Properties and Applications of Zeolites

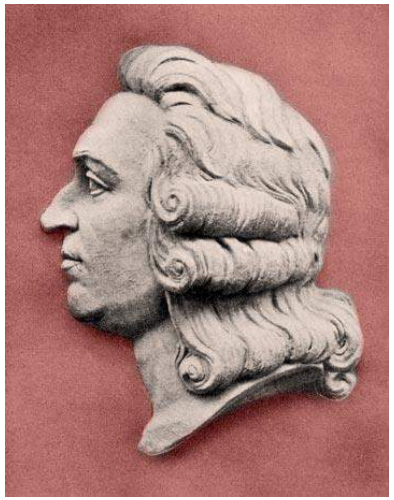
Content

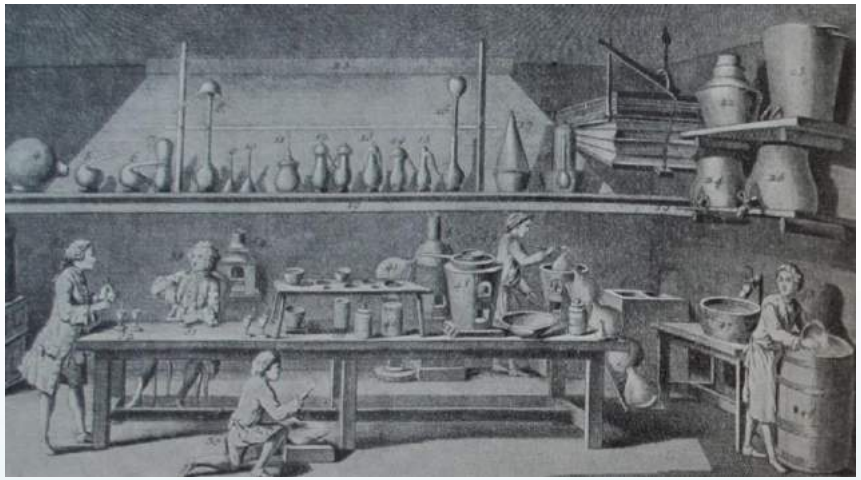
1. Discovery
2. Structure
3. Formation and synthesis
4. Application

