NAMP

Savannah River National Laboratory

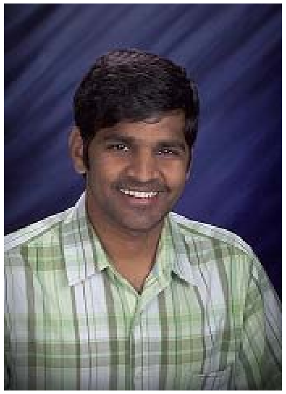
Radiochemistry Webinars

Separation of Xenon and Krypton from nuclear re-processing using Open Framework Materials

In Cooperation with our University Partners

Meet the Presenter…

Dr. Praveen Thallapally



Dr. Praveen K. Thallapally is a chief scientist at the Pacific Northwest National Laboratory. He obtained his PhD in 2003 from the University of Hyderabad working with Prof. Gautam R. Desiraju in the area of Crystal Engineering of organic and metal organic solids. He moved to the University of Missouri Columbia as a post-doctoral fellow working with Prof. Jerry L. Atwood in the area of supramolecular chemistry, gas storage and separation. He leads research efforts in the design of porous materials for energy conversion, catalysis, immobilization of radionuclides and electro-optic responsive metal organic frameworks . He published more than 120 research articles with an H-index of 45. He s is an advisory board member for Crystal Growth & Design, CrystEngComm and Journal of Coordination Chemistry.

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Pacific Northwest
NATIONAL LABORATORY

Acknowledgements

Interns, Postdocs and Co-workers










Not shown

- Mr. Paul Reiss (Intern, UK), Dr. Carlos Fernandez, Todd Schaef, Dr. Nune Satish
- Prof. Wen Zhang, China

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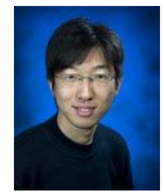
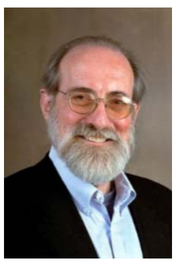
BNL NSLS-II



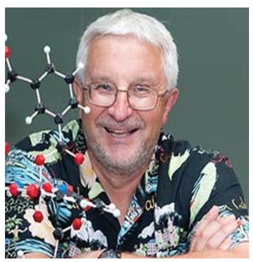

ANL - Adv photon source

Collaborators:

Prof. Smith, Berkeley USA



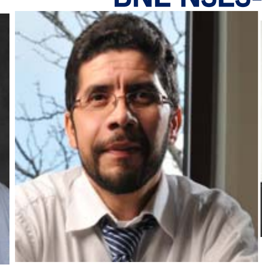
Prof. Atwood Columbia, MO



Prof. Zaworotko Ireland

Prof. Cooper UK

Prof. Parise



Prof. Moises USA


Dr. Denis Strachan & Dr. Pete McGrail, PNNL

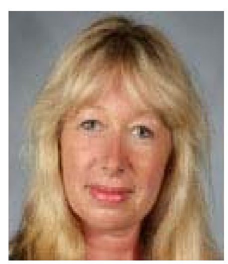
Dr. Troy Garn, Dr. Mitch Greenhalgh & Dr. Amy K. Welty (not shown), INL

Prof. Brian Space, USA (not shown)
Prof. Maciej Haranczyk, Berkeley

Programmatic and Technical Advise:







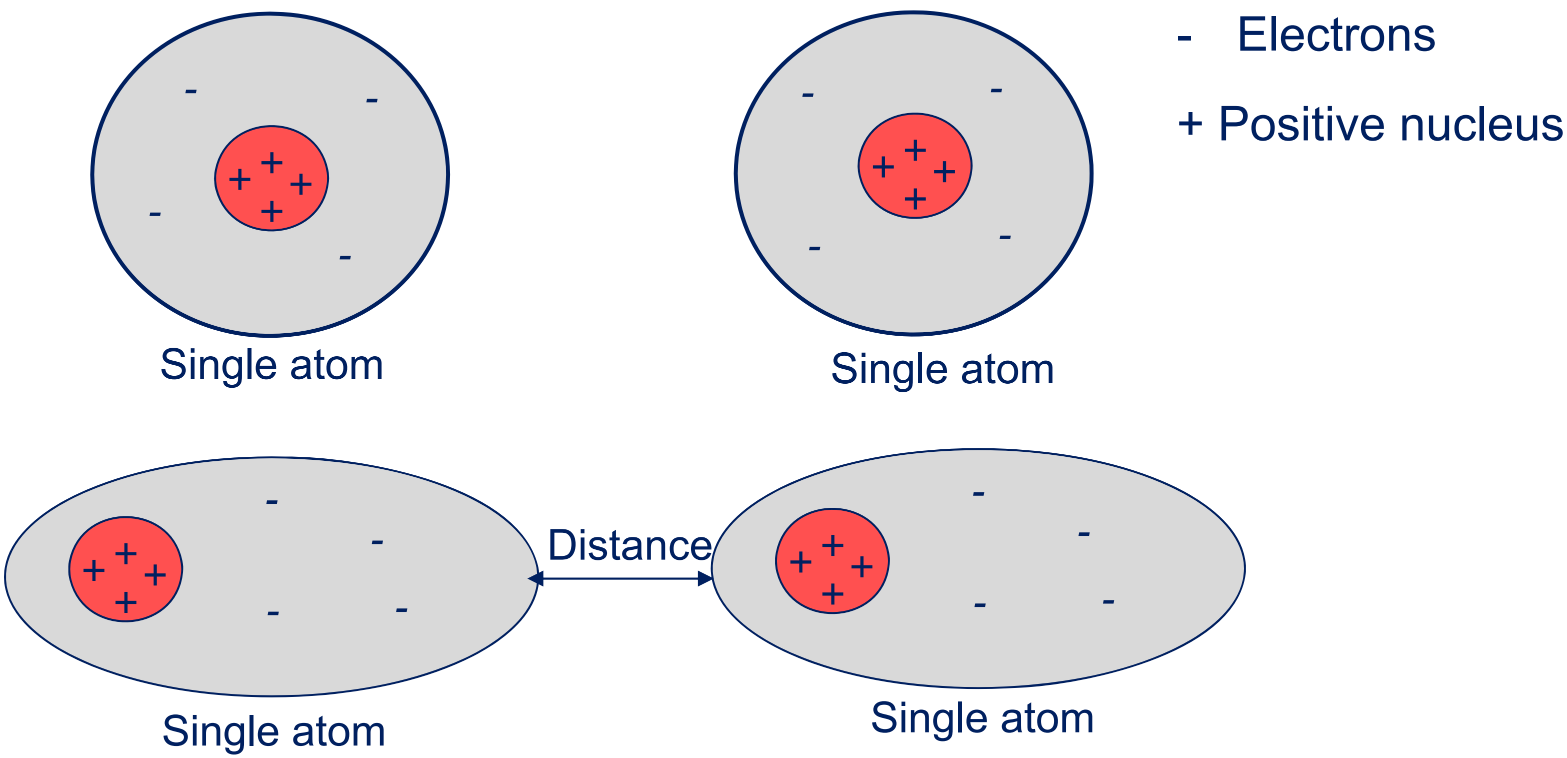
Outline

- Definitions
- History of Xenon and Krypton
- Nuclear re-processing
- Porous materials – Metal organic frameworks
- Synthesis and characterization
- Adsorption and separation
- Conclusion
- Questions?

Definitions

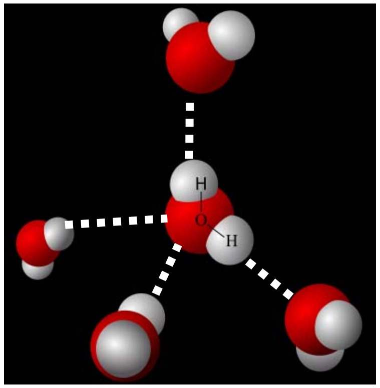
Porous/Pores: Tiny spaces or holes through which liquid or gas molecules penetrate (ultramicropore < 0.5 nm, micropore >0.5 - 2 nm, mesopore 2 – 5 nm, or macropore >5nm)

Van der Waals Forces: When two atoms come close to each other, a slight interaction between them causing polarity and slight attraction



Definitions

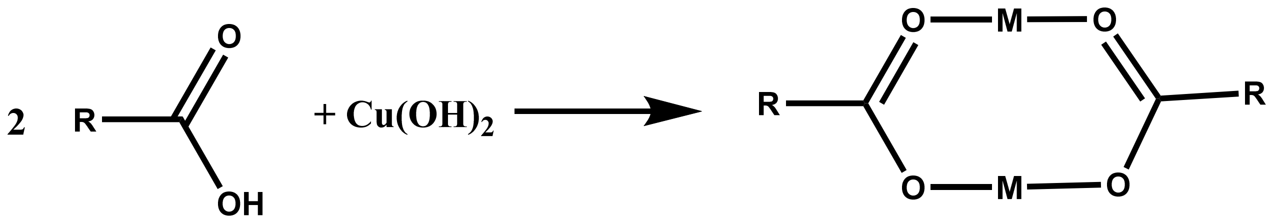
Electrostatic Attraction or Hydrogen bonding: attraction between two polar groups when hydrogen atom covalently bound to a highly electronegative atom



Hydrogen bonding strength

- F−H···:F (38.0 kcal/mol)
- O−H···:N (6.0 kcal/mol)
- O−H···:O (5.0 kcal/mol)
- N−H···:N (3.1 kcal/mol)
- N−H···:O (1.9 kcal/mol)

Coordination complex in which each metal atom connected to multiple molecules or ligands depending on their coordination number

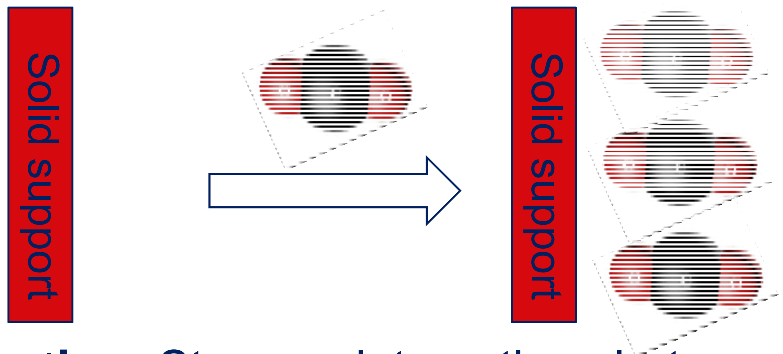


> 100 kcal/mol

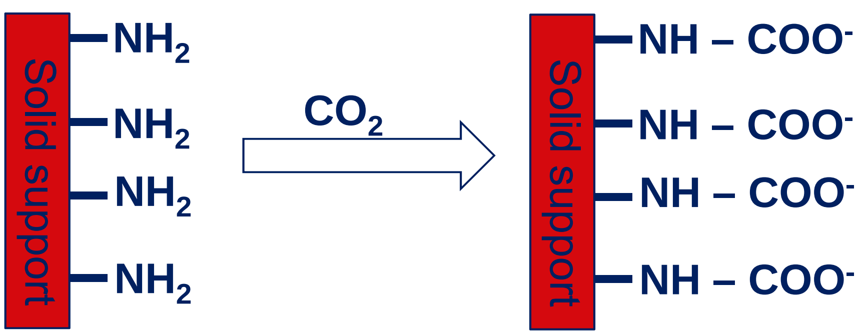
Definitions

Adsorption: is phenomenon in which gas/liquid molecules are attached to solid surface by intermolecular interactions

Physical adsorption: attached to solid surface by weaker interactions between solid and gas/liquid



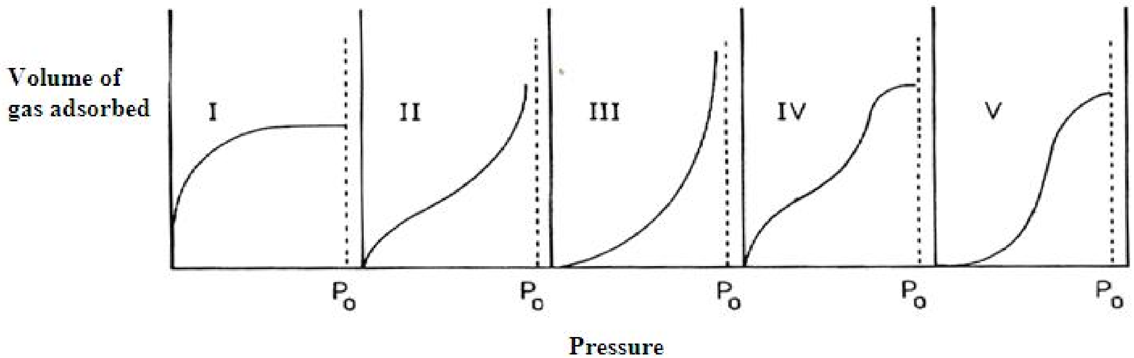
Chemical Adsorption: Stronger interactions between the solid and gas/liquid



Desorption in which the adsorbed gas/liquid released from the surface by heating or vacuum.

Definitions

Adsorption isotherm: a graph between the amount of gas/vapor adsorbed on a solid and pressure at constant temperature.



Breakthrough Curve is a plot of the composition at the outlet against time, relative to the initial inlet composition. The breakthrough curves can be used as a rapid method to compare the potential performance of new materials for gas separation applications

Flow rate

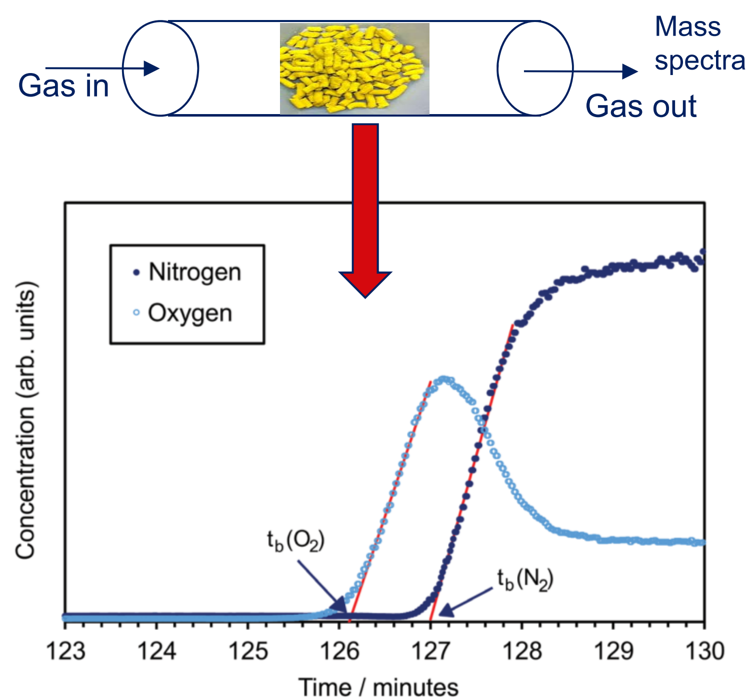
Partial pressure of the inlet gas

$$\text{Breakthrough capacity (q in mmol/kg)} = \frac{Cvt}{MTg} \times 10^6$$

Gas constant

Selectivity of Gas A over B $S_{AB} = \dfrac{x_A / y_A}{x_B / y_B}$

x_A and x_B are the mole fractions of gases A and B in the adsorbed phase, and y_A and y_B are the mole fractions of gases A and B in the bulk phase,



Breakthrough plot

History of Xenon and Krypton

- ✓ Xenon and Krypton – discovered by Sir William Ramsay and Morris Travers 1898
- ✓ Xenon and Krypton are odorless, colorless, tasteless and chemically non reactive
- ✓ In 1962 Neil Bartlett discovered Xe and Kr will react with fluorine to form fluorine derivatives.

Xenon

Atomic number	54
Atomic mass	131.29 g.mol $^{-1}$
Density	5.9 x10^{-3}g.cm^{-3} at 20°C
Melting point	- 112 °C
Boiling point	- 107 °C
Diameter	0.4 nm

Krypton

Atomic number	36
Atomic mass	83.80 g. mol $^{-1}$
Density	3.73 10^{-3} g. cm^{-3} at 20°C
Melting point	- 157 °C
Boiling point	- 153° C
Diameter	0.36 nm

Source of Xenon and Krypton

- Xenon and Krypton occur naturally in the atmosphere at 0.087 ppmv (Xe) and 114 ppm (Kr)
- Xe has nine and Kr has six naturally occurring stable isotopes.

Radioactive Xe and Kr

- Fission of uranium, plutonium or other radioactive decay of fission products
- Production of medical isotopes
- Nuclear accidents - Fukushima Daiichi Nuclear Power Plant in Japan
- Dissolution of the spent fuel in nuclear reprocessing

- Radioactive Xe isotopes are monitored around the globe to detect nuclear explosions
- These systems detected and tracked Xe isotopes from the Japanese nuclear accident

Statistic on spent fuel

❖ Spent fuel is a nuclear fuel that is irradiated in the nuclear reactor

• Love It or Hate It We Have It: What to do with It is the Issue

• We have about 70,000 tonnes

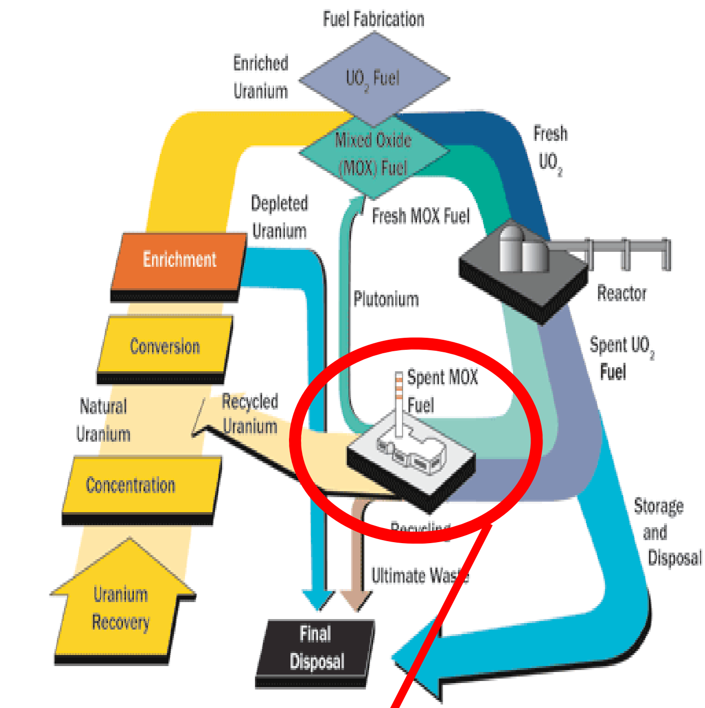
• Current reactors will produce 60,000 tonnes more over their lifetimes

Nuclear Waste Legacy (EM, NE) for USA and the world

Elements, Dec 2006

Reprocessing the spent fuel

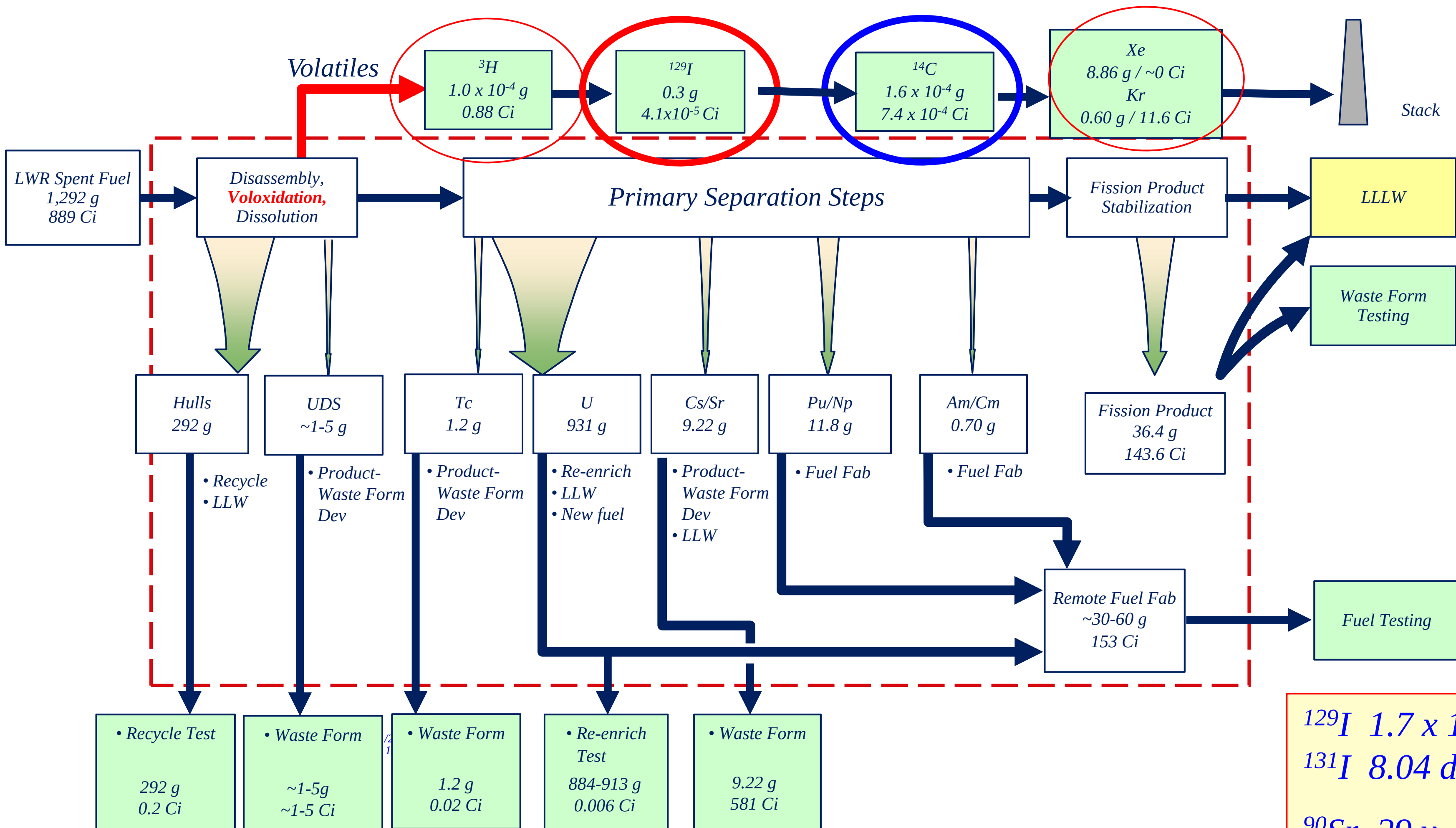
- ✓ Spent fuel can be reprocessed to recover fissile and fertile materials to provide fresh fuel to new and existing nuclear plants saving up to 30% of the natural uranium otherwise required
- ✓ Reduce the volume of material to be disposed of as high-level waste to about one-fifth
- ✓ In addition, the level of radioactivity in the waste from reprocessing is much smaller compared to before reprocessing



Source: U.S. Nuclear Regulatory Commission

Separations of non-burnable volatile fission products and lesser actinides

Reprocessing flow diagram



^{129}I 1.7 x 10^{7} y
^{131}I 8.04 d
^{90}Sr 29 y
^{81}Kr 2.1 x 10^{5} y
^{133}Xe days

Mass Basis: 1 kg SNF; 55 GWD/MTIHM; 5 year Cooling

Provided by R. Jubin, ORNL

Separations and applications

- Capture of Xe provides an economic incentive

- **High purity of Xe**
  - Buildings - Commercial lighting
  - Automotive – Head lights
  - Space Industry – Propellant
  - Medical – Anesthesia, Imaging
  - Science – NMR

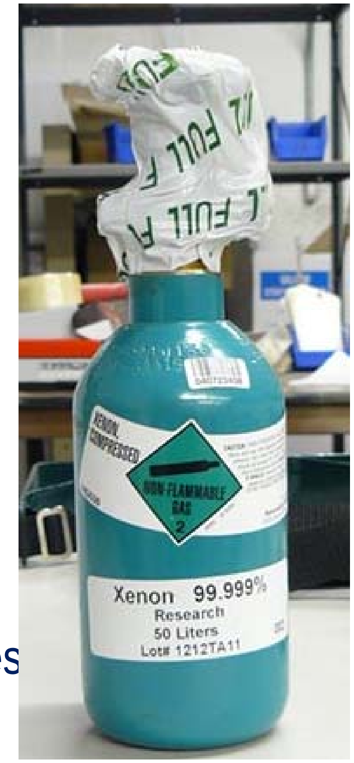
- **High Purity of Kr**
  - Insulation – Efficiency is 6 times higher than normal windows
  - Flat panel display manufacturing

Objectives and existing technologies

- **Objective:** The objective is to develop and test alternative materials to capture volatile radioactive gas components (most specifically Kr) released during Used Nuclear Fuel Reprocessing operations

- **Existing Technology**
  - Cryogenic distillation to remove Xe and Kr
    - Projected to be expensive
    - Potential to accumulate O_3 due to radiolysis of O_2 $\Rightarrow$ Explosion hazardous

- **Immobilization**
    - Elevated pressure in a stainless steel canisters
    - ^{85}Kr decay product Rb is a liquid at storage temperatures
    - Corrosive to storage canisters

