

Ζεολίτε

Barrer
1948

1756

Cronstedt



2D zeolity Ζεολίτε

aneb Nový rozměr zeolitové chemie

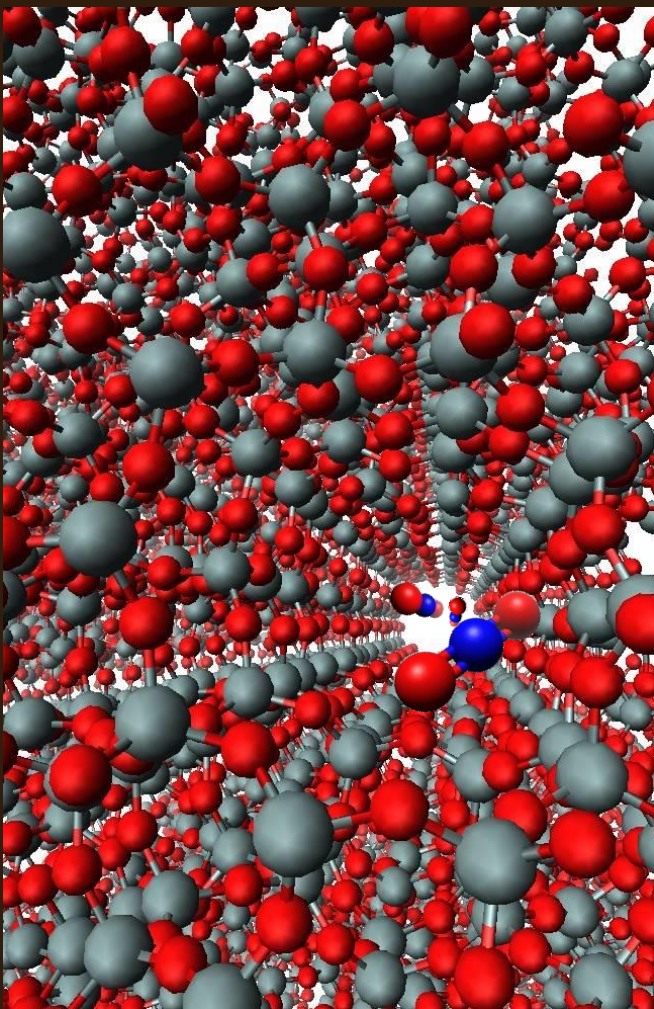
R. Bulánek

Ζεολίτε

Barrer
1948

1756

Cronstedt



Proč jsou zeolity vyjimečné?



Jednotné póry a kanály



Tvarová selektivita a molekulově
síťový efekt



Silně kyselá centra



Iontově výměnná schopnost



Termálně stabilní nad 600°C



Ekologicky nezávadné, chemicky odolné

Ζεολίτε

Barrer
1948

1756

Cronstedt



prací prášky

petrochemie

adsorbenty

zemědělství

pigmenty

klenotnictví



Ζεολίτε

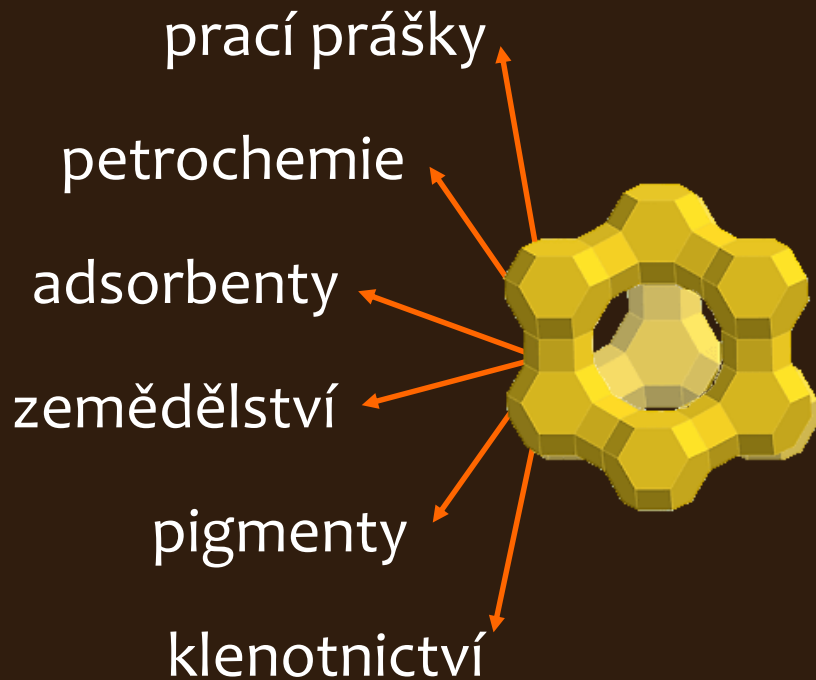
Barrer
1948

1756

Cronstedt



Molekulárně síťový efekt



Ζεολίτε

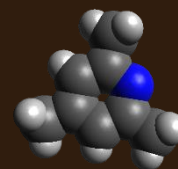
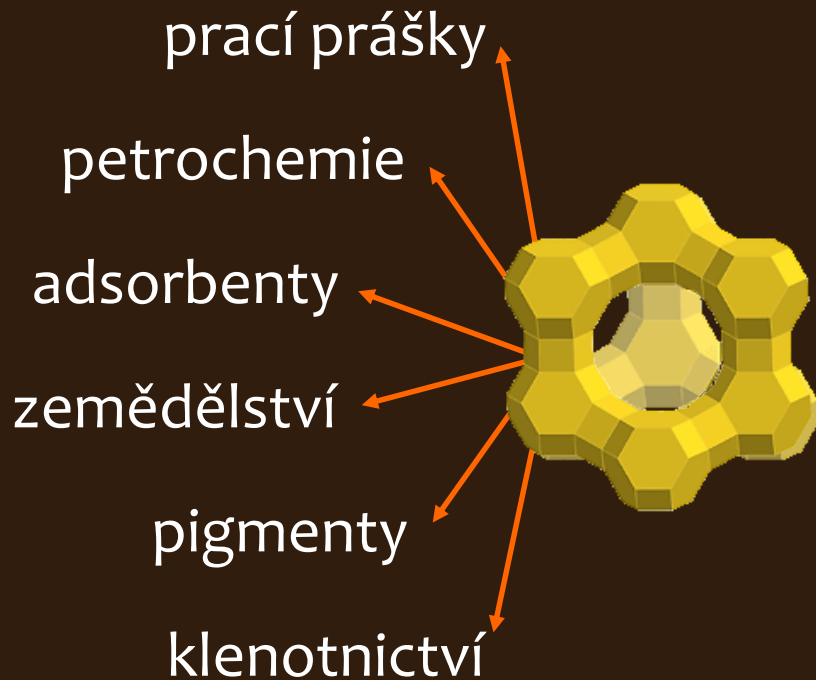
Barrer
1948

1756

Cronstedt



Molekulárně síťový efekt



trimethyl pyridin

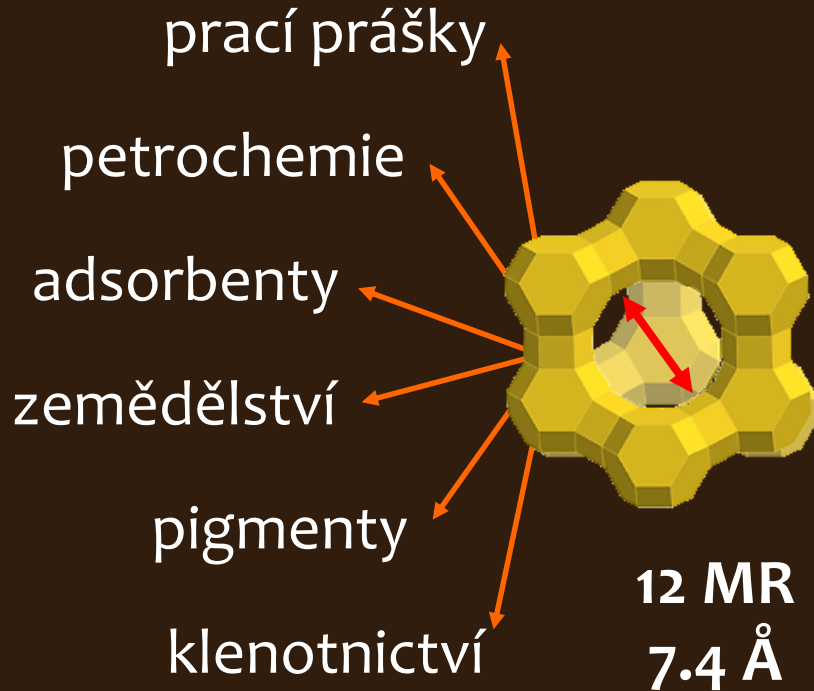
Ζεολίτε

Barrer
1948

1756

Cronstedt

Molekulárně síťový efekt

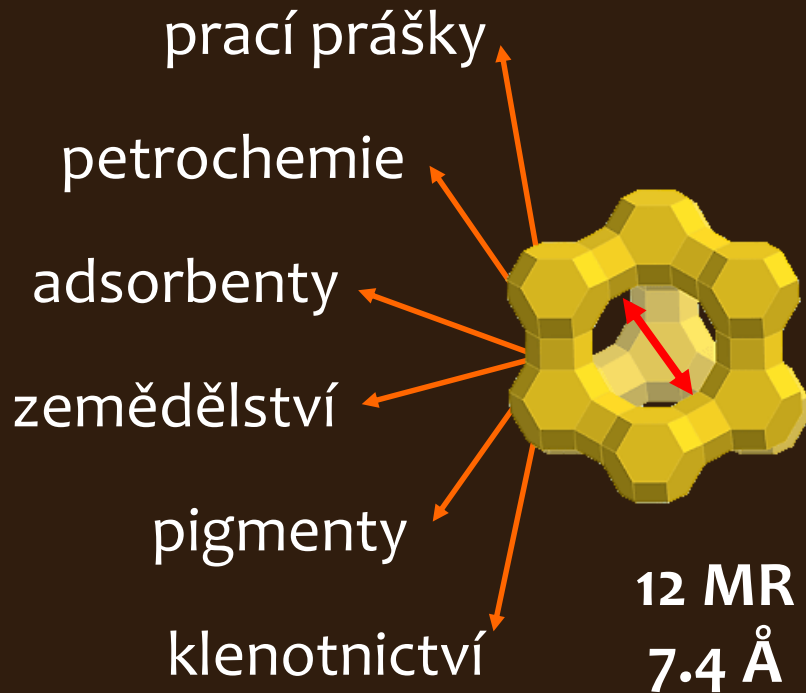


Ζεολίτε

Barrer
1948

1756

Cronstedt



Molekulárně síťový efekt

Jak zpracovat objemnější molekuly?

těžší ropné frakce
biomasa



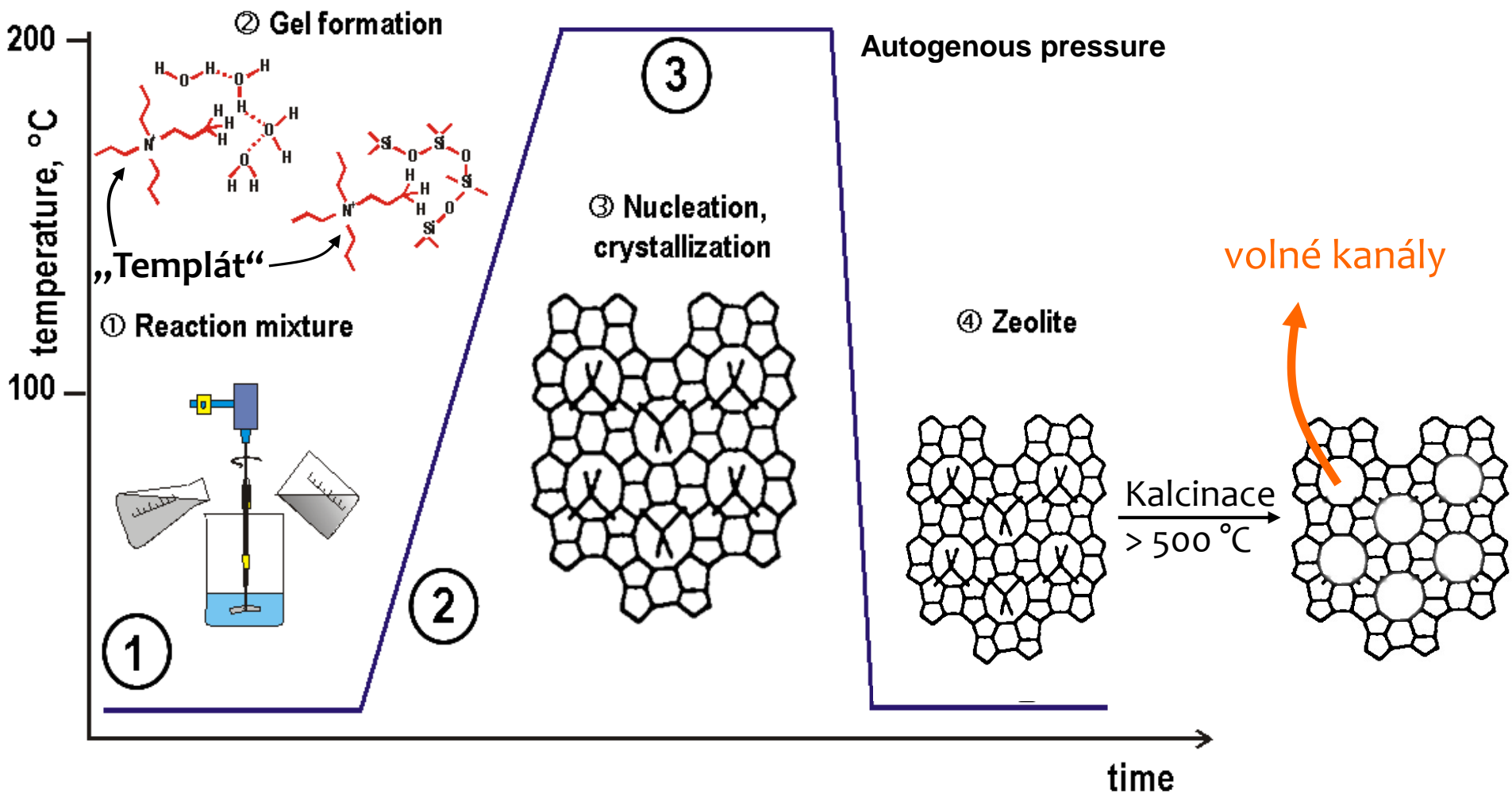
syntéza zeolitů s většími póry

Ζεολίτε

Barrer
1948

1756

Cronstedt



Ζεολίτε

Barrer
1948

1756

Cronstedt



Jak vyrobit širokoporézní zeolity?

Objemnější templát = širší pór

Ζεολίτε

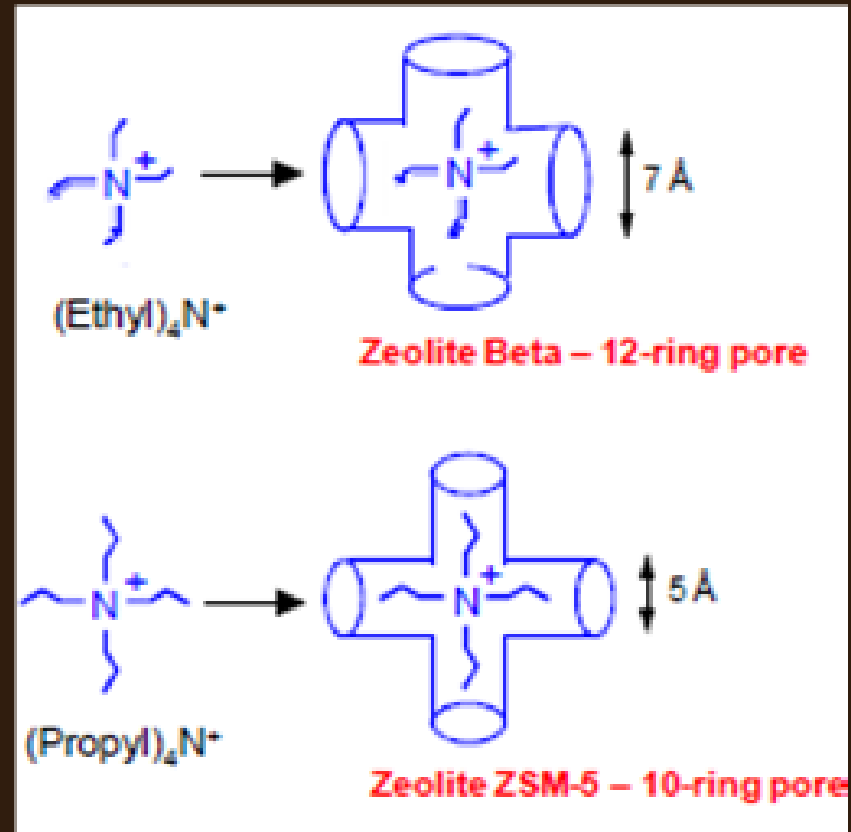
Barrer
1948

1756

Cronstedt

Jak vyrobit širokoporézní zeolity?

Objemnější templát \neq širší pór



Ζεολίτε

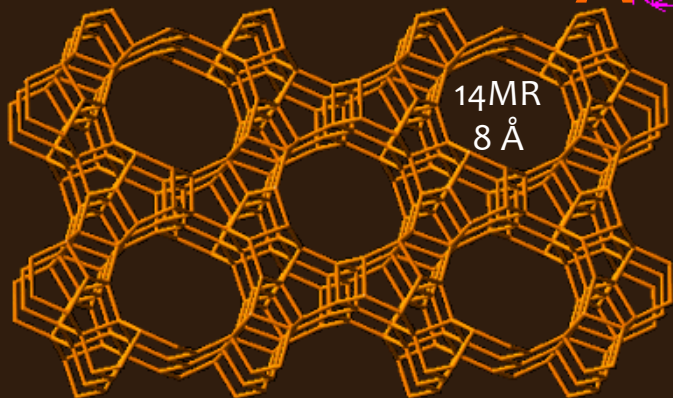
Barrer
1948

1756

Cronstedt

Jak vyrobit širokoporézní zeolity?

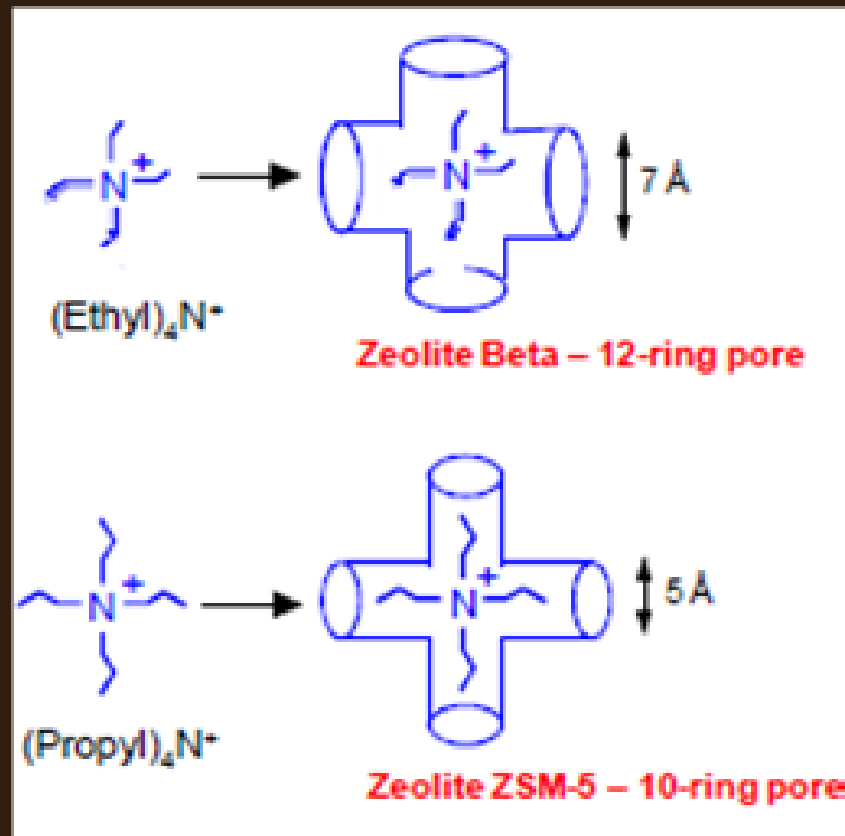
Objemnější templát ~~X~~ širší pór



CIT-5 (CFI)
Methylsparteinium



Wagner, P., Yoshikawa, M., Lovallo, M., Tsuji, K., Tsapatsis, M. and Davis, M.E.: *Chem. Commun.*, , 2179-2180 (1997)



Ζεολίτε

Barrer
1948

1756

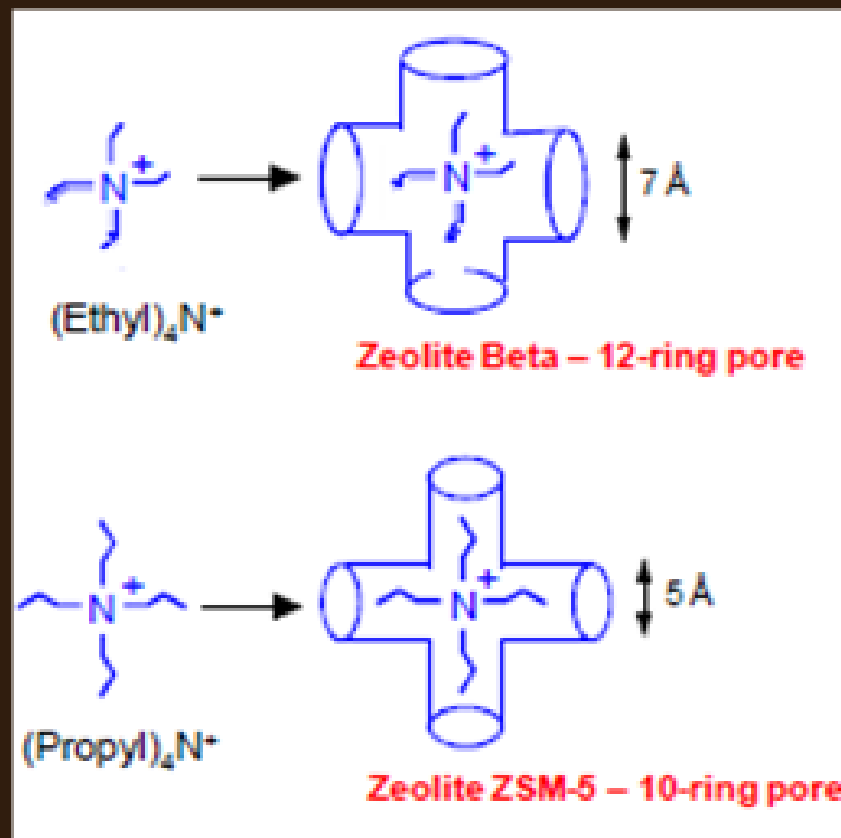
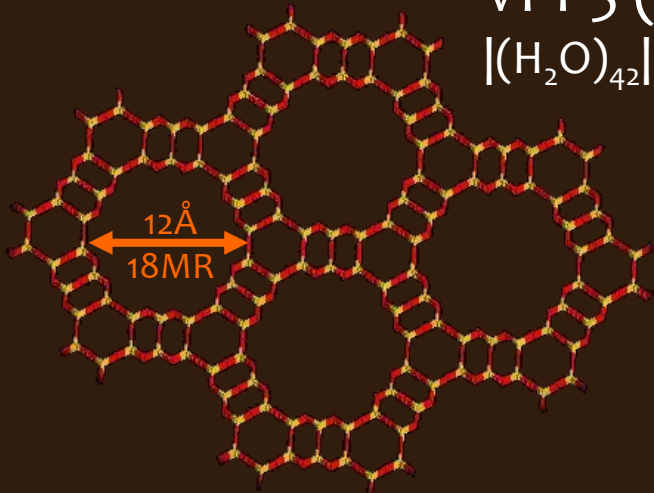
Cronstedt

Jak vyrobit širokoporézní zeolity?

