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"Some Recent Developments in Nanoporous Materials"

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SOME RECENT DEVELOPMENTS IN NANOPOROUS MATERIALS

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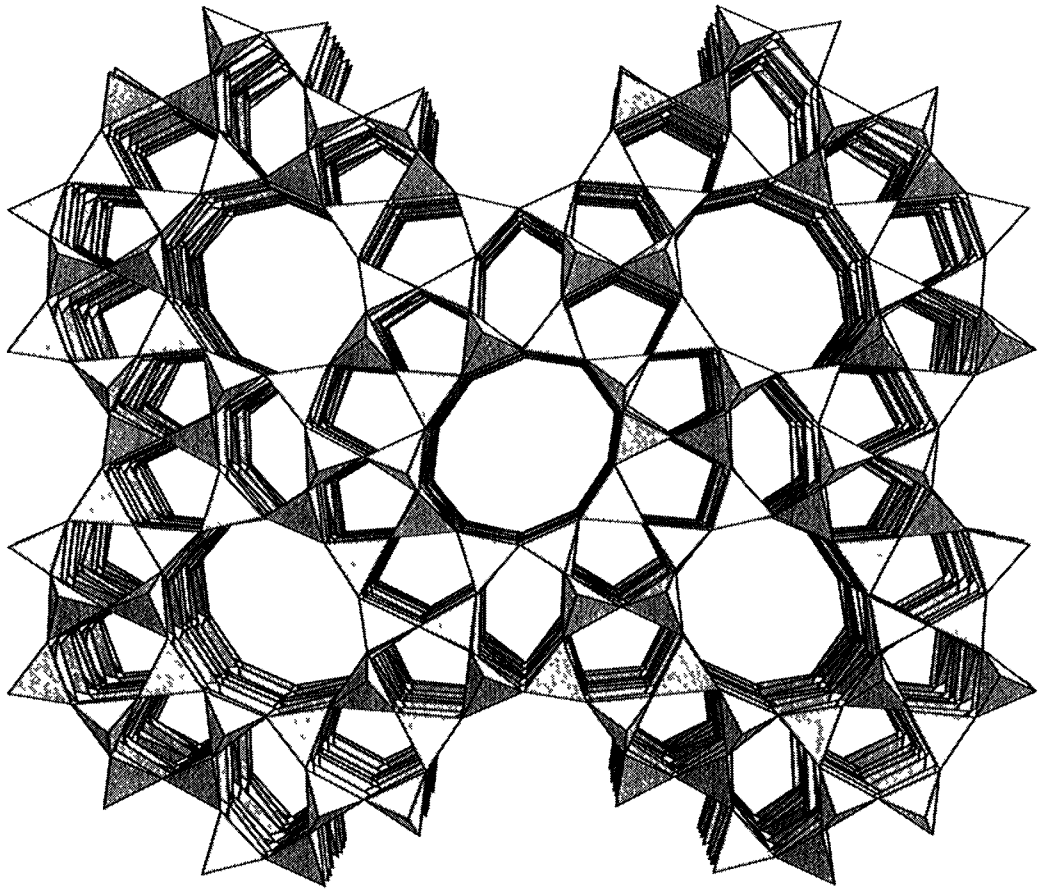
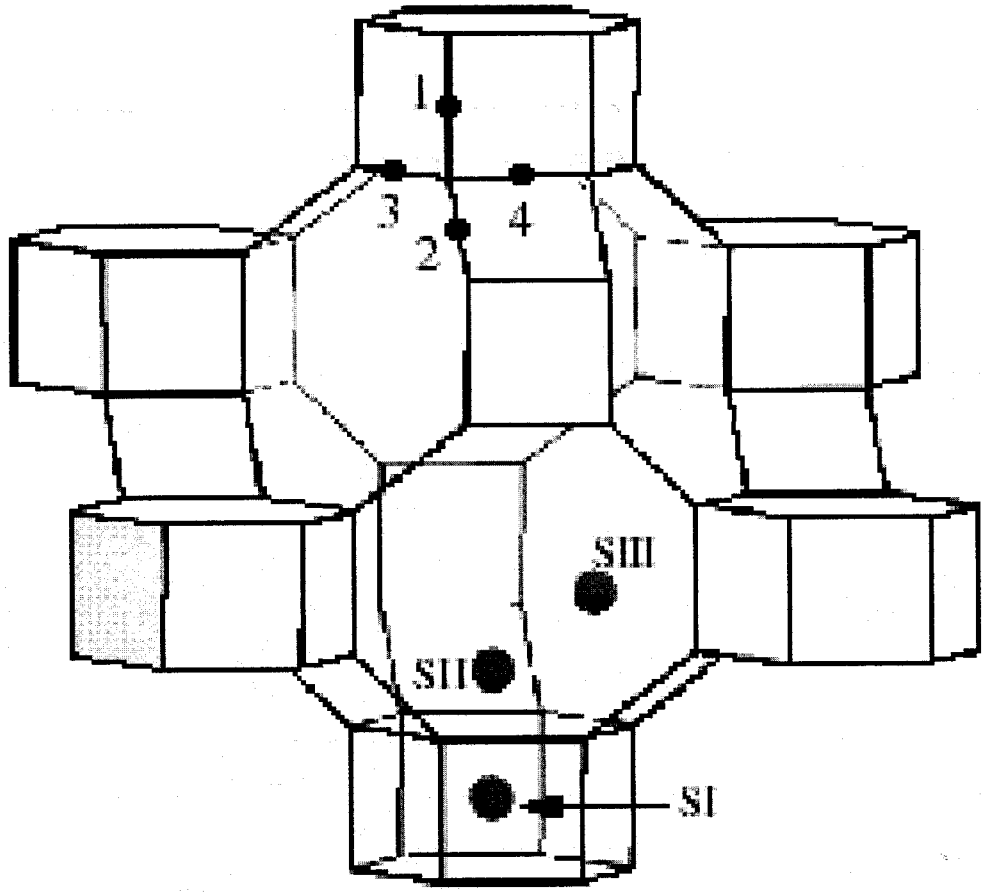
Santa Barbara, CA 93106

- **Introduction to nanoporous materials**
  - Chemical and structural diversity
  - Applications
- **Nanoporous phosphates of nickel**
  - Magnetic and catalytic properties
- **Nickel dicarboxylates**
- **Conclusions**

Zeolite ZSM-5 in its pure silica form with corner sharing SiO_4 tetrahedra; channel diameter is about 5.5 Å



Schematic figure of an aluminosilicate zeolite (chabazite) showing locations of charge-compensating cations (e.g.Na^+); $Na_x(Si_{1-x}Al_xO_2).nH_2O$



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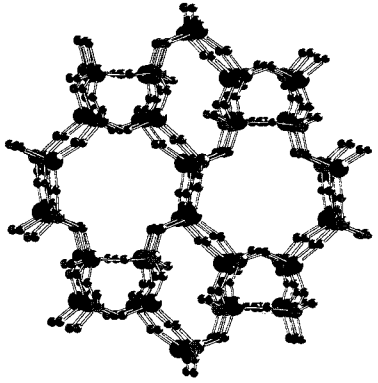
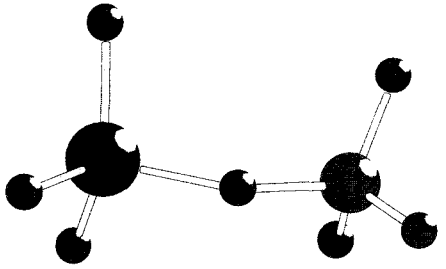
Evolution of Open Framework Materials

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



Aluminosilicate zeolites
in the 1950s/1960s



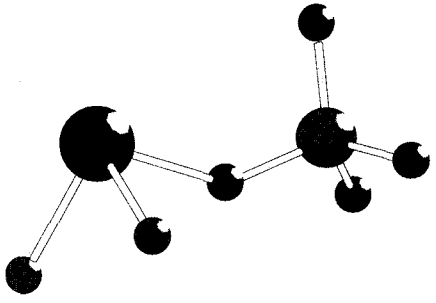
Aluminum phosphates
in the early 1980s

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

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

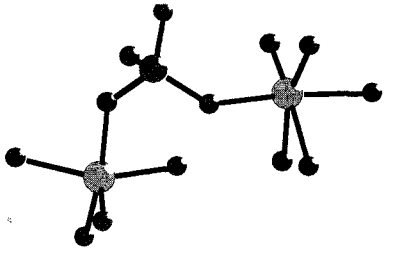
Non TO_4 Frameworks

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



The Development of Open-Framework Phosphates

- **The phosphates of aluminum, e.g. $AlPO_4$ -Synthesized at Union Carbide during the 1980s (Flanigen, Wilson), and subsequently elsewhere!**
- **The phosphates of gallium and indium, e.g. $GaPO_4$ -Synthesized with Ga à Stony Brook, Mulhouse, Le Mans, Oxford, Versailles and Santa Barbara during the 1990s; $InPO_4$s at Oxford in 1997**
- **The phosphates of the transition metals and Zn -Developed by several teams in the 1990s, including Oxford, R.I., Santa Barbara, Versailles, Taiwan, Berlin, NEC.....**
- **The phosphates of tin(II) et antimony(III) - Made in Santa Barbara and Bangalore at the end of the 1990s**
- **The phosphates of uranium - made at Oxford, 1999**

Applications of Nanoporous Materials

Ion Exchange with Hydrated Zeolites

Water softening

Detergency

Radwaste remediation, e.g. for Cs and Sr removal

Separation Processes (size, shape, chemistry)

Branched from linear hydrocarbons

Polar from non-polar molecules (e.g. CO_2 from H_2)

Nitrogen from oxygen over Li-containing zeolites

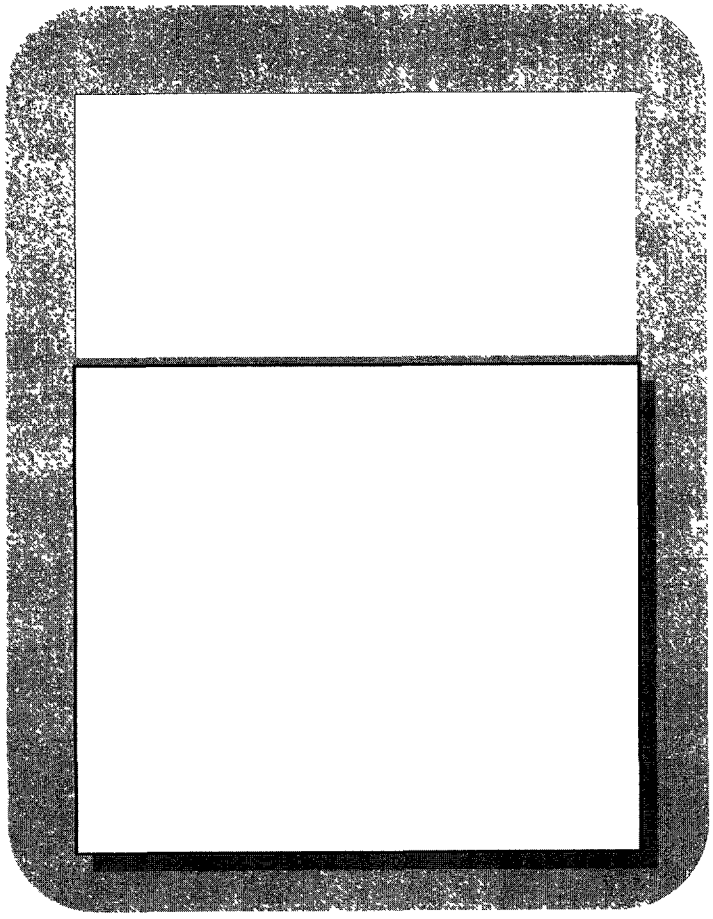
Shape-Selective Catalysis with Zeolites, AlPOs

Catalytic cracking in gasoline manufacture (acid catalysis)

Isomerizations, e.g. xylenes for polyesters (acid catalysis)