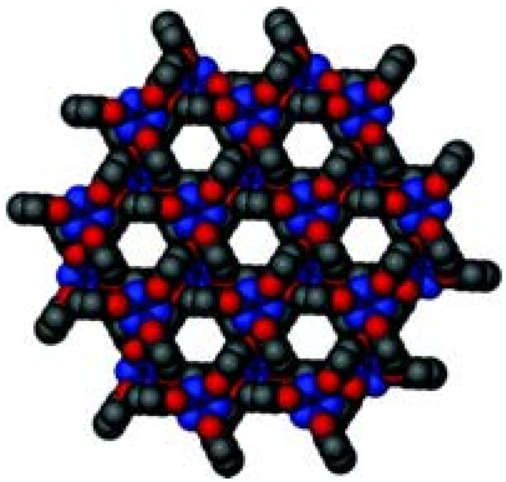


$5,000 per kilogram

Alternate materials/methods

- **Porous Materials**
  - Separation at higher temperatures
  - Remove Xe and Kr in separate steps
  - Remove Xe at ambient temperature

    Recover process costs by selling Xe?
  - Remove Kr at near room temperature

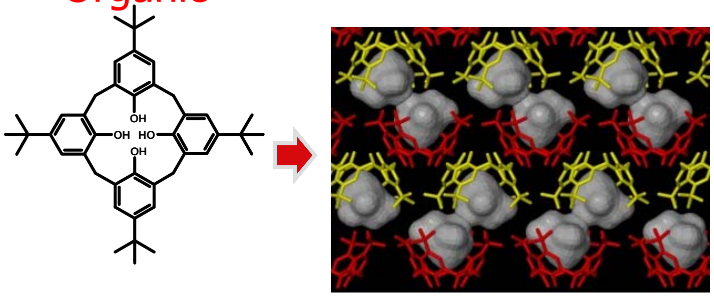


Thallapally *et. al.*, Chem Commun., 2013

- **Porous Materials allow**
  - More gas to be stored in the canister at lower pressures
  - The decay product Rb would be isolated from the metal canister
  - Porous materials have capacities 3 to 10 times those of currently used materials. For eg. CO_2, H_2 and Natural gas

Porous materials

Organic Solids
Organic



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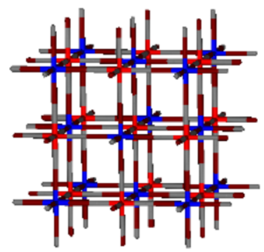
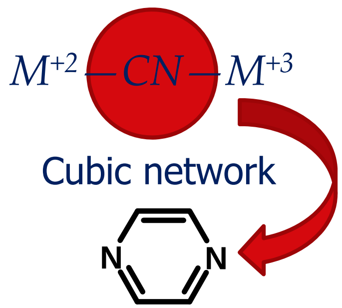
Thallapally et. al, Chem Comm., 2012
Thallapally et. al., Chem Comm 2012

Prussian Blue/Zeolites
Inorganic





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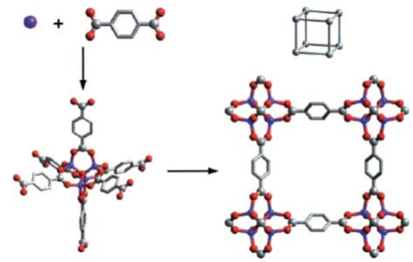
Thallapally et. al., Cryst. Eng. Comm., 2010

MOF’s/COFs
Hybrid



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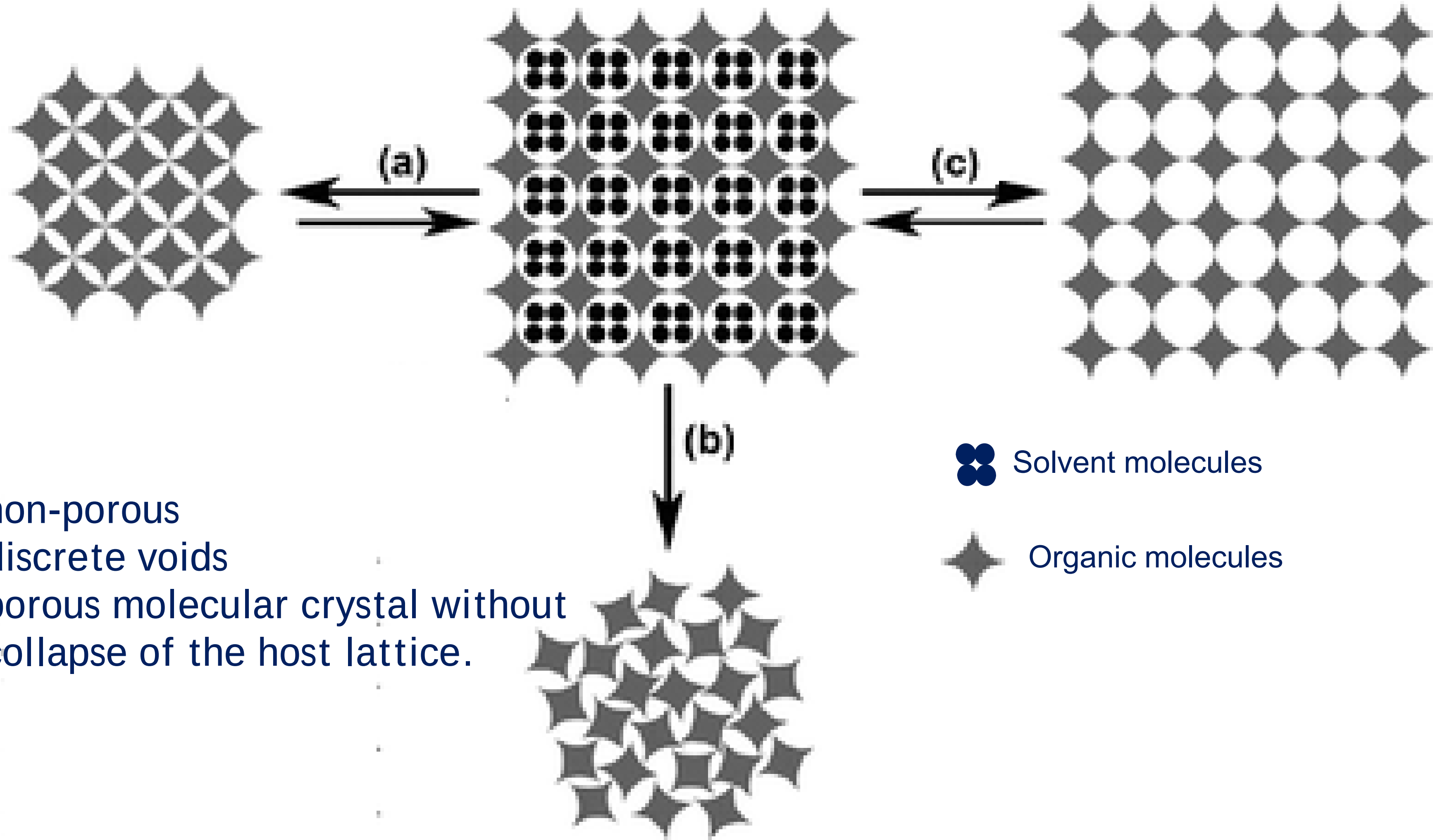
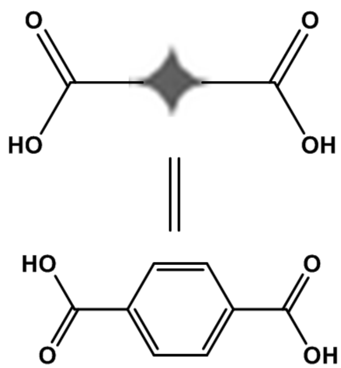
Kui et. al., Chem. Mat., 2013

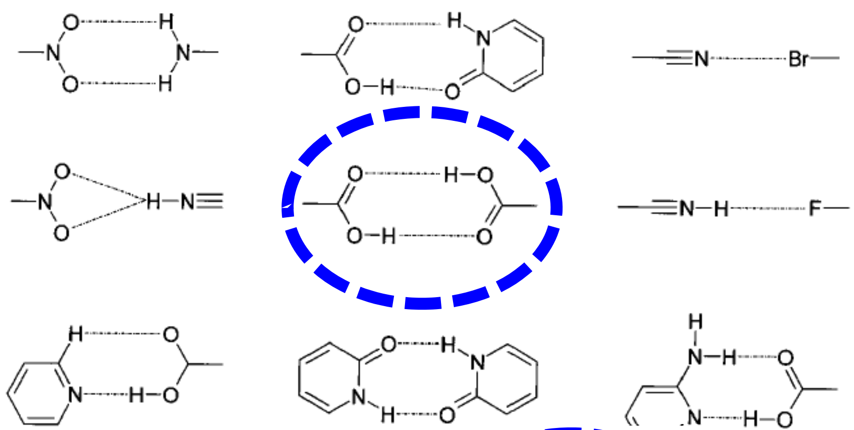
Concept

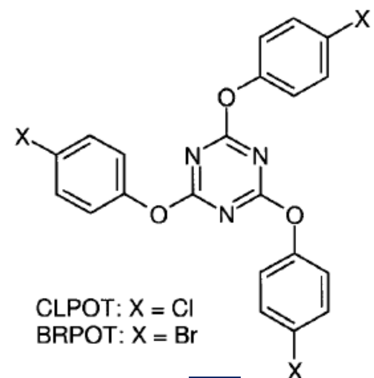


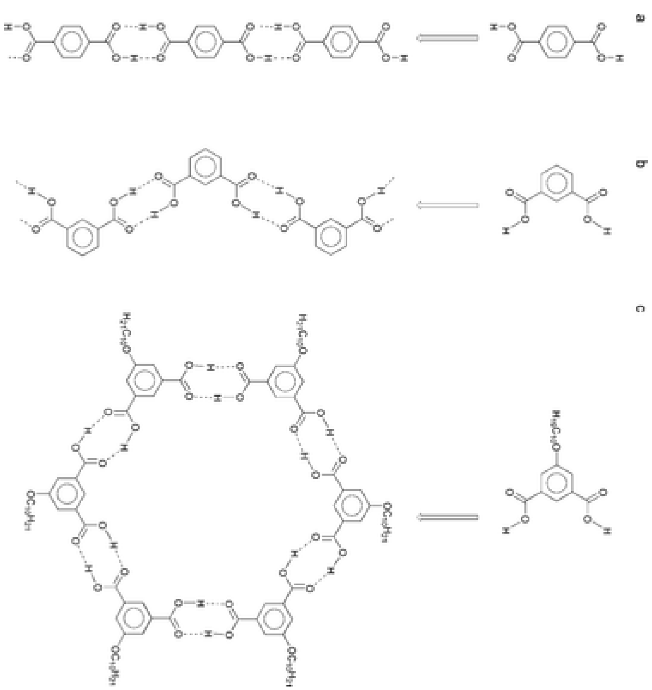
(a) non-porous
(b) discrete voids
(c) porous molecular crystal without collapse of the host lattice.

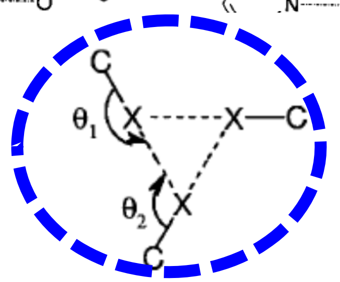
Organic Solids 101
Design Principles

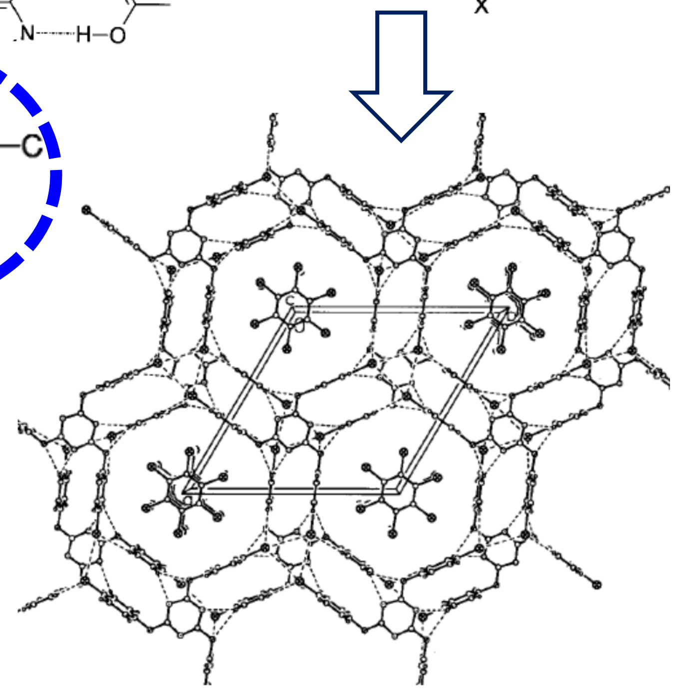






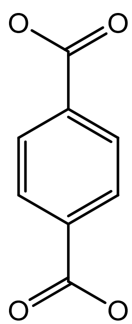






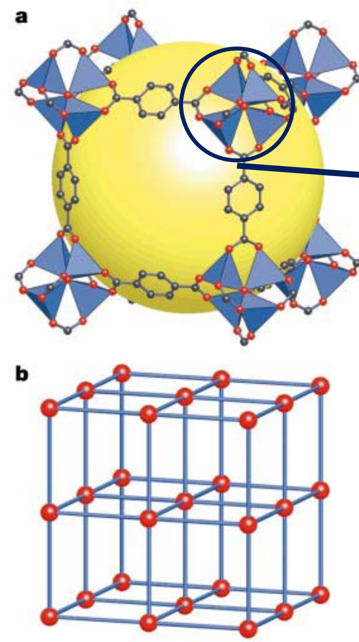
Micro Porous MOFs

2000 - present



+ Zinc Nitrate

SBU



$Zn_4O(CO_2)_6$

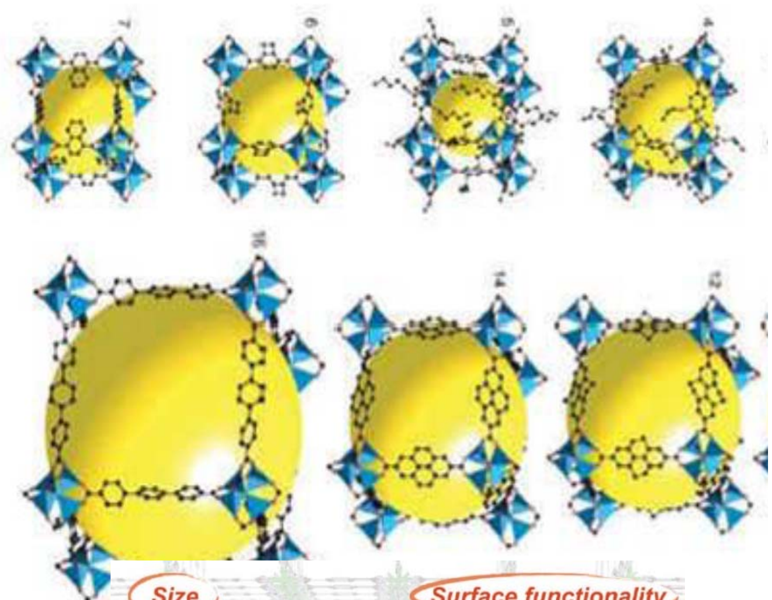
4 ZnO_4 tetrahedra

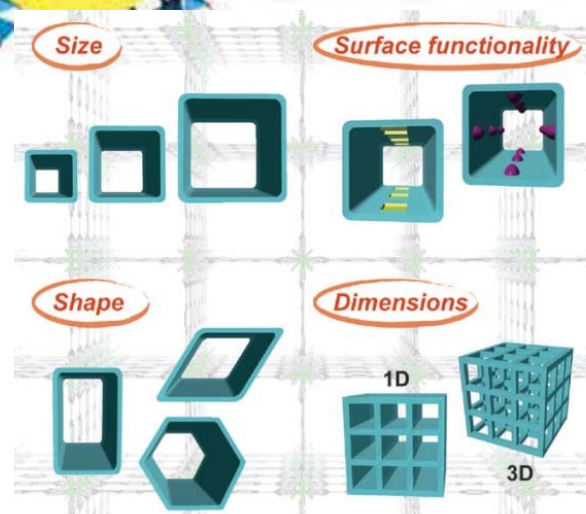
✓ The use of multiple metal ions in a cluster bridged by multiple coordinating ligands tends to enhance the robustness of the MOF

Yaghi et. al., Science 1998

Advantages

- MOFs are hybrid crystalline porous solids with a vast array of topologies constructed from metal ion clusters and organic linkers.
- More than 20,000 MOF structures are known to date
- The properties of MOFs are easier to tune synthetically than those of other porous compounds
- The MOF structures are controllable to certain degree by the choice of molecular building blocks

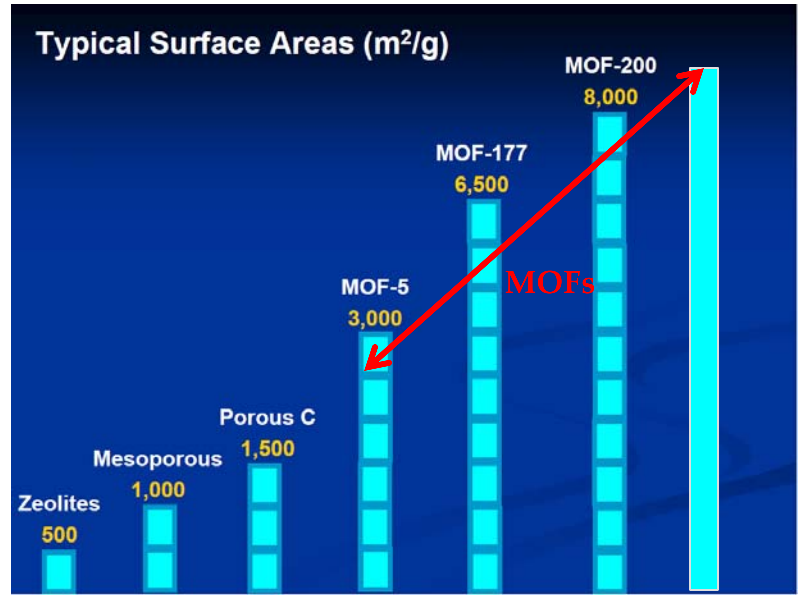


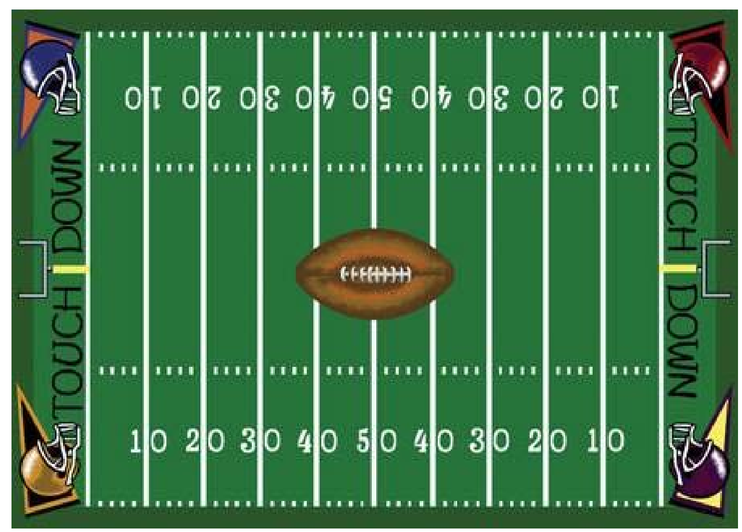


Yaghi et. al., Science 2013, 974; Kitagawa et. al., Angew Chem. 2002; Ferey et. al., Science 2002

Advantages and disadvantages

- Long cycle stability 500 – 2000
- More than 5,000 experimental and 130,000 hypothetical MOF structures are known to date
- Possess much higher specific surface area (~8,000 m^2/g) than possible in any other traditional crystalline material



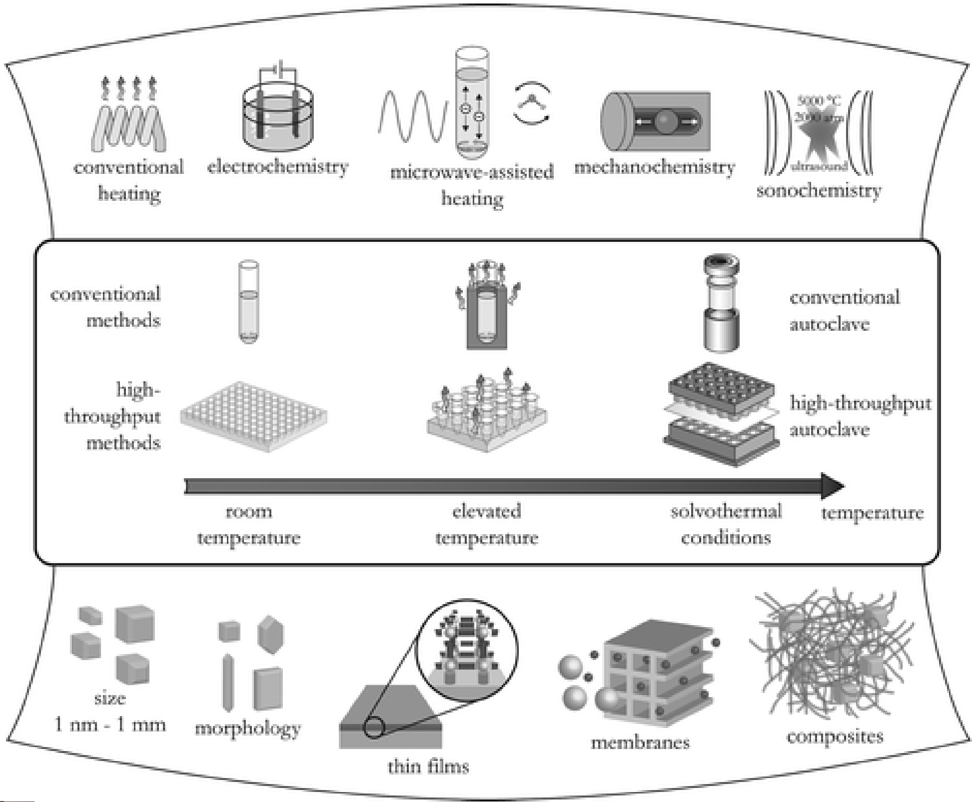


Disadvantages

- Stability 300 - 900°C
- Limited quantities

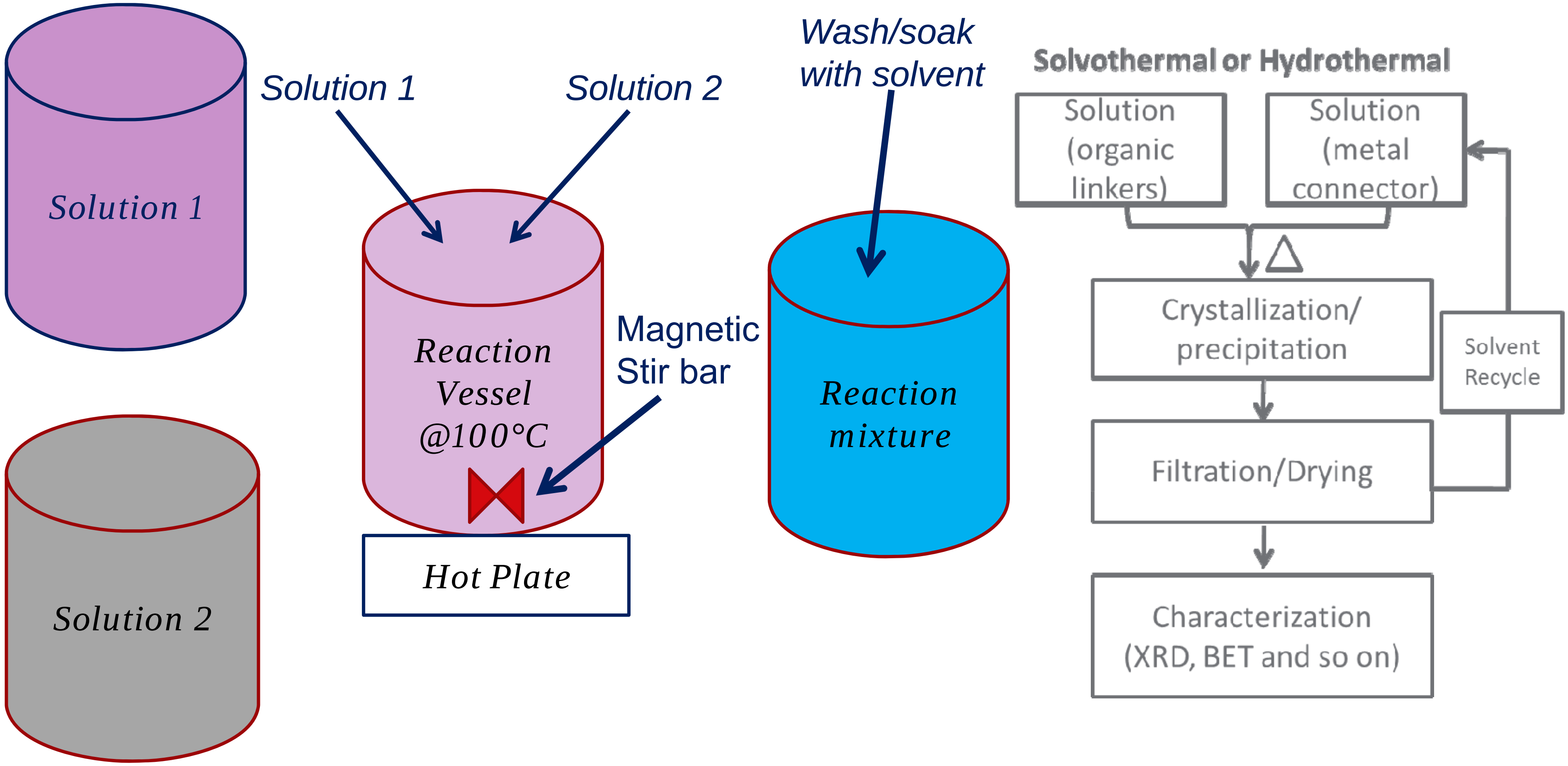
Synthesis protocol

- MOFs are constructed from precursor chemicals that in most cases are readily available
- Mild synthesis conditions provide options for in-house production as desired
- MOFs can be made in many different forms as needed:
  - Bulk powders
  - Nanoparticles
  - Fibers
  - Gels



