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Gas Hydrates : Properties and opportunities for The Energy Transition

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CRIANN Scientific Day

LCS Laboratoire Catalyse & Spectrochimie

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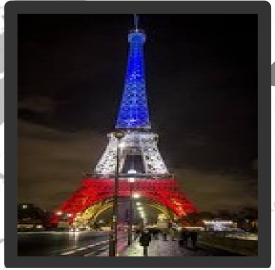
AMIChemE,SMAIChE,MSFGP and SCF

Texas A&M

R&D: Computational & Experimental studies.
Industry:

- **Gas Seperation**
- **Natural Gas Storage**
- **H_2 Storage**



H_2 and methane Storage R&D

R&D ,Different Gas and Petrochemical companies

R&D and QatarGas:Control 1/3 of LNG Exports worldwide and 2 very big GTL facilities.

Hydrate For Energy

Zeolites As A Solution

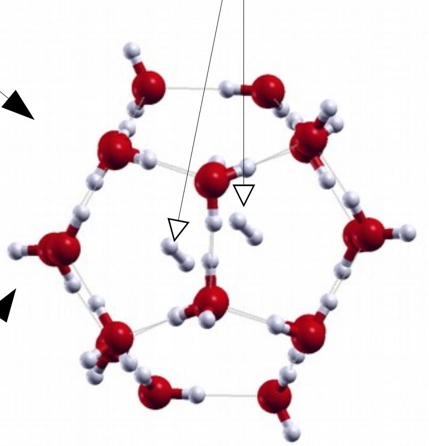
Gas molecules

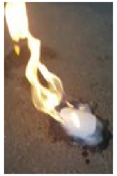
Guests (e.g. H_2)

(and/or)

Salts (e.g. QAS)

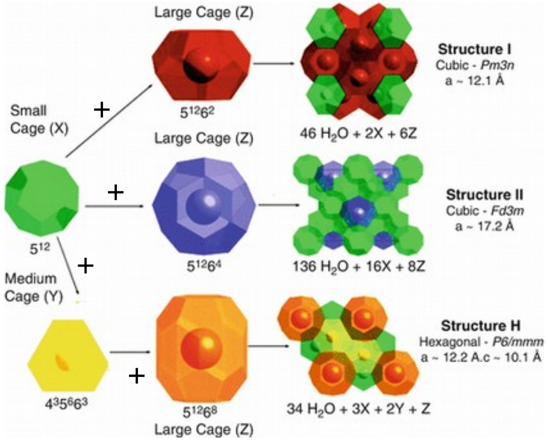
H-bonding
&
vdW forces



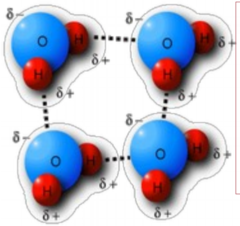


P-T conditions

Guest nature



Clathrate
Hydrates



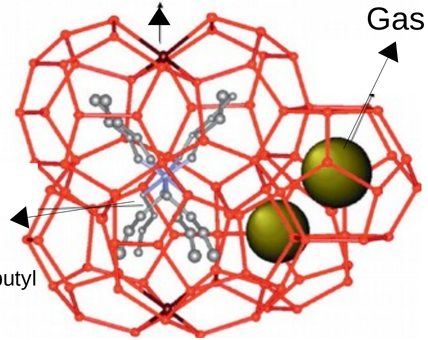
Host
Water

Challenges:

Slow kinetics, storage capacity and stability.

Br^-, F^-,..

Gas



TBA^+

TBA=*tetra*-n-butyl ammonium

Semiclathrates

1-T.A. Strobel *et al.*, **Chem. Phys. Letters** 478 (2009) 97–109
2-Tariq, M., *et al.* (2016). **Energy & Fuels**, 30(4), 2821-2832.

Beyond *vdW-Platteeuw* Model:

- Although one of the best applications of statistical thermodynamics, VdW-Platteeuw theory has its limitations

