分子篩 Molecular Sieve
沸石 Zeolite

1

References

General introduction

- J . Weitkamp, *Solid State Ionics* 131 (2000) 175.
- M. Yates, *J. Mat. Sci.* 30 (1995) 4483-4491
- 蔡振章, "沸石於環境友善性線性烷基苯生產製程之催化應用" *化學* 65(4) (2007) 385-396
- Rabo, "Future opportunities in zeolite science and technology" *Appl.Catal. A: Gen.* 229 (2002) 7–10

Reference books

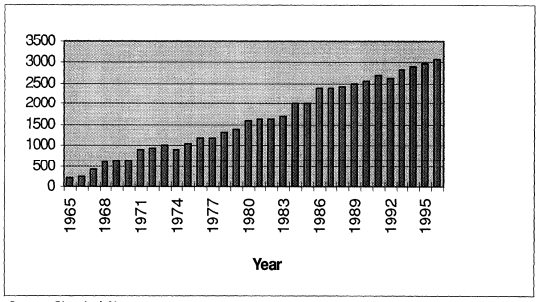
- H. van Bekkum, E. M. Flanigen & J. C. Jansen (eds.) *Introduction to Zeolite Science & Practice*, Elsevier, Amsterdam (1991)
- D. W. Breck, *Zeolite Molecular Sieves*, J. Wiley, New York (1974)
- 徐如人，龐文琴等人〈沸石分子篩的結構與合成〉吉林大學出版社 (1987)

3

Helpful References on Zeolites

- **A. Dyer, *Zeolite Molecular Sieves*, J. Wiley, New York (1988)**
- **H. van Bekkum, E. M. Flanigen, and J. C. Jansen (eds), *Introduction to Zeolite Science and Practice*, Elsevier, Amsterdam (1991)**
- **D. W. Breck, *Zeolite Molecular Sieves*, J. Wiley, New York (1974)**
- **R. M. Barrer, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, London (1978)**
- **R. M. Barrer, *Hydrothermal Chemistry of Zeolites*, Academic Press, London (1982)**
- **G. Gottardi and E. Galli, *Natural Zeolites*, Springer Verlag, Berlin (1985)**

Number of Molecular Sieve Related Publications



Source: Chemical Abstracts

Introduction

- What is a Molecular Sieve Zeolite?
- Its Brief History?
- Natural and Synthetic Zeolites
- Zeolite Nomenclature

What is a Molecular Sieve Zeolite?

8

The Word‘Zeolite’is Derived from Greek (希臘文)

- *Zeo* - “ to boil”
- *Lithos* - “a stone”
- Name was given to this class of materials by Swedish minerologist Baron Axel F. Cronstedt (1722–1765) in 1756
- Based on his experience with *stilbite* - when heated, the material bubbled as if it were boiling

9

Cronstedt’d Discovery

Cronstedt paper

(a) the Swedish specimen was light yellow, the Iceland specimen was white;

(b) the former material was composed of spherulites and wavy fragments consisting of radiating pyramids 角錐體 whose apices 頂端apparently terminate in a center, the latter was a mixture of a massive opaque 不透明chalk-like material and tangled 糾纏concentric wedges 楔形物;

(c) the hardness of both samples corresponded to that of normal spar 晶石or massive limestone earth;

(d) in the blow-pipe flame both samples emitted gas and puffed 噴的一吹up almost like borax 硼砂; in the Swedish specimen, in particular, the pyramids were initially transformed into a white spongy mass which subsequently fused with a phosphorescent glow to a white glass;

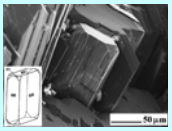
(e) when placed on charcoal the Swedish specimen, but not the Icelandic specimen, could be melted into a pure glass. Because it came from a copper mine, traces of copper impurity colored the glass in opaque reddish-brown; the green color of the flame also indicated copper.

Gualtieri, *Micro. Meso. Mat.* 105 (2007) 213–221; Deventer, *Chem. Mater.* 17 (2005) 3075-3085

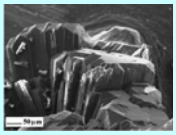
10

250 Years after

cavity of Cronstedt’s zeolite crystals (x20)

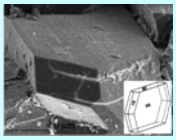


a cavity with stellerite crystals



aggregate with stellerite crystals

- the first zeolite studied by Cronstedt was actually a mixture of stellerite with minor (less than 10% volume) stilbite
- The re-discovery of Cronstedt zeolite has an undoubted valence 掛布式框架 of historical character, as this event is the first step of a long and exciting story involving the discovery and study of natural zeolites that still continues today.



stilbite crystals which accompany stellerite in some zeolitized cavities

11

Glossary

- **Unit Cell** - Smallest repeating crystallographic unit of a zeolite framework
- **T-atom** - Tetrahedrally coordinated atom (normally Si or Al)
- **Framework Density** - Number of T-atoms per nm^3, also expressed in g/cc
- **SBU** - Secondary Building Unit

12

Broadest Definition

Zeolites are porous solids consisting of corner-sharing tetrahedra, representing a three-dimensional, four-connected net with T- atoms at the vertices of the net and oxygen atoms near the midpoints of the connecting lines.

13

Broad Definition

Zeolites are crystalline inorganic polymers based on a framework of XO_4 tetrahedra linked to each other by the sharing of oxygen ions, where X may be trivalent (e.g., Al, B, Ga,...), tetravalent (e.g., Ge, Si, ...) or pentavalent (e.g., P...)

14

Narrow Definition

A zeolite is a member of a class of crystalline aluminosilicates that has the following properties:

- Consists of a 3-dimensional structure arising from a framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ coordination polyhedra linked by all of their corners
- Comprises a framework which is generally open and contains channels and cavities in which are located cations and water molecules

15

Chemically

$$M_{2/n}O.\ Al_2O_3\ .\ ySiO_2\ .\ wH_2O$$

n = Cation valence

w = water contained in voids of the zeolite

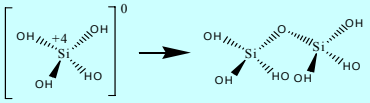
y = $SiO_2/A1_2O_3$ ratio

16

Zeolites from T-Atoms

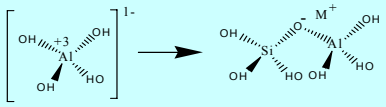
- $[Si\text{-}O\text{-}Si]^0$

  $\infty > Si/Al > 10000$



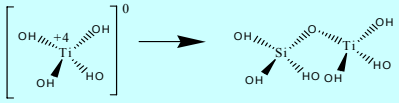
- $[Al\text{-}O\text{-}Si]^-\ M^+$

  $Si/Al > 1$



- $[Ti\text{-}O\text{-}Si]^0$

  $Si/Ti > 1$

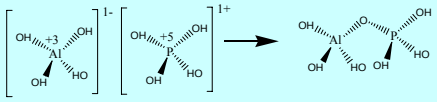


17

Zeolites from T-Atoms

- $[Al\text{-}O\text{-}P]^0$

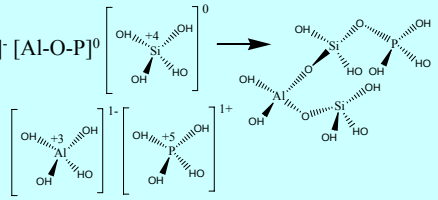
  $Al/P = 1$



- $M^+[Si\text{-}O\text{-}Al]^-\ [Al\text{-}O\text{-}P]^0$

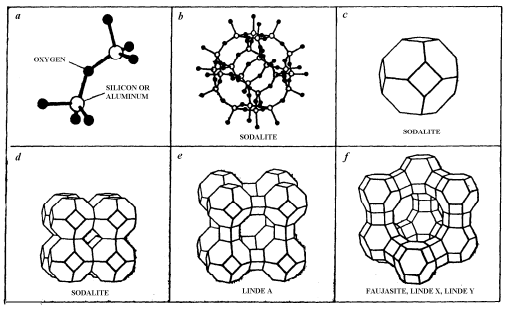
  $\infty > Si/Al > 0$

  $Si/P > 1$

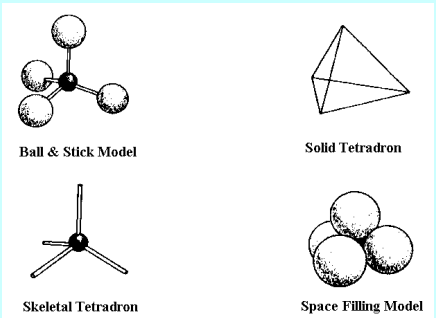


18

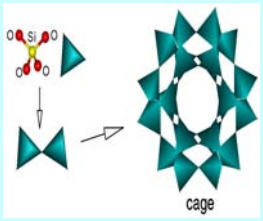
Zeolite Frameworks



Primary Building Units



Structure of Zeolites



- A defining feature of Zeolites are the 4-connected networks of atoms.
- One way of thinking about this is in terms of tetrahedral, with a silicon atom in the middle and oxygen atoms at the corners.
- These tetrahedra can then link together by their corners to form a variety of beautiful structures.

