SAND2016-2464C

Study of Nanoparticle Formation in Zeolites Using Simultaneous Pair Distribution Function & Infrared Spectroscopy Measurements

Tina M. Nenoff,[1] H. Zhao[2,3], K.A. Beyer[2], M. A. Newton[4], K.W. Chapman[2], P.J. Chupas[2]

[1] Sandia National Laboratories, Nanoscale Sciences Department, Albuquerque, NM 87185, USA; tmnenof@sandia.gov

[2] Argonne National Laboratory, X-ray Science Division, Advanced Photon Source, Argonne, Illinois, 60439, USA

[3] University of Idaho, Chemical & Materials Engineering, Idaho Falls, ID, 83402, USA

[4] European Synchrotron Radiation Facility 6, Rue Jules Horowitz, BP-220, Grenoble, F-38043, France

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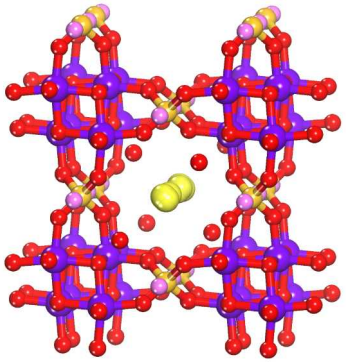
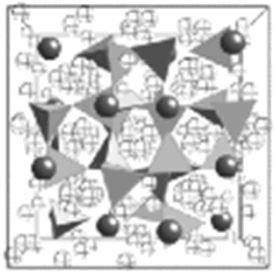
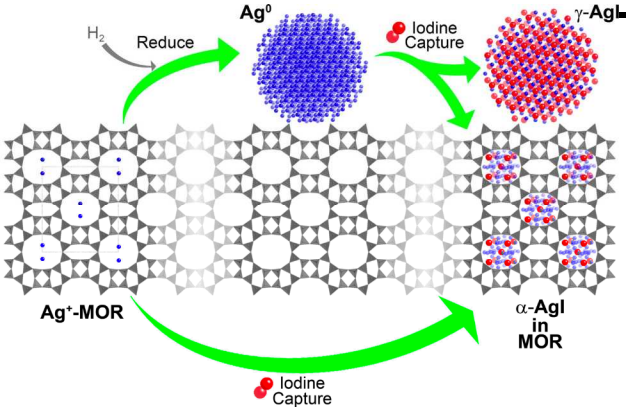
Introduction: Environmental & Energy Applications of Zeolites





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

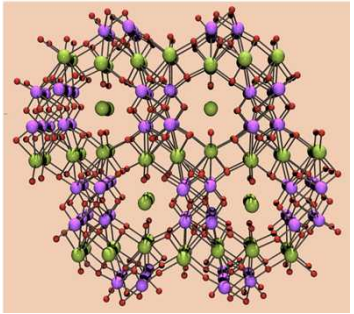
CST, Cs^+ removal from water to Pollucite Waste Form

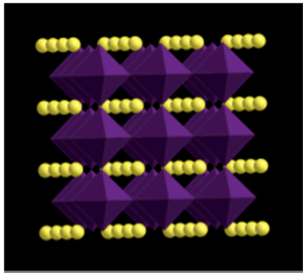


Ag-MOR I_2(g) capture & mechanisms

JACS, **2010**, *132*(26), 8897
J Phys Chem Letters, **2011**, *2*, 2742

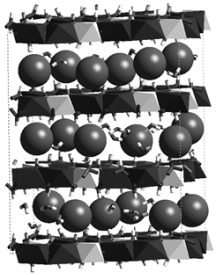
Fundamental Research to Applied to Commercial Products
Design the Separation Material To Develop the Waste Form

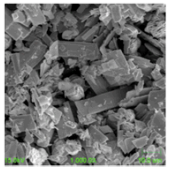




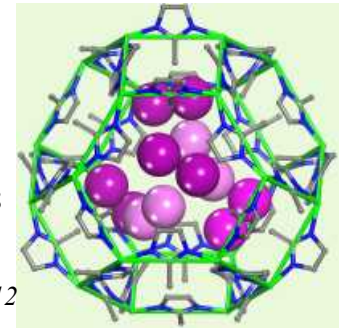
Sr^{2+} getter, 1-step to Perovksite waste form
JACS, **2002**,*124(3),* 1704

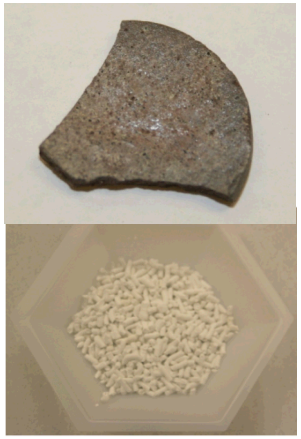
Applied Geochem, **2011**, *26*, 57



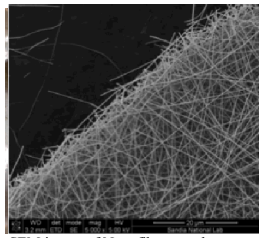


In-situ Iodine removal from water

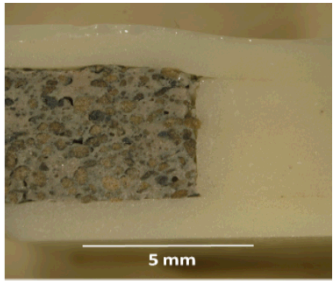




I_2/MOF, Isolation to Waste Form
JACS, **2011**,*133(32),*12398
Ind.Eng.Chem.Res, **2012**, *51*(2),614
US Patent Application, 2012



Nanoporous Nanofibers Volatile Gas Removal
US Patent Application, 2011



Universal Core-Shell Glass Waste Form Iodine & Getter
JACerS, **2011**, *94*(8), 2412

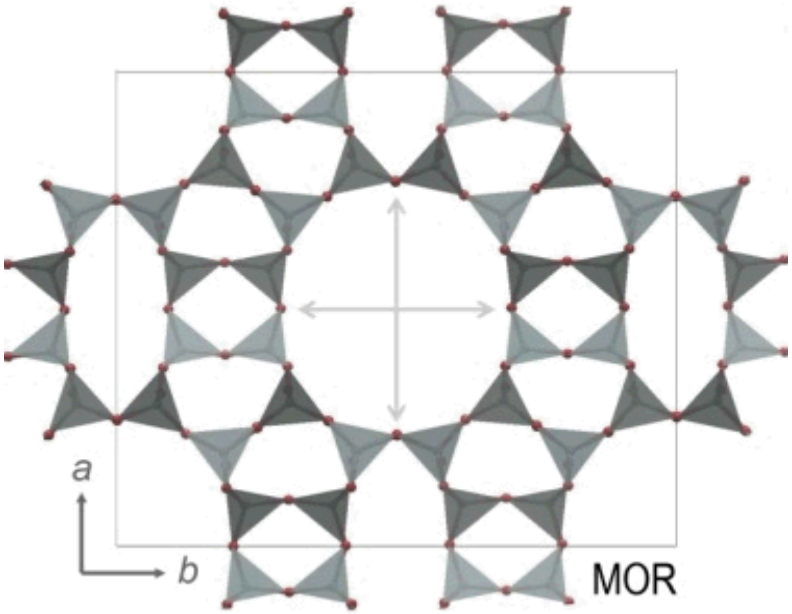
Zeolite System of Interest: Silver Mordenite

- Si:Al=5
- Ag-exchanged then reduced to Ag° (3% H_2 reducing stream)

Pore network:

- 12-member ring channels along c-direction (~7.0 x 6.5Å)
- 8-member ring pores

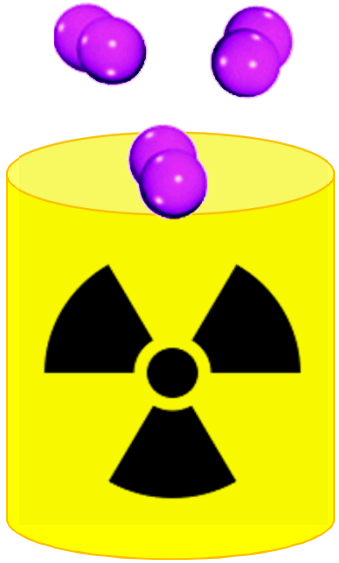
- Applications in *radioiodine* capture and *catalysis* (e.g. NO_x)



