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MOF-TEMPLATED GROWTH OF MOLECULAR AG-CLUSTERS FOR SMALL MOLECULE SENSING

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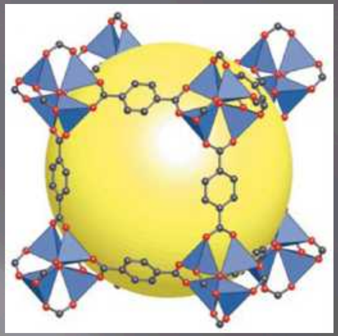
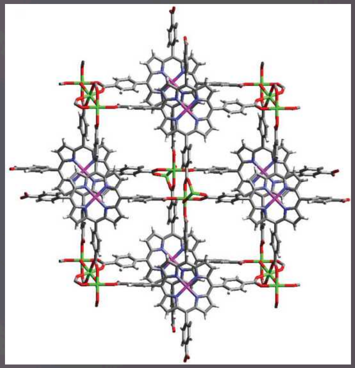
Theory

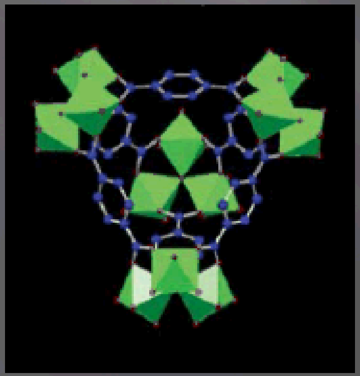
- MOFs are coordination polymers with functional properties:
  - Porosity
  - Flexibility
  - Chemical tunability
- Discreet and rigid pore structure can generate a regular array of monodisperse, non-surfactant stabilized colloidal particles



"Isoreticular" MOF-5: tunable pore size and pore chemistry (*Yaghi et al. Science 1999*)



PIZA-1: open metal coordination sites in linker (*Suslick et al., Nat. Mat. 2002*)



Cr MIL: 6000 m^2/g
(Férey et al., Science 2005)

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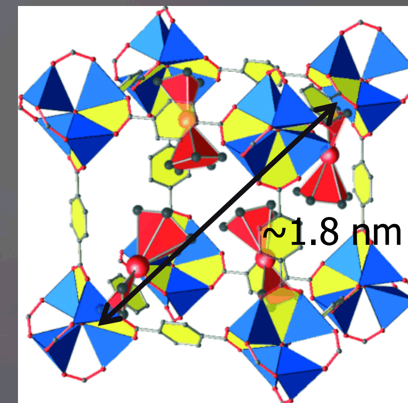
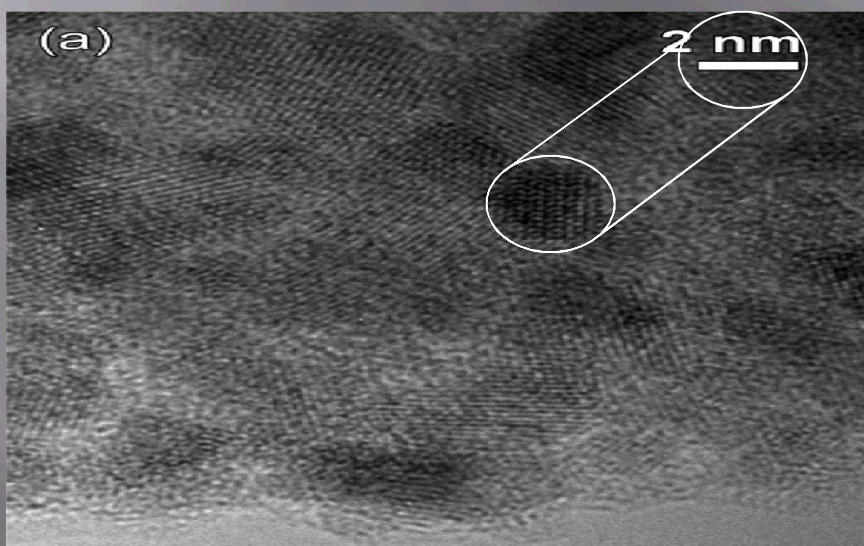
Background

- Fischer group pioneered Metal@MOF
- Metals are infiltrated using MOCVD precursors
- Pd, Au, Ru, $Fe(Cp)_2$, ZnO, TiO_2 and more have been grown in MOF-5





- MOF-5 has a pore diameter of 1.8 nm.
- In all literature on Metal@MOFs, larger-than-pore particles widely observed

Turner et al. *Chem. Mater.*, **2008**

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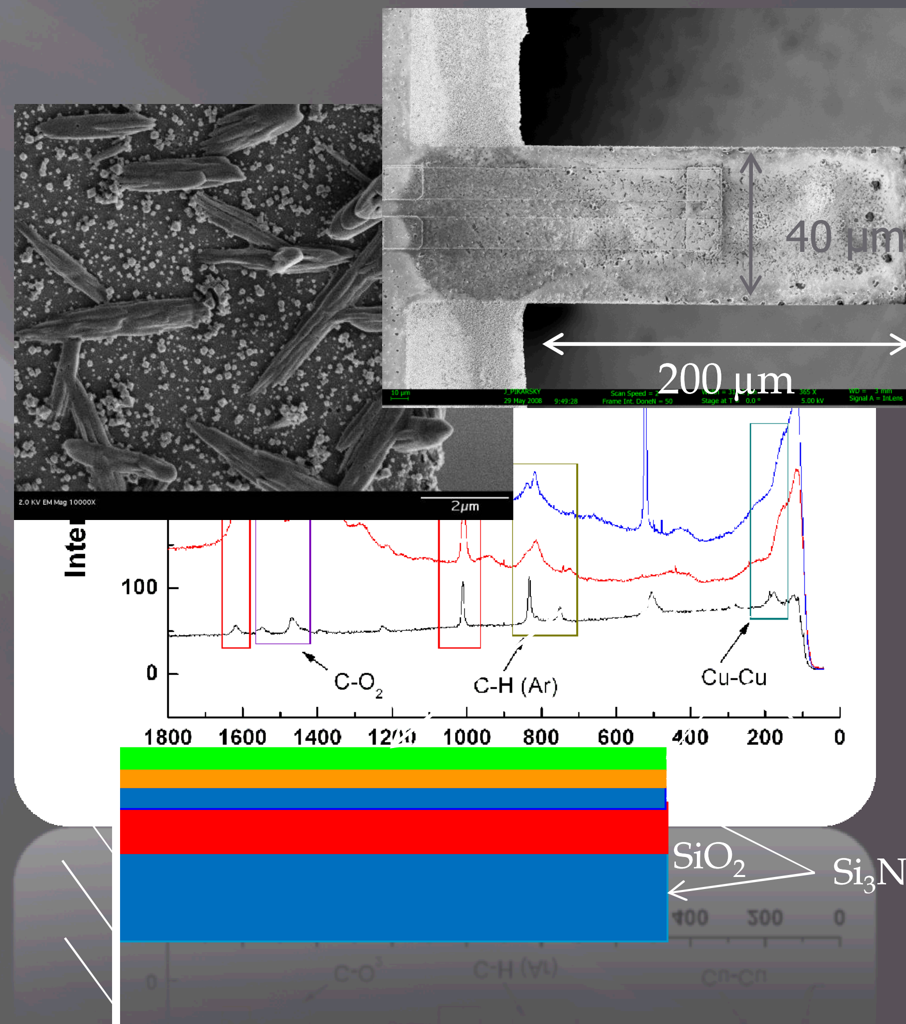
Motivation