Objemnější templát ~~X~~ širší pór

VPI-5 (VFI)

$[(H_2O)_{42}][Al_{18}P_{18}O_{72}]$



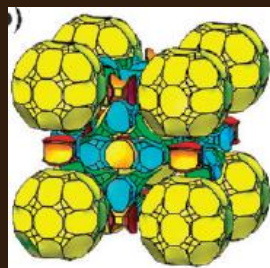
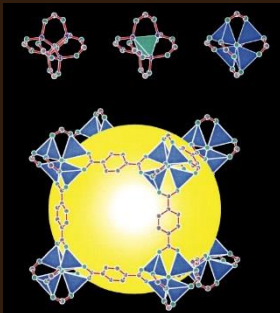
Ζεολίτε

Barrer
1948

1756

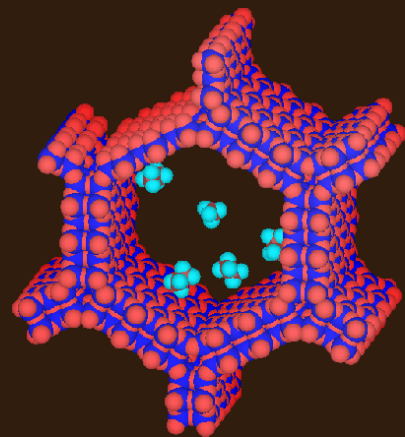
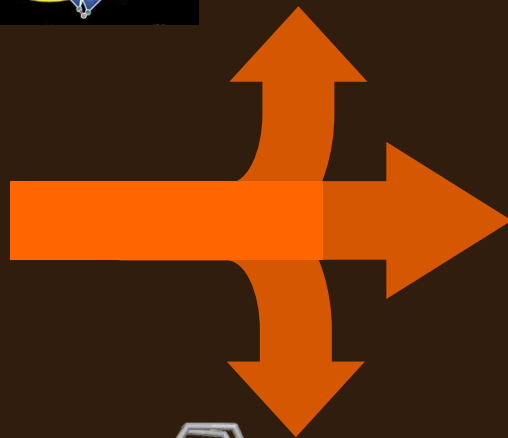
Cronstedt

MOF-5

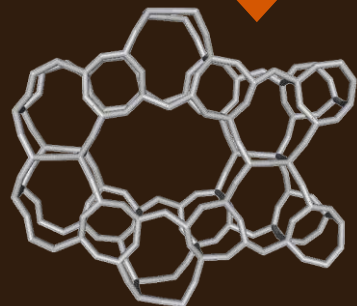


ZIF-100

- prací prášky
- petrochemie
- adsorbenty
- zemědělství
- pigmenty
- klenotnictví



MCM-41



CoAlPO-11

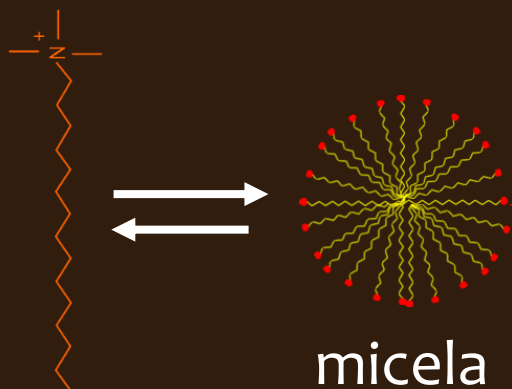
Ζεολίτε

Barrer
1948

1756

Cronstedt

Objev mesoporézních silik (Mobil 1989)



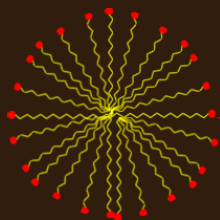
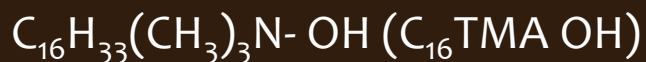
Ζεολίτε

Barrer
1948

1756

Cronstedt

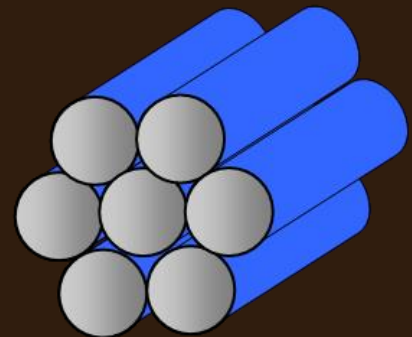
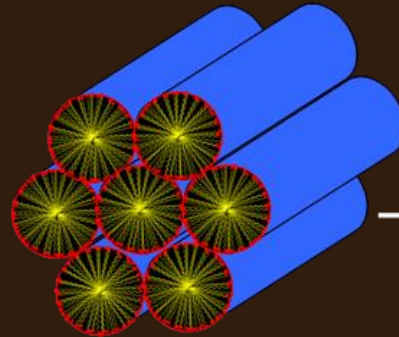
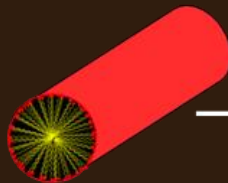
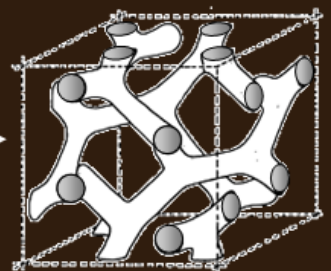
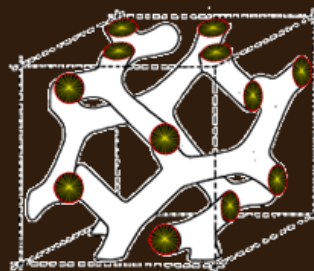
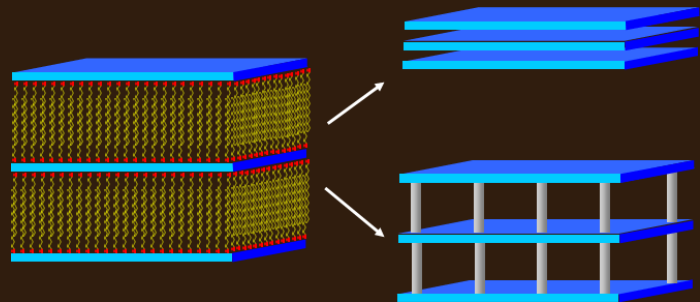
Objev mesoporézniích silik (Mobil 1989)



micela

20 – 100 Å

růst koncentrace templátu



Ζεολίτε

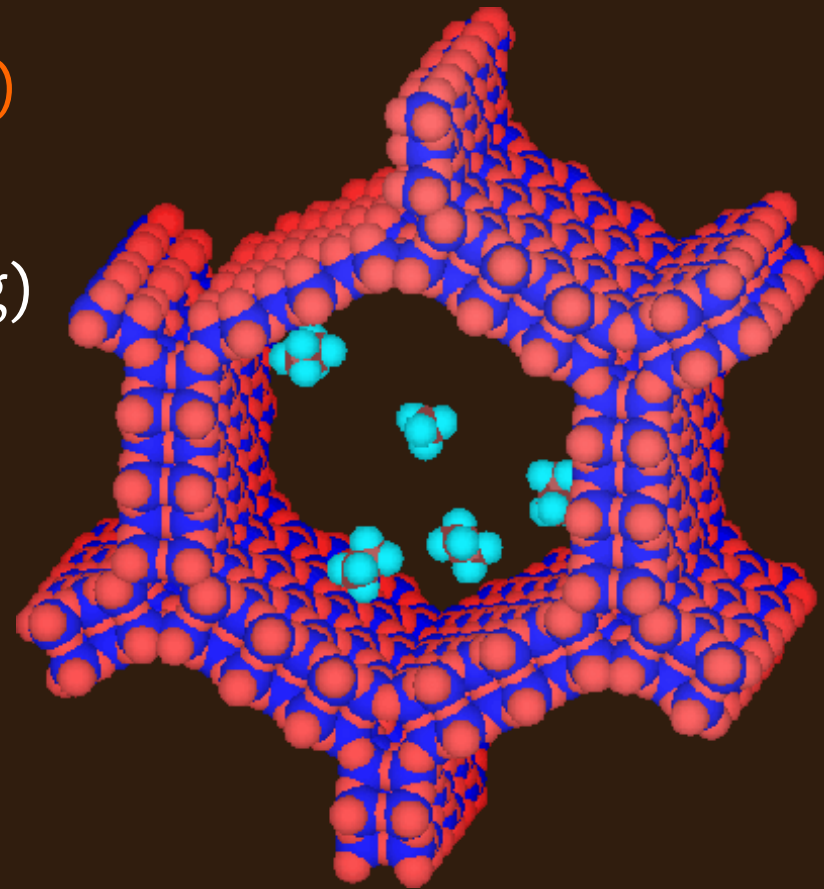
Barrer
1948

1756

Cronstedt

Objev mesoporézních silik (Mobil 1989)

- ⬡ velký specifický povrch ($\sim 1000 \text{ m}^2/\text{g}$)
- ⬡ amorfní (ne zeolitická) stěna kanálu
- ⬡ úzká distribuce pórů
- ⬡ slabě kyselá povaha materiálu
- ⬡ častěji silika než alumosilikát (možné i jiné kombinace)



Ζεολίτε

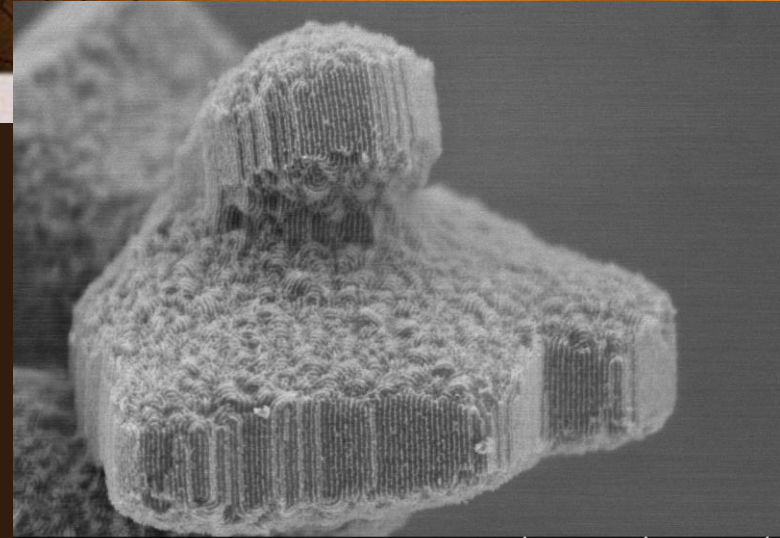
Barrer
1948

1756

Cronstedt

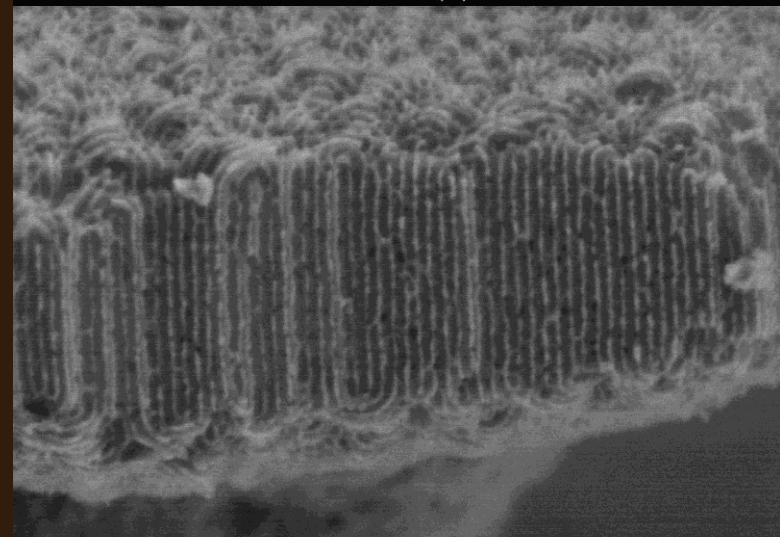
Objev mesoporézních silik (Mobil 1989)

- velký specifický povrch ($\sim 1000 \text{ m}^2/\text{g}$)
- amorfní (ne zeolitická) stěna kanálu
- úzká distribuce pórů
- slabě kyselá povaha materiálu
- častěji silika než alumosilikát (možné i jiné kombinace)



SU8030 0.5kV-D 1.4mm x80.0k SE+BSE(U)

500nm



SU8030 0.5kV-D 1.4mm x200k SE+BSE(U)

200nm

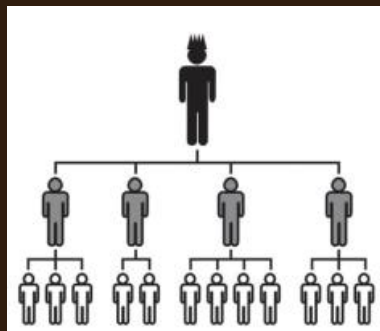
Ζεολίτε

Barrer
1948

1756

Cronstedt

Hierarchické zeolity



Paříž

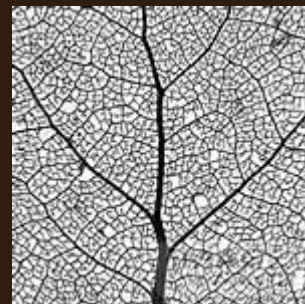
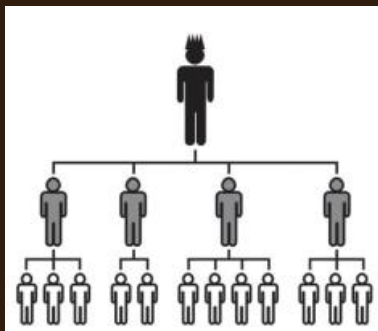
Ζεολίτε

Barrer
1948

1756

Cronstedt

Hierarchické zeolity



list



Paříž



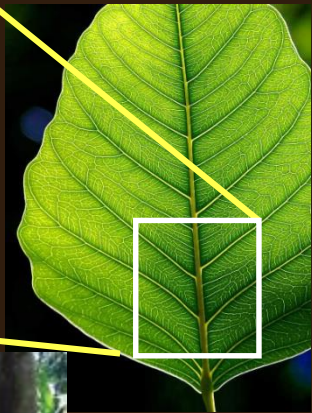
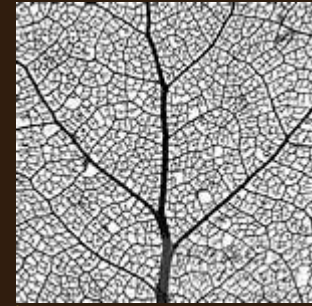
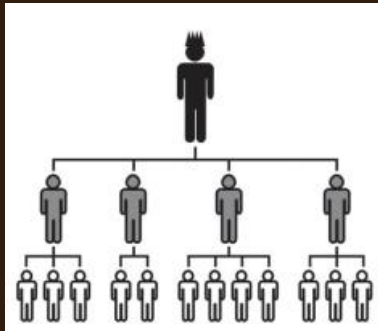
Ζεολίτε

Barrer
1948

1756

Cronstedt

Hierarchické zeolity



list



Paříž



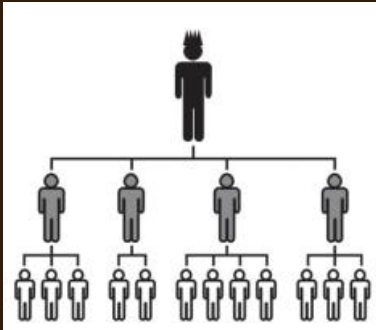
Ζεολίτε

Barrer
1948

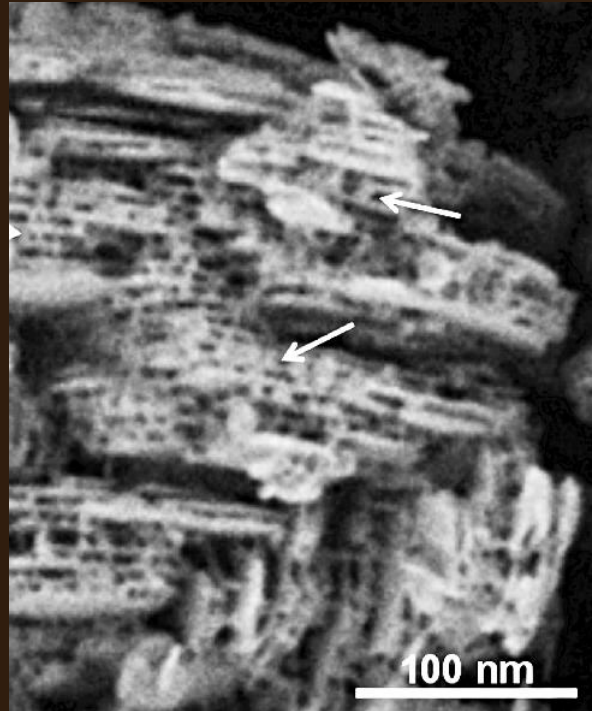
1756

Cronstedt

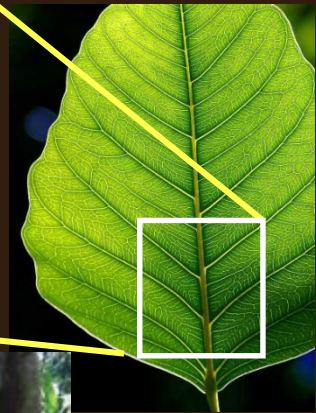
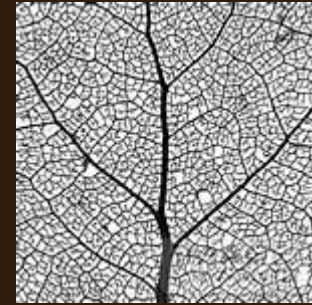
Hierarchické zeolity



Paříž



hierarchický zeolit



list



Ζεολίτε

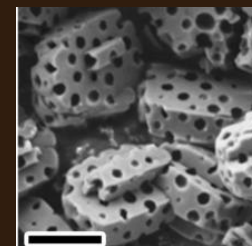
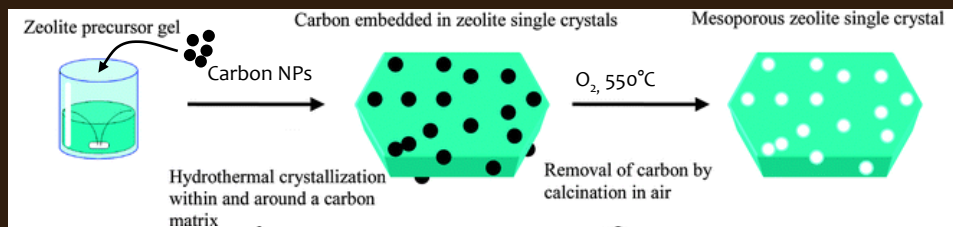
Barrer
1948

1756

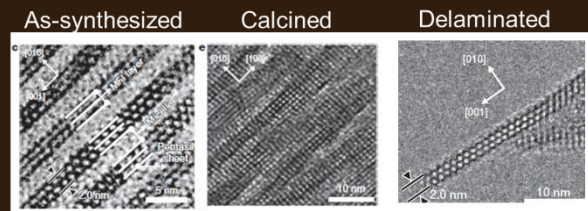
Cronstedt

Hierarchické zeolity – syntéza: bottom – up strategie

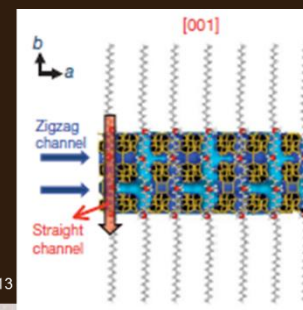
Hard templating



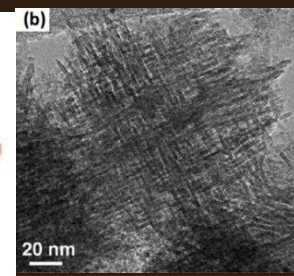
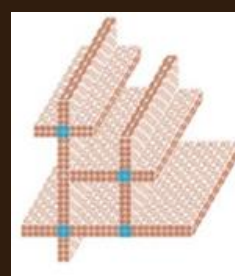
Soft templating



SDA – Diquat (C₂₂₋₆₋₆) - C₂₂H₄₅-N(CH₃)₂-C₆H₁₂-N(CH₃)₂-C₆H₁₃



Non-templating



Ζεολίτε

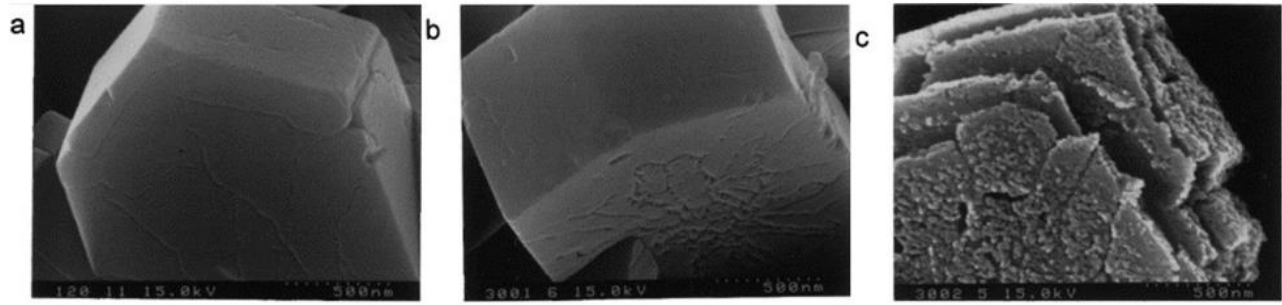
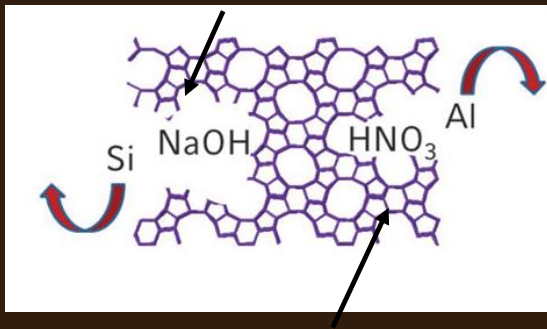
Barrer
1948

