Institut de recherches sur la catalyse et l'environnement de Lyon IRCELYON

MOFs in Catalysis

« **The Emperor's New Clothes** » ?

D. Farrusseng

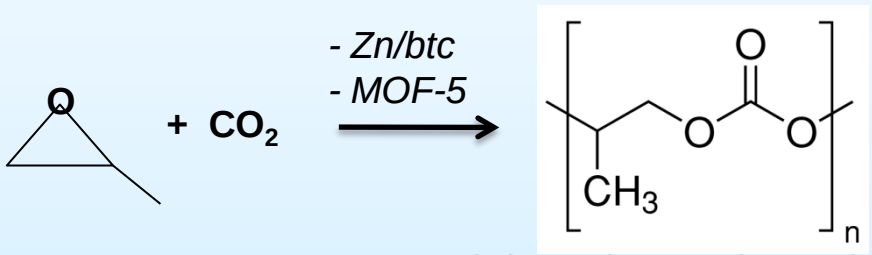
1 – Acid Catalysis
2 – Acid/Base
3 – Encapsulation
4 – Organometallics / Enantioselective Cat.
5 – Photocatalysis
6 – Polymerisation

1 – Acid Catalysis

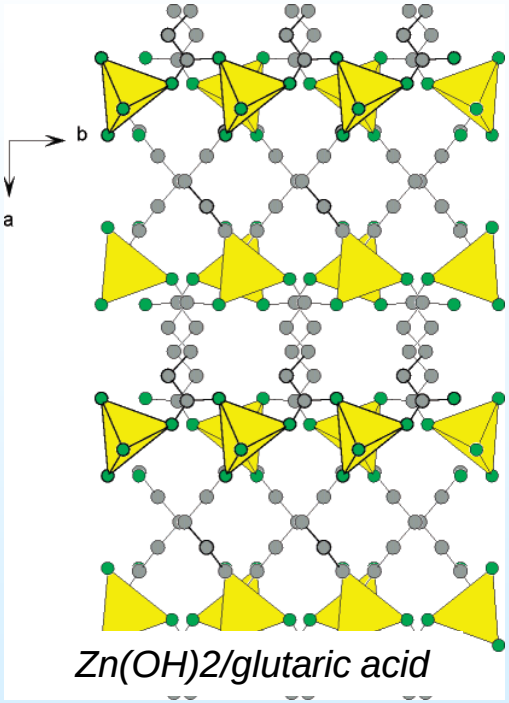
? ! ? !

- First catalyst generations

- ZnEt2/pyrogallol > ZnEt2/H2O
- ZnO/glutaric acid > Zn(OH)2/glutaric acid > Cr(OOCCH3)3



poly(propylene carbonate).
Mw = 60.000-75.000 g/mol



Zn(OH)2/glutaric acid

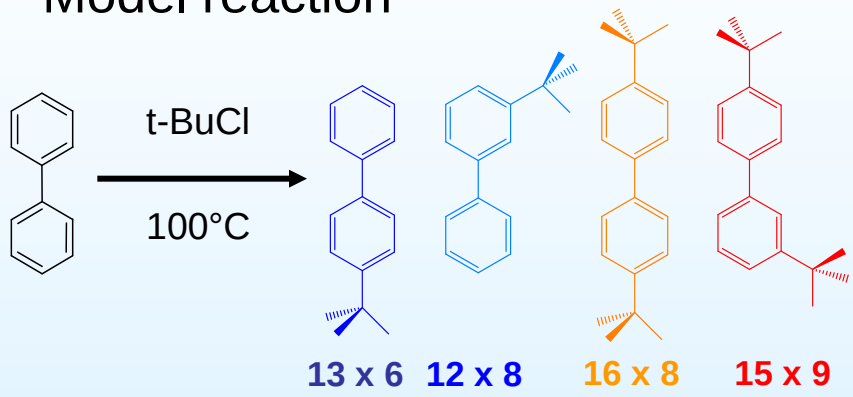
- BASF patent 2002

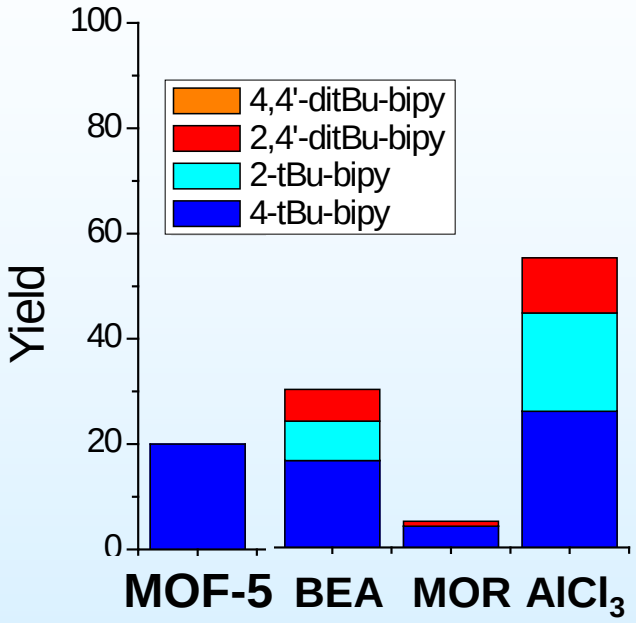
US20020279940

Inoue, S.; Tsuruta, T.; Furukawa, J. Makromol. Chem. ***1962, 53, 215***
Soga, K.; Imai, E.; Hattori, I. Polym. J. ***1981, 13, 407.***

Catalytic results on “MOF-5”

- Model reaction





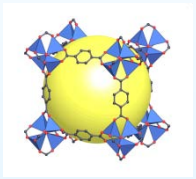
- “MOF-5” prepared by fast pecipitation
  - S_{BET} = 500-700 m^2/g
- “pure” MOF-5 (Prof. S. Kaskel)
  - S_{BET} = 2500 m^2/g
  - much less active when kept under Ar and with dried chemicals

U. Ravon, *MicroMeso Mat., 2010*

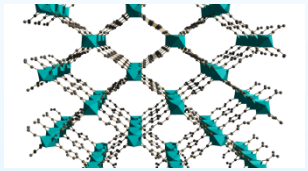
Zn-OH in “MOF-5” ?

- MOF-5 transforms to MOF-69C*

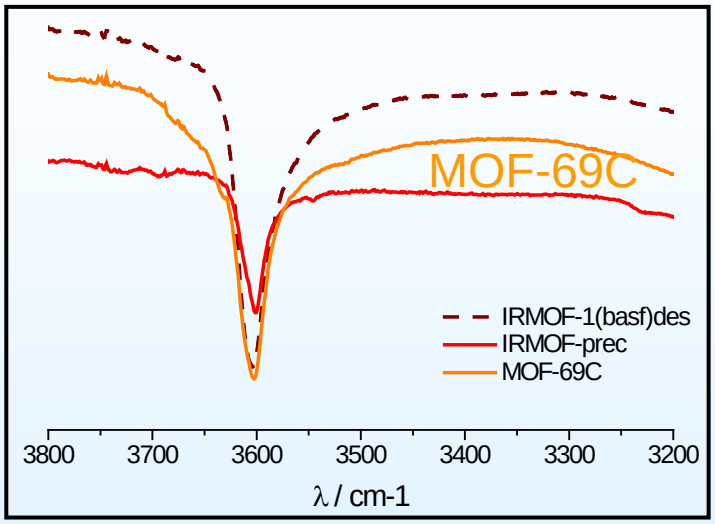
$Zn_4O(bdc)_3$•2DEF → $Zn_3(\mu_3\text{-}OH)(bdc)_2$•2DEF



Air
24hrs

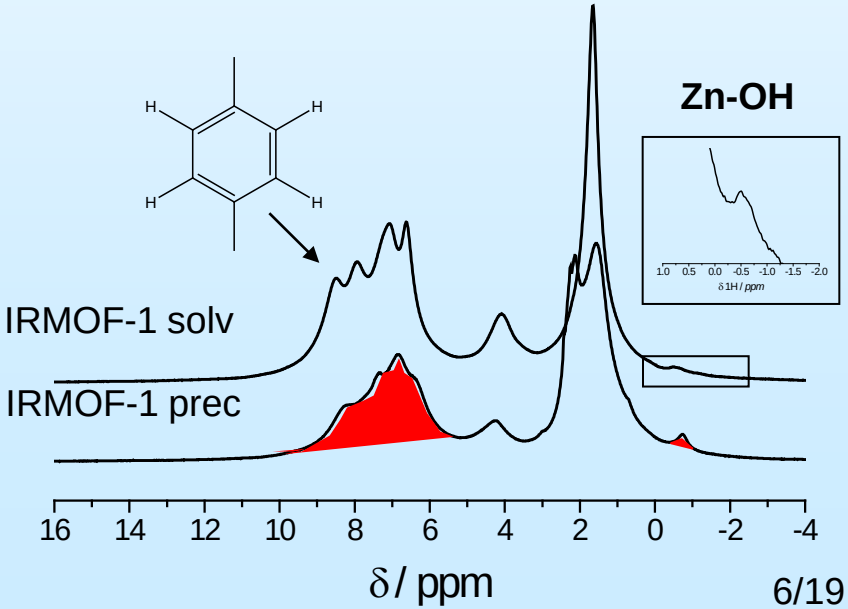


*S. Hausdorf, *J. Phys. Chem. A*, 2008, 112, 7567



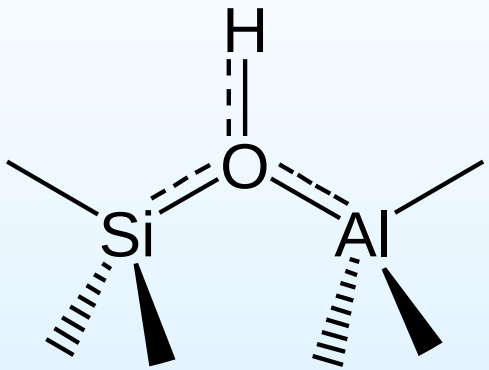
- Quantification by solid ^{1}H NMR
  - Zn(μO**H**) : dbc = 1:20-30

- MOF-5 with Zn-OH defects
  - 3-5% of Zn(O**H**)
  - S_{BET} = 500-700 m^2/g >> MOF-69C

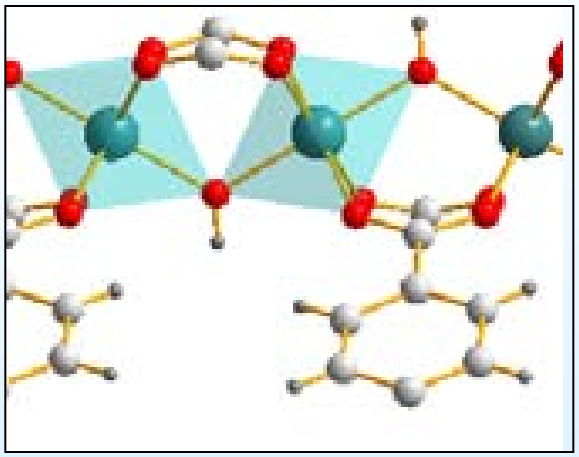


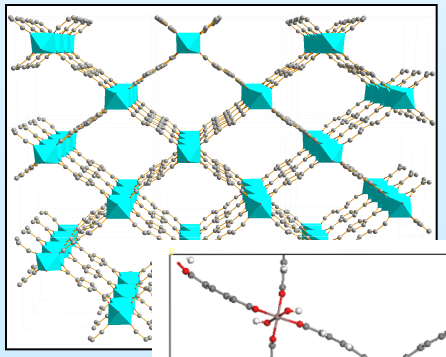
U. Ravon, *New J. Chem*, (2008), 32,937-940