Discovery

1756

Axel Fredrick Cronstedt



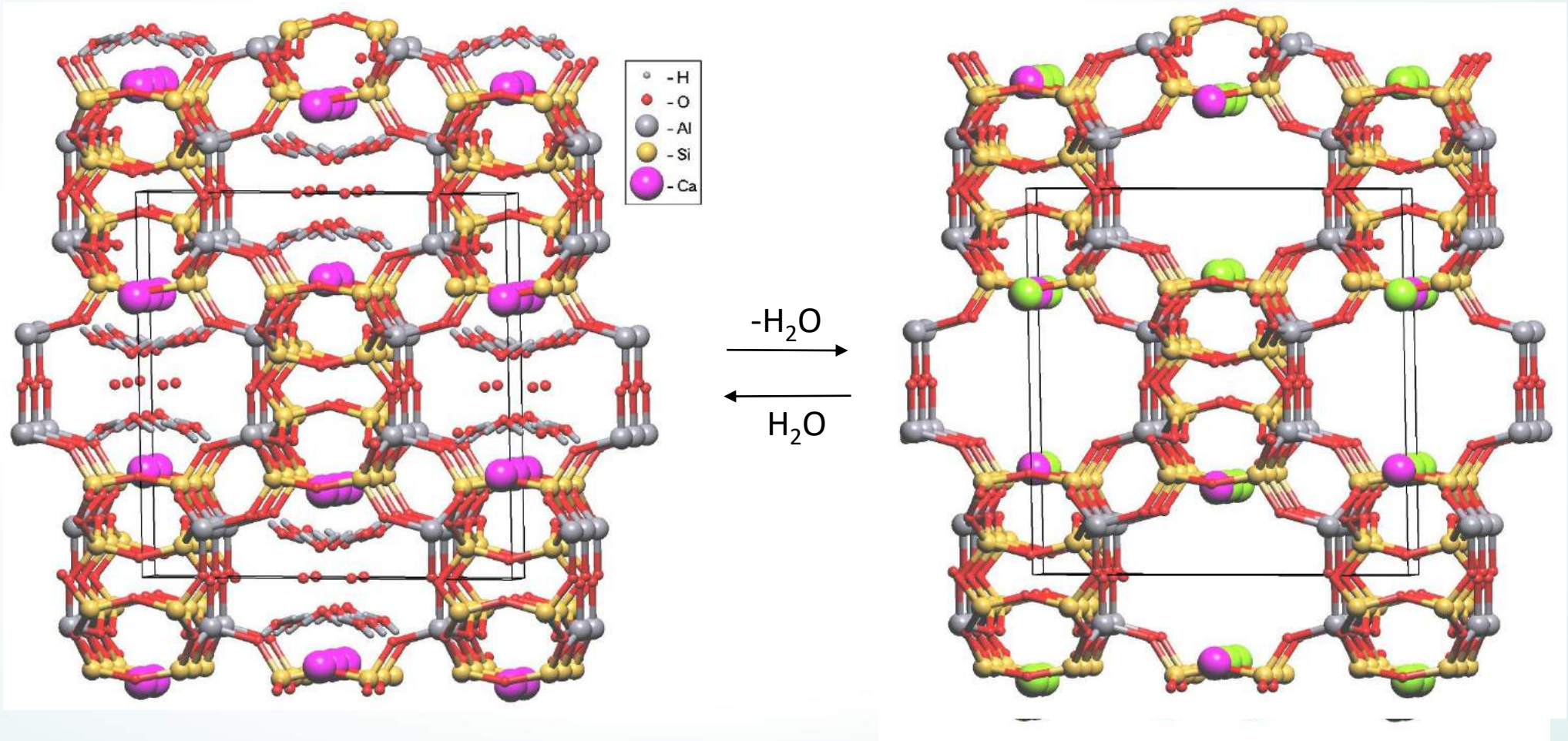


Zein - to boil

Lithos - a stone

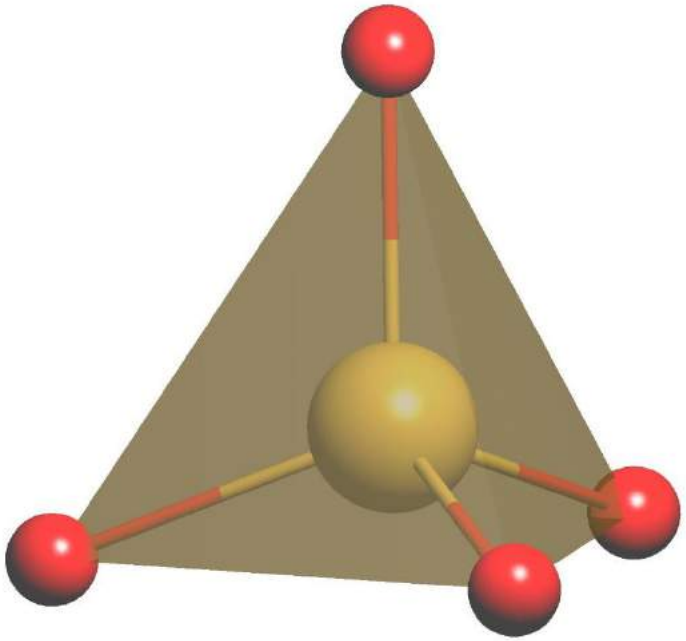
Stilbite

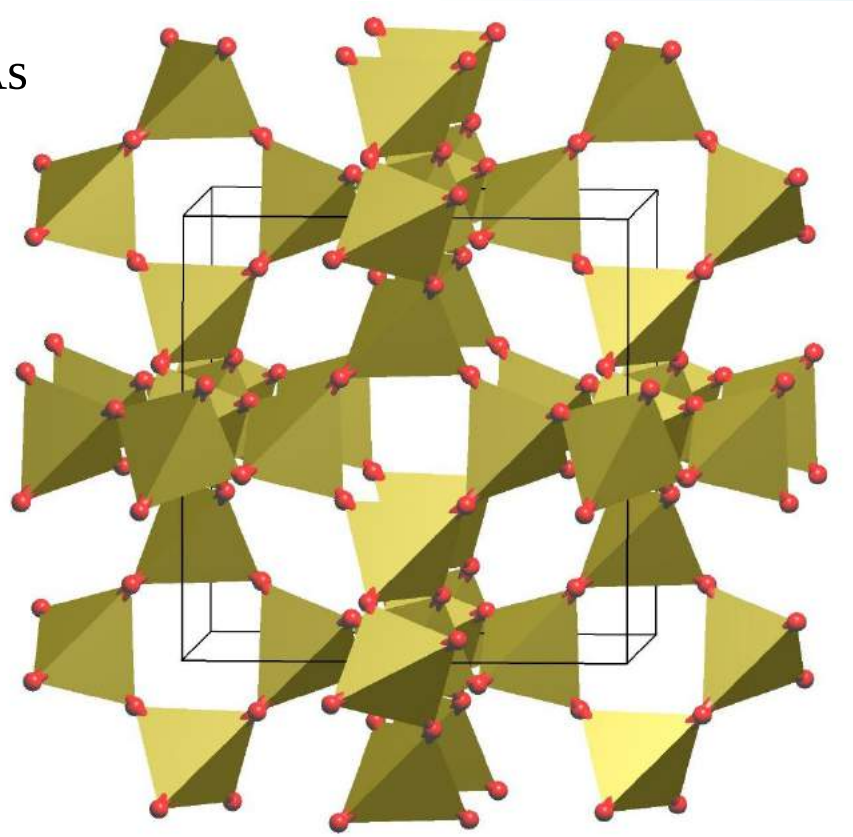
Structure



Structure

Si, Al, Be, Mg, P, Ti, Mn, Fe, Zn, Ga, Ge, Co, B, Li, As

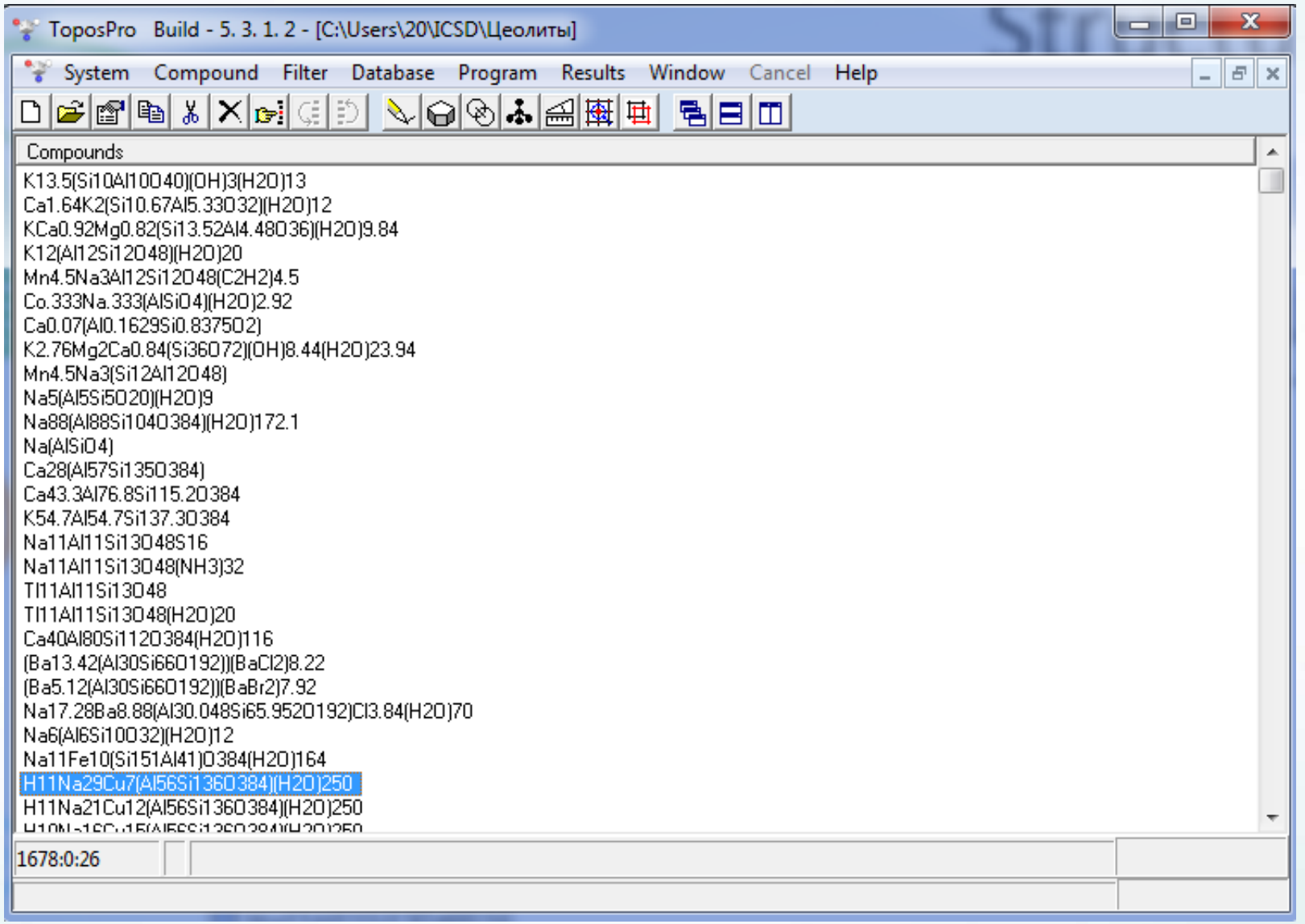




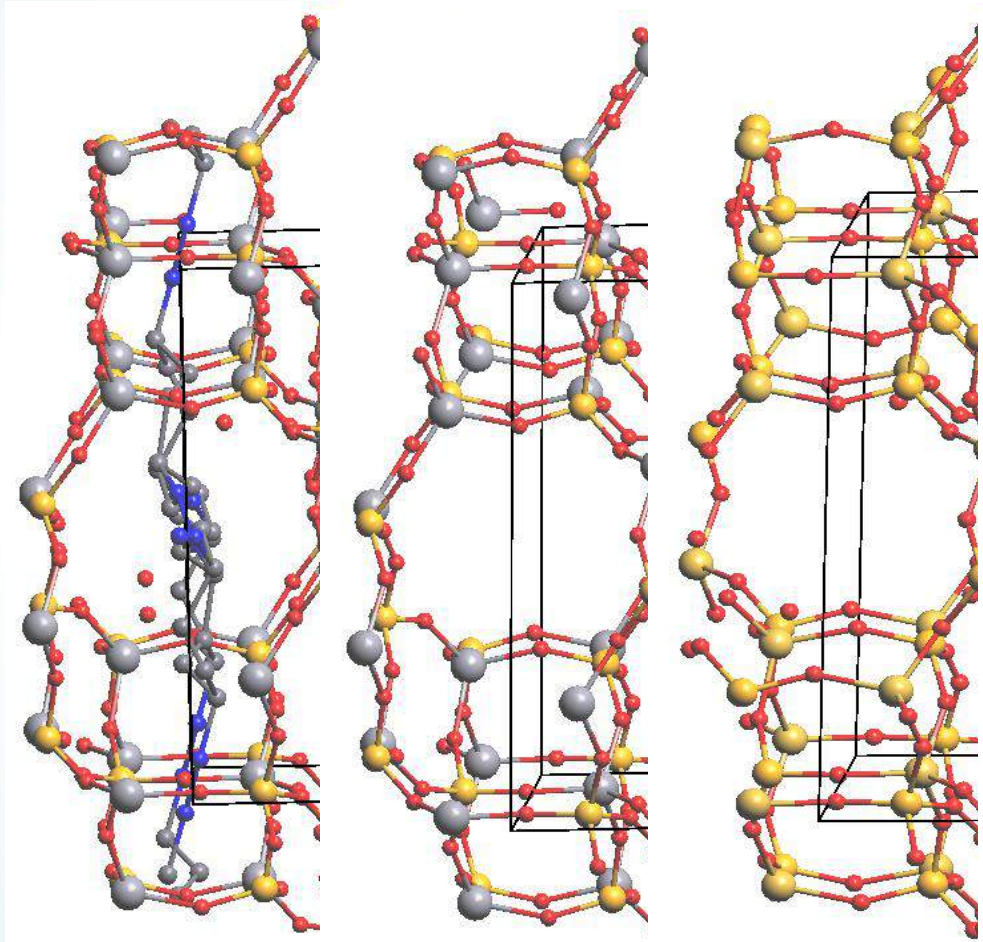
Definition

1. Crystalline substance.
2. Framework consists of linked tetrahedra.
3. Tetrahedron consists of O atoms surrounding the cation.
4. Framework contains open cavities.
5. Cavities are usually occupied by H_2O molecules and extra-framework cations that are usually exchangeable.
6. The channels are large enough to pass the guest species.
7. The framework may be interrupted.

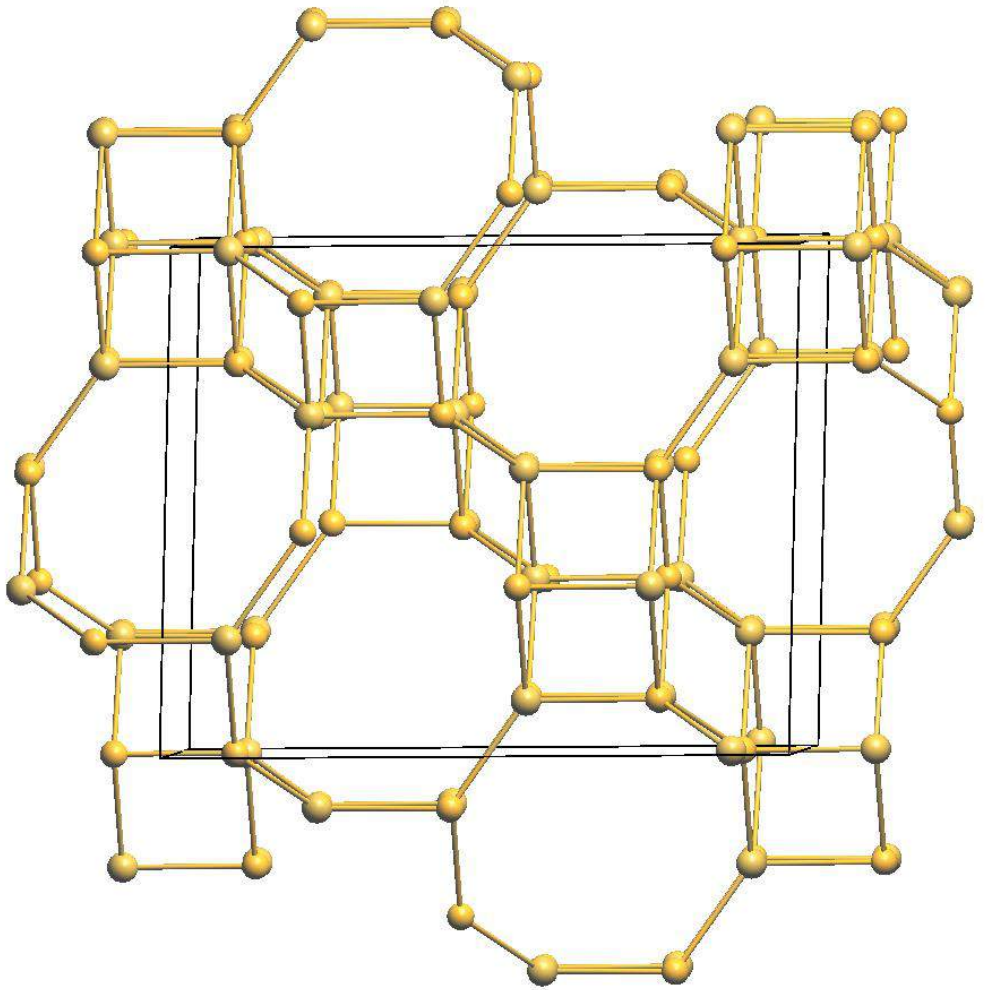
Composition



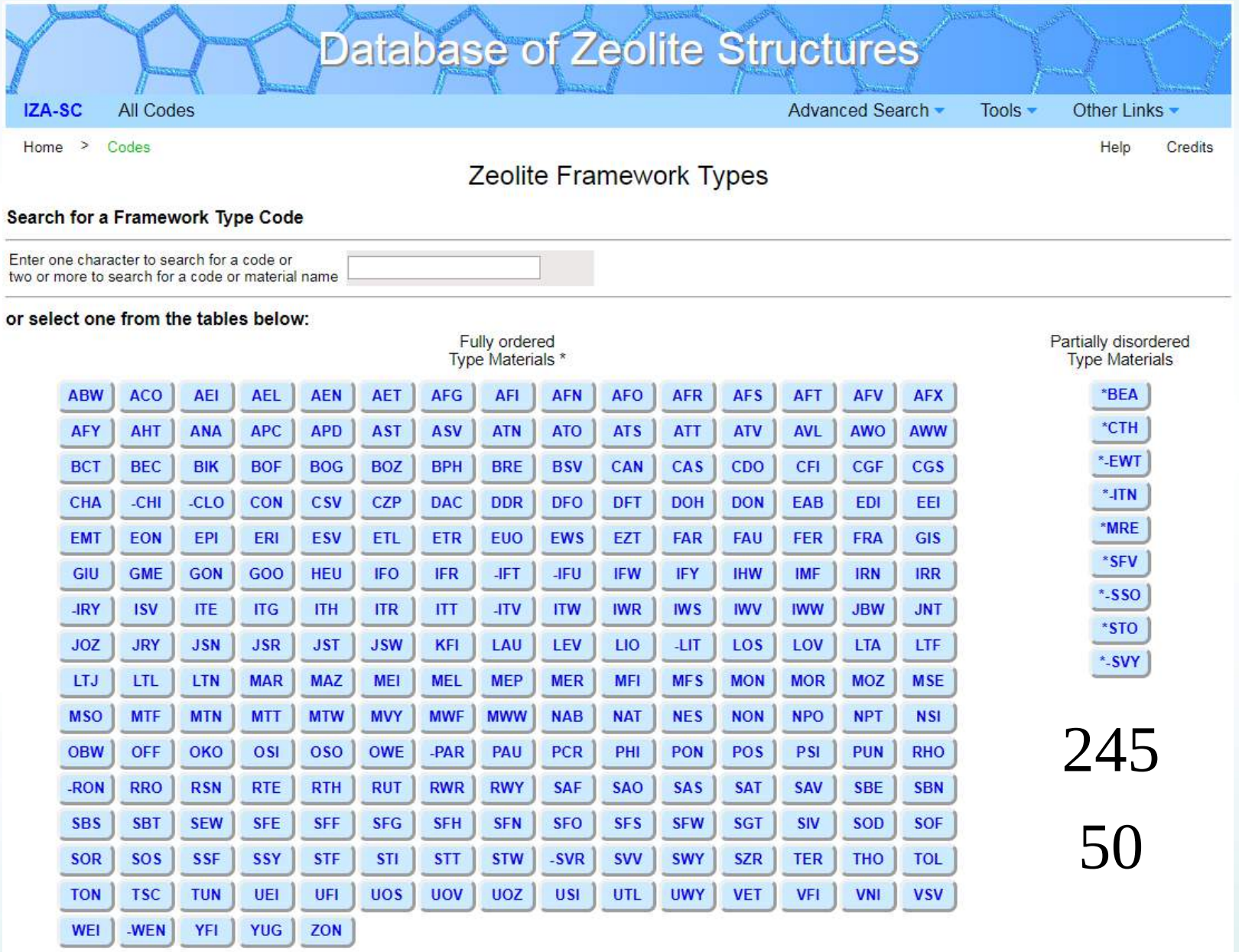
3D Framework



4-connected net



http://iza-structure.org



245

50

Building units

Database of Zeolite Structures

IZA-SC | All Codes | Framework | Material | 3D Drawing | Powder Pattern | CIF | PDF | References

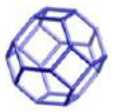
Home » Codes » Framework | Characteristic Units | Help | Credits

Framework Type **FAU**

Framework

Cell Parameters:	cubic	F d -3 m (# 227)	
	a = 24.3450 Å	*b* = 24.3450 Å	*c* = 24.3450Å
	α = 90.000°	β = 90.000°	γ = 90.000°
	Volume =	14428.8Å^3	
	R_{DLS} =	0.0009	
Framework density (FD_{Si}):	13.3 T/1000 Å^3		
Topological density:	TD_{10} = 579	TD = 0.476190	
Ring sizes (# T-atoms):	12 6 4		
Channel dimensionality:	Topological (pore opening > 6-ring): 3-dimensional		
Maximum diameter of a sphere:			
that can be included	11.24 Å		
that can diffuse along	a: 7.35 Å	b: 7.35 Å	c: 7.35 Å
Accessible volume:	27.42 %		
Secondary Building Units:	6-6 or 6-2 or 6 or 4-2 or 1-4-1 or 4		
Composite Building Units:			

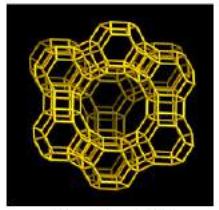
d6r (t-hpr)



sod (t-toc)

Natural Tiling *t-fau* *t-hpr* *t-toc*

Framework images
(click on icon for larger image)



Viewed along [111]

viewed along [110]

Polyhedral model viewed along [110]

an 'artist impression' of a catalytic reaction

Year code assigned 1978
Data last updated Jul 1, 2007

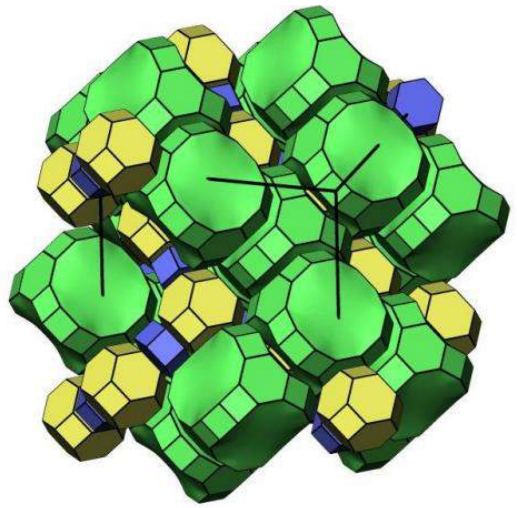
FAU $Fd\bar{3}m$ $2[4^6.6^2]+[4^6.6^8]+[4^{18}.6^4.12^4]$ **1 4 5 3**