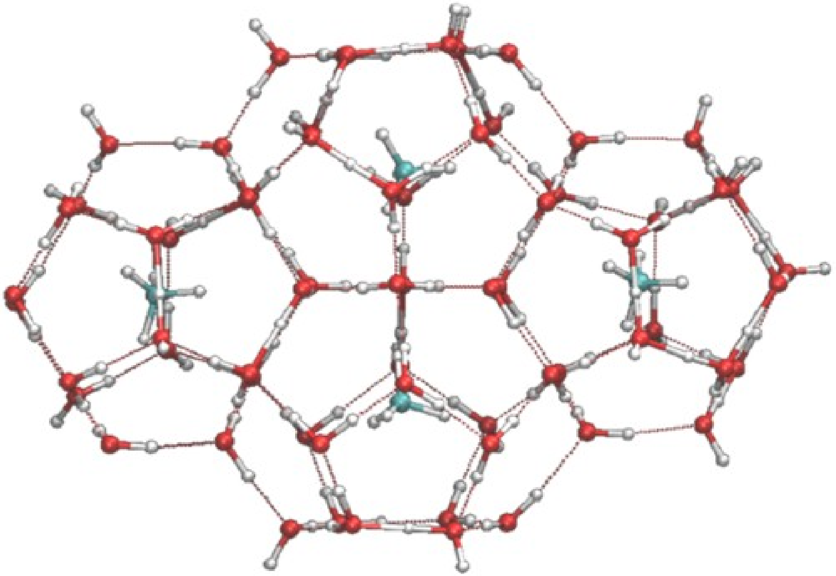
- Understanding the different molecular interactions and their effect on the stability and capacity gas hydrate and hydrate formation condition.

- 3 Main interactions:

  1) Guest-Host Interaction ($hilfsgase$).

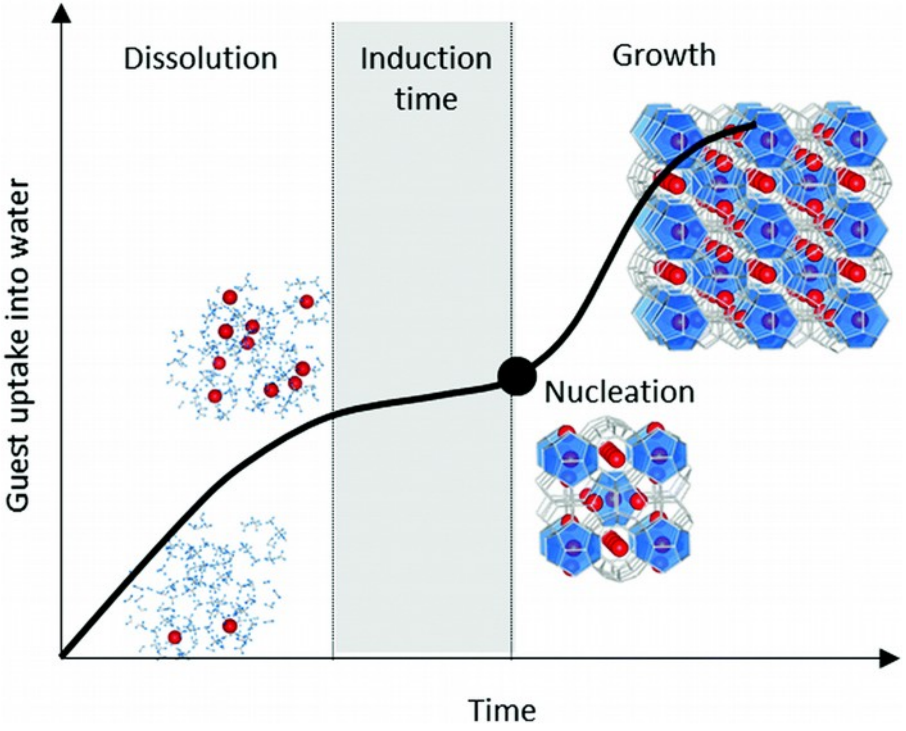
  2) Guest-guest Interactions.

  3) Host-Host Interaction.

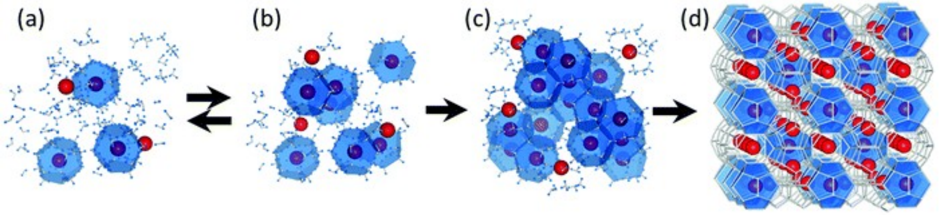


Tariq, M. et al. (2016). Energy & Fuels, 30(4), 2821-2832.

