



Catalysis by Zeolites

The role of hydrogen bonding and entropy

Shashikant Kadam, Arnaud Travert

Laboratoire Catalyse et Spectrochimie
University of Caen, France

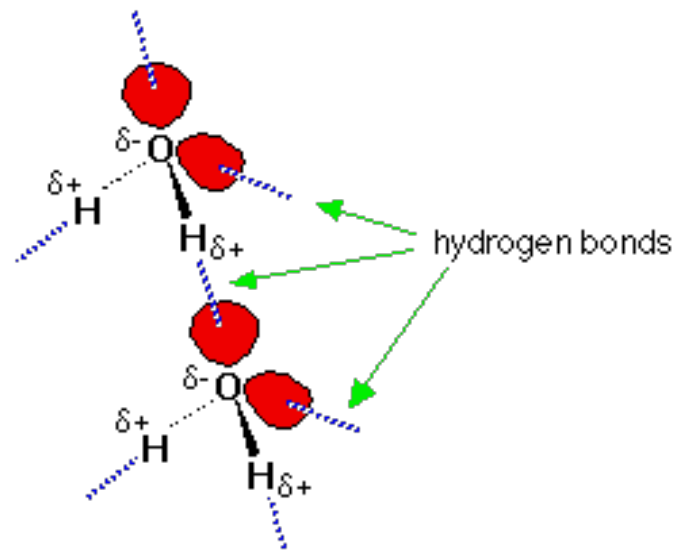
shashikant.kadam@ensicaen.fr





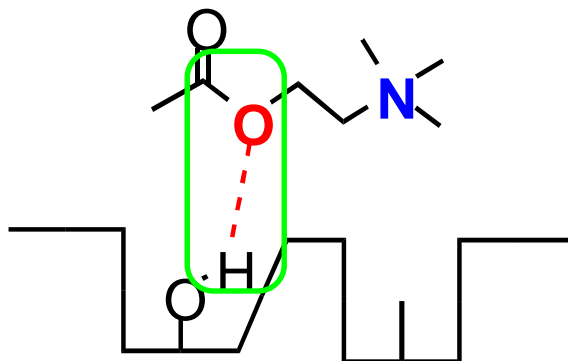
The Hydrogen Bond

A weak chemical bond in which a hydrogen atom of one molecule is attracted to an electronegative atom such as oxygen, nitrogen, or fluorine atom of another molecule.



Eg. Hydrogen bonding in water

Hydrogen bond in catalysis



The action of a **Neurotransmitter** is a result of Hydrogen bond

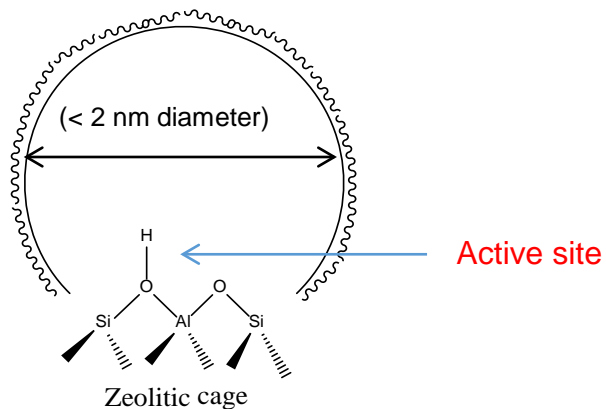
Enzymes

- Most complex catalytic system
- Presence of different active sites
- Speed up chemical reactions
- Catalyst to over 4000 biochemical reactions!

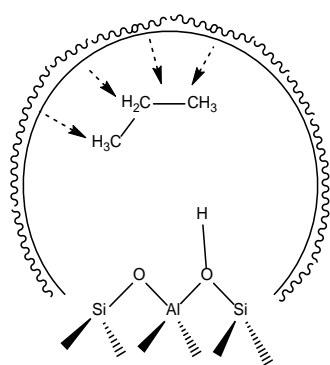
Difficult to mimic the enzymatic actions artificially !

