SAND2017-XXXX

SAND2017-12289PE

Light Gas Separations and Storage with MOFs; Tying the nanoscale science to bulk scale energy and environment applications

Tina M. Nenoff, Leo J. Small,
Dorina Sava Gallis, Jeffrey Greathouse, Marie Parkes,
Karena W. Chapman*

*Chemical, Physical, Nano Sciences Center
Sandia National Laboratories
Albuquerque, NM USA

*Advanced Photon Source
Argonne National Laboratory
Argonne, IL USA

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Outline

Introduction to Nenoff Group Research

Materials of Interest

Activated Charcoals/Carbons, Zeolites, MOFs, layered/clays

Oxygen Separations Materials, Design by High Performance Computing to Real-World Testing

Direct Electrical Readout Sensors, Development and Testing

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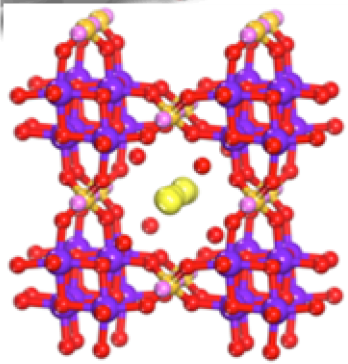
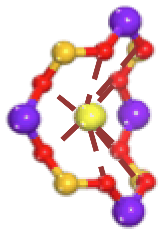
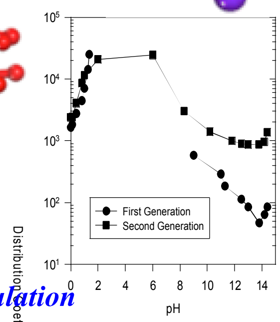
Example 1: Nanoporous Materials (Zeolites, Molecular Sieves & MOFs), Radiological Ion and Gas Capture

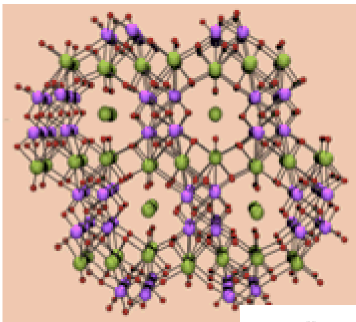




CST, Molecular Sieve:
R&D100 1996
JACerS, 2009, *92(9)*, 2144
JACerS, 2011, *94(9)*, 3053
Solvent Extr. & Ion Exch, 2012, *30*, 33

CST, Cs^+ removal from water to Pollucite Waste Form
US Patents *6,479,427; 6,110,378*



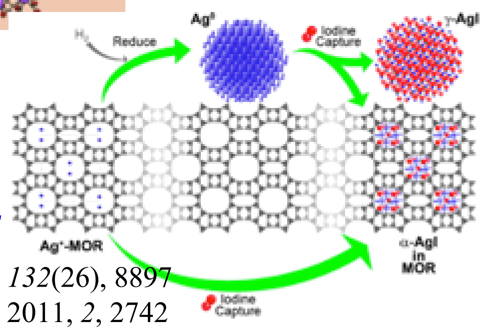


SOMS Molecular Sieve,
Sr^{2+} getter,
1-step to Perovksite WF
JACS, 2002,*124(3)*, 1704
US Patent *7,122,164;* 2006

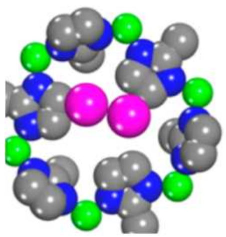
I_2/ZIF-8 MOF, *Encapsulation to Waste Form*
JACS, 2011,*133(32)*,12398
JACS 2013, *135*, 16256

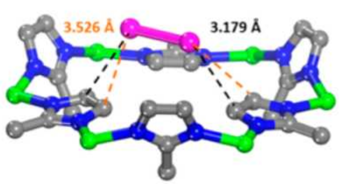
Fundamental Research to Applied to Commercial Products
Design the Separation Material To Develop the Waste Form

Ag-MOR Zeolite,
$I_2(g)$ capture & mechanisms

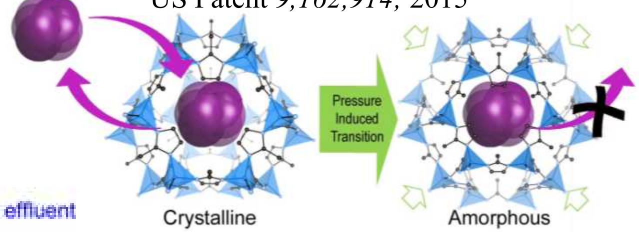


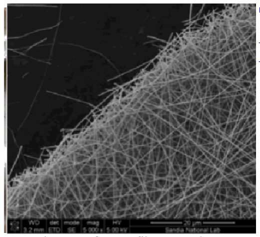
JACS, 2010, *132*(26), 8897
JPC Letters, 2011, *2*, 2742



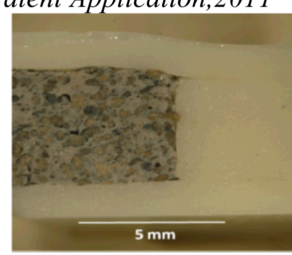


MOF *Amorphization for Gas Storage*
JACS, 2011,*133*(46),18583
US Patent *9,162,914;* 2015

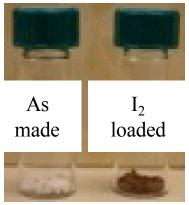




TiO_2 Nanoporous Nanofibers
Volatile Gas Removal
US Patent Application,2011



MOF Cu-BTC*:*
I_2 from Humid Gas Stream
Chem. Mater. 2013, *25*(13), 2591



Binder Free **MOF** *Pelletization*
US Patent Pending 2014

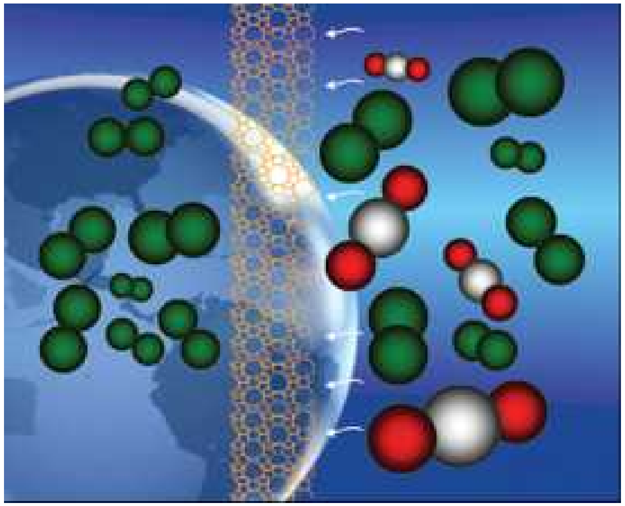
Glass Composite Materials:
Universal Core-Shell Iodine Glass Waste Form & Getter
JACerS, 2011, *94*(8), 2412
US Patent *8,262,950*; 2012

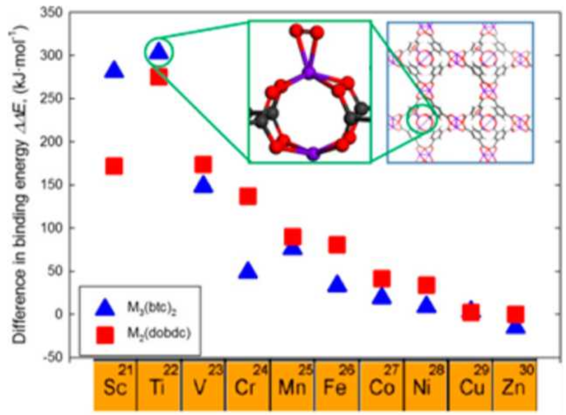
Example 2: Zeolite/MOF Membranes for Light Gas & Hydrocarbon Separations

H_2 Purification

Nature Mater., **2015**, *7*, 377; *Chem. Rev.* **2007**, *107*, 4078

MRS Bulletin, **2006**, 31(10), 735 (cover; Editor Nenoff)





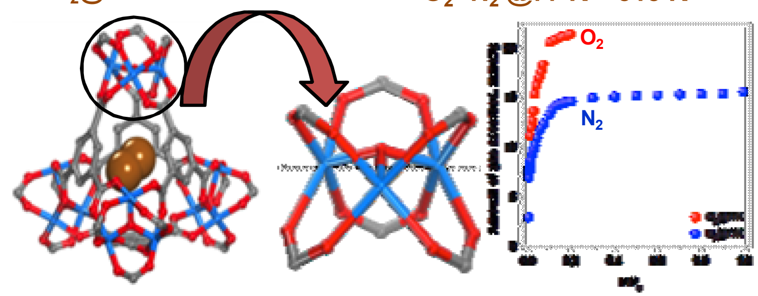
O_2 Separations with MOFs for Energy Efficient Oxyfuel Combustion

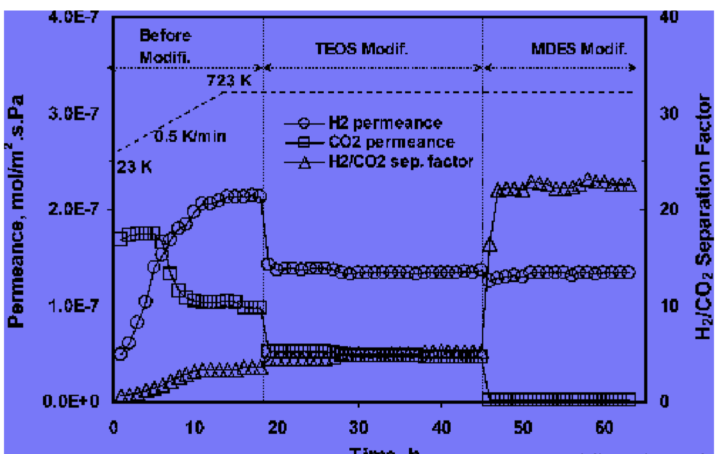
Chem. Mater. **2016**, 28(10), 3327-3336

Chemical Science **2016**, *18*, 11528

J. Phys. Chem. C, **2015**, *119*, 6556

Chem. Mater. **2015**, *27*(6), 2018



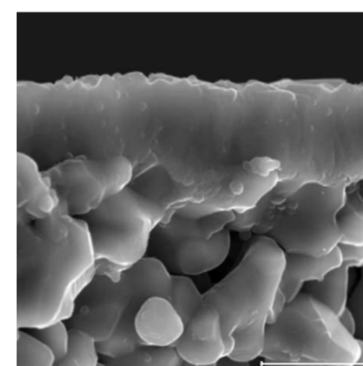


H_2 Purification from Syngas

Langmuir, **2009**, *25*(9), 4848

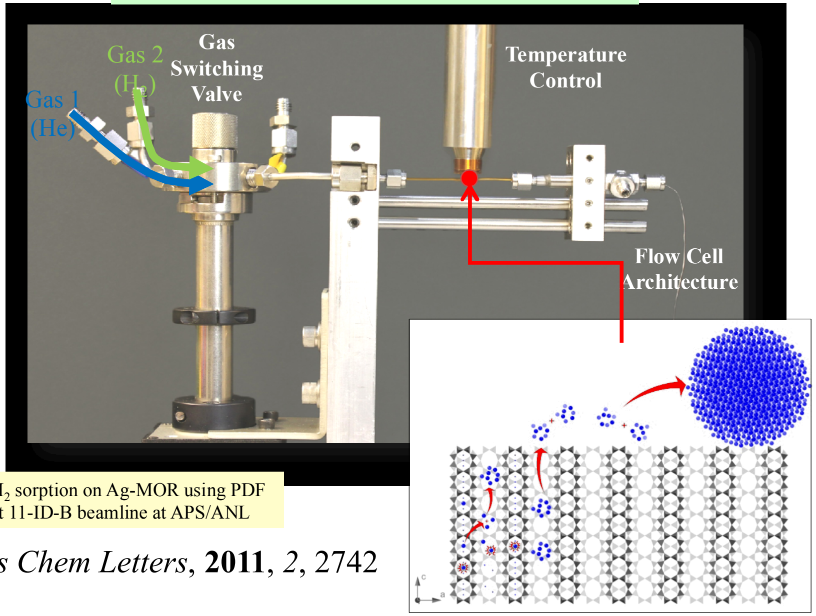
ZSM-5 Zeolite membrane for H_2 from CO_2 separations

Micro Meso Mater, **2003**, *66*, 181



Example 3: Nanoparticle Formation for Heterogenous Catalysis, Gas Capture

Determine Mechanism of Ag^+ to Ag° NPs in MOR

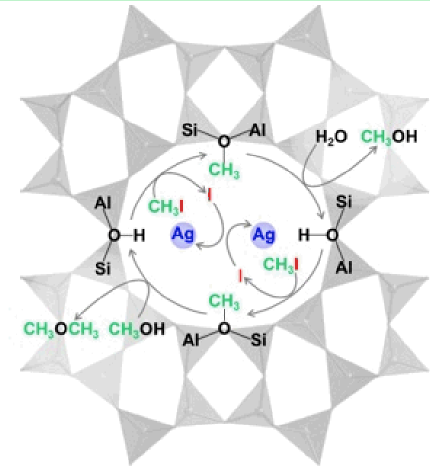


In situ I_2 sorption on Ag-MOR using PDF setup at 11-ID-B beamline at APS/ANL

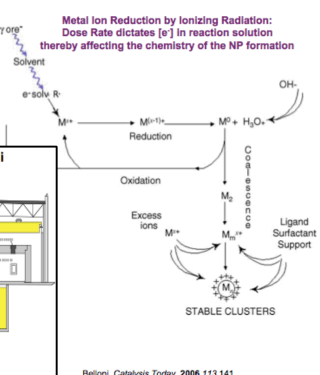
J Phys Chem Letters, **2011**, *2*, 2742

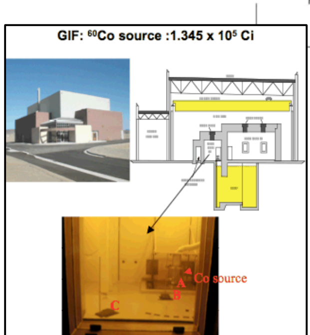
Mechanism of Iodine Capture on Ag-MOR from Acidic Humid CH_3-I Stream: Catalytic Cleaving of CH_3-I and I Capture

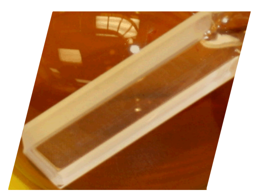
Micro. Meso. Mater., **2014**, *200*, 297 (invited)

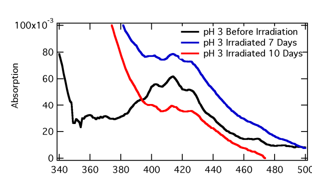


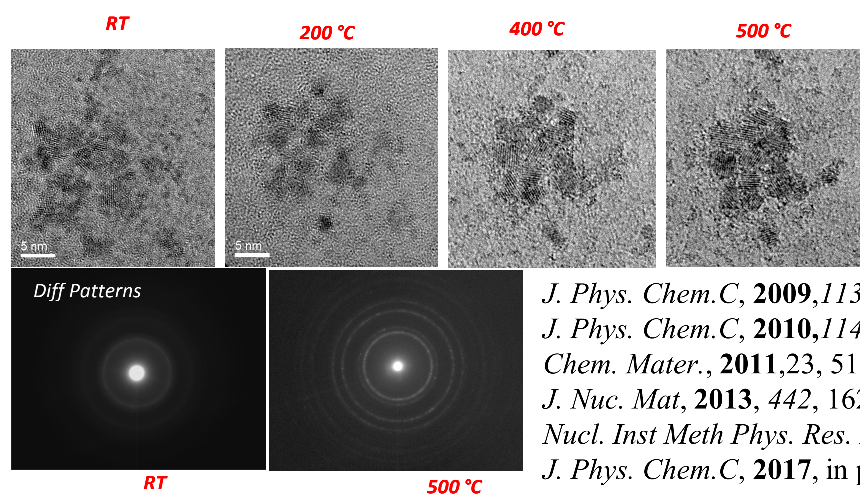
γ-irradiation NP formation and growth via sintering





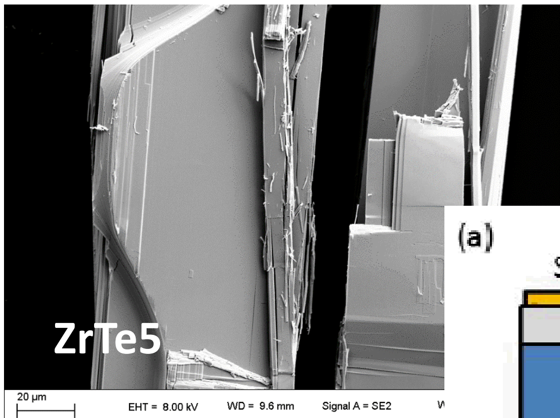




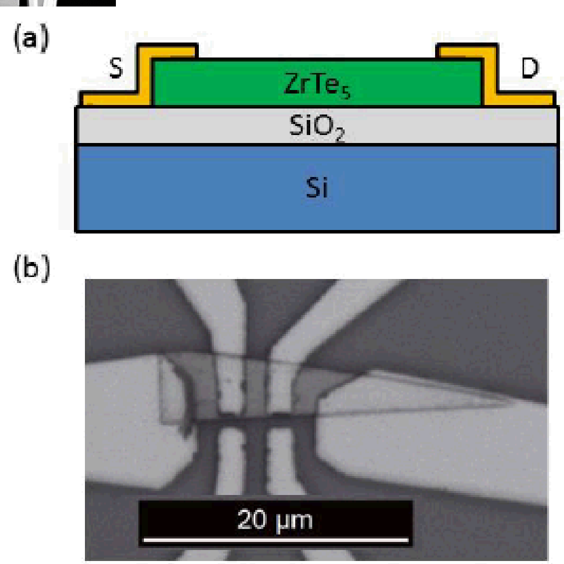


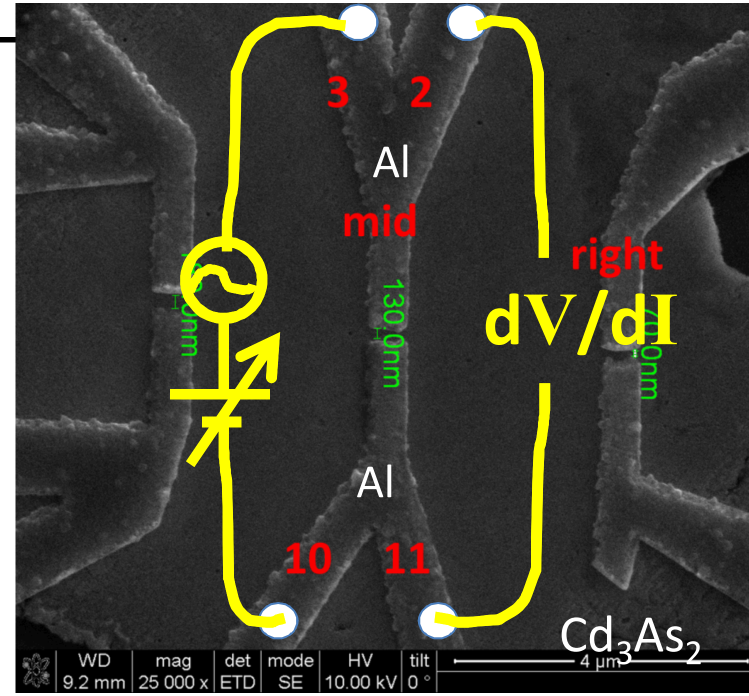
J. Phys. Chem.C, **2009**,*113*, 1155
J. Phys. Chem.C, **2010**,*114,* 14309
Chem. Mater., **2011**,23, 5185
J. Nuc. Mat, **2013**, *442*, 162
Nucl. Inst Meth Phys. Res. B; 2017
J. Phys. Chem.C, **2017**, in prep.