Partial oxidations with H_2O_2 over Ti silicates

Hydrothermal Synthesis



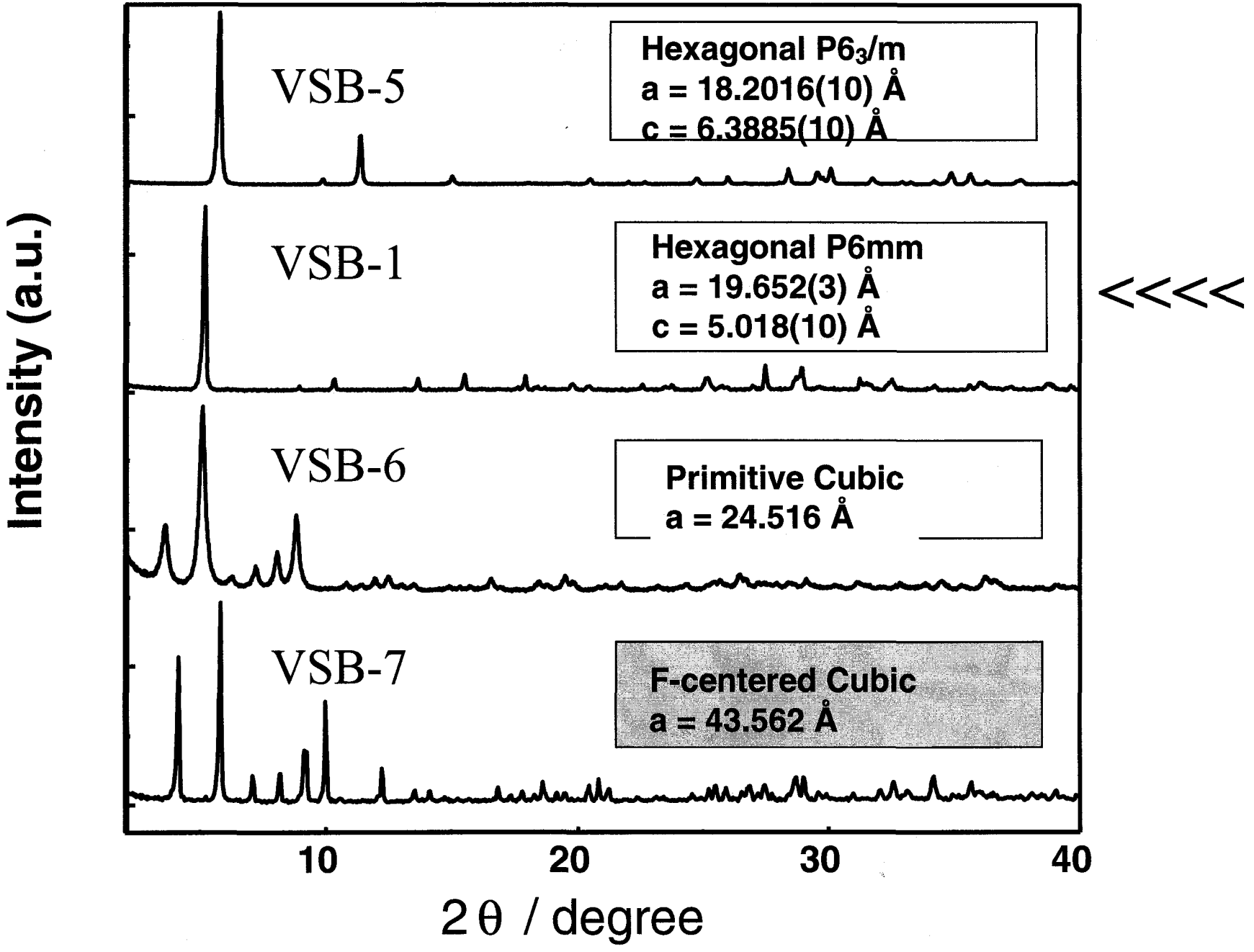
For Ni-P-O systems:

Temperature 150-180 C

Aqueous solution contains:

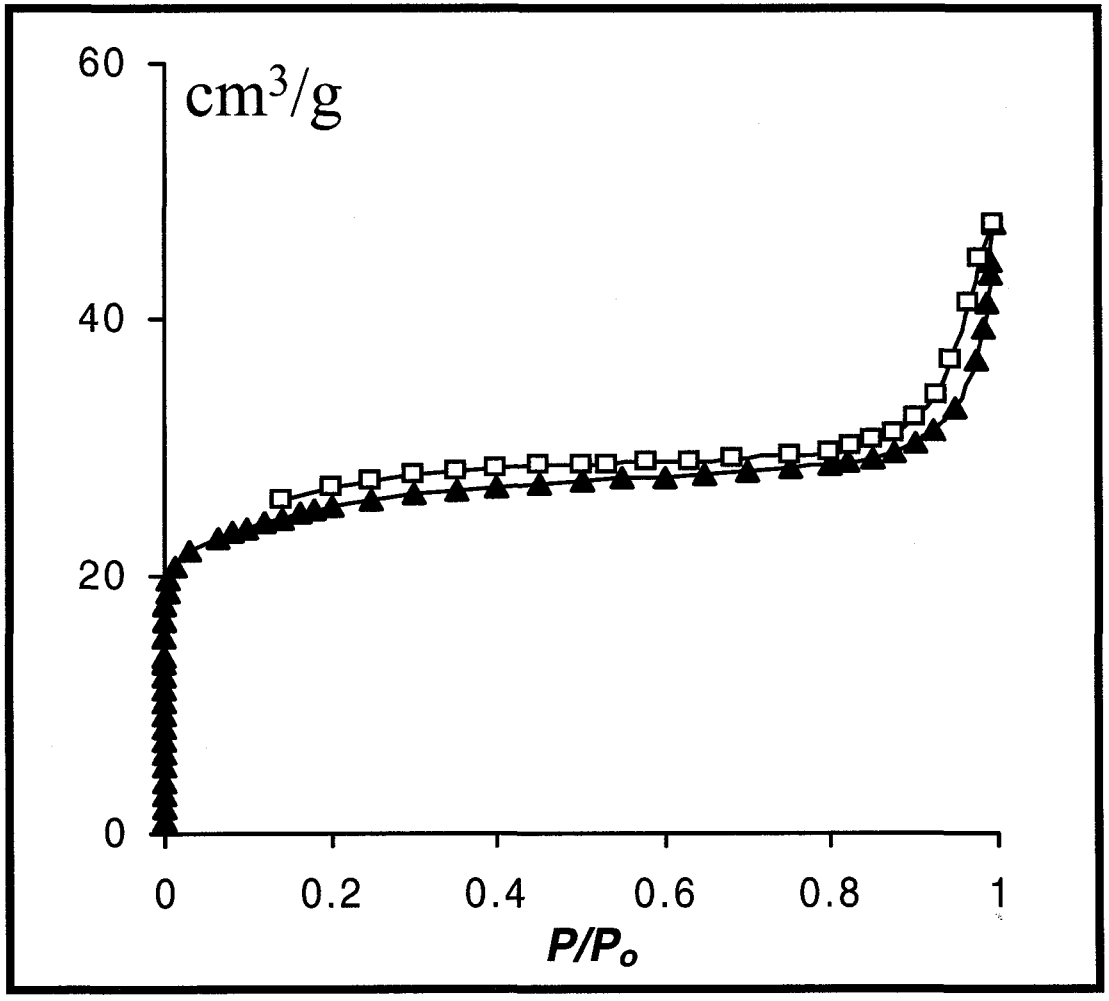
- A nickel Salt
- Phosphoric acid
- **<u>An amine</u>**, e.g. R_4N^+, (to act as a template that will be trapped in the structure)

