Horizon2020
Materials Networking

Molecular dynamics simulations applied to industrial processes

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Introduction

Our group of research (Applied Computational Chemistry and Molecular Modeling Group) is studying different industrial processes by means of Molecular Dynamics:

CO_2 capture in post-combustion flows

How to increase the CO_2 capture/sequestration by adsorbent materials?

how molecular dynamics simulations have helped in the processes behind the two former topics

Introduction

Our group of research (Applied Computational Chemistry and Molecular Modeling Group) is studying different industrial processes by means of Molecular Dynamics:

Sensible thermal storage

How to increase the C_p in molten salts (solar salts) for using in solar plants?

how molecular dynamics simulations have helped in the processes behind the two former topics

Introduction

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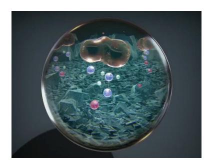


Enhanced Oil Recovery Techniques

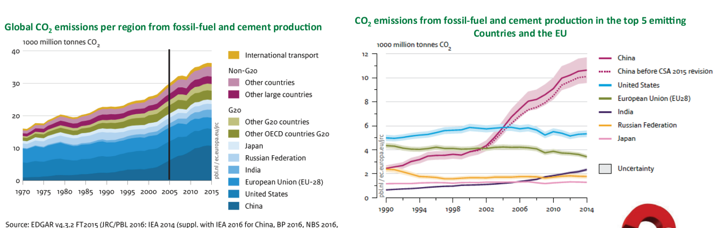
How to increase the amount of oil recovered in third stage technologies?

how molecular dynamics simulations have helped in the processes behind the two former topics

CO_2 capture in post-combustion flows

Carbon Emission Problem

After a decade of very high annual growth rates of global CO_2 emissions of 4% on average, the growth in emissions almost stalled in 2014 with an increase of only 0.5% to 35.7 billion tonnes CO_2. Power plants are responsible for about 40% of the total.

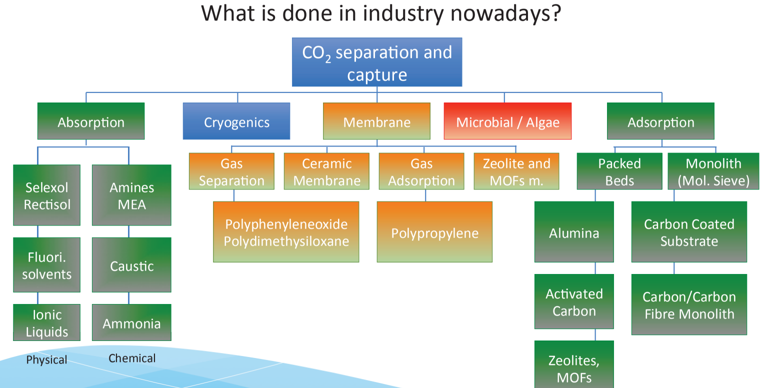


It is a "good new" but it is necessary to keep on decreasing carbon emissions

CO_2 capture in post-combustion flows

Technologies for CO_2 capture

What is done in industry nowadays?



Technologies for CO_2 capture

What is done in industry nowadays?

Separation with Sorbents (adsorption)

Post-combustion CO_2 capture

(Flue gas composition: 14-16%)

Pressure Swing Adsorption (PSA):

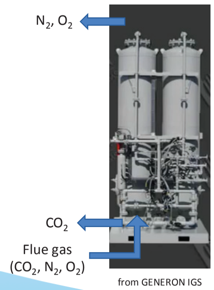
1st. the flue gas mixture enters into bed 1 (at 1 bar).

2nd. the mixture pressurizes bed 1 in the range (7-30 bars).

at this conditions CO_2 adsorbs and the other components not, exiting from the top of the bed.