$Ag_2Al_2Si_{10}O_{24}•7(H_2O)$

12 MR, 7.0 x 6.5Å

Example Target Radiological Gas: Iodine (I_2, HI, Org-I)



^{129}I half life ~ 17 million years

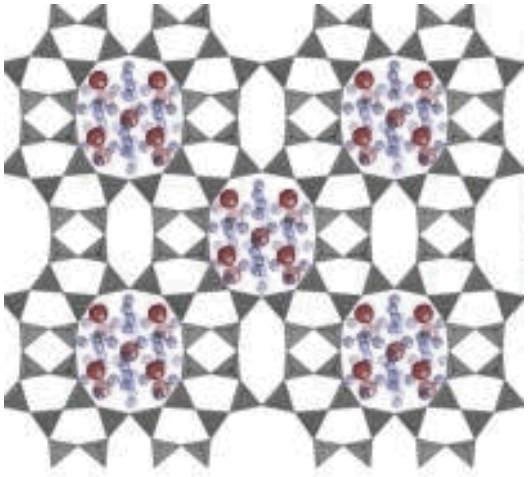
^{131}I half life ~ 8 days

involved in metabolic reactions in humans (thyroid)

Ag-exchanged mordenite (MOR)

Benchmark $^{129}I_2$ "getter"

Forms AgI within pores



- Must be Captured in Nuclear Energy & Environmental Settings
- Ag^+ in Zeolite Pores is reduced Ag^0 before use in sorbent beds
- The distribution of supported Ag^0 (inside vs outside pores) impacts the distribution of AgI (inside vs outside pores)

Challenge: *To understand AgI nanoparticle (NP) formations on the nanoscale and to ultimately control the (1) synthesis of Ag-MOR and (2) Ag distribution in MOR*

Nanoscale Structure-Property Analysis Utilizing Pair Distribution Function (PDF) Analysis

The PDF, ***G(r),*** is related to the ***probability*** of finding an atom at a distance ***r*** from a reference atom.
It is the Fourier transform of the total structure factor, ***S(Q)***.

$$G(r) = 4\pi r\,\rho_0[g(r)-1] = (2/\pi)\int Q[S(Q)-1]\sin(Qr)dQ$$

probability — structure factor

The structure factor, ***S(Q)***, is related to coherent part of the diffraction intensity

$$S(Q) = 1 + [I^{coh}(Q) - \sum c_i|f_i(Q)|^2]/\,|\sum c_i f_i(Q)|^2$$

diffraction intensity (corrected)

Apply corrections for background, absorption, Compton & multiple scattering

Function of r/distance
Intensity is related to probability of finding pair atoms separated by given distance
Opportunity to see ALL atoms

PDF measurements: APS/ANL Collaboration

Does it matter which synchrotron?

Yes. Only higher energy storage rings produce significant fluxes of high energy X-rays

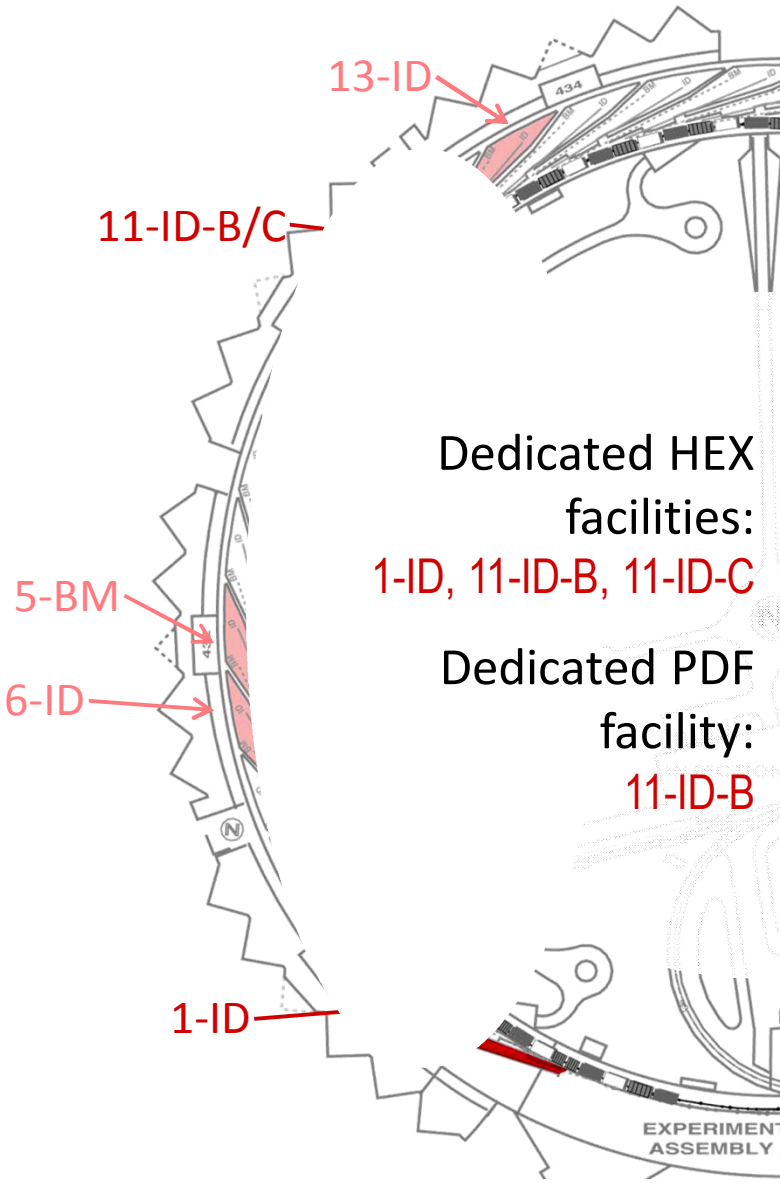
High energy X-rays are a unique strength of the *Advanced Photon Source* (in the western hemisphere)

- 3 dedicated high energy beam lines
- 1 dedicated PDF beamline

APS 11-ID-B: Dedicated PDF facility
- 58 or 90KeV high energy X-rays
- typical wavelengths = 0.1 - 0.2Å