TILES

Face symbol:	$[4^6.6^2]$	$[4^6.6^8]$	$[4^{18}.6^4.12^4]$
			
V, E, F:	(12, 18, 8)	(24, 36, 14)	(48, 72, 26)
Symmetry:	$\bar{3}m$	$\bar{4}3m$	$\bar{4}3m$
Wyckoff:	16*c*	8*a*	8*b*
Label:	t-hpr	t-toc	t-fau

Special features: ***simple***

TILING



ZSM-5

Zeolite
Socony
Mobil-five

Database of Zeolite Structures

IZA-SC | All Codes | Framework | Material | 3D Drawing | Powder Pattern | CIF | PDF | References

Home » Codes » Type Material | Characteristic Units | Help | Credits

Framework Type **MFI**

Type Material

Material Name: ZSM-5

Chemical Formula§: $|Na^{+}_{n}(H_2O)_{16}|[Al_nSi_{96-n}O_{192}]$-**MFI**, $n < 27$

Unit Cell§:

orthorhombic	*P n m a (# 62)*	
a' = 20.0700Å	*b'* = 19.9200Å	*c'* = 13.4200Å
α' = 90.000 °	β' = 90.000°	γ' = 90.000°

Framework density: 17.9 T/1000 Å^3

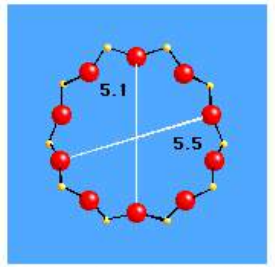
Channels: {[100] **10** 5.1 x 5.5 <-> [010] **10** 5.3 x 5.6}***

Dimensionality

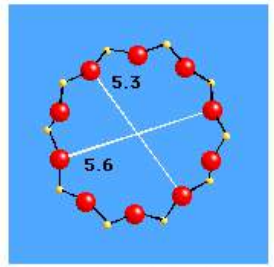
Sorption (molecular cross section > 3.4Å): 3-dimensional

Topological (pore opening > 6-ring): 3-dimensional

Limiting Rings



10-ring viewed along [100]



10-ring viewed along [010]

References:

Kokotailo, G.T., Lawton, S.L., Olson, D.H. and Meier, W.M.
"Structure of synthetic zeolite ZSM-5"
Nature, **272**, 437-438 (1978)

§ Olson, D.H., Kokotailo, G.T., Lawton, S.L. and Meier, W.M.
"Crystal Structure and Structure-Related Properties of ZSM-5"
J. Phys. Chem., **85**, 2238-2243 (1981)

van Koningsveld, H., van Bekkum, H. and Jansen, J.C.
"On the location and disorder of the tetrapropylammonium (TPA) ion in zeolite ZSM-5 with improved framework accuracy"
Acta Crystallogr., **B43**, 127-132 (1987)

Name and Code derivation:

Zeolite Socony Mobil - five
→ ZSM-5 (five)
→ **MFI**

§ *Chemical Formula and Unit Cell taken from the reference marked with this sign*

Materials

Database of Zeolite Structures

IZA-SC | All Codes | Framework | Material | 3D Drawing | Powder Pattern | CIF | PDF | References

Home » Codes » Framework

MFI Type Material
MFI Related materials

Characteristic Units | Help | Credits

F … MFI

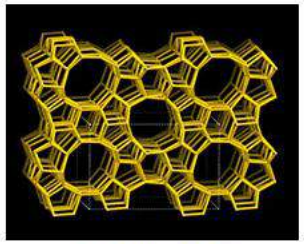
Framework

Cell Parameters:	orthorhombic	P n m a (# 62)	
	a = 20.0900 Å	*b* = 19.7380 Å	*c* = 13.1420Å
	α = 90.000°	β = 90.000°	γ = 90.000°
	Volume =	5211.3Å^3	
	R_{DLS} =	0.0020	
Framework density (FD_{Si}):	18.4 T/1000 Å^3		
Topological density:	TD_{10} = 960	TD = 0.825819	
Ring sizes (# T-atoms):	10 6 5 4		
Channel dimensionality:	Topological (pore opening > 6-ring): 3-dimensional		
Maximum diameter of a sphere:			
that can be included	6.36 Å		
that can diffuse along	a: 4.7 Å	b: 4.46 Å	c: 4.46 Å
Accessible volume:	9.81 %		
Secondary Building Units:	5-1		
Composite Building Units:			

mor (t-tes) | *cas* | *mfi (t-pen)* | *mel*

Natural Tiling *t-bog-1* *t-kah* *t-mel* *t-mel-1* *t-mel-2* *t-mfi-1* *t-mfi-2* *t-pen* *t-pes* *t-tes*

Framework images
(click on icon for larger image)



Viewed along [010]

framework, viewed along [100]

projection along [010]

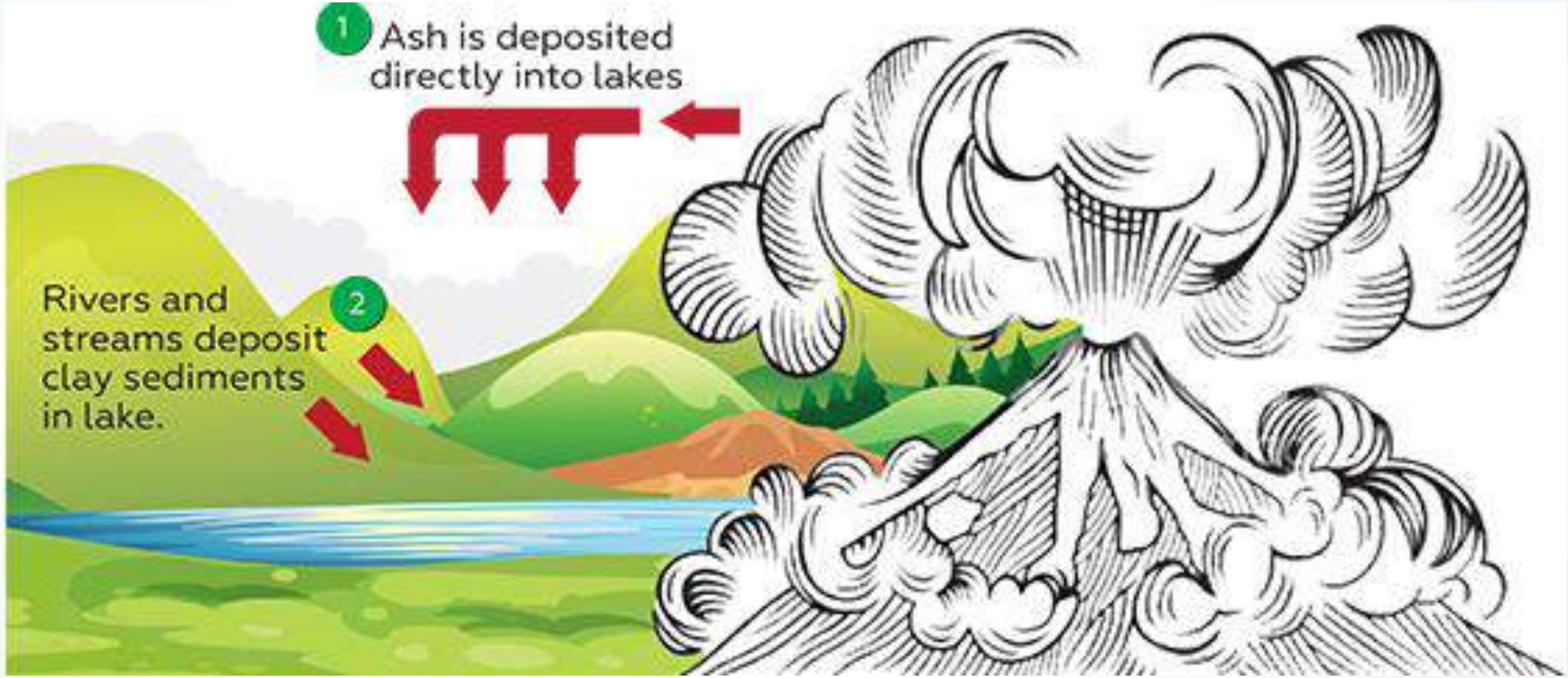
10ring straight channel

complex of 10rings viewed along [010]

complex of 10rings viewed along [100]

- ZSM-5
- FeS-1
- MnS-1
- Mutinaite
- [As-Si-O]-MFI
- [Ga-Si-O]-MFI
- [Fe-Si-O]-MFI
- NU-4
- TSZ-III
- ZBH
- Encilite
- AZ-1
- TSZ
- ZKQ-1B
- TS-1
- USI-108
- ZMQ-TB
- NU-5
- TZ-01
- USC-4
- AMS-1B
- FZ-1
- LZ-105
- Bor-C
- Boralite C
- Silicalite

Formation


1
Ash is deposited directly into lakes
2
Rivers and streams deposit clay sediments in lake.

Deposits


Пастбищное
Ягоднинское
Сокирницкое (Украина)
Хотынецкое
Хогуруу
Серёдочное
Чеховское
Лютогское
Татарско-Шатрашанское
Ванчинское
Радденское
Чутуевское
Сахаптинское
Пегасское
Пашенское
Холинское
Шивьяртуйское
Тайжузгенское (Казахстан)
Бадинское
Айдатское (Азерб.), Ноемберянское (Армения)
Тедзамское, Дзегвское (Грузия)