3rd. the first bed is depressurized to atmospheric pressure.

at this conditions the CO_2 is removed and driven to a receiver tank and the adsorbent material is regenerated. At the same time the cycle is repeated in bed 2.



from GENERON IGS

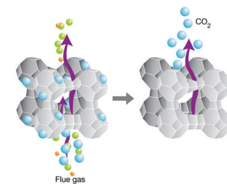
Technologies for CO_2 capture

What is done in industry nowadays?

Separation with Sorbents (adsorption)

Other Swing Adsorption-Desorption processes:

	ADSORPTION STEP	DESORPTION STEP
PSA	High pressure	Atmospheric pressure



Technologies for CO_2 capture

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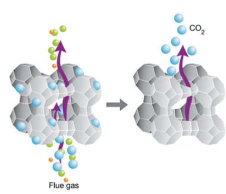
Other Swing Adsorption-Desorption processes:

	ADSORPTION STEP	DESORPTION STEP
PSA	High pressure	Atmospheric pressure
VSA	Atmospheric pressure	Vacuum



VSA: Vacuum Swing Adsorption

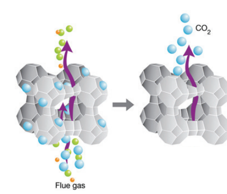
Technologies for CO_2 capture

What is done in industry nowadays?

Separation with Sorbents (adsorption)

Other Swing Adsorption-Desorption processes:

	ADSORPTION STEP	DESORPTION STEP
PSA	High pressure	Atmospheric pressure
VSA	Atmospheric pressure	Vacuum
TSA	Ambient temperature	High temperature



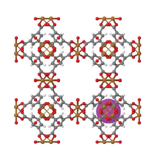
VSA: Vacuum Swing Adsorption

TSA: Temperature Swing Adsorption

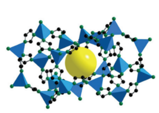
Materials for CO_2 capture

How the materials for CO_2 capture should be?

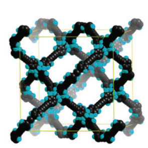
- High CO_2 working capacities
- High selectivity towards CO_2
- Suitable for a wide range of temperatures and pressures
- No degradable in presence of impurities
- Easy to regenerate
- Small increase in the price of electricity



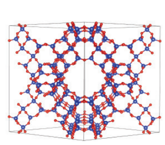
Metal-organic frameworks (MOFs)
e.g. CuBTC



Zeolitic imidazolate frameworks (ZIFs)
e.g. ZIF-8



Porous polymer networks (PPNs)
e.g. PPN-I

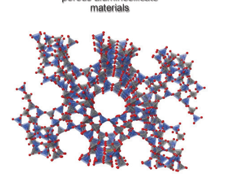


Zeolites
e.g. Faujasite 13X

Materials for CO_2 capture

Zeolites

porous aluminosilicate materials



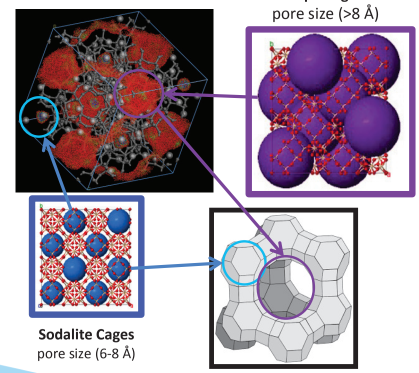
Faujasite 13X $Na_{88}[Si_{104}Al_{88}O_{384}]$

Porous Material of Si/Al ratio 1.2 (88-FAU)

is the one used today in industrial processes

Na:gray / Al:pink / Si:yellow / O:red

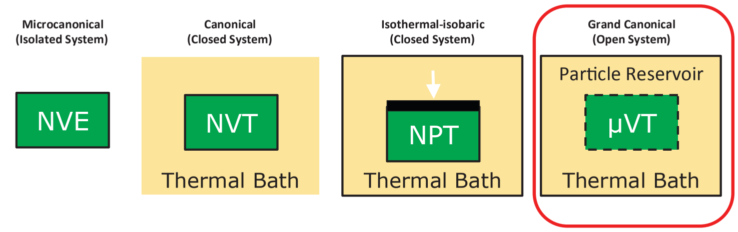
Supercages
pore size (>8 Å)



Sodalite Cages
pore size (6-8 Å)

How do we simulate the capture process by adsorbents?

