metal organic frameworks (MOFs) for CO2 capture

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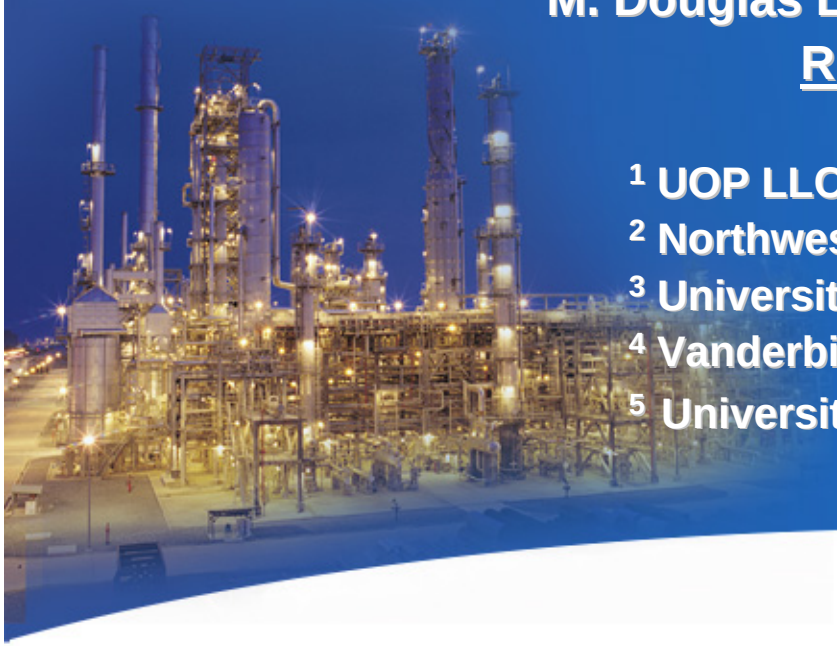

07 April 2008

AIChE Spring National Meeting

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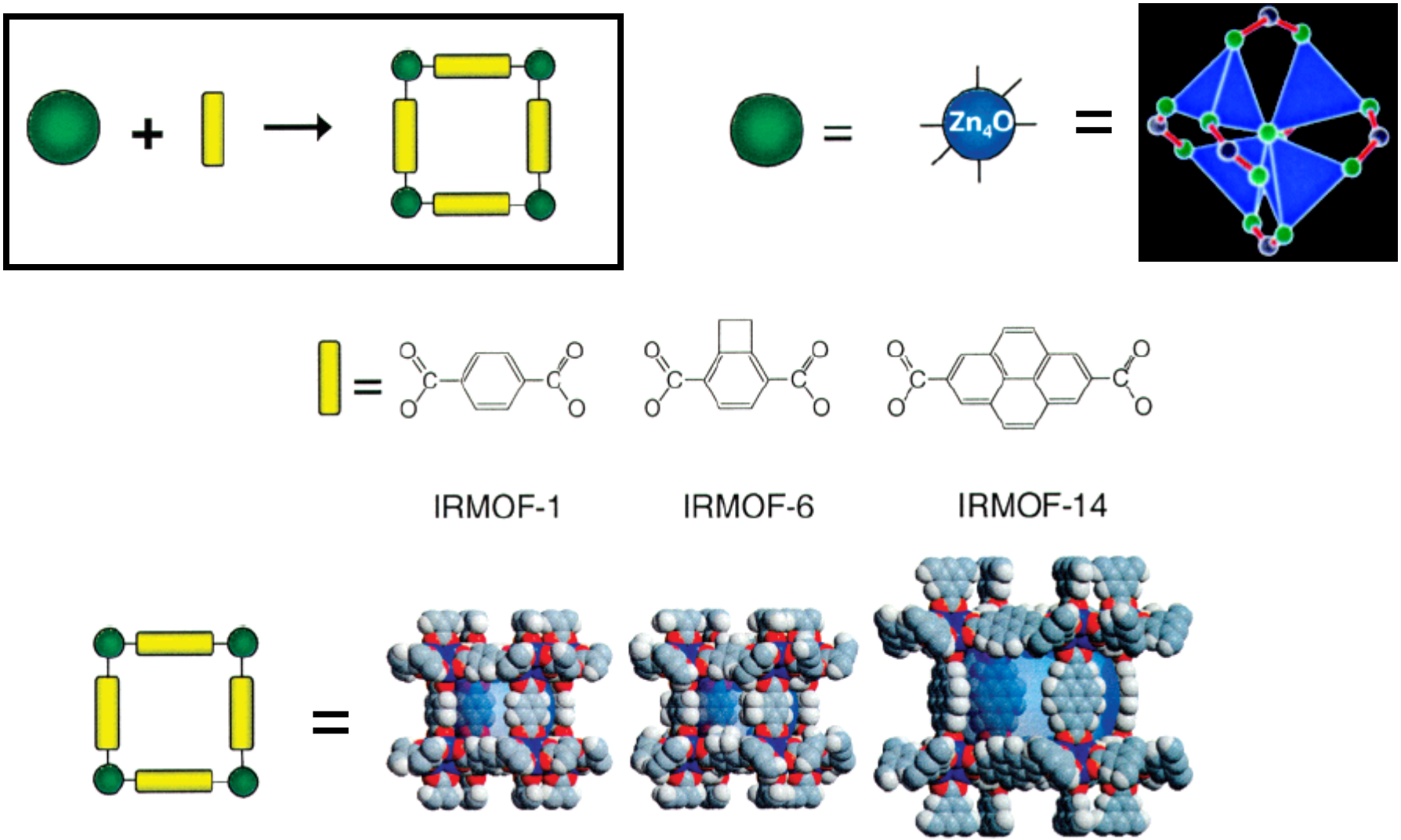
outline

- short introduction
  - MOF primer
  - relationships between zeolites and MOFs
- CO2 capture application
  - current progress vs. success criteria
- hydrothermal stability
  - laboratory vs. theory
- summary

MOF construction



some graphics from Yaghi, et al, Nature, 423 (2003) 705

synthesis: zeolite vs. MOF

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typical zeolite synthesis

crystallization → **solid-liquid separation** → **post synthesis treatments**

hydrothermal
hours to several days
ambient to 225 °C

filtration
centrifugation

heat treatment
ion exchange
forming

typical MOF synthesis

crystallization → **purification** → **activation** → **post synthesis treatments**

solvothermal
vapor diffusion
microwave
hours to several days
ambient to 225 °C

isolation
- density separation
- filtration

calcination
- remove starting materials

solvent exchange
calcination
- remove water
- remove solvent

forming
- graphite
- polymer

metal addition

MOF synthesis more specialized than zeolite synthesis

properties to exploit

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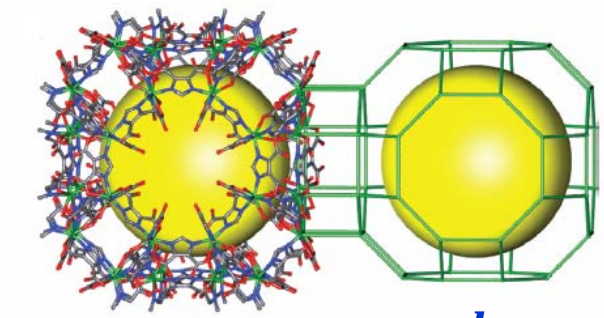
similarities to molecular sieves:

- synthesis conditions
- good yields
- crystalline
- tunable hydrophil(phob)icity and acid(basic)ity

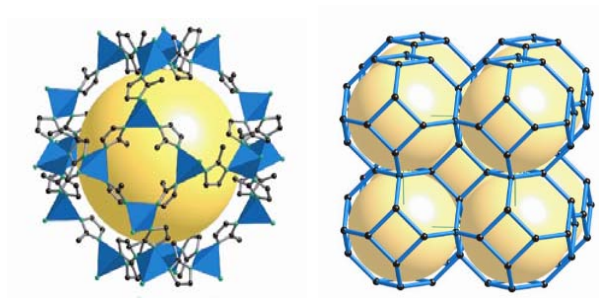


rho

ZMOF-rho from Eddaoudi, et al, *Chem Comm* **2006**, 1488

differences from molecular sieves

- lower temp stability (up to 450 ^{o}C reported)
- much higher SA/ PV
- more unobstructed gas diffusion
- much more diverse chemistry
  - many more metals/ metal clusters available
  - organic linkers can contain functionality



sod

ZIF-8 from Yaghi, et al, *PNAS* **2006**, *103*, 10186

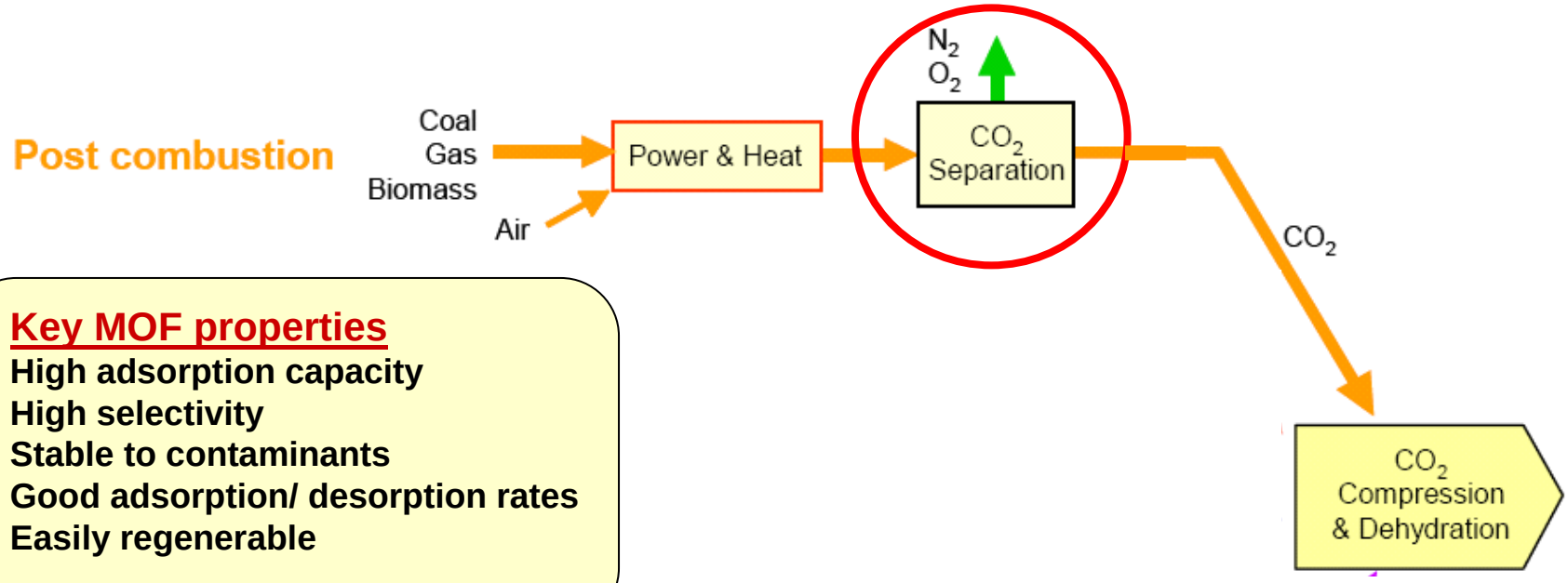
material	surface area, sq m/g	crystal density, g/cc	% free volume	pore size, Å	stability, deg C	CO2 heat adsorp, kJ/mol
NaX	700	1.91	49	7.4	> 700	50
IRMOF-1	3800	0.62	79	12	400	15