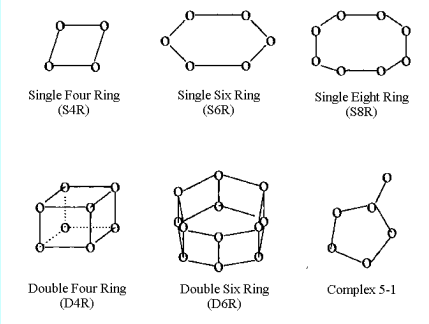
21

Structure of Zeolites

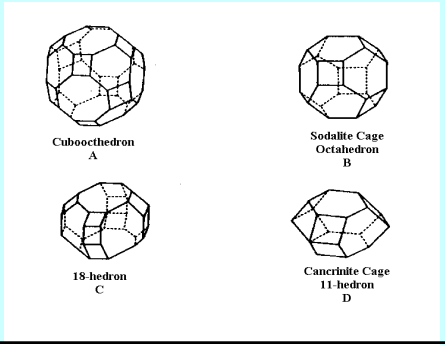
- These tetrahedra can then link together by their corners to form a variety of beautiful structures.
- The framework structure may contain linked cages, cavities or channels, which are the right size to allow small molecules to enter.
- Zeolites have basically three different structural variations.
  - Chain-like crystals
  - Sheet-like crystals
  - Equal in dimension

22

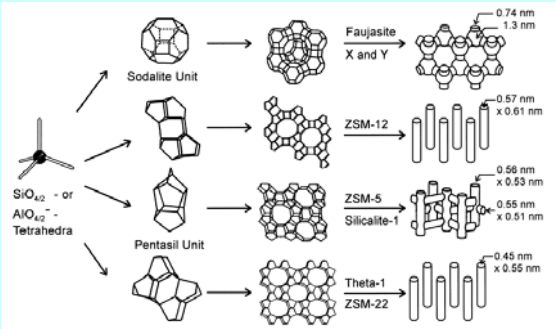
Secondary Building Units (SBU)



Some Cage Structures



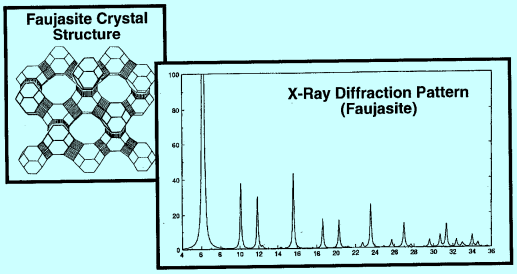
沸石之一級構造、二級構造與三維骨架結構



25

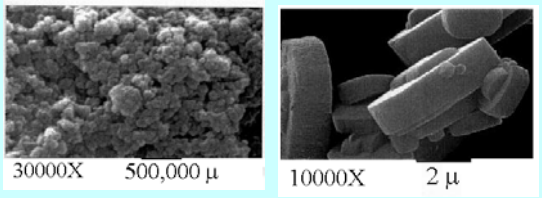
Weitkamp, Solid State Ionics 131 (2000) 175–188

X-Ray Diffraction Pattern vs. Crystal Structure



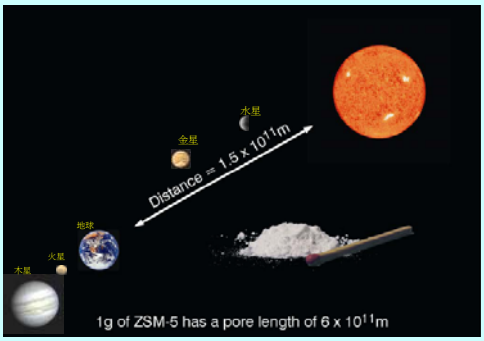
26

SEM of ZSM-5 Crystals
Size measurement by SE Detector



27

The Incredible Pore System of Zeolites



28

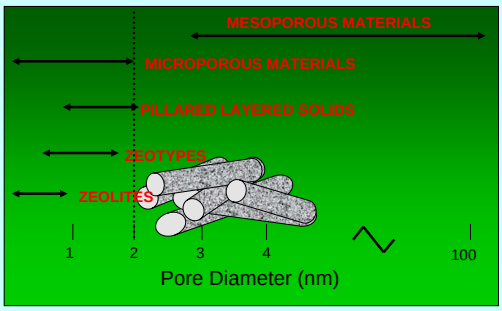
Egeblad, K, Christensen, C. H., Kustova, M., Christensen, C. H.,(2007) (Eds.) Roth, W., Cejka, J., Perez-Pariente, P.

Structure - Property Relationships

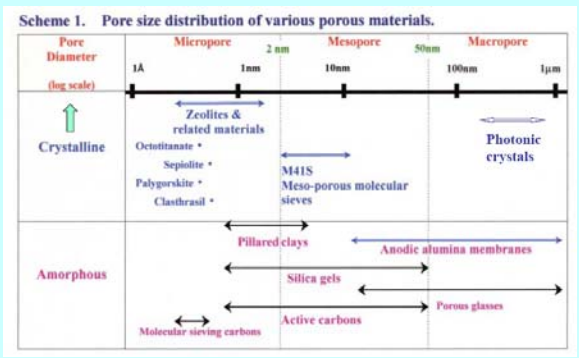
- Implications
- Structural Units
- Ordered & Disordered Structures
- Zoning
- Acid Sites

29

無機孔洞材料

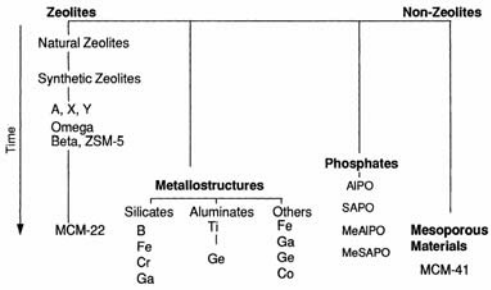


30



31

History of Molecular Sieves

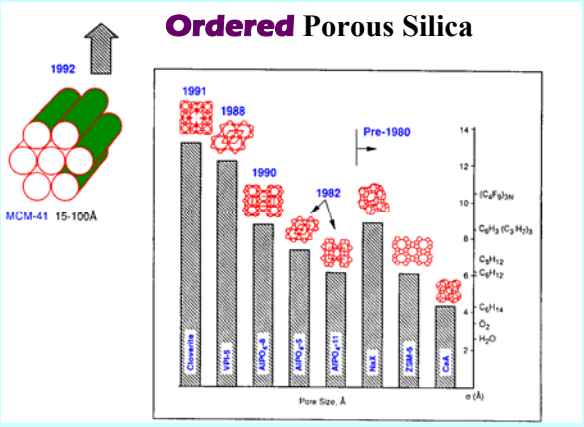


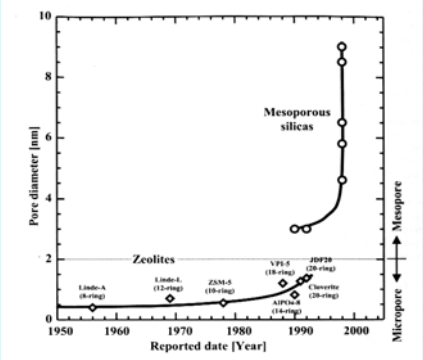
32

Evolution of Molecular Sieve Materials

- 1842 Discovery of Faujasite
- 1864 Discovery of Mordenite
- 1930-1934 First zeolite structure resolution
- Late 40's to early 50's Low SiO_2/Al_2O_3 ratio zeolites
- Mid- to Late 60's High SiO_2/Al_2O_3 ratio zeolites
- Early 70's High siliceous zeolites
- Late 70's Metallosilicates and metalloaluminosilicates
- Late 70s to early 80s $ALPO_4$, SAPO and MeAlPO molecular sieve
- Mid 80's VPI-5
- Early 90's MCM-41S materials