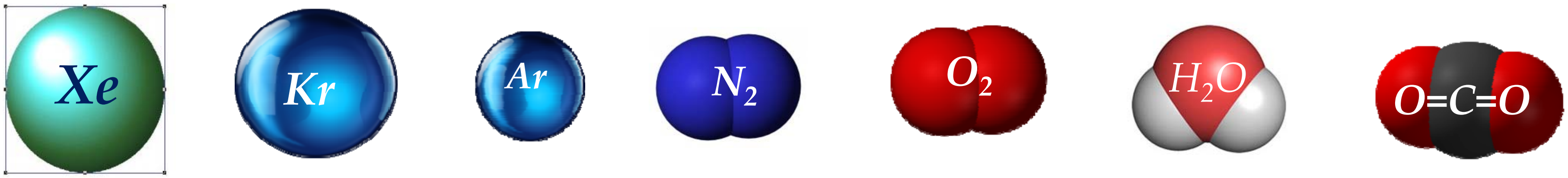
Stock, N., Chem. Rev., **2012**, 112 (2), pp 933-969

Batch process

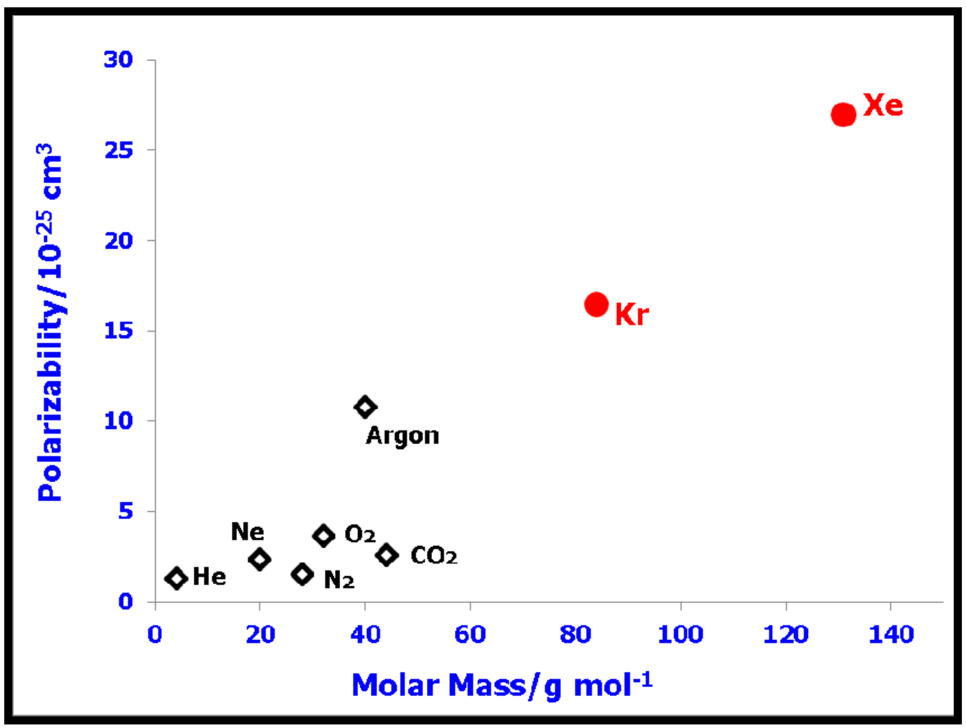


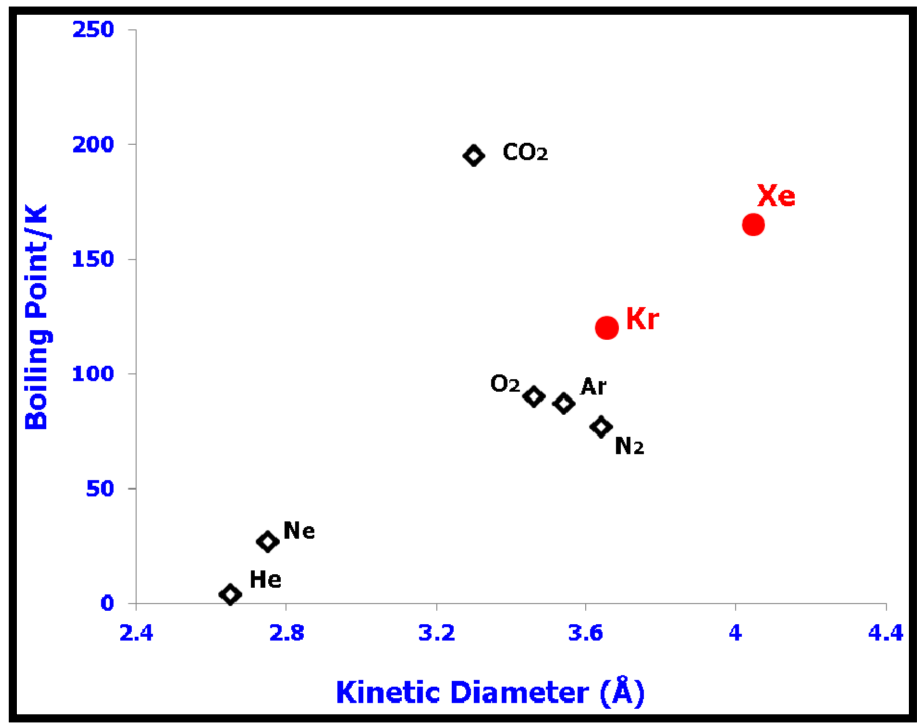
Physical and chemical properties

- **Gas composition in nuclear re-processing plants**



400 ppm | 40 ppm | 0.9% | 78% | 21% | very low | 0.03%

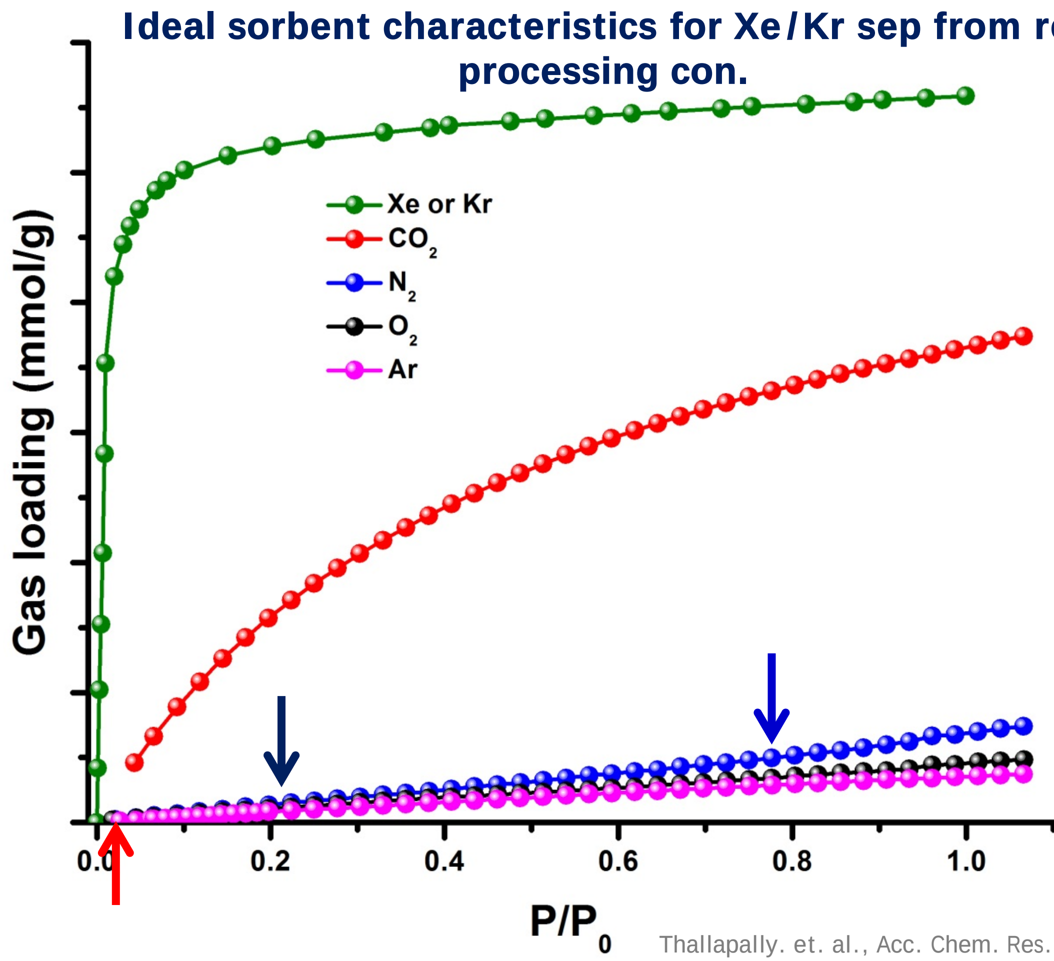




Thallapally. et. al., Acc. Chem. Res., 48, 211, 2015

Ideal adsorbent

	Xe	Kr	Ar	N_2	O_2	H_2O	CO_2
Con. =	400 ppm	40 ppm	0.9%	78%	21%	very low	0.03%
P mbar =	0.4	0.04	9	780	210	very low	0.3



Thallapally. et. al., Acc. Chem. Res., 48, 211, 2015

High Capacity (Xe or Kr)

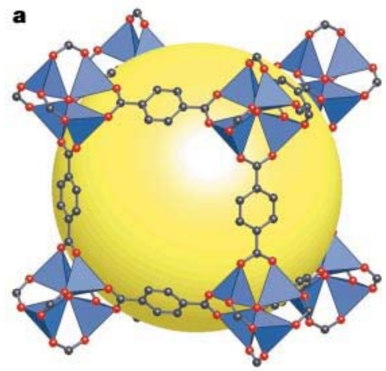
High Selectivity (N_2, O_2, H_2O, Ar, CO_2 etc.)

Faster Kinetics

Stability/Radiation over 1000 cycles

Types of MOFs studied

1. MOF-5, a proto-type
2. MOFs functionalized with polar groups
3. MOFs containing open metal sites
4. Hydrophobic MOFs with small pore size
5. MOFs impregnated with Ag^0 nano particles



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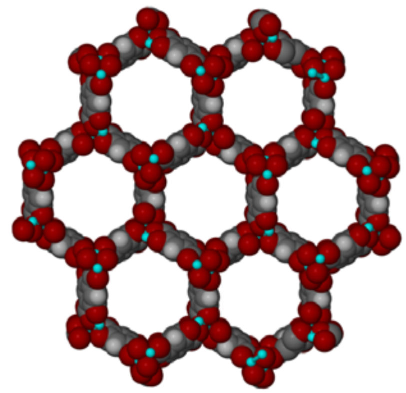

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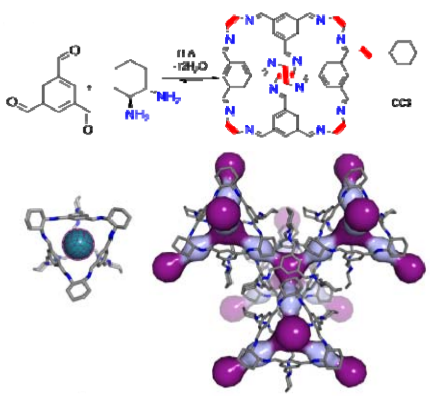
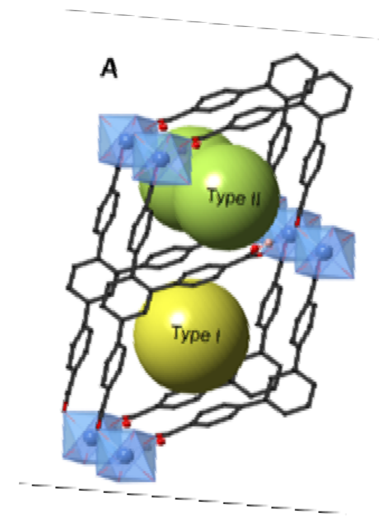


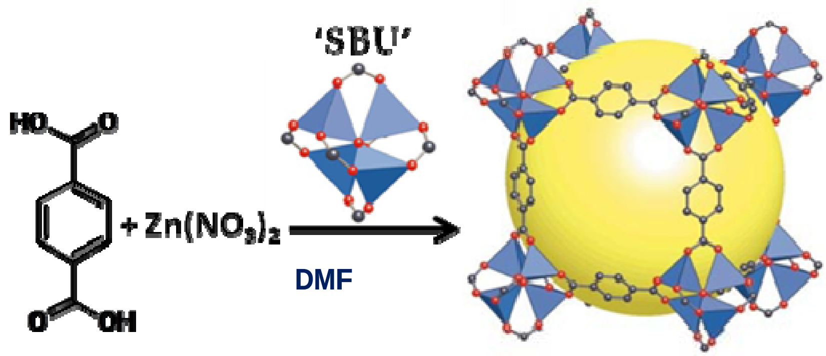
Thallapally, Cooper et. al., Nature Materials., 13, 954, 2014

- ➢ Role of surface area
- ➢ Open metal sites
- ➢ Small pores/polar groups
- ➢ Nanoparticles

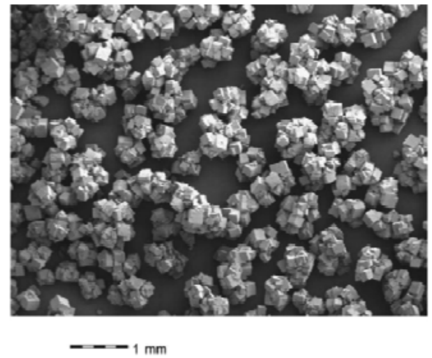


Thallapally et. al., J. Am. Chem. Soc., 134, 9046, 2012

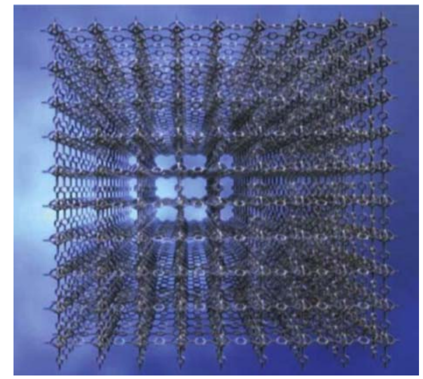
MOF-5 synthesis and characterization



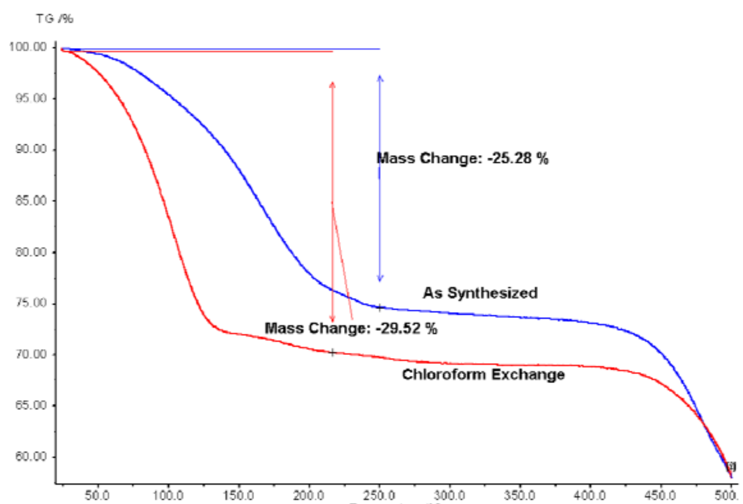
Mol For: $Zn_4O(BDC)_3$

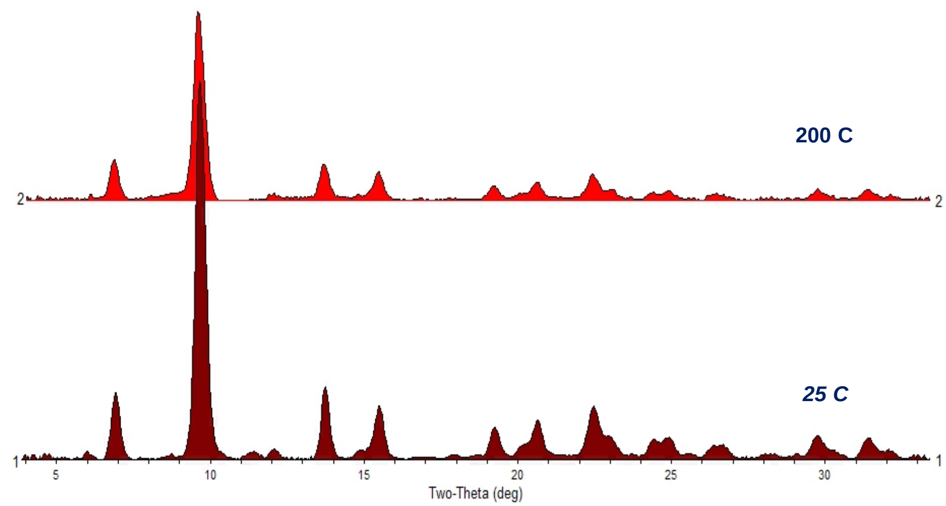


Xtal/particle morphology



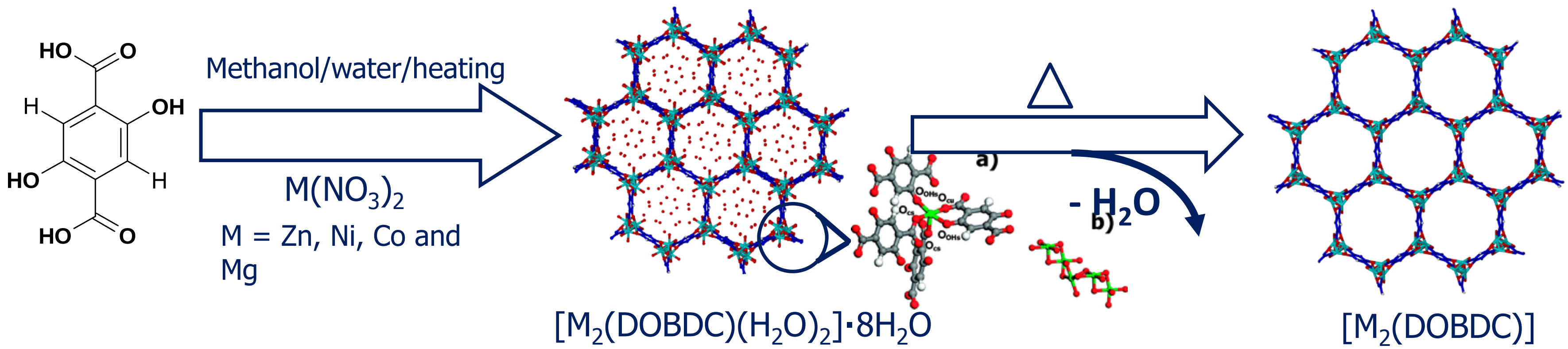
3D Structure





Yaghi et. al., Science 2002

Synthesis of a Mdobdc family of MOFs

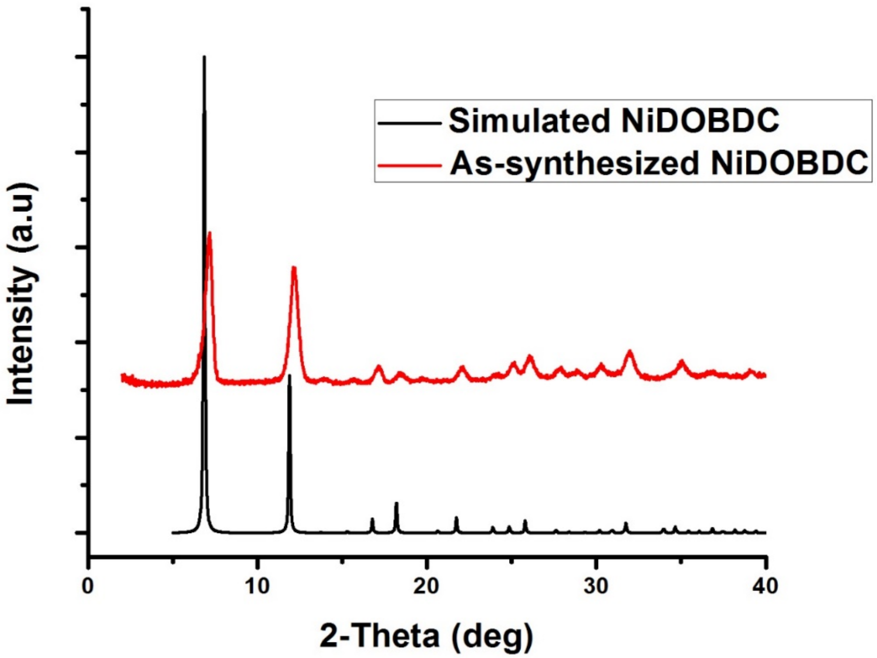


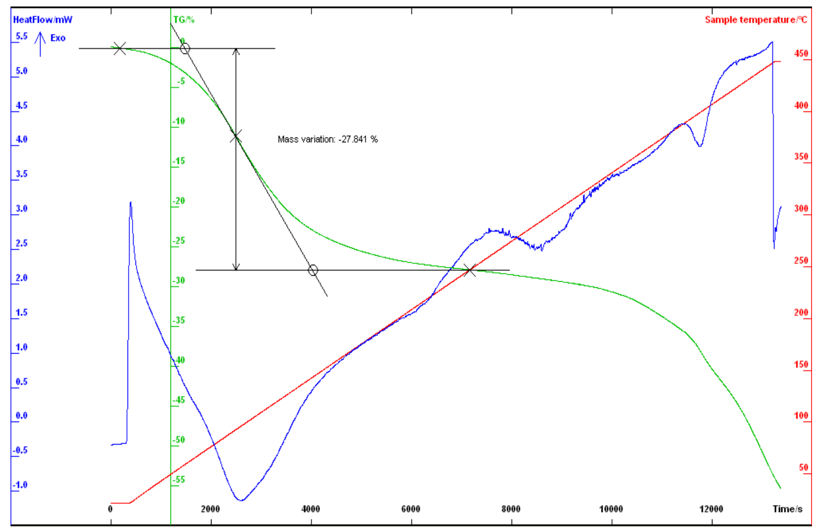
Scale up

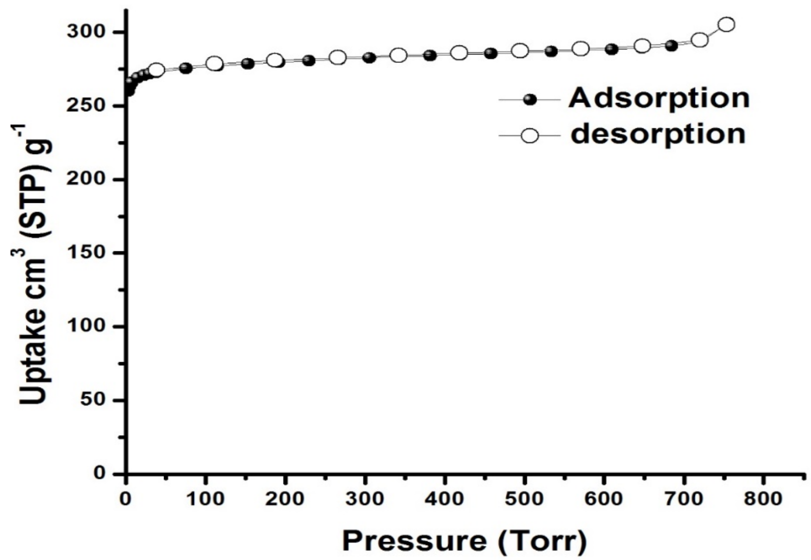
PNNL engineered form

Yaghi et. al., PNAS., 2006
Thallpally et. al., J. Physc. Chem. C. 116, 9575, 2012.