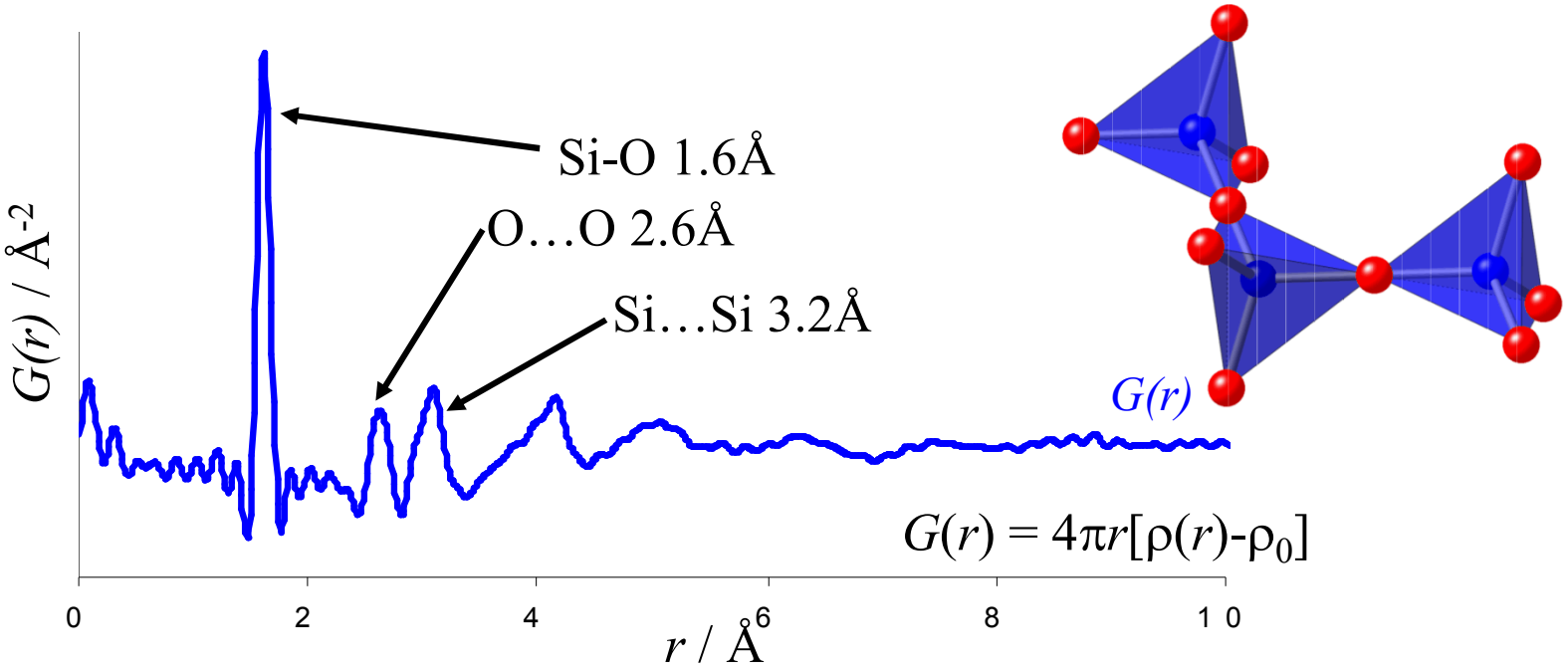
For our experiments:

$Q > 20Å^{-1}$; CuK_α to $2\Theta = 180$ results in $Q_{max} = 8Å$



PDF Provides Insight Into Short Range Structural Order
eg., Amorphous SiO_2 (Glass)

- a weighted histogram of ALL atom-atom distances



Peak position ⟷ Bond length / distance

Peak area ⟷ Coordination #, scattering intensity

Peak width ⟷ Disorder, bond angle distribution

Peak r_{max} ⟷ Particle size, coherence

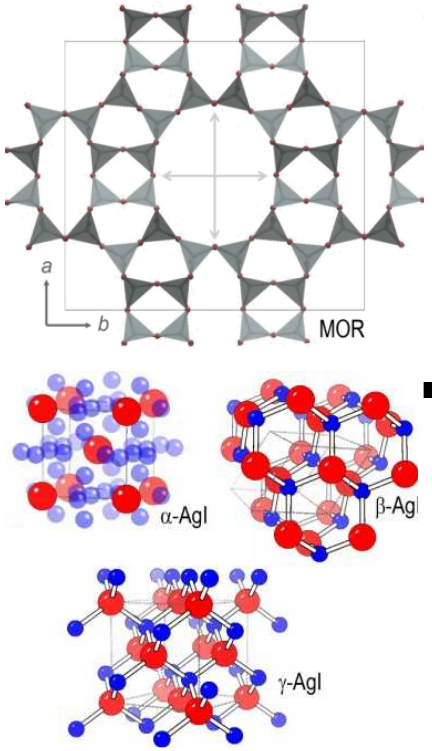
→ **Structural Modeling**

Application to Zeolites to Examine Short Range Interactions of Guests in Pores

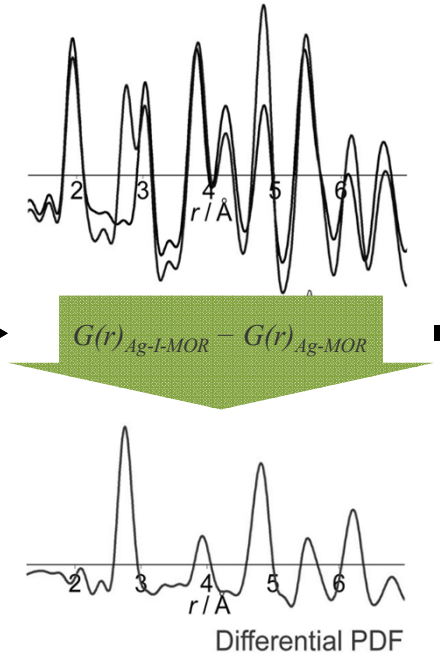
Determine Mechanism of AgI Nanoparticle (NP) Formation in Zeolite MOR

Allows for determining short range guest interactions (eg., AgI) within porous materials