It corresponds to a mechanical **system of particles in thermodynamic equilibrium (thermal and chemical) with a reservoir of gas** (*i.e.*, the system can exchange energy and particles with the reservoir).



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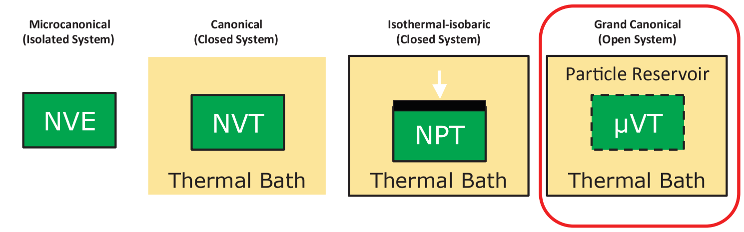
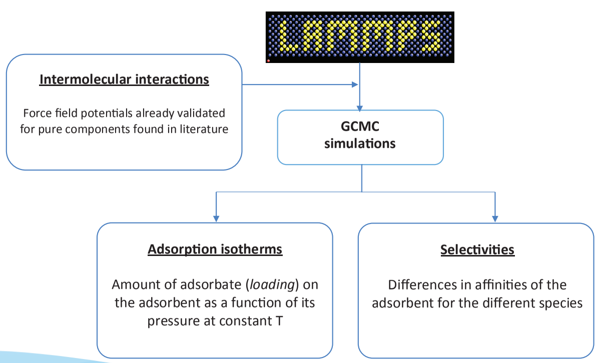


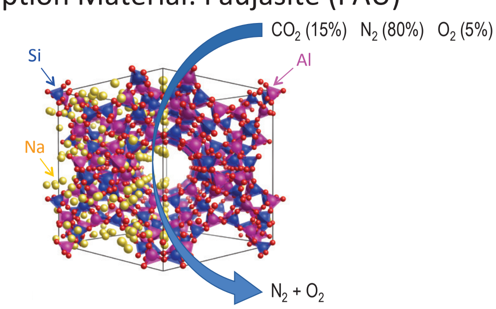
The interaction of particles is described by validated force fields and these particles are inserted, moved or eliminated from the system in order to achieve the equilibrium state when chemical potentials of reservoir and system become equal at a fixed P and T of the reservoir.

How do we simulate the capture process by adsorbents?



Adsorption Material: Faujasite (FAU)

for every Si atom substituted by Al one Na^+ atom is also introduced to cancel the negative charge



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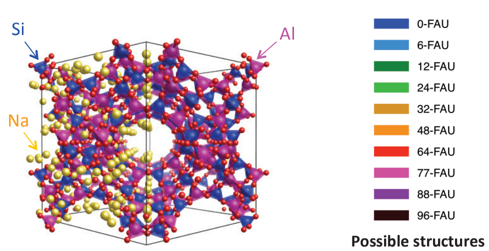
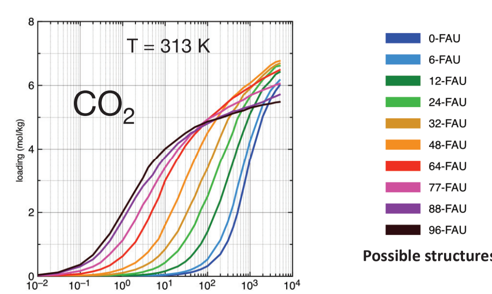


- from totally silicalited (*silicalite*, **0-FAU**)
- to **96-FAU**, maximum number of Al per unit cell (according to Lowenstein's rules)