CO2 capture

DOE Target (2012):

90% CO_2 removal from flue gas at no more than 10% increase in electricity cost

Develop a low cost, novel adsorbent to remove CO_2 from flue gas and gasification streams



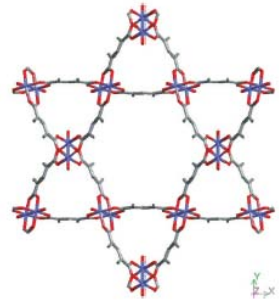
Key MOF properties

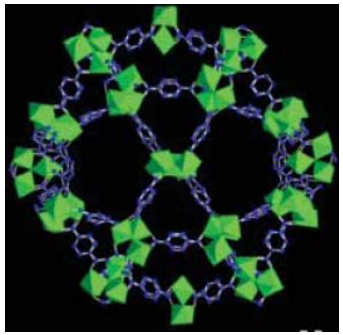
High adsorption capacity
High selectivity
Stable to contaminants
Good adsorption/ desorption rates
Easily regenerable

goal: 15wt% CO2 at 38 °C and 0.1atm

approach

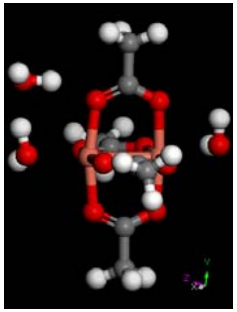
- **make MOF materials**
  - **team ideas**
  - **literature compounds**

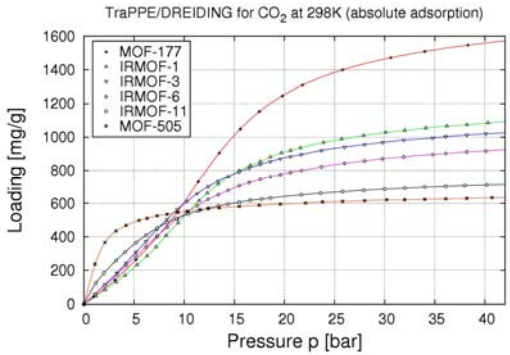




MIL-101 from Ferey, et al, *Science* **2005**, *309*, 2040

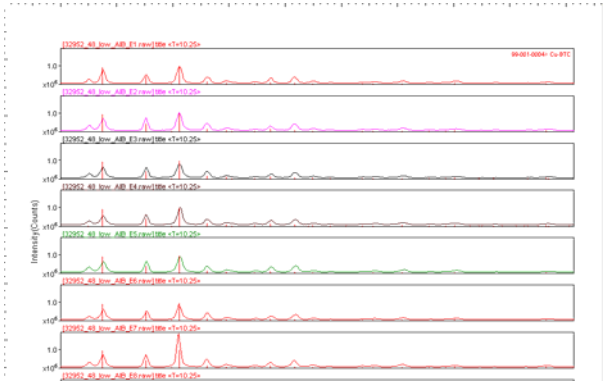
- **model interesting materials**
  - **isotherms**
  - **maximum theoretical surface areas**

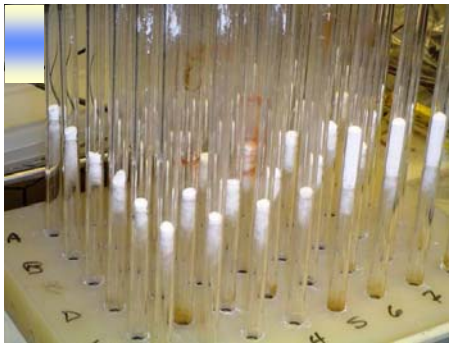




CuBTC from Williams, et al, *Science* **1999**, *283*, 1148

- **evaluate materials**
  - **adsorptive properties**
  - **hydrothermal stability**





early results

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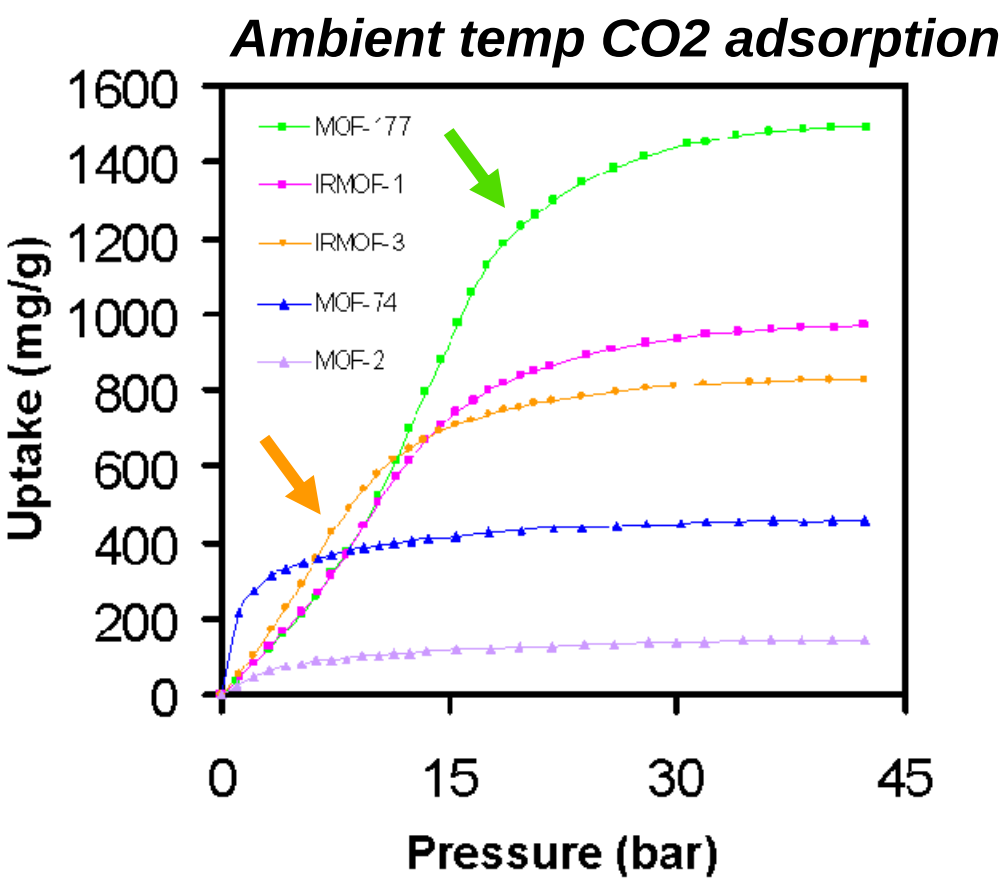
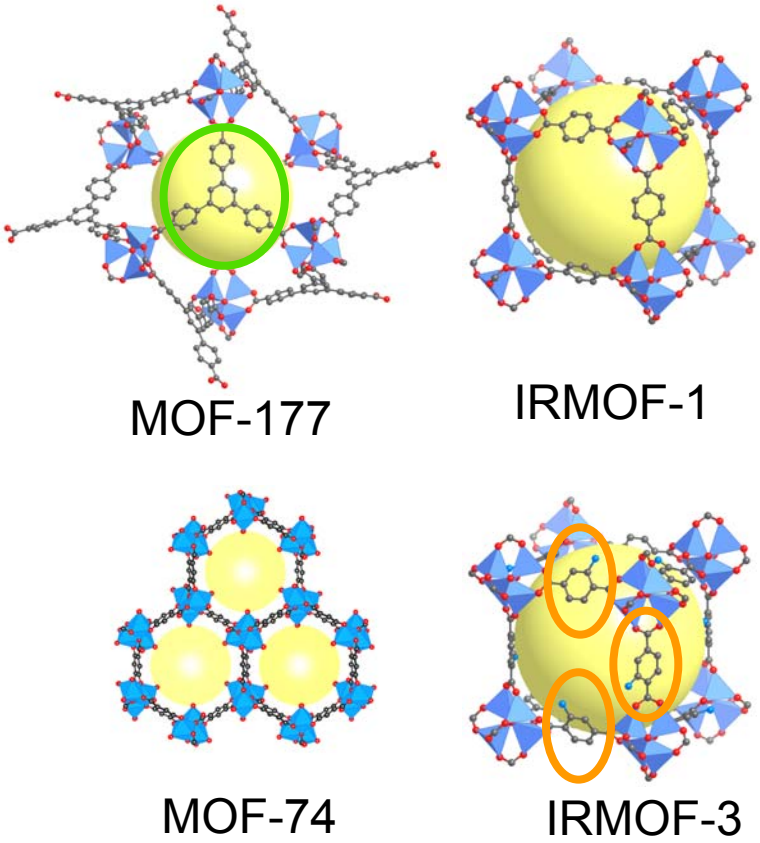
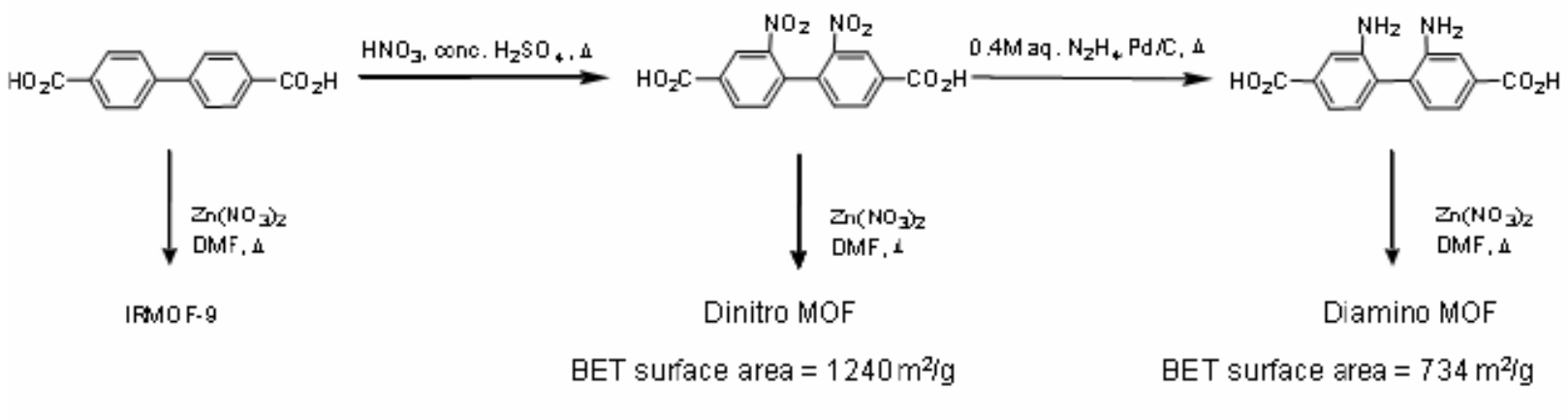
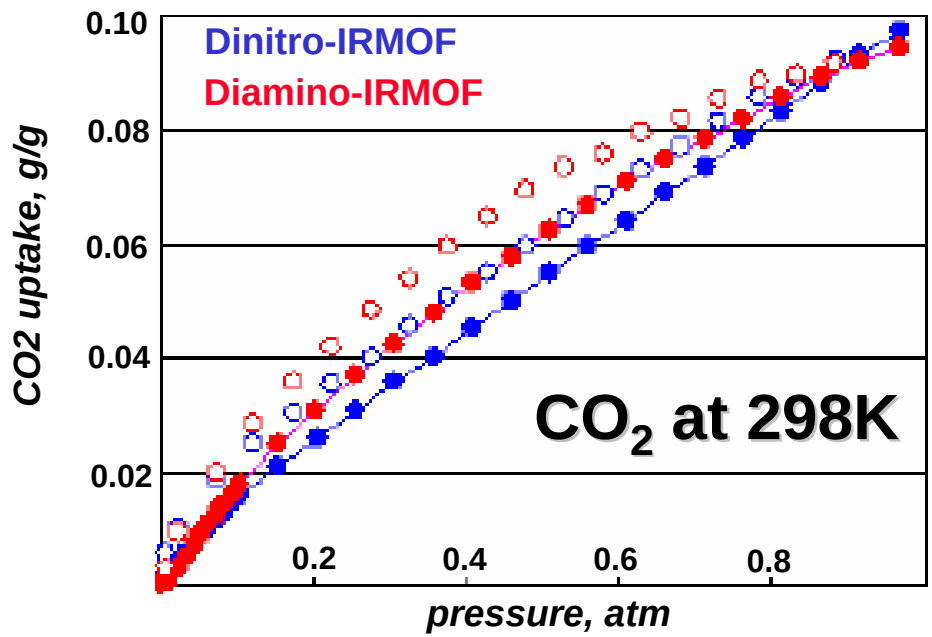