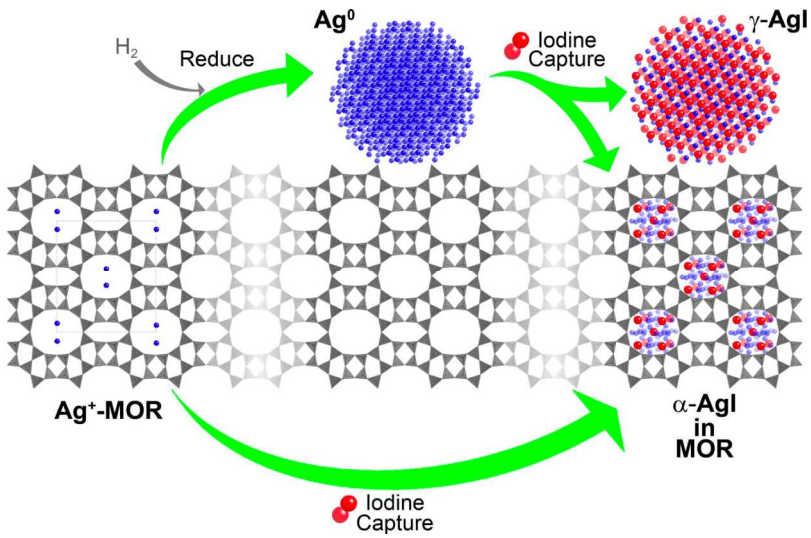
JACS, **2010**, *132*(26), 8897



Components



d-PDF = AgI-MOR – MOR framework

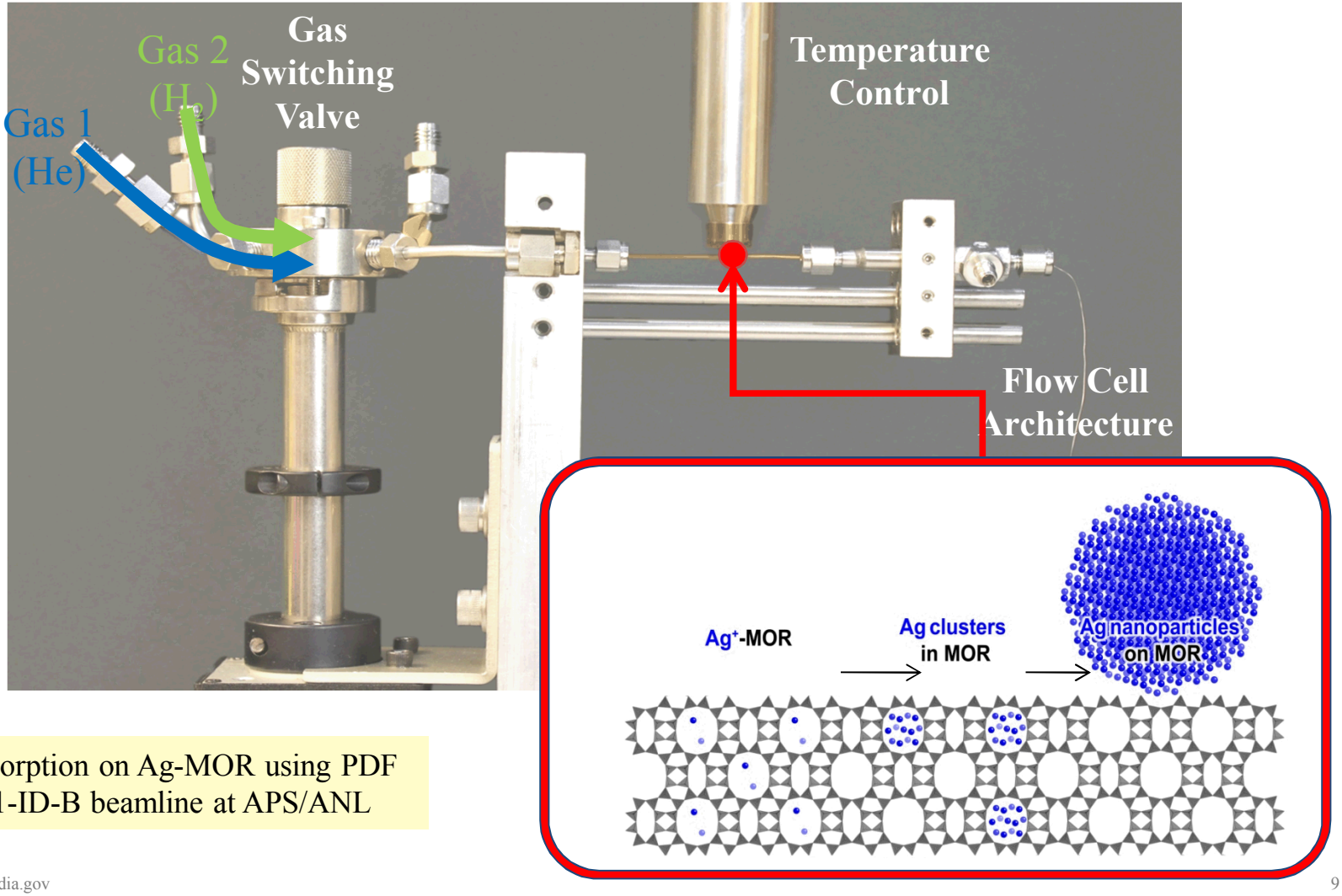


Mechanism of AgI formation & phase determination

Challenge: *To understand Ag nanoparticle (NP) formations (time, temp) on the nanoscale and to ultimately control the (1) synthesis of Ag-MOR and (2) Ag distribution in MOR*

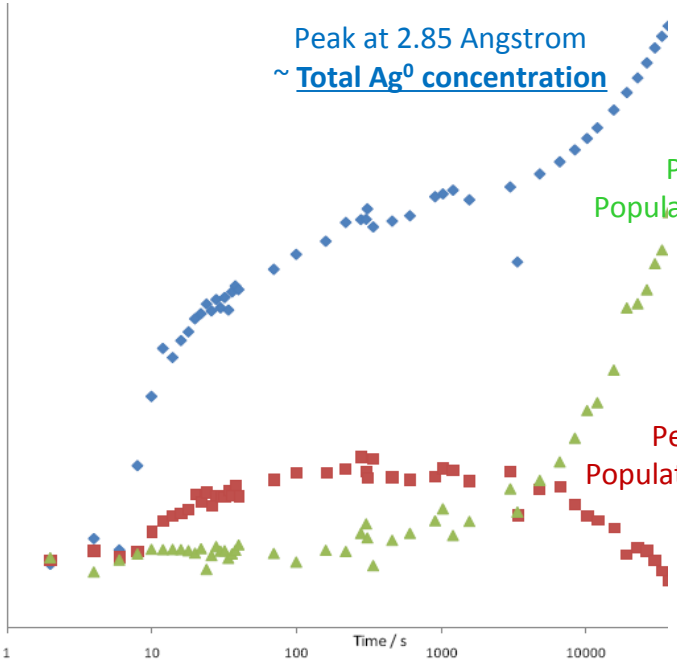
Determine Mechanisms and Kinetics of Ag^+ to Ag NP Formation in Zeolites

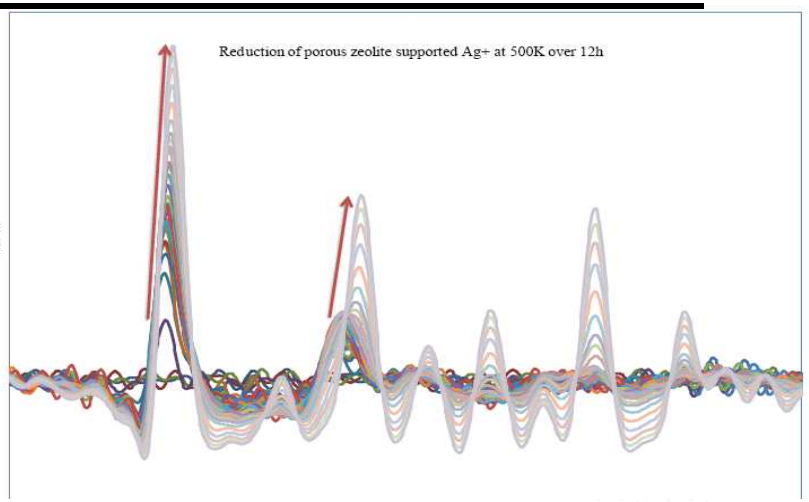
Study Conversion and Migration of Ag^+ to Ag° in MOR

