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Nanoporous Materials for Environmental and Energy Applications

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Technical Focus

- Technical Focus:
  Chemical study of confinement and reactivity of ions and molecules in micro- and nano-porous materials
  - zeolites, metal-organic frameworks (MOFs), clays and amorphous silicas

- The study of Structure-Property Relationships on the nanoscale enabling the informed testing of the materials for a wide range of interests.

- Structure analysis of host-guest systems on the nanoscale has led to strong collaborations with staff scientists at the APS for synchrotron data collection & Pair Distribution Function (PDF) analysis

- Strong Interdisciplinary Teams working in concert.
  diverse programs require diverse teams
  chemists, engineers, computational modelers
  national labs, universities and industry

- Mentoring: postdocs, young staff and collaborating young professors, strong support of women and minorities into the sciences

Program Development & Management - Nenoff

- Raised $35+ Million raised in individual PI grants
  150+ publications, 13 US Patents, 4 book chapters, *h*-index = 33

- Developed strong relationships at DOE, resulted in *long running* programs
  - DOE/EERE/Office of Industrial Technologies (Advanced Materials)
  - DOE/EERE/Hydrogen
  - DOE/Environmental Management
  - DOE/Office of Nuclear Energy

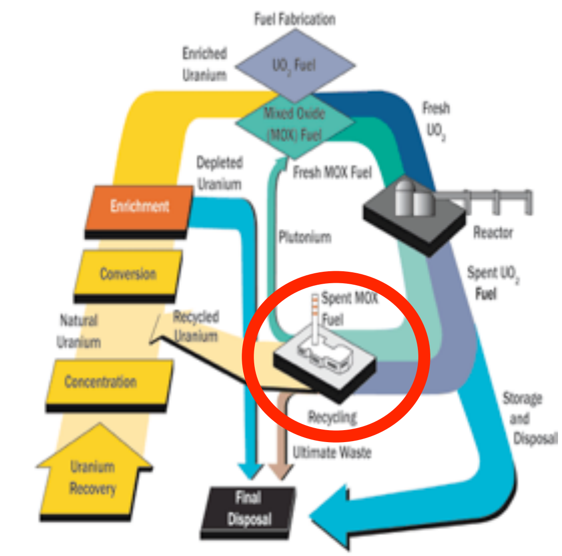
Building customers with ARPA-E, DOE/BES, and DOE/Fossil Energy (NETL)

- Research Group works in *TRL 1 - 9*

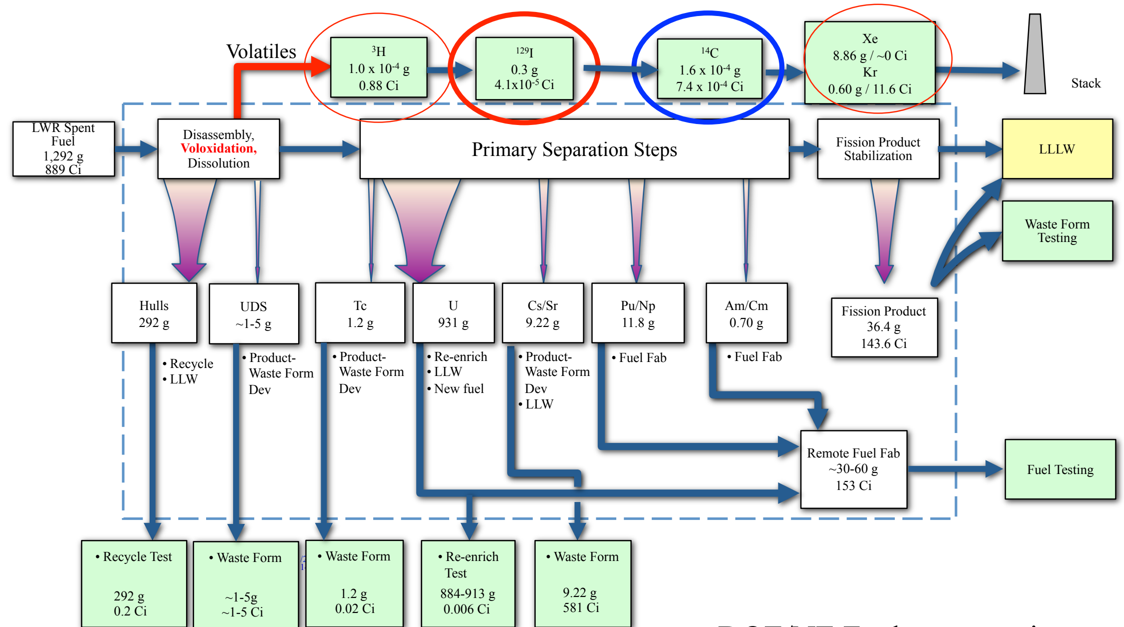
- Led 2 different multiyear, multimillion $ CRADAs
  - SNL, BP, Temec, Coors Ceramics, University Cincinnati:
    Zeolite Membranes for HC isomer feedstock purification
  - SNL, Goodyear Chemicals, University Cincinnati:
    Membranes for Separations of High Volume $C_4/C_5/C_6$ Mixtures