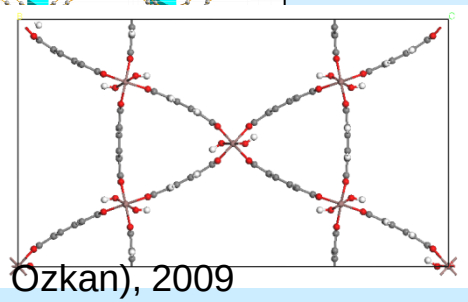
Bronsted function



1D Class with bridging OH



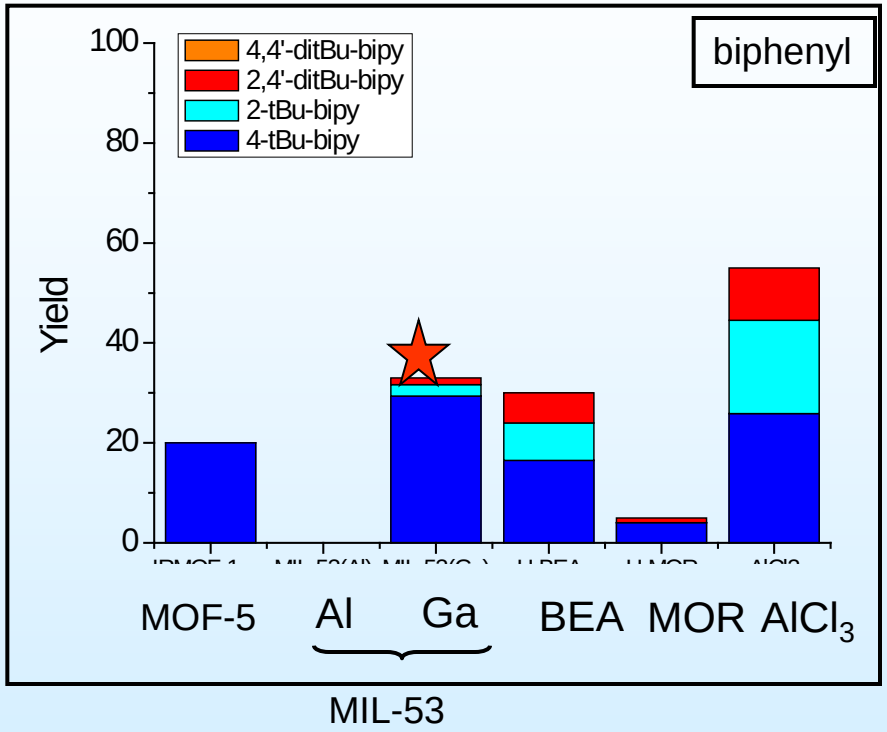


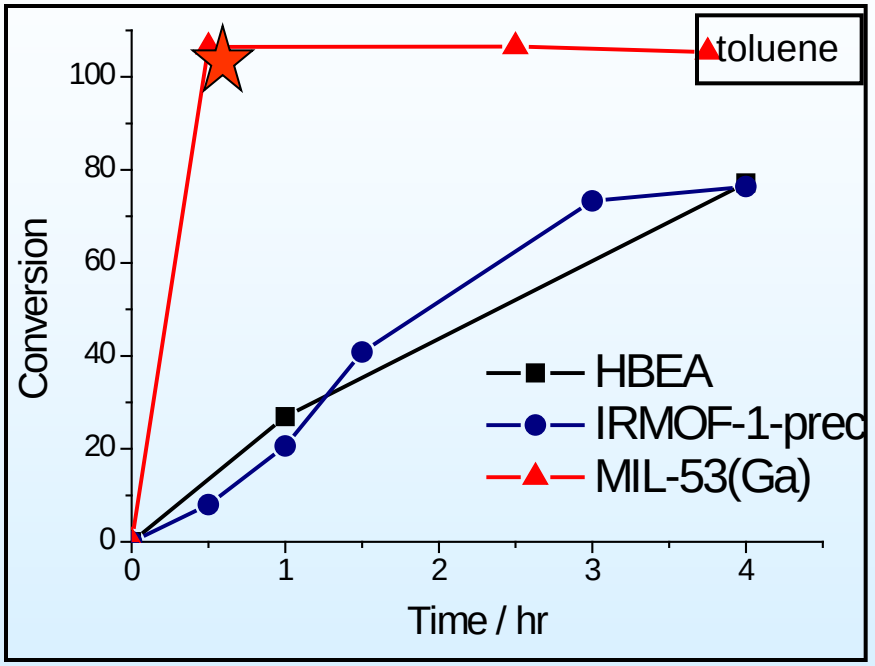


- MOF-69C (Zn) : $Zn_3(\mu_3\text{-}OH)_2(bdc)_2$
- MIL-53 (Ga) : $Ga(\mu_2\text{-}OH)(bdc)$
- MIL-68 (In) : $In(\mu_2\text{-}OH)(bdc)$

D. Farrusseng, in “Handbook of heterogeneous Catalyst Design”, Wiley (Ed. U. Özkan), 2009

Alkylation on MIL-53(Ga)



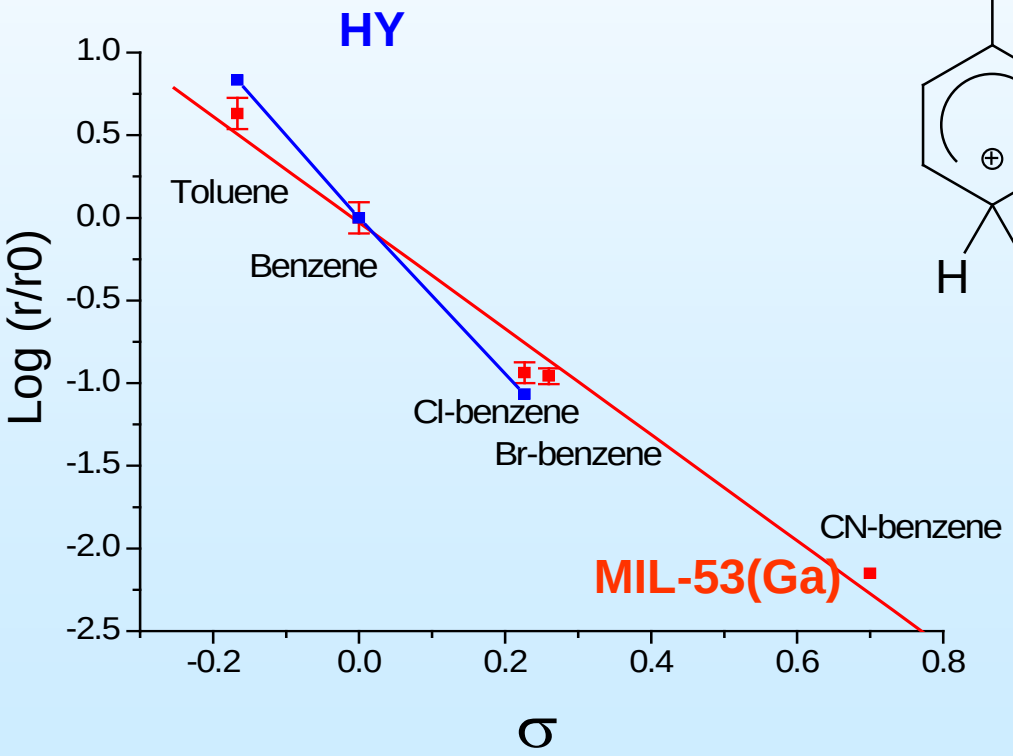


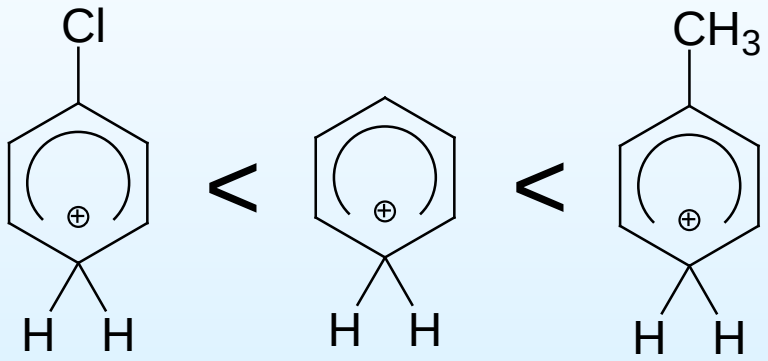
- MIL-53(Ga)>>>MIL-53(Al)
- MIL-53(Ga) active at room temperature !

Patent FR 08/01.089

Brønsted mechanism ?

- Effect of inductive groups on reactivity (Hammett constant σ)
- Charge of the transition state (ρ)
  - Protonation of the aromatics





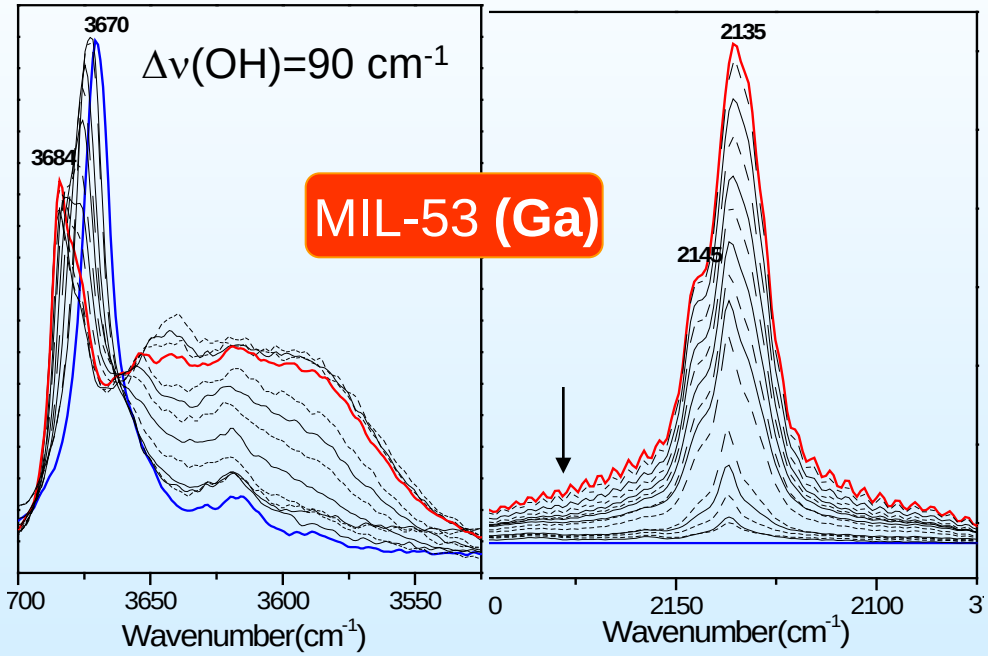
$$\text{Log(rate)} = \text{Cst} + \sigma.\rho$$

ρ> 0, acylation (basic)
ρ=0, Fe-beta (redox)
ρ<0, H-zeolite (acid)

B. Coq et al, Applied Cat. A, 100(1993) 69

Brønsted acidity: Measurements

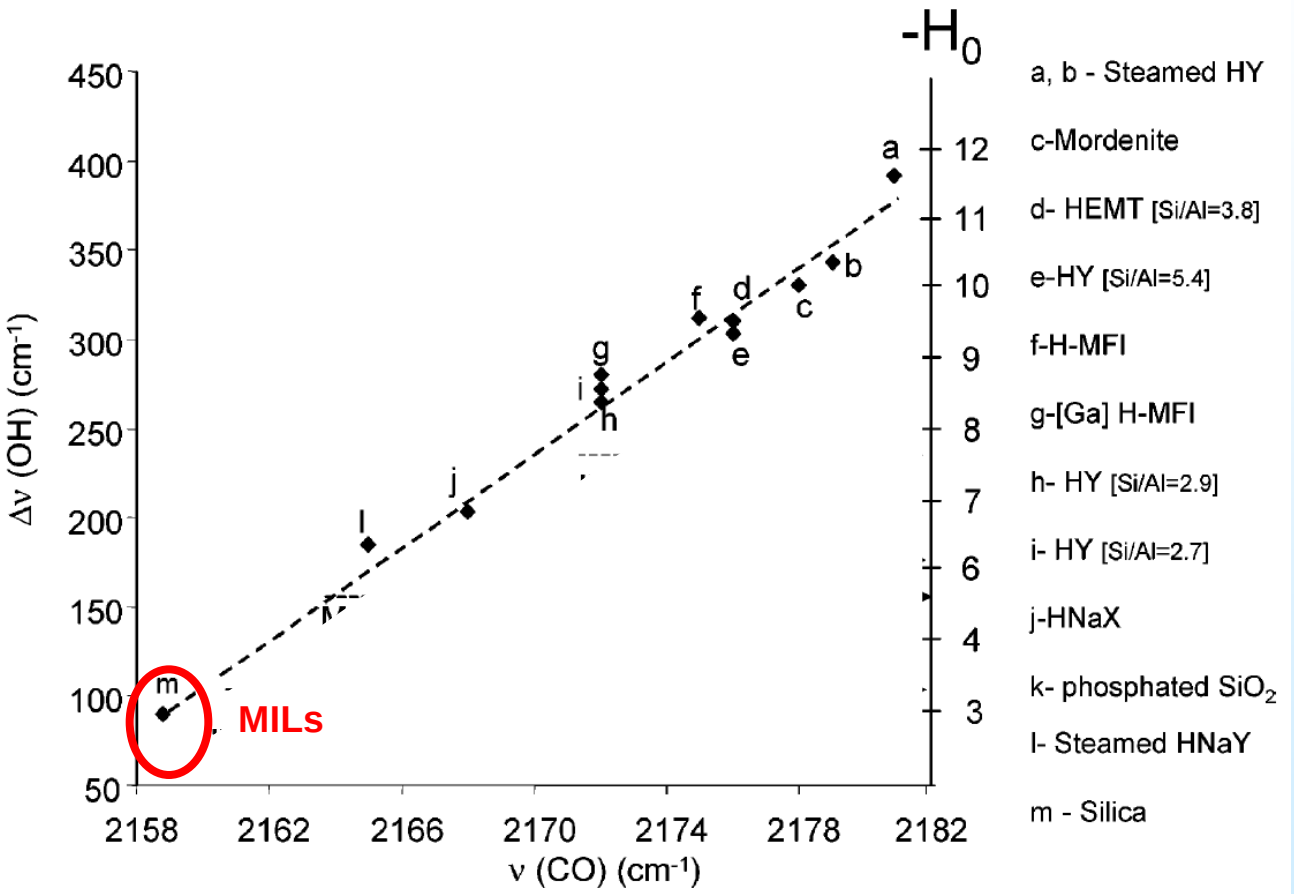
- Site probing by CO adsorption at 100K (Prof. S. Bordiga)



- Brønsted acidity: MIL-53(Ga) > MIL-53(Al)
- No evidence of Lewis centers

D. Farrusseng, ChemCatChem, 2010

Ga-MIL-53 vs. zeolite



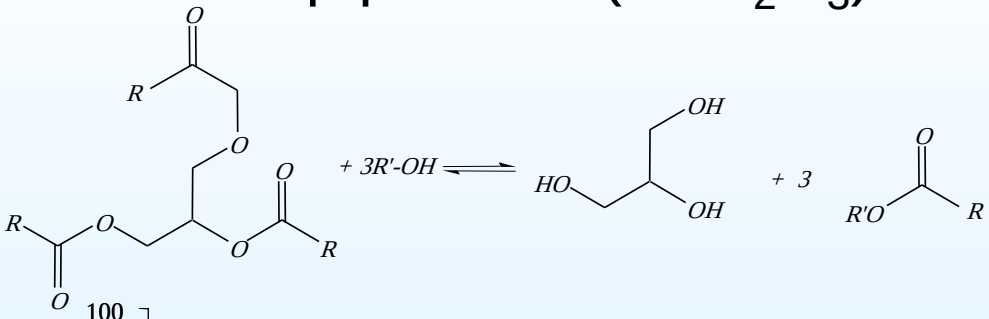
Not in the same range !

