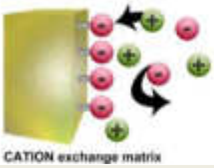
Physical properties of minerals: how and why to dive into their knowledge

12-15 febbraio 2018, Casa della Gioventù Universitaria, via Rio Bianco 12, 39042 Bressanone

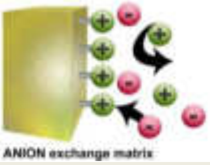
MINERALOGICAL SCHOOL OF THE
NATIONAL MINERALOGICAL GROUP (GNM)
AND
ITALIAN SOCIETY OF MINERALOGY AND
PETROLOGY (SIMP)

Sponsored by University of Calabria, University of Modena e Reggio Emilia University of Napoli "Federico II, University of Padova, University of Pisa, University of Trieste

Main topics



CATION exchange matrix



ANION exchange matrix

POROUS MATERIALS:

- *Concept of Porosity*
- *Main Characteristics of Powders and Porous Solids;*
- *Overview of hierarchical structured porous materials.*

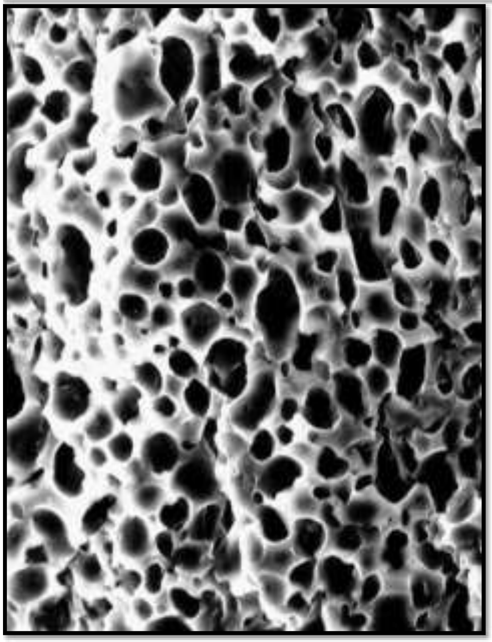
SELECTED ADVANCES IN FUNCTIONAL POROUS SOLIDS:

- *Natural and Synthetic Zeolites;*
- *Metal Organic Frameowrks (MOFs);*
- *Mesoporous materials;*
- *Porous Clay Heterogeneous Structures (PCHSs).*

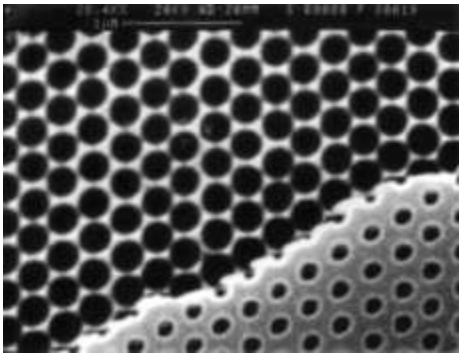
DIFFUSION IN POROUS CRYSTALLINE MATERIALS:

- *Ion exchange processes;*
- *Ion exchangers: relations between structural features and Properties.*
- *How to use porous exchangers: applications.*

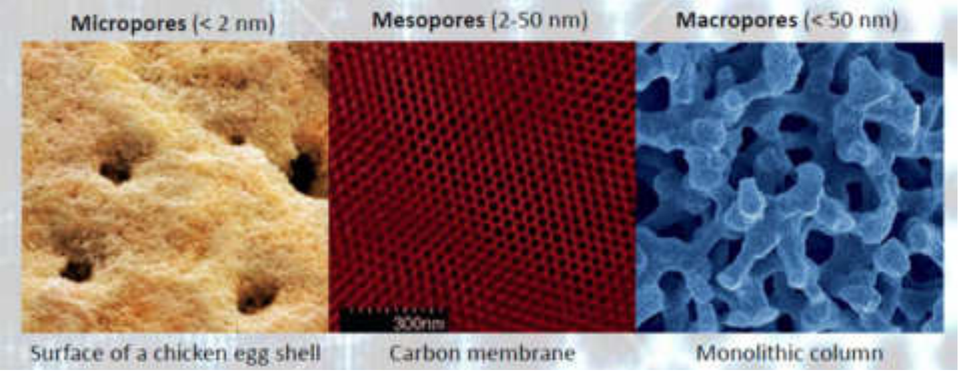
Porous materials



Porous materials are materials with pores (cavities, channels or interstices). The characteristics of a porous material vary depending on the size, arrangement and shape of the pores, as well as the porosity (the ratio of the total pore volume relative to the apparent volume of the material) and composition of the material itself.



Main Characteristics of Powders and Porous Solids

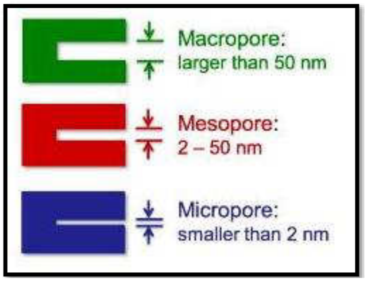


Surface of a chicken egg shell

Carbon membrane

Monolithic column

Porous materials are classified according to the size of pores: material with pores less than <u>2 nm are called micropores,</u> materials with pores between <u>2 and 50 nm are called mesopores,</u> and material with pores <u>greater than 50 nm are macropores</u>.

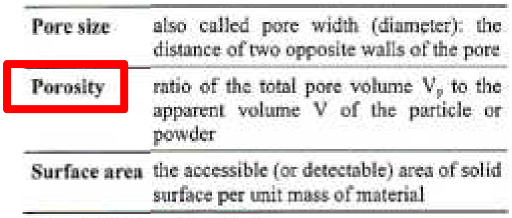


Concept of Porosity: Open vs. Closed Pores

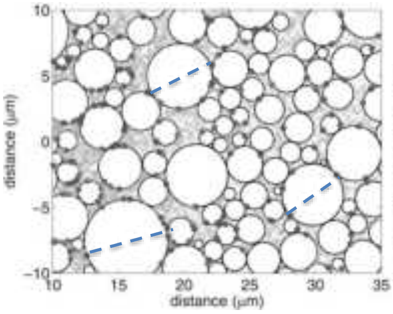
Porosity is a measure of the void fraction in a material. Voids can either be 'closed', and inaccessible or 'open' and connected to other voids and thence to the exterior of the material. The total porosity (φ) is defined by the ratio of the volume of void space (VV) to the total, or bulk volume of the material (VT):

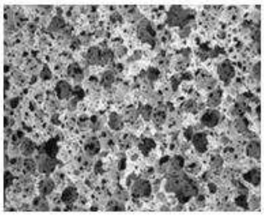
$$\phi = \frac{V_V}{V_T}$$

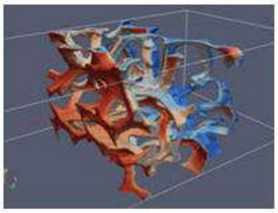
Porosity can also be expressed as a percentage of the bulk volume of the material.



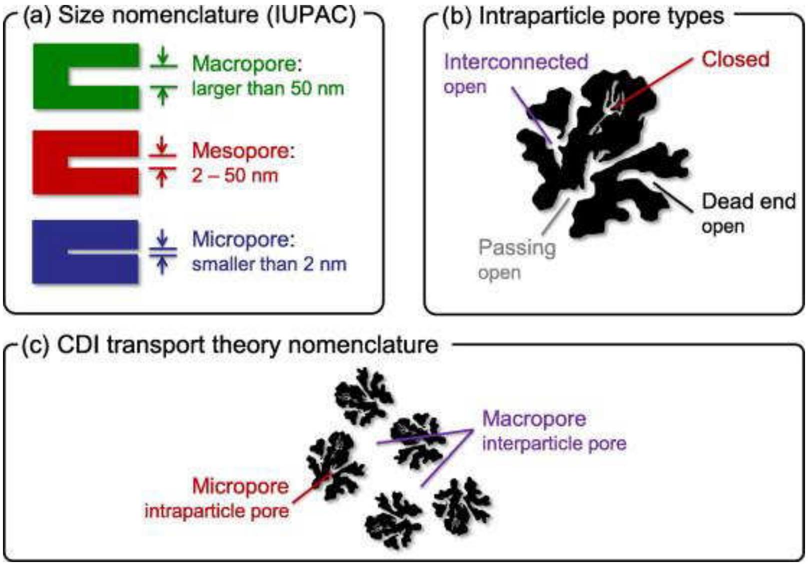
Pore size	also called pore width (diameter): the distance of two opposite walls of the pore
Porosity	ratio of the total pore volume V_p to the apparent volume V of the particle or powder
Surface area	the accessible (or detectable) area of solid surface per unit mass of material





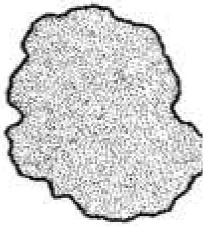


Main Characteristics of Powders and Porous Solids



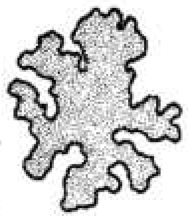
Pore nomenclature according to IUPAC (a), classification of intraparticle pores (b), and nomenclature in porous media transport theory (c).

Measurement of Porosity and Specific Surface Area
What are Porous Materials?



Non-porous solid

- **Low specific surface area**
- **Low specific pore volume**



Porous solid

- **High specific surface area**
- **High specific pore volume**

Porous materials have highly developed internal surface area that can be used to perform specific function.

Almost all solids are porous except for ceramics fired at extremely high temperatures

F. Rouquerol , J. Rouquerol , K. S. W. Sing, Adsorption by Powders and Porous Solids, Academic Press, 1-25, 1999

Overview of hierarchical structured porous natural materials

Chem. Soc. Rev., 2017, 46, 481 Copyright 2011, Wiley-VCH. Copyright 2011, Wiley-VCH.

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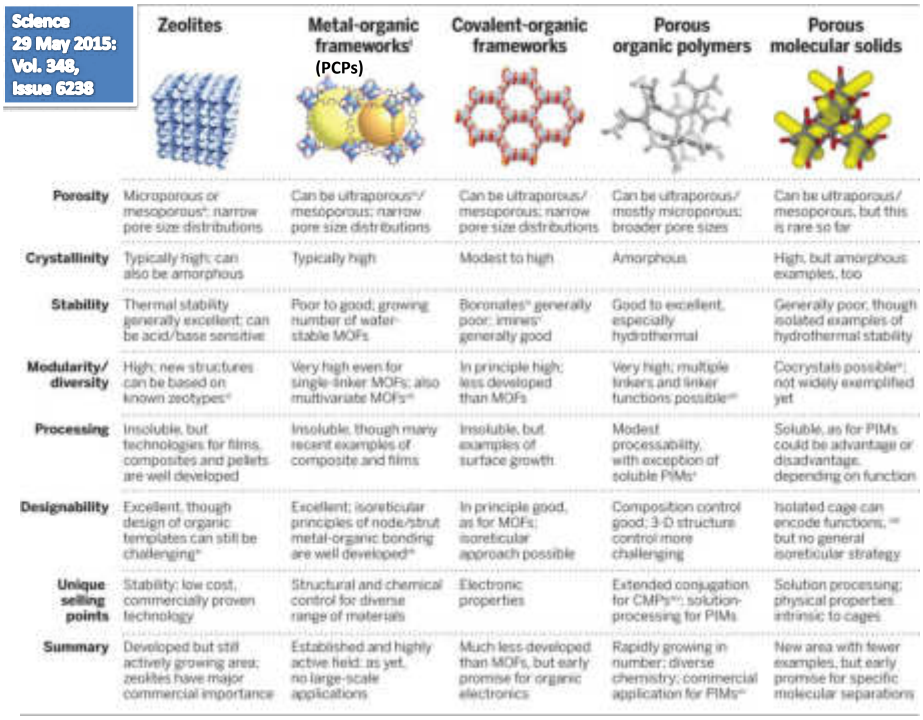
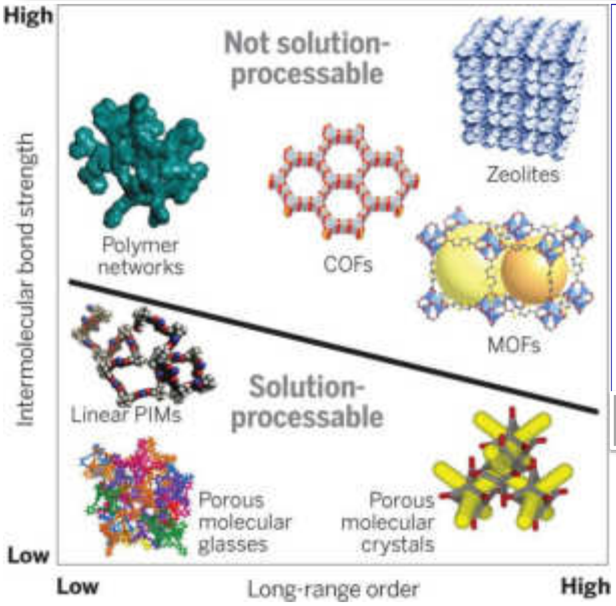
29 May 2015:
Vol. 348,
Issue 6238



	Zeolites	Metal-organic frameworks (PCPs)	Covalent-organic frameworks	Porous organic polymers	Porous molecular solids
Porosity	Microporous or mesoporous; narrow pore size distributions	Can be ultraporous/ mesoporous; narrow pore size distributions	Can be ultraporous/ mesoporous; narrow pore size distributions	Can be ultraporous/ mostly microporous; broader pore sizes	Can be ultraporous/ mesoporous, but this is rare so far
Crystallinity	Typically high; can also be amorphous	Typically high	Modest to high	Amorphous	High, but amorphous examples, too
Stability	Thermal stability generally excellent; can be acid/base sensitive	Poor to good; growing number of water-stable MOFs	Boronates generally poor; imines generally good	Good to excellent, especially hydrothermal	Generally poor, though isolated examples of hydrothermal stability
Modularity/ diversity	High; new structures can be based on known zeotypes	Very high even for single-linker MOFs; also multivariate MOFs	In principle high; less developed than MOFs	Very high; multiple linkers and linker functions possible	Cocrystals possible; not widely exemplified yet
Processing	Insoluble, but technologies for films, composites and pellets are well developed	Insoluble, though many recent examples of composite and films	Insoluble, but examples of surface growth	Modest processability, with exception of soluble PIMs	Soluble, as for PIMs could be advantage or disadvantage, depending on function
Designability	Excellent, though design of organic templates can still be challenging	Excellent; isoreticular principles of node/strut metal-organic bonding are well developed	In principle good, as for MOFs; isoreticular approach possible	Composition control good; 3-D structure control more challenging	Isolated cage can encode functions, but no general isoreticular strategy
Unique selling points	Stability; low cost, commercially proven technology	Structural and chemical control for diverse range of materials	Electronic properties	Extended conjugation for CMPs; solution-processing for PIMs	Solution processing; physical properties intrinsic to cages
Summary	Developed but still actively growing area; zeolites have major commercial importance	Established and highly active field; as yet, no large-scale applications	Much less developed than MOFs, but early promise for organic electronics	Rapidly growing in number; diverse chemistry; commercial application for PIMs	New area with fewer examples, but early promise for specific molecular separations

FUNCTIONAL CLASSIFICATION OF POROUS SOLIDS



One way to classify porous materials is by their degree of long-range order and their intermolecular bond strengths. These parameters affect function; for example, long-range order may be useful in molecular sieving applications, and strong intermolecular bonds may promote chemical or thermal stability. Only molecular porous solids can be processed as true solutions.

Science 29 May 2015:
Vol. 348, Issue 623


V.

Beſchreibung und Unterſuchung

einer unbekannten Bergart,

Zeolithes genannt.

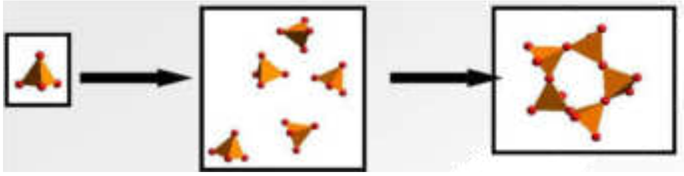
Von Axel Fr. Cronſtedt.

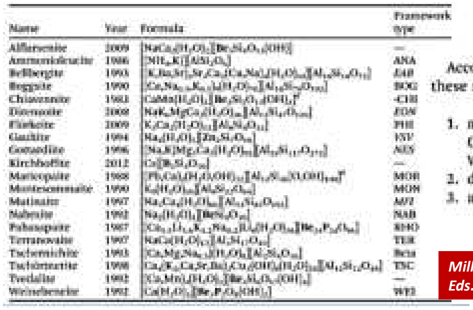
- In 1756, **Axel Cronstedt**—best known as the discoverer of nickel—coined the name "zeolite" because it literally means "**boiling stone".**
- **St. Claire Deville** reported the **first hydrothermal synthesis** of a zeolite, levynite, in 1862.
- In 1896 **Friedel** developed the idea that the structure of dehydrated zeolites consists of **open spongy frameworks** after observing that various liquids such as alcohol, benzene and chloroform were occluded by dehydrated zeolites .
- **Grandjean** in 1909 observed that dehydrated **chabazite adsorbs ammonia**, air, hydrogen and other molecules, and in 1925 Weigel and Steinhoff reported the first molecular sieve effect .

- In 1927 Leonard described the first use of X - ray diffraction for identification in mineral synthesis .
- Taylor and Pauling described the first single crystal structures of zeolite minerals in 1930.
- In 1932 McBain established the term “ molecular sieve ” to define porous solid materials that act as sieves on a molecular scale .
- Richard M. Barrer began his pioneering work in zeolite adsorption and synthesis in the mid - 1930s to 1940s. in 1948 he reported the first definitive synthesis of zeolites, including the synthetic analog of the zeolite mineral mordenite and a novel synthetic zeolite much later identified as the KFI framework.
- Barrer ’ s work in the mid - to late 1940s inspired Robert M. Milton of the Linde Division of Union Carbide Corporation to initiate studies in zeolite synthesis in search of new approaches for separation and purification of air. Between 1949 and 1954 Milton and coworker Donald W. Breck discovered a number of commercially significant zeolites, types A, X and Y.