1756

Cronstedt

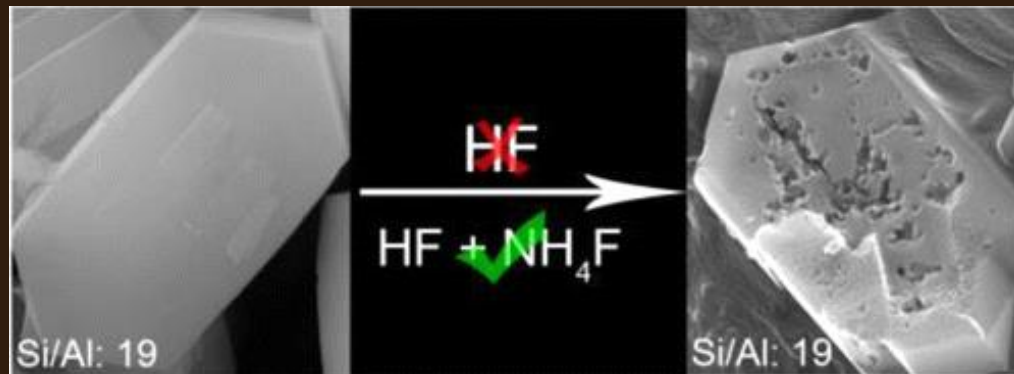
Hierarchické zeolity – syntéza: top - down strategie

desilikace



dealuminace

Leptání fluoridy

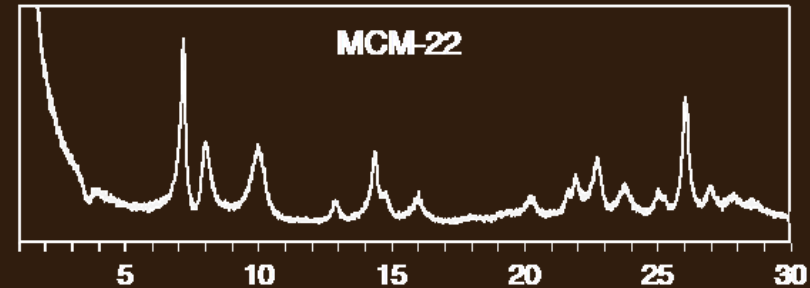
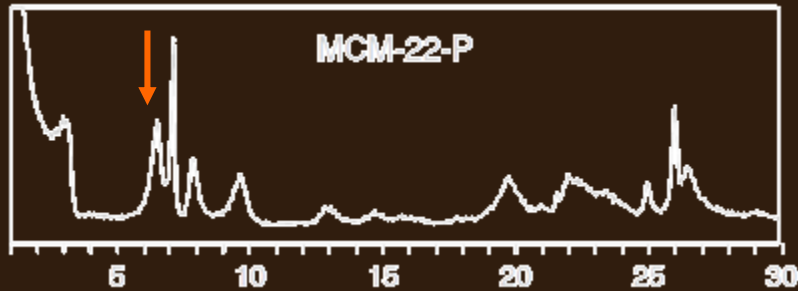


Ζεολίτε

Barrer
1948

1756

Cronstedt

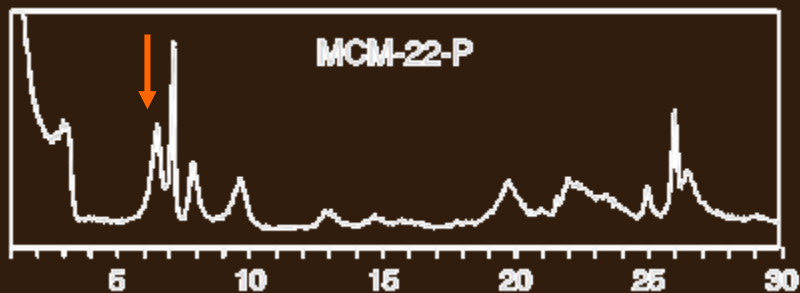


Ζεολίτε

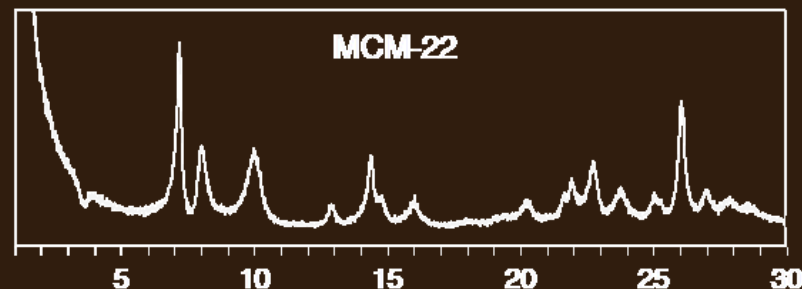
Barrer
1948

1756

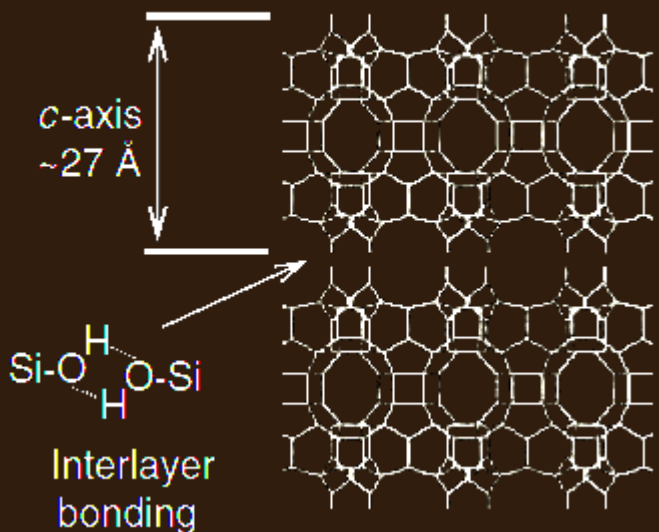
Cronstedt



Layered MCM-22-P

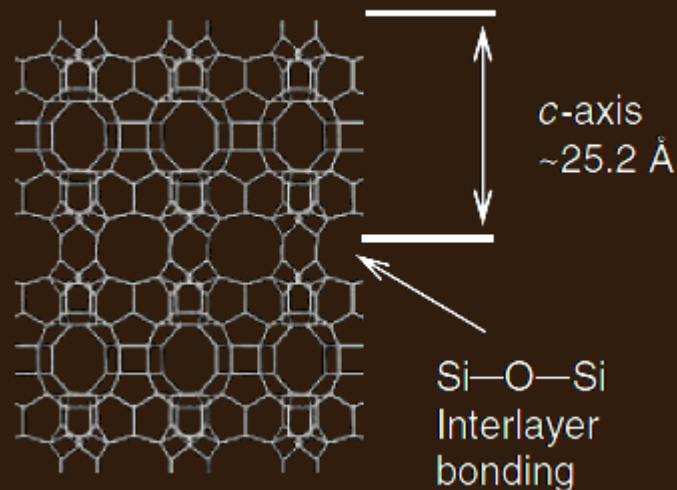


Zeolite MCM-22



zahřátí

- H₂O



Ζεολίτε

Barrer
1948

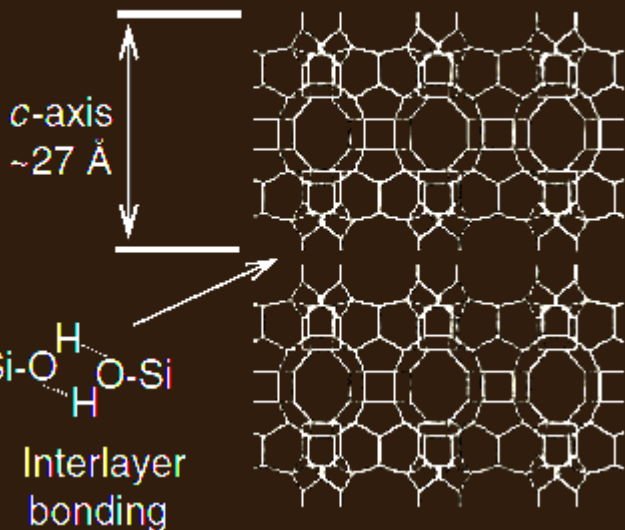
1756

Cronstedt

MWW

2D prekurzor

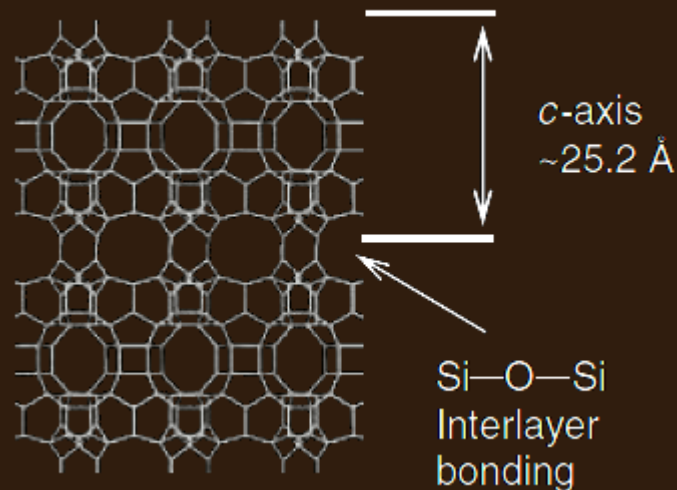
Layered MCM-22-P



zahřátí
- H_2O

3D zeolit

Zeolite MCM-22



Ζεολίτε

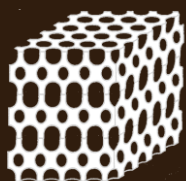
Barrer
1948

1756

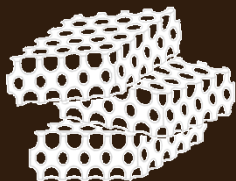
Cronstedt



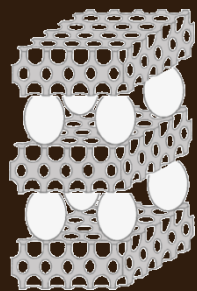
MCM-22-P



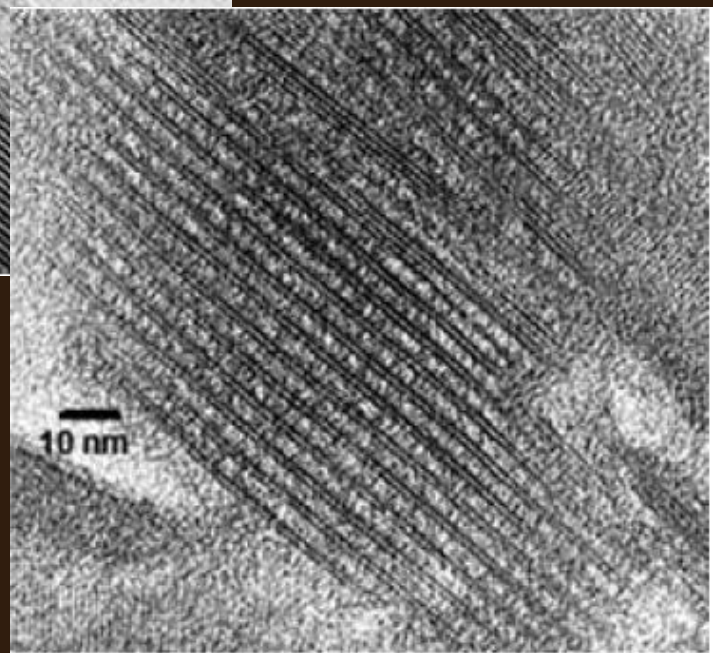
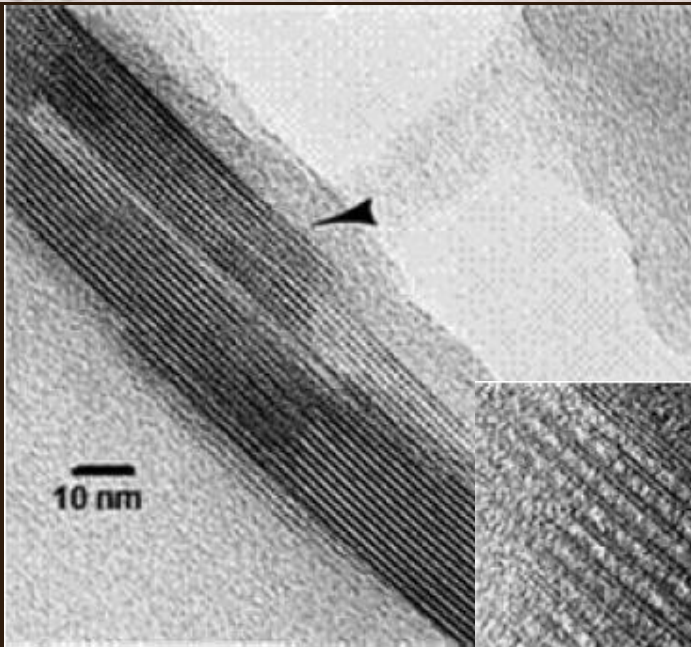
MCM-22



MCM-56



MCM-36



Ζεολίτε

Barrer
1948

1756

Cronstedt



Vrstevnatý prekurzor



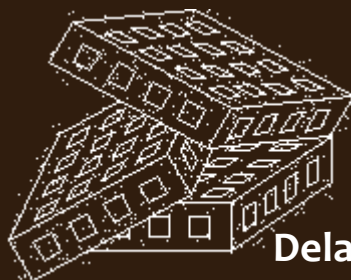
záhřev



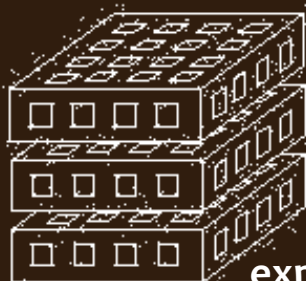
3D zeolit



Pilřovaný zeolit



Delaminovaný zeolit



IEZ – vrstevnatý
expandovaný zeolit

LEGO CHEMISTRY

2D zeolites = Infinite possibilities for inter layer distances, orientation, connectivity, functionalization

W. Roth

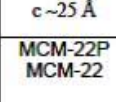

Ζεολίτε

Barrer
1948

1756

Cronstedt

2D zeolitové vrstvy

Conventional 3-D zeolite Frameworks	Conventional 3-D zeolite	Layered precursor				Delaminated	Swollen/ pillared
		Ordered		Dis-ordered			
		Unmodified	Stabilized	Unmodified	Stabilized		
FAU	Synthesis	Synthesis	Treatment	Synthesis	Treatment	Synthesis, treatment	Treatment
MWW							
FER							
CDO							
CAS							
NSI	c ~25 Å c ~25 Å	c >26 Å c ~25 Å	c >26 Å c >26 Å	c >26 Å c ~25 Å	c >26 Å c >26 Å	c ~25 Å c ~25 Å	c >50 Å c ~50 Å
MFI	MCM-49 MCM-22	MCM-22P MCM-22	IEZ-MWW EMM-13P EMM-13	EMM-10P EMM-10 ITQ-30	EMM-12P EMM-12	MCM-56; ITQ-2 (treatment)	Swollen MCM-22P, MCM-36
SOD							
RWR							
RRO							
AFO							
Remaining frameworks still without layered form							

Různé uspořádání vrstev

Roth WJ, *Microporous Mesoporous Mater.* 142 (2011) 32-46

Ζεολίτε

Barrer
1948

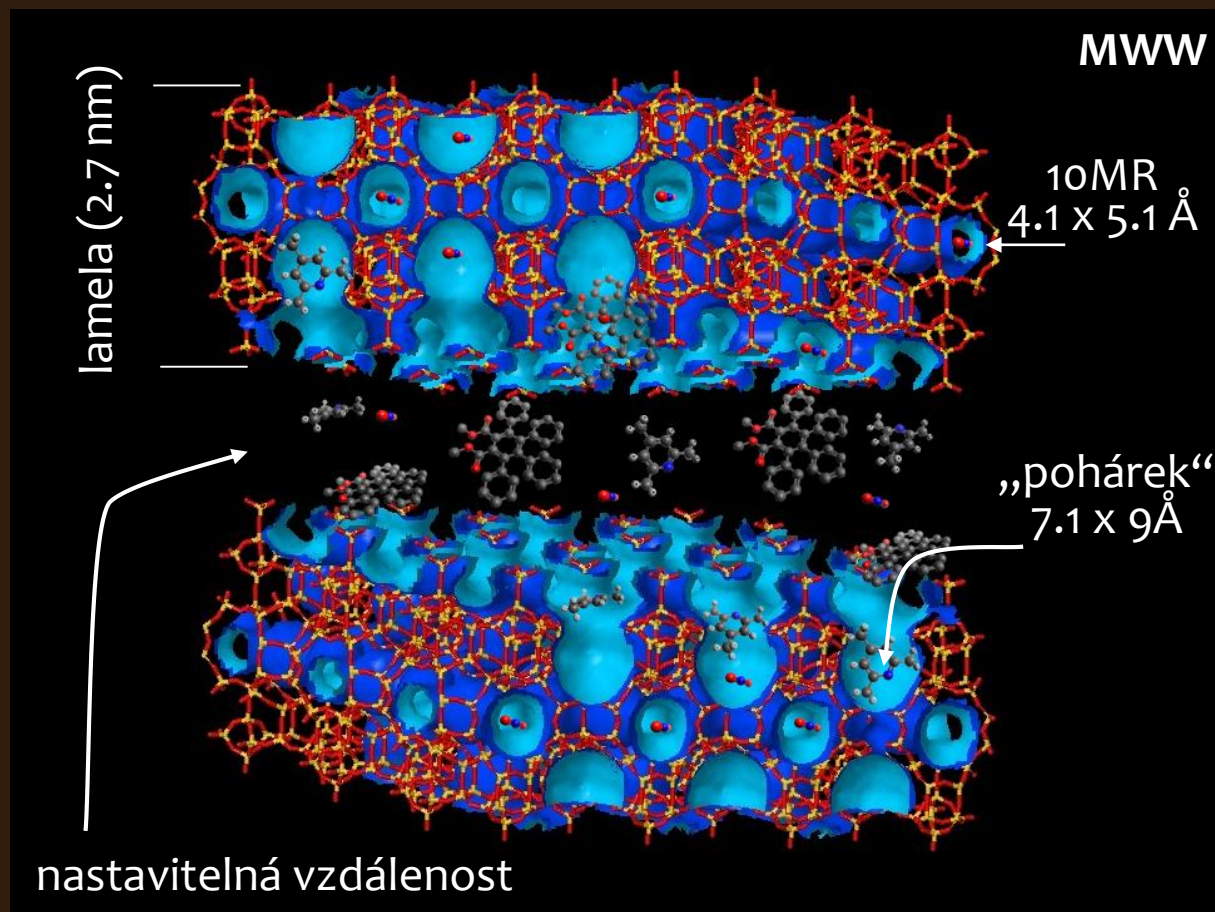
1756

Cronstedt

Výhody lamelárních forem zeolitů



aktivní centra přístupná i
pro objemné molekuly



Ζεολίτε

Barrer
1948

1756

Cronstedt

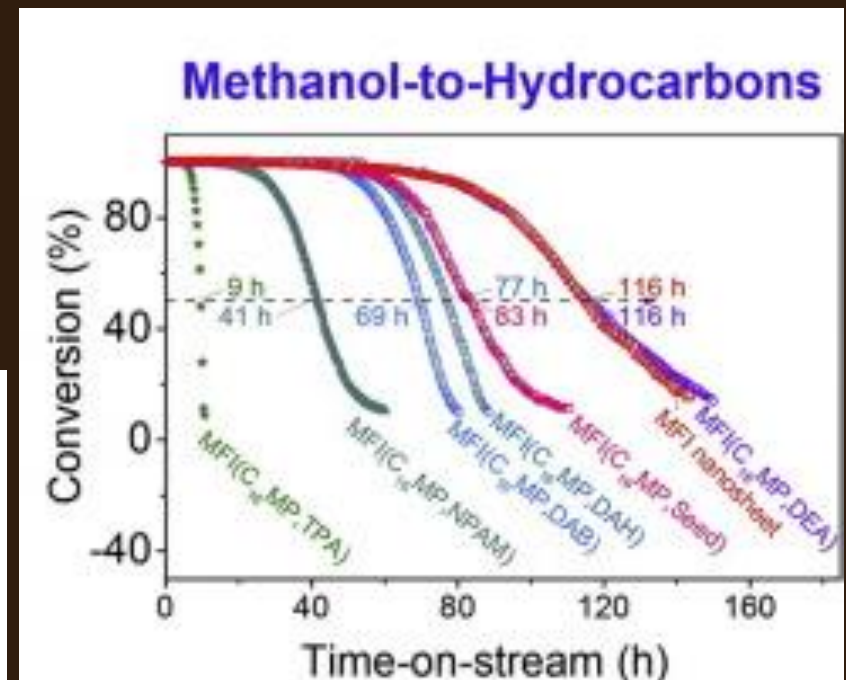
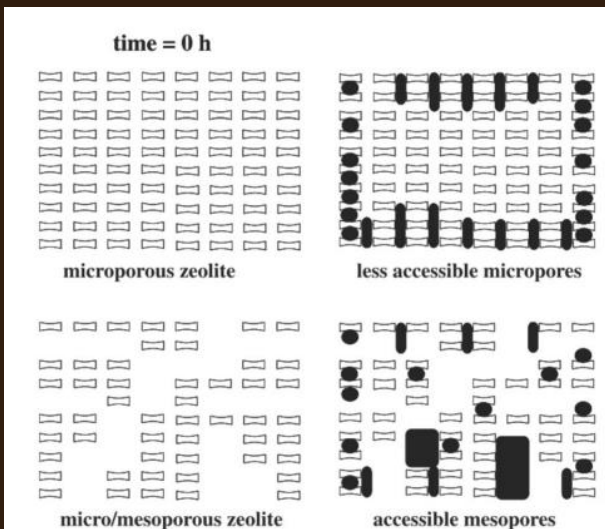
Výhody lamelárních forem zeolitů



aktivní centra přístupná i pro objemné molekuly



potlačení deaktivace katalyzátoru



Ζεολίτε

Barrer
1948

1756

Cronstedt

Výhody lamelárních forem zeolitů



aktivní centra přístupná i pro objemné molekuly

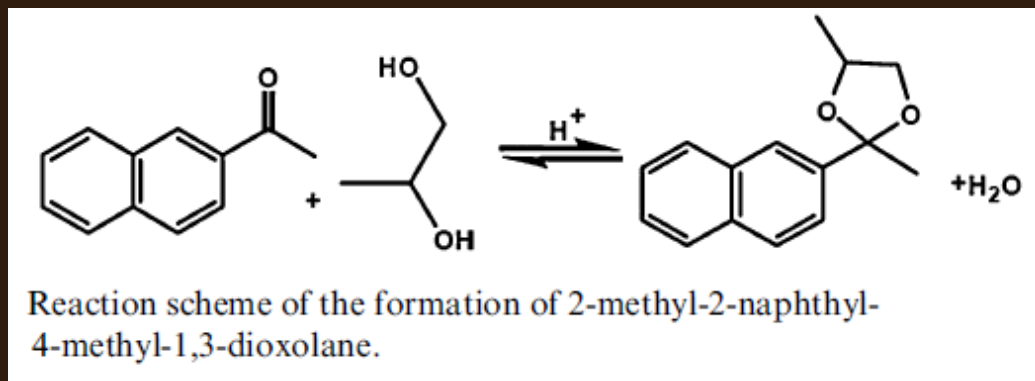


potlačení deaktivace katalyzátoru



vznik center nového typu – zcela jiná reaktivita

Acetylizace 2-acetonaftalenu pomocí propylenglykolu



Výtěžek: ITQ-2 (63%) > MWW (20%) > BEA (5%)





