CHARLES UNIVERSITY
CENTRE OF ADVANCED MATERIALS

Faculty of Science
CHARLES UNIVERSITY IN PRAGUE

3D *vs* 2D ZEOLITES

Petr Nachtigall

Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, 128 43 Prague 2, Czech Republic

petr.nachtigall@natur.cuni.cz

CUCAM Kick-off meeting

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS

3D vs 2D Zeolites

2D → 3D transition

- Structures of “ADORable” zeolites
- Layer arrangement and re-organization (SDA, pressure)

2D vs 3D properties

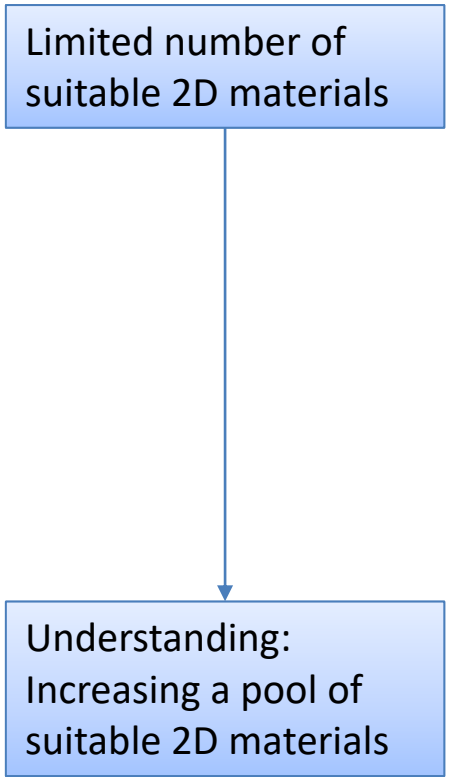
- Lewis acidity
- Brønsted acidity
- Catalysis

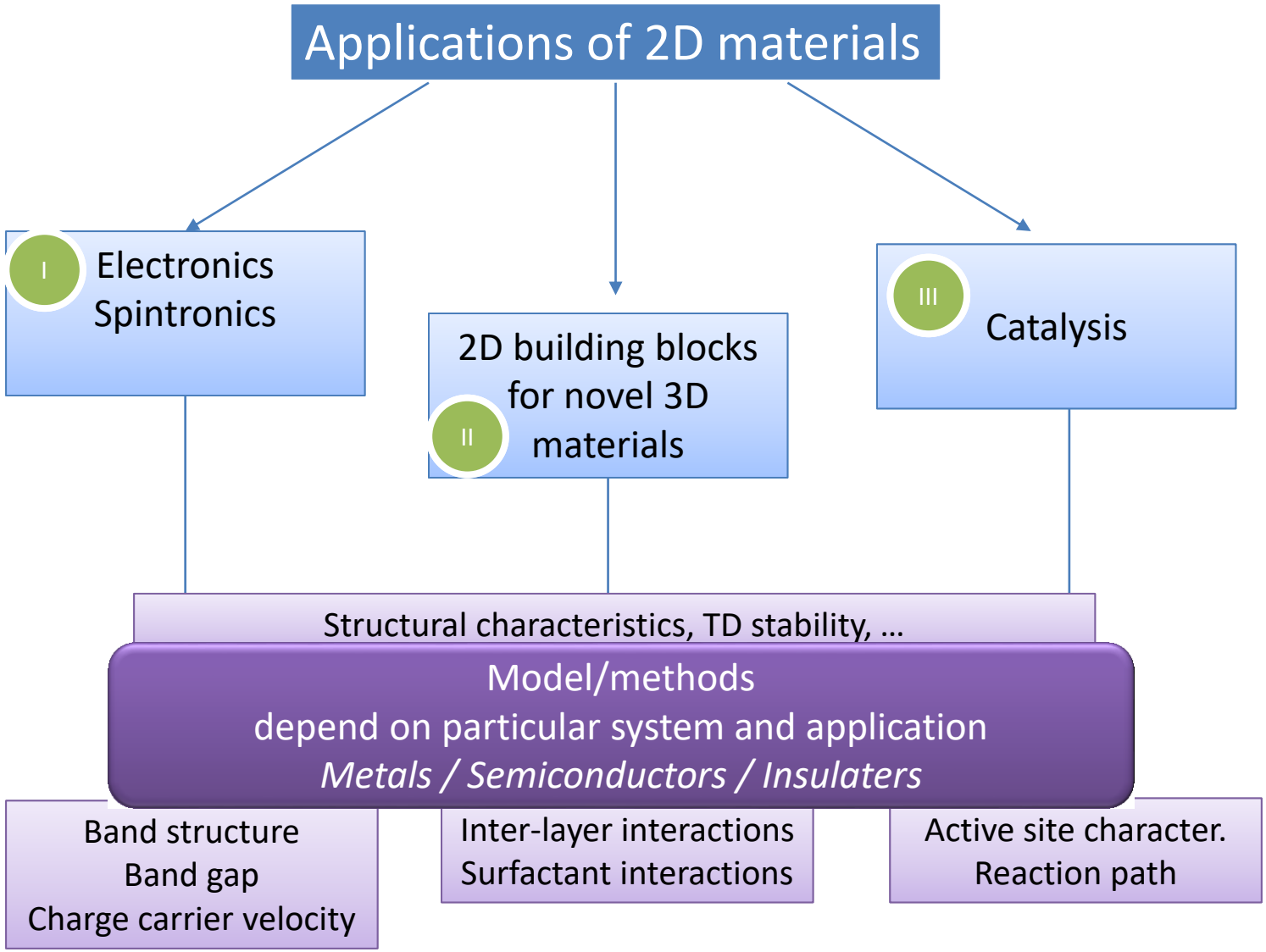
3D → 2D transition

- Exploring the weaknesses of 3D structure
- Zeolite hydrolysis

Hybrid materials

- Interlayer interactions/arrangement
- Spintronics




Applications of 2D materials
I
Electronics
Spintronics
II
2D building blocks for novel 3D materials
III
Catalysis
Structural characteristics, TD stability, …
Model/methods
depend on particular system and application
Metals / Semiconductors / Insulaters
Band structure
Band gap
Charge carrier velocity
Inter-layer interactions
Surfactant interactions
Active site character.
Reaction path

2D materials – a favored area for computational chemistry

(i) Easier to model than surfaces of 3D materials

(ii) Mostly we know the structure (including surfaces) *(At least we believe…)*

More 2D materials modeled than synthesized !

All of them were modeled as free-standing ! *(Experiment will never catch up…)*

2D materials were investigated *in silico* well before they were synthesized.

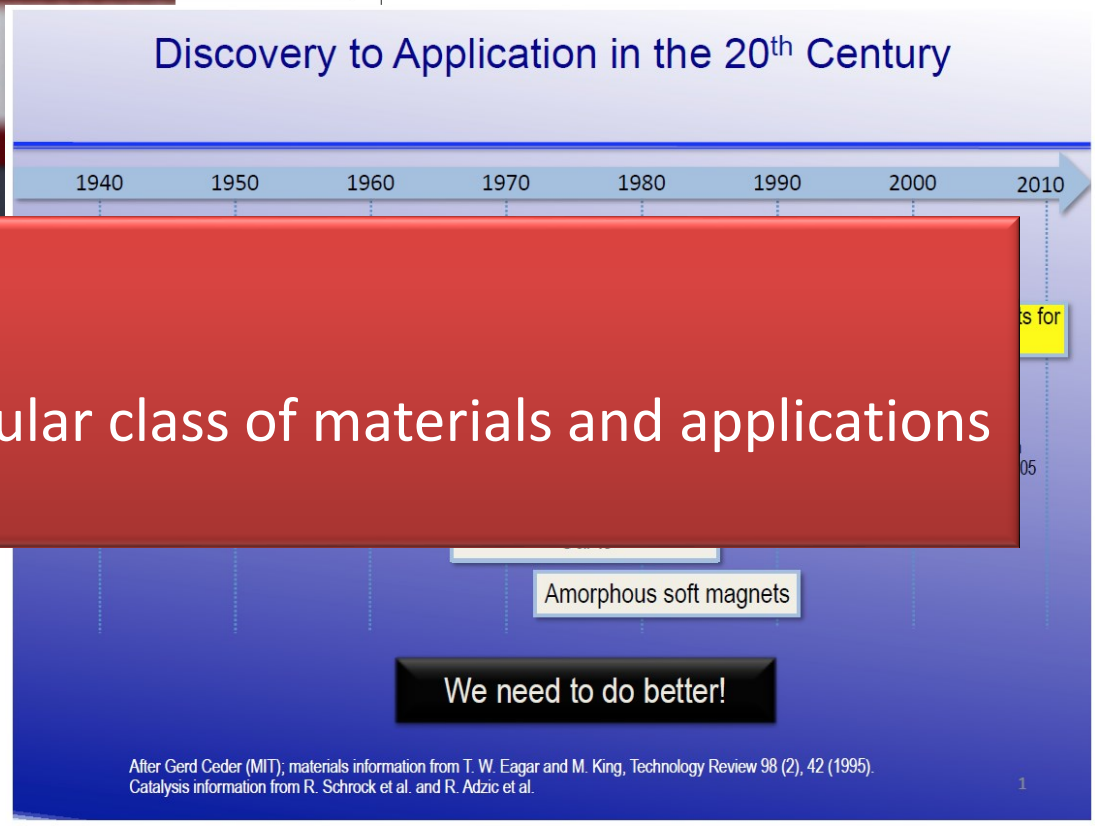
And it is getting worth and worth…

Materials Genome Initiative

"To help businesses discover, develop, and deploy new materials twice as fast, we're launching what we call **the Materials Genome Initiative**.

The invention of silicon circuits and lithium ion batteries made computers and iPods and iPads possible, but it took years to get those technologies from the drawing board to the market place. **We can do it faster.**"

-President Obama (6/11)



Hard to compete !

⇒ Focus on just for particular class of materials and applications

https://www.whitehouse.gov/sites/default/files/docs/microsites/mgi/wadia_mgi_talk.pdf

2D building blocks for novel 3D materials

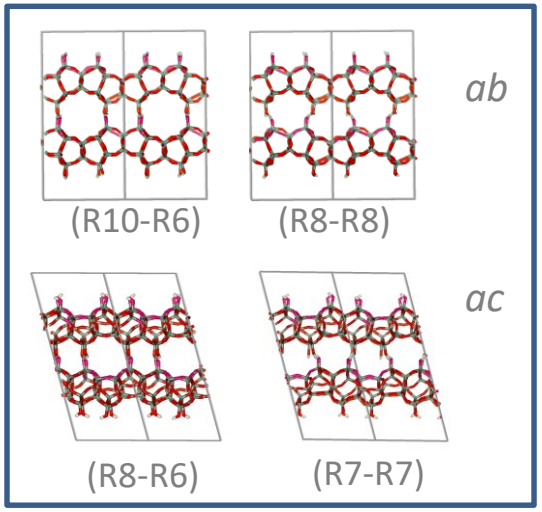
II

In silico ADOR

Interaction and arrangement of IPC-1P layers

Synthesis of zeolites formed by topotactic condensation of IPC-1P

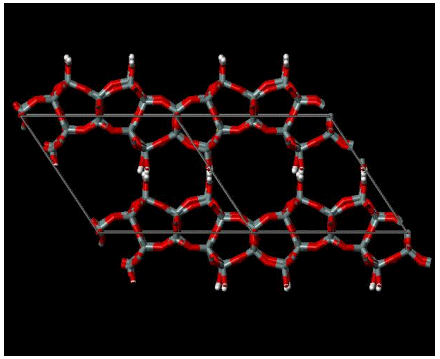
Assembly – Disassembly – Organization - Reassembly



1. **Organization**
   - **number of possible inter-layer arrangements**
     - various inter-layer shifts
     - number of inter-layer H-bonds
     - H-bond orientation
   - **interaction driven by inter-layer H-bonds**
     - ~ 25 kJ mol^{-1}/SiOH
     - 6 H-bonds/SiOH quadruplet

Energetically the most stable arrangment

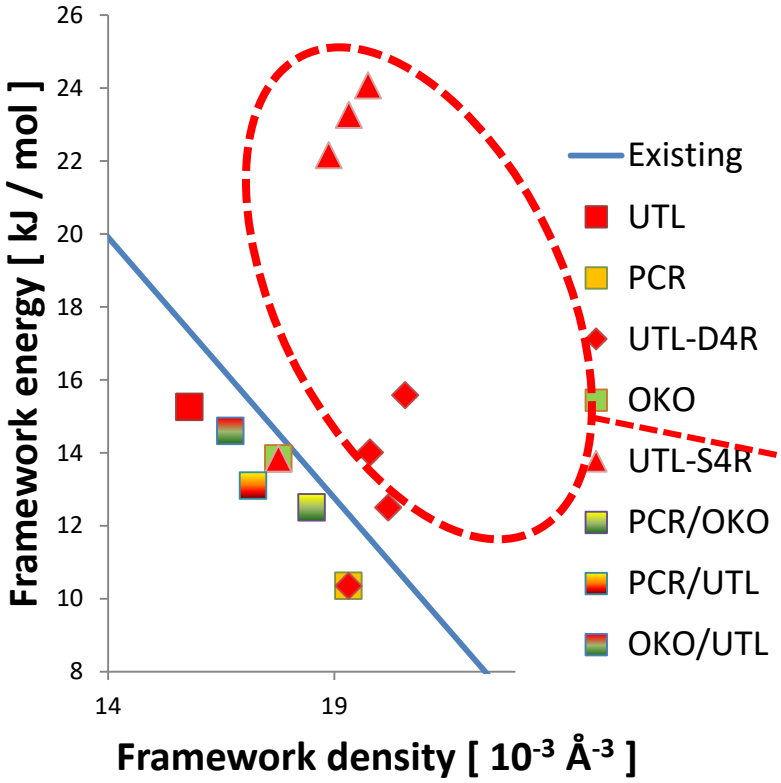
Without lateral shift – more than 2.5 kJ mol^{-1}/SiOH below other arrangements

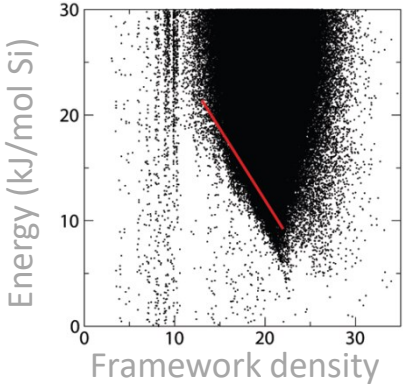


No shift

4 unique arrangments
8 “hypothetical” new zeolites can be obtained
+ combinations