Characterization of Mdobdc MOF

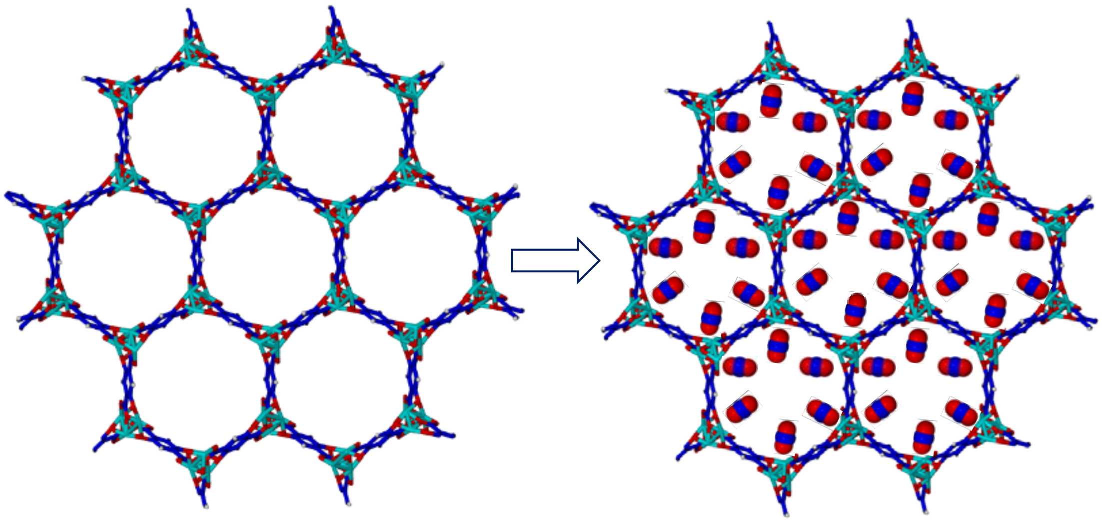


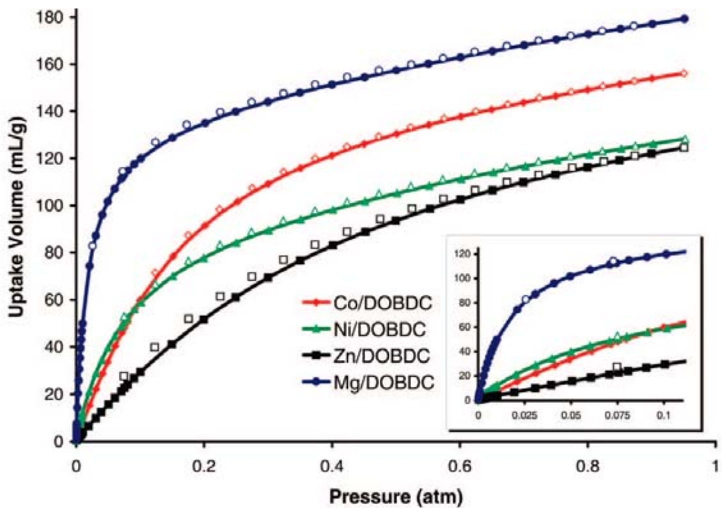


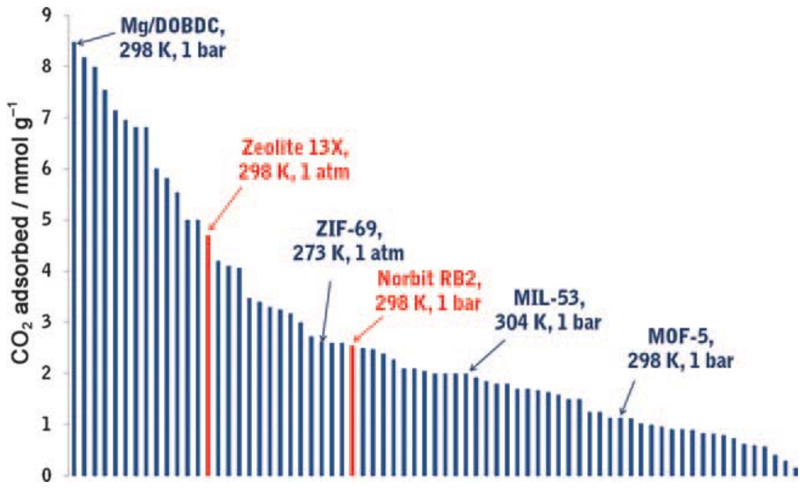


- Identical PXRD indicate the successful synthesis and identical topology
- Thermogravimetric analysis indicate ~30% of weight loss between RT to 250 °C
- 1200 m^2/g surface area

Mdobdc family of MOFs



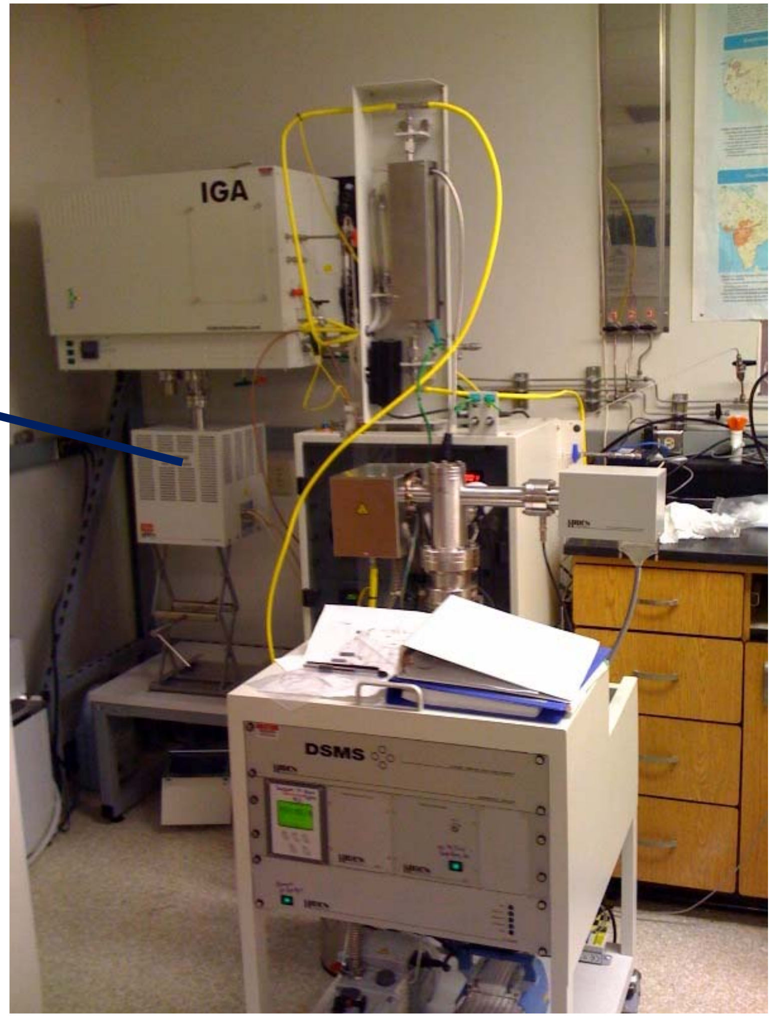


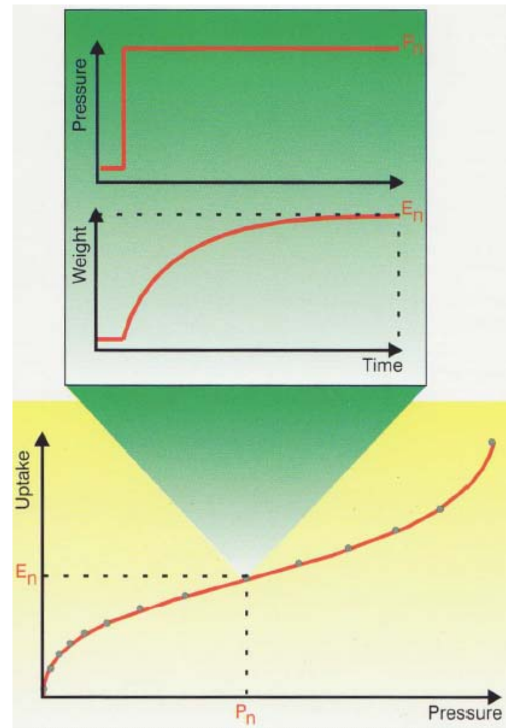


- 36 mass% at 100 kPa (1 bar)
- Reversible adsorption and desorption
- Selective towards CO_2 over N_2
- Better CO_2 capacity than any other sorbent

Matzger and co-workers., J. Am. Chem. Soc., 2008
Thallapally et. al., J. Physc. Chem. C., 2012

Gravimetric gas analyzer

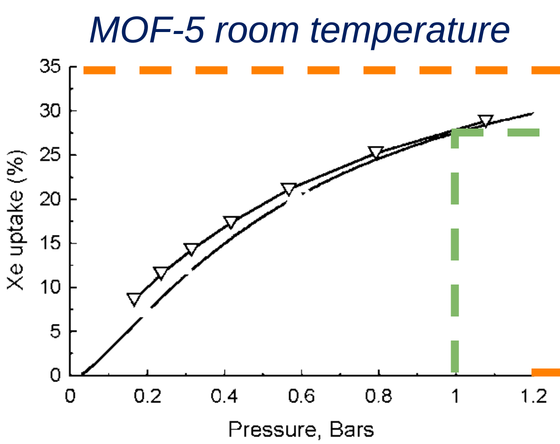


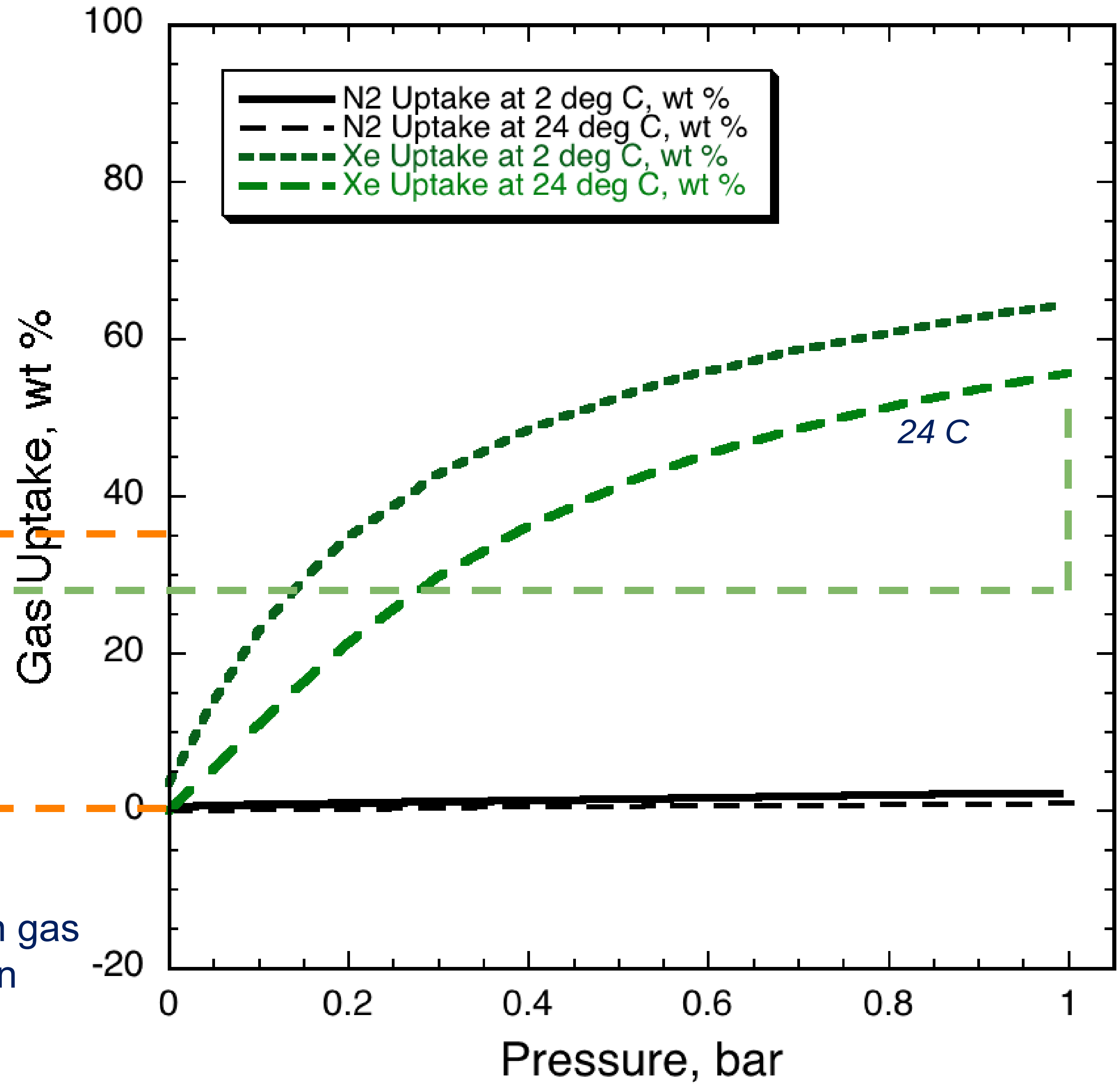


- Pressure/gas composition changed and held constant to set point P_n
- Weight data is acquired and analyzed in real time to determine the equilibrium uptake
- Equilibrium points are collected and plotted as an isotherm

What about Xenon and Krypton MOF -5 Vs Nidobdc

- MOF-5 to NiDOBDC
- Doubled Xe uptake
  - From 28% @ 1 bar
    - To 56% @ 1 bar
    - Reversible at all temperatures
    - Increase capacity at lower temperatures





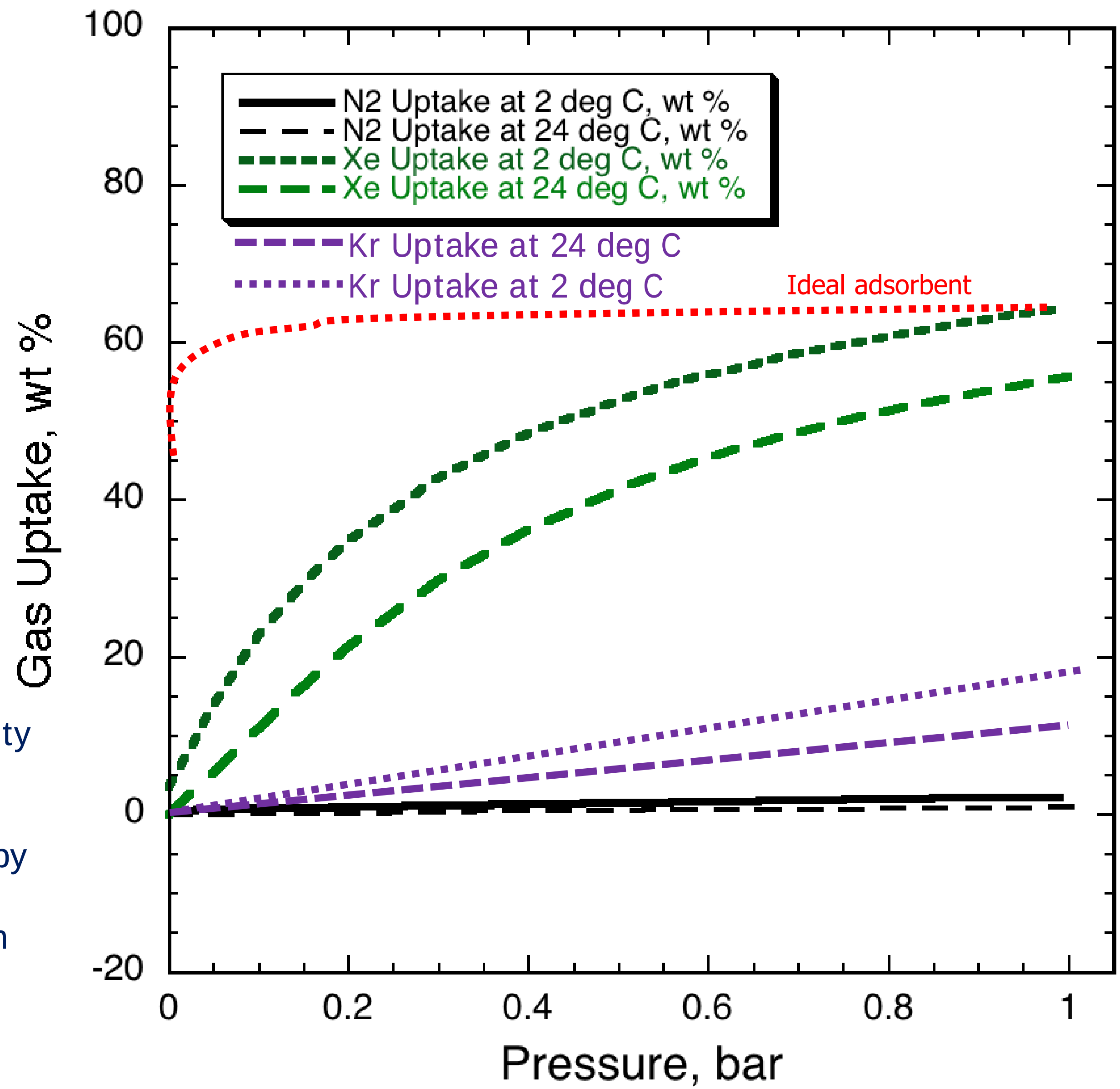
- Active site playing a key role in gas adsorption at low pressure than surface area.

Thallapally et. al., Chem. Comm., 2012

Nidobdc MOF

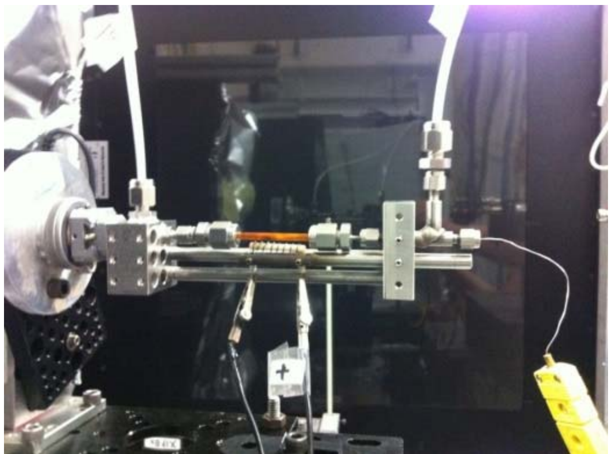
- Corresponds to seven Xe per cavity.
- Highly selective to Xe over Kr, N_2

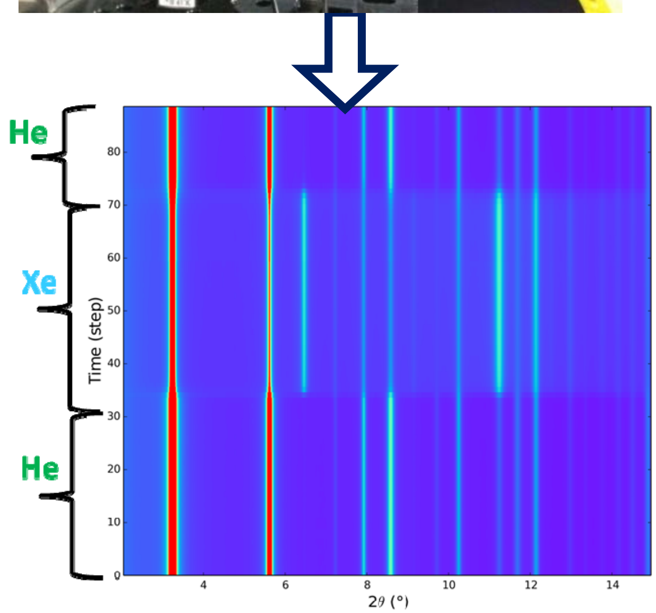
- The only mechanism for Xenon to interact is based on its polarizability.
- Metal cations are very polarizing, which may enhance the interaction with polarizable adsorbents
- Additionally, high surface area, uniform porosity, and high diffusivity make NiDOBDC more attractive.
- The ability to tune the properties by replacing nickel with another transition metal center (Mg, Co, Zn and Mn) is advantageous compared to other materials



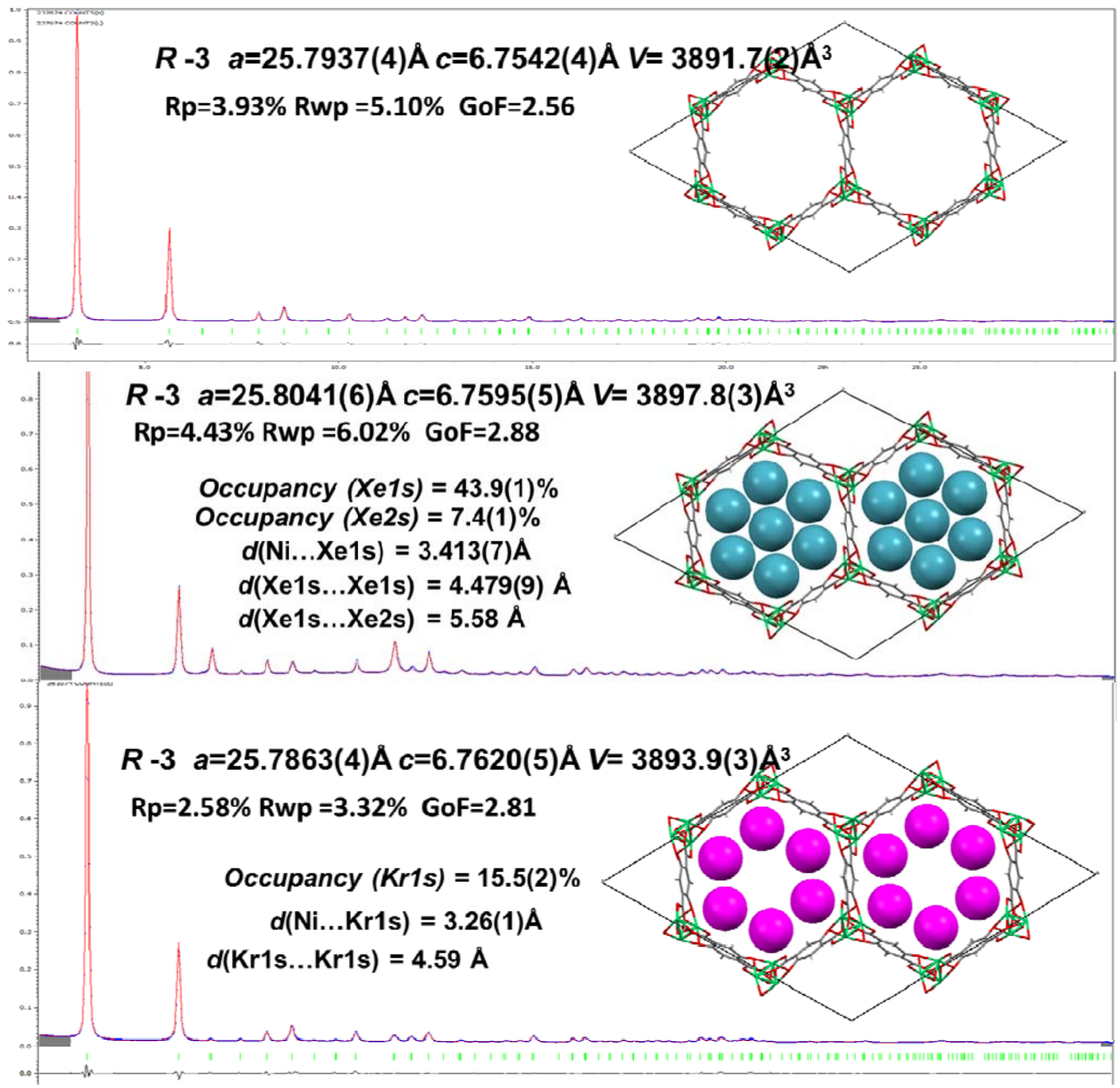
Thallapally et. al., Chem. Comm., 2012, 48, 347

In-situ XRD on Nidobdc with Xe/Kr flow NSLS/PETRA III





Thallapally et. al., J. Phys. Chem. Lett., 6, 1790, 2015



Breakthrough measurements apparatus

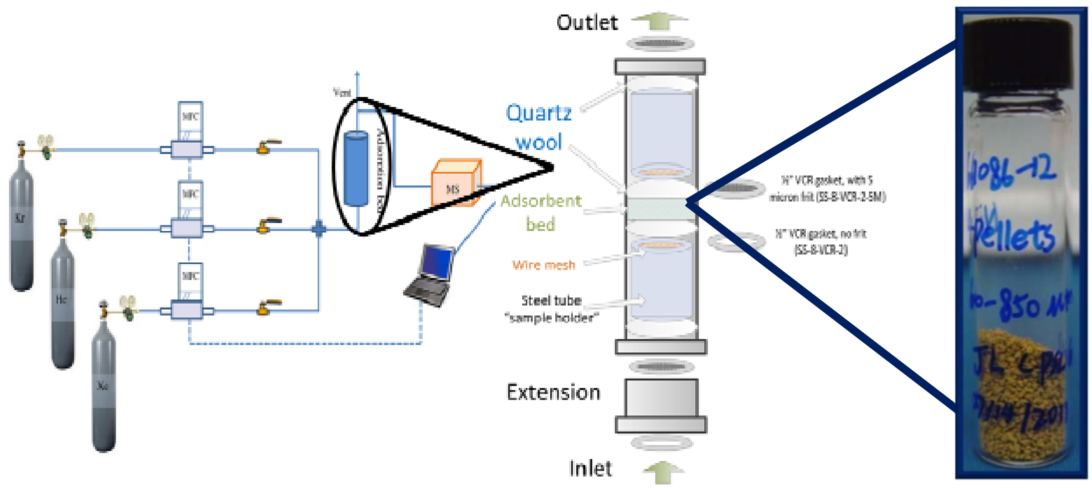
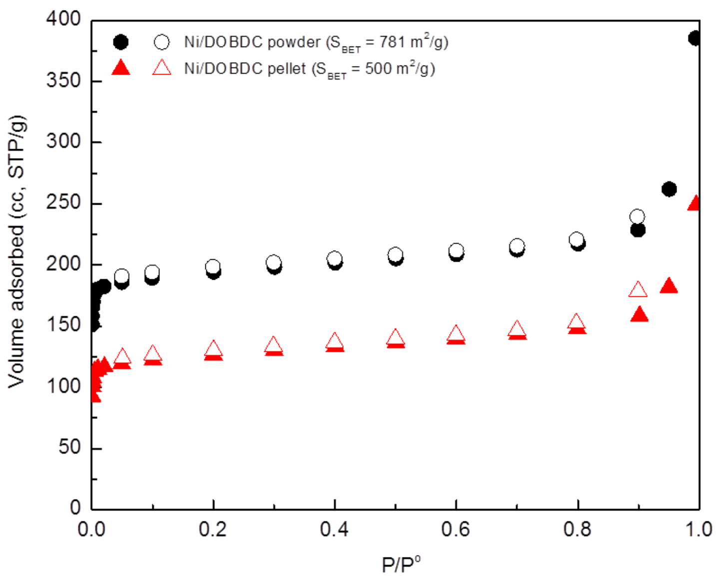


