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# Structure-property Relationships in acid gas stable RE-MOFs and Zeolite supported nanoparticle catalysts

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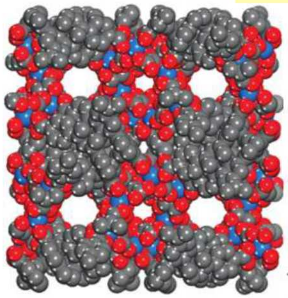
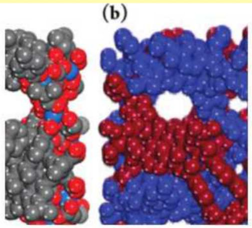
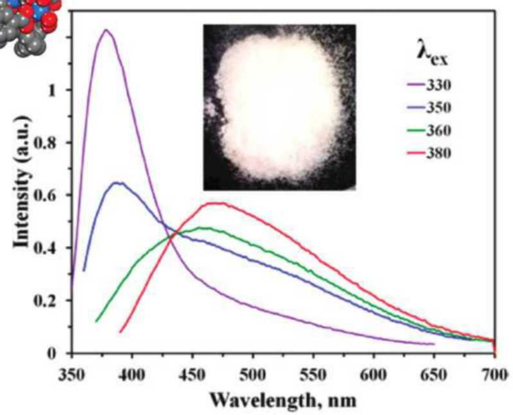
# RE-MOFs: Structure-Property relationships for Stability to acid gases

SMOF-1: white light emitter

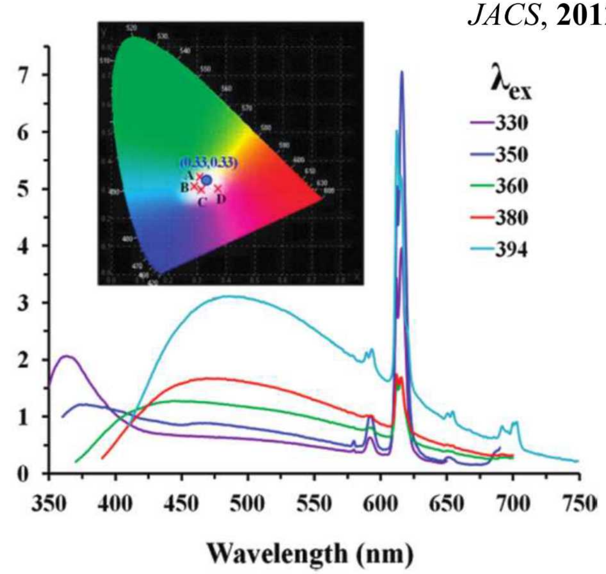
*JACS*, **2012**, *134*, 3983



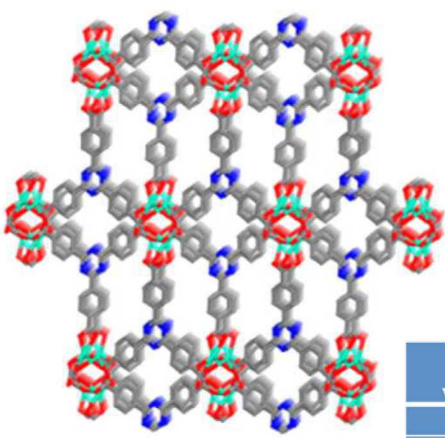



MOF tuned to "warm" white light

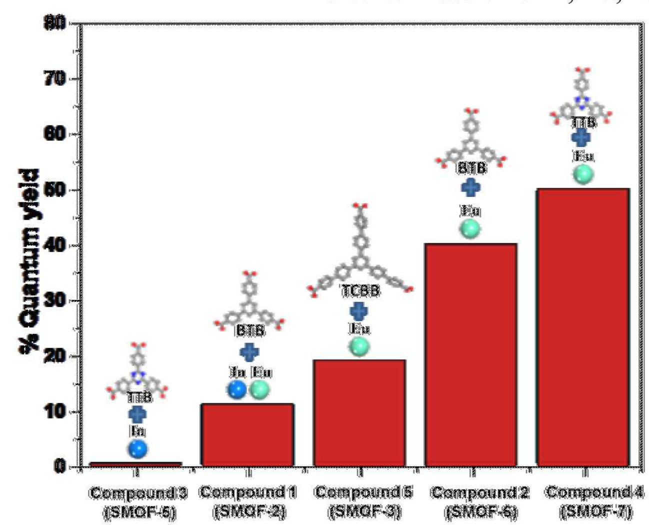



*Chem. Mater.* **2014**, *26*, 2943



SMOF-7: red light emitter, high quantum yield with thermal stability for OLED applications

| Excitation wavelength, nm | 25°C | 100°C | 150°C |
|---|---|---|---|
| 340 | 46% | 50% | 48% |
| 394 | 22% | 22.3% | 19% |

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# Rare Earth – MOFs
# PL & Acid Gas Durability

***Team of modelers, synthesis and characterization of zeolites and MOFs with caustic gases***

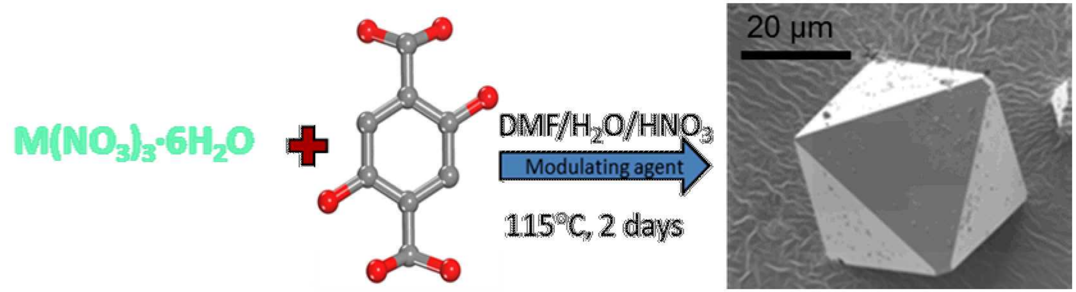
Goal: Investigate the structure-property relationship in a series of isostructural rare-earth MOF materials platform for NOx adsorption

- Probe the effect of metal ion identity in the adsorption/selectivity for NOx (Dorina Sava Gallis, **Grace Vincent, UNM undergrad (SNL))**
- Preliminary testing in house at SNL; Complementary modeling work for **Jon Vogel (SNL postdoc)**
- **Team with Ryan Lively (GeorgiaTech) for mixed gas testing and Katharine Page (ORNL) for characterization**

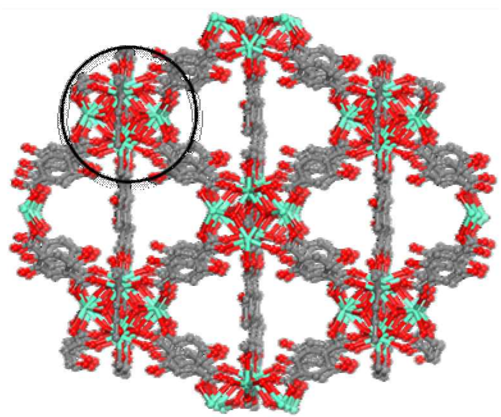
## Activities/Findings

- Preliminary tests indicate that the materials remain crystalline upon NOx exposure for 24 hrs
- XRD studies reveal noticeable peak shifts to the right in the higher two-theta region indicative of host-guest interactions
- Correlated and complimentary VASP modeling to describe MOF strength and acid gas binding energies.
- Refs for RE-MOFs:

Dalton Trans., 2016, 45, 928
Anal.Chem, 2013, 85,22,11020
ACS Appl Mater Inter. 2017, 9, 22268




$M_6(\mu_3\text{-}OH)_8(C_8H_4O_6)_5(C_2H_6O_6)_1(H_2O)_6\cdot 24H_2O$
M= Eu, Nd, Yb, Y, Tb and tuned compositions of Nd/Yb