- In 1954 Union Carbide commercialized synthetic zeolites as a new class of industrial materials for separation and purification.
- In 1955 T.B. Reed and D.W. Breck reported the structure of the synthetic zeolite A .
- In 1959 Union Carbide marketed the " ISOSIV " process for normal – isoparaffin separation, representing the first major bulk separation process using true molecular sieving selectivity. Also in 1959 a zeolite Y - based catalyst was marketed by Carbide as an isomerization catalyst.
- In 1962 Mobil Oil introduced the use of synthetic zeolite X as a hydrocarbon cracking catalyst.
- In 1969 Grace described the first modification chemistry based on steaming zeolite Y to form an " ultrastable " Y.
- In 1967 – 1969 Mobil Oil reported the synthesis of the high silica zeolites beta and ZSM - 5.
- In 1974 Henkel introduced zeolite A in detergents as a replacement for the environmentally suspect phosphates.
- In 1977 Union Carbide introduced zeolites for ion - exchange separations.
- By 2008 industry - wide approximately 367 000 t of zeolite Y were in use in catalytic cracking

aluminosilicate with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion-exchange and reversible dehydration".[19]





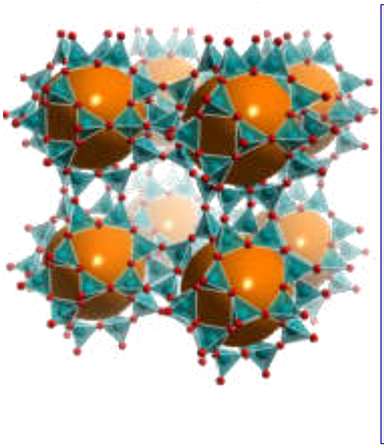
Name	Year	Formula	Framework type
Alflarsenite	2009	[illegible]	—
Ammonioleucite	1986	[illegible]	ANA
Bellbergite	1993	[illegible]	EAB
Boggsite	1990	[illegible]	BOG
Chiavennite	1983	[illegible]	-CHI
Direnzoite	2008	[illegible]	EON
Flörkeite	2009	[illegible]	PHI
Gaultite	1994	[illegible]	VSV
Gottardiite	1996	[illegible]	NES
Kirchhoffite	2012	[illegible]	—
Maricopaite	1988	[illegible]	MOR
Montesommaite	1990	[illegible]	MON
Mutinaite	1997	[illegible]	MFI
Nabesite	1992	[illegible]	NAB
Pahasapaite	1987	[illegible]	RHO
Terranovaite	1997	[illegible]	TER
Tschernichite	1993	[illegible]	Beta
Tschörtnerite	1998	[illegible]	TSC
Tvedalite	1992	[illegible]	—
Weinebeneite	1992	[illegible]	WEI

According to the definition proposed by J. V. Smith, it is clear that some of these minerals:

1. are not aluminosilicates, but contain Be or Zn instead of Al (*e.g.* Chiavennite, Gaultite, Nabesite) or are beryllophosphates (Pahasapaite, Weinebeneite);
2. do possess an interrupted framework (*e.g.* Chiavennite, Maricopaite);
3. are anhydrous (*e.g.* Ammonioleucite)

Millini and Bellussi, Zeolites in Catalysis: Properties and Applications. Eds.Jiří Čejka,Russell E. Morris. Royal Society of Chemistry, 2017

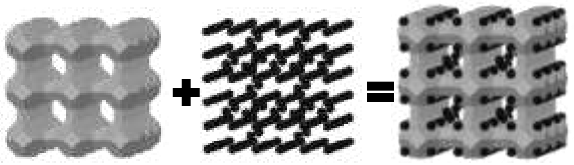
RECOMMENDED NOMENCLATURE FOR ZEOLITE MINERALS: REPORT OF THE SUBCOMMITTEE ON ZEOLITES OF THE INTERNATIONAL MINERALOGICAL ASSOCIATION, COMMISSION ON NEW MINERALS AND MINERAL NAMES



A zeolite mineral is a crystalline substance with a structure characterized by *a framework of linked tetrahedra*, each consisting of four O atoms surrounding a cation. This framework contains open cavities in the form of channels and cages. These are usually occupied by *H_2O molecules and extra-framework cations that are commonly exchangeable*. The channels are large enough to allow the passage of guest species. In the hydrated phases, *dehydration occurs at temperatures mostly below about 400°C and is largely reversible.* The framework may be *interrupted by (OH,F) groups*; these occupy a tetrahedron apex that is not shared with adjacent tetrahedra.

The Canadian Mineralogist Vol. 35, pp. 1571-1606 (1997)

Framework density, defined as the number of tetrahedral sites in 1000 Å^3, was used as the criterion for inclusion in the Atlas of Zeolite Structure Types (Meier et al. 1996).



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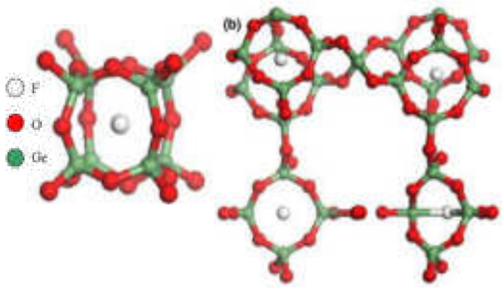
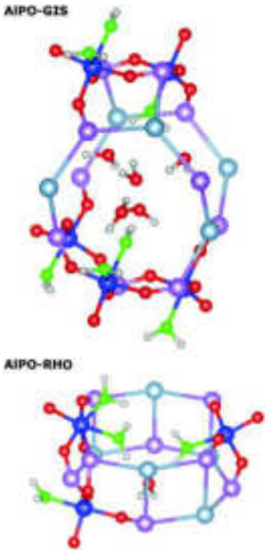
In some minerals with a tetrahedral framework structure and other zeolitic characteristics as described, namely parthéite, roggianite, maricopaite, and chiavennite, one apex of some tetrahedra is occupied by an (OH) group or F atom instead of being occupied by an O atom. This (OH) group or F atom does not form a bridge with an adjacent tetrahedron. The framework is thus interrupted. *Such minerals are here accepted as zeolites.*

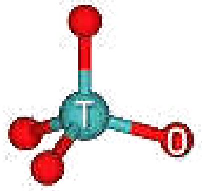


The D4R unit and one of the interrupted germanate zeolite frameworks containing structurally related components : (a) the $Ge_8O_{12}(OH)_8F^-$ anion, (b) layer B of the STAG-1 structure (in the *a*, *b* plane) showing one of each of the two SBUs.



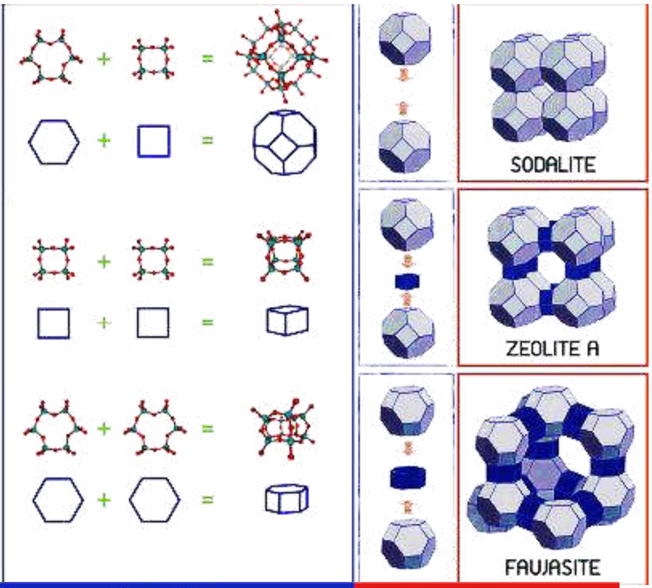
Top: One gis cage of AlPO-GIS. Bottom. One d8r unit of AlPO-RHO.
Phys. Chem. Chem. Phys., 2016, 18, 15738-15750

2001 IUPAC, Pure and Applied Chemistry 73, 381–394



TO_4

T = Si or Al



Primary Building Unit (PBU)

Secondary Building Units (SBU)

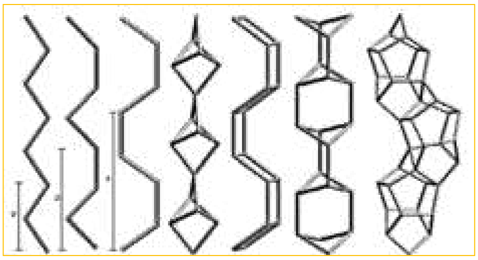
Zeolites

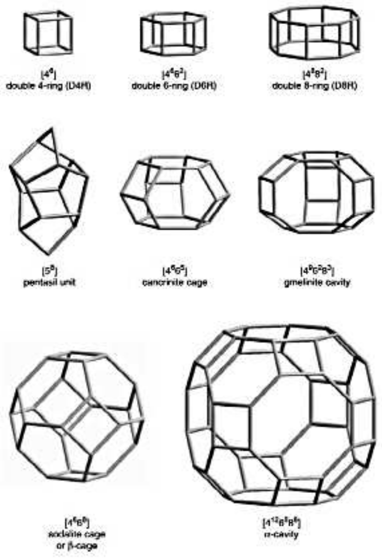
2001 IUPAC, Pure and Applied Chemistry 73, 381–394

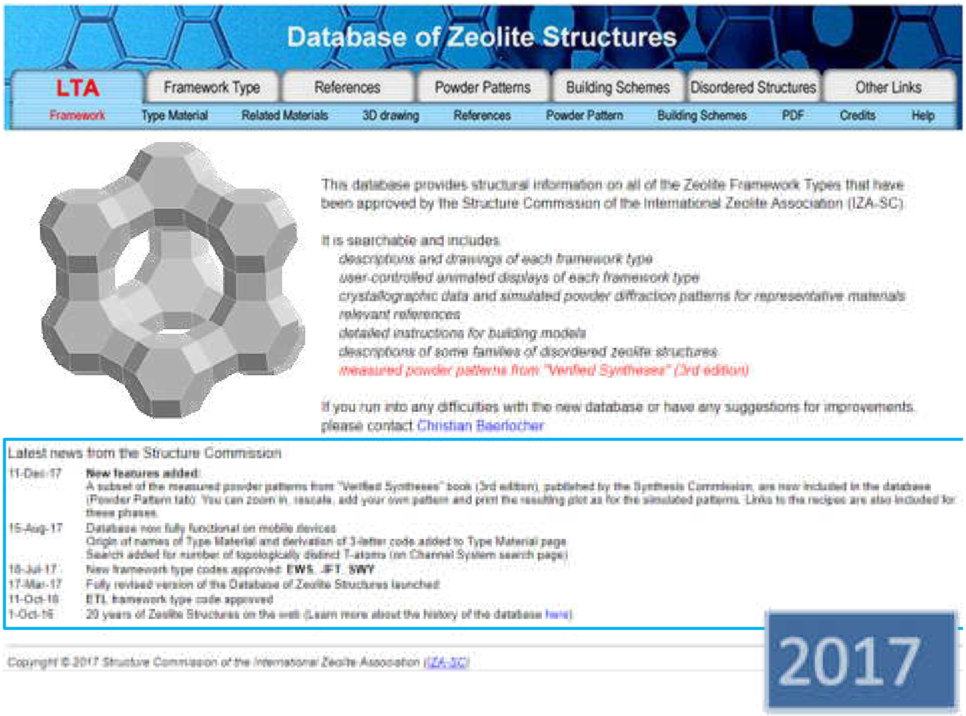
Zeolite framework type Microporous materials with an inorganic, 3-dimensional host structure composed of fully linked, corner-sharing tetrahedra and the same host topology constitute a zeolite framework type. Each confirmed zeolite framework type is assigned a three-letter code by the Structure Commission of the International Zeolite Association (IZA), and details of these framework types are published in the Atlas of Zeolite Framework Types.

Windows

The *n*-rings defining the faces of a polyhedral pore are called windows.







Database of Zeolite Structures

This database provides structural information on all of the Zeolite Framework Types that have been approved by the Structure Commission of the International Zeolite Association (IZA-SC).

It is searchable and includes:

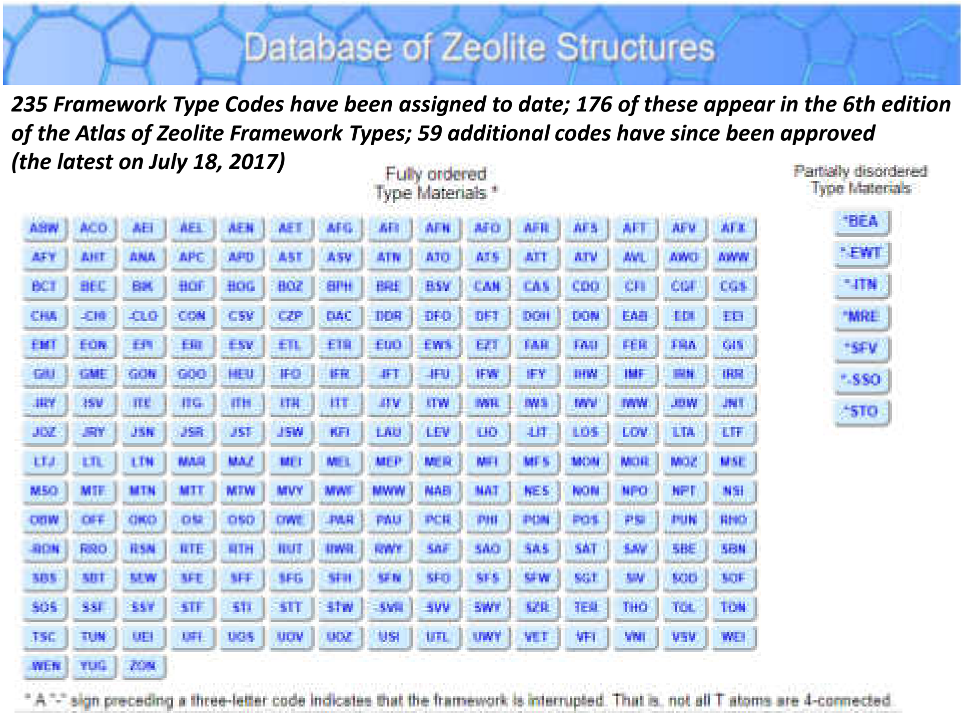
descriptions and drawings of each framework type
user-controlled animated displays of each framework type
crystallographic data and simulated powder diffraction patterns for representative materials
relevant references
detailed instructions for building models
descriptions of some families of disordered zeolite structures
measured powder patterns from "Verified Syntheses" (3rd edition)

If you run into any difficulties with the new database or have any suggestions for improvements, please contact Christian Baerlocher

Latest news from the Structure Commission

11-Dec-17	**New features added:** A subset of the measured powder patterns from "Verified Syntheses" book (3rd edition), published by the Synthesis Commission, are now included in the database (Powder Pattern tab). You can zoom in, rescale, add your own pattern and print the resulting plot as for the simulated patterns. Links to the recipes are also included for these phases.
15-Aug-17	Database now fully functional on mobile devices Origin of names of Type Material and derivation of 3-letter code added to Type Material page Search added for number of topologically distinct T-atoms (on Channel System search page)
18-Jul-17	New framework type codes approved: **EWS**, **-IFT**, **SWY**
17-Mar-17	Fully revised version of the Database of Zeolite Structures launched
11-Oct-16	ETL framework type code approved
1-Oct-16	20 years of Zeolite Structures on the web (Learn more about the history of the database here)

2017



235 Framework Type Codes have been assigned to date; 176 of these appear in the 6th edition of the Atlas of Zeolite Framework Types; 59 additional codes have since been approved (the latest on July 18, 2017)

Database of Zeolite Structures

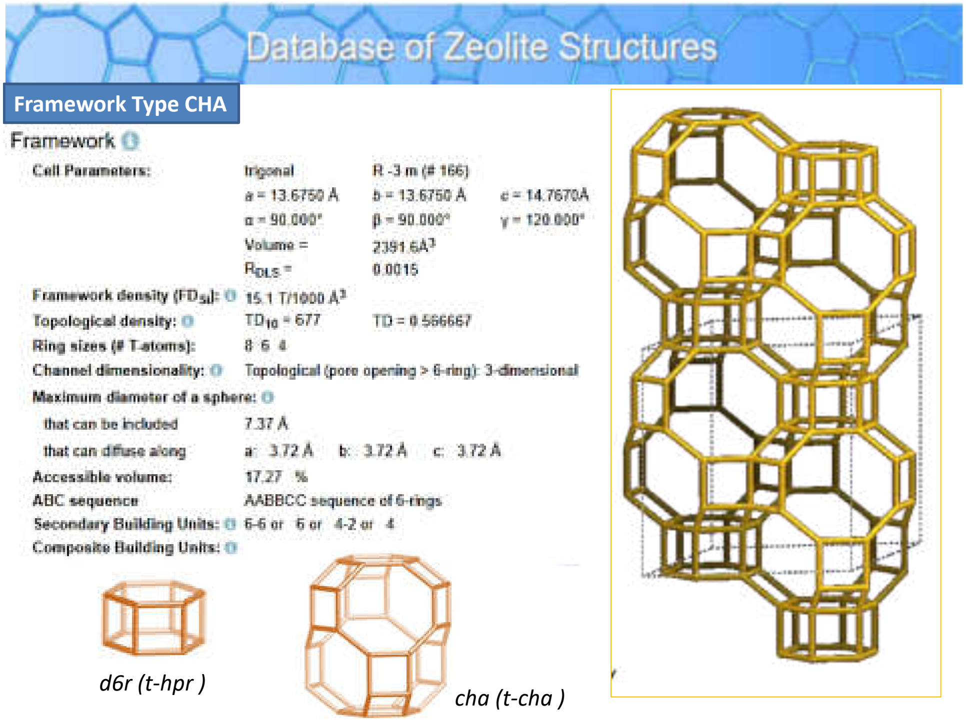
Fully ordered Type Materials *

ABW	ACO	AEI	AEL	AEN	AET	AFG	AFI	AFN	AFO	AFR	AFS	AFT	AFV	AFX
AFY	AHT	ANA	APC	APD	AST	ASV	ATN	ATO	ATS	ATT	ATV	AVL	AWO	AWW
BCT	BEC	BIK	BOF	BOG	BOZ	BPH	BRE	BSV	CAN	CAS	CDO	CFI	CGF	CGS
CHA	-CHI	-CLO	CON	CSV	CZP	DAC	DDR	DFO	DFT	DOH	DON	EAB	EDI	EEI
EMT	EON	EPI	ERI	ESV	ETL	ETR	EUO	EWS	EZT	FAR	FAU	FER	FRA	GIS
GIU	GME	GON	GOO	HEU	IFO	IFR	-IFT	-IFU	IFW	IFY	IHW	IMF	IRN	IRR
-IRY	ISV	ITE	ITG	ITH	ITR	ITT	-ITV	ITW	IWR	IWS	IWV	IWW	JBW	JNT
JOZ	JRY	JSN	JSR	JST	JSW	KFI	LAU	LEV	LIO	-LIT	LOS	LOV	LTA	LTF
LTJ	LTL	LTN	MAR	MAZ	MEI	MEL	MEP	MER	MFI	MFS	MON	MOR	MOZ	MSE
MSO	MTF	MTN	MTT	MTW	MVY	MWF	MWW	NAB	NAT	NES	NON	NPO	NPT	NSI
OBW	OFF	OKO	OSI	OSO	OWE	-PAR	PAU	PCR	PHI	PON	POS	PSI	PUN	RHO
-RON	RRO	RSN	RTE	RTH	RUT	RWR	RWY	SAF	SAO	SAS	SAT	SAV	SBE	SBN
SBS	SBT	SEW	SFE	SFF	SFG	SFH	SFN	SFO	SFS	SFW	SGT	SIV	SOD	SOF
SOS	SSF	SSY	STF	STI	STT	STW	-SVR	SVV	SWY	SZR	TER	THO	TOL	TON
TSC	TUN	UEI	UFI	UOS	UOV	UOZ	USI	UTL	UWY	VET	VFI	VNI	VSV	WEI
-WEN	YUG	ZON												

Partially disordered Type Materials

*BEA
*-EWT
*-ITN
*MRE
*SFV
*-SSO
*STO

* A "-" sign preceding a three-letter code indicates that the framework is interrupted. That is, not all T atoms are 4-connected.