Ζεολίτε

Barrer
1948

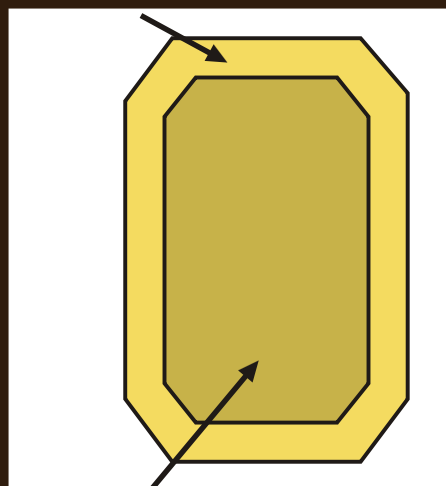
1756

Cronstedt

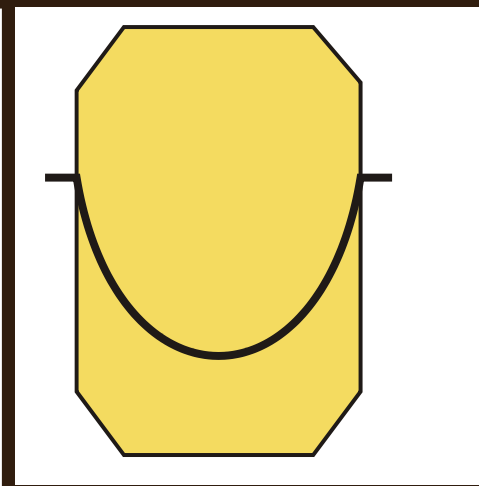
Výhody lamelárních forem zeolitů

-  aktivní centra přístupná i pro objemné molekuly
-  potlačení deaktivace katalyzátoru
-  vznik center nového typu – zcela jiná reaktivita
-  potlačení difuzních limitací

reakční zóna



koncentrační profil



„nereaktivní“ zóna

Ζεολίτε

Barrer
1948

1756

Cronstedt

Výhody lamelárních forem zeolitů



aktivní centra přístupná i pro objemné molekuly



potlačení deaktivace katalyzátoru

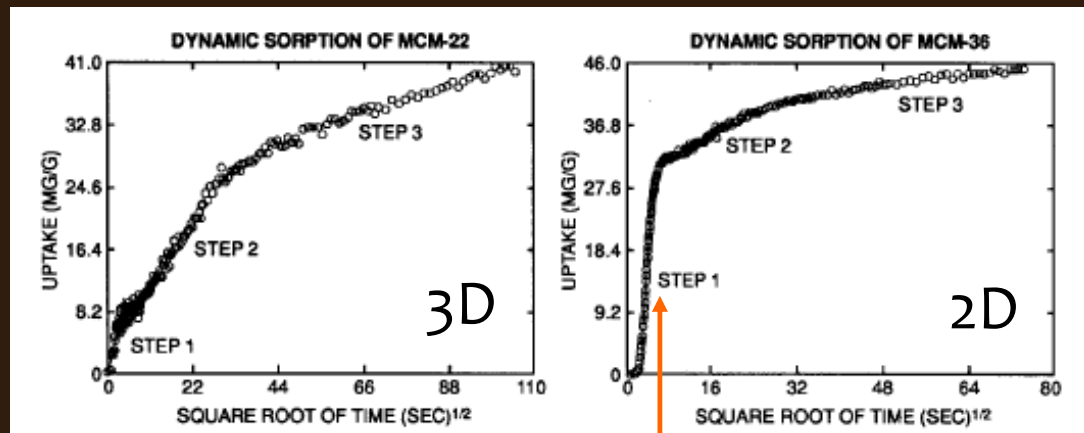


vznik center nového typu – zcela jiná reaktivita



potlačení difuzních limitací

Adsorpce 2,2-dimetylbutanu



oblast rychlé adsorpce

Ζεολίτε

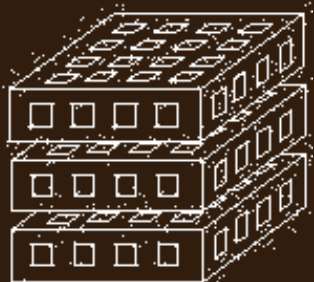
Barrer
1948

1756

Cronstedt



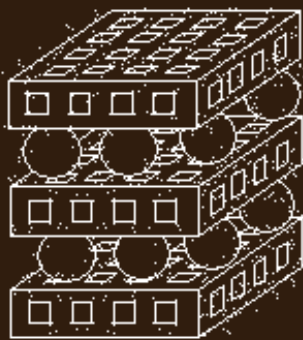
Vrstevnatý prekurzor



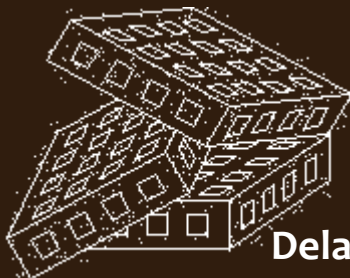
záhřev



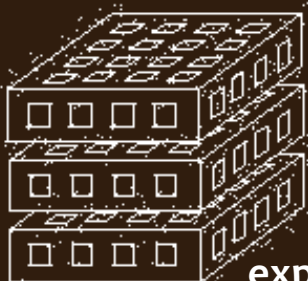
3D zeolit



Pilřovaný zeolit



Delaminovaný zeolit



IEZ – vrstevnatý
expandovaný zeolit

LEGO CHEMISTRY

2D zeolites = Infinite possibilities for inter layer distances, orientation, connectivity, functionalization

W. Roth

Ζεολίτε

Barrer
1948

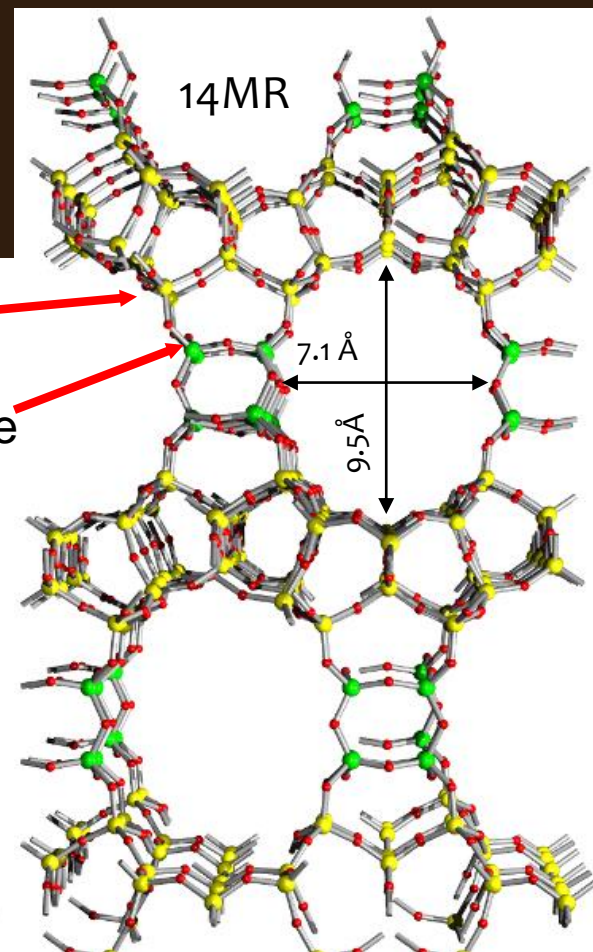
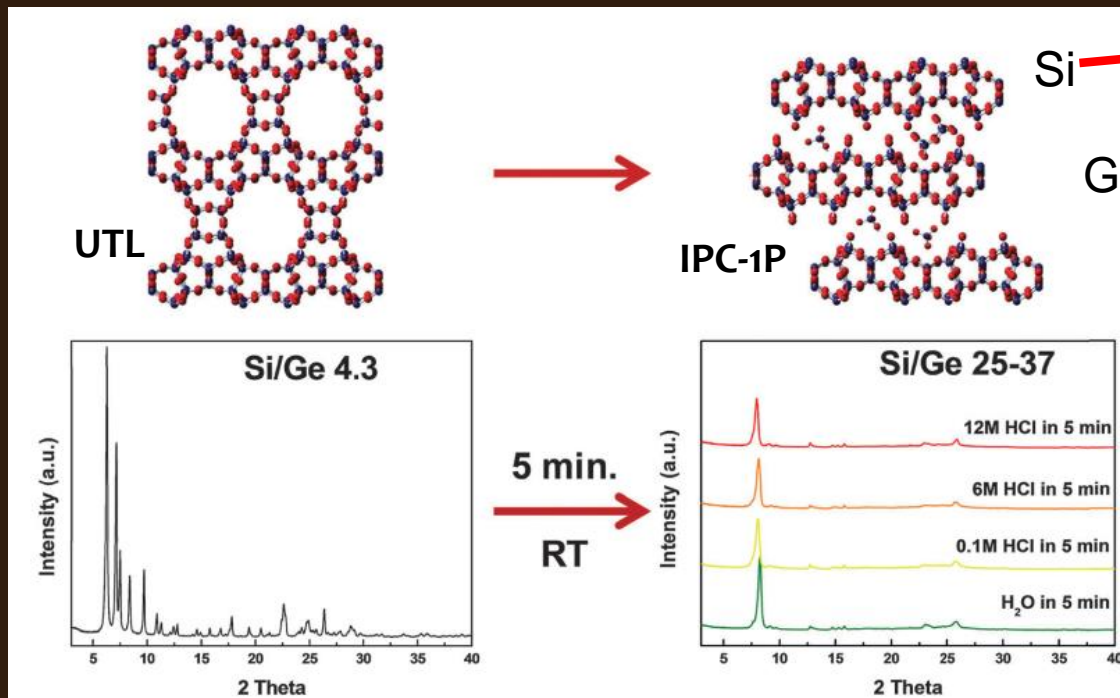
1756

Cronstedt

IPC
IPC-1P
Institute of Physical Chemistry
hydrolyzed UTL

UTL
 $[Ge_{13.8}Si_{62.2}O_{152}]$

Paillaud, J.-L., Harbuzaru, B., Patarin, J. and Bats, N.:
Science, **304**, 990-992 (2004)



Ζεολίτε

Barrer
1948

1756

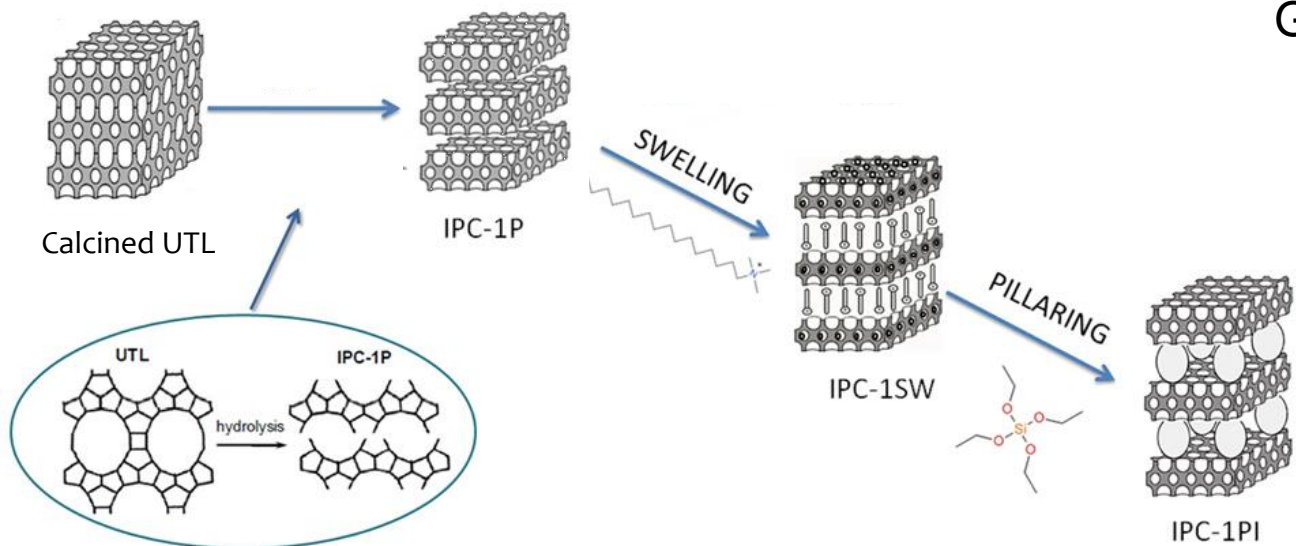
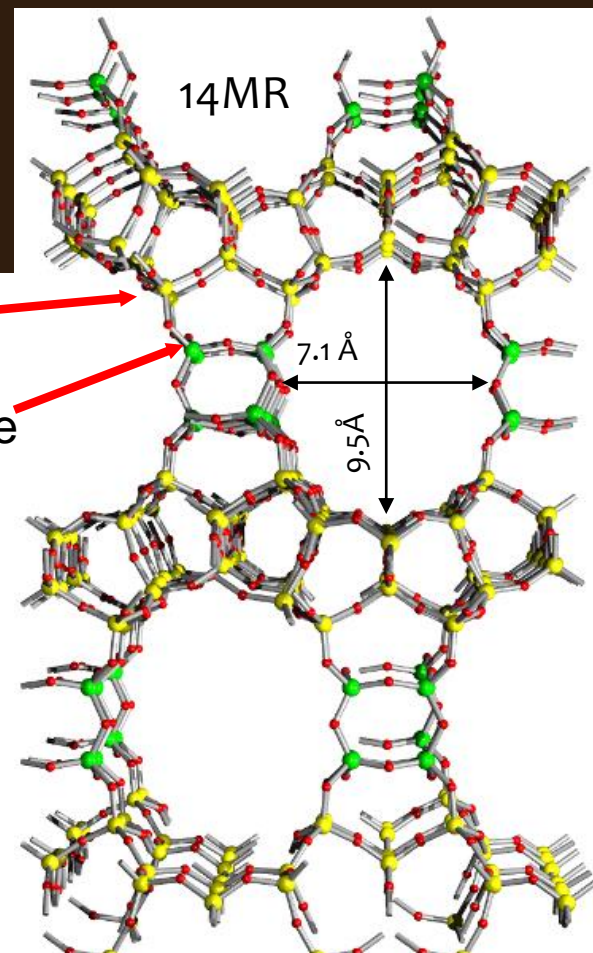
Cronstedt

IPC Institute of Physical Chemistry
IPC-1P hydrolyzed UTL
IPC-1 hydrolyzed calcined UTL
IPC-1SW swollen material

UTL



Paillaud, J.-L., Harbuzaru, B., Patarin, J. and Bats, N.:
Science, **304**, 990-992 (2004)



Ζεολίτε

Barrer
1948

1756

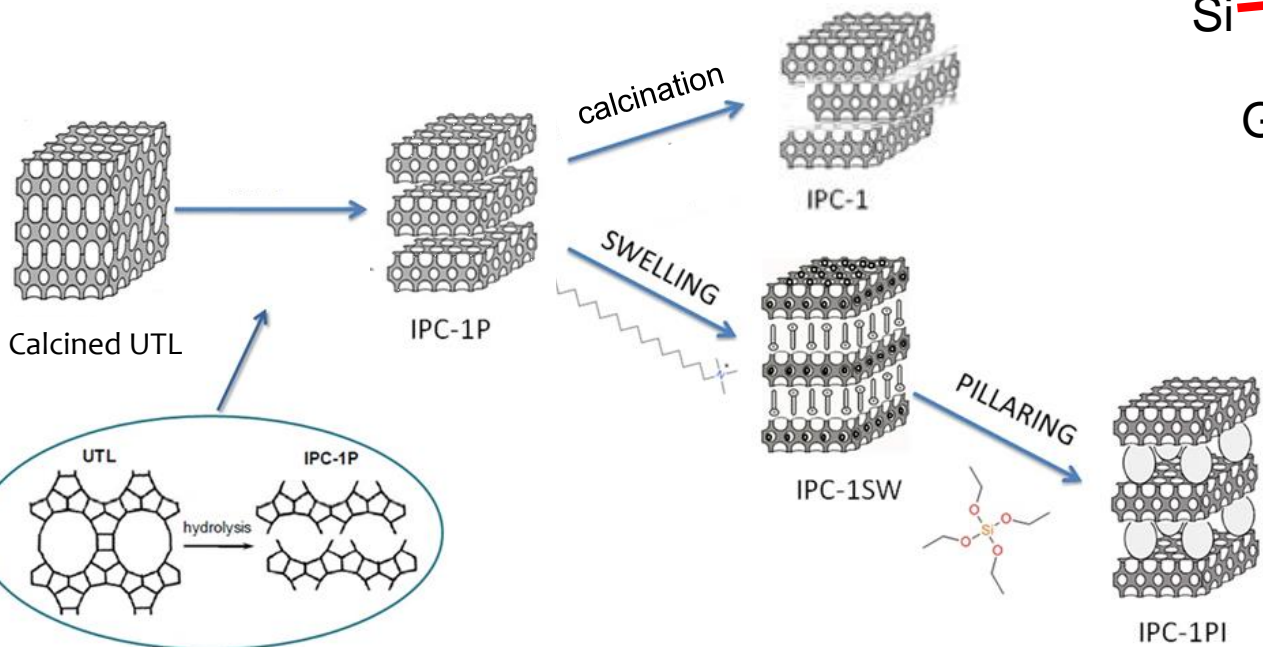
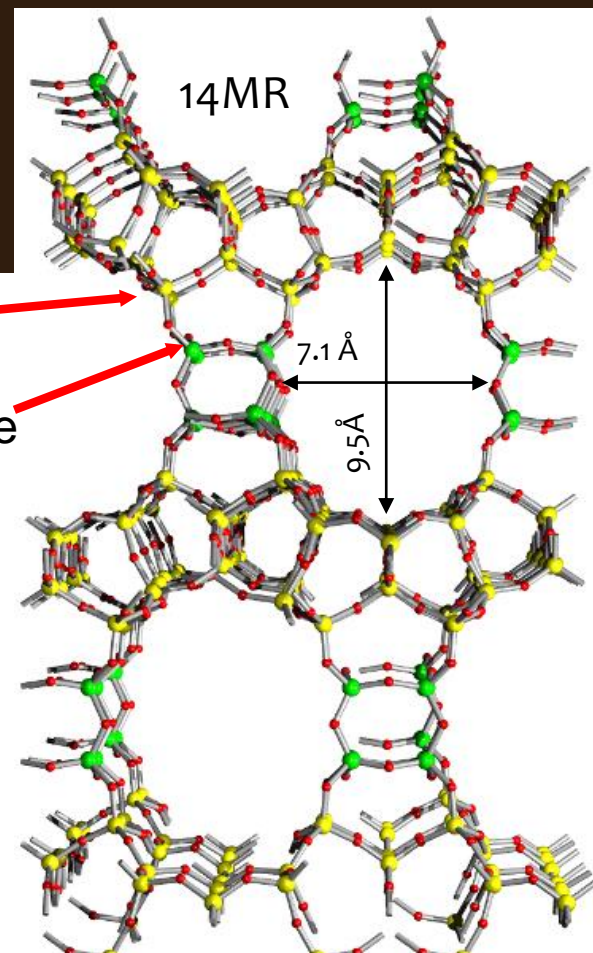
Cronstedt

IPC Institute of Physical Chemistry
IPC-1P hydrolyzed UTL
IPC-1 hydrolyzed calcined UTL
IPC-1SW swollen material

UTL



Paillaud, J.-L., Harbuzaru, B., Patarin, J. and Bats, N.:
Science, **304**, 990-992 (2004)



Ζεολίτε

Barrer
1948

1756

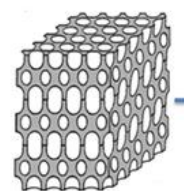
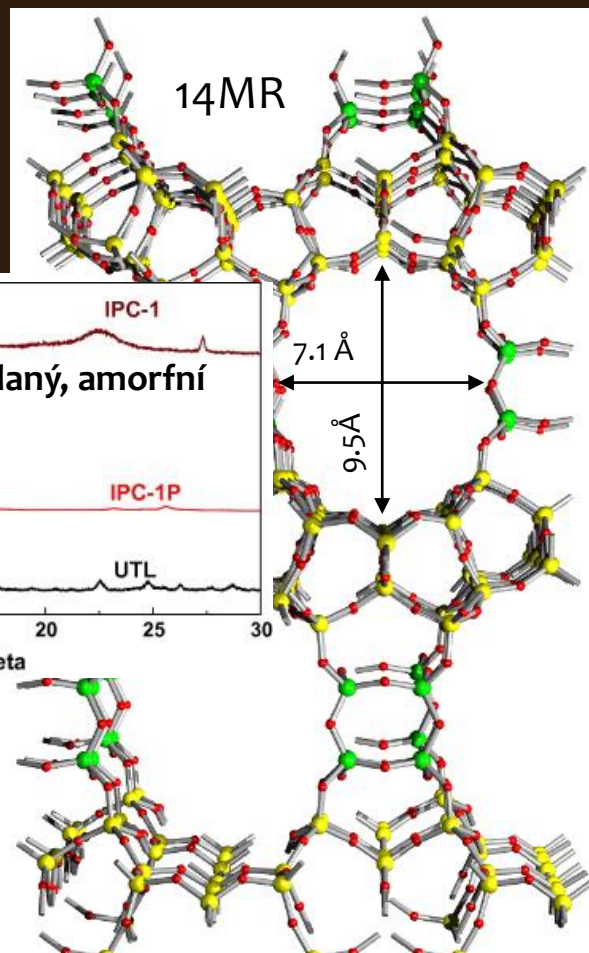
Cronstedt

IPC Institute of Physical Chemistry
IPC-1P hydrolyzed UTL
IPC-1 hydrolyzed calcined UTL
IPC-1SW swollen material

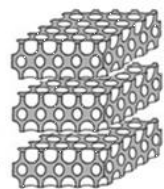
UTL



Paillaud, J.-L., Harbuzaru, B., Patarin, J. and Bats, N.:
Science, **304**, 990-992 (2004)

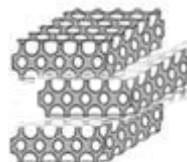


Calcined UTL



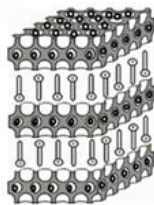
IPC-1P

calcination



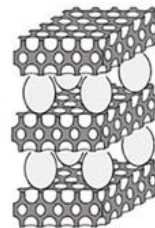
IPC-1

SWELLING

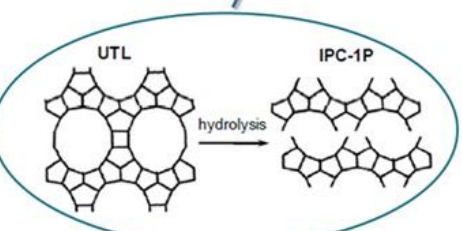
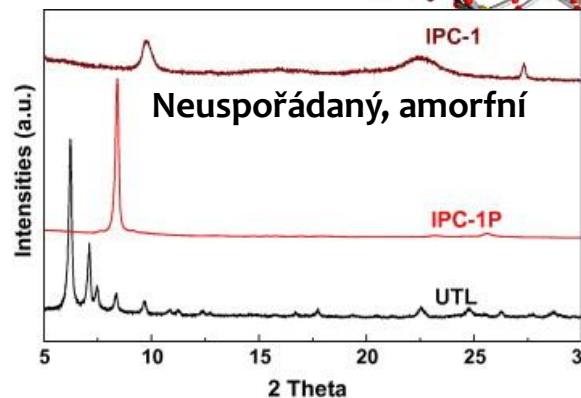