- **Increasing the length/ size of the organic linker increases capacity and decreases curvature of isotherm.**
- **Adding amine to IRMOF-1 linker increases capacity at lower pressure, decreases capacity at higher pressure and increases curvature of isotherm.**

today: amino-functionalized linker





boosting amine function did not increase CO2 adsorption!

today: meso-microporous MOFs

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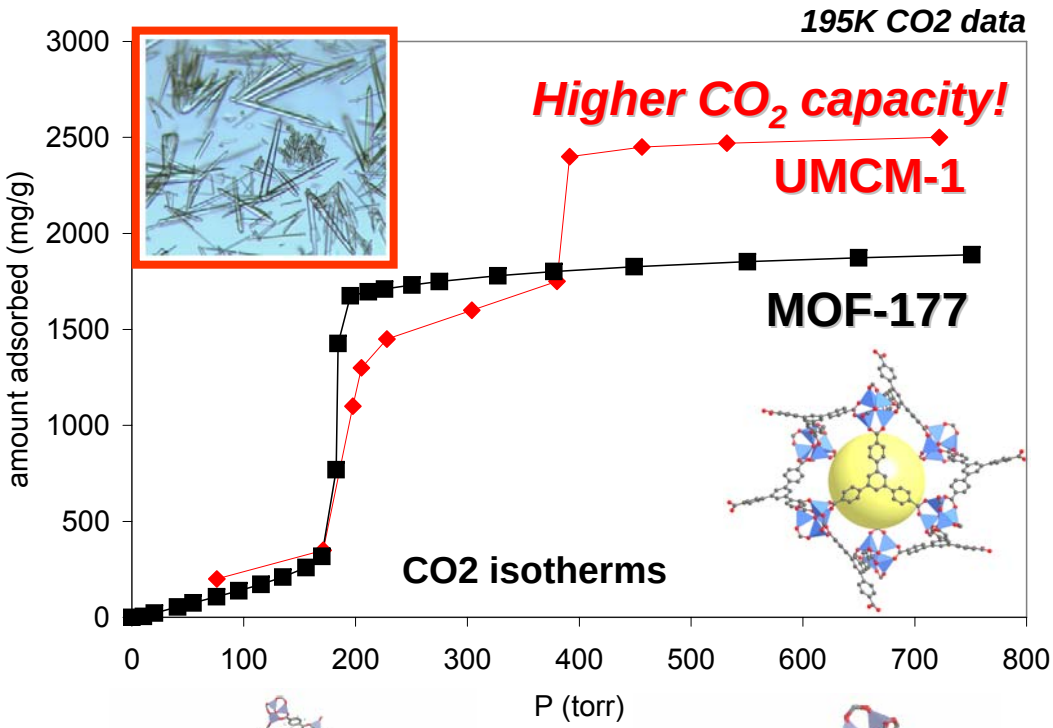
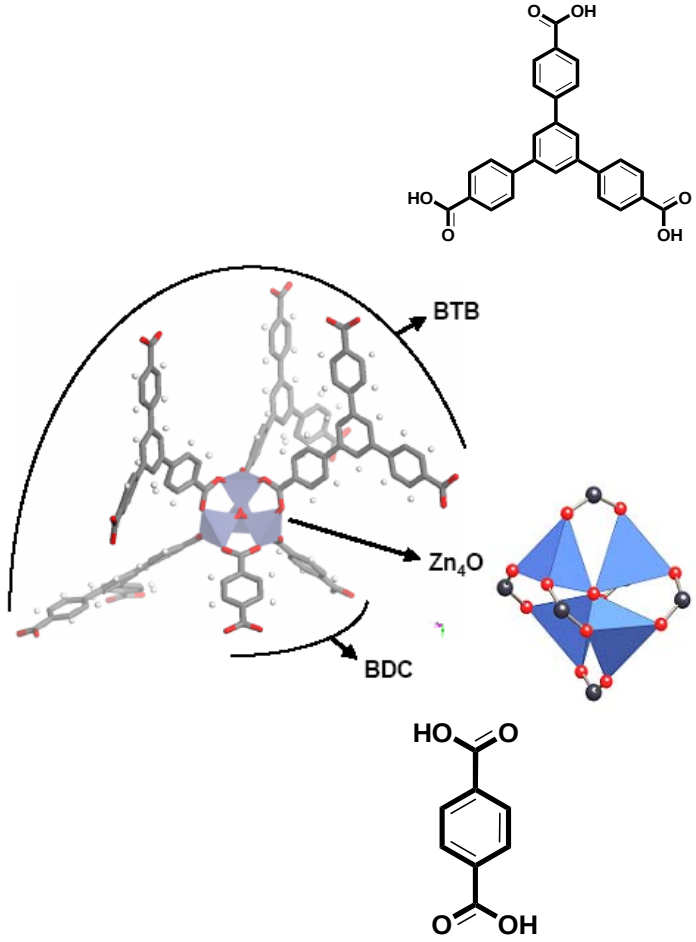
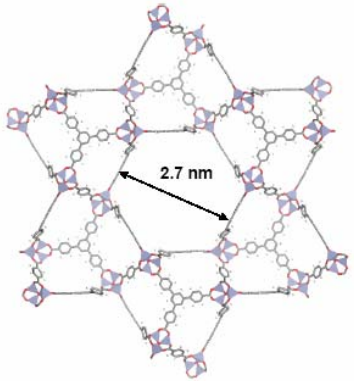
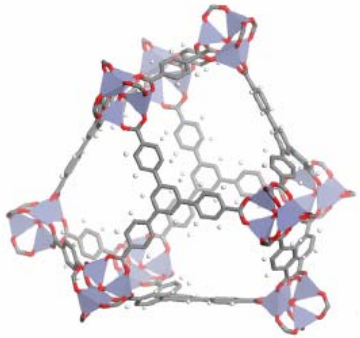
New mixed-linker MOF: UMCM-1







mesoporous channel



microporous cage

Matzger, et al, *Angew. Chem.* **2008**, *47*, 677

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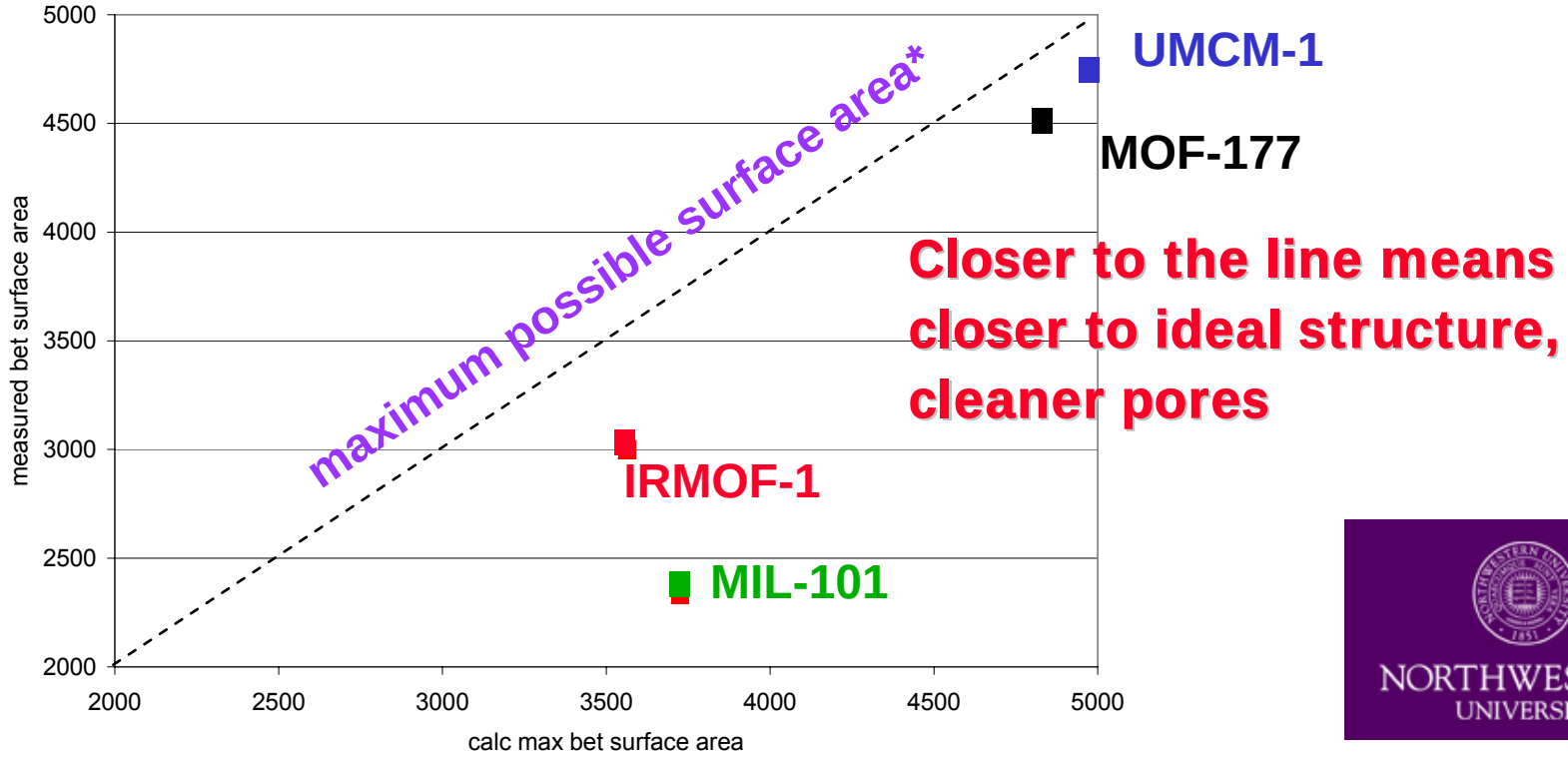
ultra-high surface area MOFs