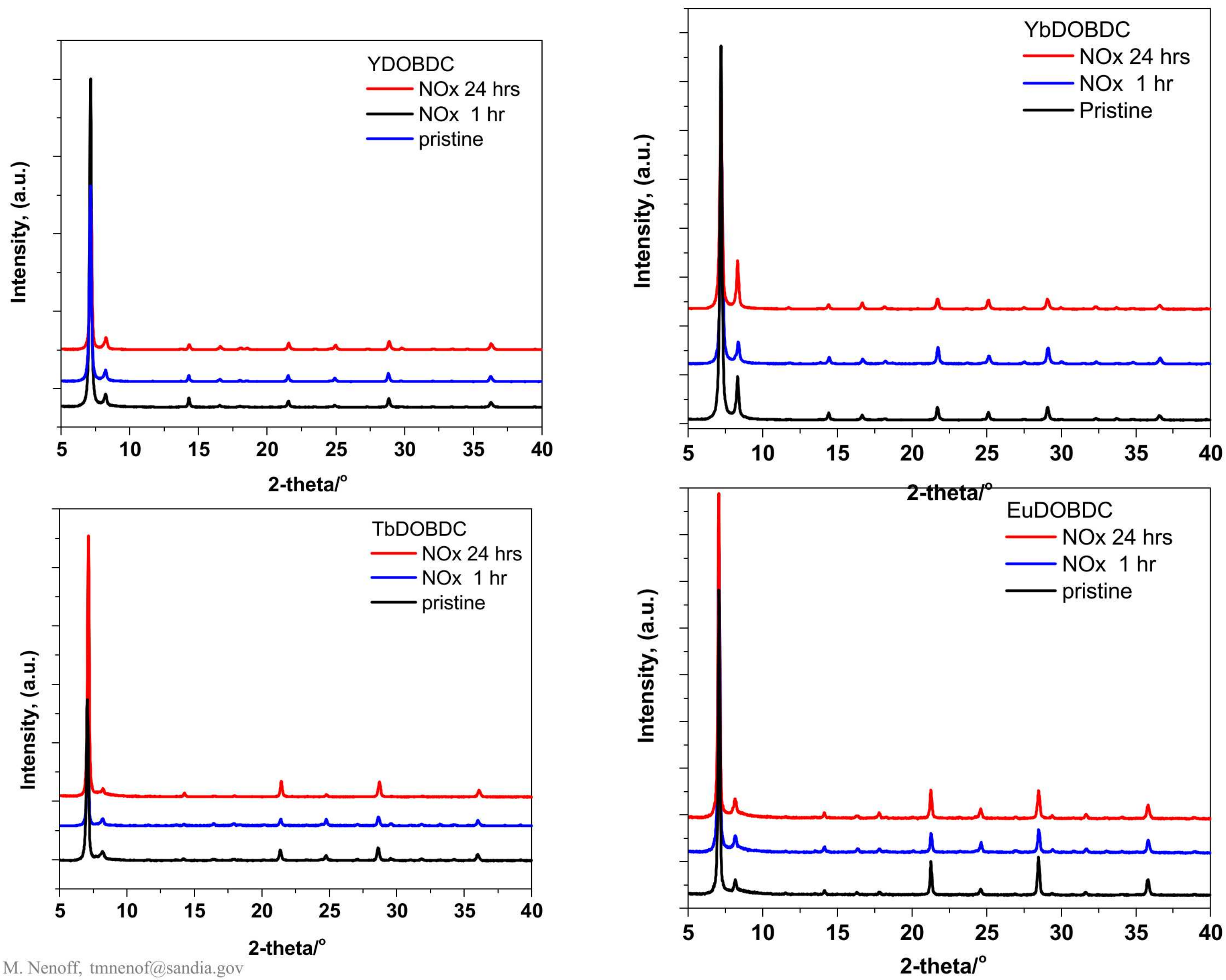
Rare Earth (RE) metals
8 Fold coordination, but unsaturated enables energetically favorable bonding of acid gases to metal center

# XRD pre- and post-$NO_x$ exposure in M-DOBDC M=Y, Yb, Tb, Eu

The NOx was generated in an adsorption chamber at room temperature

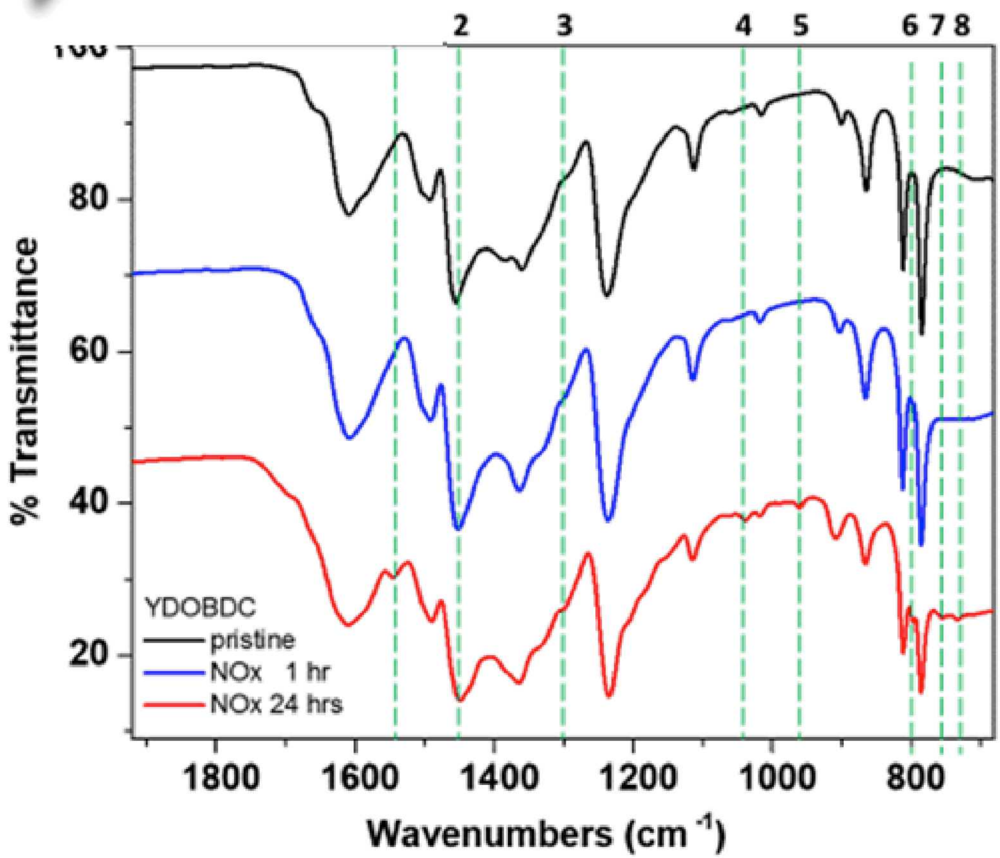
**1st step**: *Generation of nitrous acid via acidification with $H_2SO_4$*
$2\ NaNO_2 + H_2SO_4 \rightarrow 2\ HNO_2 + Na_2SO_4$

**2nd step**: *Nitrous acid decomposition*
$2\ HNO_2 \rightarrow NO_2 + NO + H_2O$




*No change in XRD patterns after 24 hr exposure*

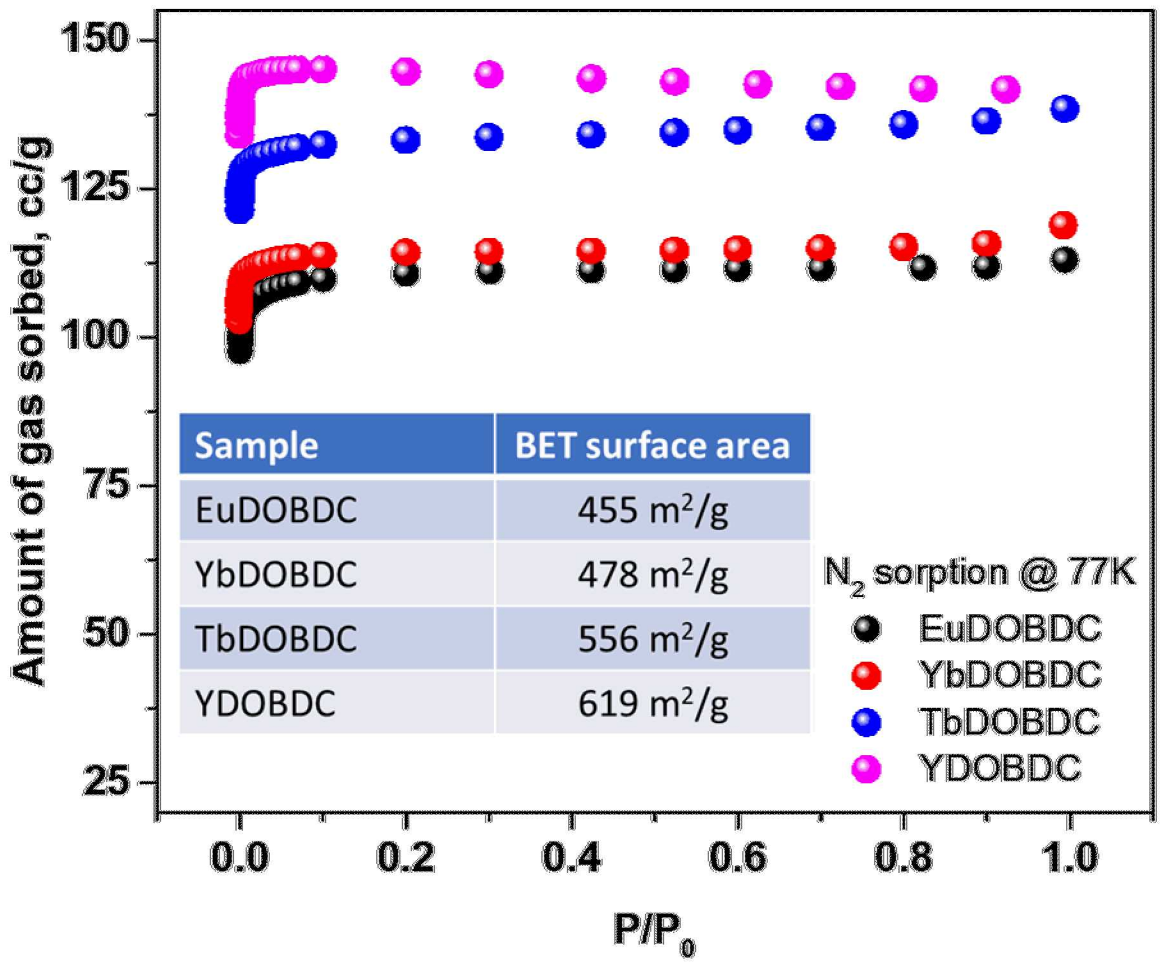
# IR data showing NOx species (new peaks, broader peaks, etc)




| Peak number | Wavenumber ($cm^{-1}$) | Peak assignment |
|---|---|---|
| 1 | 1544 | Asym. $NO_2$ stretching |
| 2 | 1489 | N=O stretching |
| 3 | 1297 | Asym. $NO_2$ stretching |
| 4 | 1037 | Sym. stretching $NO_2$ |
| 5 | 959 | TBD |
| 6 | 796 | N-O stretching |
| 7 | 755 | $NO_2$ bending |
| 8 | 732 | $NO_2$ bending |