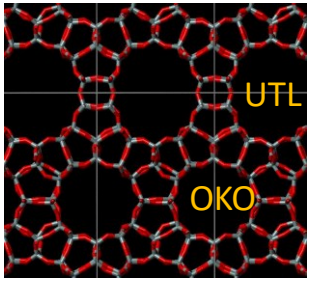
In silico ADOR

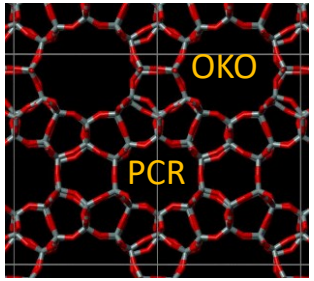


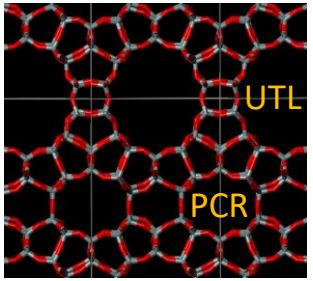


Deem at al.
J. Phys. Chem. C 113 (2009) 21353

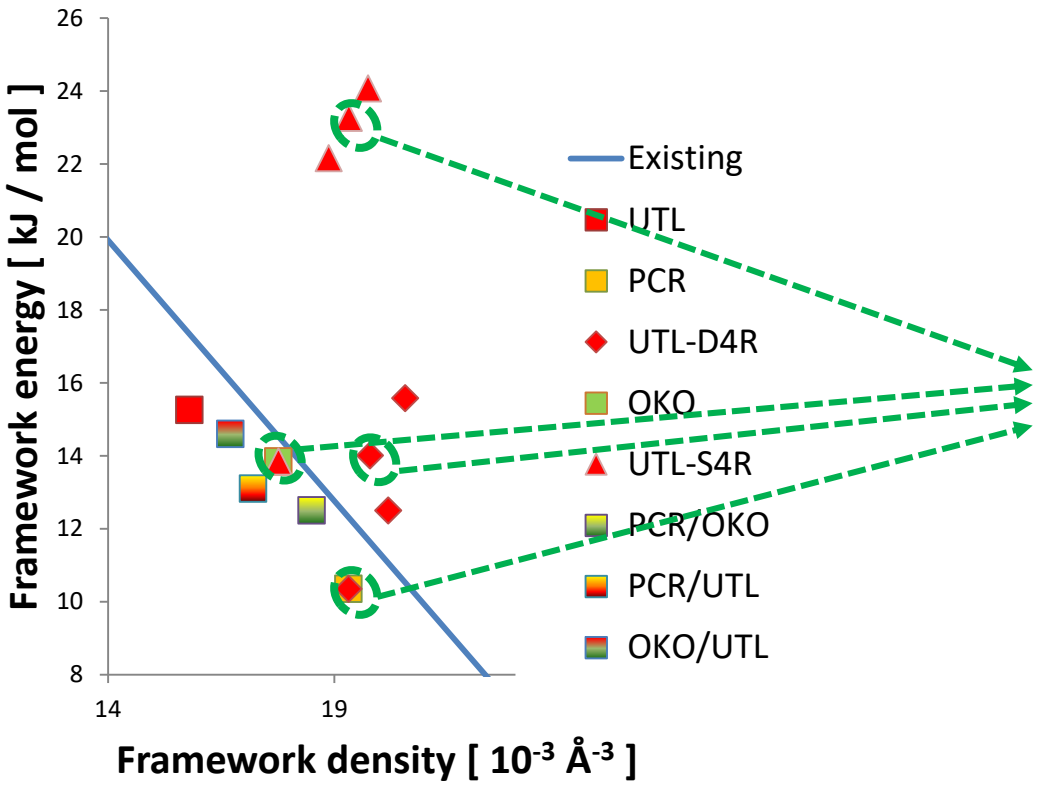
Unfeasible zeolites







In silico ADOR



Experimentally achieved !

- IPC-2
- IPC-4
- IPC-9
- IPC-10

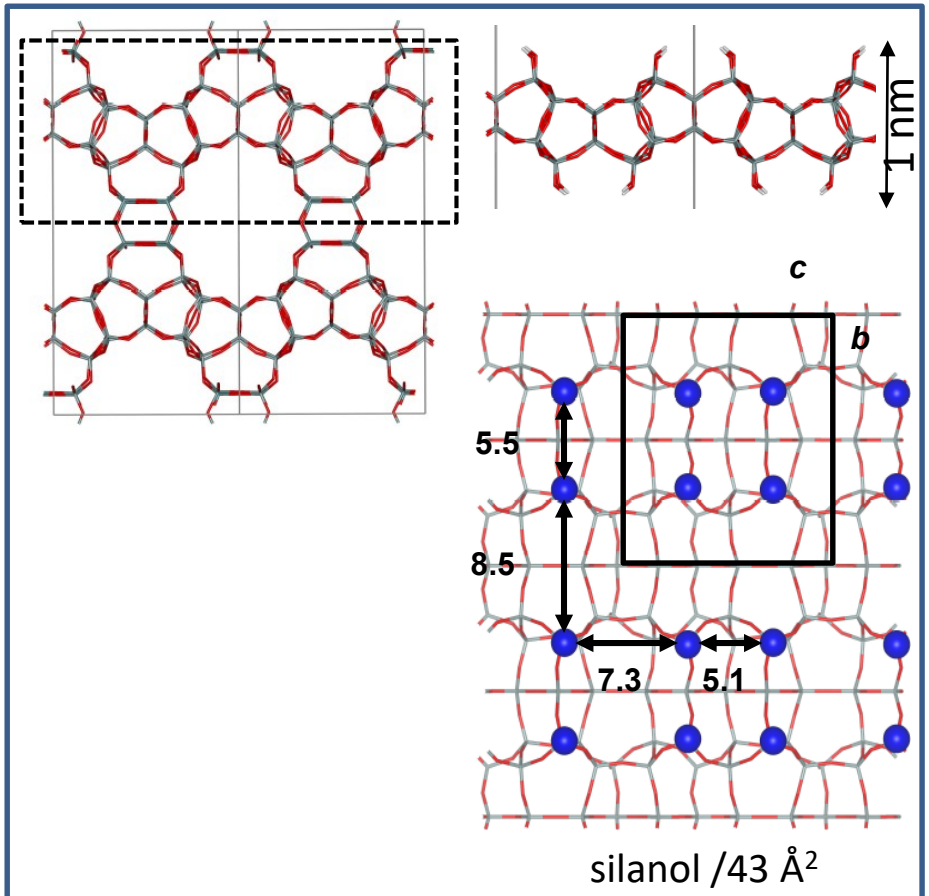
Can all 8 possible new zeolites be obtained?

Simple answer – NO – they are unfeasible.

Better answer – more than 4 should

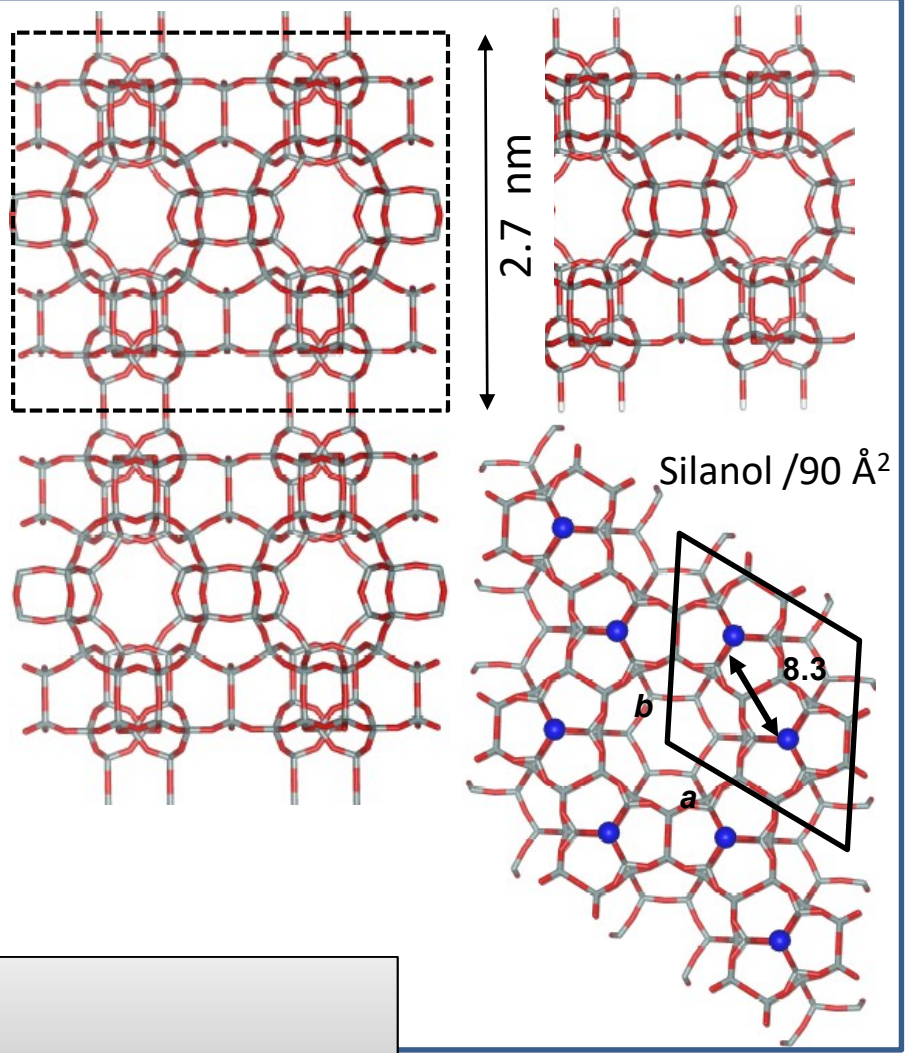
IPC-1P zeolite family

UTL (IPC-1P)



silanol /43 Å^2

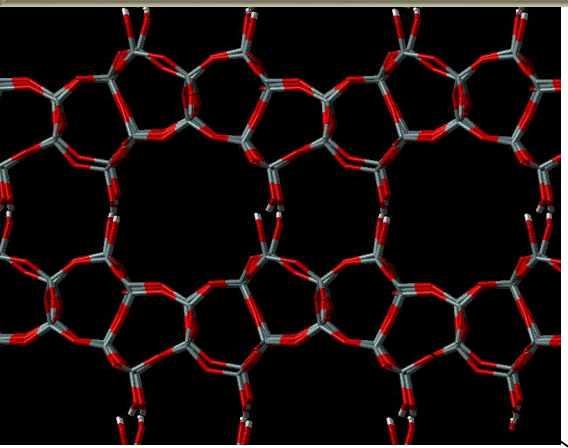
MCM-22 (MCM-22P/MWW)



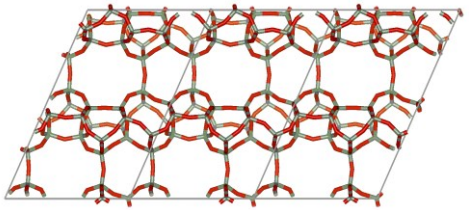
Differences:

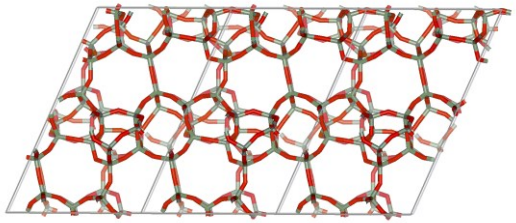
- Layer thickness
- Silanol concentration and arrangement

IPC-1P zeolite family

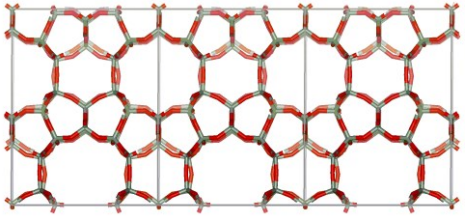


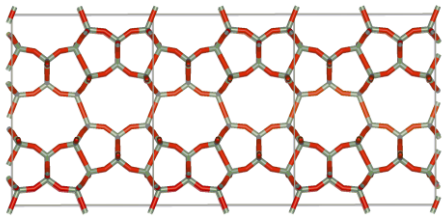
ac plane projection

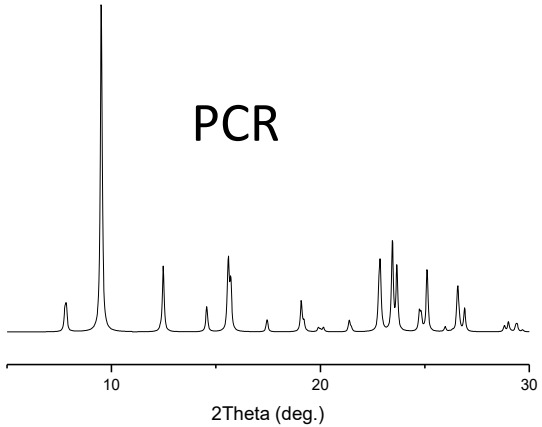


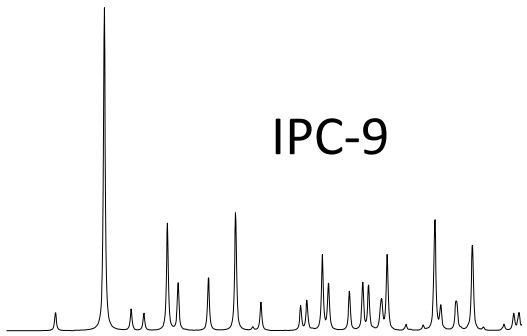


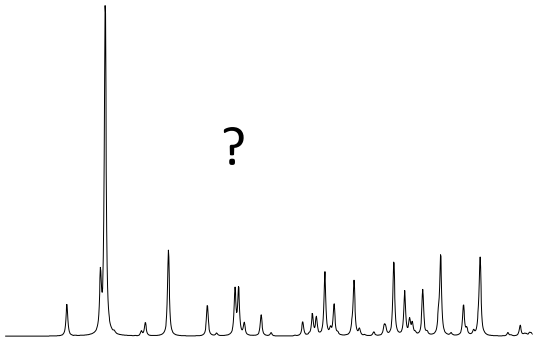
ab plane projection

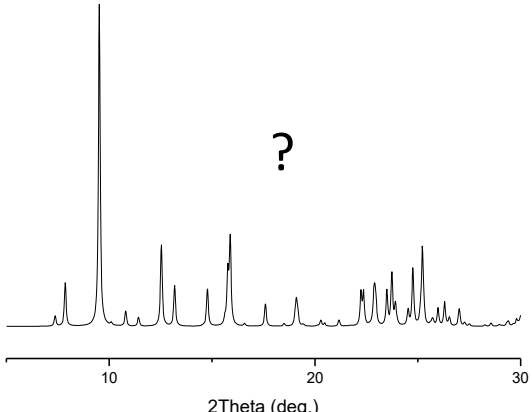












Roth et al, Nature Chemistry 5 (2013) 628-633

IPC-1P zeolite family

Organization step crucial

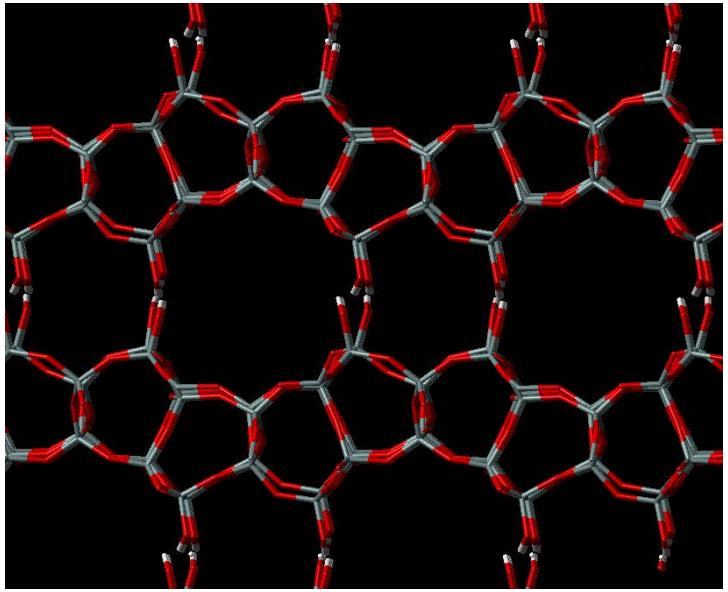
- various inter-layer shift – different H-bonding between layers