Ordered Porous Silica





K. Okada and K.J.D. MacKenzie, "Nanoporous Materials from Mineral and Organic Templates", Elsevier (2006)

Natural Zeolites

- Occur mainly in cavities of igneous rocks, such as basaltic and volcanic
- Some are known to be formed from natural alteration of volcanic ash in alkaline environments
- Most common natural zeolites in use: chabazite, erionite, mordenite and clinoptiolite

References

- http://www.bza.org/zeolites.html
- http://mineral.galleries.com/minerals/silicate/zeolites.htm
- http://members.aol.com/vbetz/Zeolites.html
- http://www.curriehj.freeserve.co.uk/skye6.htm

Natural Zeolites - Time Line

Date	Mineral	Described and named by
1756:	ZEOLITE GROUP	CRONSTEDT
1792:	CHABAZITE	BOSC D'ANTIC
1801:	S11LBITE	HAUEY
1801:	ANALCIME	HAUEY
1801:	HARMOTOME	HAUEY
1803:	NATROLITE	KLAPROTH
1808:	LAUMONTITE	HAUEY
1813:	SCOLECITE	GEHLEN & FUCHS
1816:	MESOLITE	FUCHS & GEHLEN
1817:	GISMONDINE	LEONHARD
1820:	THOMSONITE	BROOKE
1820:	HEULANDITE `	BROOKE
1822:	BREWSTERITE	BROOKE

Natural Zeolites - Time Line

Date	Mineral	Described and named by
1825	EDINGTONITE	HAIDINGER
1825	PHILLIPSITE	LEVY
1825	HERSCHELITE	LEVY
1825	GMELINITE	BREWSTER
1825	LEVYNE	BREWSTER
1826	EPISTILBITE	ROSE
1842	FAUJASITE	DAMOUR
1846	POLLUCITE	BREITHAUPT
1864	MORDENITE	HOW
1890	OFFRETITE	GONNARD
1896	GONNARDITE	LACROIX
1897	WELLSITE	PRATT & FOOTE
1898	ERIONITE	EAKLE

39

Natural Zeolites - Time Line

Date	Mineral	Described and named by
1906	DACHIARDITE	D'ACHIARDI
1909	STELLERITE	MOROZEWICZ
1918	FERRIERITE	GRAHAM
1932	CLINOPTILOLITE	SCHALLER
1952	YUGAWARALITE	SAKURAI & HAYASHI
1955	WAIRAKITE	STEINER
1957	BIKITAITE	HURLBUT
1960	PAULINGITE	KAMB & OKE
1962	GARRONITE	WALKER
1974	MAZZITE	GALLI, PASSAGLIA, PONGILUPPI, RINALDI
1975	BARRERITE	PASSAGLIA & PONGILUPPI
1975	COWLESITE	WISE & TSCHERNICH
1977	MERLINOITE	PASSAGLIA, PONGILUPPI, RINALDI

40

Natural Zeolites - Time Line

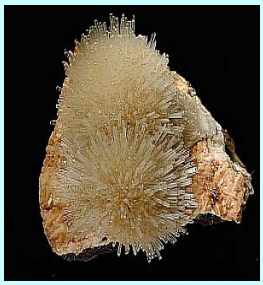
Date	Mineral	Described and named by
1979	AMICITE	ALBERTI, HENTSCHEL, VEZZALINI
1980	PARANATROLITE	CHAO
1980	TETRANATROLITE	CHEN & CHAO
1980	GOOSECREEKITE	DUNN, PEACOR, NEWBERRY, AND RAMIK
1982	GOBBINSITE	NAWAZ & MALONE
1984	WILLHENDERSONITE	PEACOR, DUNN, SIMMOMS, TILLMANNS, FISCHER
1984	PERLIALITE	MEN'SHIKOV
1990	BOGGSITE	HOWARD, TSCHERNICH, SMITH, KLEIN
1991	MONTESOMMAITE	ROUSE, DUNN, GRICE, SCHLENKER, HIGGINS
1992	TSCHERNICHITE	B+OGGS, HOWARD, SMITH, KLEIN

Source: R. W. Tschemich, ***Zeolites of the World***, Geoscience Press, Inc. (1992)

41

Structural Variations of Zeolites

- There are chain-like structures whose minerals form needle-like prismatic crystals, i.e. Natrolite.



42

Structural Variations of Zeolites

- Sheet-like structures where the crystals are flattened or tubular, i.e. Heulandite.

43

Structural Variations of Zeolites

- Framework structures where the crystals are more equal in dimensions, i.e. Chabazite.

44

ZEOLITE GROUP

Reference: **Fleischer's Glossary of Mineral Species**
M.E. Back & J.A. Mandarino, Miner. Rec. Ed., Tuscon (AZ), 2008, 345 pp

MINERAL GROUPS

A mineral group, consisting of **at least 3 species**, involves members having **similar chemical formulae** and, ideally, the **same general structure**, thus belonging to the same crystal system
(not often respected)

ZEOLITE GROUPS

(Alumino)silicates ("and related"?) with framework structures containing **open cavities** in the form of **channels** and **cages**, usually occupied by H_2O and **extra-framework** (charge-compensating) **cations**.
Crystallography varies within the group.

90 officially recognized species (as for August 2008, including Direnzoite) are partitioned between series species and non-series species

45

SERIES

Series can be defined on the basis of **dominant extra-framework cations**

In the case of zeolites, series were established for **15 generic species**, each involving 2 or more species:

BRE (Monoclinic): Ba, Sr ➔ Ex: **Brewsterite-Ba**

CHA (Trigonal): Na, K, Ca, Sr
Note: **Herschellite** (discredited) ➔ **Chabasite-K**

CLI (Monoclinic): Na, K, Ca

DAC (Monoclinic): Na, Ca

ERI (Hexagonal): Na, K, Ca

FAU (Cubic): Na, Ca, Mg
Note: Kaiserstuhl: presence of both **FAU-Na** & **FAU-Mg**
FAU-Ca exclusively found at Vogelsberg

46

SERIES

FER (Orth. & Mon.): Na, K, Mg

GME (Hexagonal): Na, K, Ca

HEU (Monoclinic): Na, K, Ba, Ca, Sr

LEV (Trigonal): Na, Ca

MAZ (Hexagonal): Na, Mg
Note: Mt Semiol = **Mazzite-Mg**; **Mazzite-Ca** = Boron (CA)

PAU (Cubic): K, Ca

PHI (Monoclinic): Na, K, Ca

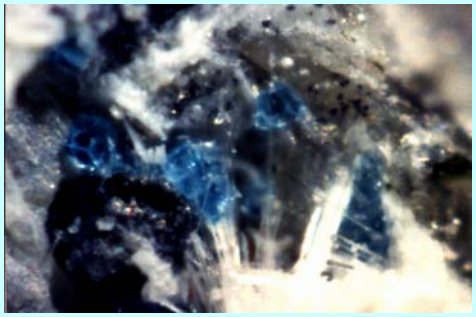
STI (Monoclinic): Na, Ca

THO (Orthorhombic): Ca, Sr

Total: 41 valid species

47

RARE ZEOLITES, UNUSUAL COLORS, UNEXPECTED COMPOSITIONS



48

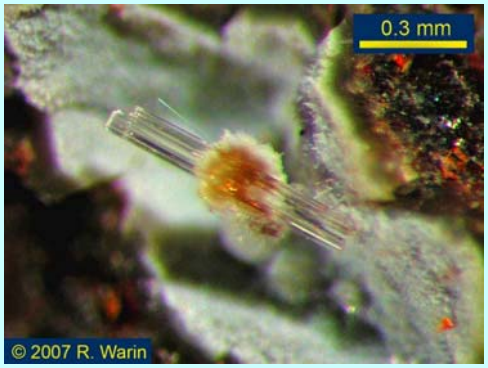
RARE ZEOLITES, UNUSUAL COLORS, UNEXPECTED COMPOSITIONS

49

RARE ZEOLITES, UNUSUAL COLORS, UNEXPECTED COMPOSITIONS

50

RARE ZEOLITES, UNUSUAL COLORS, UNEXPECTED COMPOSITIONS



51

RARE ZEOLITES, UNUSUAL COLORS, UNEXPECTED COMPOSITIONS

52

RARE ZEOLITES, UNUSUAL COLORS, UNEXPECTED COMPOSITIONS

53

RARE ZEOLITES, UNUSUAL COLORS, UNEXPECTED COMPOSITIONS

54

NEW TOPOLOGIES ?