Applications

Reprocessing: capture on nonburnable volatile fission products and lesser actinides



Source: U.S. Nuclear Regulatory Commission



DOE/NE Fuel reprocessing Scheme, ORNL

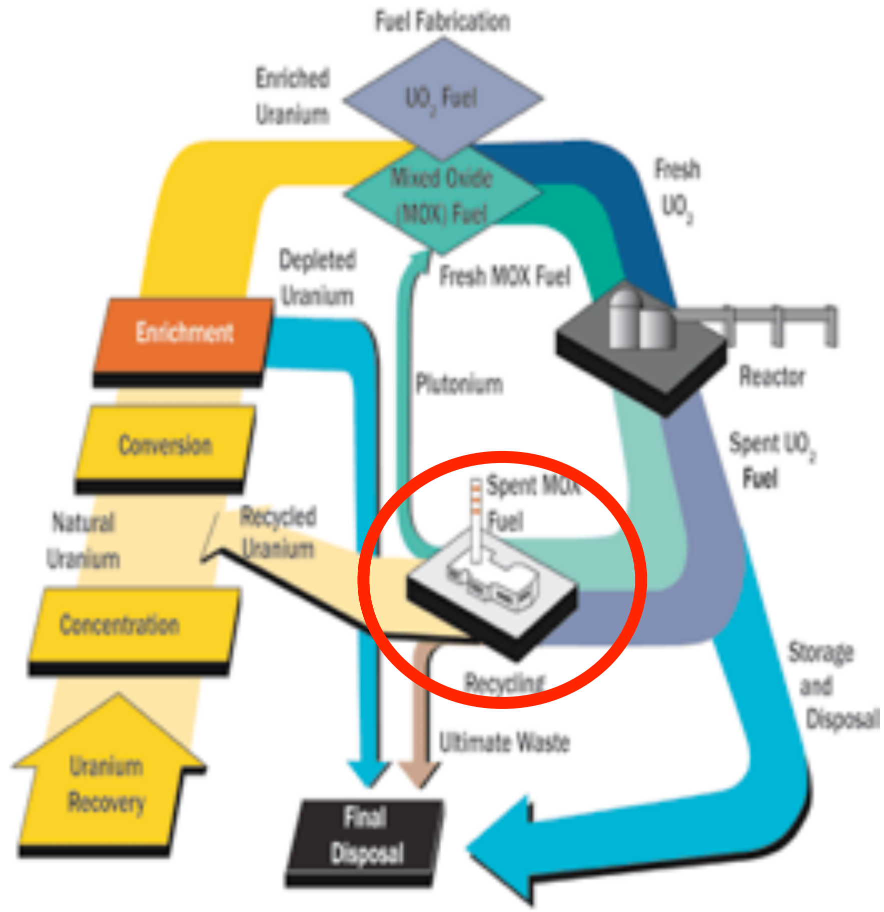
Legacy, Accident or Produced rad aqueous waste requiring highly specific ion capture