X-ray Powder patterns of the VSB-n



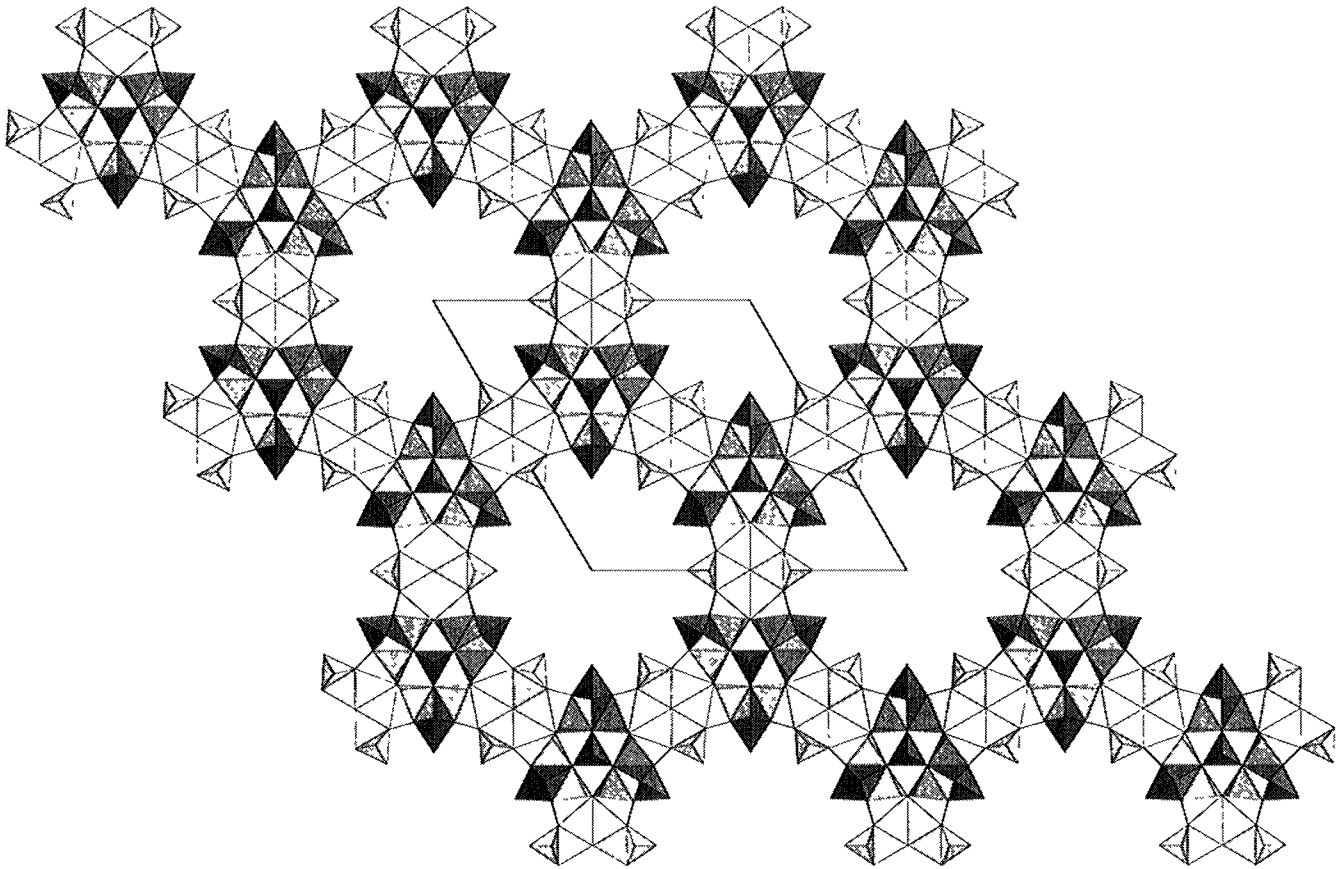
Porosimetry of VSB-1

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



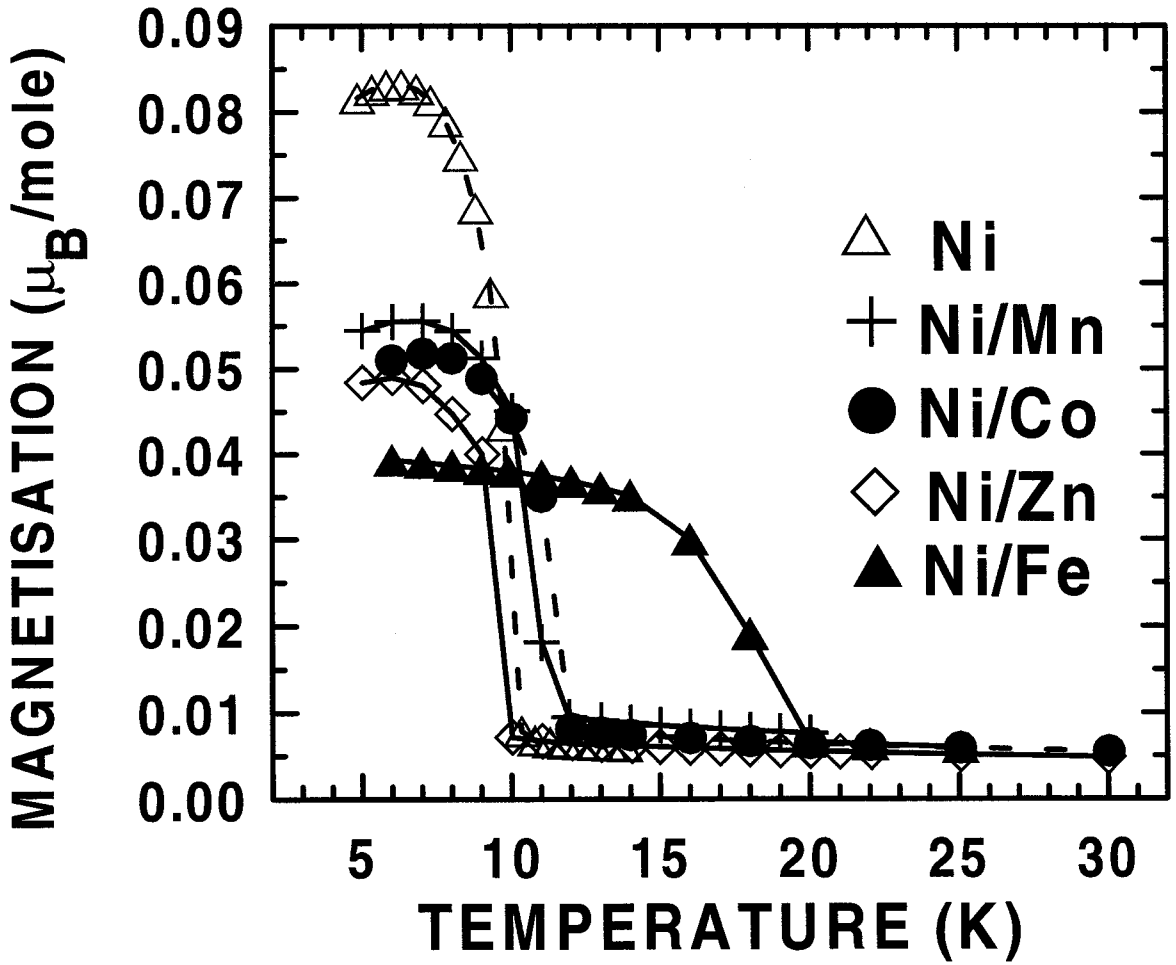
Structure of Nickel Phosphate, VSB-1

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

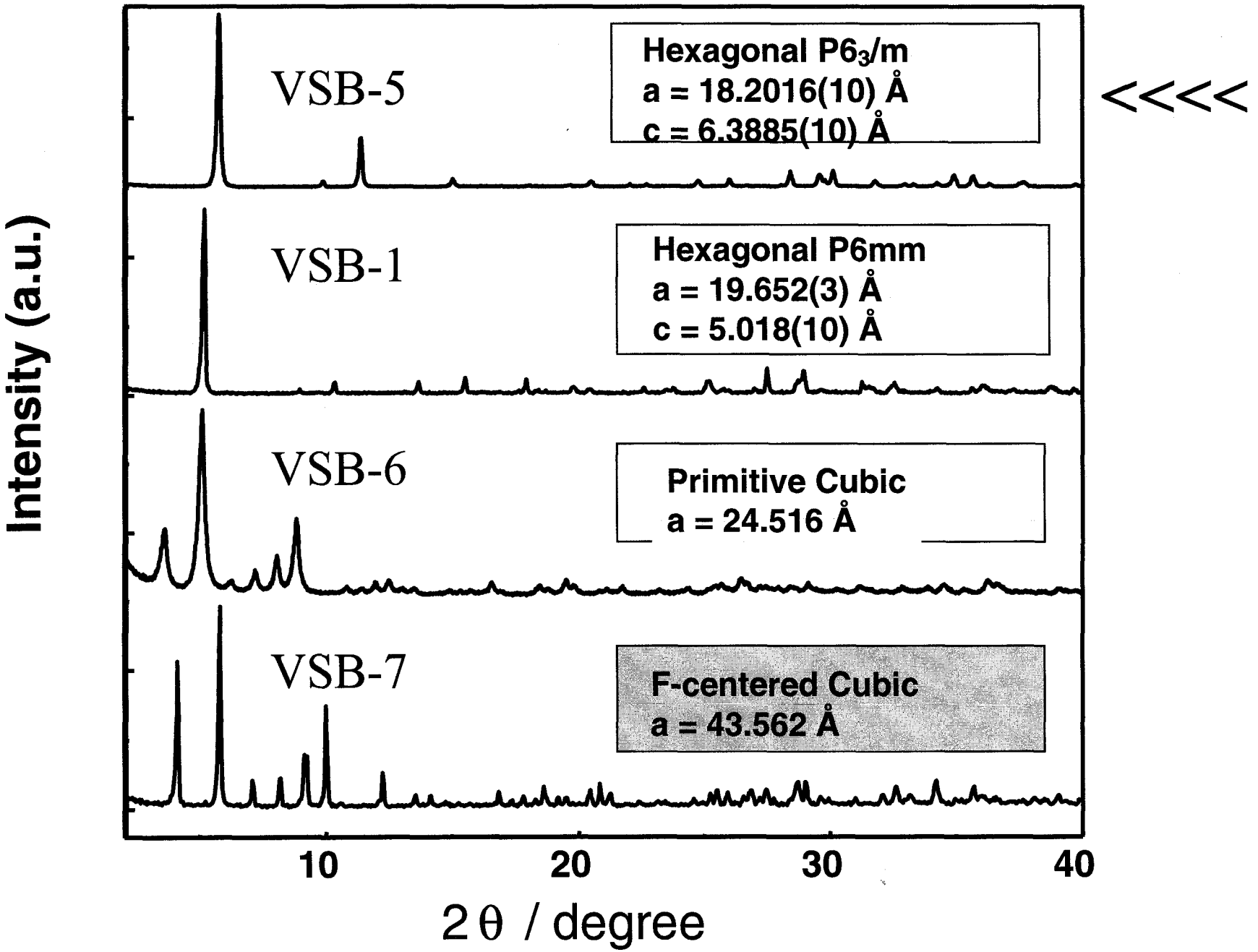


Magnetic Properties of VSB-1

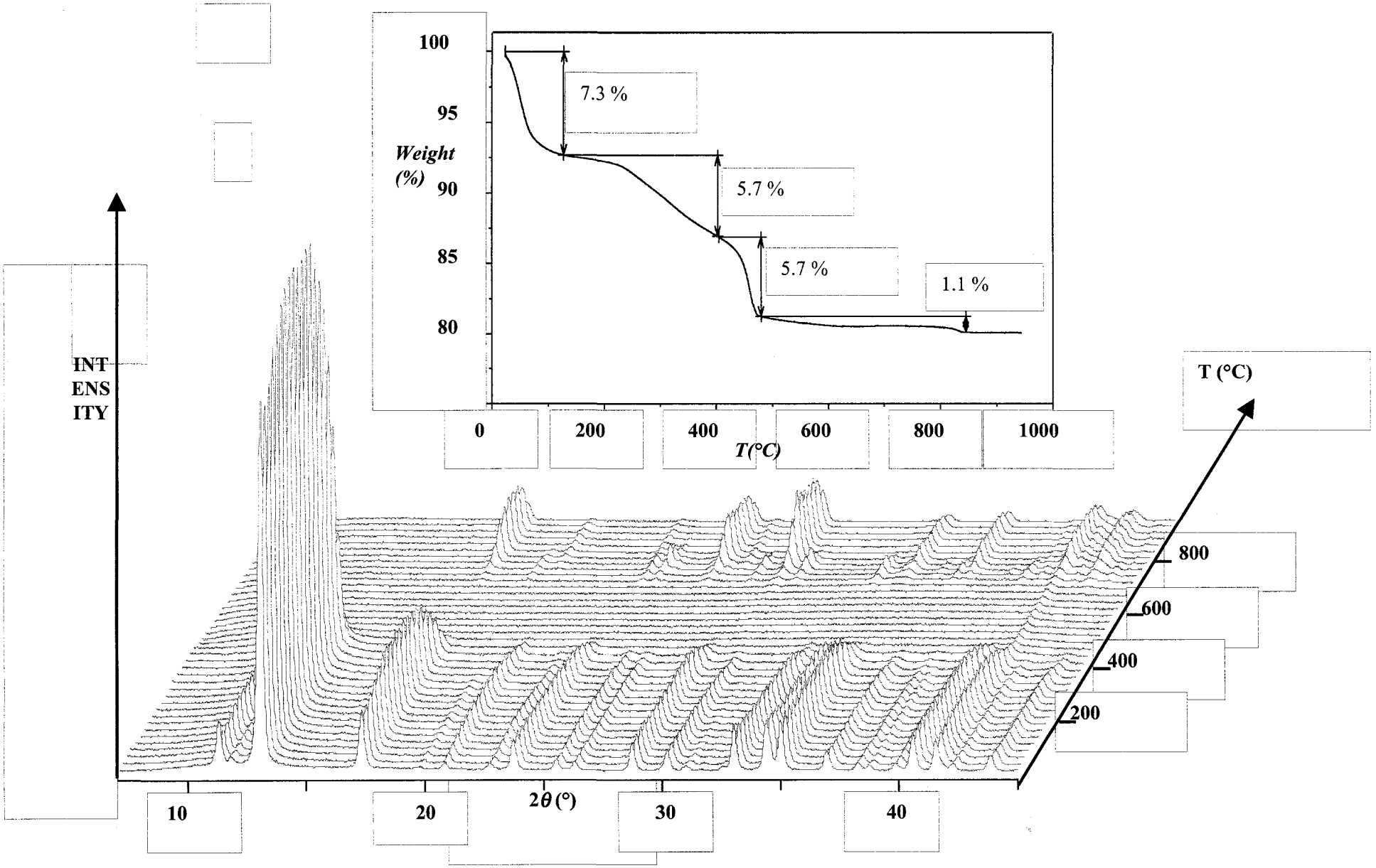
Guillou et al, Compte Rendu Ser. IIC, 387 (1999)



X-ray Powder patterns of the VSB-n

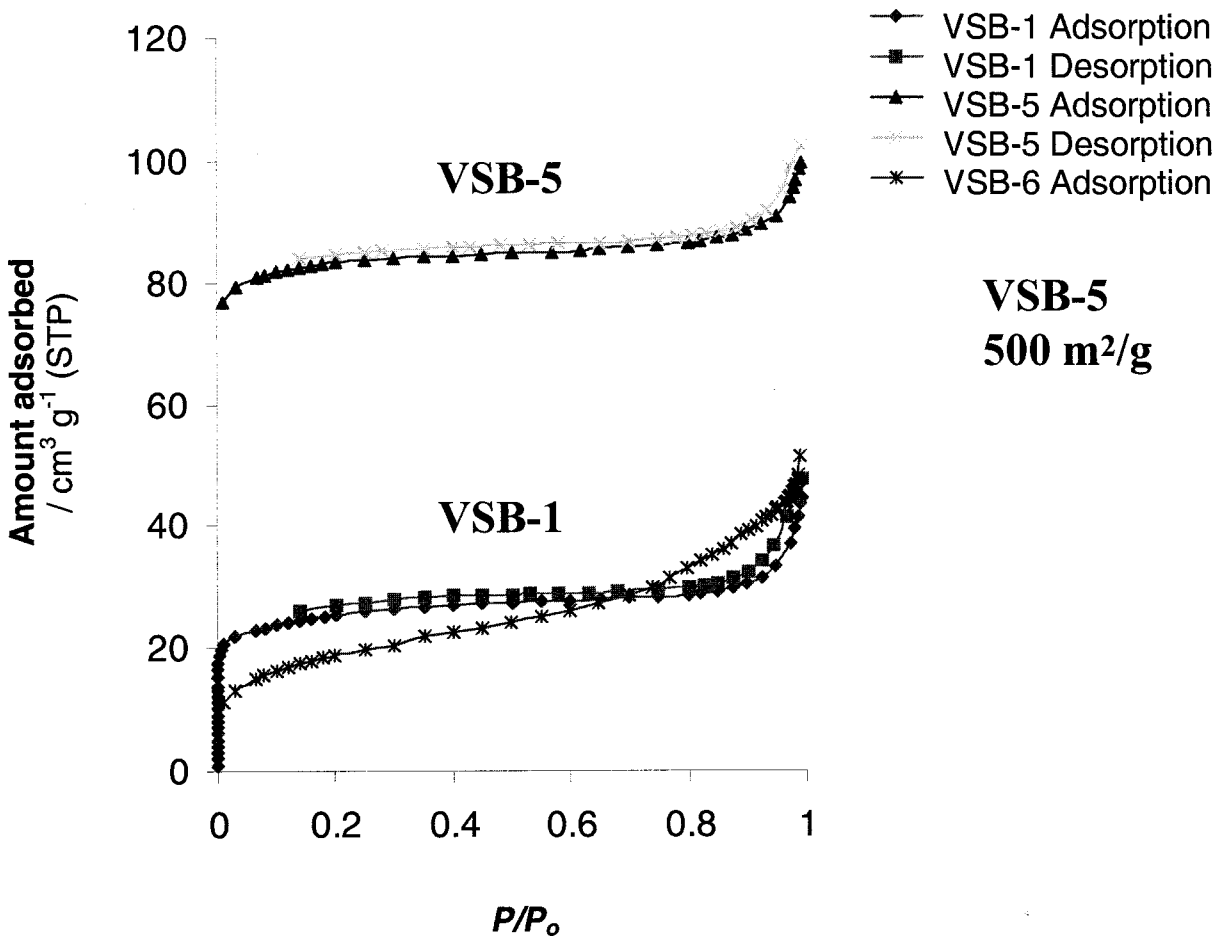


Thermal evolution of VSB-5



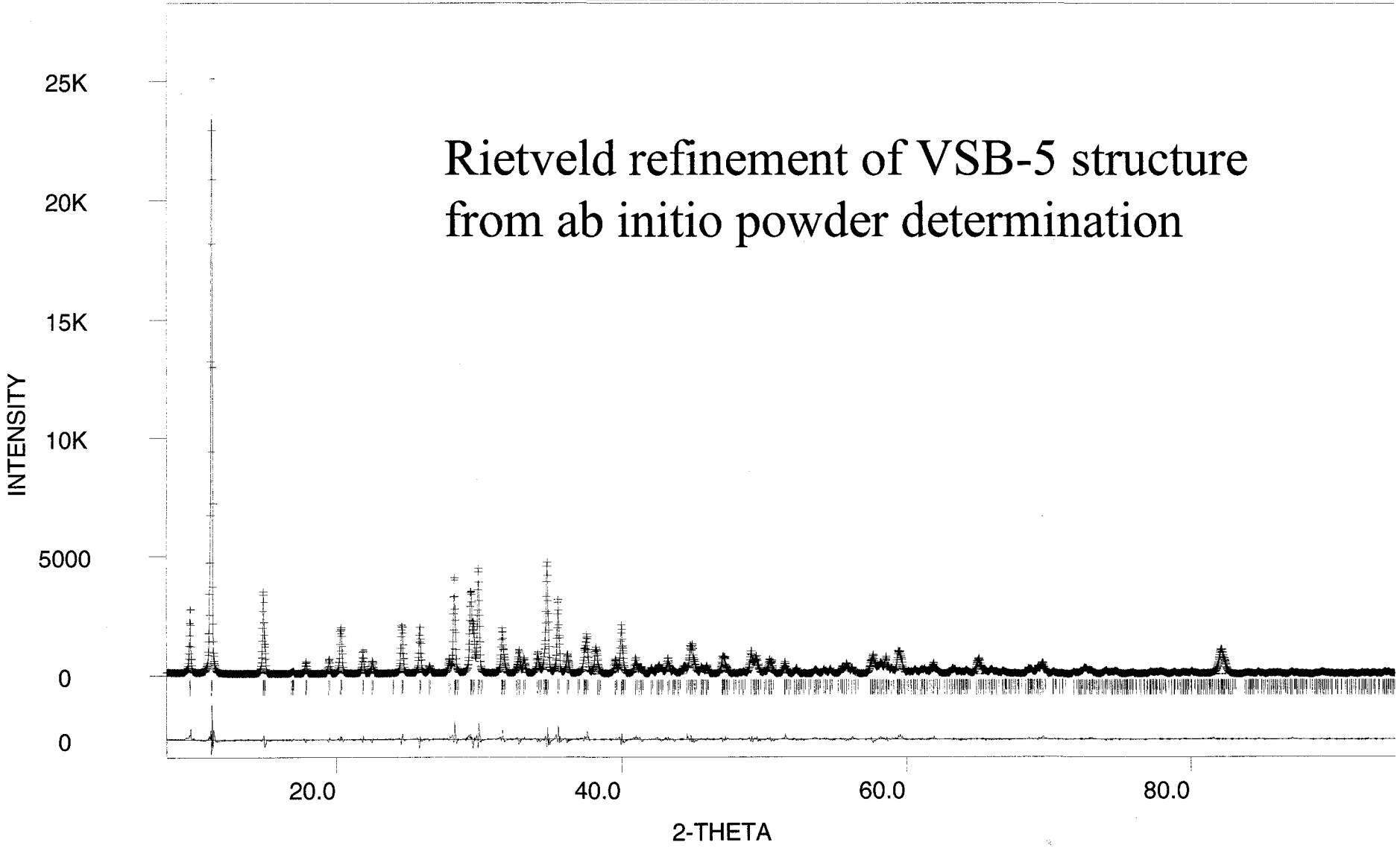
Porosimetry of VSB-5

Guillou et al,
Angew. Chemie (in press)