- PCR – IPC-1P layers stay in the same arrangement as in UTL
  - the most stable arrangement
    - 2.5 kJ/mol / SiOH without SDA

NEW ZEOLITES → SDA

- octylamine – $E_{diff} > 7$ kJ/mol / SiOH
- ethylendiamine – $E_{diff} < 1$ kJ/mol / SiOH

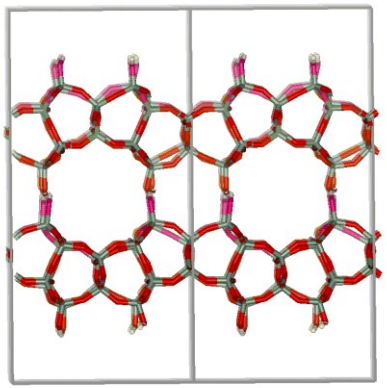
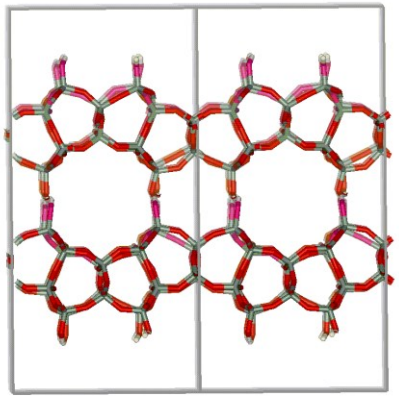
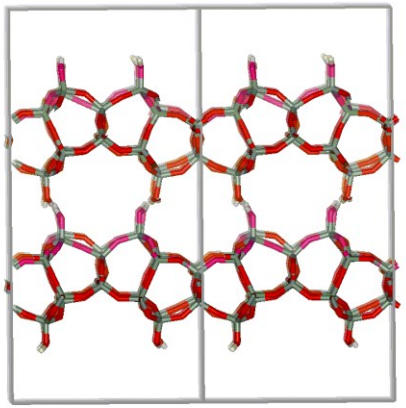
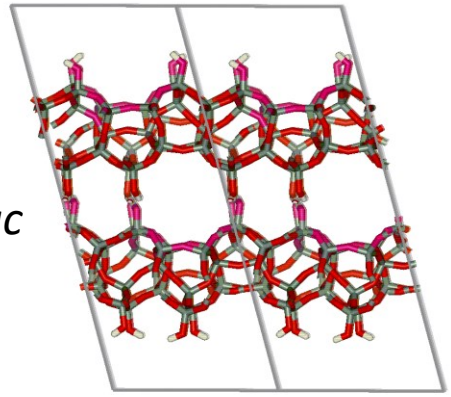
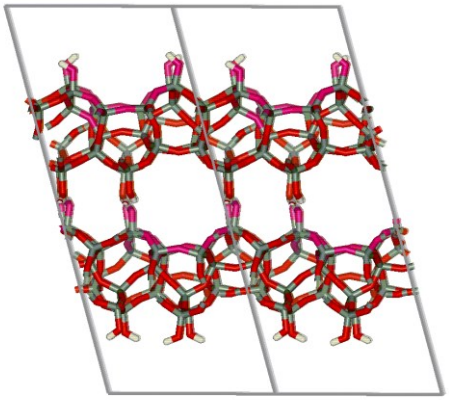
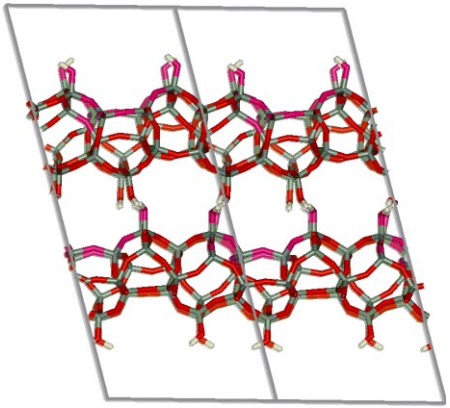
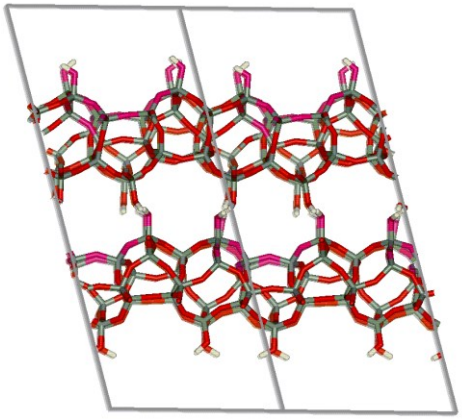
- other SDA?
  - Experiment: Choline, DEDMA



Grajciar et al, Catalysis Today 204 (2013) 15-21

IPC-1P zeolite family

Energy of periodic system:

0 kJ/mol	9 kJ/mol	25 kJ/mol	--
PCR-precursor		IPC-9-precursor	IPC-1P structure not found
ab 			
(R10-R6)	(R8-R8)	(R10-R6)	(R8-R8)
ac 			
(R8-R6)	(R8-R6)	(R7-R7)	(R7-R7)

MODELS

Single IPC-1P layer:

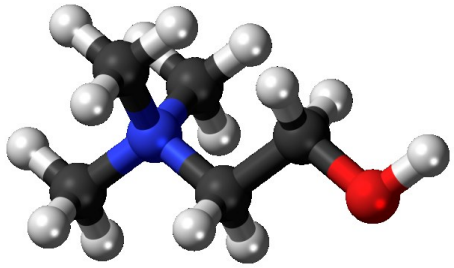
- non-interacting layers separated by vacuum (along an *a* vector)

- UC composition: *a*=30.0 Å, *b*=14.0 Å, *c*=12.4 Å, α=γ=90 °, β=105.2 °
- UC parameters: $Si_{30}O_{64}H_8$ (+ SDA)

Interacting IPC-1P layers:

- periodic system of interacting layers forming an infinite stack

- UC composition: $Si_{30}O_{64}H_8$
- UC parameters optimized in each caluclation



IPC-1P/SDA:

- choline cation $(CH_3)_3N\text{-}CH_2CH_2OH^+$ chosen as a representative SDA
- SDA charge ballanced by formation of silanolate groups on the surface
- water not considered

IPC-1P/choline interaction

ICP-1P surface charged to compensate for choline cation charge

- silanolate groups instead of some surface silanols
- experimental conditions (high pH)support the silanolate formation

$$\text{CholineOH} + \text{IPC-1P} \rightarrow \text{choline(+)/IPC-1P(-) complex} + H_2O$$

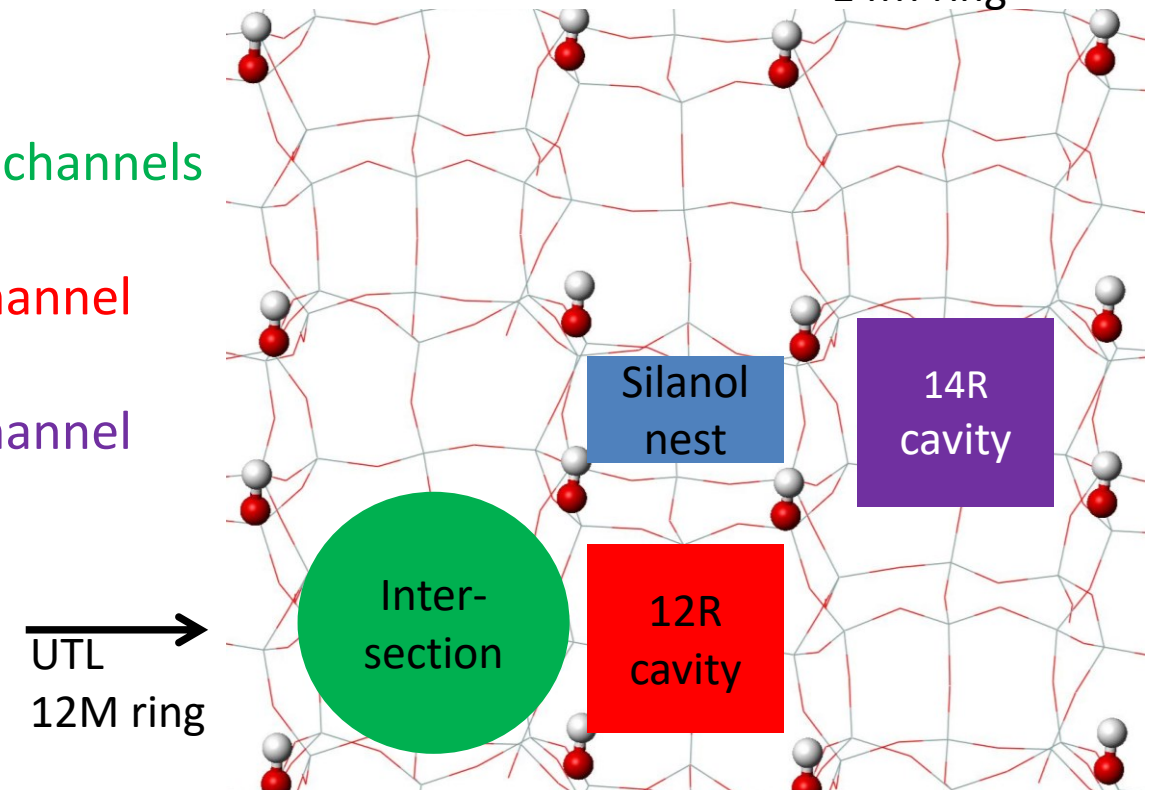
Preferential positions of choline on the IPC-1P surface:

Possible positions:

1) Intersection of former UTL channels

2) Cavity in the former 12R channel

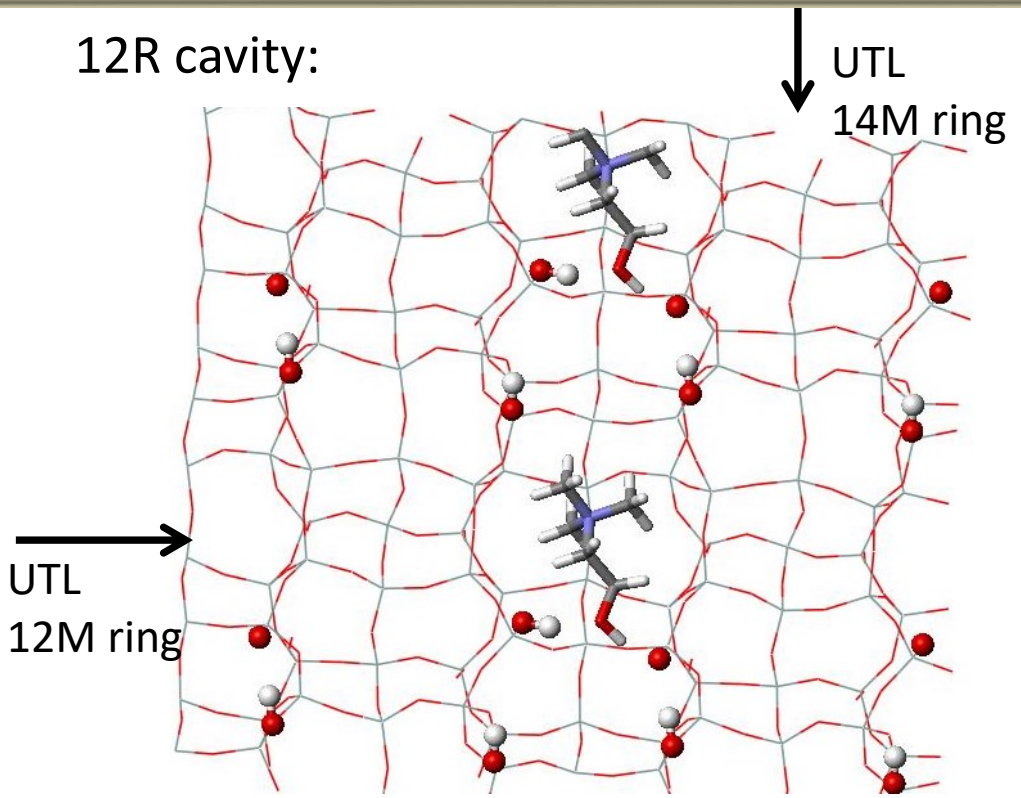
3) Cavity in the former 14R channel



IPC-1P/choline interaction

	DFT Erel / kJ/mol	FF Erel / kJ/mol
Intersection: 14M ring direction	0.0	0.0
Intersection: 12M ring direction	8.4	2.9
12R cavity	-30.4	9.1
14R cavity	-23.4	17.5

12R cavity:



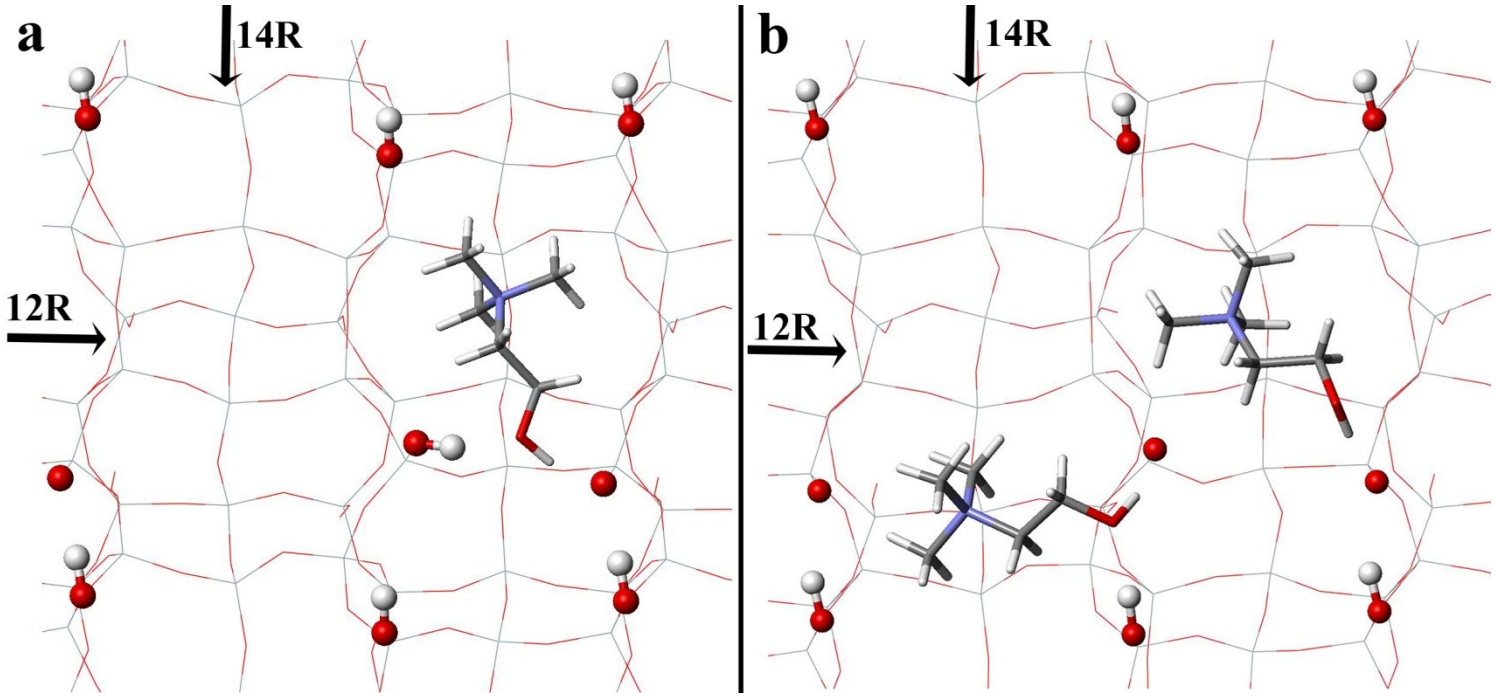
Force Field is now not an option!

- problem probably due to the presence of silanolate groups

- <u>New FF has to be developed</u> for SDA interaction with zeolite surface

IPC-1P/choline interaction

The interaction energy of the second choline increased
due to the higher ionicity of the layer



E_{int}(1st choline) = 168 kJ mol^{-1}

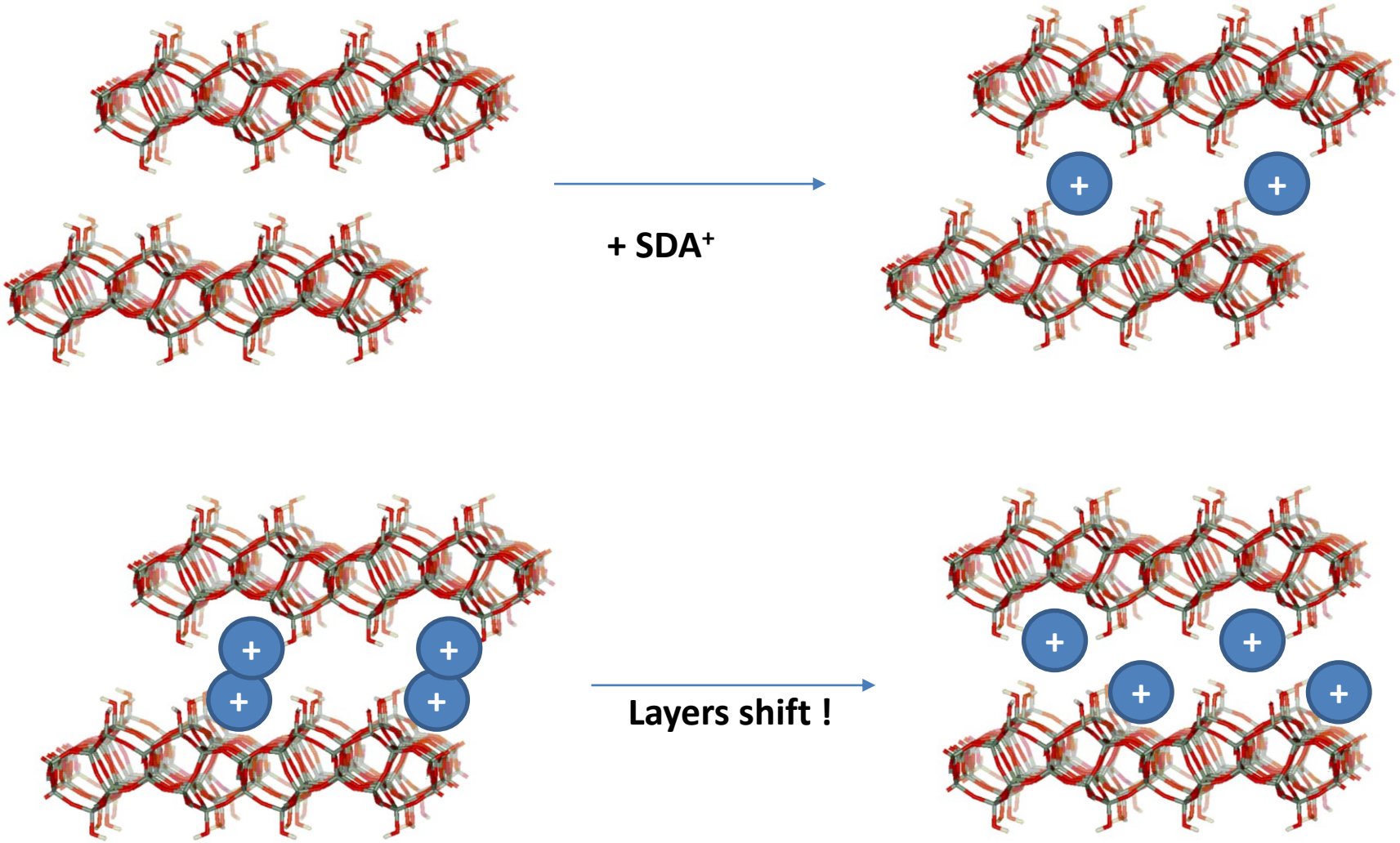
E_{int}(2nd choline) = 201 kJ mol^{-1}

Very strong preference for the channel interior sites

-> Approximate model of IPC-1P/SDA complex as a starting structure

- layers with SDA in preferential sites
- no water

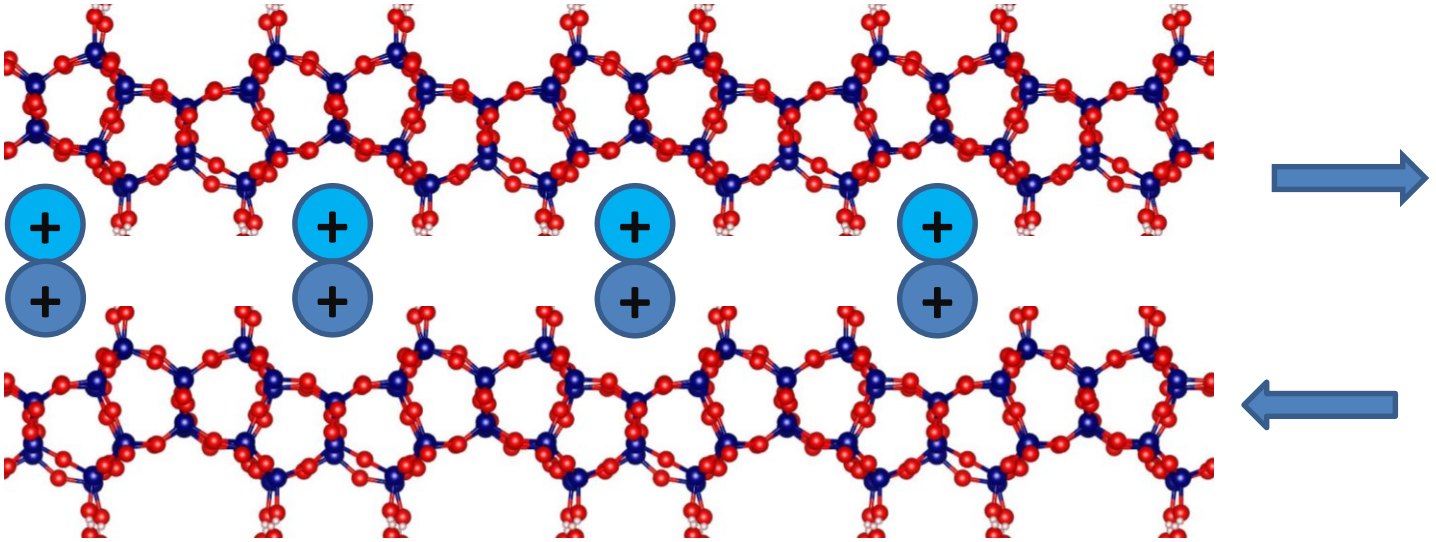
ADOR



Choline as SDA – 1 choline / silanol nest

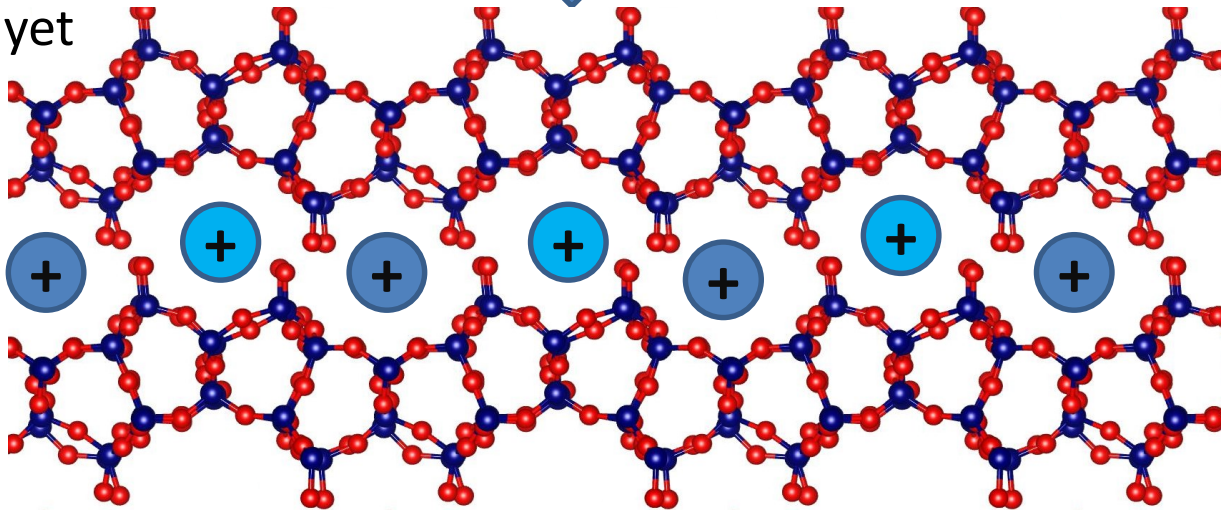
IPC-1P structure changes after adsorption of choline – electrostatic repulsion

IPC-1P (C2/m)
- PCR precursor



E_{rel}= 103 kJ/mol

IPC-1P (Pm)
- Not synthetized yet



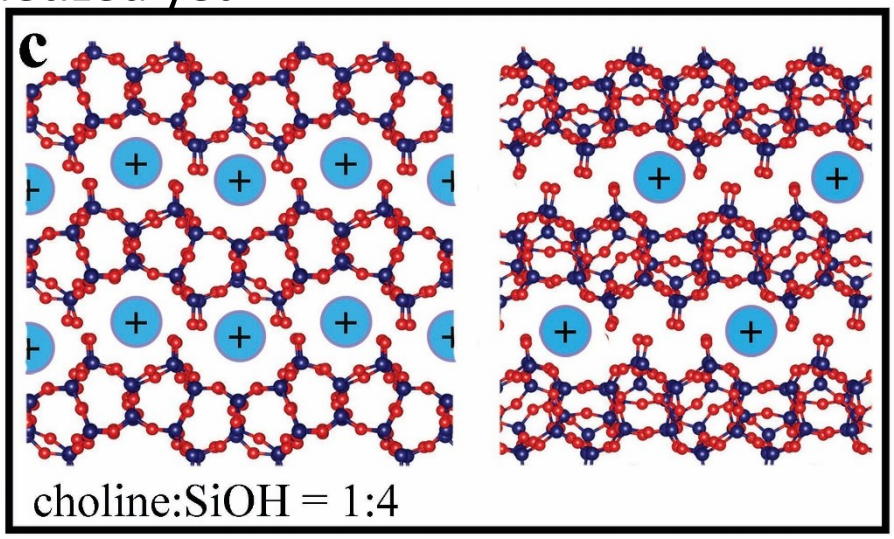
E_{rel}= 0 kJ/mol

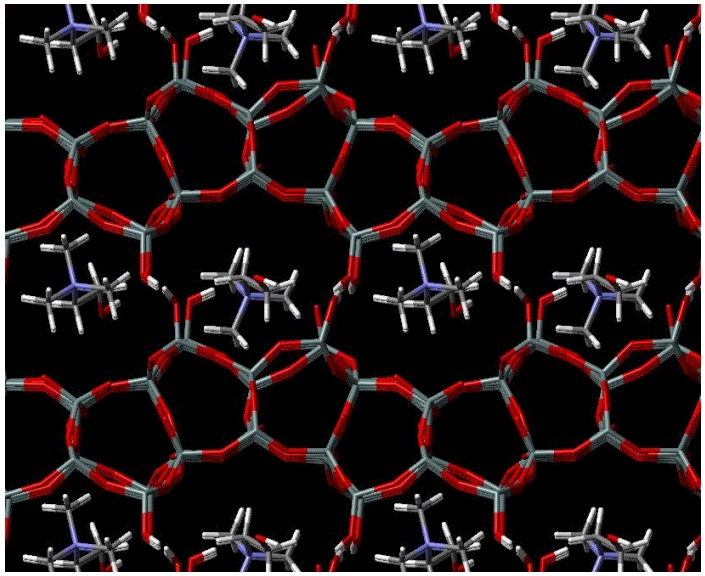
Choline as SDA – 2 cholines / silanol nest