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)

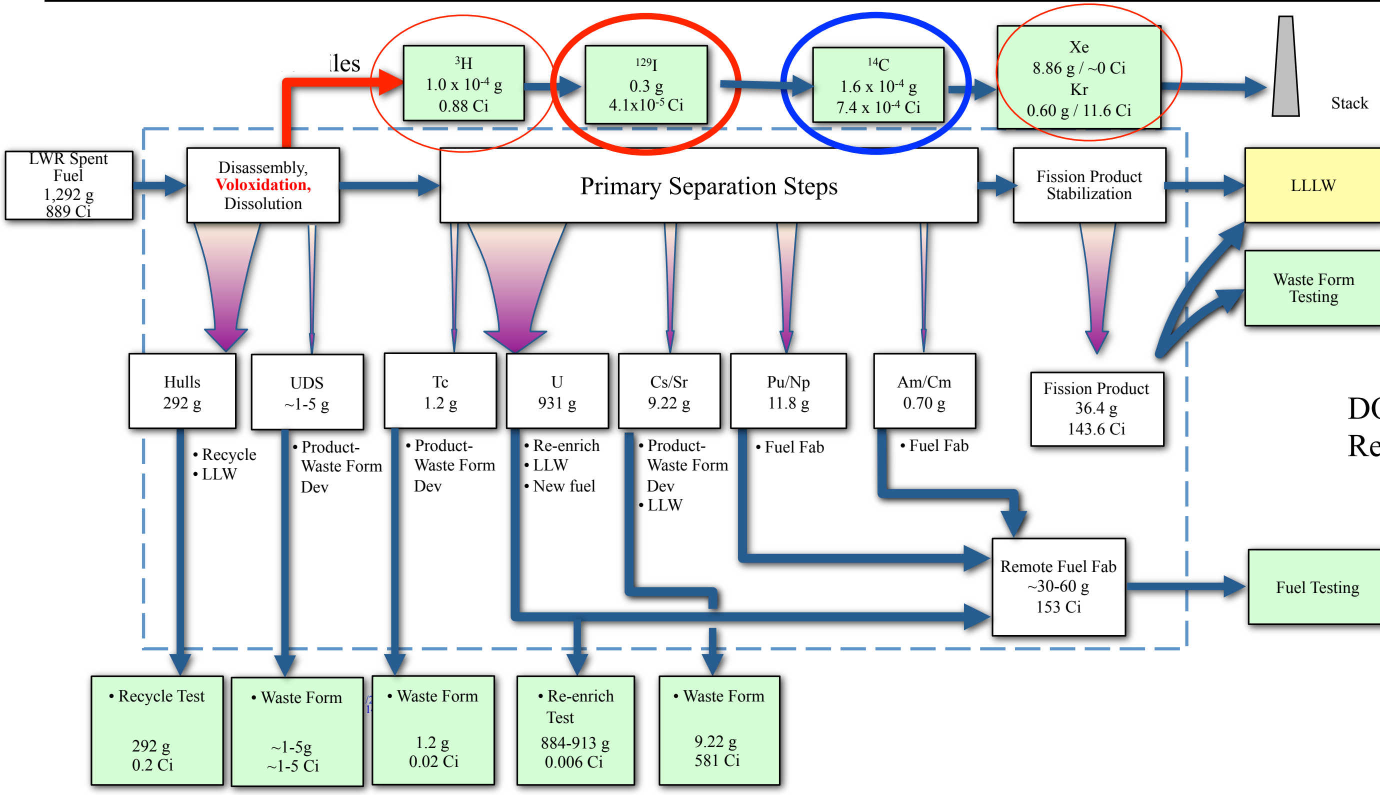
Applications: Fission Gases

Reprocessing: capture on nonburnable volatile fission products and lesser actinides