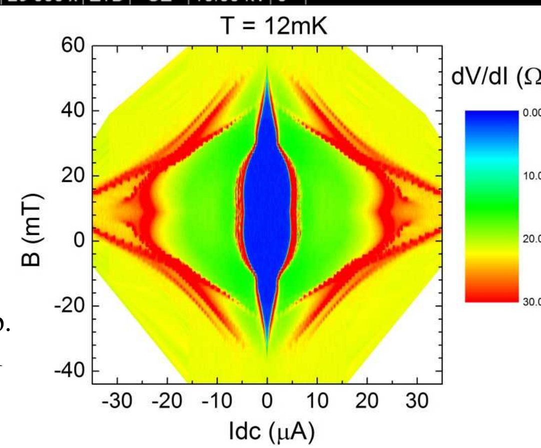
Example 4: Topological Quantum Materials

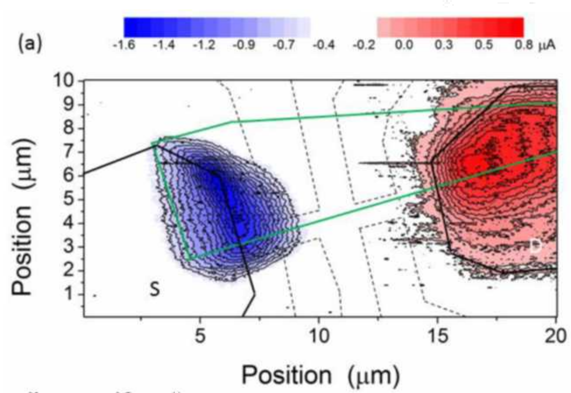


The Search for Majorana Fermion









Chem. Mater., **2017**, invited review, in prep.
ACS Appl. Mater. Interfaces 2017, 9, 37041

Superconducting Al (low temp) with the Cs_3As_2 (TQM) enables the p-wave superconductor, requirement for creating Majorana fermions

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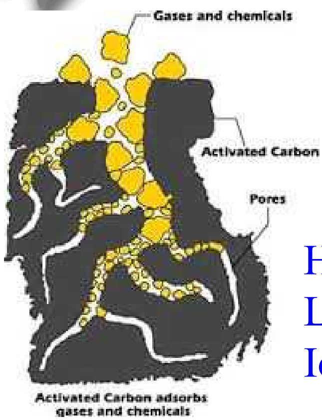
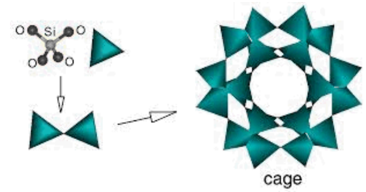
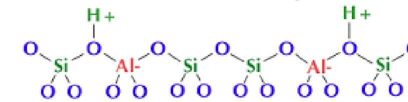
Nanoporous Adsorption Materials

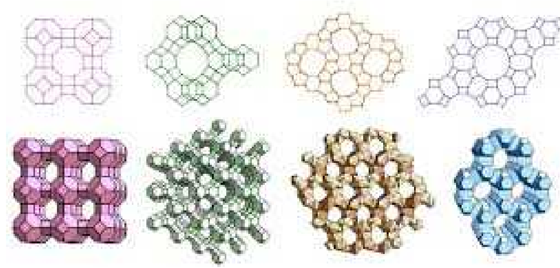


Higher sorption capacity
Lower Selectivity
Iodine background

Activated Carbon/Charcoal > 500 m^2/g





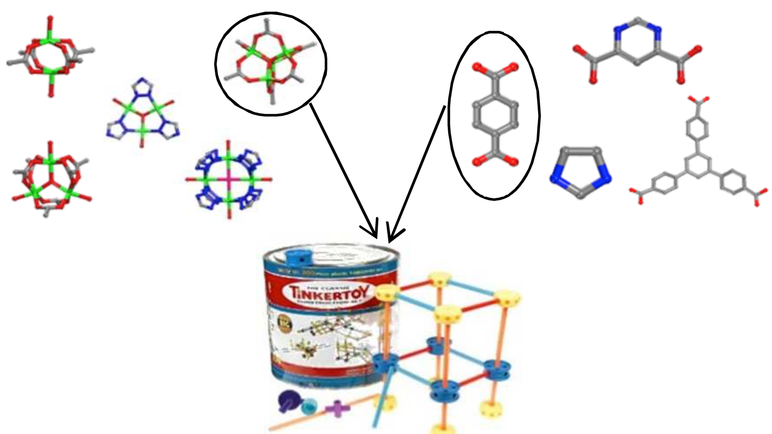


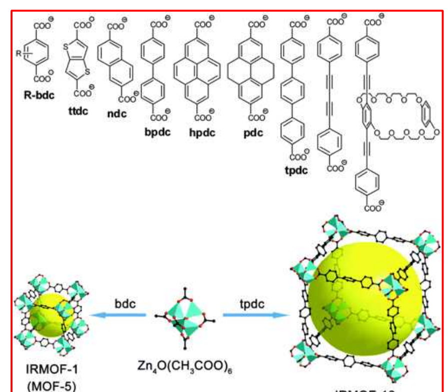
Lower Sorption Capacity
Selectivity (?)

Ag-MOR:
I_2, ^3H, Kr/Xe

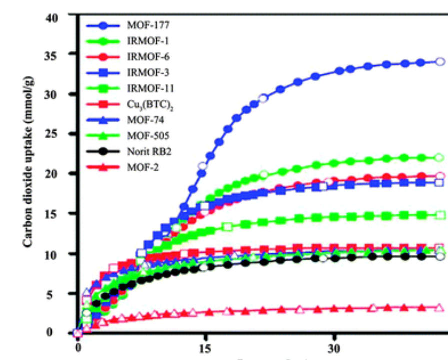
Zeolite~100 m^2/g

Metal-Organic Frameworks (MOFs) >1000m^2/g





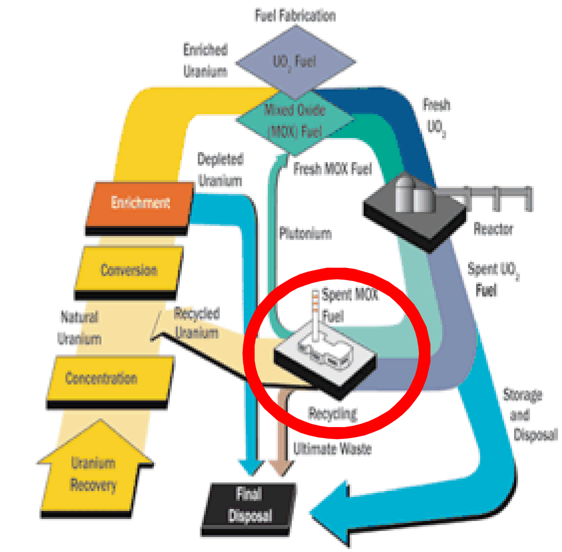
Target: Extremely
High Selectivity
High Capacity



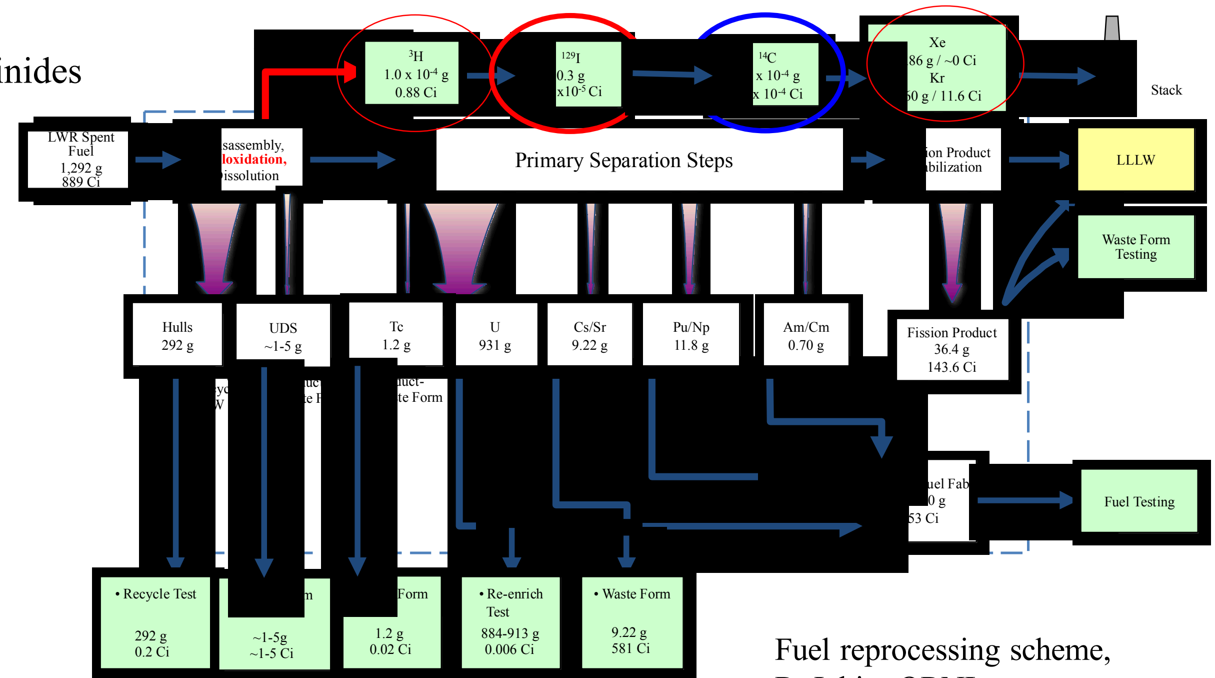
Yaghi, JACS, 2005,127, 17998

Application: Environmental Rad Waste Capture

Reprocessing: capture on nonburnable volatile fission products and lesser actinides



Source: U.S. Nuclear Regulatory Commission

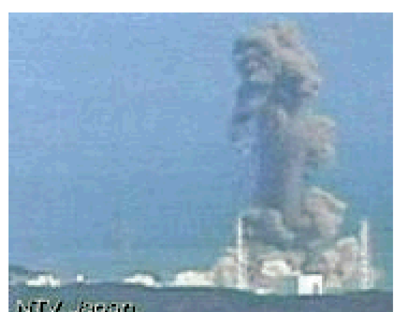


Fuel reprocessing scheme, R. Jubin, ORNL, FCRD-SWF-2011-000306

Legacy, Accident or Produced rad aqueous waste requiring highly specific ion capture

Fukashima Daiichi Nuclear Power Plant explosion 2011 I^{129}, I^{131} volatile gas released; Cs^{135}, Cs^{137} & Sr^{90} aqueous released

(www.IAEA.org)



Ag-MOR zeolite, Traditional Iodine Capture Material

- While I^{129} is only found in small concentrations in nuclear effluent, the effective capture and storage of iodine is critically important to public safety due to its involvement in human metabolic processes and its long half-life (~10^7 years).

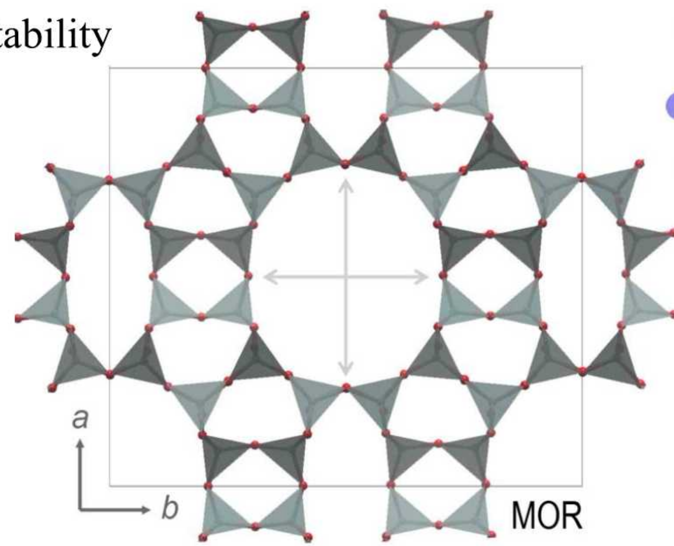
- Silver Mordenite (MOR) is a standard iodine-getter, although the iodine binding mechanism remains poorly defined. Presumably an iodide forms within the zeolite's pores

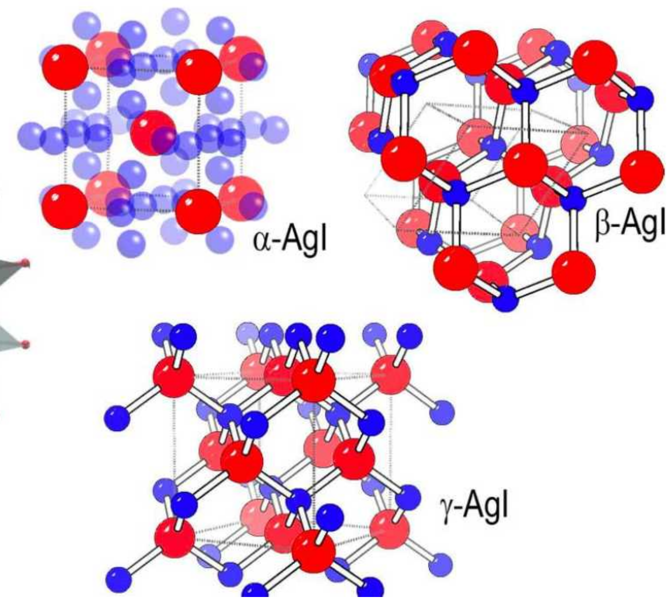
- Understanding **Structure-Property Relationship between Nanoscale and Bulk effects**
  - To optimize capture
  - Impacts processing for long term storage
  - To predict long term stability

MOR, Mordenite

$X_2Al_2Si_{10}O_{24} \cdot 7(H_2O)$

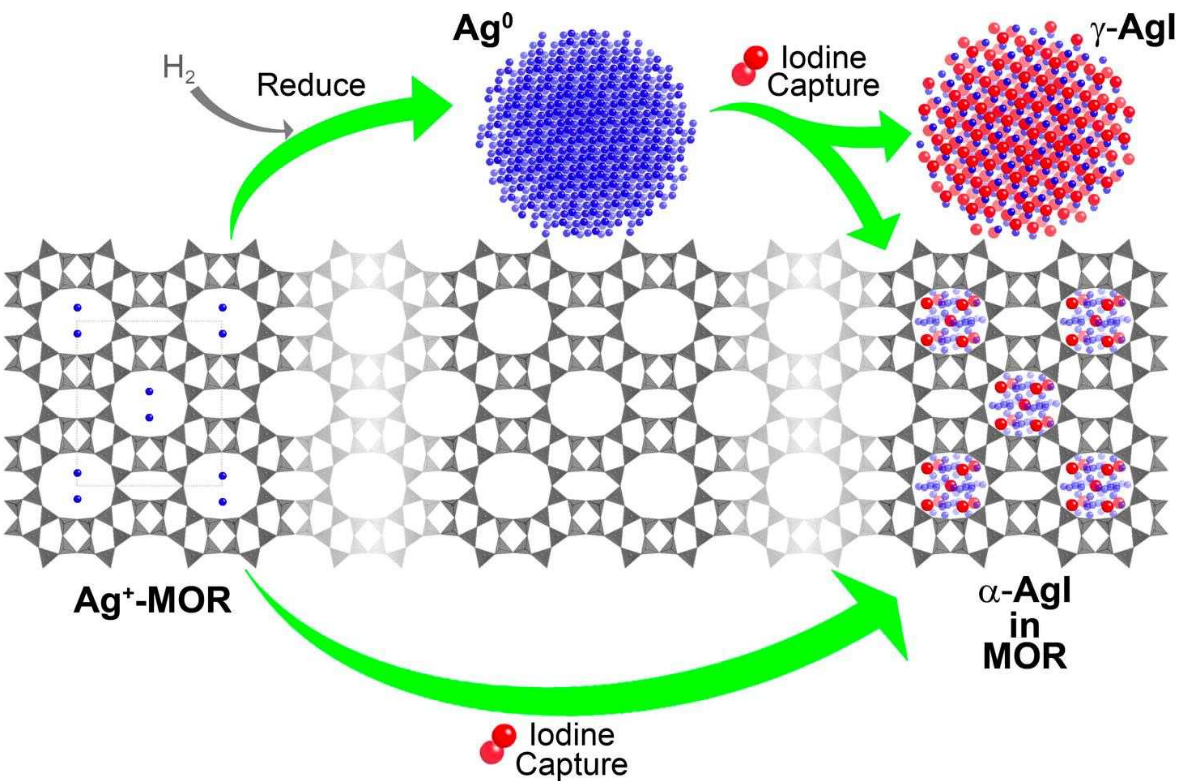
12 MR, 7.0 x 6.5Å





Mechanism Determined: State of the Ag determines I capture

Ag°-MOR + I_2 yields a mixture of γ-AgI bulk surface nanoparticles and sub-nanometer α-AgI.
Ag^+-MOR + I_2 produces exclusively sub-nanometer α-AgI ("**perfect fit**", confined in pores)