Natural zeolites

analcime

chabasite

heulandite

clinoptilolite

natrolite

sodalite

stilbite

phillipsite

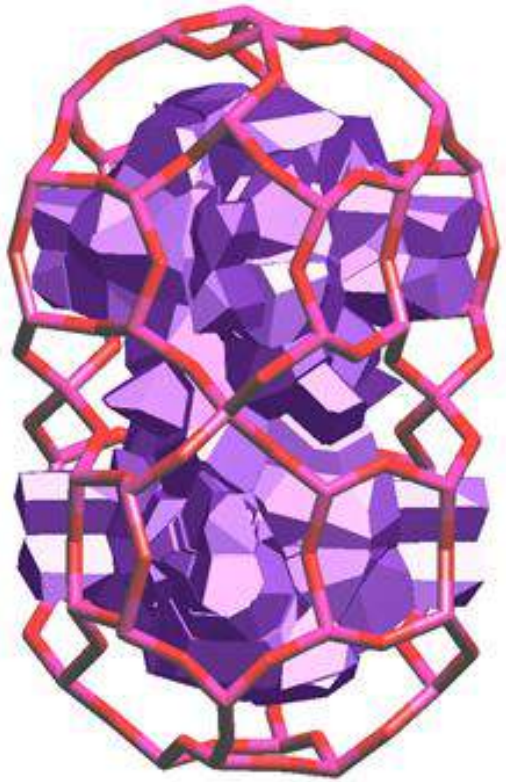
Synthesis

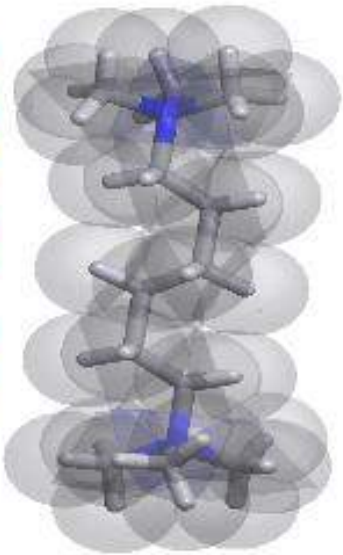
Mixing

$NaAl(OH)_4+Na_2SiO_3+NaOH$ +template, 25^0C gel formation

$Na_n(Al($ 5-175^0C

H)n





Synthesis

Composition

Concentrations and reactant ratio

Order of mixing

Temperature

Ageing time

Crystallization time

pH

Stirring/No stirring

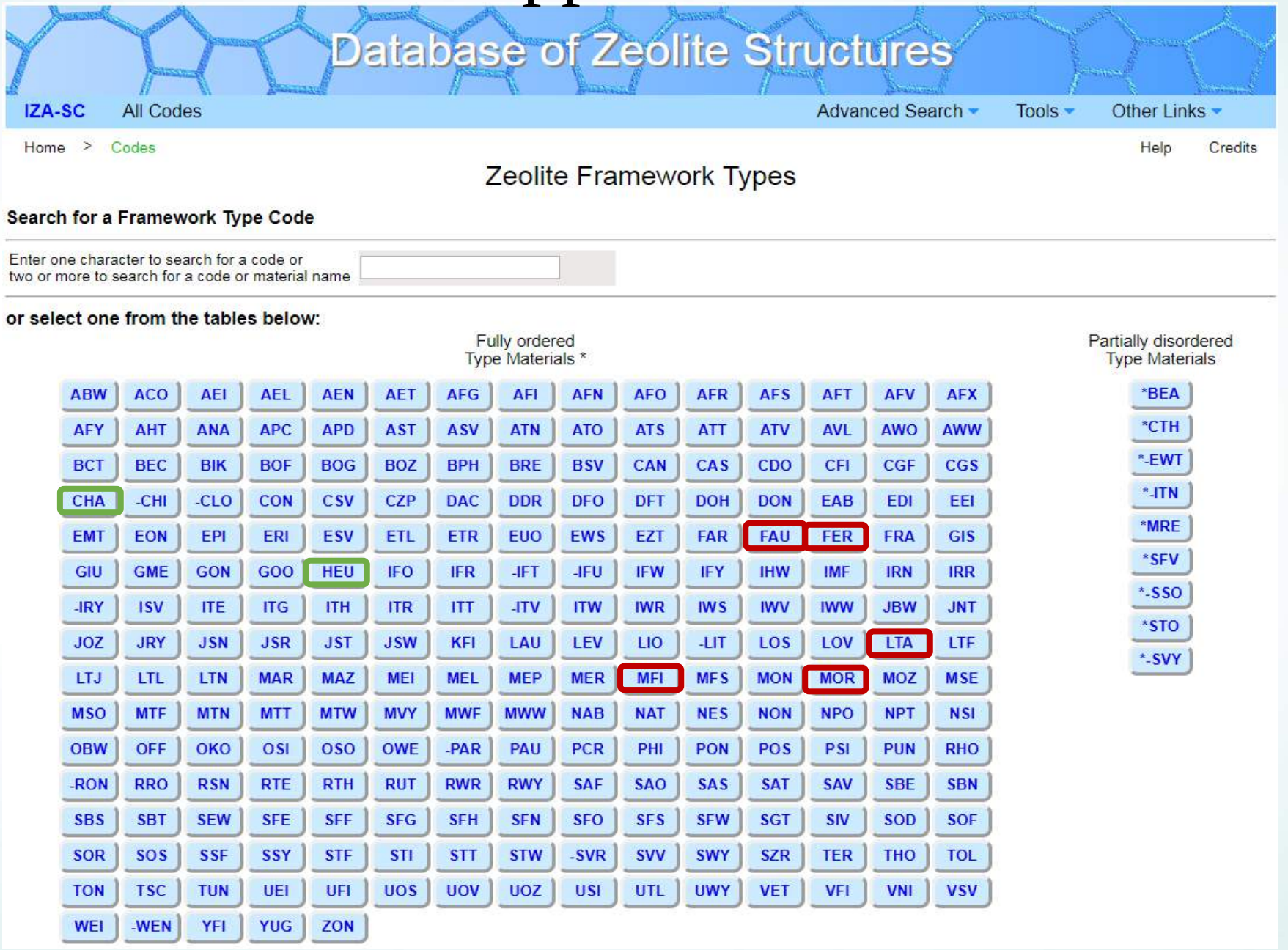
Seeding

Templates

Hypothetical zeolites

1. M. M. J. Treacy, I. Rivin, E. Balkovsky, K. H. Randall, M. D. Foster, Enumeration of Periodic Tetrahedral Frameworks. II. Polynodal Graphs. *Micropor. Mesopor. Mater.* **2004**, *74*, 121.
2. R. Pophale, P. A. Cheeseman, M. W. Deem, A database of new zeolite-like materials. *Phys. Chem. Chem. Phys*. **2011**, *13*, 12407.
3. Y. Li, J. Yu, R. Xu, Criteria for Zeolite Frameworks Realizable for Target Synthesis. *Angew. Chem. Int. Ed.* **2013**, *52*, 1673.

Application



Database of Zeolite Structures

IZA-SC | All Codes | Framework | Material | 3D Drawing | Powder Pattern | CIF | PDF | References

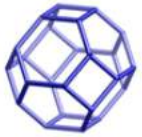
Home » Codes » Framework | Characteristic Units | Help | Credits

Framework Type **LTA**

Framework

Cell Parameters:	cubic	P m -3 m (# 221)	
	a = 11.9190 Å	*b* = 11.9190 Å	*c* = 11.9190Å
	α = 90.000°	β = 90.000°	γ = 90.000°
	Volume =	1693.2Å^3	
	R_{DLS} =	0.0026	
Framework density (FD_{Si}):	14.2 T/1000 Å^3		
Topological density:	TD_{10} = 641	TD = 0.533333	
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	11.05 Å		
that can diffuse along	a: 4.21 Å	b: 4.21 Å	c: 4.21 Å
Accessible volume:	21.43 %		
Secondary Building Units:	8 or 4-4 or 6-2 or 6 or 1-4-1 or 4		
Composite Building Units:			

d4r (t-cub)

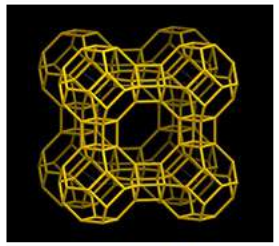


sod (t-toc)

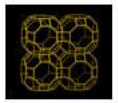
lta (t-grc)

Natural Tiling *t-cub* *t-grc* *t-toc*

Framework images
(click on icon for larger image)

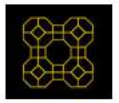


Viewed along [100]



framework, showing the alpha cages

alpha-cage, sodalite cage and 4MR



projection along [100]

Year code assigned	1978
Data last updated	Jul 1, 2007

Zeolite A

Database of Zeolite Structures

IZA-SC | All Codes | Framework | Material | 3D Drawing | Powder Pattern | CIF | PDF | References

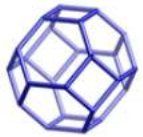
Home » Codes » Framework | Characteristic Units | Help | Credits

Framework Type **FAU**

Framework

Cell Parameters:	cubic	F d -3 m (# 227)	
	a = 24.3450 Å	*b* = 24.3450 Å	*c* = 24.3450Å
	α = 90.000°	β = 90.000°	γ = 90.000°
	Volume =	14428.8Å^3	
	R_{DLS} =	0.0009	
Framework density (FD_{Si}):	13.3 T/1000 Å^3		
Topological density:	TD_{10} = 579	TD = 0.476190	
Ring sizes (# T-atoms):	12 6 4		
Channel dimensionality:	Topological (pore opening > 6-ring): 3-dimensional		
Maximum diameter of a sphere:			
that can be included	11.24 Å		
that can diffuse along	a: 7.35 Å	b: 7.35 Å	c: 7.35 Å
Accessible volume:	27.42 %		
Secondary Building Units:	6-6 or 6-2 or 6 or 4-2 or 1-4-1 or 4		
Composite Building Units:			

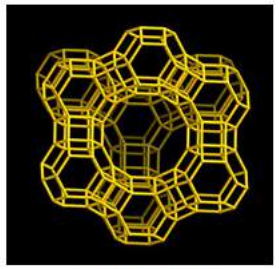
d6r (t-hpr)



sod (t-toc)

Natural Tiling *t-fau* *t-hpr* *t-toc*

Framework images
(click on icon for larger image)



Viewed along [111]

viewed along [110]

Polyhedral model viewed along [110]

an 'artist impression' of a catalytic reaction

Year code assigned	1978
Data last updated	Jul 1, 2007

Zeolite X Si/Al 1.25
ZeoliteY Si/Al 2.3
USY (Ultra-Stable-Y) Si/Al 5.6

Database of Zeolite Structures

IZA-SC | All Codes | Framework | Material | 3D Drawing | Powder Pattern | CIF | PDF | References

Home » Codes » Type Material | Characteristic Units | Help | Credits

Framework Type **MFI**

Type Material

Material Name: ZSM-5

Chemical Formula§: $|Na^{+}_{n}(H_2O)_{16}|\ [Al_nSi_{96-n}O_{192}]$-**MFI** , n < 27

Unit Cell§: orthorhombic *P n m a (# 62)*

a' = 20.0700Å	*b'* = 19.9200Å	*c'* = 13.4200Å
α' = 90.000 °	β' = 90.000°	γ' = 90.000°

Framework density: 17.9 T/1000 Å^3

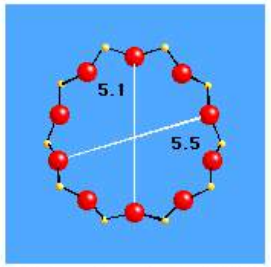
Channels: {[100] **10** 5.1 x 5.5 <-> [010] **10** 5.3 x 5.6}***

Dimensionality

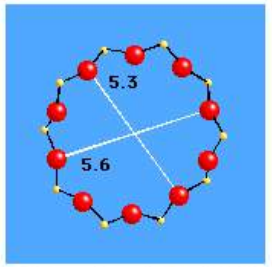
Sorption (molecular cross section > 3.4Å): 3-dimensional

Topological (pore opening > 6-ring): 3-dimensional

Limiting Rings



10-ring viewed along [100]



10-ring viewed along [010]

References:

Kokotailo, G.T., Lawton, S.L., Olson, D.H. and Meier, W.M.
"Structure of synthetic zeolite ZSM-5"
Nature, **272**, 437-438 (1978)

§ Olson, D.H., Kokotailo, G.T., Lawton, S.L. and Meier, W.M.
"Crystal Structure and Structure-Related Properties of ZSM-5"
J. Phys. Chem., **85**, 2238-2243 (1981)

van Koningsveld, H., van Bekkum, H. and Jansen, J.C.
"On the location and disorder of the tetrapropylammonium (TPA) ion in zeolite ZSM-5 with improved framework accuracy"
Acta Crystallogr., **B43**, 127-132 (1987)

Name and Code derivation:

Zeolite Socony Mobil - five
→ ZSM-5 (five)
→ **MFI**

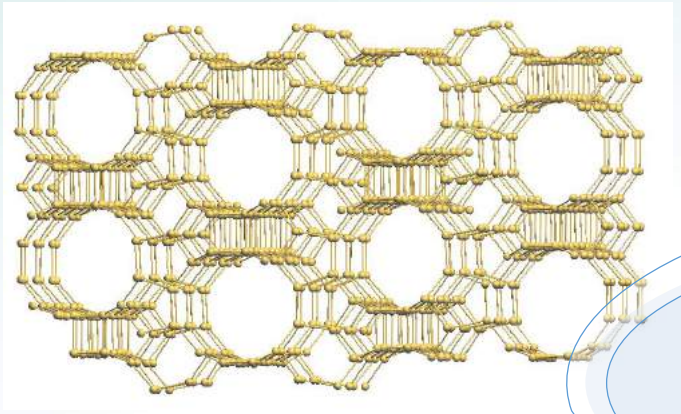
§ *Chemical Formula and Unit Cell taken from the reference marked with this sign*