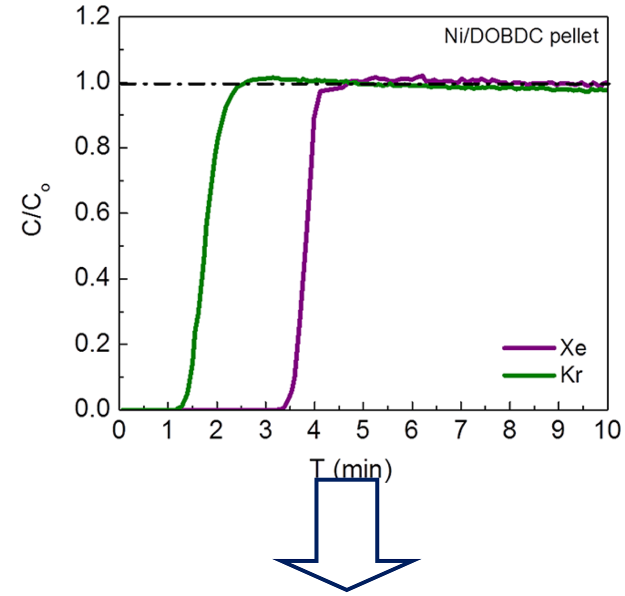
Table 1. Properties of the Ni/DOBDC Pellet

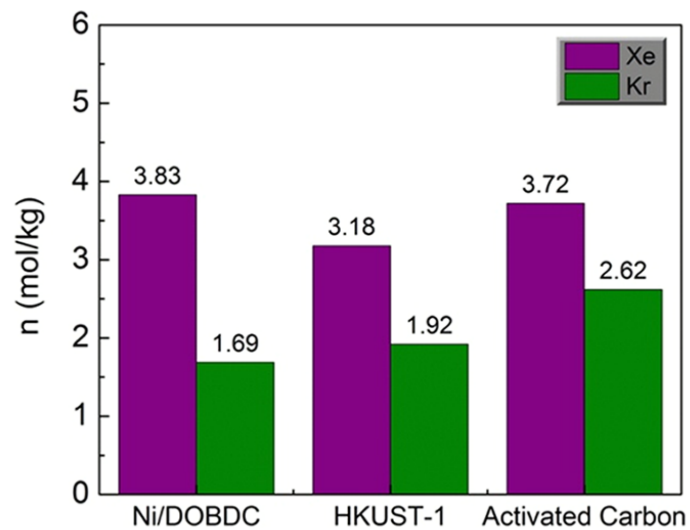
property	value
pressed pressure	12 MPa
size	600–850 μm
pellet density	0.78 g/cm^3
packing density	0.40 g/cm^3
BET surface area	1147 m^2/g
original weight	1.51 g
activated weight	1.01 g

Thallapally et. al., Langmuir 2012, 28, 11584

Nidobdc pellet characterization



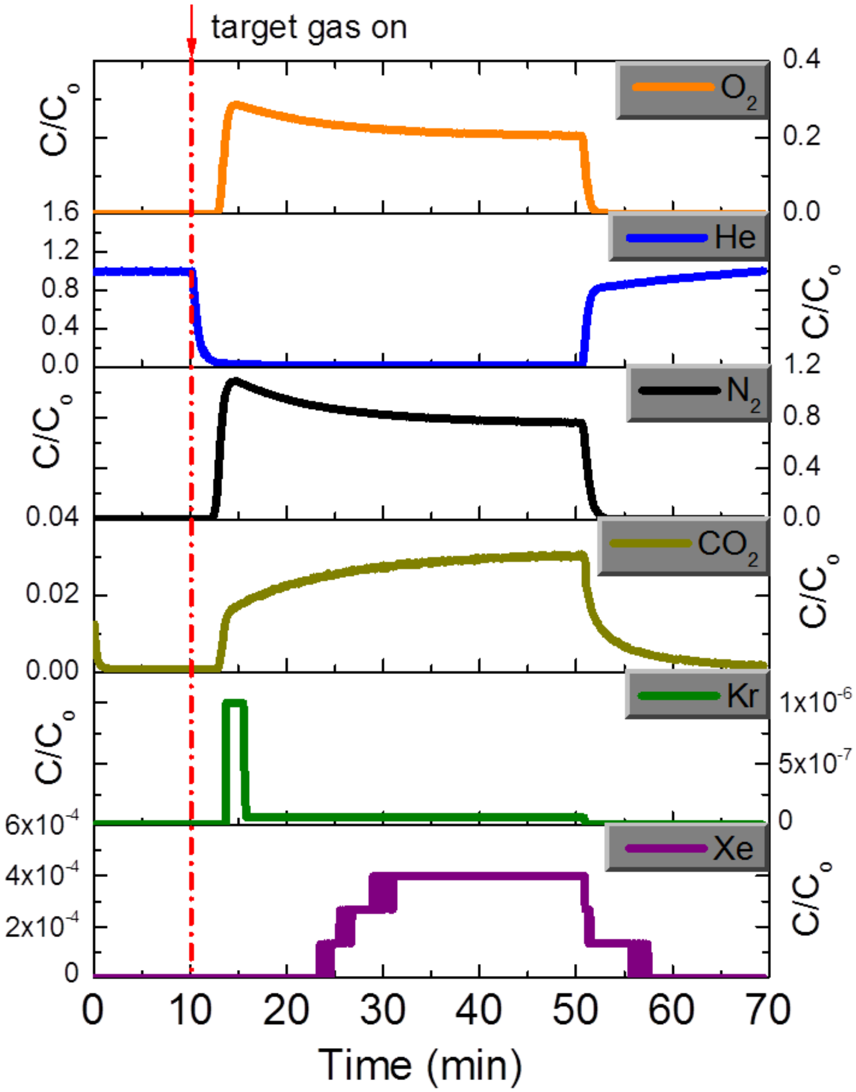




- ❖ PXRD confirms the crystallinity of the sample
- ❖ No amorphization of upon pressurization
- ❖ Reduced surface area of the pellets compare to powder
- ❖ Uptake of Xe/Kr using breakthrough matches with static method

Thallapally et. al., Langmuir 2012, 28, 11584

Single column experiments with off-gas mixture



Thallapally et. al., Langmuir 2012, 28, 11584

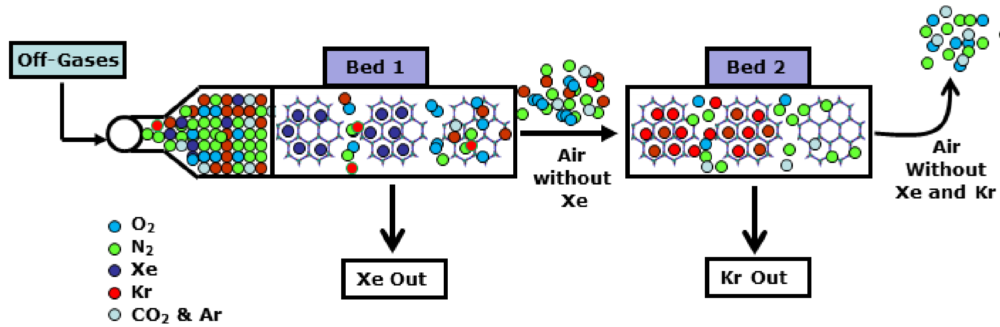
Air = 400 ppm Xe, 40 ppm Kr, 78% N_2, 21% O_2, 0.9% Ar, 0.03% CO_2 etc

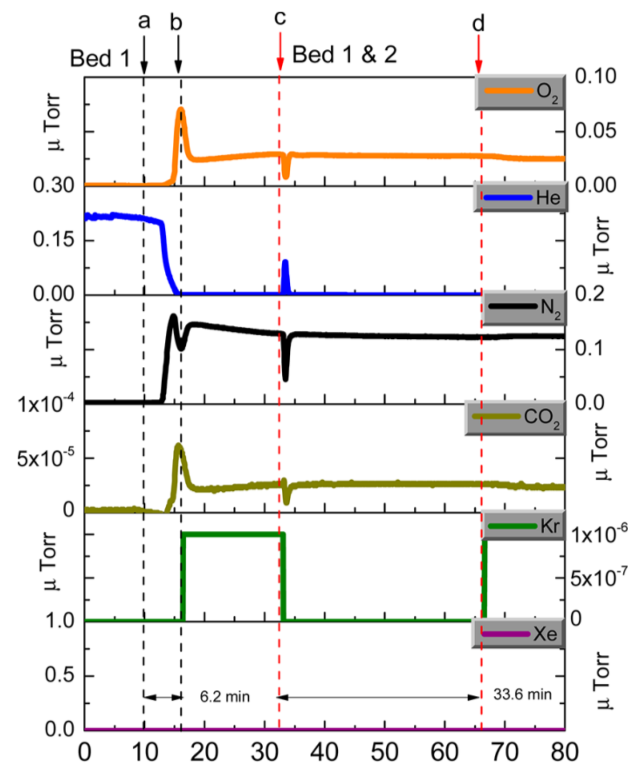
- He flow rate and the flow rate of Xe and Kr in air is 20 sccm.
- NiDOBDC adsorbs Xenon preferentially over other gases
- >95% of Xenon is captured from air using NiDOBDC
- Ni/DOBDC is able to separate 400 ppm Xe from 40 ppm Kr mixture in air with a Xe/Kr overall selectivity of 7.3.
- The uniform cylindrical pores are believed to be favorable to maximize the Xe/Ke selectivity

Two-column breakthrough experiments with off-gas mixture

Air = 400 ppm Xe, 40 ppm Kr, 78% N_2, 21% O_2, 0.9% Ar, 0.03% CO_2 etc

- **A two-bed technique to remove and separate**
  - Bed 1 remove Xe from air
    - NiDOBDC MOF
    - Yields air with Kr
  - Bed 2 remove Kr
    - Yields air without Xe and Kr
    - Off-gas can be released
- **Results**
  - Air: 400 ppmV Xe, 40 ppmV Kr
  - Removal of Xe first (Bed 1) removes competition on Bed 2
  - NiDOBDC capacity
    - 0.24 mmol/kg w/ Xe
    - 0.61 mmol/kg w/o Xe

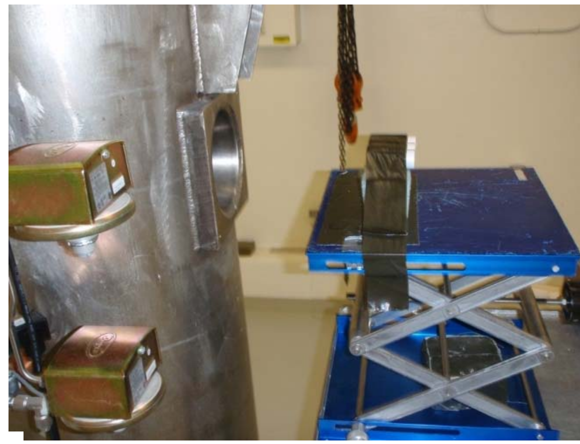
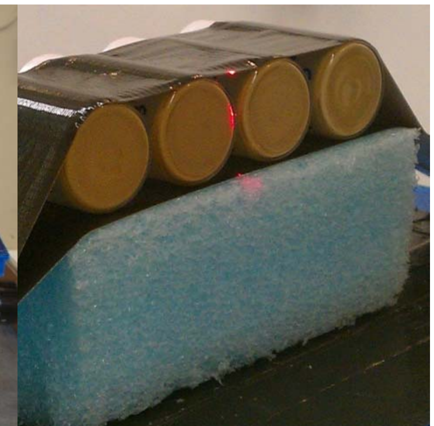




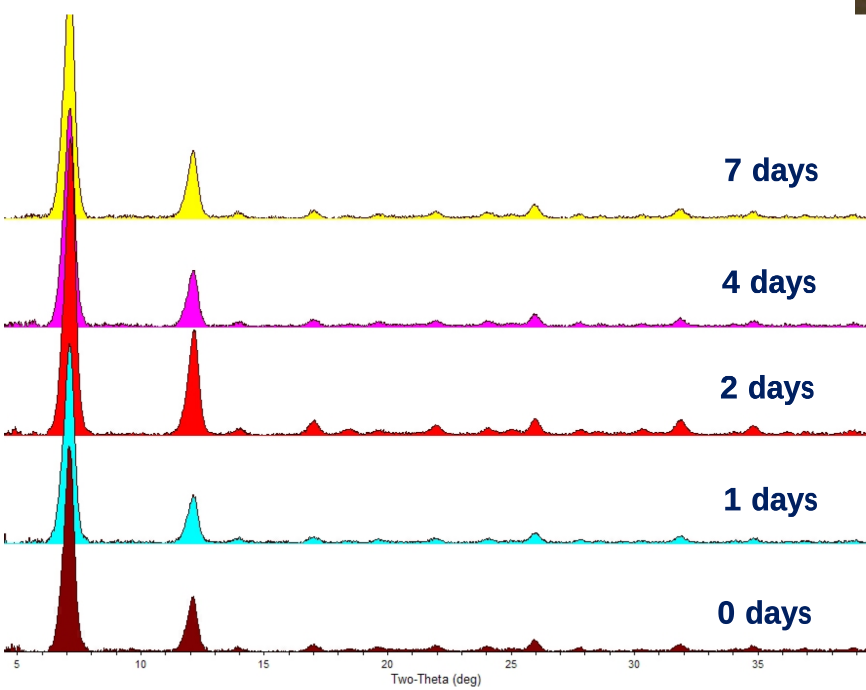
Thallapally et. al., Ind. Eng. Res. & Chem., 53, 12893, 2014

Effect of γ radiation (^{60}Co)

- The goal is to deliver the same amount of radiation exposure to the material using ^{60}Co as would be delivered by the ^{85}Kr
- Needed 1.4×10^{13} R
- Max about 7×10^{6} R

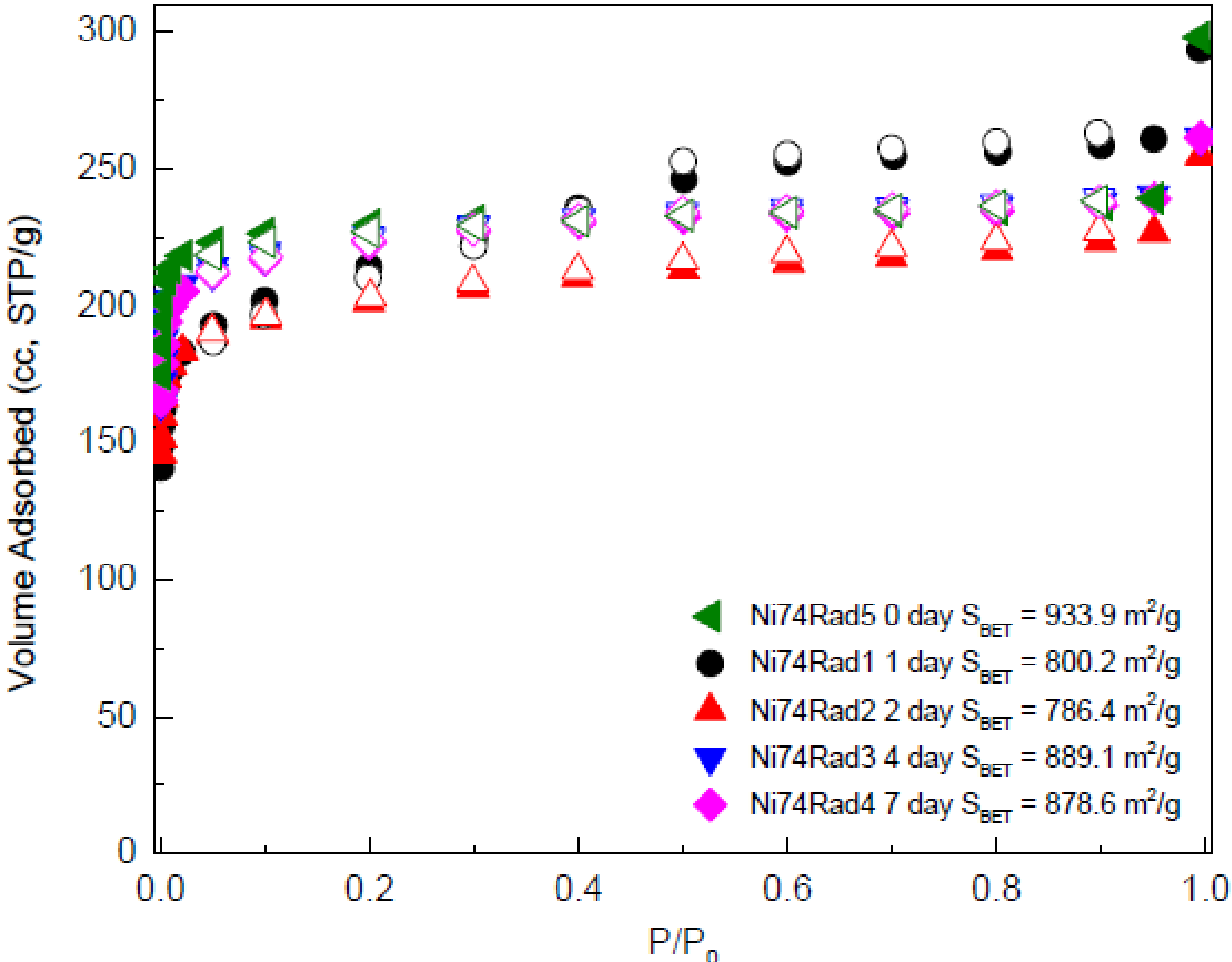



- This view shows the distance between the source and the collimator



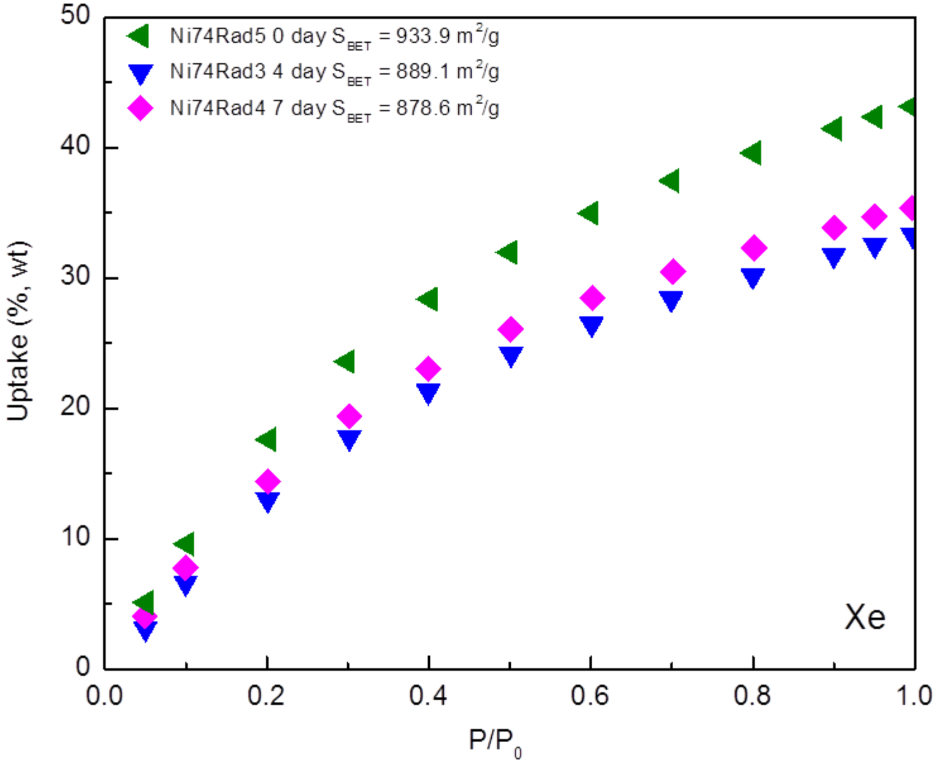
	Dose rate 40000 R/h	
Sample	**Dose**	**Days**
1	960 000	1
2	1920 000	2
3	3840 000	4
4	6720 000	7

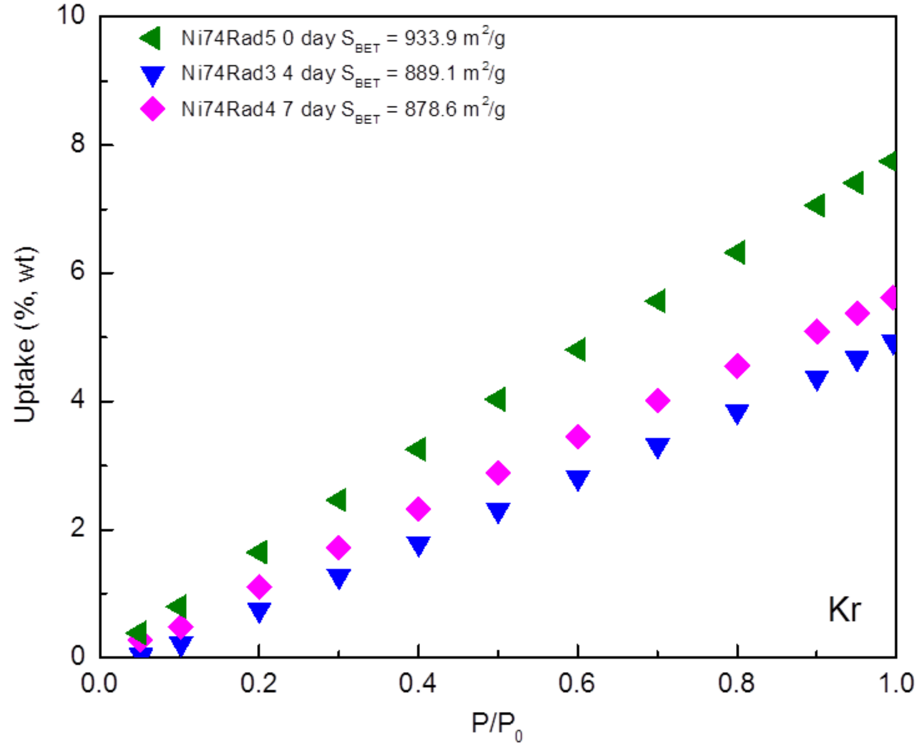
Surface area measurement on radiation irradiated samples



- Only a minor change in the surface area with radiation
- Due to the presence of an impurity

Xenon and Krypton loading





- Slightly reduced Xe/Kr at 1 bar and RT
- Might be due to the 10% of impurity (Nickel formate) in the samples studied
- Nickel formate was confirmed from the XRD powder patterns.

Techno economic evaluation of MOF-based separation

- **Techno-economic considerations for noble gas capture from UNF processing**

Process	Decontamination Factor	Total Project Capital ($\$10^6$)	Proposed Annual Consumables[A] ($)
Cryogenic Distillation	67	8.77	267,000[A]
MOF Adsorption	100[B]	8.42	78,000

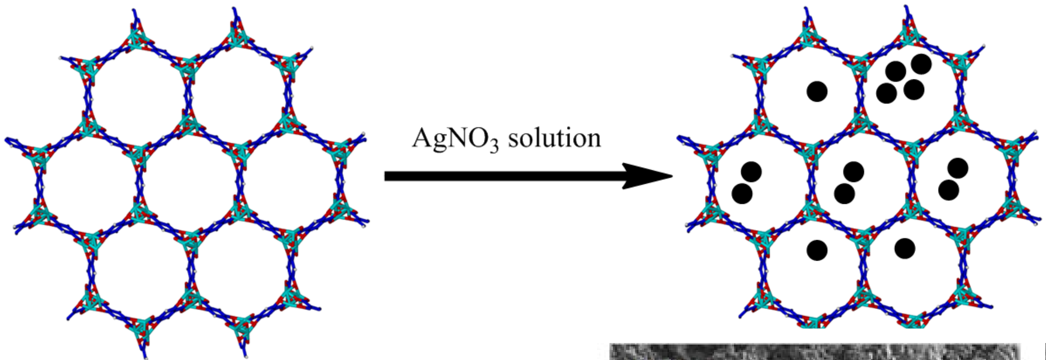
A: Includes compressor/pump utility loads adjusted to capacity factor and $0.10/kWh, and annual consumables (hydrogen for cryogenic and MOF for the adsorbent process).

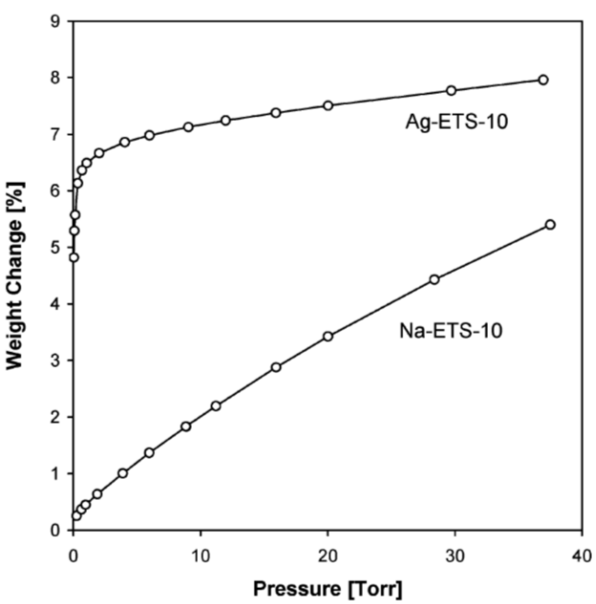
B: The MOF DF is theoretical and neither measured nor calculated. The model assumed complete adsorption based on experimental data and performance criteria established in bench scale testing.