Database of Zeolite Structures

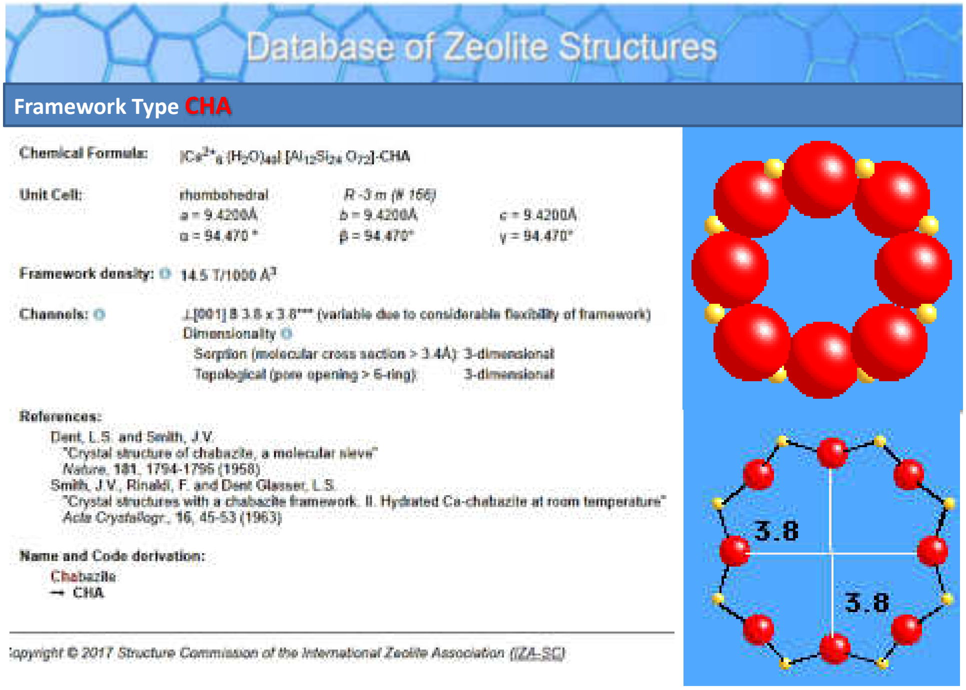
Framework Type CHA

Framework

Cell Parameters:	trigonal	R -3 m (# 166)	
	a = 13.6750 Å	b = 13.6750 Å	c = 14.7670Å
	α = 90.000°	β = 90.000°	γ = 120.000°
	Volume =	2391.6Å^3	
	R_{DLS} =	0.0015	
Framework density (FD_{Si}):	15.1 T/1000 Å^3		
Topological density:	TD_{10} = 677	TD = 0.566667	
Ring sizes (# T-atoms):	8 6 4		
Channel dimensionality:	Topological (pore opening > 6-ring): 3-dimensional		
Maximum diameter of a sphere:			
that can be included	7.37 Å		
that can diffuse along	a: 3.72 Å	b: 3.72 Å	c: 3.72 Å
Accessible volume:	17.27 %		
ABC sequence	AABBCC sequence of 6-rings		
Secondary Building Units:	6-6 or 6 or 4-2 or 4		
Composite Building Units:			

d6r (t-hpr)

cha (t-cha)



Database of Zeolite Structures

Framework Type CHA

Chemical Formula:	$|Ca^{2+}_6(H_2O)_{40}|[Al_{12}Si_{24}O_{72}]$-CHA		
Unit Cell:	rhombohedral	R -3 m (# 166)	
	a = 9.4200Å	b = 9.4200Å	c = 9.4200Å
	α = 94.470 °	β = 94.470°	γ = 94.470°
Framework density:	14.5 T/1000 Å^3		

Channels: ⊥[001] 8 3.8 x 3.8*** (variable due to considerable flexibility of framework)
Dimensionality
Sorption (molecular cross section > 3.4Å): 3-dimensional
Topological (pore opening > 6-ring): 3-dimensional

References:

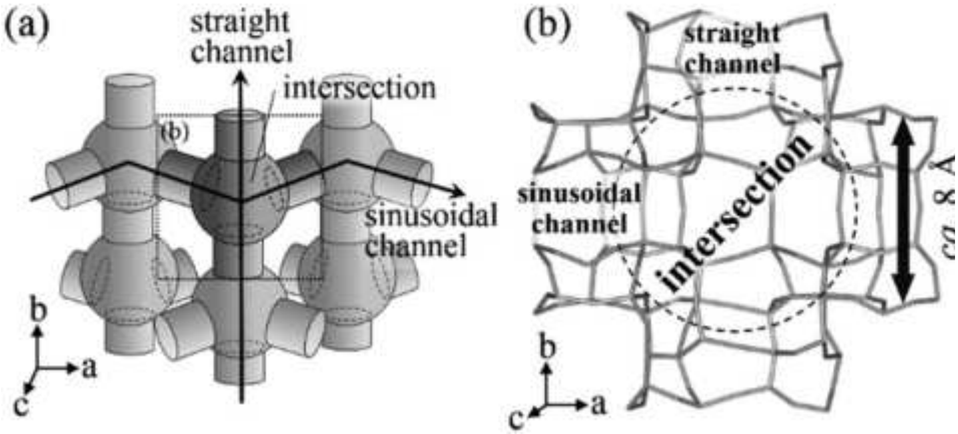
Dent, L.S. and Smith, J.V.
"Crystal structure of chabazite, a molecular sieve"
Nature, **181**, 1794-1796 (1958)
Smith, J.V., Rinaldi, F. and Dent Glasser, L.S.
"Crystal structures with a chabazite framework. II. Hydrated Ca-chabazite at room temperature"
Acta Crystallogr., **16**, 45-53 (1963)

Name and Code derivation:

Chabazite
→ CHA

8-ring viewed normal to [001]

Representative zeolite frameworks, (with pore openings). (a) zeolite A (3D, 4.2 Å); (b) zeolite Y (3D, 7.4 Å); (c) Zeolite L (1D, 7.1 Å); (d) ZSM-5 (silicalite) (2D, 5.3 × 5.6 Å, 5.1 × 5.5 Å) D—dimensions of channel system.

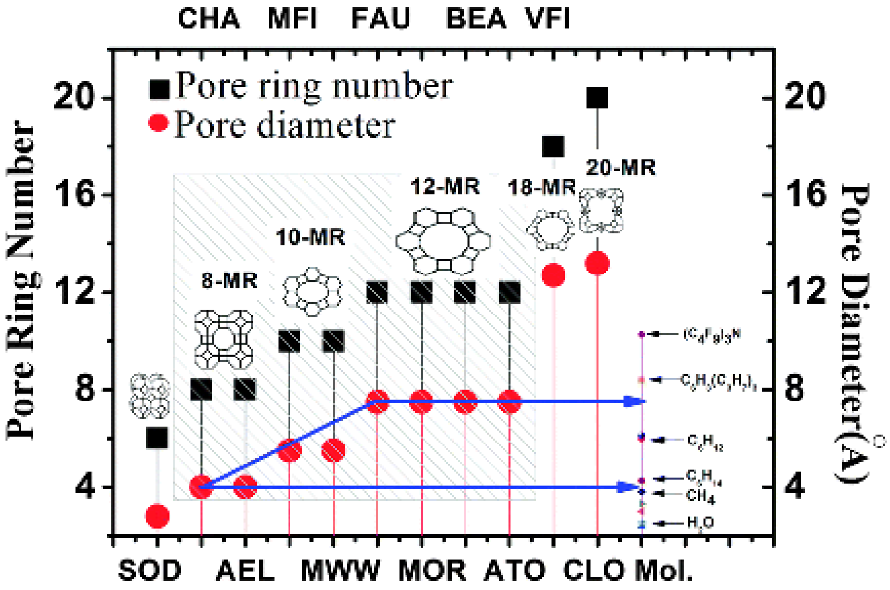


3D, 4.2 Å

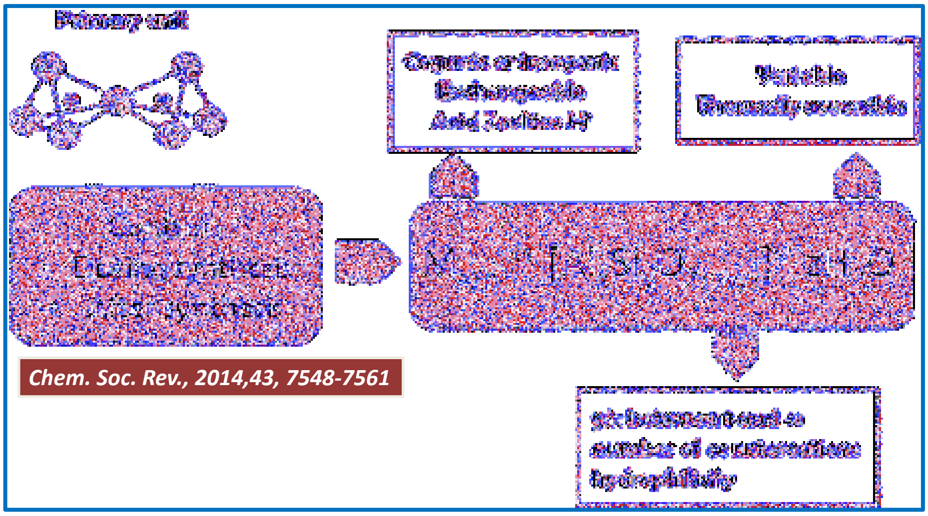
3D, 7.4 Å

1D, 7.1 Å

2D, 5.3 × 5.6 Å,
5.1 × 5.5 Å



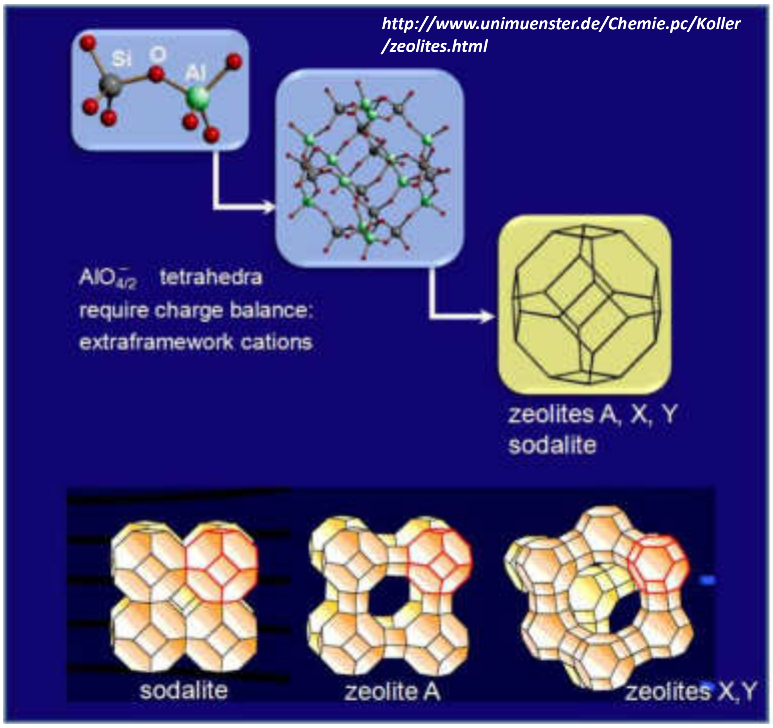
Chem. Soc. Rev., 2015,44, 8877-8903



Chem. Soc. Rev., 2014,43, 7548-7561

$(Li,Na,K)_a(Mg,Ca,Sr,Ba)_b[Al_{(a+2b)}Si_{n-(a+2b)}O_{2n}]\cdot mH_2O$

$M_xN_y[T'_pT''_q\dots O_{2(p+q+\dots)-e}(OH)_{2e}]\ .\ nQ$



http://www.unimuenster.de/Chemie.pc/Koller/zeolites.html

$AlO_{4/2}^{-}$ tetrahedra require charge balance: extraframework cations

The Evolution/Transition in Properties as framework Si/Al increases from 1 to ∞

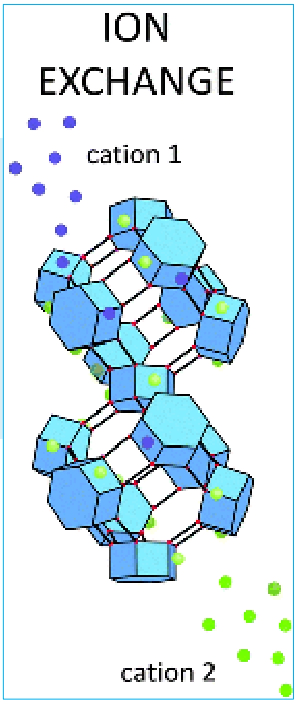
☐ **Natural zeolites.**

Si/Al ratio between 1.0 (e.g. gismondine) and 7.6 (mutinaite). The negative charge of the framework is compensated by alkali cations (mainly Na, K, Ca, Mg) in extraframework sites.

☐ **Synthetic zeolites**

Low Si/Al ratio, between 1.0 (e.g. zeolite A, zeolite X) and 9-10 (e.g. synthetic mordenite) if synthesized using alkali as counter-cations.

High Si/Al ratio (10 < Si/Al ≤ ∞) if synthesized using an organic molecule as structure direct agent (SDA) or template material.



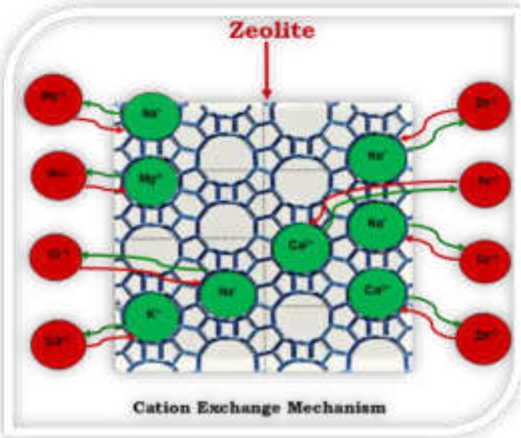
Low to high Si/Al:

- **Stability from ≤700°C to ~ 1300°C**
- **Surface selectivity from hydrophylic (with cations) to hydrophobic (SiO$_2$ or AlPO$_4$)**
- **Increase in acid strength**
- **Structure from 4, 6 & 8-rings to 5-rings**

Characteristics and Physicochemical properties of Zeolites

The properties of zeolites are closely related to both structure and chemistry.

- *High surface area,*
- *Uniform micropore size,*
- *High hydro thermal stability,*
- *Intrinsic acidity,*
- *Ability to accommodate active metal species,*
- *Introducing constraints to undesired species by molecular sieving effect (shape selectivity),*
- *Environmentally harmless,*
- *Non-corrosive,*
- *Show ease of separation from reaction mixture compared with homogeneous catalysts.*



Oceanography and Fisheries (OFOAJ); ISSN: 2476-0536

Size Constraints or Molecular sieving or Shape selectivity

Due to rigid skeletal system, zeolite window has intact window size due to which molecules having size larger than this window dimensions often experience constraints in accessing the intrinsic sites. Thus, prevents undesired large molecules to enter network. Shape selective

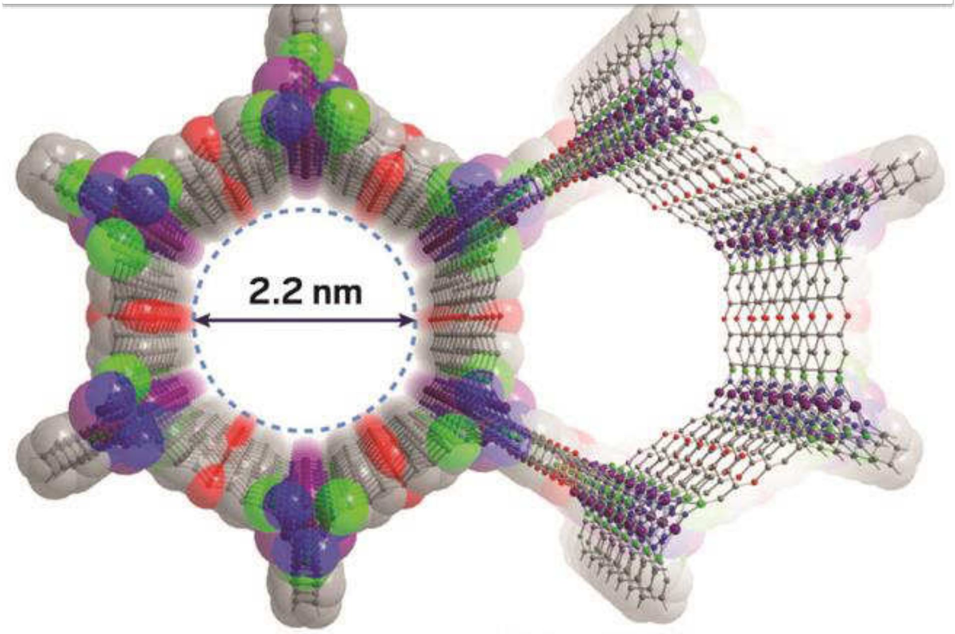
Characteristics and Physicochemical properties of Zeolites

The cation exchange properties of zeolites are of great importance, and *vary strongly* from one structure to the next, *in terms of both selectivities and extent of ion exchange* due to strong effects of structure on cation exchange, and vice versa.
For many low silica zeolites, complete ion exchange is possible (for example with zeolites A, X, chabazite, Rho), whereas for some, such as zeolite L, it is possible to exchange extra-framework cations in the main channels but not those held within the cancrinite cages.

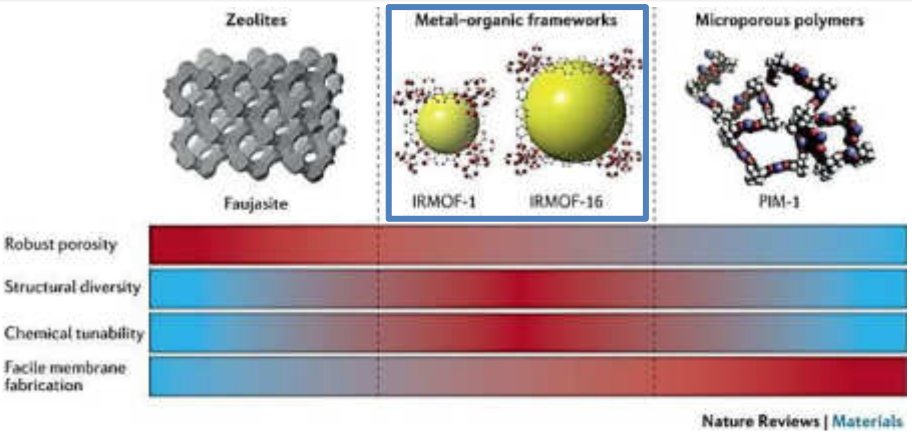
For flexible zeolites, the ion exchange can cause structural effects.
Upon ion exchange with K+, Rb+ and Cs+, for example, the zeolite Na-natrolite is found to exhibit volume expansion of 10, 16 and 18 %, the largest observed for zeolites. This arises through the flexibility of the link between natrolite chains, so that the linking TÔT angle changes from 176º to 130º and the channel cross-section changes from strongly elliptical to nearly circular as hydrated sodium cations are replaced by larger hydrated cesium cations.