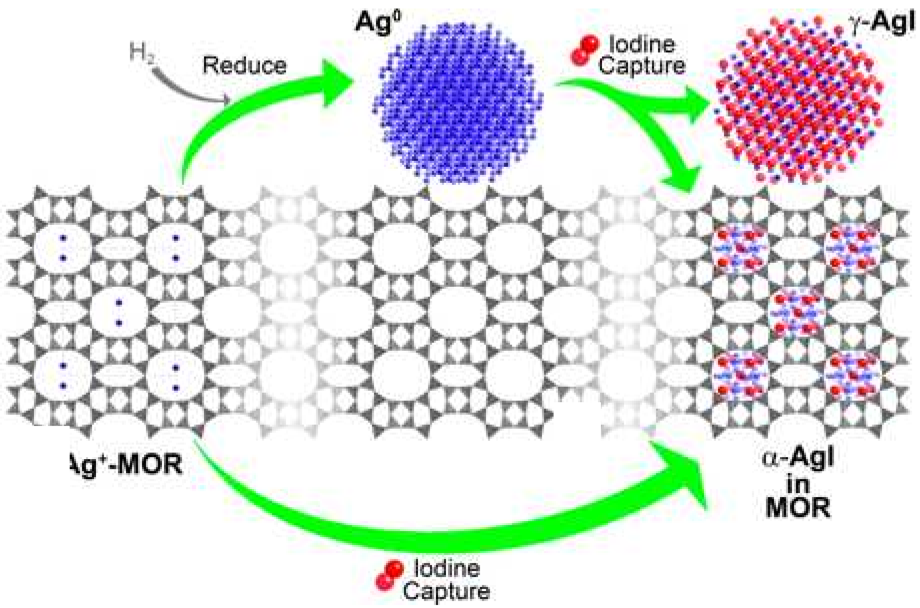
JACS, **2010**, *132* (26), 8897

Issue associated with Zeolites do include the ***need for Ag*** *and the difficulty of working with zeolites that* ***selectively adsorb I_2 and Org-I,*** *but* ***not ^3H_2O, and Xe***

AgI nanoparticle formation in MOR (from Ag^+-MOR + iodine species)

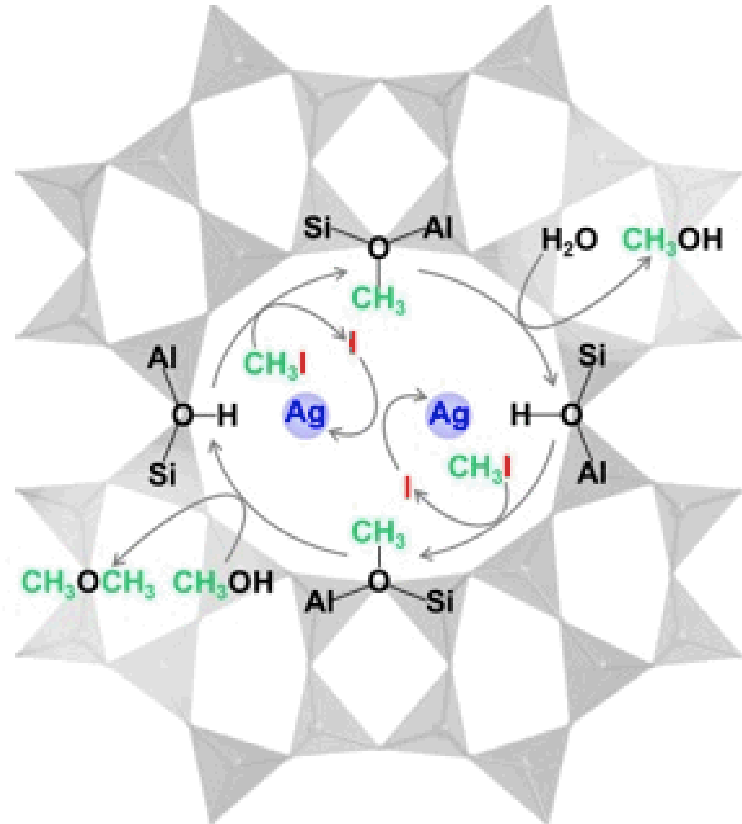
JACS, **2010**, *132*(26), 8897

Ag-MOR + I_2



MMM, **2014**, *200*, 297

Ag-MOR + CH_3-I

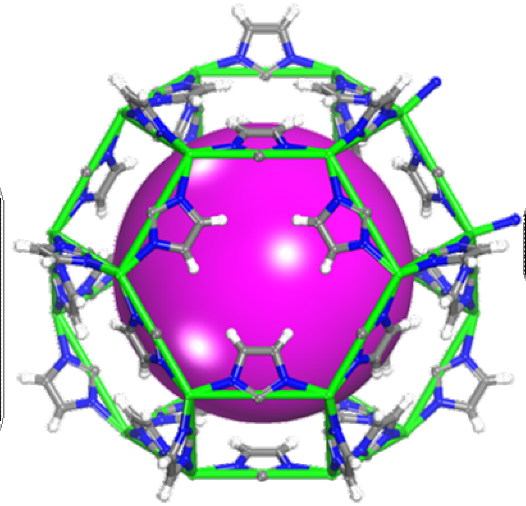


Mechanism of AgI formation & phase determination

Metal Organic Frameworks (MOFs) for fission gas adsorption: iodine (I_2)

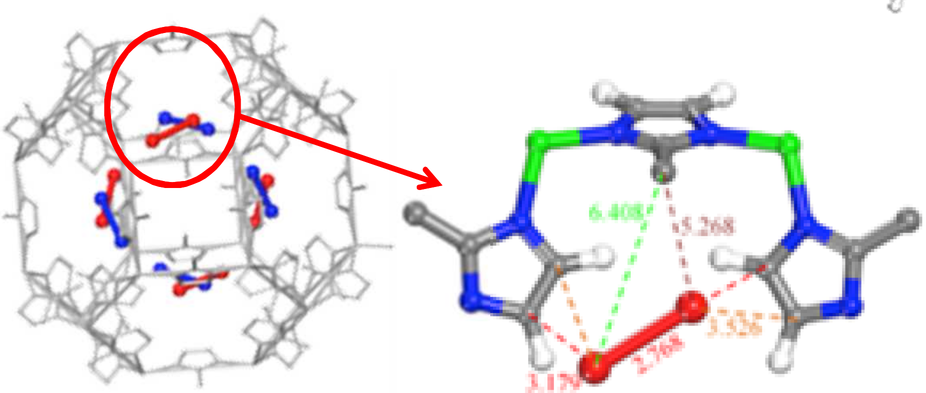
Traditionally zeolites/molecular sieves are used as baseline materials for selectivity and sorption. Cutting edge materials are tuned for high selectivity and high capacity.

Basolite Z1200, ZIF-8
Constricted Pore Opening (≈ 3.4Å)
1100 – 1600 m^2/g
Pore Volume = 0.636 cc/g
stable in Air & H_2O

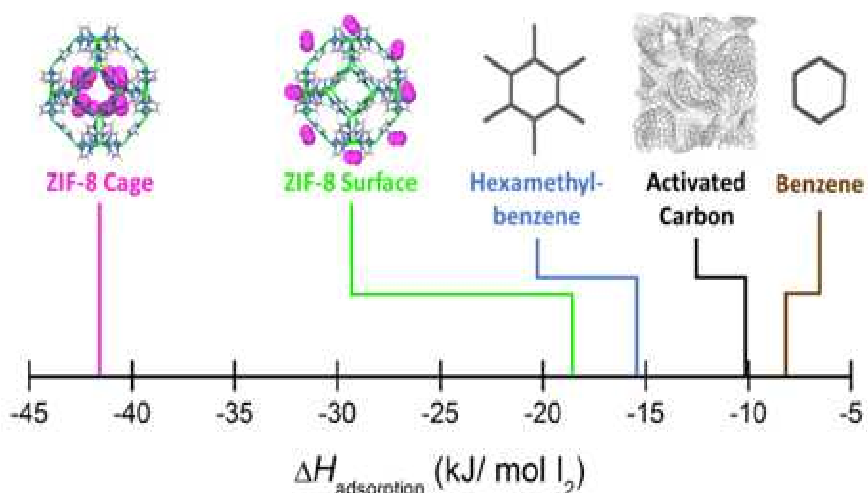


I_2@ZIF-8 ~ 125 wt.% I_2

JACS, **2011**, *133*(32), 12398



I_2 is selectively captured by ZIF-8 due to:
- *Size selectivity*
- *Iodine bound to organic ligand*

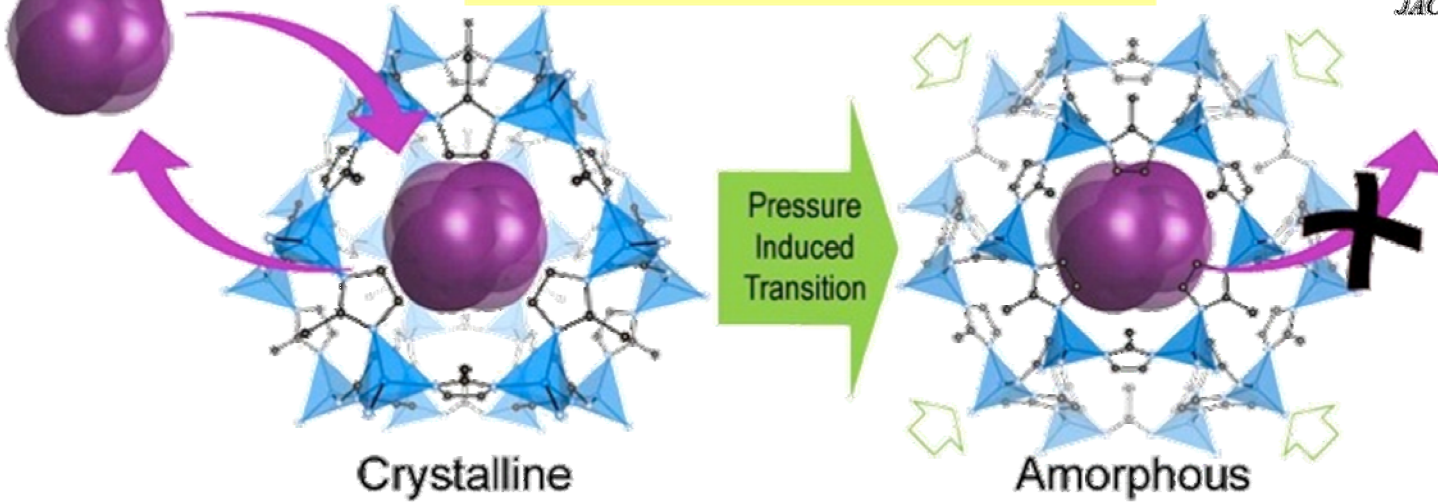


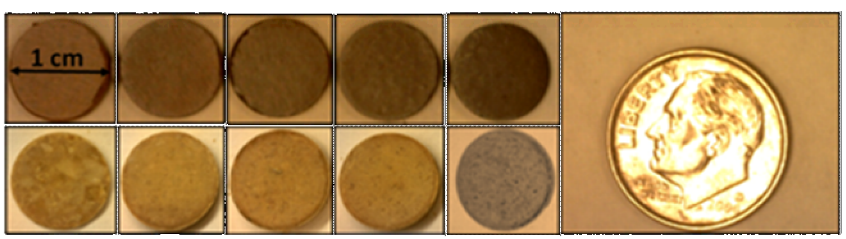
JACS, **2013**

I_2@ZIF-8 Pressure-Induced Amorphization of Trapped Gases: Enhanced Retention

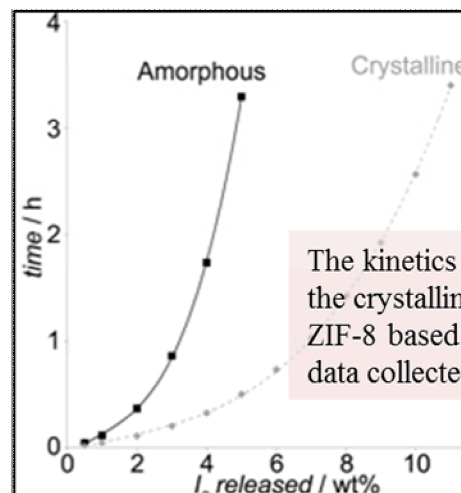
Secure consolidated interim storage before incorporation into a long term waste form.

Chapman, Nenoff, et.al., *JACS* **2011**, *133*(46), 18583.





Crack free pellets of iodine loaded ZIF-8 powders were obtained by applying uniaxial mechanical pressure.

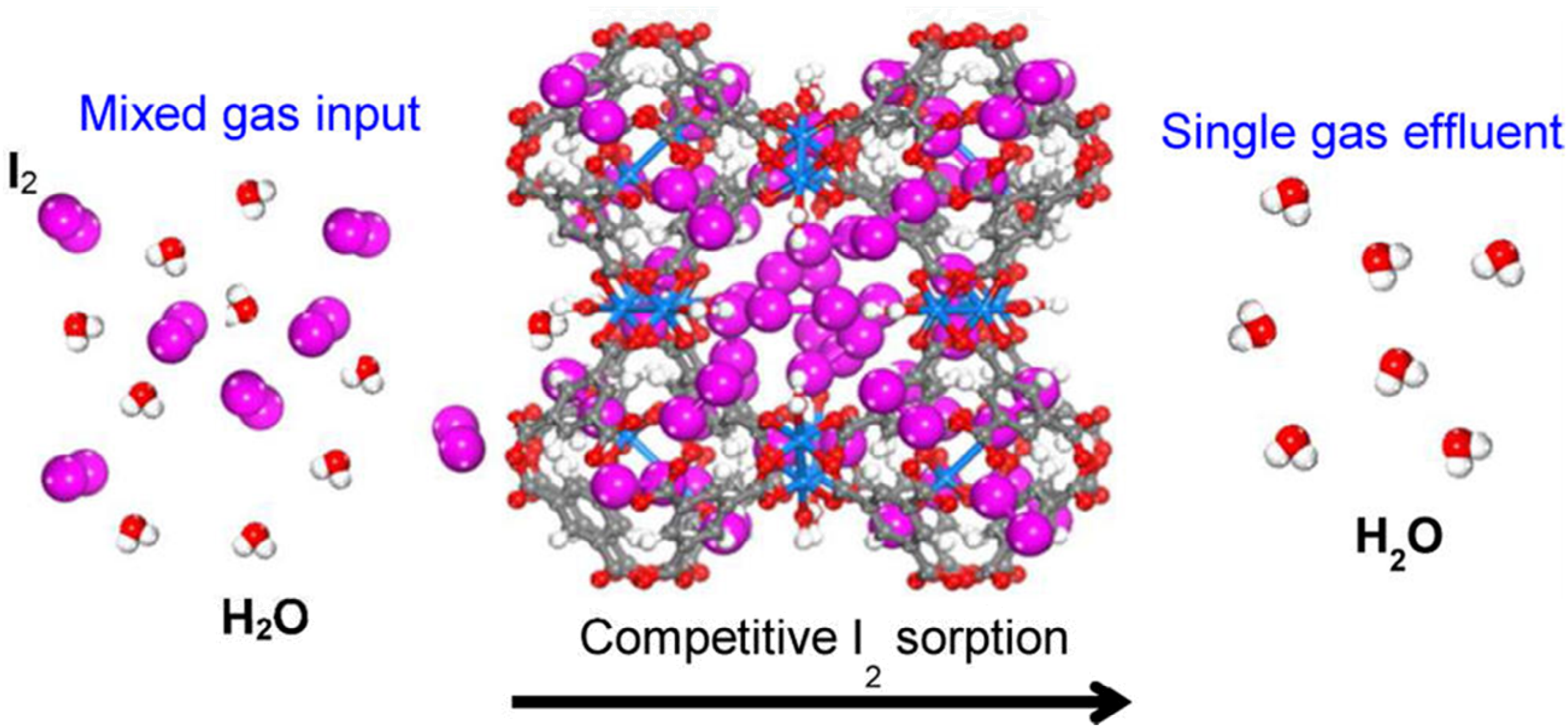


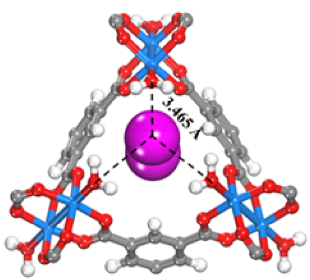
The kinetics of I_2 release from the crystalline and amorphized ZIF-8 based on isothermal TGA data collected at 200°C, 4hours

Crystal Structure of I_2@HKUST-1, selectivity of I_2 over H_2O

I_2/HKUST-1 **3.3 I/Cu**

Sava Gallis, Nenoff, et.al., *Chem. Mater.*, **2013**, *25* (13), 2591





Iodine – Metal center (Cu) strongly bound
High Selectivity!
Trumps hydrophilicity of MOF

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↓

Oxygen Separations Materials, Design by High Performance Computing to Real-World Testing

Direct Electrical Readout Sensors, Development and Testing

Tunable Impedance Spectroscopy Sensors via Selective Nanoporous Materials

The ability to sense and identify *individual gases* from the complexity of the environment requires highly selective materials.

- Current conductivity-based devices generally fall into two categories:,
  - Solid state - (oxide based) require higher temperatures (>200°C) for interaction of the gas with the surface oxides; heating devices are needed.
  - Fuel cell – room temperature liquid electrolyte, easily fouled, short lifetime

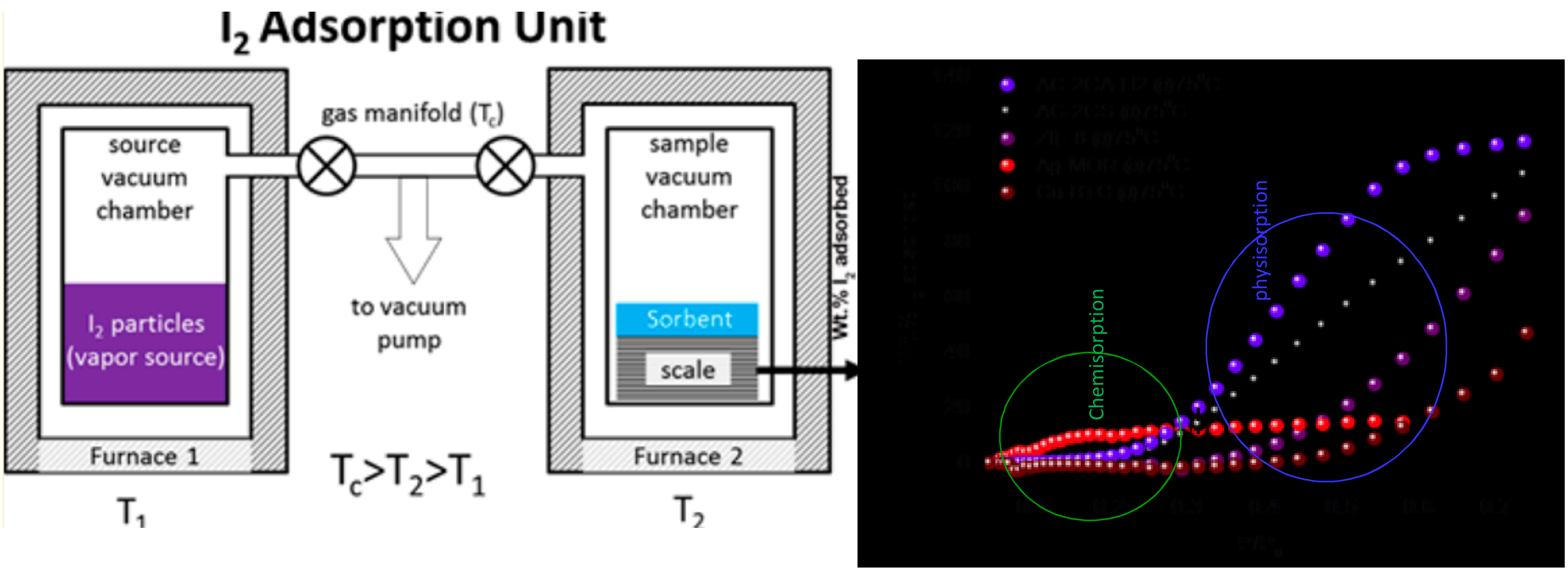
- Utilization of *nanoporous metal organic frameworks (MOFs;* exceptionally high selectivity of gases of interest (eg., I_2) under ambient conditions) with *impedance spectroscopy* allows for novel sensing technologies

Sensors, **2009**, *9*, 1574

Comparison studies of I_2 adsorption on Various Nanoporous Materials

Using a combination of Modeling (GCMC) and Iodine (I_2) Adsorption Studies to compare various nanoporous phases for iodine adsorption

MOFs, Zeolites/Molecular Sieves, Activated Carbons/Charcoals:



P/P$_o$ <0.3: I_2 adsorption occurs in **small pores** & **strong chemisorption interactions** with framework or extra framework

Ind. Eng. Chem. Res., **2017**, 56(8), 2331

Iodine Sensors with High Selectivity in Environmental Conditions

Impedance spectroscopy,
polarizable molecules increase the capacitance and thereby decrease the impedance.