Microscopic Induction Time : Gas dissolution



KPIs* : Induction time, t_{90}, uptake and conversion

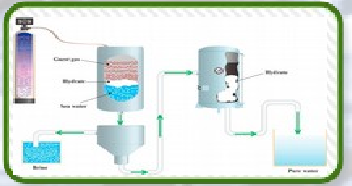


Labile-cluster model of hydrate nucleation: (a) labile-clusters, (b) agglomeration of clusters, (c) primary nucleolus, and (d) hydrate crystal

KPI*: key performance indicators

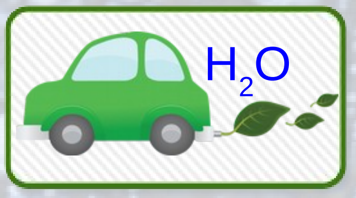
Hassanpouryouzband, A. *et al*(2020). **Chemical Society Reviews**, 49(15), 5225-5309.

Hydrate-Based Applications For Energy Transition



Desalination

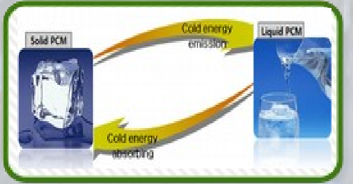
Hydrogen Storage



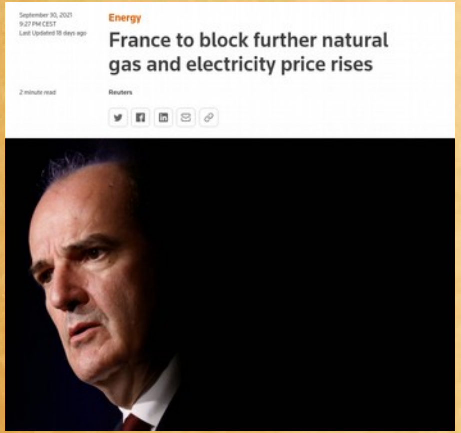
Solid Electrolytes for Fuel Cells

Methane Storage

Combined CCS and Energy Recovery



PCM for Cold Energy Storage



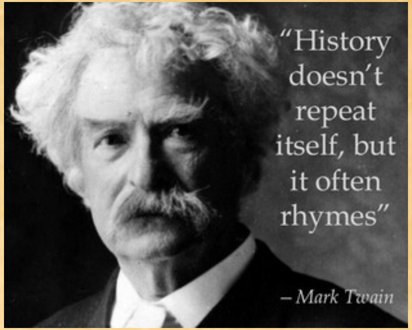
https://www.reuters.com/

Safe and long term Storage (CH_4, H_2, CO_2)?

Discrete gas resources (fuel gas, shale gas)?

Strategic Storage Plan!

Gas Crisis 2021



Energy Policy and Conservation Act of 1975 (EPCA)

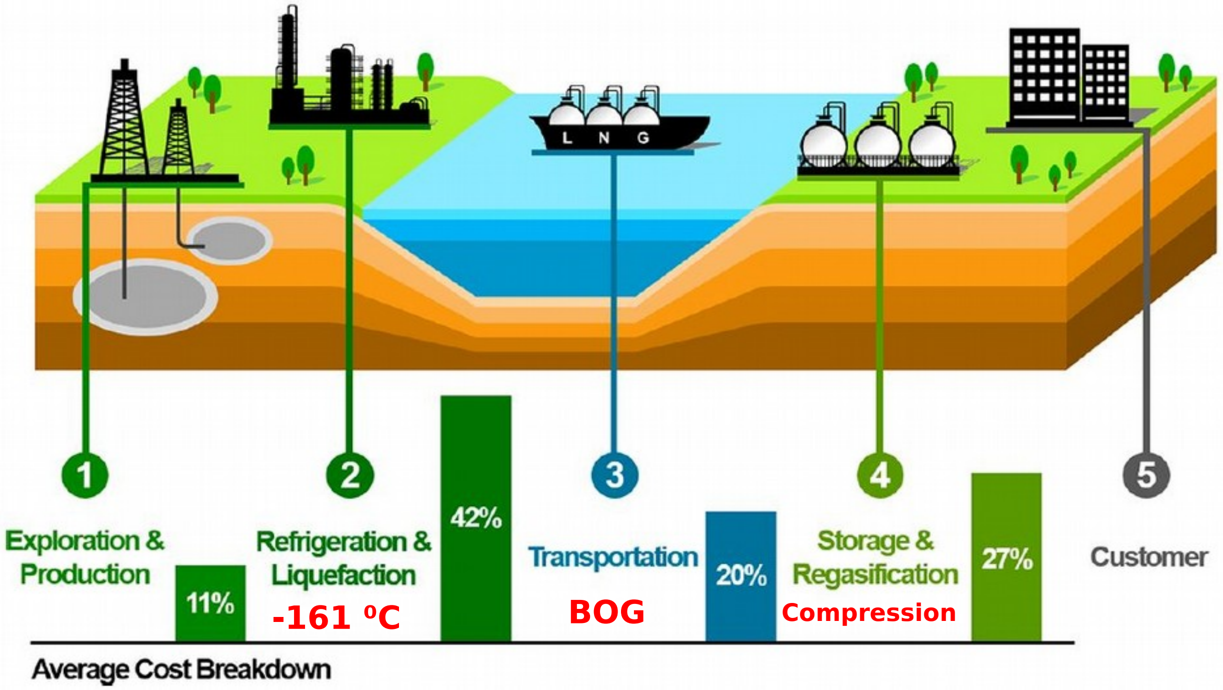
Storage!