Chapter 1: Structural Chemistry and Properties of Zeolites (PDF Download Available). Available from: https://www.researchgate.net/publication/271384764_Chapter_1_Structural_Chemistry_and_Properties_of_Zeolites [accessed Feb 10 2018].

Metal Organic Framework



So what are MOFs?



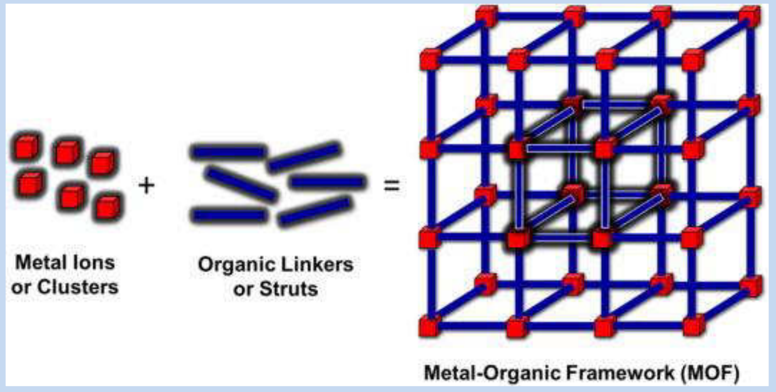
Nature Reviews | Materials

MOF$_s$ are solid materials with regular honeycomb-like structures – a little like the steel frame of a skyscraper – which can be prepared in the laboratory from organic molecules which form the links between metal atoms. The size and shape of the pores or holes in these materials can be altered by merely modifying the structure of the link or changing the metal salt.

So what are MOFs?

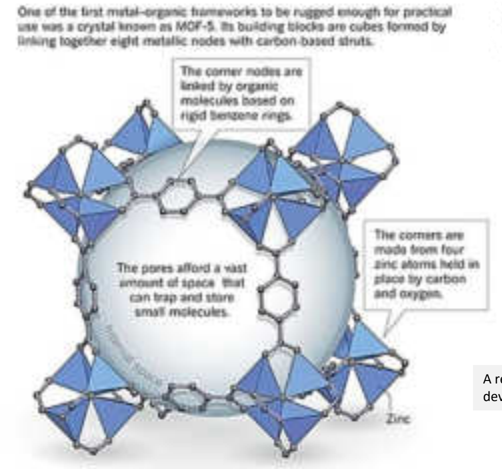
By definition, two secondary building units (SBUs) are involved in the formation of a crystalline MOF structure. The first SBU is the organic linker, which may be ditopic (having two types of coordinative functionalities), tritopic (three types) or polytopic (more than three types). The second SBU is a metal atom, a finite polyatomic inorganic cluster with two or more metal atoms, or an infinite inorganic unit such as an infinite periodic rod of metal atoms.

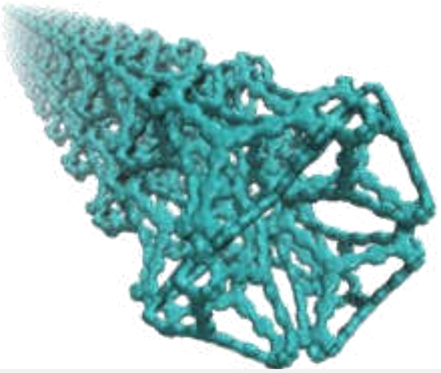
Nature Reviews Materials **1**, Article number: 15018 (2016)



Since MOF structure depends on the choice of metals and ligands, various organic ligands of different shape and size have also been utilized to control the architecture.

So what are MOFs?


One of the first metal-organic frameworks to be rugged enough for practical use was a crystal known as MOF-5. Its building blocks are cubes formed by linking together eight metallic nodes with carbon-based struts.

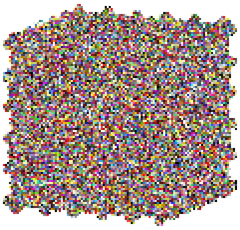

A representation of one of the two ultra-high surface area compounds developed by Farha and colleagues, named NU-110. Northwestern University

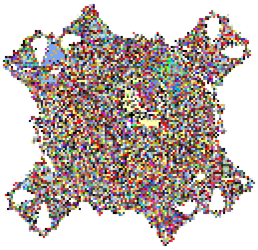
The organic units are ditopic or polytopic organic carboxylates (and other similar negatively charged molecules), which, when linked to metal-containing units, yield architecturally robust crystalline MOF structures with a typical porosity of greater than 50% of the MOF crystal volume. The surface area values of such MOFs typically range from 1000 to 10,000 m^2/g, thus exceeding those of traditional porous materials such as zeolites and carbons.

Omar M. Yaghi
Department of Chemistry & Biochemistry, UCLA
Professor
PhD, University of Illinois-Urbana; NSF Postdoctoral Fellow, Harvard University
http://yaghi.chem.ucla.edu

Metal-Organic Frameworks

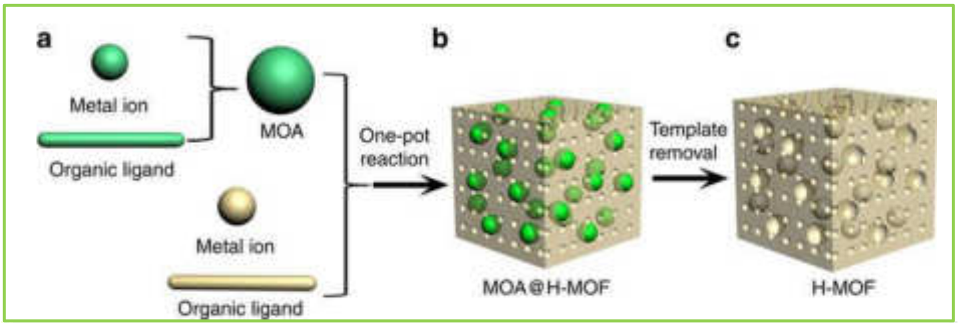
- Metal ions linked by organic chains
- Very low density
- Crystalline and "tunable"
- Vast number of possible structures
- Large voids, voids of ~ 10 – 20 Å for molecular storage and separation
- Complex unit cell makes computation modeling challenging
- Significant van der Waals interactions





MOF:FRAMEWORK

Frameworks obtained by using various connectors linked by linear linkers.
3-D MOF materials are among those with the largest pores for crystalline materials.
When synthesized the pores will be filled by guest or template molecules.
In order to obtain porosity it is necessary to remove the guest species. This is difficult due to a generally low thermal stability of the materials. (May also fill space by forming e.g. two interpenetrating frameworks). Also exceptionally high surface areas may be obtained. (several thousand square meters per gram)



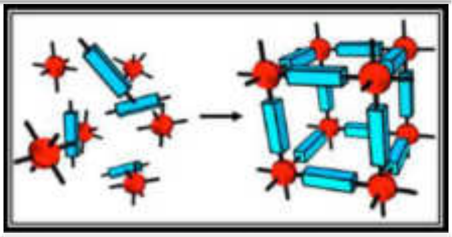
(a) In situ self-assembly of MOA through the reaction between metal ion and organic ligand. (b) MOA@H-MOF composite formed by one-pot self-assembly reaction. (c) H-MOF formed through removing MOA template.

•*Nature Communications* **6, Article number: 8847 (2015)**

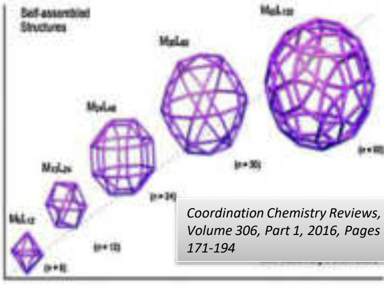
MOF:SYNTHESIS

- The variety of different connectors and linkers makes it possible to construct a variety of 1-, 2- and 3-dimensional structures. The design of linkers is especially efficient in attempting to form new structure types.
- Standard coordination chemistry methods are used, where metal ions are reacted with an organic ligand.
- **The conditions are low temperature and hydrothermal/solvothermal synthesis**. This may be seen as "self-assembly" of basic building units. **The products are usually not kinetically but thermodynamically determined.**
- The flexibility/rigidity of the linker is important for the properties, e.g. the possibility of forming porous materials. Most used linker are fairly rigid. Also during formation the rigidity of the linkers are important; **a very flexible linker may enable several possible conformations, resulting in poorly crystalline materials**.

Millini and Bellussi, Zeolites in Catalysis: Properties and Applications. Eds.Jiří Čejka,Russell E. Morris. Royal Society of Chemistry, 2017

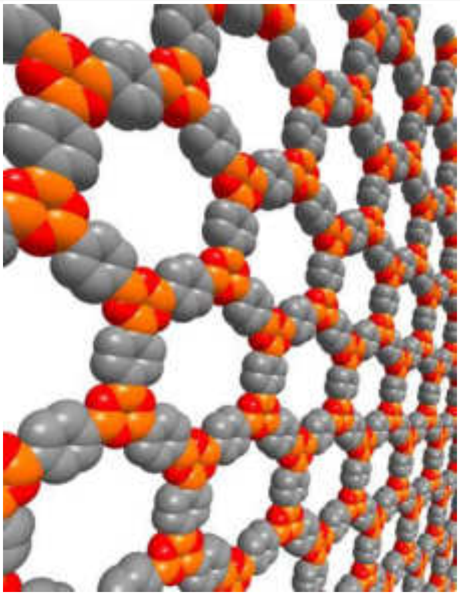


Metal-organic frameworks (MOFs) self-assemble from rigid building blocks into porous crystals consisting of metal nodes (red) and organic linkers (blue).
http://web.stanford.edu/group/gcep/cgi-bin/gcep-research/all/new-materials-and-processes-for-energy-efficient-carbon-capture-in-the-presence-of-water-vapor/



Coordination Chemistry Reviews, Volume 306, Part 1, 2016, Pages 171-194

MOF classification



- 1st generation: The framework is only maintains with the guest molecules present, and collapses upon removal of the guests.
- 2nd generation: The framework is stable and robust, and have porosity when removing the guest species.
- 3rd generation: the framework is flexible and dynamic and responds to external stimuli. 2nd and 3rd generation materials may be used for gas storage or as catalysts.

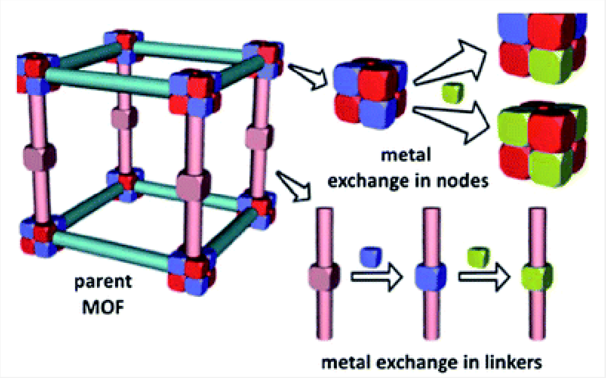
Advantages:

- In principle the dimensions and shape of the channels are easily tunable by changing the organic linkers.
- Functionality may be built into the linkers.
- The materials are light weight, making it possible to obtain large surface areas.

Millini and Bellussi, Zeolites in Catalysis: Properties and Applications. Eds.Jiří Čejka,Russell E. Morris. Royal Society of Chemistry, 2017

MOF PROPERTIES

Ion-exchange is one of the interesting properties of anionic or cationic MOFs that do not have neutral frameworks. If we can predict which MOFs are capable to ion-exchange, it will become a logical tool for synthesizing new materials with targeted properties.

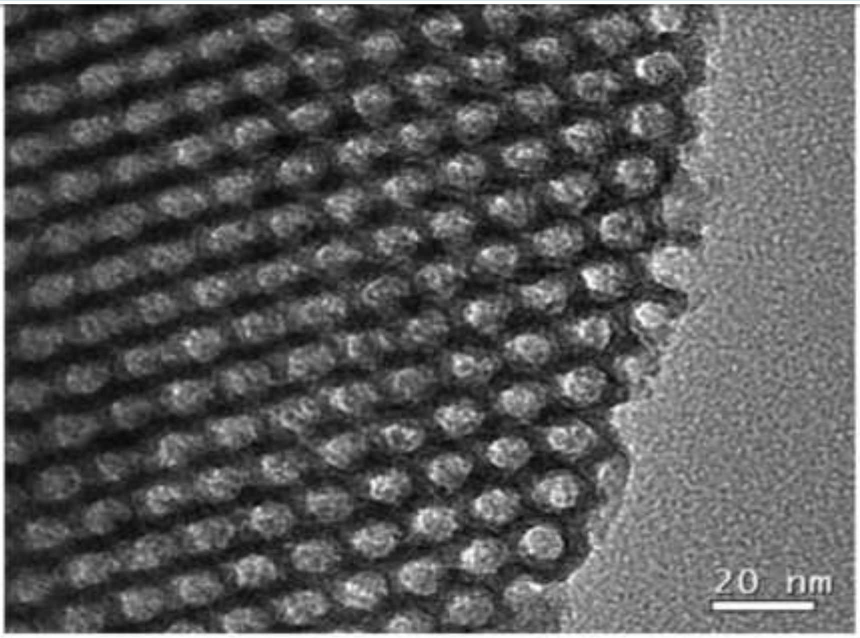


Metal-exchange within MOF nodes and metal-exchange in metal-containing linkers. Reproduced with permission from M. Lalonde, W. Bury, O. Karagiaridi, Z. Brown, j. t. Hupp and O. K. Farha, J. Mater. Chem. A, 2013, 1, 5453–5454

When the factors that generate exchangeable ions in the pores are elucidated, particular materials may be selected for ion-exchange including cation-exchange and anion-exchange, and their exact compounds may be designed.

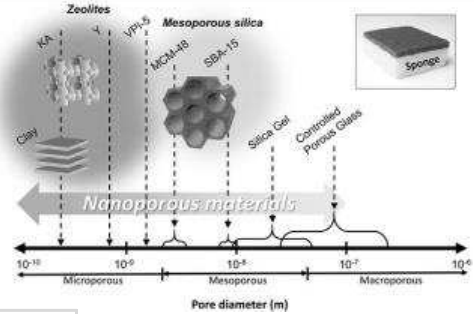
RSC Adv., 2017, 7, 1782-1808

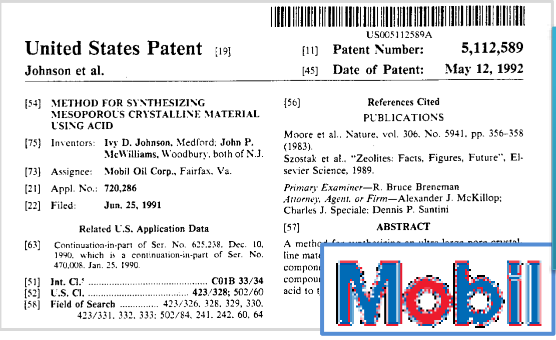
MESOPOROUS MATERIALS



MESOPOROUS MATERIALS

A mesoporous material is a material containing pores with diameters between 2 and 50 nm, according to IUPAC notation. The procedure for producing mesoporous materials (silica) was patented around 1970 and methods based on the Stöber process from 1968 were still in use in 2015.




US005112589A

United States Patent [19]

Johnson et al.

[11] **Patent Number:** **5,112,589**

[45] **Date of Patent:** **May 12, 1992**

[54] METHOD FOR SYNTHESIZING MESOPOROUS CRYSTALLINE MATERIAL USING ACID

[75] Inventors: **Ivy D. Johnson**, Medford; **John P. McWilliams**, Woodbury, both of N.J.

[73] Assignee: **Mobil Oil Corp.**, Fairfax, Va.

[21] Appl. No.: **720,286**

[22] Filed: **Jun. 25, 1991**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 625,238, Dec. 10, 1990, which is a continuation-in-part of Ser. No. 470,008, Jan. 25, 1990.

[51] **Int. Cl.^{5}** **C01B 33/34**
[52] **U.S. Cl.** **423/328**; 502/60
[58] **Field of Search** 423/326, 328, 329, 330, 423/331, 332, 333; 502/84, 241, 242, 60, 64

[56] **References Cited**

PUBLICATIONS

Moore et al., Nature, vol. 306, No. 5941, pp. 356–358 (1983).
Szostak et al., "Zeolites: Facts, Figures, Future", Elsevier Science, 1989.

Primary Examiner—R. Bruce Breneman
Attorney, Agent, or Firm—Alexander J. McKillop; Charles J. Speciale; Dennis P. Santini

[57] **ABSTRACT**

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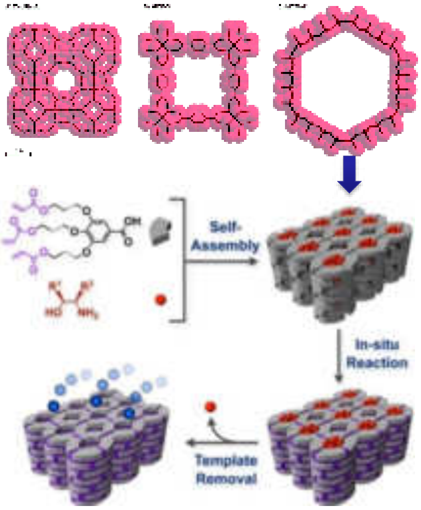
Mesoporous silica nanoparticles (MSNs) were independently synthesized in 1990 by researchers in Japan.
They were later produced also at Mobil Corporation laboratories and named Mobil Crystalline Materials, or MCM-41.

MCM-TYPE MATERIALS: REMOVAL OF TEMPLATE

In order to create porosity the template must be removed. Several different ways are possible:

- Solvent extraction
- Calcination
- Oxygen plasma treatment
- Supercritical drying Extraction often with organic solvents with dissolved acids. (e.g. EtOH w. HCl) (Cannot remove covalently bonded molecules)

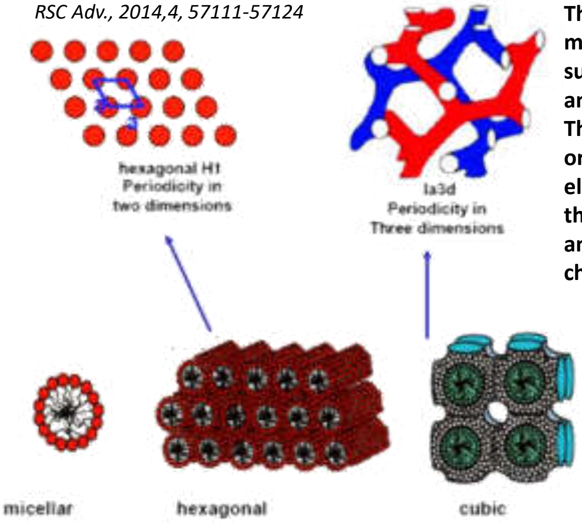
Calcination typically at 400-600˚C in e.g. N_2 or air. Framework structures (hexagonal or cubic MCM phases) may survive template removal. Lamellar phases collapse. Design of mesoporous ordered materials with different pore sizes is possible by tuning the template molecules. ***Mesoporous materials containing elements other than Si have been produced.***



MESOPOROUS MATERIALS

According to the IUPAC, a mesoporous material can be disordered or ordered in a mesostructure.

