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Effect of LiCl aqueous solutions on the energetic performances of Silicalite-1

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OUTLINE

- ⇨ Generalities on Zeosils
- ⇨ Basic idea : intrusion of aqueous solution into hydrophobic solids
- ⇨ Energetic performances of Silicalite-1
- ⇨ Conclusion

- GENERAL REMARKS ON MICROPOROUS SOLIDS -

Zeolites and related materials

More than 253 structure types
(3 code letter): FAU, LTA, MOR, MFI,…..

$0.3 \leq D$ Pores ≤ 1.3 nm
Specific surface area 400-900 $m^2.g^{-1}$
Porous volume: 0.2-0.3 $cm^3.g^{-1}$

Inorganic framework built from TO_4 tetrahedra
(T = Si, Al, Ge, P, …)

Zeosils

Silicates T = Si

Non-charged framework

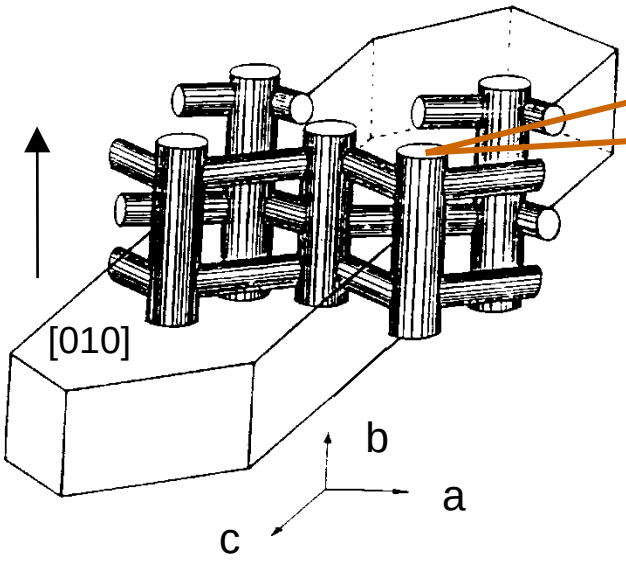
Hydrophobic materials

Zeosils

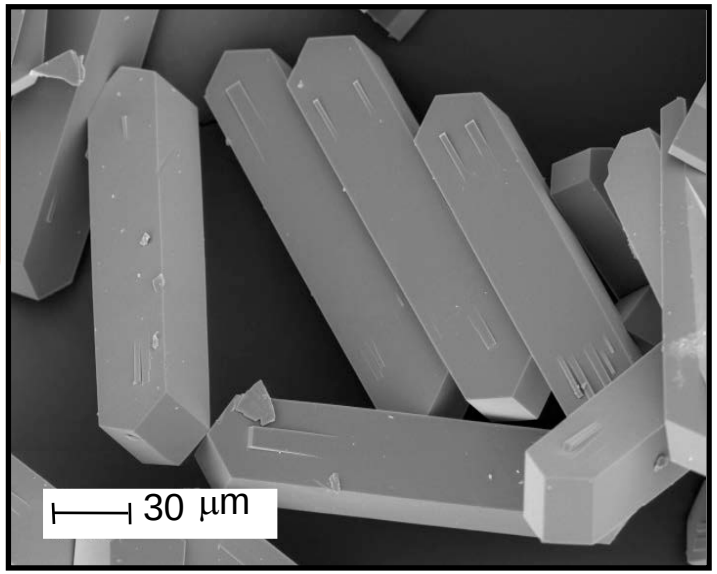
3D multichannel zeosils

Silicalite-1 (SiO_2, MFI-structure type)

Unit cell formula of the calcined material $Si_{96}O_{192}$



3D channel system
Pore openings
(0.55 x 0.56 nm)