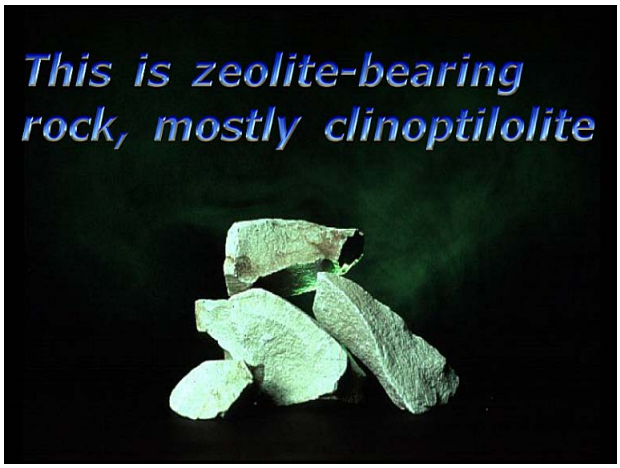
55

NEW TOPOLOGIES ?

56

NEW TOPOLOGIES ?

57



Zeolite-based products in various grain sizes, from Mexico.

"ZEOLITHE INFAILLIBLE" : FIRST APPLICATION ?

60

Zeolite / Clinoptilolite

Chemical composition Zeolite % by vol.

Composition	
SiO_2	81.13
Al_2O_3	9.66
K_2O	6.188
CaO	1.957
Na_2O	0.327
Fe_2O_3	0.898
MgO	0.376
Si/Al ratio	7.12

Formula $\cdots N_2(Al\ Si\ O_{12})x6H_2O$

Physical properties

Surface area (m^2/g)	22.0
Pore volume (cm^3/g)	0.052
Mean pore diameter (nm)	9.49

Cation exchange capacity

Exchange cap. 1.3mg eqv./g
Full exchange cap. 1.9-2.4 mg eqv./g

Major exchangeble cations: Rb, Li, K, Na, Ag, Cd, Pb, Zn, Ba, Sr, Cu, Hg, Fe, Co, Al, Mg,

Primary absorbing gases: CO, CO_2, SO_2, H_2S, NH_3, C_2H_2 CH_3OH, CH_3NH_2, CH_3Cl, H_3Br

Zeolite Nomenclature

- There is no systematic nomenclature for zeolites
- Natural zeolites are often named after minerologists or locations where the crystal was discovered:
  - goosecreekite, brewsterite, tschernichite, barrerite
- Synthetic zeolites were systematically named by companies who patented the materials:
  - Union Carbide: A, L, X, Y, LZ
  - Mobil: ZK-, Greek alphabet, ZSM-, MCM-
  - Exxon: ECR
  - Chevron: SSZ
  - ICI: NU-, FU-, EU-

62

Other Nomenclatures

ALPO SAPO MAPO MEAPO
VPI CIT CF
Theta AMS AZ
EMC ECR CSZ TPZ TS TSZ
Silicalite

63

Zeolite Nomenclature

- Formalized Procedure Administered by the International Zeolite Association (IZA)
  - Three-letter codes given to unique zeolite topologies

Examples: ZSM-5 - MFI
Y and X - FAU
ZSM-12 - MTW
Beta - BEA
$ALPO_4$-5 - AFI

Source: W.M. Meier, D.H. Olson and Ch. Baerlocher, ***Atlas of Zeolite Structure Types***, Elsevier, 4th edition (1996)

64

Zeolite framework topologies by 3-letter code and framework type

Silicates			Silicates and phosphates	Phosphates
ABW	GOO	MOR	AFI	AEI
AFG	HEU	MTN	ANA	AEL
BEA	KFI	MTT	AST	AET
BIK	JBW	MTW	BPH	AFO
BOG	LAU	NAT	CAN	AFR
BRE	LIO	NES	CHA	AFS
CAS	LOS	NON	SRI	AFT
CHI	LOV	OFF	FAU	AFY
DAC	LTL	PAR	GIS	APC
DDR	LTN	PAU	LEV	APD
DOH	MAZ	PHI	LTA	ATN
EAB	MEI	ROG	RHO	ATO
EDI	MEL	SGT	SOD	ATS
EMT	MEP	STI	ATT	
EPI	MER	THO	ATV	
EUO	MFI	TON	AWW	
FER	MFS	WEN	CLO	
GME	MON	YUG	VFI	

65

Metalloaluminophosphates

Designation	Structure Type	Designation	Structure Type
Very Lg. Pore		**Small Pore**	
VPI-5	Novel, determined	14	Novel, determined
Large Pore		17	Erionite
5	Novel, determined	18	Novel
36	Novel	26	Novel
37	Faujasite	33	Novel
40	Novel	34	Chabazite
46	Novel, determined	35	Levynite
		39	Novel
		42	Linde Type A
Intermed Pore		43	Gismondine
11	Novel, determined	44	Chabazite - like
31	Novel	47	Chabazite - like
41	Novel		
		Very Small Pore	
		16	Novel
		20	Sodalite
		25	Novel
		28	Novel

66

Representative ALPO/SAPO/Zeolite

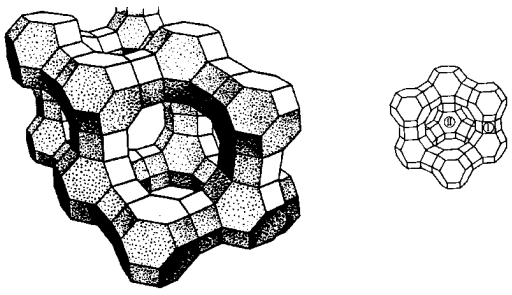
Code	Name	MR	Channel	Pore size(Å)
CHA	**ALPO/SAPO-34**[a]	8	3D	3.8 x 3.8
AEL	**ALPO-11/SAPO-11**[b]	10	1D	4.0 x 6.5
AFO	ALPO-41/SAPO-41	10	1D	4.3 x 7.0
MTT	ZSM-23	10	1D	4.5 x 5.2
ATO	ALPO-31/SAPO-31	12	1D	5.4 x 5.4
MTW	ZSM-12	12	1D	5.6 x 6.0
ATS	ALPO-36/~~SAPO~~/MAPO-36	12	1D	6.5 x 7.5
IWV	ITQ-27	12	2D	6.2 x 6.9
AFR	ALPO-40/SAPO-40	12	1D/2D	6.7 x 6.9
SFO	SSZ-51	12	1D/2D	6.9 x 7.1
AFT	ALPO-5/SAPO-5	12	1D	7.3 x 7.3
FAU	~~ALPO-37~~/SAPO-37	12	3D	7.4 x 7.4
AET	ALPO-8/~~SAPO-8~~	14	1D	7.9 x 8.7

[a]Isodewaxing
[b]Amination; MTO

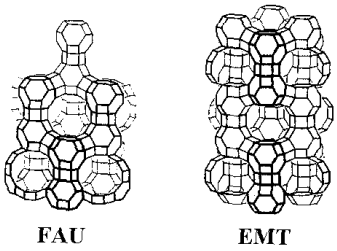
http://www.iza-structure.org/databases/

67

Faujasite Structure

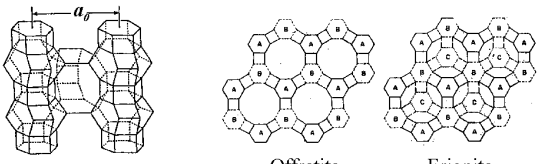


FAU (Cubic Faujasite) & EMT (Hexagonal Faujasite) Framework



FAU EMT

Erionite & Offretite



Hexagonal Offretite Erionite

	Volume(Å^3)	a	b	c(Å)	α	β	γ (°)
OFF	1159.95	13.29	13.29	7.58	90	90	120
ERI	2295.19	13.27	13.27	15.05	90	90	120

1	m	meter	Gm	Gram
1.00E-03	mm	millimeter	MG	milligram
1.00E-06	μm	micron	μg	microgram
1.00E-09	nm	nanometer	NG	nanogram
1.00E-10	A	Angstrom		
1.00E-12			PG	picogram
1.00E-15			FG	
1.00E-18			AG	

72

TYPES OF STRUCTURE

Code	Full Name	Secondary Building Units				Cage Units	Framework Density No. of T Atoms/nm^3
FAU	Faujasite	S4R	S6R		D6R	B	12.70
LTA	Linde Type A	S4R	S6R	S8R	D4R	A,B	12.90
RHO	Rho	S4R	S6R	S8R		A,B	14.30
CHA	Chabazite	S4R	S6R		D6R		14.60
KFI	ZK-5	S4R	S6R	S8R	D6R	A,C	14.70
OFF	Offretite	S4R	S6R		D6R	D	15.50
PHI	Phillipsite	S4R		S8R			15.80
ERI	Erionite	S4R	S6R		D6R	D	15.60
LTL	Linde Type L		S6R		D6R	D	16.40
MOR	Mordenite		5-1				17.20
MEL	ZSM-11		5-1				17.70
MFI	ZSM-5		5-1				17.90

