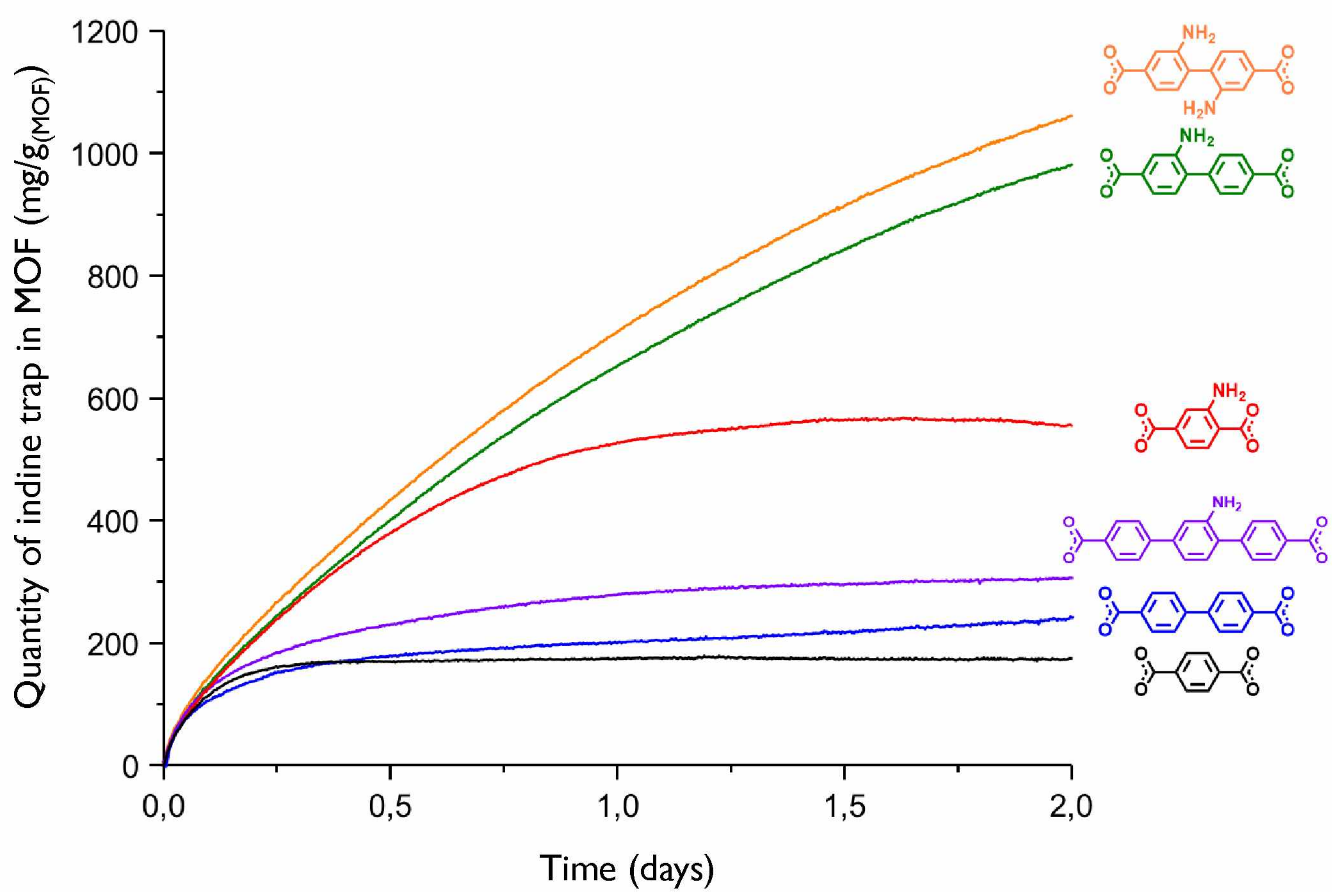
UiO-67-(Zr)

UiO-67-(NH_2)-(Zr)

UiO-67-($(NH_2)_2$)-(Zr)

UiO-68-(NH_2)-(Zr)

1.06 $g/g_{(MOF)}$



UiO-67-($(NH_2)_2$)-(Zr) best combination of pore size and fonctionalization :

- donor fonction (amino)
- immobilization of the iodine (pore size)

M. Leloire, *et al., manuscipt in preparation.*

Conclusions

MOFs are promising efficient porous materials for the I_2 and RuO_4 capture

Important results : RuO_2 : 1,17 $g.g^{-1}$
I_2 : 1,06 $g.g^{-1}$

Other studies :

- Stability under gamma irradiations (IRMA@IRSN)
- Filtration tests under accidental conditions (EPICUR@IRSN)

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September 7 - 10
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Thanks to my teams UCCS and IRSN

Thank you for your attention

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