APPLICATION

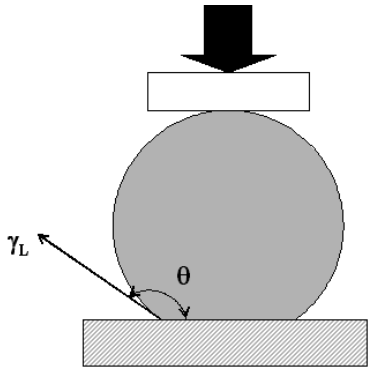
Energy storage

Generalities – Basic idea

Principle :

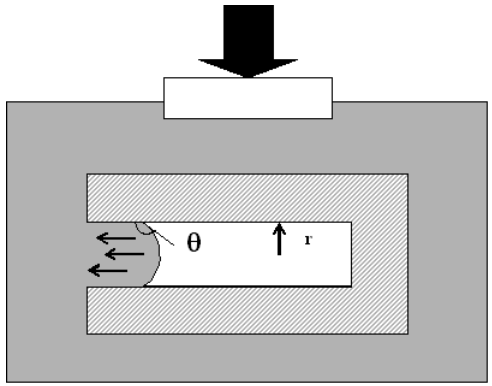
➢ to spread a non-wetting liquid droplet on the surface of a solid, a certain pressure must be applied.

➢Similarly to make this liquid penetrate a porous matrix the applied pressure has to be higher than the capillary pressure P_{int} which follows the Laplace-Washburn relation :



$$P_{int} = - (2 \gamma_L \cos \theta) / r$$

γ_L: liquid-vapor interface energy
θ: contact angle.
r: pore radius



During this process, mechanical energy is converted into interfacial energy

Generalities – Basic idea

Intrusion of a non wetting liquid into a lyophobic porous solids [1, 2]

Solid: porous silica gel, porous glass

Liquid: metal with low melting point (mercury,…)

[1] V. Eroshenko C.R. Acad. Sc. Ukraine, Series A 10, 1990, 79

[2] V. Eroshenko Patent: WO 96/18040

Generalities – Basic idea

Our work [1-13]

Intrusion of water into hydrophobic porous inorganic frameworks

Advantages:

Water: **Liquid at room temperature**

High surface tension

Non-polluting

Low cost

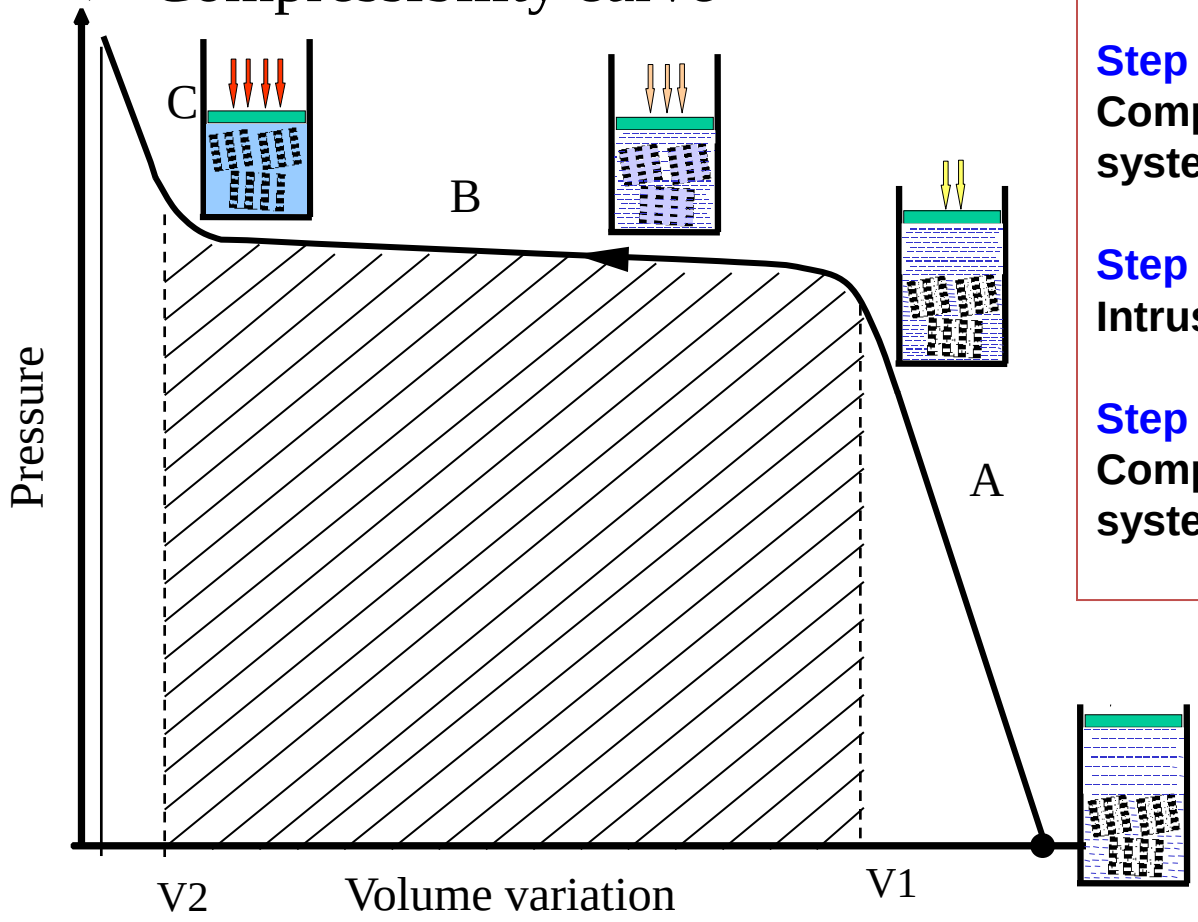
kinetic diameter 0.28 nm → **Zeosils**

[1] V.Eroshenko *et al.*,J. Am. Chem. Soc. 123, 2001, 8129
[2] N. Debiens *et al*, Angew. Chem. Int. Ed., 2005, 44, 5310
[3] M. Trzpit *et al*., Langmuir, 2007,23 (20), 10131
[4] M. Trzpit *et al.*, Chem. Letters, 2007, 36 (8), 980-981
[5] M. Trzpit *et al*., The Journal of Physical Chemistry B, 112 (2008), 7257
[6] F. Cailliez *et al.*, Phys. Chem. Chem. Phys., 10 (2008), 4817-4826
[7] M.Trzpit *et al.*, Micro. and Mesoporous Mater, 117 (2009), 627-634.
[9] M. Trzpit *et al.*, J. of Mater. Science , 44, (2009), 6525 – 6530
[9] M. Saada *et al*., The Journal of Physical Chemistry C, 114 (2010), 11650
[10] T. Karbowiak *et al*., Phys. Chem. Chem. Phys, 12 (2010), 11454
[11] M.A. Saada *et al.*, , Journal of Physical Chemistry C, 115 (2011), 425-430
[12] L. Tzanis *et al.*, Micro. and Mesoporous Mater, 146 (2011),119-126
[13] L. Tzanis *et al.*, Journal of Physical Chemistry C, 116 (2012), 4802-4808