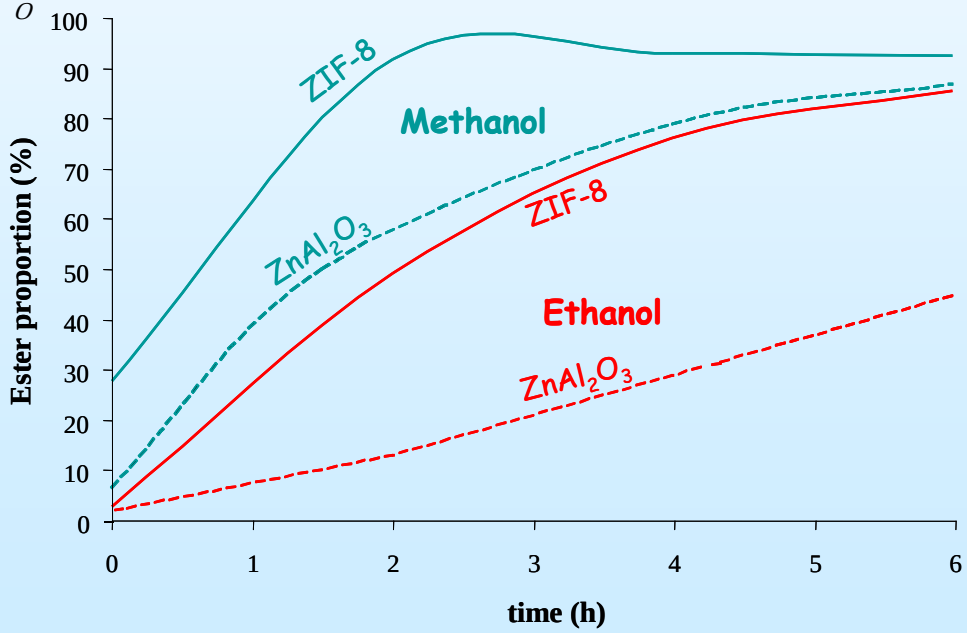
A. Vimont et al, . Phys. Chem. C, Vol. 111, No. 1, 2007

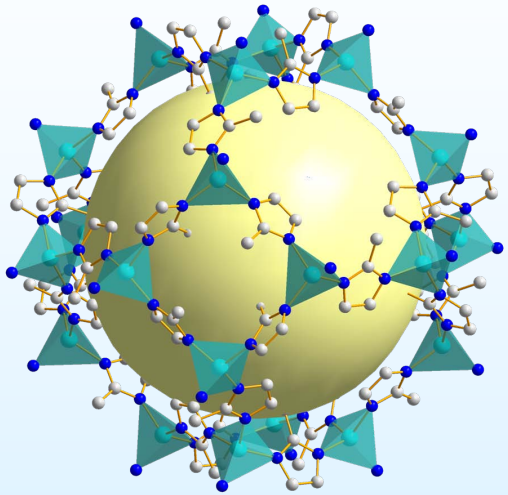
2 – ACID BASE

? ! ? !

- Esterfip process ($ZnAl_2O_3$)





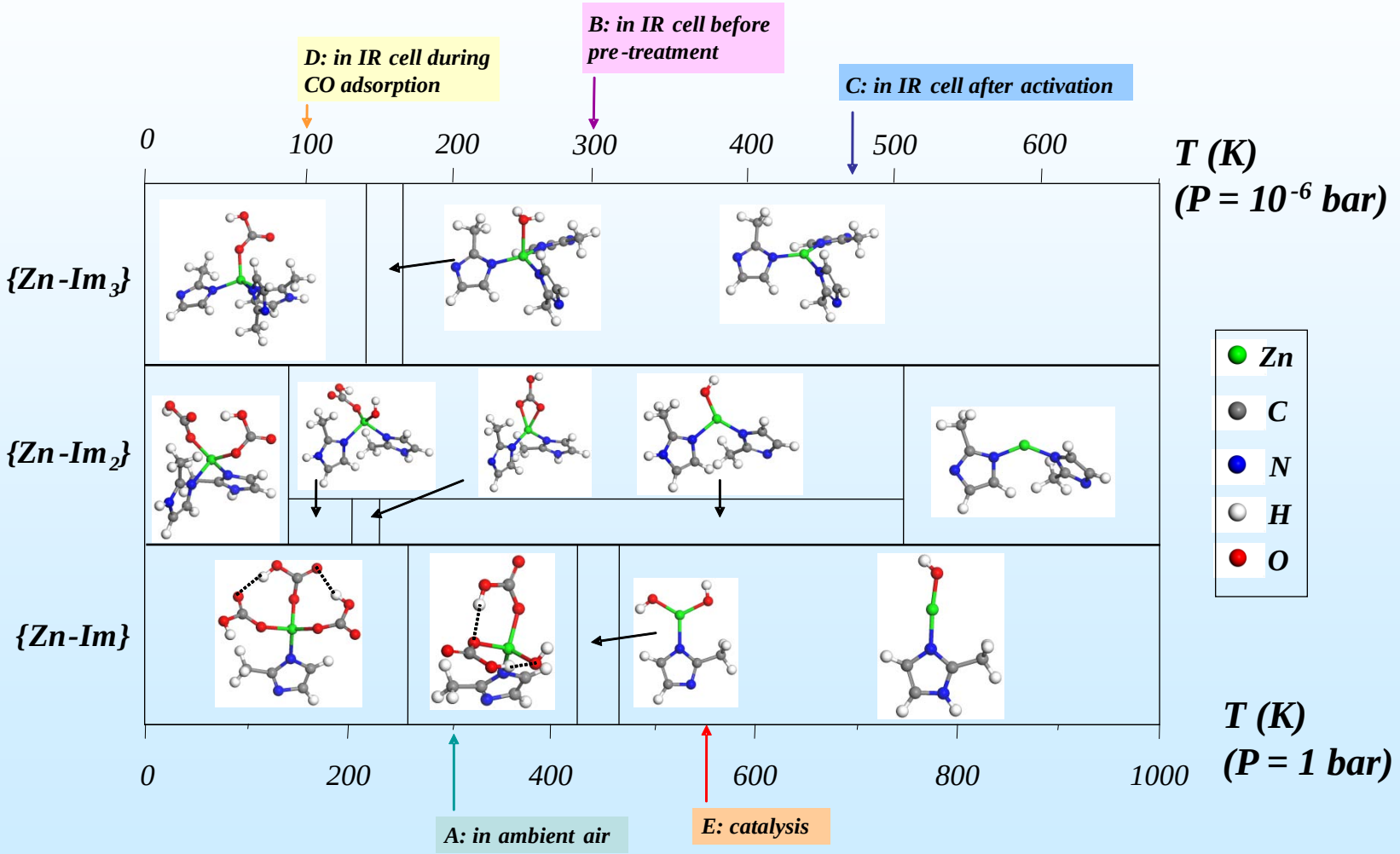


ZIF-8

Triglyceride > pore aperture

C. Chizallet, et al., JACS, **2010**, 132, 12365

External surface models of ZIF-8

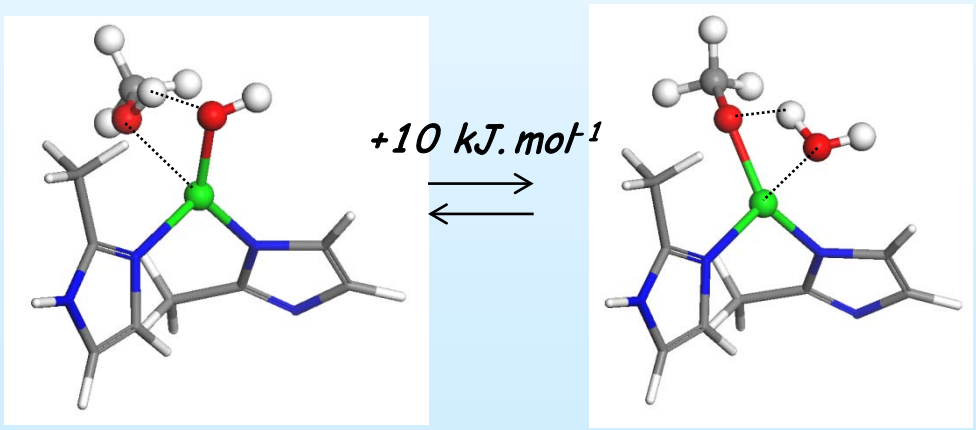


C. Chizallet, N. Bats, J. Phys. Chem. Lett, 2010, 1, 349

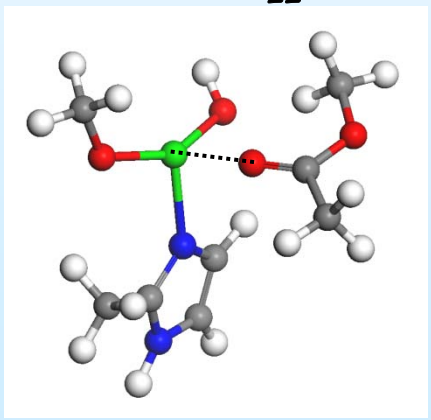
Activation studies

- Bulk can not activate MeOH
- Actives centers : Zn-OH
- at external surfaces and/or structural defects

Dissociation of MeOH on Zn_{III} and Zn_{II}



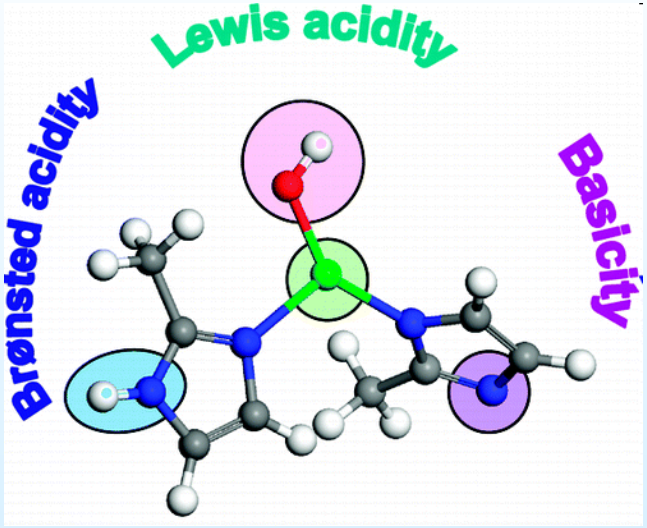
Co-activation MeOH and Ester on Zn_{II}

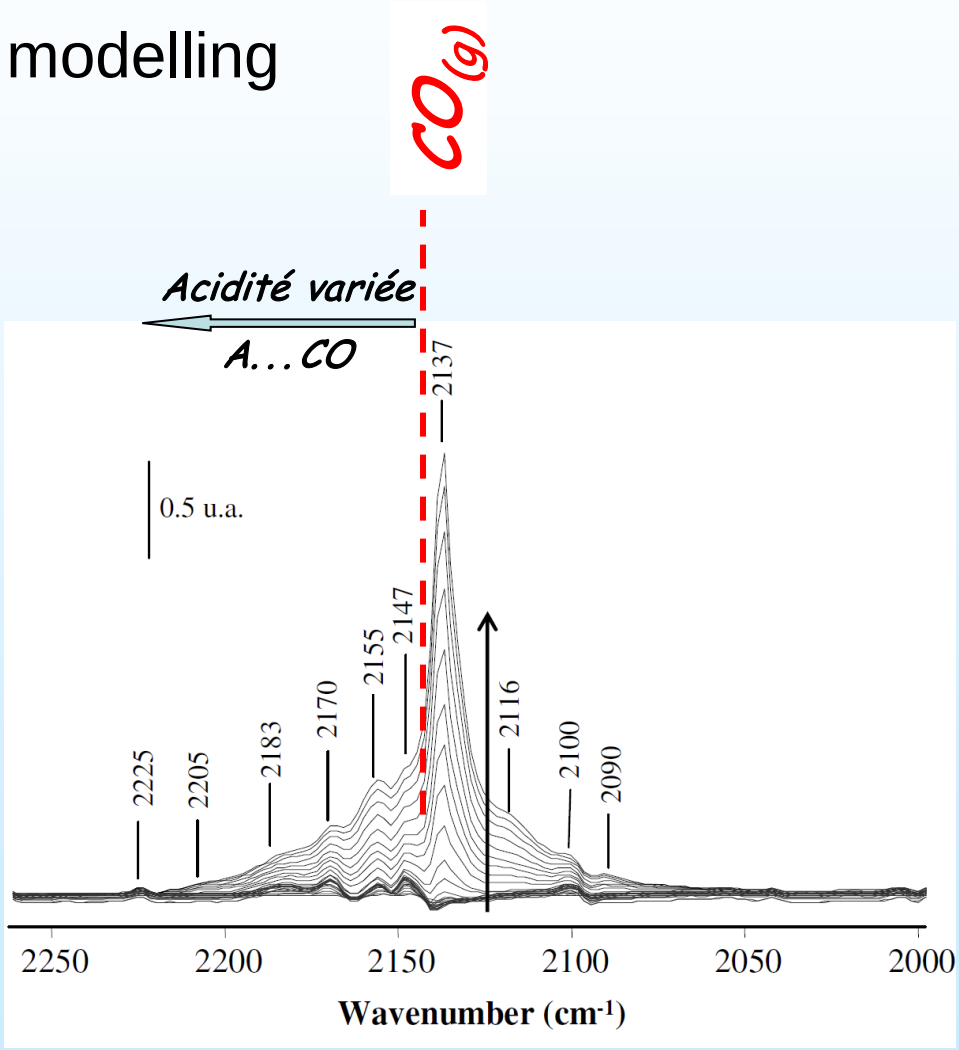


C. Chizallet, et al., JACS, **2010**, 132, 12365

Nature of acid/base centers ?