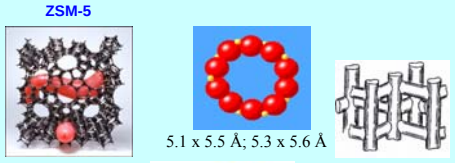
73

Framework Density (T-atoms/nm^3)

LTA	Zeolite A	12.7
FAU	Zeolite Y	12.5 – 12.9
ERI	Erionite	15.1
LTL	Zeolite L	16.1
MAZ	Mazzite (ZSM-4)	16.5
MOR	Mordenite	17.2
MFI	ZSM-5	17.9

74

C_6異構物與ZSM-5沸石孔洞



Hexane Isomer

n-hexane 4.1 x 4.1 x 9.0 Å 3.9 x 4.3 x 9.0 Å

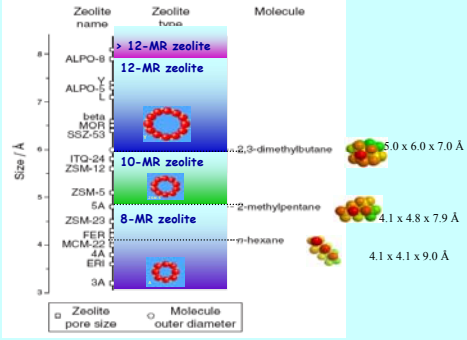
2-methylpentane 4.1 x 4.8 x 7.9 Å 4.6 x 5.8 x 8.6 Å

2,3-dimethylbutane 5.0 x 6.0 x 7.0 Å 5.9 x 6.2 x 6.7 Å

75

Chester, *Stud. Surf. Sci. Catal.* 28 (1986) p 547

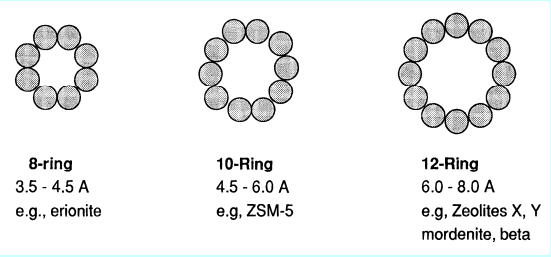
沸石孔洞口徑與已烷分子尺寸



Tsai, J. Chem. Edu. 2008

76

Typical Pore Sizes



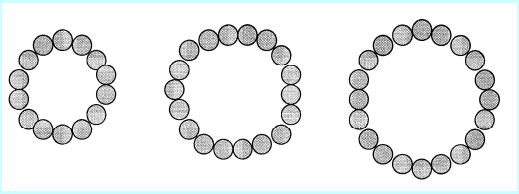
8-ring
3.5 - 4.5 A
e.g., erionite

10-Ring
4.5 - 6.0 A
e.g, ZSM-5

12-Ring
6.0 - 8.0 A
e.g, Zeolites X, Y
mordenite, beta

78

Some Newer Molecular Sieves Have Larger Pore Diameters



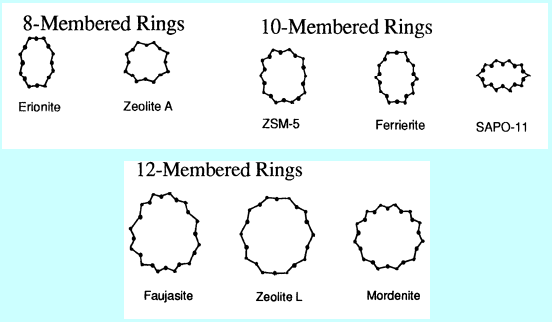
14-Ring
7.5 to 9 Å
ALPO-8

18-Ring
11.5 to 12.5 Å
VPI-5

20-Ring
12.5 to 14 Å
Cloverite

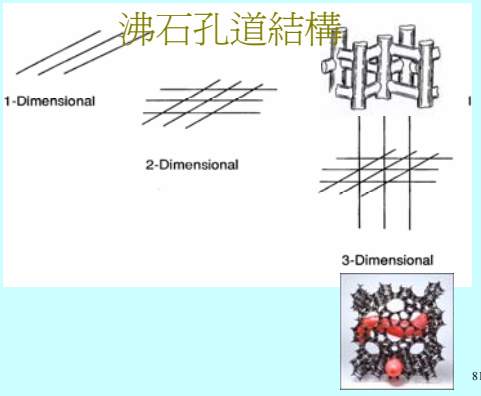
79

Pore Size and Shape



80

沸石孔道結構



81

Zeolite Matrix-Pore System

	1-Dimensional	2-Dimensional	3-Dimensional
12-MR	Zeolite L		Faujasite[i]
12MR X 10 MR	-	CIT-1[i]	
12MR x 8MR	-	Mordenite[i]	Gmelinite
10-MR	SAPO-11		ZSM-5[i]
10MR x 8MR	-	Ferrierite	Wenkite

82

Void Volume

Zeolite	Window No. O atoms	Window Size Å	Void Vol cc H_2O/cc
Zeolite A	8	4.5	0.47
Zeolite X, Y	12	7.8	0.53
Zeolite L	12	7.1	0.28
Mordenite	12	6.7 x 7.0	0.26
	8	2.9 x 5.7	
ZSM-5	10	5.6 x 5.4	0.32

83

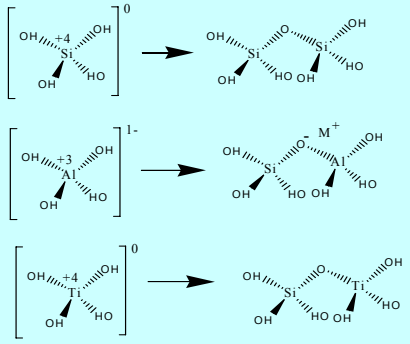
Zeolite Matrix-Pore System

	1-Dimensional	*2-Dimensional*	*3-Dimensional*
12-MR	Zeolite L		Faujasite[j]
12MR X 10 MR	-	CIT-1[i]	
12MR x 8MR	-	Mordenite[j]	Gmelinite
10-MR	SAPO-11		ZSM-5[j]
10MR x 8MR	-	Ferrierite	Wenkite

84

Zeolites from T-Atoms

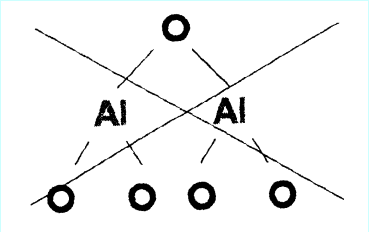
- $[Si\text{-}O\text{-}Si]^0$
  $\infty > Si/Al > 10000$
- $[Al\text{-}O\text{-}Si]^- M^+$
  $Si/Al > 1$
- $[Ti\text{-}O\text{-}Si]^0$
  $Si/Ti > 1$



85

Lowenstein's Rule

No two aluminum atoms can share the same oxygen atom:



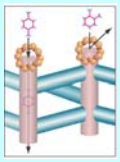
86

Zeolite SiO_2/Al_2O_3 Ratio

Classification	SiO_2/Al_2O_3 Ratio (Molar)	Examples
Low Silica	$2 < SiO_2/Al_2O_3 < 4$	A, X, Erionite
Intermediate Silica	$4 < SiO_2/Al_2O_3 < 10$	Y, Mordenite, L, Offretite
High Silica	$10 < SiO_2/Al_2O_3$	ZSM-5, beta, most synthetic zeolites

Si/Al ratio

- Low-silica (Si/Al <2): strong acidity, unstable at high temperature
  - Hydrated low-silica zeolites: ion-exchange applications
    - High cation content leads to high exchange capacities
  - Dehydrated form: adsorption and separation applications
    - Interactions between the under-coordinated cations and the sorbate molecules are a crucial feature of this process
- High-silica (Si/Al >2): more thermal stability
  - Shape-selective catalysis
    - Acid-catalyzed reaction: exchangeable cation is replaced by a proton that provides Bronsted acidity
    - Shape and size of pores add the selectivity in the reaction
  - Isomerization catalysis in p-xylene production
- Pure-silica (Si/Al = infinity)
  - Candidate of low-k material for integrated circuit