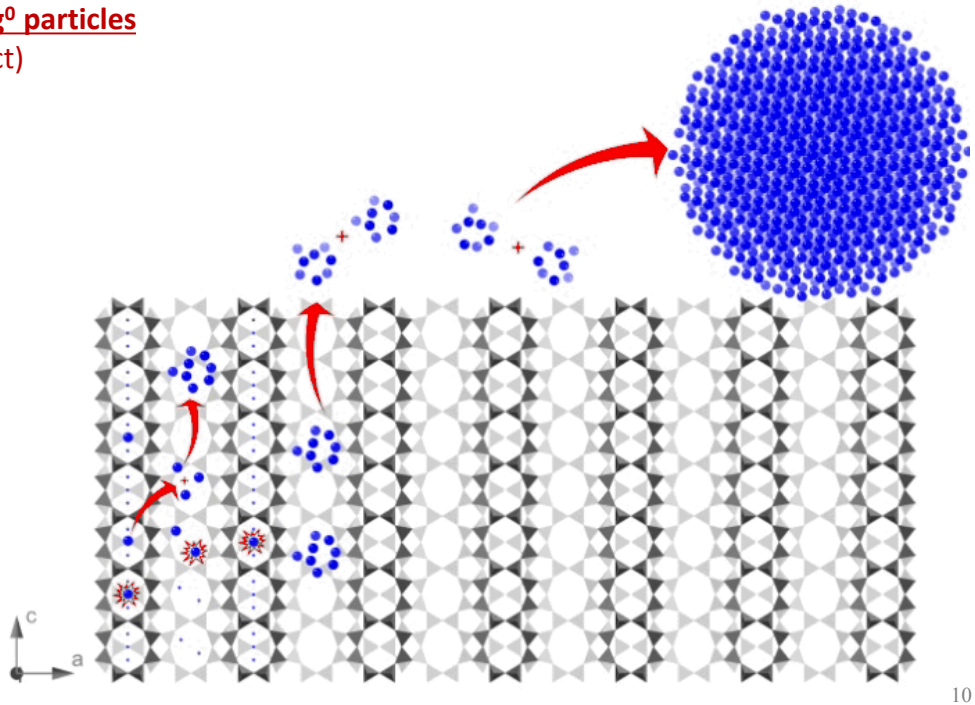


In situ I_2 sorption on Ag-MOR using PDF setup at 11-ID-B beamline at APS/ANL

Multi-step Mechanism for Silver Particle Growth on a Porous Zeolite





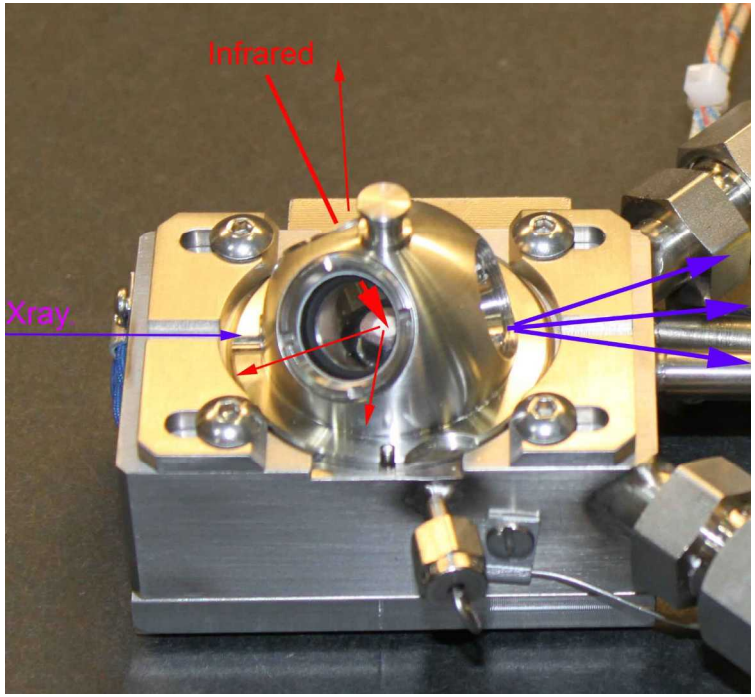


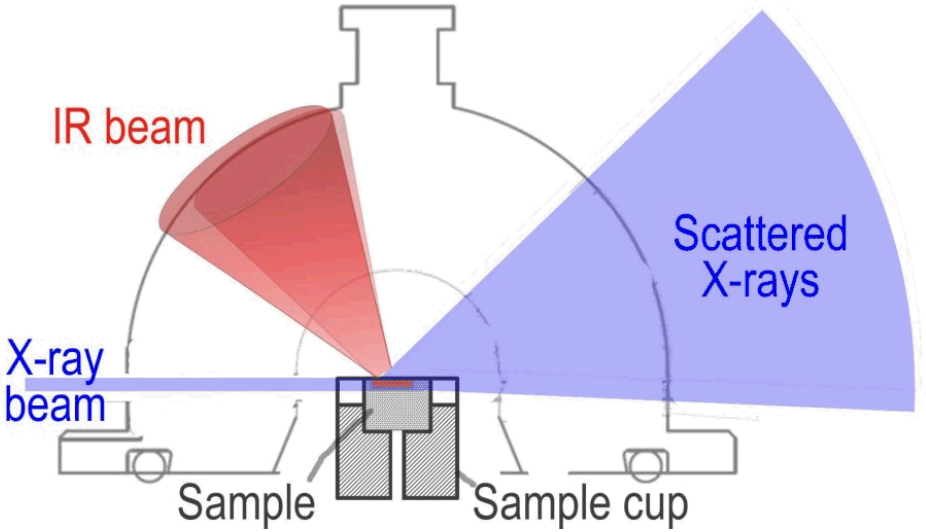
Mechanism Pathway Determined

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

i) Ag^+ reduction in 12MR and 8MR "Red star"
ii) Ag° migration from 8MR to 12MR
iii) Ag° form clusters within 12MR channels
iv) Clusters migrate to zeolite surface
v) Clusters aggregate as nanoparticles

Simultaneous Diffuse Reflectance IR Spectroscopy (DRIFTS) and PDF Analysis

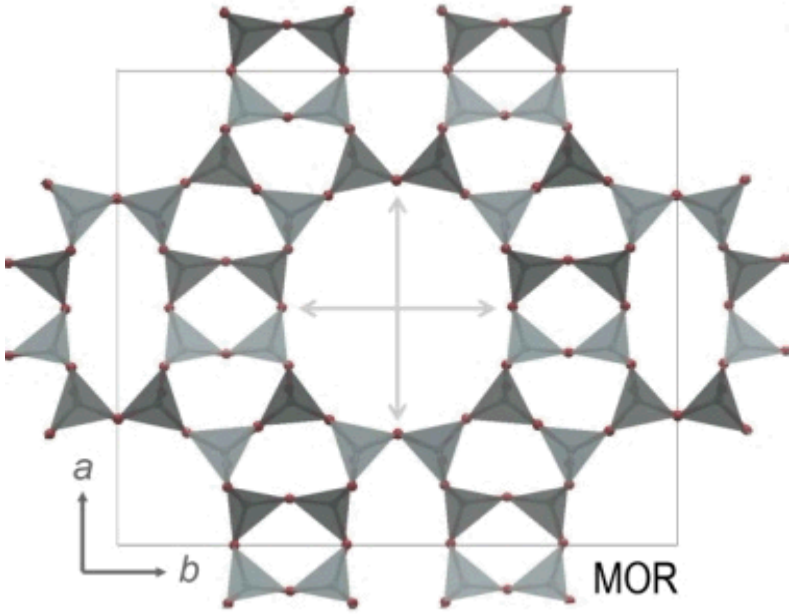




- Infra-red spectroscopy is highly sensitive to H_2O/OH molecular speciation
- PDF+IR measurements can be performed simultaneously on the same sample region without compromise to the data

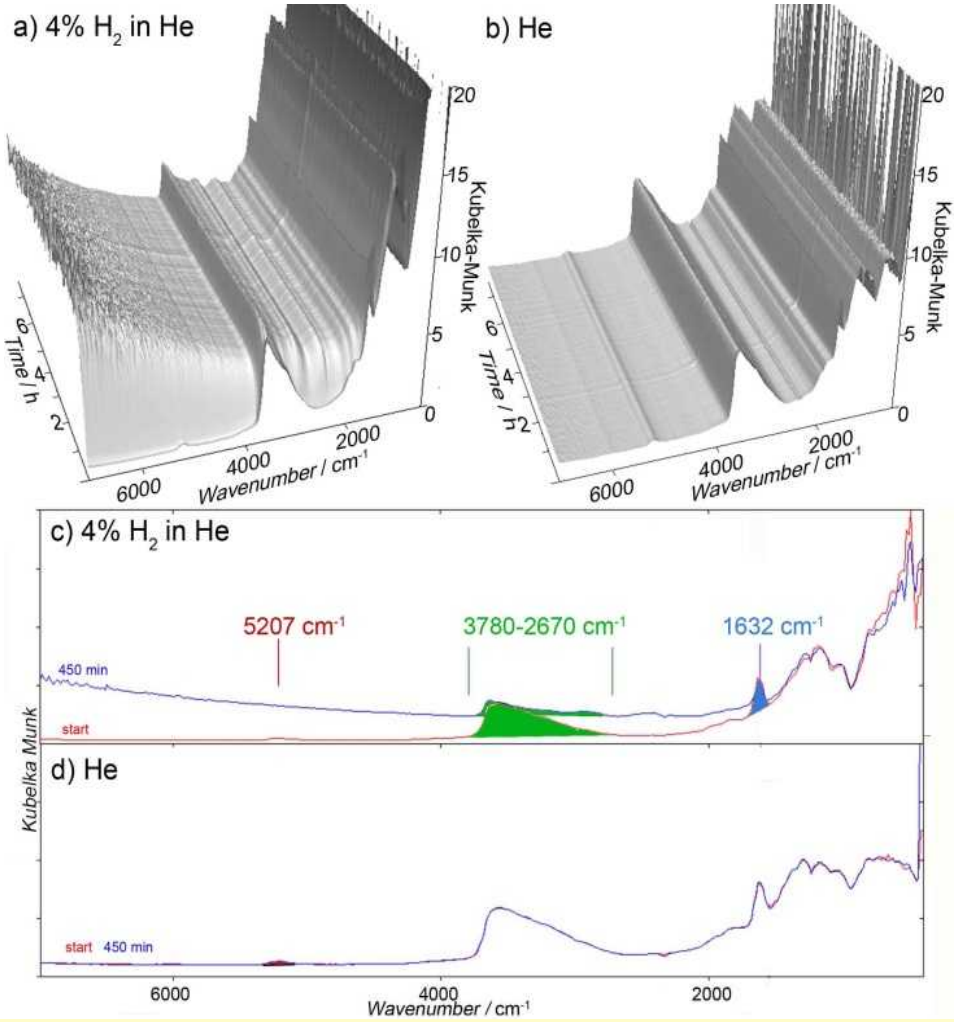
How does adsorbed water and –OH species in pores affect Ag cluster formation in Zeolites?