https://www.cvce.eu/

Oil Crisis 1973

Methane Storage

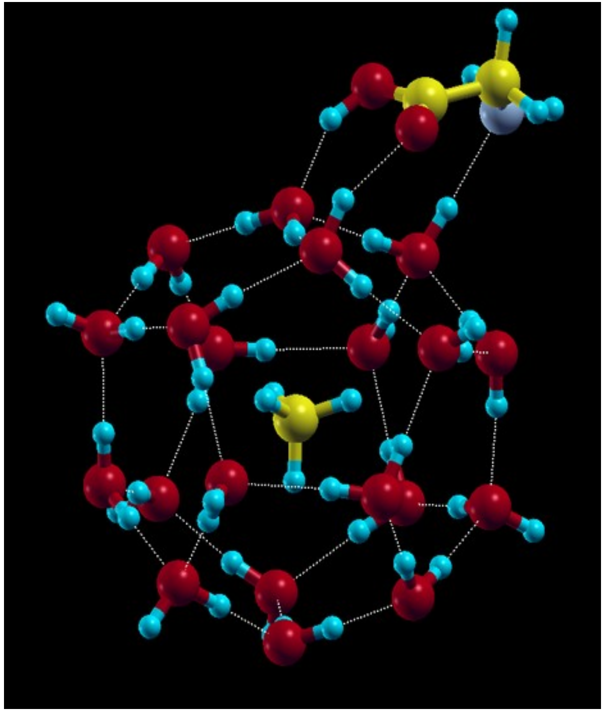
Energy Storage: SNG *vs* LNG



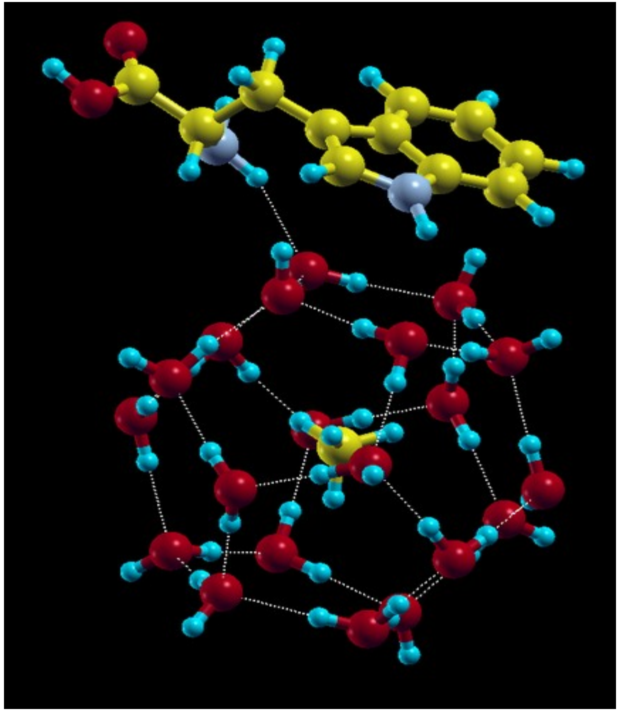
- LNG can reach 600 v/v but with extensive energy cost to achieve -161 **⁰C**[1].
- **SNG** plant has **almost half cost of LNG** one of the same capacity (CAPEX).
- Transportation and storage will require high compression power. **18-25% cost reduction is estimated in case of NGH transport[2].**

1-Lee, I. *et al.* (2017). Industrial & Engineering Chemistry Research, 57(17), 5805-5818.
2- Kanda, H. (2006, June). In *23rd world gas conference, Amsterdam*.