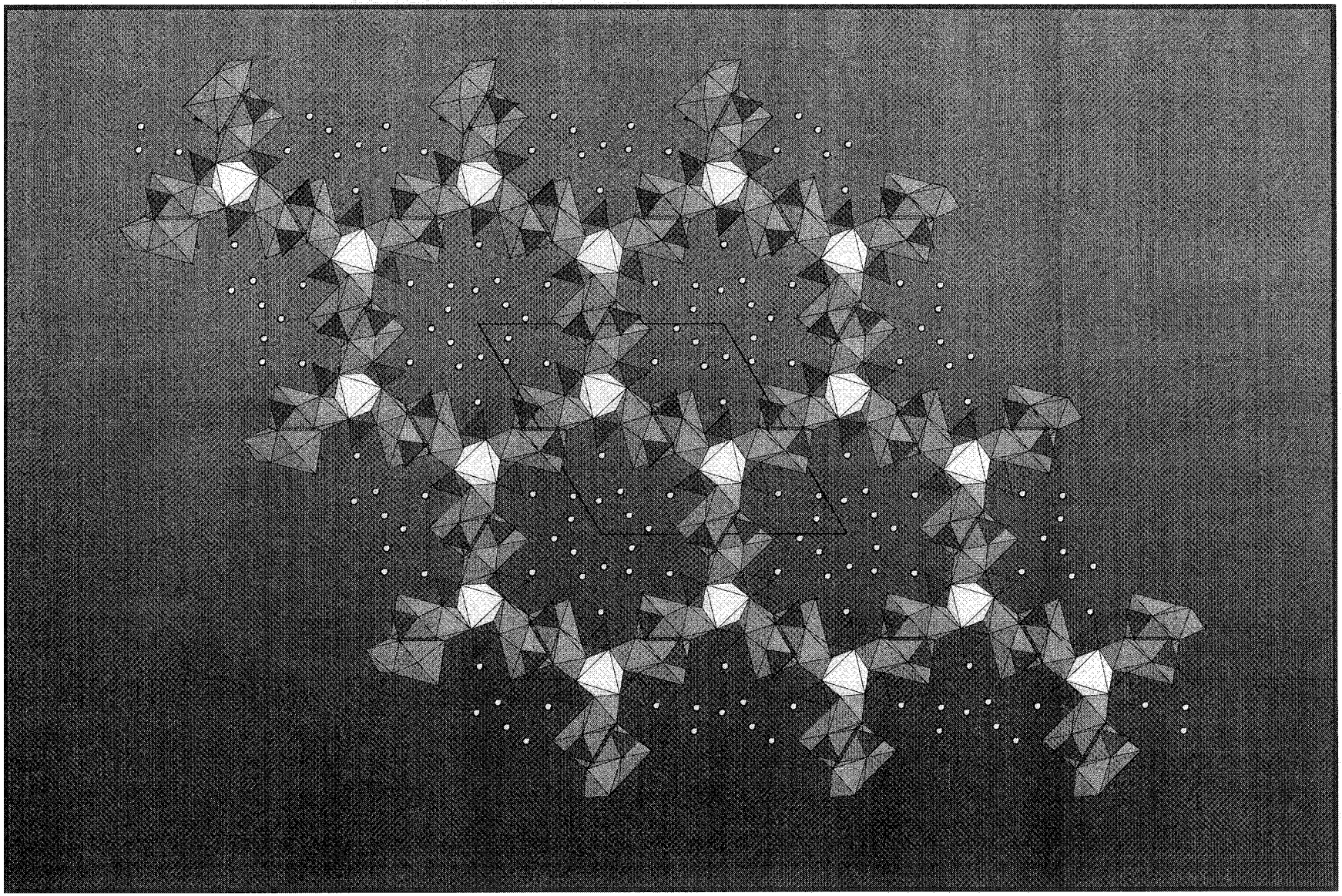


VSB-5
500 m²/g

Guillou et al, Angew. Chemie (in press)



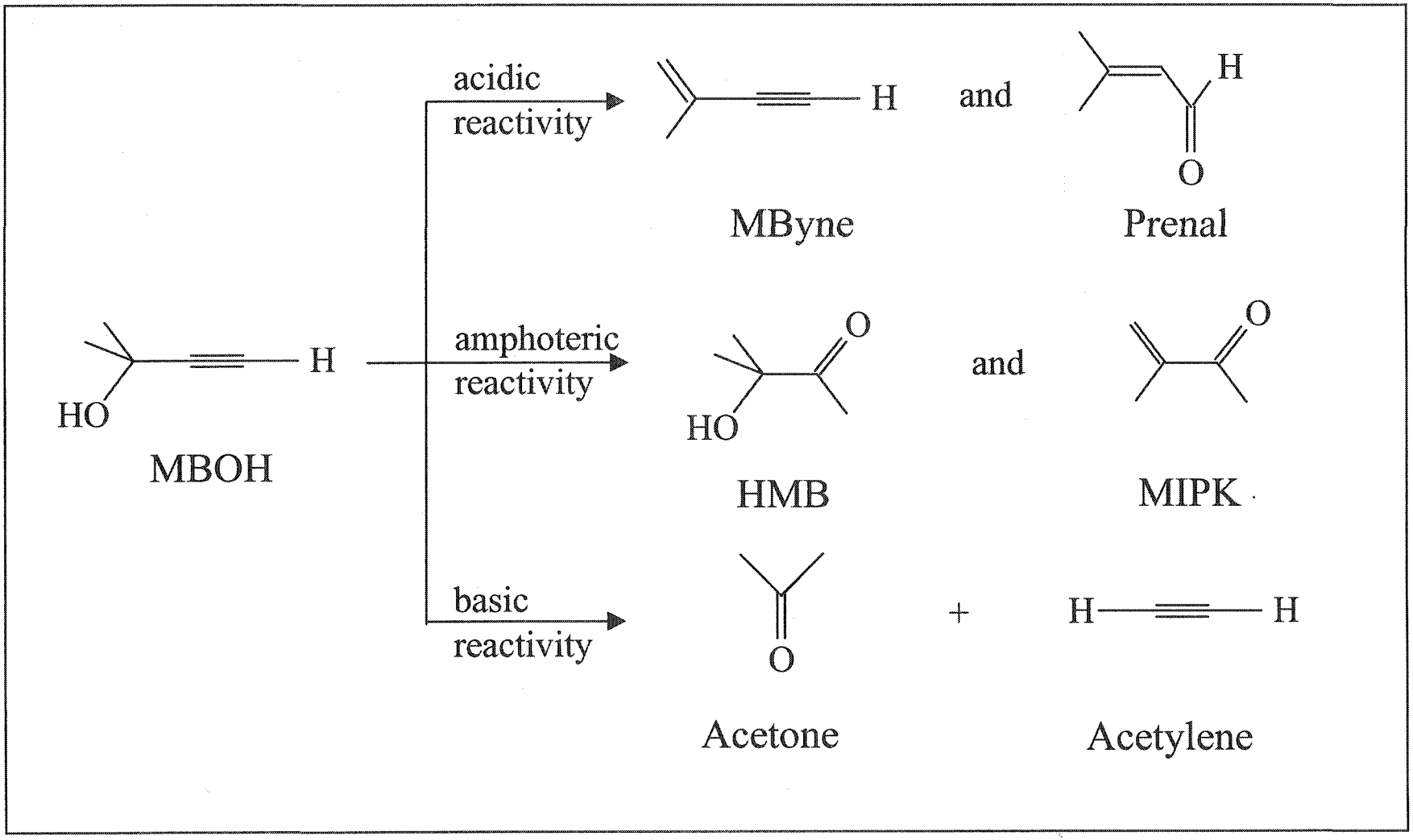
VSB-5: $[Ni_{20}(OH)_4(H_2O)_{14}(PO_4)_{12}] \cdot 12\ H_2O$



Catalytic Applications of Nanoporous Materials

- Shape-selective catalysis with aluminosilicate zeolites and $AlPO_4$s
- Primarily for acid catalysis
- Redox reactions
  - Ti-silicates, Cu-ZSM-5
- Major problems with alkene conversions due to coke formation
- Need for new classes of catalysts

Catalytic Conversion of 2-methyl-3-butyn-2-ol (MBOH)



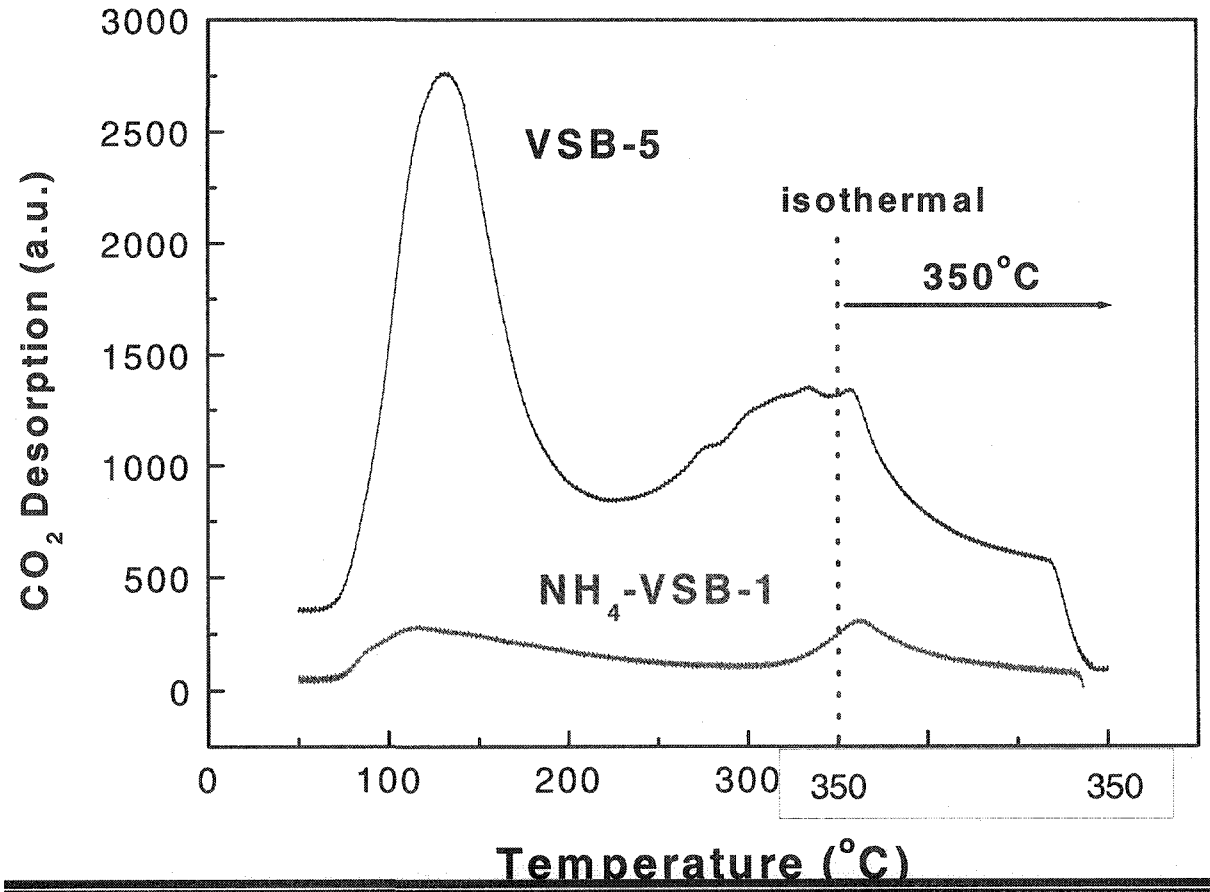
Conversion of 2-methyl-3-butyn-2-ol over nickel phosphates and zeolites[a]