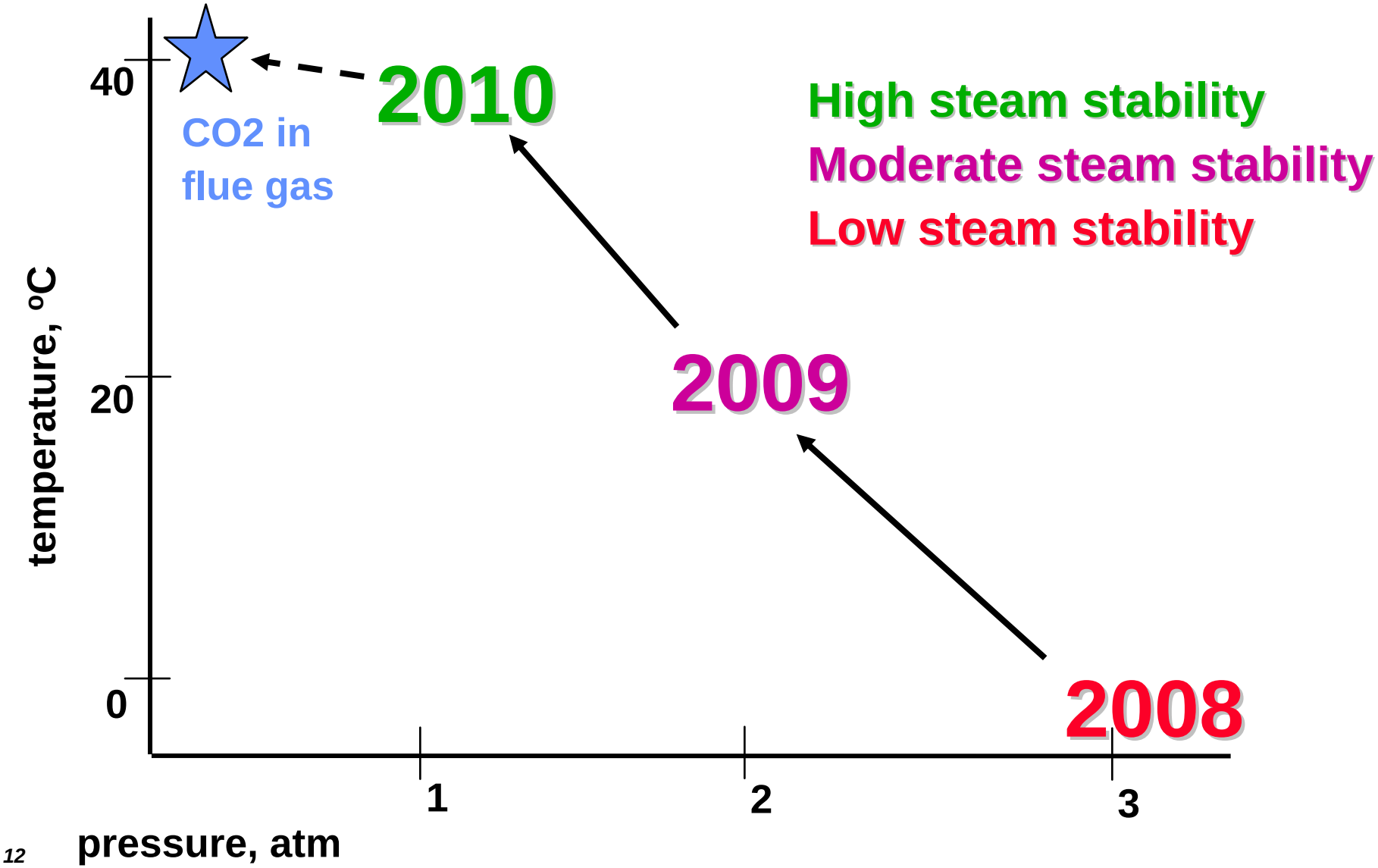
Material	crystal density, g/cc	calculated* surface area, (sq m/g)	measured** surface area (sq m/g)	reported surface area (sq m/g)
IRMOF-1	0.593	3563	3000	up to 4170
MIL-101	0.327	3725	2334	4100 to 5900
MOF-177	0.427	4833	4500	4500
UMCM-1	0.338	4972	4730	4730