- Cu(BTC) growth on Microcantilever substrates gave multiple morphologies
- Substrates too small for standard chemical characterization techniques
- Evaporation of silver onto devices generates a strong Raman enhancement
- SEM does not show presence of silver on Cu(BTC) surface



Allendorf et al. *JACS*, **2008**
Xia et al. *MRS Bull.*, **2005**

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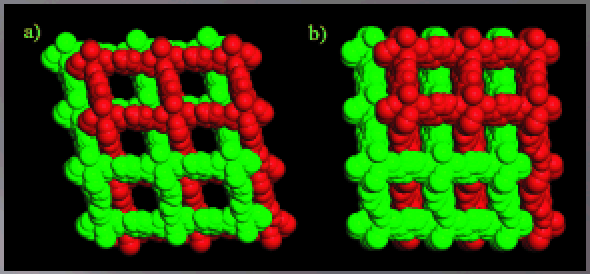
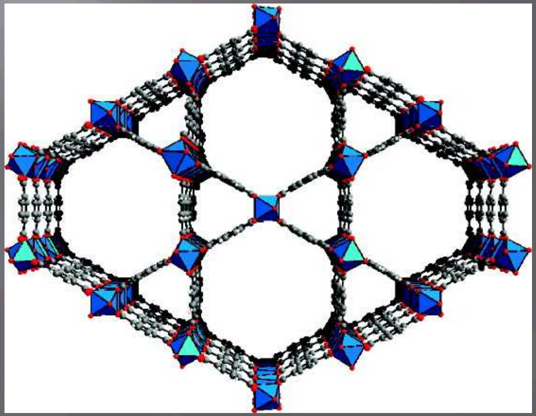
MOFs for Ag-Infiltration

- **MOF-508:** Doubly interpenetrated, shows reversible guest-induced flexibility *(Chen et al. Angew. Chem.* ***2006****)*



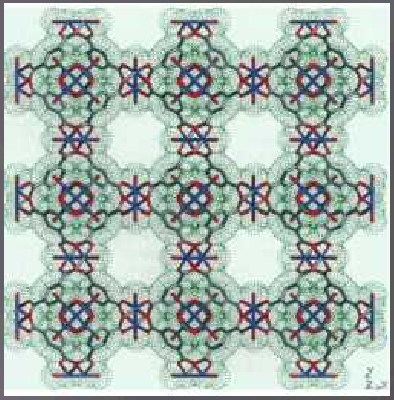
~6-7 Å diameter 1D channels

- **MIL-68(In):** Non-interpenetrated, largest molar uptake of Ag *(Volkringer et al. Inorg. Chem.* ***2008****)*



Large channels = 2 nm
Small channels = 1 nm

- **Cu(BTC):** Cubic, non-interpenetrated network; open Cu-coordination sites. *(Chui et al. Science* ***1999****)*



Spherical 1.56 nm pores

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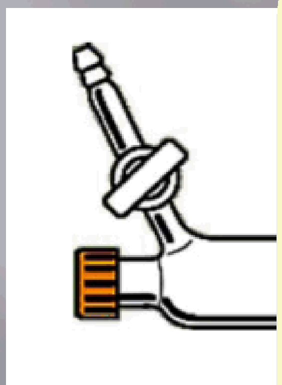
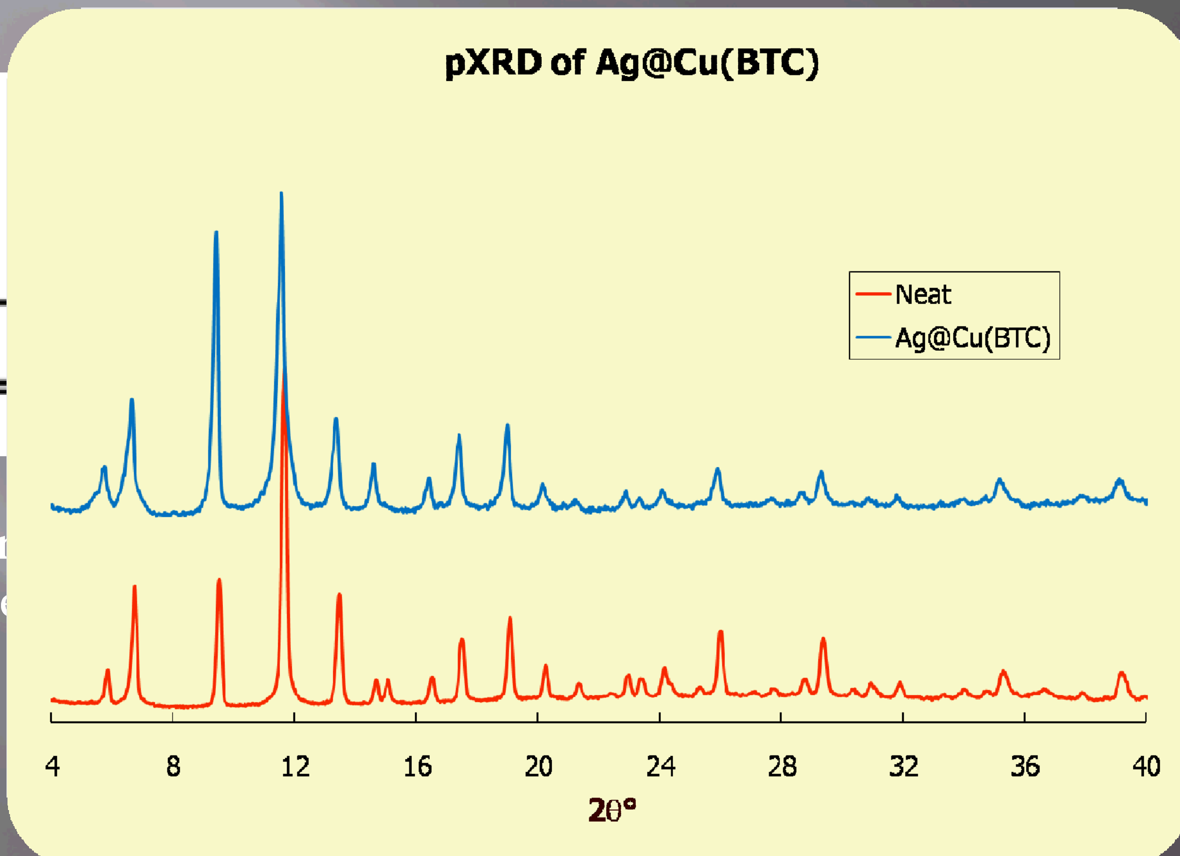
Method of Infiltration

- Infiltration achieved by immersing activated MOF crystals in an ethanolic solution of $AgNO_3$



Gas Phase In
air-free, schl



$AgNO_3$

ltration:
open air

- pXRD shows little to no change from the neat material.