- ❑ Improve Xe/Kr adsorption at room temperature
- ❑ Selectivity

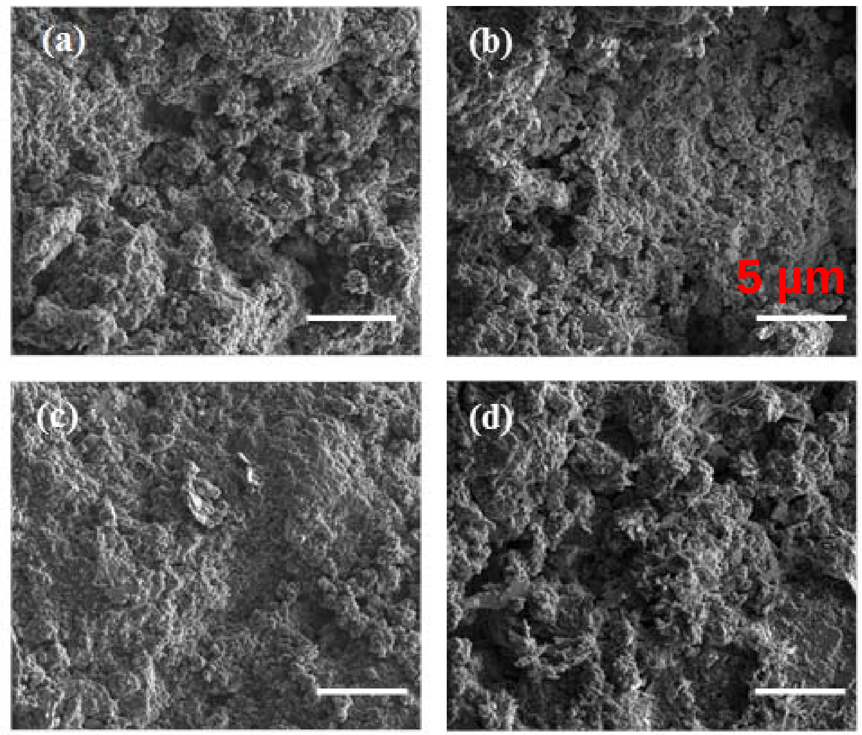
Cabe, J and Thallapally et. al., 2013

Impregnation of silver nanoparticles in Nidobdc



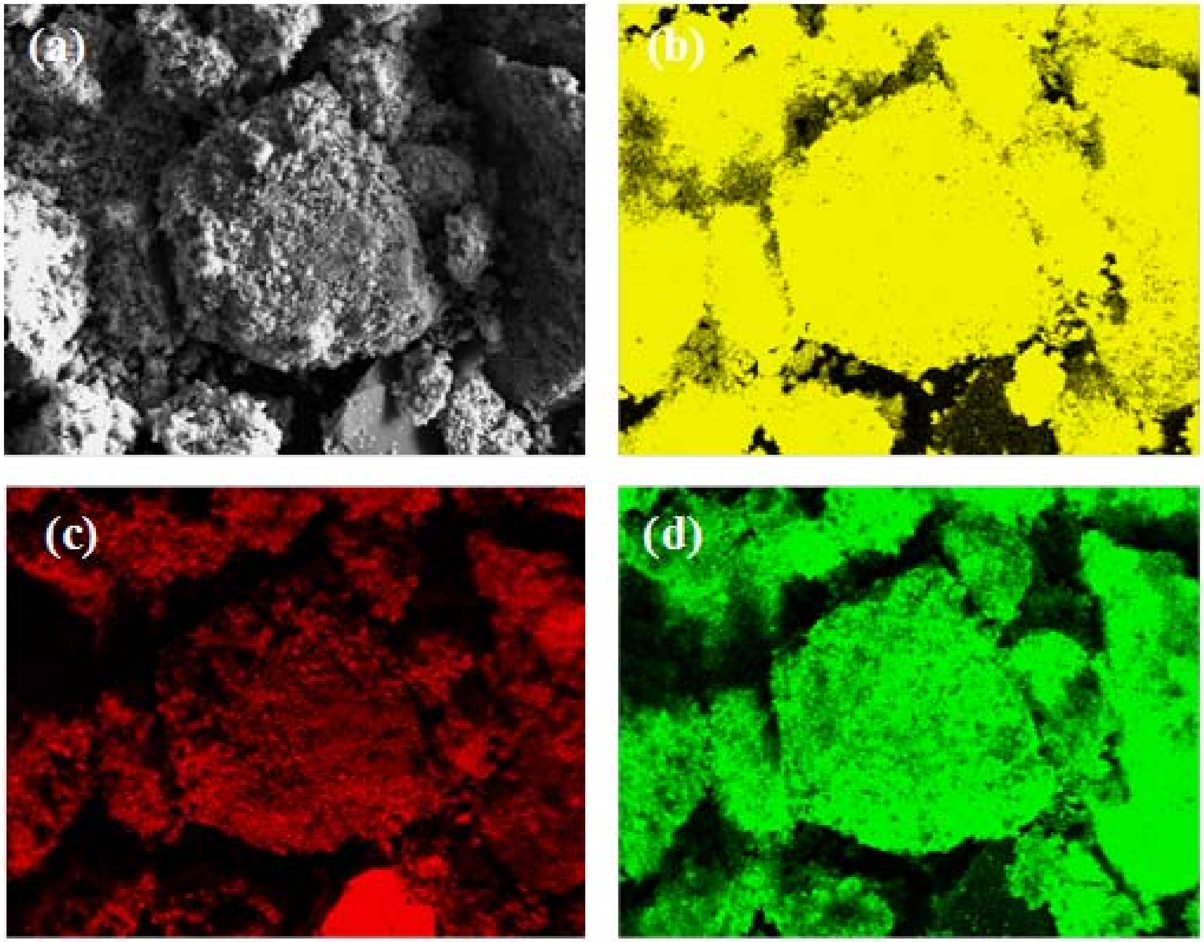


J. Physc. Chem. Lett **2007,** *111,* 1560-1562



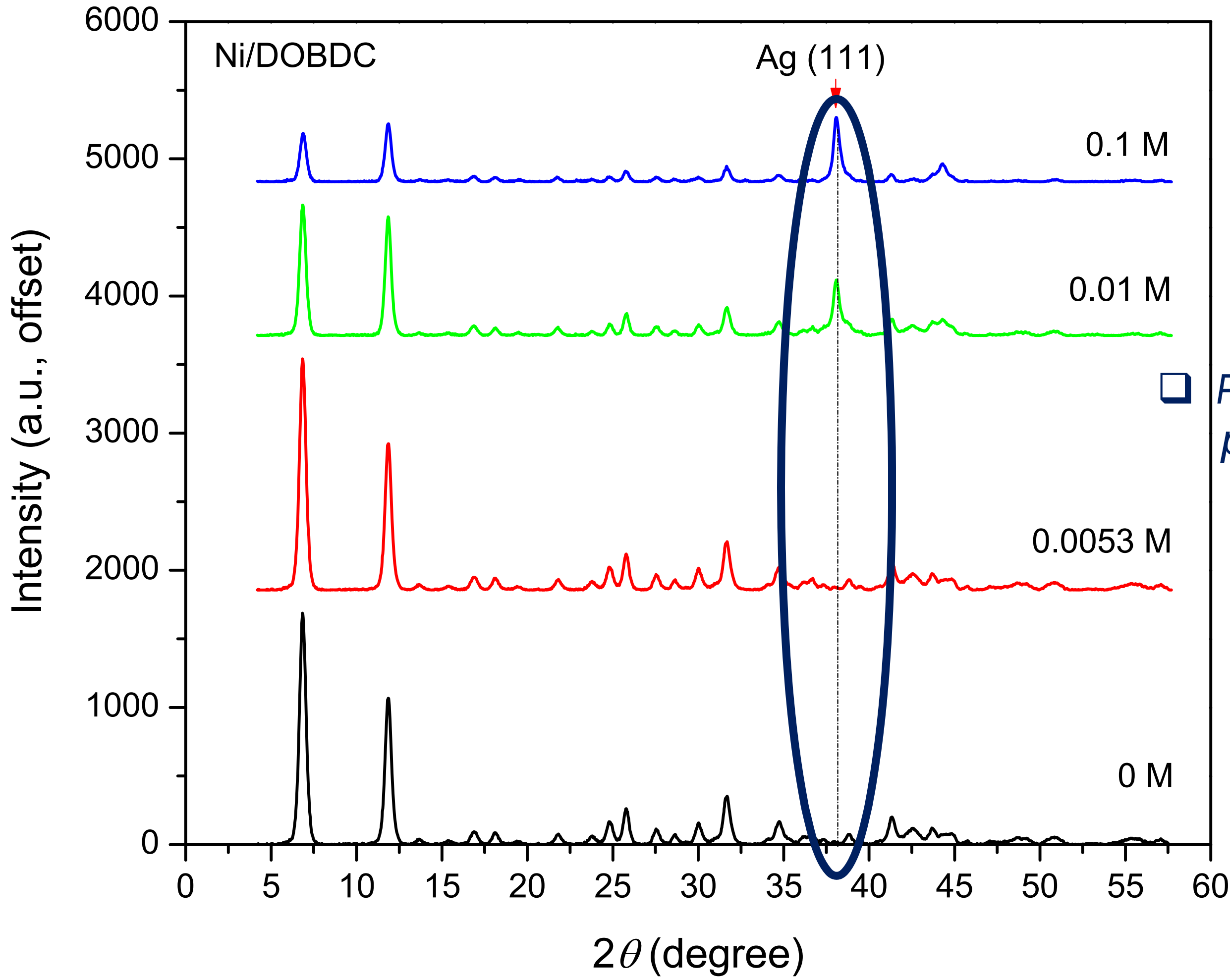
Thallapally et. al., Chem. Commun., 2013

Elemental mapping of Ag@Nidobdc



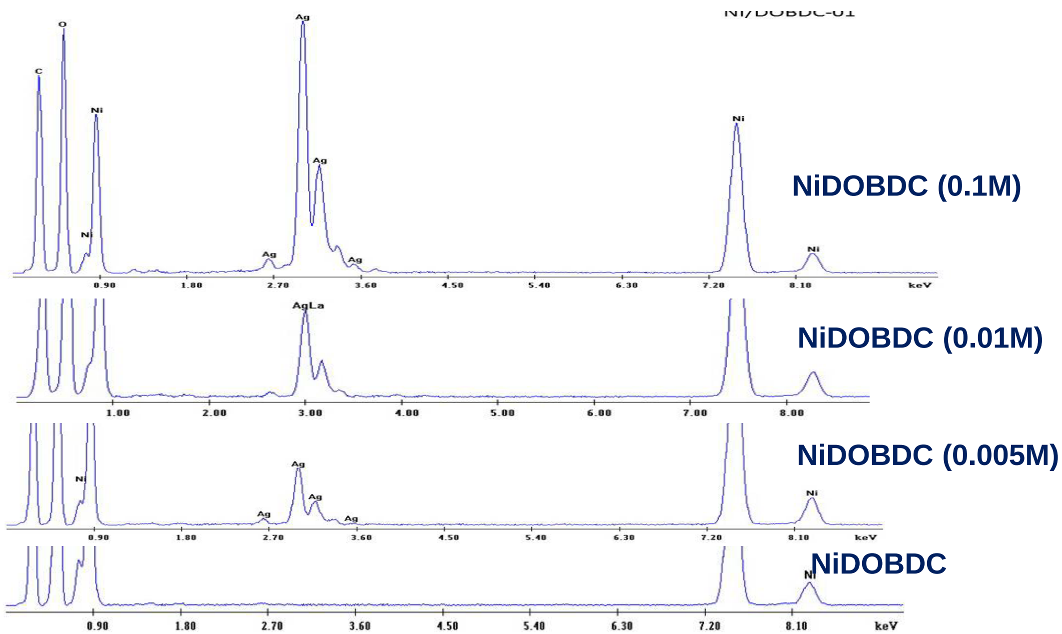
a) SEM image NiDOBDC; b) Ni; c) O; d) Ag

Powder X-ray Diffraction of Ag@NiDOBDC



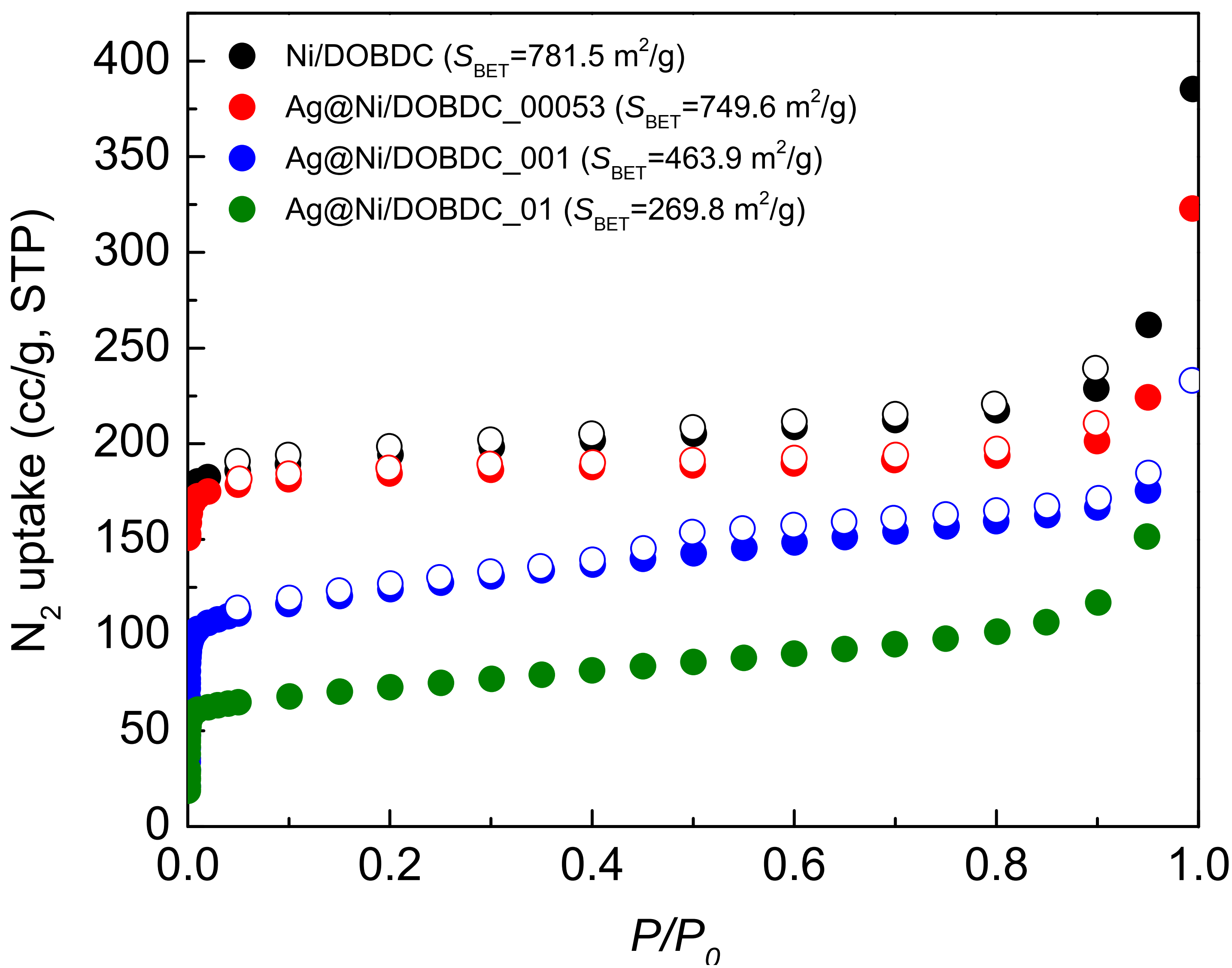
- Peak @ 39º represent the presence of Ag^0

Ag@Nidobdc X-ray photoelectron spectroscopy

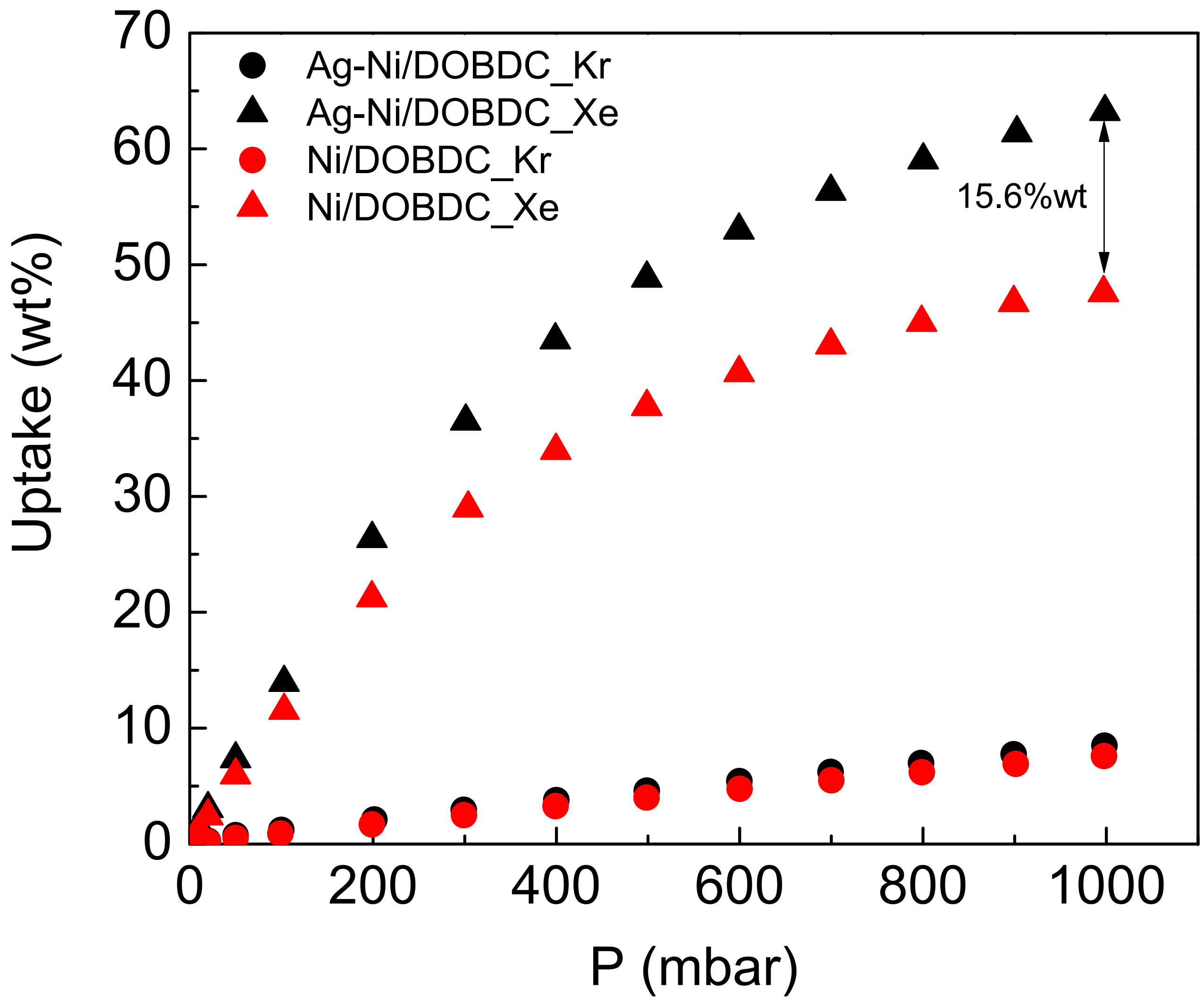


Sample	Surface area (m^2/g)	Ag loading (%)
Ni/DOBDC	781.5	0
Ni/DOBDC-0005	749.7	1.47
Ni/DOBDC-001	463.9	1.92
Ni/DOBDC-01	269.9	6.59

Surface area of Ag@Nidobdc



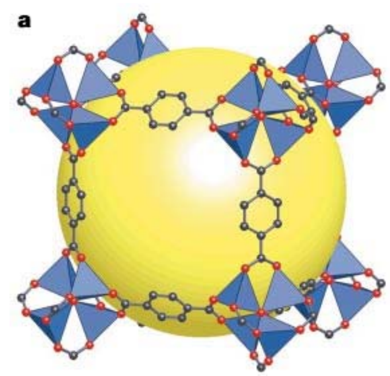
Xe/Kr adsorption in Ag@Nidobdc



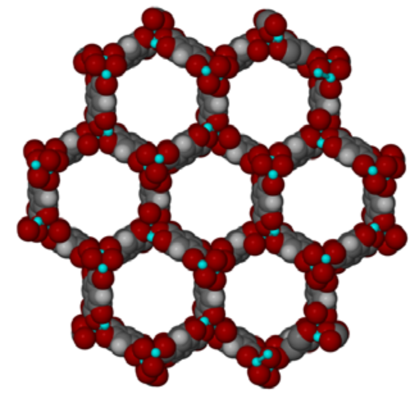
Types of MOFs studied

1. MOF-5, a proto-type
2. MOFs containing open metal sites
3. MOFs functionalized with polar groups
4. MOFs impregnated with Ag^0 nano particles
5. Hydrophobic MOFs with small pore size
6. Computational approach

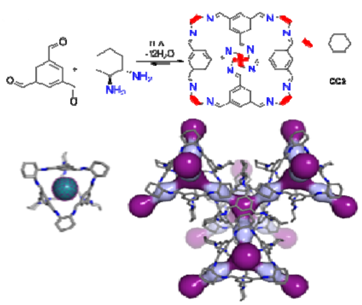
Increase in Xe/Kr capacity and selectivity at RT



Thallapally et. al., Chem. Comm., 2012, 48, 347

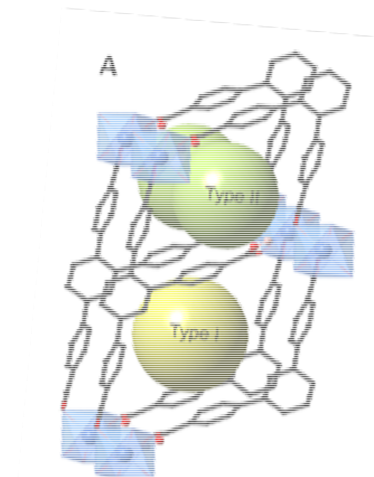


Thallapally et. al., J. Am. Chem. Soc., 137, 7007, 2015
Thallapally et. al., JACS 2012



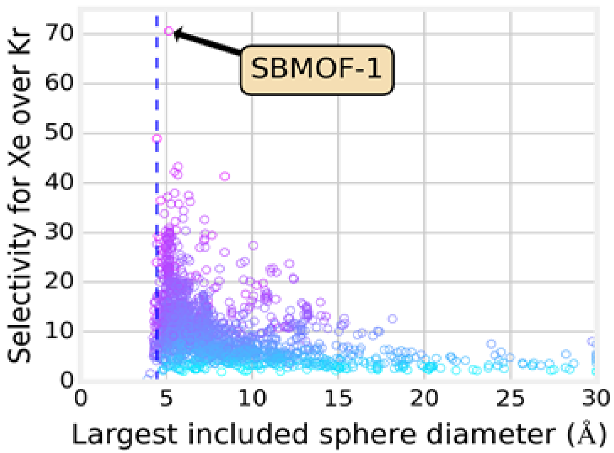
Thallapally, Cooper et. al., Nature Materials., 13, 954, 2014

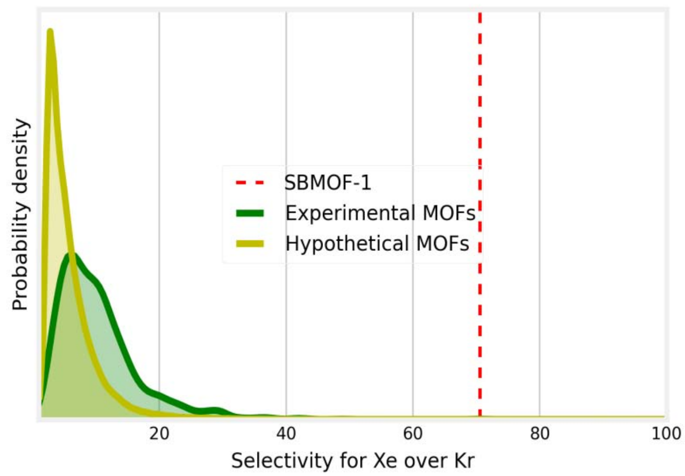
- Synthesis and Characterization
- Gas sorption properties at 1 bar and various temperatures
- Breakthrough measurements
- Economic analysis



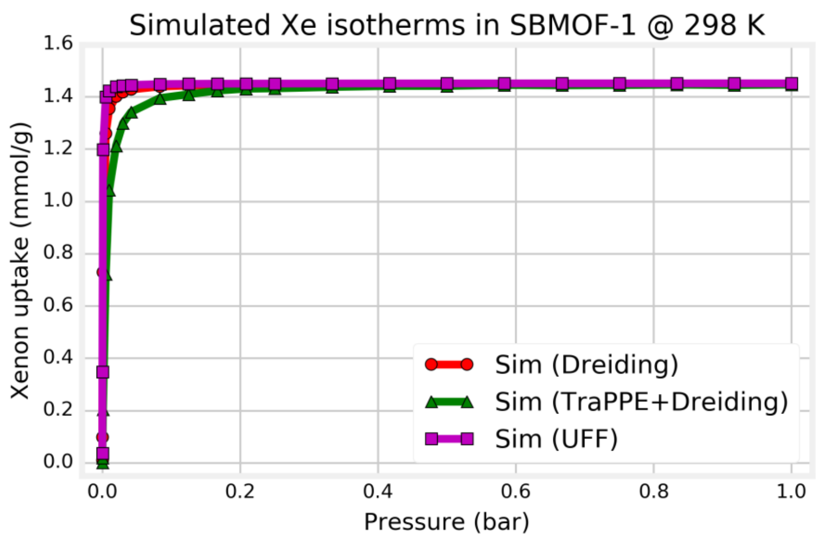
Thallapally et. al., J. Am. Chem. Soc., 134, 9046, 2012
Thallapally et. al., Angew Chem. Int. Ed., 2016

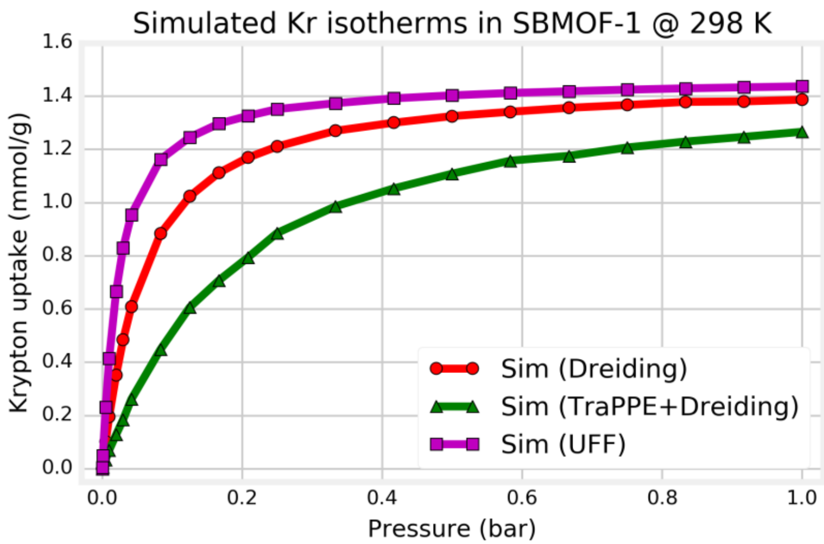
Material discovery using computational approach





Modelling predicts the SBMOF-1 is the best among 5000 experimental and 125,000 hypothetical MOFs.