IPC-1SW

PILLARING



IPC-1PI

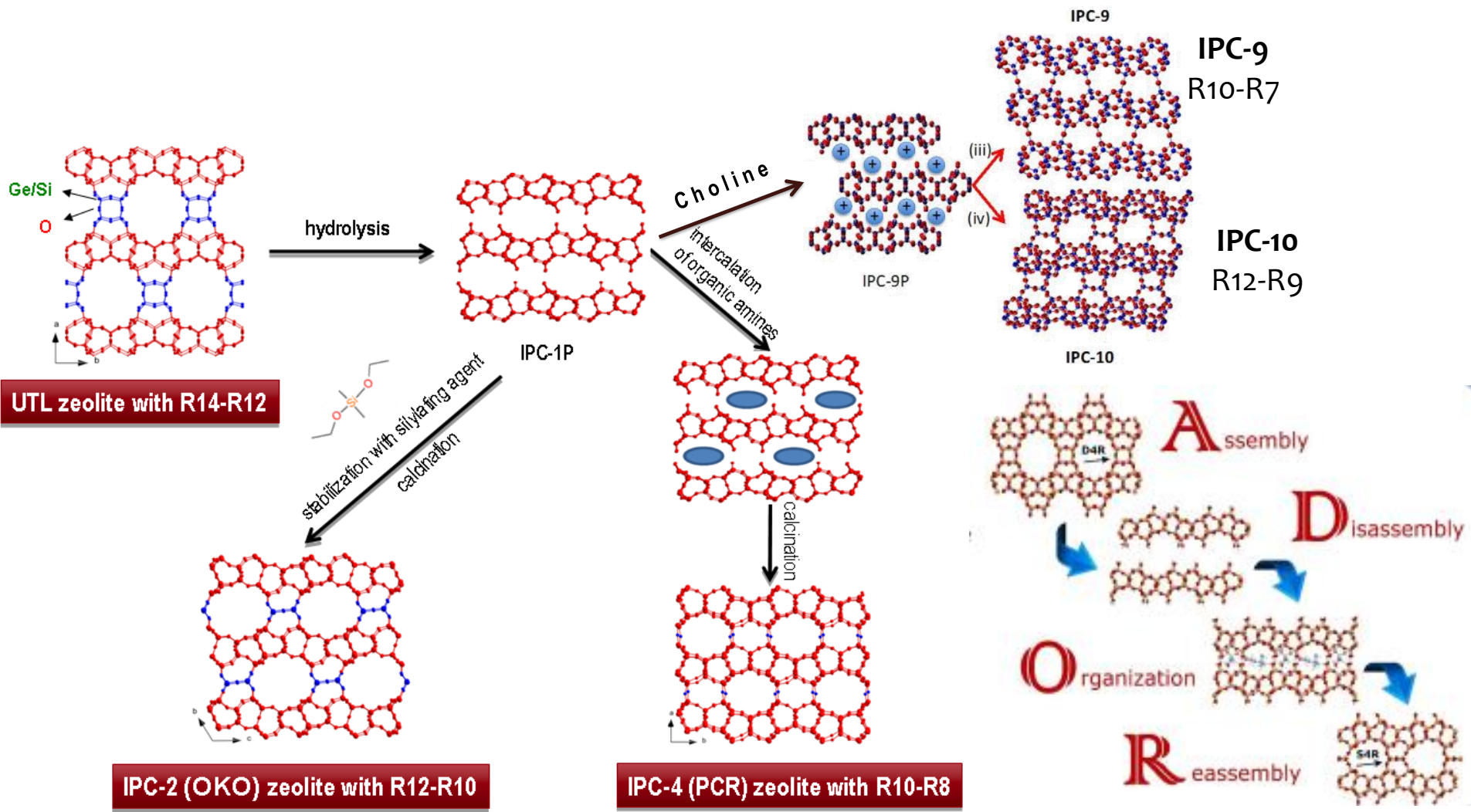


Ζεολίτε

Barrer
1948

1756

Cronstedt

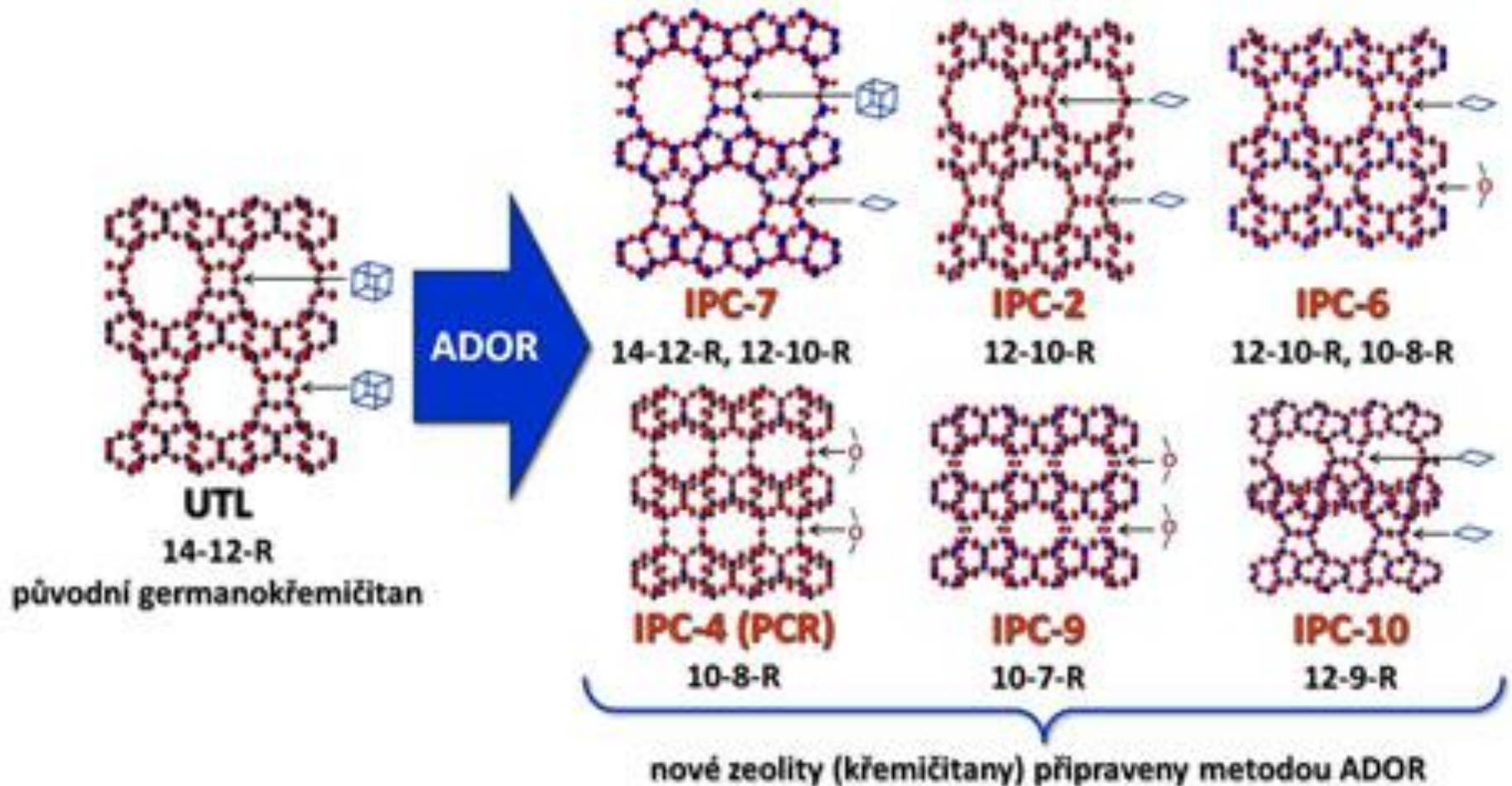


Ζεολίτε

Barrer
1948

1756

Cronstedt



Ζεολίτε

Barrer
1948

1756

Cronstedt



Table 3 The list of germanosilicates containing D4R/D3R units. Adopted from the IZA website⁷⁰

IZA code	Type material	Channel dimensionality	Channels	Type of double-ring unit	Location of double-ring in	First reported (patent/paper)
BEC	FOS-5 beta polymorph C	3-Dimensional	12-12R	D4R	3D	2000 ¹⁴⁹
IRN	ITQ-49	1-Dimensional	8R	D4R	2D	2012 ¹⁶²
IRR	ITQ-44	3-Dimensional	18-12R	D3R, D4R	3D	2010 ¹⁵⁰
-IRY	ITQ-40	3-Dimensional	16-15R	D3R, D4R	3D	2010 ¹⁶⁴
ISV	ITQ-7	3-Dimensional	12-12R	D4R	2D	2002 ^{144 a}
ITG	ITQ-38	3-Dimensional	12-10-10-10R	D4R	1D	2012 ¹⁸⁰
ITH	ITQ-13	3-Dimensional	10-10-9R	D4R	1D	2002 ¹⁵³
ITR	ITQ-34	3-Dimensional	10-10-9R	D4R	1D	2008 ¹⁵⁴
ITT	ITQ-33	3-Dimensional	18-10R	D4R	2D	2006 ¹⁸¹
-ITV	ITQ-37	3-Dimensional	Mesoporous	D4R	3D	2009 ¹⁵⁶
IWR	ITQ-24	3-Dimensional	12-10-10R	D4R	1D	2003 ¹⁶⁵
IWS	ITQ-26	3-Dimensional	12-12R	D4R	3D	2008 ¹⁵⁷
IWW	ITQ-22	3-Dimensional	12-10-8R	D4R	1D	2003 ⁸¹
LTA	ITQ-29	3-Dimensional	8R	D4R	3D	2004 ^{174 b}
POS	PUK-16	3-Dimensional	12-11R	D4R	2D	2014 ¹⁶³
SOF	SU-15	3-Dimensional	12-10R	D4R	3D	2008 ¹⁵⁸
STW	SU-32	3-Dimensional	10-8R	D4R	3D	2008 ¹⁵⁸
SVV	SSZ-77	0-Dimensional	6R	D4R	1D	2008 ¹⁵⁹
UOS	IM-16	3-Dimensional	10-8-8R	D4R	1D	2007 ¹⁷¹
UOZ	IM-10	0-Dimensional	6R	D4R	3D	2004 ¹⁴⁶
UTL	ITQ-15/IM-12	2-Dimensional	14-12R	D4R	1D	2004 ^{71,72}
UWY	IM-20	3-Dimensional	12-10-10-10-10R	D4R	2D	2010 ¹⁶¹
	ITQ-21	3-Dimensional	12R	D4R	3D	2002 ⁷⁸
	ITQ-43	3-Dimensional	28-12-12-12R	D4R	2D	2011 ¹⁸²

^a ISV was first reported in 1999 as pure silica zeolites, later in 2002 prepared as germanosilicates. ^b LTA was first reported in 1956 as aluminosilicates, later in 2004 prepared as aluminogermanosilicates.

Ζεολίτε

Barrer
1948

1756

Cronstedt



Πůvodní
zeolit

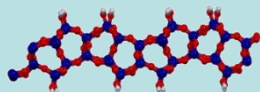
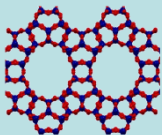
Vrstevnatý
prekurzor

-s4R

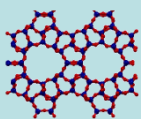
-d4R

Posunuté vrstvy

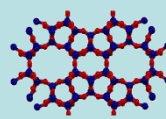
UTL



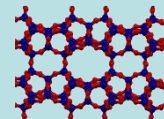
IPC-1P



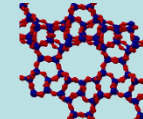
IPC-2 (OKO)



IPC-4 (PCR)

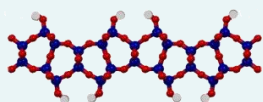
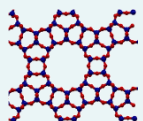


IPC-9

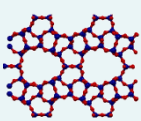


IPC-10

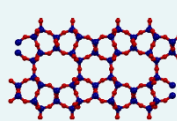
SAZ-1



SAZ-1P

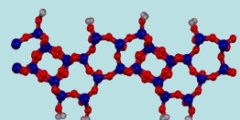
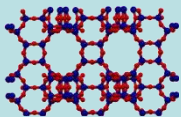


IPC-16

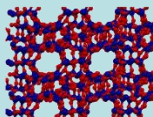


IPC-15

IWW

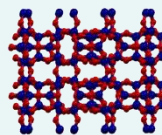
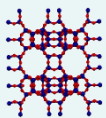


IPC-5P



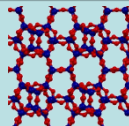
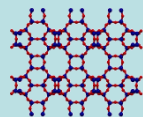
IPC-18

UOV



IPC-12

IWR



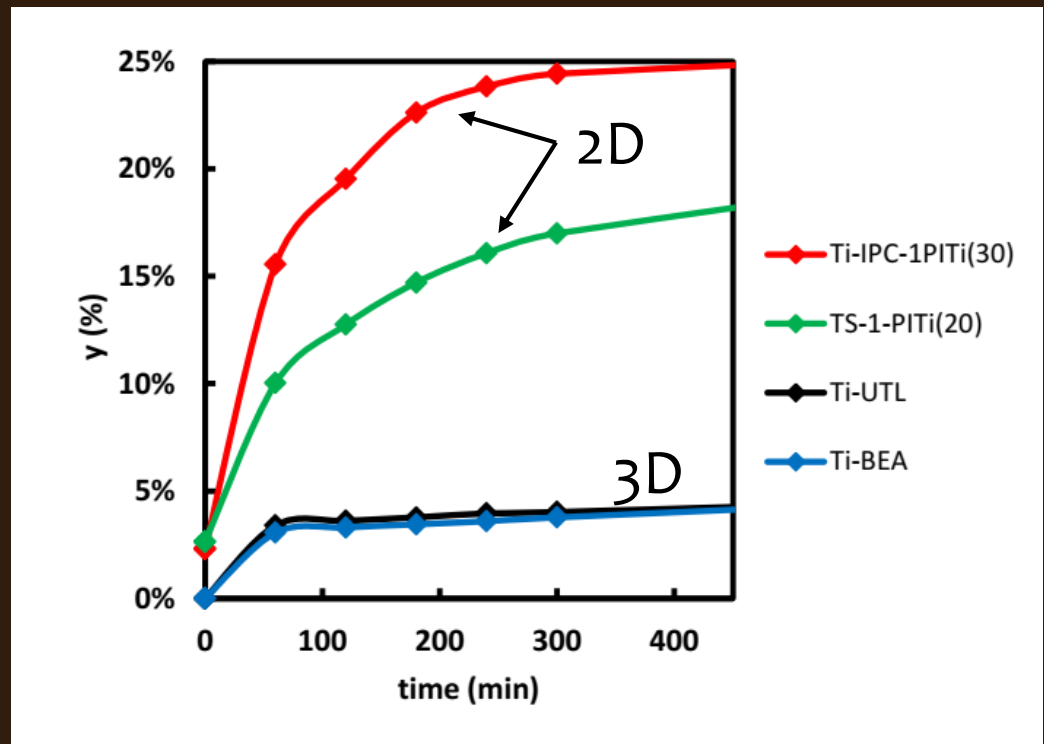
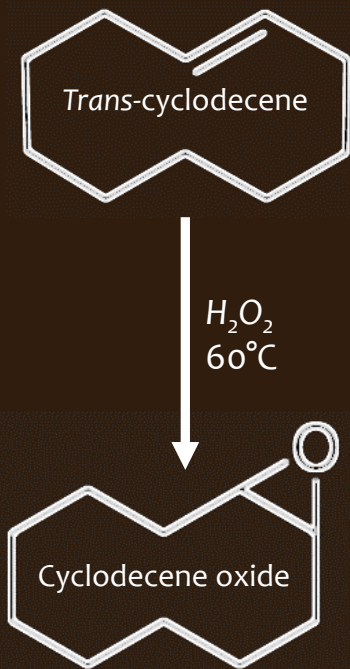
IPC-17

Ζεολίτε

Barrer
1948

1756

Cronstedt



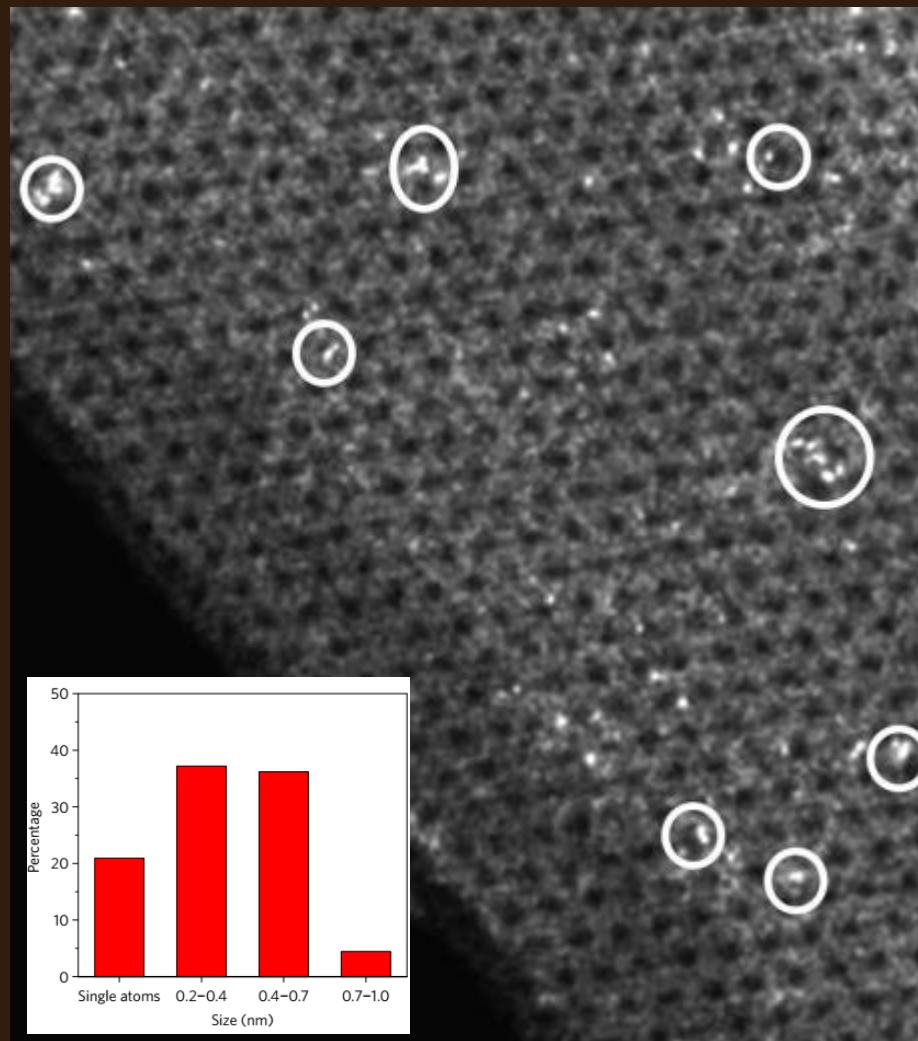
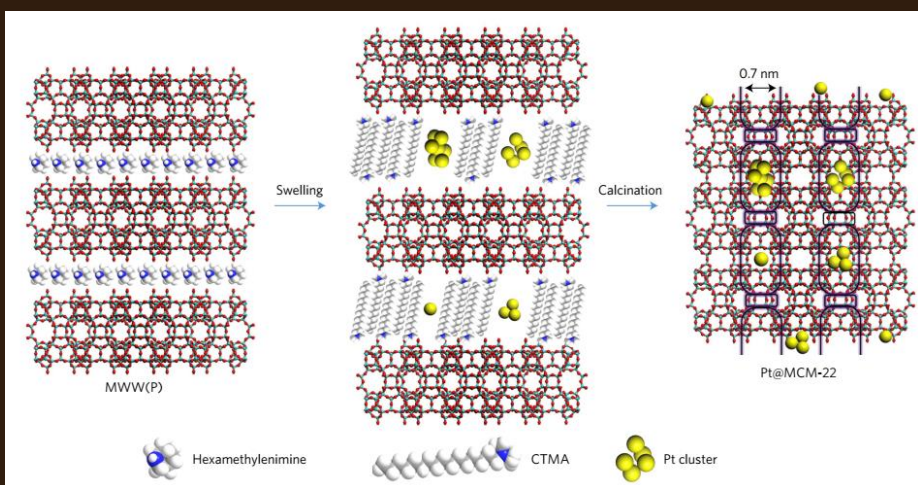
Ζεολίτε

Barrer
1948

1756

Cronstedt

Nanočástice Pt @ MWW



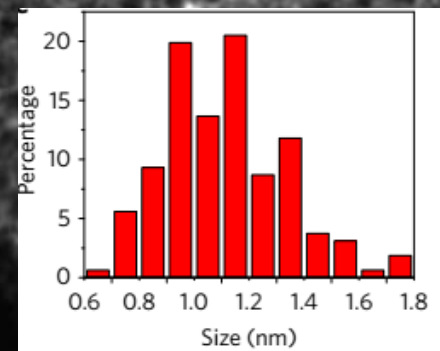
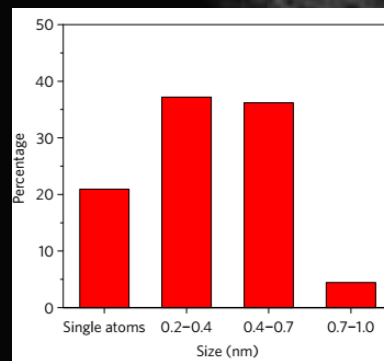
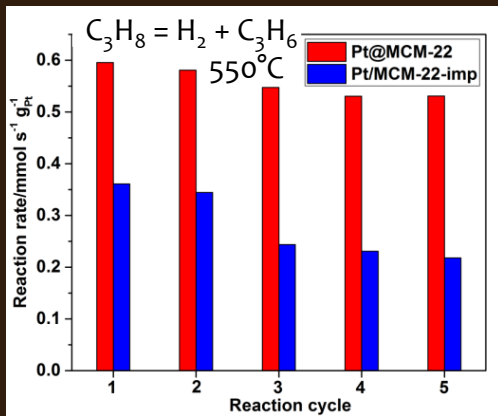
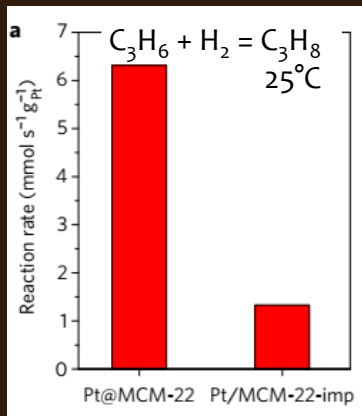
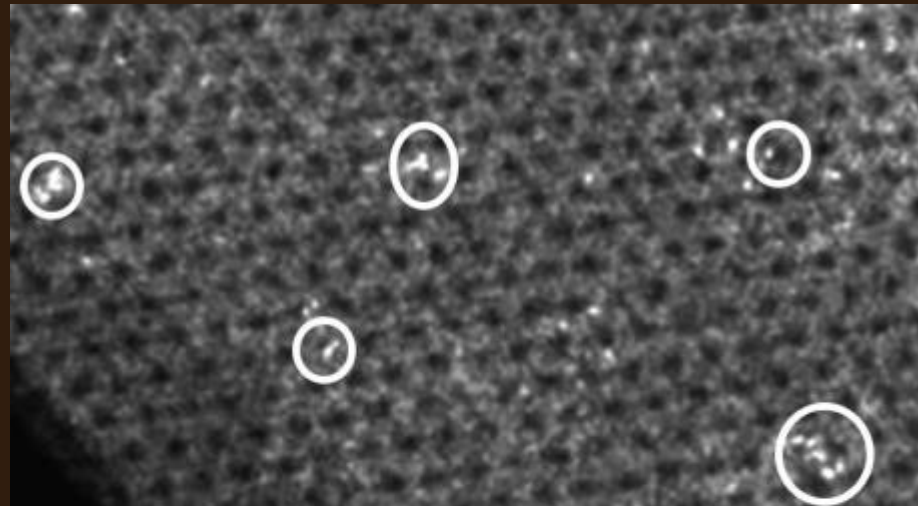
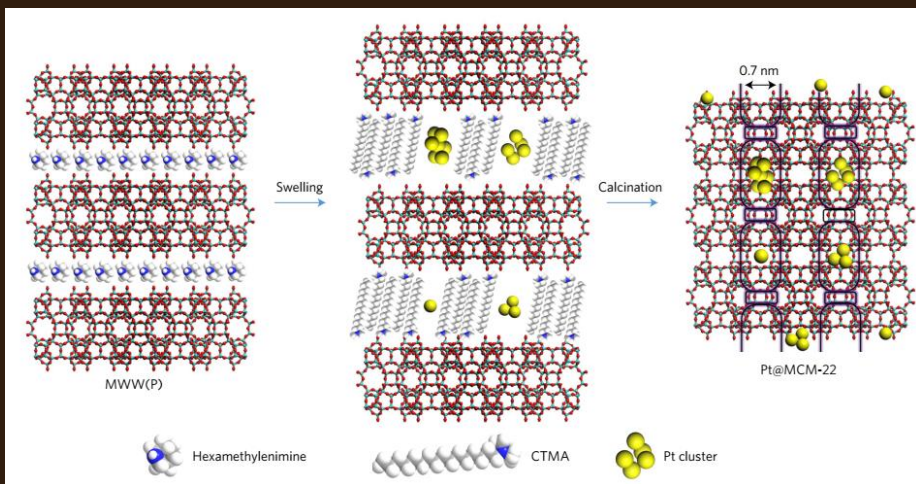
Ζεολίτε