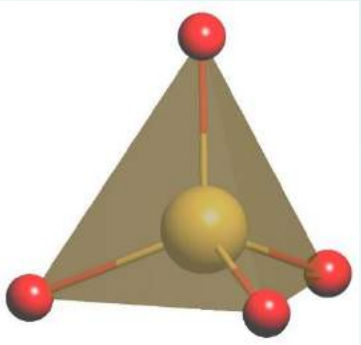
H-ZSM-5

Application: building

4 000 000 t

Si, Al, Be, Mg, P, Ti, Mn, Fe, Zn, Ga, Ge, Co, B, Li, As



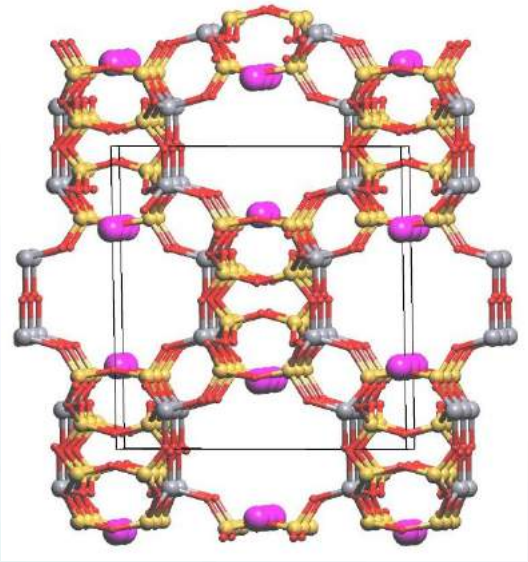


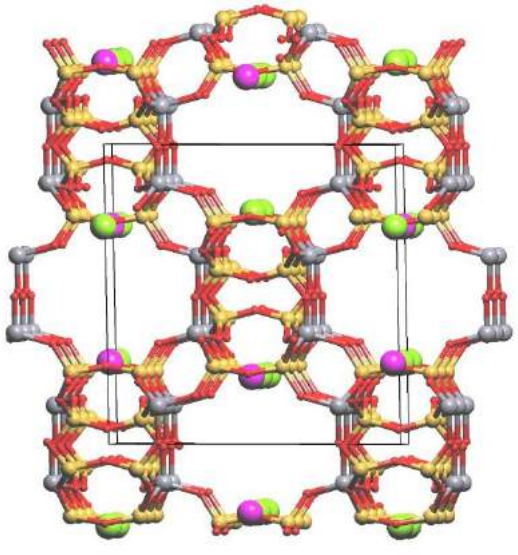
Channels & cavities

Various T-atoms

Many actives centers

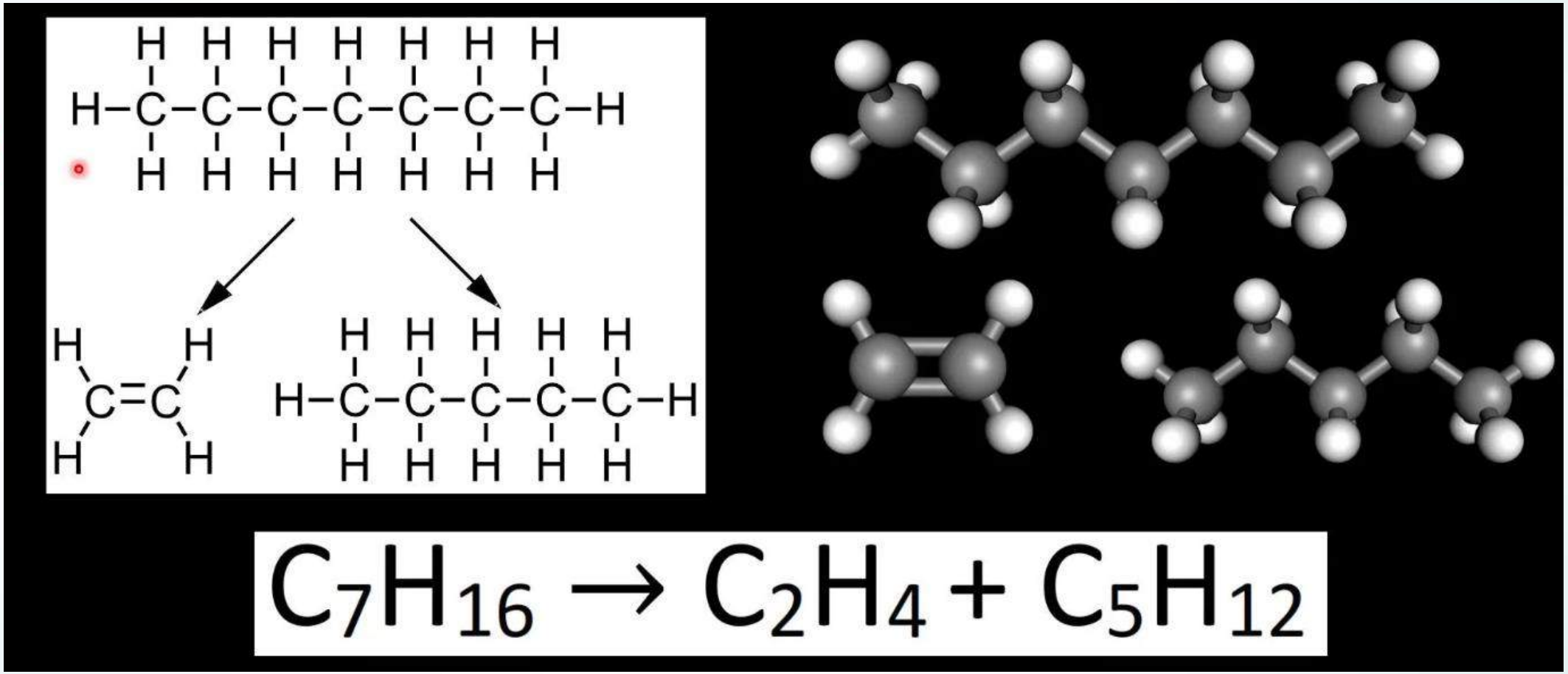
Kt-exchange





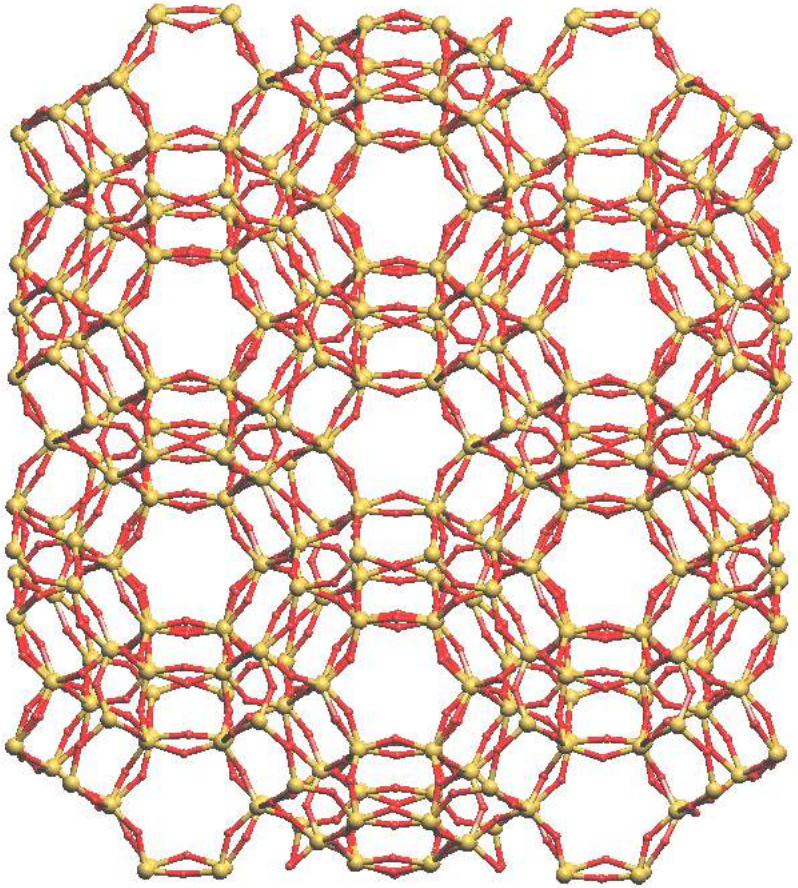
Adsorbents
Molecular sieves
Catalysis
Kt-exchange

Applications: catalysis



Applications: catalysis

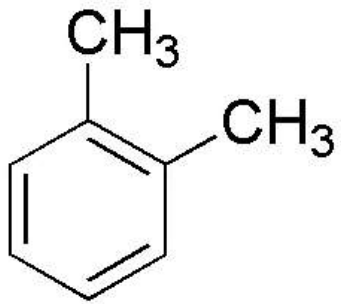
Zeolite Y (FAU) 300 000 t



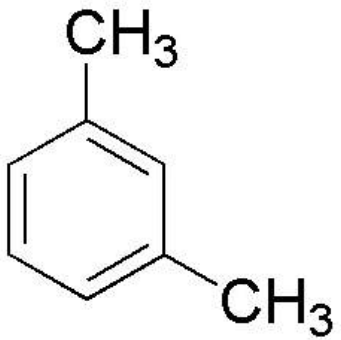
Applications: catalysis

H-ZSM-5 (MFI)

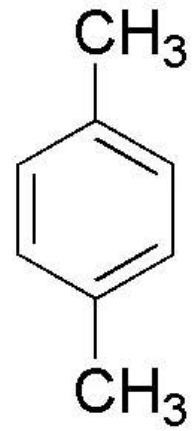
"Polyester" industry



ortho-xylene
(1,2-dimethylbenzene)



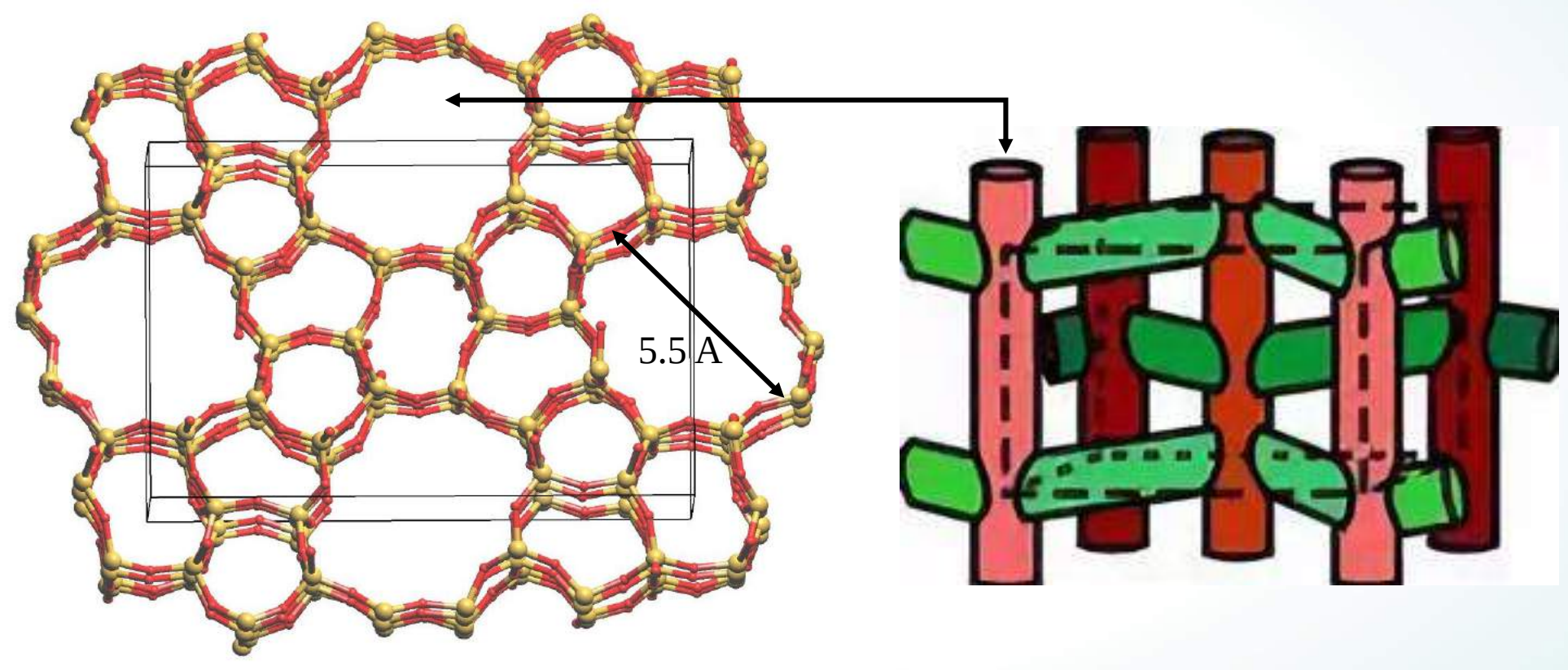
meta-xylene
(1,3-dimethylbenzene)



para-xylene
(1,4-dimethylbenzene)

Applications: catalysis

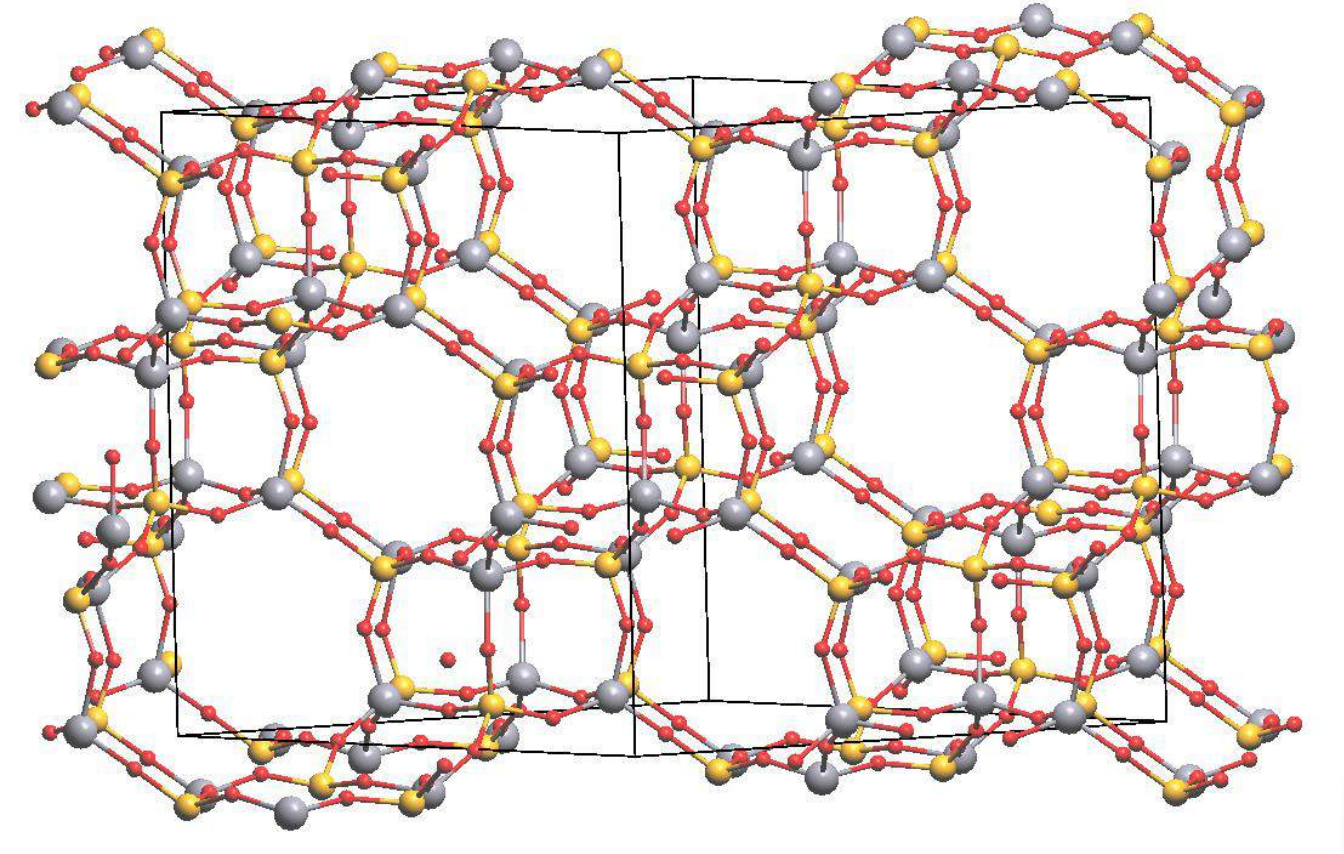
Methanol to Gasoline (MTG) Process



H-ZSM-5 (MFI)