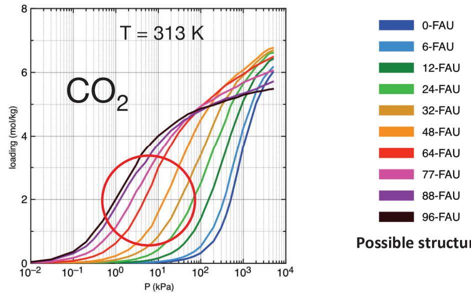
Pure gas adsorption isotherms



the quantity of CO_2 adsorbed depends strongly on the Si/Al ratio

Optimal Faujasite structures for post combustion CO_2 capture and separation in different swing adsorption processes
H. Prats, D. Bahamón, G. Alonso, X. Giménez, P. Gamallo, R. Sayós, *J. CO_2 Util. 19 (2017) 100-111 & 21 (2017) 261-269* .

Pure gas adsorption isotherms

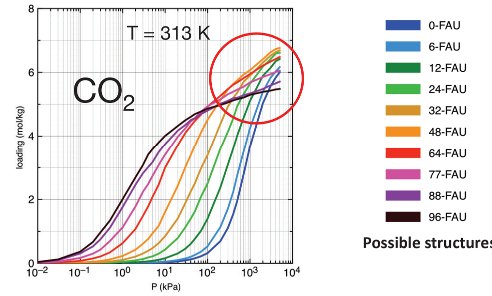


Possible structures

the quantity of CO_2 adsorbed depends strongly on the Si/Al ratio

as the Al and Na+ content increases, the amount of **CO_2 adsorbed is higher**, specially at low pressures

Pure gas adsorption isotherms

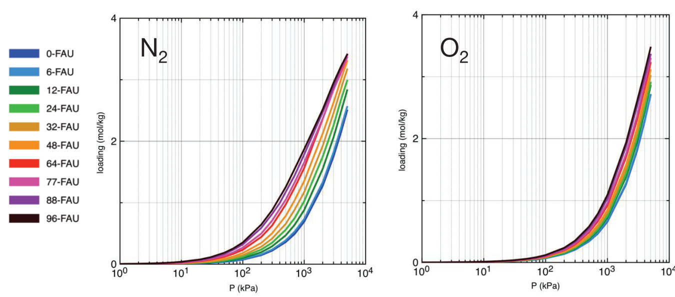


Possible structures

the quantity of CO_2 adsorbed depends strongly on the Si/Al ratio

High Al content faujasites saturate faster with a lower quantity of CO_2, due to the volume reduction by Na+

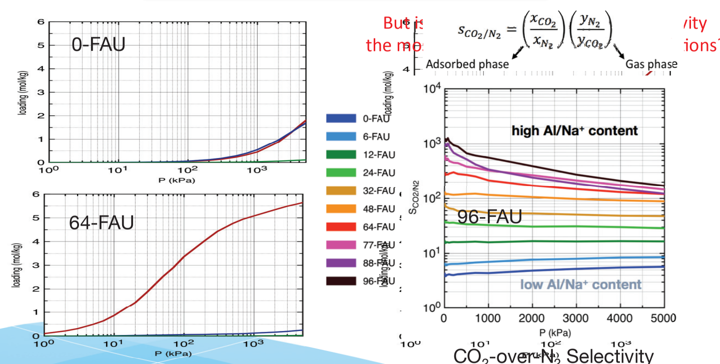
Pure gas adsorption isotherms



the quantity of N_2 and O_2 adsorbed does not depend strongly on the Si/Al ratio

Mixture results

15% CO_2 / 80% N_2 / 5% O_2 (T = 313 K)