Catalyst	Temp. (°C)	MBOH Conversion		Ratio of Acetone/MByne	
		10 min	30 min	10 min	30 min
NH_4-VSB-1	250	2.7	1.9	1.69	2.24
	300	10.0	7.6	1.82	2.32
	350	24.7	19.6	1.53	1.89
K-VSB-1	250	2.3	1.5	6.74	6.59
VSB-5	250	22.6	12.7	26.2	28.2
	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

(to measure the basicity)



Calcination: 350°C for 4 h

(in air)

TPD Analysis:

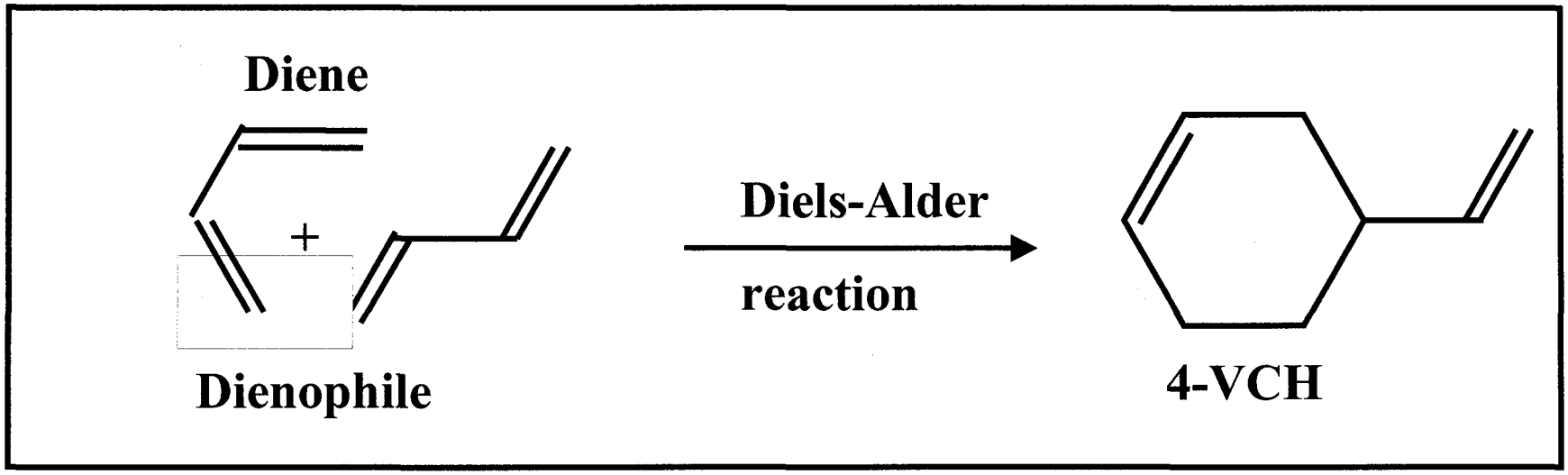
$T_{adsorption}$: 30°C

Desorption: 50°C to 350°C

Ramp rate (β): 5°C/min

Carrier flow rate: 50 ml/min

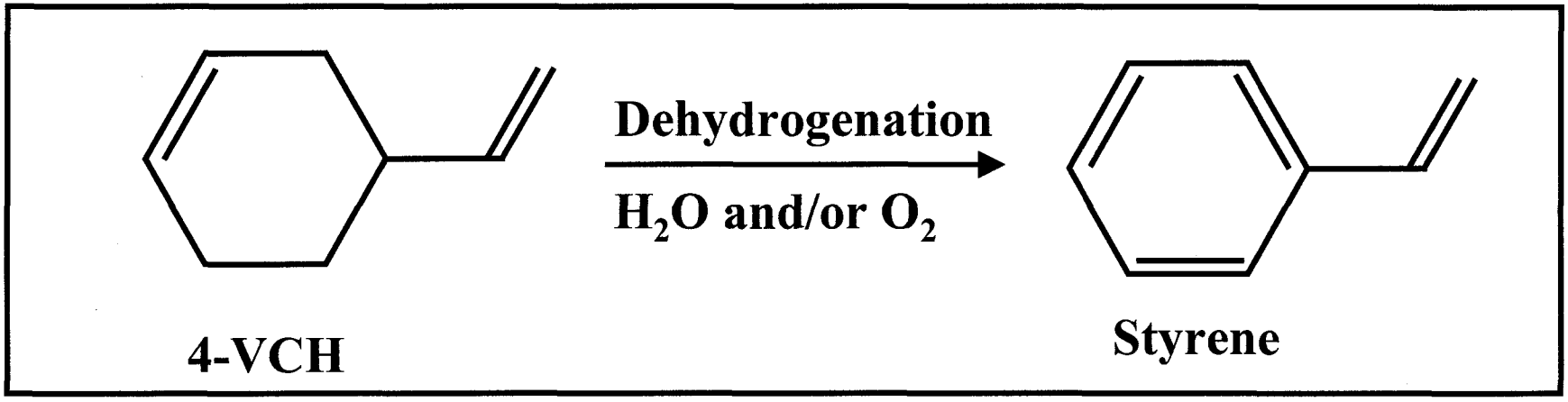
Diels-Alder Cyclodimerization of Butadiene



Effective Catalyst for Butadiene to Vinylcylcohexene

1. I.E. Maxwell (England), *J. Catal.*, 61, 485 (1980).
   Catalyst: CuY zeolite - 60% Conv., 99% Selectivity at 100°C, 25 atm
2. Dow Chemicals (USA), US Patent 5,329,057 (1994).
   Catalyst: 2-Allyl-$FeO(NO)_2$ - 97% Yield at 100°C
3. A. Mortreux (France), Tetrahedron Lett., 35, 413 (1994).
   Catalyst: Phosphane Ni complex - 99% yield at 80°C.

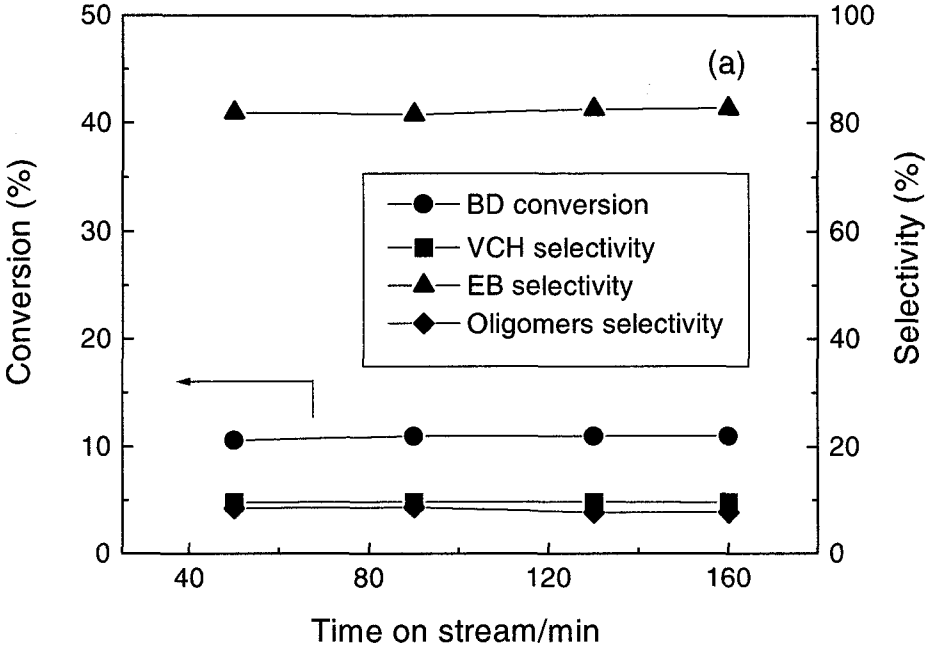
VCH Dehydrogenation to Styrene Monomer



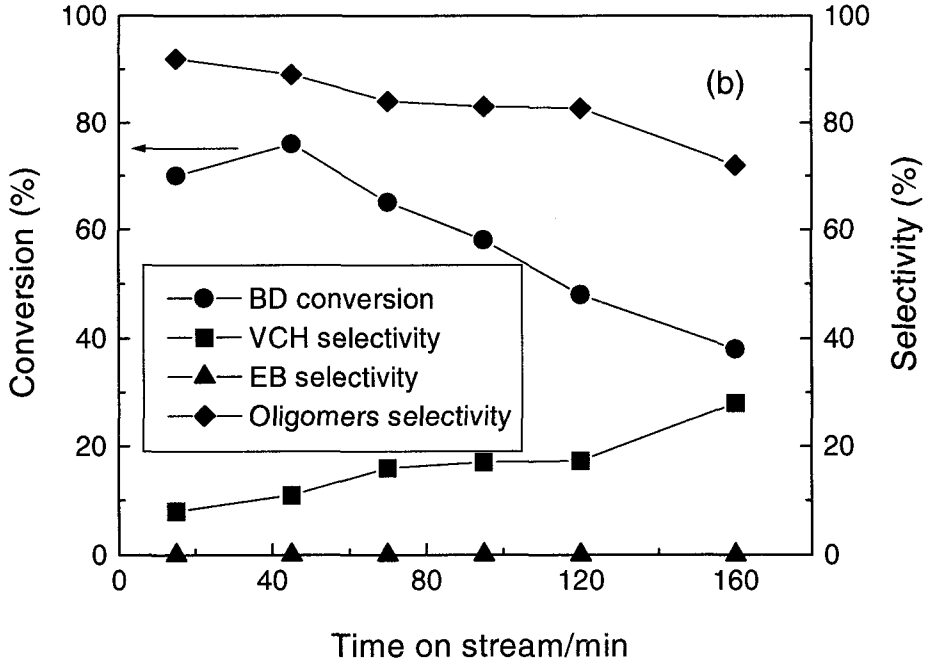
Proposed Catalyst for Vinylcylcohexene to Styrene

1. Dow Chemicals, US Patent 5,336,822 (1994).
   Sn/SbOx - 91% yield for VCH/H_2O/O_2 at 380°C, LHSV = 0.3 h^{-1}
2. Mitsubishi Chemical Industry, US Patent 4,165,441 (1979).
   Sn/SbOx(2:1) - 82% Conv., 59% SM selectivity at 400°C
3. R. Neumann (Israel), *Appl. Catal. A: General*, 172, 67 (1998).
   $H_5PV_2Mo_{10}O_{40}$ on carbon - 65% Conv., 48% SM selectivity at 260°C
   Drawback: short lifetime (< 260 min)

VSB-1



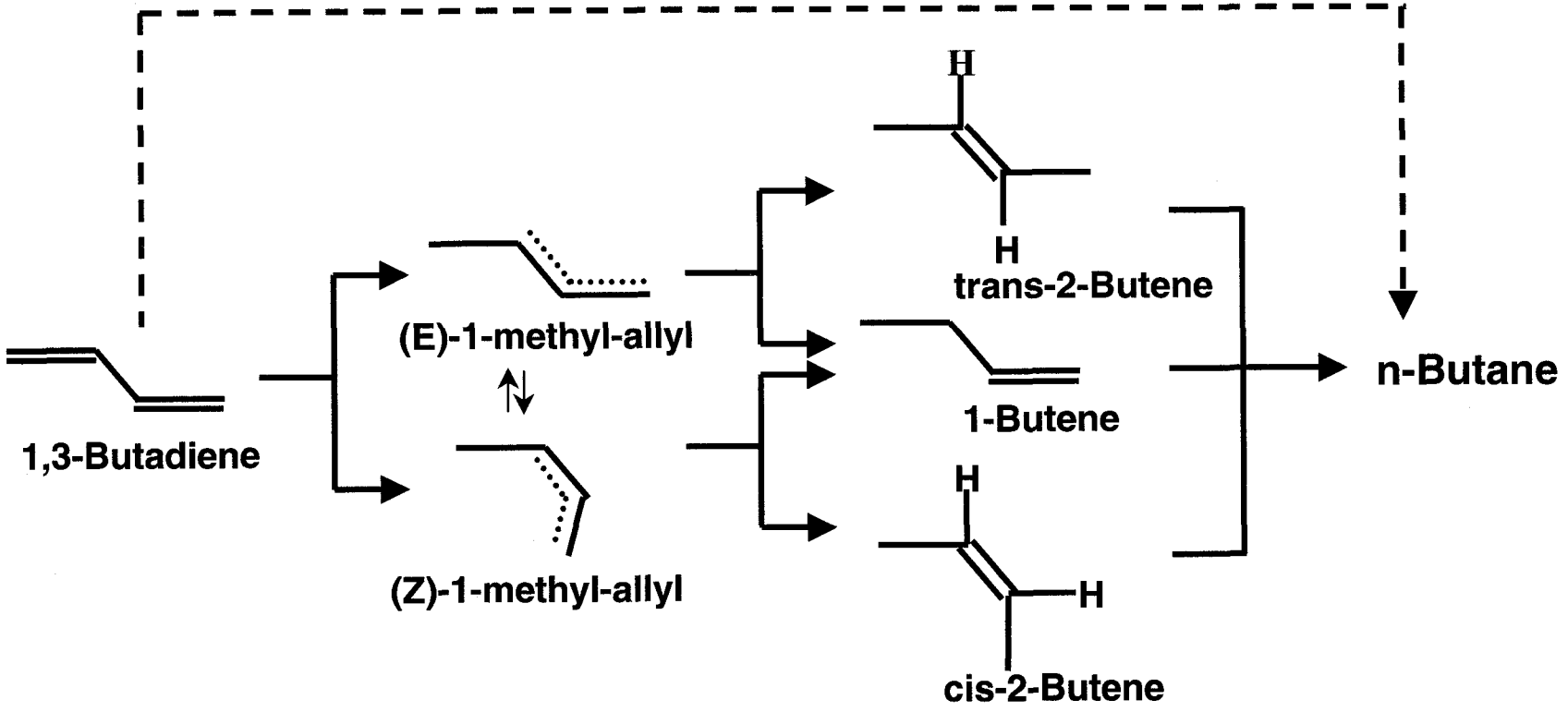
Na-X



BD cyclodimerization and dehydrogenation to Ethylbenzene with VSB-1:

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

Reaction Scheme for Selective 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.