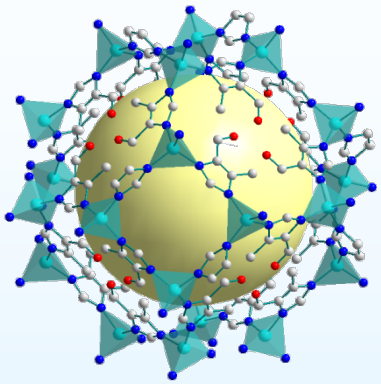
- CO adsorption at 77K / DFT modelling



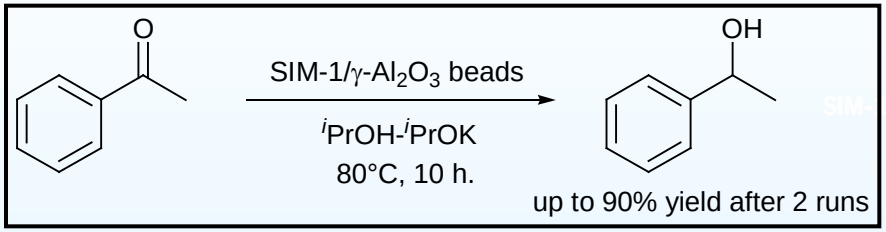


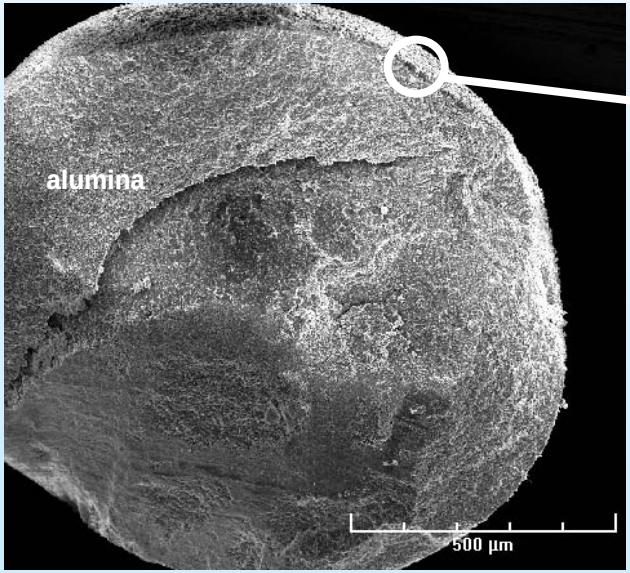
- Strong Zn(II) Lewis centers
- Strong Bronsted acid NH
- Weak basic sites OH and N^-
- Activity at the surface

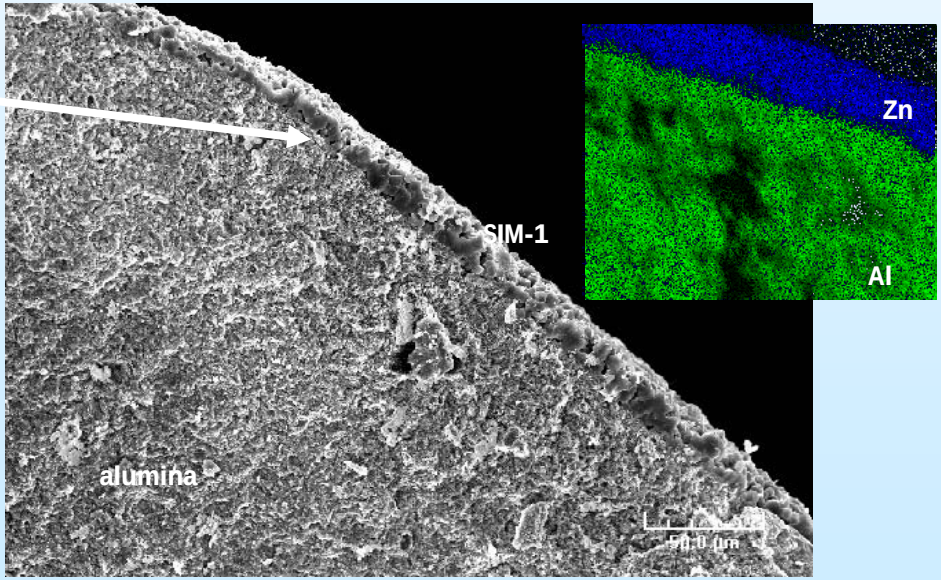
Enginnering: egg-shell catalyst



SIM-1

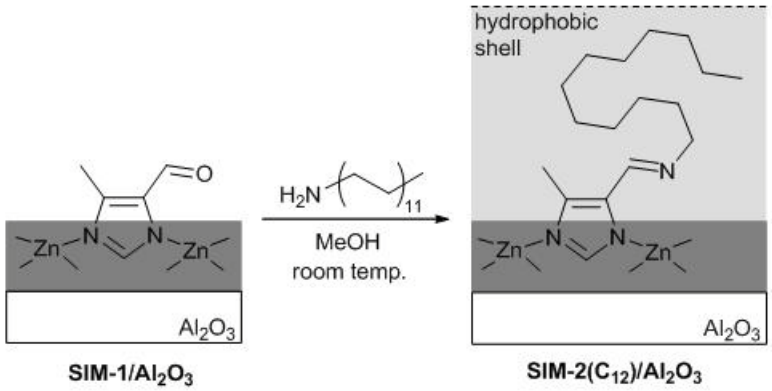




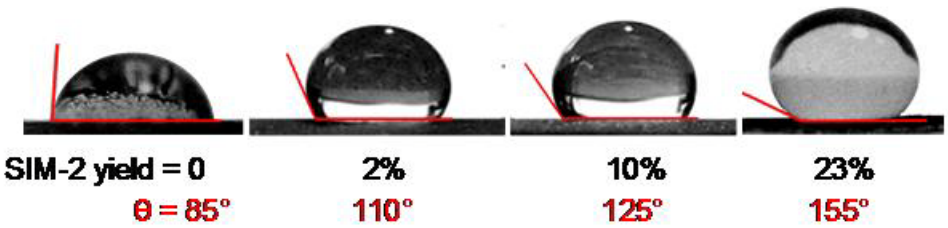


Aguado et al, Chem. Commun. ***2010****, 46, 7999-8001*

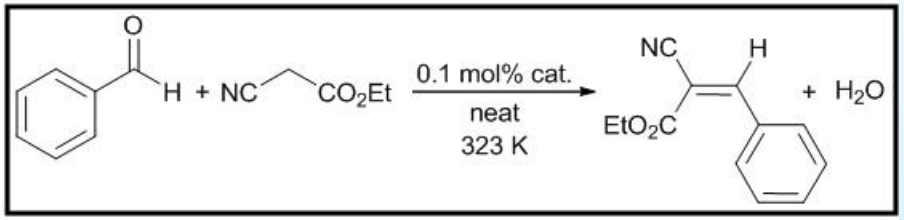
Engineering : post-hydrophobisation

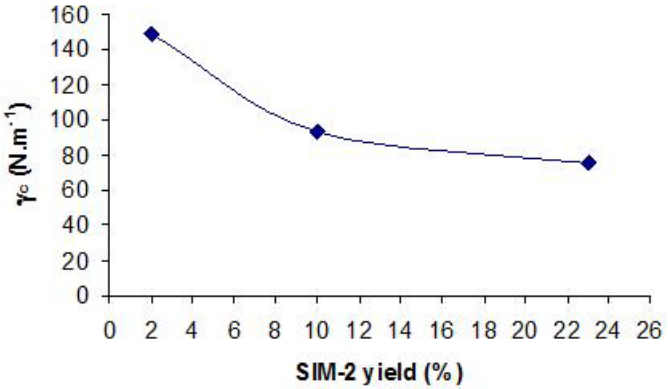


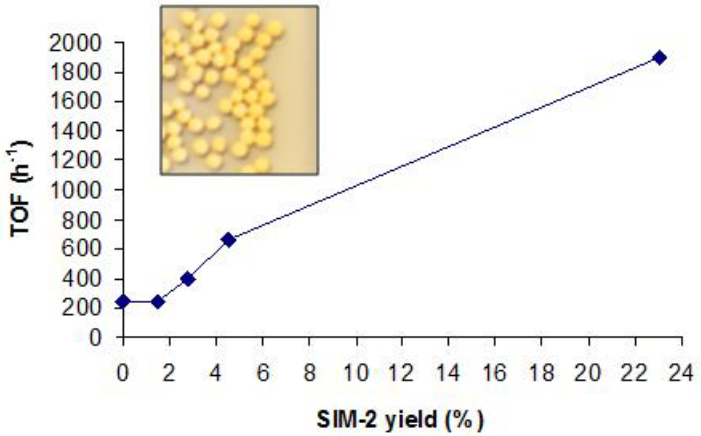
SIM-1/Al_2O_3 **SIM-2(C_{12})/Al_2O_3**



SIM-2 yield = 0	2%	10%	23%
θ = 85°	110°	125°	155°



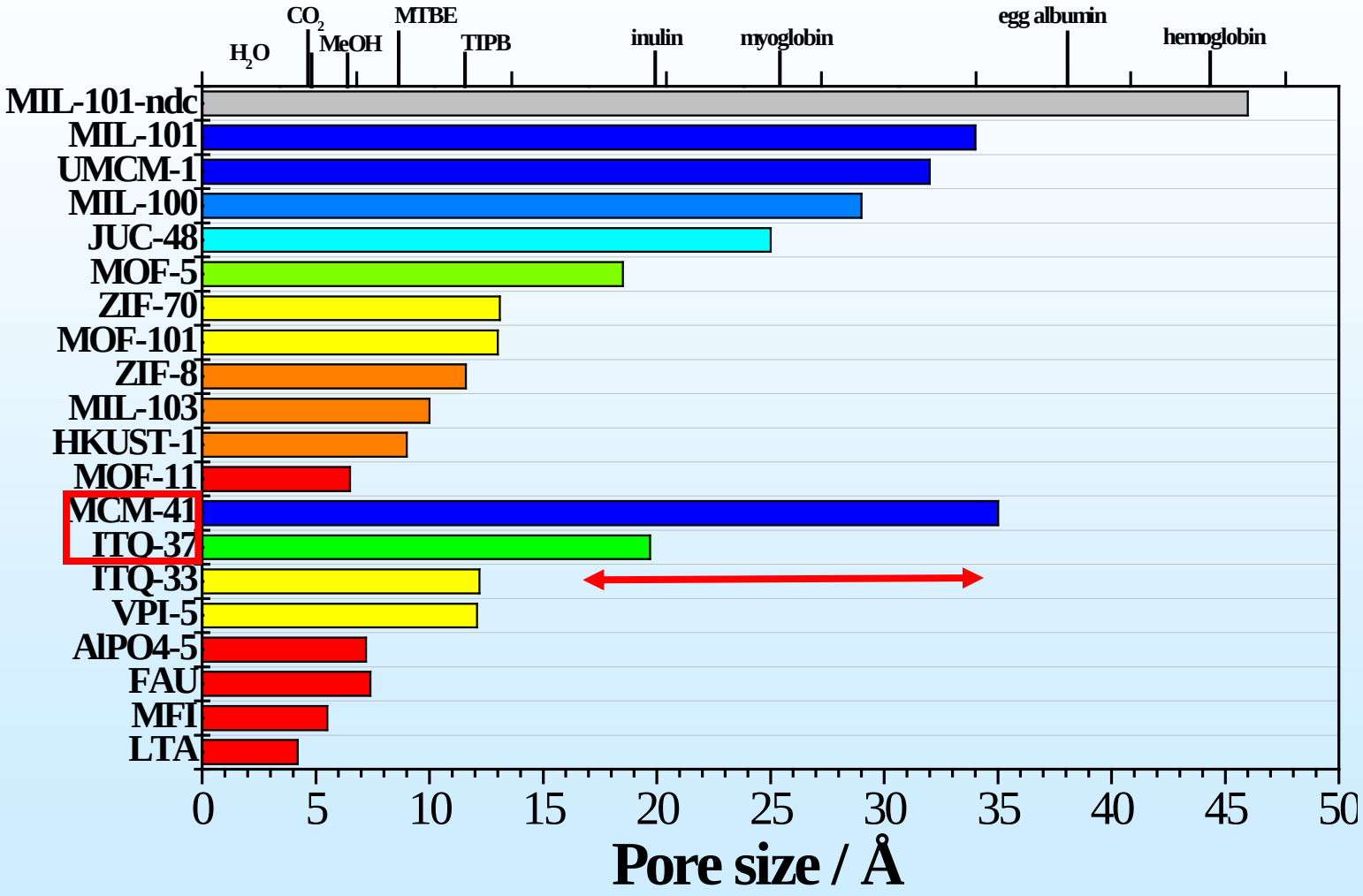




Canivet et al, *ChemCatChem*. **2011**, *3*, 675-678.
Aguado et al, *Journal of Material Chemistry*, *in press*

3 - ENCAPSULATION

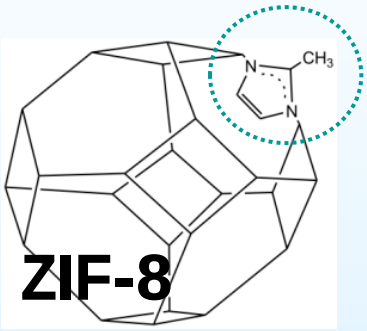
MOFs: bridging pore size gap

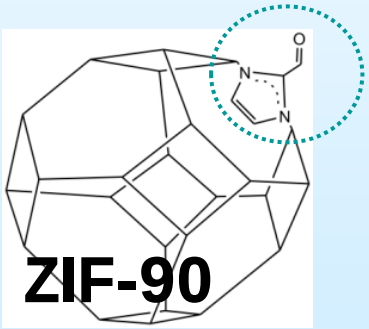


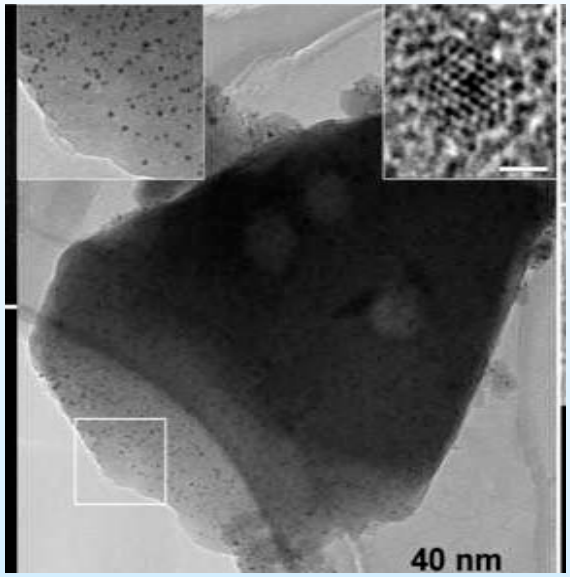
Metal Nanoparticle (Au@ZIF)