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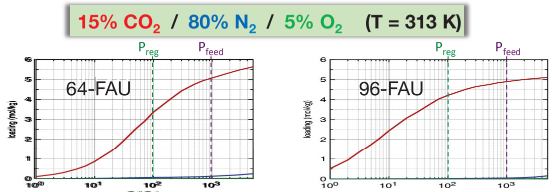
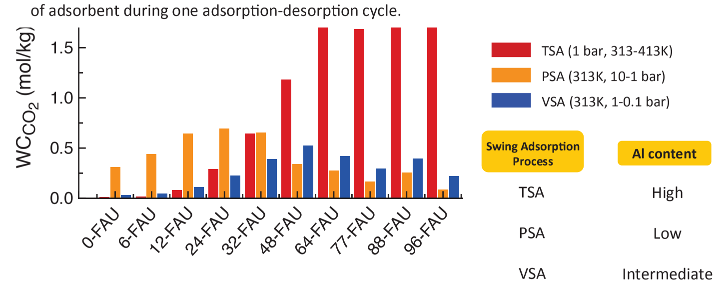


- The effectiveness for CO_2 capture and separation in FAU structures is highly dependent on the Al content **but also on the process conditions (feeding and regeneration pressure)**.
- FAU with **high Al or Na+ content** would adsorb **more CO_2 molecules** under adsorption conditions (*i.e.*, high pressure), but at the desorption step (*i.e.*, low pressure) the number of desorbed molecules will be lower, due to the **high isosteric heat** of adsorption.
- **Selectivity is not enough**, for a given operative conditions it is necessary to select the most suitable FAU.

Adsorbent evaluation criteria

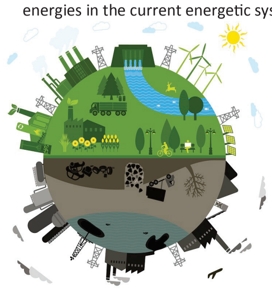
- **Working capacity** is the amount of CO_2 that can be expected to be captured by a specified amount of adsorbent during one adsorption-desorption cycle.



- There is no best structure. Instead, depending on the process and the operating conditions (*i.e.*, T_{ads}, T_{des}, P_{ads}, P_{des}) one or another structure should be chosen in order to maximize the WC.

Thermal Storage

Energy Storage systems are the key point for the introduction of renewable energies in the current energetic system.

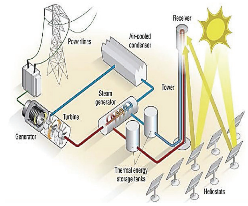


BBVA, momentum. Lorean Energy

Types of storage:

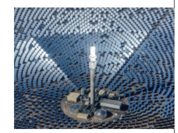
- Mecanic
- Electrochemical
- Thermal (sensible, latent, chemical)
- Chemical
- Electromagnetic

Concentrate Solar Power Stations



from General Electric

Solar Platform Extremadura (Spain) source: ABENGOA SOLAR



SandStone Plant Nevada (USA) source:PROTERMOSOLAR

The fluids used as thermal storage in Solar Power Stations are molten salts. Concretely, "solar salts":

40% sodium nitrate ($NaNO_3$)
+
60% potasium nitrate (KNO_3)

Why molten salts?

Requirements for a Material for Sensible Thermal Storage:

- High density
- High temperature of stability
- High energetic den
- High thermal cond
- Low thermal diffus
- High heat or therm

Contrarily to conventional thermal storage materials (i.e., paraffin, oils,...) molten salts present thermal stability at high temperatures.

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BUT NO MODEL IS VALIDATED FOR EXPLAINING THE ANOMALOUS EFFECT OF INCREASING THE THERMAL CAPACITY OF SOLAR SALTS.