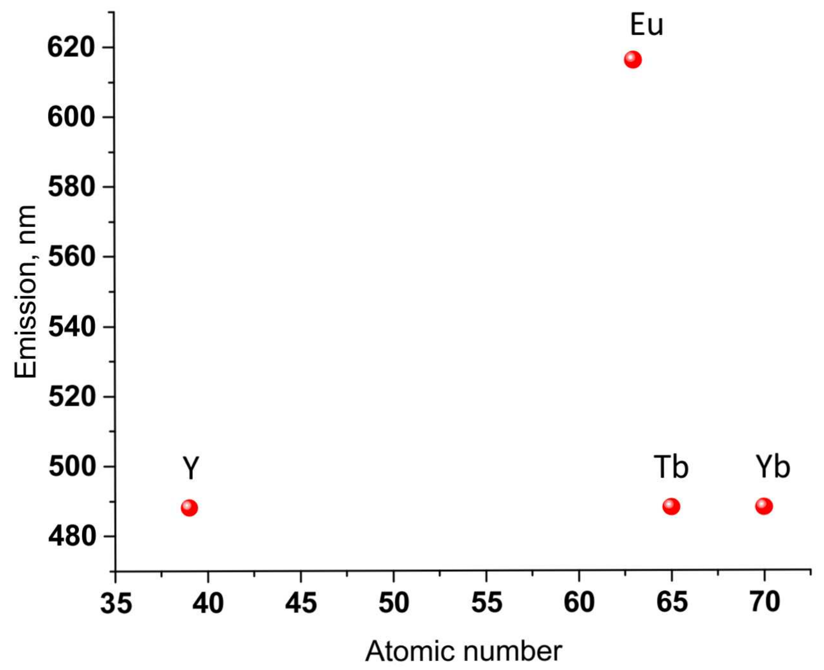
Peak assessments gathered from *Chem. Mater. 2017, 29, 4227*

# BET adsorption data confirming open porosity

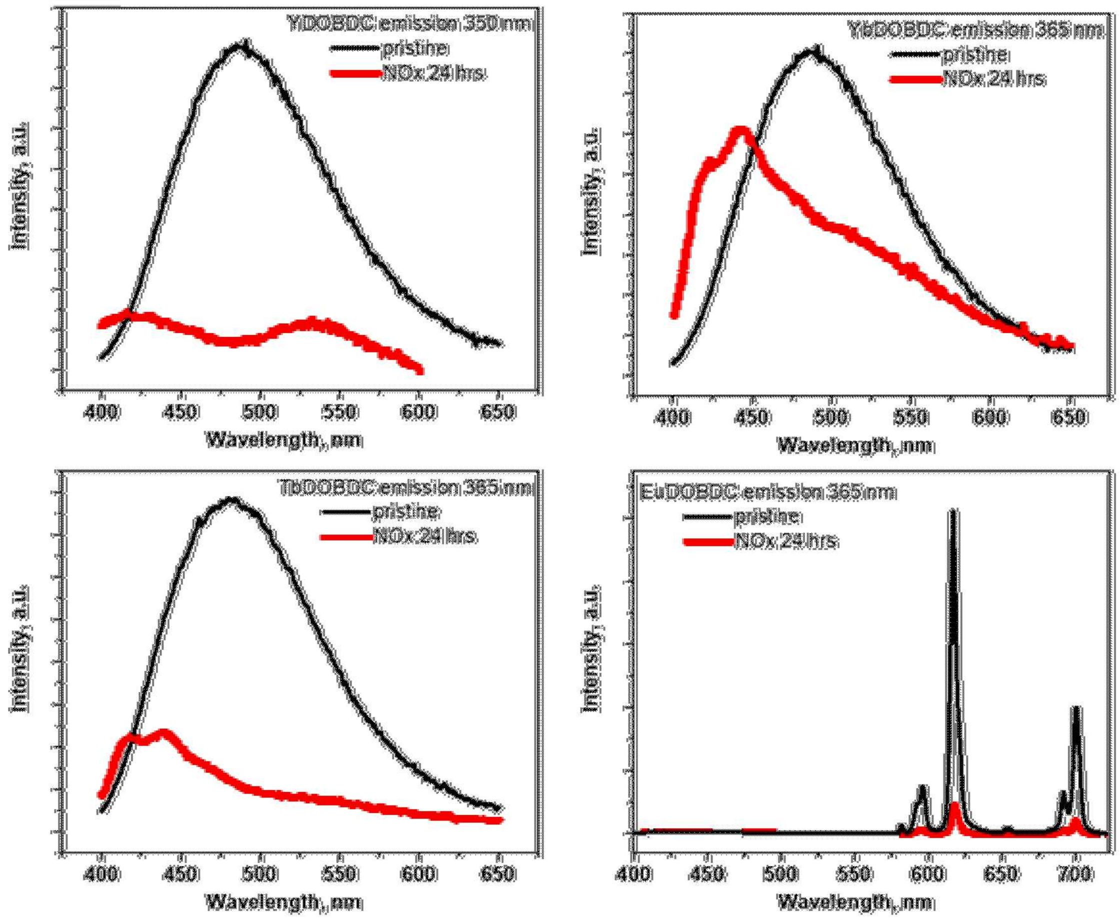



| Sample | BET surface area |
|---|---|
| EuDOBDC | 455 $m^2/g$ |
| YbDOBDC | 478 $m^2/g$ |
| TbDOBDC | 556 $m^2/g$ |
| YDOBDC | 619 $m^2/g$ |