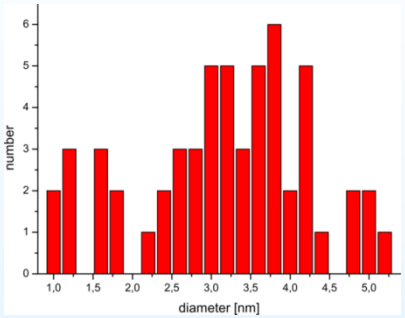
***D.Esken* R. Fischer, RUB**

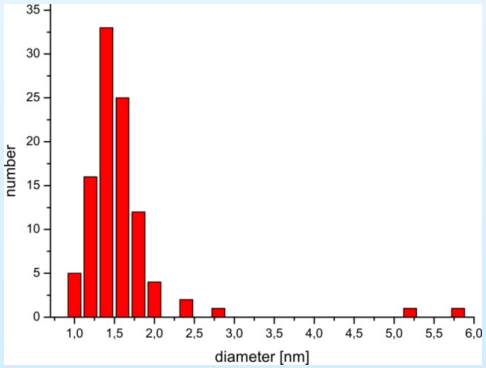
- CVI of [AuCOCl] / 30wrt%loading





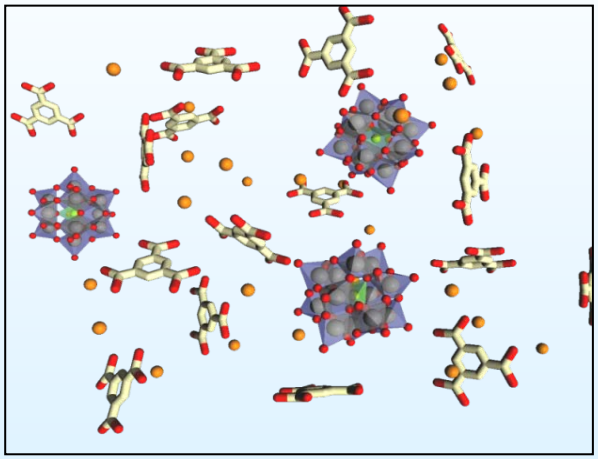


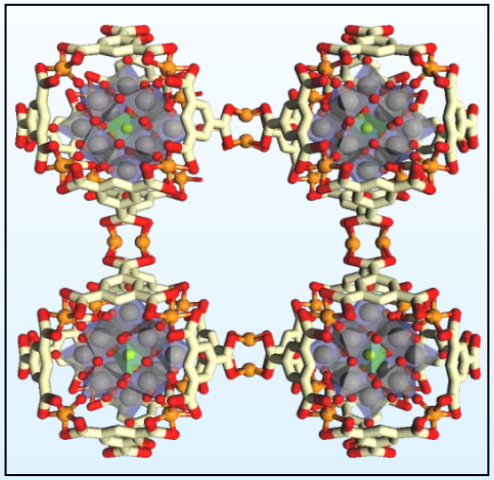


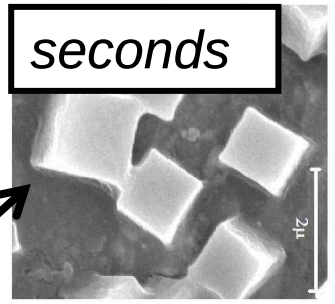


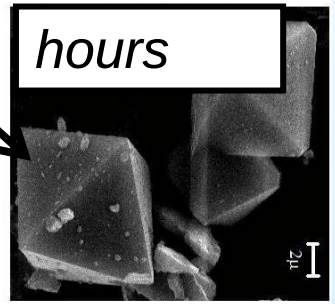
Heteropoly acids HPW/MOF

- HPA templating in HKUST-1



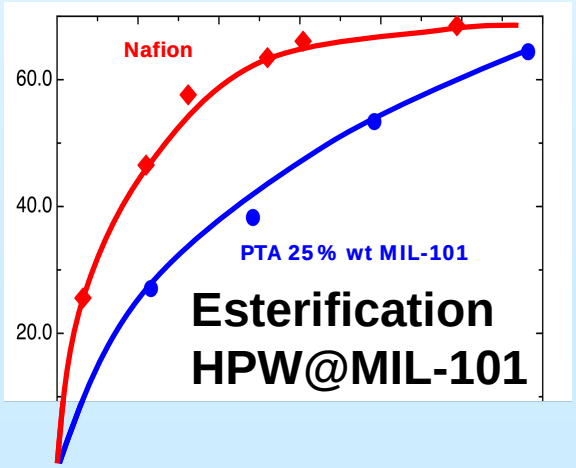




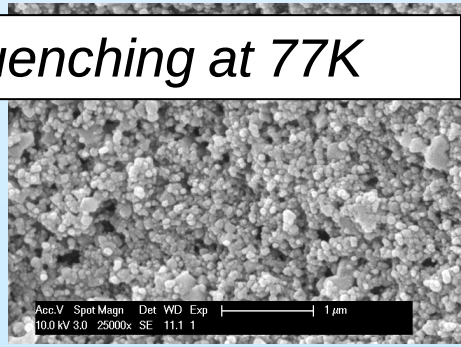


$Cu(NO_3)_2$ + HPW + H3BTC

- Catalysis
  - Knoevenagel
  - MeOH deydration
  - Esterfication



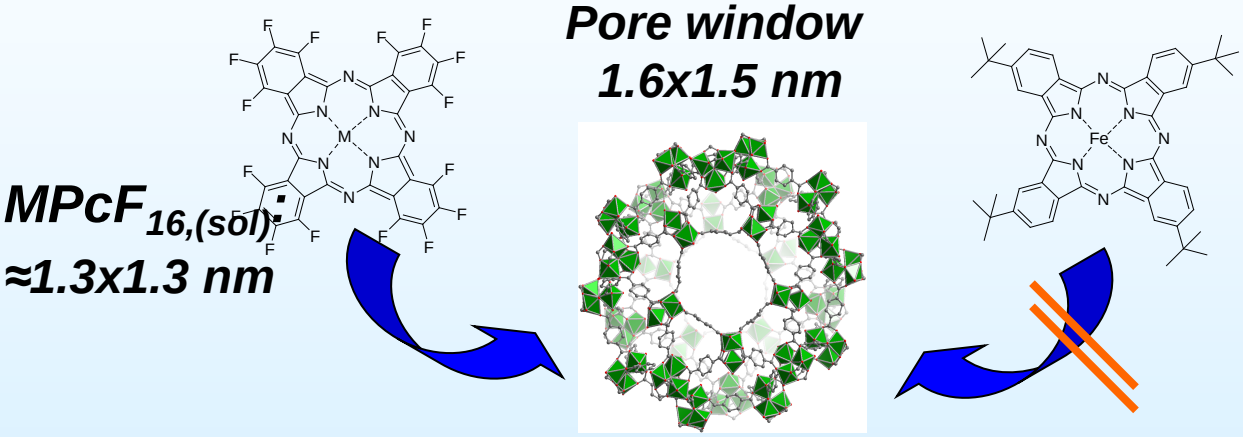
Quenching at 77K

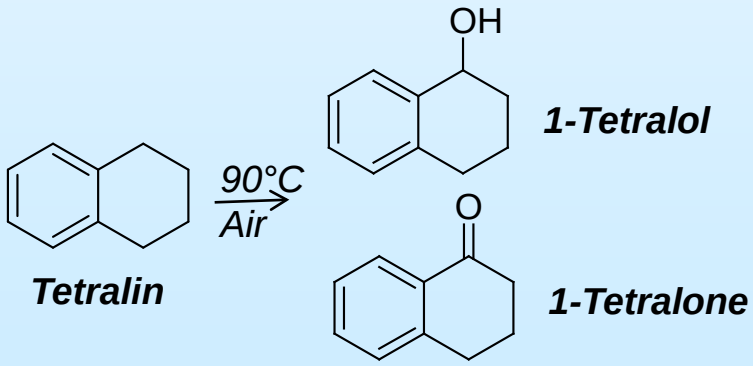


Bajpe et al. Chem. Eur. J. 2010
L. H. Wee et al, Chem. *Comm, 2010*
F. Kapteijn, J. Catal, 2009

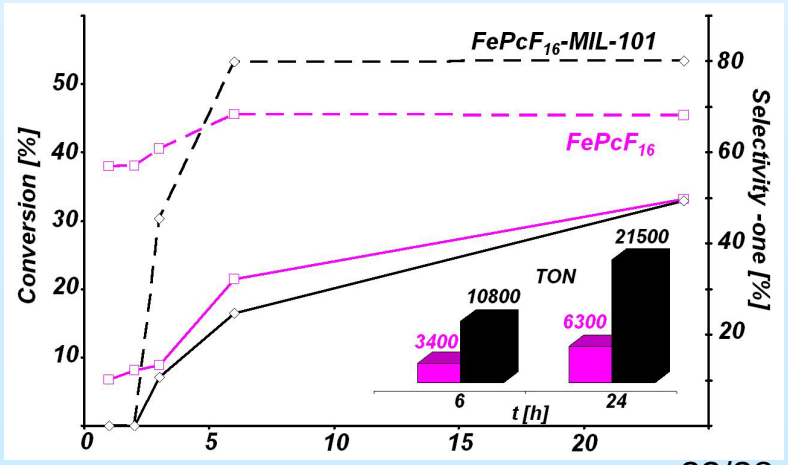
Complexes in MOFs

- Encapsulation of metallo-phthalocyanines





n(Tetralin):n(complex)=64000:1

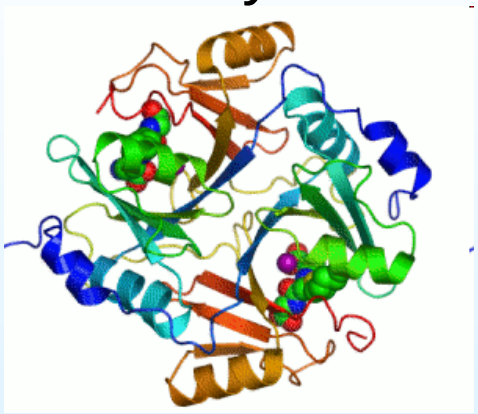


Kockrick et al, Chem. Commun. ***2010***

4 – Functional Ligands

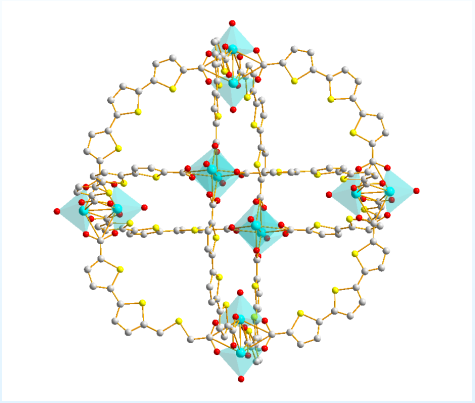
Sources of inspiration

Enzymes



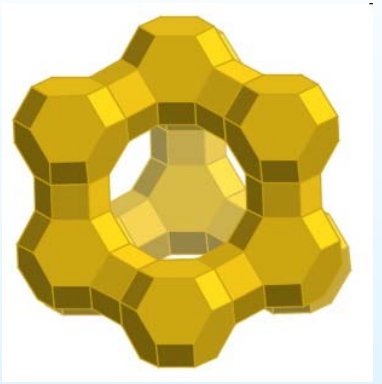
- Organic
- Multinuclear sites
- Flexible
- Low thermal stability

MOFs



- Hybrid
- Multinuclear sites
- “Semi-rigid”
- 200-400°C

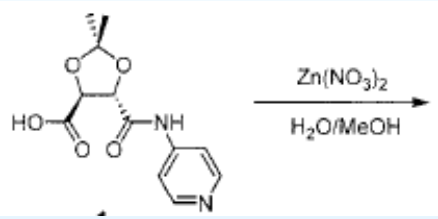
Zeolites

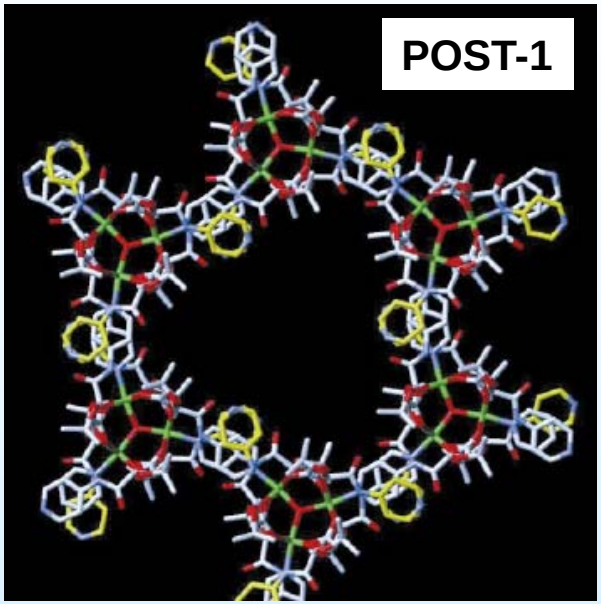


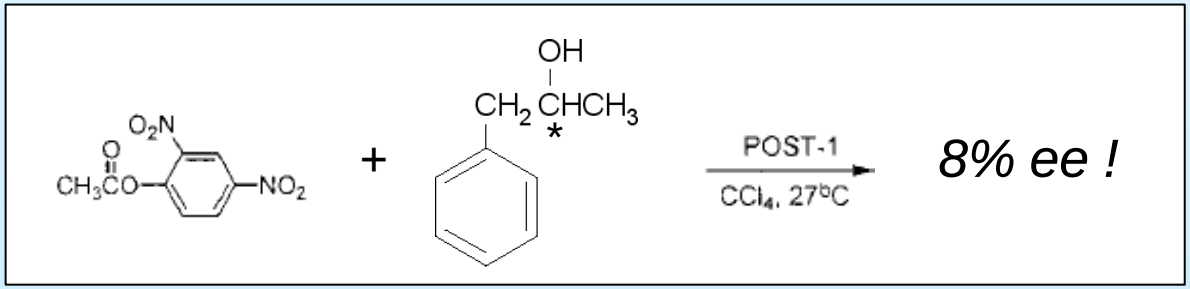
- Inorganic
- Isolate acid sites
- Rigid
- High thermal stability

? ! ? !