Generalities – Water intrusion

Hydrophobic porous solids +**water**

➢ Compressibility curve



Step A :
Compression of the water-zeosil system

Step B :
Intrusion of water into the pores

Step C :
Compression of the water-zeosil system

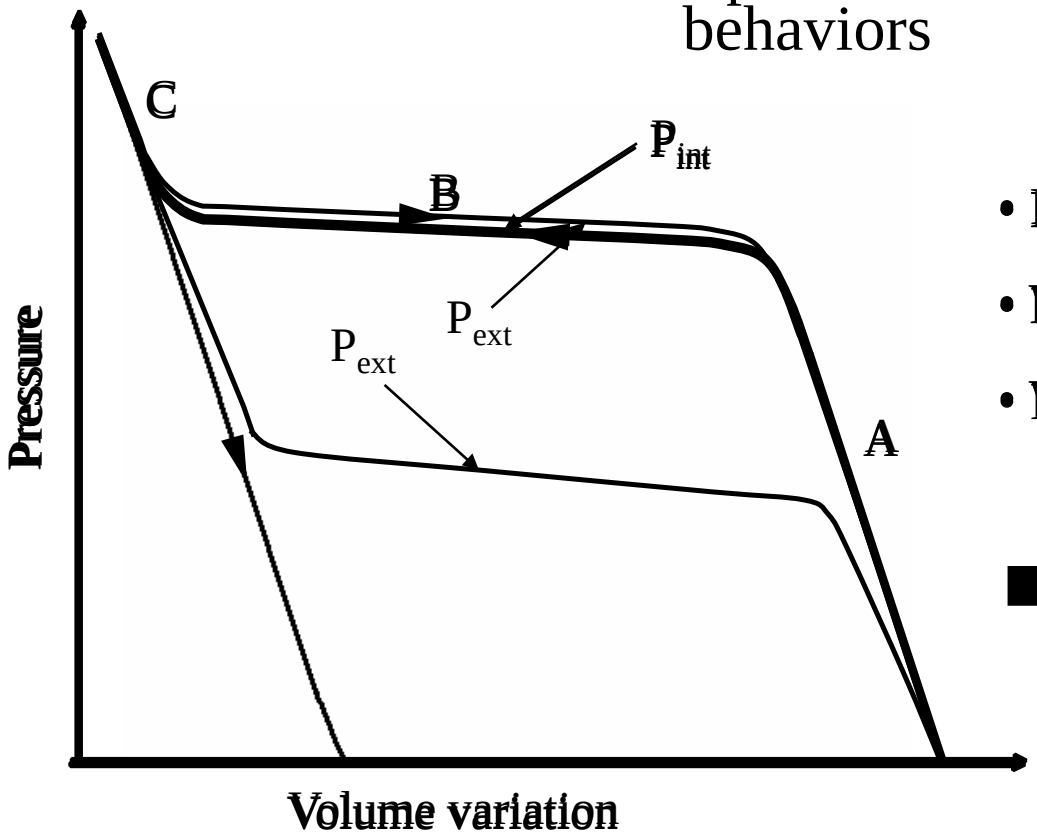
- Stored energy (W) :