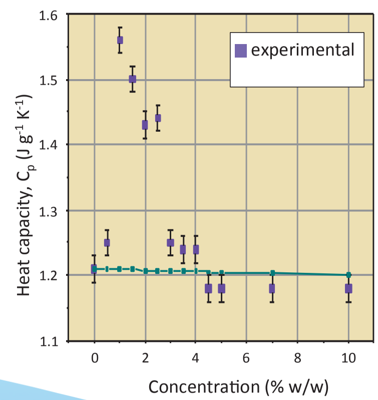
Moderate C_p values

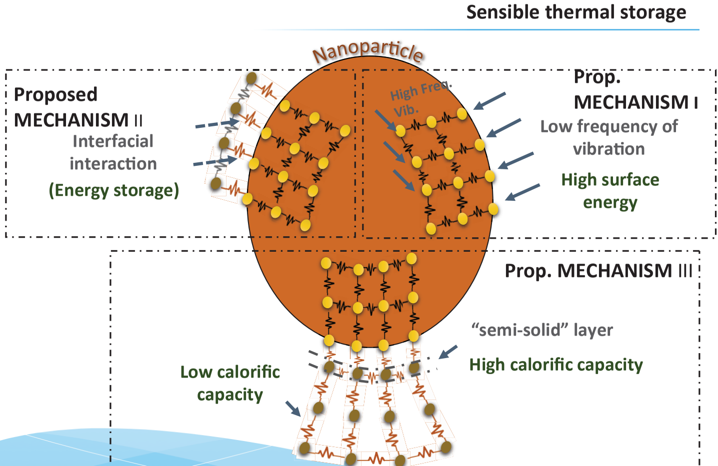
In the last years:

NANOFLUIDS → **Introduction of nanoparticles in molten salts systems** → Incresing Cp between 10-50% at low concentrations of nanoparticles.

Introducing Nanoparticles of SiO_2 in $NaNO_3$

Since the controversial among experimental results, we have performed the experimental calculations of C_p with nanoparticles of SiO_2 of 5-15 nm of diameter.





try to visualize these mechanisms with the help of molecular dynamics simulations

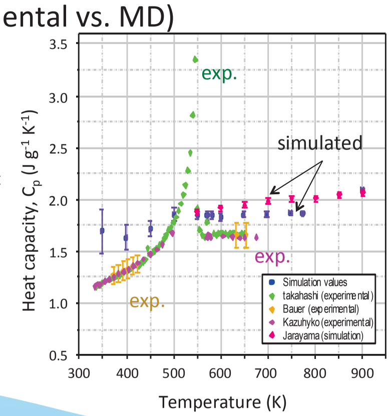
Thermal Capacity pure $NaNO_3$ (experimental vs. MD)

$$Q_{sensible} = \int_{T_1}^{T_2} C_p \cdot dT$$

Density values are also in close agreement with experimental results (3%), then validating the force field used.

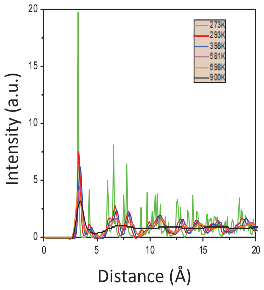
C_p (500°C) = 1.5 J g^{-1} K^{-1}

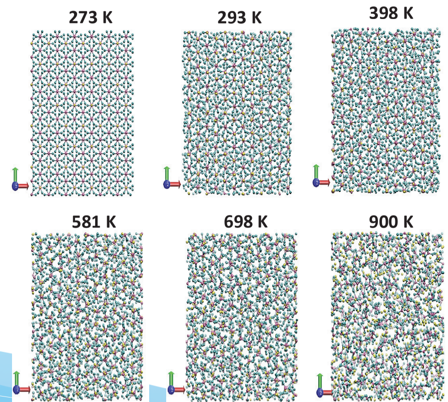
C_p (500°C) = 1.8 J g^{-1} K^{-1} (simulated)



Sensible thermal storage

Radial distribution pure $NaNO_3$

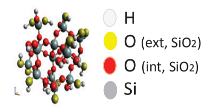




- Lost of crystalline order
- melting temperature range **[550-600]K**
  $T_{m,\ exp.}$=581K