Barrer
1948

1756

Cronstedt

Nanočástice Pt @ MWW



Ζεολίτε

Barrer
1948

1756

Cronstedt

ABW	ACO	AEI	AEL	AEN	AEI	AFG	AFI	AFN	AFO	AFR	AFS
AFT	AFX	AFY	AHT	ANA	APC	APD	AST	ASV	ATN	ATO	ATS
ATT	ATV	AWO	AWW	BCT	*BEA	BEC	BIK	BOG	BPH	BRE	CAN
CAS	CDO	CFI	CGF	CGS	CHA	CHI	CLO	CON	CZP	DAC	DDR
DFO	DFT	DOH	DON	EAB	EDI	EMT	EON	EPI	ERI	ESV	ETR
EUO	EZT	FAR	FAU	FER	FRA	GIS	GIU	GME	GON	GOO	HEU
IFR	IHW	IMF	ISV	ITE	ITH	ITW	IWR	IWV	IWW	JBW	KFI
LAU	LEV	LIO	LIT	LOS	LOV	LTA	LTL	LTN	MAR	MAZ	MEI
MEL	MEP	MER	MFI	MFS	MON	MOR	MOZ	MSE	MSO	MTF	MTN
MTT	MTW	MWW	NAB	NAT	NES	NON	NPO	NSI	OBW	OF	OSI
OSO	OWE	PAR	PAU	PHI	PON	RHO	RON	RRO	RSN	RTE	RTH
RUT	RWR	RWY	SAO	SAS	SAT	SAV	SBE	SBN	SBS	SBT	SFE
SFF	SFG	SFH	SFN	SFO	SGT	SIV	SOD	SOS	SSF	SSY	STF
STI	*STO	STT	SZR	TER	THO	TOL	TON	TSC	TUN	UEI	UFI
UOZ	USI	UTL	VET	VFI	VNI	VSV	WEI	WEN	YUG	ZON	

Ζεολίτε

Barrer
1948

1756

Cronstedt

ABW	ACO	AEI	AEL	AEN	AEI	AFG	AFI	AFN	AFO	AFR	AFS			
AFT	AFX	AFY	AHT	ANA	APC	APD	AST	ASV	ATN	ATO	ATS			
ATT	ATV	AWO	AWW	BCT	*BEA	BEC	BIK	BOG	BPH	BRE	CAN			
CAS	CDO	CFI	CGF						CZP	DAC	DDR			
DFO	DFT	DOH	DOM						ERI	ESV	ETR			
EUO	EZT	FAR							GON	GOO	HEU			
IFR	IHW	IMF							IWW	JBW	KFI			
LAU	LEV	LIO		2D - pilřřované					LTN	MAR	MAZ	MEI		
MEL	MEP		2D - lamelarnř					MOR	MOZ	MSE	MSO	MTF	MTN	
MTT	MTW	3D					NAT	NES	NON	NPO	NSI	OBW	OF	OSI
OSO	OWE	PAR	PAU	PHI	PON	RHO	RON	RRO	RSN	RTE	RTH			
RUT	RWR	RWY	SAO	SAS	SAT	SAV	SBE	SBN	SBS	SBT	SFE			
SFF	SFG	SFH	SFN	SFO	SGT	SIV	SOD	SOS	SSF	SSY	STF			
STI	*STO	STT	SZR	TER	THO	TOL	TON	TSC	TUN	UEI	UFI			
UOZ	USI	UTL	VET	VFI	VNI	VSV	WEI	WEN	YUG	ZON				

Ζεολιτε

Barrer
1948

1756

Cronstedt



Děkuji za pozornost

Ζεολιτε

Barrer
1948

1756

Cronstedt

Project EXCELLENCE

InDeNAC

Intelligent Design of Nanoporous
Adsorbents and Catalysts

2D zeolity

Ζεολίτε

Barrer
1948

1756

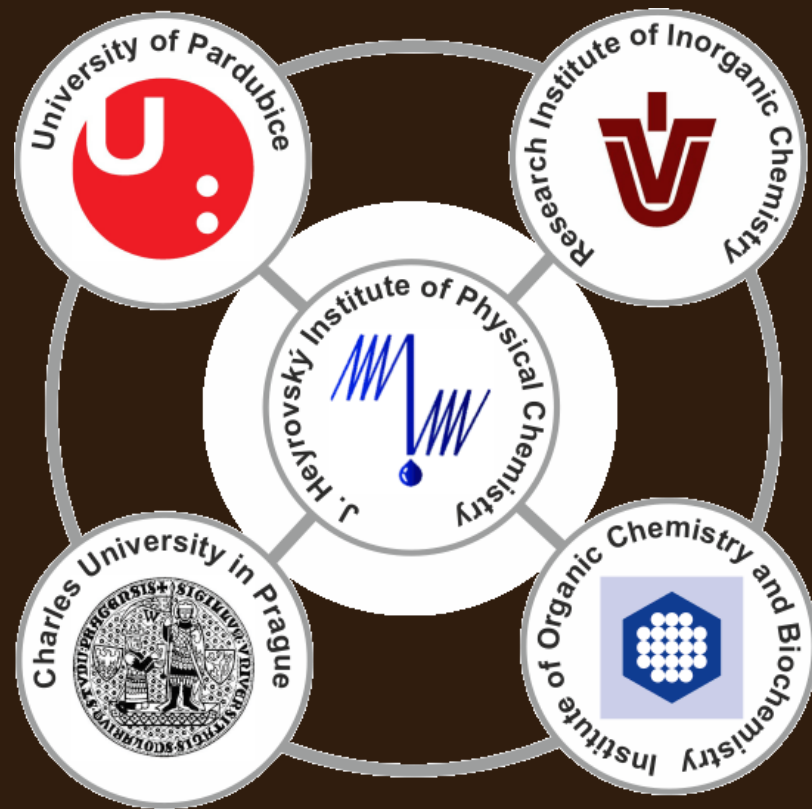
Cronstedt

Project EXCELLENCE

InDeNAC

Intelligent Design of Nanoporous
Adsorbents and Catalysts

2D zeolity



Ζεολίτε

Barrer
1948

1756

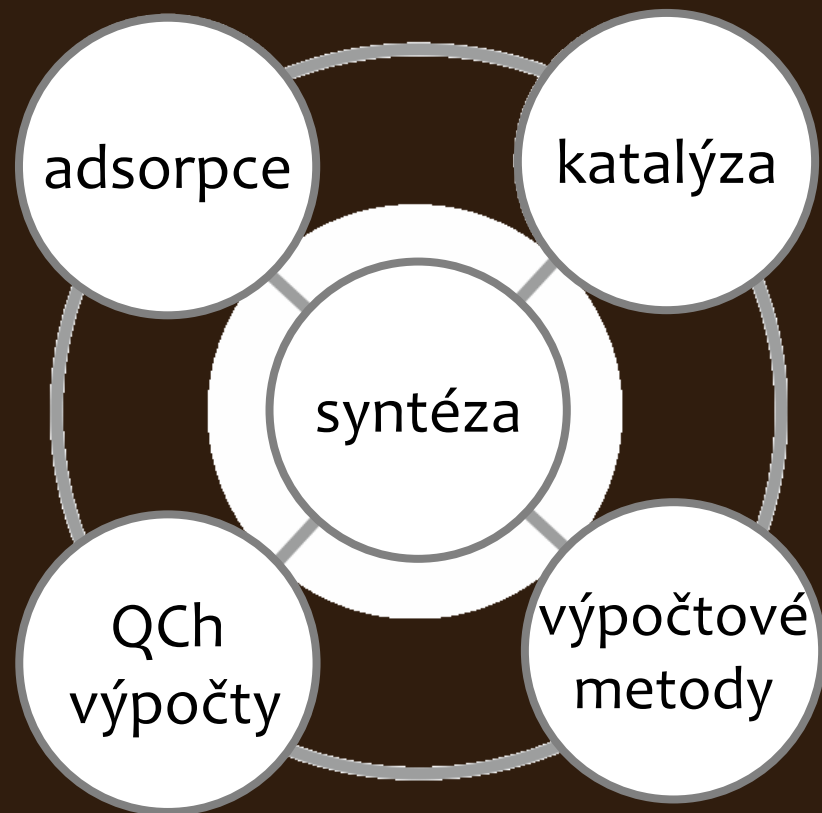
Cronstedt

Project EXCELLENCE

InDeNAC

Intelligent Design of Nanoporous
Adsorbents and Catalysts

2D zeolity



Ζεολίτε

Barrer
1948

1756

Cronstedt



Cíle projektu



Syntéza nových 2D zeolitů, nalezení nových metod cílené přípravy.



Pochopení vztahu syntéza-struktura-vlastnosti.



Zhodnocení adsorpčních vlastností nově připravených materiálů.



Zhodnocení přínosu 2D zeolitů ke katalytickému zpracování lignocelulosové biomasy a pod.



Vývoj metodologie teoretického popisu 2D zeolitů a interakce jednotlivých lamel.



Vytvoření představy o struktuře povrchu lamel na atomární úrovni.

Ζεολίτε

Barrer
1948

1756

Cronstedt

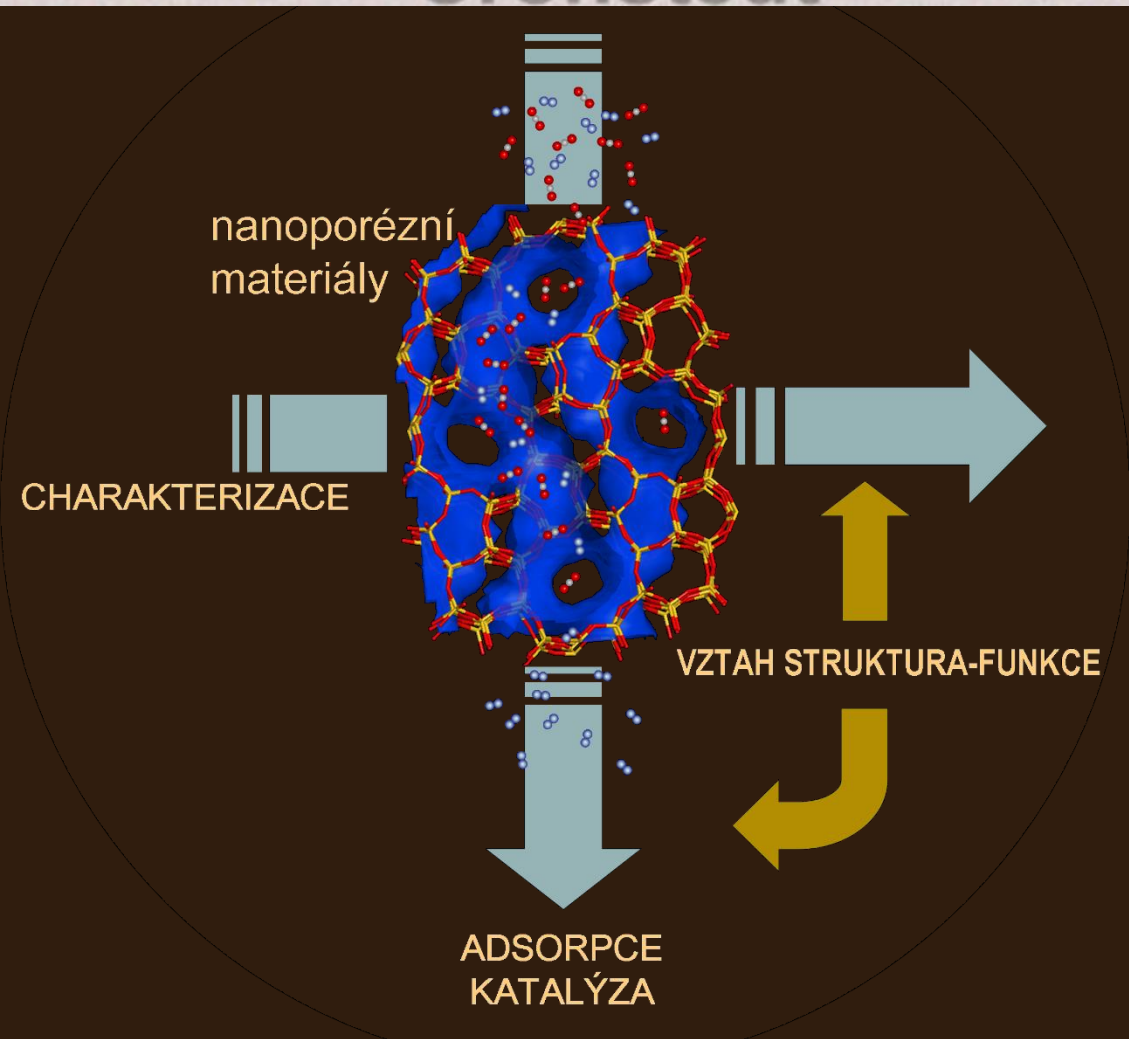


nanoporézní
materiály

CHARAKTERIZACE

VZTAH STRUKTURA-FUNKCE

ADSORPCE
KATALÝZA



Ζεολίτε

Barrer
1948

1756

Cronstedt



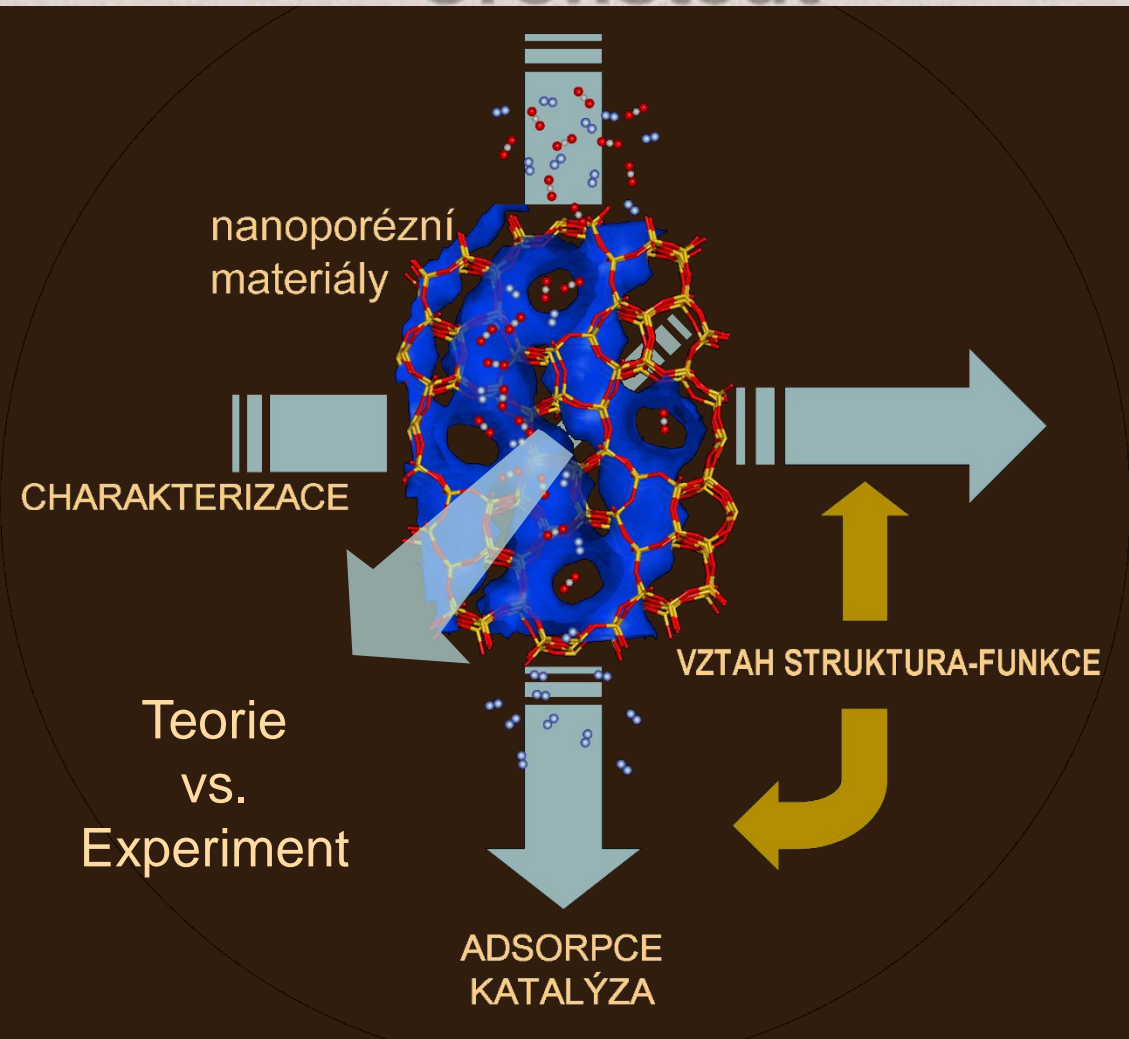
nanoporézní
materiály

CHARAKTERIZACE

VZTAH STRUKTURA-FUNKCE

Teorie
vs.
Experiment

ADSORPCE
KATALÝZA

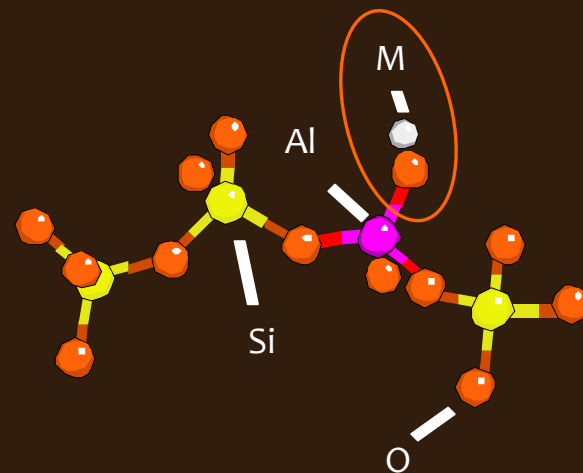
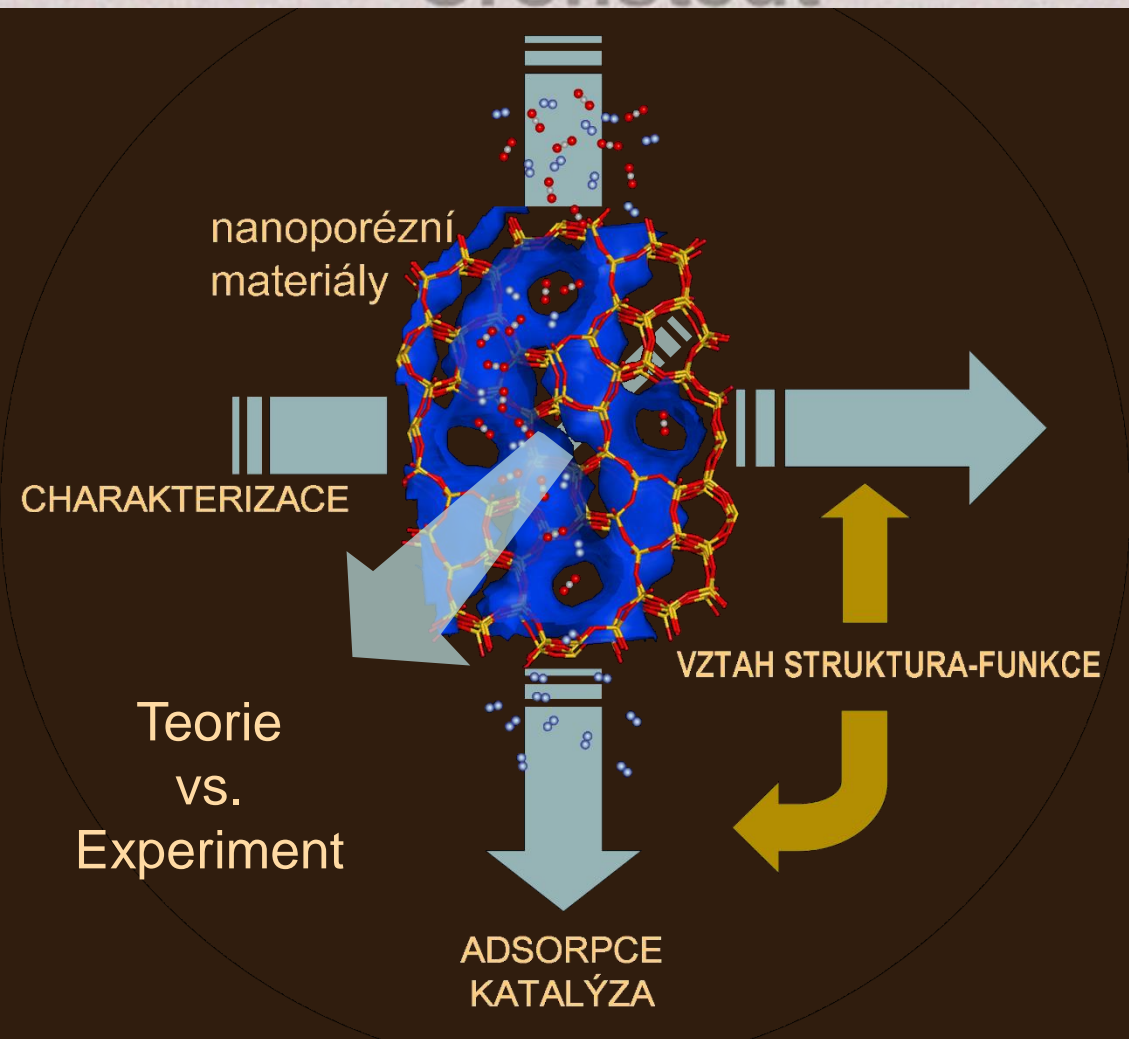