RSC Adv., 2014,4, 57111-57124

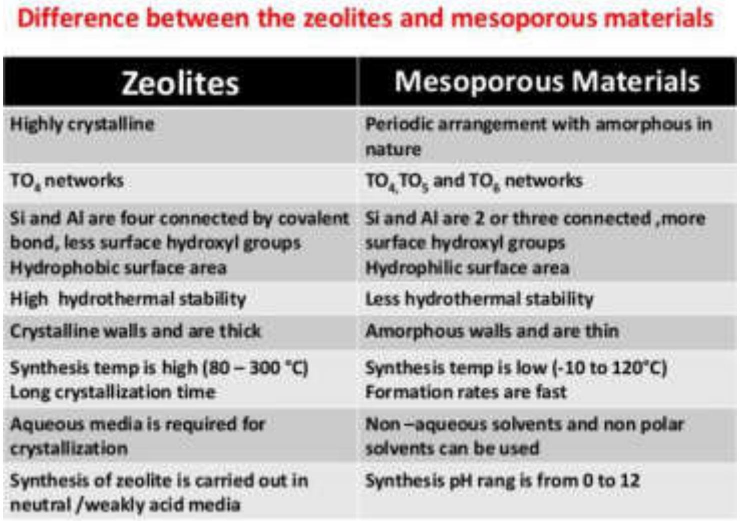


The first-ordered mesoporous materials were prepared from ionic surfactants, such as quaternary ammonium ions.

The formation of the inorganic–organic composites is based on electrostatic interactions between the positively charged surfactants and the negatively charged silicate species in solution.

MESOPOROUS MATERIALS

According to the IUPAC, a mesoporous material can be disordered or ordered in a mesostructure.



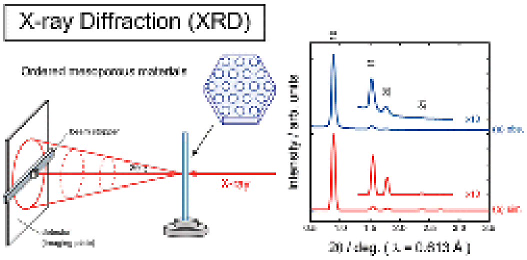
Difference between the zeolites and mesoporous materials

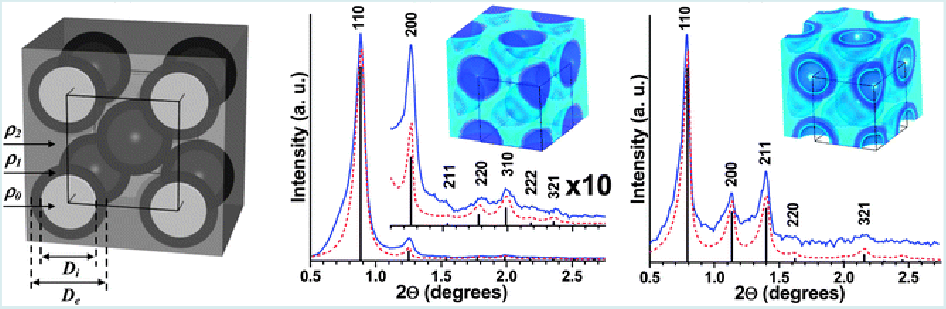
Zeolites	Mesoporous Materials
Highly crystalline	Periodic arrangement with amorphous in nature
TO_4 networks	TO_4, TO_5 and TO_6 networks
Si and Al are four connected by covalent bond, less surface hydroxyl groups Hydrophobic surface area	Si and Al are 2 or three connected ,more surface hydroxyl groups Hydrophilic surface area
High hydrothermal stability	Less hydrothermal stability
Crystalline walls and are thick	Amorphous walls and are thin
Synthesis temp is high (80 – 300 °C) Long crystallization time	Synthesis temp is low (-10 to 120°C) Formation rates are fast
Aqueous media is required for crystallization	Non –aqueous solvents and non polar solvents can be used
Synthesis of zeolite is carried out in neutral /weakly acid media	Synthesis pH rang is from 0 to 12

MESOPOROUS MATERIALS: X-RAY DIFFRACTION

By analyzing the small-angle powder XRD pattern, it can successfully determined not only the pore-to-pore distance but also the pore diameter of the mesoporous materials having a quasi two-dimensional hexagonal pore structure.

J. Phys. Chem. C, 2013, 117 (35), pp 18120–18130



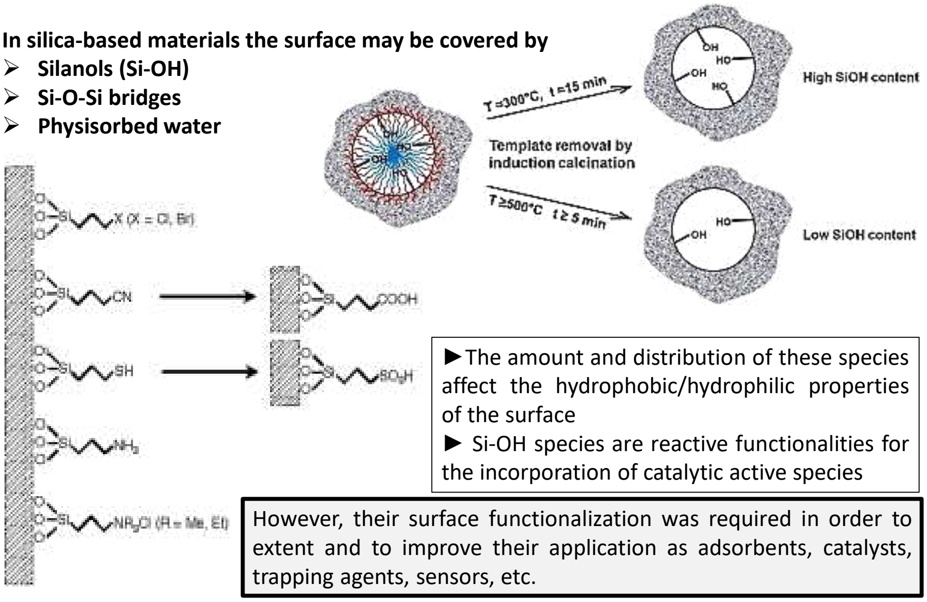


Chem. Soc. Rev., 2013,42, 3708-3720

Periodic mesoporous organosilicas, commonly named as "PMOs", are a new class of ordered organic-inorganic hybrid materials in which the organic units are homogenously distributed into the silica framework

In silica-based materials the surface may be covered by

- **Silanols (Si-OH)**
- **Si-O-Si bridges**
- **Physisorbed water**

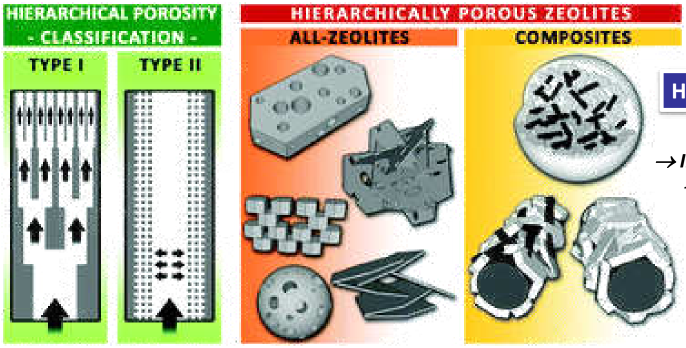


►The amount and distribution of these species affect the hydrophobic/hydrophilic properties of the surface
► Si-OH species are reactive functionalities for the incorporation of catalytic active species

However, their surface functionalization was required in order to extent and to improve their application as adsorbents, catalysts, trapping agents, sensors, etc.

POROUS CLAY HETEROSTRUCTURES (PCHS)

Barrer and MacLeod [Trans. Faraday Soc. 51, *1290* (1955)] first introduced the concept of transforming a lamellar solid into a porous structure by inserting laterally spaced molecular props between the layers of a smectite clay mineral.



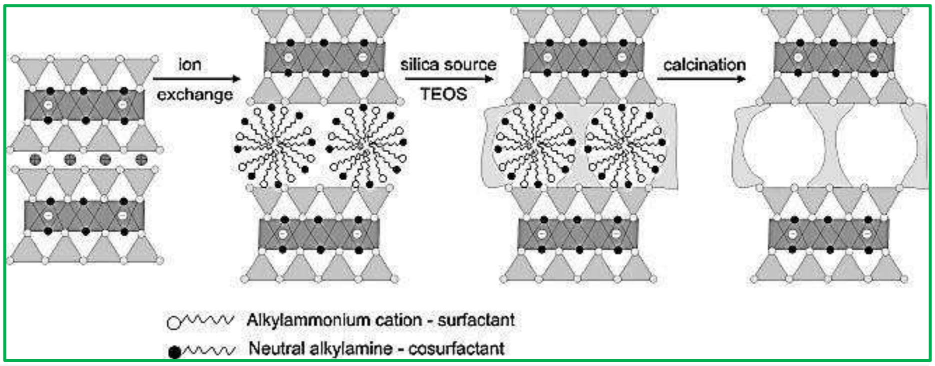
HIERARCHY OF MATERIALS

LAYERED COMPOUNDS
→INTERCALATION COMPOUNDS
→PILLARED COMPOUNDS.

__Pillaring__ is the process by which a layered compound is transformed into a thermally stable micro- and/or mesoporous material with retention of the layer structure.
__The material obtained is a pillared compound or a pillared layered solid.__
A pillared derivative is distinguished from an ordinary intercalate by virtue of intracrystalline porosity made possible by the lateral separation of the intercalated guest.

1999 IUPAC, Pure Appl. Chem. 71, 2367±2371

POROUS CLAY HETEROSTRUCTURES (PCHS)

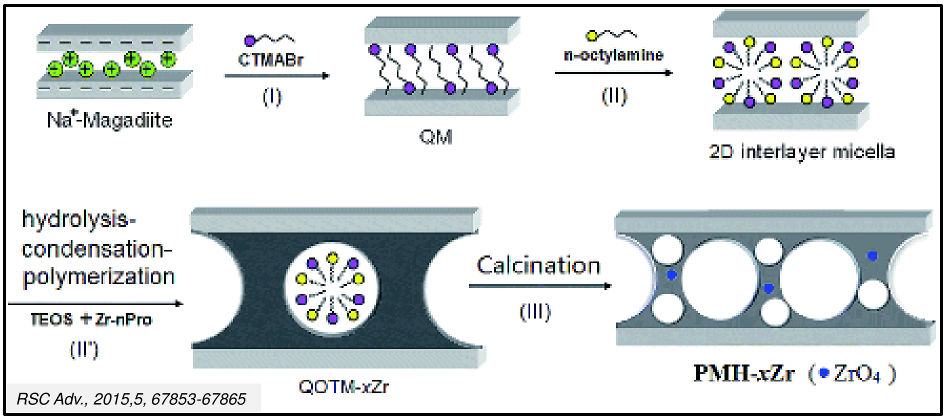


The synthesis of such materials consists of the following steps:
(i) cationic templates and neutral amine co-templates are intercalated in the interlayer space of the host clay forming the micelle structures;
(ii) the silica pillars are created by in-situ
polymerization of a silica source around the micelle structures. The silica source was allowed to hydrolyze and condense, surrounding the added amine within the interlayer gallery.
(iii) the organic templates are removed from the material by a classical calcination (above 550 C in an air atmosphere), producing materials with a high surface area and combined micro and mesoporous structure.

This new class of materials is called porous clay heterostructure (PCH).

POROUS CLAY HETEROSTRUCTURES (PCHS)

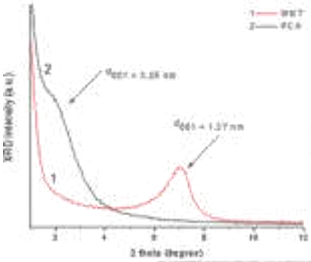
Various types of the cationic layered clays characterized by different surface acidity were used as precursors for the synthesis of the PCH materials.

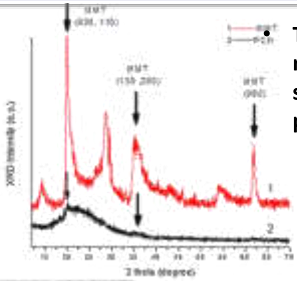


RSC Adv., 2015,5, 67853-67865

These types of materials combine the structural elements of a mesostructure with the intrinsic acidity of a lamellar smectite clay. The acidity of PCH materials can be controlled by the selection of the starting clay minerals (fluorohectorite, montmorillonite, synthetic saponite, magadiite, vermiculite) , the post-grafting of aluminum or copper and iron species in the mesostructured silica or the acid activation of the clay mineral prior to expansion with cationic templates and neutral amine co-templates cations and reaction with TEOS and neutral amines.

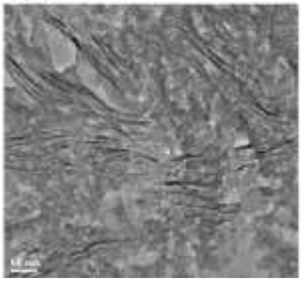
POROUS CLAY HETEROSTRUCTURES (PCHS): PROPERTIES





- The shift in 2θ value to lower range and increase in d (001) spacing indicate the success of pillaring process.

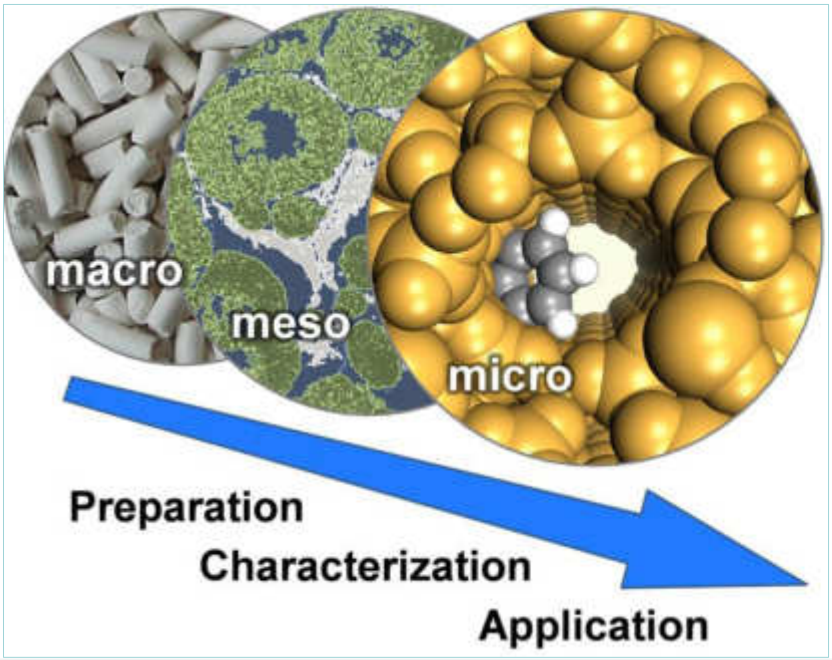
International Journal of Pharmaceutics Volume 491, Issues 1–2 1 August 2015, Pages 299-309



- *Surface area, pore volume, average pore size etc. increased dramatically as a result of pillaring process.*
- *PCHs attracted particular attention due to its high surface area (250-1000 m^2/g), ion exchange capacity, surface acidity, mesoporosity with narrow pore size distribution, good thermal stability and mechanical strength.*

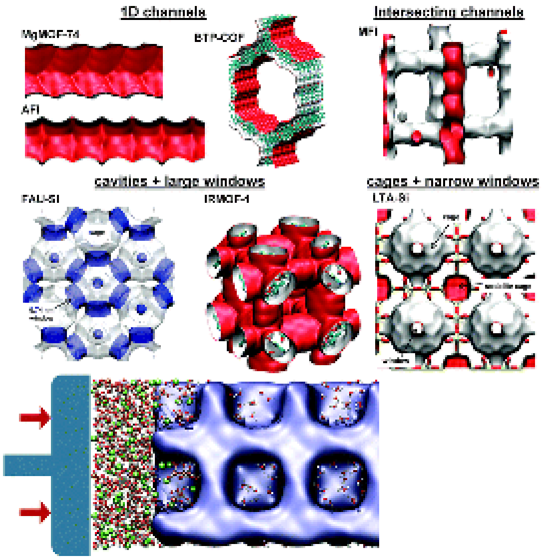
https://dyuthi.cusat.ac.in/xmlui/bitstream/handle/purl/4977/Dyuthi-T2048.pdf?sequence=1

PCH have properties inherent to both components, the properties of clays (e.g; CEC and acidity) and properties of silica network (e.g; ability to be functionalized).



https://www.copybook.com/companies/micromeritics-instrument-corporation/articles/micromeritics-and-eth-zurich-presenting-advanced-porous-materials-workshop

DIFFUSION IN POROUS CRYSTALLINE MATERIALS

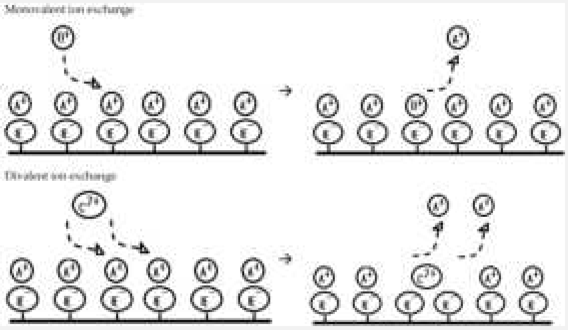


Chem. Soc. Rev., 2012,**41**, 3099-3118

In meso-porous materials, with pore sizes 2 nm < dp < 50 nm, there is a central core region where the influence of interactions of the molecules with the pore wall is either small or negligible; meso-pore diffusion is governed by a combination of molecule–molecule and molecule–pore wall interactions. Within micro-pores, with dp < 2 nm, the guest molecules are always under the influence of the force field exerted with the wall and we have to reckon with the motion of adsorbed molecules, and there is no "bulk" fluid region.

ION EXCHANGE PROCESSES

IUPAC recommendations for ion-exchange nomenclature define the following capacity types: "Theoretical (specific) capacity, apparent capacity (effective capacity)", "Practical (specific) capacity", "Useful capacity" and "Breakthrough capacity"
[Inglezakis VJ (2005) The concept of "capacity" in zeolite ion-exchange systems. *J.Colloid Interf. Sci. 281:68-79*].



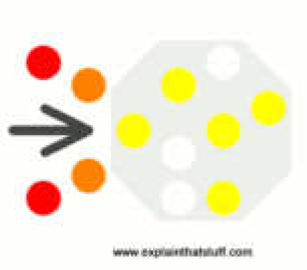
Examples of the monovalent and divalent exchange processes. In this diagram, it is easy to see the importance of charges in the stoichiometric process.