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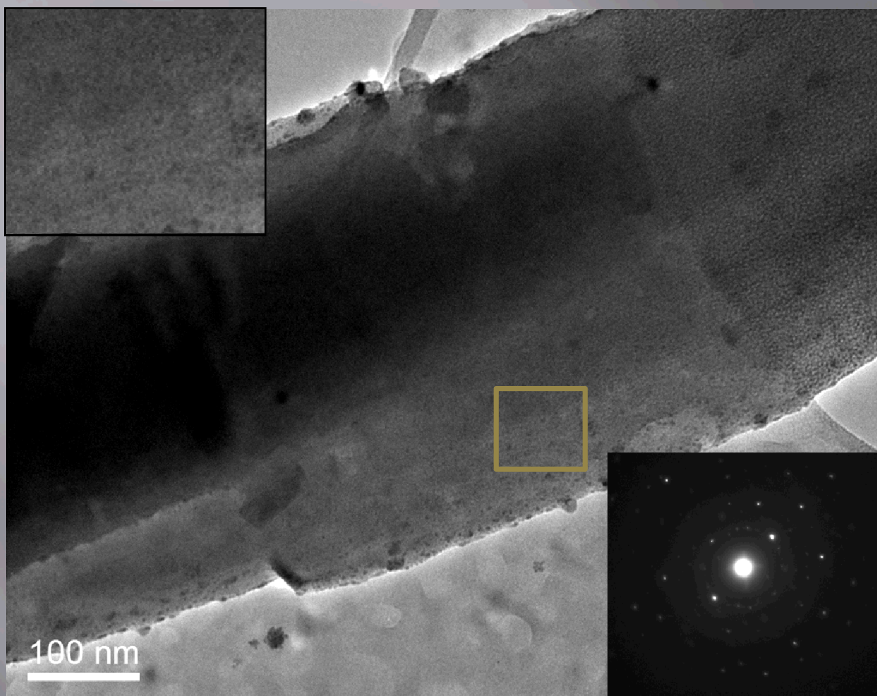
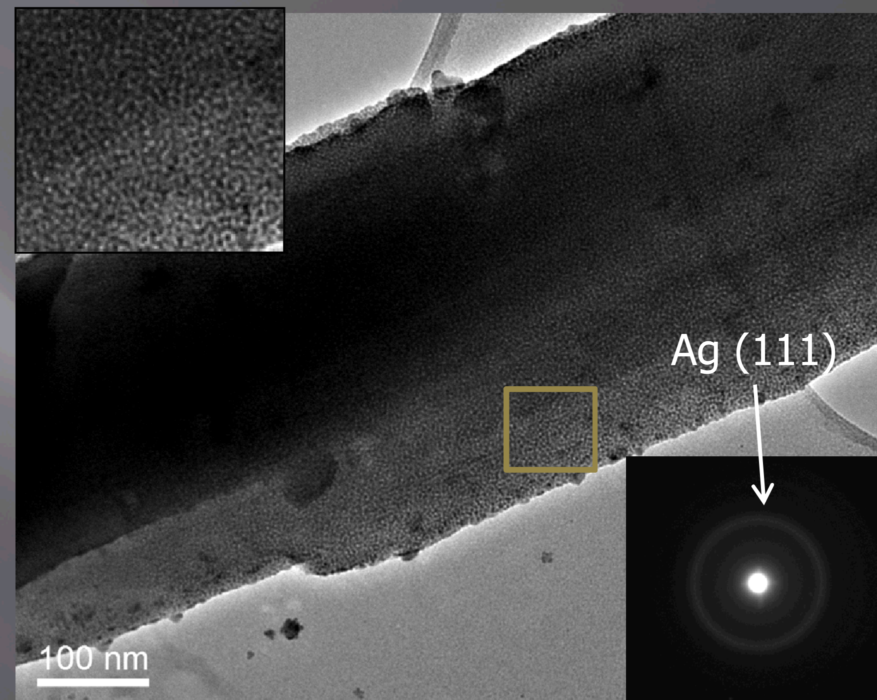
Electron Microscopy

Ag@MIL-68(In) – before beam degradation



Ag@MIL-68(In) – after beam degradation



- MOFs are extremely susceptible to electron beam damage
- As synthesized Ag-clusters are much smaller than initially believed