DRIFTS: Data Collection of Ag^+ - MOR Under Reducing or Inert Atmosphere



$Ag_2Al_2Si_{10}O_{24}•7(H_2O)$

12 MR, 7.0 x 6.5Å

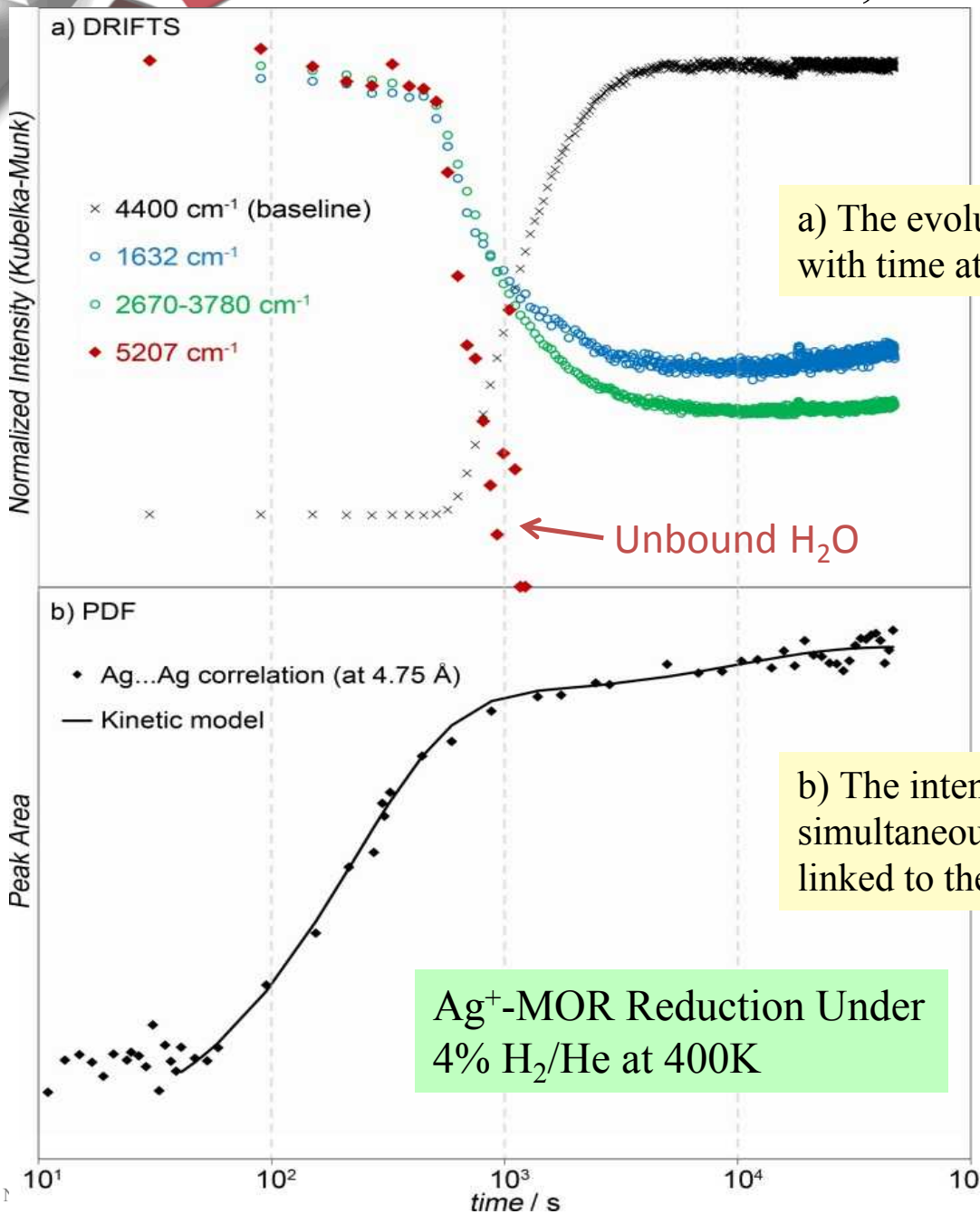


The **time resolved DRIFTS** data for Ag^+-MOR during heating at 400 K under (a) reducing and (b) inert atmospheres, and (c and d, respectively) corresponding before-and-after data

Position and Assignments of Peaks in DRIFTS data

Peak / cm^{-1}	Assignment
1632	Molecular H_2O (free/weakly bound to Ag^+ cations and bound to Bronsted acid sites)
3250	Acidic OH group
3450	Molecular H_2O (free/weakly bound and bound to aluminosilicate lattice)
3585, 3605, 3610	Si-OH
3680	AlOH group
5207	Molecular H_2O (free/weakly bound, combined bending and stretching)

As 400K, Water/-OH Species Evolve Out, Ag NPs Form

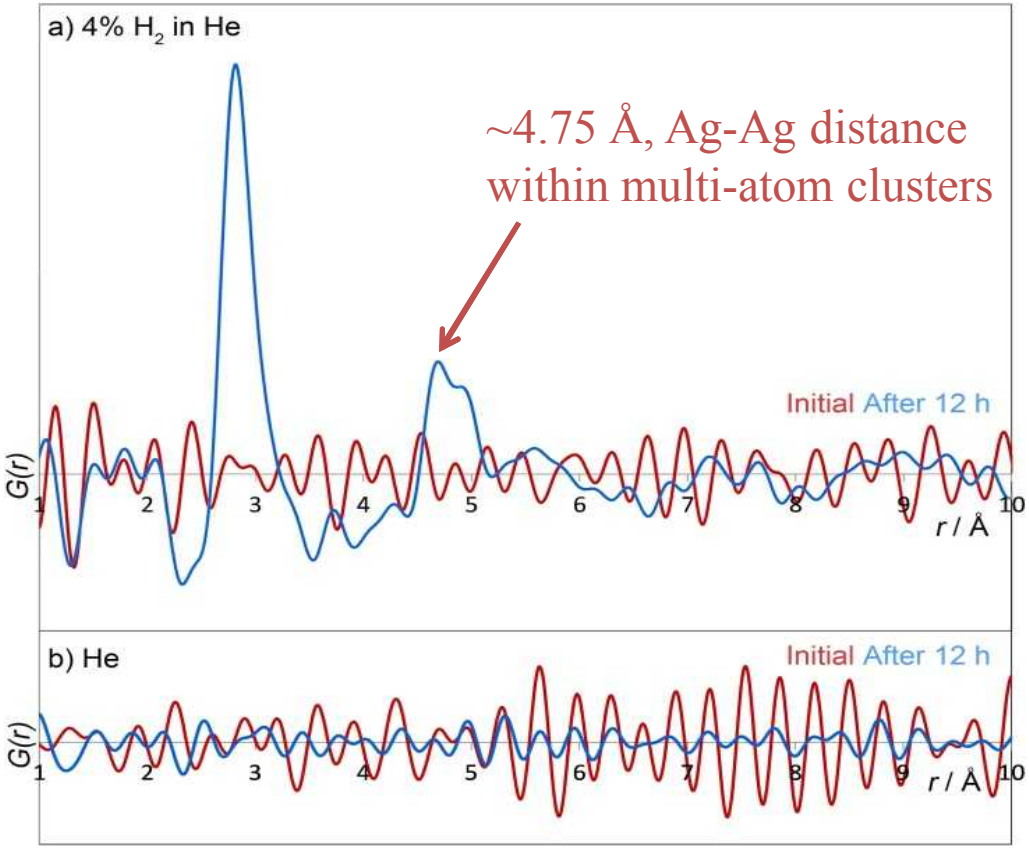


a) The evolution of water and –OH molecules with time at 400K; from time-resolved DRIFTS data.

b) The intensity of the peak at 4.75 Å in the simultaneously collected time resolved PDF data, linked to the multi-atom Ag cluster population.