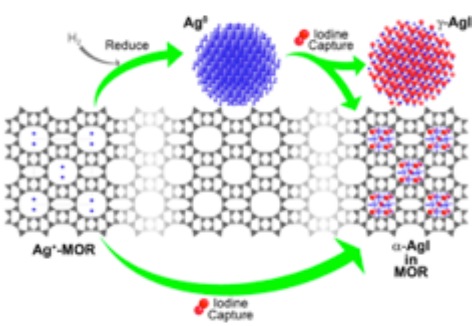
Source: U.S. Nuclear Regulatory Commission

Applications: Fission Gases

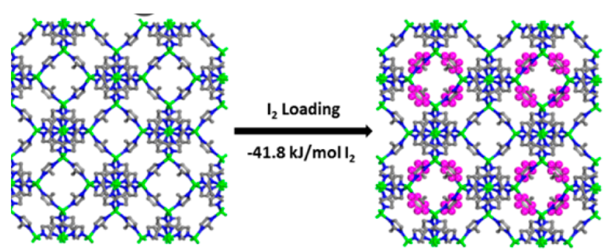


DOE/NE Aqueous Fuel Reprocessing Scheme, ORNL

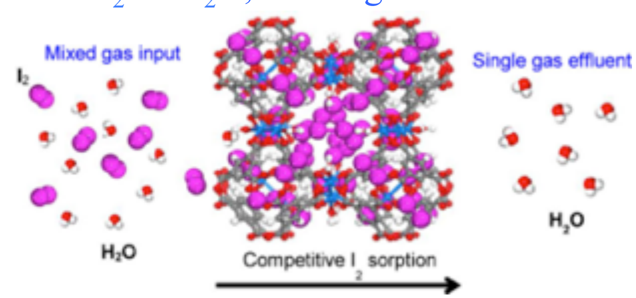
Zeolites – I_2 capture/storage



MOFs – small pore for large quantity I_2 capture



MOFs – large pore for competitive I_2 vs H_2O, and large volumes



Applications: Rad Ion Capture

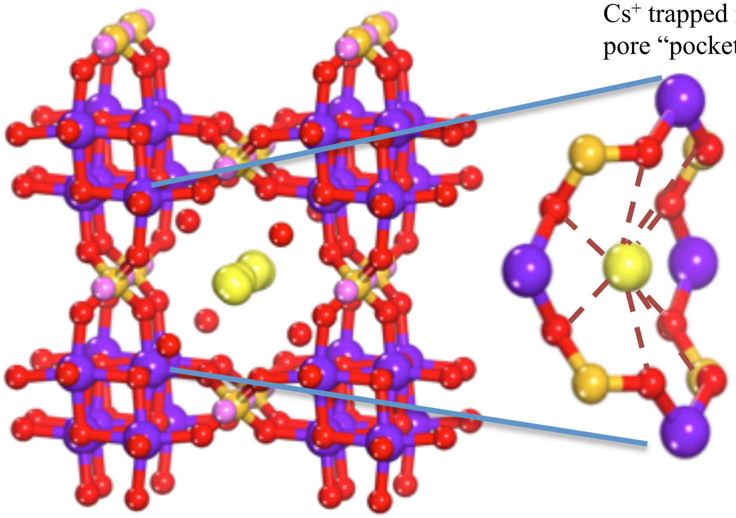
Legacy, Accident or Produced rad aqueous waste requiring highly specific ion capture.