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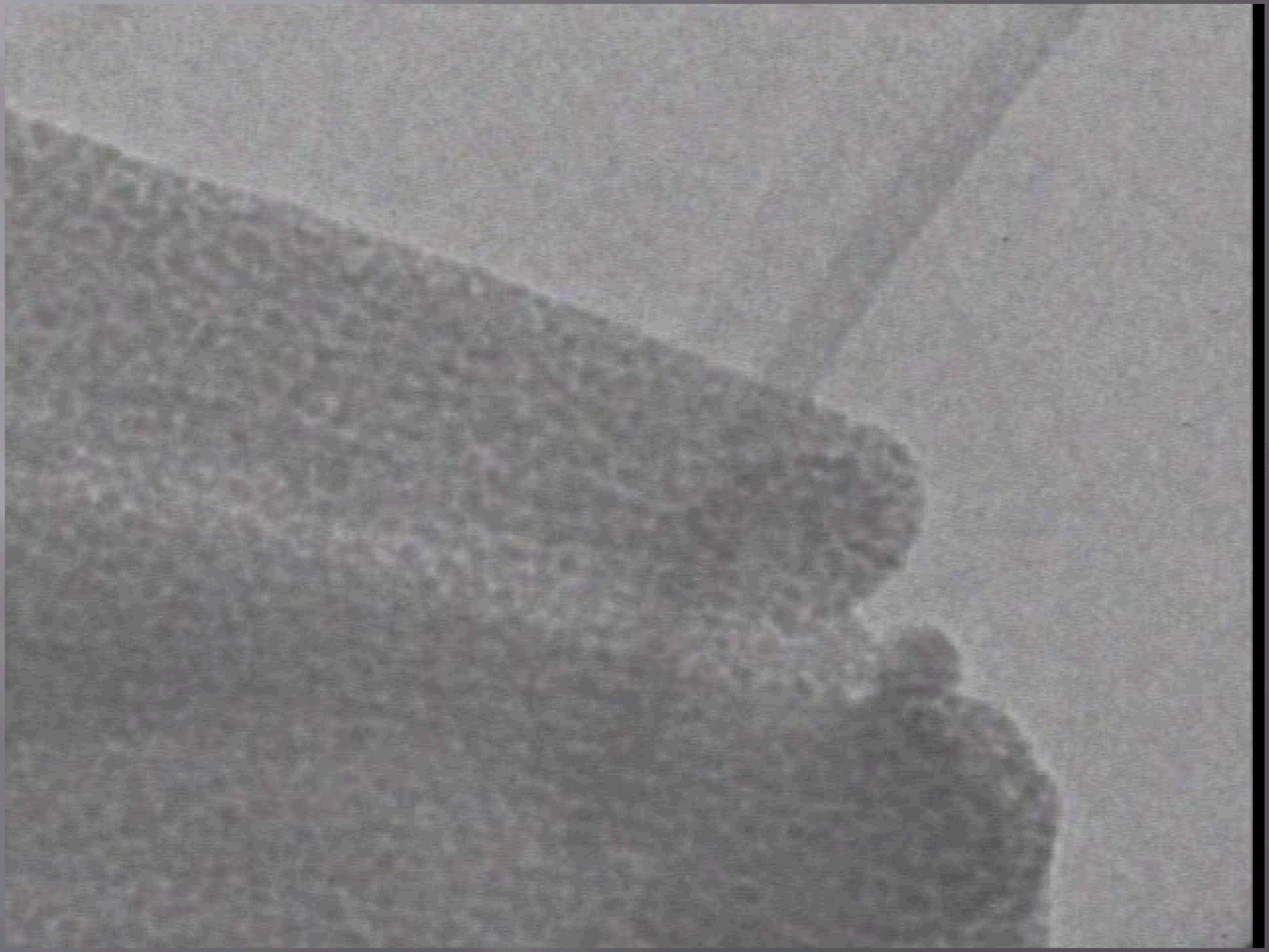
Evidence of Lattice Collapse

MIL-68(In) framework collapsing and Ag particles forming

MOF-508 collapsing and silver particles



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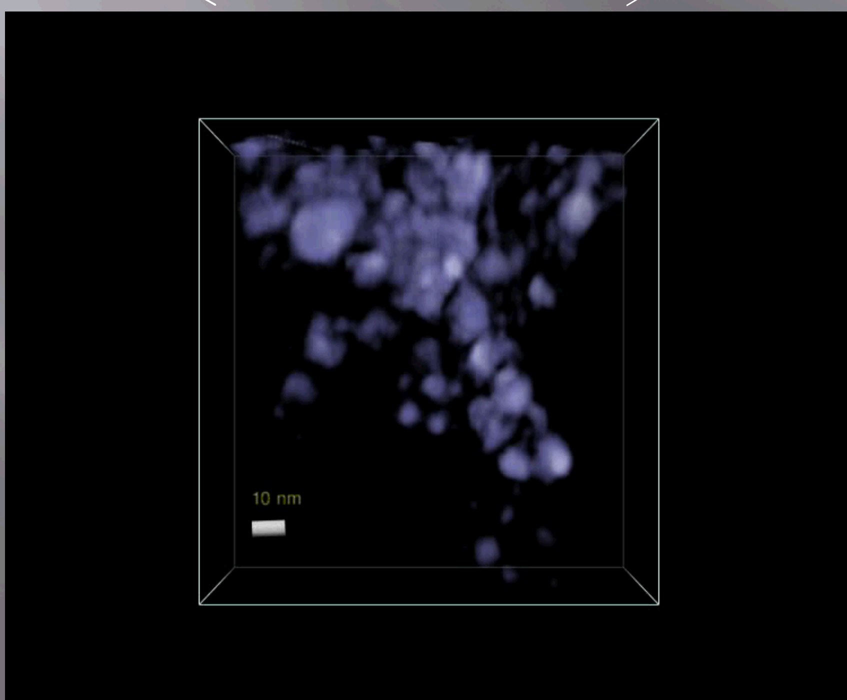
Effectiveness of Infiltration

- Lack of x-ray diffraction but strong IR evidence of interaction leads to conclusion that particles are well dispersed and small.

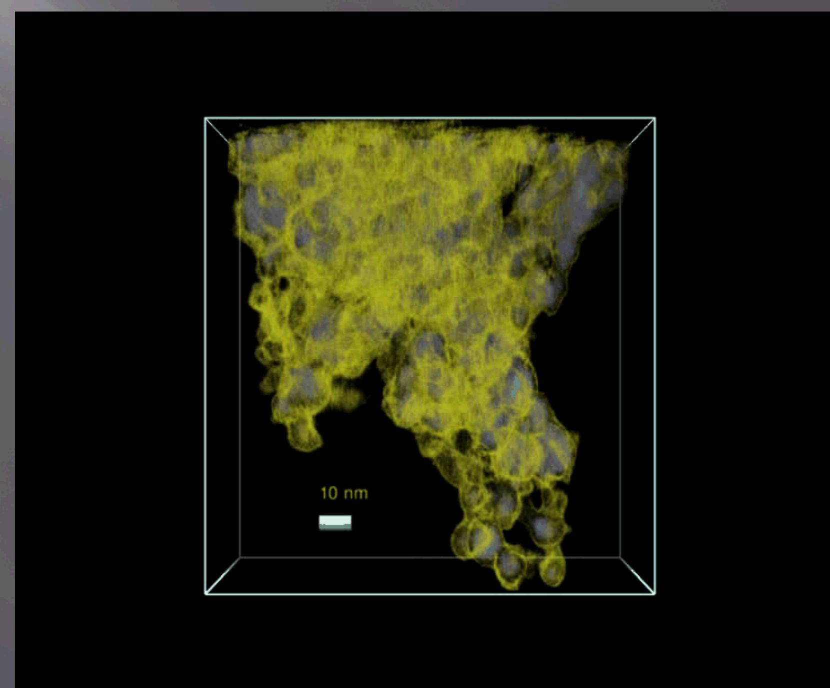
MOF	Ag w%	Ag:M (mol)	Ag/Pore
Cu(BTC)	8%	0.2	1.7
MOF-508	29%	1.51	3.2
MIL-68(In)	31%	1.8	19.25