Zeolites : The wonder materials

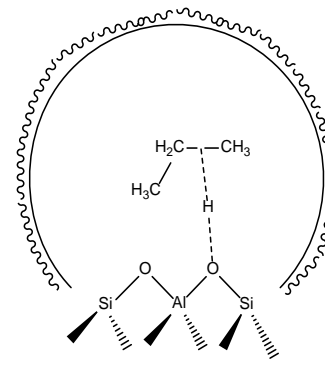
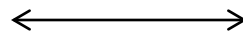
<http://www.chemtube3d.com/solidstate/SS-Z-Faujasite.htm>



Two dimensional representation of zeolite framework with active site



Pure van der Waals interaction
"Molecules are mobile"

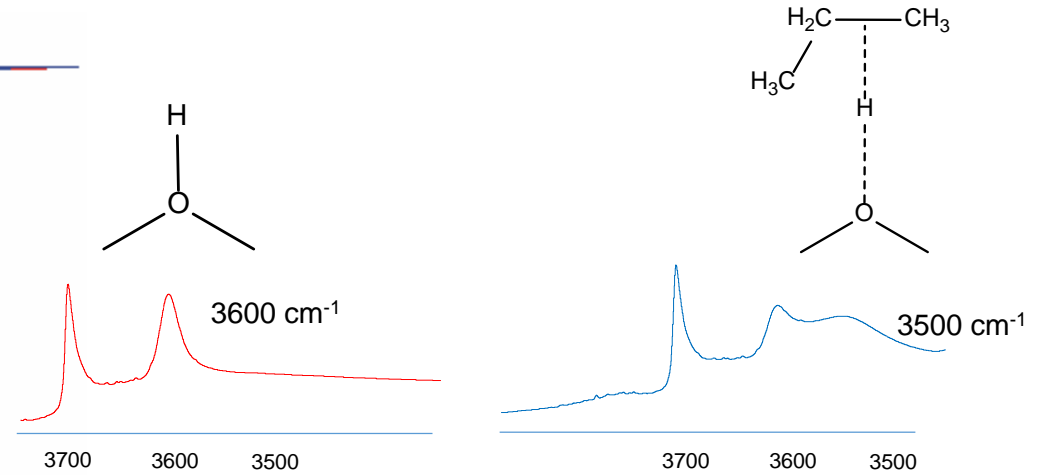
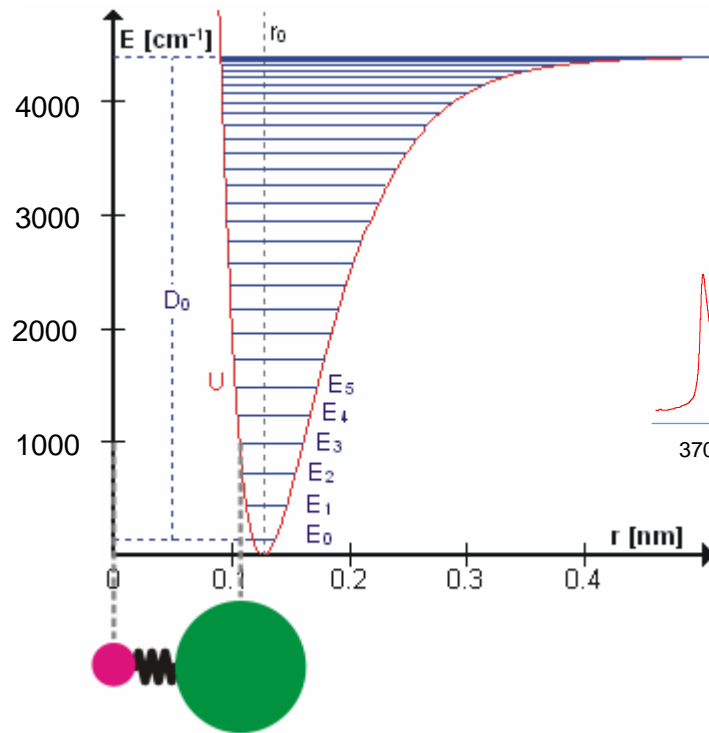


Hydrogen bond formation
"Restricted mobility"



How can we observe this hydrogen bond in zeolite?