Cs+ ion capture: Crystalline Silicotitanates (CSTs)

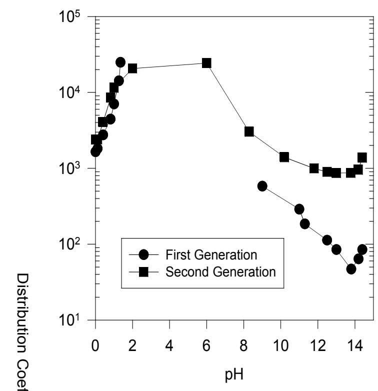
Fukashima Daiichi Nuclear Power Plant explosion 2011 I^{129}, I^{131} volatile gas released; Cs^{135}, Cs^{137} & Sr^{90} aqueous released
(www.IAEA.org)

Cs^{+} captured in CST cage

Cs^{+} trapped in pore “pocket”



Distribution Coefficient of Cs on CST

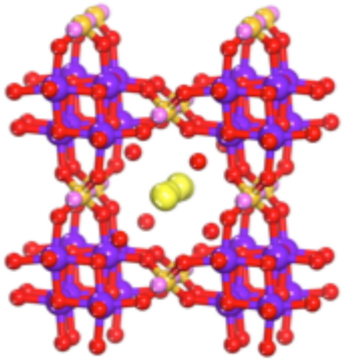


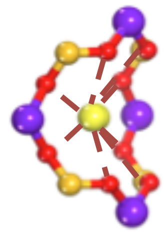
UOP IONSIV™ IE-911:
LDRD idea to Commercial product in 5 years

Augmentation of accumulated water processing facility (SARRY)

CSTs used in Cs^{+} cleanup of 160M+ gallons from seawater in Fukushima buildings

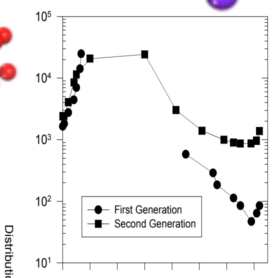
Example 1: Nanoporous Materials (Zeolites, Molecular Sieves & MOFs), Radiological Ion and Gas Capture

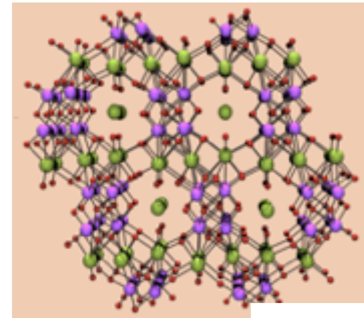




CST, Molecular Sieve:
R&D100 1996
JACerS, 2009, *92(9)*, 2144
JACerS, 2011, *94(9)*, 3053
Solvent Extr. & Ion Exch, 2012, *30*, 33

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



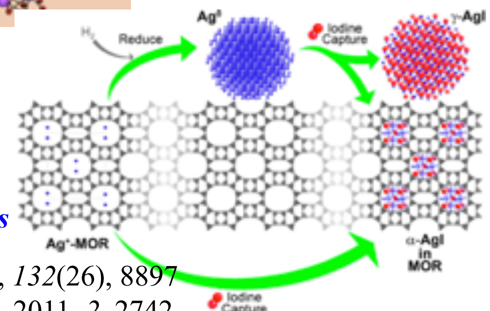


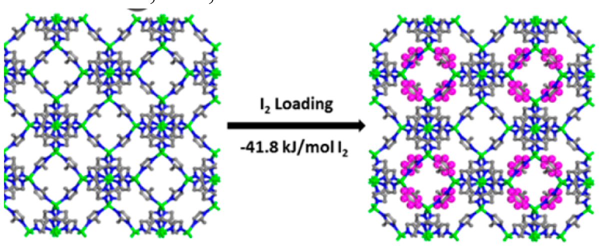
SOMS Molecular Sieve,
Sr^{2+} getter,
1-step to Perovksite WF
JACS, 2002,*124(3),* 1704
US Patent *7,122,164;* 2006

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

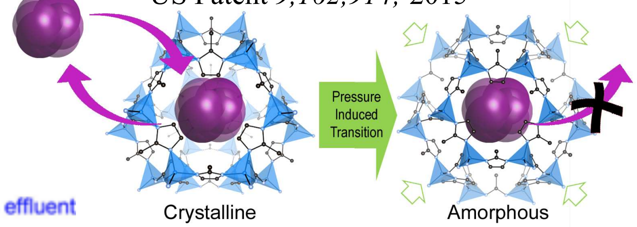
Design, Produce, Test and Commercialize Materials with Specific Selectivity to Ion/Gas by Size & Chemistry of Nanopore