IPC-1P (Pm)

- Not synthetized yet

E_{rel}= 82 kJ/mol



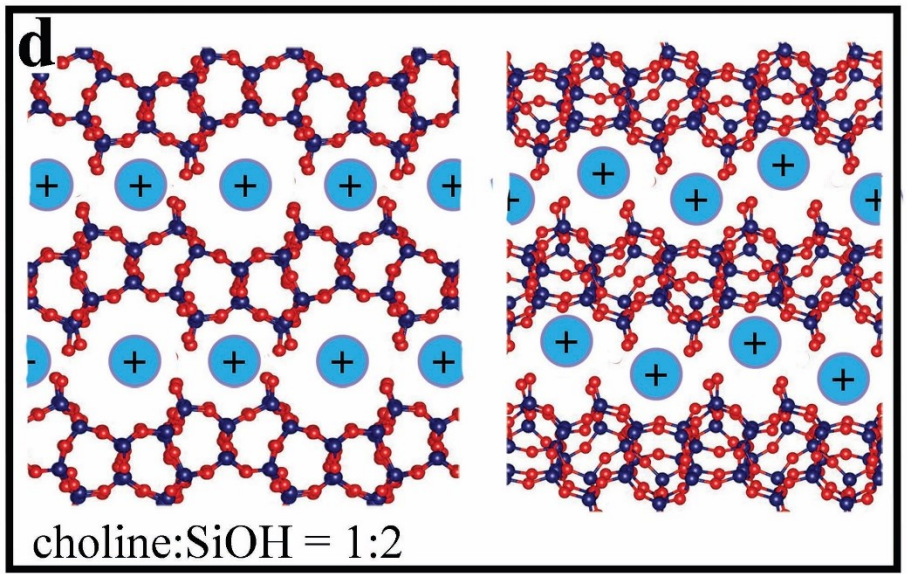


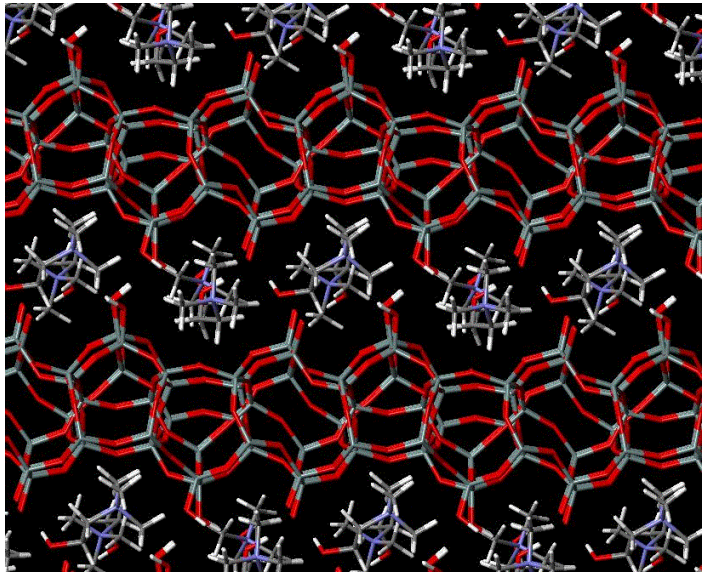
+ choline$^+$

IPC-1P (P1)

- IPC-9 zeolite

E_{rel}= 0 kJ/mol





Choline as SDA

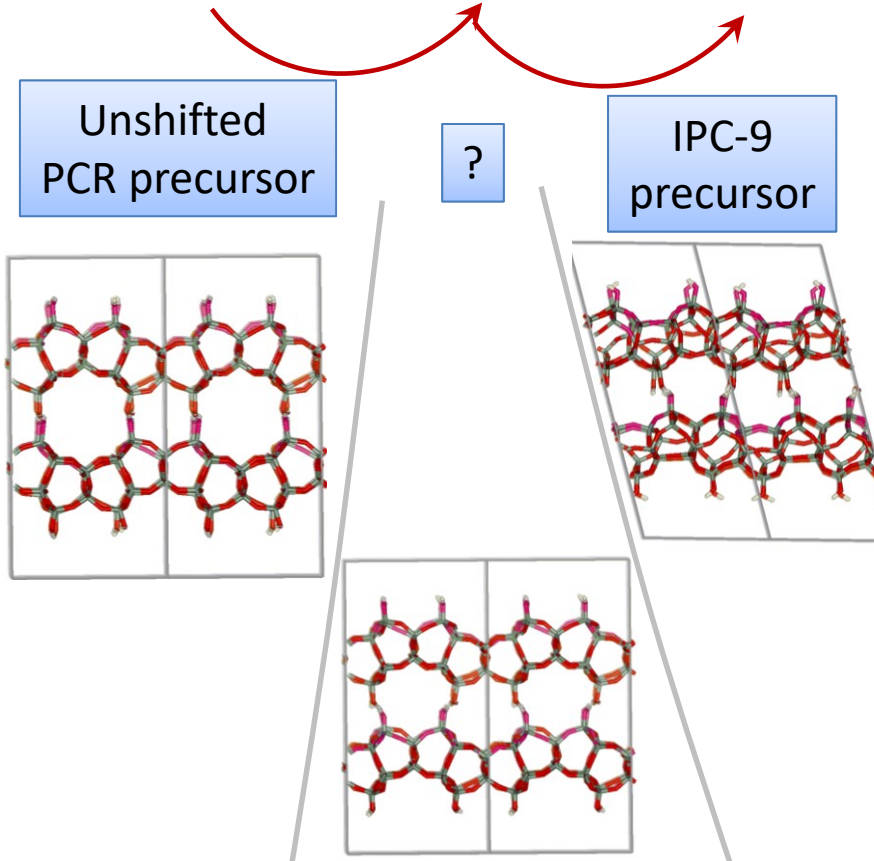
Structure		Shift along *b*	Shift along *c*	E_{rel}[b]		
Notation	Corresponding zeolite[a]			0 chol$^+$	2 chol$^+$	4 chol$^+$
IPC-1P-10R/8R	-D4R(C2/m)	no	no	**0.0**	103.0	164.7
IPC-1P-10R/7R	-D4R(P1)	no	yes	24.8	21.5	**0.0**
IPC-1P-8R/8R	-D4R(Pm)	yes	no	8.7	**0.0**	82.5
IPC-1P-8R/7R	-D4R(Pm')	yes	yes		58.3	

Original IPC-1P structure strongly destabilized

10R/7R IPC-1P ≈IPC-9 precursor formed at high SDA coverage

8R/8R IPC-1P stable at low coverage

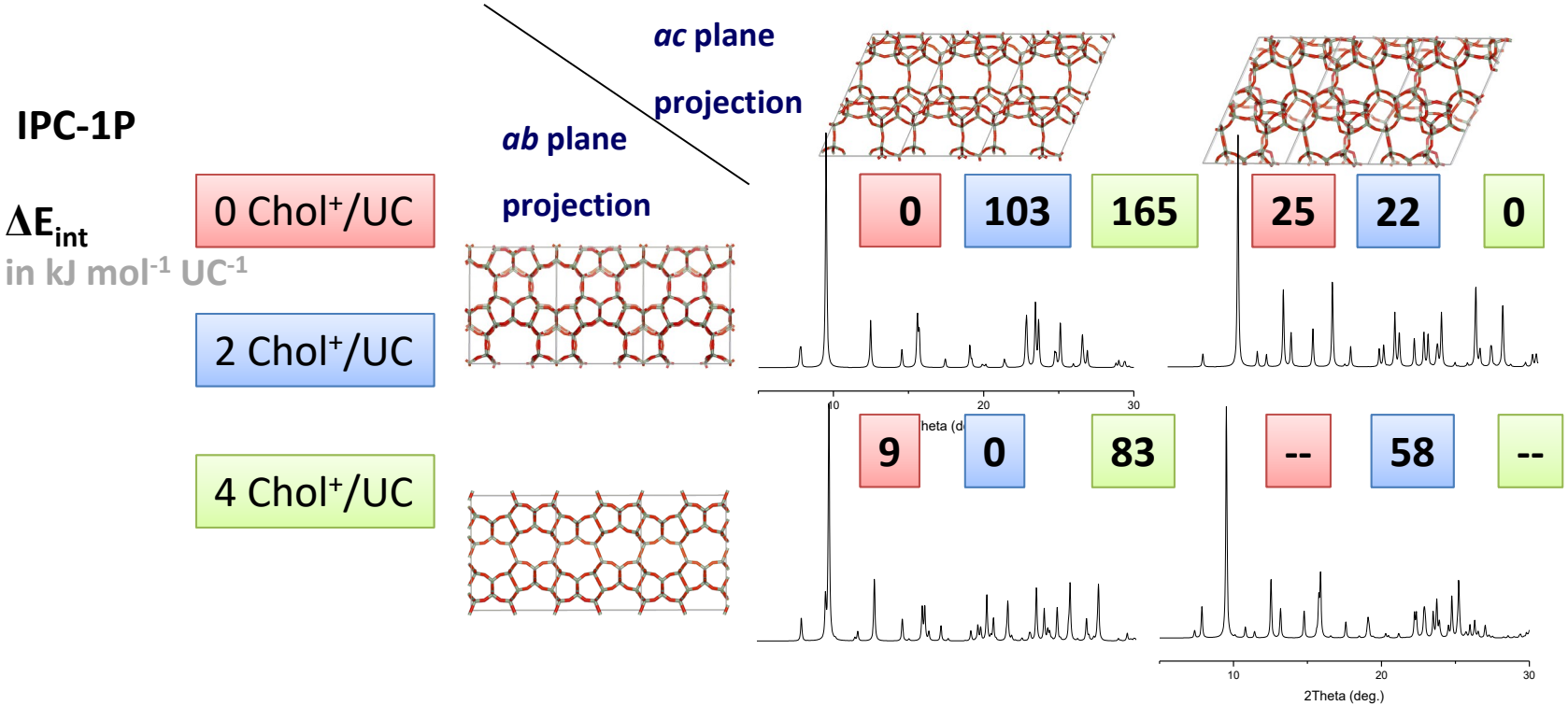
– <u>can it be obtained experimentally?</u>



Mazur et al, Nature Chemistry (2016)

Inter-layer interactions

1) Choline cation has a strong preference for the particular adsorption sites on the IPC-1P
2) Even low loading of SDA causes a strong destabilization of original unshifted arrangement (PCR-precursor) of IPC-1P
   - Higher loadings lead to the shifted



Inter-layer interactions under high pressure

IPC-1P Layers

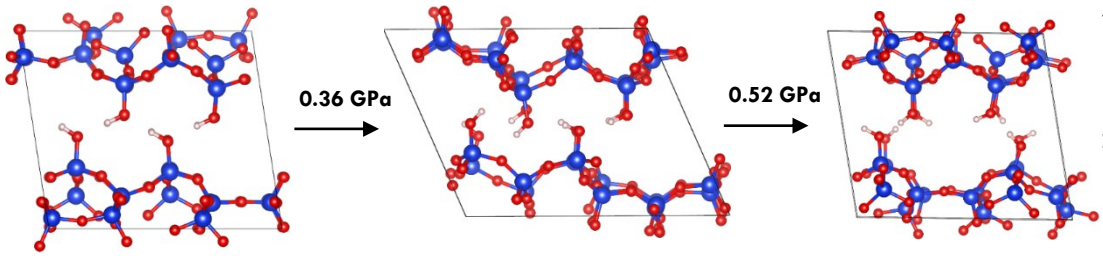
Notation	3D zeolite UTL-	Shift along b	Shift along c
IPC-1P-10R/8R	-D4R (C2/m)	no	no
IPC-1P-10R/7R	-D4R (P1)	no	yes
IPC-1P-8R/8R	-D4R (Pm)	yes	no
IPC-1P-8R/7R	-D4R(Pm')	yes	yes

M. Mazur *et al.* Nature Chem. 2016
M. Trachta *et al.* Catal. Today 2015
M. Trachta *et al.* Chem. Phys. Chem. 2014
L. Grajciar *et al.* Catal. Today 2013.