In an ion exchange process, the balancing ion (the one previously detected in the solid phase) is replaced by the counter ion (previously in the liquid phase) always when the exchange has a higher affinity to the counter ion.
It is important to emphasize that the stoichiometric replacement involves charges. Nevertheless, normality is much more adequate to describe the phenomenon than molarity.

DIFFUSION IN POROUS CRYSTALLINE MATERIALS

The word **diffusion** comes from the Latin *diffusione*, which means action of spread, which in turn comes from the Latin *diffundere*, to spread everywhere, to spread widely, which perfectly describes what happened during the mentioned phenomenon.

Now, formally the diffusion (ordinary) is defined as the net movement of particles due to a concentration gradient, that is, it is the process by which matter (atoms, molecules or other particles) is transported or transferred from a region of high concentration to a region of lower concentration (the concentration is the amount of substance contained in a certain volume).



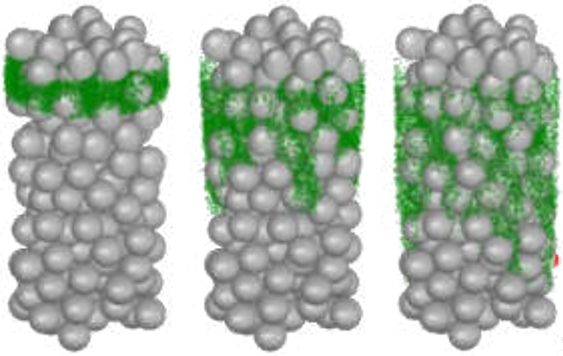
www.explainthatstuff.com

A brief Historical Survey

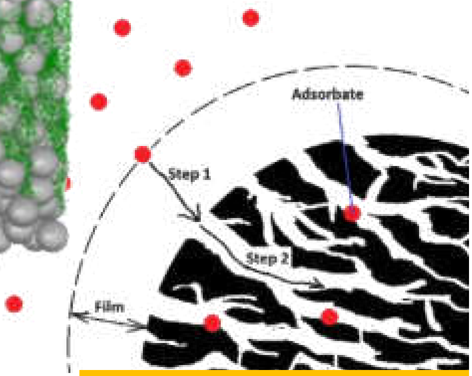
1827	Navier –	Momentum equation
1829	Graham –	Mass diffusion in gas
1839	Hagen, Poiseuille –	Flow in pipe
1845	Stokes –	Momentum equation
1855	Fick –	Law of mass transport
1856	Darcy –	Empirical flow equation
1859	Maxwell –	Distribution of velocity in gas
1870	Kelvin –	Capillary condensation
1878	Gibbs –	Thermodynamics treatment of interfaces
1885	Boltzmann –	General transport equation
1905	Einstein –	Random walk diffusion equation
1909	Knudsen –	Flow of rarified gases

GENERAL THEORY

Ion exchange is generally controlled by diffusion, a consequence of the material structure. Ion exchange framework, size of the beads, and any other physical chemistry characteristics have important roles in this process. Nevertheless, in all cases, it is accomplished by transfer of ions to and from the interphase boundary, the exchange itself followed by the diffusion of the ion inside the solid phase and the diffusion in the surrounding solution.



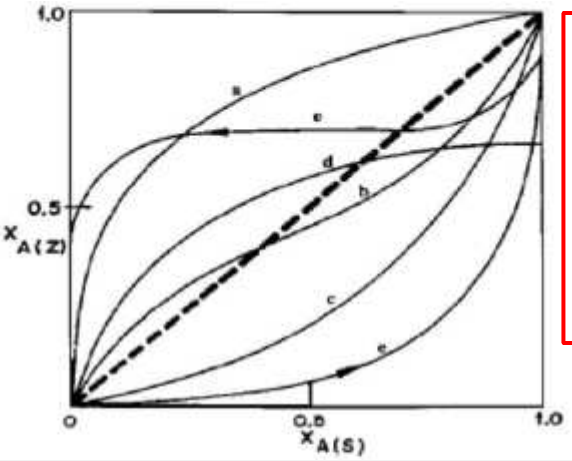
https://www.victoria.ac.nz/scps/research/research-groups/magnetic-resonance/porous-media



Ion Exchange Fundamentals and New Challenges
http://dx.doi.org/10.5772/60864

DIFFUSION IN POROUS CRYSTALLINE MATERIALS: KINETICS

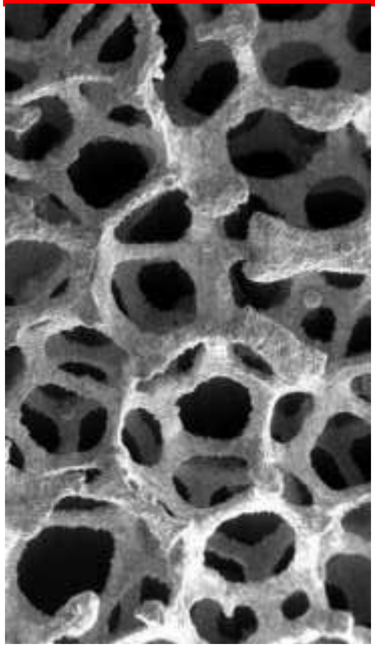
Besides kinetic data, ion exchange equilibrium data are also of great value. Isotherms may be classified in five different types, as shown in Figure .



Isotherm shapes indicate whether or not the ion is solution is preferably exchanged.
However, they provide no information on the type of exchange sites or even whether they have similar energies.
This is outstanding information as it is directly related to the ion exchange mechanism.

Ion exchange isotherms: xa(z): equivalent fraction of the counter ion in the exchanger; xa(s): equivalent fraction of the counter ion in solution . (a) Favorable isotherm; (b) isotherm with reversal behavior, from favorable to unfavorable; (c) unfavorable isotherm; (d) incomplete favorable isotherm; (e) isotherm with hysteresis.

ION EXCHANGERS: POROUS MATERIALS

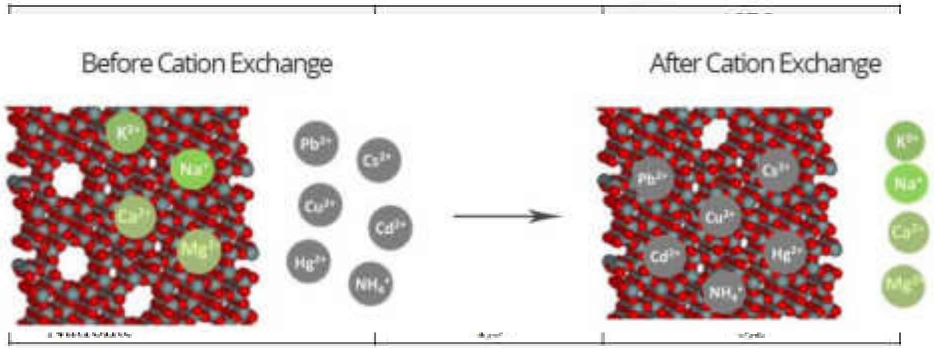


Ion exchangers are porous matrixes from different sources, with positive or negative excess charge, insoluble in aqueous solutions and in many organic solvents. The excess charge of the matrix should be compensated by the balancing ions, which may be replaced by the in-going ion depending on the selectivity and affinity of the exchanger to the ions involved

Mechanical resistance as well as regeneration capacity is quite important when packed beds are considered.
There are acid and basic exchangers being the anionic exchangers that have basic superficial groups and cationic exchangers those containing superficial acid groups. Exchangers may be also classified according to complete or incomplete dissociation based on the pH range where the exchange process is efficient.

ION EXCHANGERS: ZEOLITES MATERIALS

Selectivity is a property of the exchanger to show different preferences for particular ions and it depends of field strength in zeolite pore. Zeolites with low field strength and with higher Si content, such as clinoptilolite, are more selective for <u>cations with lower charge density</u> (K+, NH4+, Ag+, Cs+). Zeolites with high field strength, i.e. higher Al content, are more selective <u>toward the high charge density cations</u> (Na+, Li+).



*Cation-exchange capacities of different zeolitic materials (*CEC is operationally defined –determine the amount of a cation that can be removed by a specific substance once the material and solution have come to equal) [Breck DW (1974) Zeolite molekular sieves, John.Wiley&Sons, New York].*

At room temperature and low concentration of the solution ions are exchanged, the advantages of the amendment have ions with higher charge. Increasing the concentration of the solution, the difference in ion exchange affinities of different charges is reduced. ***If the solution contains different ions of the same charge, the selectivity increases with increasing atomic number (Li+, Na+, NH4 +, K+).***

The selectivity of clinoptilolite towards alkali metals exist in the sequence:

Cs+> K+> Rb+> Na+> Li+

and the alkaline earth metals:

$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$

The selectivity of clinoptilolite towards heavy metal ions (cations) exist in the series:

$Pb^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Cr^{2+} > Zn^{2+} > Mn^{2+} > Hg^{2+}$

and selectivity by anions exists in the series:

$SO_4^{2-} > I > NO_3^- > HCrO_4^- > Br > Cl > OH$.

[Armbruster T (2001)Stud.Surf.Sci.Cataly. 135:13-27; Langella A, Pansini M, Cappelletti P, de Gennaro B, de Gennaro M, C. Colella (2000) Micropor. Mesopor.Mater. 37:337-343]

ION EXCHANGERS: ZEOLITES MATERIALS

	Zeolite	R_a	CSC (meq/g)
MOR	Mordenite	0.80-0.86	1.8-2.0
HEU	Clinoptilolite	0.73-0.85	2.0-2.3
CHA	Chabazite	0.67	3.0-3.5
PHI	Phillipsite	0.69	3.0-3.5
GIS	Gismondina	0.50	6-7
	Montmorillonite		0.8-1.0

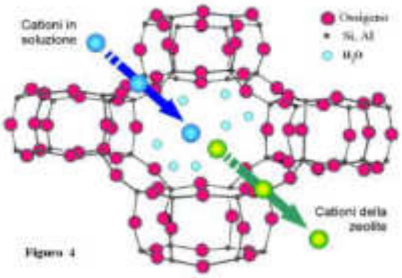


Figura 4

Removal of heavy metals & ammonia

Natural zeolites are ***excellent ion exchangers*** for the **removal and recovery of heavy metal** cations (Pb, Cu, Cd, Zn, Co, Cr, Mn and Fe; Pb, Cu as high as 97%) from drinking and waste-waters.

Ammonia is a major issue for the treatment of municipal wastewater. This remarkable mineral has a ***huge capacity for adsorbing ammonia*.** Ammonia levels in municipal wastewaters can be reduced to 10-15 ppm after treatment facilities.

The processes of ion exchange and adsorption on natural zeolite occur concurrently with the process of **HYDROLYSIS** in aqueous solutions. Determination of hydrolytic activity and stability of zeolites is a very important aspect of technological applications, and hydrolytic activity indicates the chemical stability.

The hydrolysis process (1) is a reaction following the process of ion exchange. Understanding and studying zeolite hydrolysis is of great importance to understanding the properties of zeolite.

The hydrolysis process of zeolite is usually observed by monitoring the pH levels and electric conductivity during which a sudden increase in the pH value can be seen at beginning of the hydrolysis process after which the zeolite-water system tends to stabilize the pH value.

$$\text{Me-Z (s)} + H_2O(l) \leftrightarrow \text{H-Z(s)} + Me^{n+}\,(l) + n\,OH\,(l) \qquad (1)$$

n – cation charge, Me – exchangeable cations (Na+, K+, Ca2+,Mg2+), Z – zeolite

The created OH ions cause an increase in the pH value of the system. A reaction of the metallic ions occurs at the same time (2).

$$Me^{n+}\,(ls) + H_2O\,(l) \leftrightarrow [MeOH]^{+}\,(l) + H^{+}(l) \qquad (2)$$

Increase in the concentration of OH ions at the beginning of hydrolysis causes thus created OH ions to adsorb onto the surface of zeolitic particles, which in turn causes melting of the surface layer of zeolitic particles. Anions on the zeolite surface form with exchangeable cations more or less stable complexes, depending on the stability constant (3).

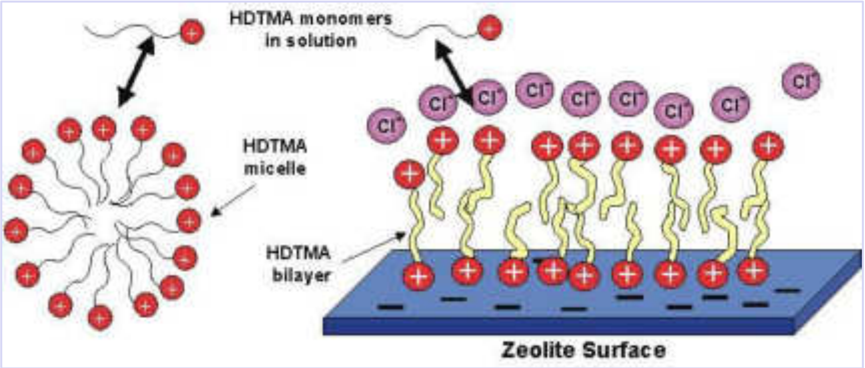
$$Me^{n+}\,(l) + mAy^{-}\,(l) \leftrightarrow (MeAm)^{n-my}\,(l) \qquad (3)$$

Hydrolysed cations in the channels have good mobility and ability to exchange with the cations from the solution because they are connected by weak electrostatic bonds to the basic aluminium-silicate structure.

ION EXCHANGERS: SURFACTANT MODIFIED ZEOLITES (SMZ)

To enhance the simultaneous adsorption capacity of zeolite toward specific hydrophilic and hydrophobic solutes (adsorbates), several researchers have developed an amphiphilic adsorbent by adsorption of certain substances (i.e. cationic surfactants) onto its external surface. The surfactant-modified zeolite (SMZ) became organozeolite.

The removal of anions was made possible on SMZ, prepared through the sorption of cationic surfactant, such as hexadecyltrimethylammonium (HDTMA), on the zeolite surface



Da http://www.zeoliteproducer.com/soilconditioner.html

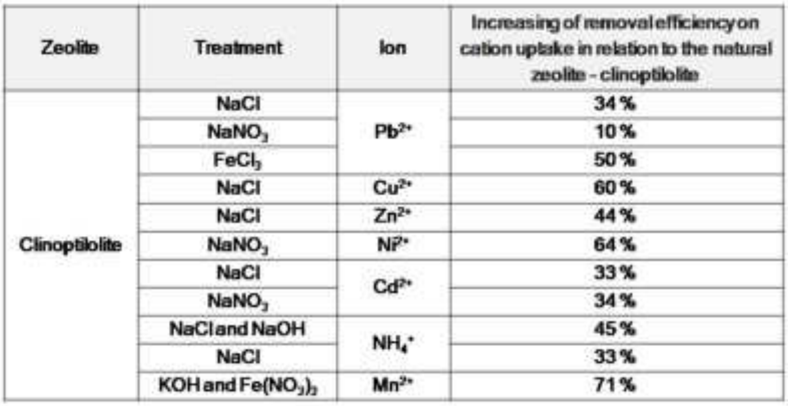
Zeolites are slow release fertilisers. Plant nutrients such as nitrogen and potassium are held by the negatively charged clinoptilolite structure, and released on demand.
Zeolite is very porous with an incredibly large surface area. The selectivity of zeolite for ammonium helps buffer the soil and prevents toxicity, which occurs when excess ammonium is applied.

Strong affinity for ammonium provides superior odour control and a healthy environment
Reduction of gastrointestinal diseases

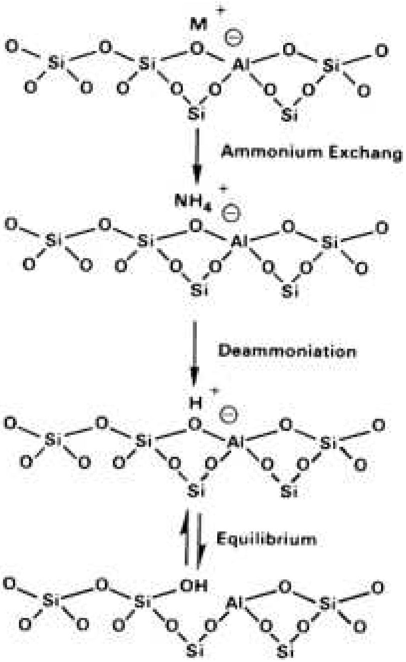
.

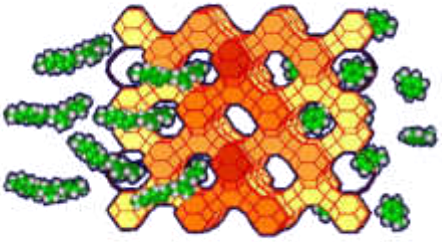
RADIOACTIVE WASTE TREATMENT:
Natural zeolite has a high ion exchange capacity and a particular affinity for heavy metal cations. It can absorb elements such as strontium 90, caesium 137 and other radioactive isotopes from solution, and hold them in its 3 dimensional crystal framework. Zeolites react readily with cement and glass systems thus allowing the radioactive waste to be entrapped and contained safely. Zeolites are physically robust and resistant to nuclear degradation, and they are less expensive than organic ion exchange resins.

ION EXCHANGERS: ZEOLITES MATERIALS



Zeolite	Treatment	Ion	Increasing of removal efficiency on cation uptake in relation to the natural zeolite - clinoptilolite
Clinoptilolite	NaCl	Pb^{2+}	34 %
	$NaNO_3$		10 %
	$FeCl_3$		50 %
	NaCl	Cu^{2+}	60 %
	NaCl	Zn^{2+}	44 %
	$NaNO_3$	Ni^{2+}	64 %
	NaCl	Cd^{2+}	33 %
	$NaNO_3$		34 %
	NaCl and NaOH	NH_4^+	45 %
	NaCl		33 %
	KOH and $Fe(NO_3)_3$	Mn^{2+}	71 %





ADSORBIMENTO/DESORBIMENTO DI INQUINANTI EMERGENTI SU MATRICI MICROPOROSE

Mineralogical Magazine, October 2014, Vol. 78(5), pp. 1115–1140

Recent advances in clean-up strategies of waters polluted with sulfonamide antibiotics: a review of sorbents and related properties

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A. Avogadro, Via T. Michel 11, 15121 Alessandria, Italy
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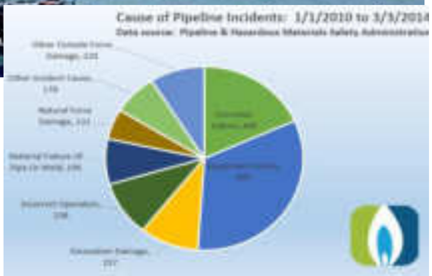
ABSTRACT

Several strategies are available to reduce or eliminate recalcitrant sulfonamide antibiotics (sulfa drugs) from aqueous media. These contaminants are bioactive and ubiquitous pollutants of soils and watercourses and are known to induce bacterial resistance. Here the biological, chemical and physical methods developed over the last 5 years to decontaminate waters polluted with sulfa drugs are reviewed with special attention to procedures that make use of porous adsorbent materials and their applicability to real waters.