DFT Calculation of Interaction Energy and H-bonding:



Gly



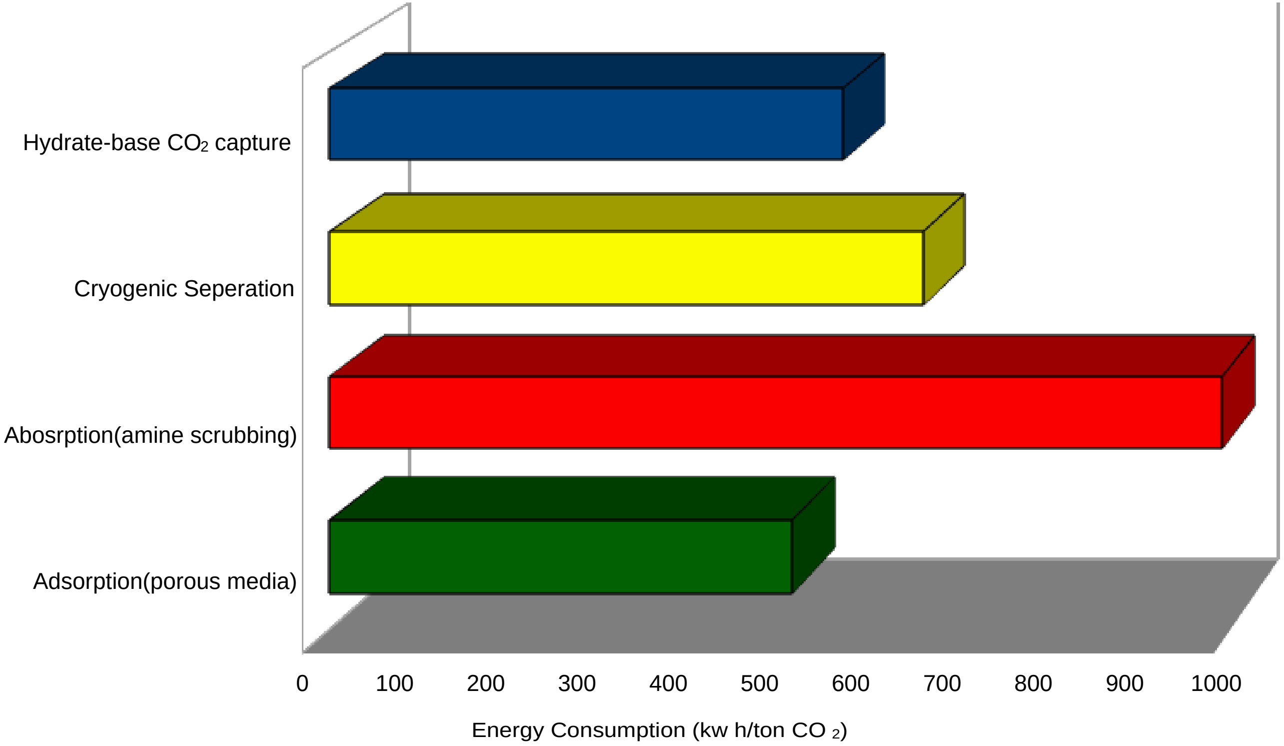
Try


CCS

Carbon Capture Technologies

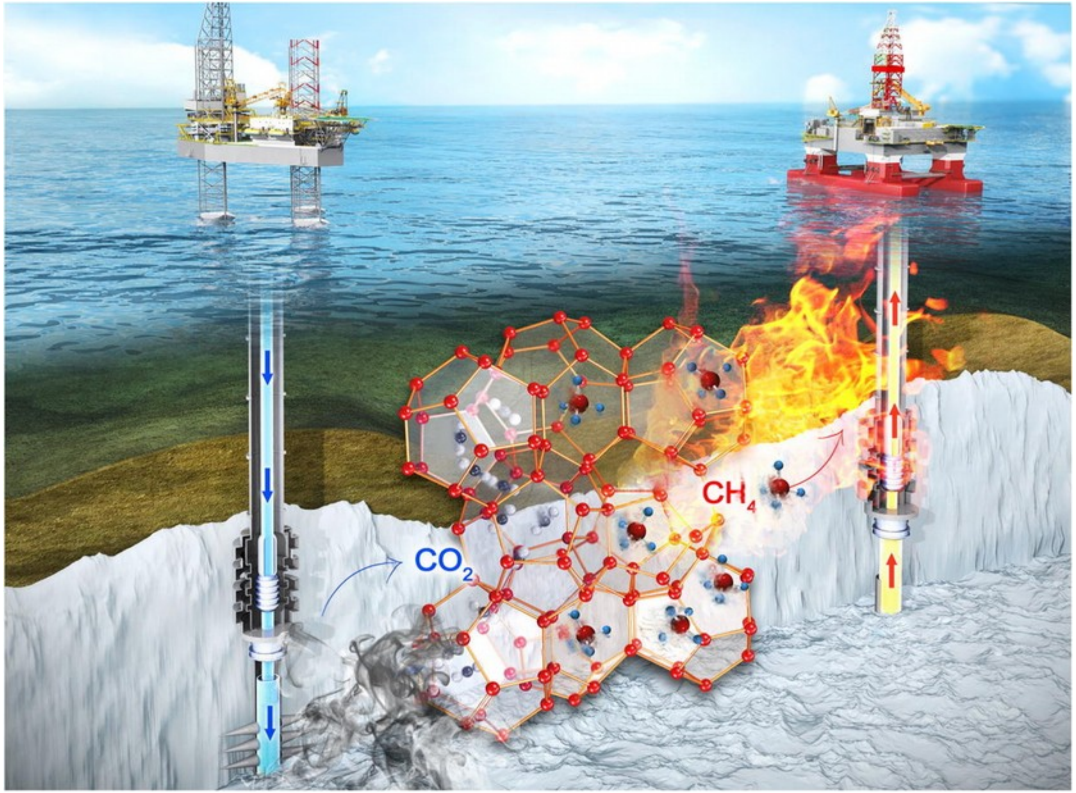
- Current capture technologies has its drawbacks.
- Membranes cost 24-48$ per ton.
- MOFs sustainability affected by impurities, humidity and pressure drop.
- Absorption is energy intensive

What about sequestration?



Yu, Y., ZHANG, X. W., Liu, J. W., Lee, Y., & Li, X. **(2021). Energy & Environmental Science.**