Ζεολίτε

Barrer
1948

1756

Cronstedt



Ζεολίτε

Barrer
1948

1756

Cronstedt

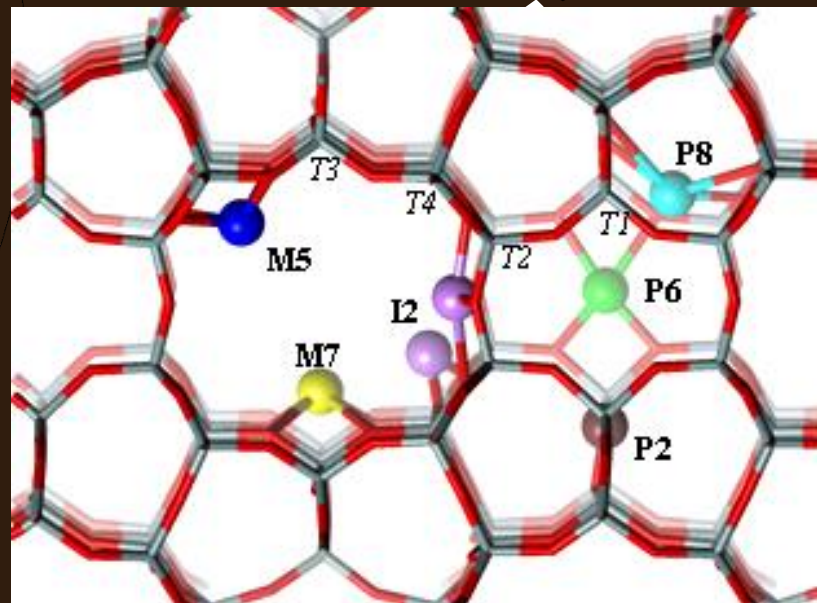
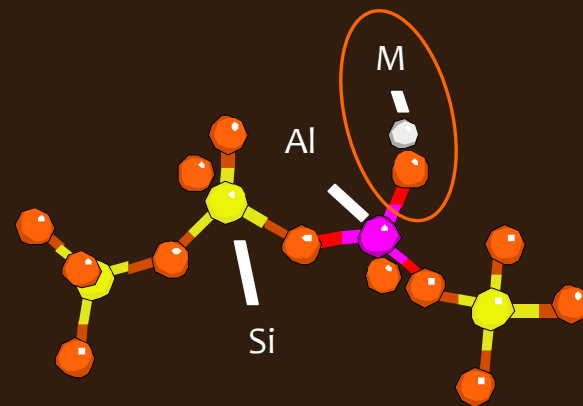
nanoporézní
materiály

CHARAKTERIZACE

Teorie
vs.
Experiment

ADSORPCE
KATALÝZA

VZTAH STRUKTURA-FUNKCE

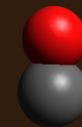
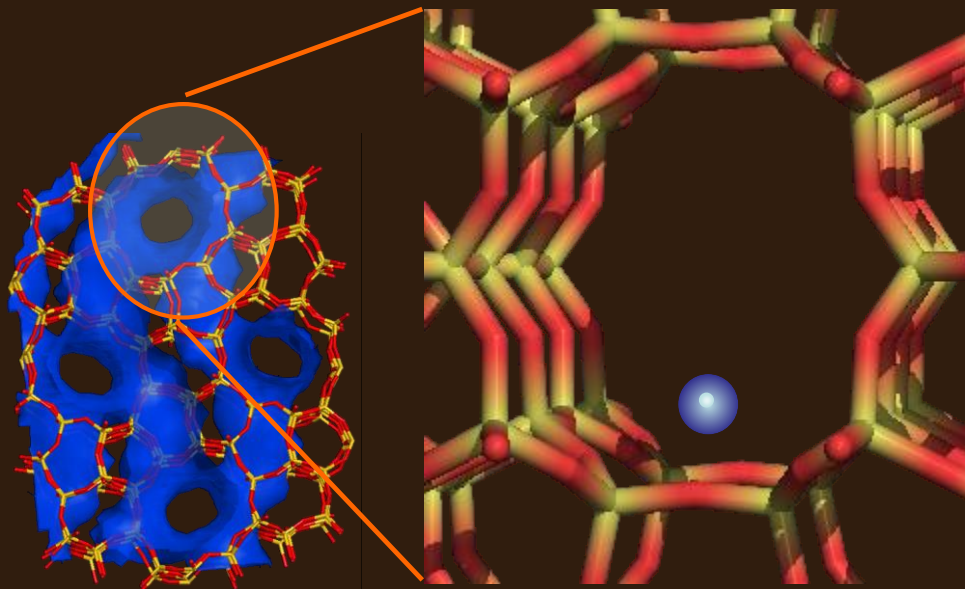


Ζεολίτε




Barrer
1948

1756

Cronstedt



testovací molekula

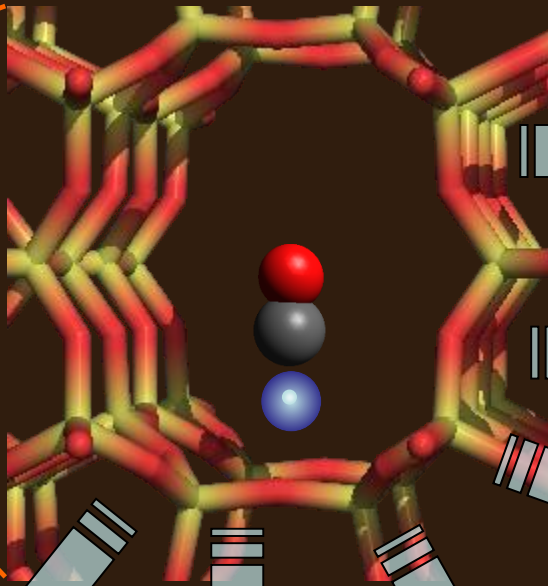
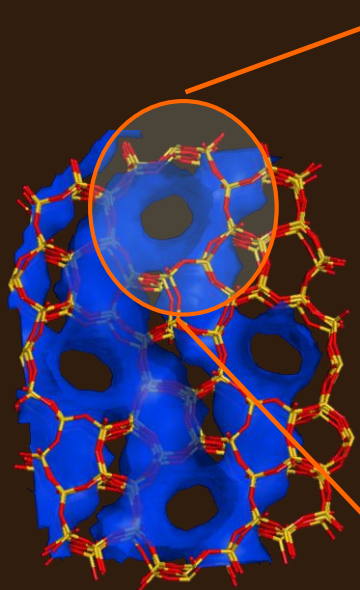
-  specifická adsorpce či reaktivita
-  vlastnosti citlivé na koordinaci
-  snadná sledovatelnost

Ζεολίτε

Barrer
1948

1756

Cronstedt



IČ spektroskopie

DR UV-vis spektroskopie

Teplotně programované
techniky

katalýza

kalorimetrie

volumetrie

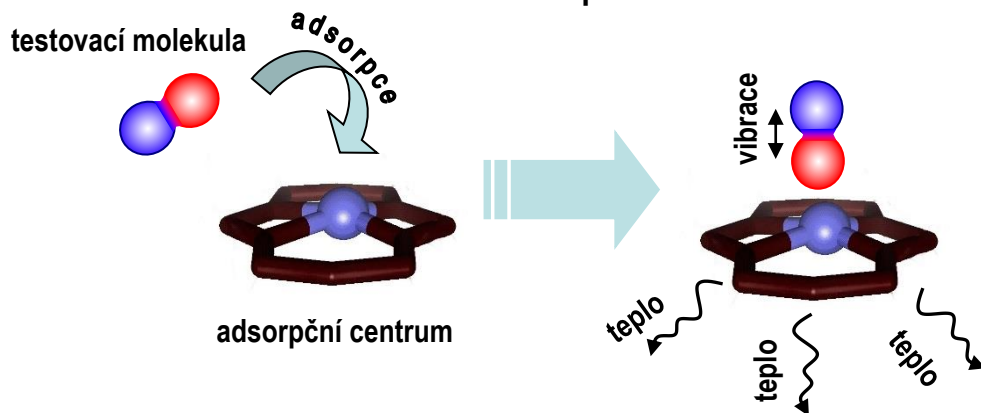
Ζεολίτε

Barrer
1948

1756

Cronstedt

■ Charakterizace adsorpčních center



Ζεολίτε

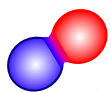
Barrer
1948

1756

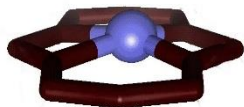
Cronstedt

■ Charakterizace adsorpčních center

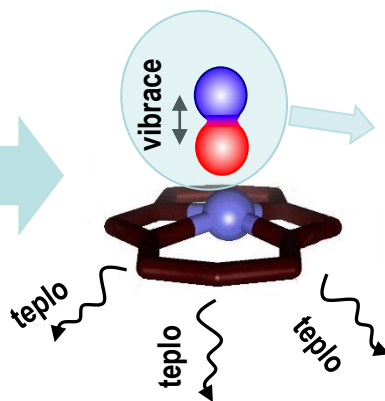
testovací molekula



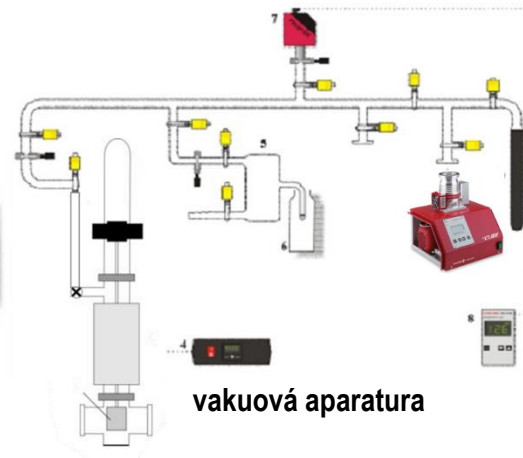
adsorpce



adsorpční centrum



FTIR



vakuová aparatura

Ζεολίτε

Barrer
1948

1756

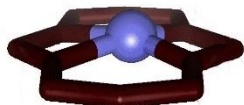
Cronstedt

■ Charakterizace adsorpčních center

testovací molekula

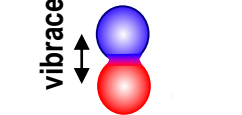


adsorpce



adsorpční centrum

vibrace



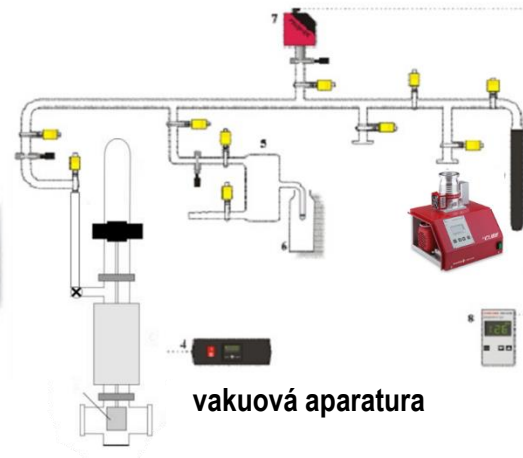
teplo

teplo

teplo



FTIR



vakuová aparatura



volumetrická aparatura + kalorimetr

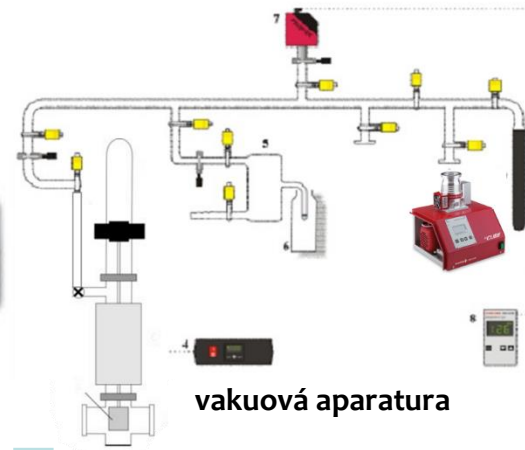
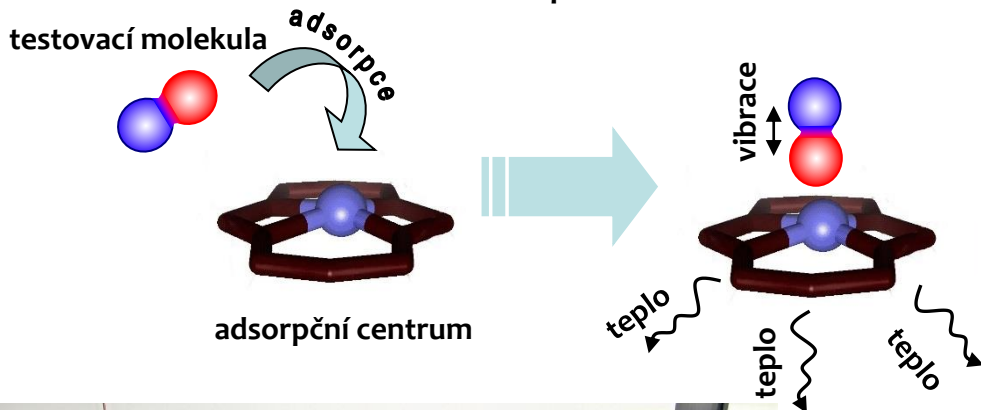
Ζεολίτε

Barrer
1948

1756

Cronstedt

■ Charakterizace adsorpčních center



- adsorpční izoterma – kvantita
- kalorimetrická křivka – distribuce interakčních energií
- IČ spektra – rozlišení různých adsorpčních komplexů, odhad int. energií (VTIR),

Ζεολίτε

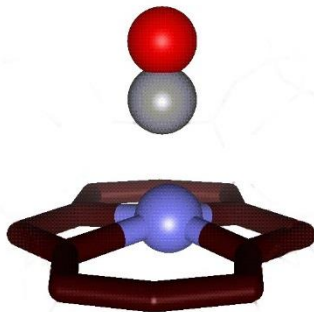
Barrer
1948

1756

Cronstedt

Adsorpce CO

- velice citlivé k povaze adsorpčního centra a jeho okolí (v , ΔH_{ads})
 - typ adsorpčního centra
 - koordinace v povrchu
 - lokální složení povrchu



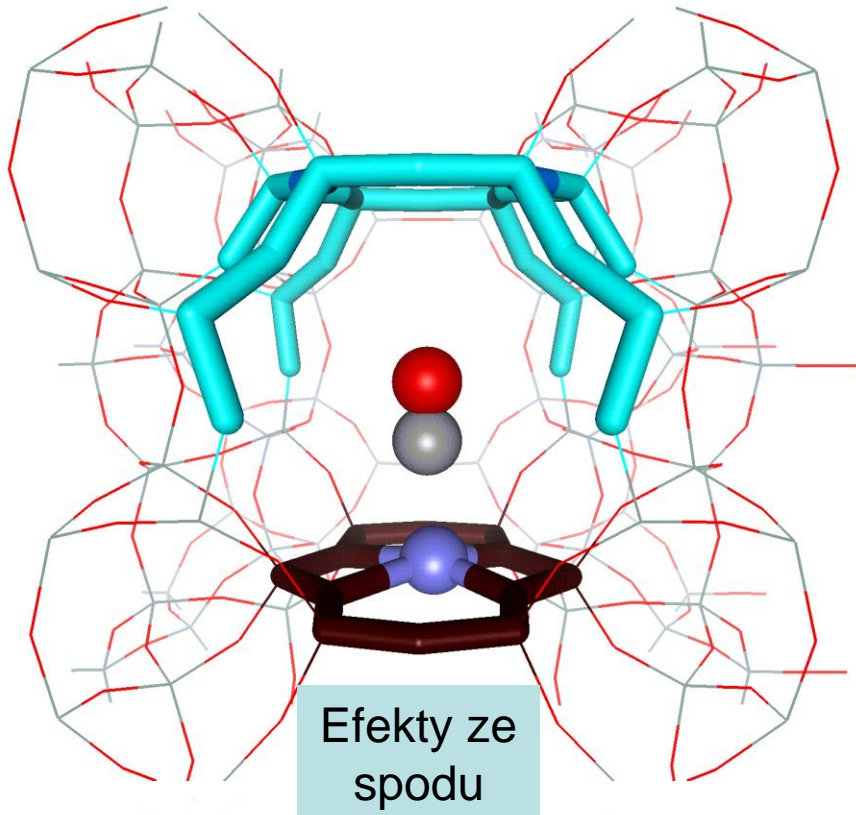
Ζεολίτε

Barrer
1948

1756

Cronstedt

Adsorpce CO



- velice citlivé k povaze adsorpčního centra a jeho okolí (v , ΔH_{ads})

- typ adsorpčního centra
- koordinace v povrchu
- lokální složení povrchu

stísněný prostor strukturního póru

Ζεολίτε

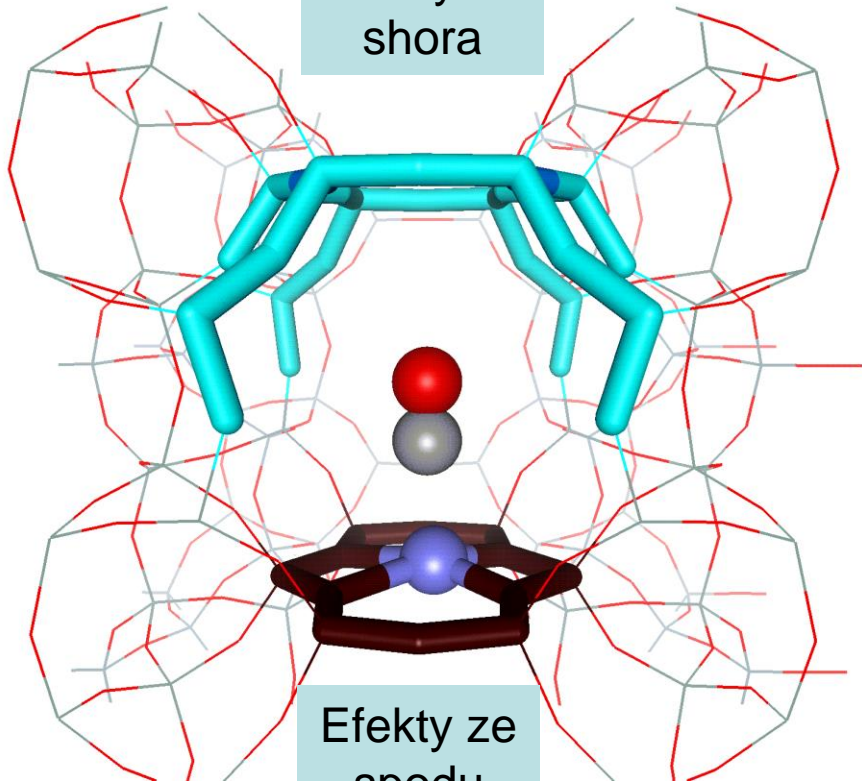
Barrer
1948

1756

Cronstedt

Adsorpce CO

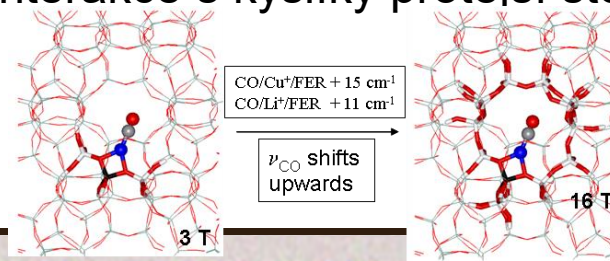
Efekty ze
shora



Efekty ze
spodu

stísněný prostor strukturního póru

- velice citlivé k povaze adsorpčního centra a jeho okolí (ν , ΔH_{ads})
 - typ adsorpčního centra
 - koordinace v povrchu
 - lokální složení povrchu
- vliv stísněného prostoru póru (efekty ze shora)
 - interakce s kyslíky protější stěny



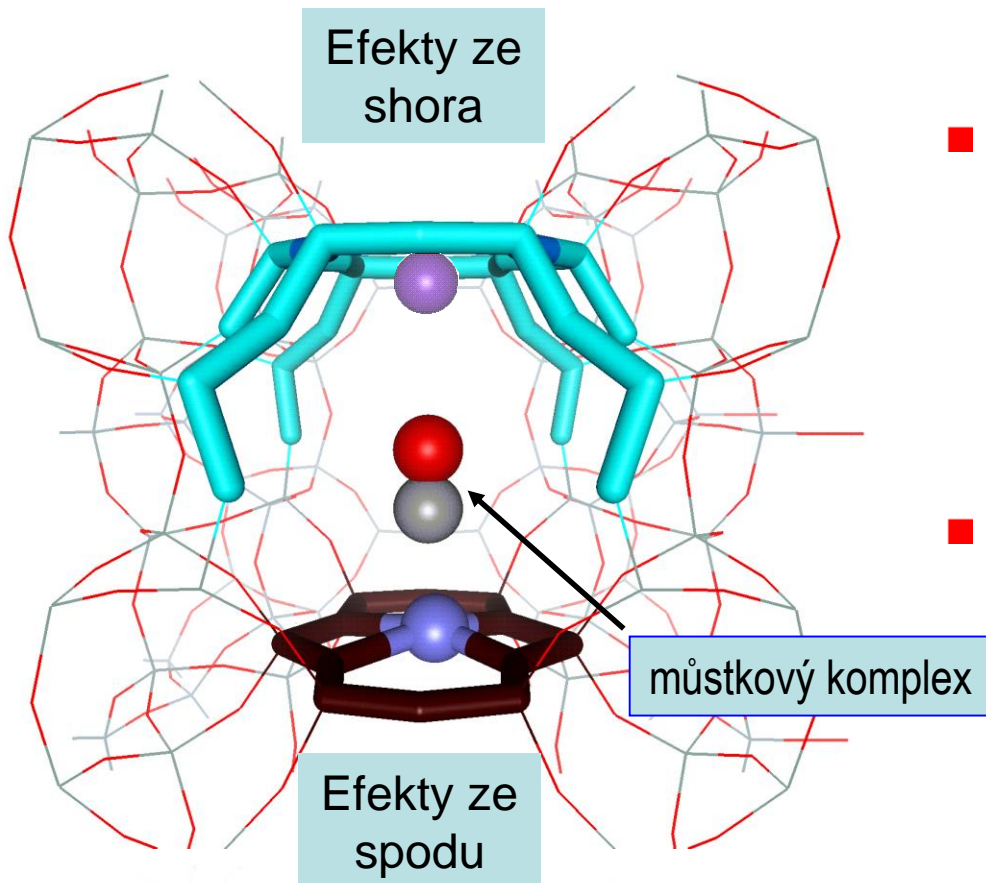
Ζεολίτε

Barrer
1948

1756

Cronstedt

Adsorpce CO



- velice citlivé k povaze adsorpčního centra a jeho okolí (v , ΔH_{ads})
 - typ adsorpčního centra
 - koordinace v povrchu
 - lokální složení povrchu
- vliv stísněného prostoru póru (efekty ze shora)
 - interakce s kyslíky protější stěny
 - interakce s druhým kationtem