# Element atomic number vs. emission

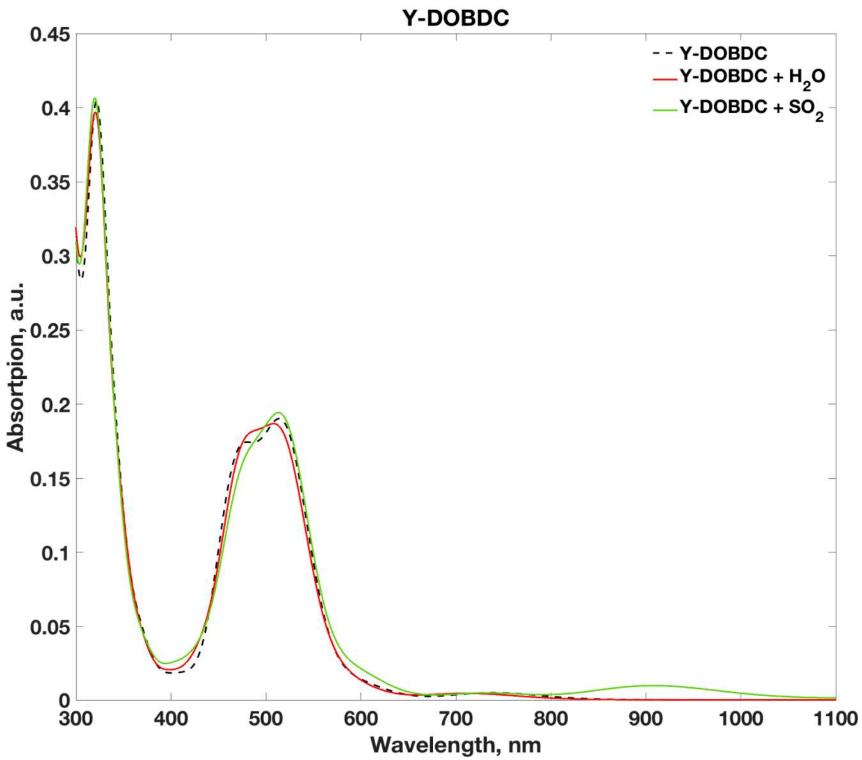


# Emission data per unique metal centers, only Eu has metal emission transitions

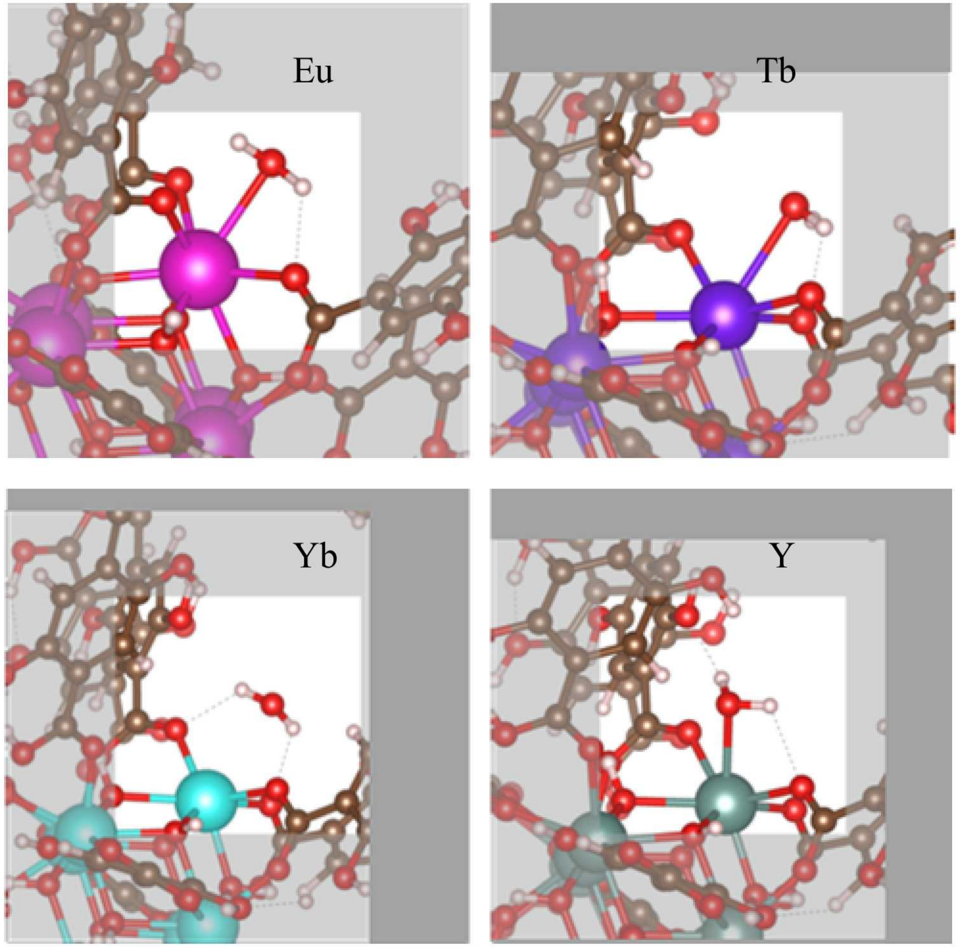


# Preliminary modeled emissions for M-DOBDC with $SO_2$ adsorbed, with $H_2O$ adsorbed

*See Jon Vogel's poster*




Optical emissions modeled
Pre- and post adsorption of $SO_2$




Ligand reorganization:
Optimized $H_2O$ gas interactions with metal centers

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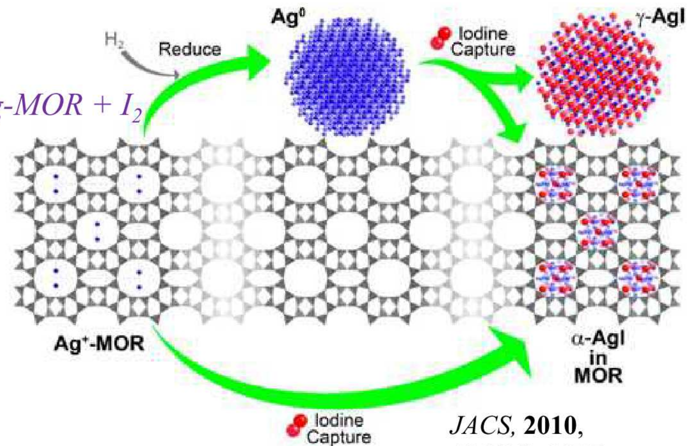
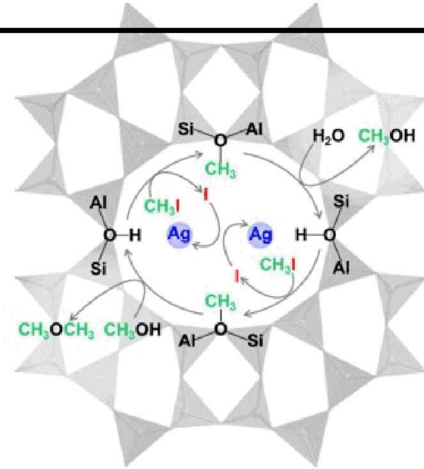
# Supported Nanoparticle Catalysts: Formation and Characterization

## *I. Chemical loading, reduction and activity*

*Ag-MOR + $I_2$*




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

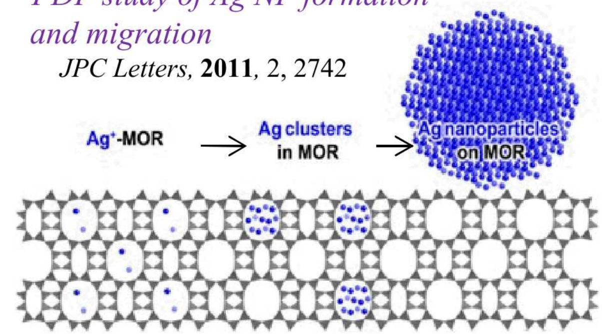



*Ag-MOR + $CH_3$-I*

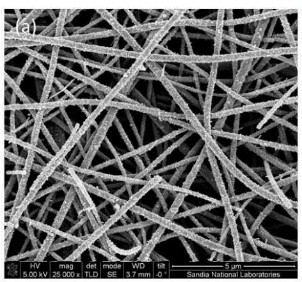
*MMM,* **2014**, *200*, 297

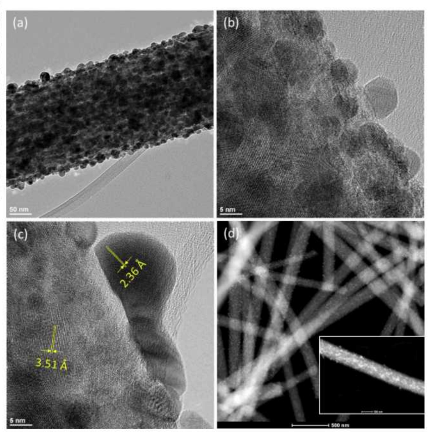
*PDF study of Ag NP formation and migration*

*JPC Letters*, **2011**, 2, 2742




## *III. Radiolysis for the generation of $e^-_{aq}$, Chem reduction of metal salts NPs, free standing or supported*



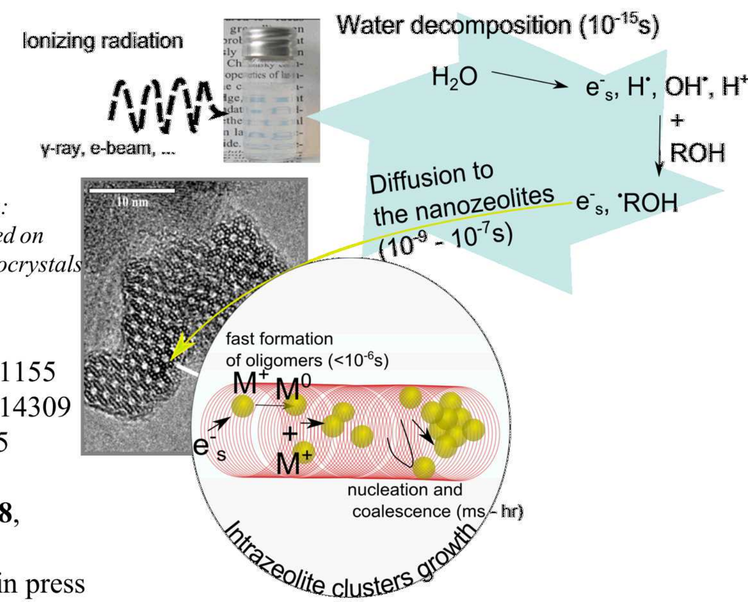

## *II. Electrospun*

*nonwoven $TiO_2$ crystalline mesoscale fibers & Ag. $Ag^+$ spun, NPs reduced both in nanopores and on nanofibers. Also AgI, and ZIF-8 NPs.*

Patent pending, 2019

SAND2012-8025

*Pulse Radiolysis: Ag NPs supported on BEA zeolite nanocrystals*




*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
**Invited Review:** *JPCC*, **2018**, *122*(24), 12573
*Nanoscale Advances*, **2019,** in press

# Materials Thrust 1 Project: In-situ PDF/IR studies of the formation of zeolite-supported *nanoparticle* catalysts. Tina Nenoff, SNL, Monthly Report

**Summary of Activities:** ***Zeolite supported Ag nanoparticles: synthesis & characterization. Leveraged with GENESIS EFRC (K. W. Chapman) for in-situ simultaneous PDF/IR structural studies of mechanism and kinetics of NP formation.***

- Controlling the size and shape of nanoparticles is key to controlling their functional behavior. Functionality can deviate significantly from bulk materials properties such as in catalytic, optical, electronic behaviors.
- Understanding how the size and structure of NPs evolve during synthesis and how they are influenced by a support is critically important for optimization of their activity.
- Determining the mechanisms of NP formation with respect to occluded water & temperature. Plus transport properties of the NPs in pores.