*by Snurr, et al; ** BET method, measured at UOP or U Michigan

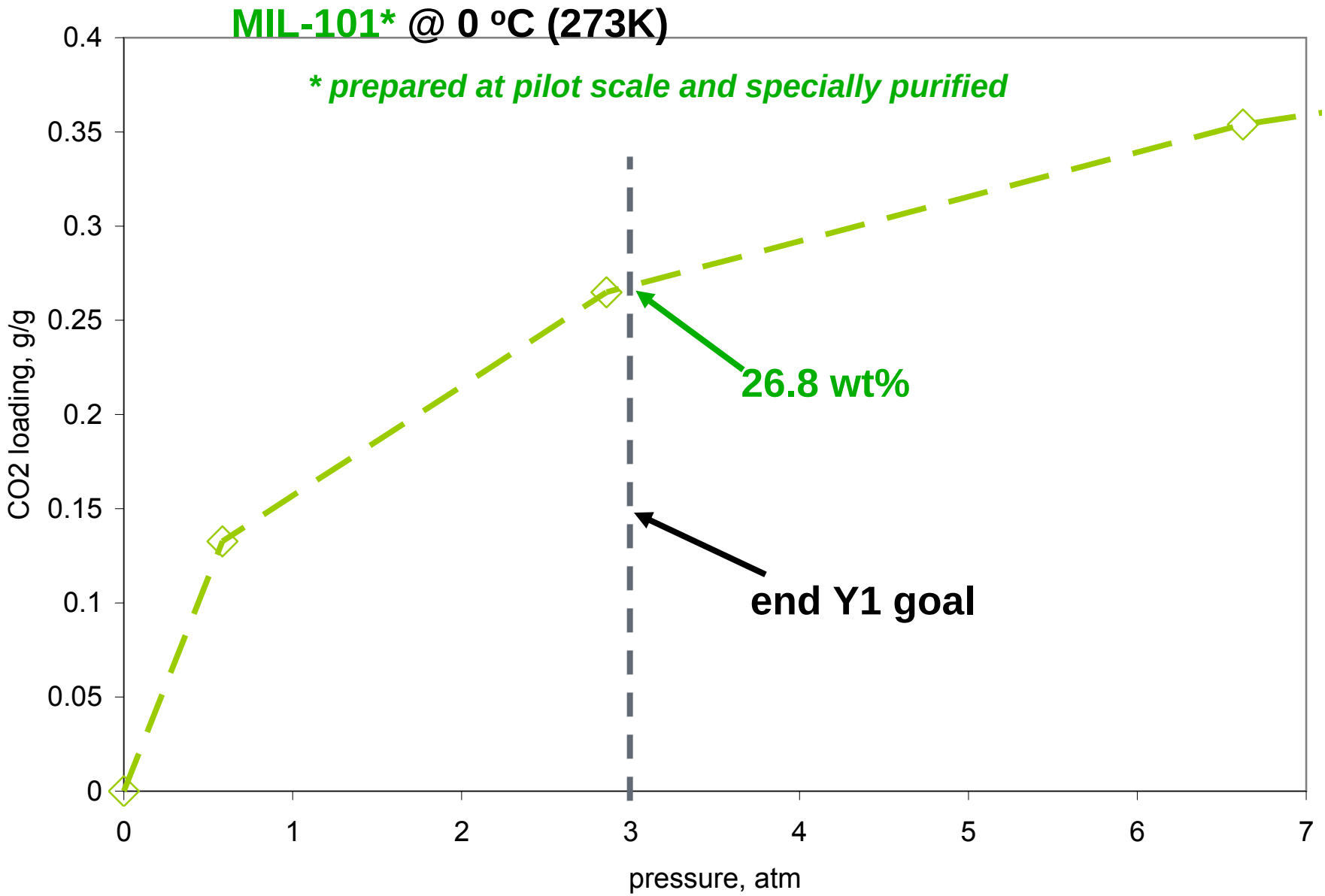


success criteria summary

all at least 15wt% CO2 loading

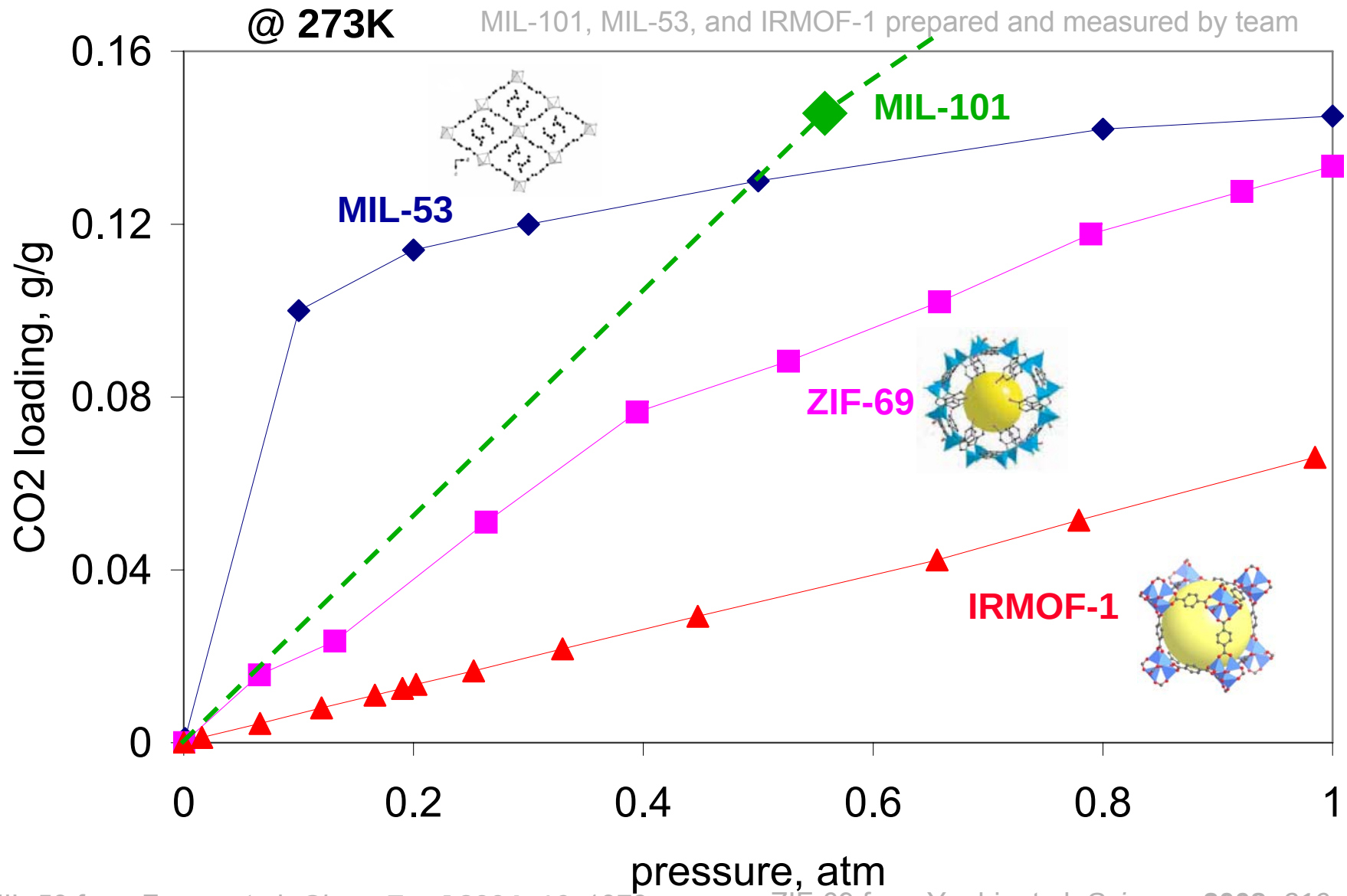


current status – *versus end Y1 goal*



also: MIL-101 has moderate steam stability

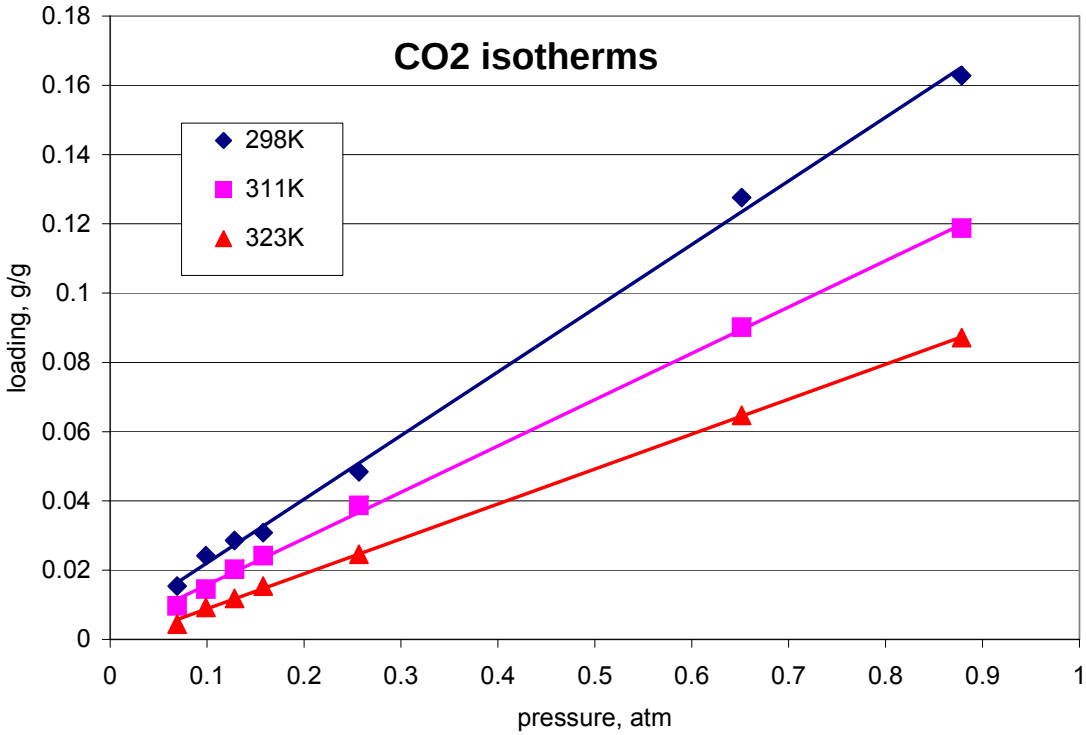
current status – *versus recent literature*

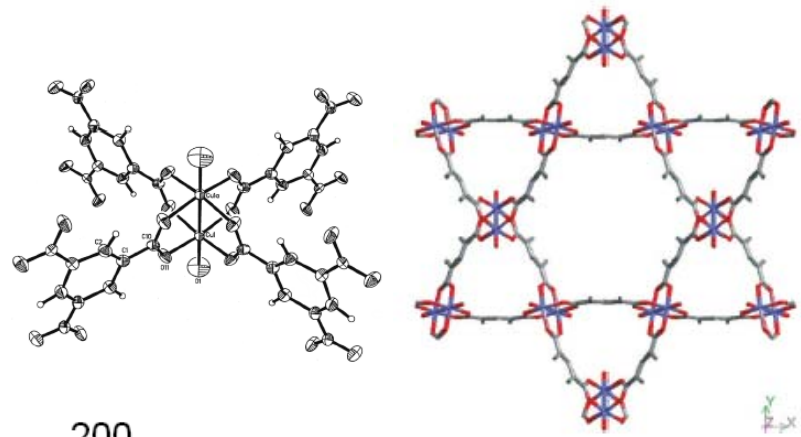


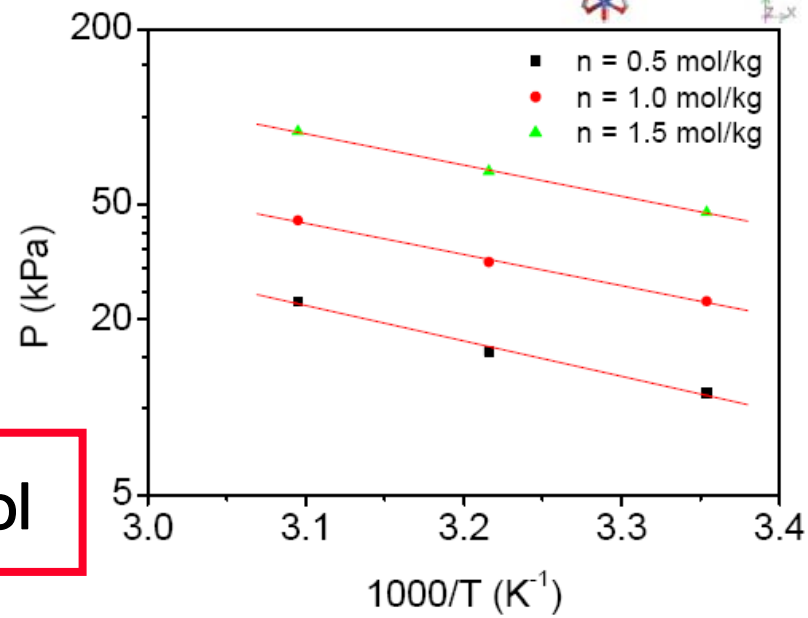
MIL-53 from Ferey, et al, *Chem Eur J* **2004**, *10*, 1373

ZIF-69 from Yaghi, et al, *Science*, **2008**, *319*, 939

CuBTC: ambient to high temperature







q_{st} of CO_2 on HKUST-1 : 23 ± 1 kJ/mol

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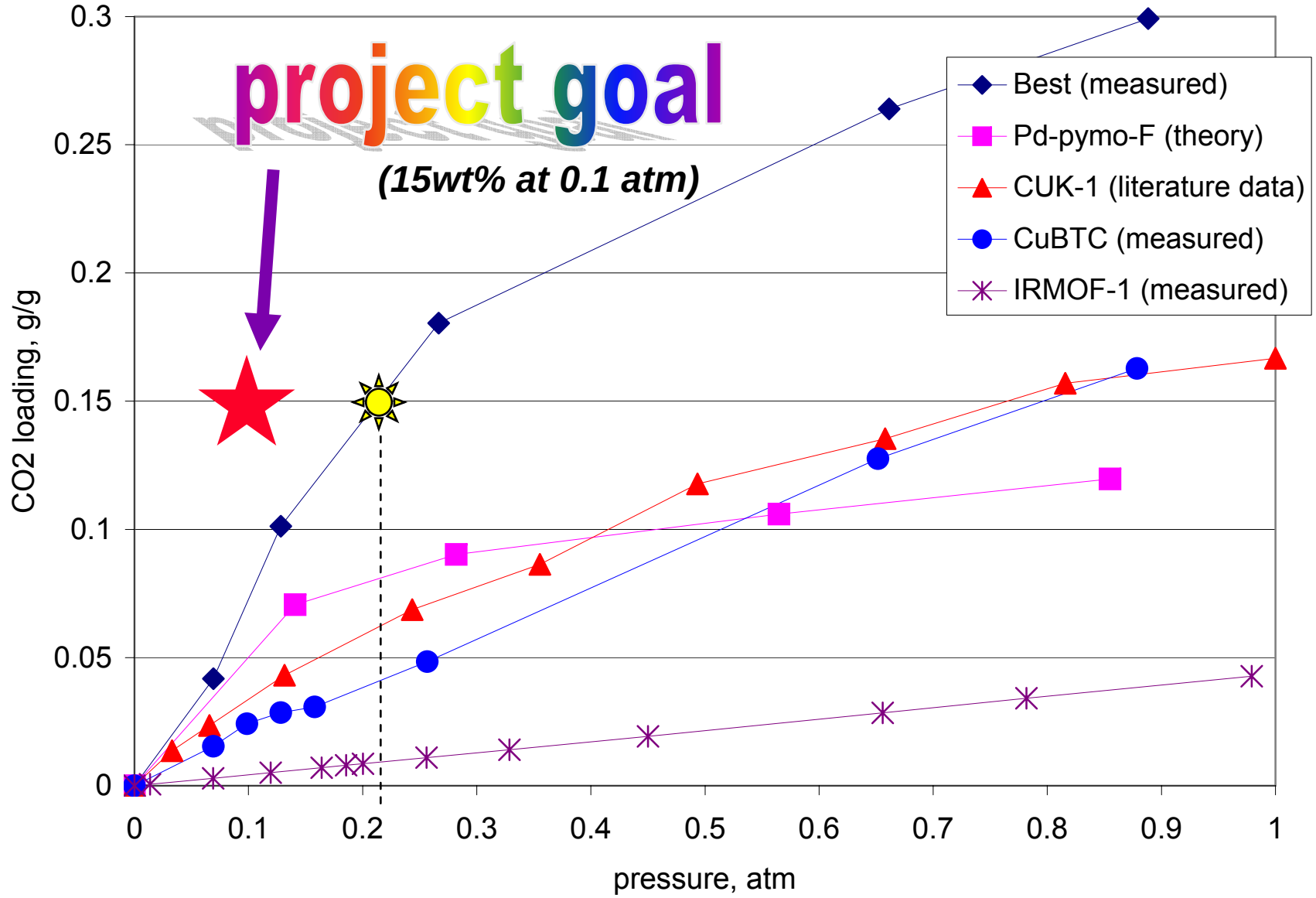
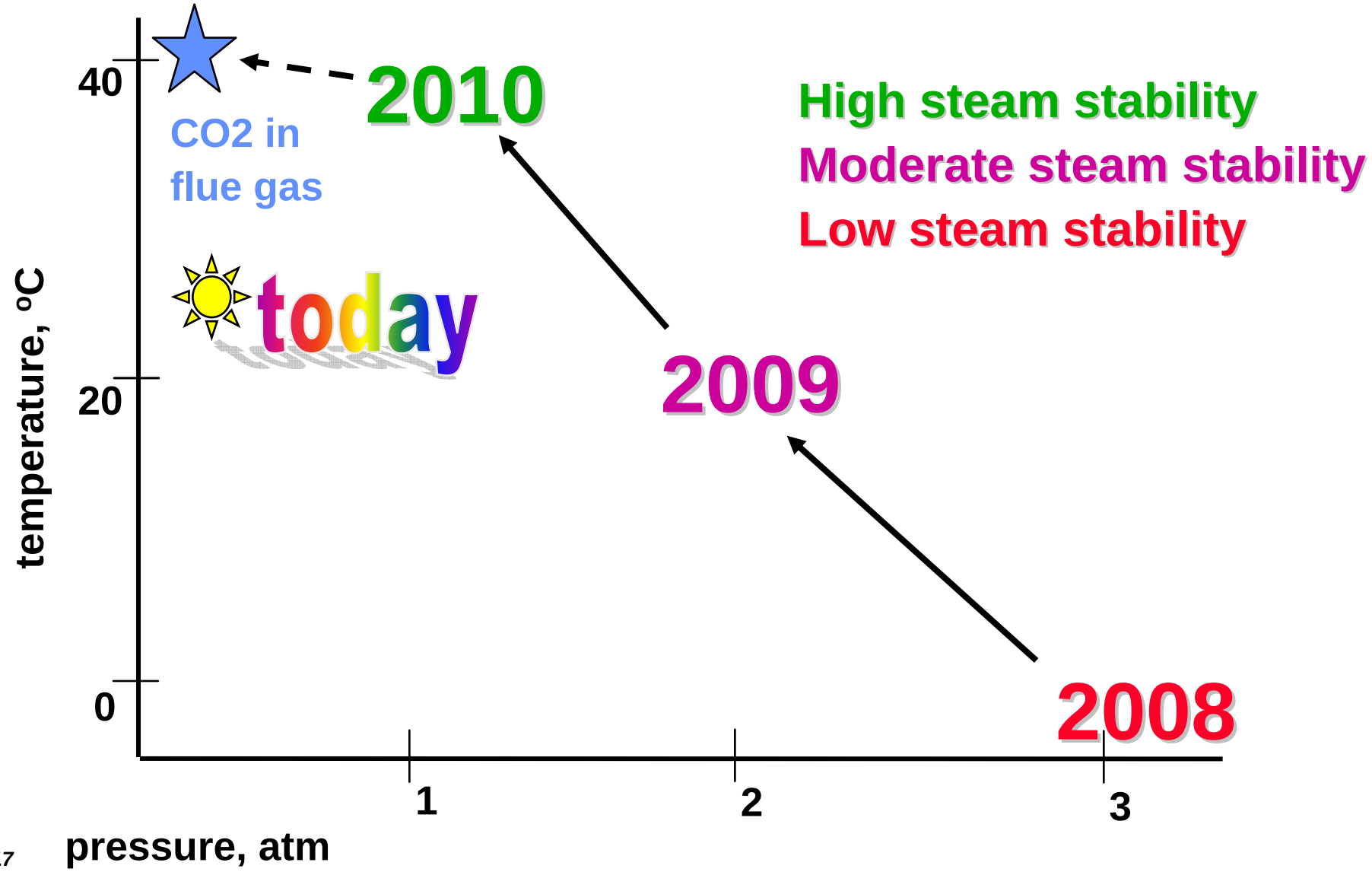
current status – *at 298K*