Ag^{+}-MOR Reduction Under 4% H_2/He at 400K

PDF: Direct Observation of the effect of Dehydration on Ag NP Formation

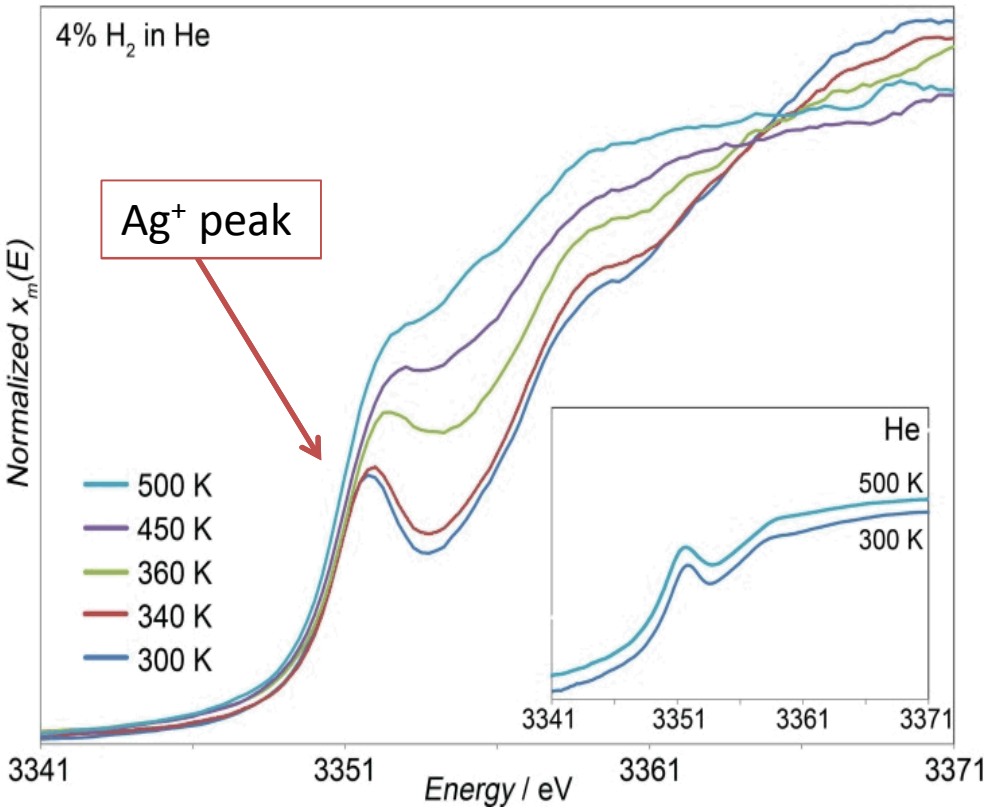


PDF for Ag^{+}MOR before and after heating at 400 K in reducing (a) and inert (b) atmosphere.

Larger amplitude artifacts in initial data reflect the shorter acquisition times used early in the reaction.

XANES: Direct Observation of the effect of Dehydration on Ag^0 NP Formation

X-ray Absorption Near Edge Spectroscopy (XANES), evidence of change in oxidation state of silver from ion (+1) to metal with temperature



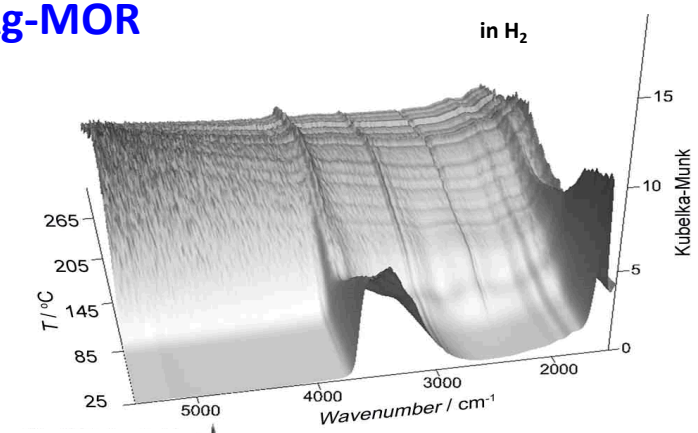
Ag L(III) edge XANES data for ramping Ag^+MOR in inert (inset) and reducing atmospheres.