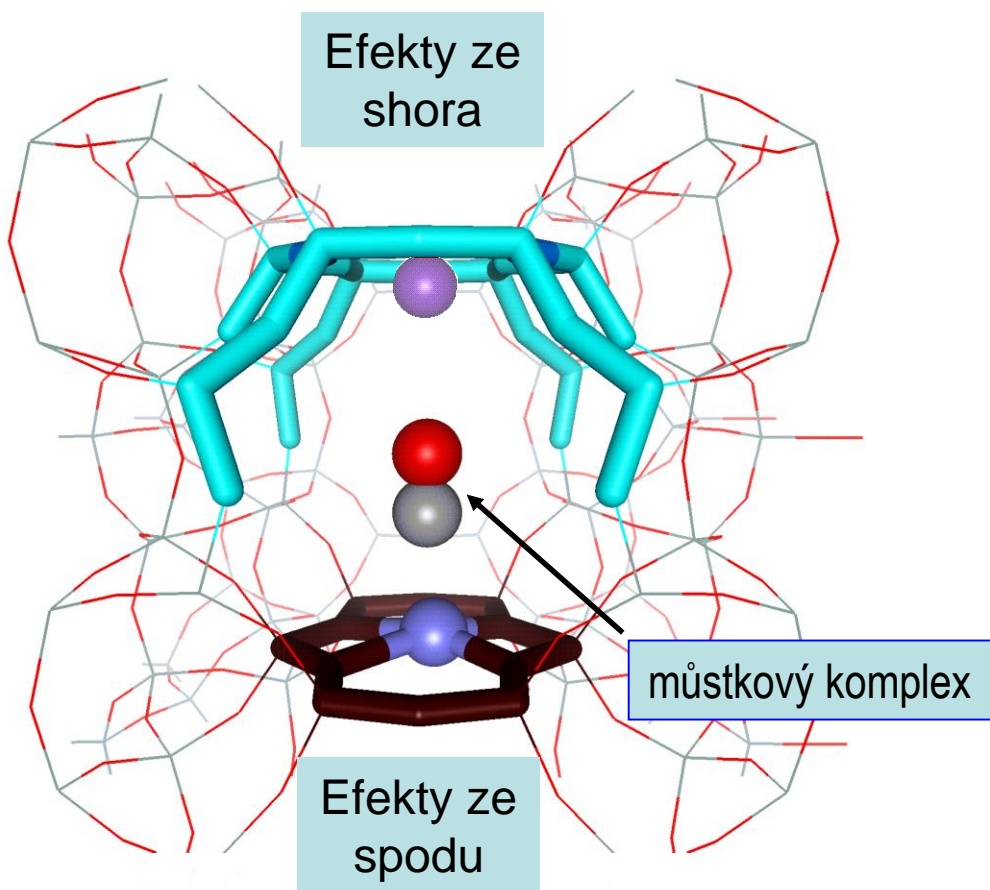
stísněný prostor strukturního póru

Ζεολίτε

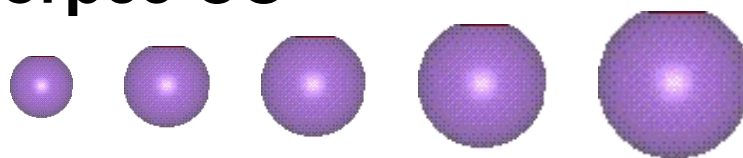
Barrer
1948

1756

Cronstedt



Adsorpce CO



velikost kationtu

vliv efektů ze shora

vliv efektů ze spodu

stísněný prostor strukturního póru

Nachtigallova et al. PCCP, 2006, 4849

Ζεολίτε

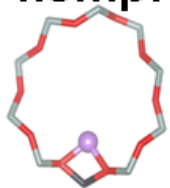
Barrer
1948

1756

Cronstedt

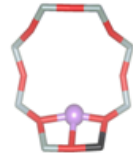
Li/CO komplexy

Improving Li^+ coordination with the framework
Decreasing CO stretching frequency



R10
MFI: 12

2193



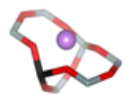
R8
FER: 12

2188



R5
MFI: M5, Z5
FER: M5

2187



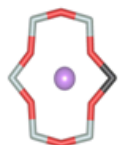
R7
MFI: M7
FER: M7

2184



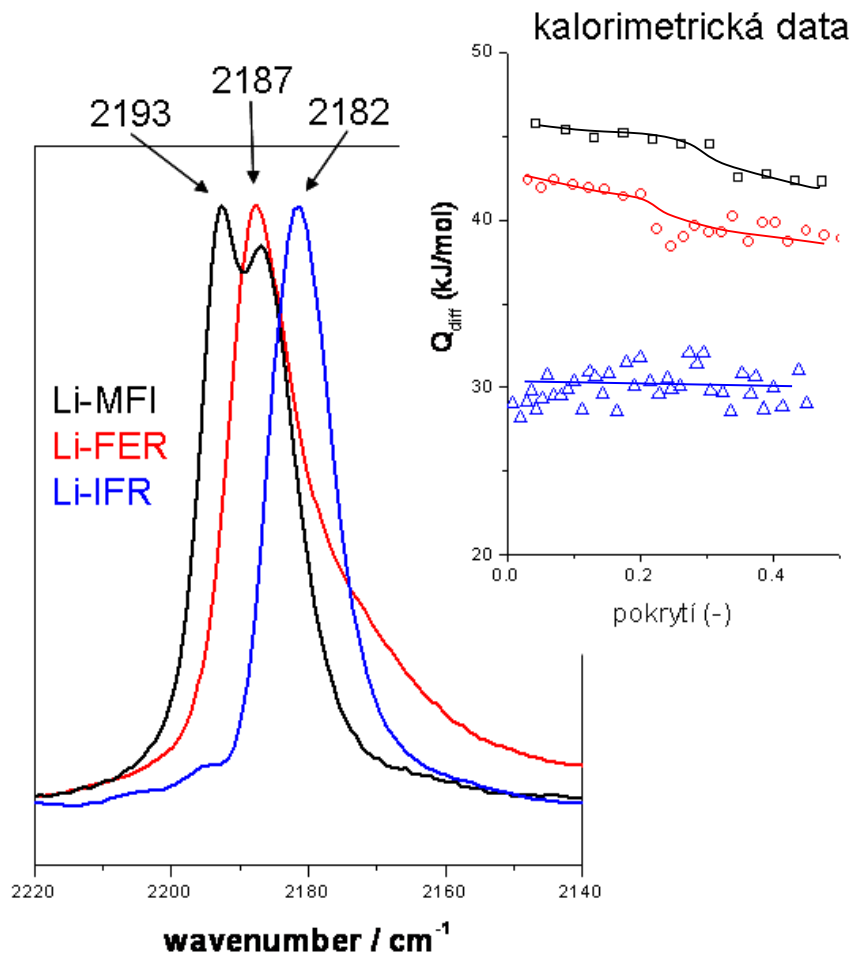
R6^c
MFI: M6^c, Z6^c
FER: P6^c

2180



R6^s
MFI: M6, Z6
FER: P6

2175



Ζεολίτε

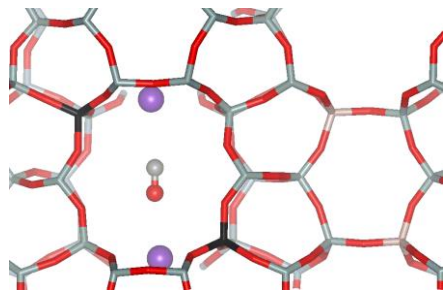
Barrer
1948

1756

Cronstedt



CO/M⁺ - FER



Li-FER

Na-FER

K-FER

2200 2175 2150 2125 2100

Wavenumber (cm⁻¹)

DCS

DCS

K-MFI

Na-FER

Rb-MFI

Si/Al
11.5
25.0
75.0

Si/Al
8.6
27.5

Si/Al
30.0

2200 2175 2150 2125 2100

2200 2175 2150 2125 2100

2200 2175 2150 2125 2100

wavenumber / cm⁻¹

Ζεολίτε

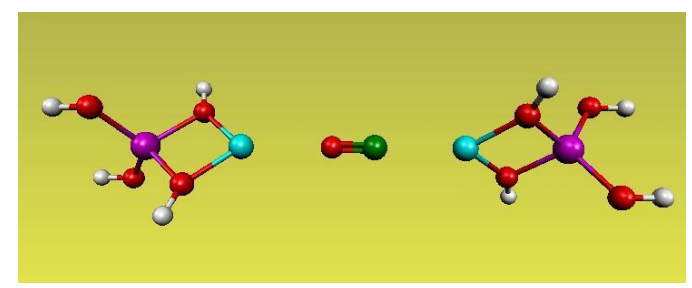
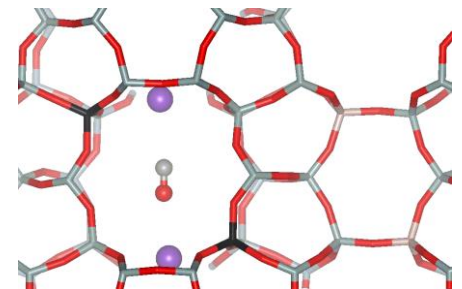
Barrer
1948

1756

Cronstedt



CO/M⁺ - FER



Li-FER

Na-FER

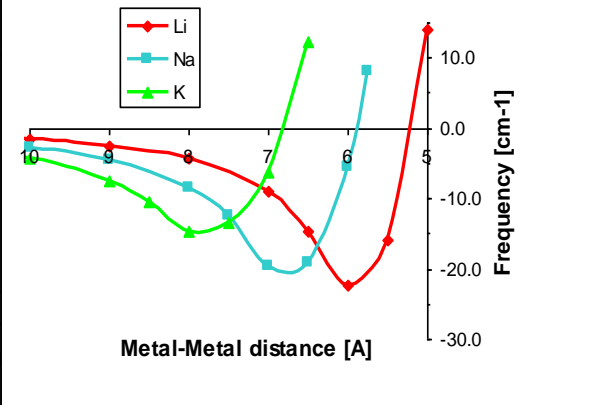
K-FER

DCS

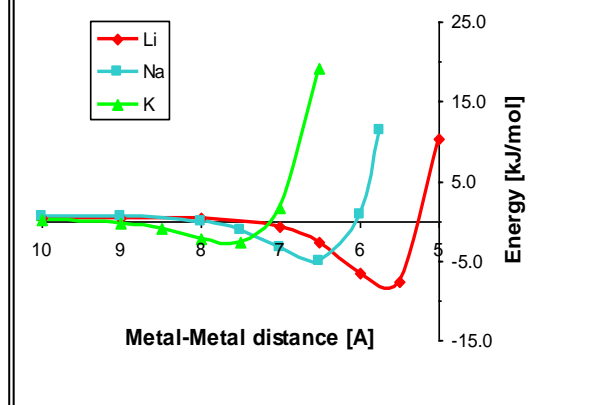
DCS

Wavenumber (cm⁻¹)

CO frequency change due to the interaction with second cation



Energy stabilization due to the second cation



Ζεολίτε

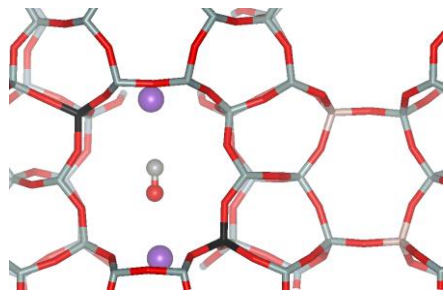
Barrer
1948

1756

Cronstedt



CO/M⁺ - FER



Li-FER

Na-FER

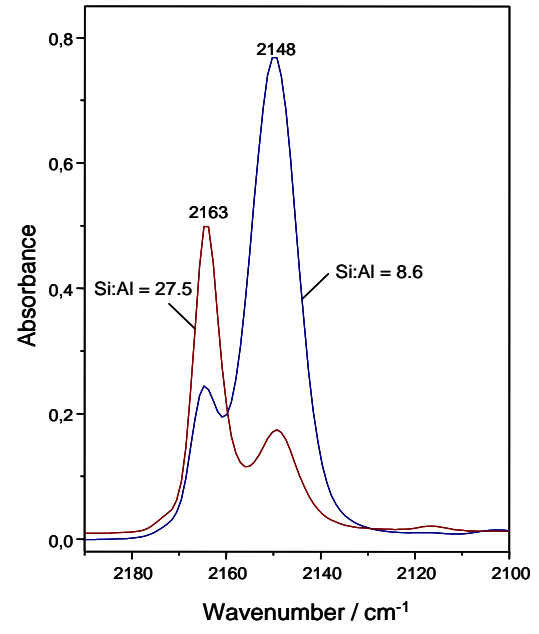
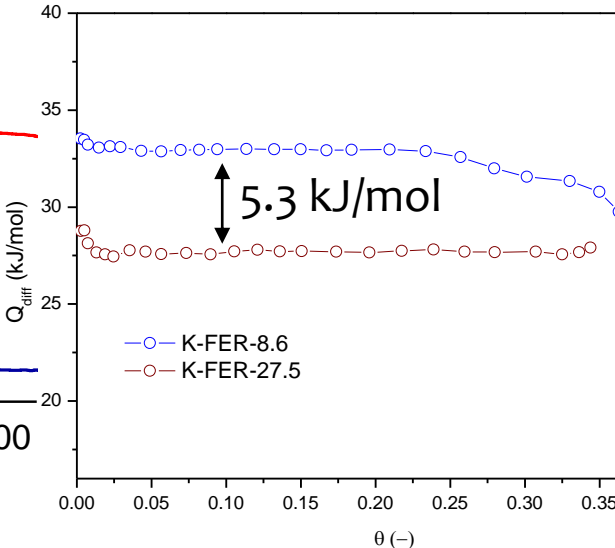
K-FER

DCS

DCS

Wavenumber (cm⁻¹)

Wavenumber (cm⁻¹)

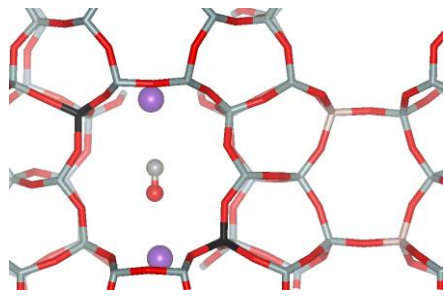
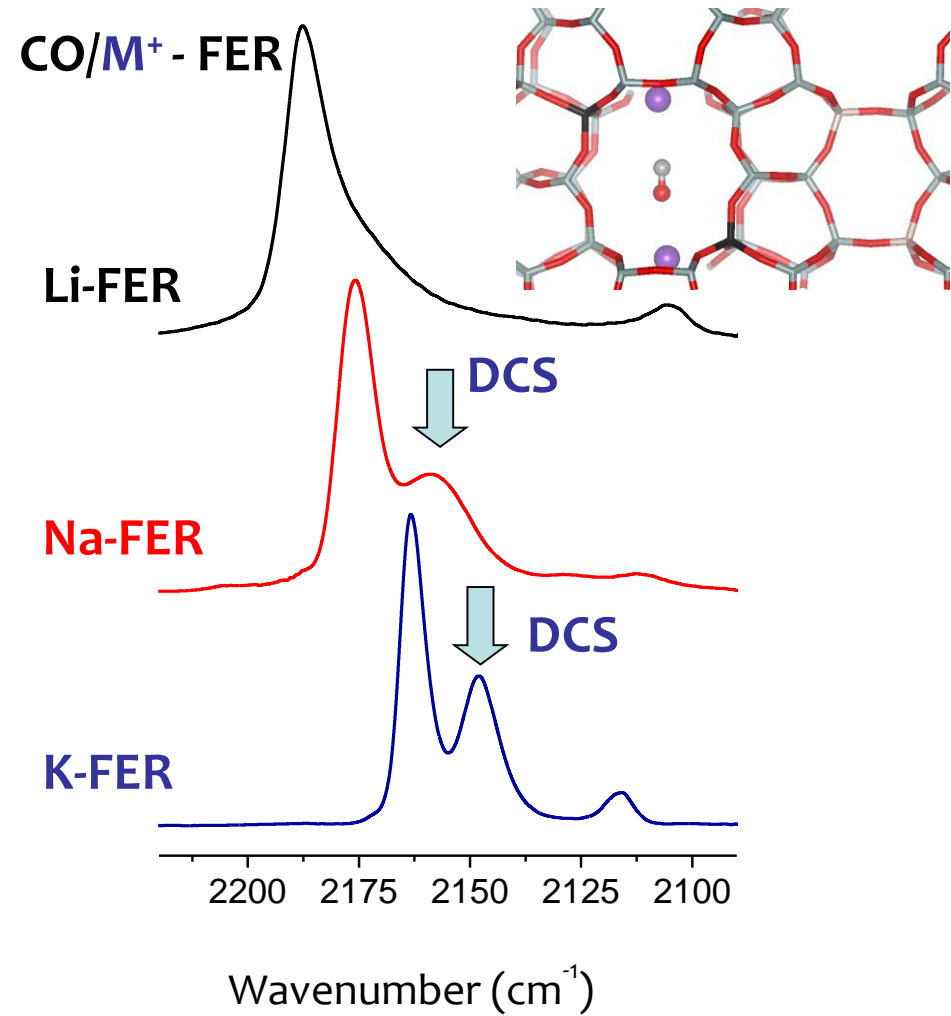


Ζεολίτε

Barrer
1948

1756

Cronstedt



Dual sites character:

1. Cations at right distance from each other

cation	Li ⁺	Na ⁺	K ⁺
distance/Å	5.5	6.5 - 7	7.5 - 8

2. The population of dual sites depends on:

cation size
Si/Al ratio
zeolite topology

3. Stability of bridged complex is higher than stability of single complex about 3 - 5 kJ/mol

4. Bridged complexes exist also for other zeolites and combination of cations (het. dual sites)

Ζεολιτε

Barrer
1948

1756

Cronstedt



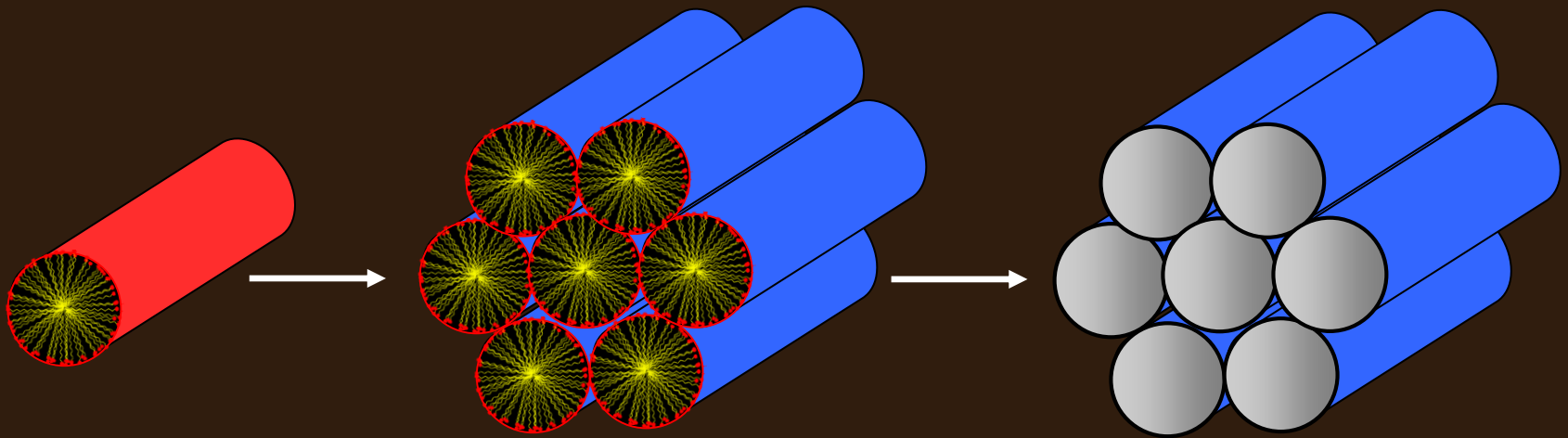
Děkuji za pozornost

Ζεολίτη

Barrer
1948

1756

Cronstedt

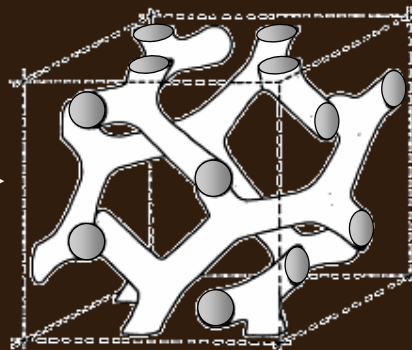
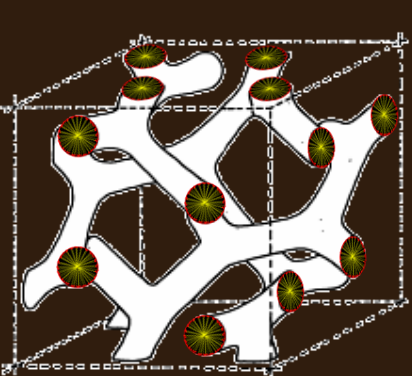
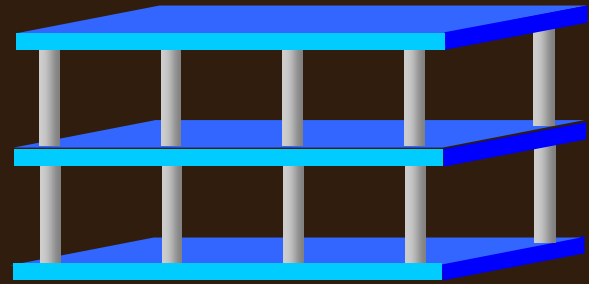
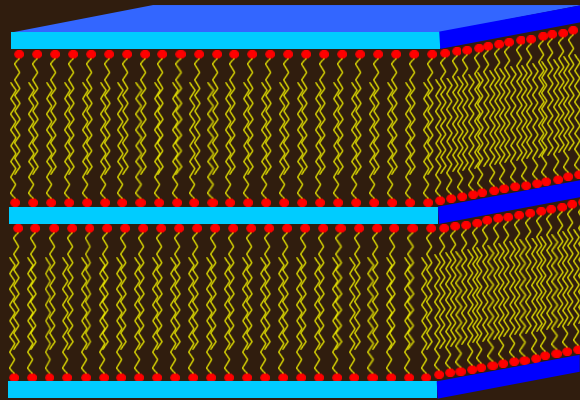
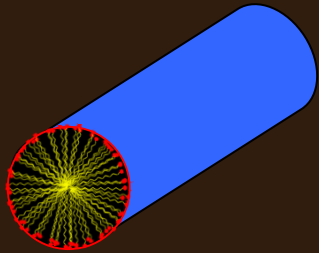


Ζεολίτε

Barrer
1948

1756

Cronstedt



Ζεολίτε

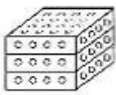
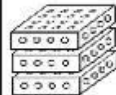
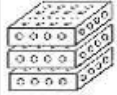
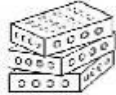
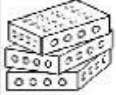


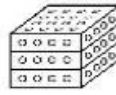
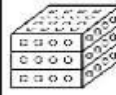
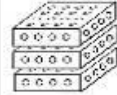
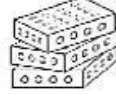
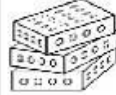

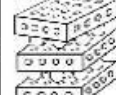
Barrer
1948

1756

Cronstedt

2D zeolitové vrstvy

Conventional 3-D zeolite Frameworks
FAU
MWW
FER
CDO
CAS
NSI
MFI
SOD
RWR
RRO
AFO
Remaining frameworks still without layered form

	Conventional 3-D zeolite	Layered precursor				Delaminated	Swollen/pillared
		Ordered		Dis-ordered			
		Unmodified	Stabilized	Unmodified	Stabilized		
As-synthesized	Synthesis 	Synthesis 	Treatment 	Synthesis 	Treatment 	Synthesis, treatment 	Treatment 
Calcined							
Unit c-cell	c ~25 Å c ~25 Å	c >26 Å c ~25 Å	c >26 Å c >26 Å	c >26 Å c ~25 Å	c >26 Å c >26 Å	c ~25 Å c ~25 Å	c >50 Å c ~50 Å
Material examples	MCM-49 MCM-22	MCM-22P MCM-22	IEZ-MWW EMM-13P EMM-13	EMM-10P EMM-10 ITQ-30	EMM-12P EMM-12	MCM-56; ITQ-2 (treatment)	Swollen MCM-22P, MCM-36

Různé uspořádání vrstev

Roth WJ, *Microporous Mesoporous Mater.* 142 (2011) 32-46