CH_4 Recovery - CO_2 Sequestration:



Energy-efficient natural gas hydrate production using gas exchange

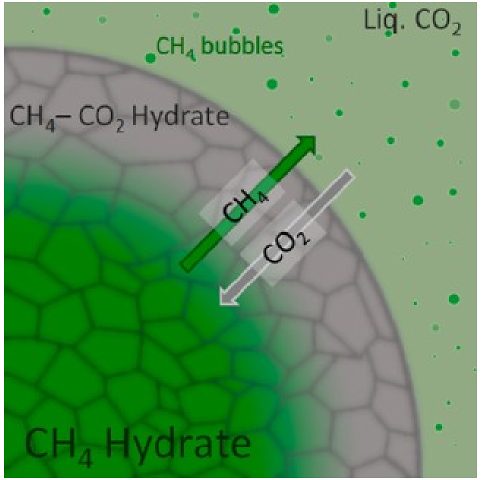
Maintain the geological structure.

-Practical, already applied in the USA (Alska) and reported in Japan and Canda.

Challenges:
Slow kinetics, storage capacity and replacement mechanism.

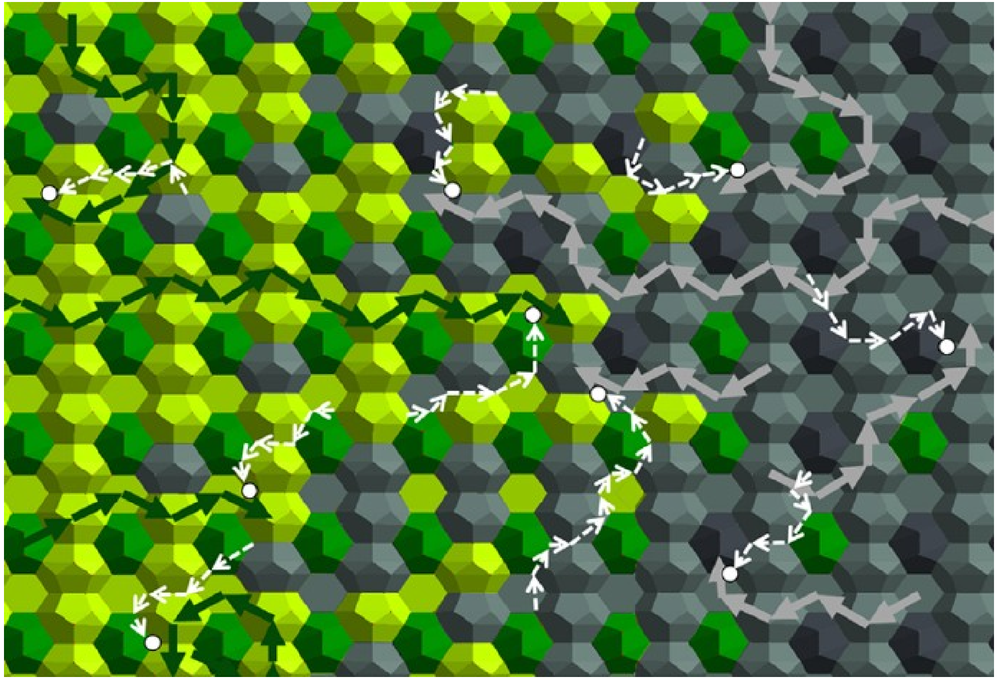
Mok, J., Choi, W., & Seo, Y. (2020). **Chemical Engineering Journal,** 389, 124434.