Applications: catalysis

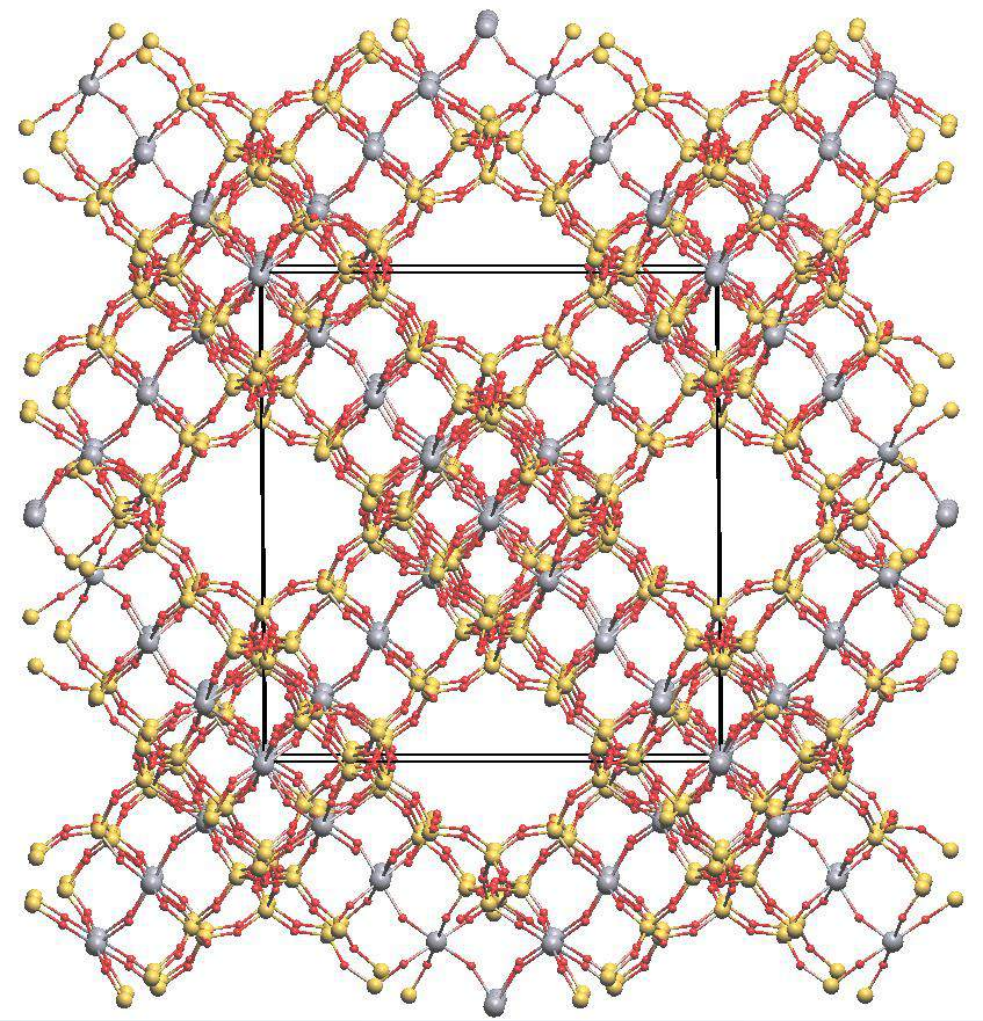
Methanol to Olefins (MTO) Process

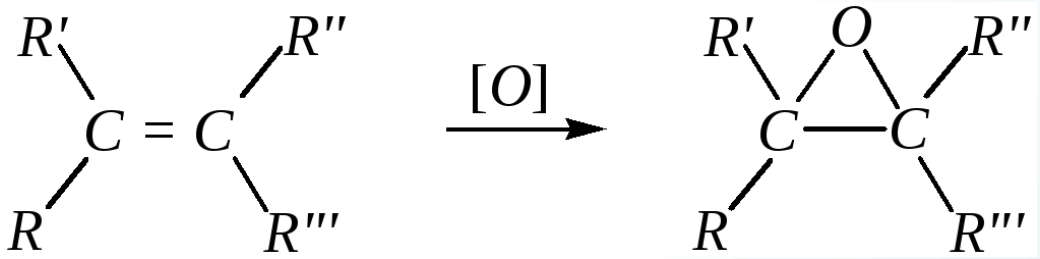


H-SAPO-34 (CHA)

Applications: Chemical oxidation

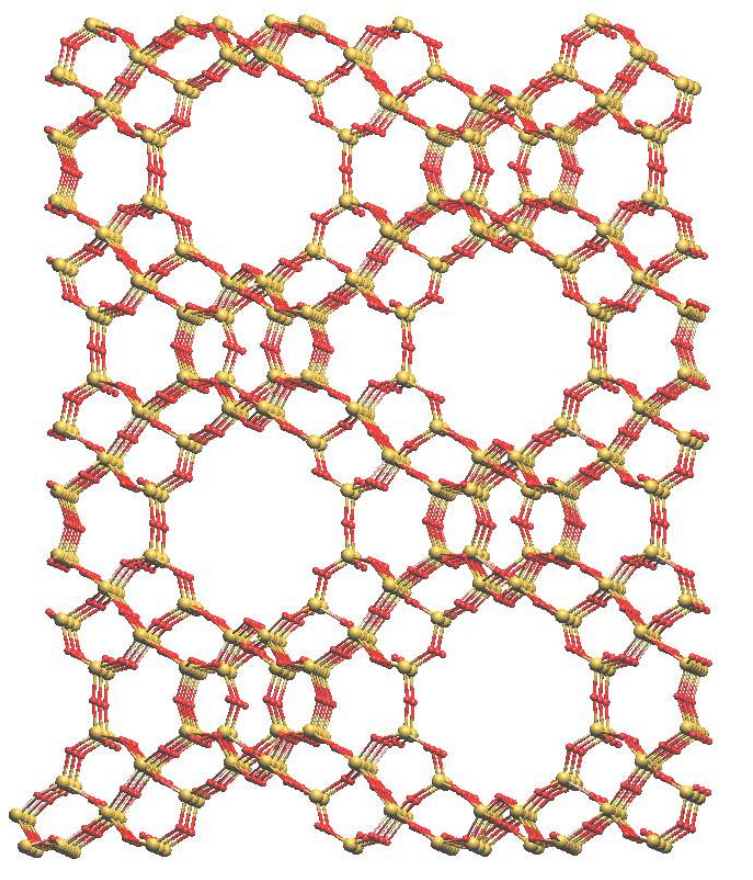
TS-1 (MFI)

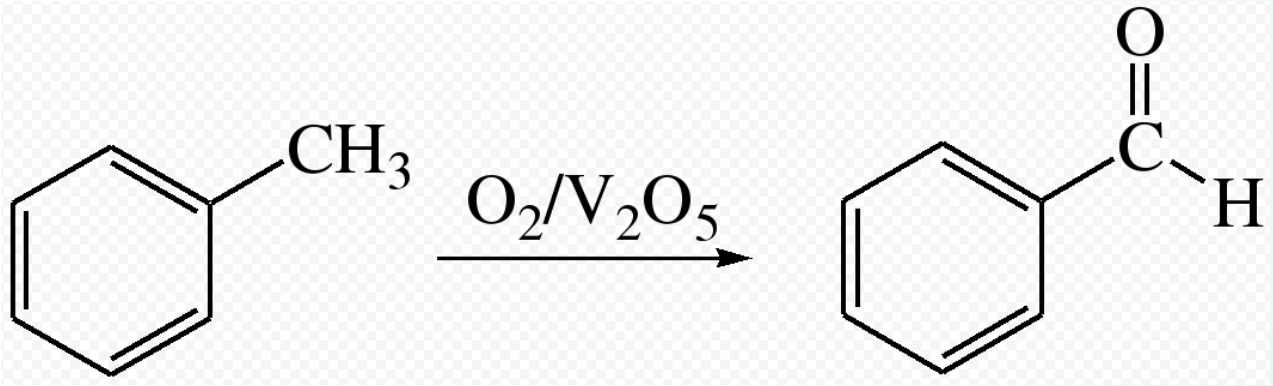




Applications: Photo-oxidation

Zeolite Y (FAU)





Application: “Ship in a bottle” complex

Applications: “Ship in a bottle” complex

Zeolite Y (FAU)

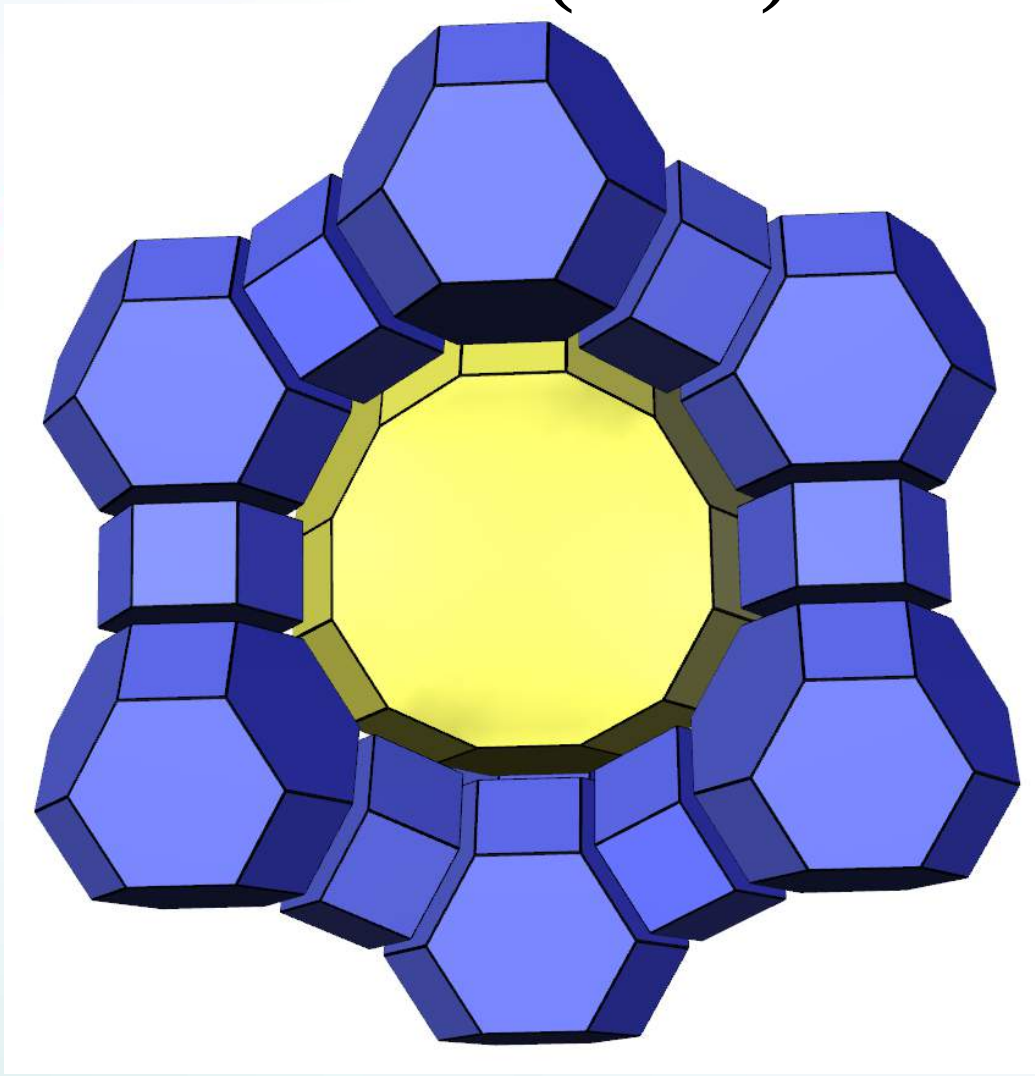
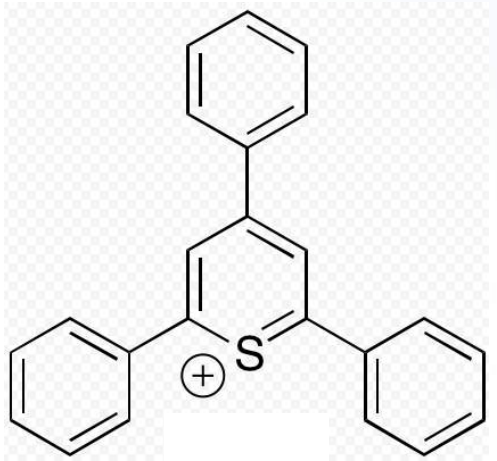
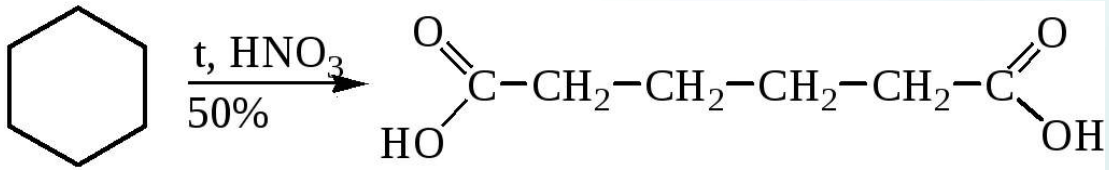