The selectivity of MOFs for I_2 under mild conditions paired with the **polarizability of the I_2** molecules, enables real-time electrical sensing (direct electrical readout) via impedance spectroscopy.
Common air component gas molecules such as Ar, O_2 and N_2 are not/not-highly polarizable molecules

Modular platform:
able to test MOFs of different configurations, metal centers and charge transfer capabilities

Real-Time sensing by impedance spectroscopy (IS):

All measurements to date are simple single sine measurements.
The electrical test equipment generates a single sine voltage wave at a given frequency,
& measures the returned current in terms of its:
- **magnitude** (this relates to the impedance, |Z| on the plots) and
- **phase angle** compared to the original voltage wave

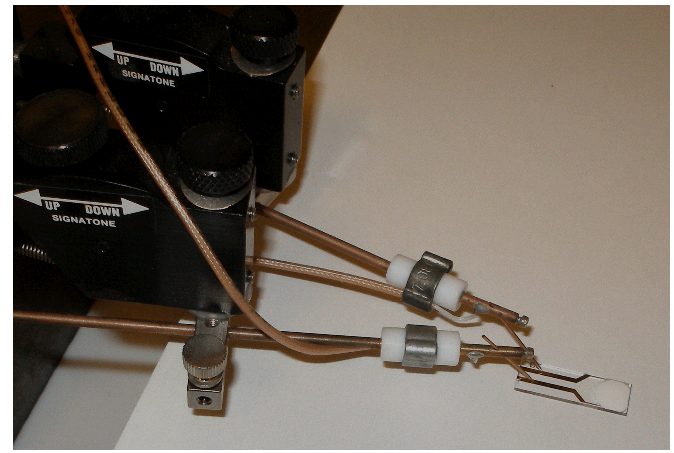
In fast fourier transform (FFT), a voltage pulse is sent out.
The pulse is the FFT of 20+ frequencies.
The measurement time is limited by the lowest frequency.
High Efficient Method: can collect ~ 20 data points in nearly the same time as the 1 lowest frequency data point.

This is all contained in commercial equipment and software.

Iodine Sensors with High Selectivity in Environmental Conditions

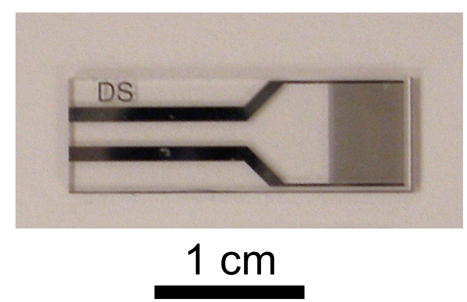
Solartron 1296 dielectric interface in series with a Solartron 1260 frequency response analyzer.
All sensor testing in a faraday cage to minimize electrical noise.

Samples are contacted with tungsten probes.



The dielectric interface allows us to **measure impedances as large as 10^{14} Ohms and frequencies 1 mHz – 1 MHz**.
Unique SNL specific: specialized high impedance, low frequency test equipment
(Common electrical test equipment has a lower input impedance than these coatings)

- Inter Digitated Electrodes (IDE's):
  10 µm wide platinum lines (125 pairs), 10 µm spacing on glass substrate
- MOF film: MOF + binder
- Film: screen printed onto platinum interdigitated electrodes
- Iodine adsorption studies: in air and humidity at 25, 40, 70 ˚C
- Test response over a broad electrical frequency response (1 MHz – 1 mHz)

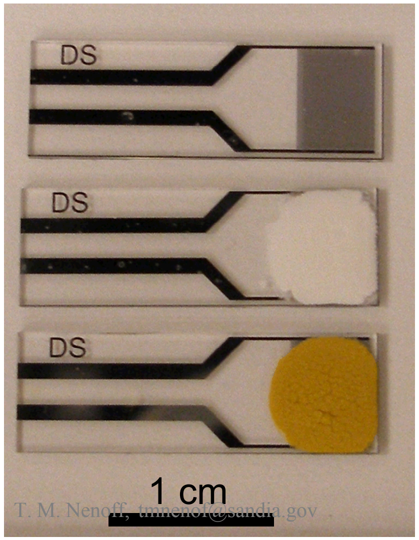


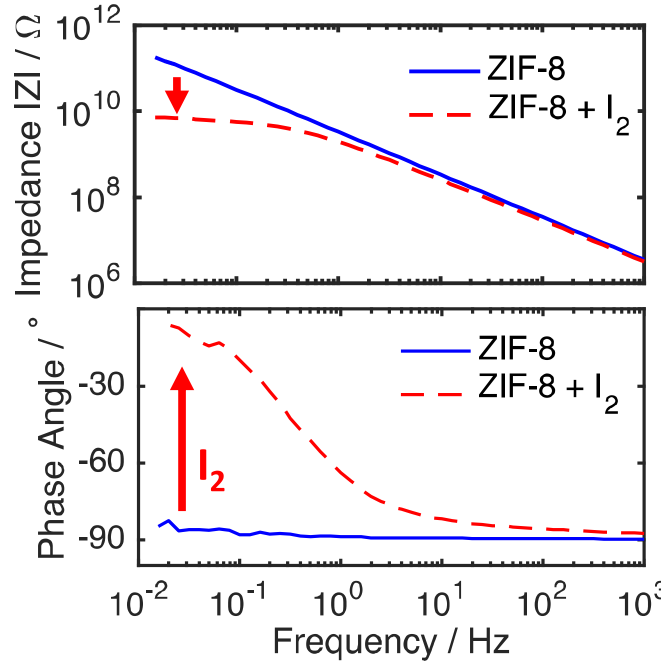
Iodine (I_2) Sensor with ZIF-8

as-received

ZIF-8

ZIF-8 + I_2 70 °C





>1 order magnitude decrease in impedance 70 °C, 30 min I_2 exposure

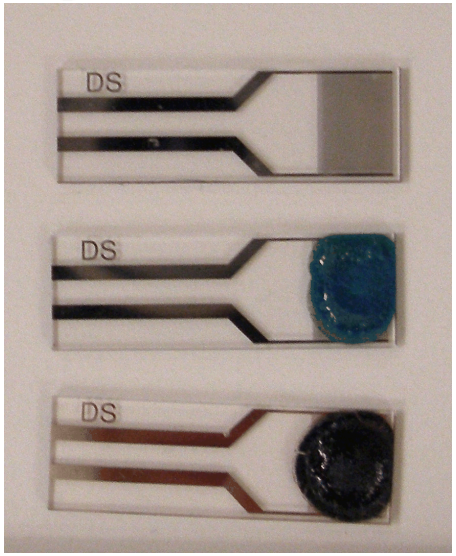
Sensor changes from ideal capacitor to nearly ideal resistor at low frequency after I_2 sorption.

Loading Temperature (˚C)	"Empty MOF" Device impedance (GΩ)	"I_2-Loaded MOF" Device impedance (GΩ)	% Change
Room temp.	171	121	-29%
40	182	20.7	-89%
70	182	7.22	-96%

|Z| recorded at 15 mHz. 10 mV AC. 0 V DC.

Small & Nenoff, **2017**, submitted.

Iodine (I_2) Sensor with HKUST-1

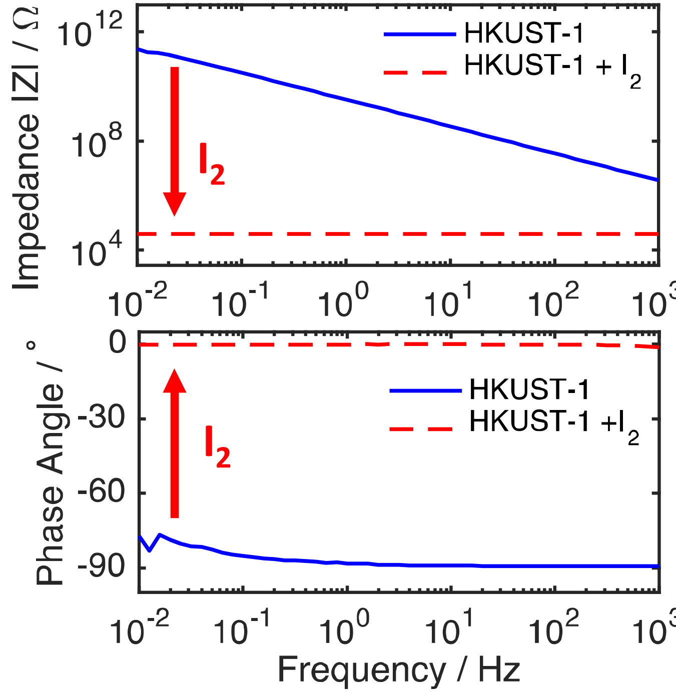


as-received

HKUST-1 + I_2 40 °C

HKUST-1 + I_2 70 °C

1 cm



>6 order magnitude decrease in impedance 70 °C, 30 min I_2 exposure

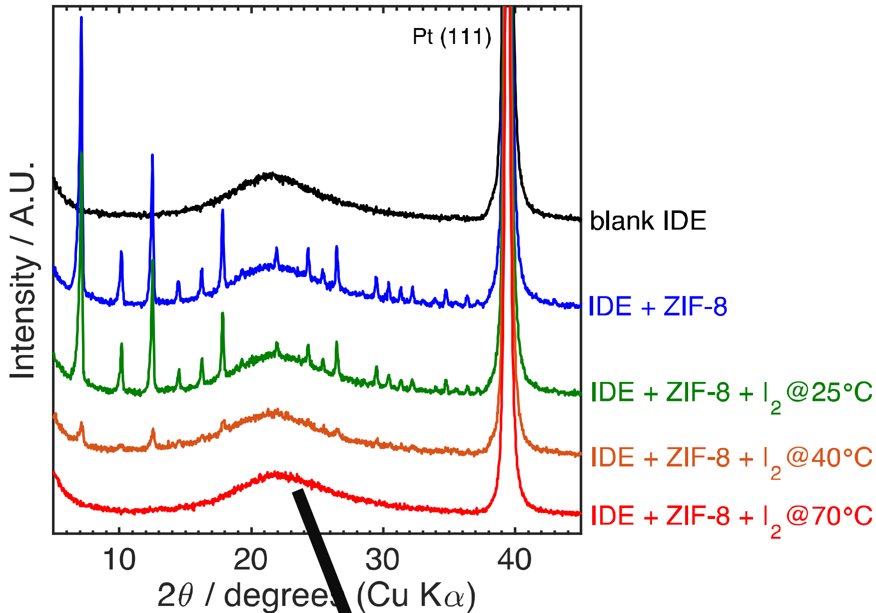
Sensor changes from ideal capacitor to ideal resistor after I_2 sorption.

Loading Temperature (˚C)	"Empty MOF" Device impedance (GΩ)	"I_2-Loaded MOF" Device impedance (GΩ)	% Change
Room temp.	105	21	-80%
40	106	4.73	-96%
70	99.0	38.8 **kΩ**	-100%

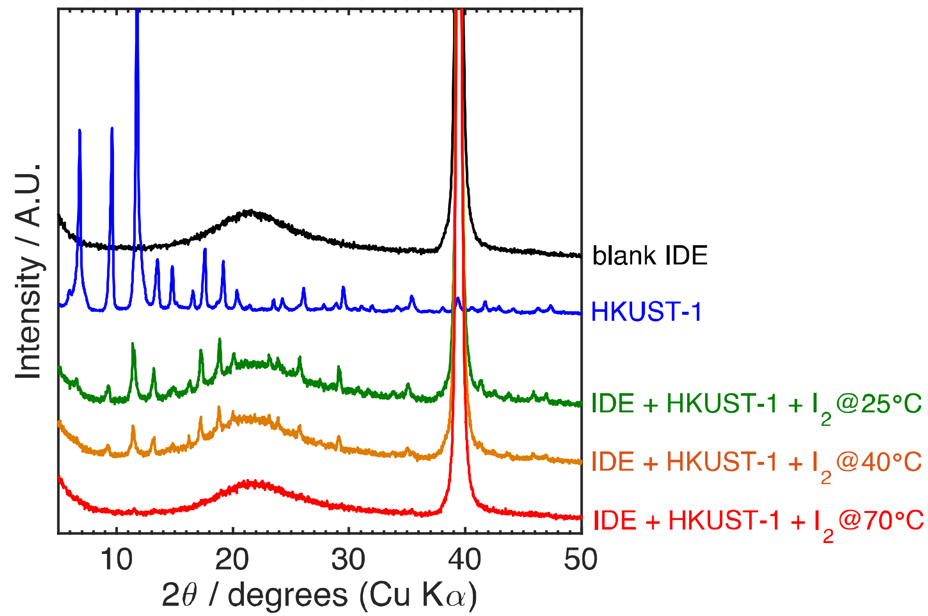
|Z| recorded at 15 mHz. 10 mV AC. 0 V DC.

MOF/Sensor Temperature Dependence

ZIF-8

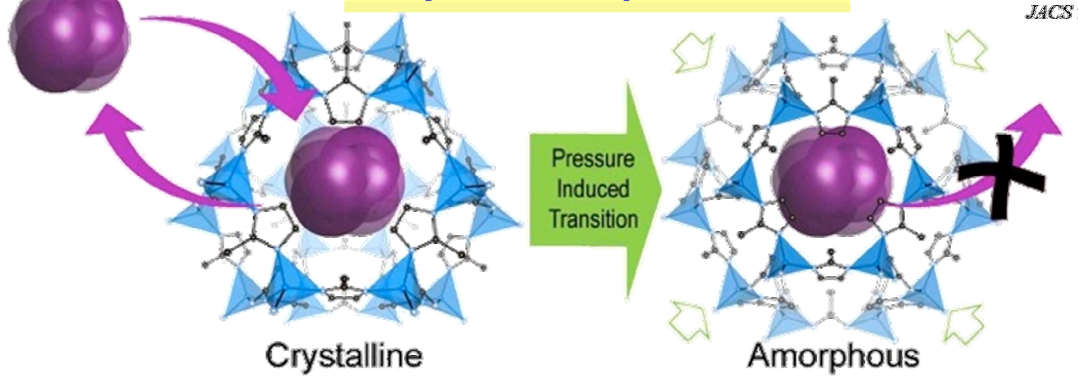


HKUST-1



Retention of Iodine in MOF due to SHORT range crystallinity

incorporation into a long term waste form.



Chapman, Nenoff, et.al., *JACS* **2011**, *133*(46), 18583.

Outline

Programmatic / Background

Novel Materials of Interest

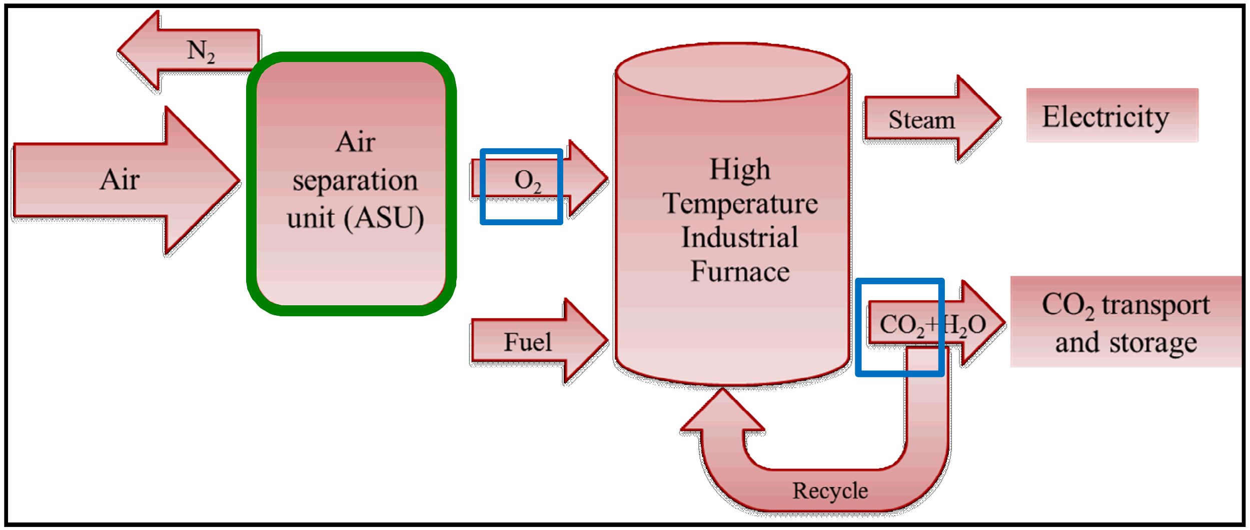
Activated Charcoals/Carbons, Zeolites, MOFs, layered/clays

Oxygen Separations Materials, Design by High Performance Computing to Real-World Testing

Direct Electrical Readout Sensors, Development and Testing

Application: Environmental Efficiency of the *ASU*, O_2/N_2 air separations with MOFs to Increase

Basic Research directed to an *Energy Efficient Process* for Oxygen purification from air.
a.k.a.: how to increase the efficiency of the air separations unit (*ASU*)?