During the 1930-2010, the losses of piping containment accounted for 21.9% of the direct causes of accidents, whose effects were mainly related to the consequent water/soil pollution and to the related fire hazards of the leaked materials.



<u>EMERGING ORGANIC ONTAMINANTS</u> (EOCs): Toluene, chlorobenzene, 1,2-dichloethane and methyl-tert-buthyl-ether are of special relevance since are toxic and commonly

Zeolites present almost all the characteristics of an ideal adsorbent for water treatment.

Regeneration of high-silica zeolites after sulfamethoxazole antibiotic adsorption: a combined *in situ* high-temperature synchrotron X-ray powder diffraction and thermal degradation study

Mineralogical Magazine, October 2014, Vol. 78(5), pp. 1141–1159

L. Leardini[1,*], A. Martucci[2], I. Braschi[3], S. Blasioli[3] and S. Quartieri[1]

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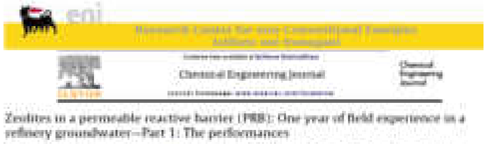
✓ easy regeneration



eni

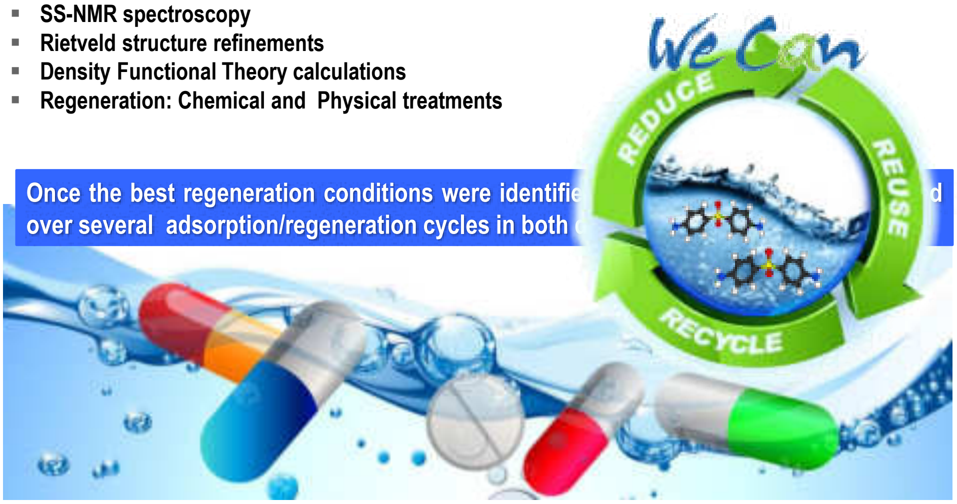
Chemical Engineering Journal

Zeolites in a permeable reactive barrier (PRB): One year of field experience in a refinery groundwater—Part 1: The performances

No significant changes of the MFI and MOR structures have been detected after one year immersion in groundwater

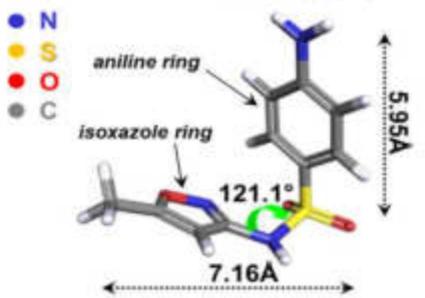
Experimental Techniques

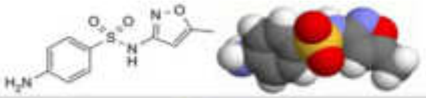
- Liquid chromatography–mass spectrometry
- Thermal analyses (TG, DTA)
- Nitrogen adsorption (196 °C; 106–760 Torr) (SSA and pore volume) and Brunauer–Emmett–Teller (BET) method (external surface area).
- XRPD and FTIR, *in-situ* adsorption/desorption experiments (temperature range 30°-600°C).
- SS-NMR spectroscopy
- Rietveld structure refinements
- Density Functional Theory calculations
- Regeneration: Chemical and Physical treatments



Once the best regeneration conditions were identifie d over several adsorption/regeneration cycles in both

Sulfamethoxazole, $C_{10}H_{11}N_3O_3S$





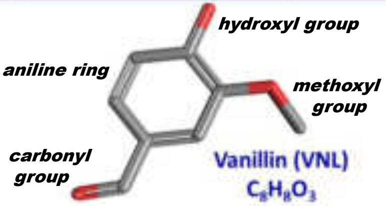
Systematic (IUPAC) name

4-Amino-*N*-(5-methylisoxazol-3-yl)
benzenesulfonamide

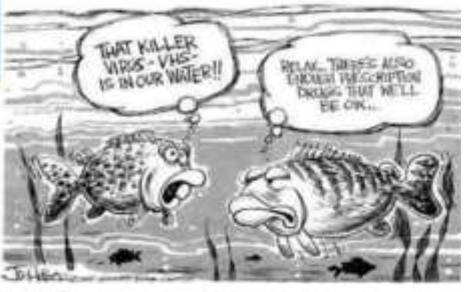
Physical data

Melting point	169 °C (336 °F)

Sulfamethoxazle (SMX) is in the listing of "priority pharmaceuticals" for human use in Italy.
In aquaculture, SMX is added to the food, which is then placed in the water where the fish. are kept.



Vanillin (VNL)
$C_8H_8O_3$

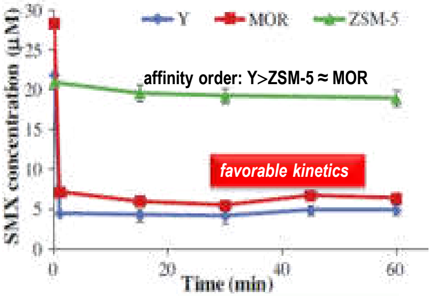


Journal of Colloid and Interface Science 419 (2014) 148–159

Removal of sulfamethoxazole sulfonamide antibiotic from water by high silica zeolites: A study of the involved host–guest interactions by a combined structural, spectroscopic, and computational approach

Sonia Blasioli, Annalisa Martucci, Geo Paul, Lara Gigli, Maurizio Cossi, Cliff T. Johnston, Leonardo Marchese, Ilaria Braschi

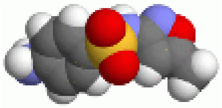
Zeolite Y and MOR adsorbed SMX with a favorable kinetics (a few minutes) up to 24% and 6% zeolite DW, respectively.
The adsorption of SMX into ZSM-5 after 24 h contact at 65 °C reached 8% zeolite DW *(relevant for applications in manure/sewage).*



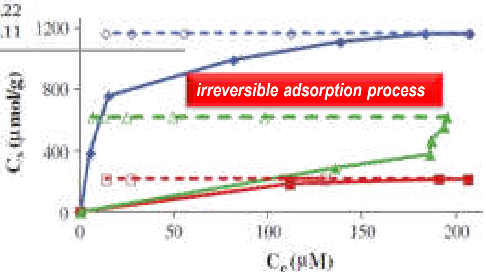
affinity order: Y>ZSM-5 ≈ MOR

favorable kinetics

Sample	Specific surface area (m^2/g)		Total pore volume at $P/P_0 = 0.99$ (cm^3/g, STP)	
	Bare zeolite	Loaded zeolite	Bare zeolite	Loaded zeolite
Y	648	135	0.57	0.29
MOR	441	301	0.28	0.22
ZSM-5	342	150	0.21	0.11



Evidence of the SMX adsorption was obtained by comparing the specific surface area (SSA) and pore volume of the 'bare' and SMX loaded zeolites.
SMX desorption revealed the irreversibility of the adsorption process for each zeolite.



irreversible adsorption process

Chemical and physical regeneration of high silica zeolite Y used to remove sulfonamide antibiotics from water

I.Braschi, S. Blasioli, E. Buscaroli, D. Montecchio and A. Martucci

In press on Journal of Environmental Sciences (2015)

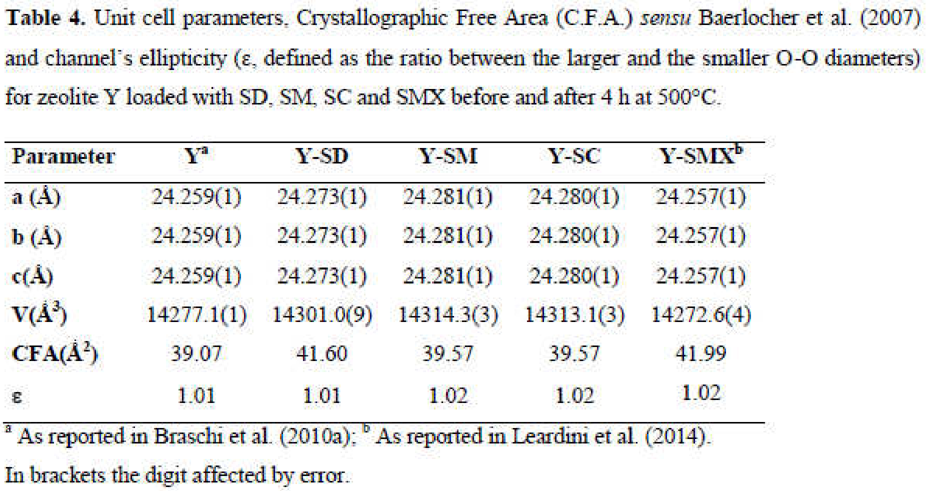


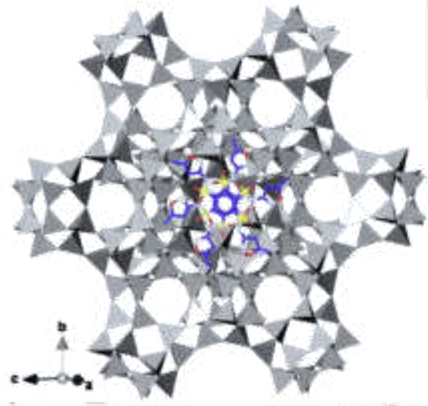
Table 4. Unit cell parameters, Crystallographic Free Area (C.F.A.) *sensu* Baerlocher et al. (2007) and channel's ellipticity (ε, defined as the ratio between the larger and the smaller O-O diameters) for zeolite Y loaded with SD, SM, SC and SMX before and after 4 h at 500°C.

Parameter	Y[a]	Y-SD	Y-SM	Y-SC	Y-SMX[b]
a (Å)	24.259(1)	24.273(1)	24.281(1)	24.280(1)	24.257(1)
b (Å)	24.259(1)	24.273(1)	24.281(1)	24.280(1)	24.257(1)
c(Å)	24.259(1)	24.273(1)	24.281(1)	24.280(1)	24.257(1)
V($Å^3$)	14277.1(1)	14301.0(9)	14314.3(3)	14313.1(3)	14272.6(4)
CFA($Å^2$)	39.07	41.60	39.57	39.57	41.99
ε	1.01	1.01	1.02	1.02	1.02

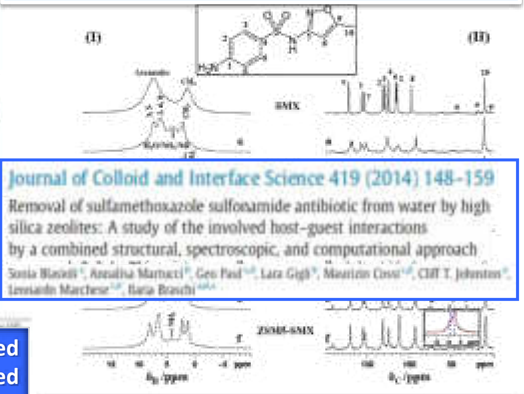
[a] As reported in Braschi et al. (2010a); [b] As reported in Leardini et al. (2014).

In brackets the digit affected by error.

The location of SMX inside the zeolite porosities was defined by XRPD Rietveld analysis.



Medium-weak and cooperative H-bonds and van der Waals forces occur between zeolite porosity walls and the antibiotic.



Journal of Colloid and Interface Science 419 (2014) 148–159

Removal of sulfamethoxazole sulfonamide antibiotic from water by high silica zeolites: A study of the involved host–guest interactions by a combined structural, spectroscopic, and computational approach

Sonia Blasioli, Annalisa Martucci, Geo Paul, Lara Gigli, Maurizio Cossi, Cliff T. Johnston, Leonardo Marchese, Ilaria Braschi

Its efficiency was also positively evaluated to clean-up fresh natural water collected from an Italian river (Reno) in Bologna municipality.

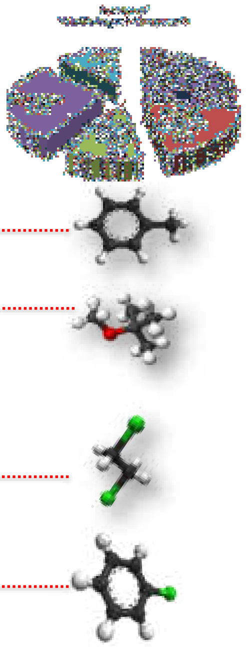
HPLC measurements indicated that zeolite Y adsorbed SMX with a favorable kinetics (a few minutes) up to 20% zeolite DW.

Based on the sorption, structural and spectroscopic data presented, zeolite Y showed the highest affinity for SMX and can be thus considered optimal for sulfonamide removal from impacted waters.

Materials: selected zeolite and pollutants

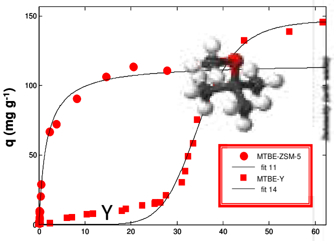
[IUPAC, International Union of Pure and Applied Chemistry; CAS, Chemical Abstract Services; —, not applicable]

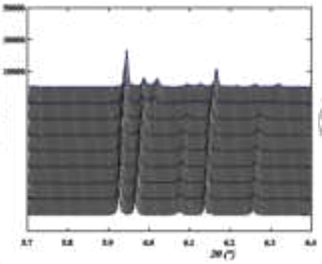
IUPAC name[1]	Common or alternative name (synonyms)[2]	Other possible names[3]	Predominant source
		Alkyl benzenes	
1,2-dimethylbenzene 1,3-dimethylbenzene 1,4-dimethylbenzene	*o*-xylene *m*-xylene *p*-xylene	The X in BTEX, dimethyltoluene, Xylol	gasoline
ethylbenzene	—	The E in BTEX, Ethylbenzol, phenylethane	gasoline
methylbenzene	toluene	The T in BTEX, phenylmethane, Methacide, Toluol, Antisal 1A	gasoline
		Ethers	
2-methoxy-2-methylpropane	methyl *tert*-butyl ether, MTBE	*tert*-butyl methyl ether	fuel oxygenate
		Chlorinated alkenes	
chloroethene	vinyl chloride	chloroethylene, monochloroethene, monovinyl chloride (MVC)	organic synthesis, degradation product
1,1-dichloroethene	1,1-dichloroethylene, DCE	vinylidene chloride	organic synthesis, degradation product
cis-1,2-dichloroethene	*cis*-1,2-dichloroethylene	1,2 DCE, Z-1,2-dichloroethene	solvent, degradation product
trans-1,2-dichloroethene	*trans*-1,2-dichloroethylene	1,2 DCE, E-1,2-dichloroethene	solvent, degradation product
dichloromethane	methylene chloride	—	solvent
		Chlorinated aromatics	
chlorobenzene	monochlorobenzene	benzene chloride, phenyl chloride	solvent, degreaser
1,2-dichlorobenzene	*o*-dichlorobenzene	ortho dichlorobenzol	organic synthesis
1,2,3-trichlorobenzene	1,2,6-trichlorobenzene	—	organic synthesis
1,2,4-trichlorobenzene	1,2,4-trichlorobenzol	—	organic synthesis

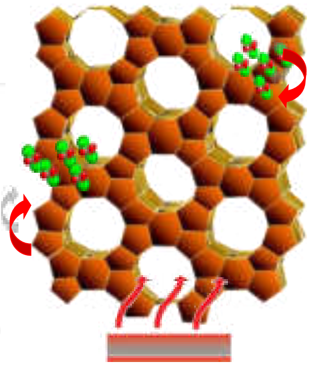


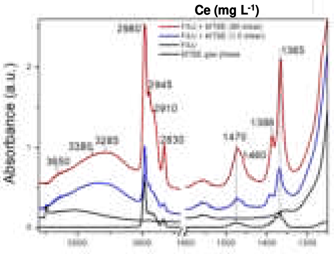
Experimental techniques

EUROPEAN SYNCHROTRON RADIATION FACILITY
INSTALLATION EUROPEENNE DE RADIATION SYNCHROTRON
A Light for Science









Liquid chromatography–mass spectrometry.

Thermal analyses (TG, DTA)

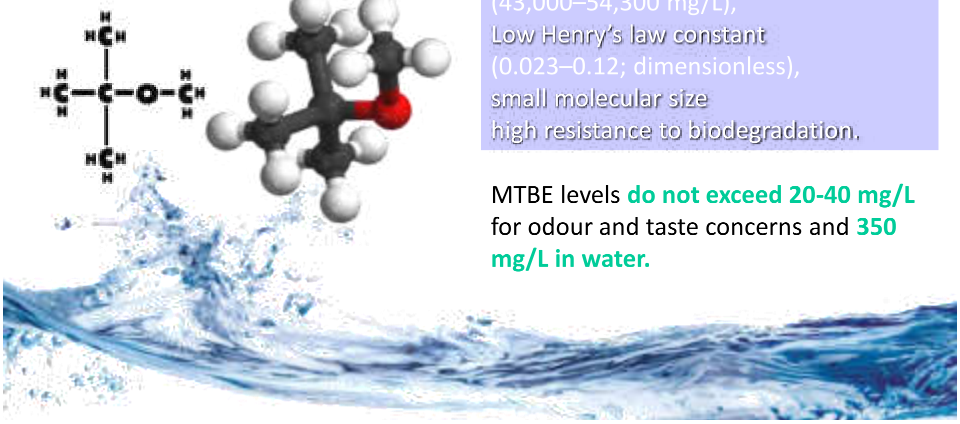
FTIR high vacuum , in-situ adsorption/desorption experiments.

"in situ" synchrotron X-ray powder-diffraction (temperature range 30°-600°C).

Structural evidences of VOCs adsorption at Room Temperature

Removal of fuels-based pollutants from water:
Methyl Tert-Butyl Ether (MTBE)

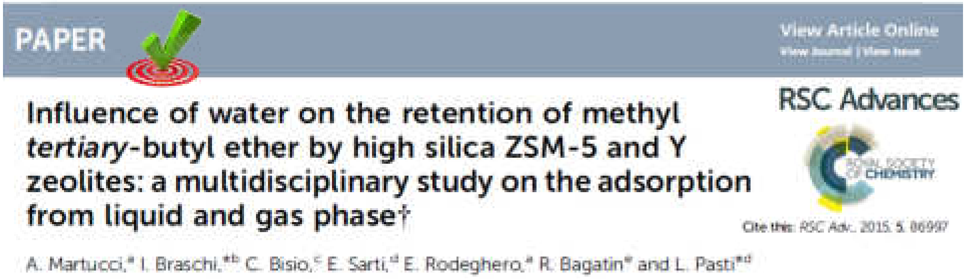
epaResearch
Climate - Water - Sustainability



Methyl Tert-Butyl Ether (MTBE), $C_5H_{12}O$

Water solubility
(43,000–54,300 mg/L),
Low Henry's law constant
(0.023–0.12; dimensionless),
small molecular size
high resistance to biodegradation.