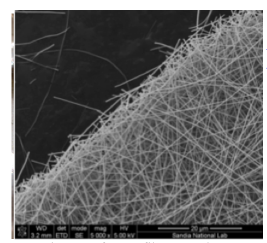
Ag-MOR Zeolite, *$I_2(g)$ capture & mechanisms*
JACS, 2010, *132*(26), 8897
JPC Letters, 2011, *2*, 2742



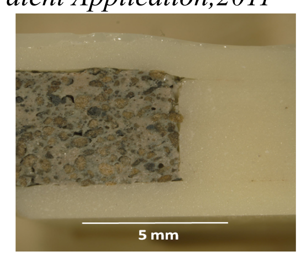


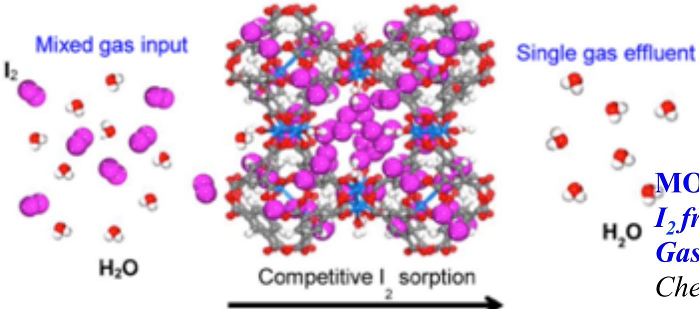
MOF *Amorphization for Gas Storage*
JACS, 2011,*133*(46),18583
US Patent *9,162,914;* 2015



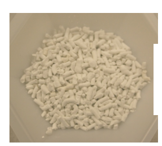


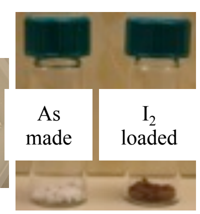
TiO_2 Nanoporous Nanofibers
Volatile Gas Removal
US Patent Application,2011





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





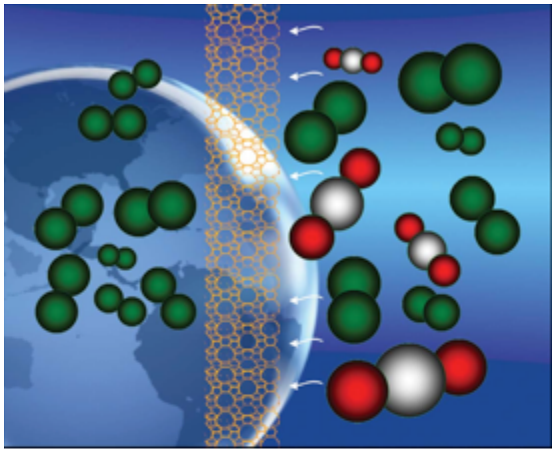
Binder Free* MOF *Pelletization
US Patent Pending 2014