Electron Tomography of Ag@MOF-508

~ 80nm



~ 80nm

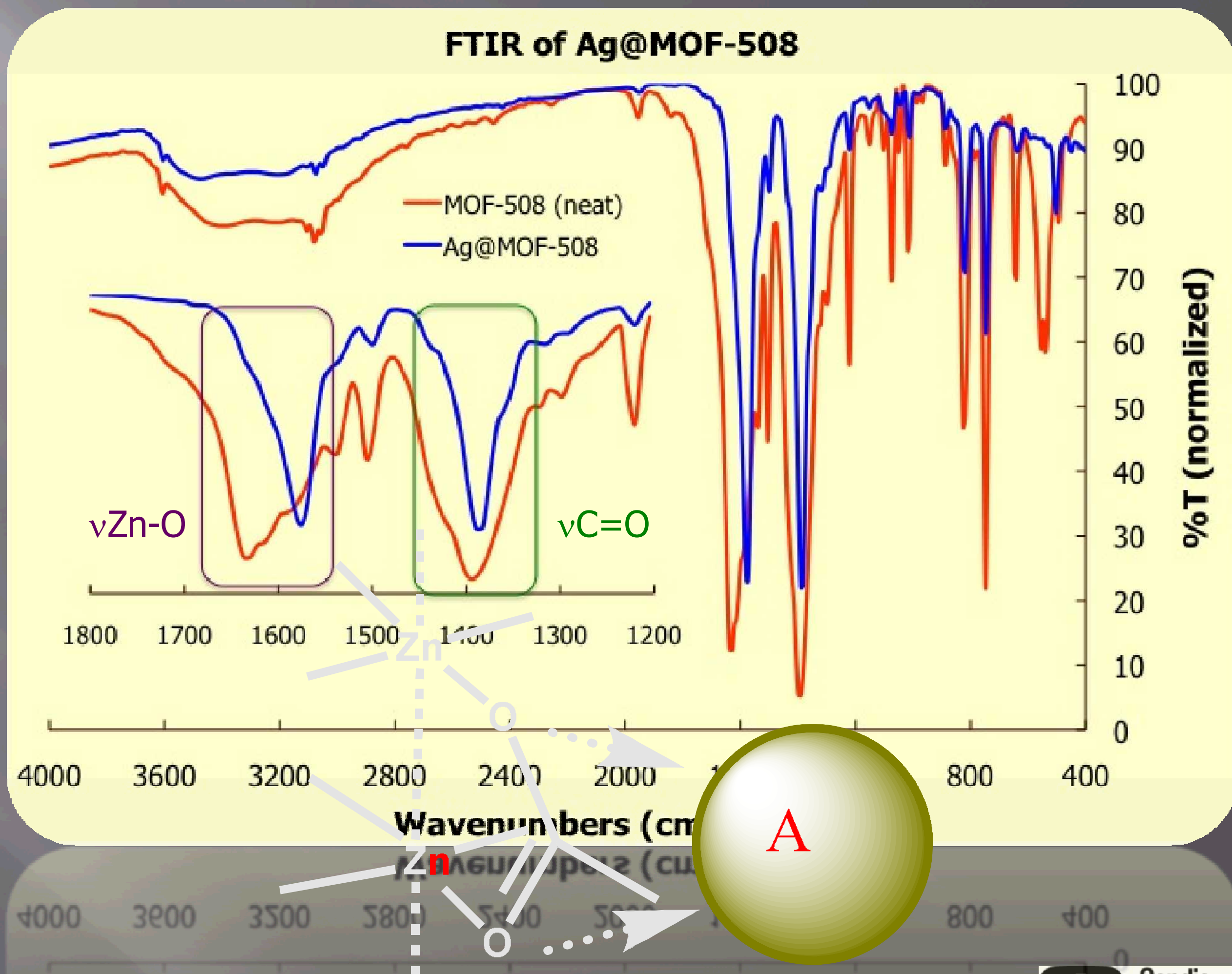


Implications

- Effect is general for every MOF we have tested
- Presence of silver in the pores is irrelevant
- Results may explain larger-than-pore particles as imaging artifacts
- Electron microscopy of MOFs and other soft materials must be interpreted with caution

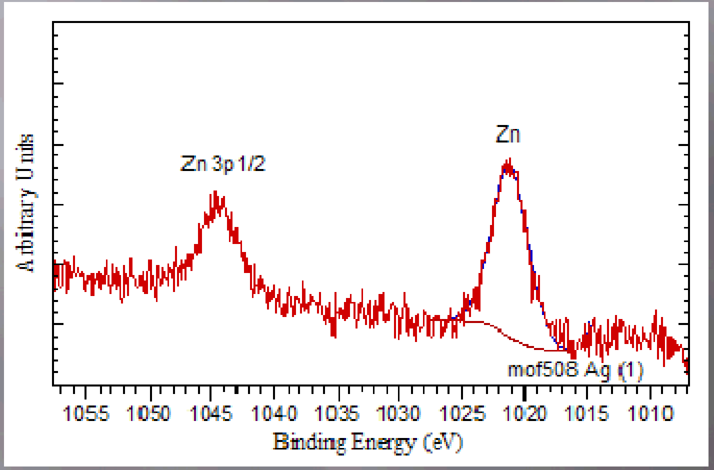
Does Ag Interact with the Frameowork?

- FTIR shows significant perturbation of C=O and M-O vibrations
- Shift of νZn-O to lower frequency shows electron withdrawal from carboxylate oxygens
- Indicates interaction of silver clusters throughout the bulk of material

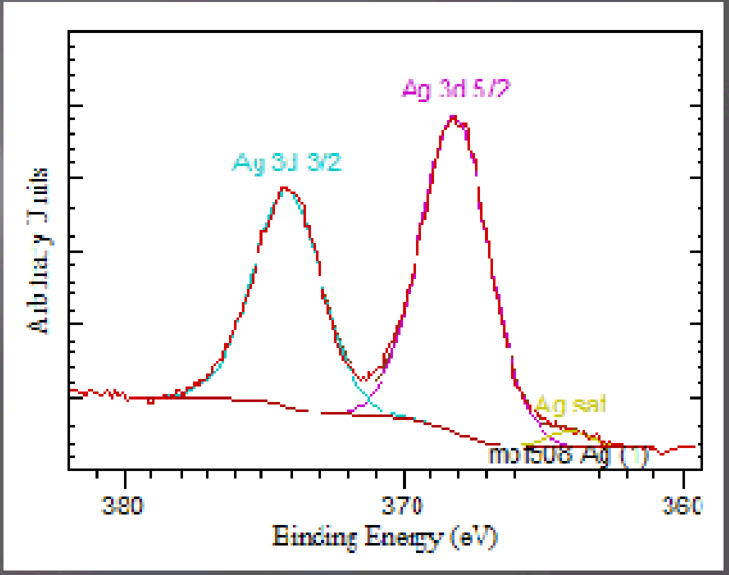


Ag(I) or Ag(0)?

- Ethanol reduces silver *in situ*.
- Zinc remains ionic



- XPS analysis of Ag@MOF-508 shows silver is metallic



- *In situ* reduction of silver removes another processing step from the infiltration procedure.