Selective Hydrogenation of 1,3-Butadiene

Selective 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 (%) $n\text{-}C_4H_{10}$	$1\text{-}C_4H_8$	$t\text{-}2\text{-}C_4H_8$	$c\text{-}2\text{-}C_4H_8$
VSB-5(350)*	4	200	10.3	97.9	2.1	48.4	30.5	19.0
VSB-5(350)	16	200	68.4	97.6	2.4	52.4	28.5	16.7
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

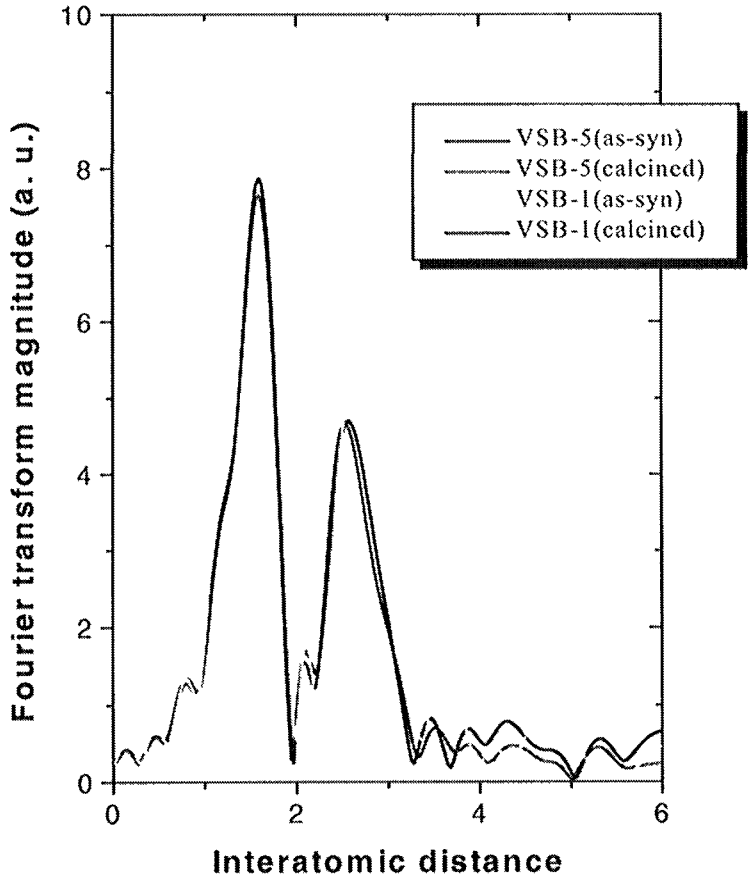
Selective Hydrogenation of 1,3-Butadiene(II)

Selective hydrogenation of 1,3-Butadiene over VSB-1 and Ni-exchanged VSB-1

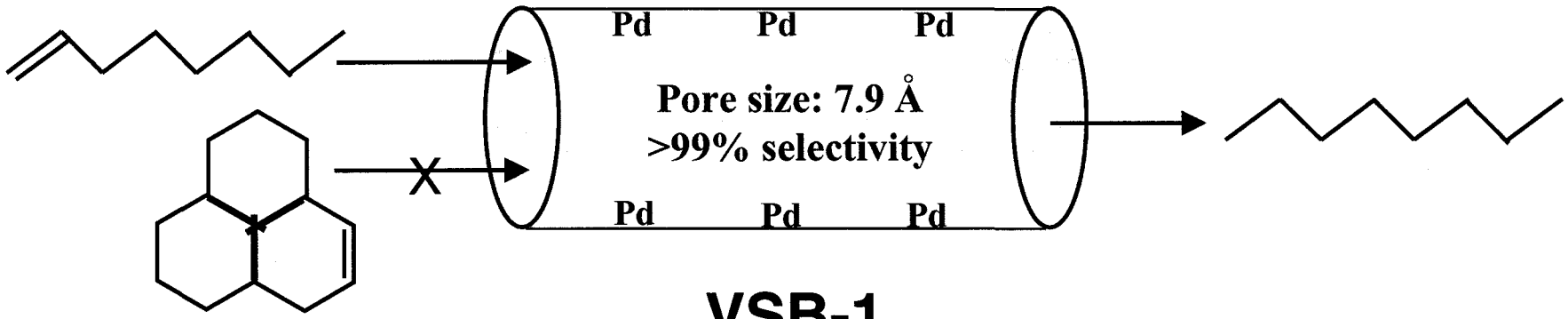
Catalyst*	BD Conv. (%)	$S_{butenes}$ (%)	Product (%)			
			$n\text{-}C_4H_{10}$	$1\text{-}C_4H_8$	$t\text{-}2\text{-}C_4H_8$	$c\text{-}2\text{-}C_4H_8$
VSB-1	0.2	99.9	0.1	36.1	38.1	25.7
Ni-VSB-1	59.8	98.8	1.2	39.4	46.3	13.1

Reaction conditions: T = 200°C, W/F = 0.6 g·sec/ml, P(BD) = 10.1 kPa, H_2/BD = 3.
***Reduction at 350°C for 16 h (VSB-1) and 2 h (Ni-VSB-1), respectively.**

FT-EXAFS spectra of VSB-1 and 5 according to treatment

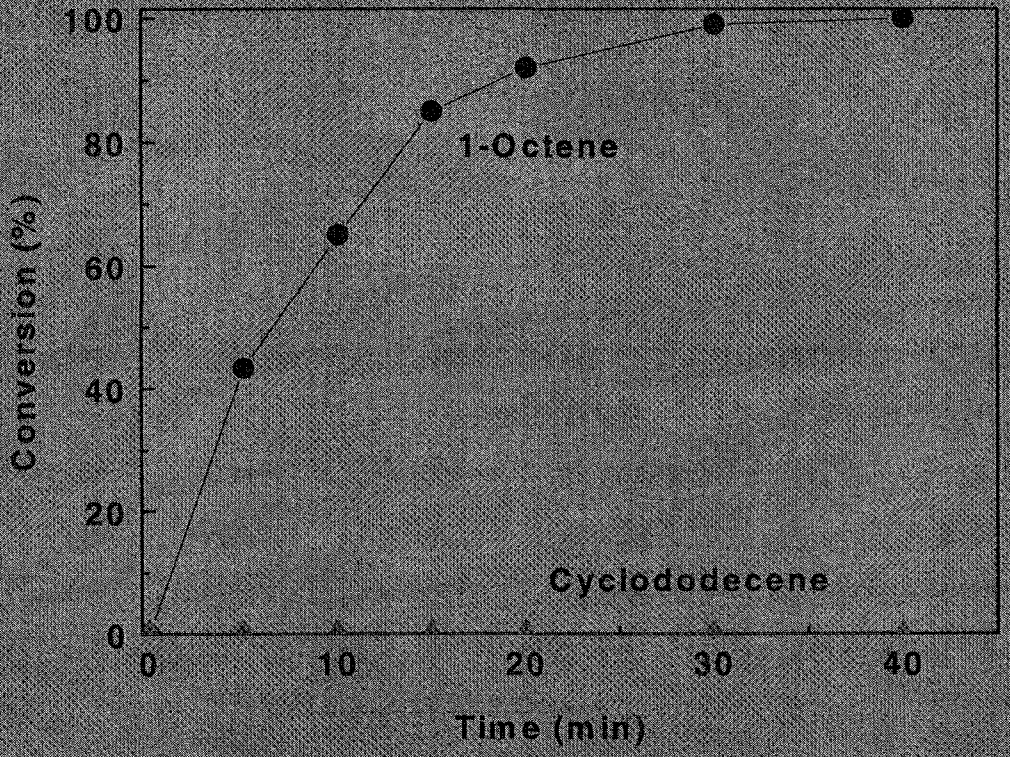


Shape Selective hydrogenation of 1-octene and cyclododecene over Pd-VSB-1



VSB-1

Competitive hydrogenation of 1-octene and cyclododecene 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.

Direct production of H_2O_2 from H_2 and air over Pd-containing microporous catalysts

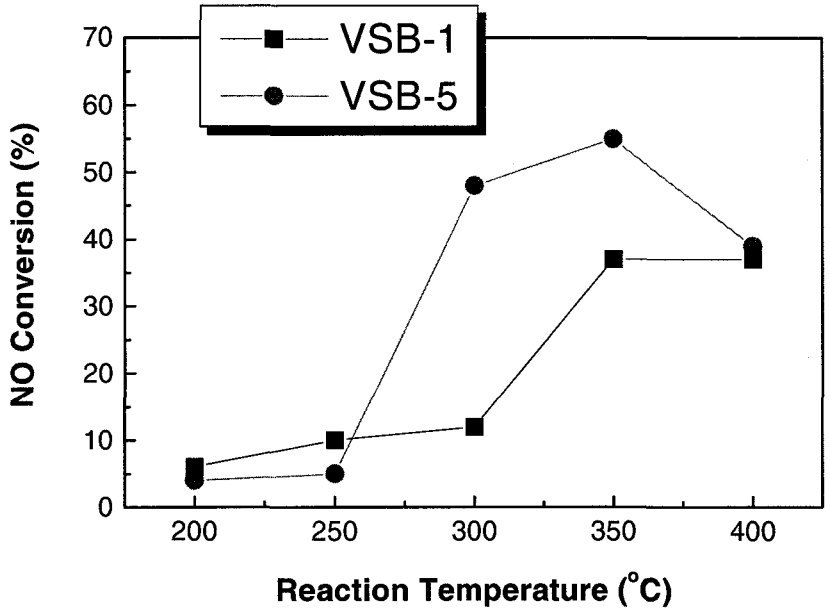
Catalyst[a]	W_{Pd} (%)[b]	$[H_2O_2]$ (mM)	TOF[c]
Pd-VSB-1	0.72	7.1	414
Pd-VSB-1	3.22	8.5	108
Pd-HBEA	0.70	5.6	338
Pd-HL	0.95	2.7	119

Reaction conditions: T = 20°C, 0.01 N HCl 400 ml, H_2 : Air = 10 : 40 ml/min.
Catalyst pretreatment: reduction with 5% H_2 in He at 300°C for 4 h.
[a]prepared by ion-exchange using aq. solution of $PdCl_2(NH_3)_4$ or $Pd(NO_3)_2$.
[b]analyzed by ICP-MS.
[c]TOF (turnover frequency) = mol-H_2O_2/(mol-Pd)·h.

Catalytic result clearly demonstrate that VSB-1 can be utilized as a microporous support for encapsulating noble metal species.

NH_3-SCR of NO over VSB Materials

$$NH_3 + NO \rightarrow N_2 + H_2O$$



Reaction conditions: GHSV = 40,000 h^{-1},
NO = 1500 ppm, NH_3 = 1500 ppm, and O_2 = 3%

Alternative bridging units between metals

Can we replace phosphate, PO_4, by longer bridges in order to make larger cavities?