Direct Observation of the effect of Dehydration on Ag NP Formation

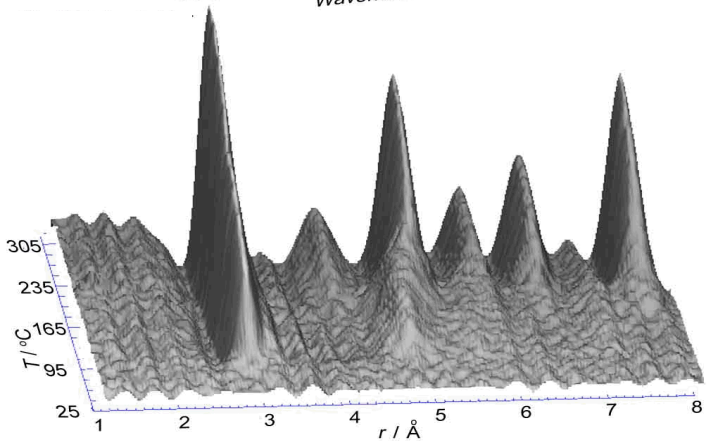
Ag-MOR

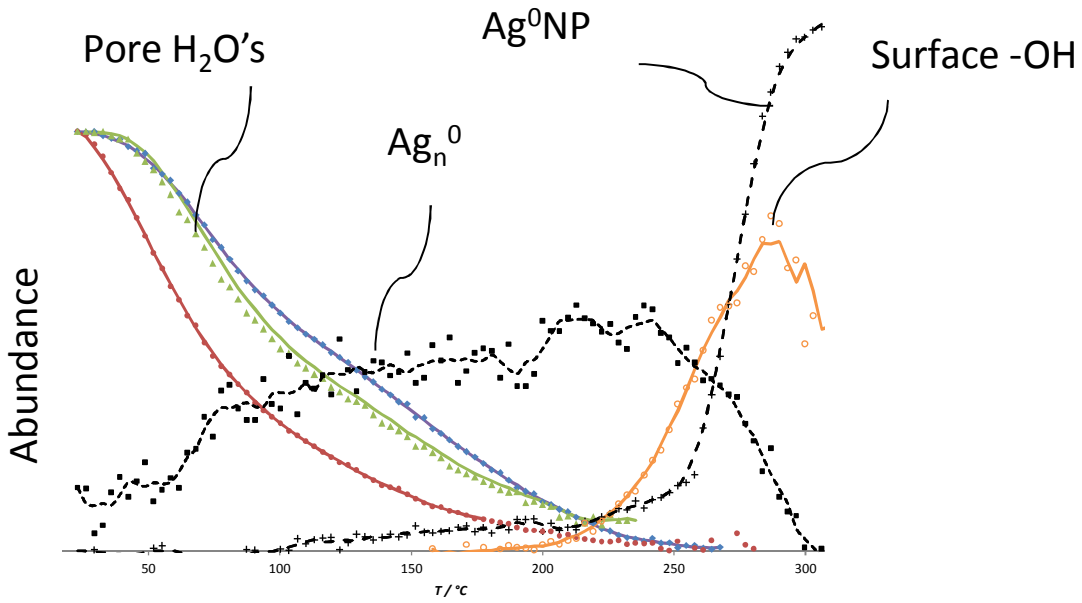
In prep, 2016

DRIFTS



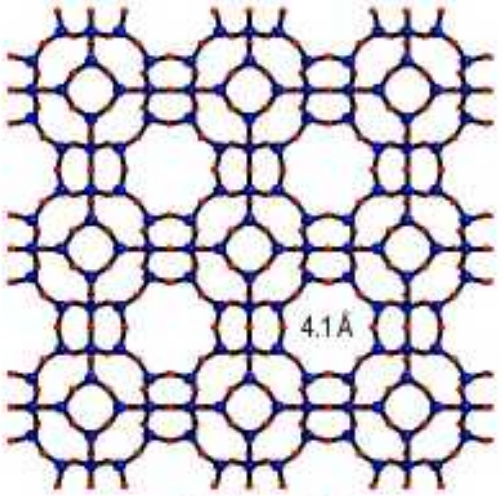
d-PDF





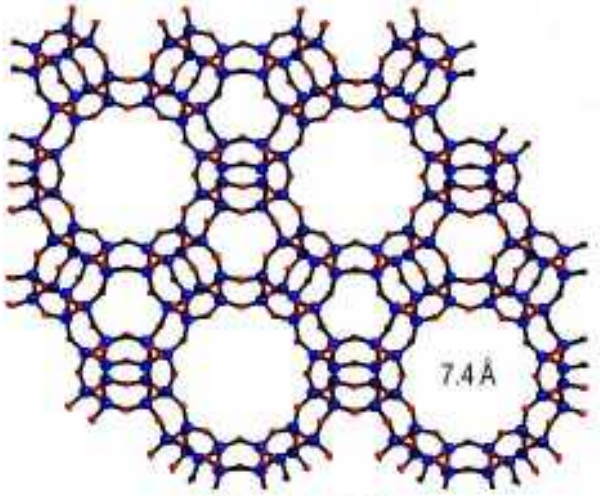
Initial Data, Ag-MOR in H_2:
Correlation identified between –OH surface functionalization and Ag NP migration to the outer surface of the MOR

Zeolite Hosts: Effect of Pore Size, Shape and Charge on Ag NP Formation



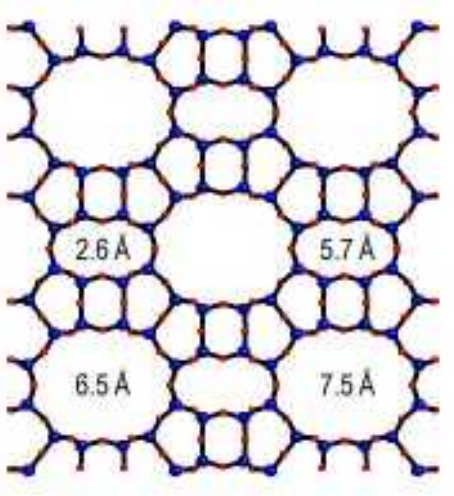
LTA (A)
Si/Al = 1

$Ag_{12}(AlO_2)_{12}(SiO_2)_{12}O_{48}.27H_2O$



FAU (Y)
Si/Al = 2.4

$Ag_{3.5}Al_7Si1_7O_{48}.\ 32H_2O$

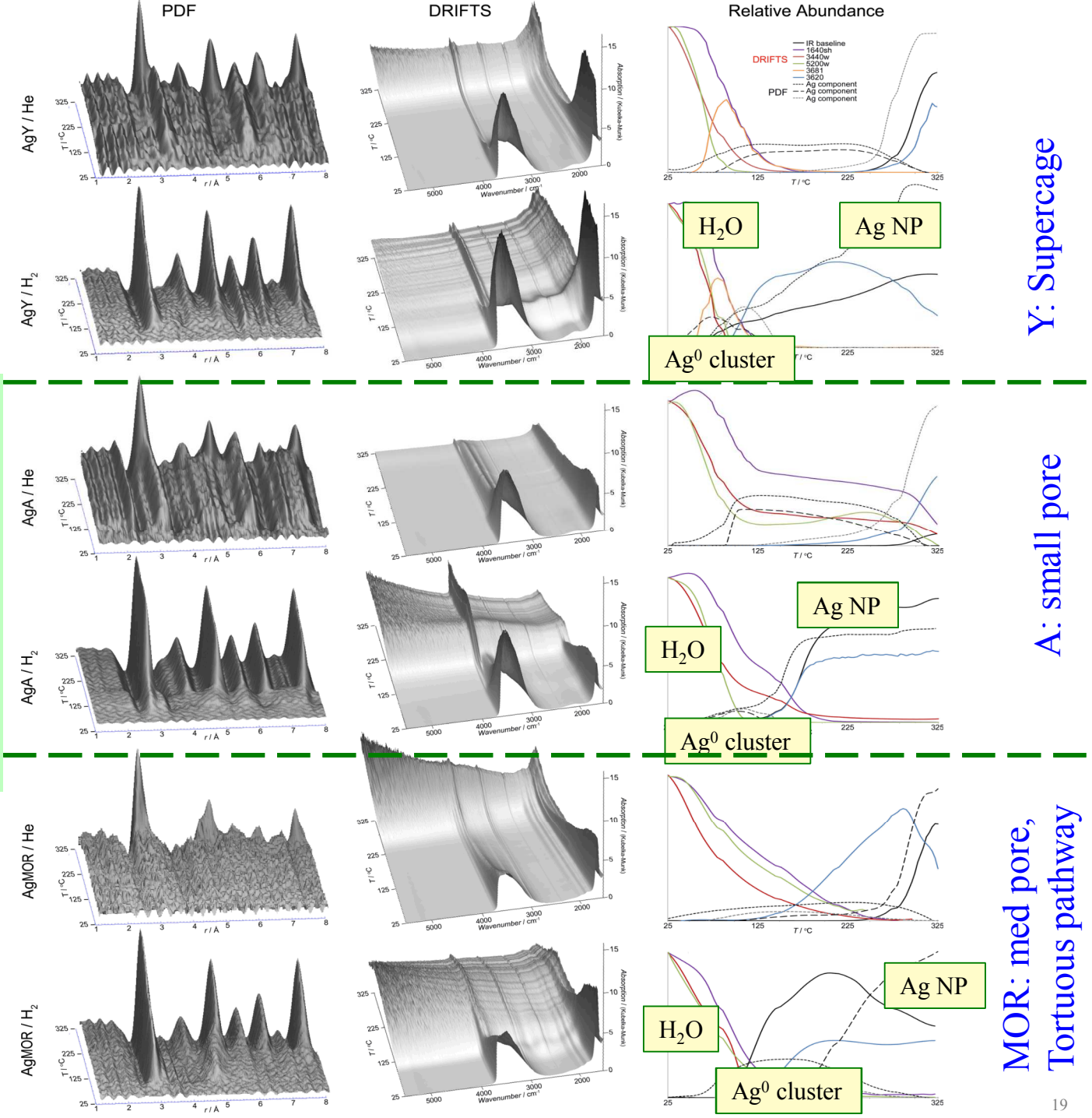


MOR
Si/Al = 5

$Ag_2Al_2Si_{10}O_2$

In situ **DRIFTS** data,
In situ **PDF** data
and the evolution
of selected features
with heating
(25 - 325°C).

Ag-Y, Ag-A, Ag-MOR Zeolites in reducing (H_2) and inert (He) atmosphere.



Conclusions

- *Success strategy for combining DRIFTS and PDF measurements, for the study of mechanisms and kinetics of silver nanoparticle formation within a zeolite*
- DRIFTS/PDF provide both an understanding of the molecular-level processes and structural changes that occur during the reaction
- Reduction of Ag^+ leads to partial dehydration of the zeolite through release of water coordinated to Ag^+
- Dehydration, itself, does not occur at these temperatures and does not contribute to reduction, confirming that the kinetics of Ag^+ reduction is dominated by chemical reaction with hydrogen at 400 K.
- Cluster formation continues following loss of water coordinated to Ag^+ ions after reduction; this is likely associated with the increased mobility of silver within the pores once water is removed.
- Simultaneous DRIFTS/PDF shows great potential to study the reactivity in heterogeneous catalysts and solid state materials.