O-H bond vibration

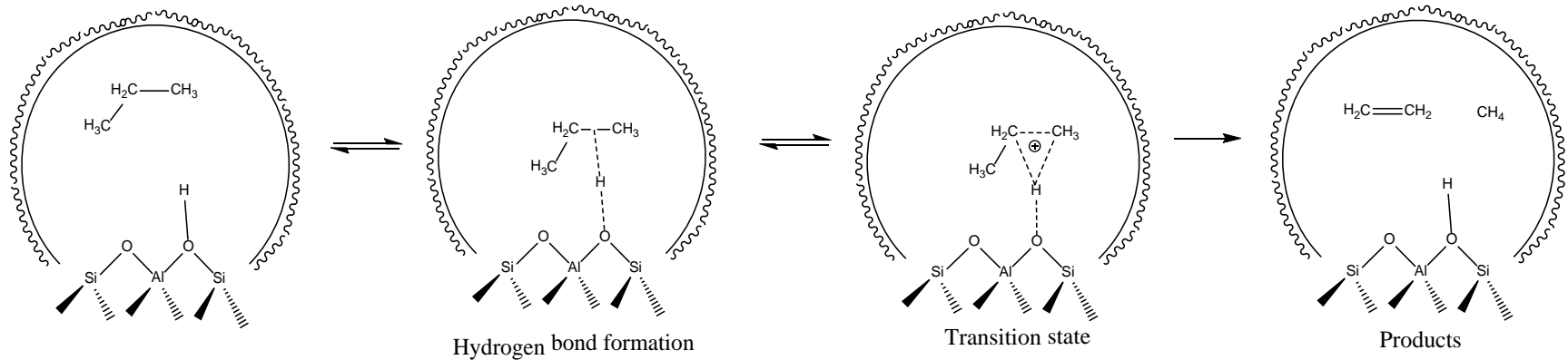


Shift in frequency due to hydrogen bond formation

By IR Spectroscopy

https://en.wikipedia.org/wiki/Molecular_vibration#/media/File:Anharmonic_oscillator.gif

Why do we study these zeolites ?



Catalytic cracking : Very important industrial reaction to produce chemicals and fuels

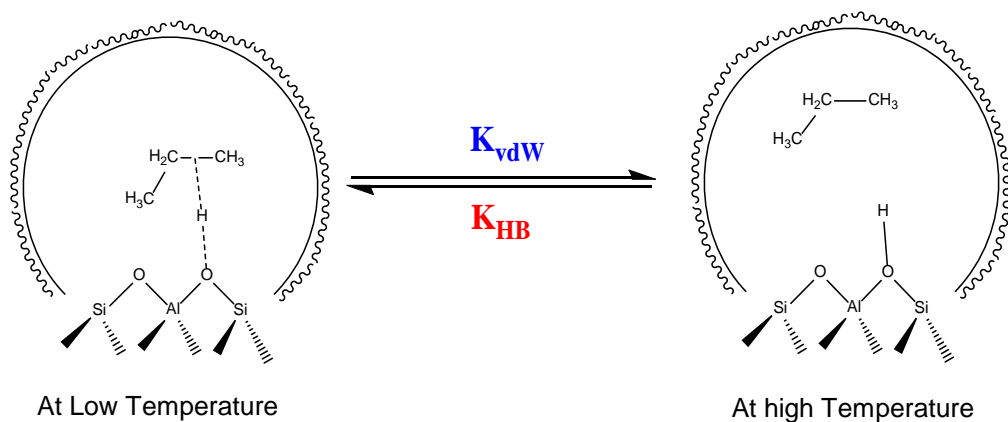
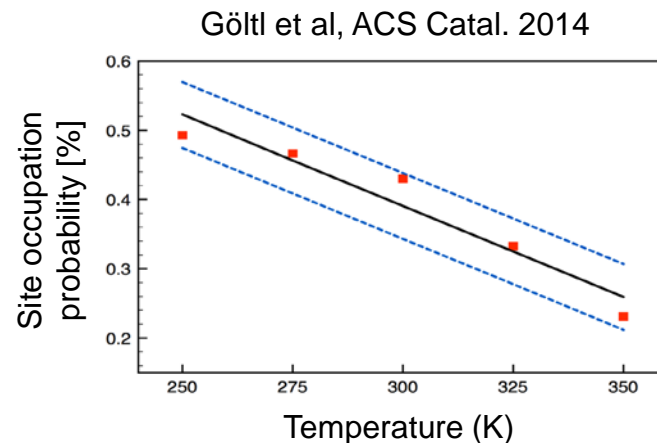
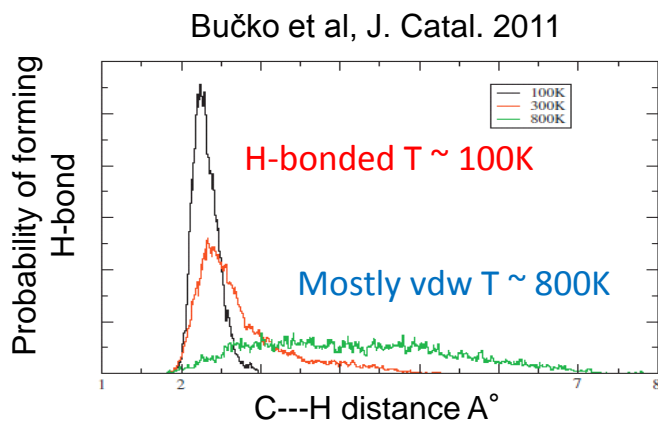
Aim of the thesis