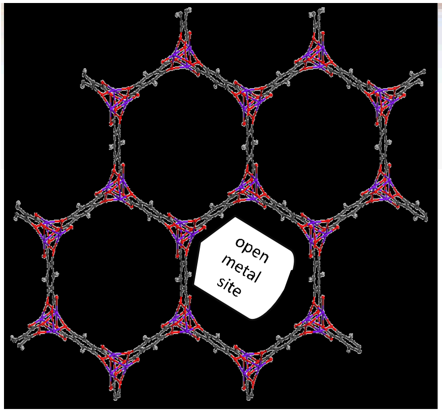


- Oxygen-enriched (oxy-fuel) combustion: burning the fossil fuel in an O_2 rich atmosphere results in a flue gas composed mainly of CO_2 (for capture) & water (little or no SO_X and NO_X emissions)
- The limiting factor of this technology is the efficiency of the cryogenic *ASU*, a costly and energy intensive process (primarily compression)
- Our study is focused on new highly selective materials (MOFs) to increase the efficiency of this separation process

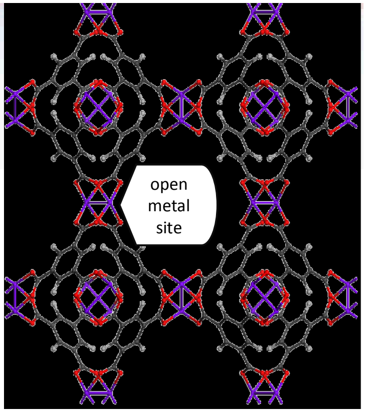
Target O_2 Selective Separations Materials, DFT & Experiments

MOFs with coordinatively unsaturated metal centers are promising materials for O_2/N_2 separations

- Two prototypical MOFs from this category, $Cr_2(BTC)_3$[1], $Fe_2(DOBDC)$[2] both show preferential adsorption O_2 vs N_2
- Plane wave DFT calculations on periodic structures: Vienna Ab initio Simulation Package (*VASP*)
    - Binding geometries for side-on and bent O_2 and bent and linear geometries for N_2 were evaluated
    - Static binding energies for O_2 and N_2 at 0 K
- Use of DFT to determine M-O_2 vs M-N_2 binding energies



$M_2(dobdc)$



$M_3(btc)_2$

MOF metal sites = separate O_2/N_2 by differences in bonding & electronic properties

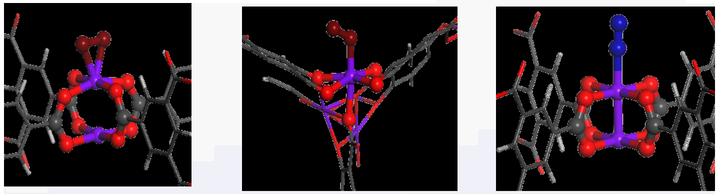
Plan wave density functional theory (DFT) calculations were performed on periodic structures of each MOF in the Vienna ab initio simulation package **(VASP)** with the Perdew-Burke-Ernzerhof **(PBE)** functional including dispersion corrections **(DFT-D2)**. Geometries were optimized and **static binding energies (ΔE_{O2}, ΔE_{N2})** were calculated by

$$\Delta E_{O2} = E_{MOF+O2} - E_{MOF} - E_{O2}$$

The **differences in binding energies ($\Delta\Delta$ E)** for oxygen and nitrogen were calculated by

$$\Delta\Delta E = -(\Delta E_{O2} - dE_{N2})$$

Side-on bonding ∠M-X-X 67° - 71° | **Bent** bonding ∠M-X-X 116° - 159° | **Linear** bonding ∠M-X-X 165° - 179°

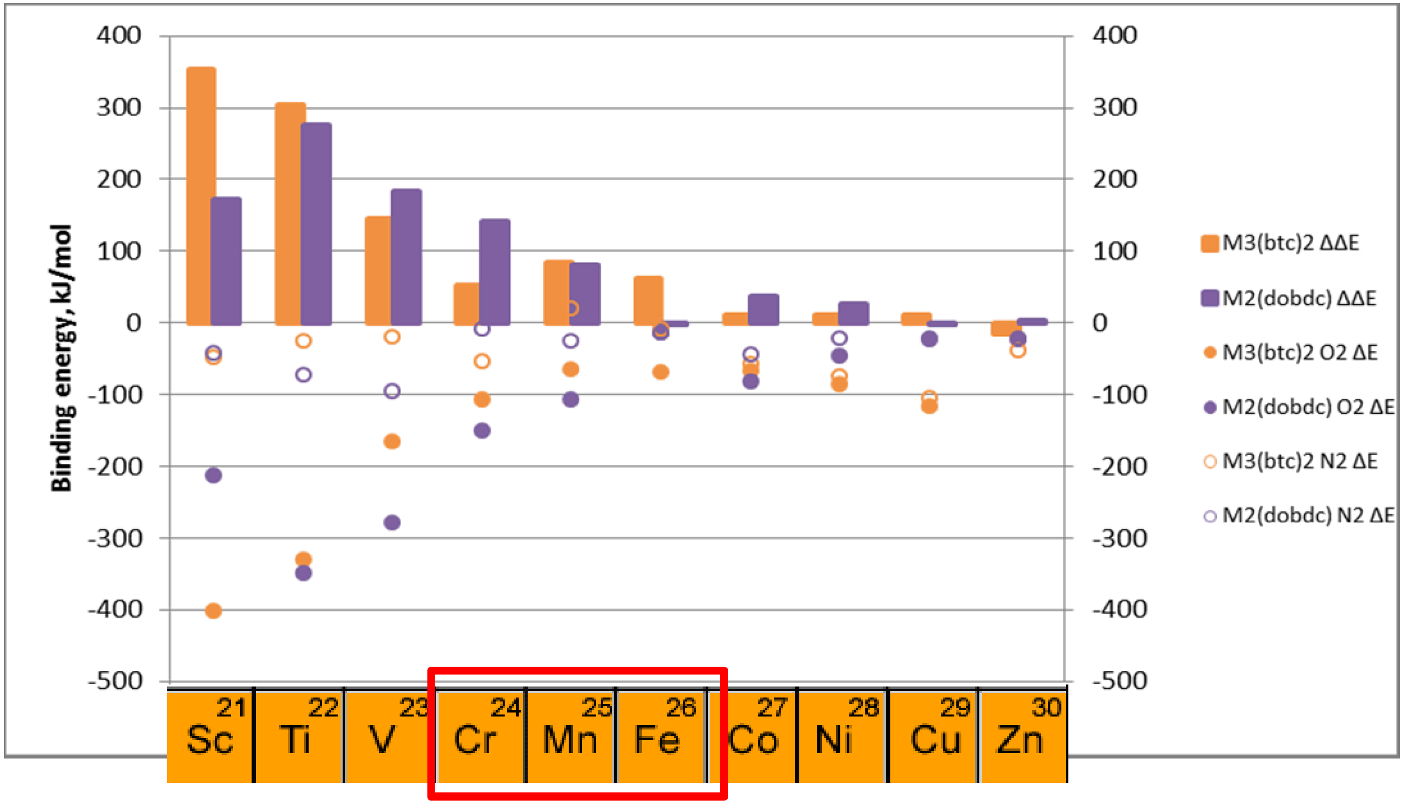


$Cr_3(btc)_2(O_2)$ | $Mn_2(dobdc)(O_2)$ | $Fe_3(btc)_2(N_2)$

Attention Paid to Bonding Geometries

[1]*JACS* **2010**, *132*, 7856–7857;
[2]*JACS* **2011,** *133*, 14814-14822

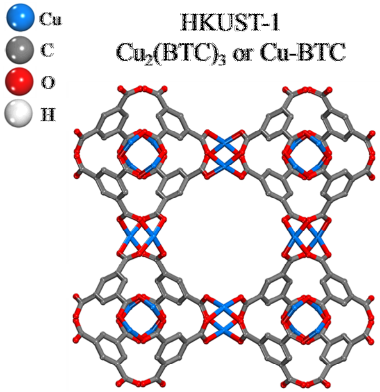
O_2 and N_2 Binding Energies Trends Across the First Row Transition Metal Series



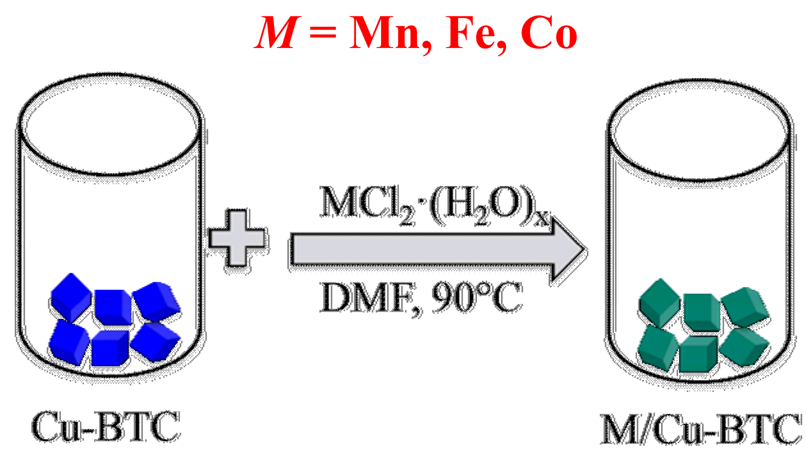
DFT predicts similar O_2 and N_2 binding to Mn, Fe, Co but with consistent stronger binding for O_2 to the metals

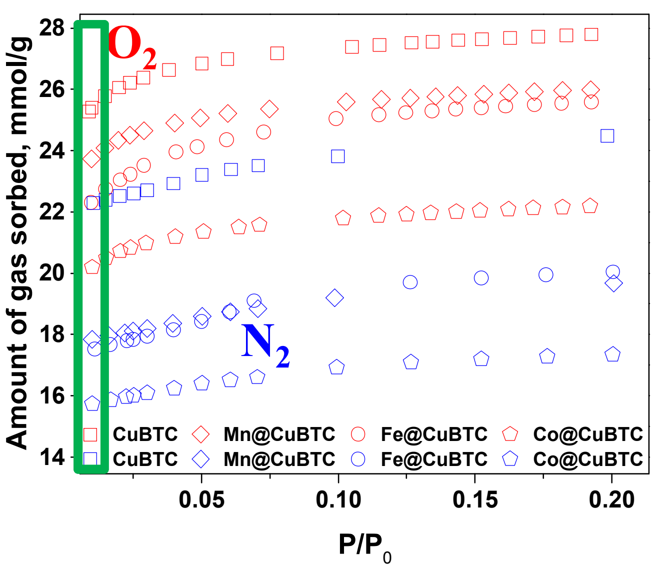
J. Phys Chem C, **2015**, *119*, 6556.

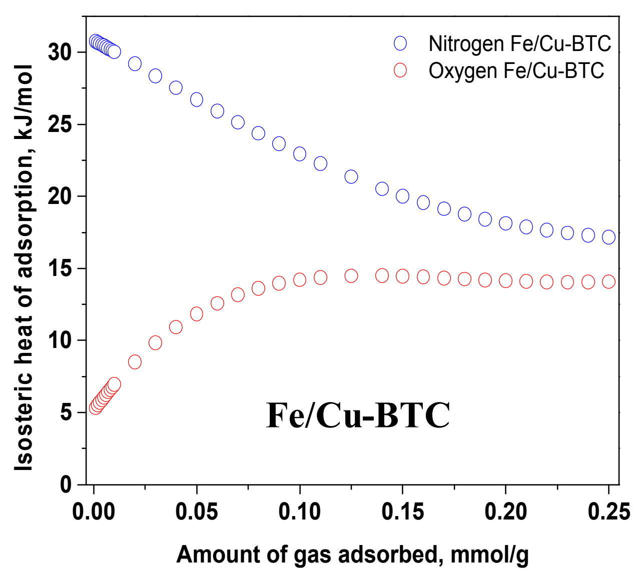
Postsynthetic Metal Ion Exchange to form Porous Mn-, Fe- and Co- Analogues of Cu-BTC



Chui, S. S. Y et.al Science **1999**, 283, 1148.







0 K *DFT binding energy*: Excellent prediction for 77K experiments,

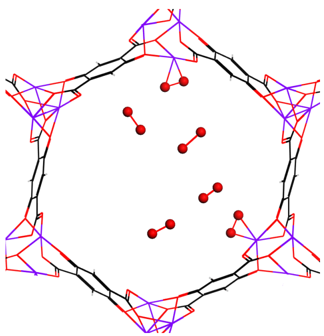
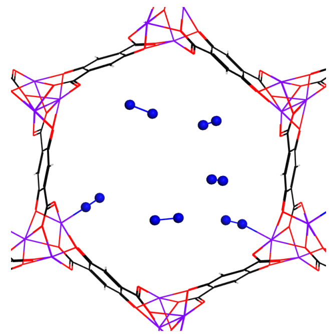
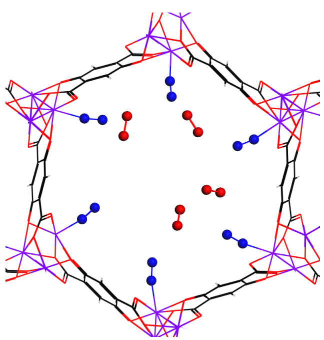
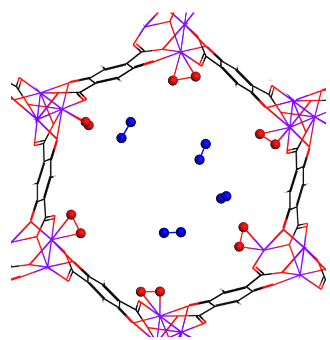
Do not correlate as well with experimental data 273-298 K - N_2 is preferred over O_2

Chem. Mater., **2015**, *27*(6), 2018.

AIMD Simulations with Temperature Considerations

M_2(dobdc) analogs

NVT ensemble: 27.5 ps, 0.5 fs timestep
PBE density functional with dispersion correction (PBE-D2),
PAW potentials for core electrons, spin polarization

Guests	2 O_2 bound 4 O_2 unbound	2 N_2 bound 4 N_2 unbound
Single component		
Mixed gas Competitive binding		
	6 N_2 bound 4 O_2 unbound	6 O_2 bound 4 N_2 unbound