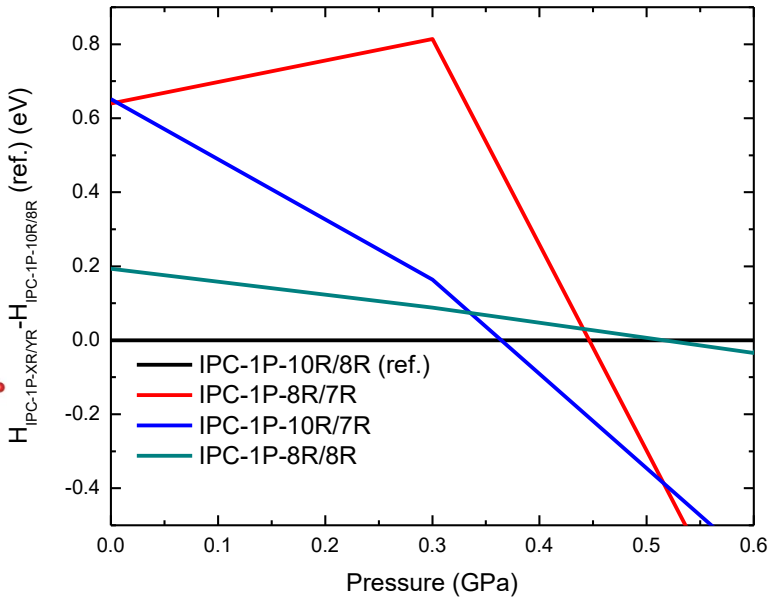
VASP code
PBE

Hydrostatic conditions

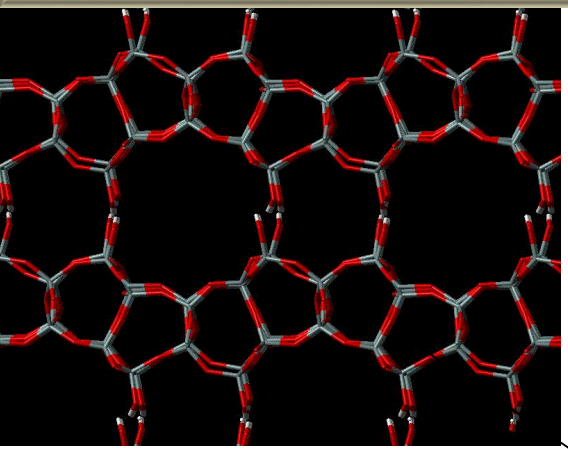
$$H = E + pV \qquad p = -\frac{\partial E}{\partial V}$$



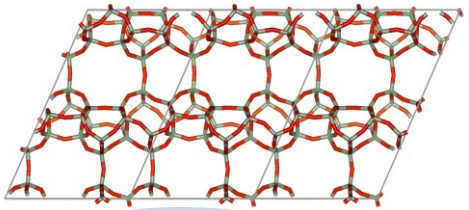
IPC-1P-10R/8R **IPC-1P-10R/7R** **IPC-1P-8R/7R**

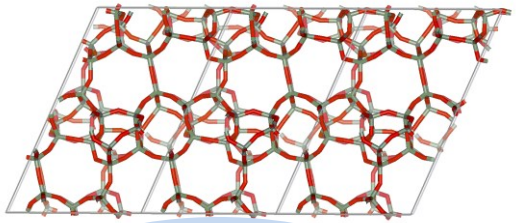


IPC-1P zeolite family

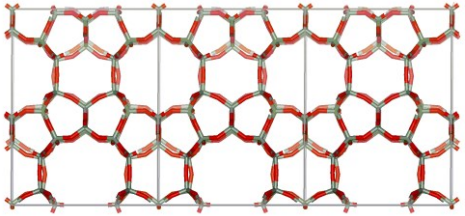


***ac* plane projection**



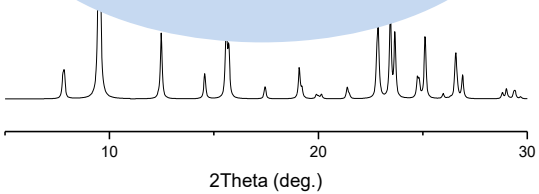


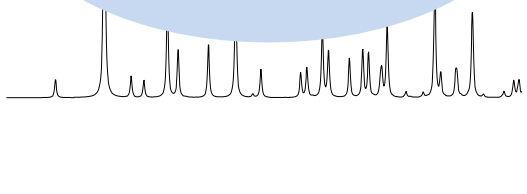
***ab* plane projection**

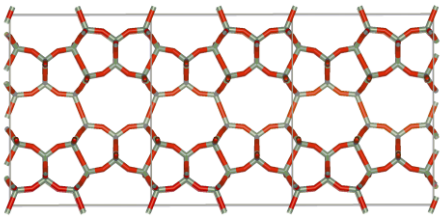


IPC-4 (PCR)
direct calcination
YES

IPC-9
Higher pH, SDA
YES

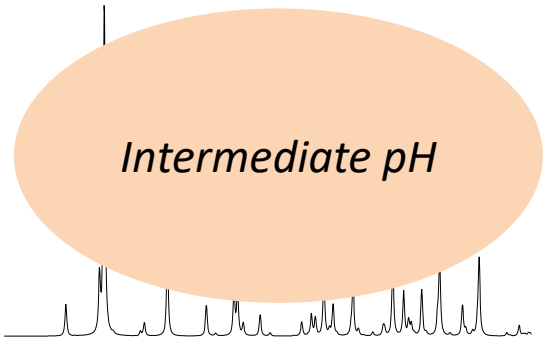


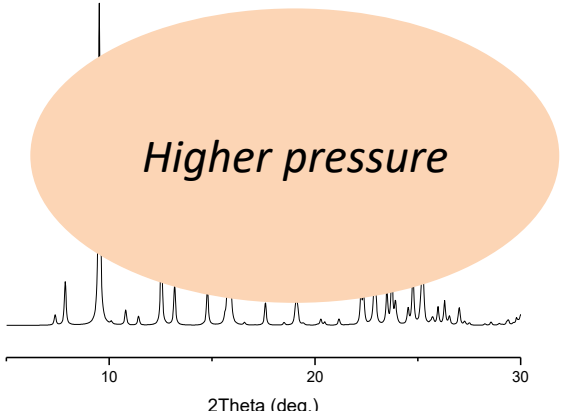




Intermediate pH

Higher pressure





Roth et al, Nature Chemistry 5 (2013) 628-633

ADOR extensions (*in silico*)

Regular shift of adjacent layers

Regular alternation of inter-layer "pillars"

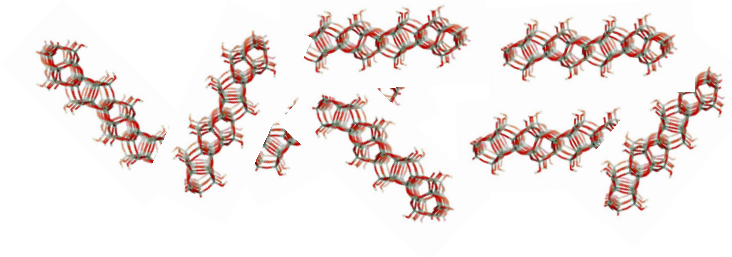
IEZ strategy (and more general approach)

ADOR extensions

Different lamellar precursors:

- zeolites with D4R
- zeolites with D3R
- other zeolites (?)

Any possible combination of ADOR extensions
⇒ almost endless number of possibilities
NEW PLAYGROUND



How many ordered 3D materials are experimentally accessible ?

ADOR extensions (*in silico*)

Database of new zeolite structures accessible by ADOR

UTL, IWW, IWV, IWR, ITH, ITR all unique 3D zeolites with regularly shifted layers investigated computationally

- **direct condensation: -D4R zeolites – 21 possible structures**

  Trachta M. et al., ChemPhysChem 2014

- **IEZ analogues: -S4R zeolites - 100 possible structures**

  Trachta M et al., Catal Today 2015

Structures and properties evaluated
XRD powder patterns generated
Accessibility criteria

Five of new zeolites generated by *in silico* ADOR were found in existing databases *e. g.*, IWR-D4R(Cmmm) = PCOD8172433

http://www.hypotheticalzeolites.net/DATABASE/DEEM/DEEM_PCOD/index.php

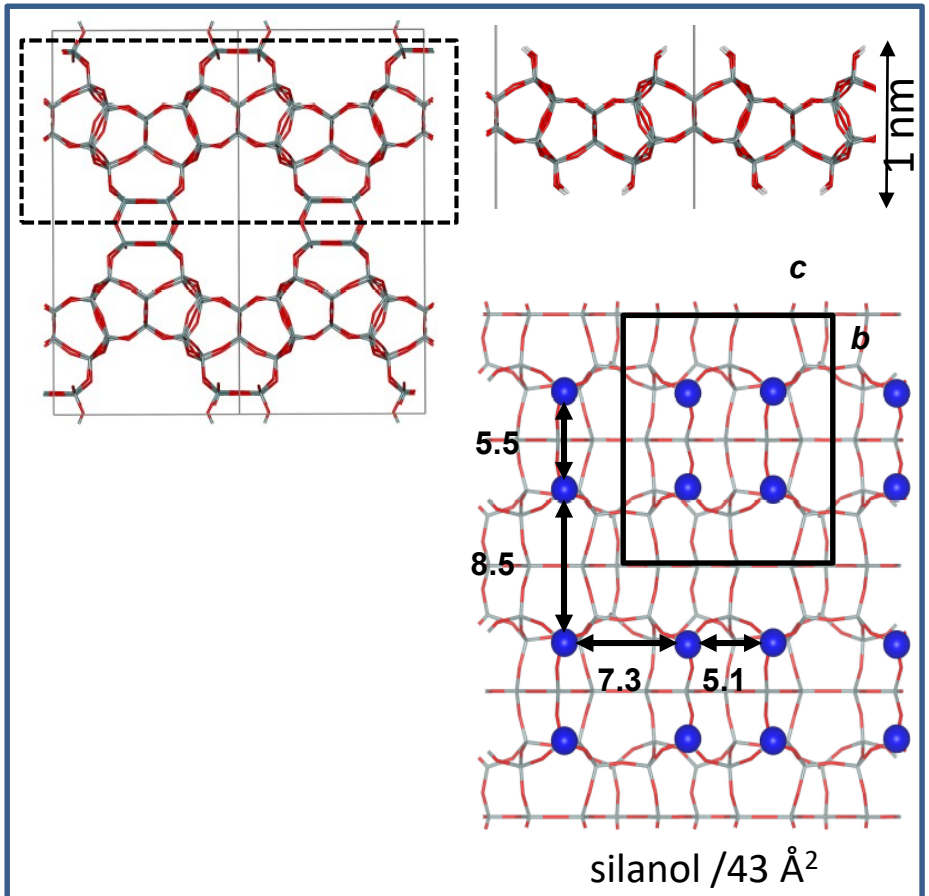
III Catalysis

Lewis Acidity of 2D zeolites

MCM-22P *vs.* IPC-1P
3D *vs.* 2D zeolite

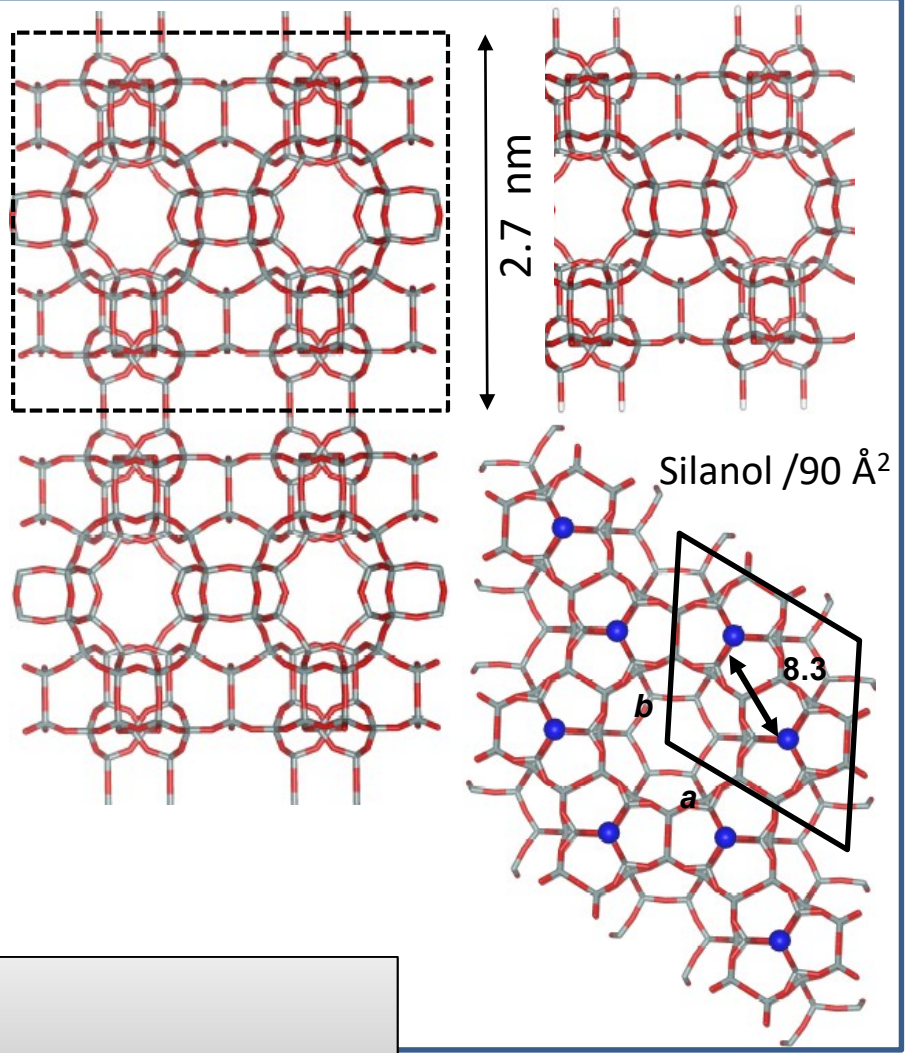
IPC-1P zeolite family

UTL (IPC-1P)



silanol /43 Å^2

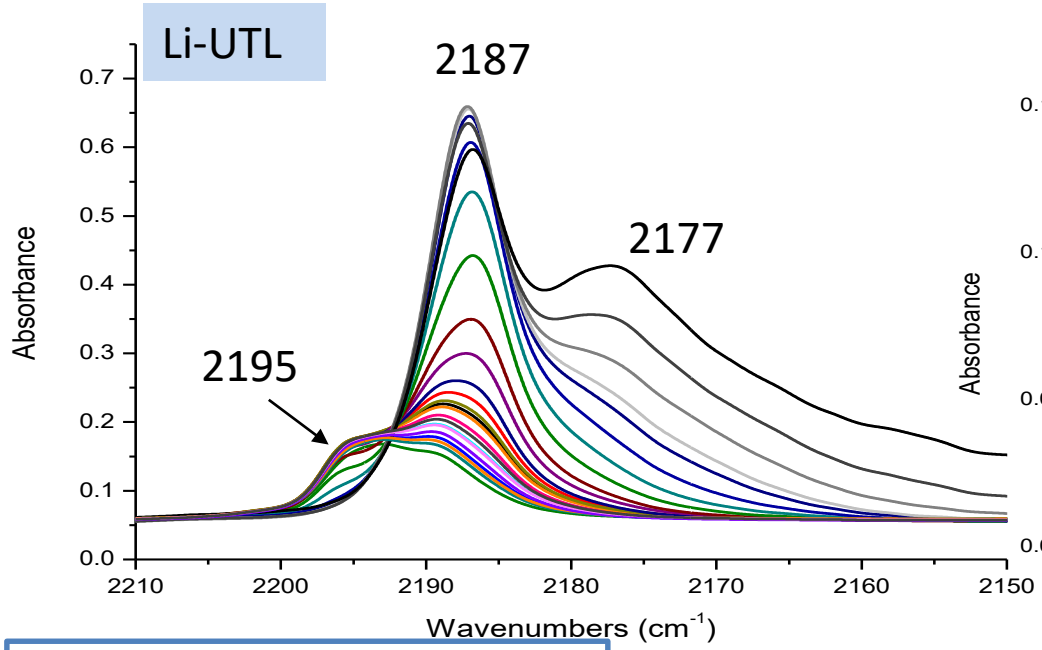
MCM-22 (MCM-22P/MWW)