1. To develop fundamental understanding of this zeolite catalyzed reaction
2. To find the factors influencing the reaction
3. To solve the discrepancy between theory and experiment
4. To understand the effect of zeolite structures
5. To find the suitable mechanism of the reaction
6. Apply this mechanistic approach to understand other zeolite catalyzed reactions
7. Apply this understanding to develop enhanced zeolite-based catalysts

Computational predictions

1. Moore et al, Phys. Chem. Chem. Phys. 2009
2. Swisher et al, J. Phys. Chem. C 2010
3. Bučko et al, J. Phys. Condens. Matter 2010
4. Bučko et al, J. Catal. 2011
5. Moore et al, J. Phys. Chem. C 2011

6. Tranca et al, J. Phys. Chem. C 2012
7. Zimmerman et al, J. Am. Chem. Soc. 2012
8. Sharda et al, J. Phys. Chem. C 2013
9. Göttl et al, ACS Catalysis 2014
10. Lercher, J. Phys. Chem. C 2015

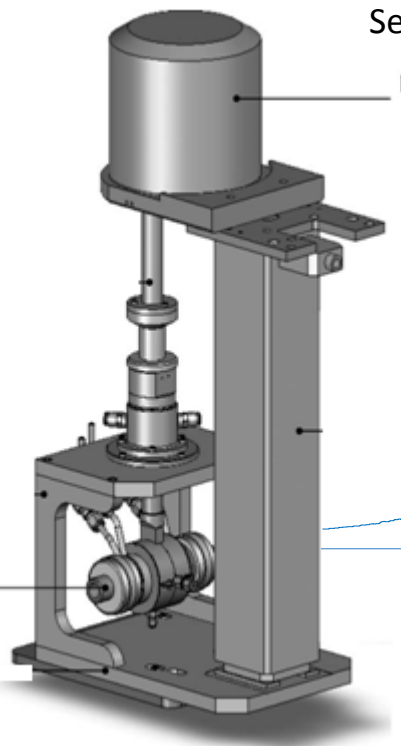


Temperature effect on H-bonding

But NO experimental study is available!