Photo-catalysts

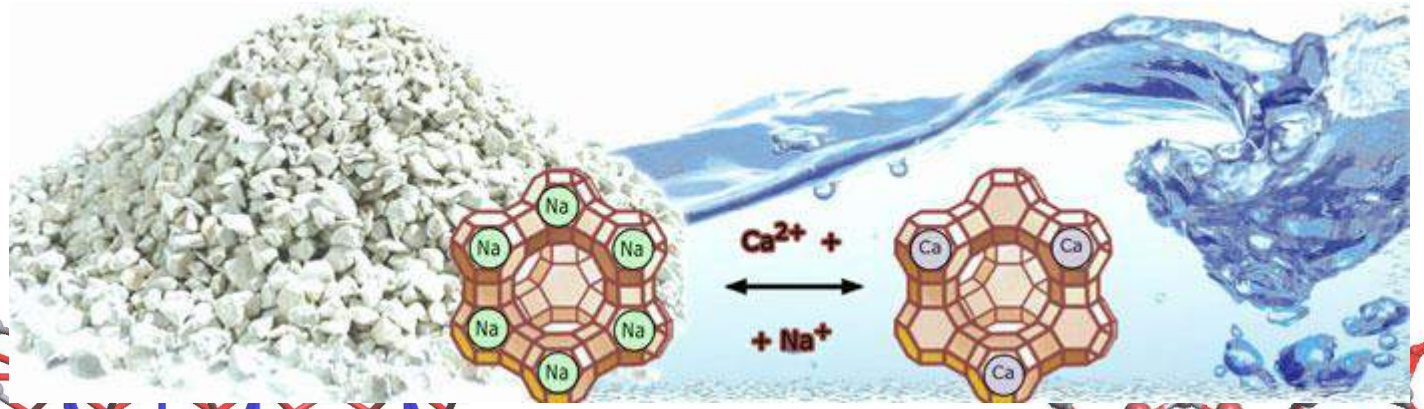


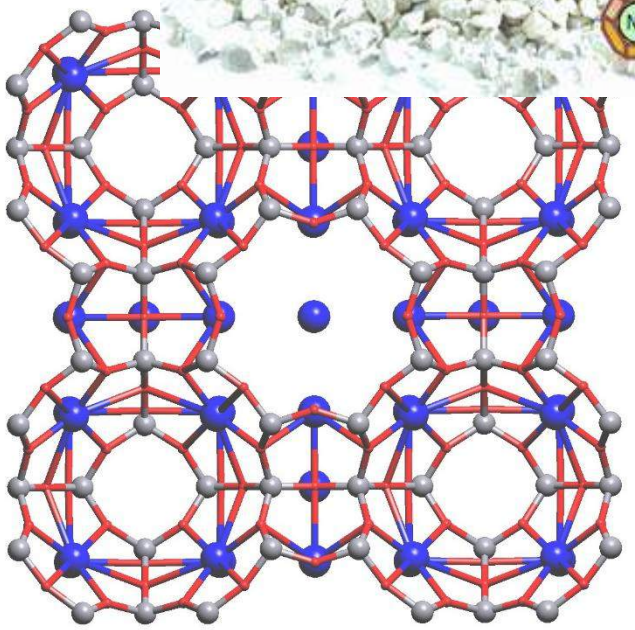
2,4,6-triphenylthiapyrylium cation



Applications: Kt-exchange

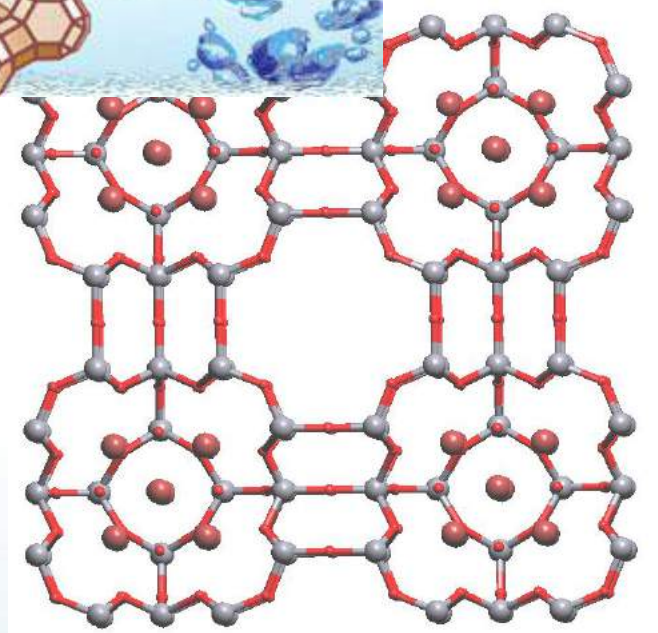
Zeolite A (LTA)
1,400 000 t





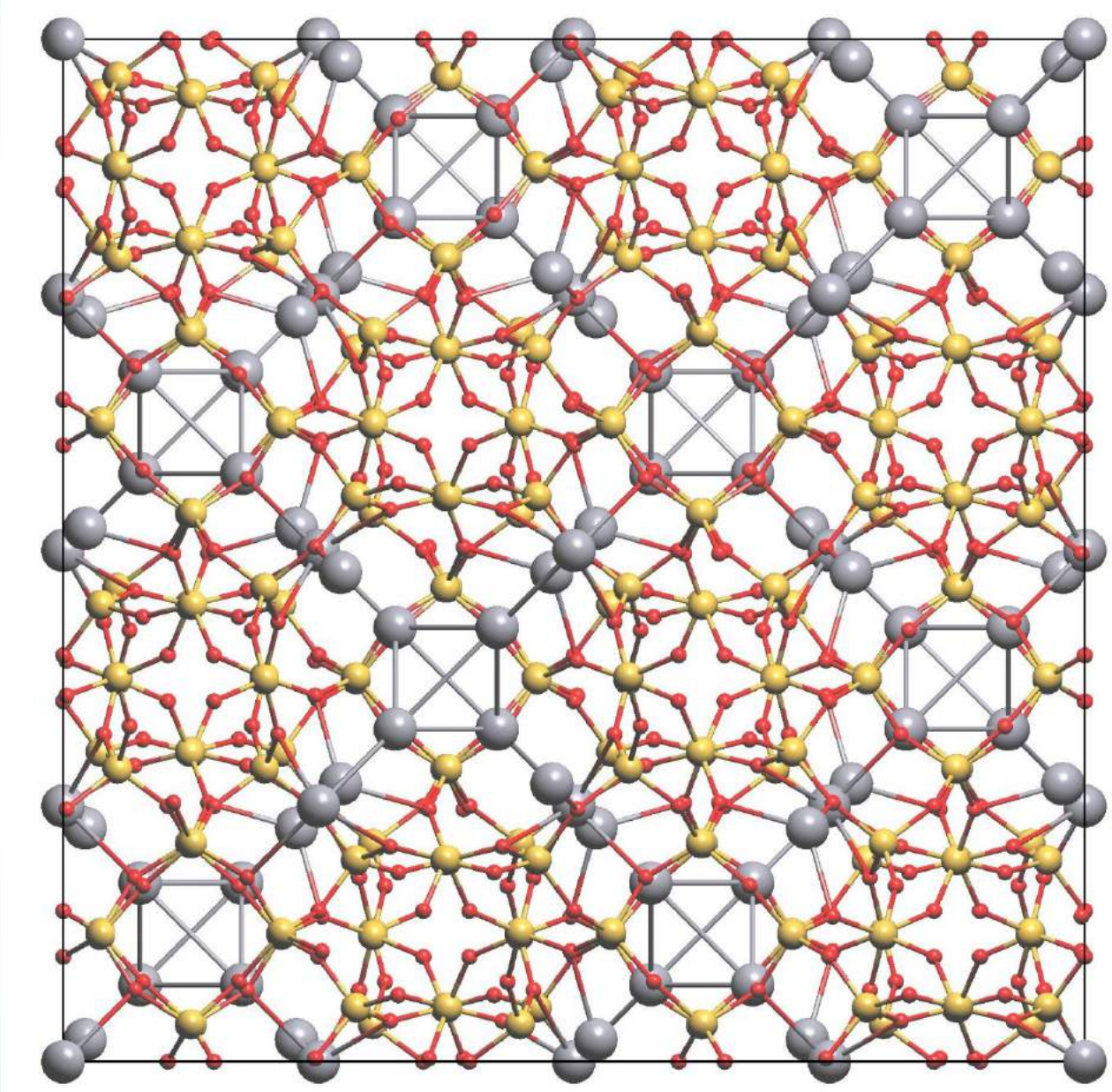
Ca^{2+}, Mg^{2+}

Pb^{2+}, Cd^{2+}, Zn^{2+}



Applications: Kt-exchange

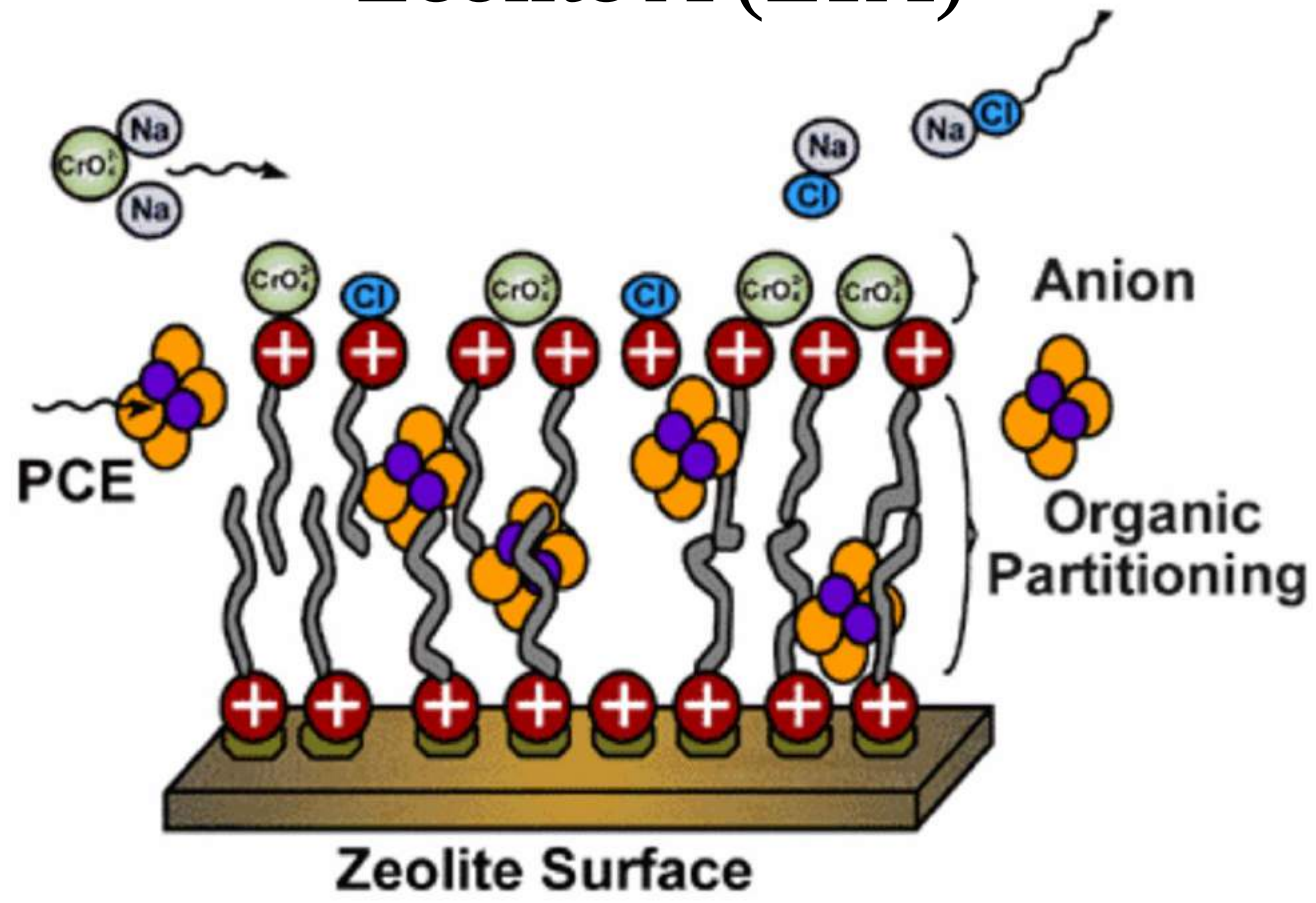
Applications: Medicine



Applications: Agriculture

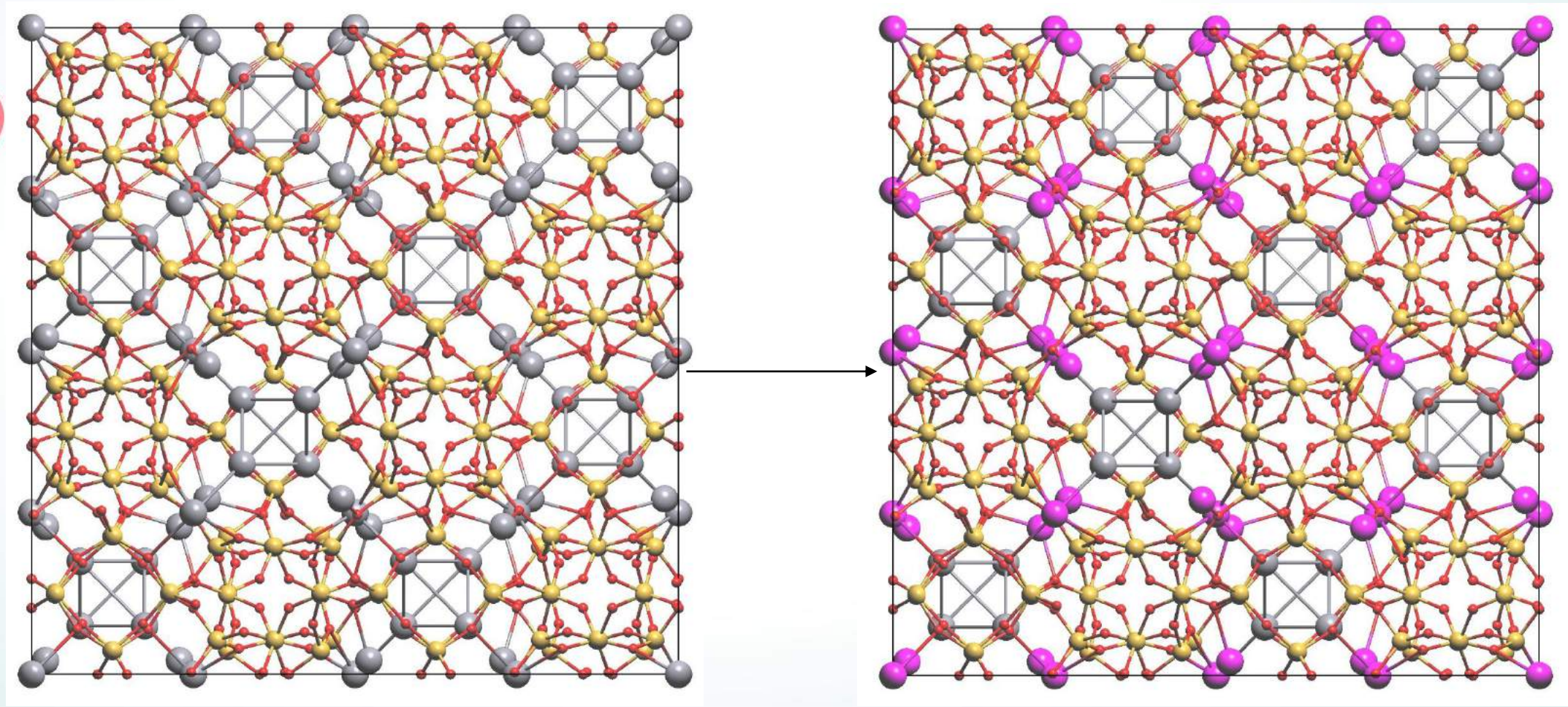
Applications: Adsorption

Clinoptilolite (HEU)
Zeolite A (LTA)

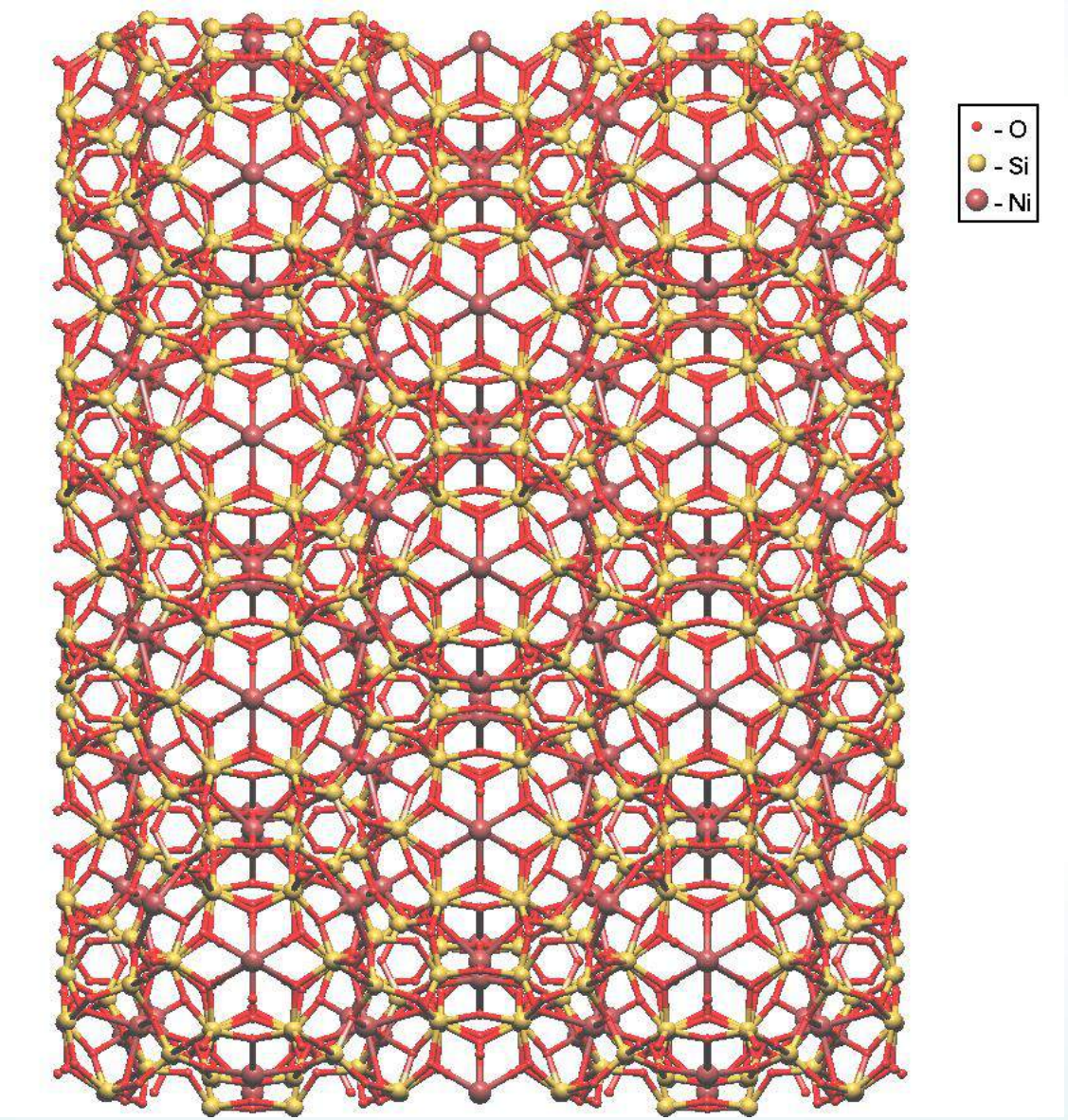


Applications: Anion adsorption

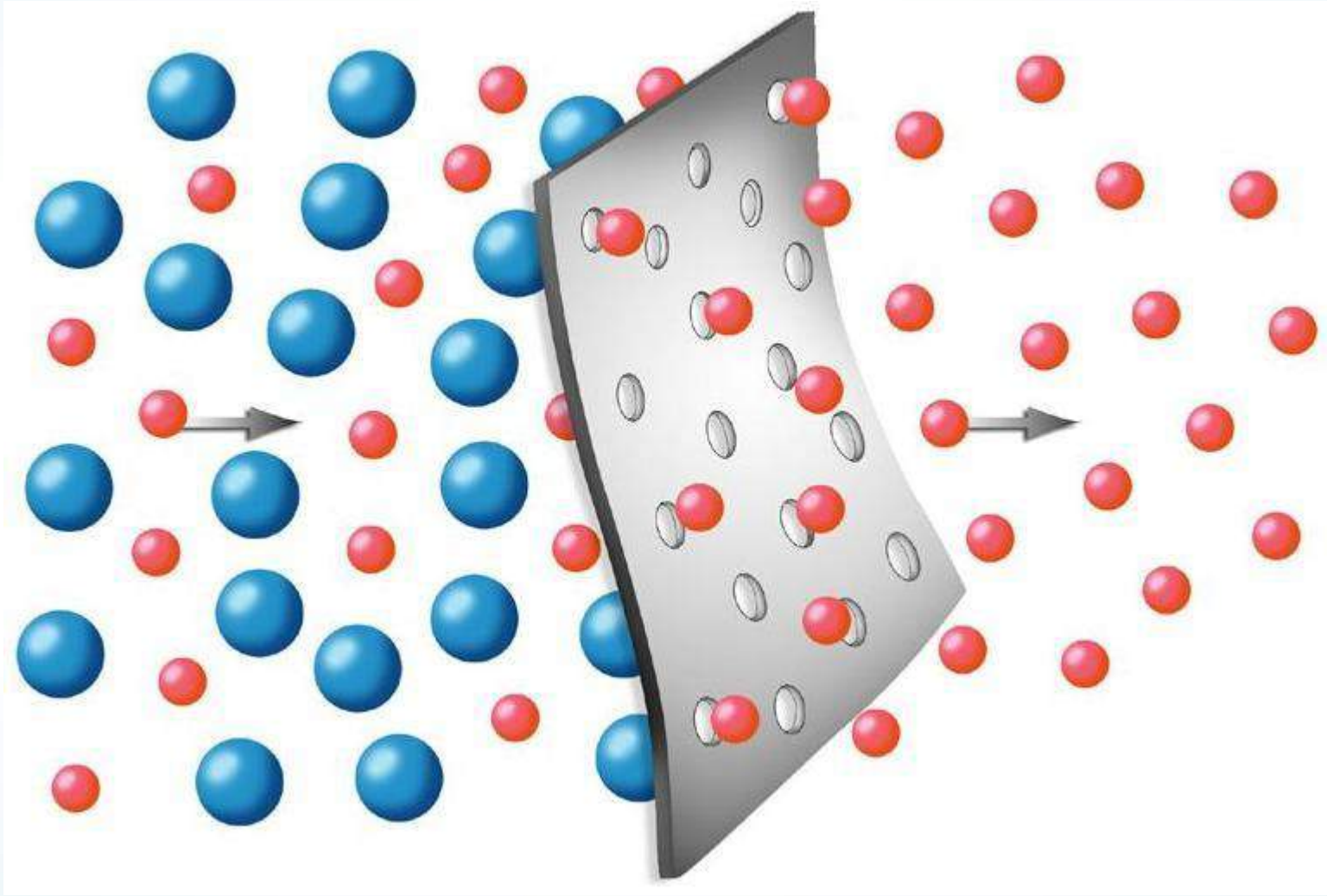