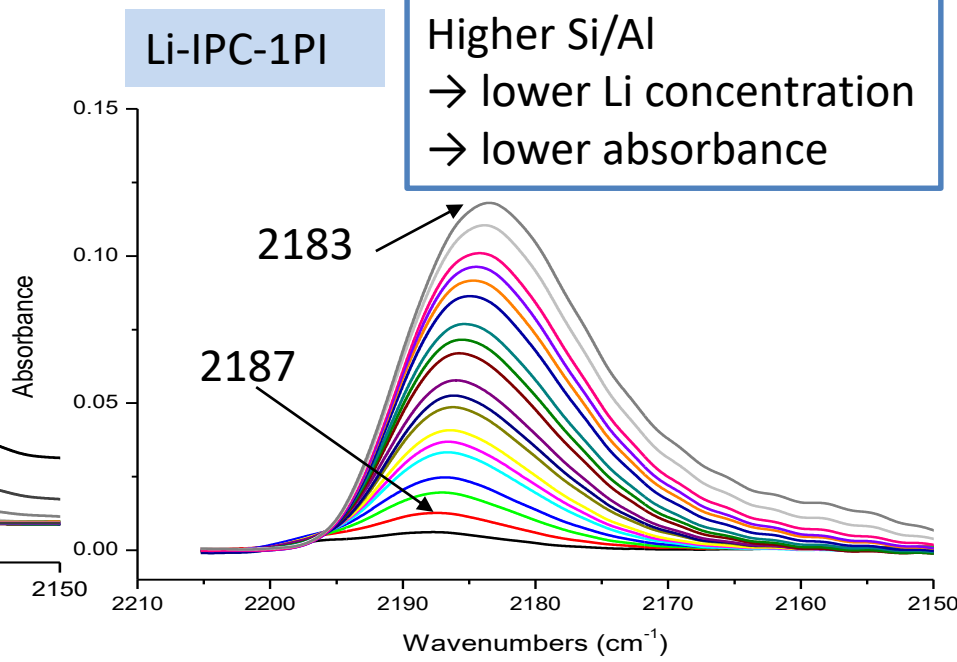


Differences:

- Layer thickness
- Silanol concentration and arrangement

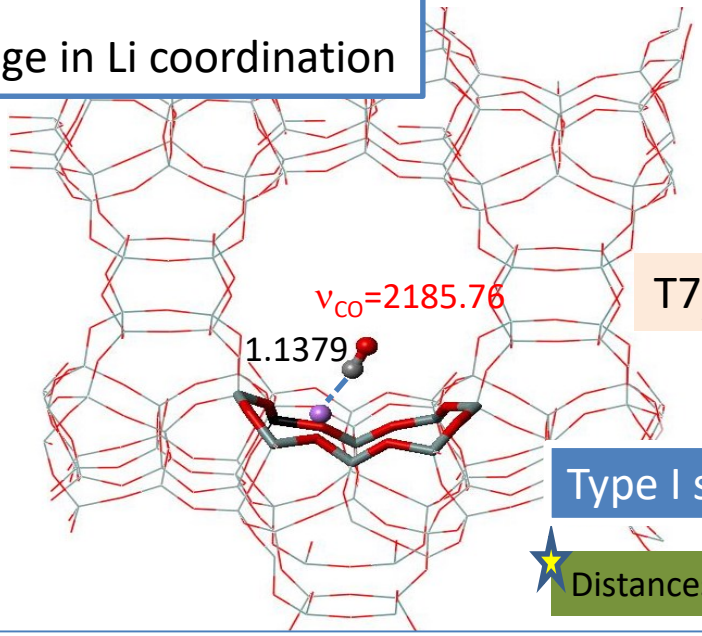
Li-UTL *vs.* Li-IPC-1PI (CO @ 77K)





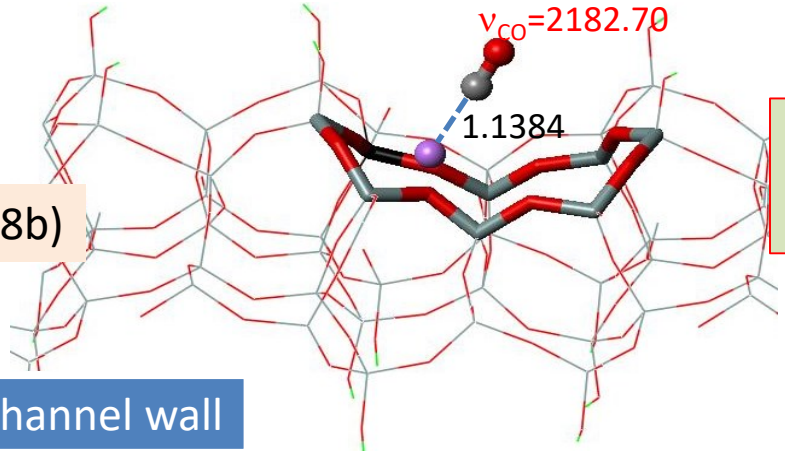
Higher Si/Al
→ lower Li concentration
→ lower absorbance

Case I
No change in Li coordination



1.94
1.95
2.08

$T7_{Al}$-Li(M8b)

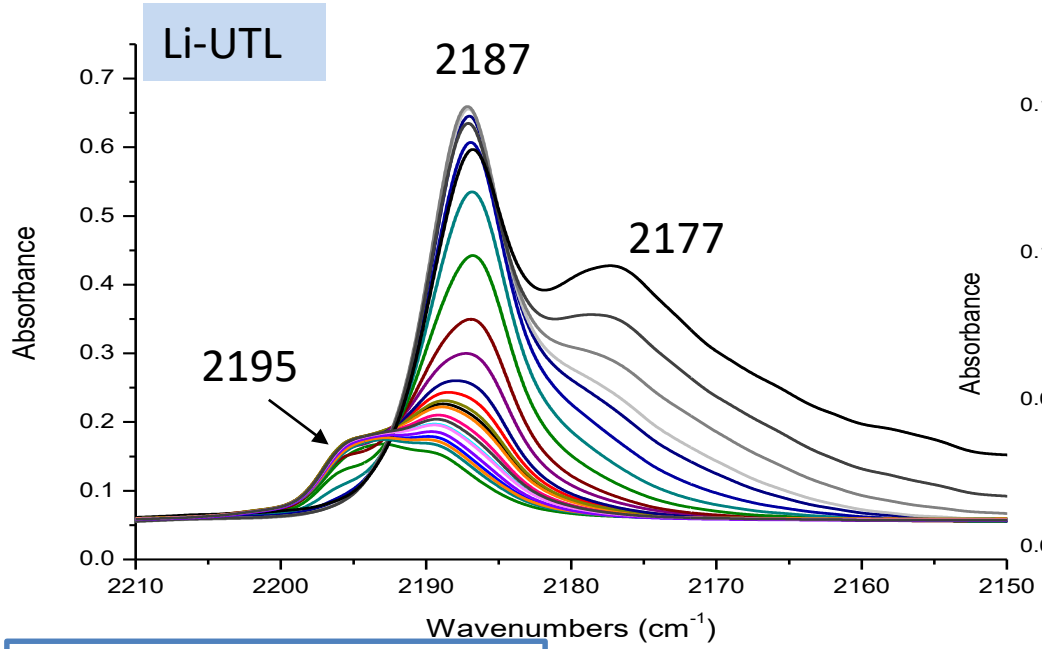


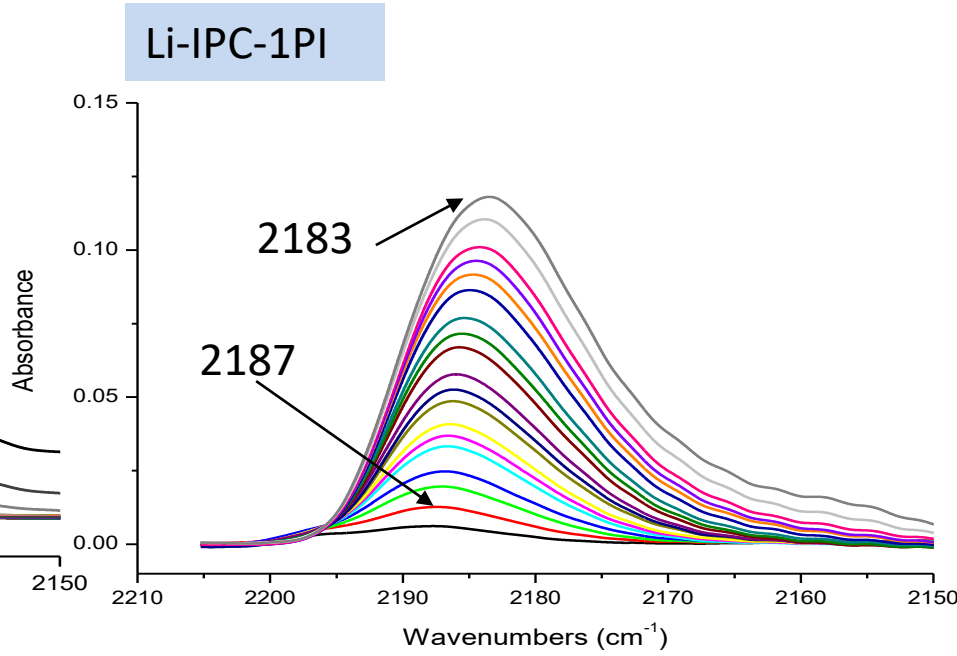
1.93
1.96
2.08

Type I site – channel wall

Distances of Li^+ ion to framework oxygen atoms in coordination with Li^+

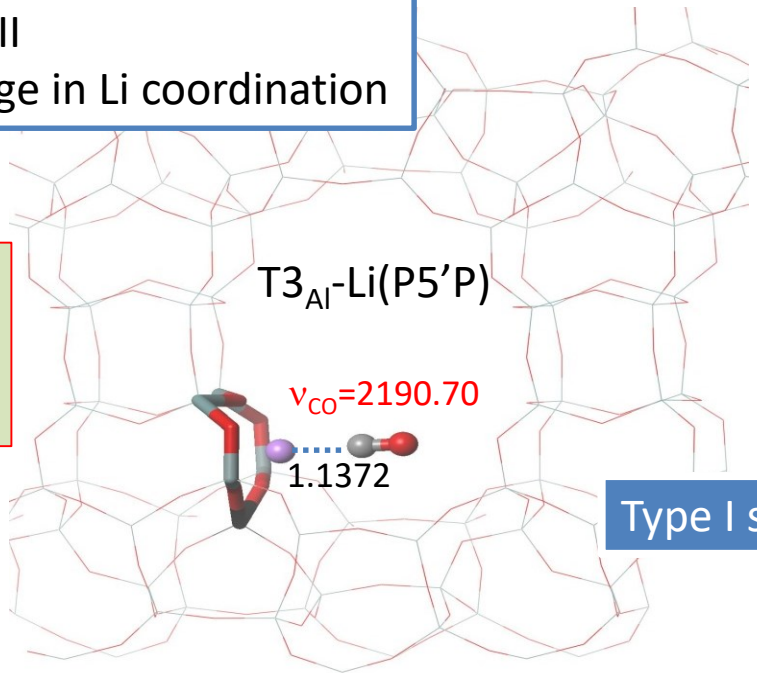
Li-UTL *vs.* Li-IPC-1PI (CO @ 77K)