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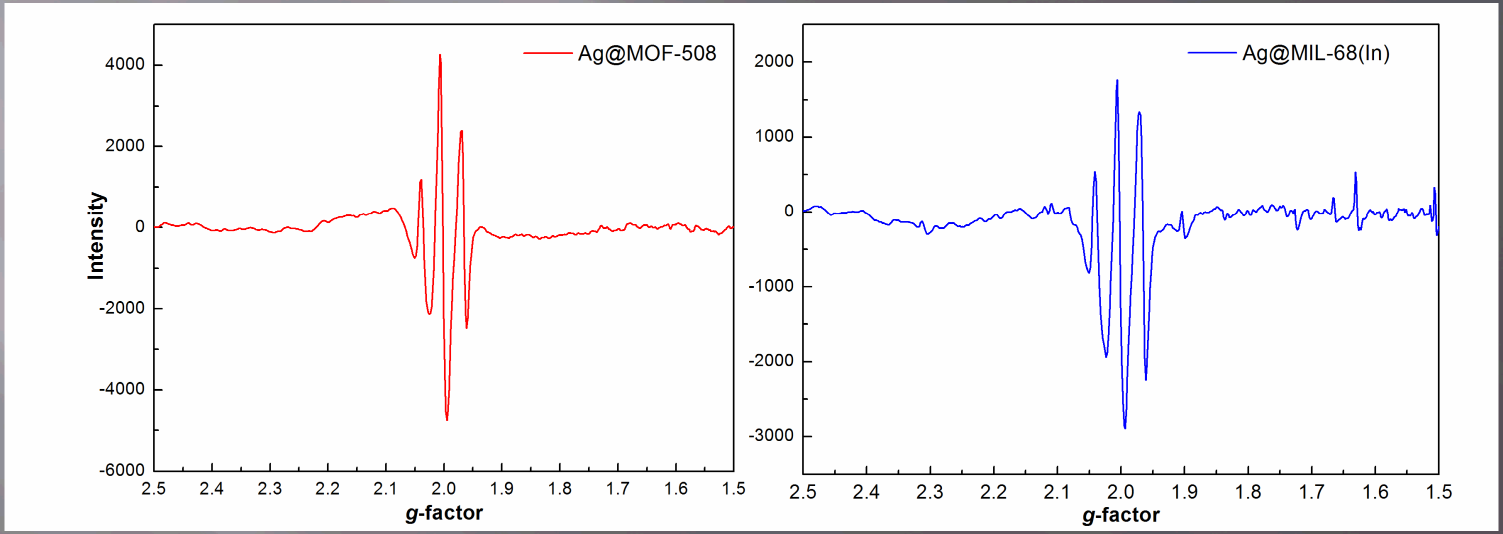
How Small Are They?

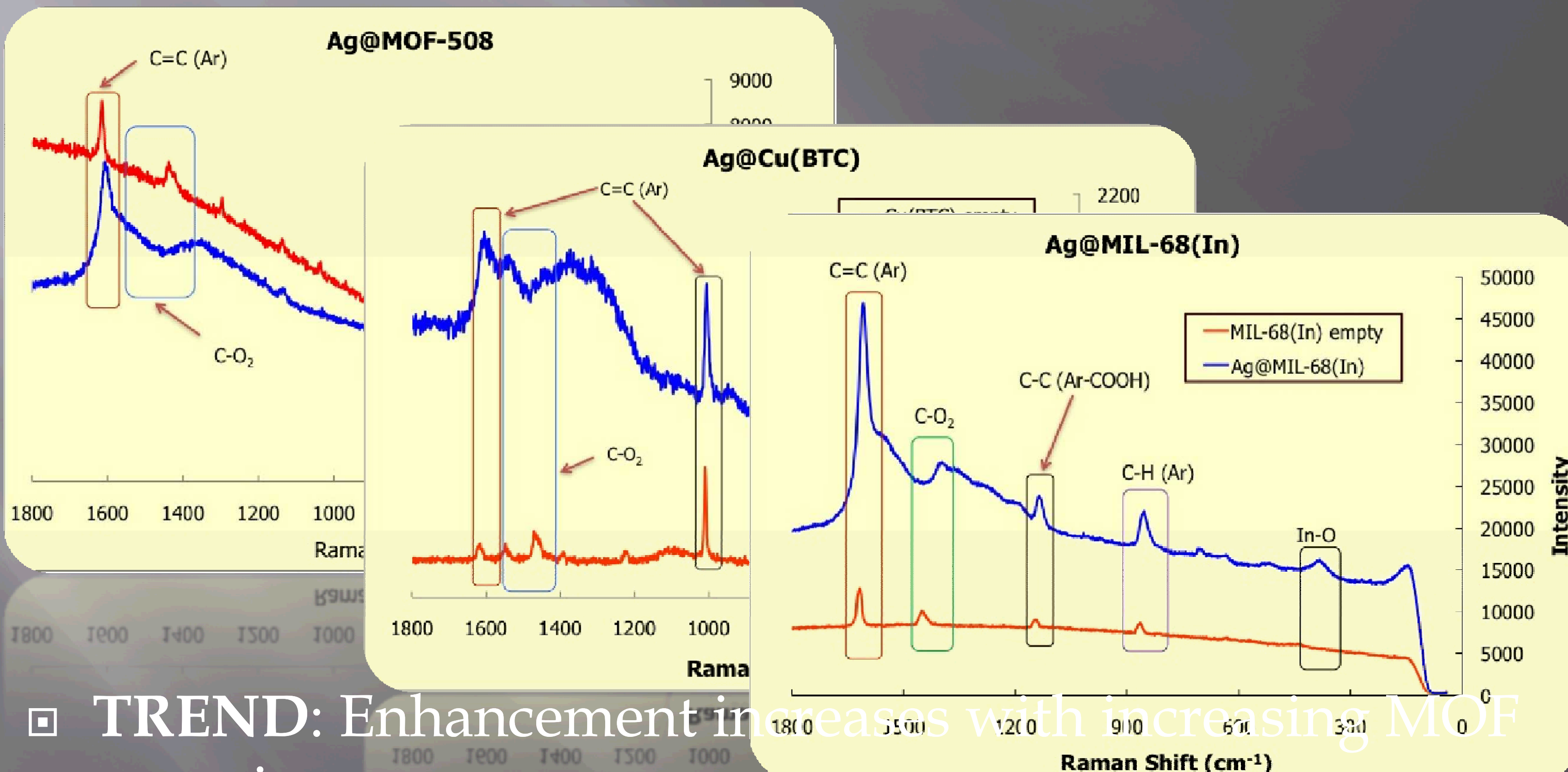
- EPR analysis suggests that a significant population of Ag_3 exists in the MOF interior



- The MOF imparts a kinetic barrier towards Ag agglomeration which is overcome by the electron beam

But do we see Raman effects?

- Raman enhancement was examined on all materials and showed weak but detectable signal enhancement.



- **TREND**: Enhancement increases with increasing MOF pore size.