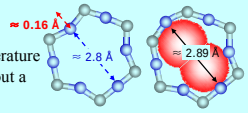


1: Cheetham A.K. et al., Angew.Chem.Int.Ed. 38 (1999), 3268-3292
2: Lai Z. et. Al., Science 300 (2003), 456

88

Thermal stability

- Framework flexibility
  - The lattice vibrations at high temperature make tetrahedra move or rotate about a bridging oxygen



- Structure Rigidity
  - Open frameworks are not the thermodynamically most stable structures compared to their condensed analogues, but the difference are quite small (≈15 kJ/mol, siliceous FAU/ α -quartz)
  - The strength of T-O bonds (e.g. ≈466 kJ/mol for Si-O bond)
    - render porous structures stable with respect to framework rearrangement and determine their thermal stability
    - Most of possible structures cannot remove organic guests in the pores without inducing the collapse of host structure
    - One family that approaches the stability of the silicates is the aluminum phosphates ($AlPO_4$)

1: van den Berg et al., J. Chem. Phys., 121(20) (2004), 10219-10216
2: van den Berg et al., J. Phys. Chem. B., 108 (2004), 5088-5094
3: Cheetham A.K. et al., Angew.Chem.Int.Ed. 38 (1999), 3268-3292

89

Thermochemistry of Silica

Framework	Framework density, Si/nm^3	Molar volume, cm^3/mol	ΔHtrans kJ/mol TO_2	ΔStrans J/(K · mol)
SBA-15		110.04	23.20	
MCM-41		71.59	19.33	
FAU	13.45	44.77	13.6	44.7
BEA	15.60	38.60	9.3	44.9
MWW	16.51	36.47	10.4	
MFI/F	17.97	33.51	6.8	45.1
MTW	19.39	31.06	8.7	
CHA	15.40	39.10	11.4	
Quartz	26.52	22.71	0.0	41.5

90

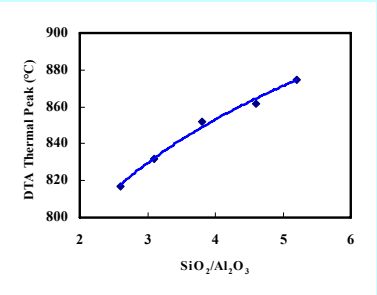
Navrotsky, Chem. Rev. 109 (**2009**) 3885

Thermal Stability
Decomposition Temperature

Type	Name	Pore Dia	SiO_2/Al_2O_3	Temp°C
LTA	NaA	4.5	2.0	600
FAU	NaX	7.8	2.4	712
FAU	NaY	7.8	4.9	793
MAZ	ZSM-4	7.5	2.5-6.0	750
LTL	L	7.1	3	850
MOR	Mordenite	6.7x7.0	10	1000
MFI	ZSM-5	5.4x5.6	> 10	>1050

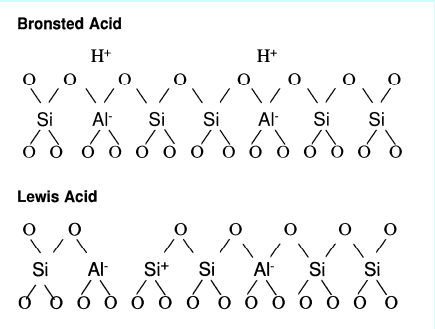
91

Thermal Stability of X- and Y- Zeolite in Sodium Form



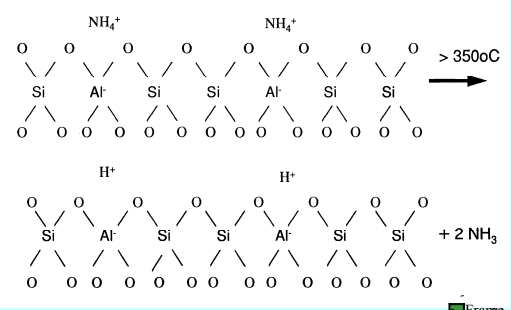
92

Acid Sites in Zeolites



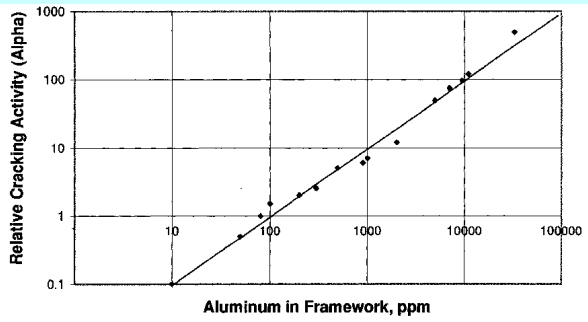
93

Conversion to the H-Form

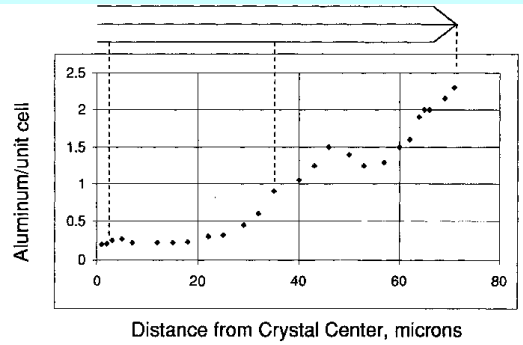


Frame Modification

Acid Activity Per Aluminum

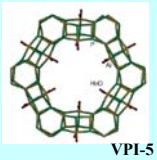


Zoning in ZSM-5 Crystal



Microporous Materials: Aluminum Phosphates

- $AlPO_4$-n
  - III-V analogues to aluminosilicates
    - Al and P are in alternating tetrahedral coordination ➡ Al/P ratio = 1
    - electrostatically neutral frameworks ➡ Modification is required regarding the chemical properties for catalysis, ion-exchange, etc.
- Partial incorporation of cations with different valences
  - Silicoaluminophosphates (SAPO-n), Metalaluminophosphates (MAPO-n), Metalsilicoaluminophosphates (MAPSO-n)
    - General formula: $(Si_xM_wAl_yP_z)O_2$, $0 \le x \le 0.20$, $0 \le w \le 0.25$
    - Si substitutes at phosphorus sites preferentially
    - Metal (M=Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}) at aluminum sites
  - Negative framework ➡ charge-compensating cations required
    - When these cations are protons, acid catalytic properties



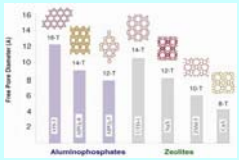
VPI-5

1: Cheetham A.K. et al., Angew.Chem.Int.Ed. 38 (1999), 3268-3292
2: Yu J., Xu R., Acc. Chem. Res., 36 (2003), 481-489

97

Greater Coordination for Aluminum

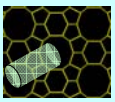
- Extra-large pore structures
  - $AlPO_4$ family usually can have more than 12-rings, while the pores in aluminosilicates are limited up to 14-ring at most
  - Poor thermal stability than aluminosilicateswer framework stability
  - Mixed metal ion coordination
    - Aluminum can adopt greater coordination numbers than 4, such as 6 coordination (octahedral)
  - Presence of non-tetrahedral framework species (H_2O, OH^-, F^-)
    - Water groups or anionic species such as hydroxide complete the coordination sphere of the aluminum



1: Davis M. E., Nature 417 (2002), 813-821
2: Francis R.J., Ohare D., J. Chem. Soc., 1998, 3133-3148

98

Mobility in Solids



Mobility of molecules
Porous materials
Intercalates
⇨ Molecular separations; Catalysis; Energy storage

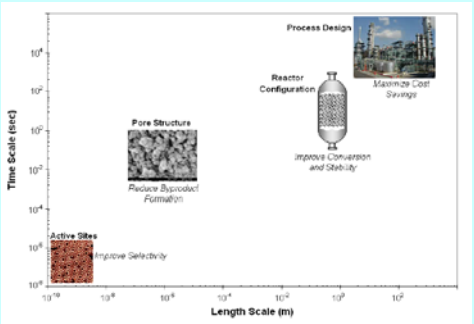
Mobility of ions
Porous materials
Intercalates
Ionic conductors
⇨ Ion-exchange separations; Batteries; Gas sensors; Fuel cell electrolytes

Immobility of molecules and ions
Dense phases
⇨ Immobilisation

Reactions in confinement
Porous materials
⇨ Control synthesis; Control polymerization