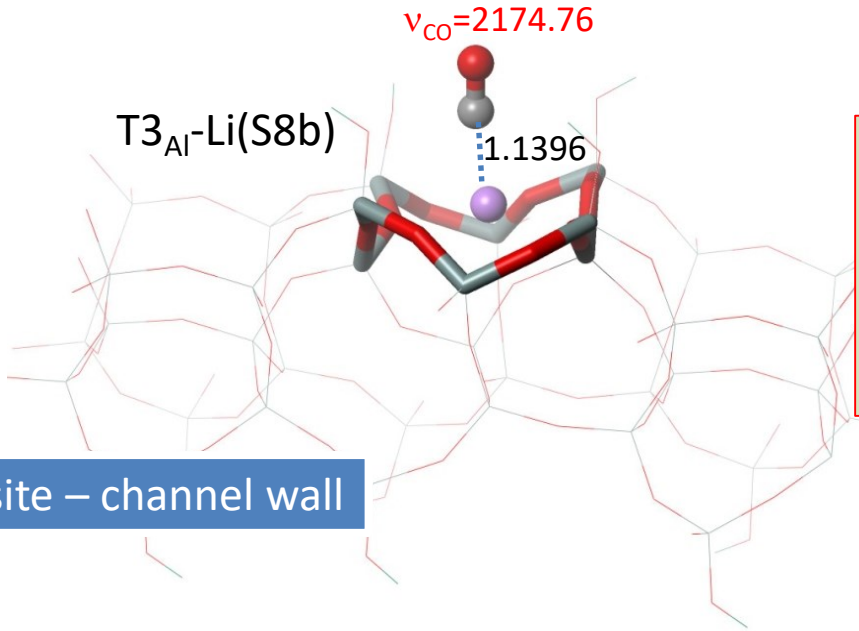




Case II
Change in Li coordination

1.90
1.94
1.95

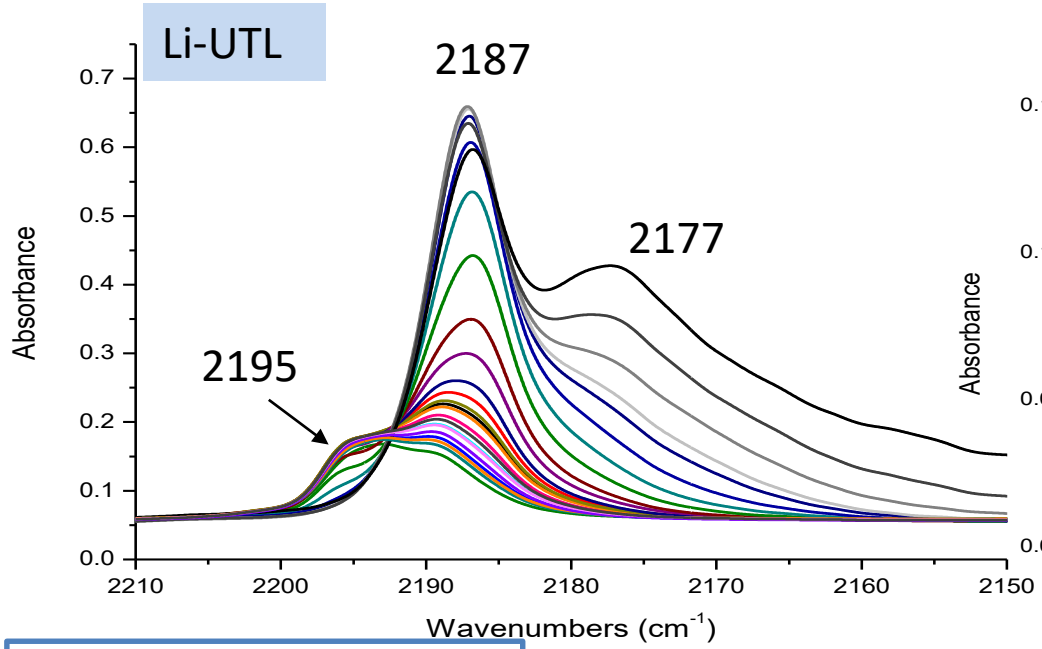


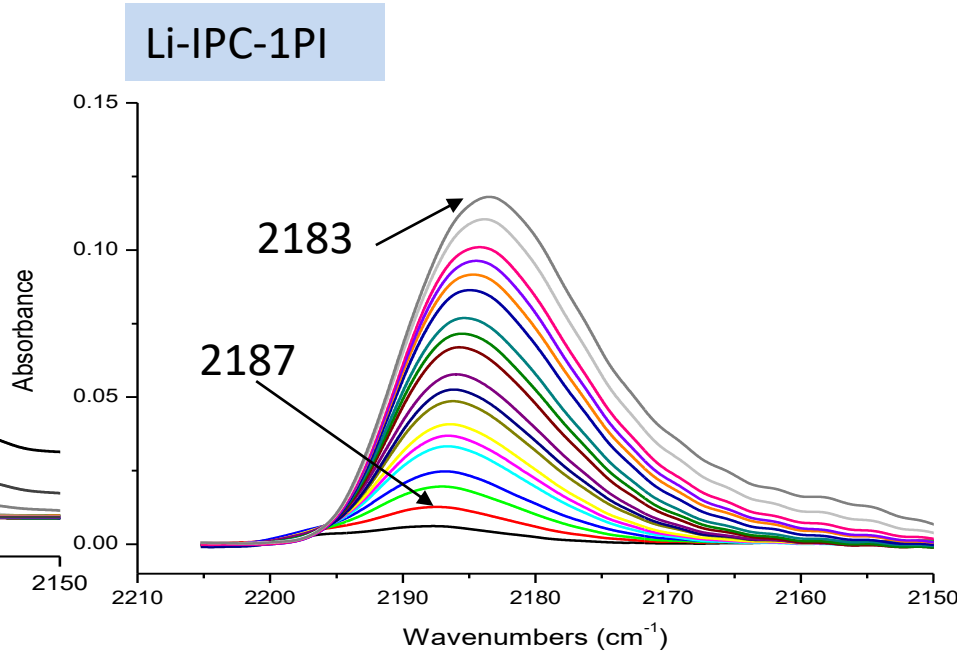


1.93
2.07
2.11
2.11

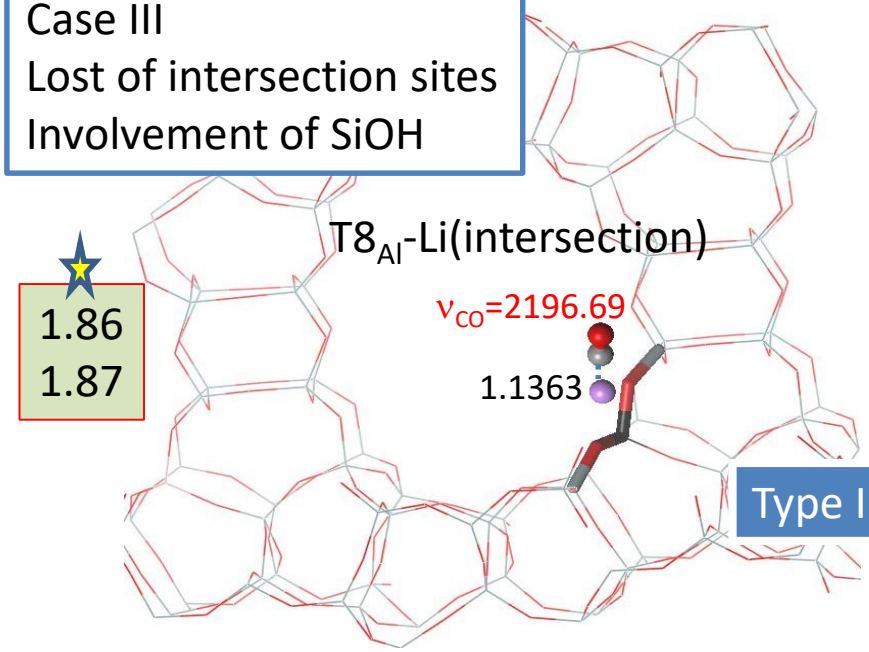
Type I site – channel wall

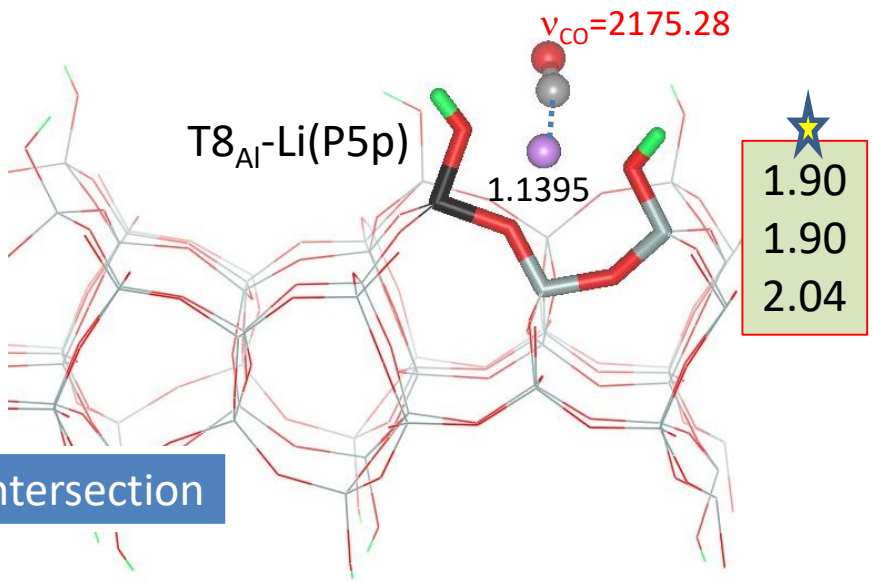
Li-UTL *vs.* Li-IPC-1PI (CO @ 77K)





Case III
Lost of intersection sites
Involvement of SiOH





Type II site – intersection

Results confirmed for other probe molecules:
vdW-DF2 level of theory

	3D → 2D		3D → 2D	
	Type I	**Type I**	**Type II**	**Type I**
CO	-47	-51	-54	-36
NH_3	-104	-106	-120	-88
CH_3CN	-105	-113	-133	-96
Pyridine	-143	-131	-155	-99

Channel wall site

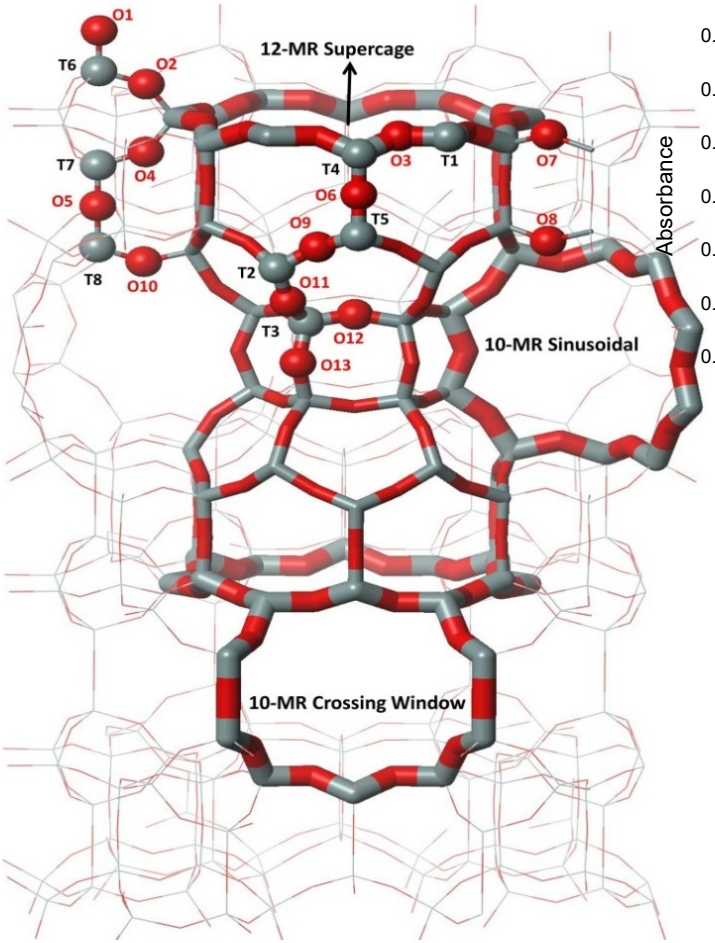
- Interaction energy and υ(CO) are both slightly lower (3 kJ/mol and 5 cm^{-1}, respectively) in 2D material

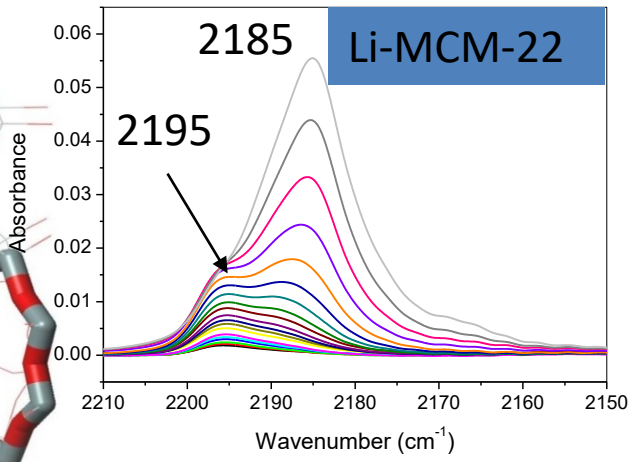
Intersection sites

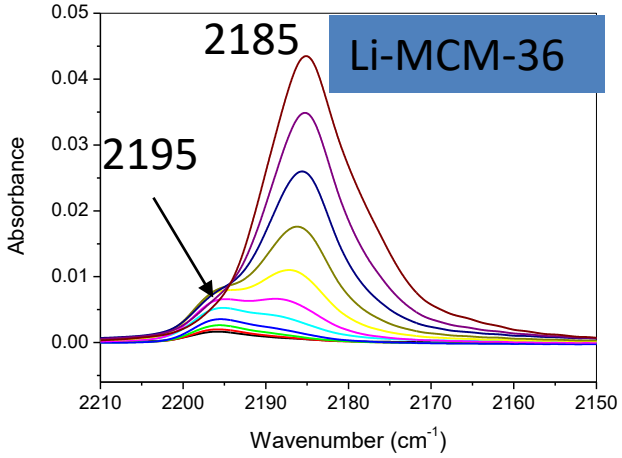
- They only exist in 3D material – highest frequencies and strongest interactions

Lost of the strongest Lewis acid sites in 2D materials (missing intersection)

Li-MCM-22 *vs.* Li-MCM-36 (CO @ 77K)







Al	Li site	MCM-22	MCM36
T1	II	2197	2189
T4	II	2196	2192
T6	I	2188	2192
T8	I	2186	2186
T3	I	2181	2180
T5	I	2180	2179
T2	I	2178	2178

Only marginal differences between 3D and 2D materials !
Good agreement between theory and experiment

Acidic/basic properties of 3D *vs.* 2D zeolites

Lewis acidty (Li^+ extra-framework)

Lewis acid sites

Strong Lewis acid sites are lost for thin IPC-1P layers

- No intersection sites in 2D material
- Large concentration of surface SiOH → number of sites influenced

No change in Lewis acidity for MCM-36 having thick layers and low surface silanol conc.

3D *vs.* 2D zeolites

Differences depends on two main factors:

- Concentration of surface silanols
- Layer thikness

2D zeolites having thicker layers and lower silanol concentration keep the Lewis acidity of corresponding 3D zeolite.

Brønsted acidty – similar, differences less pronounced

3D vs 2D Zeolites

2D → 3D transition

- Structures of “ADORable” zeolites
- Layer arrangement and re-organization (SDA, pressure)

2D vs 3D properties

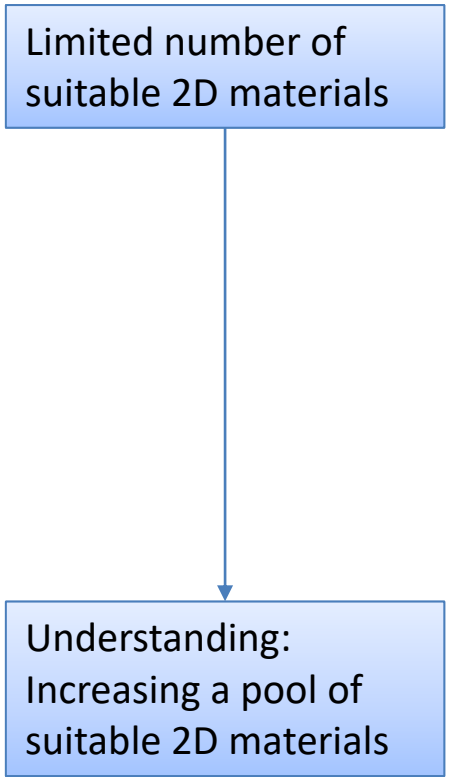
- Lewis acidity
- Brønsted acidity
- Catalysis

3D → 2D transition

- Exploring the weaknesses of 3D structure
- Zeolite hydrolysis

Hybrid materials

- Interlayer interactions/arrangement
- Spintronics



Acknowledgement

Calculations:

M. Položij, L. Grajciar, M. Rubeš, H. V. Thang,

Junjie He, Pengbo Lyu **(Charles University, Prague)**

O. Bludský, M. Trachta **(Institute of Organic Chemistry, Prague)**

Experimental work:

J. Čejka and his group **(Institute of Physical Chemistry, Prague)**

R. Bulánek and his group **(University of Pardubice)**

GAČR GRANTOVÁ AGENTURA ČESKÉ REPUBLIKY *Center of Excellence 2012-2018 (Grant Agency of the Czech Republic)*

CHARLES UNIVERSITY CENTRE OF ADVANCED MATERIALS

cascatbel www.cascatbel.eu

EUROPEAN UNION European Structural and Investing Funds Operational Programme Research, Development and Education

MINISTRY OF EDUCATION, YOUTH AND SPORTS