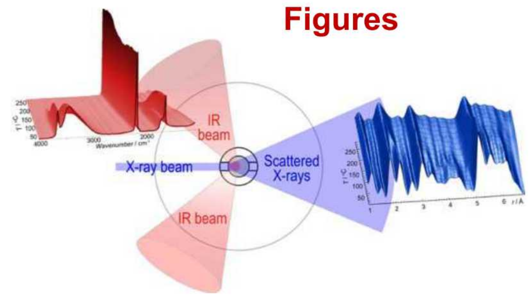
## Activities- On going

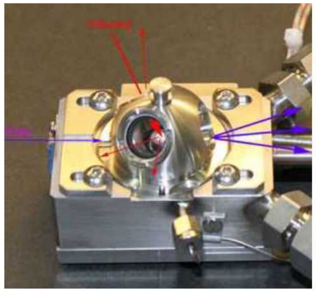
• (**FAU/Y, MOR, A**) zeolites of varying:
- Poe size
- Pore topology
- Si/Al ratio

• NP formation either in reforming stream ($H_2$/He) or autocatalytic (He)

• Monitor Ag nanoparticles Formation: address the
- role of water and dehydration of occluded pore waters on NP phase (AgO vs Ag)
- transport/location in zeolite,
- mechanism from ion to cluster to NP

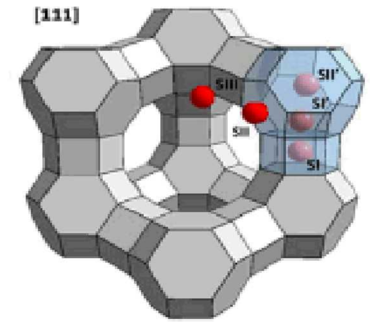
## Figures

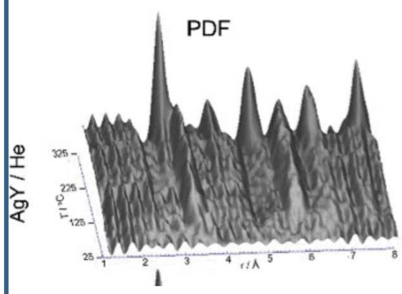


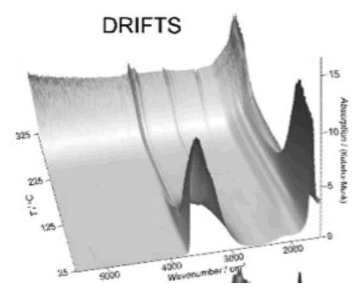



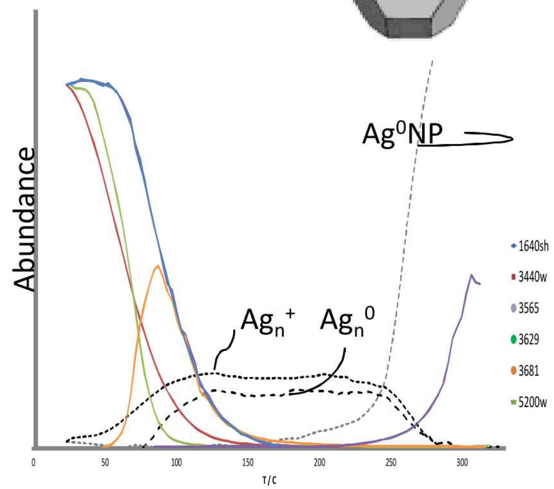
*DRIAD-X: Diffuse Reflectance Infrared Angular Dispersive X-ray Studies*

AgY Autoreduction (He stream)



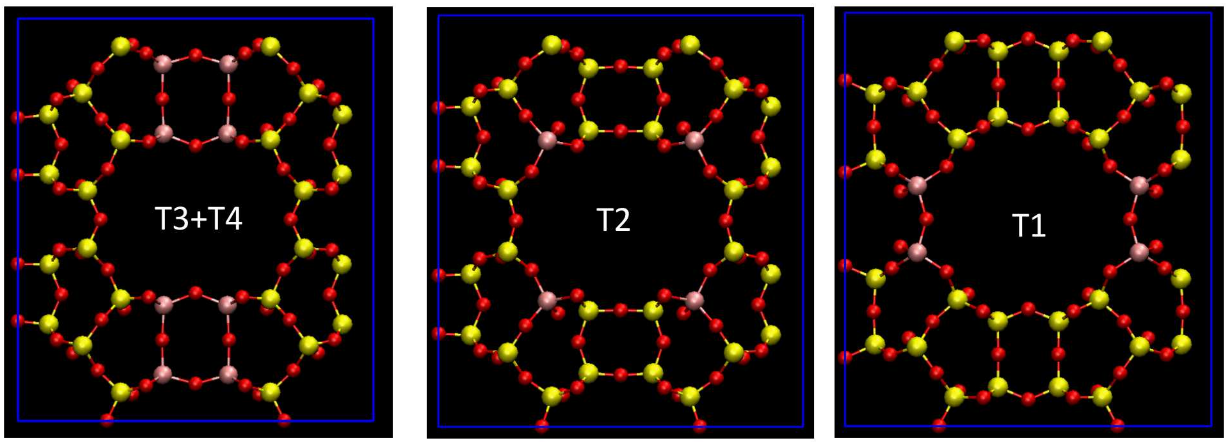



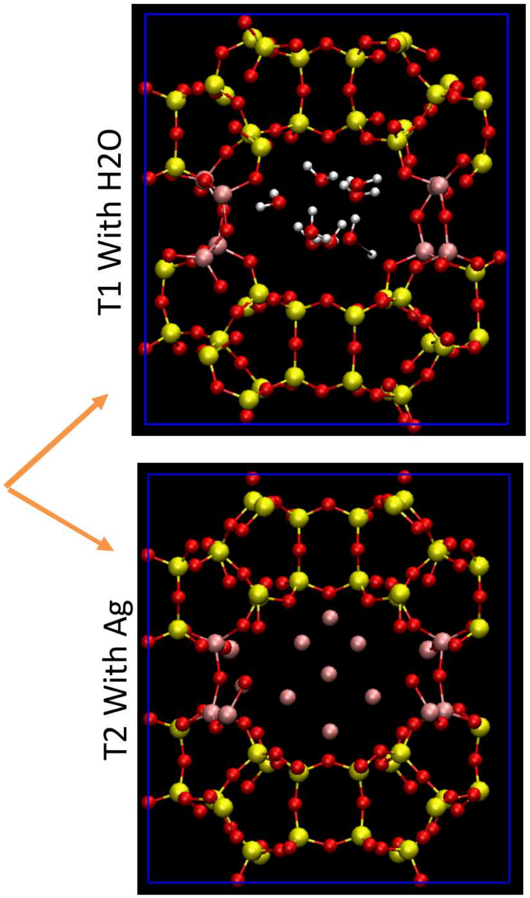
# Modeling of $Ag^+$ nanoparticles in zeolites to support experimental findings

Jessica Rimsza, SNL

Structure:
- Mordenite (MOR) framework
- Si/Al ratio = 5
- Energetics of Ag+ formation in main channel and side pocket




Snapshots of MOR framework structures with Al in four different tetrahedral locations (T1, T2, and T3+T4). Colors: silicon (yellow), oxygen (red), and aluminum (pink)




Computational Methods:
- Vienna *ab initio* Simulation Program (VASP)
- Periodic electronic structure calculations
- Methfessel-Paxton scheme with smearing of 0.1eV
- Gamma k-point sampling, 500eV energy cut-off

# *Broader Question*: Does Dehydration play a role in Ag-Zeolite nanoparticle formation?

***PDF + DRIFTS provides both complimentary methods***

X-ray see heavy species well (Ag) but not the surface molecules ($H_2O$, OH, etc) that control the surface chemistries of the zeolites:

**Ag nanoparticle formation induced by:** Reduction or Dehydration?

**Experiment:**

Variable temperature PDF + DRIFTS studies in reducing & inert atmosphere

- Three zeolites of differing framework and pores structure, and Si/Al ratio
- Heat 25 - 330$^{o}$C while collecting data
- Monitor NP formation with transitions in water/hydroxides bonding & presence in zeolite
- Determine most important parameters & mechanisms

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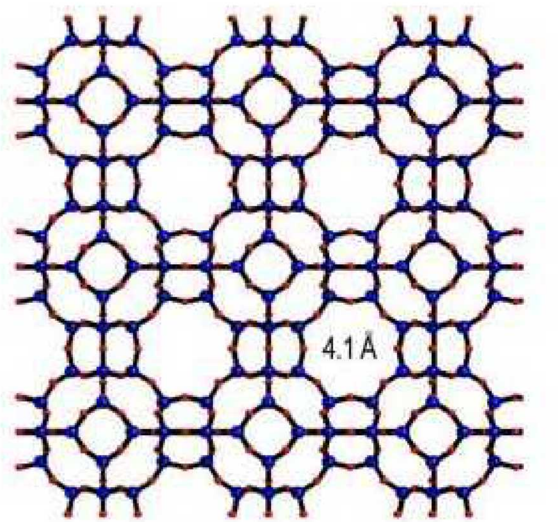
# Tuning the reaction environment in other zeolites