Ag^{+}-Zeolite+NaI→Na^{+}-Zeolite+AgI↓



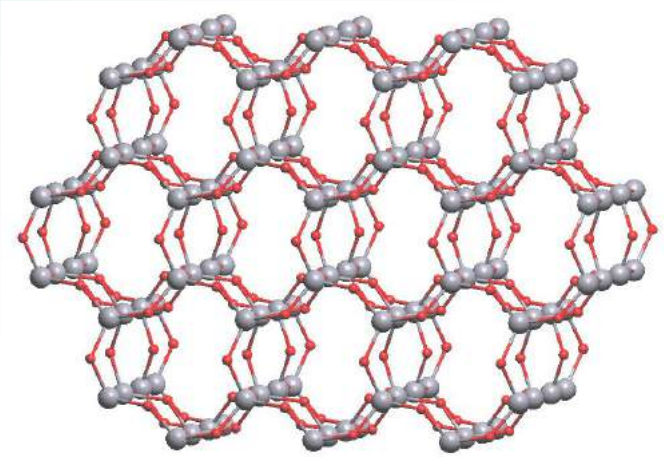
Applications: Adsorption



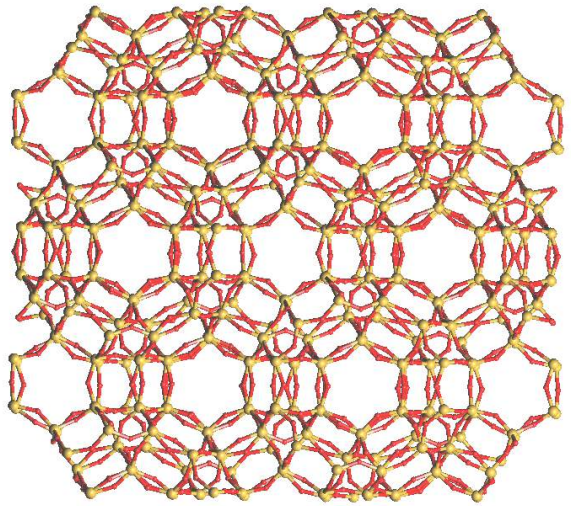
Applications: Molecular sieves



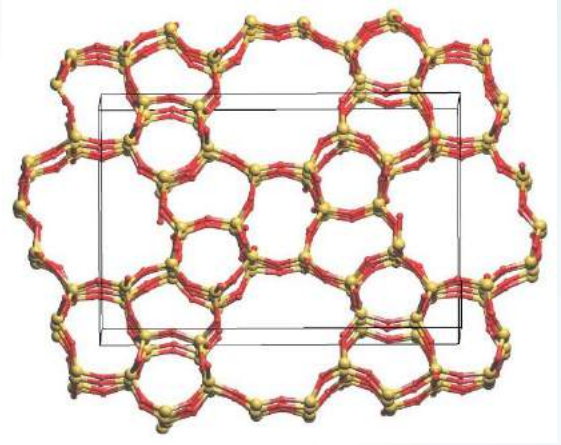
Applications: Molecular sieves



Zeolite A (LTA)



Zeolite Y (FAY)



H-ZSM-5 (MFI)

Drying agent

Hydrocarbon sieving

Separation of gases

References

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3. Christopher J. Rhodes Properties and applications of zeolites Science Progress (2010), 93(3), 1–63
4. Haw, J.F. (2002) Phys. Chem. Chem. Phys., 4, 5431.
5. Corma, A. and Garcia, H. (2004) Eur. J. Chem., 1143

Thank you for your attention