Temperatures

201 K
258 K
298 K

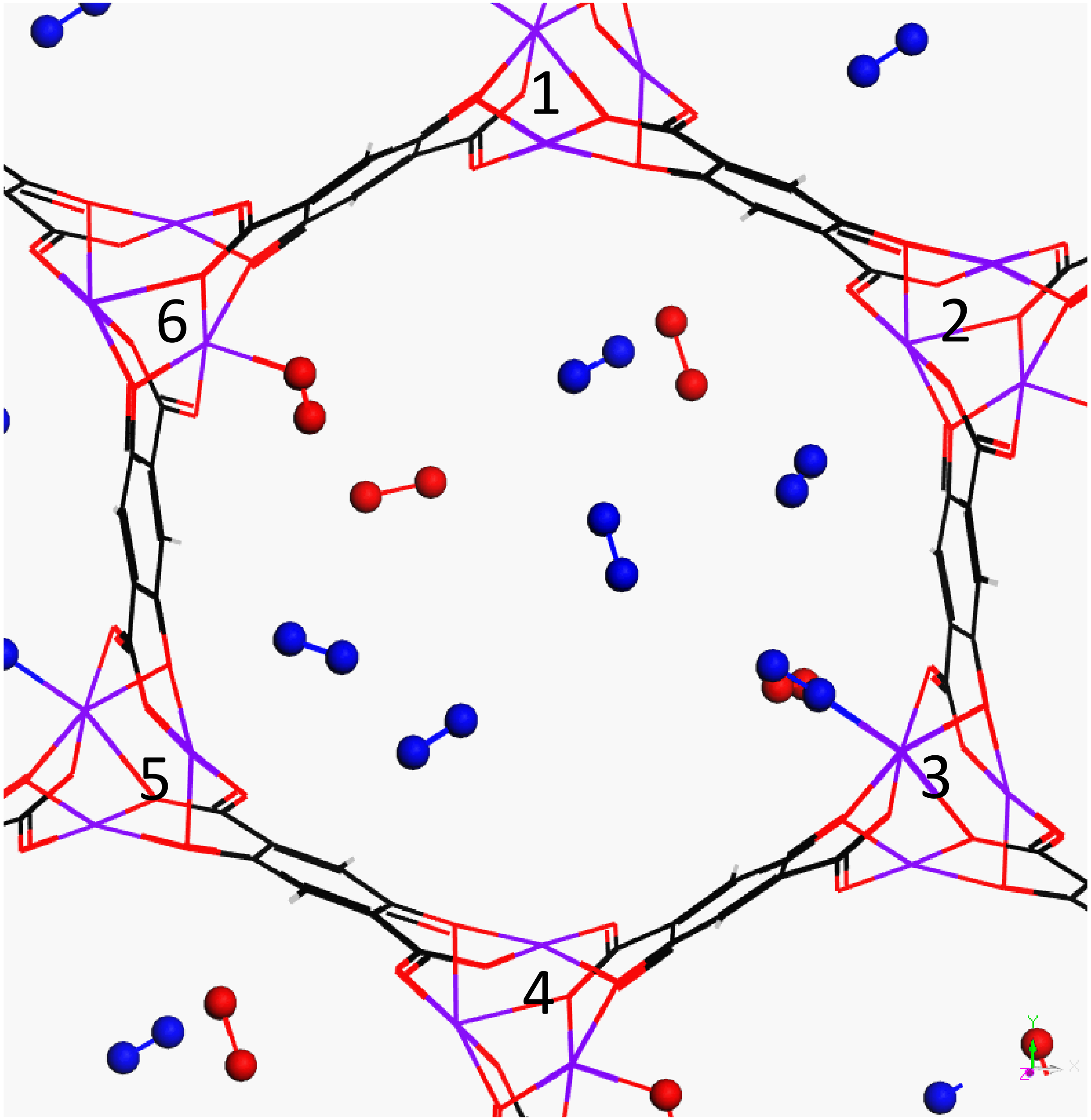
Metals

24 Cr	25 Mn	26 Fe

Red Sky Supercomputer
36 Simulations

3,800 processor-days each

http://hpc.sandia.gov/



Cr_2(dobdc)
6 N_2 + 4 O_2
298 K

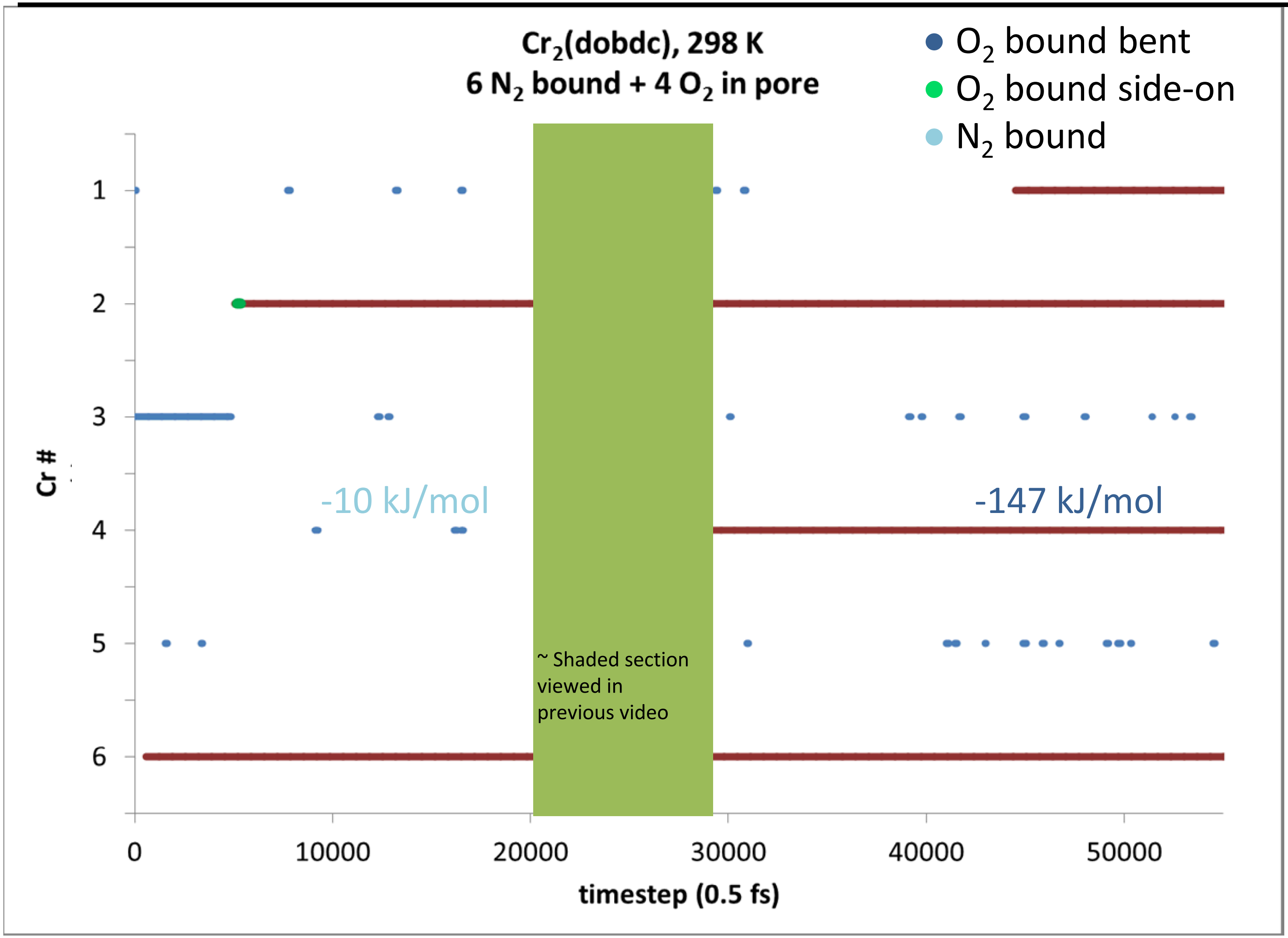
NVT
Time 2 ps – 15 ps

1 frame = 25 fs

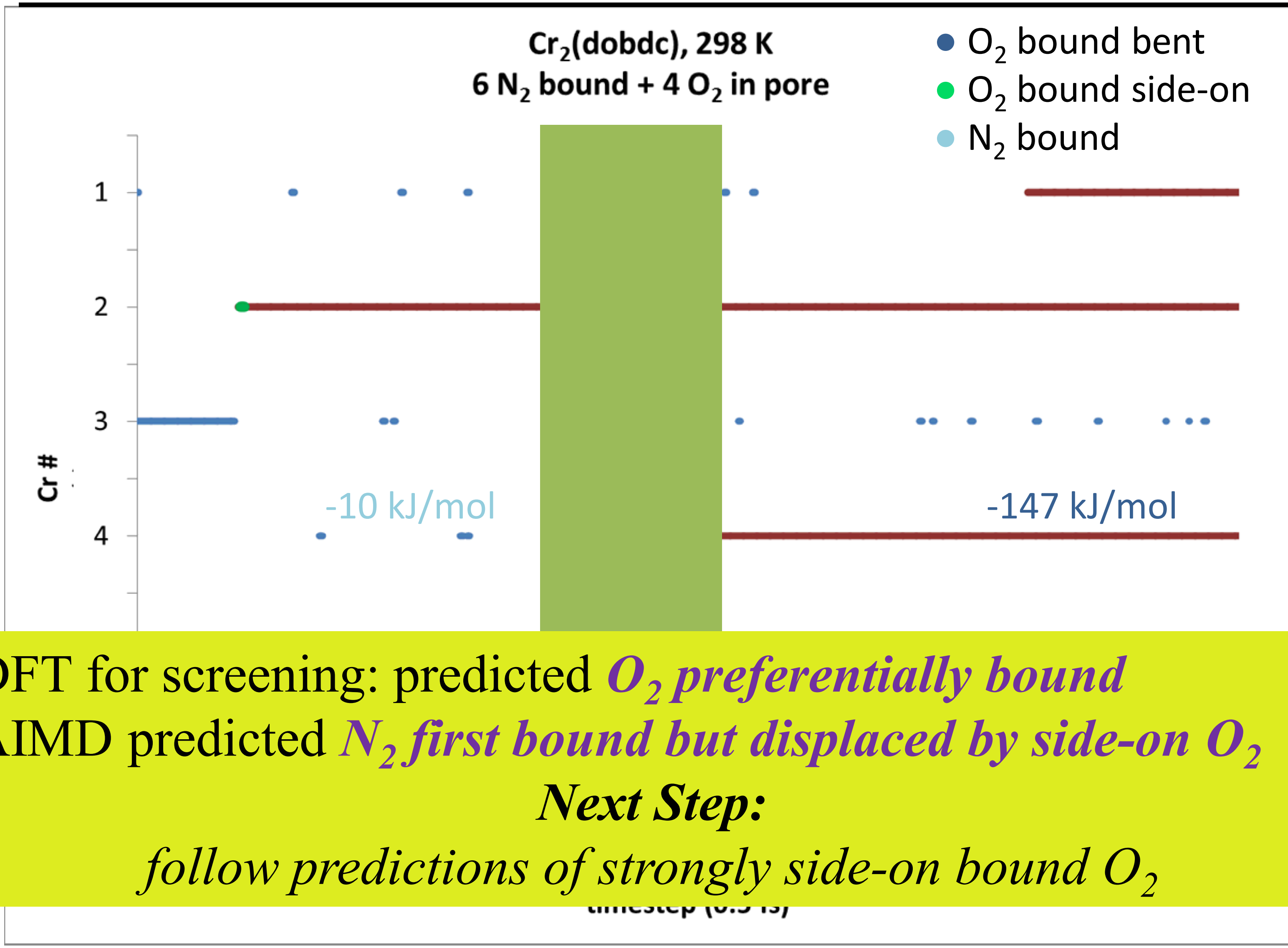
- O_2 slow to bind, but once on metal center, binding holds
- N_2 rapid bind and release from metal centers
- O_2 long term binding is consistently 'bent'
- Selective for O_2

PCCP, **2016**, 18, 11528

Gas Occupancy at Each Metal Site



Gas Occupancy at Each Metal Site



DFT for screening: predicted ***O_2 preferentially bound***

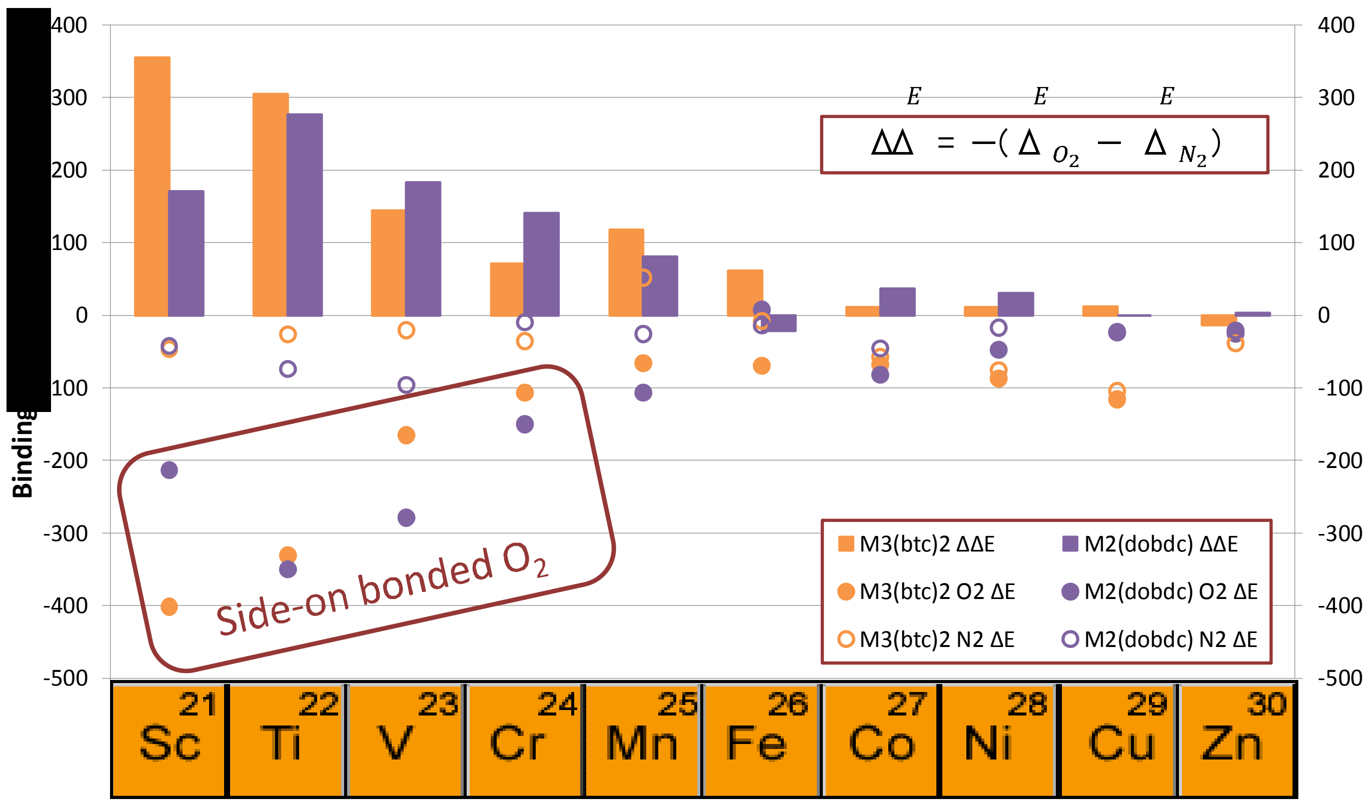
AIMD predicted ***N_2 first bound but displaced by side-on O_2***

Next Step:

follow predictions of strongly side-on bound O_2

Use of Strongest ***Side-On Binding*** Predictions

Binding Energy Calculated as a Function of Metal Site



J. Phys Chem C, **2015**, *119*, 6556.

MD Simulation Inspired MOF Synthesis: Sc/BTC/DMF/HCl

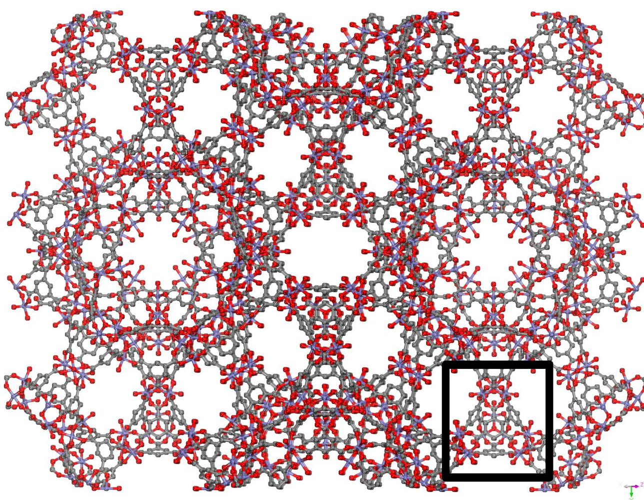
US provisional Patent filed 2016

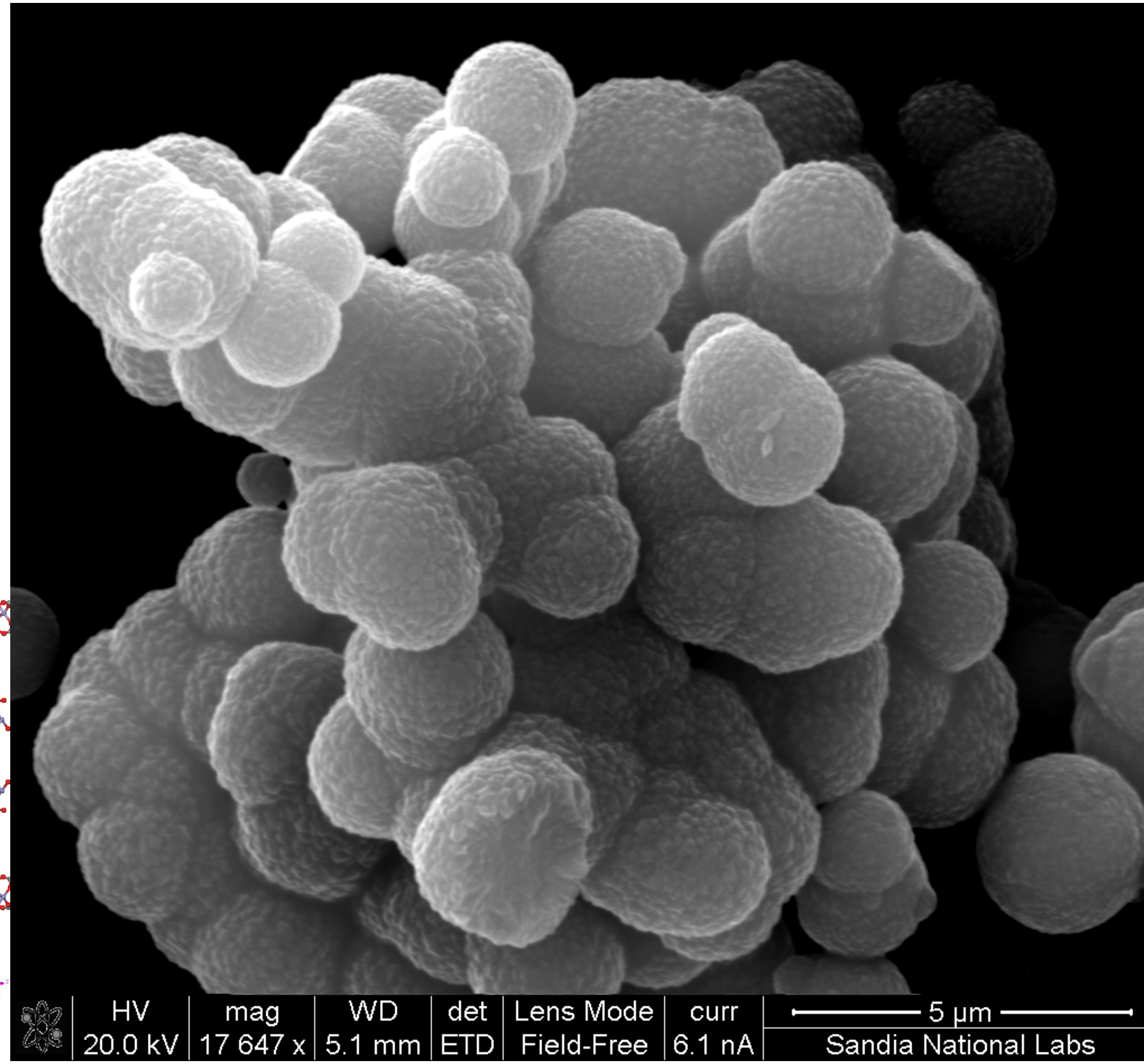
Sc-MIL-100

Unique synthesis:

Mixed $Sc(NO_3)_3 \cdot xH_2O$ and 1,3,5–benzetricarboxylic acid in N,N'-dimethylformamide and HCl.