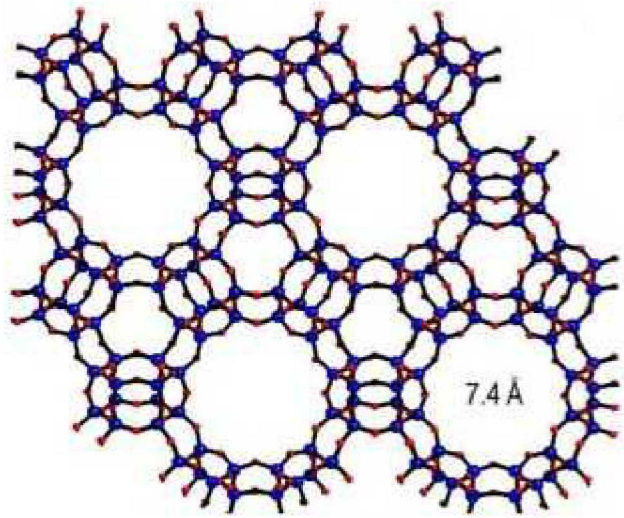



LTA (A)

Si/Al = 1

Most $Ag^+$
/surface -OH

Small pores only

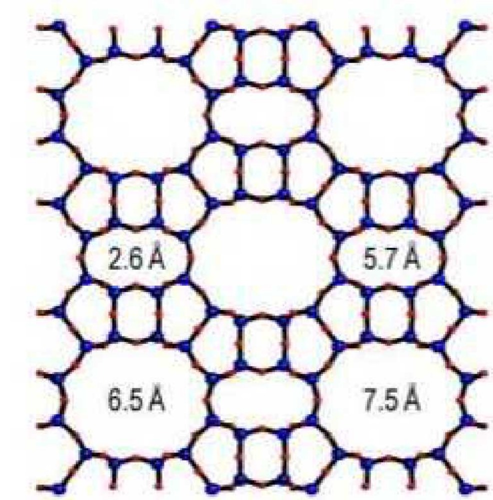



FAU (Y)

Si/Al = 2.4

Intermediate $Ag^+$
/surface -OH

Large pores




MOR

Si/Al = 5

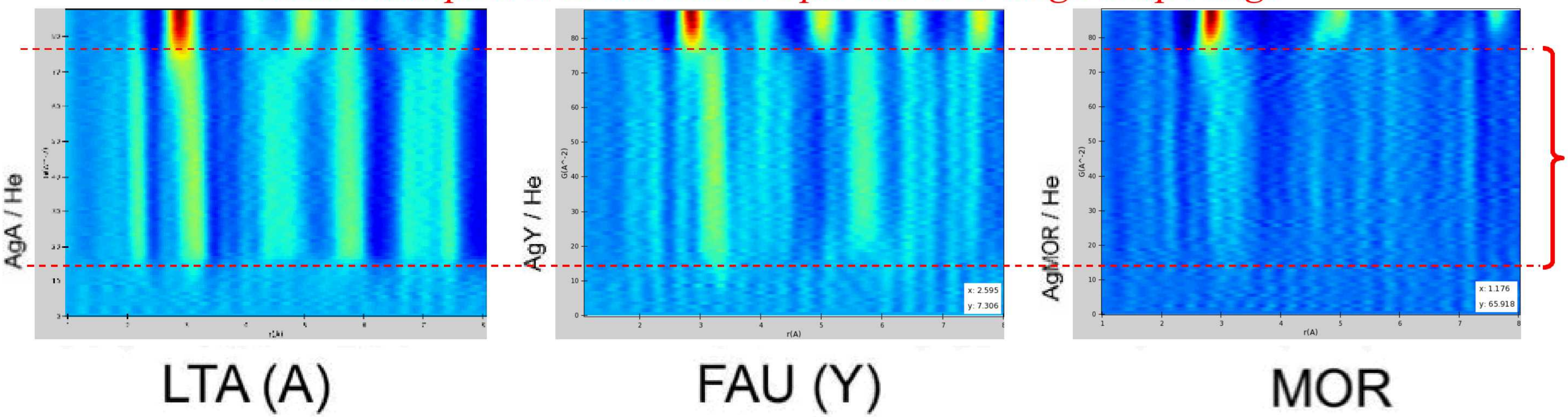
Least $Ag^+$
/surface -OH

Large & small pores

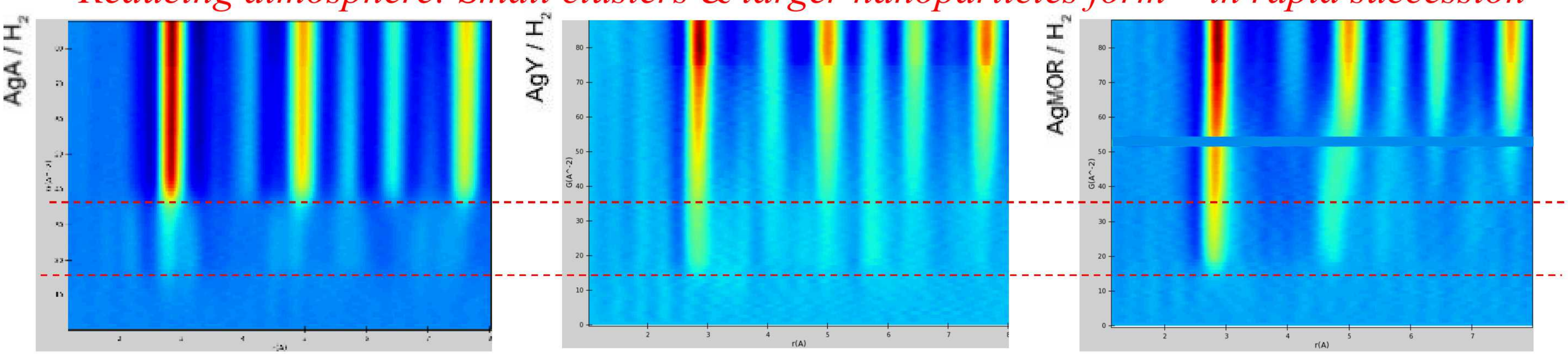
# Nanoparticle formation pathway varies widely

Different onset temperatures, stability window for Ag clusters, final NP size

*Inert atmosphere: Small clusters persist over large temp range*




*Reducing atmosphere: Small clusters & larger nanoparticles form ~ in rapid succession*

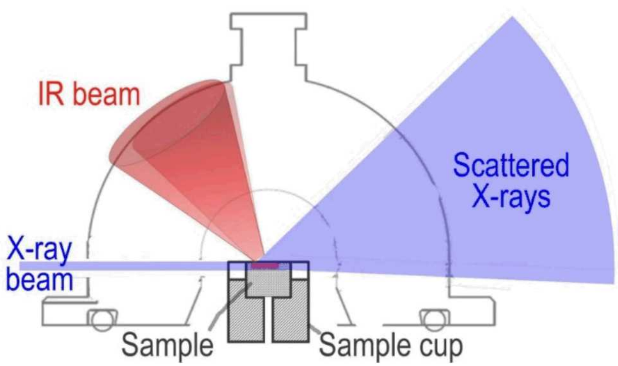


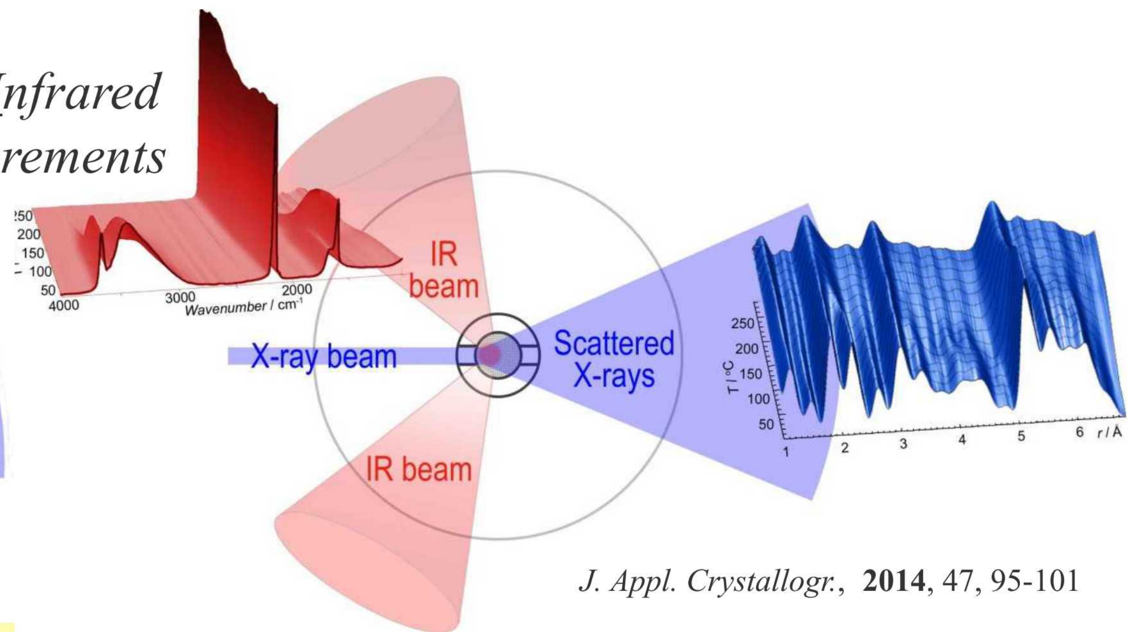
# Filling in the missing pieces - PDF$^+$
## *Complementary insights from multimodal measurements*