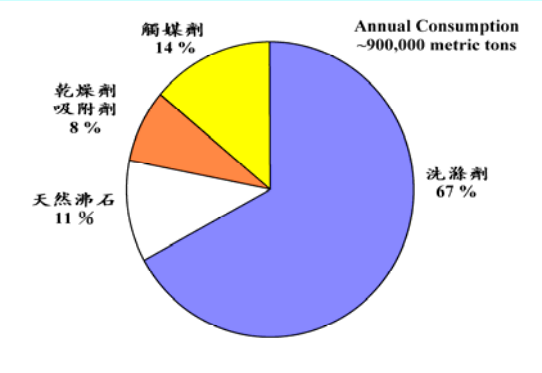
99

Nano – Macro Scale



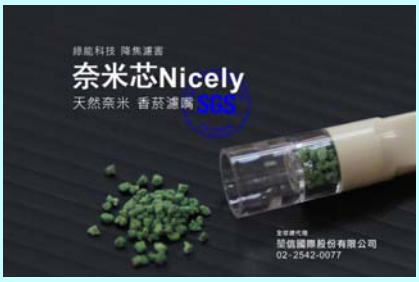
100

Worldwide Zeolite Consumption



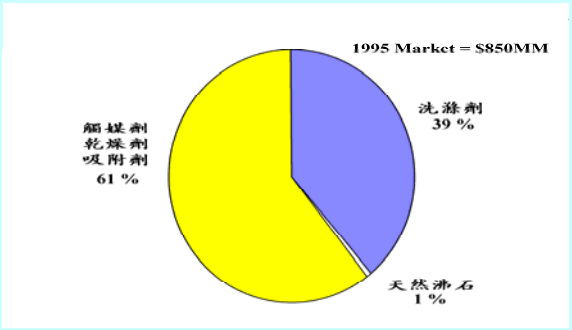
吸煙有害健康

- 吸附亞硝酸胺、多環芳香烴、自由基



102

U. S. Zeolite Market



103

Specialty Zeolite Market - Catalysis

Zeolite	Annual Market (mTons)	Market Value ($)
ZSM-5	1,000	
Mordenite	450	12 Million
Beta	400	
Others	80	4.5 Million

Source: Catalyst Consultants, 1992

How Zeolites Work

- Zeolites have the ability to act as catalysts for chemical reactions which take place within the cavities.
- Catalysis occurs by hydrogen-exchanged Zeolites, whose framework-bound protons give rise to very high acidity.

105

How Zeolites Work

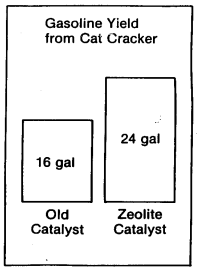
- Catalysis is used in many organic reactions.
  - Crude oil cracking
  - Isomerization
  - Fuel synthesis

106

等到二個世紀之後
Higher FCC Productivity by Zeolites

Introduced 1962

- 50% Increase in Gasoline Yield
- Saved 3.5 Billion Barrels of Crude
- Spurred Search for New Zeolites



1756
Discovery of Natural Zeolites by Cronstedt
1959
Catalytic Application in Gas Oil Cracking (FCC)

107

What is a Zeolite? How does it work?

- A variety of micropore sizes, shapes and connectivities:

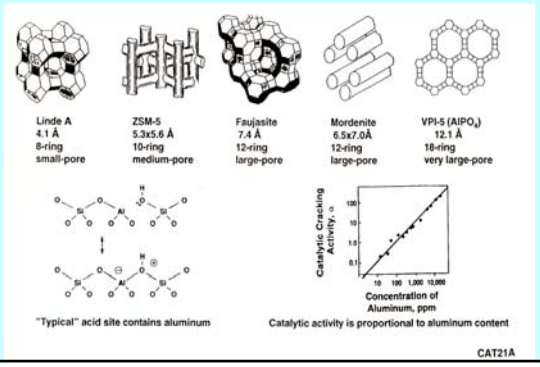
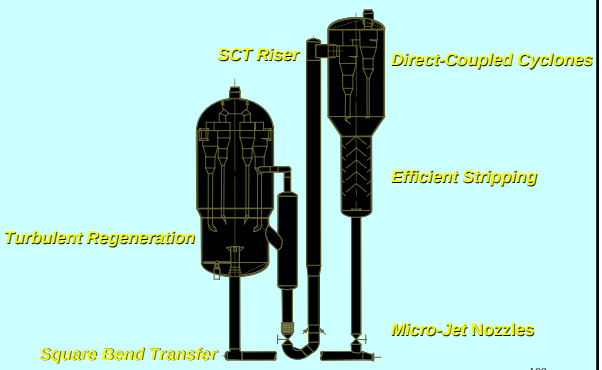
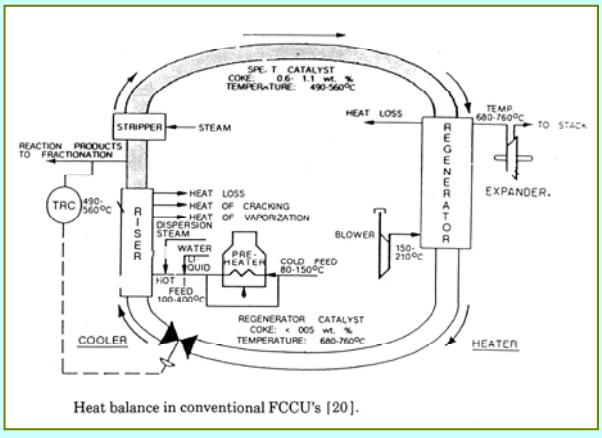


ABB Lummus FCC Process



109



Heat balance in conventional FCCU's [20].

How Zeolites Work

- The shape-selective properties of Zeolites are also the basis for their use in molecular absorption.
- This ability to absorb certain molecules, while excluding others, has opened a wide range of molecular sieving applications and purification processes.

111

How Zeolites Work

- Cation-containing Zeolites are extensively used as desiccants due to their high affinity for water, and also find application in gas separation.
- Organic solvents can be absorbed using silica Zeolites.
- Zeolites can separate molecules based on differences of size, shape and polarity.

112

How Zeolites are used Today

- Zeolites have many useful purposes
  - Ion-exchange
  - Filtering
  - Odor removal
  - Chemical sieve
  - Gas absorption tasks

113

How Zeolites are used Today

- The most well known use for Zeolites is in water softeners.
- Calcium in water can cause it to be “hard” and capable of forming scum and other problems.
- Zeolites charged with much less damaging sodium ions can allow hard water to pass through its structure and exchange the calcium for the sodium ions.

114

How Zeolites are used Today

- Since Zeolites can absorb ions and molecules they can act as a filter for odor control, toxin removal and chemical sieve.
- Most municipal water supplies are processed through Zeolites before public consumption.

115

Commercial catalytic uses of molecular sieves (refining and petrochemicals)

Zeolite	Y	L	MOR	BETA	MCM-22	ZSM-5	SAPO-11	Ferrierite	Rho	SAPO-34	Not identified
IZA code	FAU	LTL	MOR	BEA	MWW	MFI	AEL	FER	RHO	CHA	
Process											
Ethylbenzene					×	×					×
Cumene	×		×	×	×	×					
Other aromatics						×					
Xylene isomer						×					×
C_4 isomer			×								
C_8^{2-} isomer						×		×			×
C_7^{2-} isomer						×					×
Iso-dewaxing							×				
Amination			×			×			×	×	
C_3, C_4/aromatic						×					
Naphtha aromatic		×									
FCC	×					×					
Dewaxing						×					
Hydrocracking	×					×					
MTG						×					
MTO						×				×	
Toluene											
Trans-alkylation						×					×

Rabo, *Appl. Catal. A Gen.* 222 (2001) 261-275

116

Application of Molecular Sieves in Industrial Adsorption Processes

Fields of application	*Uses*		
	Drying	*Purification*	*Separations*
Refineries and petrochemical industry	Paraffins, olefins, acetylenes, reformer gas, hydrocracking gas, solvents	Sweetening* of ‘liquid petrol gas’ and aromatics, removal of CO_2 from olefin-containing gases, purification of synthesis gas	Normal and branched-chain alkanes
Industrial gases	H_2, N_2, O_2, Ar, He, CO_2, natural gas	Sweetening and CO_2 removal from natural gas, removal of hydrocarbons from air, preparation of protective gases	Aromatic compounds
Industrial furnaces	Exogas, cracking gas, reformer gas	Removal of CO_2 and NH_3 from exogas and from ammonia fission gas	Nitrogen and oxygen

*‘Sweetening’ is the removal of sulphur-containing compounds.