$O_3P\text{-}(CH_2)_n\text{-}PO_3$

$O_3P\text{-}(CH_2)_n\text{-}CO_2$

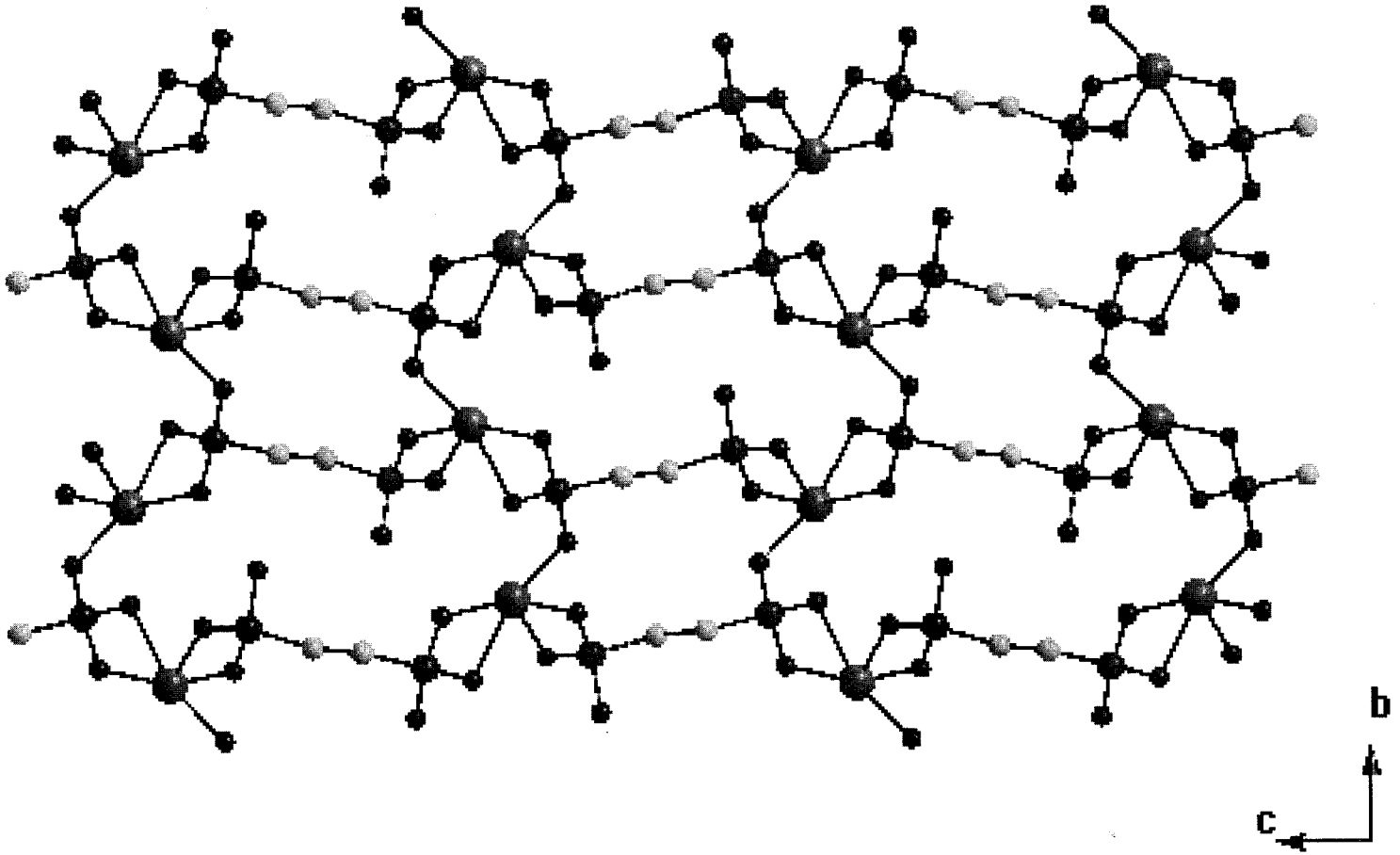
$O_2C\text{-}(CH_2)_n\text{-}CO_2$

$O_2C\text{-}(CH_2)_n\text{-}(CHR)\text{-}CO_2$

R=NH_2, OH etc for chirality!

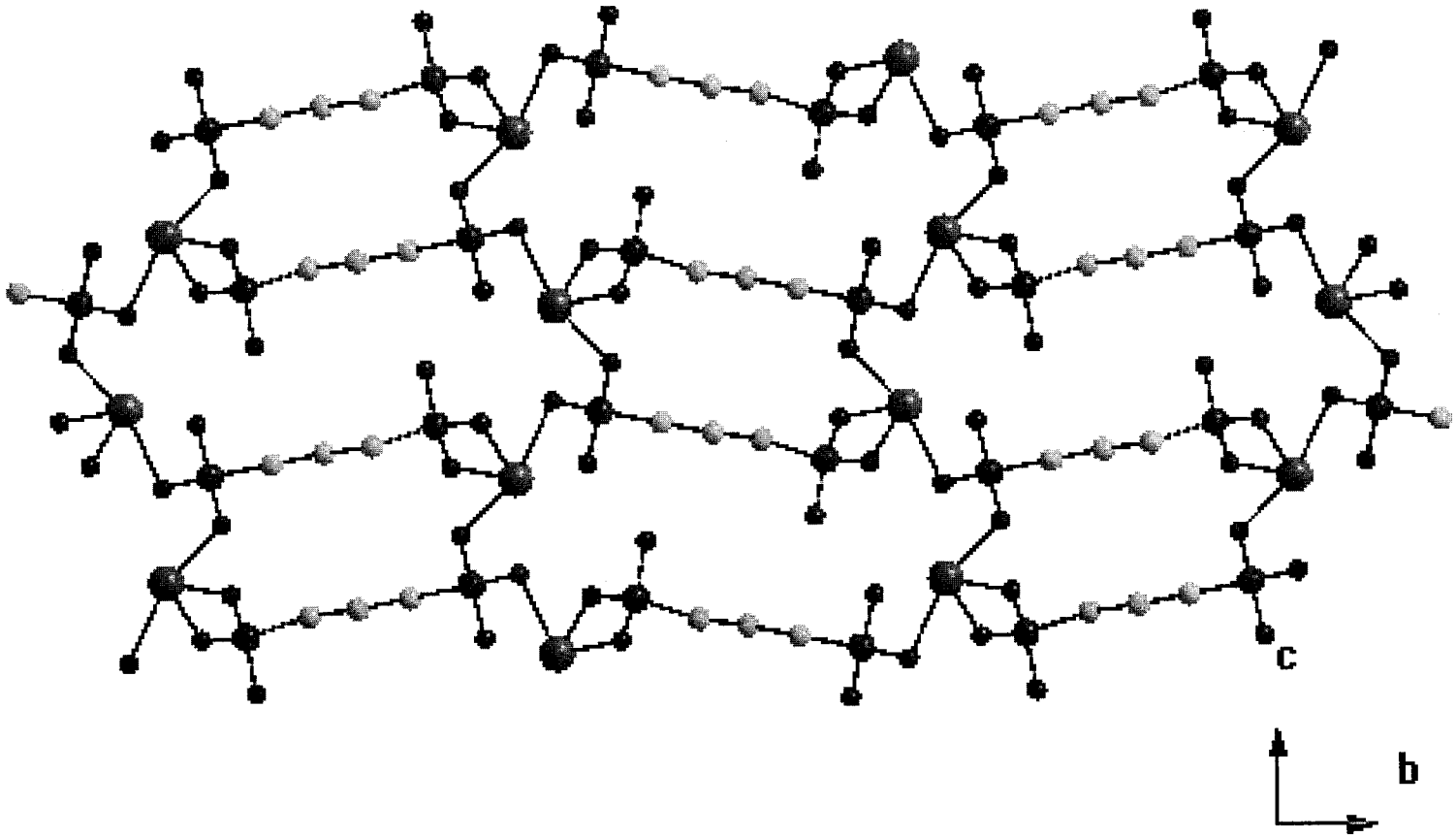
Antimony (III) Ethyldiphosphonate

Adair et al. Solid State Sciences 2, 119 (2000)

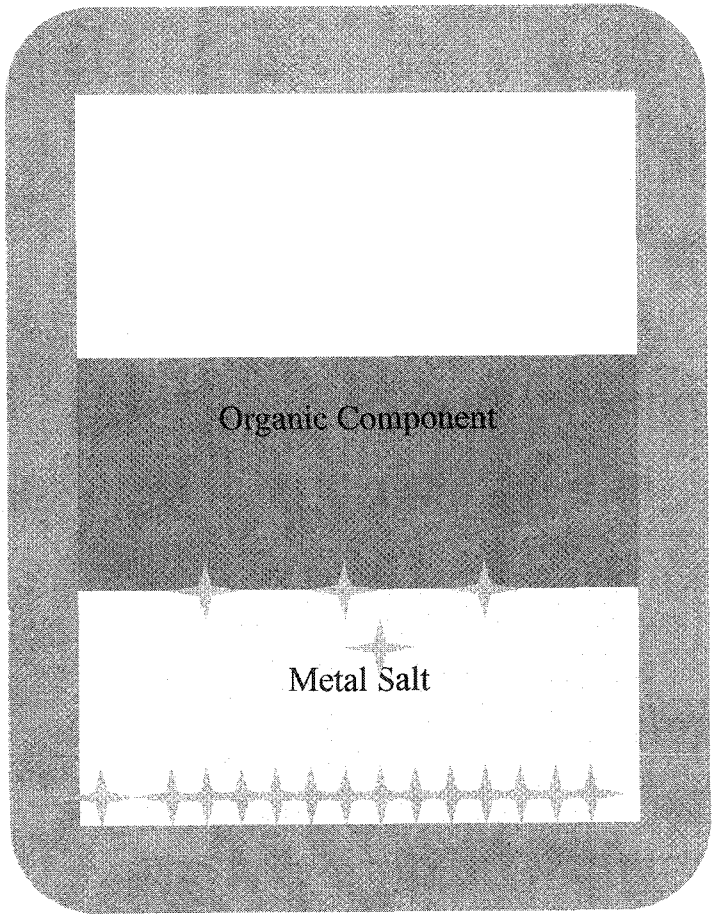


Antimony (III) Propyldiphosphonate

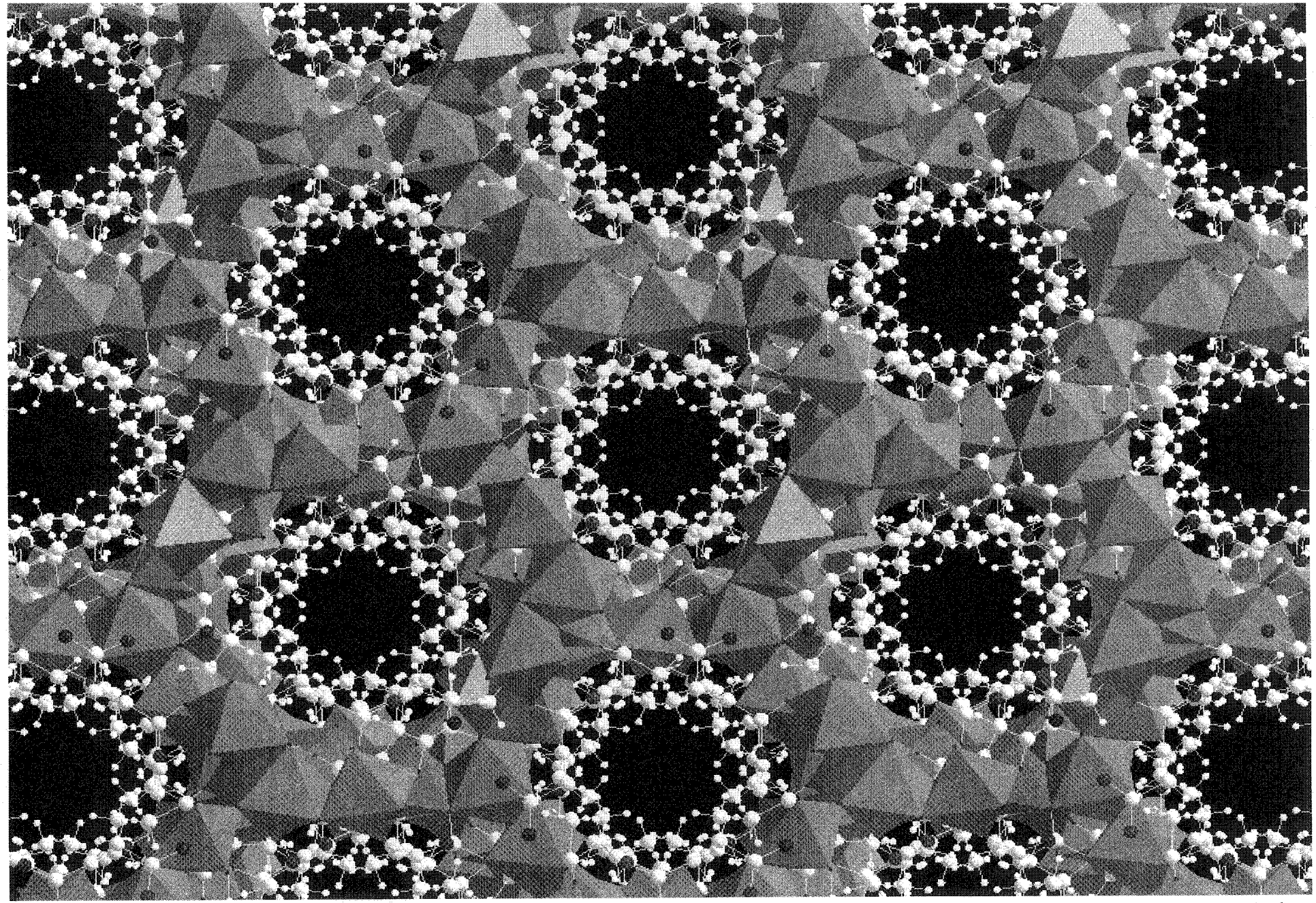
Adair et al. Solid State Sciences 2, 119 (2000)