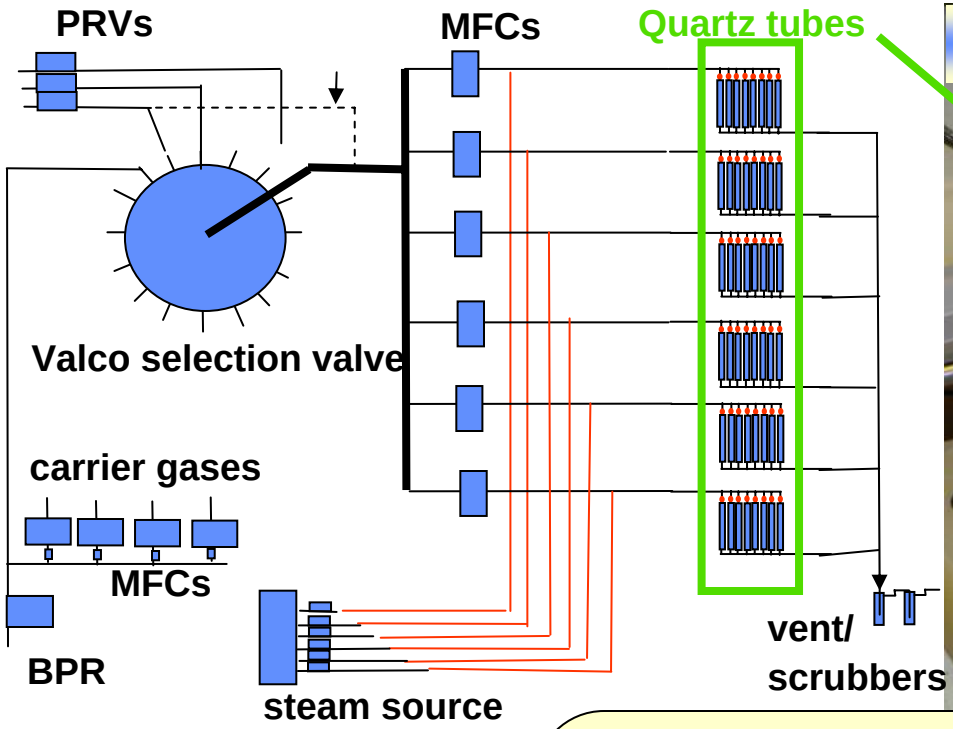


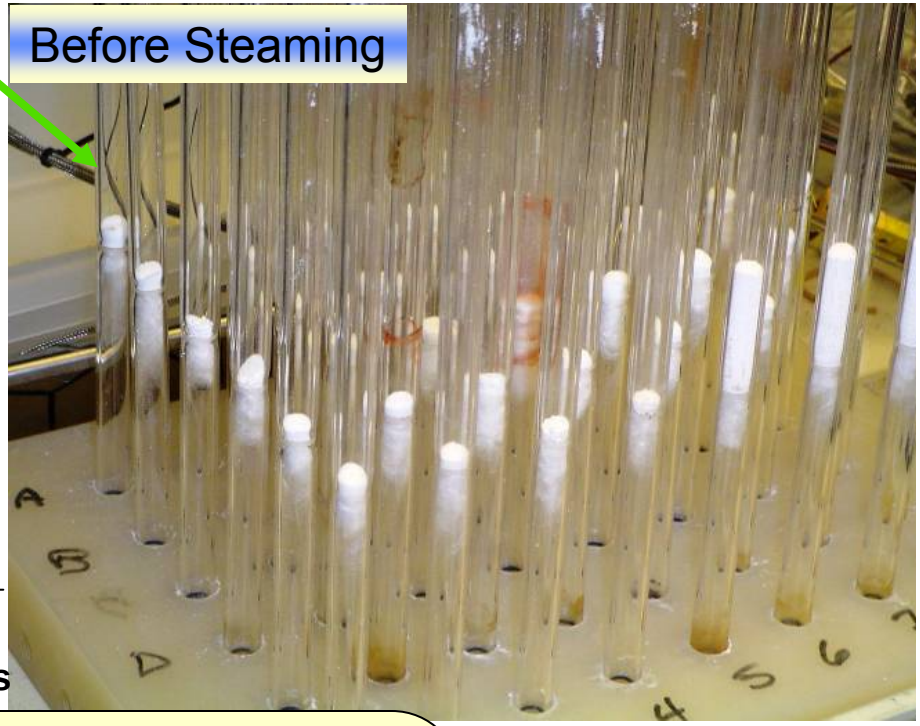
success criteria summary

all at least 15wt% CO2 loading



high-throughput hydrothermal stability testing



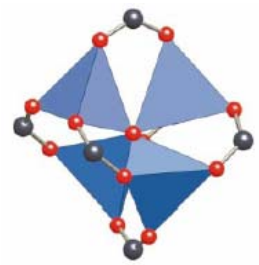


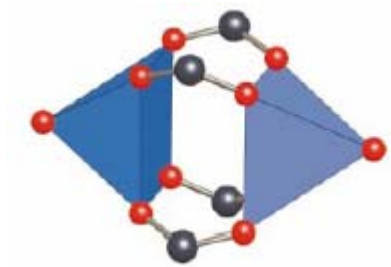
<u>as-synthesized samples:</u>

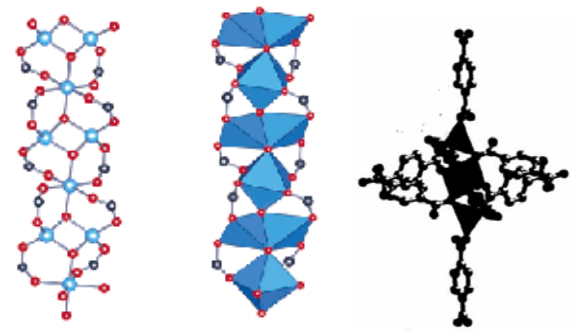
solvent exchanged
dried at 100C in N_2
loaded in air
activated 125C N_2 overnight
Steam 0 - 50%, 40 - 400C, 2 hours
Unload in air, XRD in air

for flue gas, hydrothermal stability will be critical

example study:
zinc in different coordination environments







4-coordinate

IRMOF series
ZIF-8

5-coordinate

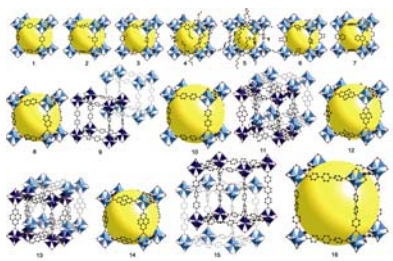
MOF-508*
Zn-IDC**

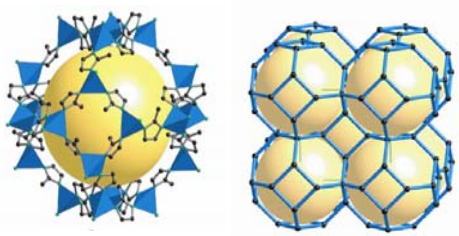
6-coordinate

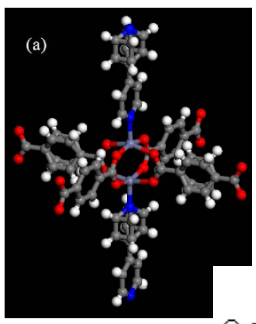
MOF-74

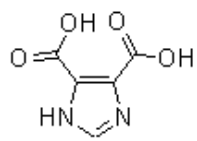
4- + 6-coordinate

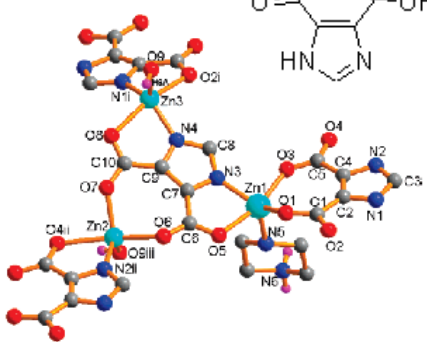
MOF-69C
MOF-144

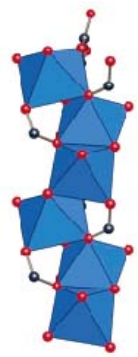


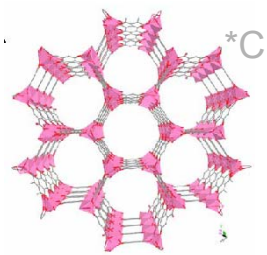


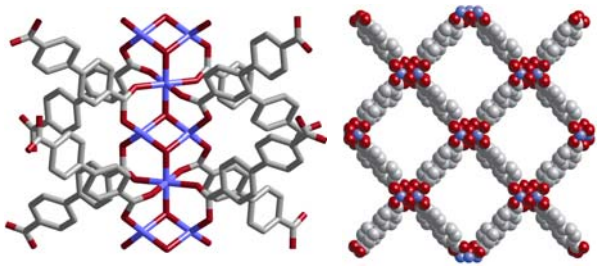












*Chen, et al, *Angew Chem*, **2006**, *45*, 1390

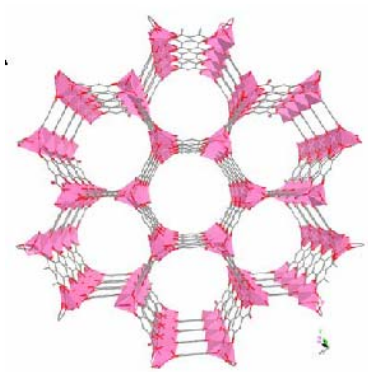
** Zhou, et al, *Inorg Chem*, **2007**, *46*, 5835