*What role does dehydration play in the Ag nanoparticle formation?*

- The PDF signal is dominated by high Z species
- Complementary, compatible infra-red spectroscopy is sensitive surface species ($H_2O$/OH)

*DRIAD-X: Diffuse Reflectance Infrared Angular Dispersive X-ray Measurements*




*J. Appl. Crystallogr.*, **2014**, 47, 95-101

In collaboration with
Prof. Karena Chapman, Stonybrook
GENESIS EFRC

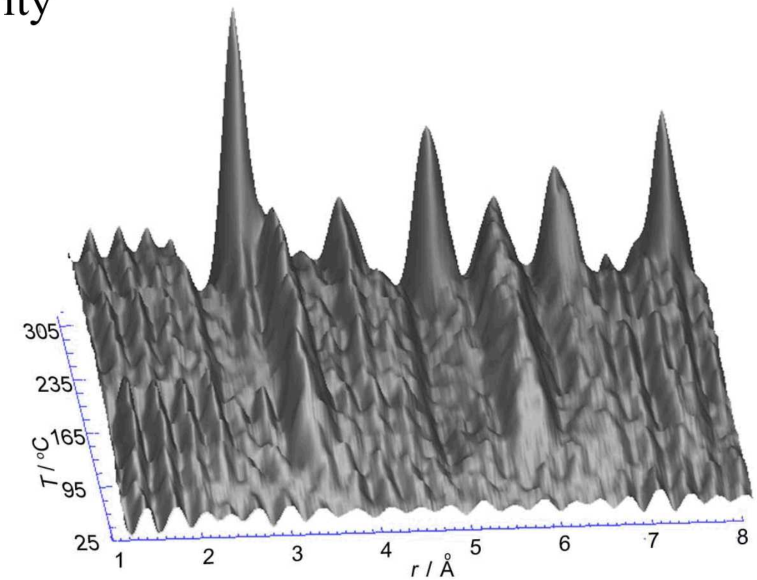
# New approaches to quantify chemical reactivity

*Operando PDF*

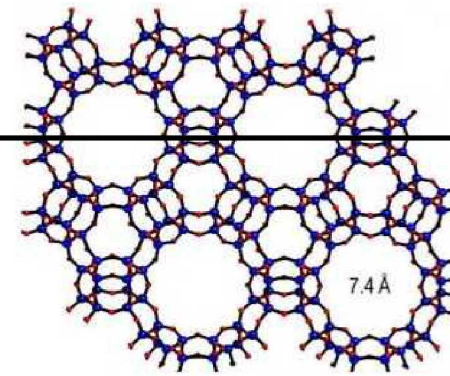
- Captures entire reaction
- Provides detailed structure mechanism and quantitative kinetics

*Multimodal measurements (PDF+IR)*

- Provides enhanced chemical insight & sensitivity
- Because a singular sample is being probed simultaneously, data can be compared directly without offsets associated with different sample environments

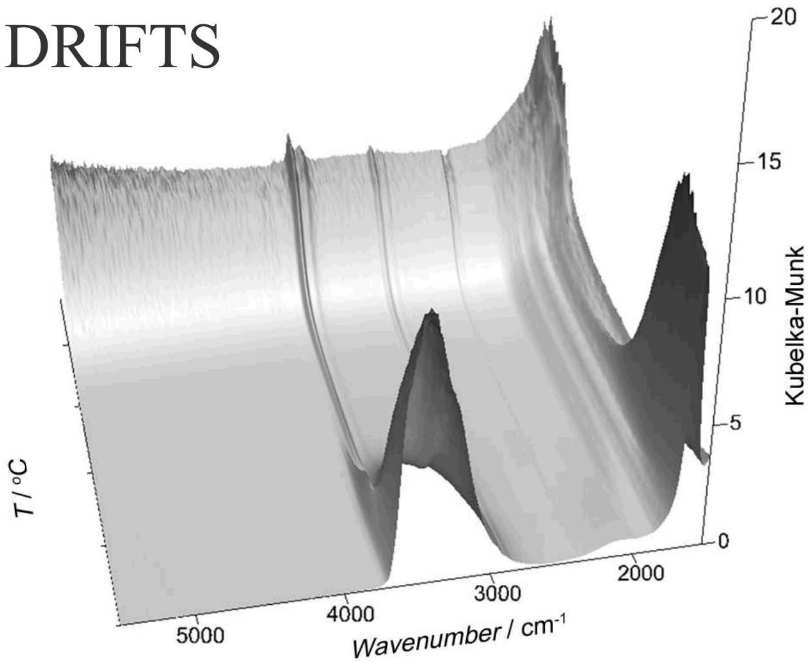


# Example of AgY Autoreduction



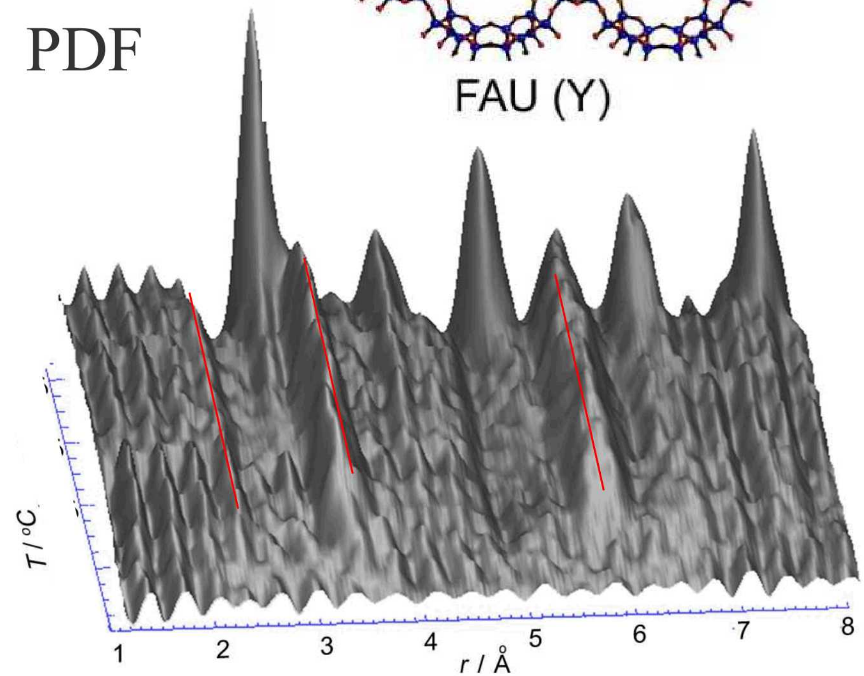

FAU (Y)