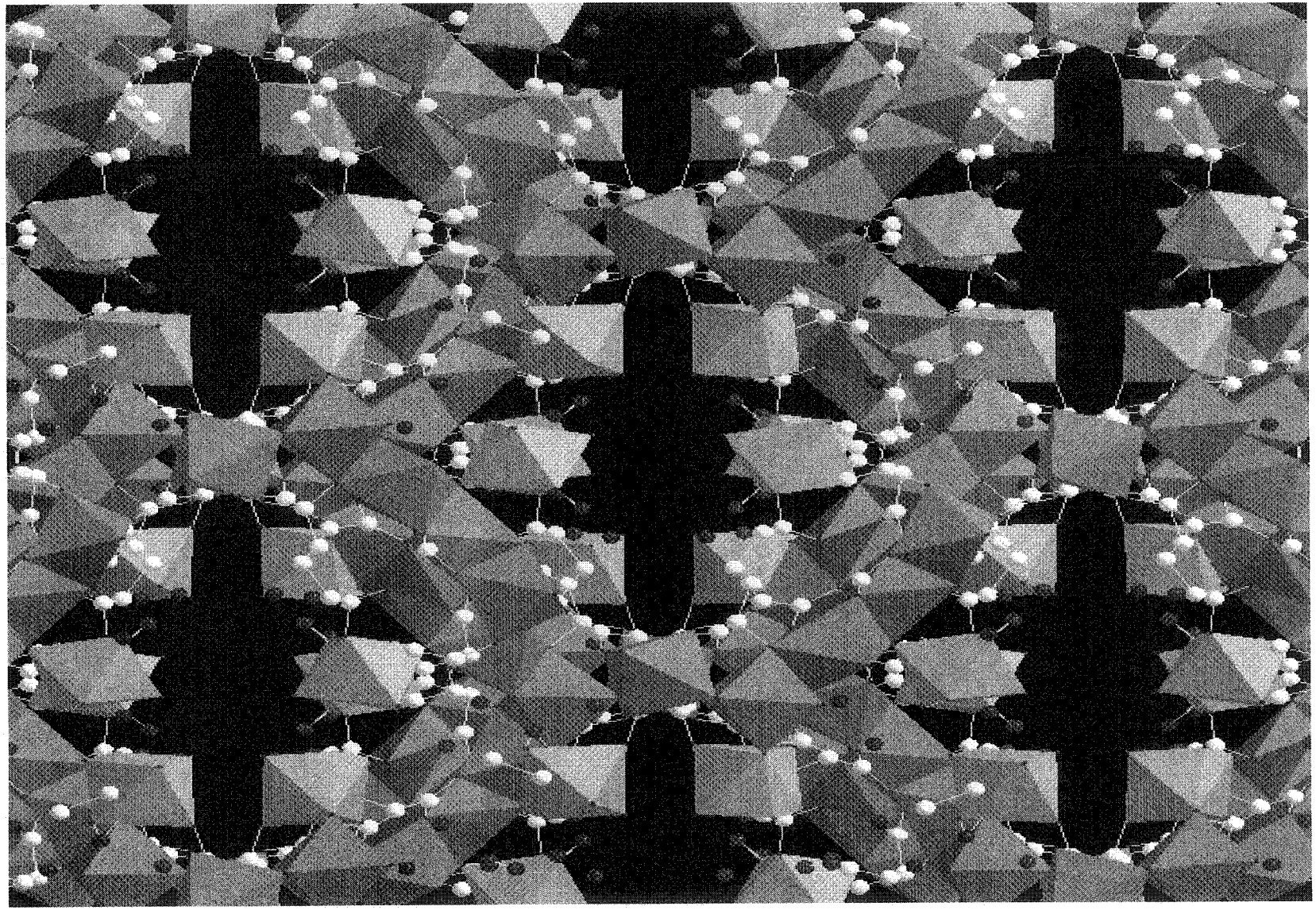
Biphasic Solvothermal Synthesis



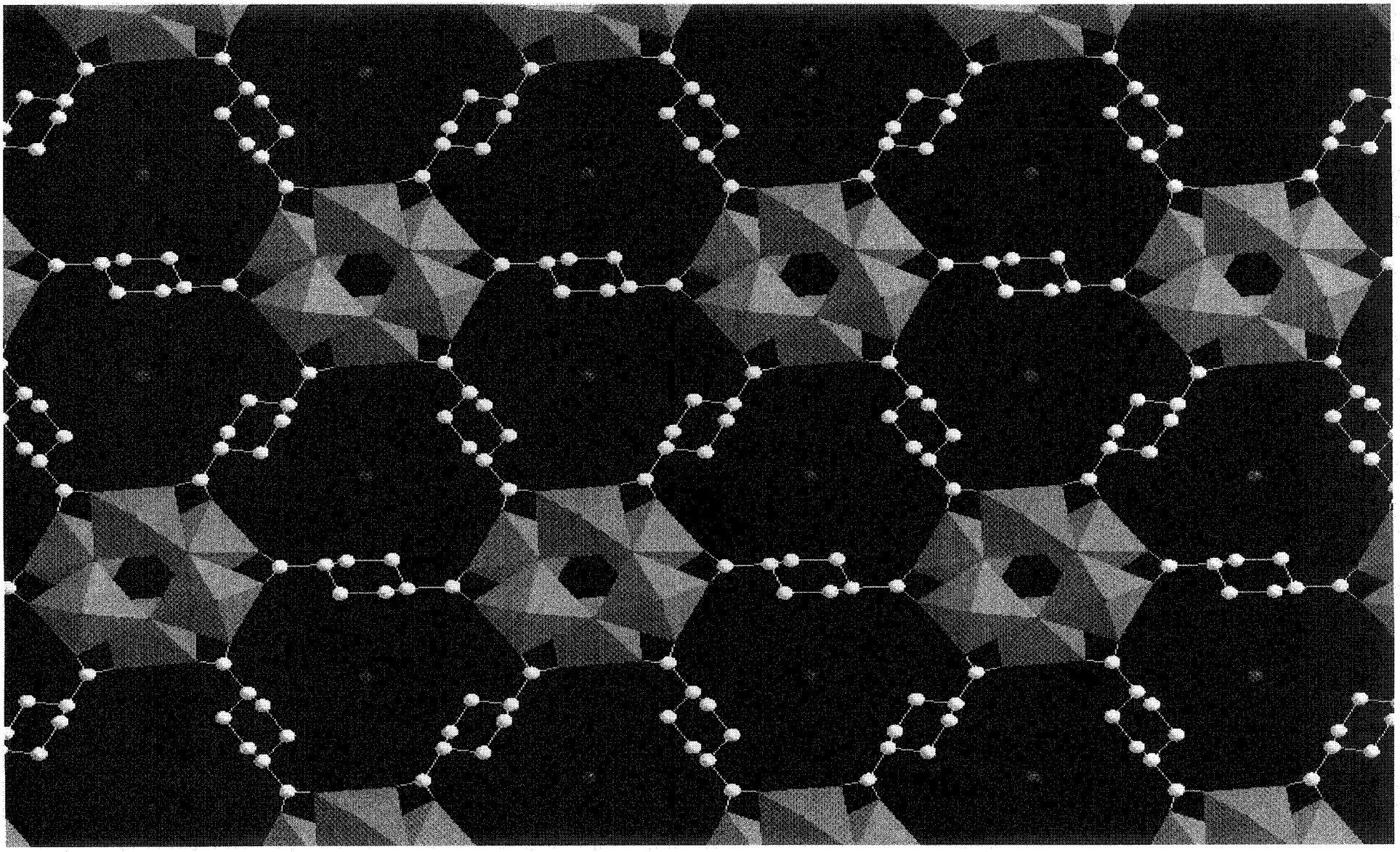
In our technique, the inorganic reactant is dissolved in water, and the organic component in a water immiscible alcohol. Reaction only occurs at high temperatures, with product formed at the interface.



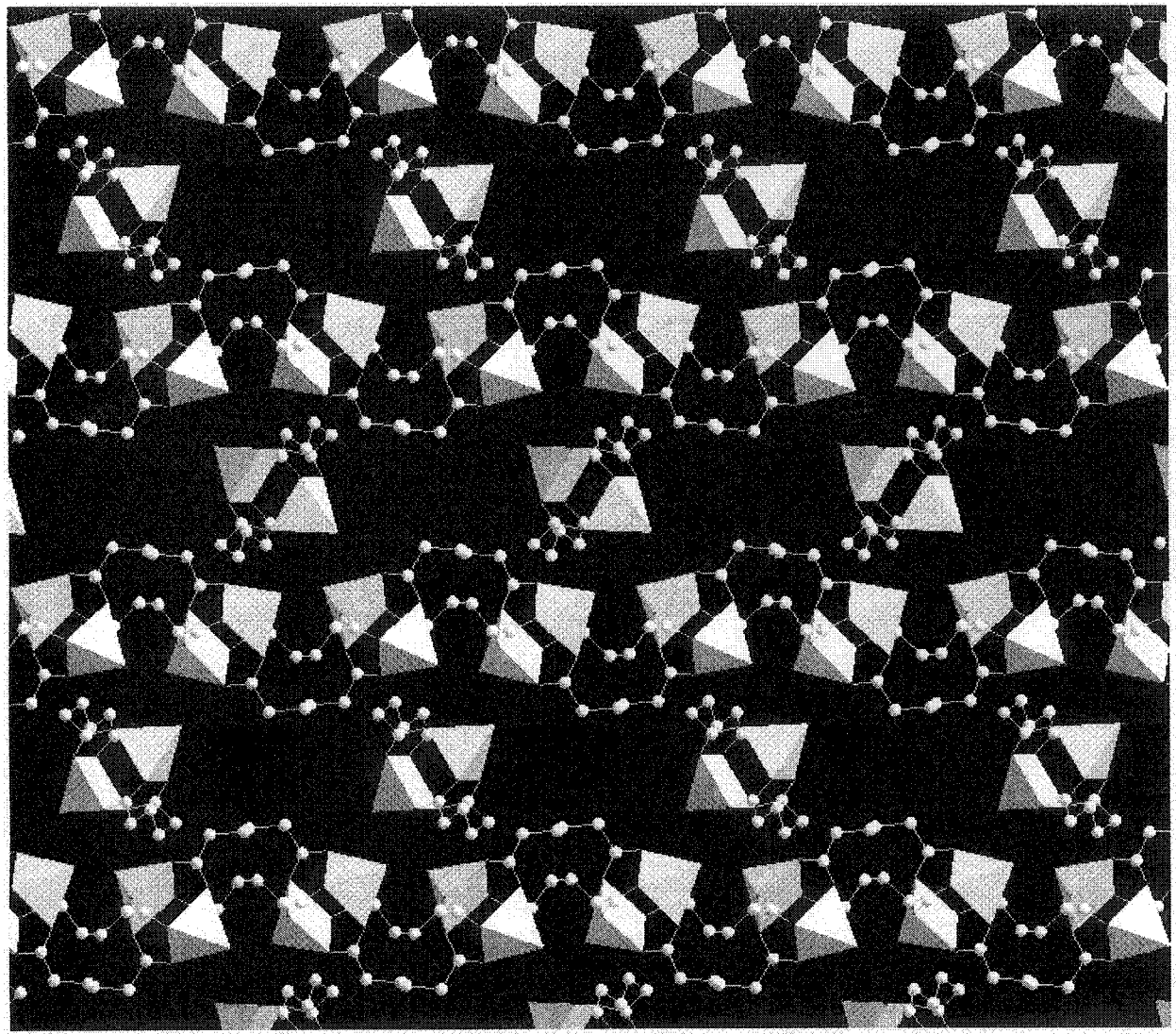
Nickel succinate, the most stable metal carboxylate known, with the structure persisting past 400 °C.

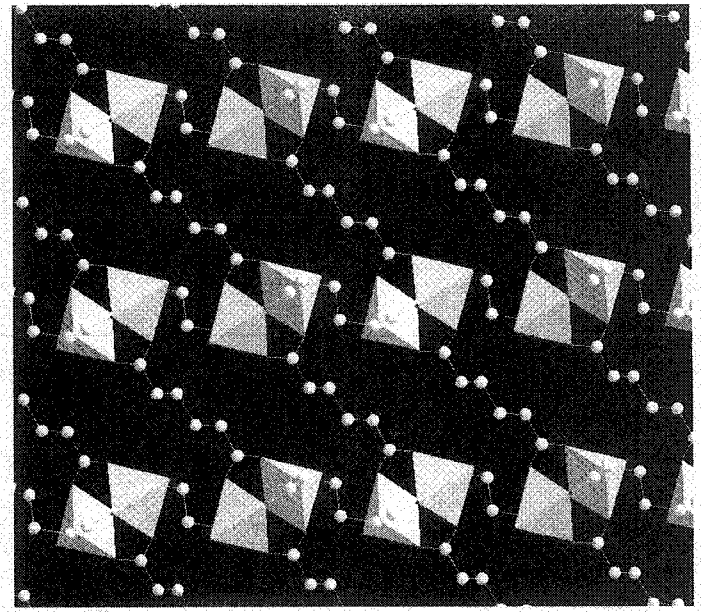


Nickel glutarate. This framework is also stable to 400 °C and the channels contain unsaturated Ni sites, ? for catalytic activity.

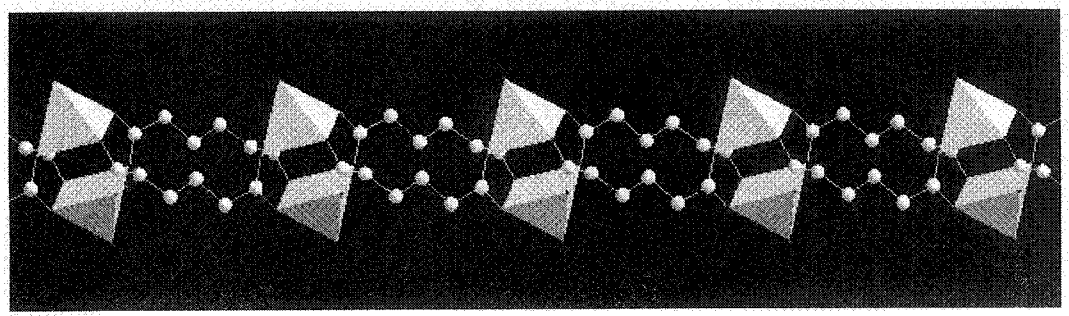


Nickel 1,4 Cyclohexanedicarboxylate





Copper adipate contains discrete 1 and 2-dimensional components.



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