- Homochiral MOF
- Lewis Base

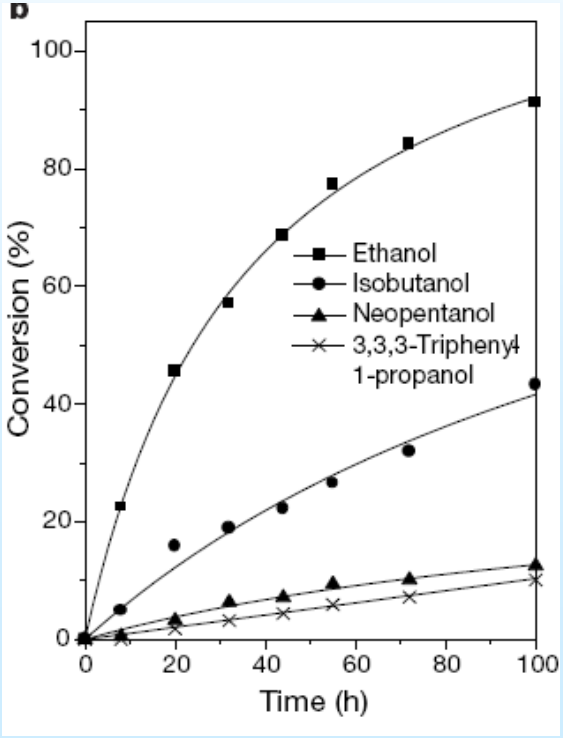






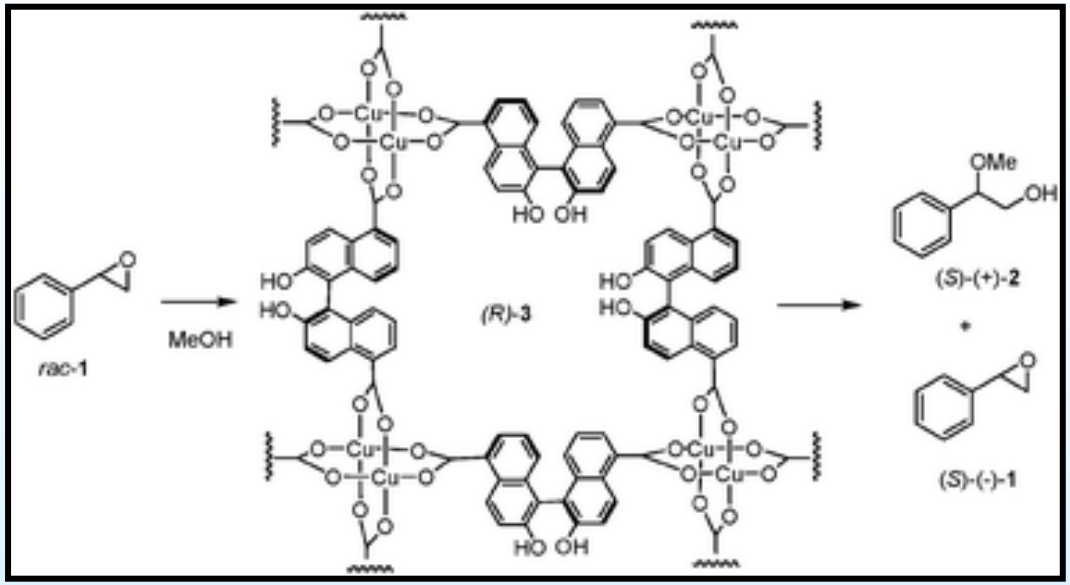
- Enantioselectivity ?
- Pore size effect ?

Esterification



Kim et al. Nature, 404 (2000), 982

Asymmetric alcoholytic kinetic resolution of styrene oxide



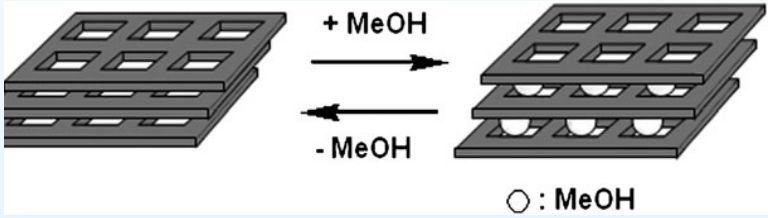


Table 1 Kinetic resolution of styrene oxide in the presence of (*R*)-**3**[a]

				Unreacted **1**		Product **2**	
Entry	Epoxide	Alcohol	Temp/°C	Yield (%)	ee[b] (%)	Yield (%)	ee[b] (%)
1	*rac*-**1**	MeOH	25	83	5 (*S*)	5	81 (*S*)
2	*rac*-**1**	MeOH	40	64	19 (*S*)	20	62 (*S*)
3	*rac*-**1**	MeOH	60	29	98 (*S*)	66	37 (*S*)
4	(*R*)-**1**	MeOH	40	50	>99 (*R*)	48	>99 (*S*)
5	(*S*)-**1**	MeOH	40	92	>99 (*S*)	5	>99 (*R*)
6	*rac*-**1**	EtOH	40	81	0.4[c]	3	12[c]
7	*rac*-**1**	*i*-PrOH	40	84	0.3[c]	2	4[c]
8	*rac*-**1**	*t*-BuOH	40	86	0.3[c]	0	—

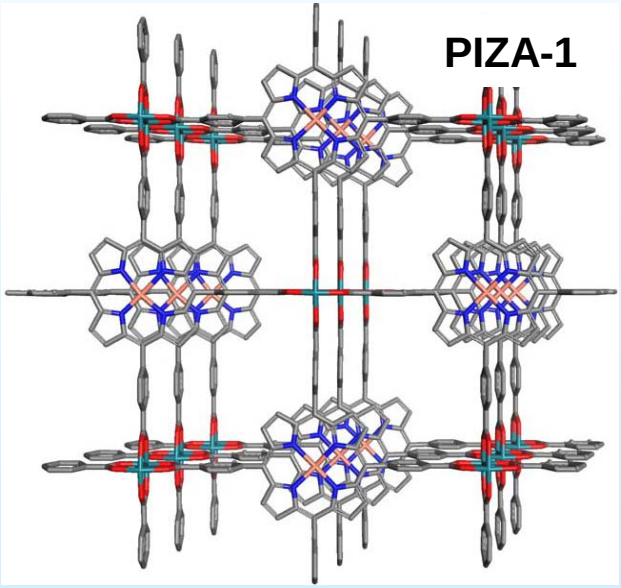
[a] Reactions were carried out for 24 h. [b] Determined by HPLC. [c] Determined by GC.

Tanaka, New Journal of Chemistry, 2010

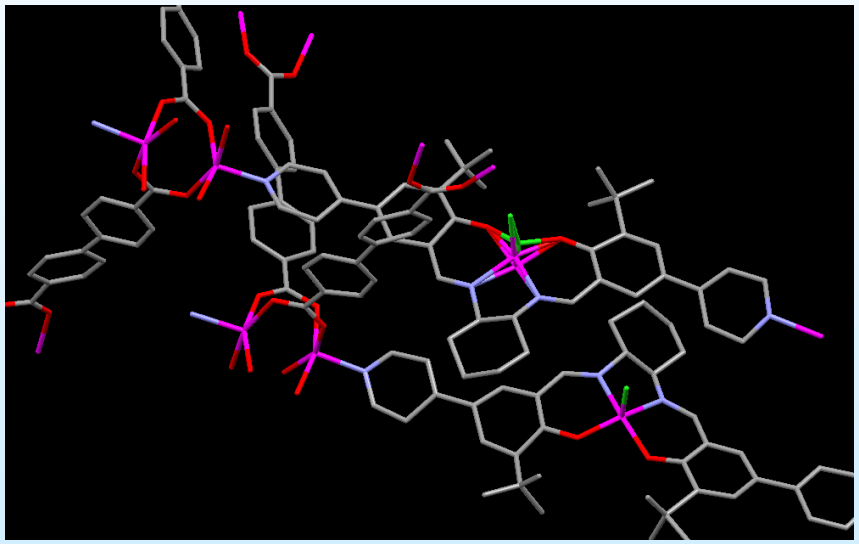
Bio-mimetic metallo-ligands

- Linker = bio-mimetic catalyst

Porphyrin

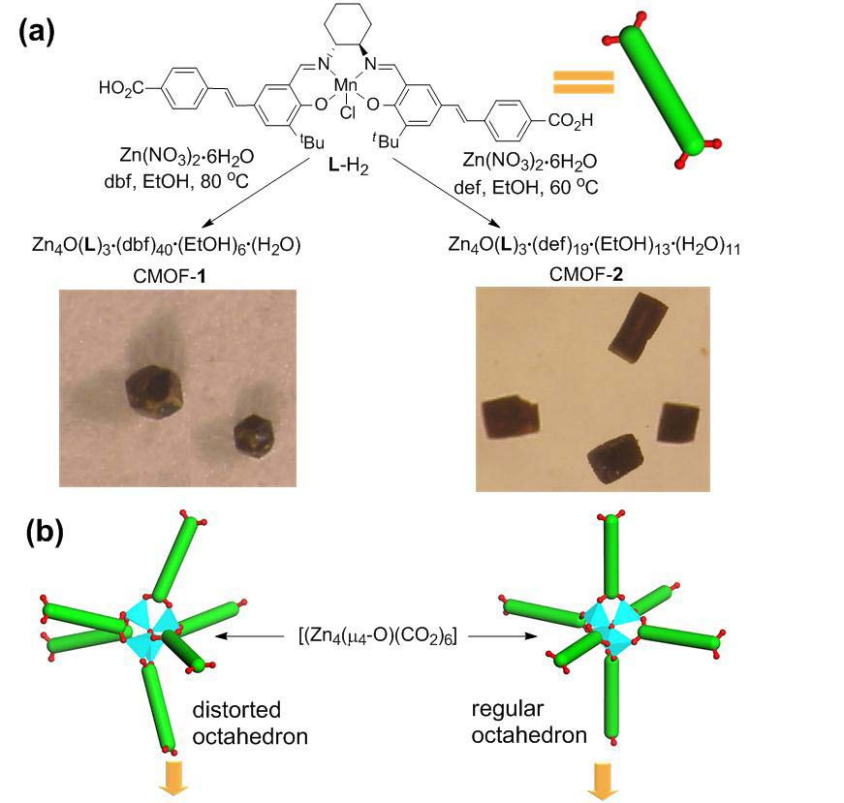


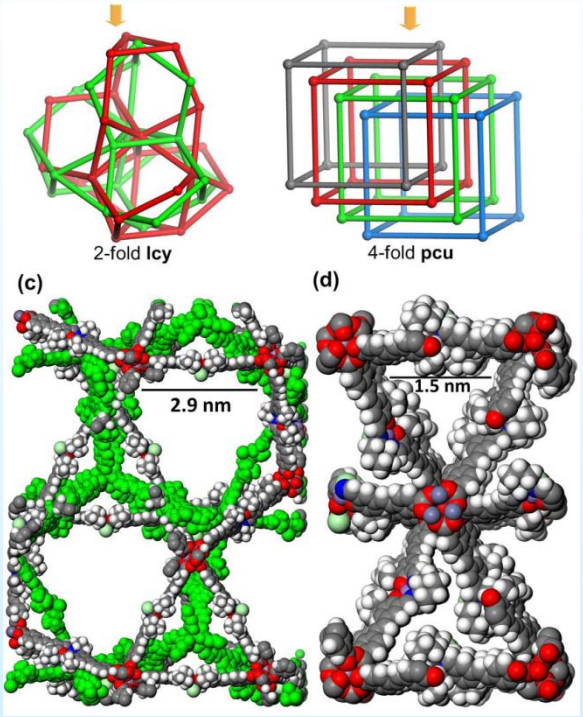
Mn(Salen)

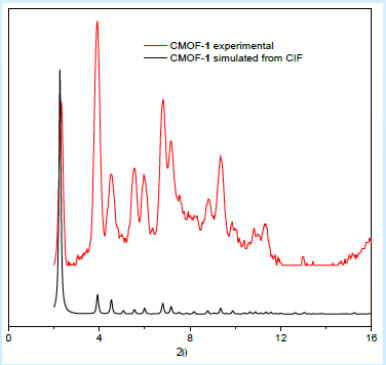


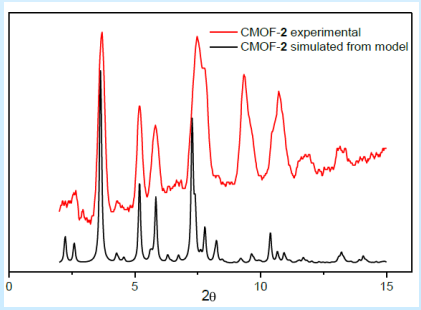
Hupp, Chem Comm, 2006
Goldberg, Chem Comm, 2005

Net interpenetration to adjust pore size





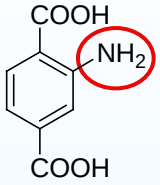


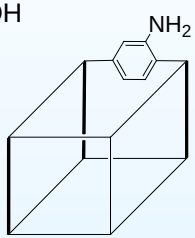


Characterisation….
Activity rate vs. Cost ?