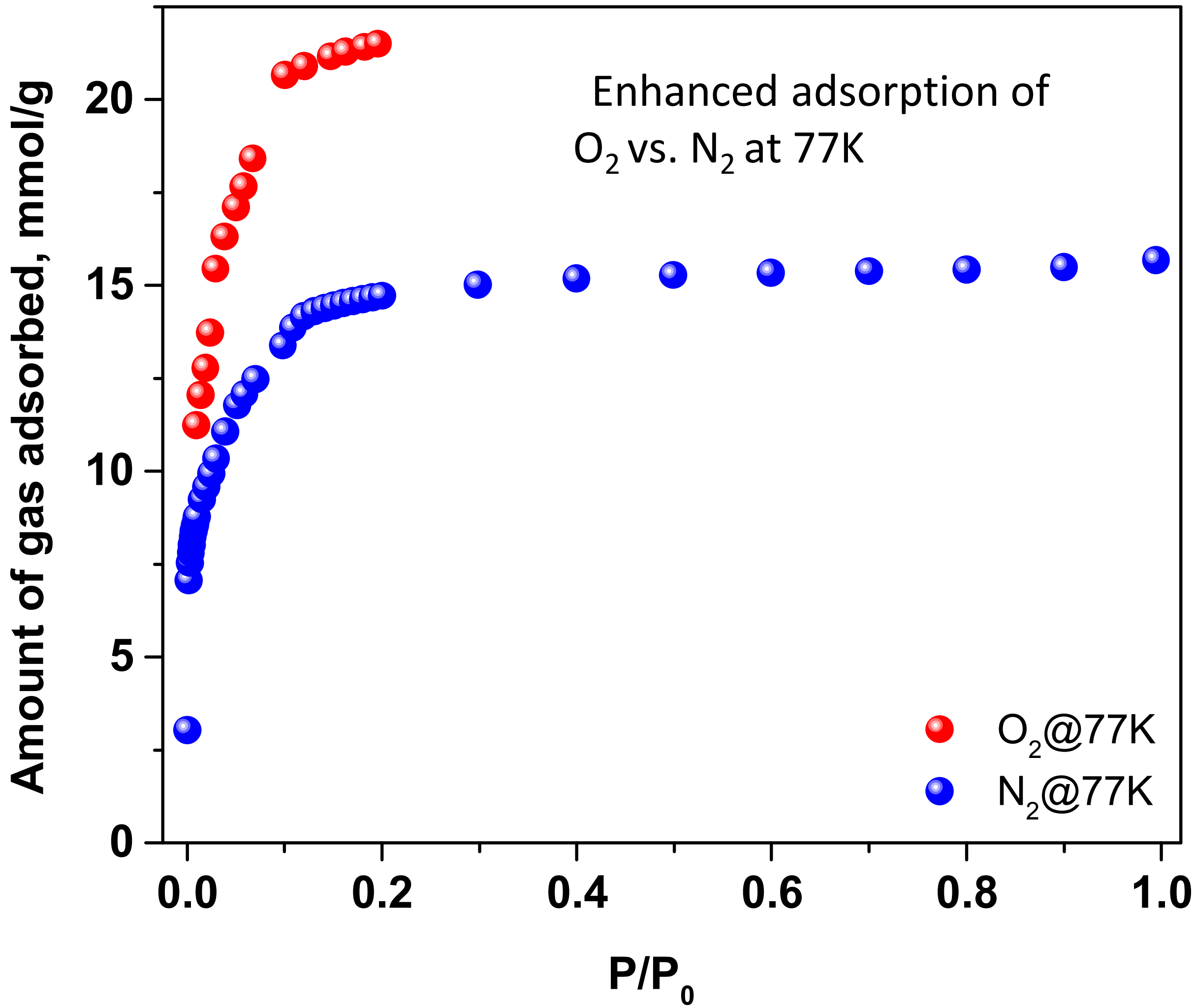
Heated to 373K overnight





Chem. Mater. **2016**, 28(10), 3327-3336

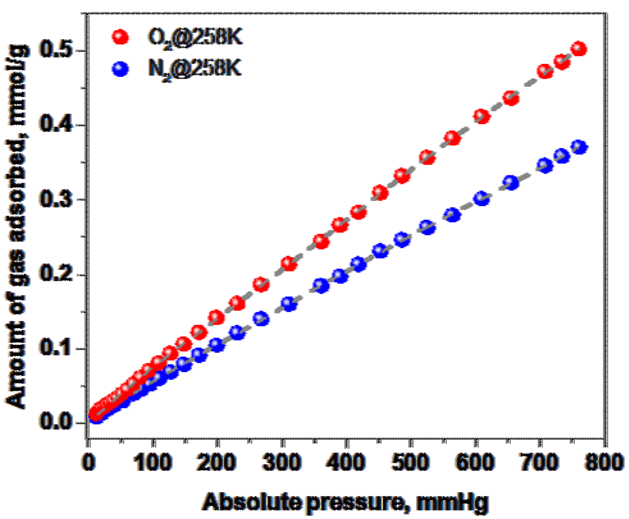
Sc-MIL-100: Metal-Center has a role at 77K



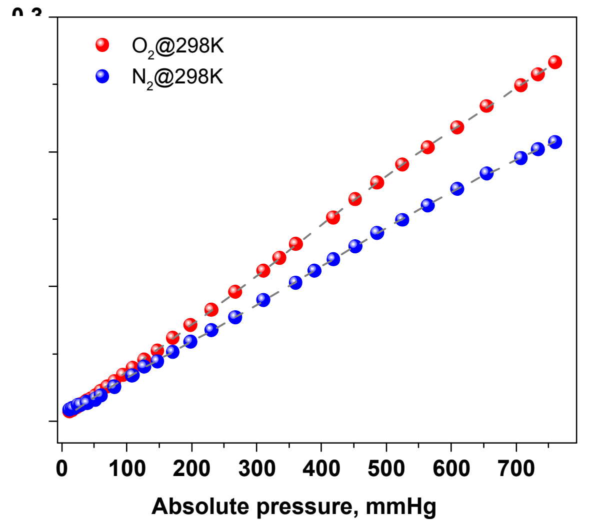
How does Sc-MIL-100 behave at more realistic operational temperatures?

Sc-MIL-100: Enhanced Quantity of O_2 vs N_2 Adsorbed over Wide Temperature Range (at least to 313K)

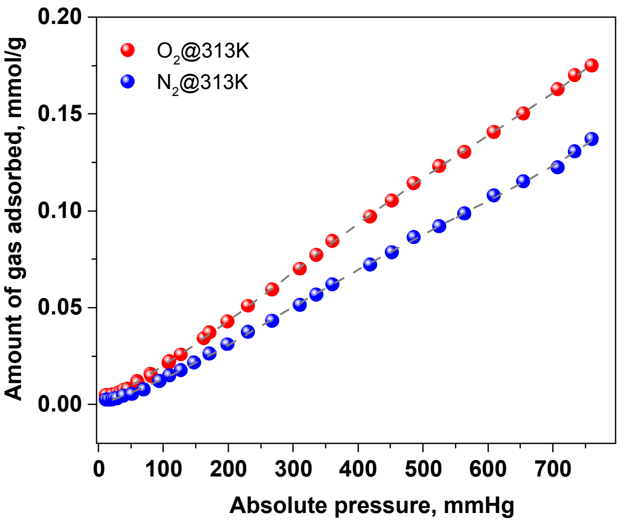
O_2 vs. N_2 @**258K**



O_2 vs. N_2 @**298K**



O_2 vs. N_2 @**313K**



Fit using the virial eq.

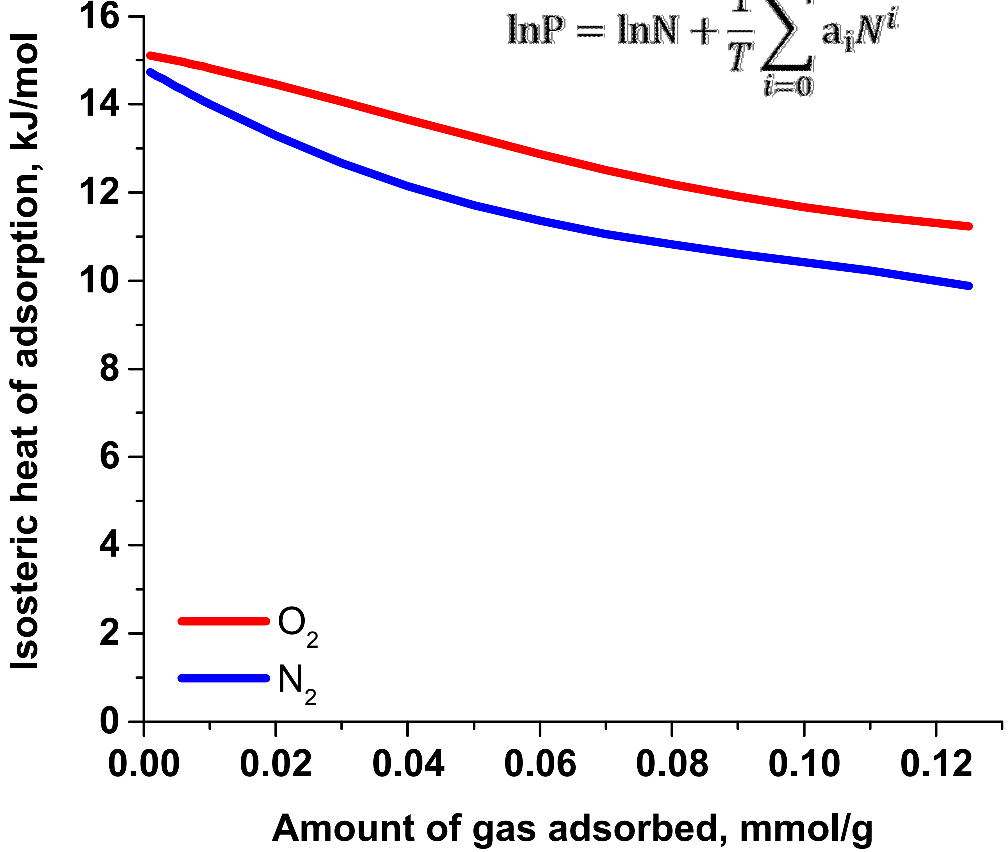
Isotherm trends mimic those predicted by GCMC

Sc-MIL-100: Isosteric Heat of Adsorption (kJ/mol) Higher Binding Energy for O_2 vs N_2

Qst derived from 258K, 298K and 313 K

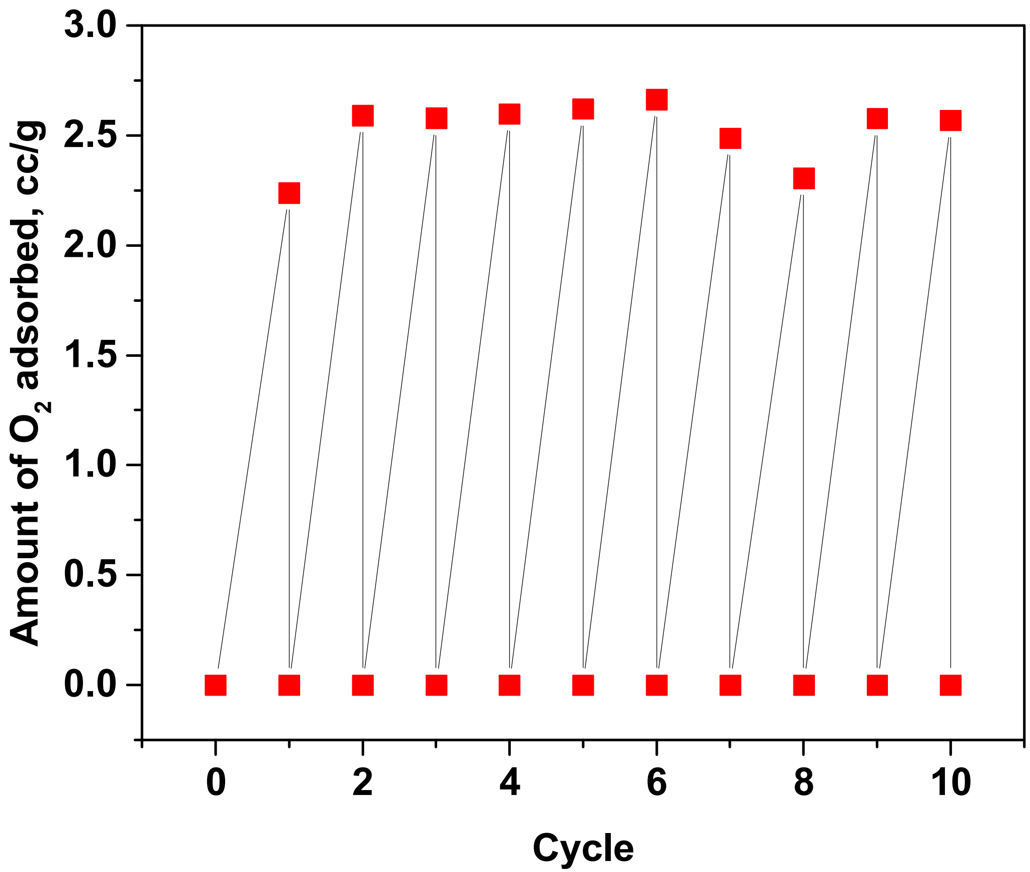
Independent Virial Fit HOA

$$\ln P = \ln N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i$$



Sc-MIL-100 Performance: O_2 adsorption & Desorption over 10 cycles, 298 K, 1 atm

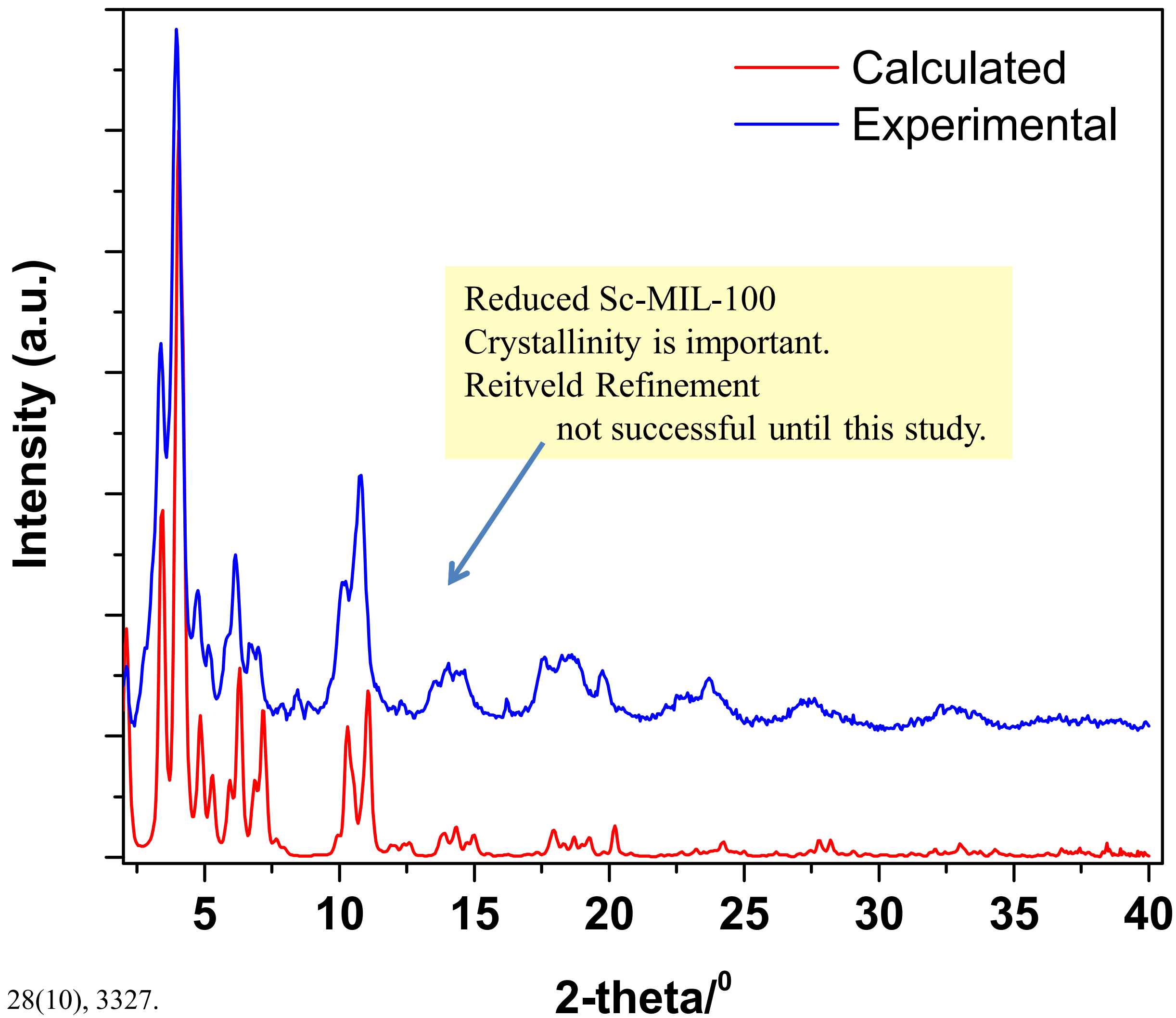
US provisional Patent 2016



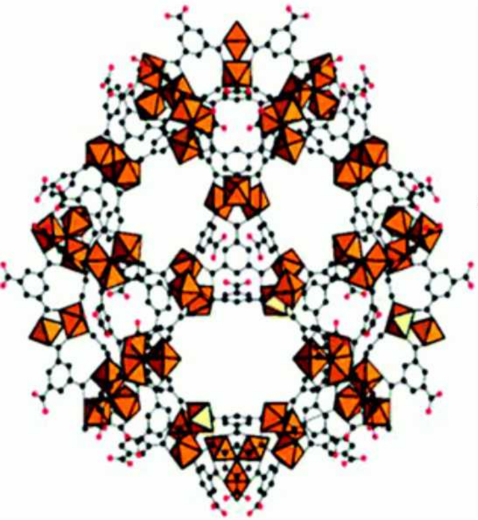
What about the structure is making Sc-MIL-100 O_2 strongly adsorbing?

Structure-Property Relationship Understanding of Sc-MIL-100 Oxygen Selectivity

High Energy Synchrotron X-ray, APS/ANL



Chem. Mater. **2016**, 28(10), 3327.