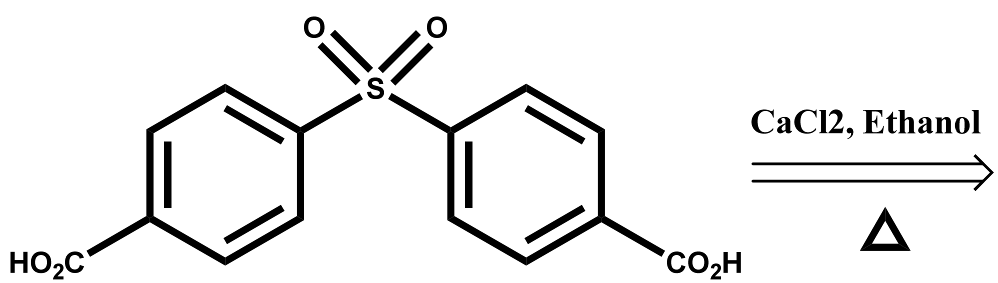


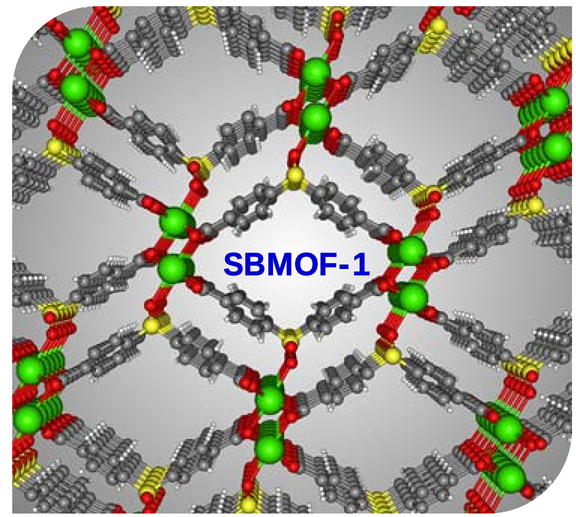


Bernard Smith et. al., Chem. Mat., 2015
Thallapally et. al., Nature Communication, 2016

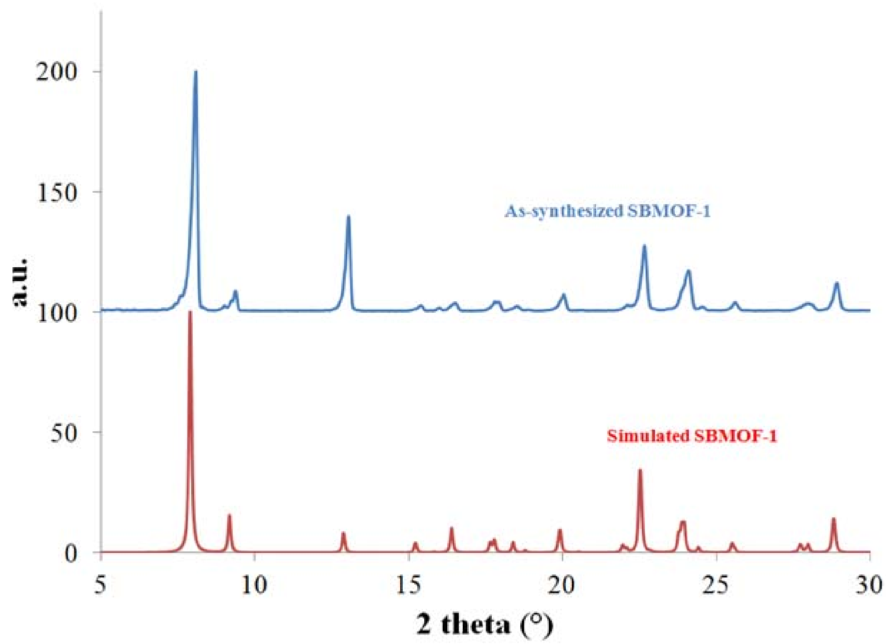
In Collaboration with Prof. Berend Smit @ University of Berkeley, CA

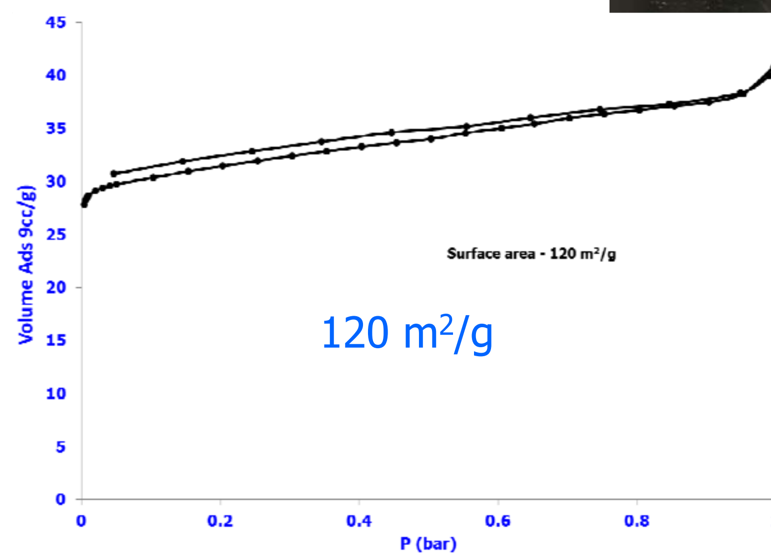
Leading MOF material @ RT?





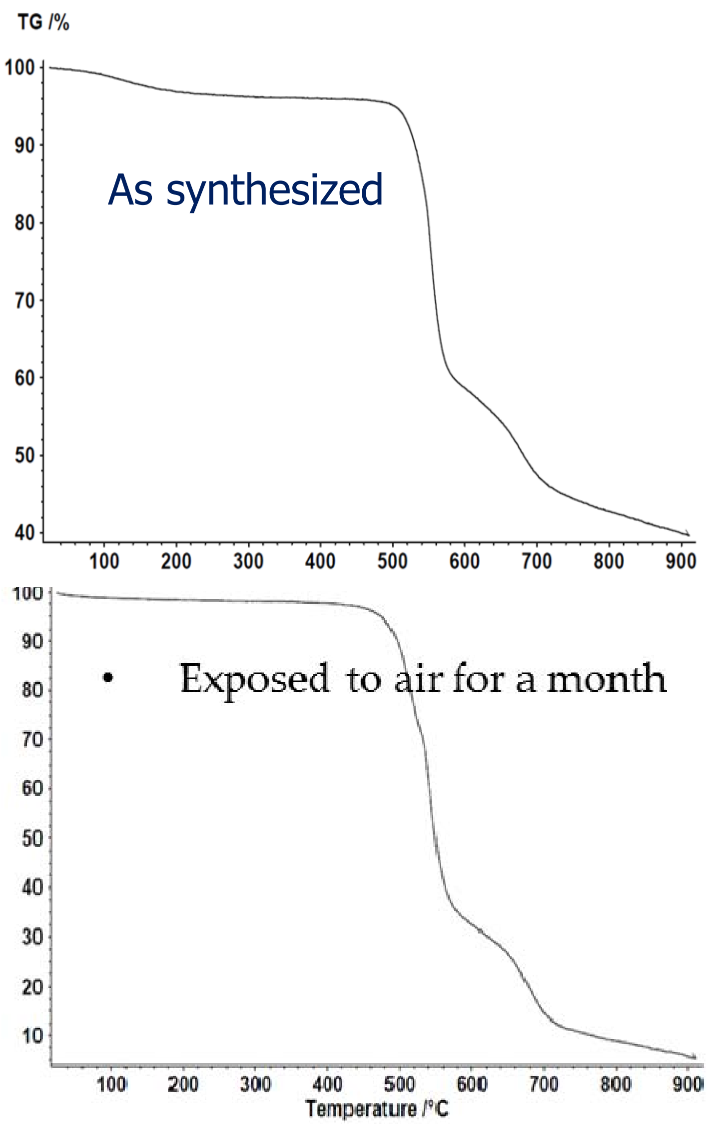
- 3D network structure connected with CaO units
- Pore diameter is about 4.1 Angstroms.

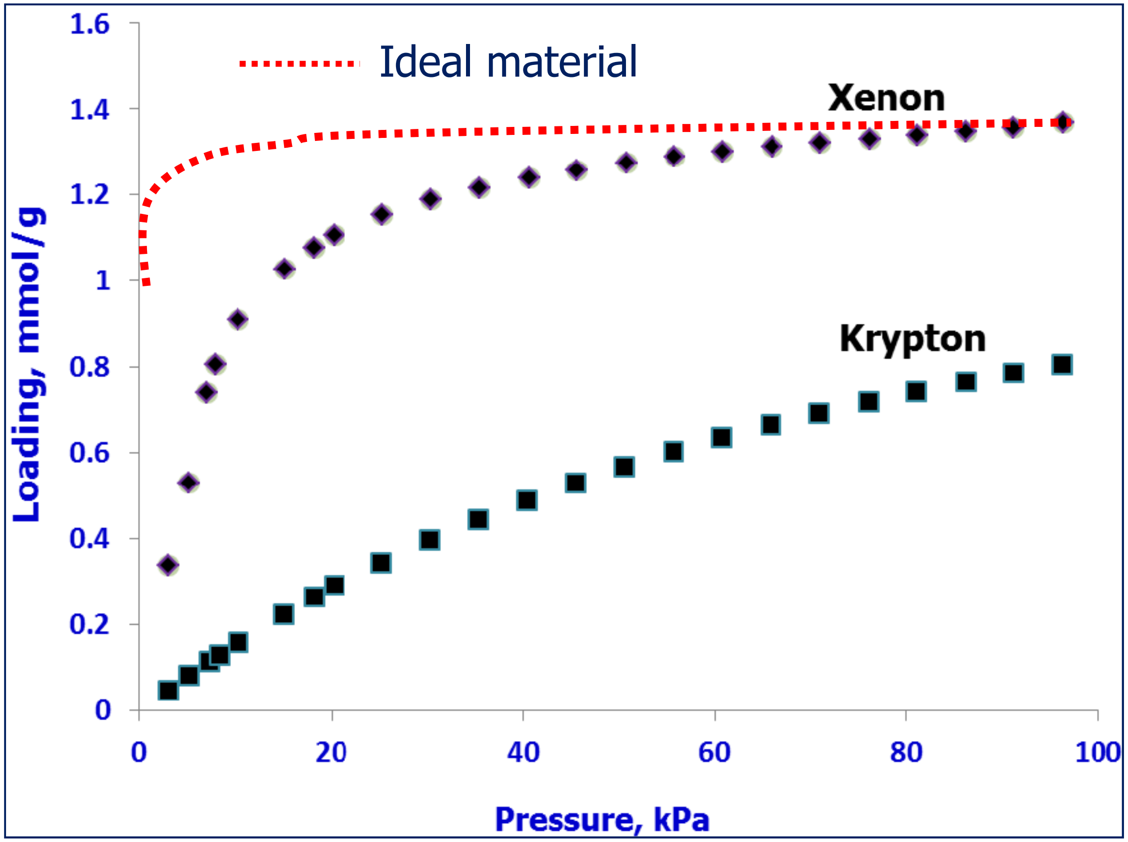




Thallapally et. al., Nature Communication, 2016

Thermal analysis and gas adsorption

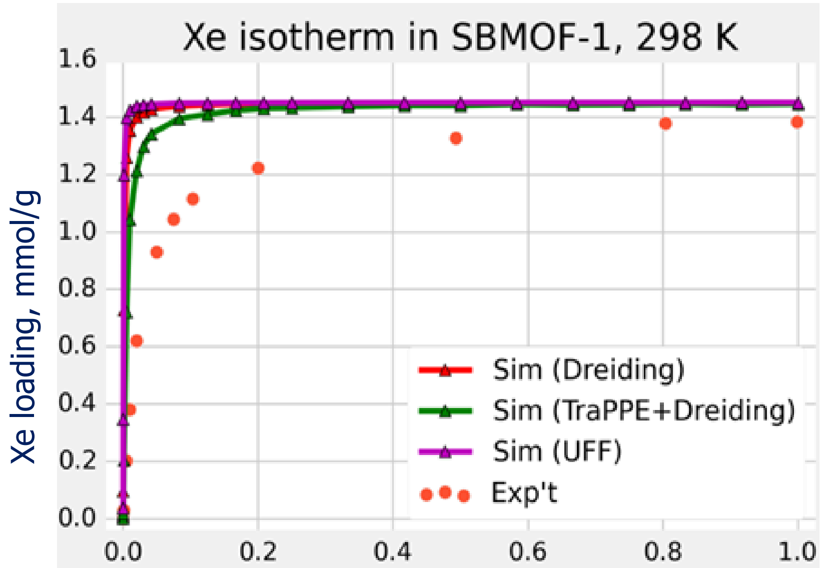


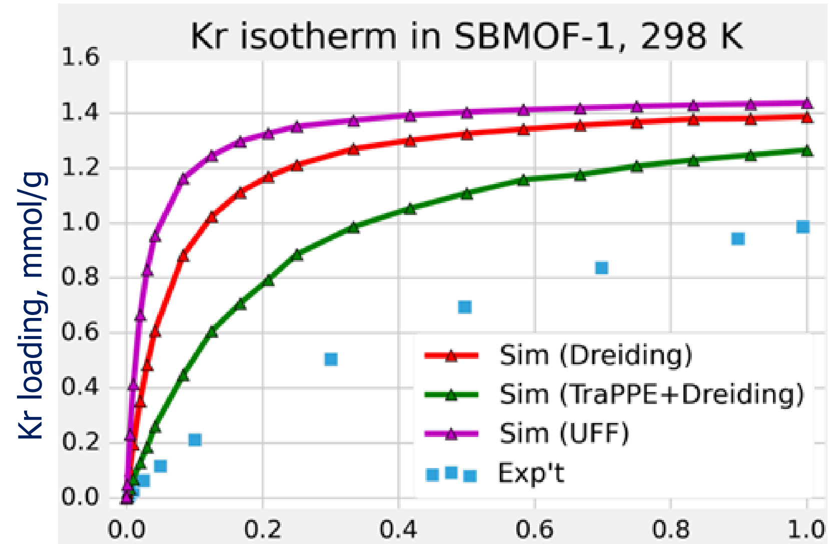


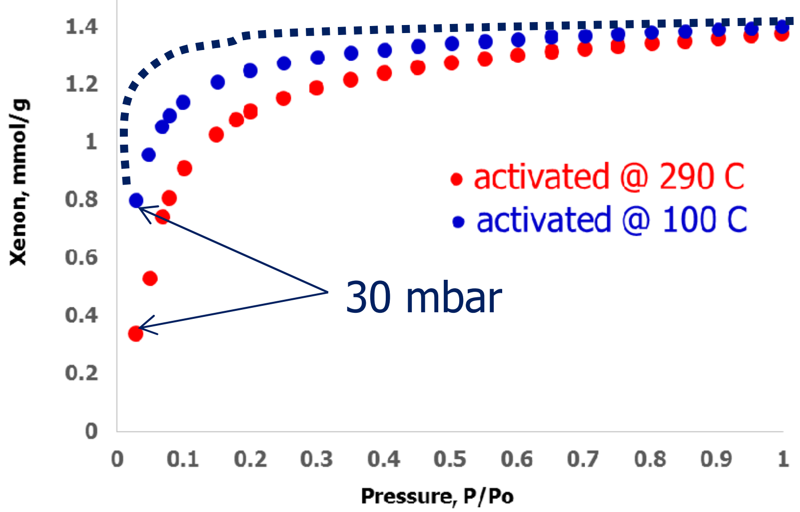
- No Weight loss or decomposition until 500 ^{o}C, indicating the robustness
- Activated at 290 C

Thallapally et. al., Nature Communication, 2016

A rare example of computationally inspired material discovery



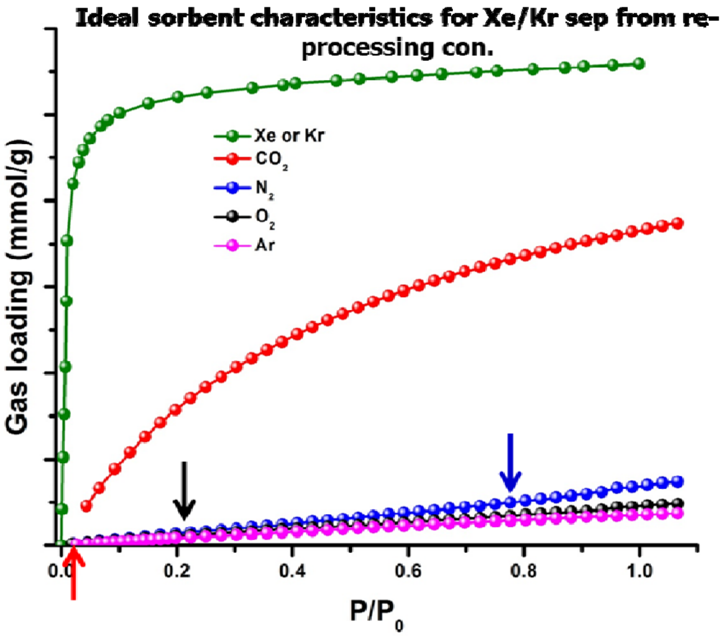


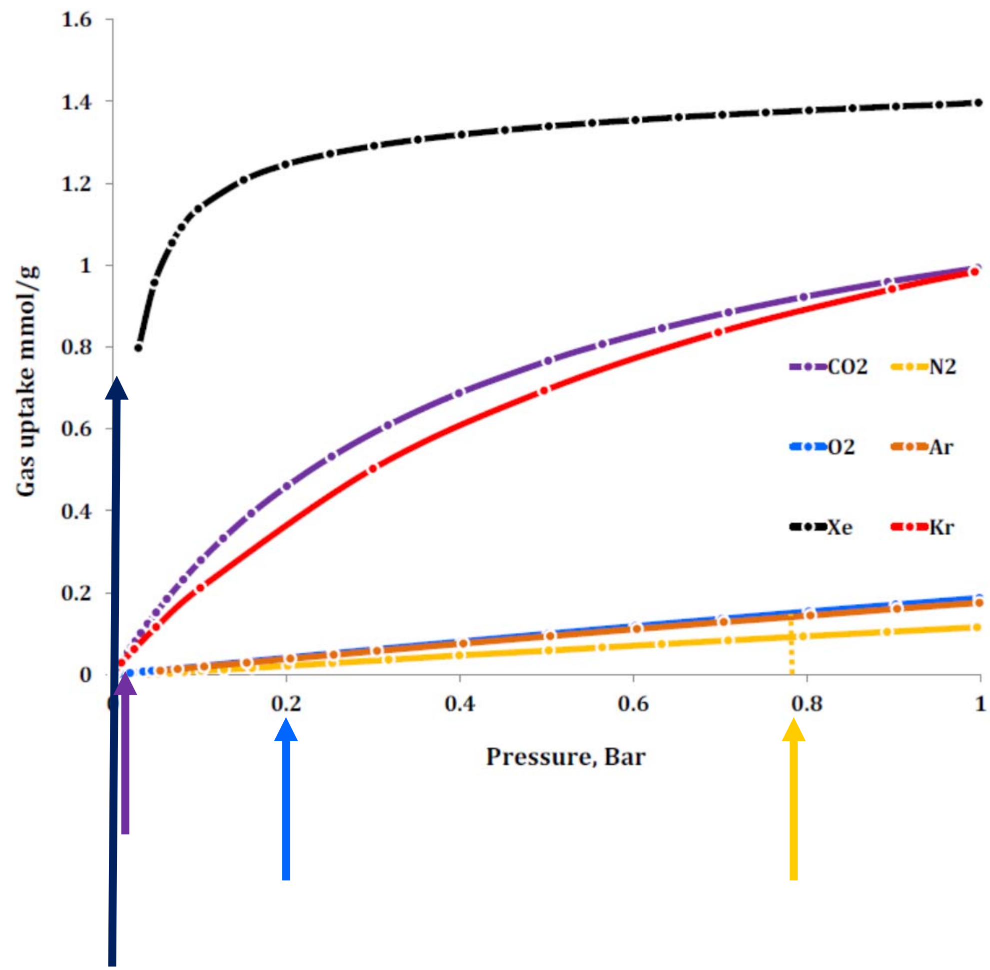


Thallapally et. al., Nature Communication, 2016

- Based on SXRD, it is evident that –phenyl rings turned by 45° to each other as a result blocks the pore when activated at 290 C
- Due to the ring rotation, the pore size in SBMOF-1 activated at 290 C is less than optimal for Xe atom to fit.
- At lower pressure (~30 mbar) Xe loading is dramatic, 2.5 times more Xe uptake capacity in sample activated at low temperature

Other gas ads in SBMOF-1

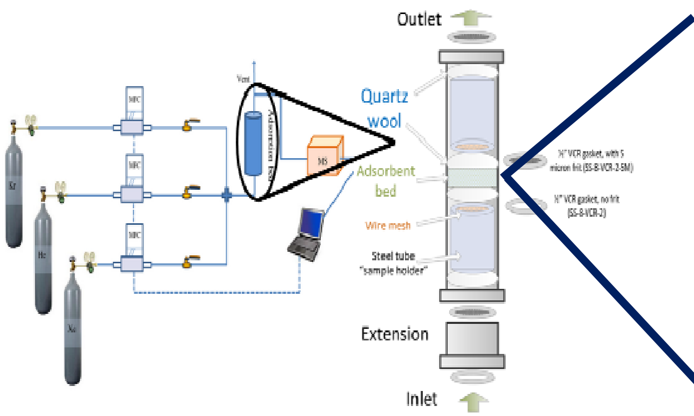




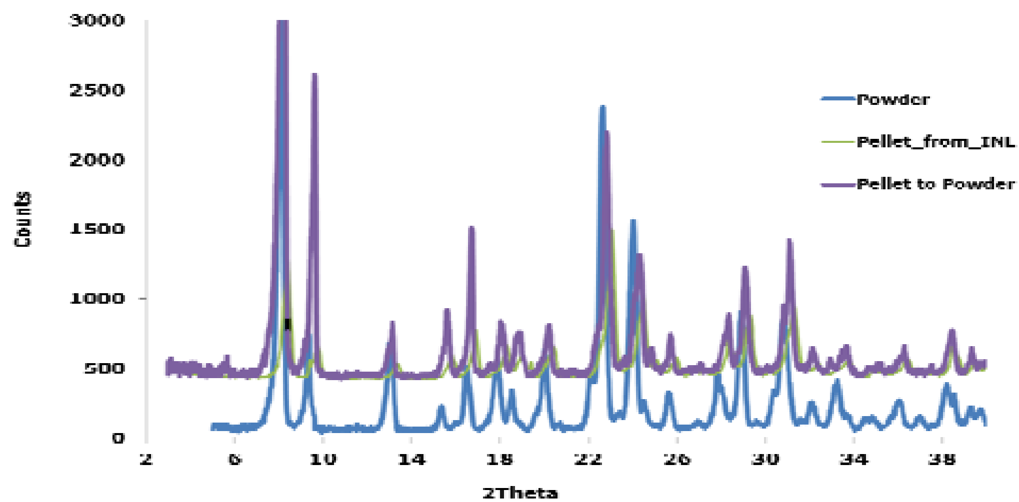
✓ SBMOF-1 is very selective towards Xe compare to other gases