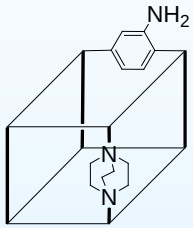
W. Lin, Nat. Chem, 2010

MOF-NH_2 library for post-functionlisation

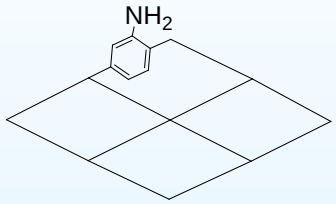




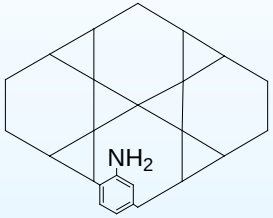
IRMOF-3[1]



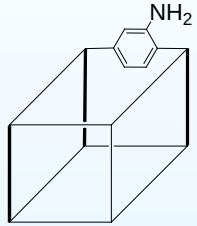
DMOF-1[2]



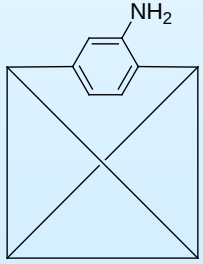
MIL-53(Al[3]*, Fe*[4]*)*



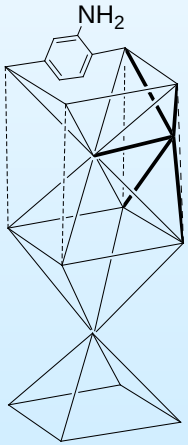
MIL-68 (In)[5]



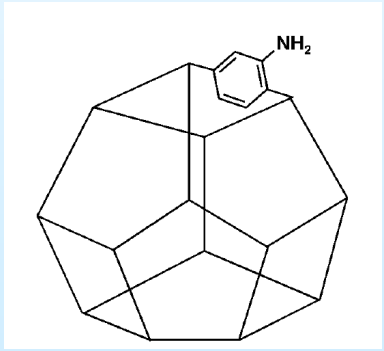
MOF-LIC-1[6]



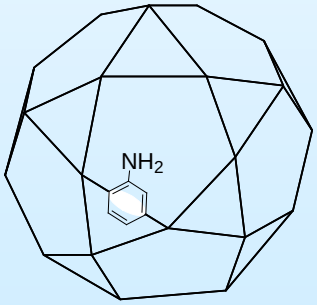
UiO-66[7]



CAU-1[8]



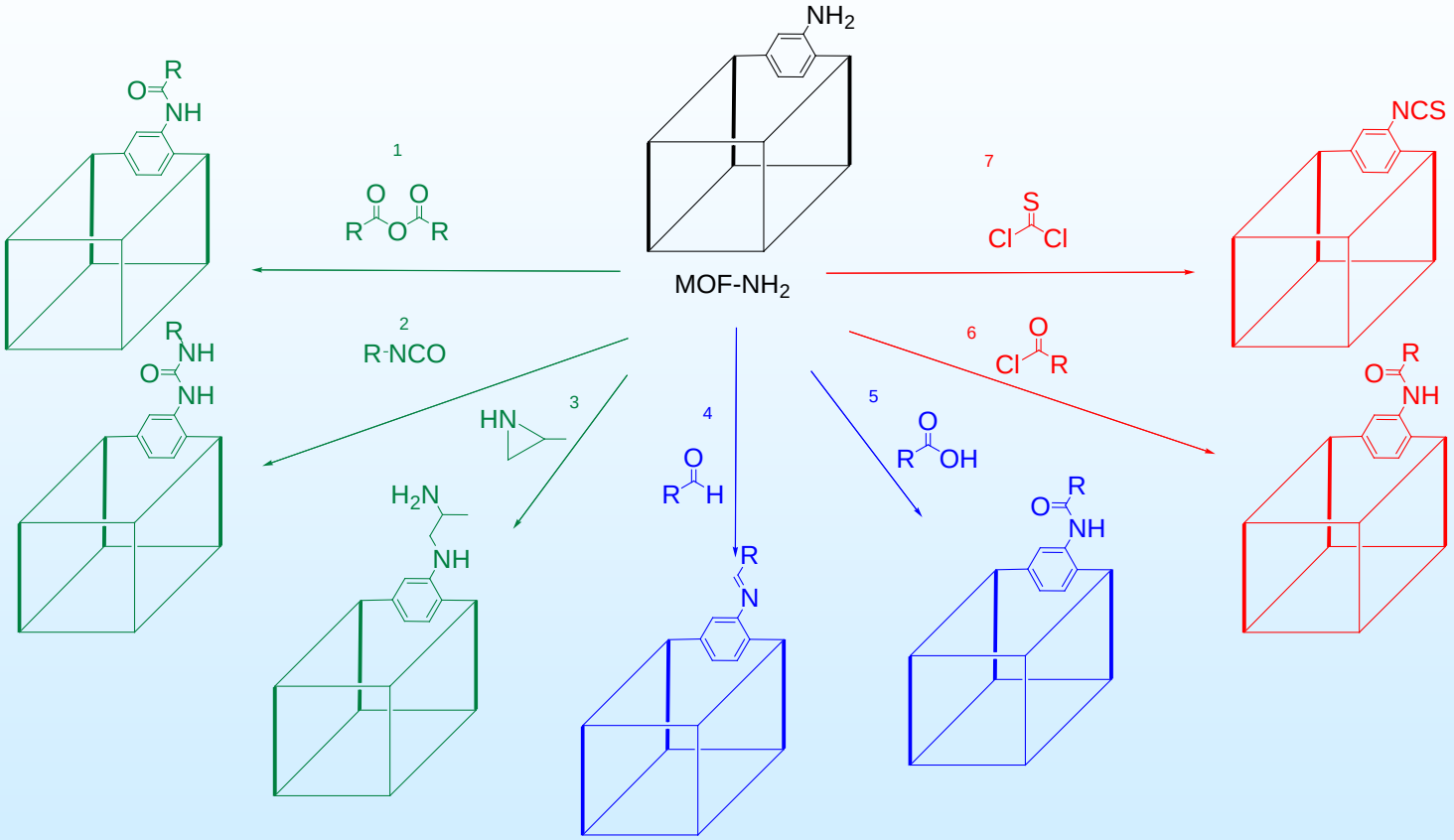
UMCM-1[2]



MIL-101 (Fe)[4] .....

[1] *Eddaoudi, M. et al, Science, **2002**, 295, 469-472.*
[2] *Wang, Z. et al, Inorg. Chem. **2009**, 48, 296-306.*
[3] *Ahnfeldt, T. Inorg. Chem., **2009**, 48, 3057-3064.*
[4] *Bauer, S. et al, Inorg. Chem., **2008**, **47**, 7568.*
[5] *Savonnet, M. et al, **2009**, FR Patent 09/05.101.*
[6] *Gamez, P. et al, Eur. J. Inorg. Chem., **2008**, 1551-1554.*
[7] *Cavka, J. H. et al, J. Am. Chem. Soc., **2008**, 130, 13850 –13851.*
[8] *Ahnfeldt, D. et al, Angew. Chem.-Int. Edit. **2009**, 48, 5163-5166.*

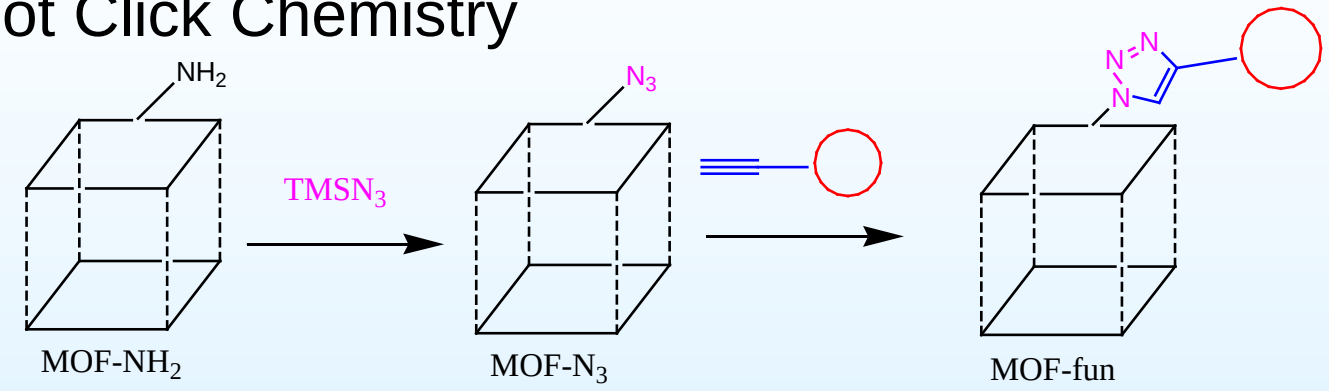
Post-functionalisation methods

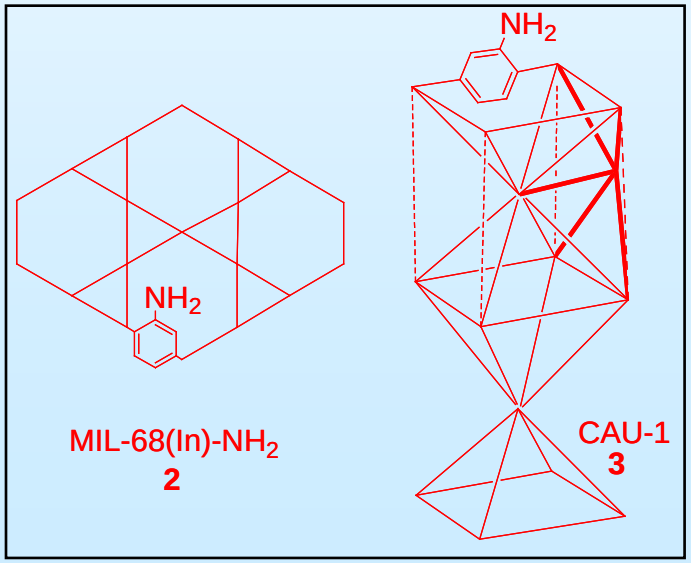


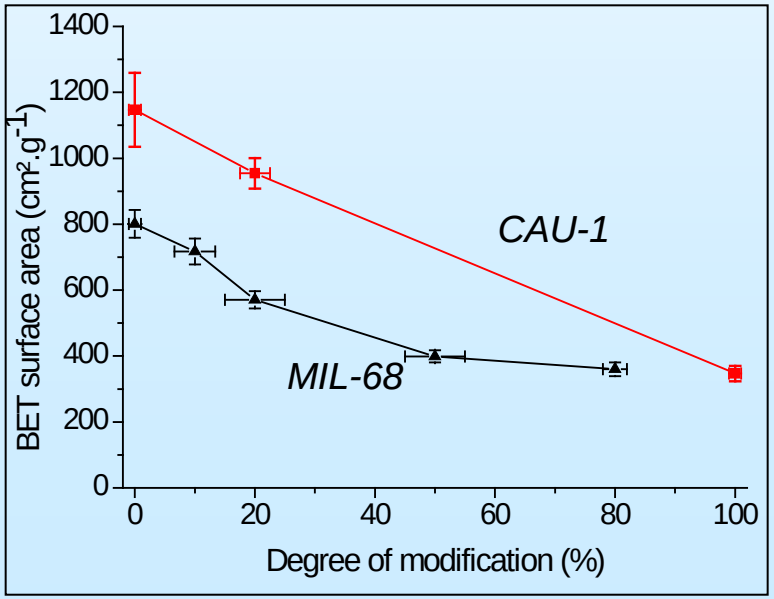
[1] *Wang, Z. Q et al, Chem. Soc. Rev.* ***2009****, 38, 1315-1329.*
[2] *Dugan, E. et al, Chem. Commun.,* ***2008****, 3366-3368.*
[3] *Ingleson, M. J.et al, Chem. Commun.,* ***2008****, 1287-1289.*
Gamez, P. et al, Eur. J. Inorg. Chem., ***2008****, 1551-1554.*
[4] *Britt, D. et al, Inorg. Chem.,* ***2010****, 49, 6387-6389.*
[5] *Ahnfeldt, T. Inorg. Chem.,* ***2009****, 48, 3057-3064.*
Gamez, P. et al, Eur. J. Inorg. Chem., ***2008****, 1551-1554.*
[6] *Savonnet, M et al, Green Chem.* ***2009****, 11, 1729-1732.*
[7] *Christophe V.et al, Angew. Chem. Int. Ed.,* ***2010****,* ***49****, 4644-4648.*

Post-functionalisation vs. Porosity ?

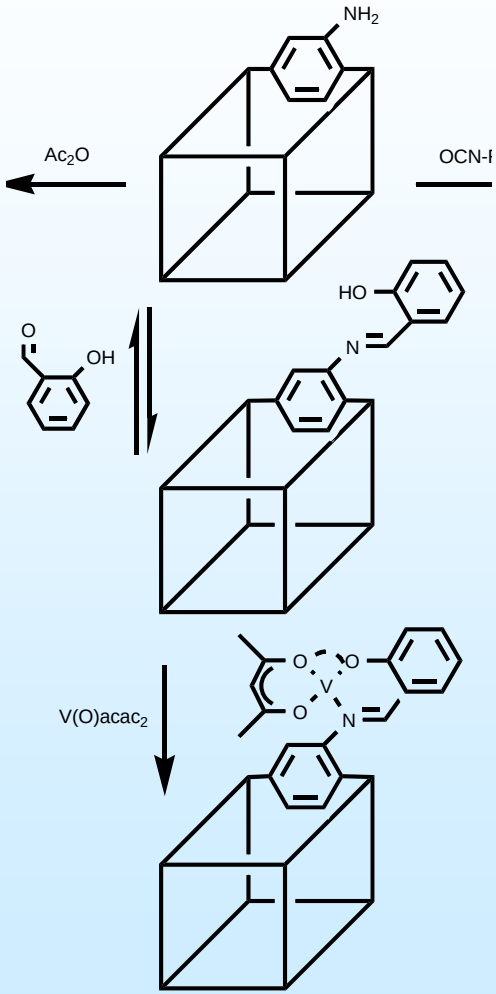
- One pot Click Chemistry

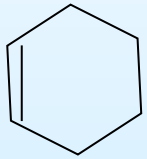






Surface Organometallic species





tBuOOH
THF/65°C
72h

40% conversion

Lack of short range characterisation….

Rosseinsky, Chem.Com, 2008

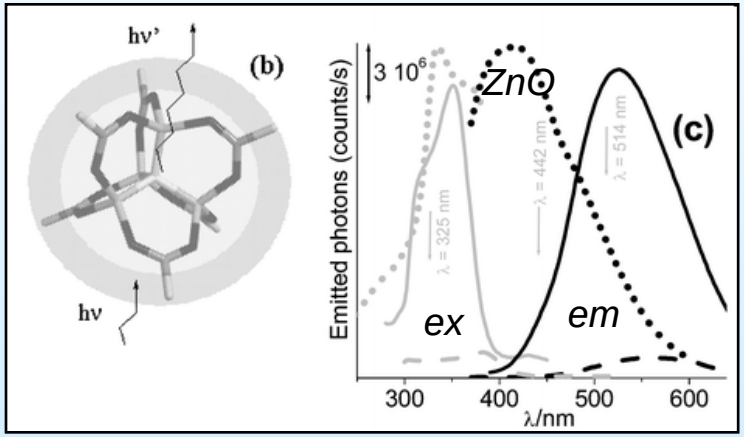
S. Cohen, Chem. Soc. Rev., 2009

5 – PhotoCatalysis

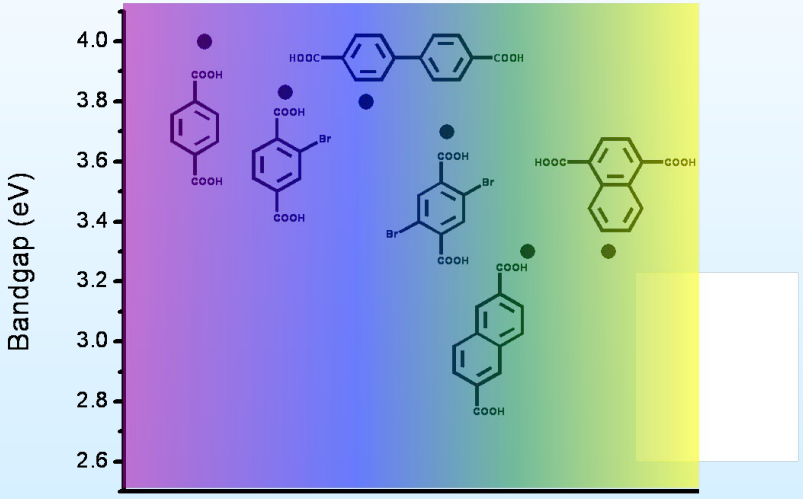
MOFs: Photocatalysis

- MOF-5 : photoluminescent material

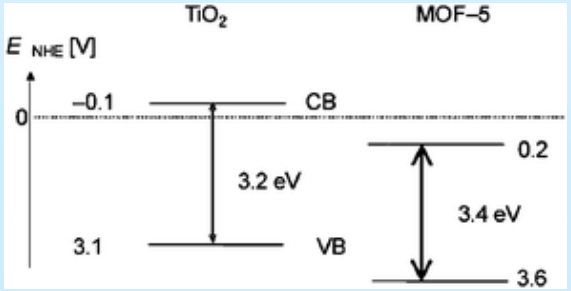
Zn4O13 node = Quantum dots
Linkers = antenna for hv



Effect of the linker on the bandgap



- MOF-5 : Strong oxidizing semi-conductor



Corma et al., J. Mater. Chem , 2010

Gascon et al., ChemSusChem, 2008

S. Bordiga et al, Chem.Commun. 2004

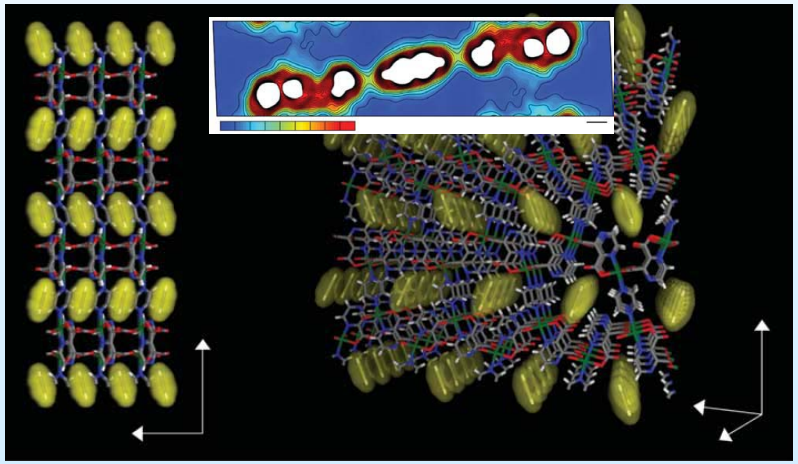
Polymerisation

- Topotactic polymerization in 1D MOF

Kitagawa et al, Angew. Chem., 2004

Mw/Mn=1.6

7.8 x 7.8



- Anionic polymerization of acetylene in 1D MOF

Kitagawa et al, Nature, 2005

- Polycarbonates from epoxides & CO_2 in 3D MOF(Zn)

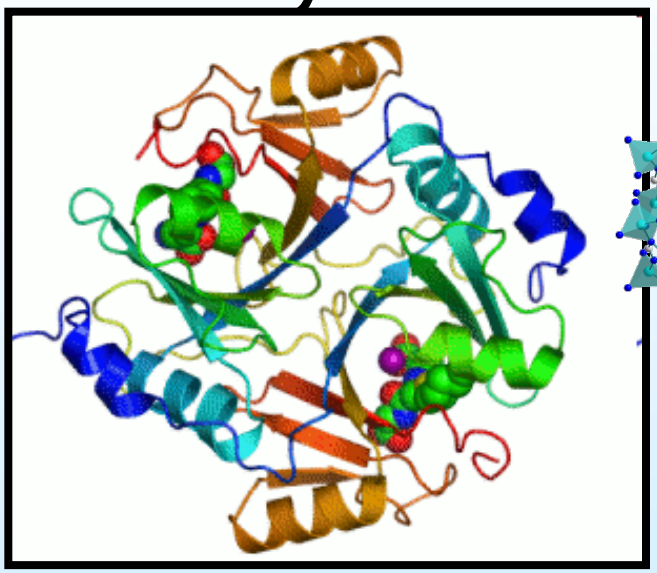
Mueller, US patent, 2003

Zinc glutarate = 2nd catalyst generation

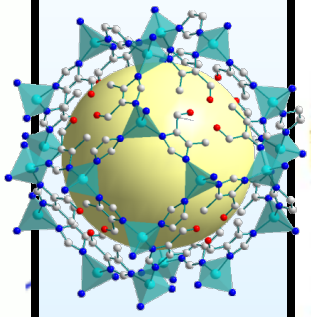
Mw = 60.000-75.000 g/mol

Marketing ?

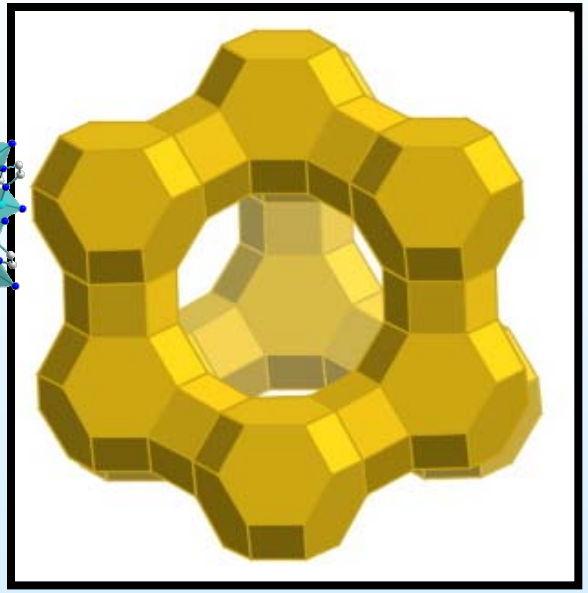
Enzymes



MOFs

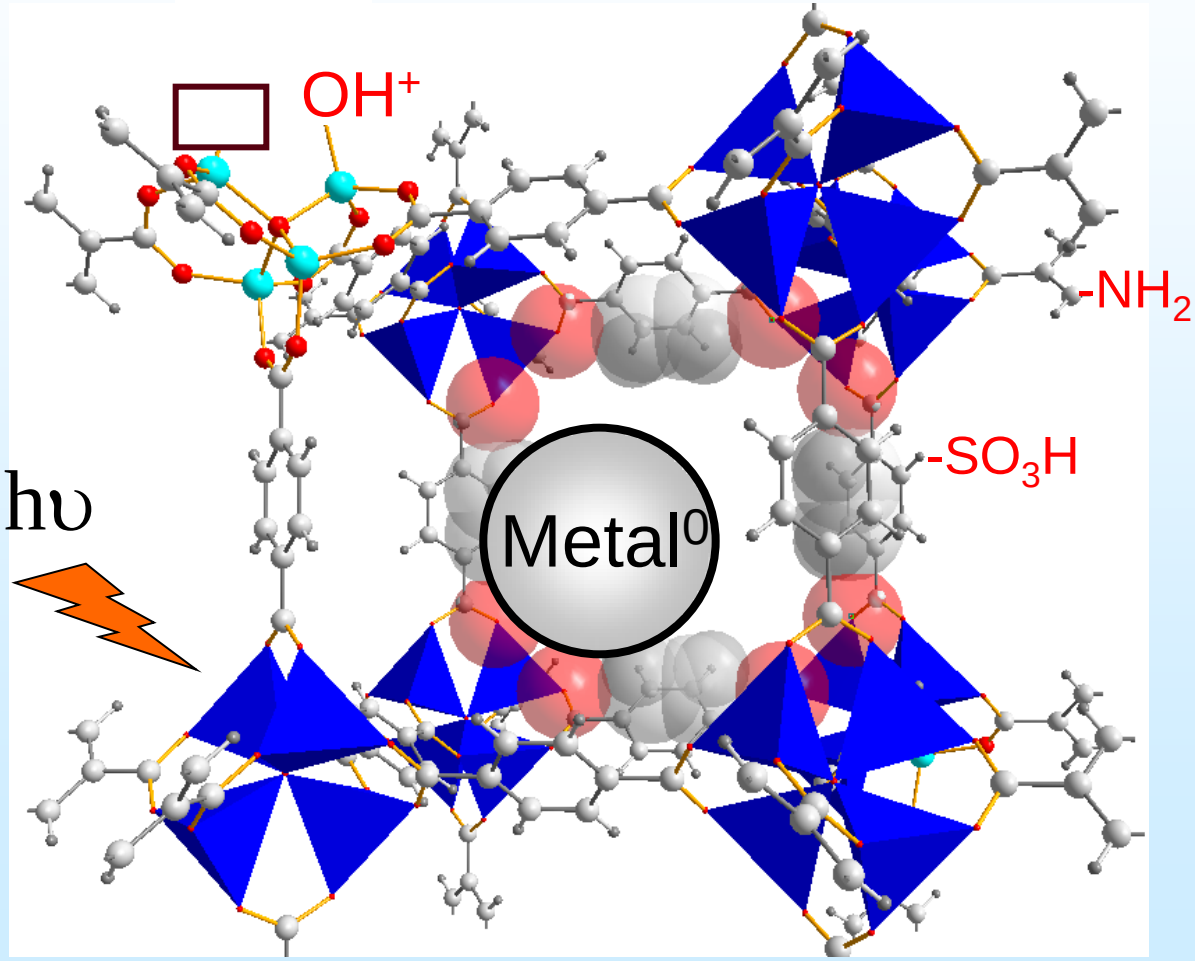


Zeolites




Think different.

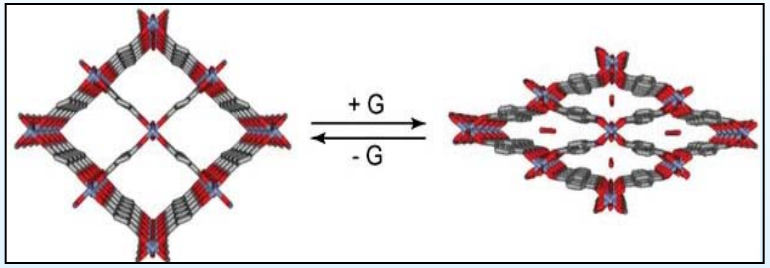
Think different !

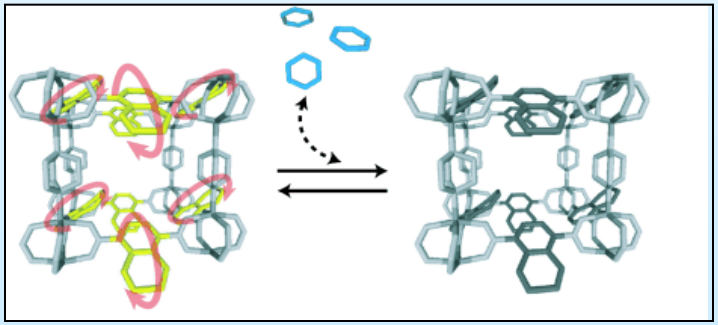


Flexibility & molecular recognition

- Pore flexibility upon guest adsorption
- Rotating ligand with Temperature

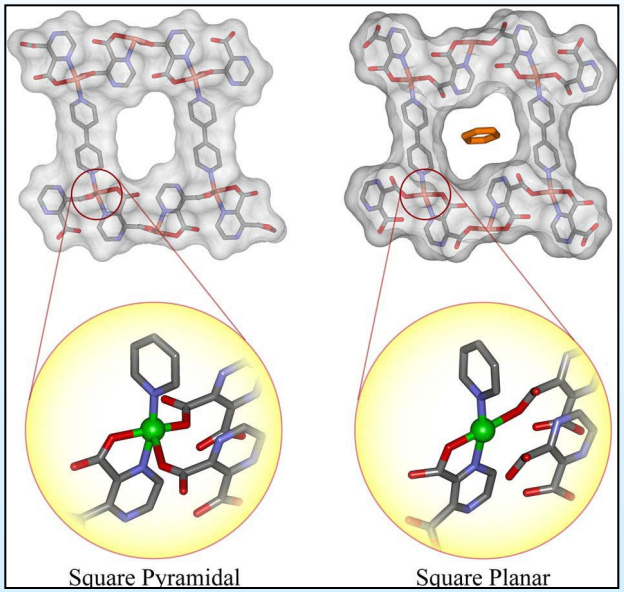
MIL-53





$[Zn_2(1,4\text{-ndc})_2\text{-(dabco)}]n$

CPL-2



S. Kitagawa et al, Angew. Chem. 2006, 118, 5054

Towards biomimetism

Thanks

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