$$\Delta W = \int_{V1}^{V2} - P dV$$

Generalities – Water intrusion

Hydrophobic porous solids +**water**

➢ When the pressure is released



3 possible behaviors

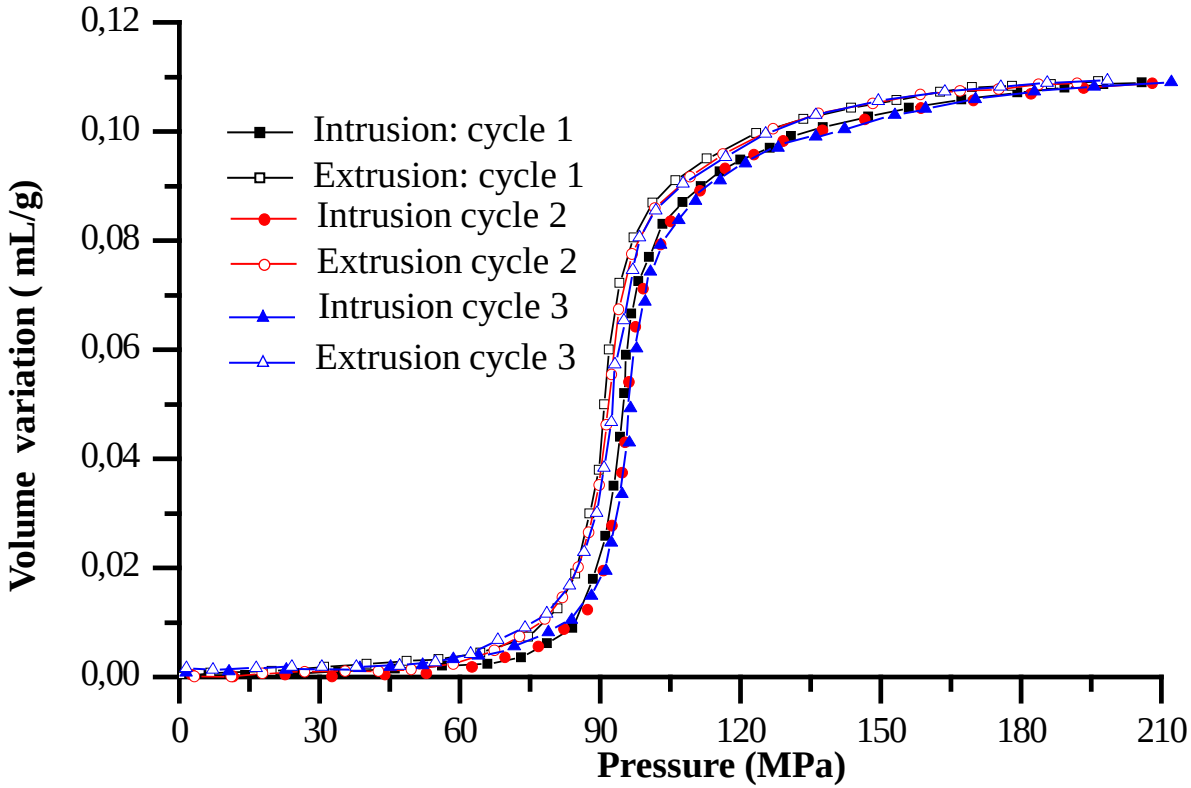
- ➢ Bumper
- ➢ Shock absorber $P_{ext} << P_{int}$
- ➢ Spring $P_{ext} \approx P_{int}$

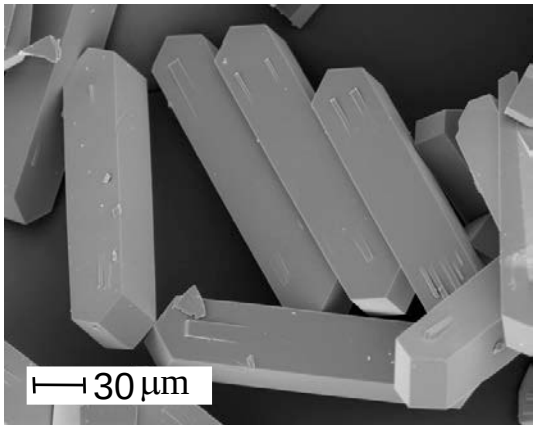
- Reversible phenomenon
- Without hysteresis
- Restitution of all the water

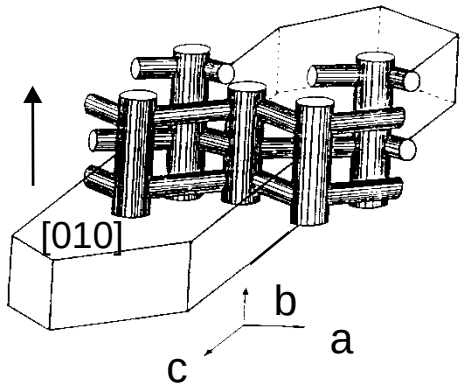
- Irreversible phenomenon
- Large hysteresis
- Water spontaneously expelled