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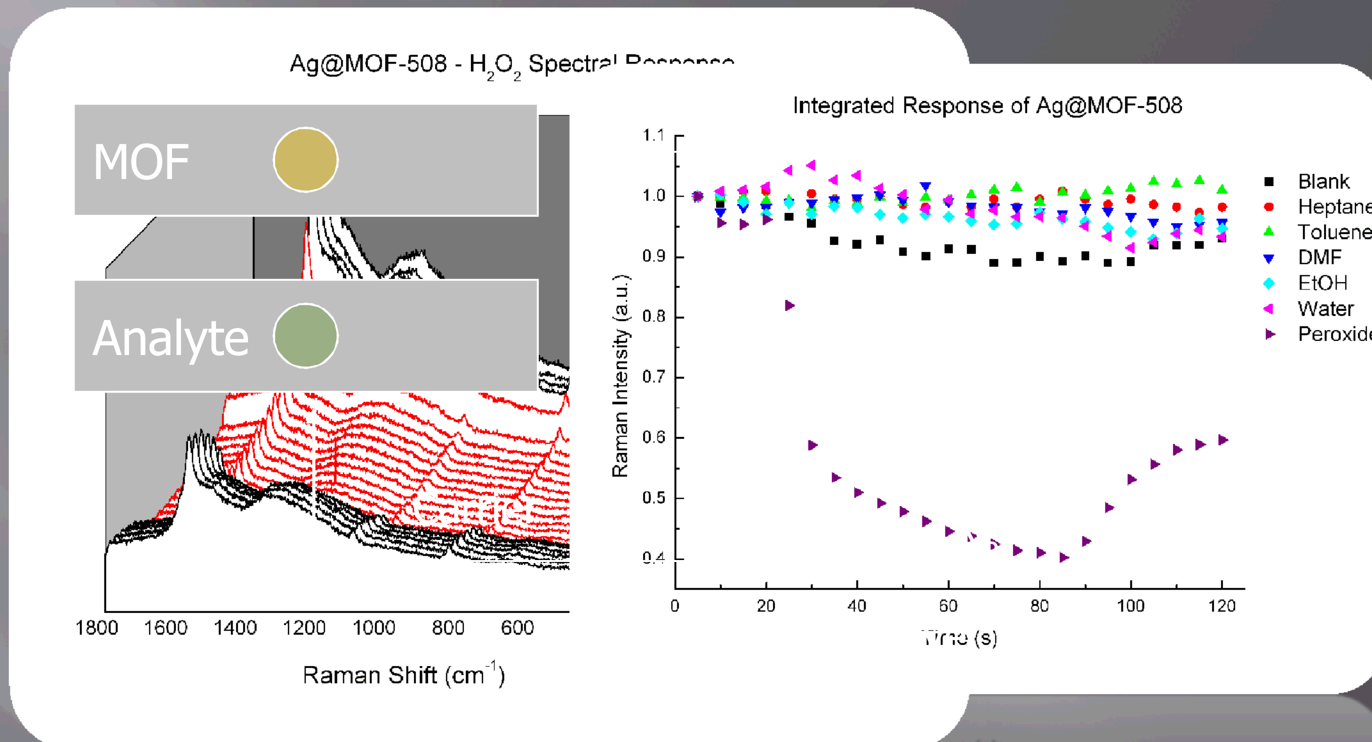
Sensing of Peroxide

- Ag@MOF-508 tested against a variety of volatile analytes.



- System shows rapid, selective and semi-reversible response to H_2O_2
- Likely mechanism of response is oxidation of the Ag_3 leading to drastic changes in the vibrational interaction with the framework.

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Conclusions

- Silver has been infiltrated into several MOFs using a general and gentle solution-based infiltration
- The MOFs impart a large kinetic barrier towards Ag agglomeration leading to molecular sized Ag clusters
- TEM analysis reveals the delicacy of MOFs and gives insight into previous imaging artifacts
- The infiltrated materials show enhanced Raman activity with greater enhancement with increasing pore size
- Preliminary results show that Ag@MOF-508 provides a rapid and strong indicator for the presence of H_2O_2