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

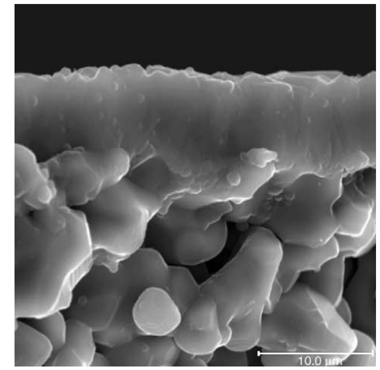
T. M. Nenoff, tmnenof@sandia.gov

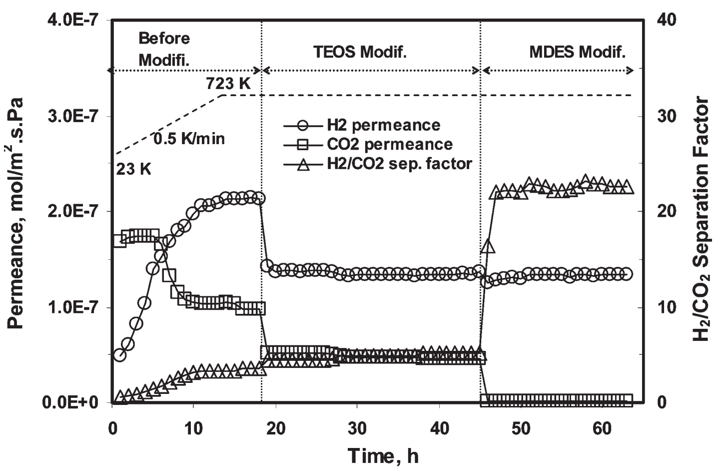
Example 2: Zeolite/MOF Membranes for Light Gas & Hydrocarbon Separations

H_2 Purification
Nature Mater., **2015**, *7*, 377; *Chem. Rev*. **2007**, *107*, 4078
MRS Bulletin, **2006**, 31(10), 735 (cover; Editor Nenoff)

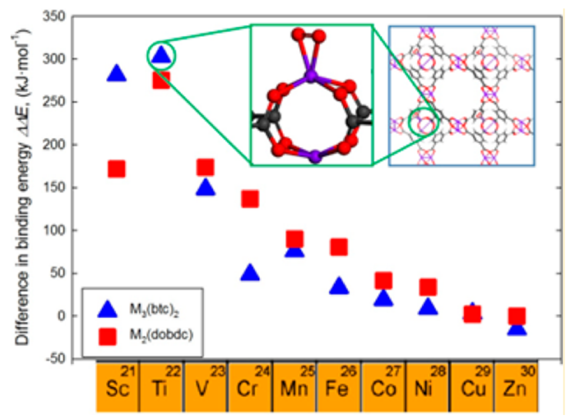


ZSM-5 Zeolite membrane for
H_2 from CO_2 separations
Micro Meso Mater, **2003**, *66*, 181



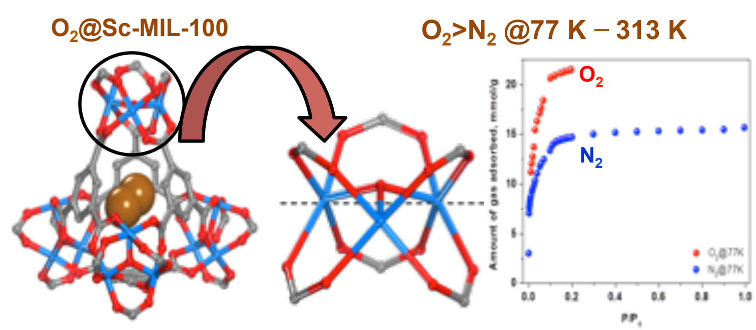


H_2 Purification from Syngas
Langmuir, **2009**, *25*(9), 4848



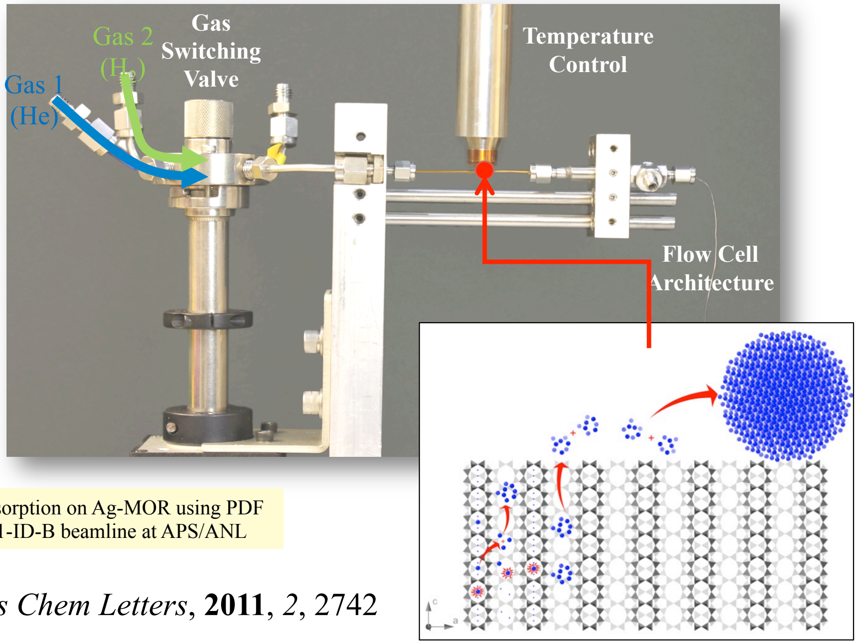
O_2 Separations with MOFs for
Energy Efficient Oxyfuel Combustion