➡ System able to store and restore energy

Silicalite-1 – Water intrusion





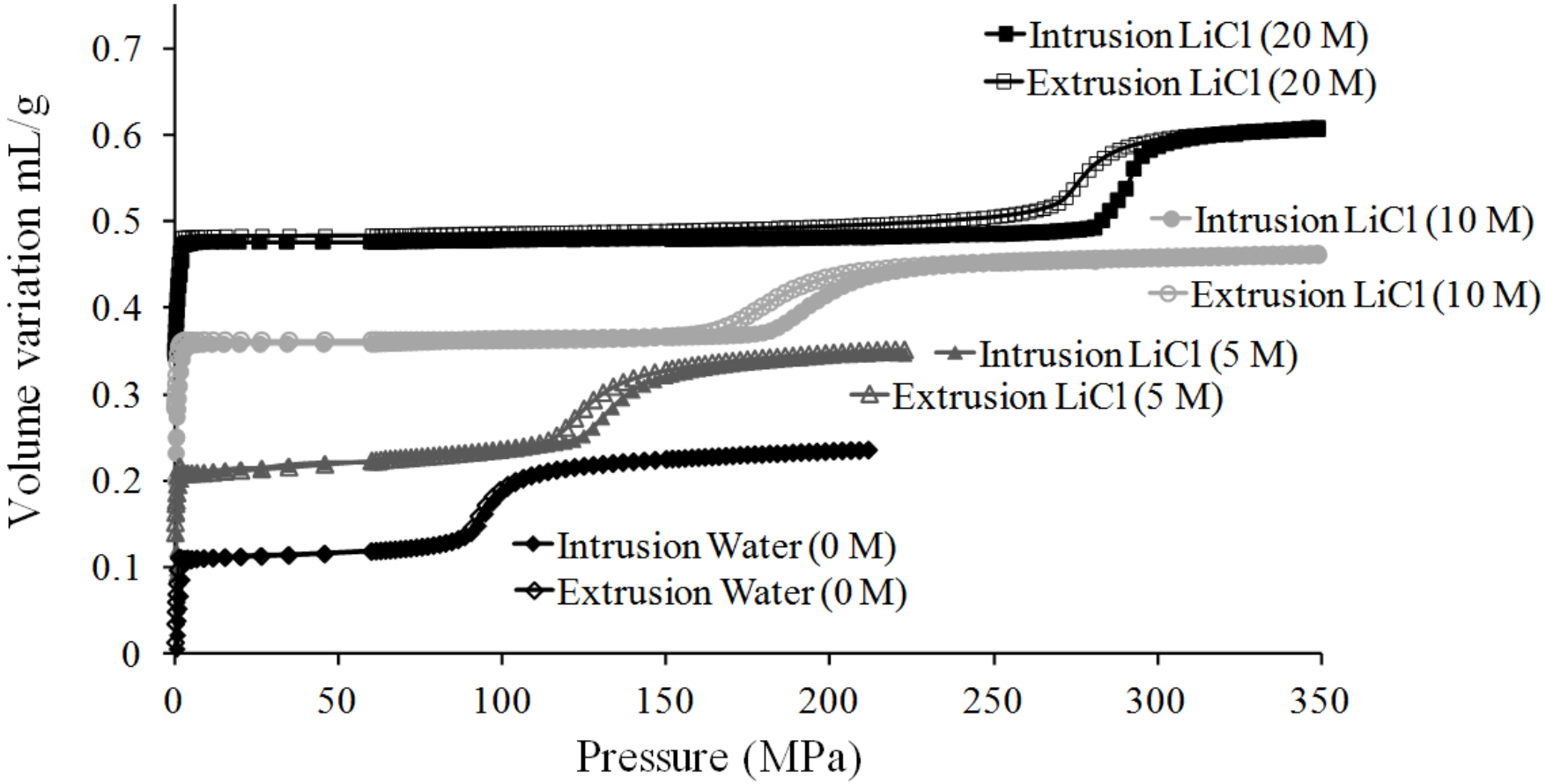


Stored energy ~10 J/g Yield > 98%

Pore openings: 0.55-0.56 nm

Silicalite-1 – LiCl aqueaous solution intrusion

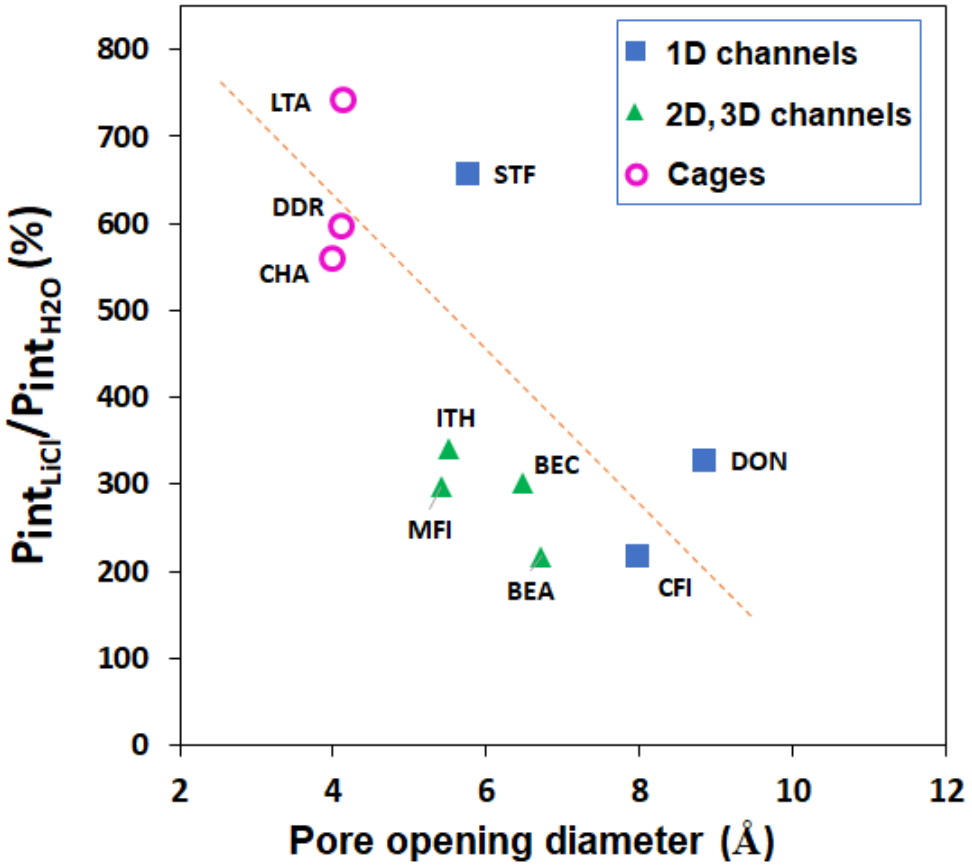
Intrusion of LiCl aqueous solutions



[LiCl] ↑ ➡ P_{int} relative increase ↑ ➡ E_S ↑

Khay, I. et al., J. Phys. Chem. C, 118, (2014), 3935.

Intrusion-extrusion of salt aqueous solutions in Zeosils – Performance



- Increase of P_{int} - up to 7.4 times
- E_s up to 93 J/g
- P_{int} ↑ relative when pore opening diameter↓
- Increase of P_{int}: Distortion and desolvation of solvated ions under penetration into micropores

Potential applications

To **store** and **restore** energy

Concern space and transport domains

- **Spreading of solar panels of satellites**
- **Opening of landing gear of aircraft**
- **Shock-absorbers or bumpers for motor vehicles**

……

Perspectives

- **Increase the stored energy**

  Synthesis of new porous solids with large pore volume,….

- **Developing new applications in this field**

- **Study the influence of the aqueous medium on the energetic performances of zeosils**

Acknowledgments

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