Thallapally et. al., Nature Communication, 2016

Breakthrough measurements apparatus



Property	Value
Pressed Pressure	75 MPa
Size	500 – 850
BET Surface area	15 m^2/g
BET Surface area, Po	120 m^2/g



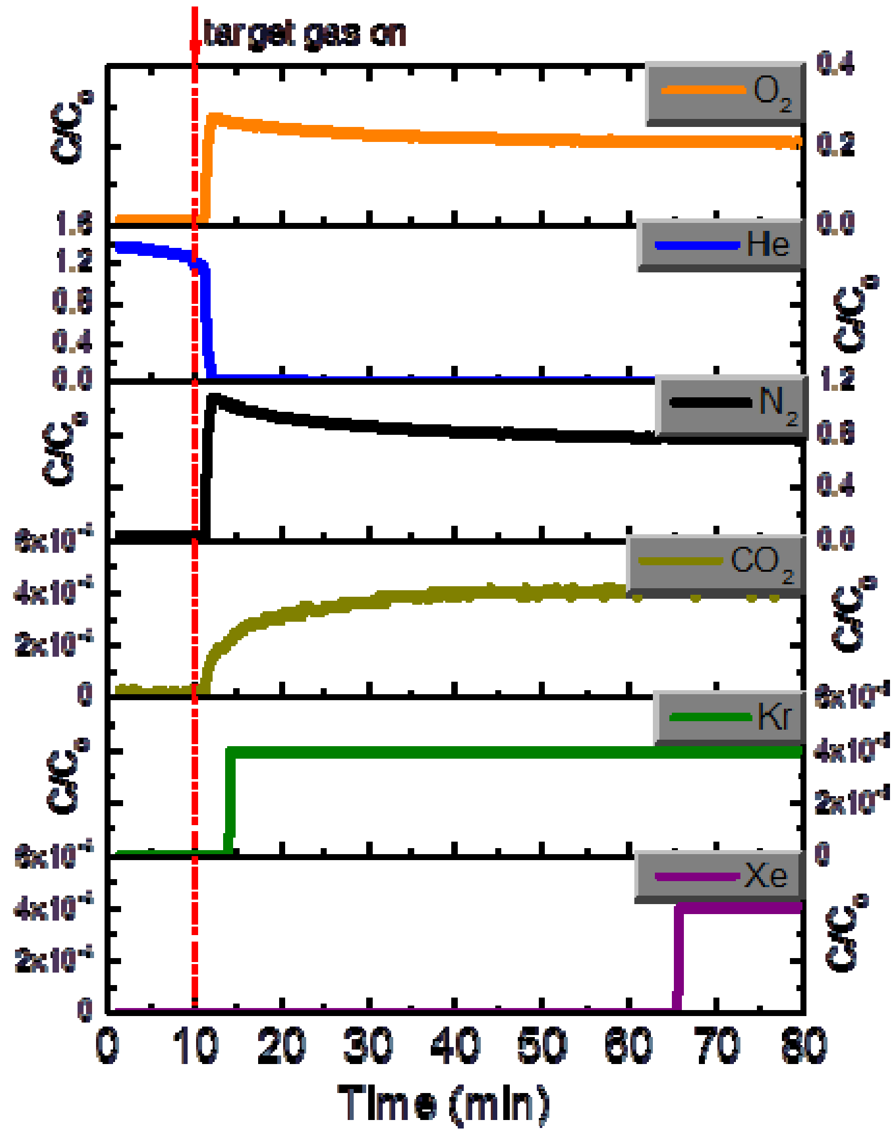
- Identical PXRD confirmed (powder to pellet)
- No amorphous phase
- Reduced BET surface area

Thallapally et. al., Nature Communications, 2016

Single column breakthrough experiments on SBMOF-1 at room temperature

- Conditions
  - Air = 78% N_2, 21% O_2, 0.9% Ar, 0.03% CO_2, 400 ppm Xe, 40 ppm Kr
  - Flow rate = 20 cm^3/min
  - T = 25 ^oC (298K)
  - MOF = SBMOF-1

- Results
  - SBMOF-1 adsorbs Xenon preferentially over other gases
  - Xe capacity = 15 mmol/kg *vs* 4.6 mmol/kg (NiMOF) and 11 mmol/kg (CC3)
  - >95% of the Xe captured from air
  - Xe/Kr (selectivity) = 15
  - Xe loading is unaffected by water (48% RH)

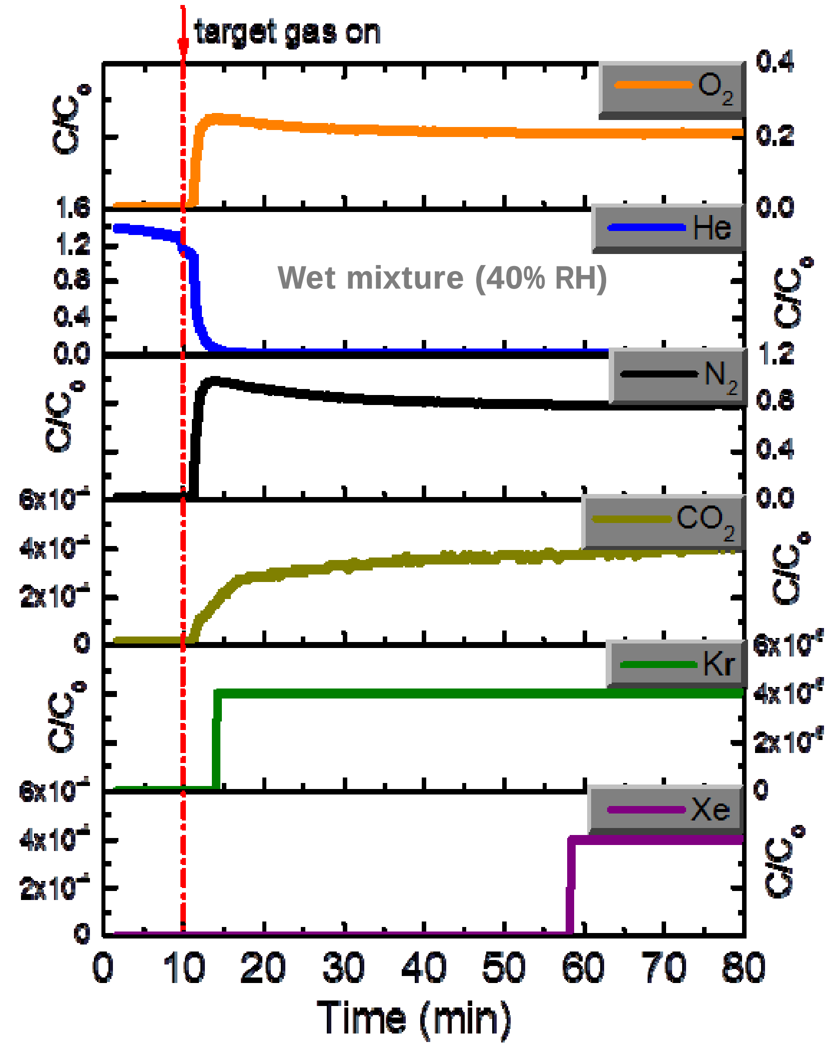


Thallapally et. al., Nature Communication, 2016

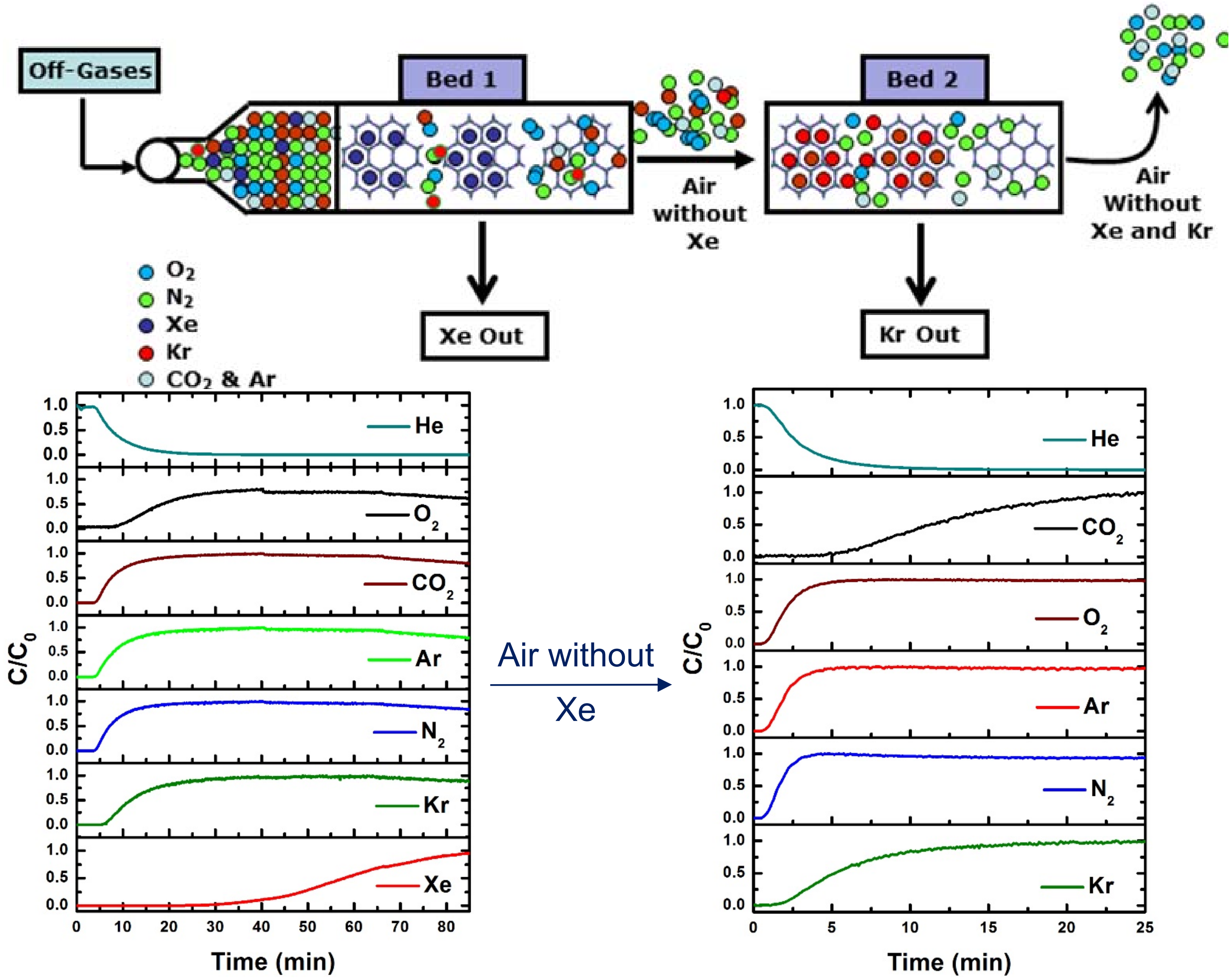
Single column breakthrough experiments with 40% RH

- Conditions
  - Air = 78% N_2, 21% O_2, 0.9% Ar, 0.03% CO_2, 400 ppm Xe, 40 ppm Kr with 40% RH
  - Flow rate = 20 cm^3/min
  - T = 25 °C (298K)
  - MOF = SBMOF-1

- Results
  - SBMOF-1 adsorbs Xenon preferentially over other gases
  - Xe capacity = 14 mmol/kg
  - >99% of the Xe captured from air
  - Xe/Kr (selectivity) = 15
  - Xe loading is unaffected by water (48% RH)



Two bed approach to capture Kr



Bed 1

Bed 2

Selectivity of CaDSB or SBMOF-1

$$\text{Breakthrough capacity (q in mmol/kg)} = \frac{Cvt}{MTg} \times 10^6$$

Flow rate

Partial pressure of the inlet gas

Gas constant

Selectivity of Gas A over B $$S_{AB} = \frac{x_A/y_A}{x_B/y_B}$$

x_A and x_B are the mole fractions of gases A and B in the adsorbed phase, and y_A and y_B are the mole fractions of gases A and B in the bulk phase,

Table 2. Co-adsorption of various gases calculated at the breakthrough point from a column containing CaSDB at room temperature. The capacity and selectivity were calculated from 20 ml/min data.

Gas	Breakthrough Time (min)	Capacity (mmol/kg)	Selectivity of Xe
Xe	18	16 (33.8)[a]	
Kr	1	0.11 (0.75)[a]	14
CO_2	5	1.2	3
N_2	0.08	47	209
Ar	0.08	5.28	210
O_2	0.08	12	206

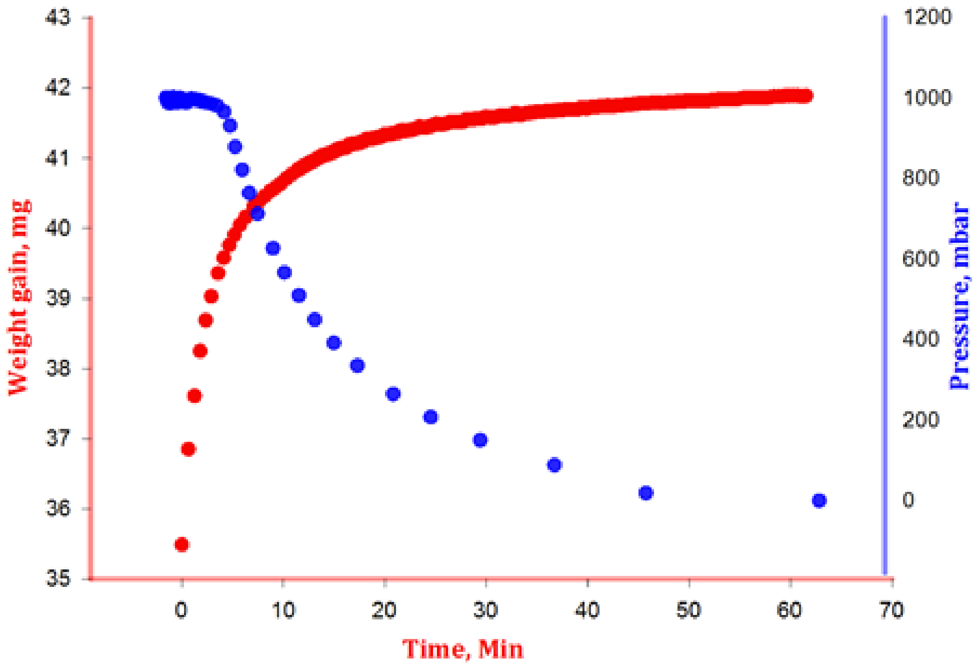
[a] Capacity at equilibrium

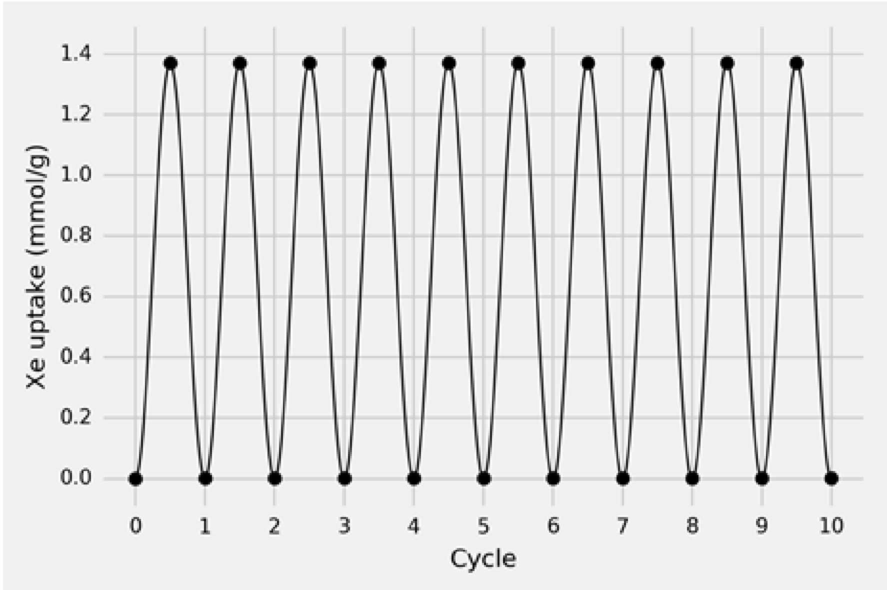
Table 4. Co-adsorption of various gases calculated at the breakthrough point from single column breakthrough experiments containing CaSDB at room temperature with a gas mixture consisting of 130 ppm Kr, 78.2% N_2, 21% O_2, 0.9 Ar, and 300 ppm CO_2 with a flow rate of 10 ml/min.

Gas	Breakthrough Time (min)	Capacity (mmol/kg)	Selectivity of Kr
Kr	2.5	0.13	
CO_2	7.5	0.90	0.3
N_2	0.25	80.8	9.9
Ar	0.25	9.09	9.3
O_2	0.25	21.2	9.3

Thallapally., DOE NE FCRD report 2016

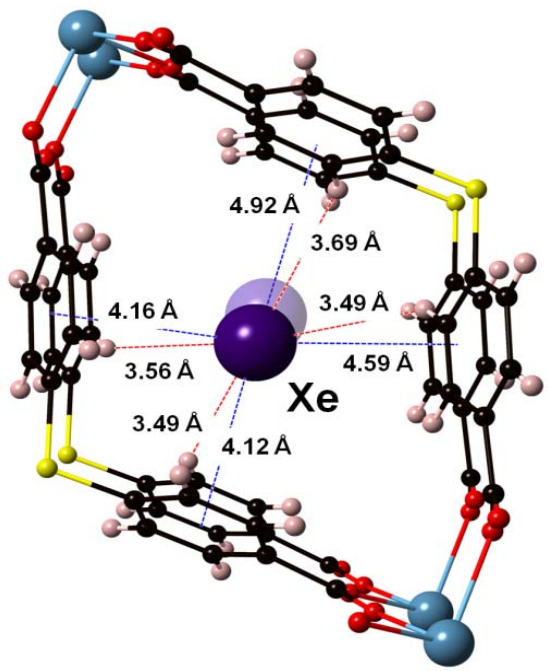
Kinetics and cycle experiments

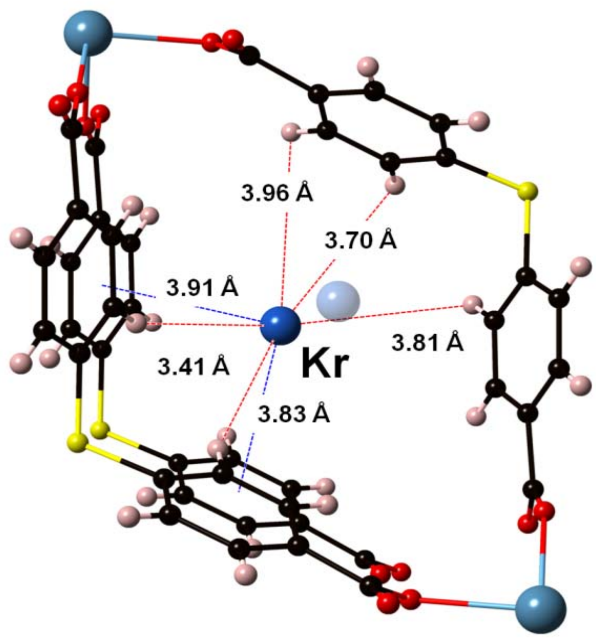




- Faster kinetics, 80% of Xe adsorbed within 10 minutes
- Cycling study indicate no loss of capacity even after 20 cycles.

Identifying Xe and Kr adsorption sites





- SBMOF-1 falls in the optimal pore size and shape for Xe/Kr separations, making it stand out among other MOFs.

Thallapally et. al., Nature Communication, 2016

CaSDB MOF vs other MOFs

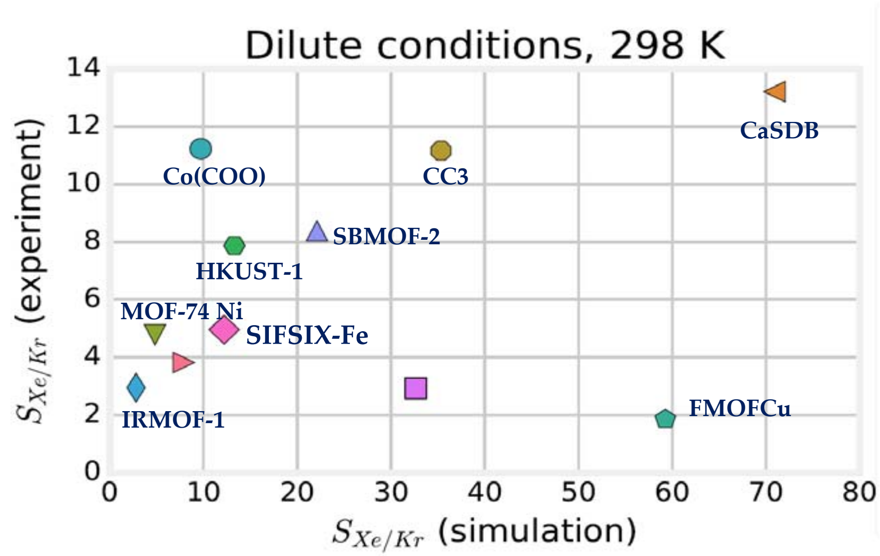
6/30/2016 Selective sorbent traps xenon and krypton | Chemical & Engineering News

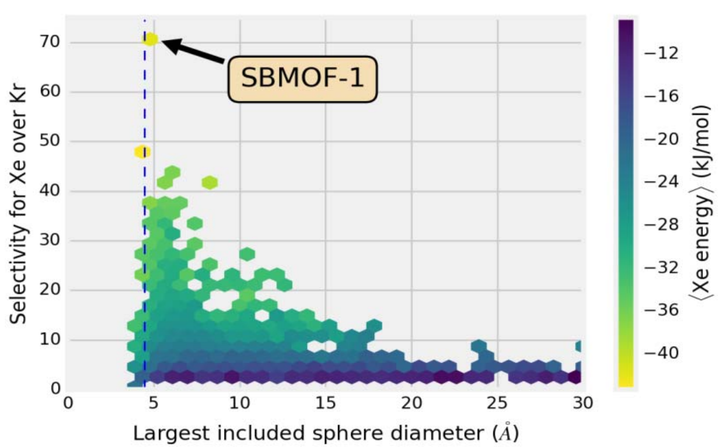
Volume 94 Issue 26 | p. 8 | Concentrates
Issue Date: June 27, 2016

Selective sorbent traps xenon and krypton

Porous material could be used to separate gases liberated during nuclear fuel reprocessing

By ***Mitch Jacoby***



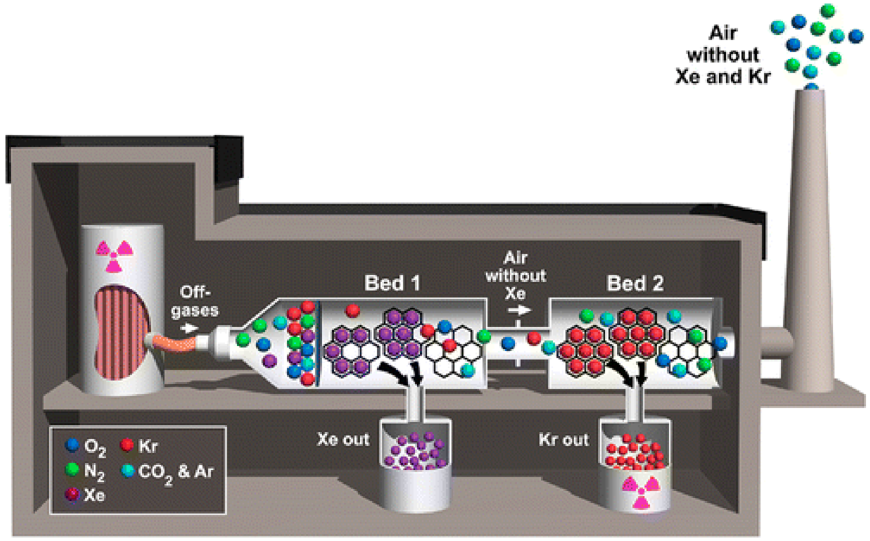


- ✓ SBMOF-1 is best among all other MOFs that PNNL tested at RT and nuclear re-processing condition.
- ✓ The capacity and selectivity, might be different at low temperature.

Thallapally et. al., Nature Communications, 2016

In conclusion

- The high capacity, selectivity and stability of MOFs allows for applications in
  - nuclear fuel reprocessing
  - pre-concentrators for sensors
- Structure – Property Relationship studies combining modeling, synthesis, testing allows for a feedback loop in the design, tuning and optimization of materials
- Preferential Xe/Kr sorption from Air
- Separation of Xe and Kr in two steps as oppose to multi column distillation
- Economic Analysis suggest: RT separation of Xe/Kr is more economical than cryo-separation.



Thallapally et. al., Nature Communications, 2016

Questions???

Upcoming Webinars

- Iodine-129 (gaseous fission products—capture and immobilization)
- Cesium
- C-14

NAMP website http://www.wipp.energy.gov/namp