MTBE levels **do not exceed 20-40 mg/L** for odour and taste concerns and **350 mg/L in water.**



PAPER

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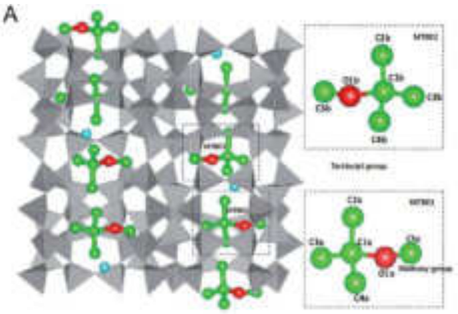
RSC Advances

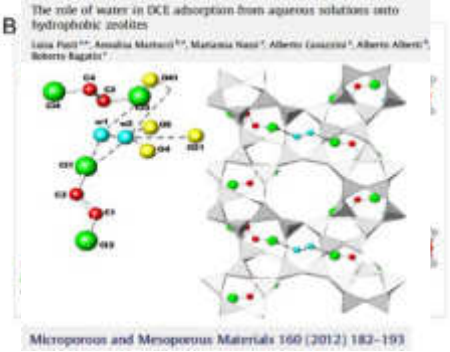
Influence of water on the retention of methyl *tertiary*-butyl ether by high silica ZSM-5 and Y zeolites: a multidisciplinary study on the adsorption from liquid and gas phase†

Cite this: *RSC Adv.*, 2015, 5, 86997

A. Martucci,[a] I. Braschi,[*b] C. Bisio,[c] E. Sarti,[d] E. Rodeghero,[a] R. Bagatin[e] and L. Pasti[*d]

Rietveld refinements indicated that in both zeolites, different organic molecules can be connected by means of hydrogen bonds through water, to form organic–water complexes.





The role of water in DCE adsorption from aqueous solutions onto hydrophobic zeolites

Luisa Pasti, Annalisa Martucci, Marianna Nassi, Alberto Cavazzini, Alberto Alberti, Roberto Bagatin

Microporous and Mesoporous Materials 160 (2012) 182–193

Structural evidences of VOCs competitive adsorption at Room Temperature

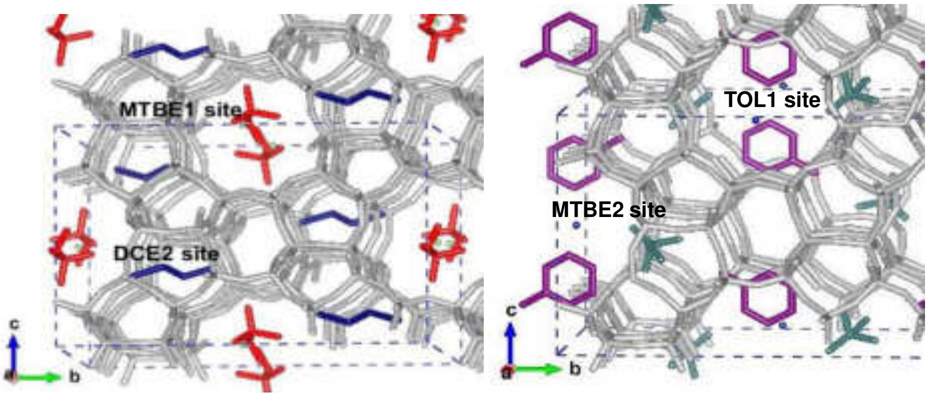
RSC Advances 2016

RSC Advances

Cite this: RSC Adv., 2016, 6, 54544

Competitive adsorption of VOCs from binary aqueous mixtures on zeolite ZSM-5†

L. Pasti,*a E. Rodeghero,b E. Sarti,a V. Bosi,a A. Cavazzini,a R. Bagatin^c and A. Martucci*b



The short interdistance values are clearly **incompatible** with a simultaneous occupancy by more than one molecule, thus highlight the pollutants competitive behaviour in mixture

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Regeneration of high-silica zeolites after sulfamethoxazole antibiotic adsorption: a combined *in situ* high-temperature synchrotron X-ray powder diffraction and thermal degradation study

Mineralogical Magazine, October 2014, Vol. 78(5), pp. 1141–1159

L. Leardini[1,*], A. Martucci[2], I. Braschi[3], S. Blasioli[3] and S. Quartieri[1]

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ABSTRACT

The thermal regeneration of sulfamethoxazole (SMX)-loaded Y and ZSM-5 zeolites was studied using a combined *in situ* high-temperature synchrotron X-ray powder diffraction and thermal degradation study. The evolution of the structural features was monitored in real time in the 30–575°C temperature range by full-profile Rietveld analysis. SMX thermal degradation pathways into high-silica zeolite antibiotic adducts, as well as the release of evolved species are similar to those for pure SMX. The adsorption/desorption process occurs without any significant loss of zeolite crystallinity, though slight deformations to the channel apertures are observed. Regenerated zeolites regain almost perfectly 'bare' (i.e. unloaded) material unit-cell parameters and only a slight memory effect, in terms of structural deformations induced by the process, is registered in the channel geometry. Interestingly, these changes do not affect the adsorption properties of the regenerated samples, which are able to re-adsorb comparable amounts of antibiotic molecules as in the first adsorption cycle.

Regeneration of high-silica zeolites after sulfamethoxazole antibiotic adsorption: a combined *in situ* high-temperature synchrotron X-ray powder diffraction and thermal degradation study

Mineralogical Magazine, October 2014, Vol. 78(5), pp. 1141–1159

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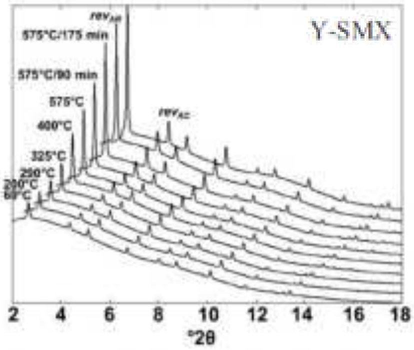
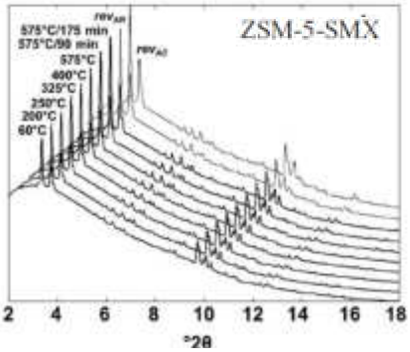


- **Remarkable increase in the low-2θ angle diffraction peak intensities above 300° and 250 °C for zeolite Y and ZSM-5, respectively.**
- **No significant broadening of the diffraction peaks**
- **No change in symmetry in Y-SMX.**
- **After regeneration ZSM-5 regains the monoclinic symmetry of the bare material, as indicated by the typical (133) reflection splitting in the rev pattern.**

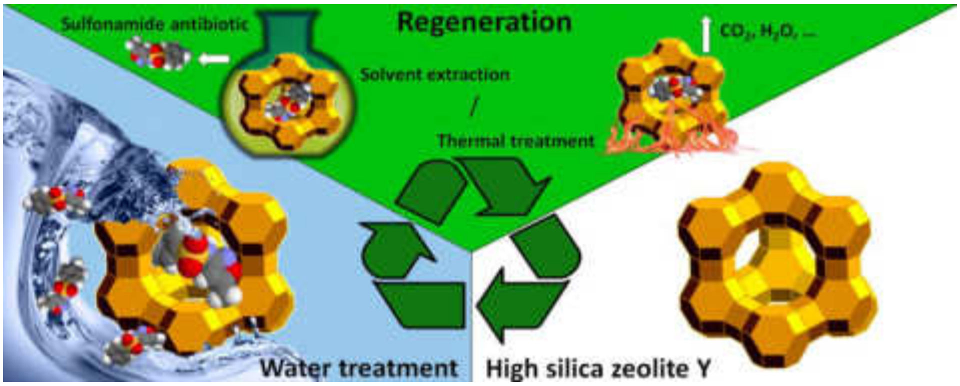


Physicochemical regeneration of high silica zeolite Y used to clean-up water polluted with sulfonamide antibiotics

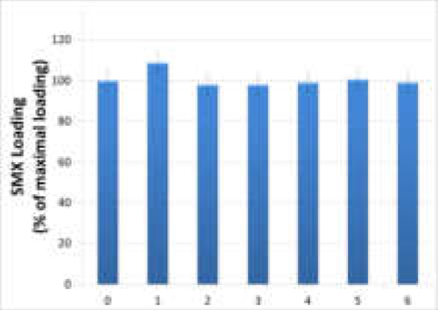
Journal of Environmental Sciences
Volume 43, May 2016, Pages 302-312

I. Braschi[1, 2], S. Blasioli[1], E. Buscaroli[1], D. Montecchio[1], A. Martucci[3]

- ❑ The zeolite aliquot loaded from **natural fresh water** was homogenized and split into sub-samples which were used to evaluate the effectiveness of the **regeneration treatments**.
- ❑ **As far as concerns photolysis, more than 90% of embedded SMX was recovered unmodified after 1 h treatment, making thus the method useless for regeneration purpose.**
- ❑ After Fenton-like treatments, the organic residue remained into the sorbent accounted for 88-100 % of the initially loaded SMX amount.



Organic residues remained into SMX loaded zeolite Y which was thermally treated under different temperatures and time durations. The least energy-consuming conditions are circled: 4 h at 500°C.



The adsorption capacity of treated zeolite resulted very close to the initial loading capacity, thus making these conditions (4 h at 500 °C) suitable for zeolite Y regeneration.

On the basis of the HPLC measurements, when the treatment was applied to the zeolite exposed to the river water, the antibiotic adsorption was found at 85% of the initial loading capacity.

Special Issue Editors *minerals*

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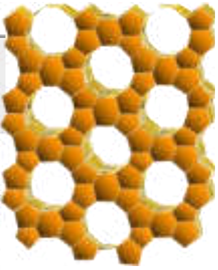
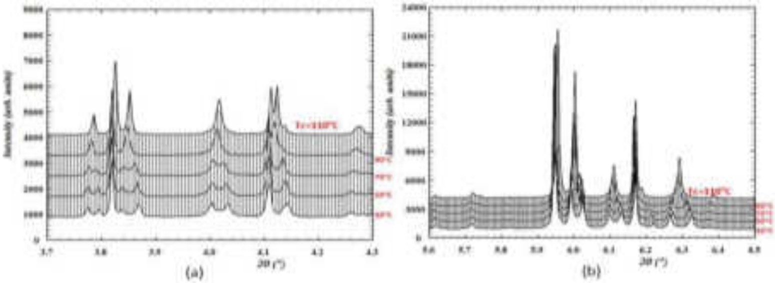
Special Issue "New Insights in Stability, Structure and Properties of Porous Materials"



Temperature-induced desorption of Methyl tert-butyl ether confined on ZSM-5: in situ synchrotron XRD powder diffraction
Elisa Rodeghero , Luisa Pasti , Elena Sarti , Giuseppe Cruciani , Annalisa Martucci



(a) (b)

The evolution of the structural features monitored by full profile Rietveld refinements revealed that a monoclinic ($P\ 2_1/n$) to orthorhombic ($P\ nma$) phase transition occurred at about 100°C. MTBE desorption process caused a remarkable change in the unit-cell parameters.

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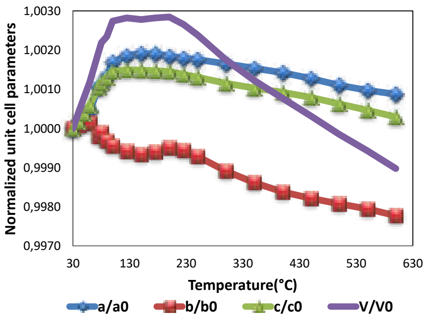
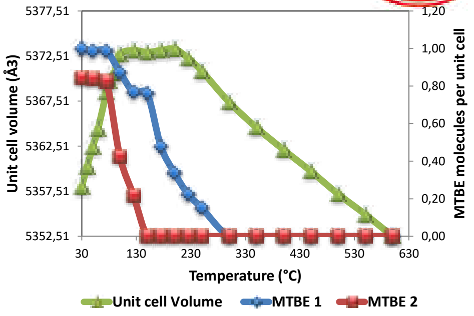
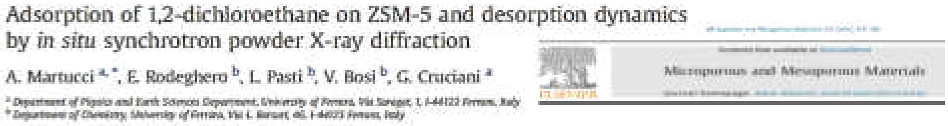
Special Issue "New Insights in Stability, Structure and Properties of Porous Materials"

Temperature-induced desorption of Methyl tert-butyl ether confined on ZSM-5: in situ synchrotron XRD powder diffraction
Elisa Rodeghero , Luisa Pasti , Elena Sarti , Giuseppe Cruciani , Annalisa Martucci

Complete MTBE desorption was achieved upon heating at about 250°C. Rietveld analysis demonstrated that the adsorption/desorption process occurred without any significant zeolite crystallinity loss, but with slight deformations in the channel apertures.







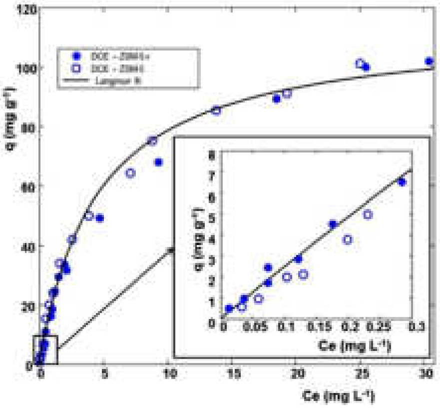
Adsorption of 1,2-dichloroethane on ZSM-5 and desorption dynamics by *in situ* synchrotron powder X-ray diffraction

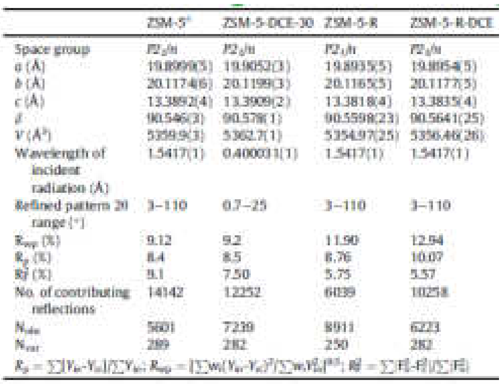
A. Martucci [a,*], E. Rodeghero [b], L. Pasti [b], V. Bosi [b], G. Cruciani [a]

[a] Department of Physics and Earth Sciences Department, University of Ferrara, Via Saragat, 1, I-44122 Ferrara, Italy
[b] Department of Chemistry, University of Ferrara, Via L. Borsari, 46, I-44121 Ferrara, Italy

Once regenerated and reloaded, zeolite does not show any significant crystallinity loss, as well as perfectly regains the unit-cell parameters of fresh material.

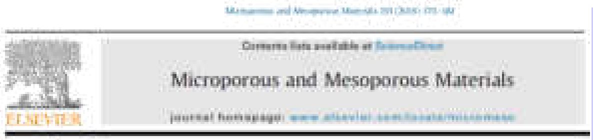
Both organic location and content remain substantially unchanged . ZSM-5 is able to re-adsorb them in amounts comparable to that adsorbed in the first cycle.





	ZSM-5[a]	ZSM-5-DCE-30	ZSM-5-R	ZSM-5-R-DCE
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	19.8999(5)	19.9052(3)	19.8935(5)	19.8954(5)
b (Å)	20.1174(6)	20.1199(3)	20.1165(5)	20.1177(5)
c (Å)	13.3892(4)	13.3909(2)	13.3818(4)	13.3835(4)
β	90.546(3)	90.578(1)	90.5598(23)	90.5641(25)
V (Å^3)	5359.9(3)	5362.7(1)	5354.97(25)	5356.46(26)
Wavelength of incident radiation (Å)	1.5417(1)	0.400031(1)	1.5417(1)	1.5417(1)
Refined pattern 2θ range (°)	3–110	0.7–25	3–110	3–110
R_{wp} (%)	9.12	9.2	11.90	12.94
R_p (%)	8.4	8.5	8.76	10.07
R_F^2 (%)	9.1	7.50	5.75	5.57
No. of contributing reflections	14142	12252	6039	10258
N_{obs}	5601	7239	8911	6223
N_{var}	289	282	250	282

$R_p = \sum|Y_{io}-Y_{ic}|/\sum Y_{io}$; $R_{wp} = [\sum w_i(Y_{io}-Y_{ic})^2/\sum w_i Y_{io}^2]^{0.5}$; $R_F^2 = \sum|F_o^2-F_c^2|/\sum|F_o^2|$



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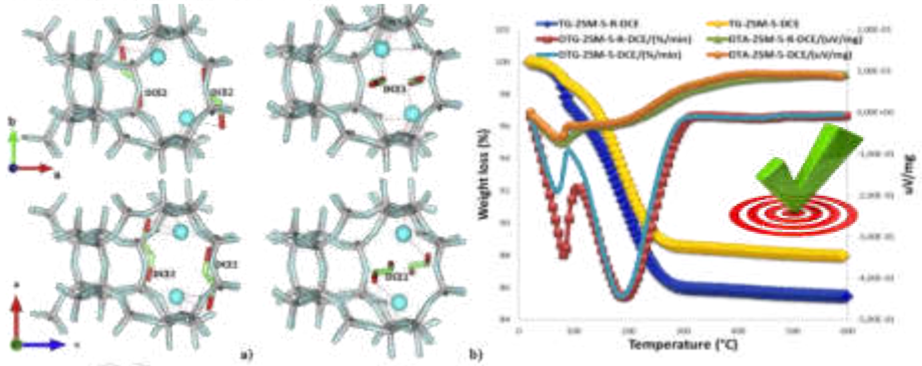
Regeneration is effective when thermally treating ZSM-5 ~ 300°C thus minimising the cost of the regeneration step of the adsorption process

In conclusion, the use of this adsorbent with unchanged adsorption performances after thermal regeneration under mild conditions appears very promising also over several cycles of the adsorption/desorption process



The refined atomic fractional coordinates and occupancies indicate minor differences in both the location and organic content

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CONCLUDING REMARKS

In situ time-resolved powder diffraction allowed a carefull investigation on EOCs theadsorption/desorption zeolites

The regeneration is effective at about 350°C without any significant difference in the saturation capacity after regeneration and without any crystallinity loss;

Hydrophobic zeolites show strong shape selectivity of ZSM-5 towards these organics

On the basis of these results we can conclude that zeolites may be suitable for integration into drinking water and wastewater treatment systems and in environmental remediation projects concerned with removal of emerging organic contaminants.