Sensible thermal storage

Introducing Nanoparticles of SiO_2 in $NaNO_3$



1 nm of diameter in concentrations in the range **0 to 10%**

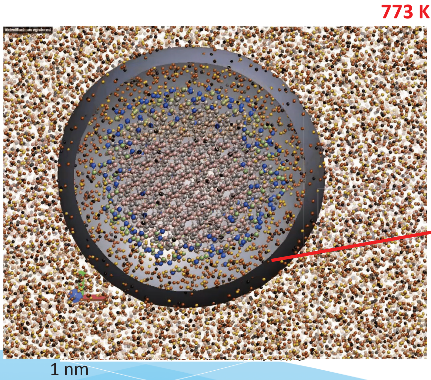
Nanoparticle concentration	Cp (ϕ=1nm)	Cp (ϕ=3nm)
(%)	$J g^{-1} K^{-1}$	
0.2	2.62	1.90
0.5	2.60	2.25
1	2.40	2.47
2	2.45	2.10
4	1.70	---
0	1.80	

The C_p value is reduced as nanoparticle size increases

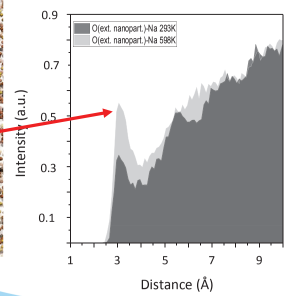
Sensible thermal storage

Introducing Nanoparticles of SiO_2 in $NaNO_3$

773 K



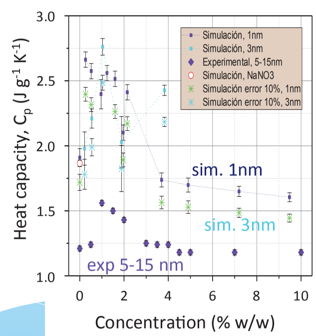
Semi-solid Layer of $NaNO_3$ around the nanoparticle: verifying the existence of Mechanism III.



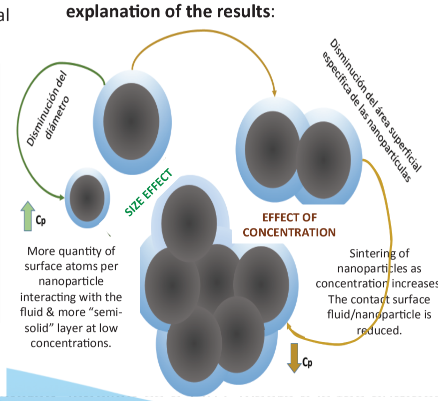
Sensible thermal storage

Introducing Nanoparticles of SiO_2 in $NaNO_3$

Comparison between experimental and simulated values.



explanation of the results:



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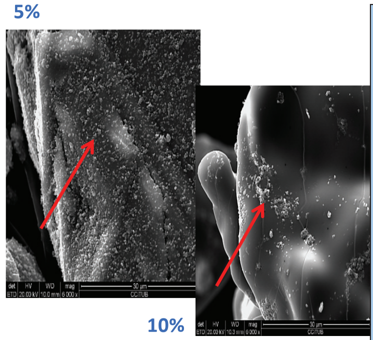

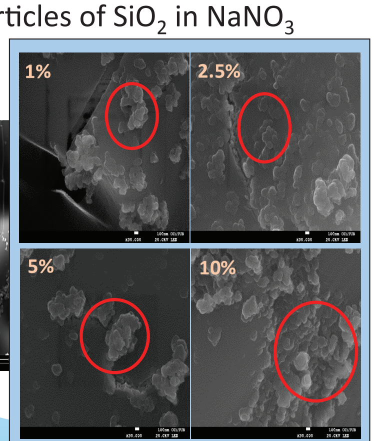

Conclusions

- ✓ Faujasite structures with different Al/Si ratio are more efficient for swing adsorption procedures.
- ✓ High Al content structures are optimum for TSA, medium content for VSA and low Al content for PSA.

- ✓ Concentration of nanoparticles plays a key role in the increase of thermal capacity in solar salts.
- ✓ All the molecular dynamics results obtained confirm the presence of the three mechanisms proposed.
- ✓ More studies are necesary for calculating the percentage of each mechanism in the overall effect.

Acknowledgements

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Ph.D. Students:
Adela Svobodova

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REPSOL

Generalitat de Catalunya

XRQTC Reference Network on Theoretical and Computational Chemistry