Hole-in-the-Cage Model



2 Steps (1)Fast Surface reaction followed by (2) **slow solid state diffusion.**

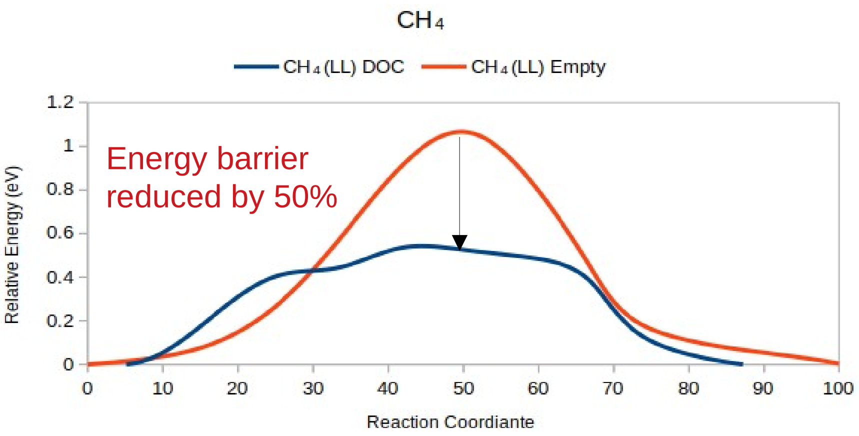
A water vacancy is needed for a successful jump of a guest molecule into a **neighboring (empty) cage.** The guest migration paths follow mostly connected LCs.