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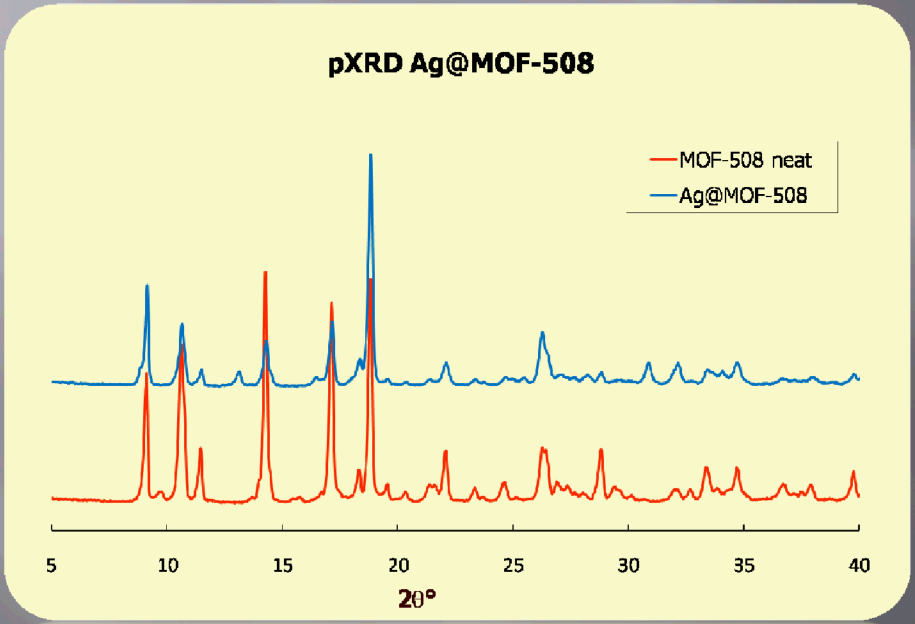
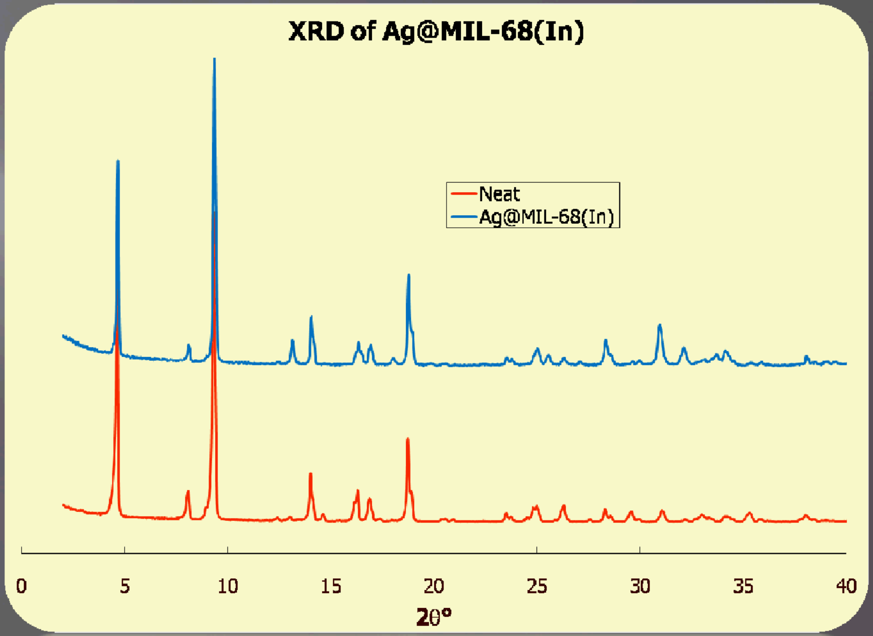
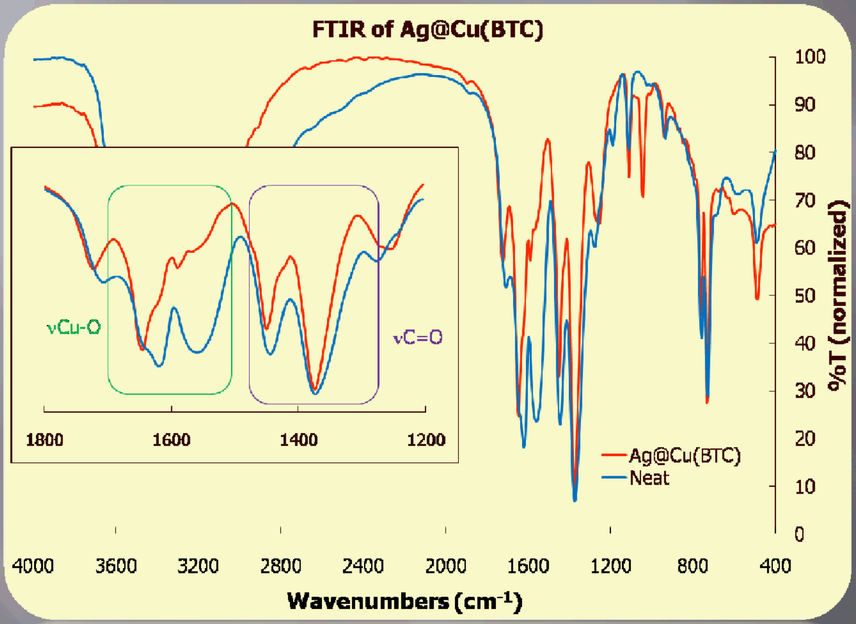
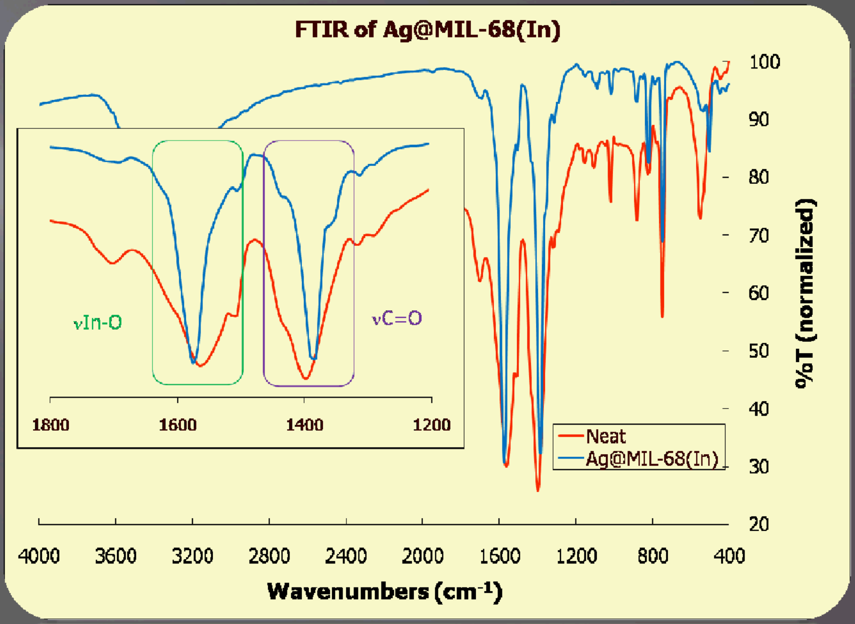
XRD of other MOFs





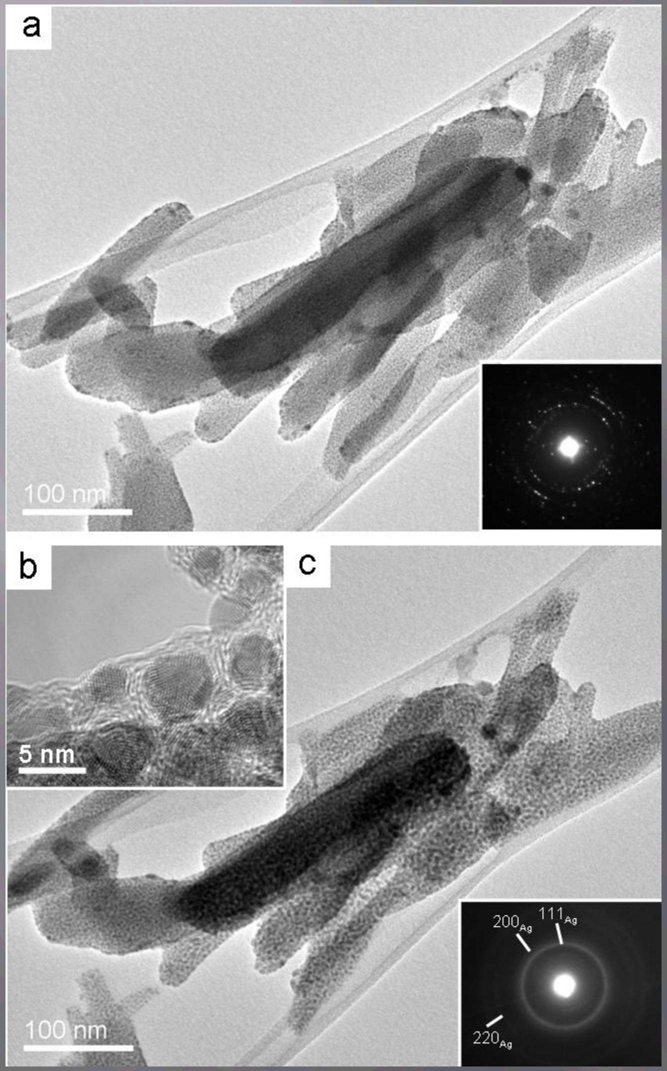
IRs of other MOFs





Before and After TEMS

Ag@MOF-508



Ag@Cu(BTC)