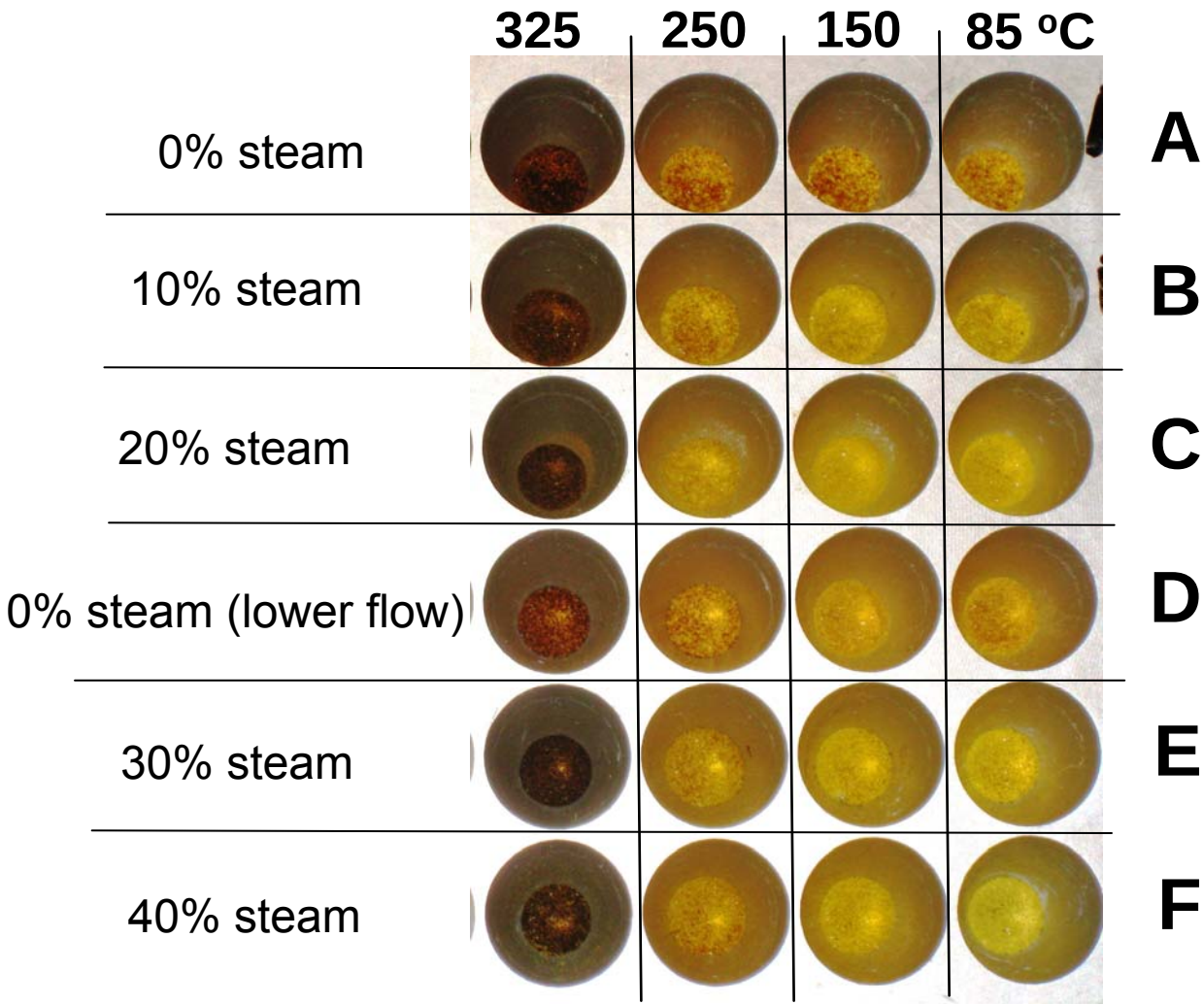
Zn-MOF-74 after steaming

6 coordinate

- color gets darker with increasing temp

- rows A and D (nominal duplicates) have comparable colors





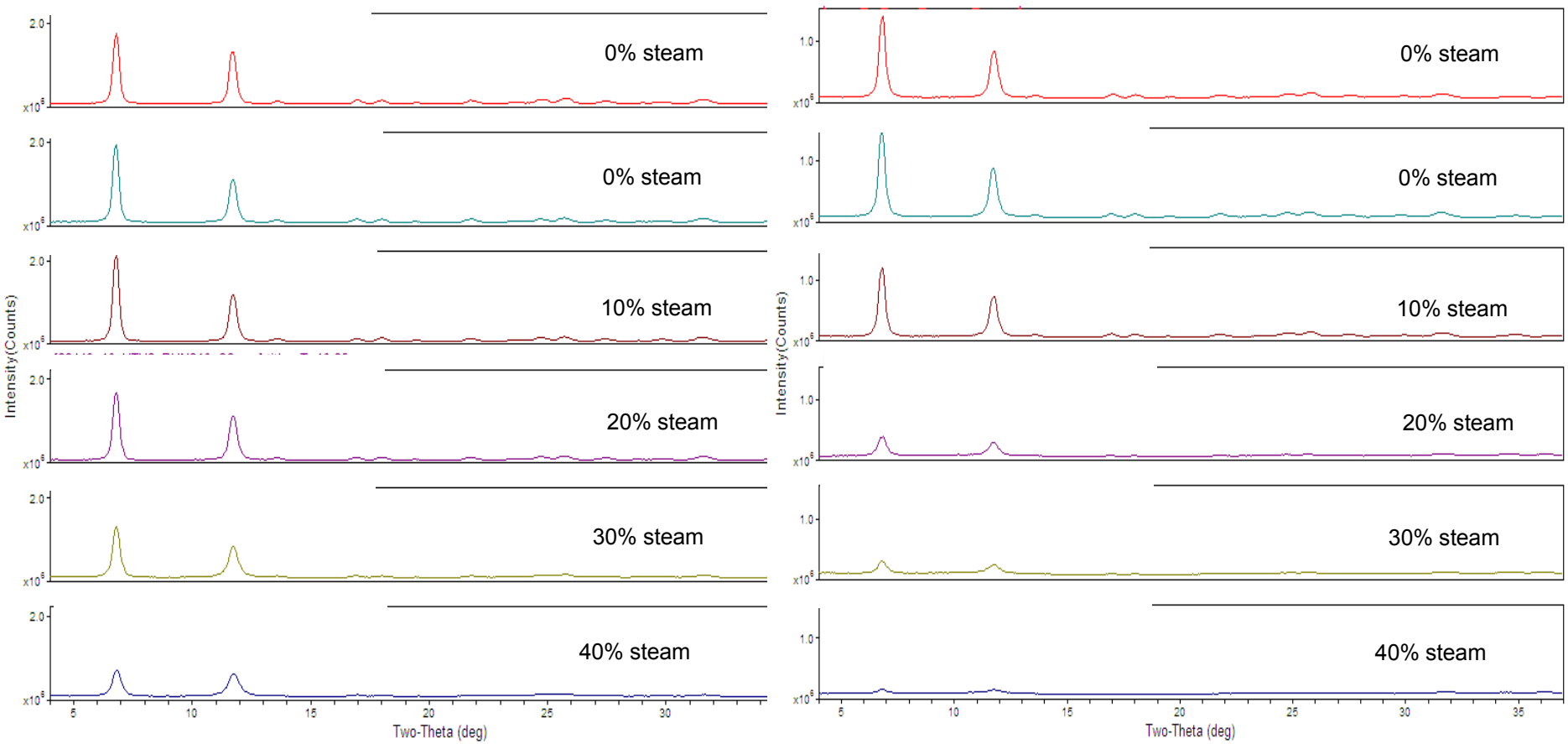
Zn-MOF-74 after steaming XRD results

- reasonable stability at 250 °C and up to 40% steam

6 coordinate

- at 325 °C, stability falls off as steam level increases

250 °C **325 °C**



in situ high temperature XRD with steam

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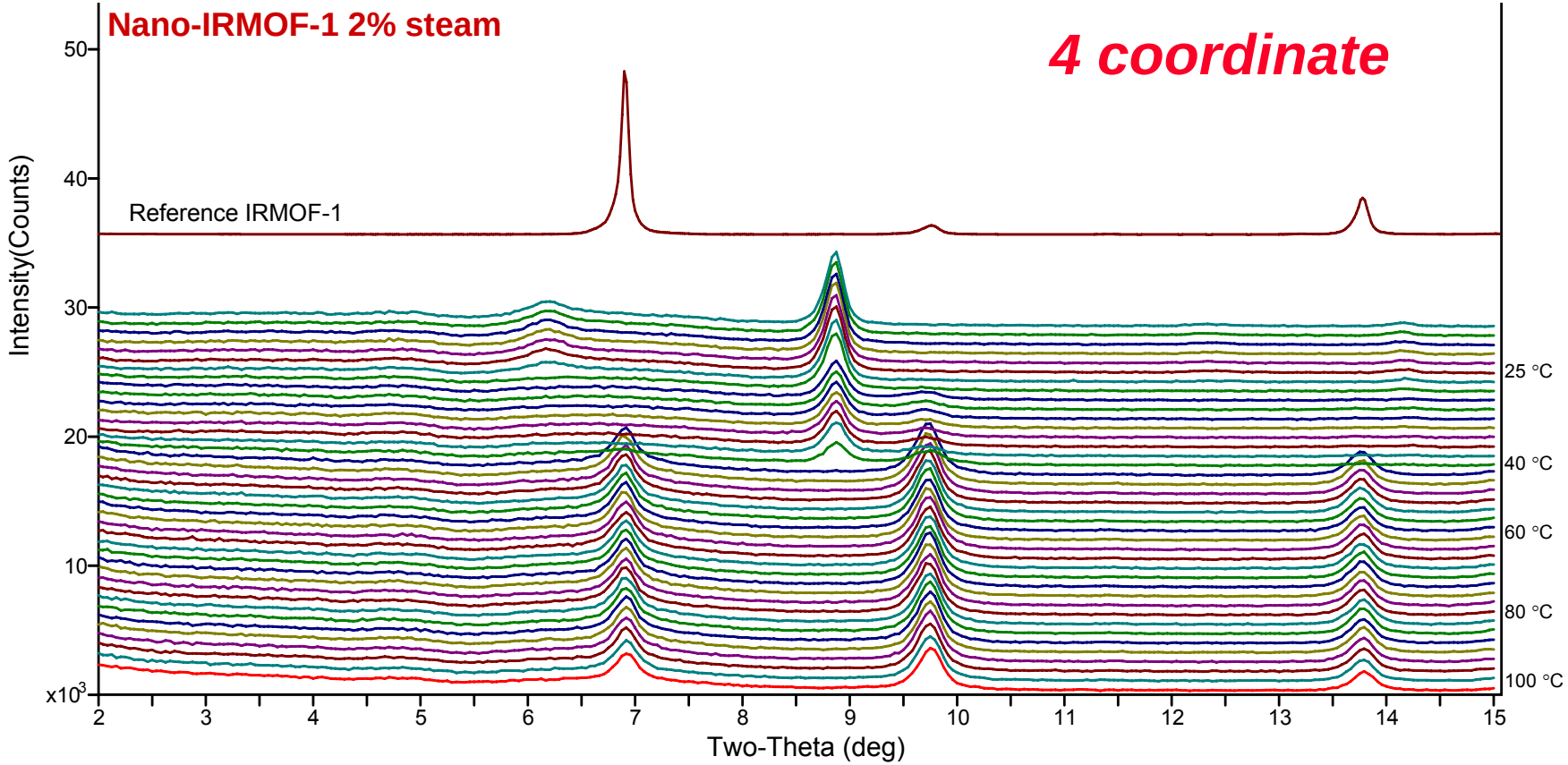
More easily investigate effects of — **time exposed to steam**
cycling