Chem. Mater. **2016**, in press
Chemical Science **2016**, *18*, 11528
J. Phys. Chem. C, **2015**, *119*, 6556
Chem. Mater. **2015**, *27*(6), 2018



Example 3: Nanoporous Zeolites for Heterogenous Catalysis and Subsequent Gas Capture

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

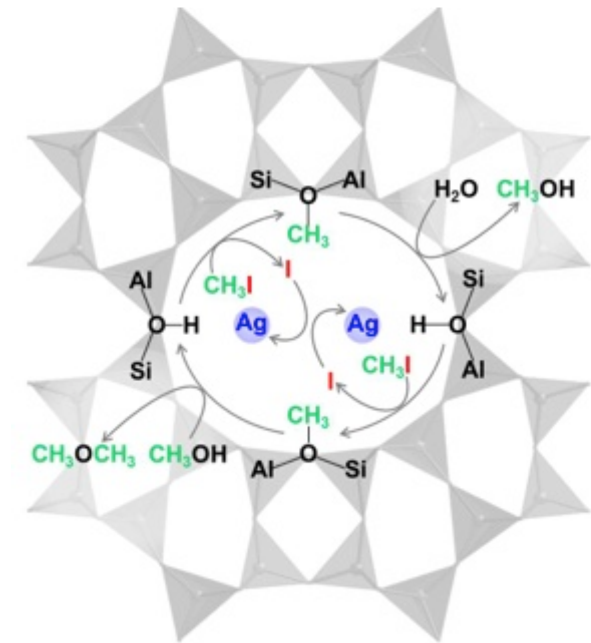


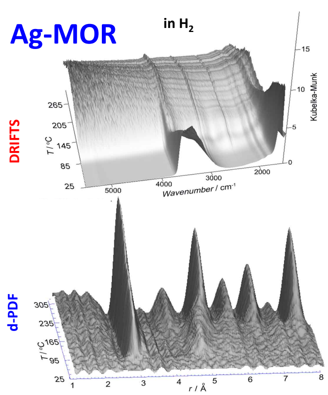
In situ I_2 sorption on Ag-MOR using PDF setup at 11-ID-B beamline at APS/ANL

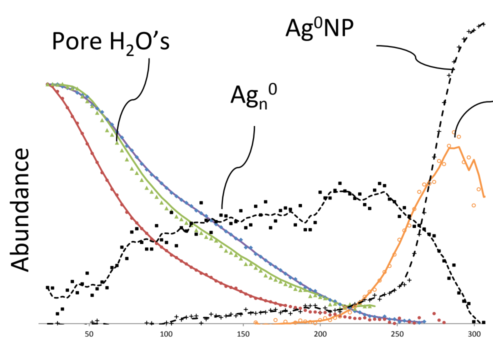
J Phys Chem Letters, **2011**, *2*, 2742

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)







Initial Data, Ag-MOR in H_2: Correlation identified between –OH surface functionalization and Ag migration to the outer surface of the MOR

On-going: Combining complementary insights from simultaneous IR and PDF.
For mechanism of NP catalyst formation

Chapman & Nenoff **2016**, in preparation