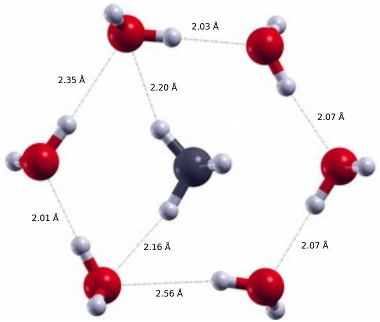


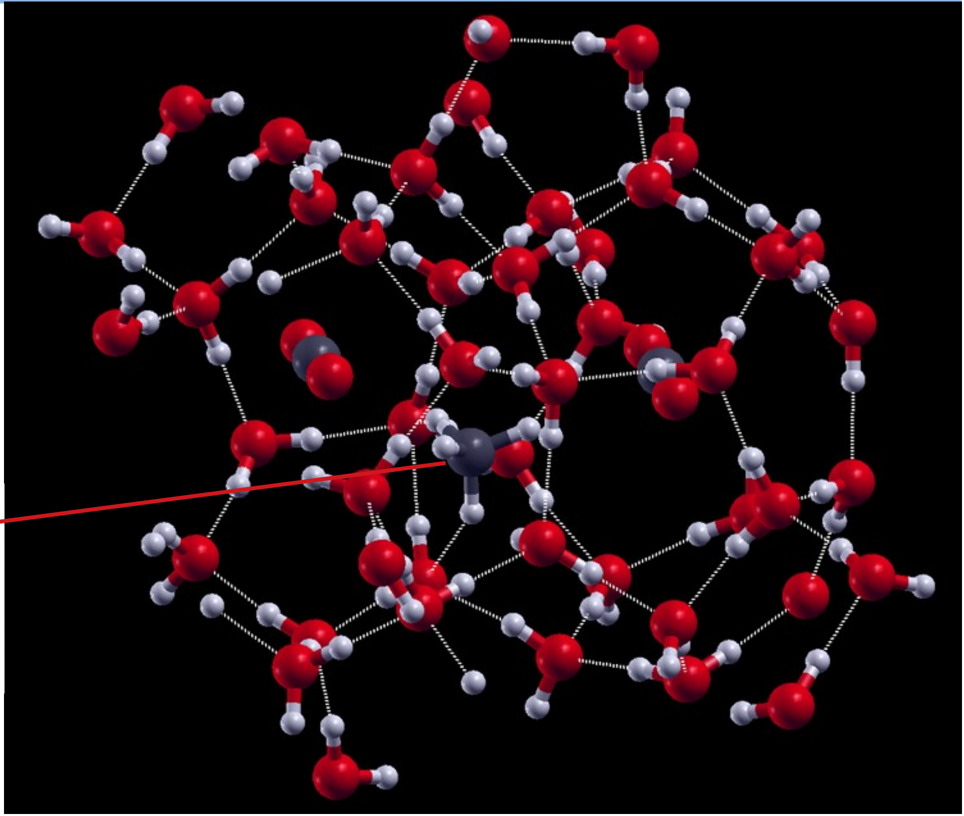
Water vacancies (white spheres and thin broken arrows)
CH_4- and CO_2-guest atoms (thick dark green and gray arrows)
Light gray (LCs) and dark gray (SCs).

A. N. Salamatin *et al* **J. Phys. Chem. C** 2017, 121, 17603−17616

CH_4 Recovery - CO_2 Sequestration







H_2 Storage

Targets: Blue Hydrogen Storage

- Check the thermodynamic stability of sI clathrate containing hydrogen.
- Possibility of double occupation of hydrogen with methane or is large cages.
- Evaluate the storage capacity of binary CH_4-H_2 compared to DOE targets.
- Study the diffusion of H_2 hopping between different cages that are either empty or pre-occupied by CH_4 or CO_2.

Hydrogen production from renewable and non-renewable is no longer problematic. It is the **safe storage** that represent the major challenge and bottleneck for sustainable hydrogen economy.

Can CH_4-H_2 system achieve the DOE target?

	H_2 wt%	kW.h/kg	kW.h/L
sII ($64H_2.136H_2O$)	5.3	1.8	1.5
sI ($10.H_2.6CH_4.46H_2O$)	**1.3**	**1.3**	**1.4**
sI ($6H_2.8CH_4.46H_2O$)	**0.5**	**0.9**	**0.9**
sI ($24H_2.2CH_4.46H_2O$)	**5.0**	**2.0**	**1.8**
2020 DOE target	4.5	1.5	1.0
2025 DOE target	5.5	1.8	1.3
Ultimate DOE target	6.5	2.2	1.7

CH_4-H_2 system could achieve compromise and achieve current and future DOE hydrogen storage targets...

- As mentioned, only 6% CH_4 of are required to stabilize sI as per thermodynamic modeling.
- As per our calculation CH_4 preferably occupy the small cages leaving the large cages to be stabilized by hydrogen.
- CH_4 can be controlled through formation conditions or using templates.

Conclusion:

- ✓ Gas Hydrate can play a central role in energy transition and can be easily integrated with existing technologies.
- ✓ Methane Hydrate represent a good opportunity for long term and large scale natural gas storage that can allow market stability and medium and long term.
- ✓ Amino acids and acidic zeolites are effective and environmental friendly kinetic hydrate promoters.
- ✓ Ab initio calculations can be **powerful tool** to determine clathrate hydrates properties.
- ✓ It is necessary to choose the proper correlation functional that approximately **accounts for dispersion interactions.**
- ✓ CO_2-CH_4 replacement mechanism goes through double occupation mechanism rather than cage-in-the-hole scenario.
- ✓ H_2 can be accommodated the large cage of sI along with CO_2 or CH_4 resulting in storage capacity of **5.00 wt%** of molecular hydrogen**. However,** the gravimetric and volumetric capacities are **2.0** kW.h/kg and **1.8** kW.h/L, respectively. This makes that system a **promising material to fulfill DOE target or large and safe storage** .

LCS

Industrial Chair (ANR-TotalEnergies)

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PROJET FINANCÉ PAR L'ANR - PROJECT FUNDED BY THE ANR

Porous nano-catalysts
for a cleaner energy & materials transition

Acknowledgment

CRIANN

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Questions?

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