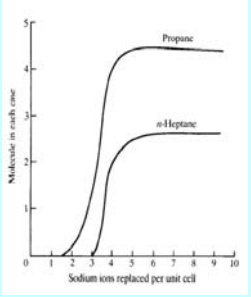
117

Ion Exchange: Fine-Tuning Pore Size

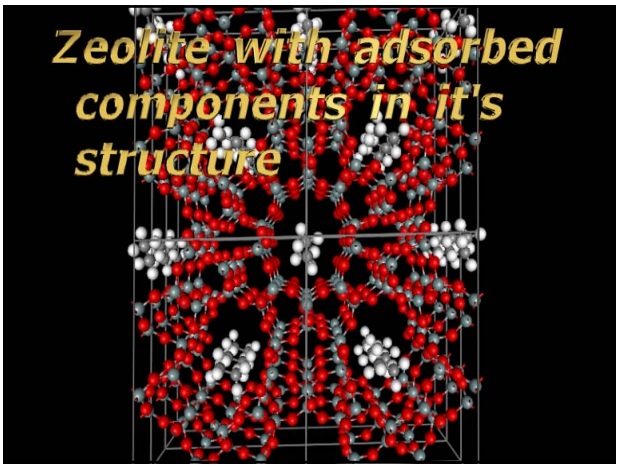
- Progressive exchange of $2Na^+$ for Ca^{2+} in Zeolite-A (LTA) leads to an increase in the pore aperture.

$Na_{12}[Al_{12}Si_{12}O_{48}]\cdot\{guests\}$
Ca^{2+} ⇵ Na^+
$Ca_6[Al_{12}Si_{12}O_{48}]\cdot\{more\ guests\}$

Ca-A is used for O_2 / N_2 separation:
O_2 diameter = 3.46 Å
N_2 diameter = 3.64 Å



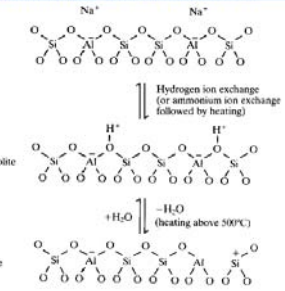
118



Microporous Catalysis

Catalytic activity is attributed to the presence of acidic sites, which may be Brønsted or Lewis in character.

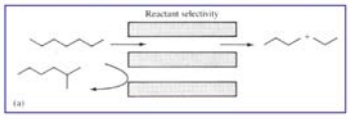
Zeolites:

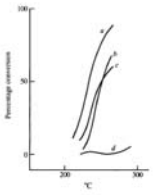


Reactant Shape Selective Catalysis

1) Reactant-selective catalysis:

Only molecules with dimensions less than a critical size can enter the pores and reach the catalytic sites, and so react there.





e.g., dehydration of butanols

a, b = *iso*-butanol, *n*-butanol in Ca-X (channel ~ 7 Å, cavity ~ 10 Å)

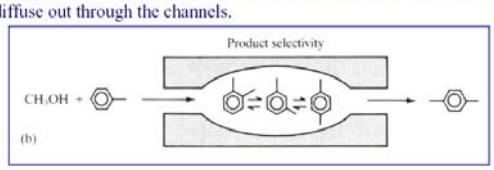
c, d = *n*-butanol, *iso*-butanol in Ca-A (channel ~ 4 Å , cavity ~ 10 Å)

121

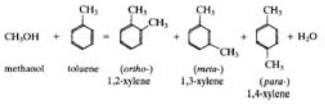
Product Shape Selective Catalysis

2) Product-selective catalysis:

Only products less than a certain dimension can leave the active sites a diffuse out through the channels.



e.g., synthesis of *para*-xylene with ZSM-5

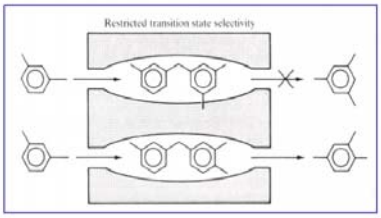


Transition-State Shape Selective Catalysis

3) Transition-state-selective catalysis:

Certain reactions are prevented because the transition state requires more space than is available in the cavities.

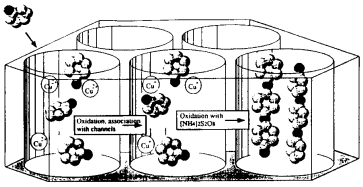
e.g., acid catalysed transalkylation of dialkylbenzenes



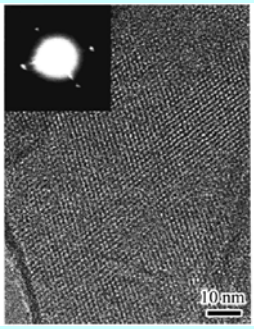
123

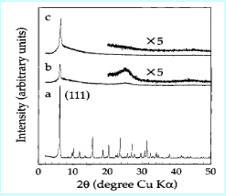
Encasement of Polymers in M41S

- Adsorb Aniline Monomer in Vapor Phase
- Conduct Polymerization (Oxidative)
- Allows Control of Polymer Morphology and Physical Properties



124

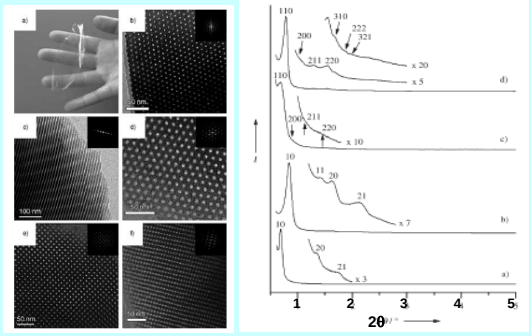




XRD patterns of zeolite Y and Carbons (a) zeolite Y; (b) the carbon prepared by the previous procedure; (c) the carbon from the present method

125

Kyotani, *Chem. Mater.* **2001,** *13,* 4413-4415

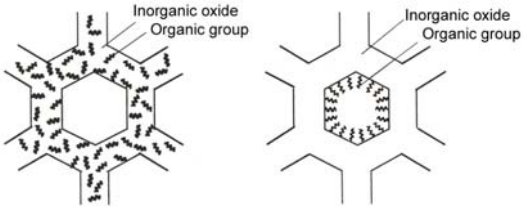


Zhao, *Angew. Chem. Int. Ed.* 2005, 44, 7053 –7059

126

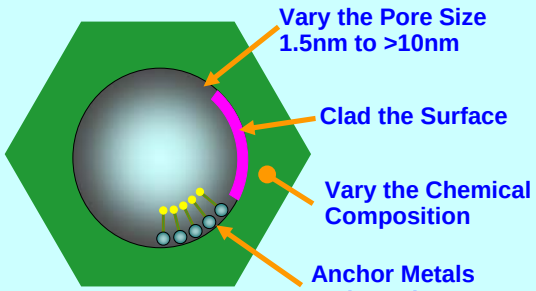
Pores Can Be Functionalized by Direct Synthesis or by Post Treatment Methods

Functionalized groups can be a component of the synthesis mixture and subsequently part of the pore wall or anchored to the pore walls using the silanol groups



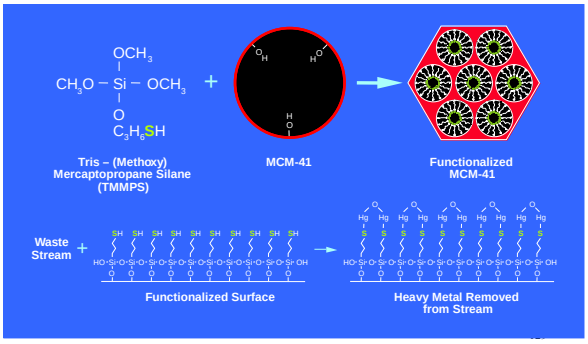
127

MCM-41: A New Class of Nanomaterials

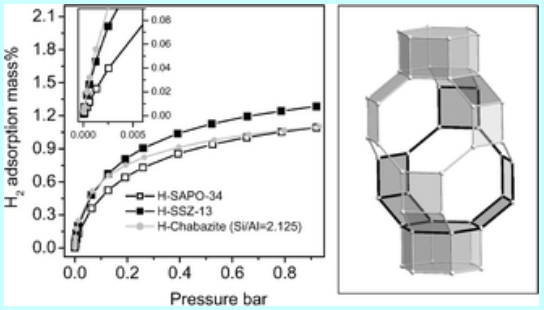


128

Functionalized MCM-41 Is Used To Remove Heavy Metals From Aqueous Waste Streams



Hydrogen storage in Chabazite zeolite frameworks



Regli, ***Phys. Chem. Chem. Phys.***, 2005, **7**, 3197 - 3203

130