Eliminates variables of — **condensation (error in steam delivered, liquid contact)**
drying between steaming and XRD

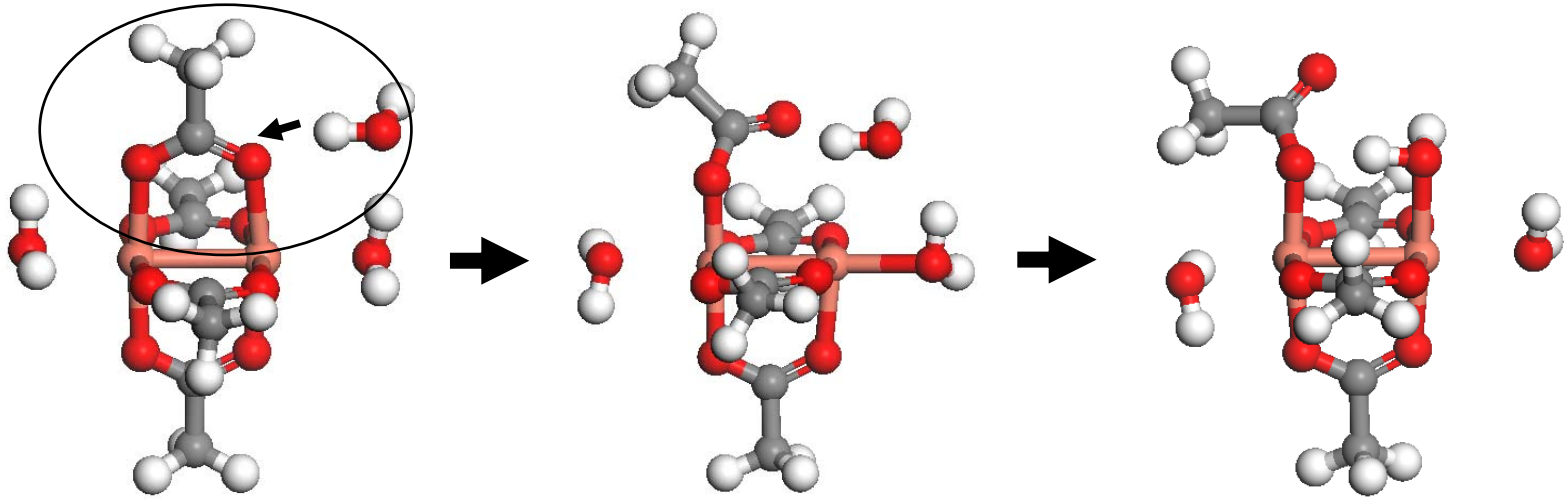


For Zn MOFs: 6 >> 5 > 4 > 4 + 6 coordinate

quantum chemistry model

MOF stability to hydrolysis:

$Cu_2(CO_2CH_3)(H_2O)_2$ model for Cu HKUST-1



Reactant	Transition State	Product
E=0	$\Delta E^{\ddagger}$=28.9 kcal/mol	ΔE=13.9 kcal/mol

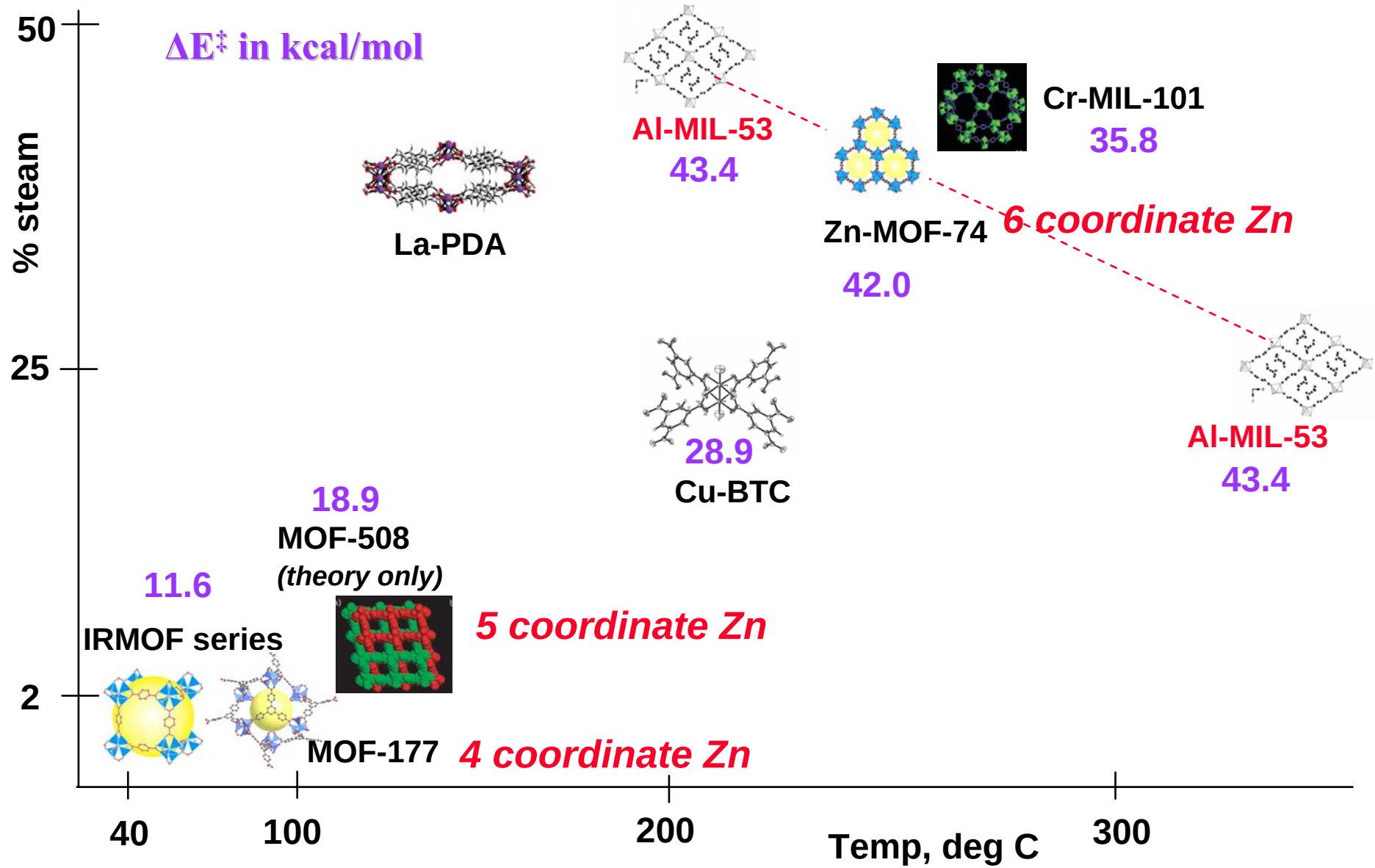
- Ligand displacement by H_2O is initial step in hydrolysis reaction.
- $\Delta E^{\ddagger}$ correlate with observed MOF stabilities (e.g., Cu HKUST-1 more stable than IRMOF-1).

(GGA/PW91) DMOL3(Accelrys) software

Water stability:

Model correlates with experiment

steam stability map



LaPDA from Wang, et al, *JACS*, **2003**, *125*, 3062

summary

- a wide variety of MOF materials successfully synthesized
  - linkers range from cheap to exotic
  - metals include Zn, Cu, Al, Cr, V, Pd and lanthanides
  - several have been prepared at large scale

- factors that make a good ambient temp, low pressure CO2 adsorbent
  - moderate pore size
  - appropriate adsorption sites
  - moderate to high surface area/ pore volume

- MOFs are hydrothermally stable
  - Highest metal coordination = best

- theory correlates well with experimental results
  - isotherms and predicted maximum surface areas match nicely
  - hydrothermal stability predictions trend with steaming studies

not discussed today

acknowledgements

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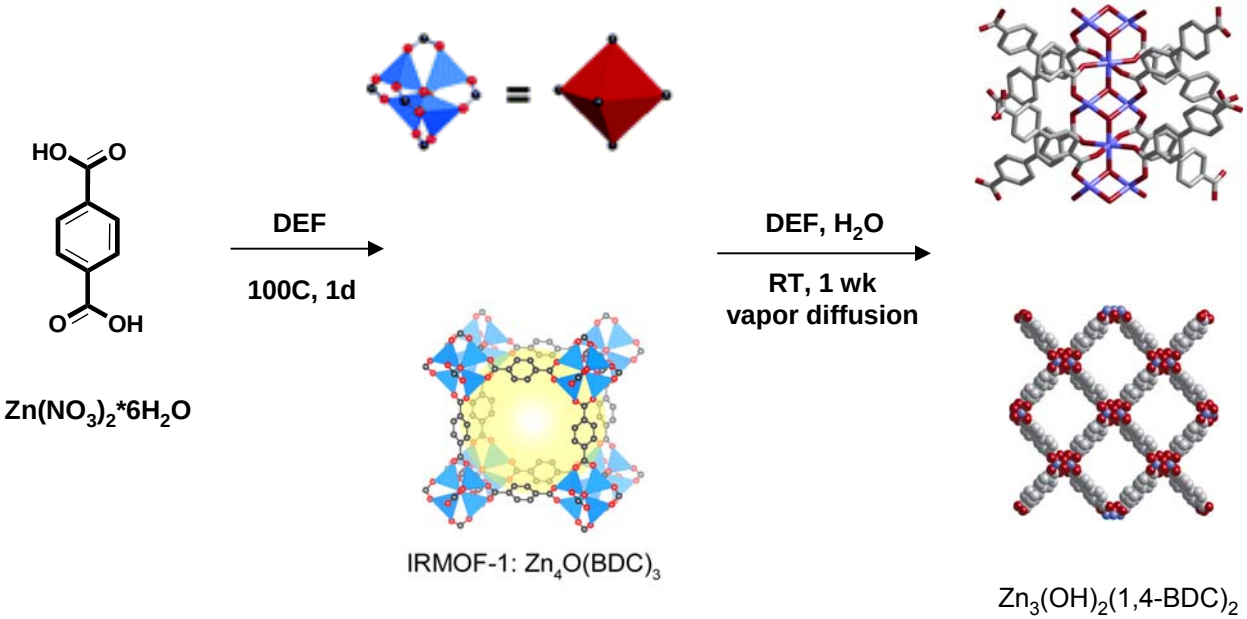
UOP Selexol™ process

- For bulk CO2 removal
  - Dimethylether of propylene glycol (liquid)
  - CO2 and/or other acid gas is captured, then sorbent is regenerated with heat
- Experience
  - Leading technology for Clean Coal to Power and Hydrogen technology
  - Over 55 units in service dating back to 1970s

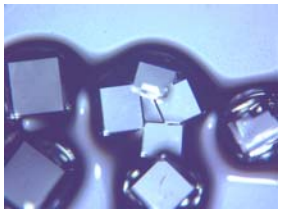
Zn-MOF-69C after steaming XRD results

- *not stable to activation!*
- *makes sense, considering synthesis:*

4 + 6 coordinate



IRMOF-1



MOF-69C

N. Rosi PhD thesis, U Michigan, 2005