## DRIFTS




1) $H_2O$, OH stretches eliminated, then
2) Reflectivity decreases

## PDF

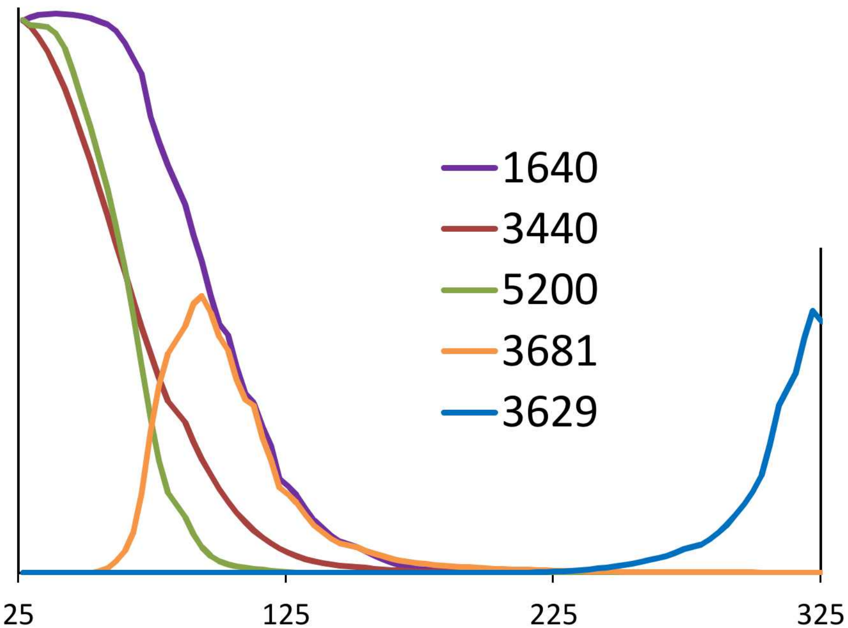



1) nm scale $Ag_2O$ nanoparticle intermediate
2) Larger Ag nanoparticles

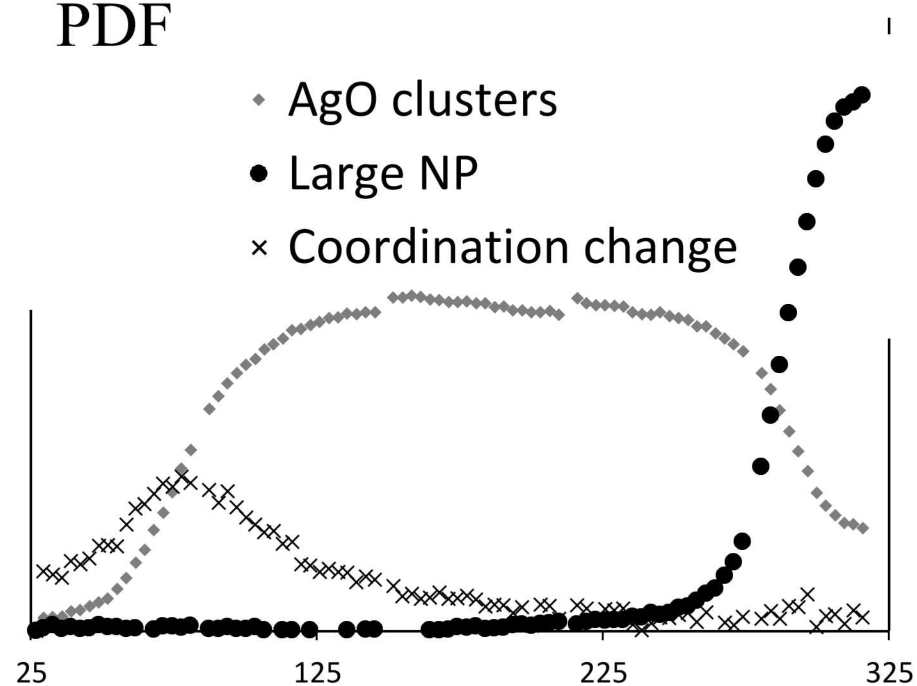
# Correlating surface chemistry & NP formation

## Surface chemistry governs cluster mobility and aggregation

DRIFTS



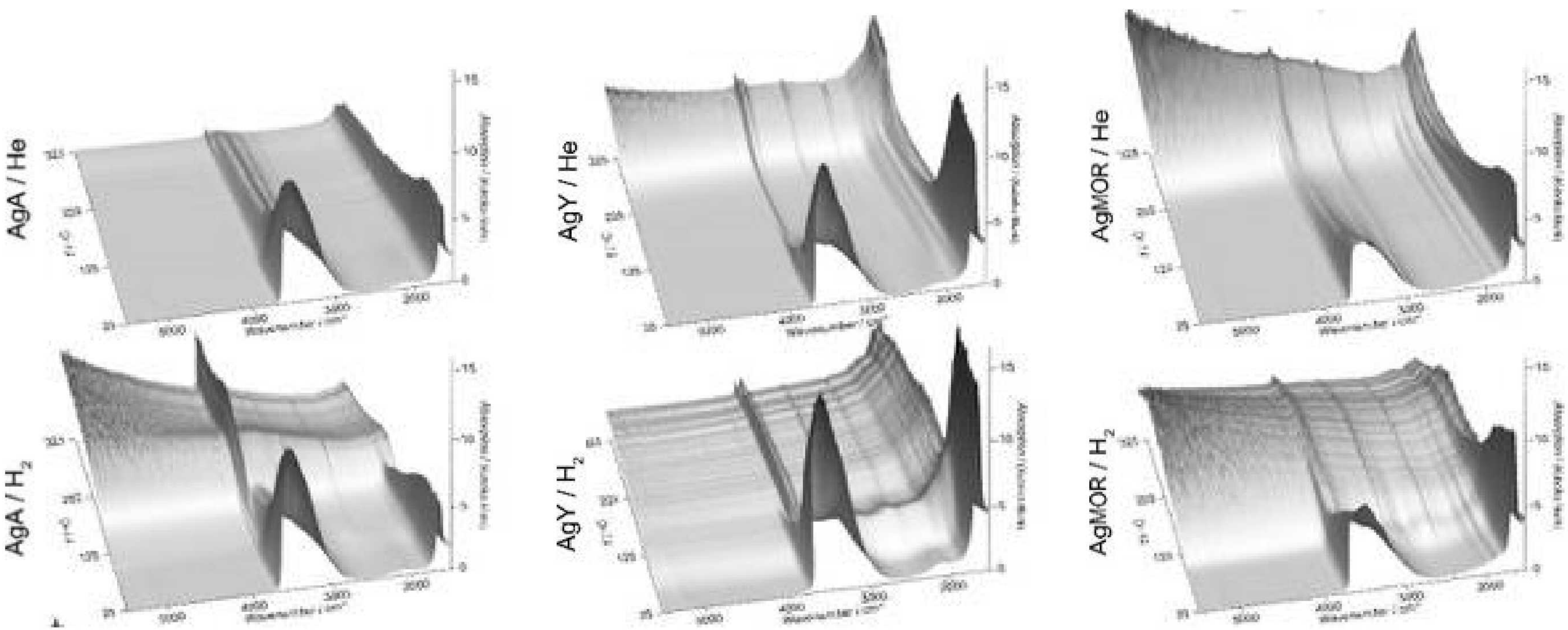

PDF




Thermal formation of small clusters (coinciding with $H_2O$ loss)
In a reducing environmental, no formation of oxide

# DRIFTS shows water and surface OH species

Loss of water and hydroxyl species evident in DRIFTS. Increasing baseline



# Highlights and Goals

**Highlights from first 6 months:**

1) New start in EFRC, hired 1 postdoc (modeling) and 1 undergrad (synthesis) who have already started on project, offer out and accepted for another postdoc (synthesis/characterization of zeolites and MOFs)

2) Proof of structural stability of Sandia La-DOBDC MOFs to NOx acid gas, supported by materials characterization (PXRD, IR, TGA-MS)

3) Collected structural and IR data at APS/ANL on catalytic Ag-zeolites (Fau(Y), Mordenite (MOR), Zeolite A) over temp range of RT-500K, analysis underway of correlations of dehydration of occluded pore water molecules and cluster/nanoparticle formation

**Future Goals (Next 12 months):**

1) Mixed caustic gas studies of RE-MOF series, adsorption (at GA Tech) and structural analysis (at SNS/ORNL), publish 2 papers

2) Successfully establish relationships between zeolites, temperature, nanoparticle formation mechanisms & mobility kinetics, publish 1 paper

3) Design next generation caustic gas stable RE-MOFs from DFT/AIMD modeling predictions, associated synthesis, characterization and testing (1-2 papers)

# Publications & Presentations FY19, to date

Pubs

| Title | Journal | Author(s) | Vol. | Iss. | Pub. Date | Page #'s | DOI | Status |
|---|---|---|---|---|---|---|---|---|
| **Iodine detection on Ag-Mordenite based sensors: Charge Conduction pathway determinations** | Micro. Meso. Mater. | Small, L.; Krumhansl, J.L.; Rademacher, D.X.; Nenoff, T.M. | 280 | | 2019 | 82-87 | 10.1016/j.micromeso.2019.01.051 | |
| **Synthesis of Rare Earth Nanostructures using In-situ Liquid Cell Transmission Electron Microscopy** | Nanoscale Advances | Taylor, C.A.; Nenoff, T. M.; Pratt, S.H.; Hattar, K. | | | | | | Submitted |
| **Uncovering the structural properties of catalytic silver clusters and nanoparticles confined in zeolites** | | Chapman, K. W.; Nenoff, T. M. | | | | | | In Preparation |
| **Adsorptive Capture of Caustic Gases in Robust Metal-organic Framework Materials** | | Zhang, X.; Nenoff, T.M.; Yang, S.; Schröder | | | | | | In preparation |

Pres

| Title | Conference Name | Author(s) | Date | Location | Comment (keynote, session chair, etc) |
|---|---|---|---|---|---|
| **Nanoparticles and Zeolites for Energy and Environmental Applications** | Univ. FL, Material science and Nuclear Engineering Dept | Tina M. Nenoff, Leo J. Small,* Karena W. Chapman, Peter J. Chupas | 10/02/18 | Gainesville, FL | Invited Speaker |
| **Direct Electrical Detection of Target Gases by a Novel Metal Organic Framework (MOF) Based Sensor** | MOF2018 | Tina M. Nenoff, Leo J. Small, Sihai Yang, Martin Schröder | 12/11/18 | Auckland, New Zealand | Keynote lecture |
| **Structure-property Relationships in Nanoporous Inorganic Frameworks: How the Pore Determines the Bulk Scale Energy & Environmental Applications** | SNS/ORNL Seminar Series | Tina M. Nenoff,* Dorina Sava Gallis, Grace Vincent, Karena W. Chapman, Luke Daemon | 3/12/19 | Oak Ridge, TN, USA | Invited Speaker |
| **Nanoscale manipulation of metal organic frameworks for tuned energy and environmental applications** | Aminoff Symposium, Swedish Academy of Sciences | Tina M. Nenoff, Dorina Sava Gallis, Grace Vincent, D. Jon Vogel, Jessica Rimsza, Karena W. Chapman | 4/1/19 | Stockholm, Sweden | Invited Speaker |

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# Questions? / Thank you