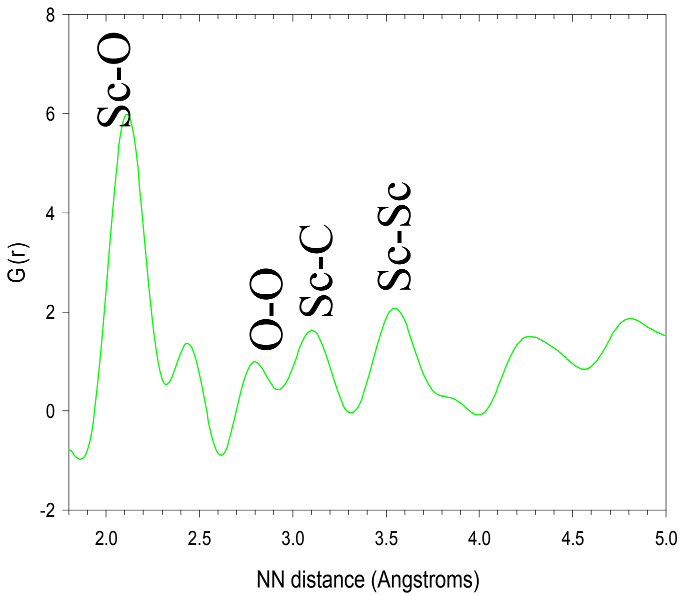


Using d-PDF, Subtract out the ligands and study only the Metal Clusters

d-PDF peak analysis

Bond	NN distance (Å)	Area	FWHM (Å)
Sc-O	2.11	1.5	0.19
O-O	2.81	0.3	0.22
Sc-C	3.08	0.8	0.26
Sc-Sc	3.53	0.5	0.24

d-Pair Distribution Function (d-PDF)



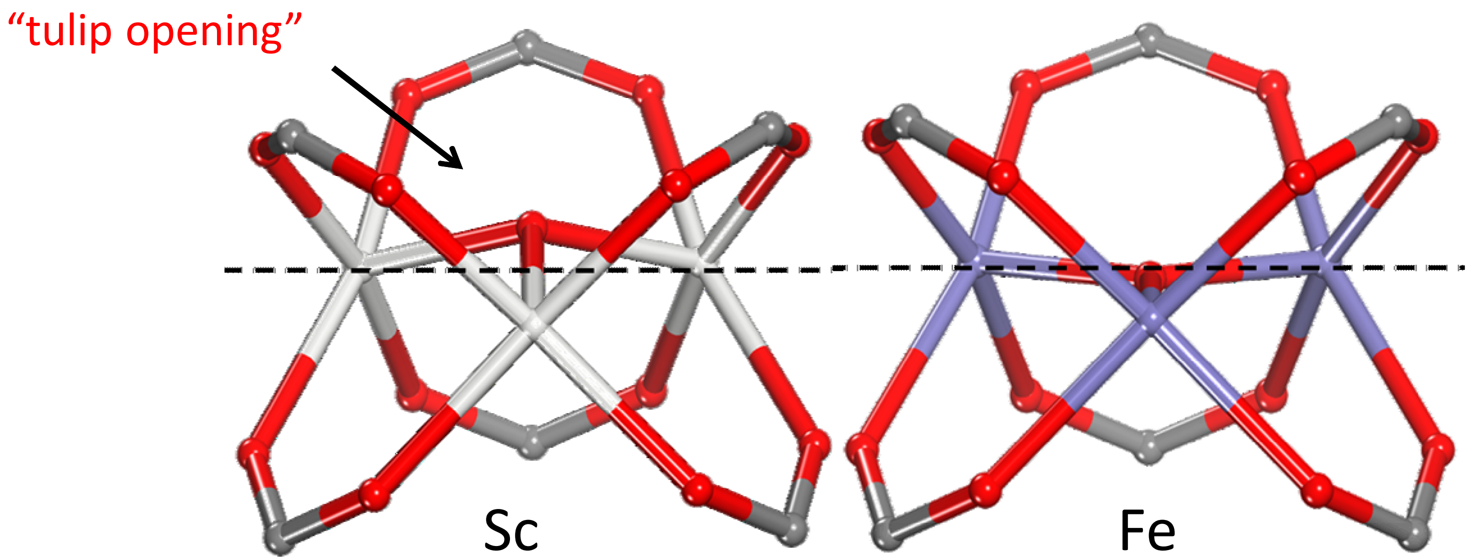
Peaks shifted to longer distances
Consistent with larger Sc incorporation
(vs. Cr-MIL-100)

- Oxo-centered trimers at nodes of MIL-100 framework inferred from M-O and M…M distances
- Narrow Sc-O peak = narrow Distribution of bond lengths
- Single M-O bond length (M-O(μ_3) or M-O (carboxylate)), suggests **M-O-M angle of 113°** << 120° of a planer trimer

Sc-MIL-100: Structure-Property relationship evaluated. Preferred O_2 sorption – Large Sc Distorts Cluster

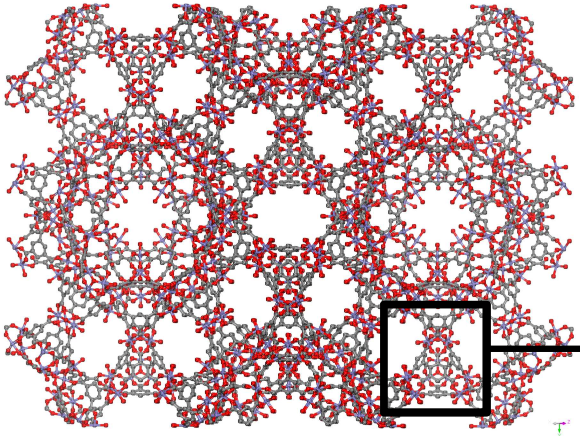
Large size of Sc atom requires **out of plane distortion** in the ozo trimer of the O(μ3) atom.

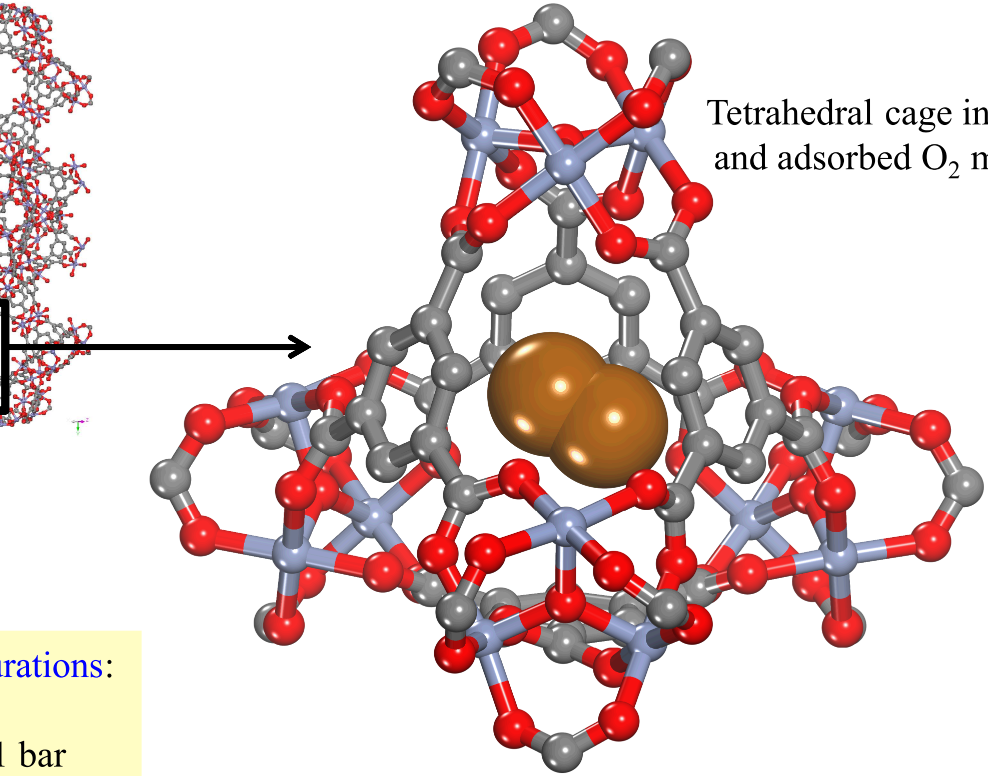
Resultant "**puckering**" of trimer and "bending" of ligand is probable route for enhanced O_2 sorption / insertion in Sc-MIL-100



Rietveld refinement unit cell for Sc-MIL-100: a = 74.518(31) Å, R = 10.7%

Sc-MIL-100: Probable Sc-O binding sites





Tetrahedral cage in the MIL-100 framework and adsorbed O_2 molecule (large spheres).

GCMC-equilibrated configurations:
Cage and pore occupancy
as determined at 298K and 1 bar

P (bar)	Gas	# in Cage	# in Pore	Total
1	N_2	21	27	48
1	O_2	47	20	67

Conclusions

- Multidisciplinary teaming allows for in-depth understanding of materials structure-properties

- The collaborative use of DFT and AIMD enabled the prediction and understanding of metals needed in MOFs for selective gas binding

- **Sc-MIL-100**: Early transition metal MOFs show preference for O_2 vs N_2 over wide temperature range (up to at least 313K), as confirmed by isosteric heats of adsorption.

- Modeling pointed us toward Sc based MOFs for O_2 preferential adsorption, chemistry, crystallography, & gas testing explained why the material worked well.

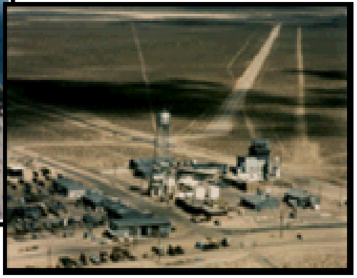
- On-going Research:
  Techno-economic Analysis Model for ion exchange resins in silica removal from Industrial Water Recycle and
  Burner Design to Oxyfuel combustion applications
  Novel MOFs designed for Fission Gas Separations

Sandia National Laboratories

Albuquerque, New Mexico

Livermore, CA

Kauai Test Facility
Hawaii



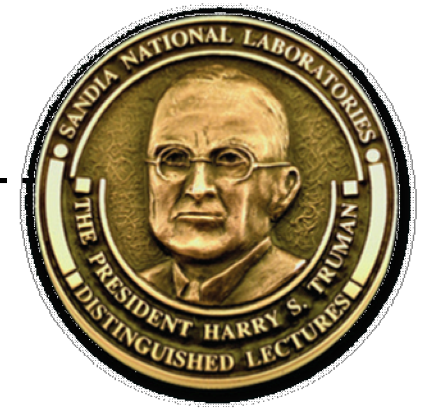
Tonopah Test
Range, Nevada

Yucca Mountain,
Nevada

WIPP,
New Mexico

Pantex, Texas

Sandia Truman Fellowship FY19



Seeking Applicants!

Sandia National Laboratories is seeking applicants for the **President Harry S. Truman Fellowship** (in National Security Science and Engineering).

Candidates for this position are expected to have solved a major scientific or engineering problem in their thesis work or have provided a new approach or insight to a major problem, as evidenced by a recognized in

The Fellowship provides the opportunity for new Ph.D. scientists and engineers to pursue independent research of their own choosing that supports Sandia's national security mission.

The appointee is expected to foster creativity and to stimulate exploration of forefront S&T and high-risk, potentially high-value research and development.

Sandia's research focus areas are: bioscience, computing and information science, engineering science, materials science, nanodevices and microsystems, radiation effects and high energy density physics, and geosciences.

The Truman Fellowship is a three-year appointment. The salary is $111,200 plus benefits and research funding for the proposal.

The deadline is November 1 of each year and normally begins on October 1 the following year.

Requirements:

Candidates must meet the following requirements:

- Ph.D. awarded within the past three years at the time of application or completed Ph.D. requirements; with strong academic achievement and evidence of exceptional technical accomplishment, leadership, and ability to team effectively
- Candidates must be seeking their first national laboratory appointment (no previous postdoc at a national laboratory)
- Ability to obtain a DOE "Q" clearance, which requires US citizenship

Visit http://sandia.gov/careers/students_postdocs/fellowships/truman_fellowship.html

Jill Hruby Fellowship FY19

Seeking Applicants!

Sandia National Laboratories is seeking applicants for the **Jill Hruby Fellowship** in National Security Science and Engineering.

This fellowship aims to develop women in the engineering and science fields who are interested in technical leadership careers in national security.

Applicants must display excellent abilities in scientific and/or engineering research and show clear promise of becoming outstanding leaders.

Jill Hruby Fellows have the opportunity to pursue independent research that supports Sandia's purpose: to develop advanced technologies to ensure global peace. **In addition to receiving technical mentorship, Jill Hruby Fellows participate in a unique, prestigious leadership development program.**

Sandia's research focus areas are: bioscience, computing and information science, engineering science, materials science, nanodevices and microsystems, radiation effects and high energy density physics, and geosciences.

The Jill Hruby Fellowship is a three-year appointment. The salary is $111,200 plus benefits.

The deadline is November 1 of each year and normally begins on October 1 the following year.

Requirements:

Candidates must meet the following requirements:

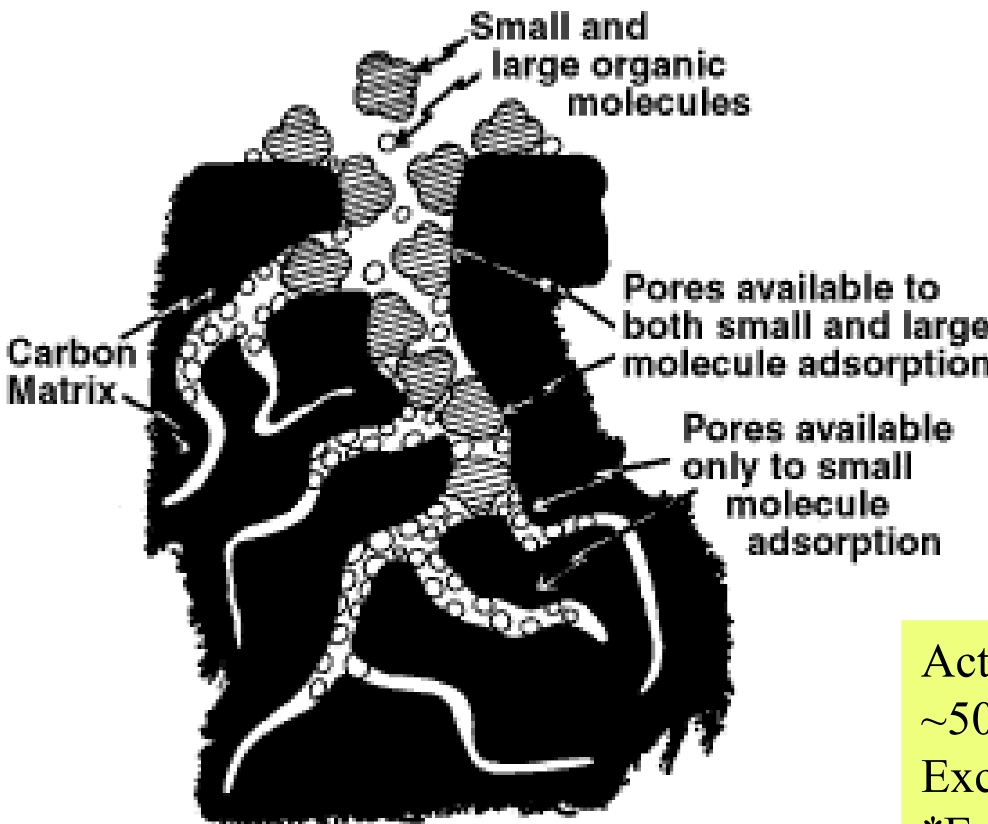
- Ph.D. awarded within the past three years at the time of application or completed Ph.D. requirements; with strong academic achievement and evidence of exceptional technical accomplishment, leadership, and ability to team effectively
- Candidates must be seeking their first national laboratory appointment (no previous postdoc at a national laboratory)
- Ability to obtain a DOE security clearance, which requires US citizenship

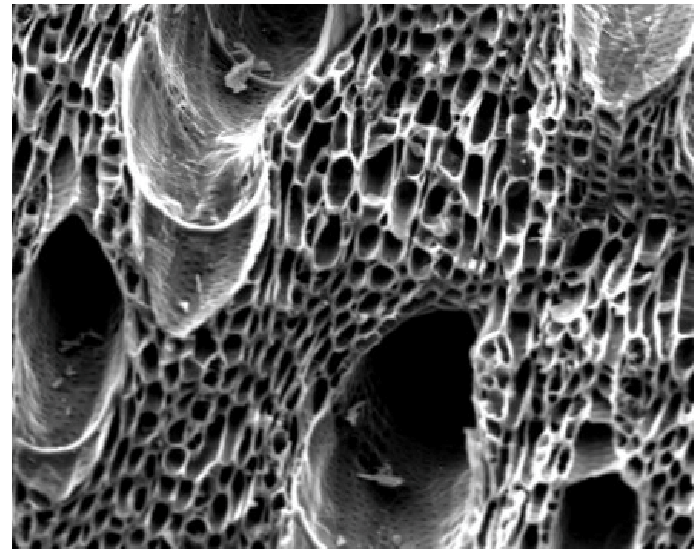
Visit http://www.sandia.gov/careers/students_postdocs/fellowships/hruby_fellowship.html

Questions? / Thank you

Extra Slides

Amorphous Carbon/Activated Charcoal: Active Capture of Iodine, and *Everything* else

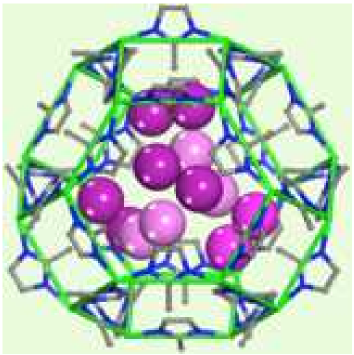




Activated Charcoals have mesoscale porosity,
~500 m^2/g surface area
Exceptional adsorption, but no selectivity
Easily “clogged”

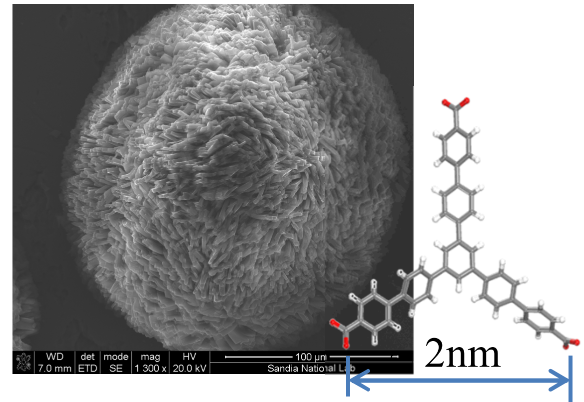
Most Charcoals are organic based,
Contain substantial quantities of natural iodine

I_2@MOFs Sensors, to date…



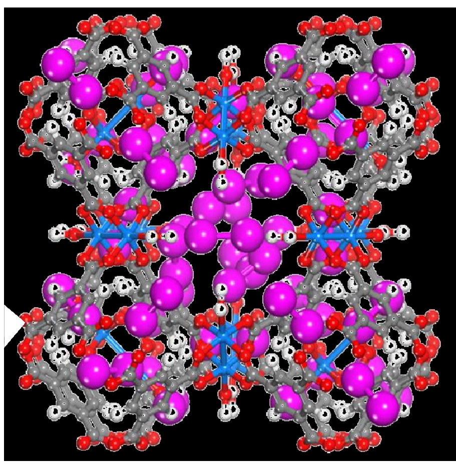
I_2@ZIF-8

JACS **2011**, *133* (32), 12398



I_2@SMOF-3

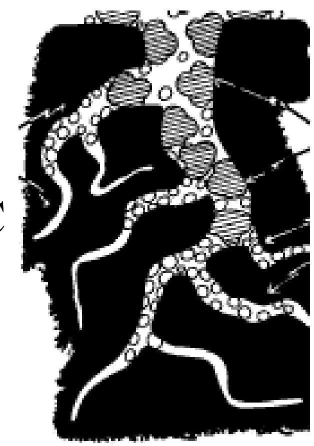
Chem. Mater. **2014**, *26* (9), 2943



I_2@HKUST-1

Chem. Mater., **2013**, *25* (13), 2591

I_2@AC



- I_2 has a low vapor pressure and is highly polarizable, once adsorbed into MOF
- Screen printed onto patterned array of IDE
- Impedance spectra measured ***in real time*** as the MOF is exposed to gas vapor at varying temperatures to **tune responses**.

Conclusion

Fission Gas selectivity for Capture and Storage is highly dependent upon local nanoscale interactions

Use of **impedance spectroscopy** enables direct electrical readout of iodine gas presence,
in ambient conditions of temperature and humidity
this is due to the *highly polarizable nature of* I_2

Success with IS is ensured due to the ability to test 100 kHz – 1 Hz in 10 s using FFT methods

Oxygen Separations Materials: