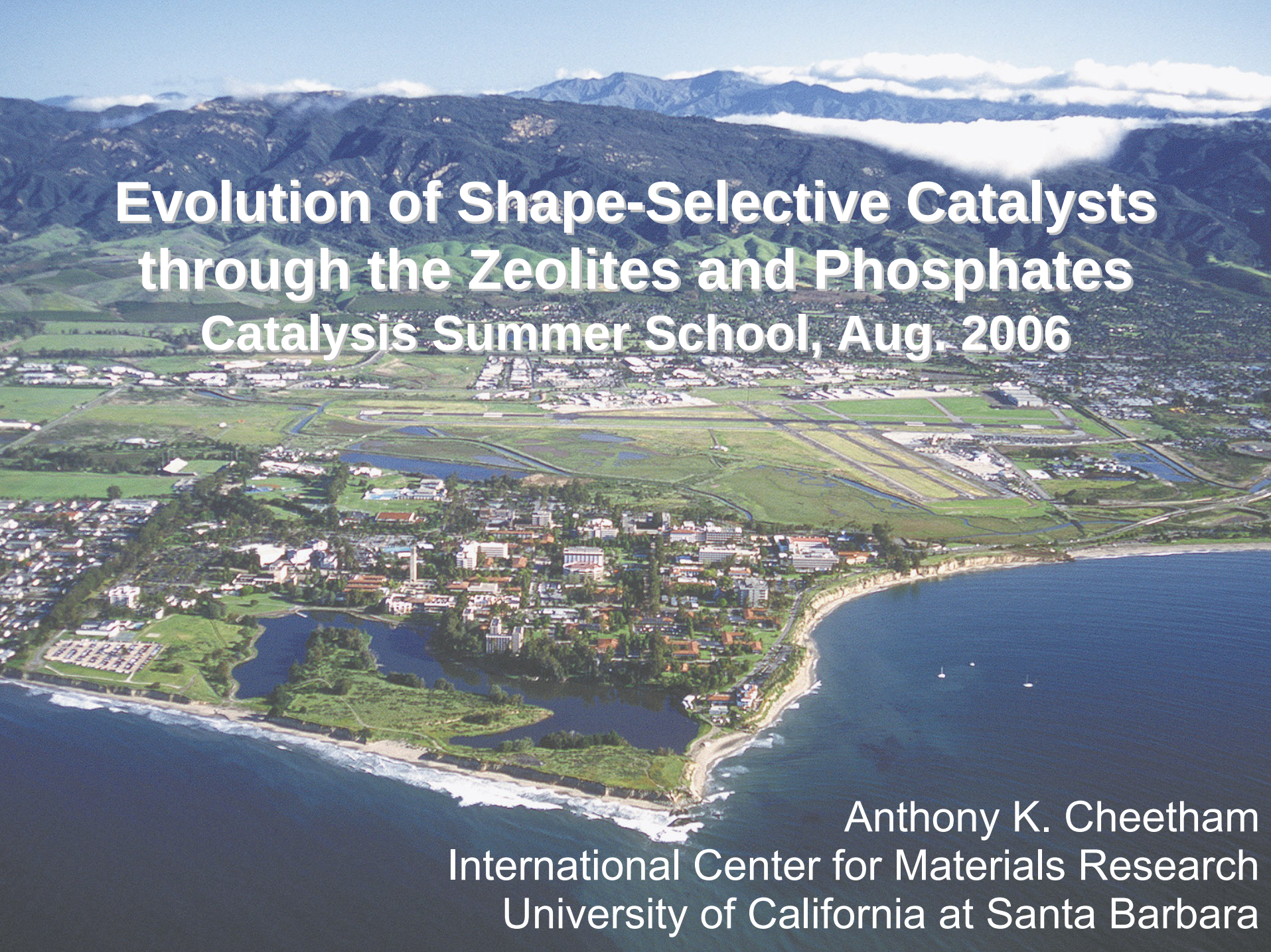


Evolution of Shape-Selective Catalysts through the Zeolites and Phosphates

Catalysis Summer School, Aug. 2006

Anthony K. Cheetham
International Center for Materials Research
University of California at Santa Barbara

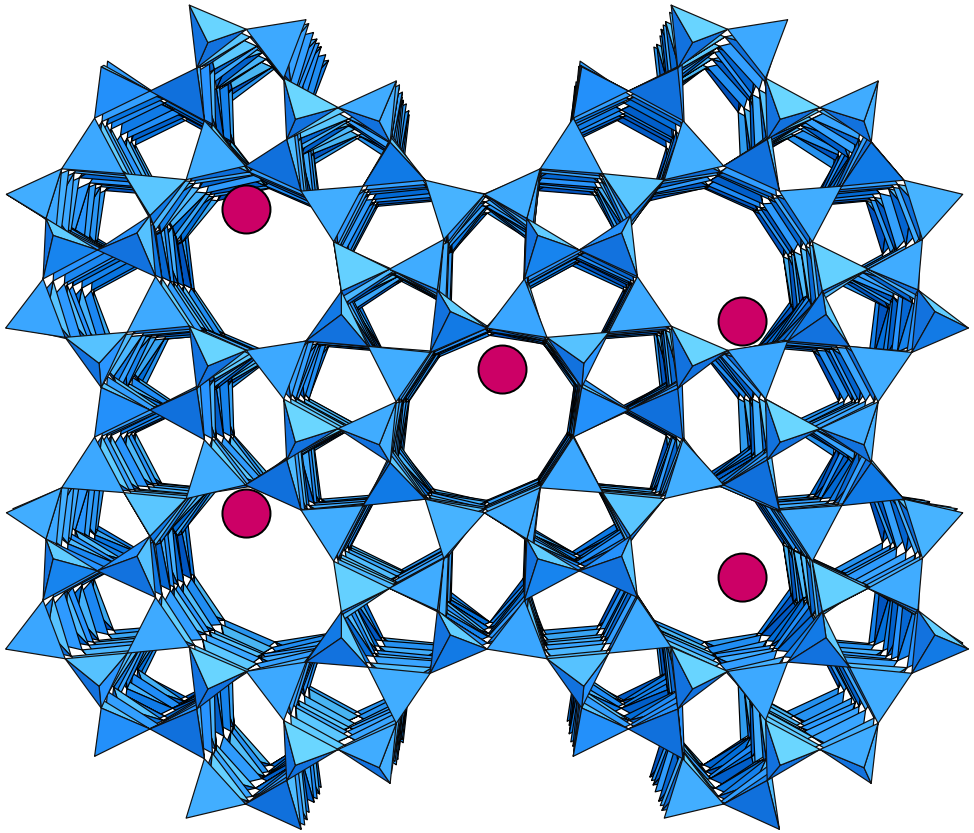
icmr

MILESTONES IN THE DEVELOPMENT OF NANOPOROUS FRAMEWORK MATERIALS

- **Inorganic open-framework structures**
  - **Aluminosilicate zeolites, $M_x[Si_{1-x}Al_xO_2].nH_2O$ 1960s →**
  - **Role of templates in synthesis; 1970 →**
  - **Aluminum phosphates; 1982 →**
  - **Other inorganic open-framework materials, especially phosphates 1990 →**
- **Mesoporous materials**
  - **1992 →**
- **Hybrid inorganic-organic frameworks**
  - **1990 → (but porous systems since ~1995)**

Zeolite ZSM-5 in its Aluminosilicate Form

Corner-sharing Si/AlO_4 tetrahedra and cations in red; channel diameter is about 5.5 Å



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Characteristics of Aluminosilicate Zeolites

- Traditionally made under hydrothermal conditions
- Reactions proceed under kinetic control
- Template molecules or structure-directing agents may be used, e.g. quaternary amines
- Excellent thermal stability on removal of solvent or templates from cages
- Nanoporosity up to ~1000 m^2/g
- Ion-exchangability, e.g. Na^+ for Ln^{3+}
- Shape-selective catalytic properties

Catalytic Applications of Zeolites

Shape-Selective Catalysis:

Acid Catalysis

Catalytic cracking in gasoline manufacture (FAU zeolites)
Isomerizations, e.g. xylenes for polyesters (ZSM-5)
Methanol to gasoline or olefins (ZSM-5)

Redox catalysis

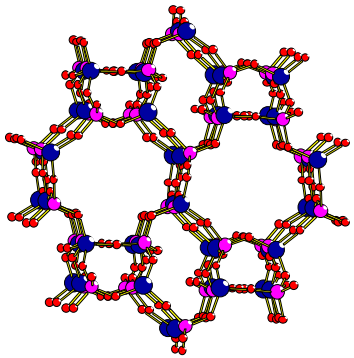
Partial oxidations with H_2O_2 over titanosilicates
Denox reactions over Cu-containing zeolites
Alkane oxidations over Co-containing AlPOs

Bifunctional catalysis

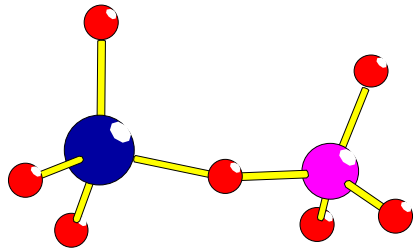
Hydrocracking over Pt-containing zeolites

Evolution of Open Framework Inorganic Materials

Cheetham, Férey, Loiseau, Angew. Chem. Int. Ed. 38, 3268 (1999)



Aluminosilicate zeolites
in the 1950s/1960s



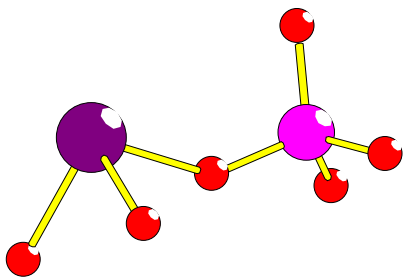
Aluminum phosphates
in the early 1980s

Metalluminophosphates
in the mid 1980s
e.g. $H(Al/M^{II})PO_4$

Other group III phosphates
from the mid 1980s;
e.g. $GaPO_4$

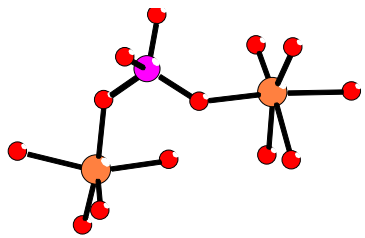
Non TO_4 Frameworks

Systems with lone pairs;
e.g. Sn^{II}, Sb^{III} in the 1990s

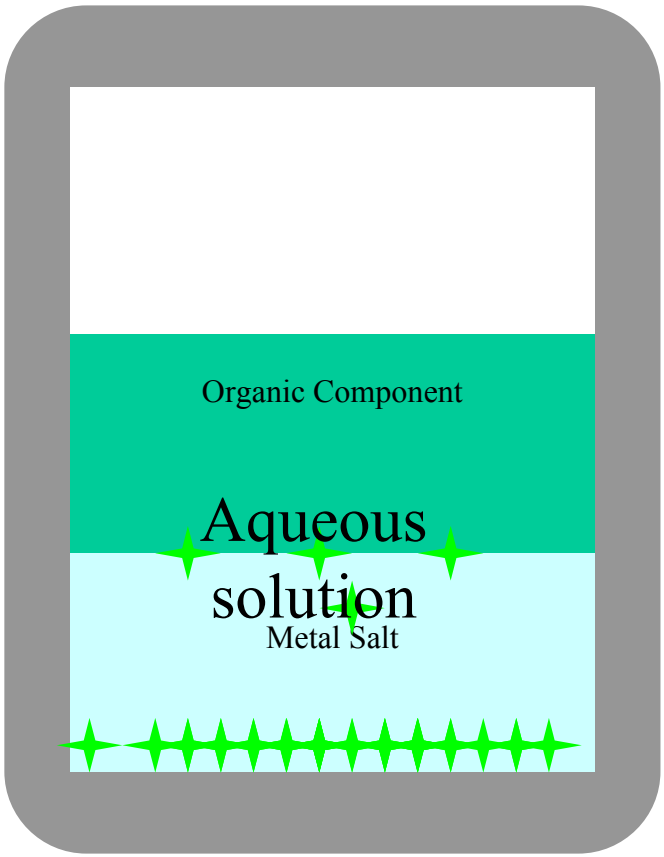


Non-oxide frameworks
e.g. sulfides, nitrides, halides
in the 1990s

Transition metal
phosphates, e.g. $FePO_4$
in the 1990s



Hydrothermal Synthesis of Metal Phosphates



e.g. for Co-P-O systems:

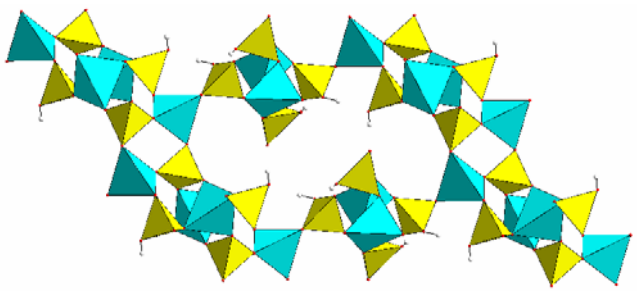
Temperature 150-200 C

An aqueous or non-aqueous solution that contains:

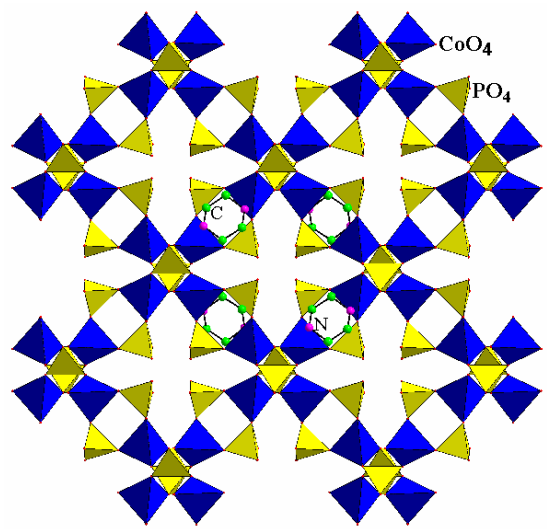
- A cobalt Salt
- Phosphoric acid
- **An amine**, e.g. R_4N^+, (to act as a template or structure-directing agent that may be trapped in the final structure)

Use of organophosphates esters as a phosphate source

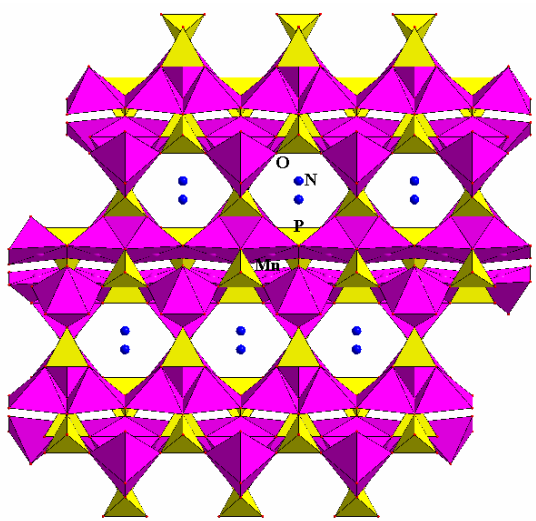
$$P(O)(OC_4H_9)_3 + 3H_2O \longrightarrow P(O)(OH)_3 + 3C_4H_9OH$$



$[C_5N_3H_{18}][Zn_3(HPO_4)_3(PO_4)]$



$[C_4N_2H_{11}][Co_2(PO_4)(H_2PO_4)_2]$



$[NH_4][Mn_4(PO_4)_3]$

Neeraj, Forster, Rao and Cheetham JCS Chem. Comm. 2716 (2001)

Neeraj, Noy, Rao and Cheetham, J. Solid State Chem, (2002)

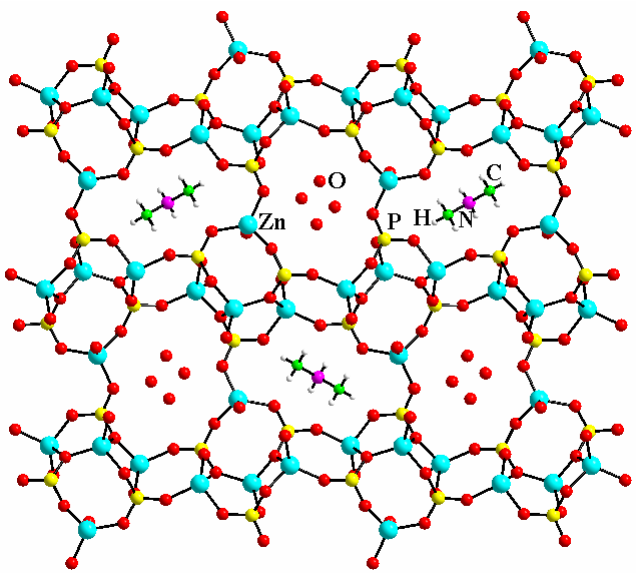
Neeraj, Noy and Cheetham, Solid State Sciences 4, 397 (2002)

Neeraj, Rao and Cheetham, J. Mater. Chem. 14, 814 (2004)

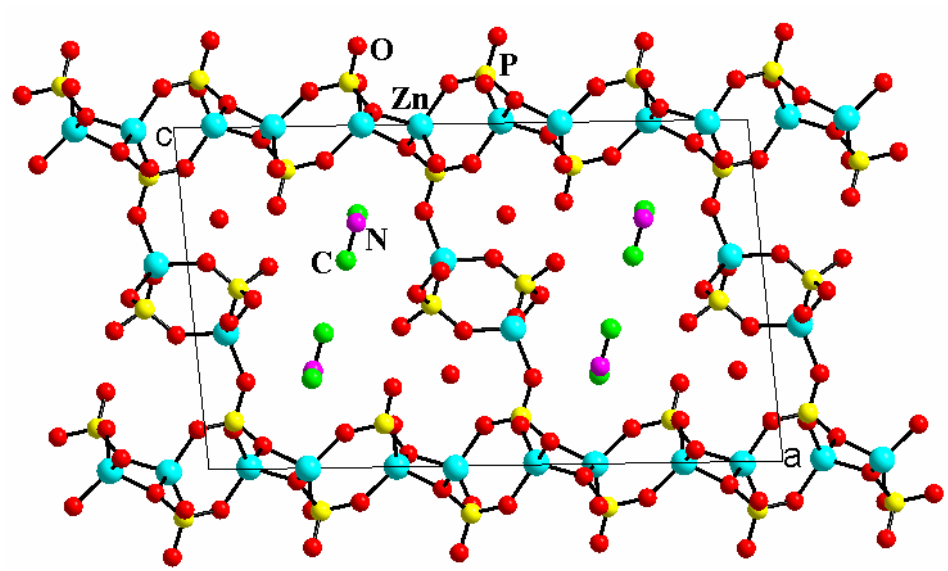
Use of Organophosphorus Amides as a Phosphate and Amine Source

$P(O)(NR_2)_3$ (R = alkyl) compounds can act as single molecule source of phosphate and amine to synthesize phosphate-based frameworks

$$PO(NR_2)_3 + 3H_2O \longrightarrow H_3PO_4 + 3R_2NH$$



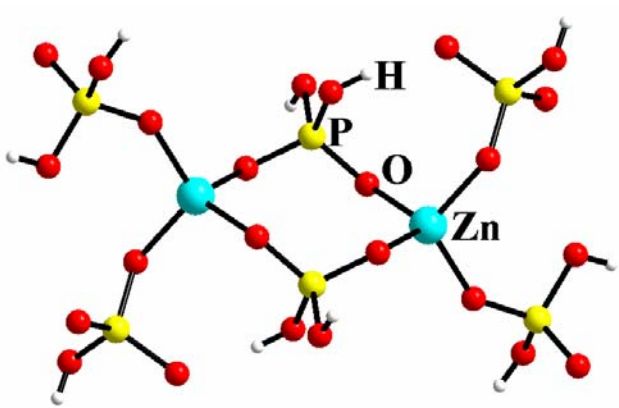
$[C_2NH_8][Zn_3(HPO_4)_2(PO_4)].H_2O$

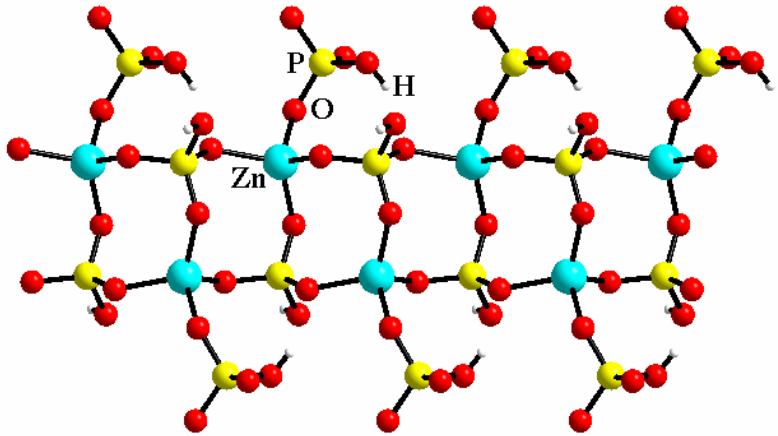


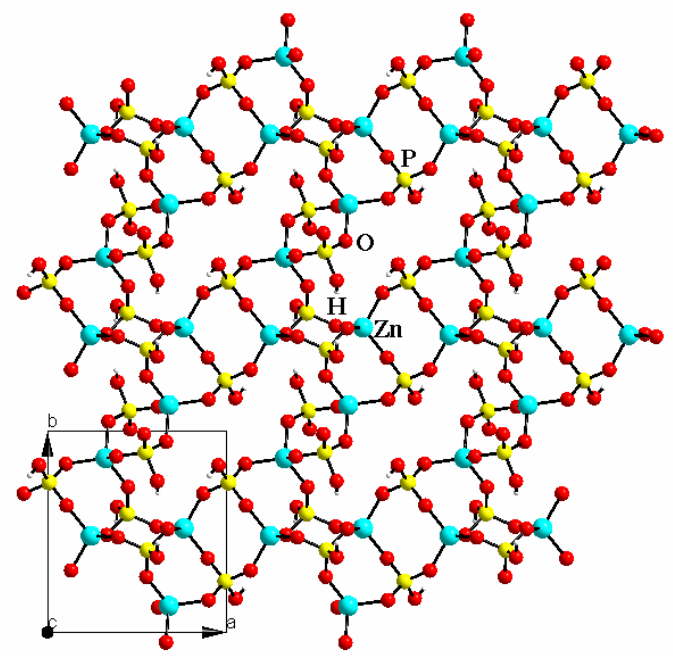
$[(C_2NH_8)(H_3O)][Zn_4(PO_4)_3(H_2O)]_2.H_2O$

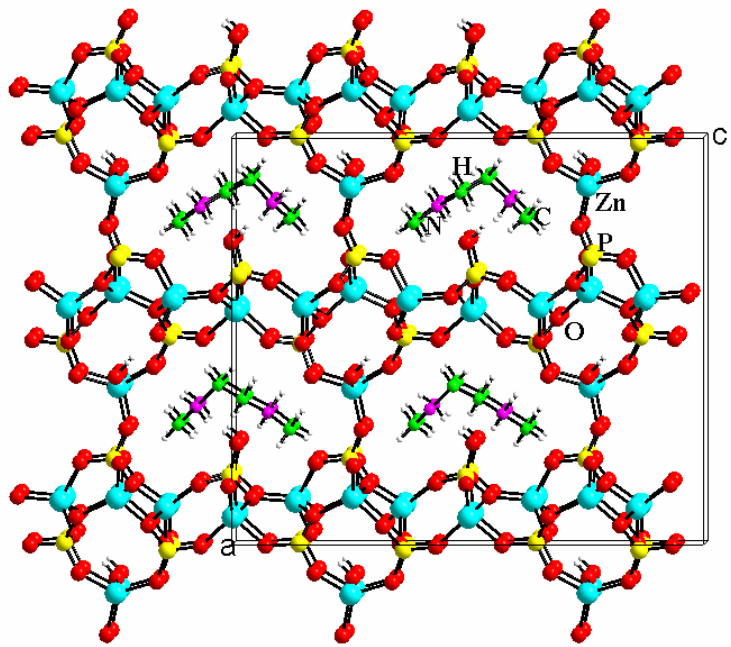
Neeraj and Cheetham, Chem. Comm. 1738 (2002)

Dimensionality in Open-framework Metal Phosphates: from monomeric to chain to sheet to 3-D structures









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The Search for New Families of Functional Nanoporous Materials

- Among the huge family of open-framework materials, the silicates and AlPOs are unique in terms of their nanoporosity and stability to 500°C and above
- They are known for their excellent reactivity as shape-selective acid catalysts
- Can we make basic catalysts based upon lone-pair cations such as Sn(II) and Sb(III)?
- Can we stabilise first transition series phosphates with ligand field effects?
- Would they exhibit shape-selective redox catalysis or sorption properties?
- Do transition metal nanoporous materials exhibit ferromagnetism or other interesting properties?

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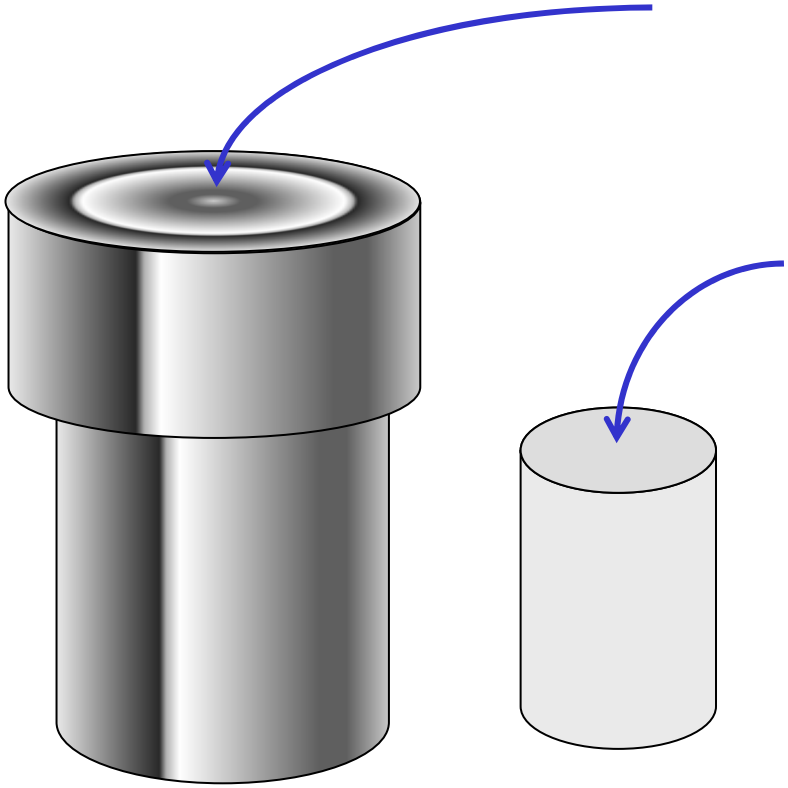
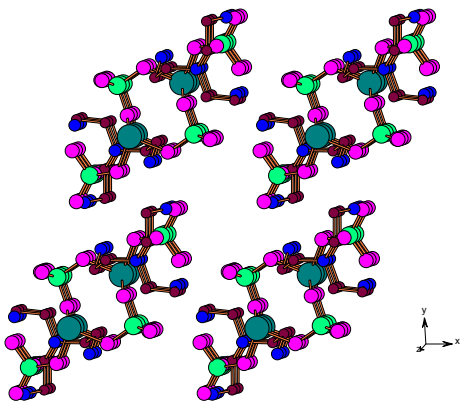
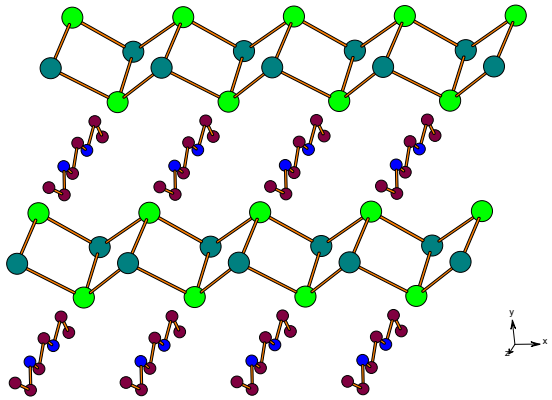
Synthesis of Sn(II) and Sb(III) Phosphates

- Hydrothermal synthesis from tin(II) oxalate, phosphoric acid (85%), amine and water/ethylene glycol
- 140-170, 2d, 60% filling, autogeneous pressure
- pH~4
- Amines used: Tris (2-aminoethyl)amine (TREN), 1,4-diaminobutane (DAB), Guanidine (GUAN), tetramethyl diaminobutane (TMDAB) and urea (as ammonium source)



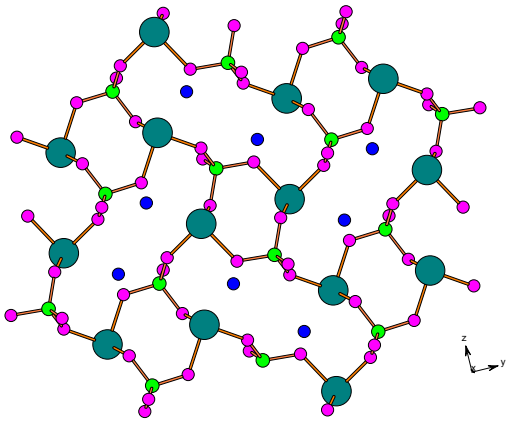
Tin(II) Phosphates of Different Dimensionalities

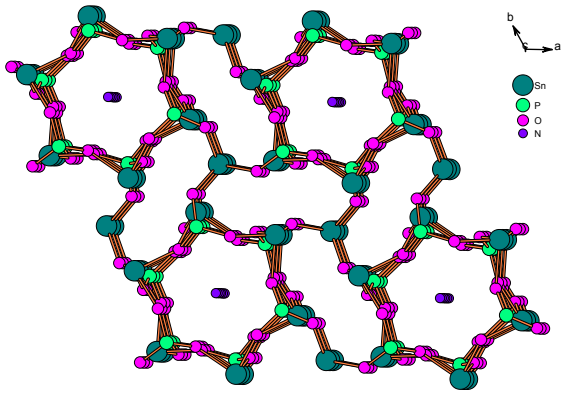




SnPO-NH$_4$

SnPO-NH$_4$





Natarajan et al. *Angew. Chem.* 36, 978 (1997); Natarajan et al. *Chem. Comm.* 1089 (1997); Natarajan et al. *Chem. Mater.* 10, 1627 (1998); Ayyappan et al. *Chem. Mater.* 10, 3308 (1998)

Ammonium Tin(II) Phosphate

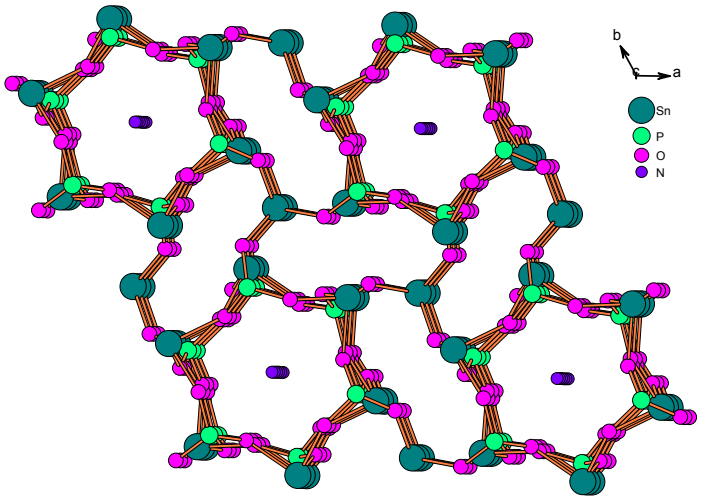
AMMON-SnPO

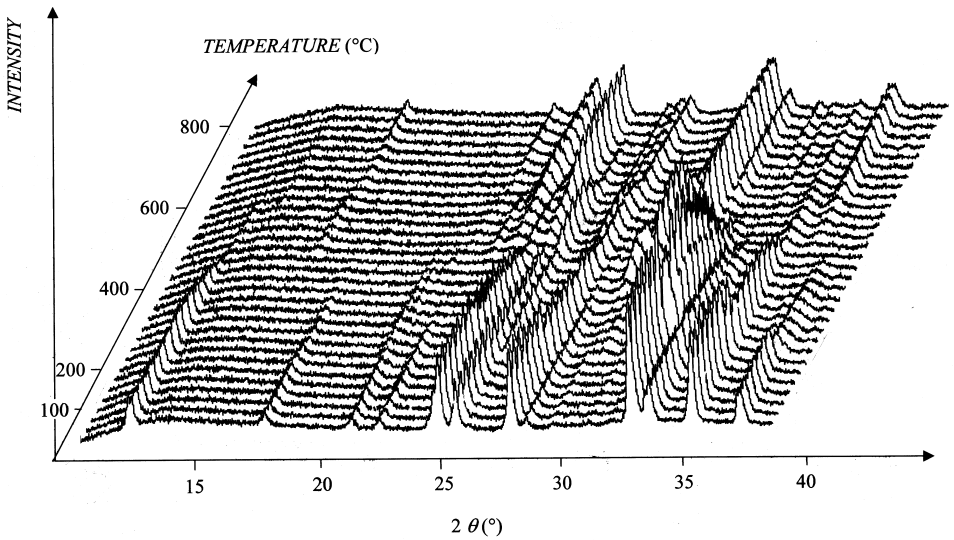
$P6_3$ (no. 173)

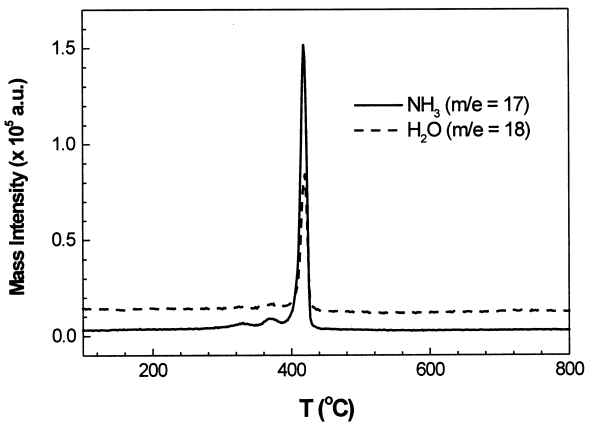
a = 9.6975(3) Å

c = 8.0938(3)Å V=659.18(4) Å^3

Z=6



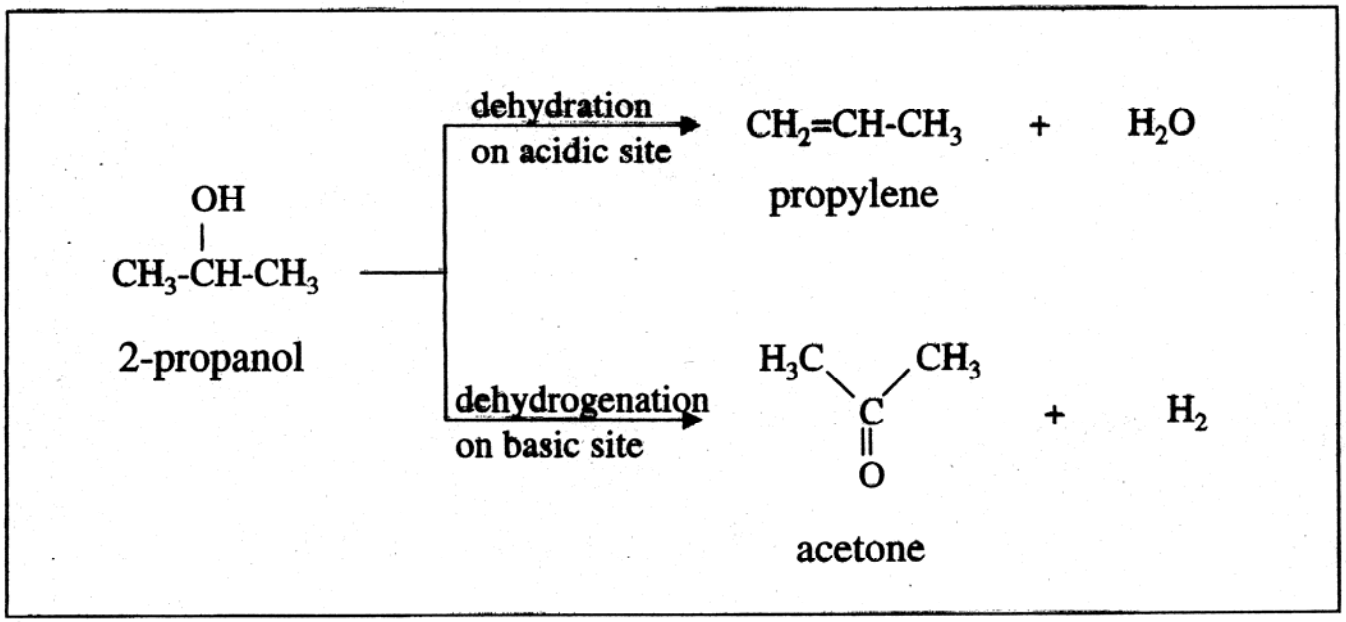




Ayyappan et al. *Intl. J. Inorg. Mater*. 2, 21 (2000)

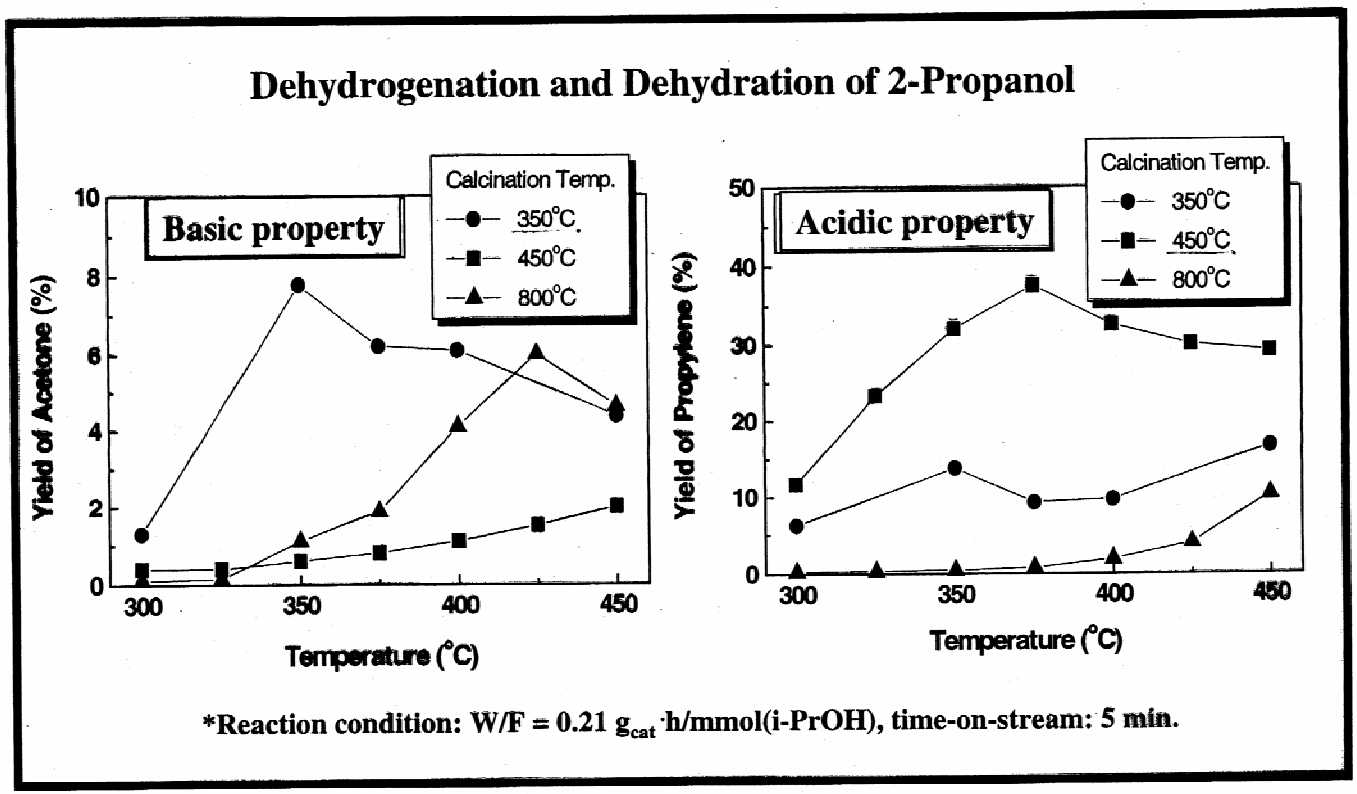
Catalysis with Ammonium Sn(II) Phosphate

Decomposition of 2-propanol as a model reaction of acid-base catalysis



Catalysis with Ammonium Sn(II) Phosphate

Catalytic Properties of Ammonium-Tin(II) Phosphate



Catalytic but not Shape-Selective!

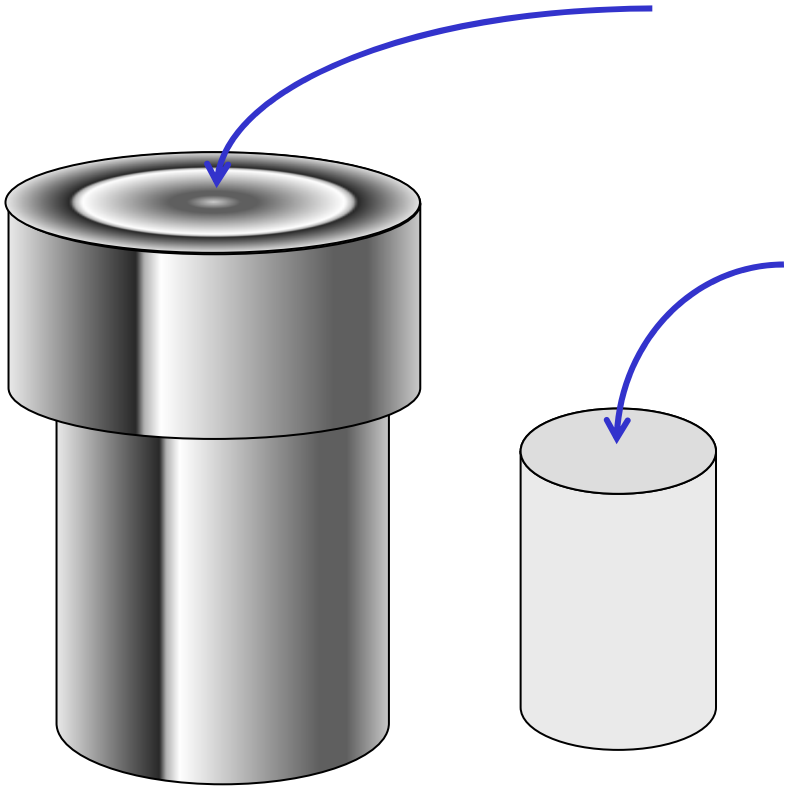
Synthesis of Sn(II) Oxalates

•Hydrothermal synthesis from tin(II) oxalate, phosphoric acid (85%), amine and water/ethylene glycol

•140-170, 2d, 60% filling, autogeneous pressure

pH~6

•Amines used: Tris (2-aminoethyl)amine (TREN), 1,4-diaminobutane (DAB), Guanidine (GUAN), tetramethyl diaminobutane (TMDAB) and urea (as ammonium source)



Sn(II) Oxalates – Hybrid Frameworks

Tin(II) Oxalate-Guanidine I

- Hydrothermal synthesis from tin(II) oxalate, phosphoric acid (85%), amine and water/ethylene glycol
- 140-170°C, 2d, 60% filling, autogeneous pressure

pH~6

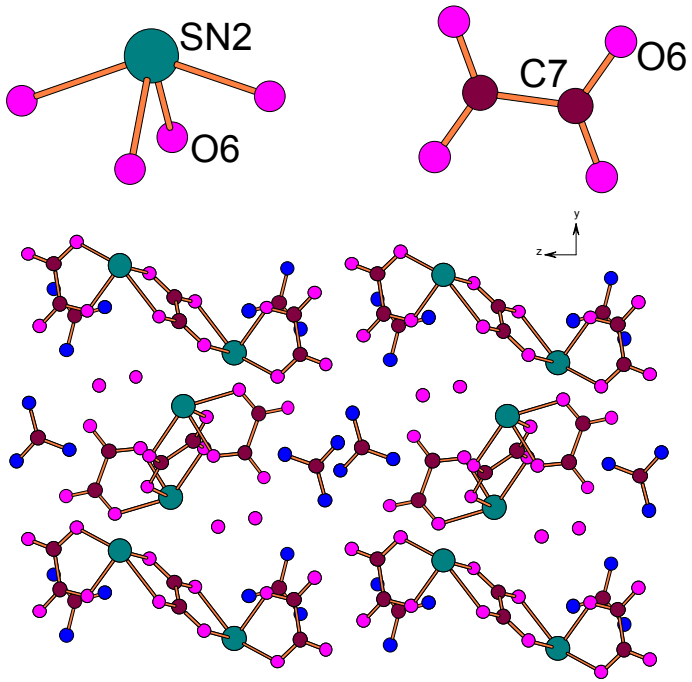
- Amines used: Guanidine carbonate, tetramethyl diaminobutane

Tin(II) Oxalate-Guanidine I

P-1

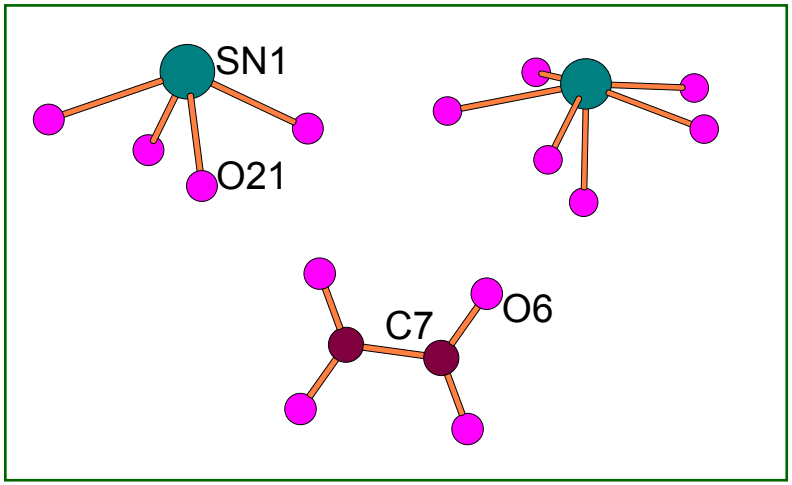
***a*=7.564, *b*=10.633, *c*=12.050Å**

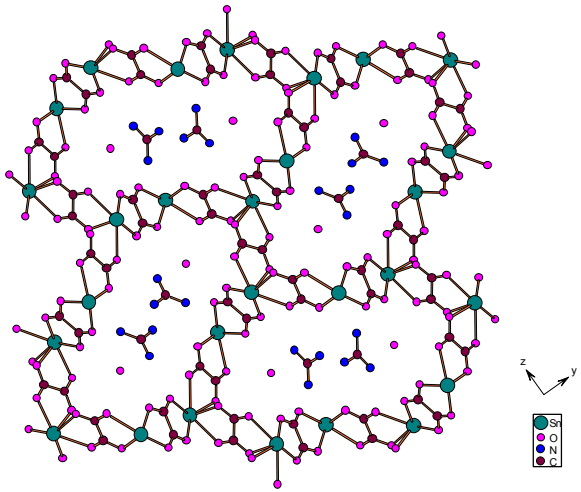
and α=87.9, β=85.2, γ=85.9°

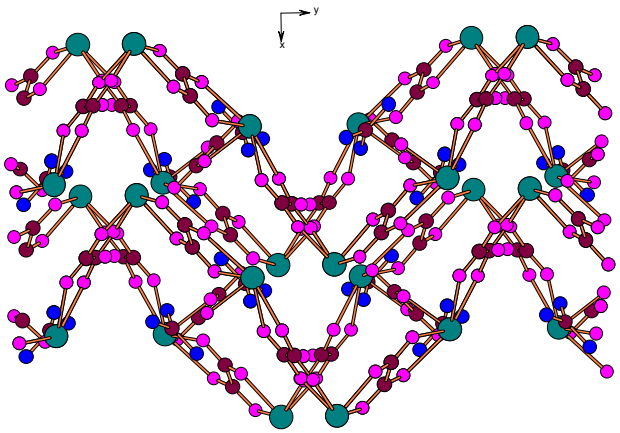


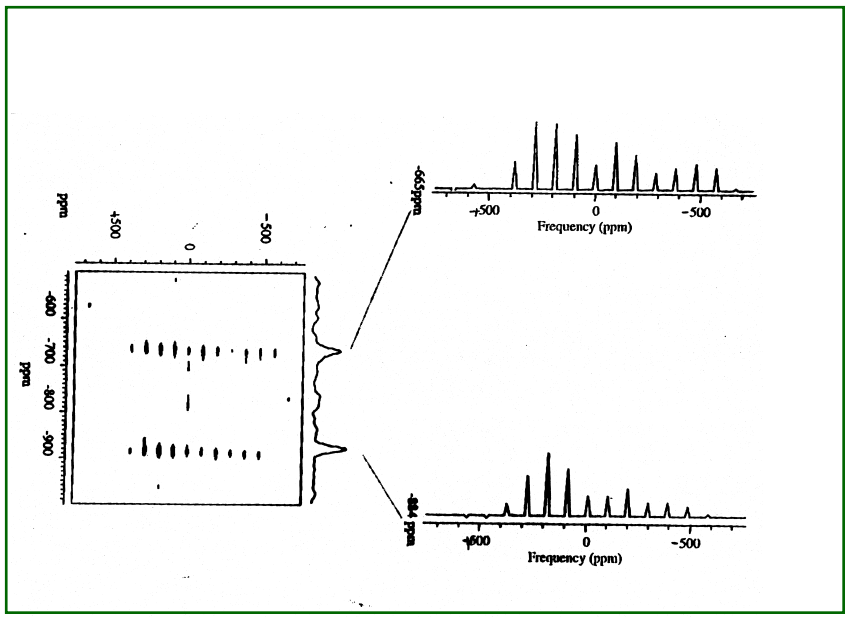
Ayyappan et al. *Chem. Mater.* 10, 3746 (1998)

Tin(II) Oxalate-GUAN II



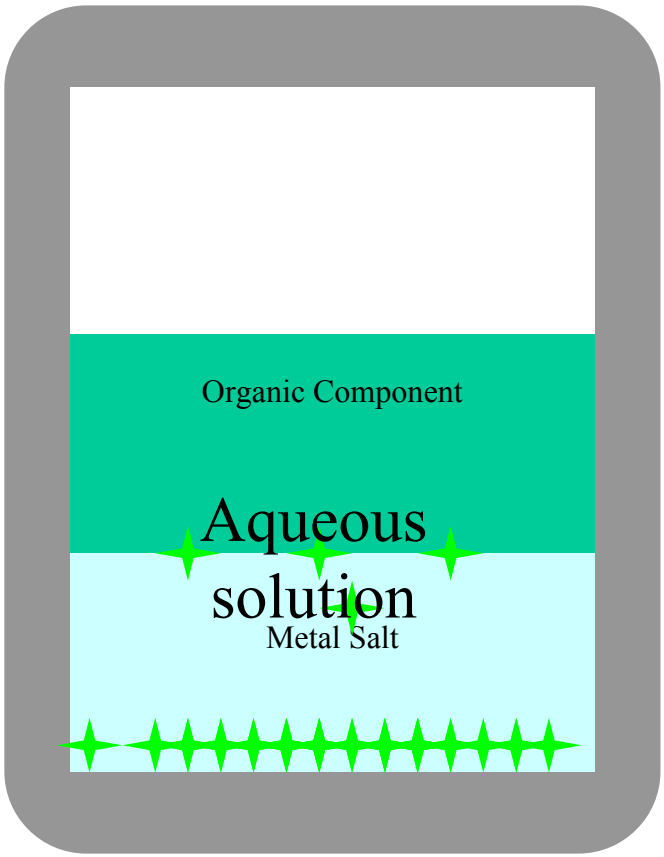






Ayyappan et al. *Chem. Mater.* 10, 3746 (1998)

Solvothermal Synthesis of Nickel Phosphates



VSB-1 conditions:

Temperature 180°C

6 days, pH 4

- $NiCl_2.6H_2O$
- Phosphoric acid
- tris(2-aminoethyl)amine (TREN)
- Pyridine/HF/water solvent

VSB-5 conditions:

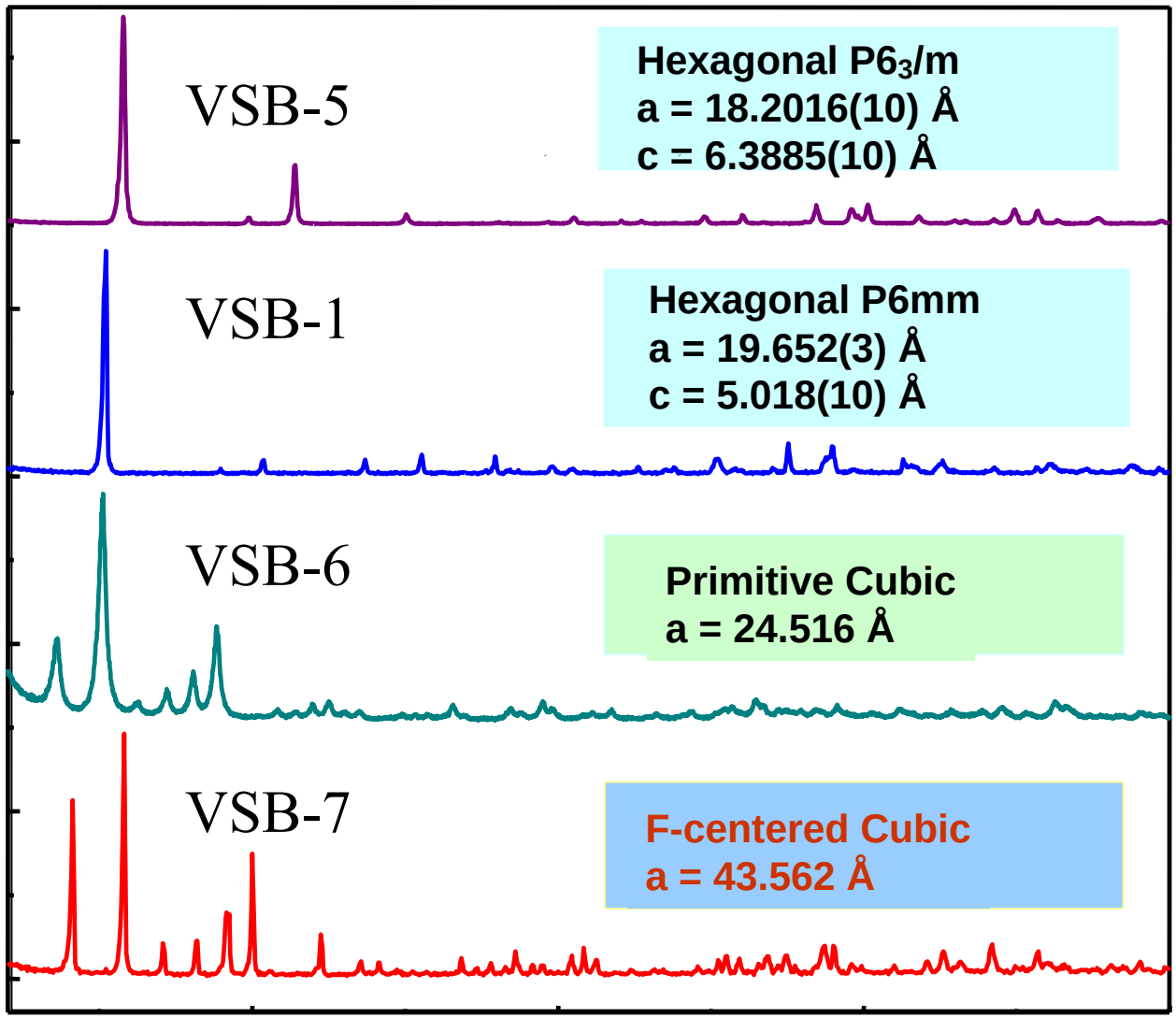
Temperature 180°C

5 days, pH 7-9

- $NiCl_2.6H_2O$
- Phosphoric acid
- 1,3-diaminopropane
- Water

Guillou, Cheetham, Ferey et al, Compte Rendu Ser. IIC, 387 (1999)
Guillou, Cheetham, Ferey et al. Angew. Chem. 40, 2831 (2001)

X-ray Powder patterns of the VSB-n



θ / degree

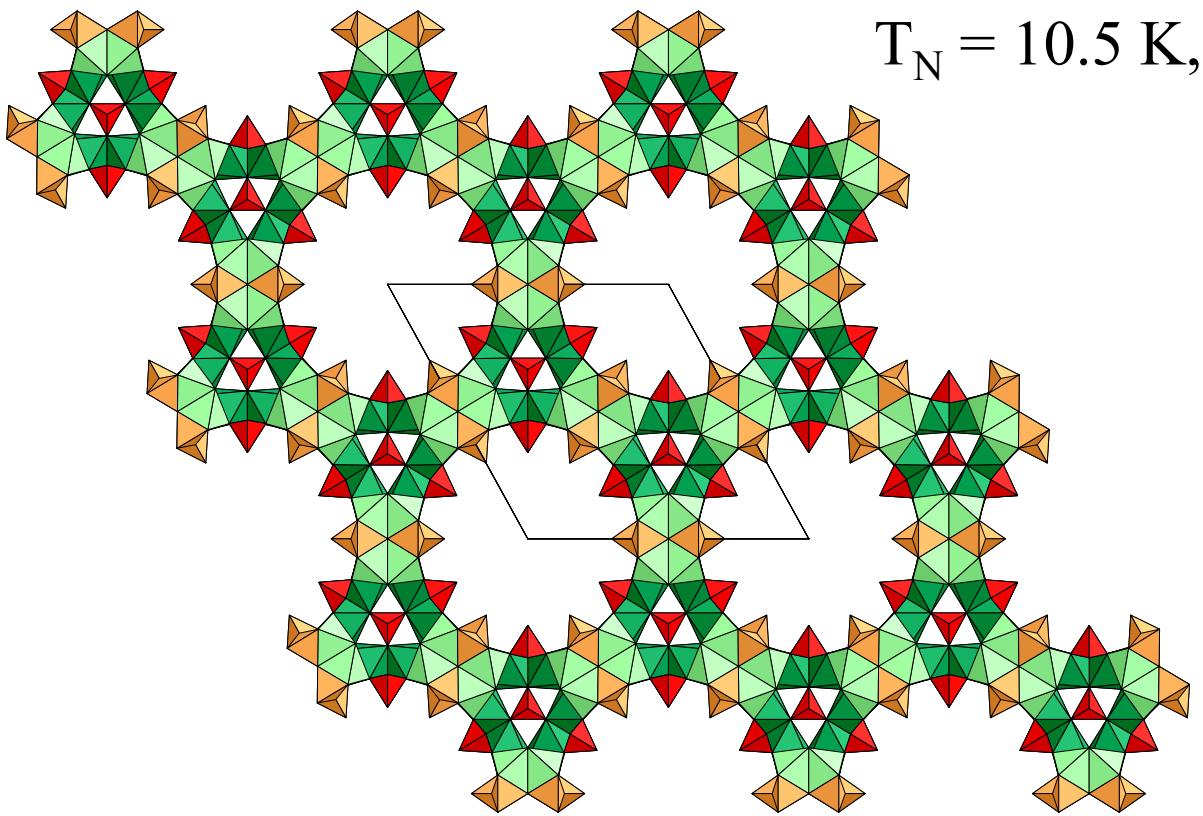
Structure of Nickel Phosphate, VSB-1

$K_4 [Ni_{18} (HPO_4)_{14}(OH)_3F_9]. 12 H_2O$

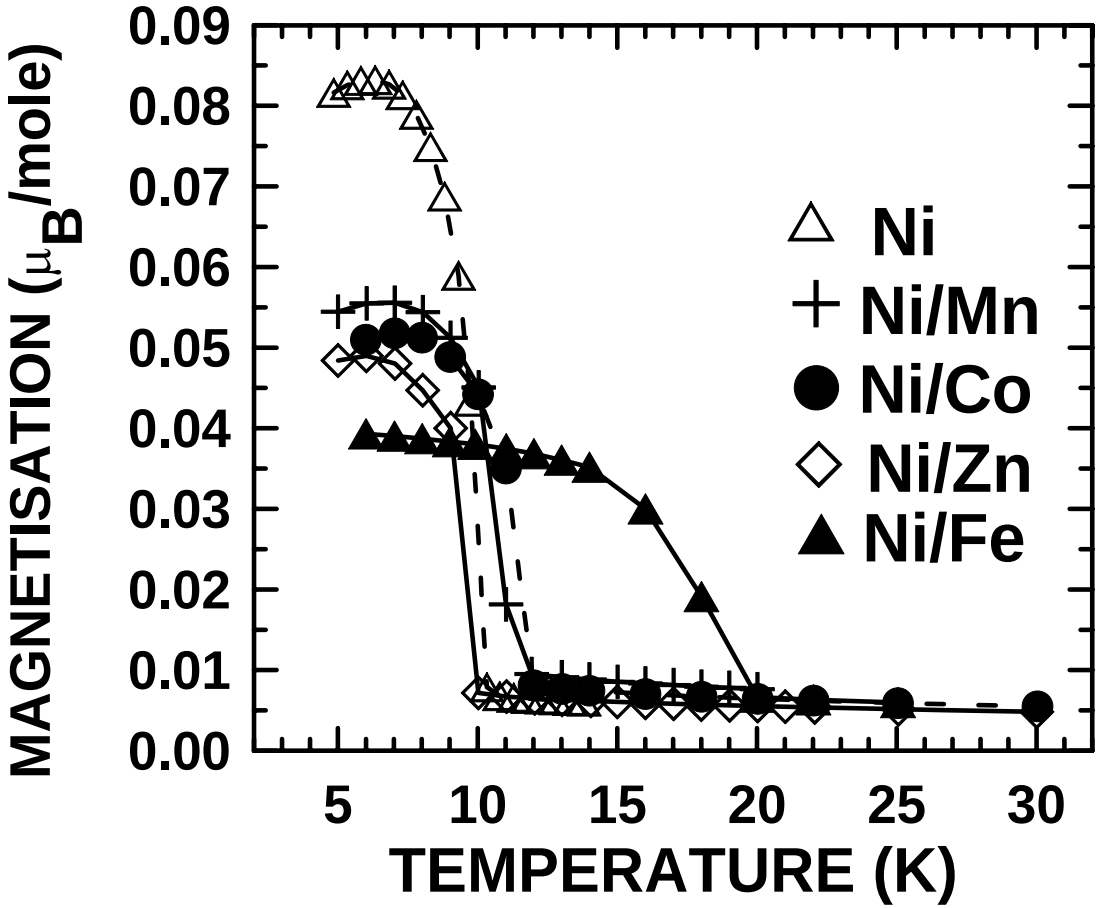
Guillou, Cheetham et al, Compte Rendu Ser. IIC, 387 (1999)

Ion-exchangeable!

$T_N = 10.5$ K, $\theta = -71$ K

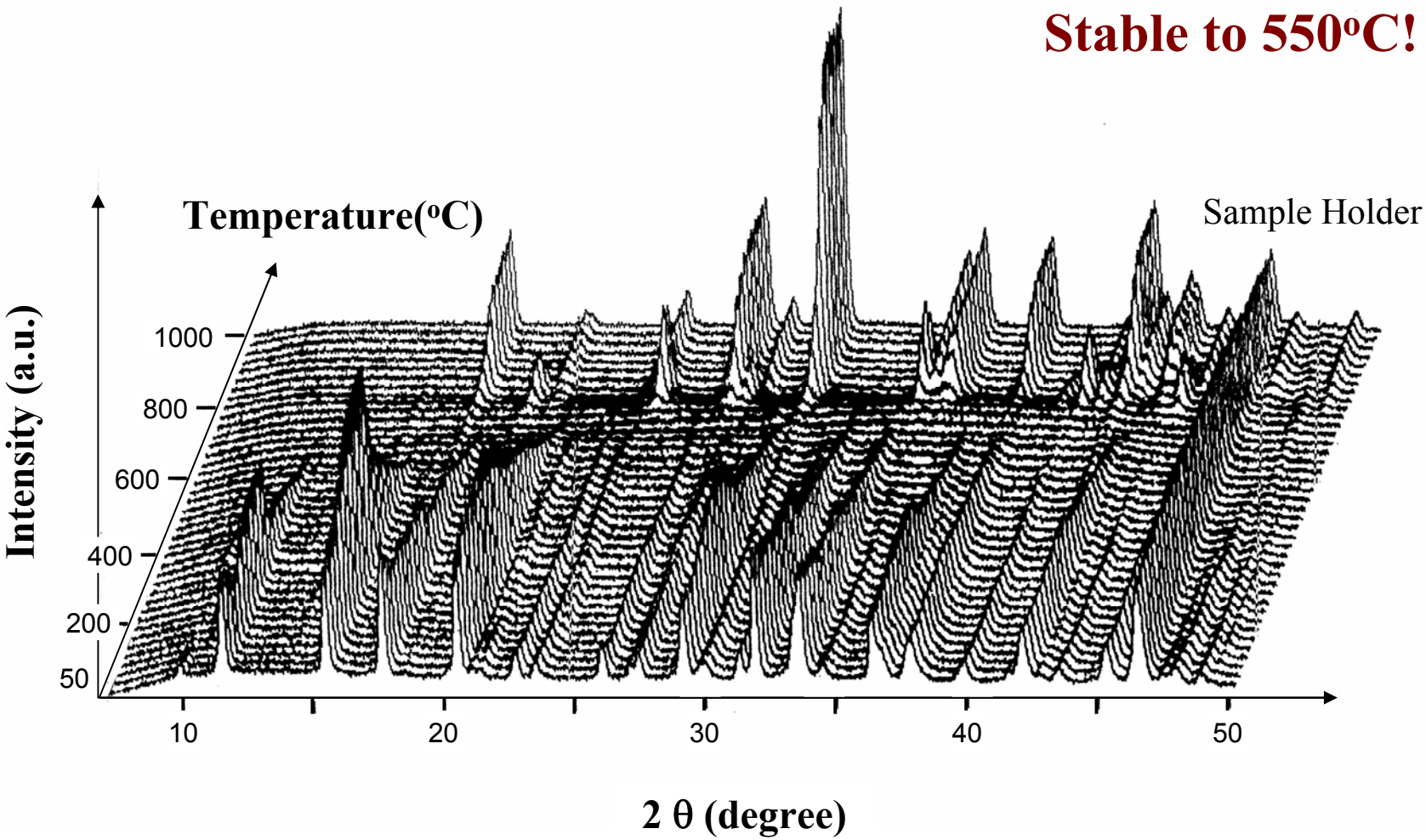


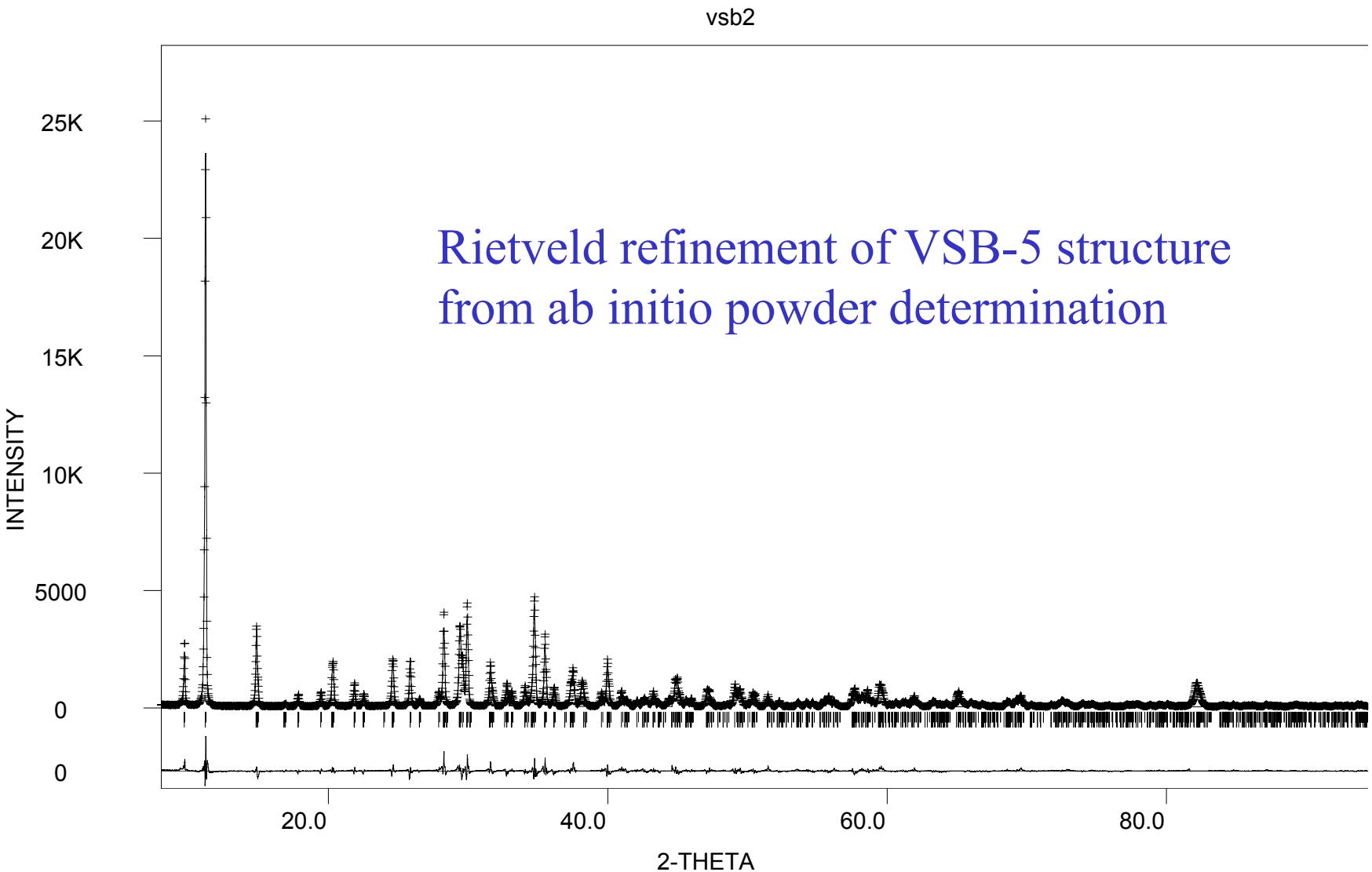
Magnetic Properties of VSB-1



Stability of Nickel Phosphate, VSB-1

$K_4 [Ni_{18} (HPO_4)_{14}(OH)_3F_9]. 12 H_2O$





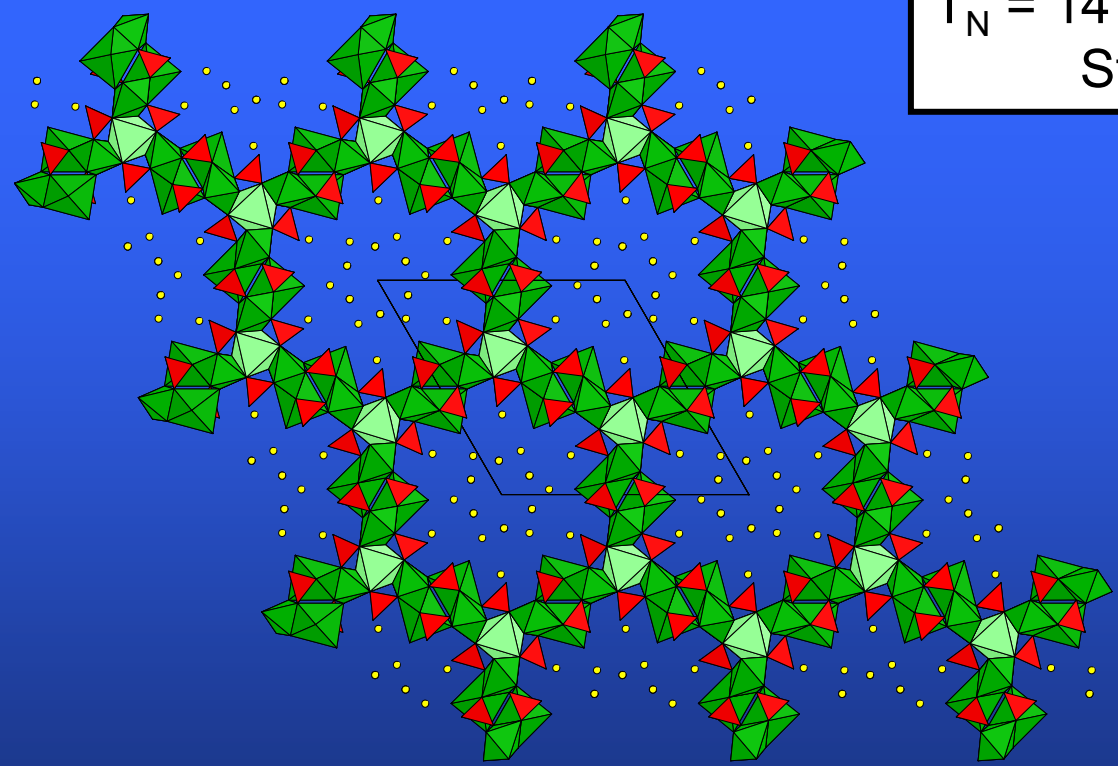
Rietveld refinement of VSB-5 structure from ab initio powder determination

Guillou et al, Angew. Chemie 40, 2831 (2001)

VSB-5: $[Ni_{20}(OH)_4(H_2O)_{14}(PO_4)_{12}] \cdot 12\ H_2O$

A Basic Molecular Sieve (Angew. Chemie. 40, 2831 (2001))

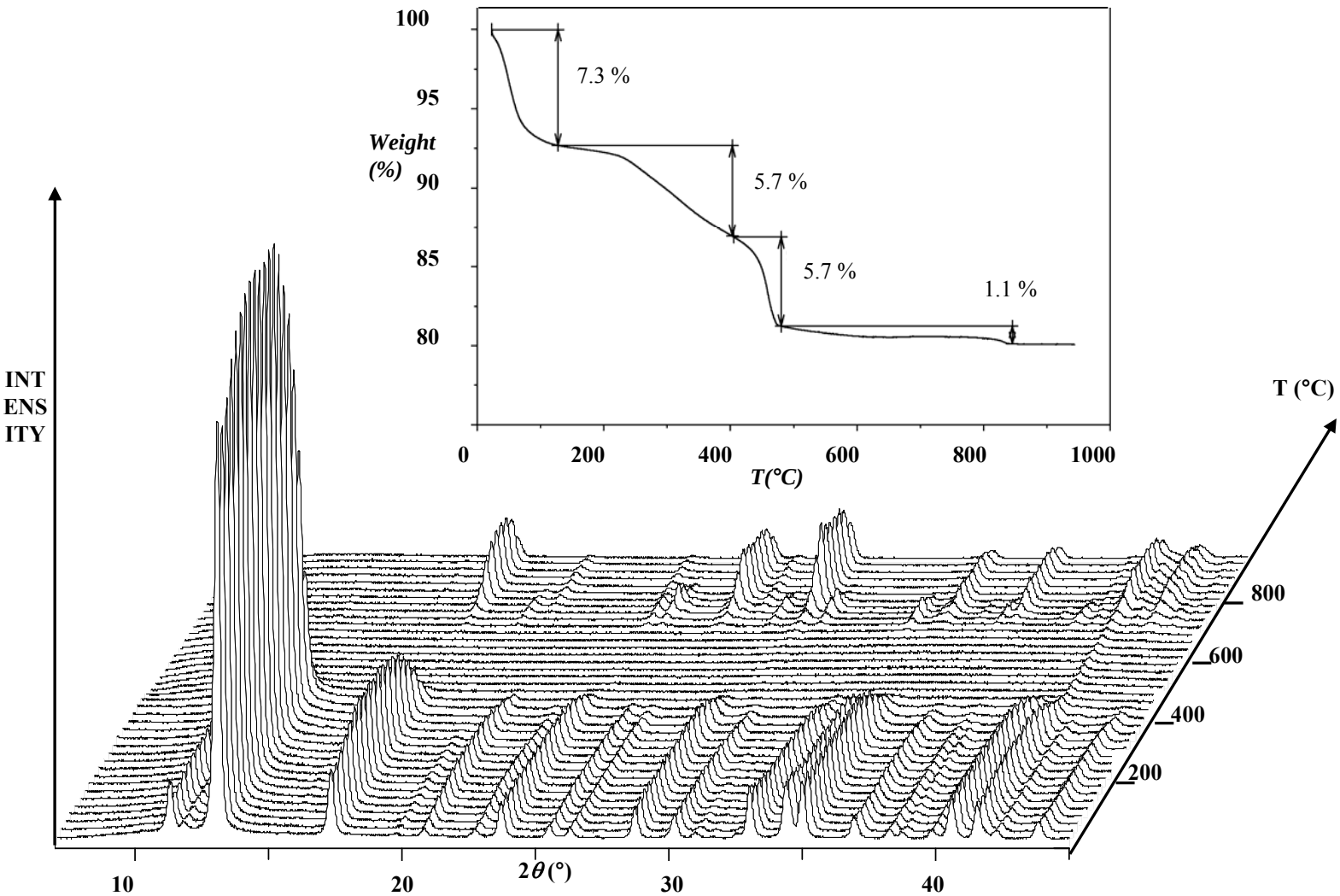
T_N = 14 K, θ = -49.5 K
Stable to 450°C



Cation substitution by Mn, Fe and V

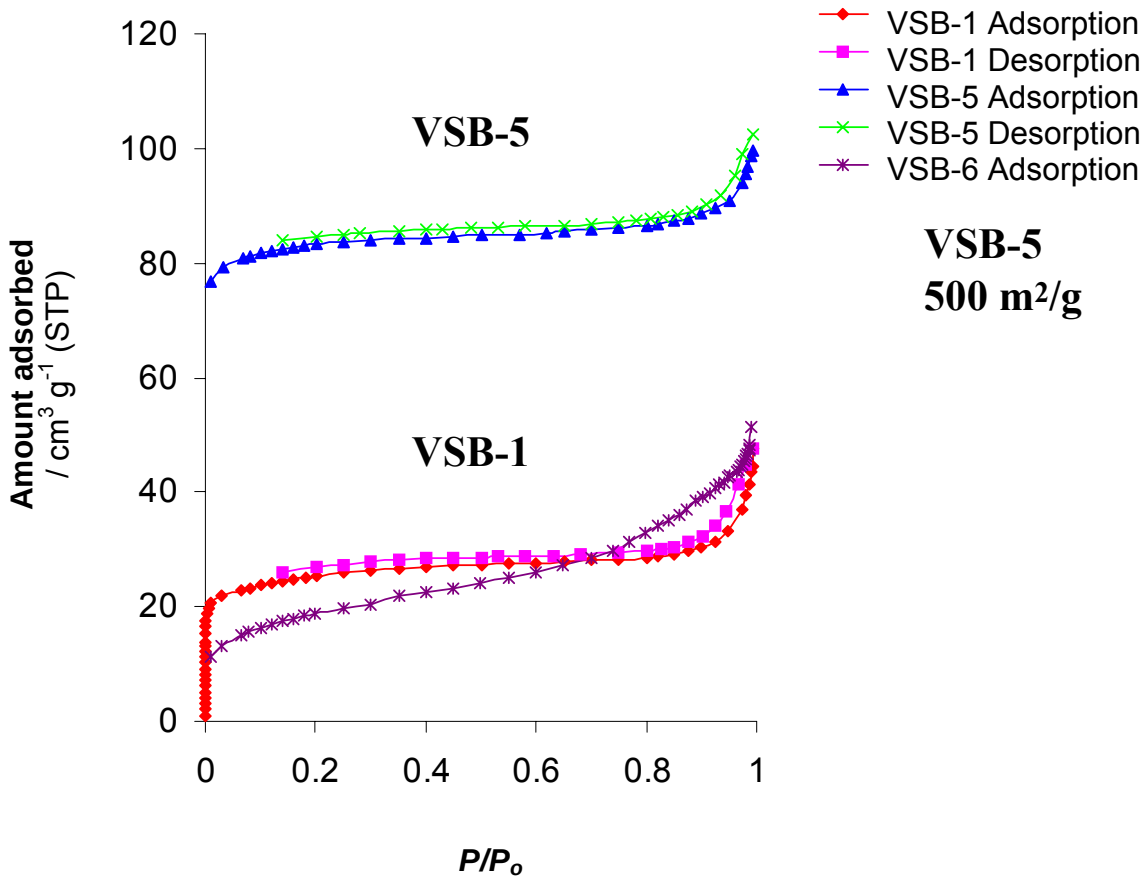
Chang, Cheetham et al. J. Phys. Chem. B109, 845 (2005)

Thermal evolution of VSB-5



Nanoporosity of VSB-1 and -5

Guillou, Férey, Cheetham et al, Angew. Chemie, 40, 2831 (2001)

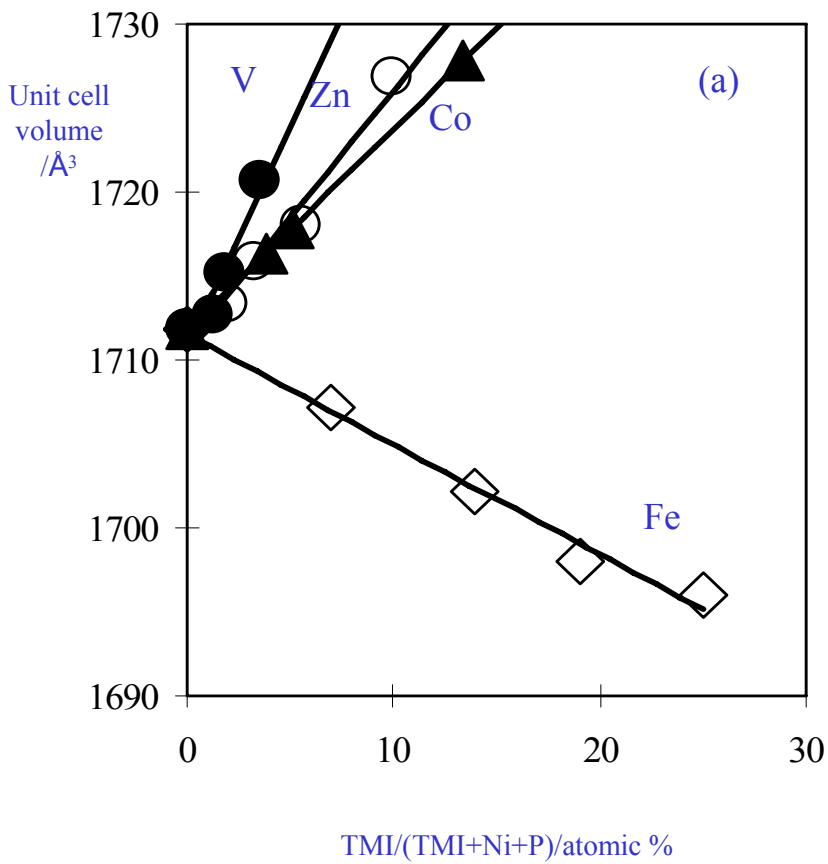


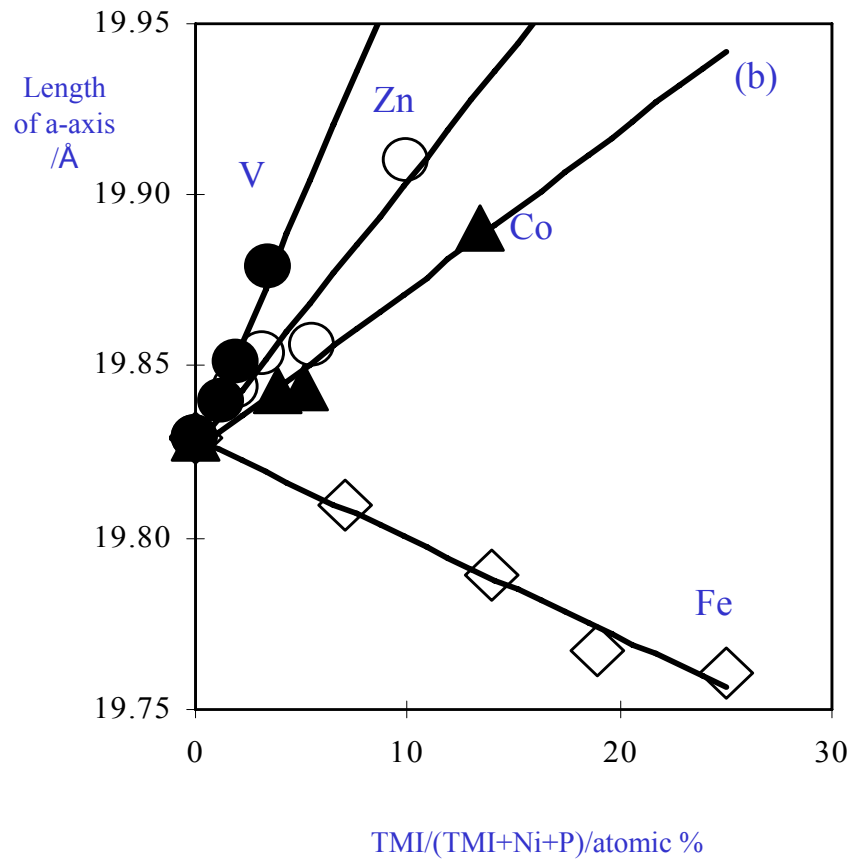
VSB-5
500 m²/g

Metal Substitution in Nickel Phosphate, VSB-1

$K_4 [Ni_{18} (HPO_4)_{14}(OH)_3F_9]. 12 H_2O$

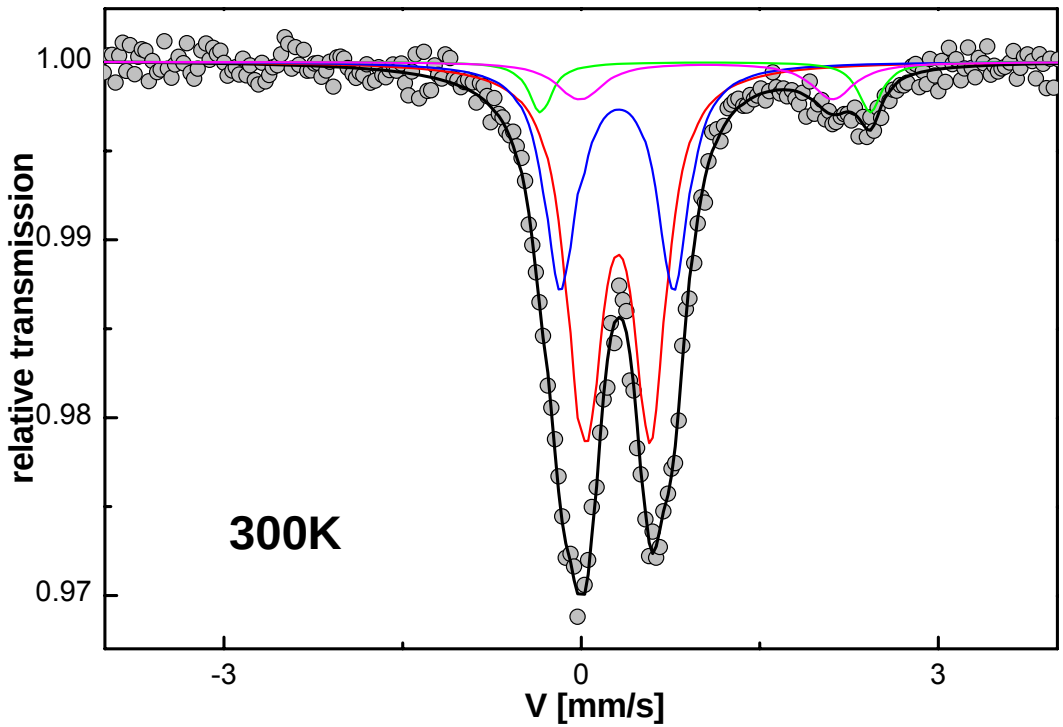
J-S. Chang, A.K. Cheetham et al, Chem. Mater. 16, 5552 (2004)





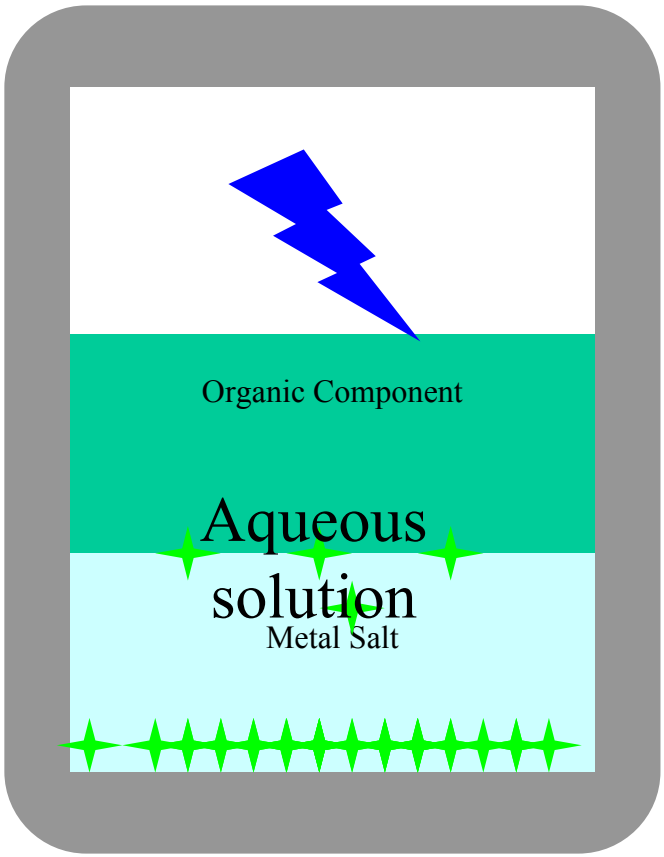
Iron Substitution in Nickel Phosphate, VSB-1
Mössbauer Spectroscopy

J-S. Chang, A.K. Cheetham et al, Chem. Mater. 16, 5552 (2004)



Fe^{2+} : 13%
Fe^{3+} : 87%

Microwave Synthesis of Nickel Phosphates



VSB-1 conditions:

Temperature 190°C, pH 3.5-4.8

1 minute 1200 W, 2 hr. 300 W

- $NiCl_2.6H_2O$
- Phosphoric acid
- HF, aq. ammonia
- water

No templates!

VSB-5 conditions:

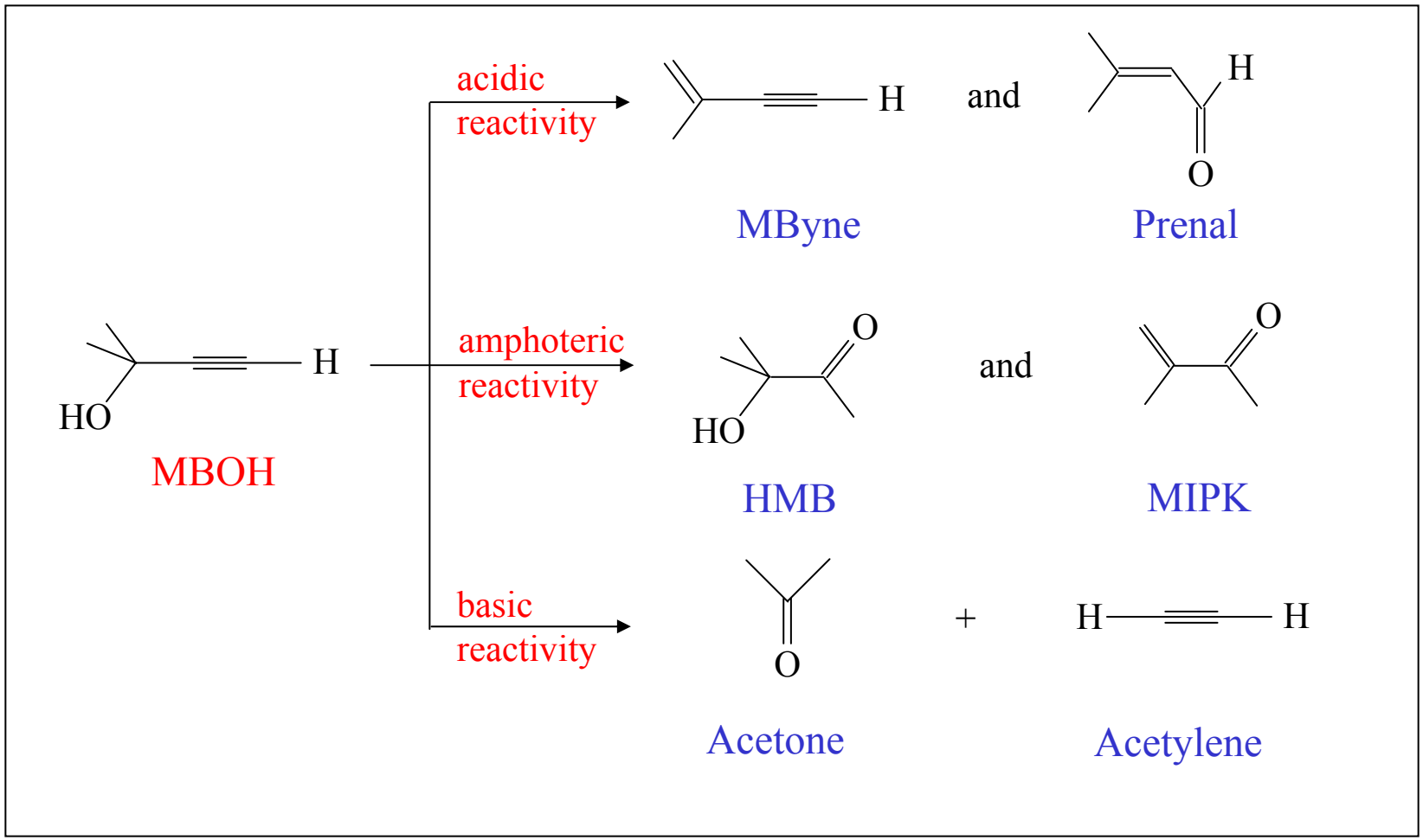
Temperature 180°C, pH 7.5-9.2

1 minute 1200 W, 1 hr. 300 W

- $NiCl_2.6H_2O$
- Phosphoric acid
- Aq. ammonia
- water

Chang, Cheetham, Jhung et al, Chem. Mater. 16, 1394 (2004)
Chang, Cheetham, Jhung et al, Chem. Mater. 17, 4455 (2005)

Catalytic Conversion of 2-methyl-3-butyn-2-ol (MBOH)
A Test for Acid-Base Character



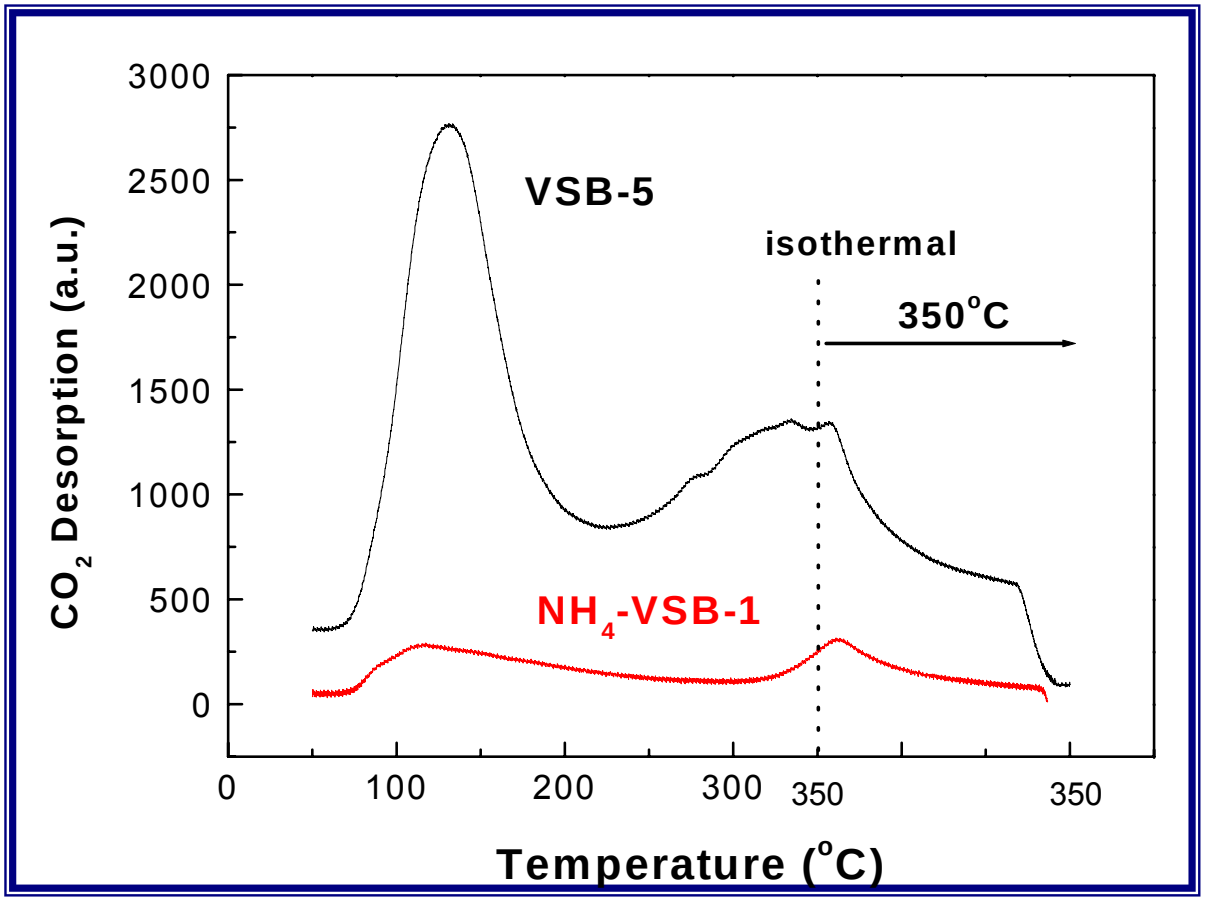
Conversion of MBOH over nickel phosphates and zeolites[a]

Catalyst	Temp. (°C)	MBOH Conversion		Ratio of Acetone/MByne	
		10 min	30 min	10 min	30 min
NH_4-VSB-1	300	10.0	7.6	1.82	2.32
VSB-5	300	99.0	97.3	38.8	42.5
NaX	200	26.1	15.2	55.7	79.7
NaY	200	18.3	10.8	0.07	0.07
ZrO_2[#]	200	-	11.7	-	0.27
				(S(HMB) = 47.1%))	

[a]Reaction conditions: p(MBOH) = 2 kPa, W/F = 125 g h mol^{-1}.
MBOH: 2-methyl-3-butyn-2-ol, Mbyne: 3-methyl-3-buten-1-yne (on acid site), acetone and acetylene: on basic site.
[#]ZrO_2 is known to be amphoteric, i.e., to have acid-base ion pairs.

CO_2-TPD Analysis of Nickel Phosphates

(as a measure of basicity)



Calcination: 350°C for 4 h (in air)

TPD Analysis:

- **$T_{adsorption}$: 30°C**
- **Desorption: 50°C to 350°C**
- **Ramp rate (β): 5°C/min**
- **Carrier flow rate: 50 ml/min**

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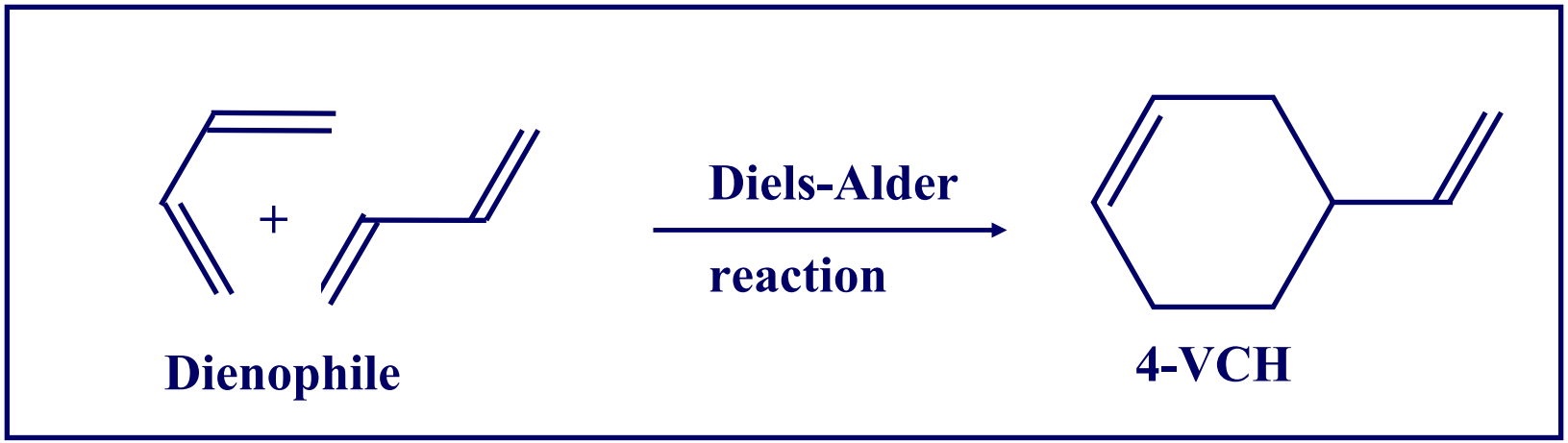
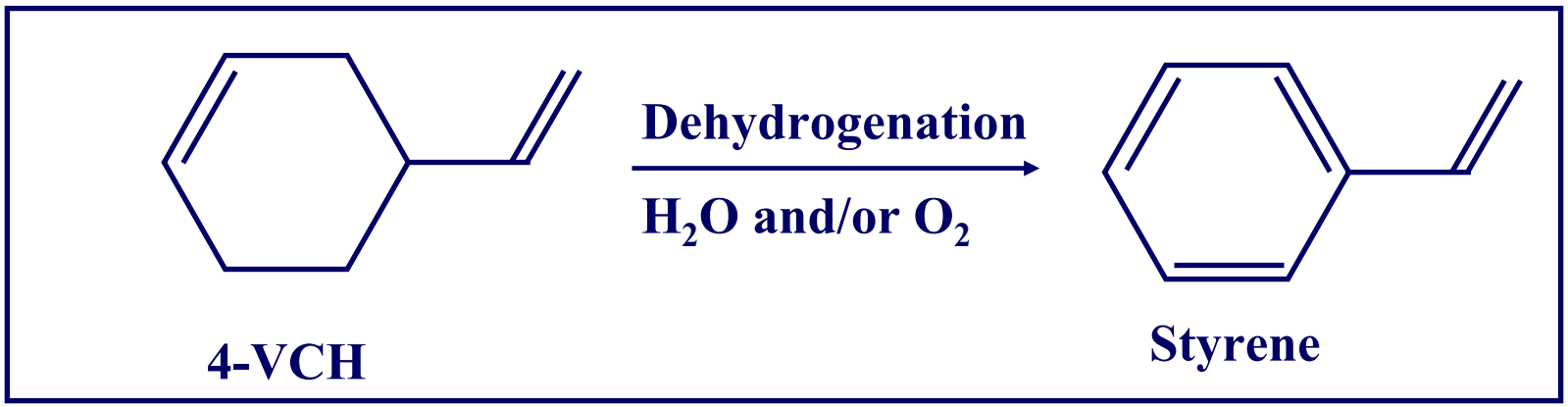
Catalytic Properties of VSB-1 and VSB-5

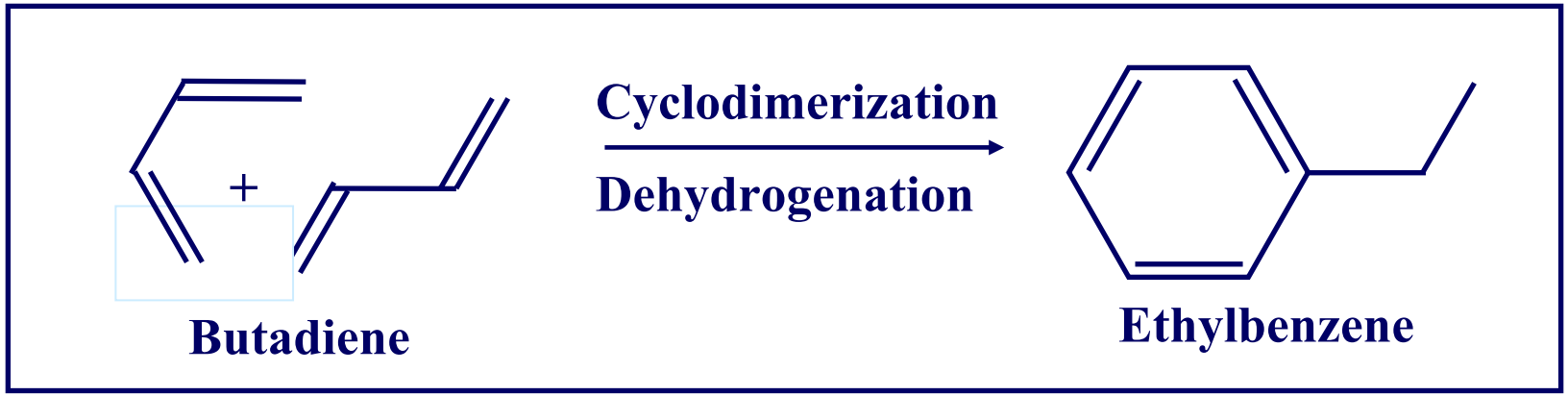
- Unlike the aluminosilicate zeolites and AlPOs, the nickel phosphates are not acidic
  - VSB-1 is mildly acidic
  - VSB-5 is basic
- This means that they can be used in reactions with alkenes that would form coke in conventional zeolite catalysts
- They may also have the potential to catalyze redox reactions…

Diels-Alder Cyclodimerization of Butadiene over VSB-1





What actually happens with VSB-1?

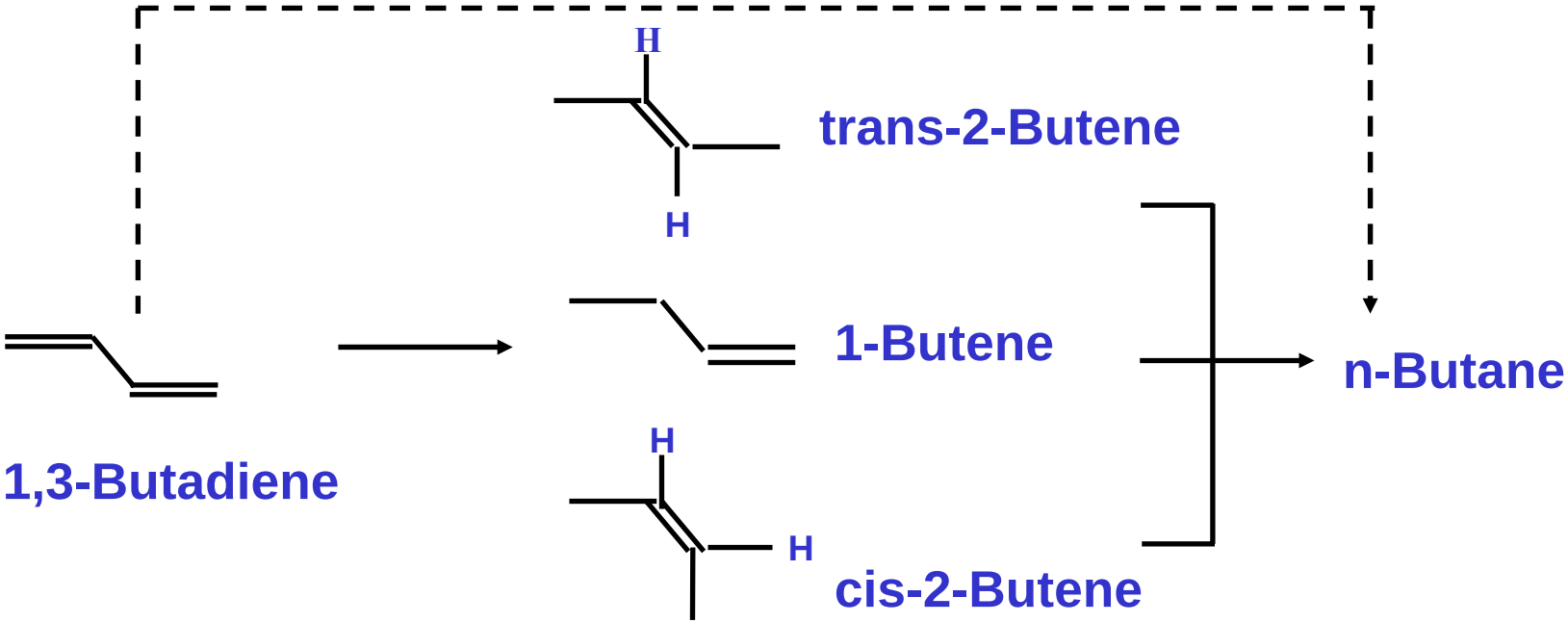


Stable catalysis with >80% selectivity, 12% conversion

VSB-1 is bifunctional, but the dehydrogenation is too mild to remove the hydrogen from the ethyl group; can we take advantage of the mild reactivity?

Chang, Cheetham et al. Chem. Comm. 859 (2001)

Partial Hydrogenation of 1,3-BD



* Isolated active species are required for selective hydrogenation of conjugated diene. VSB-5 may provide isolated Ni sites with low oxidation states upon reduction because it is hard to reduce.

Guillou, Ferey, Cheetham et al Angew. Chemie. 40, 2831 (2001)

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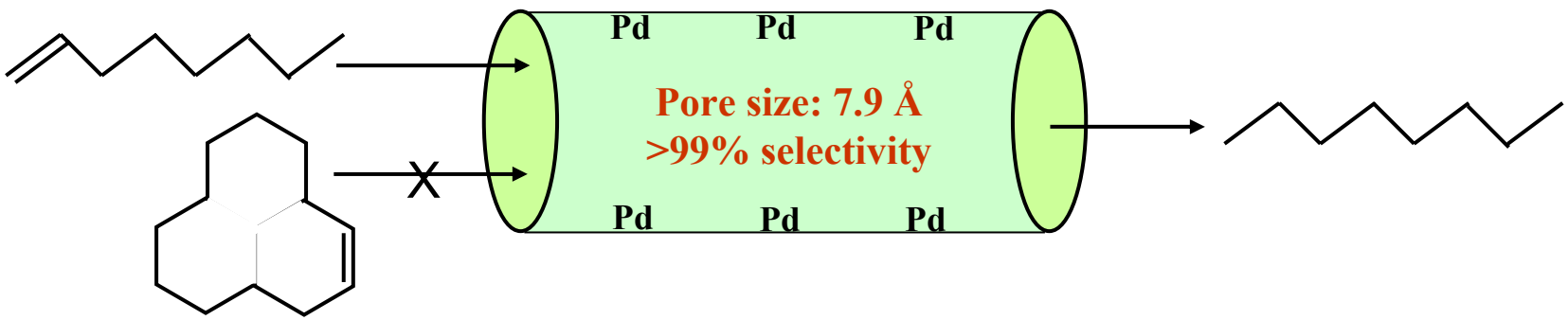
Partial Hydrogenation of 1,3-Butadiene

Partial hydrogenation of 1,3-Butadiene over VSB-5 and $Ni_3(PO_4)_2$

Catalyst	T_{red}# (h)	T_{react} (°C)	X_{BD} (%)	S_{butene} (%)	Product (%) n-C_4H_{10}	1-C_4H_8	t-2-C_4H_8	c-2-C_4H_8
VSB-5(350)	24	100	81.1	95.8	4.2	50.9	32.0	12.9
VSB-5(550)	16	100	99.6	21.4	78.6	14.0	1.3	6.1
$Ni_3(PO_4)_2$	4	100	99.5	47.7	52.3	27.4	7.3	13.0

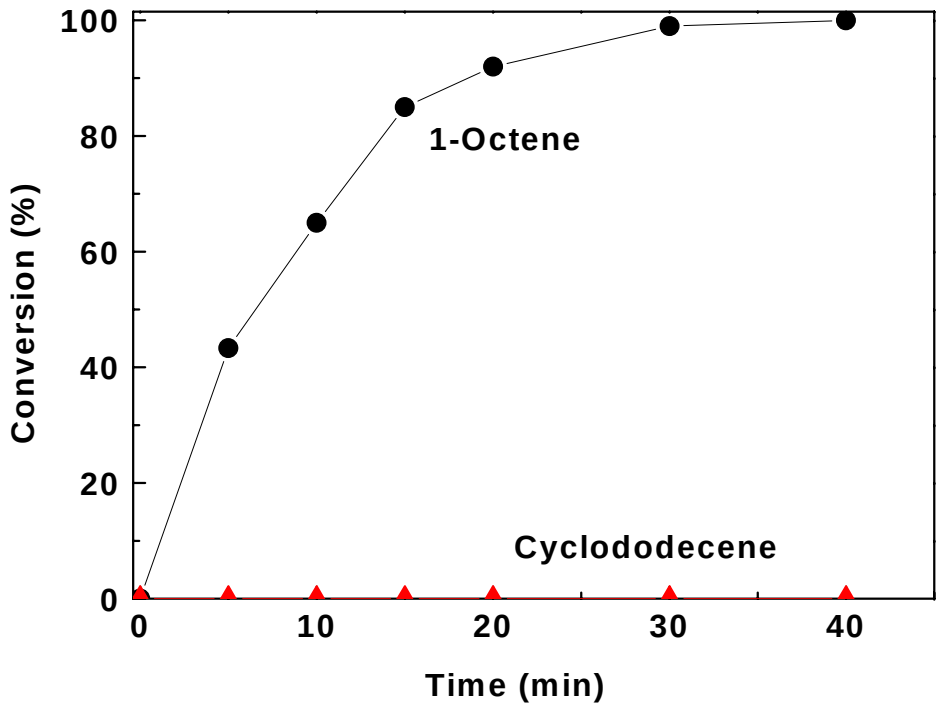
Reaction conditions: W/F = 0.6 g.ml/sec, P(BD) = 10.1 kPa, H_2/BD = 3.
* Calcination temperature, °C; #Reduction time at 350°C

Shape Selective hydrogenation of 1-octene and cyclododecene over Pd-VSB-1



Chang, Cheetham et al, Angew. Chem. 43, 2819 (2004)

Competitive hydrogenation of 1-octene and cyclo-dodecene over Pd-VSB-1 (1 wt.% exchanged)



Reaction condition:
Substrates 1 mol% each in 90 ml n-hexane, T = 30°C, P = 2 atm H_2, 0.2 g-cat.
Catalyst pretreatment: reduction with 5% H_2 in He at 300°C for 4 h.

Competitive hydrogenation result indicates that Pd species exchanged into VSB-1 are located within the pore, resulting in the shape-selectivity.

Chang, Cheetham et al, Angew. Chem. 43, 2819 (2004)

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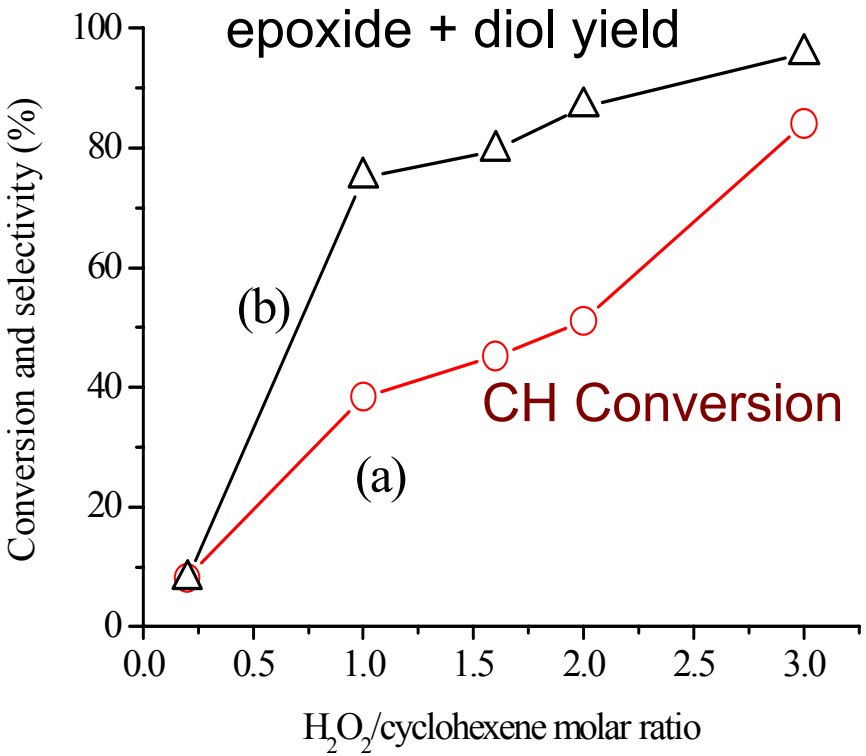
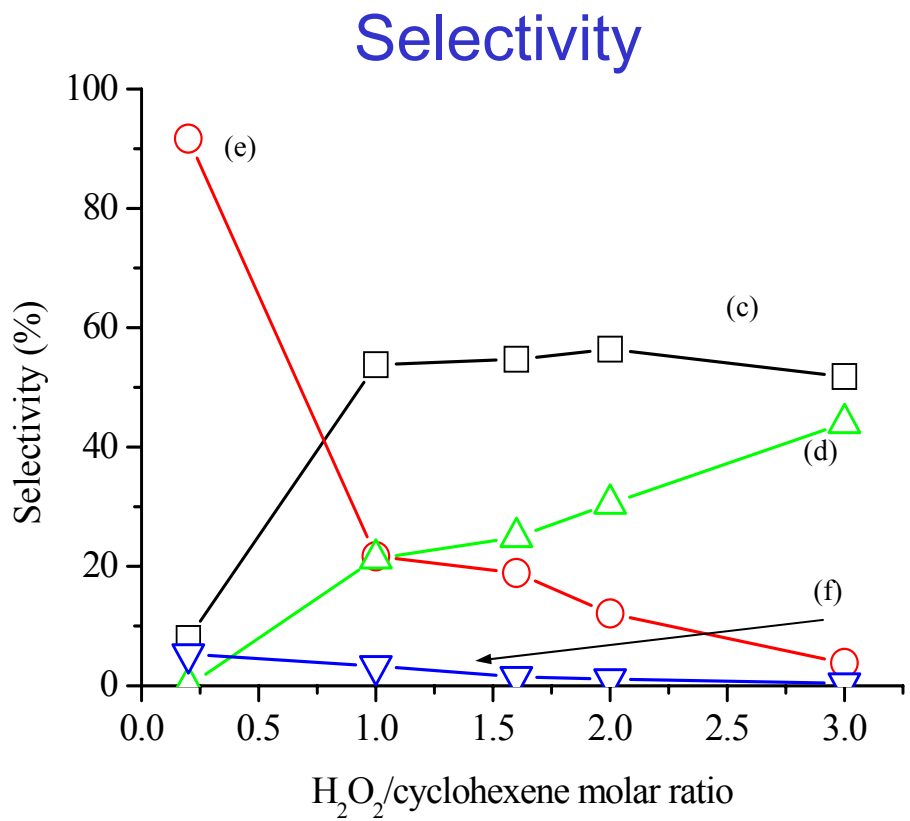
Other Catalytic Reactions with VSB-1,5

- Direct production of H_2O_2 from H_2 and air over Pd-VSB-1
- Hydroxylation of phenol to catechol with Cu-VSB-1
- Selective catalytic reduction with NO and NH_3 over VSB-1 and VSB-5
- Photocatalysis with Fe-VSB-1
- Epoxidation of cyclohexene with VSB-5

Chang, Cheetham et al, Angew. Chem. 43, 2819 (2004)

Epoxidation of cyclohexene with VSB-5





Jhung, Lee, Cheetham, Ferey, and Chang, J. Catal. 239, 97 (2006)

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Epoxidation of cyclohexene with VSB-5

Catalyst	Catalyst weight (g)	Ni content (wt %)[b]	Ni conc. (wt %)[c]	S_{BET} (m^2/g)	Conversion (%)	H_2O_2 efficiency (%)	Selectivity (mol %)			
							Cyclohexene oxide	1,2-Cyclohexane diol	2-Cyclohexene-1-one	2-Cyclohexen-1-ol
VSB-5	**0.35**	**41.0**	**3.5**	**350**	**84.1**	**53.7**	**51.8**	**44.0**	**3.8**	**0.4**
NiO	0.35	78.6	6.8	<5	13.3	7.1	58.5	0.0	40.5	1.0
$NiCl_2 \cdot 6H_2O$	1.00	24.7	6.1	-	21.3	16.0	8.5	14.9	73.0	3.6
$Ni(OAc)_2 \cdot 4H_2O$	1.00	23.6	5.8	-	27.7	18.5	3.6	0.0	91.6	4.8
None[d]	-	-	-	-	6.3	38.0	31.7	0.0	68.3	0.0

[a] Reaction conditions: 60 °C, 8 h, acetonitrile 18 ml, cyclohexene 5 ml, H_2O_2/cyclohexene=3.
[b] Ni content in the VSB-5 or Ni-containing compounds.
[c] Ni concentration based on the substrate cyclohexene.
[d] Results in the absence of catalyst.

Jhung, Lee, Cheetham, Ferey, and Chang, J. Catal. 239, 97 (2006)

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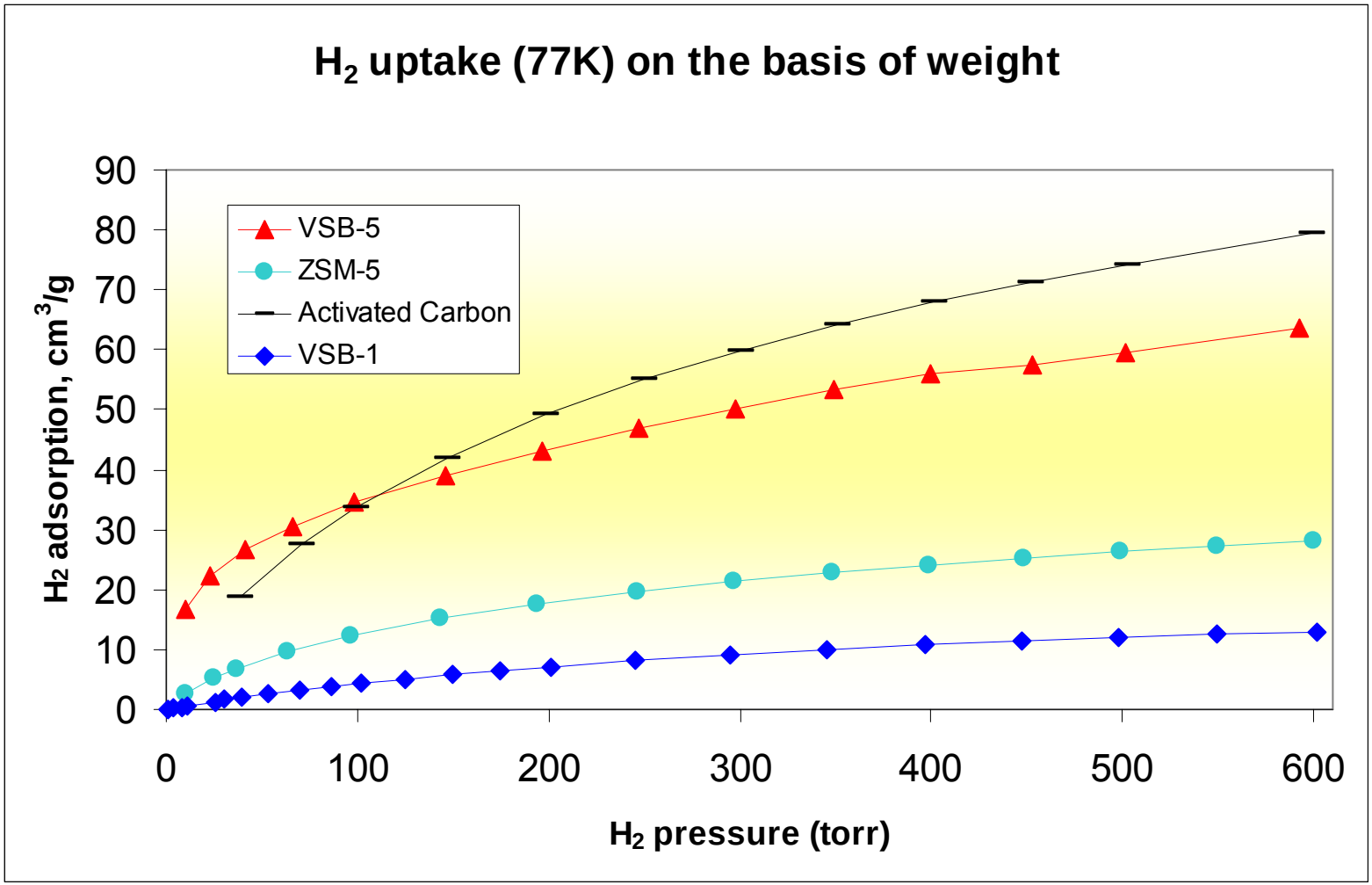
Hydrogen Storage for Fuel Cells

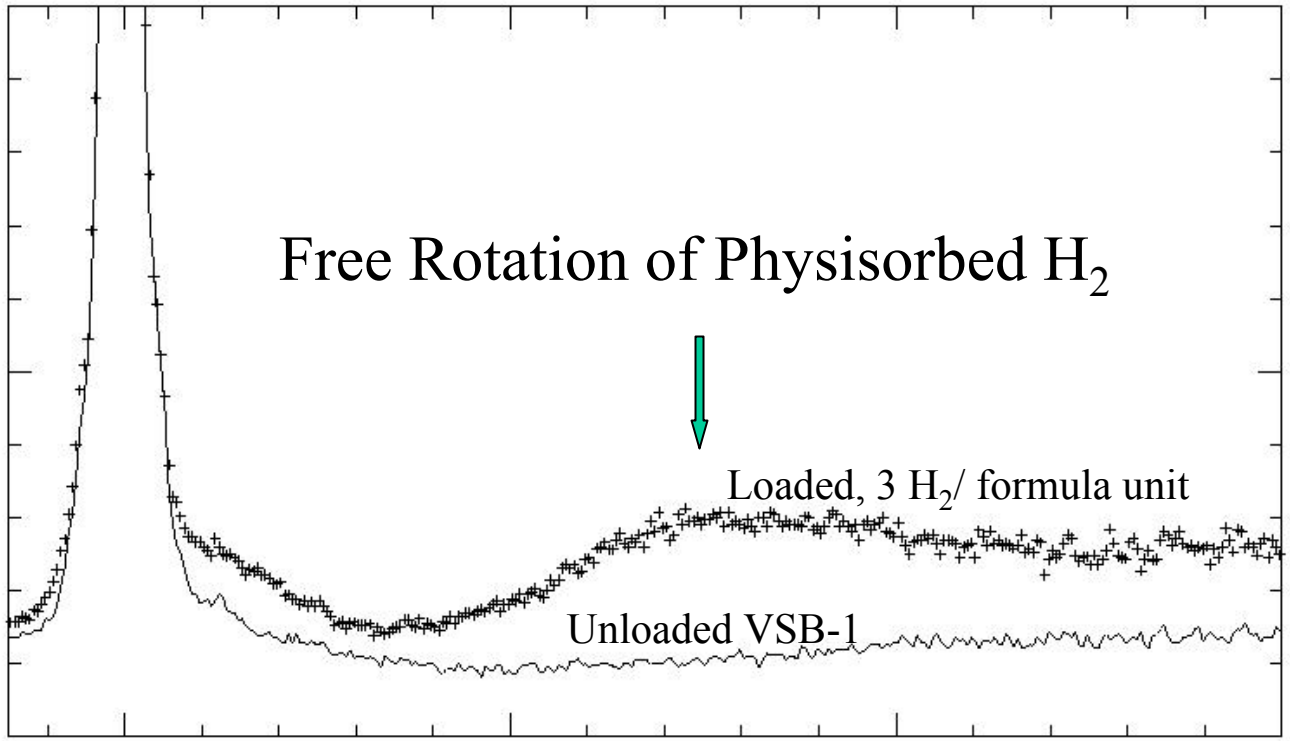
- Hydrogen storage is one of the critical challenges facing the implementation of fuel cell technology
  - See Schlapbach & Zuttel, Nature, 414, 353 (2001)
- Systems that show promise include:
  - Physisorption systems: zeolites, carbons, carbon nanotubes
  - Chemisorption: metal hydrides, $NaBH_4$ solutions
- Given that the nickel phosphate molecular sieves show remarkable hydrogenation and dehydrogenation functionality, might they be used for hydrogen storage?

Hydrogen Adsorption Isotherms
VSB-5 vs Other Porous Materials

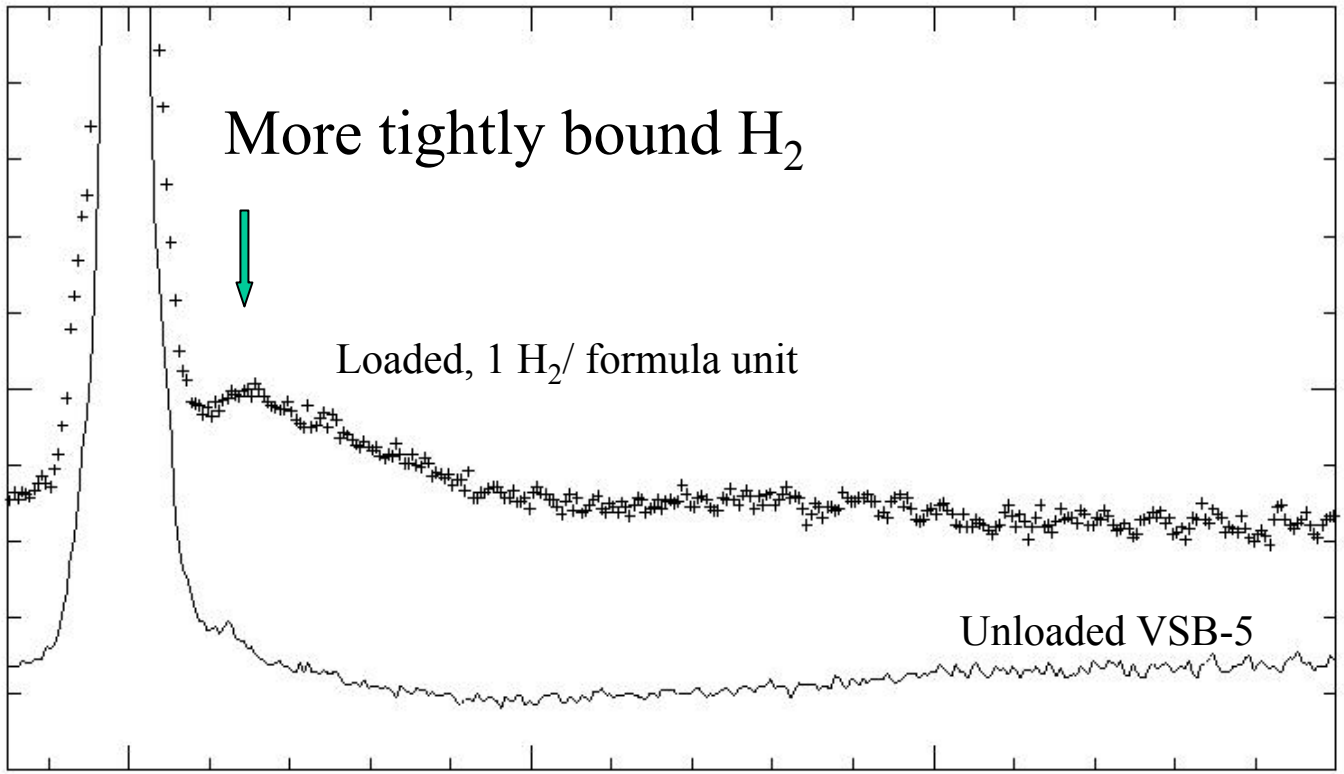
Forster, Cheetham et al. J. Amer. Chem. Soc. 125, 1309 (2003)



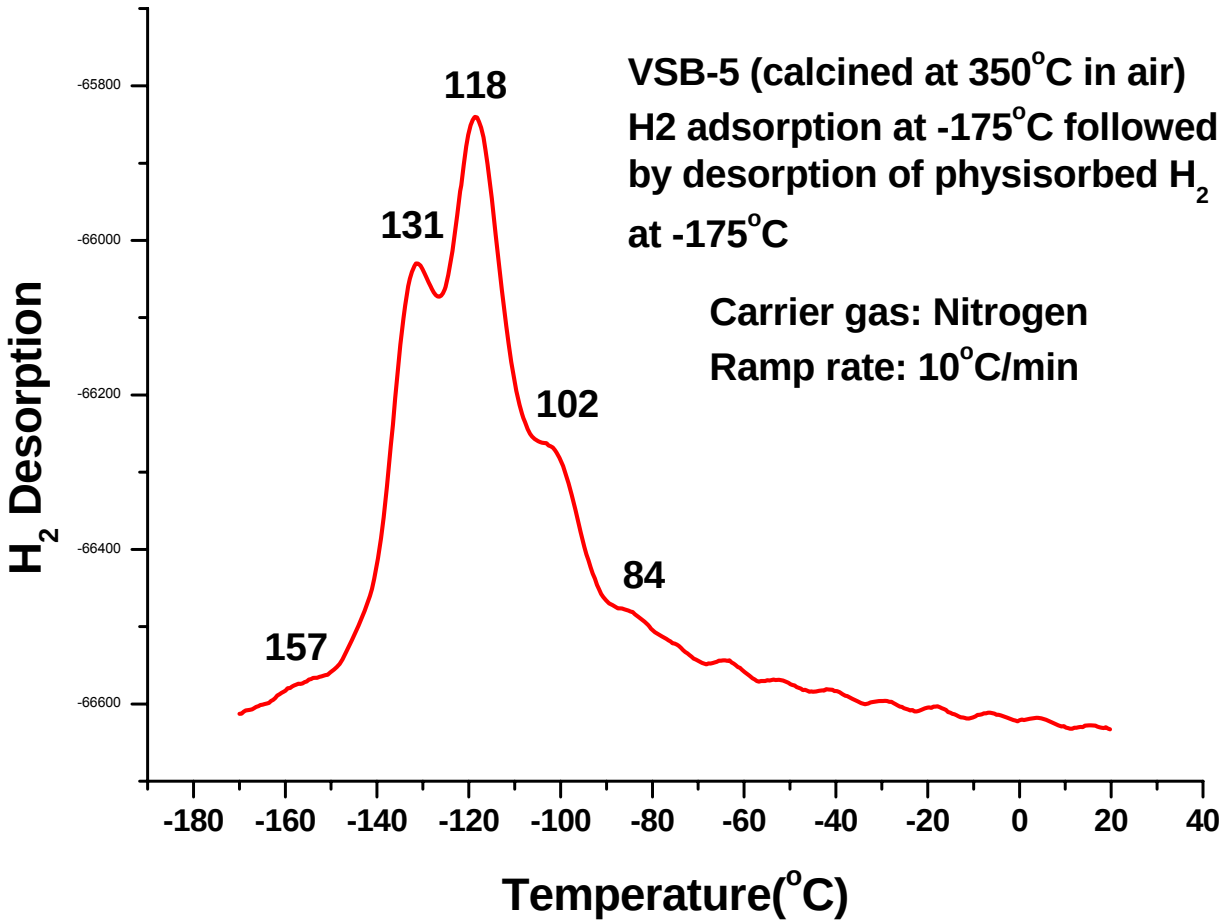
Rotational Tunnelling Spectra by Inelastic Neutron Scattering - VSB-1 at 10 K



Rotational Tunnelling Spectra by Inelastic Neutron Scattering - VSB-5 at 10 K

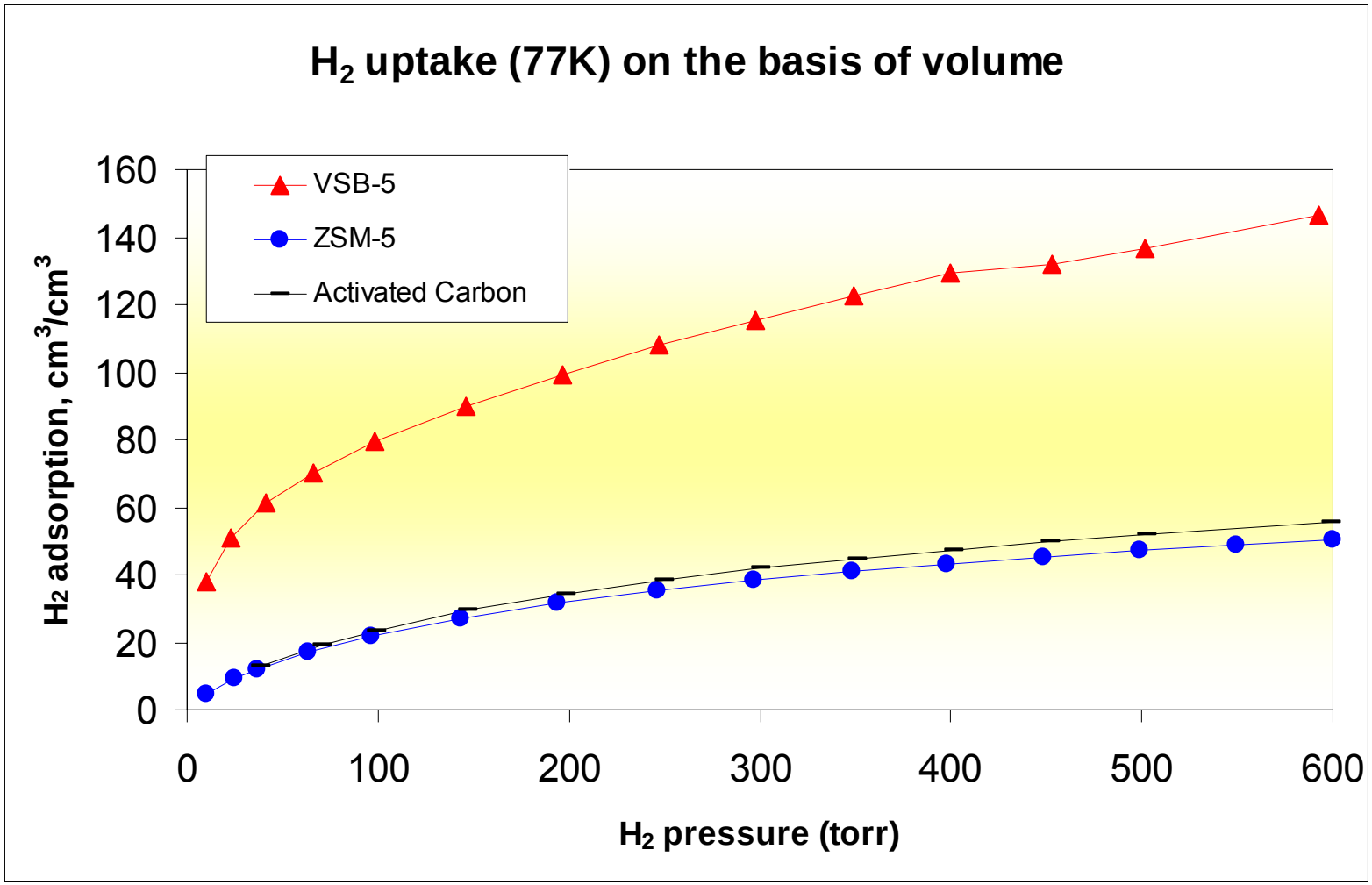


H_2-TPD Profile of VSB-5



Hydrogen Adsorption Isotherms
VSB-5 vs Other Porous Materials

Forster, Cheetham et al. J. Amer. Chem. Soc. 125, 1309 (2003)



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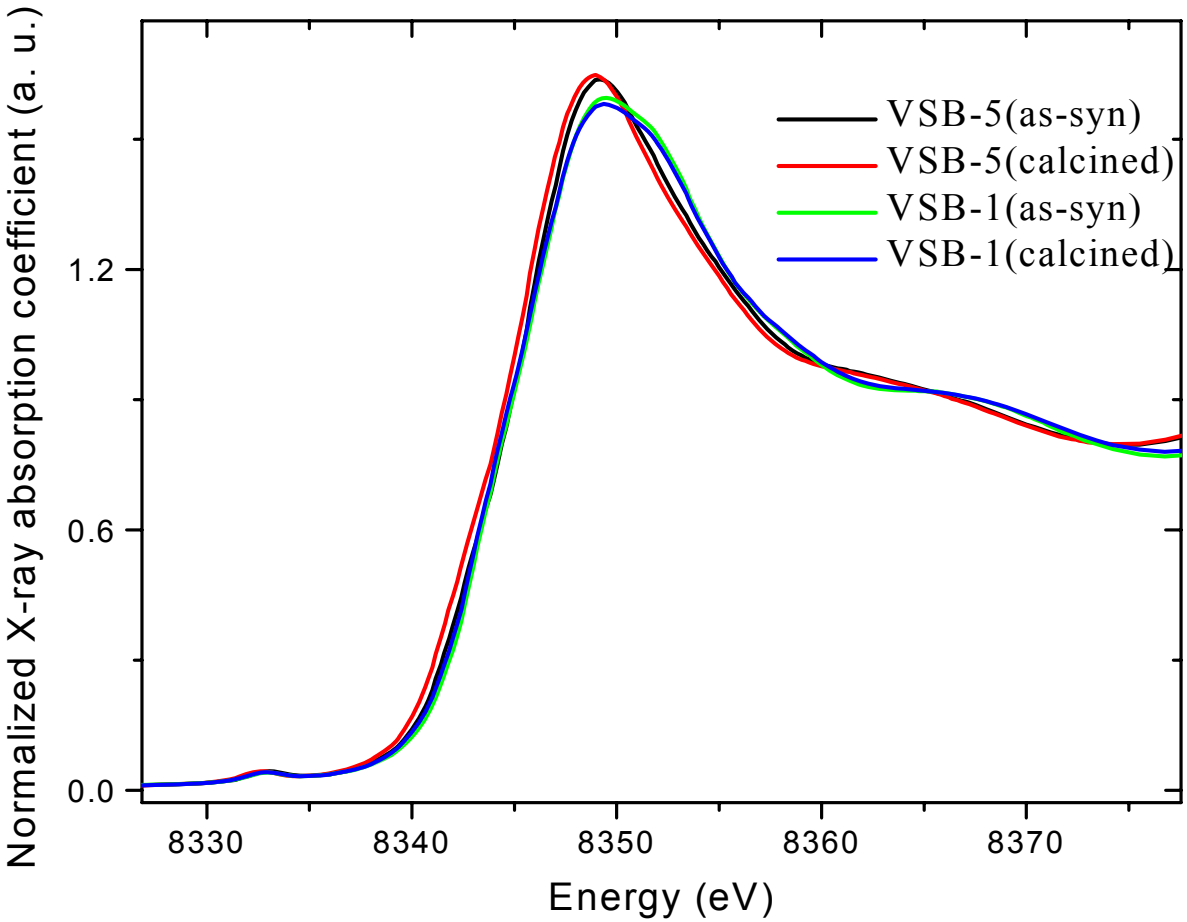
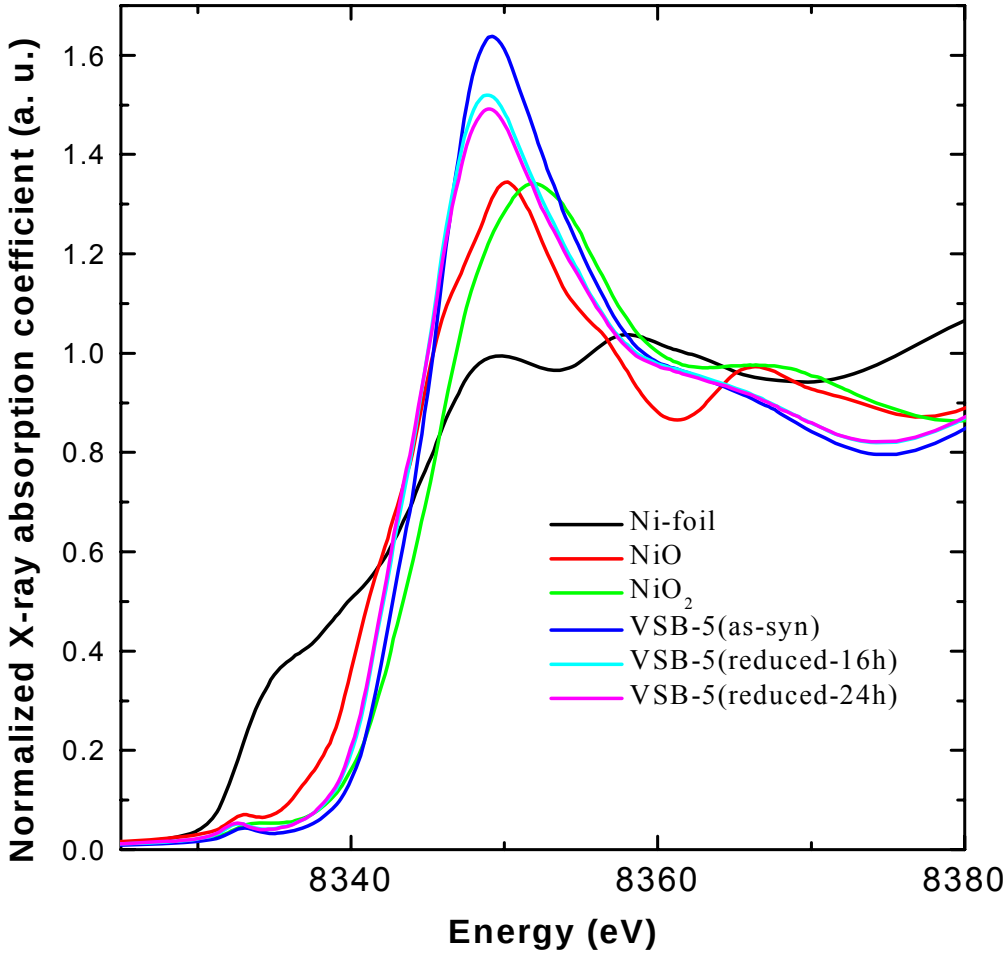
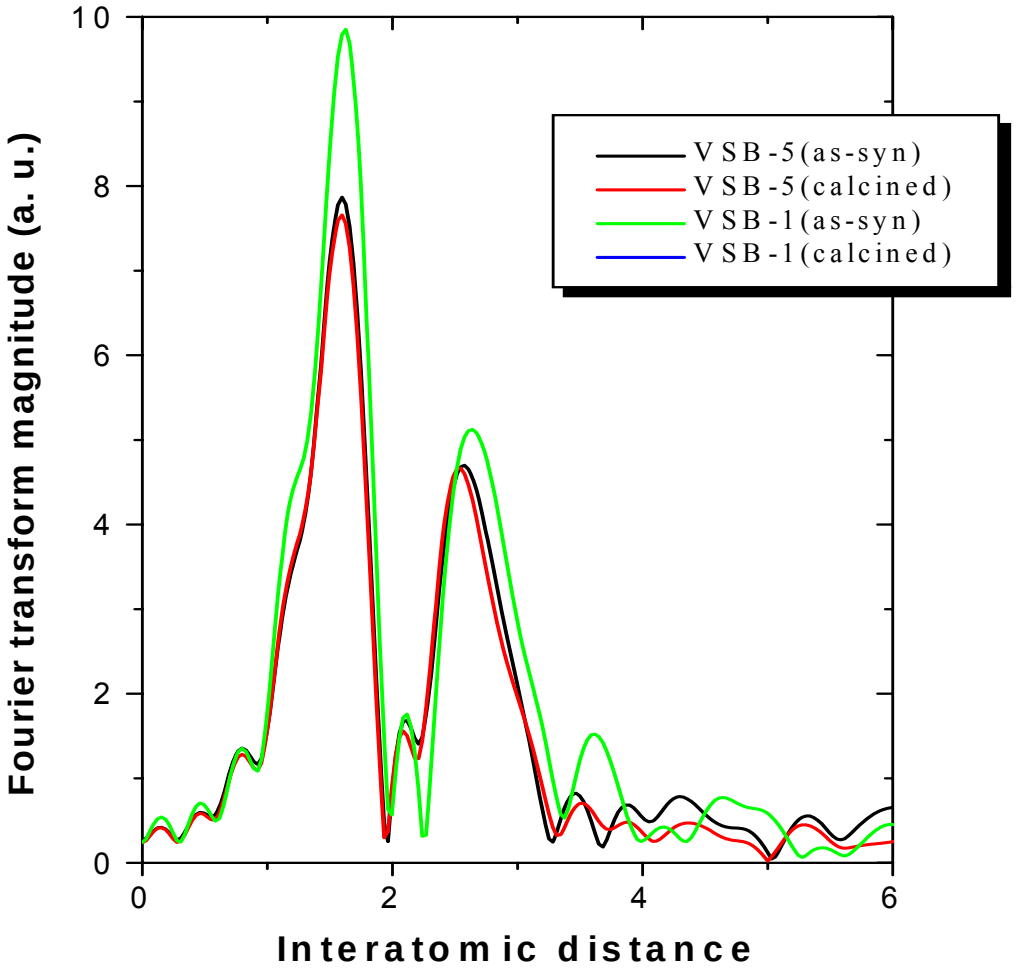
XANES of VSB-1 and 5



XANES of VSB-5 and Standards

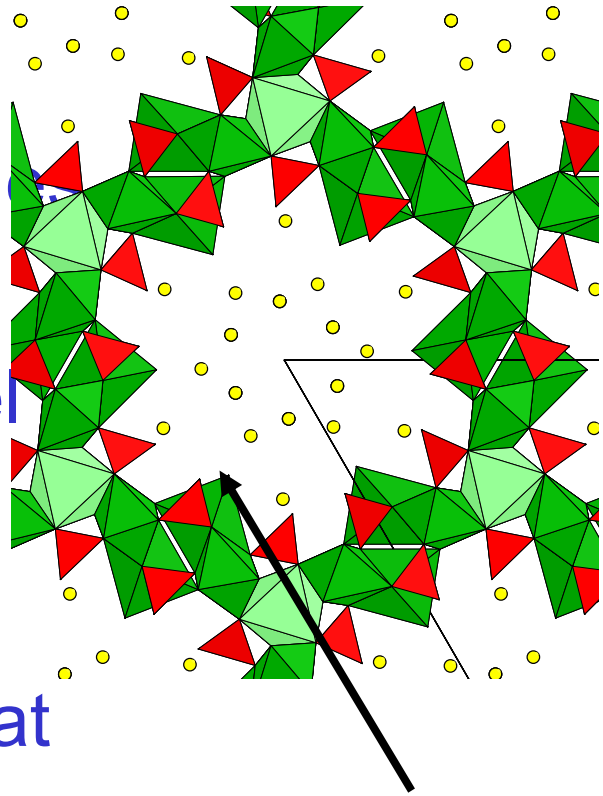


Ni EXAFS of VSB-1 and 5



Hydrogen Adsorption in VSB-5

- All the evidence points to chemisorption of H_2 at low loadings, followed by physisorption at higher on
- Hydrogen probably binds to pentacoordinated nickel sites that are exposed following dehydration
- Can we make systems that contain more of these sites?



Water lost on dehydration?

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HYBRID INORGANIC-ORGANIC MATERIALS

- **Hybrid nanocomposites**
  - Polymers containing inorganic additives
    e.g. C nanotubes or clays in organic polymers
- **Inorganics with organic guest molecules**
  - Small molecule templates in zeolites
  - Surfactant and block co-polymer templating
- **Coated nanoparticles, nanowires and nanosheets**
- **Hybrid organic-inorganic frameworks (metal-organic frameworks)**
  - Molecular nanowires and nanosheets
  - Coordination polymers
  - Extended inorganic hybirds

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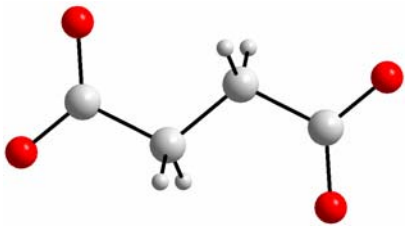
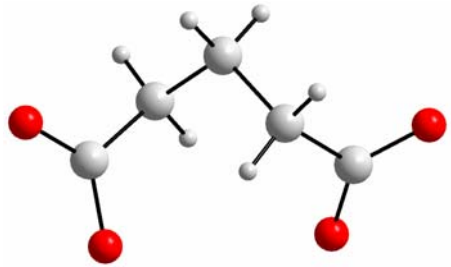
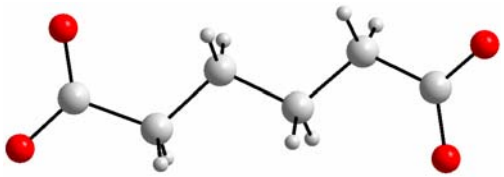
A wide range of organic ligands, both rigid and flexible, are used



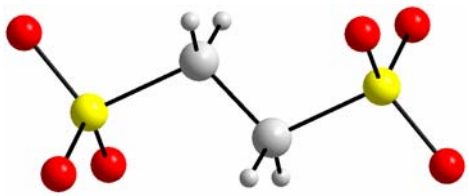
Succinate



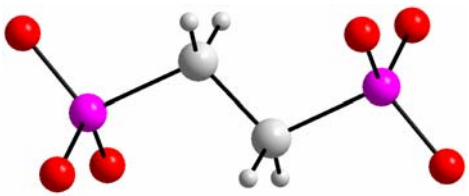
Glutarate



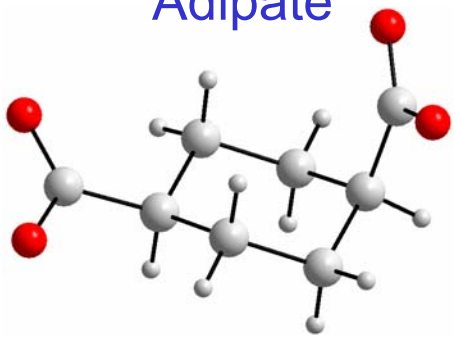
Adipate



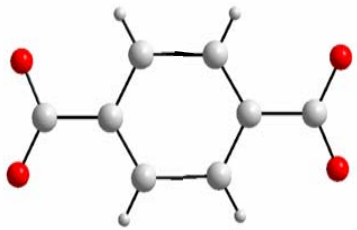
Ethanedisulfonate



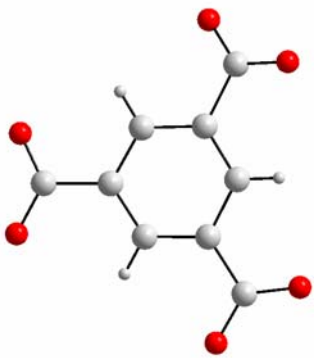
Ethylenediphosphonate



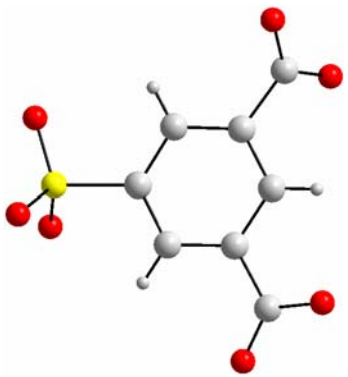
1,4 cyclohexanedicarboxylate



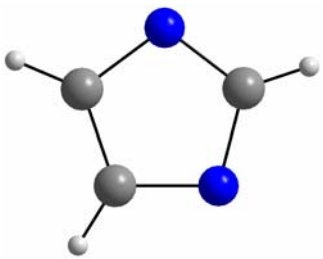
Terephthalate



Trimesate

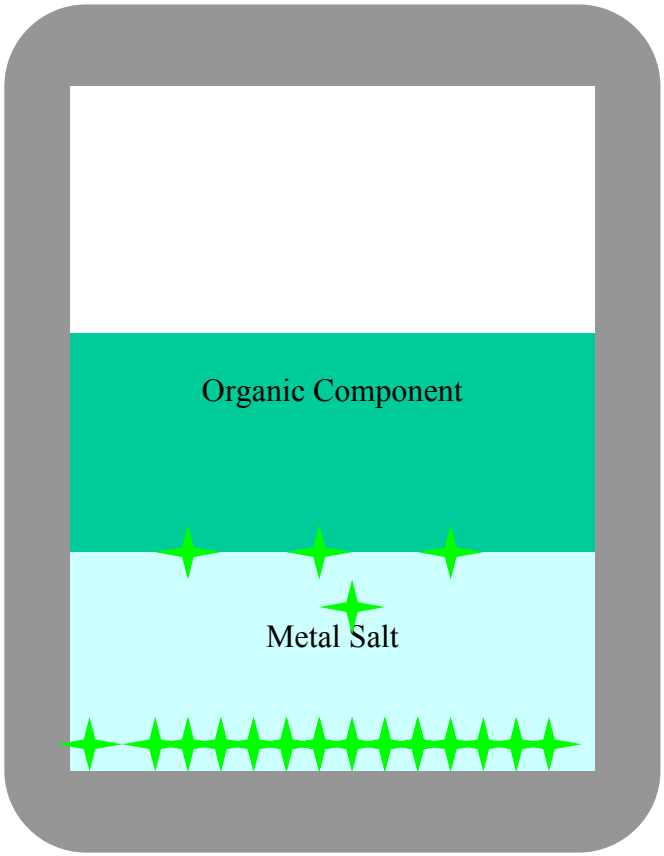


Sulfoisophthalate



Imidazolate

Hydro- or Solvothermal Synthesis



We use hydrothermal reactions at temperatures up to ~ 200C. In the absence of a compatible solvent for both reactants, the inorganic component is dissolved in water, and the organic component in a water immiscible alcohol. Reaction occurs with product forming at the interface.

Forster, Thomas & Cheetham, Chem. Mat. 14, 17 (2002)

Microwave Synthesis of Nickel Glutarates: Phase Selective and Rapid Crystallization

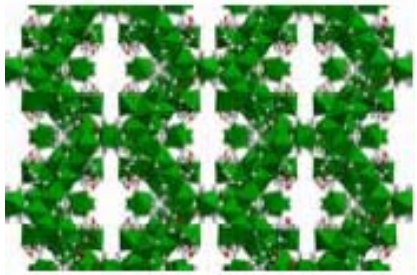
180-190°C,
2 days

Hydrothermal

$NiCl_2 \cdot 6H_2O$
Glutaric acid
KOH
H_2O/i-PrOH

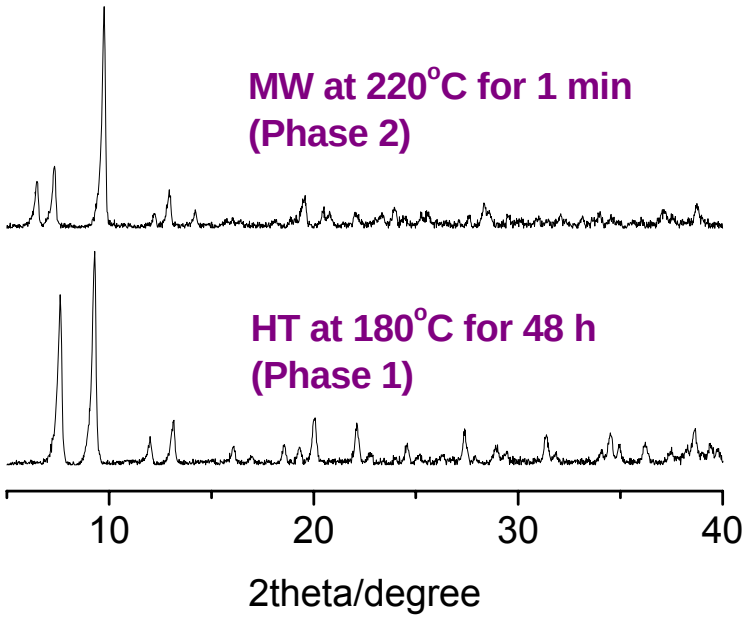
190-220°C,
1 min

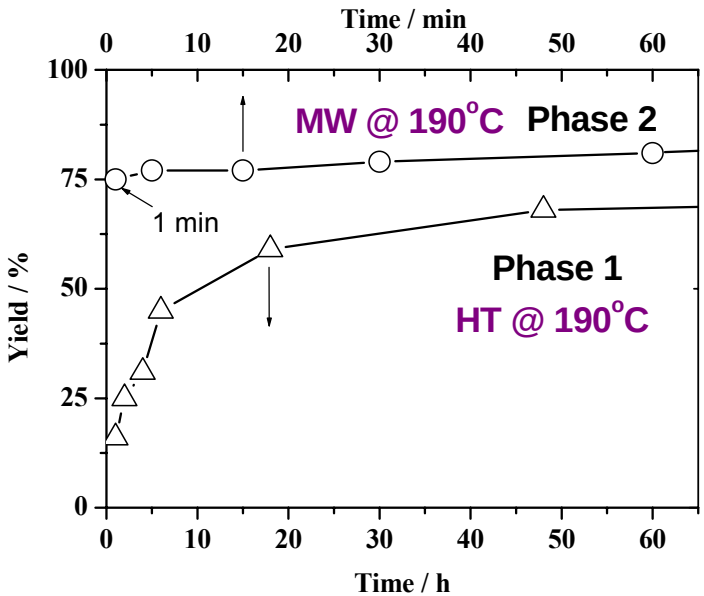
Microwave



$[Ni_{20}\{(C_5H_6O_4)_{20}(H_2O)_8\}]\cdot 40H_2O$
Cubic Phase [1]

$[Ni_{22}\{(C_5H_6O_4)_{20}(OH)_4(H_2O)_{10}\}]\cdot 38H_2O$
Tetragonal Phase [2]





Jhung, Lee, Forster, Férey, Cheetham & Chang, Chem. Eur. J., *in press* (2006)

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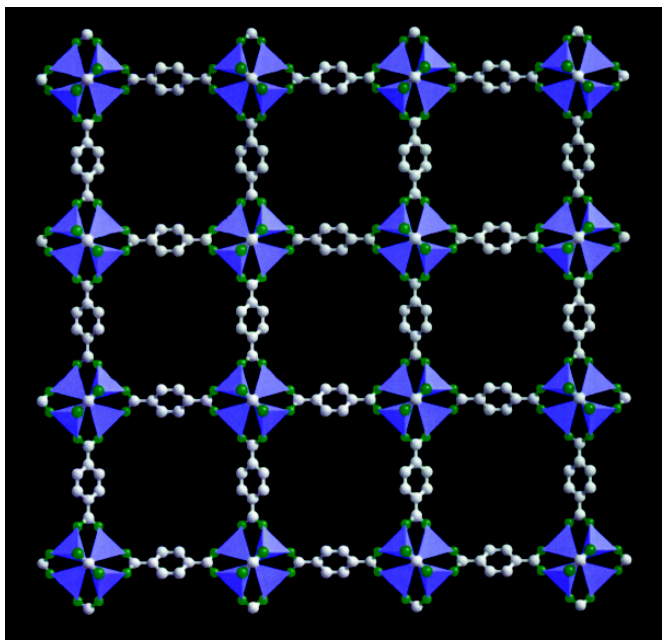
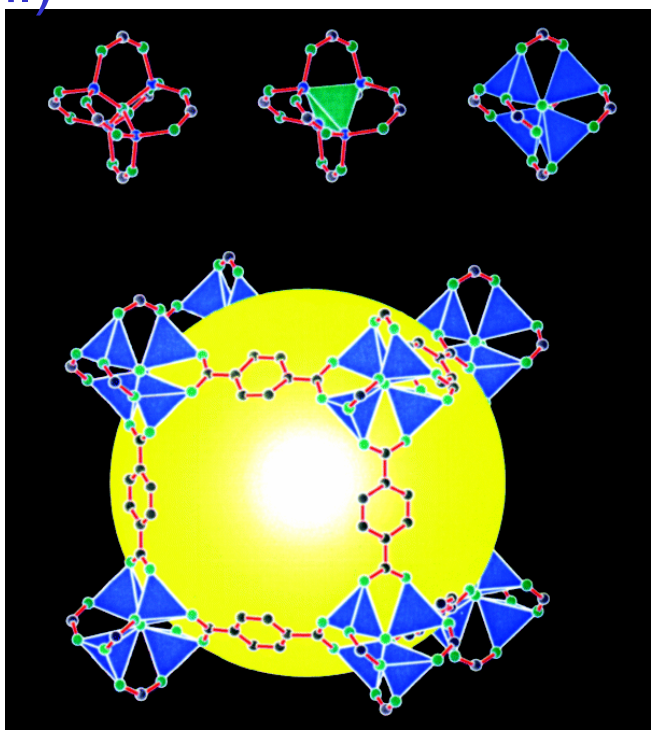
Porous Hybrid Frameworks

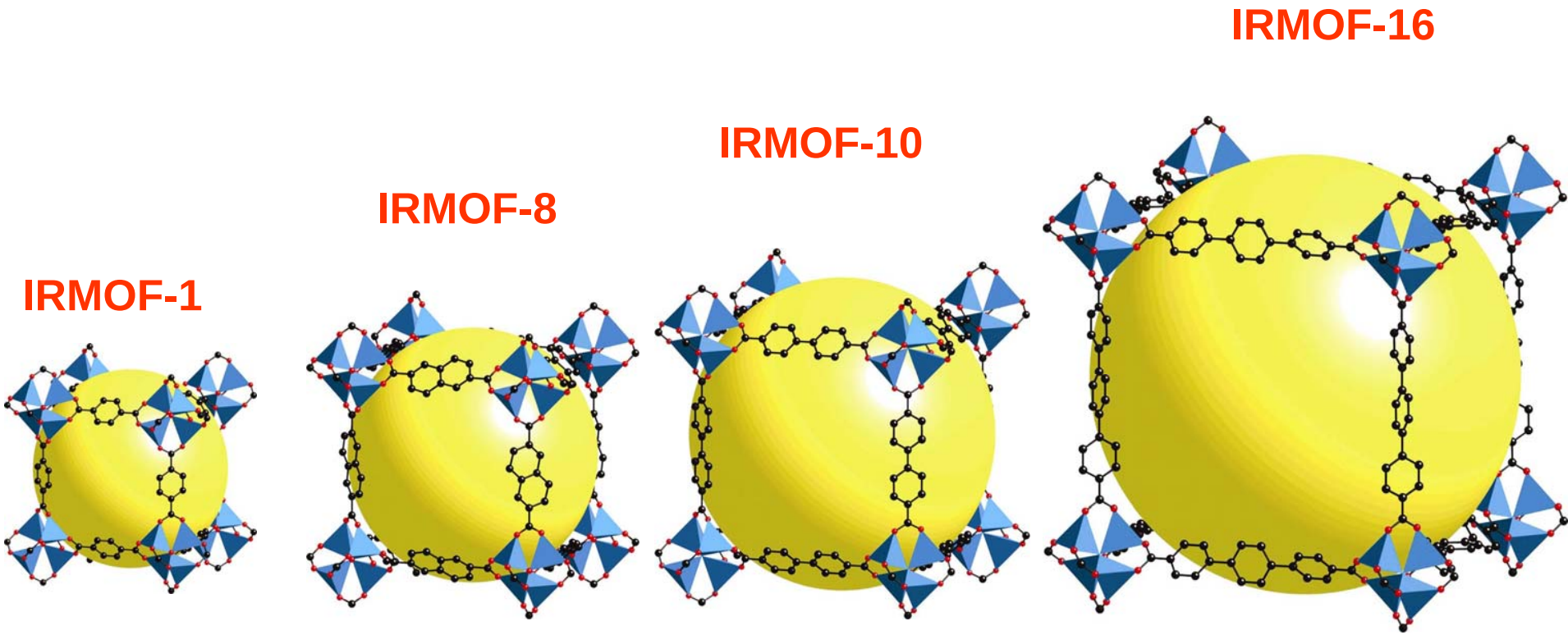
- Zn_4O(1,4 benzenedicarboxylate)[1]: MOF-5
  - Synthesized using room temperature solvent routes.
  - Structure may be modified by varying the carboxylic acids
  - Extremely Low densities (0.1-0.2 g/ml)





[1] Li, H., Eddaoudi M., O'Keeffe M., Yaghi, O.M., *Nature*, **402** 276 (1999).

Iso-Reticular MOFs



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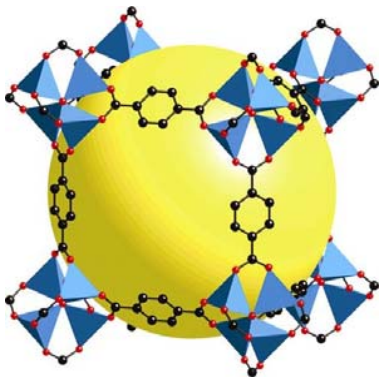
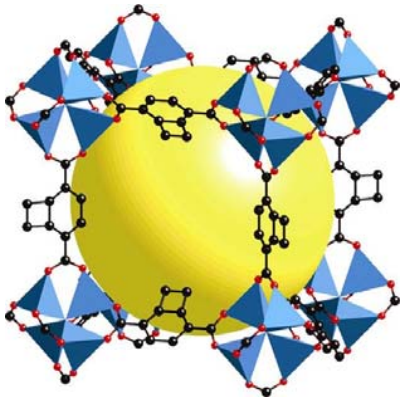
H_2 sorption @ RT and 10 bar

IRMOF-1



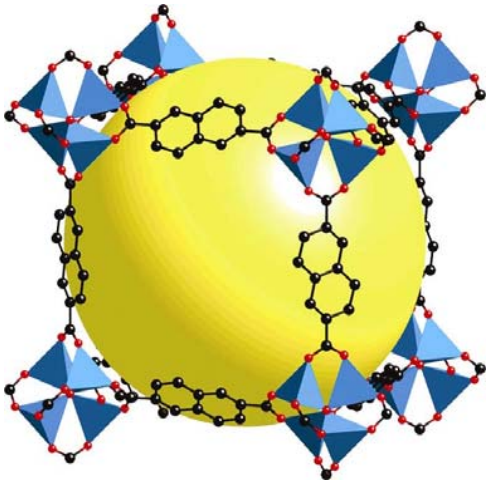
5mg/g

IRMOF-6



10mg/g

IRMOF-8



20mg/g

Activated carbon 3mg/g

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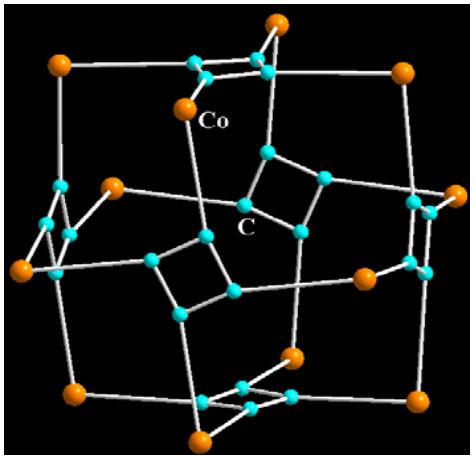
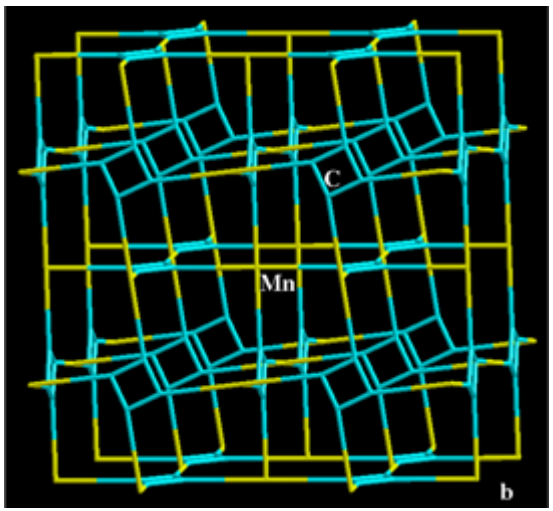
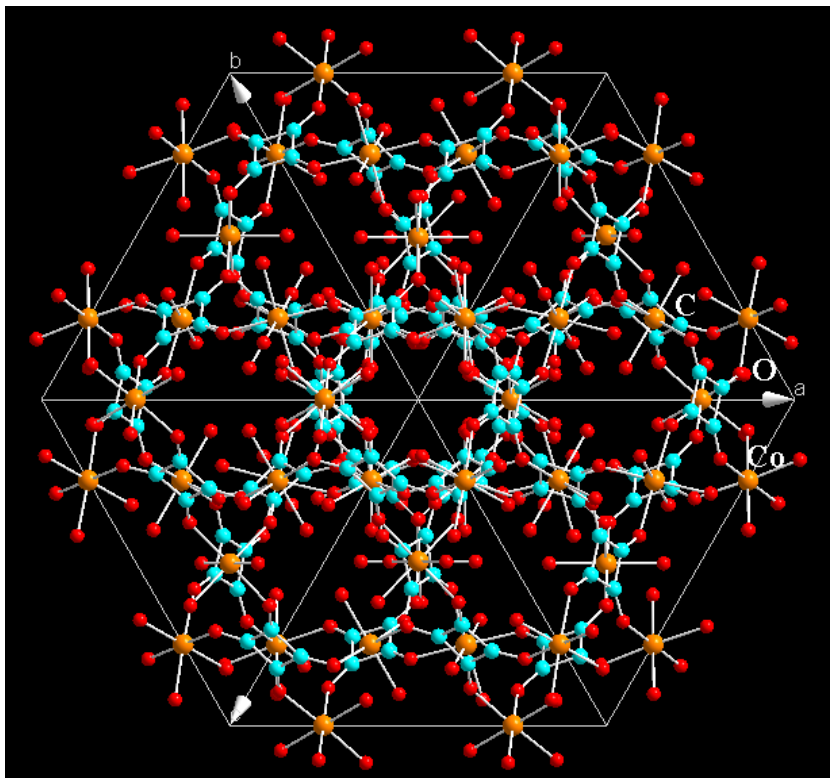
Metal Squarates with the Sodalite Structure





Predictable with the knowledge of hindsight!



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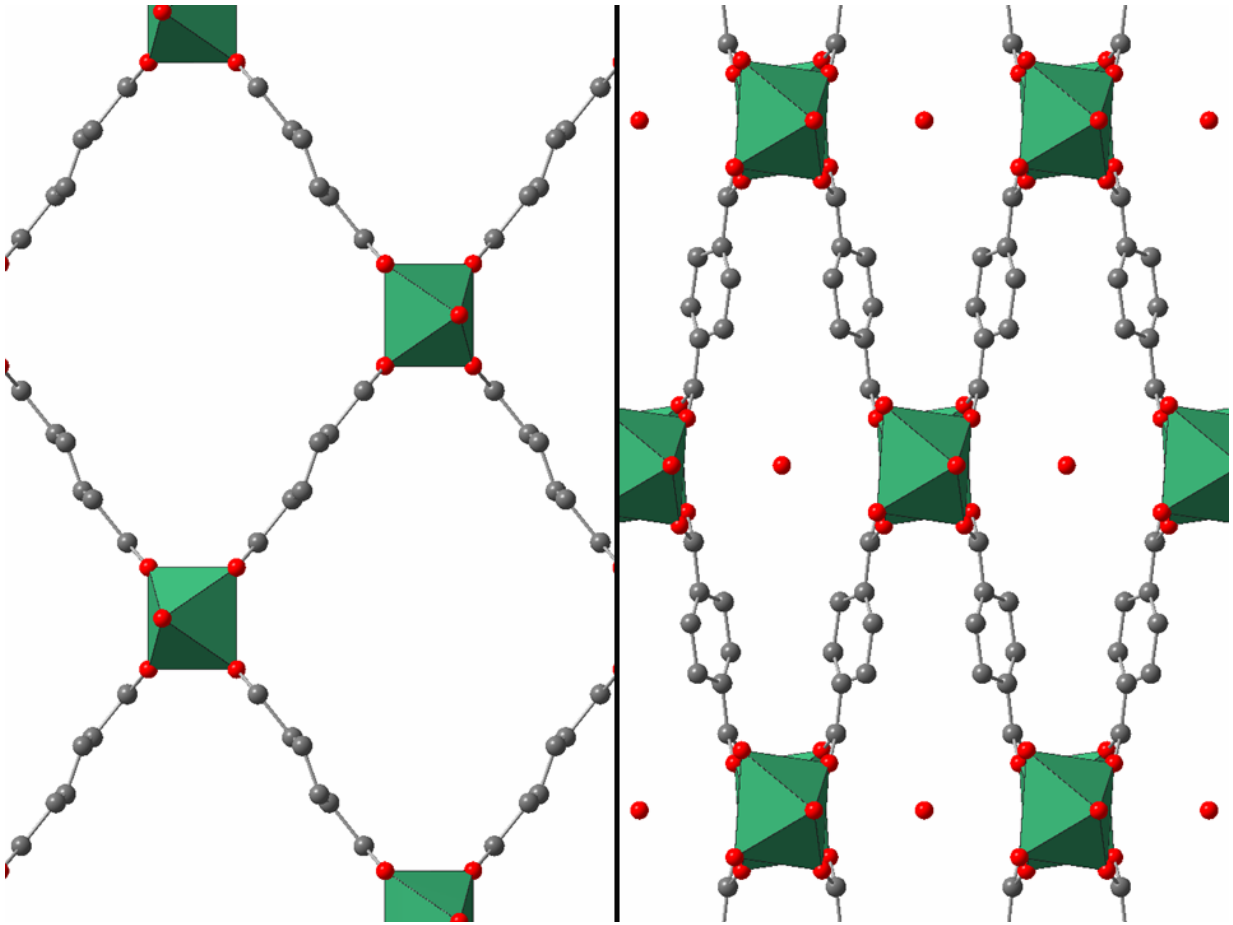
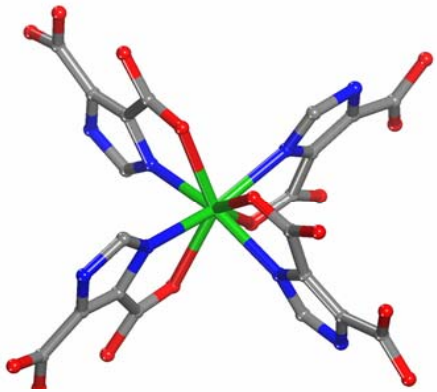
MIL-53

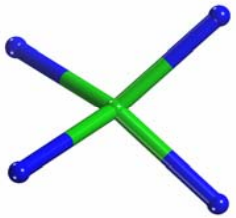
A Framework that Breaths during Adsorption

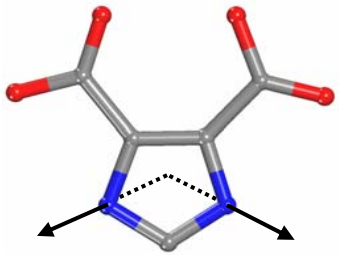


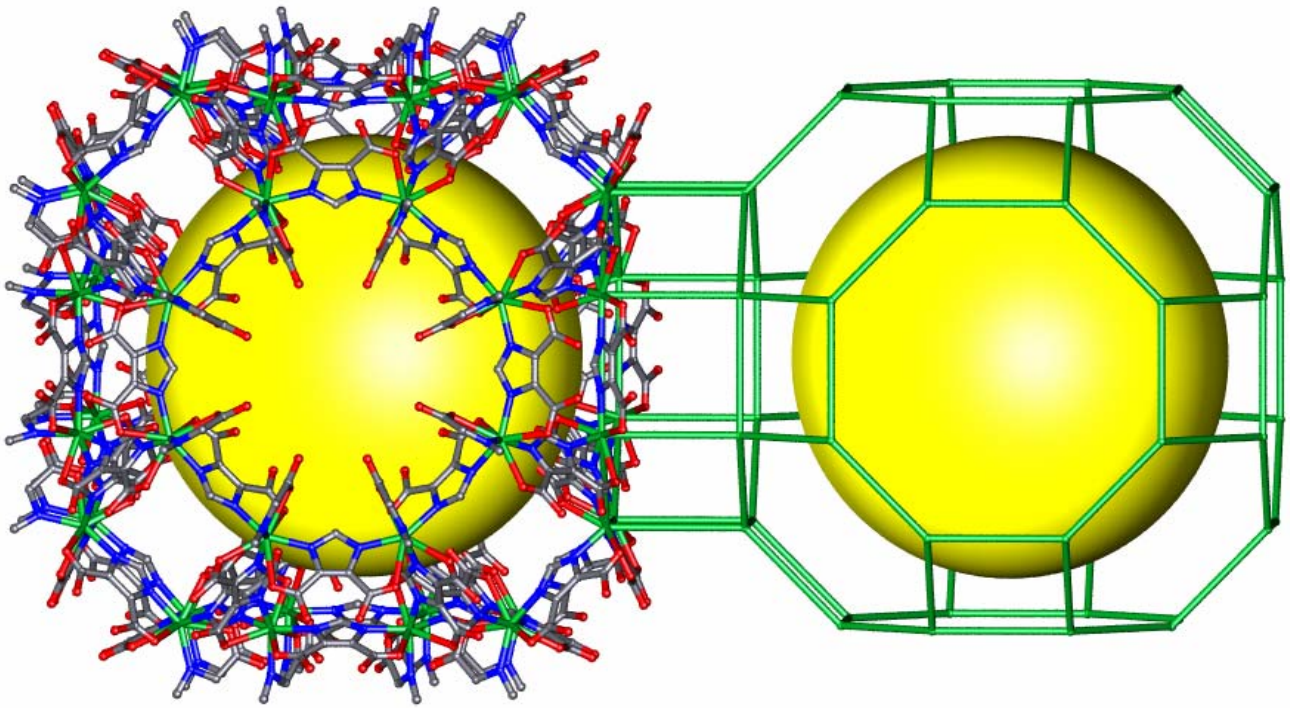
C. Serre, F. Millange, C. Thouvenot, M. Nogues, G. Marsolier, D. Louer and G. Férey, *J. Amer. Chem. Soc.* 2002, **124**, 13519

Zeolitic Hybrids - Single-metal-ion-based









cubic, *Im-3m*
a = 31.0622(7) Å
V = 29970.7(12) Å^3
Z = 48

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icmr

Relative Merits of Zeolites and Porous Hybrid Materials

	Zeolites	Hybrids
• Thermal stability	√	
• Cost	√	
• Chemical stability	depends upon conditions	
• Structural tunability		√
• Chiral separations & catalysis		√
• Chemical functionality		√
• Large pores		√
• Environmental impact	√	
• Untapped potential		√ √

Acknowledgements:

- **Students and Post docs:**

  Neeraj Sharma, Jong-San Chang, Quiming Gao, S. Natarajan, S. Ayyappan, P. Forster

- **Colleagues and Collaborators:**

  Ram Rao

  Gérard Férey,

  Nathalie Guillou

  Juergen Eckert


THANK YOU!