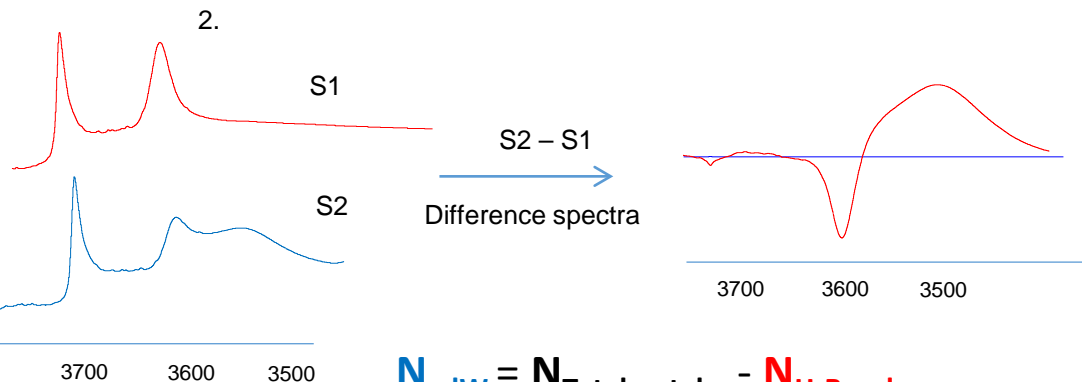


Analysis by Gravimetry and IR Spectroscopy (AGIR) (Unique experimental approach)



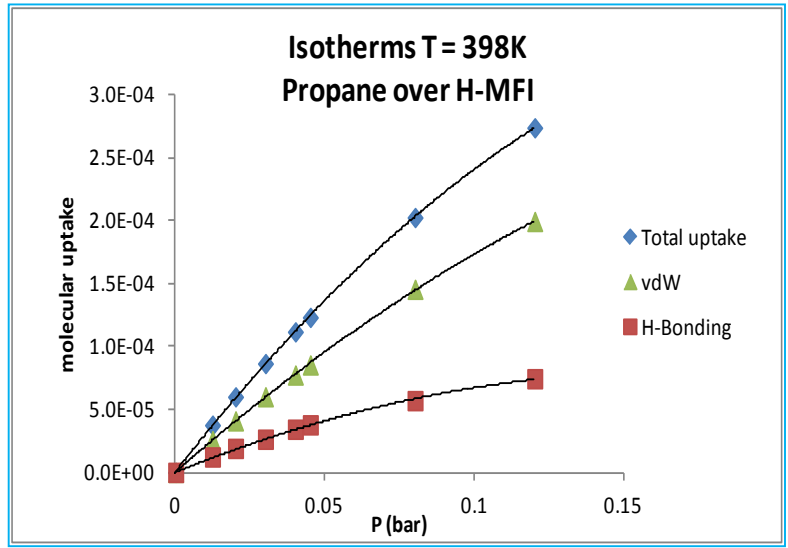
Setaram Gravimetric microbalance

1. Measures the mass of all molecules inside zeolite cage
(van der Waals + H-Bonding)

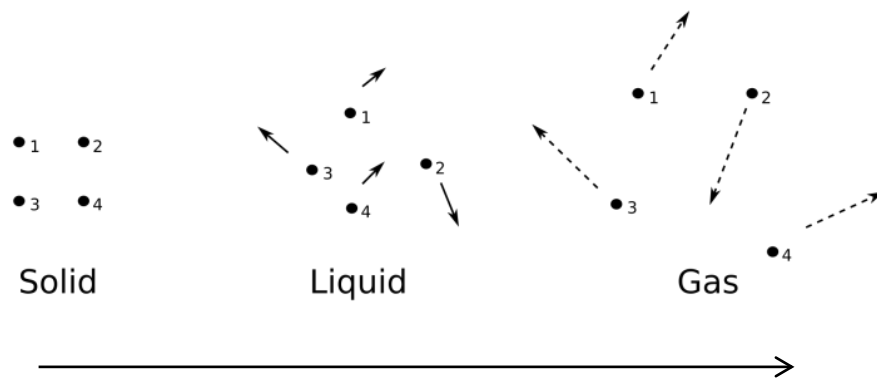


$$N_{vdW} = N_{\text{Total uptake}} - N_{\text{H-Bond}}$$

The AGIR system.

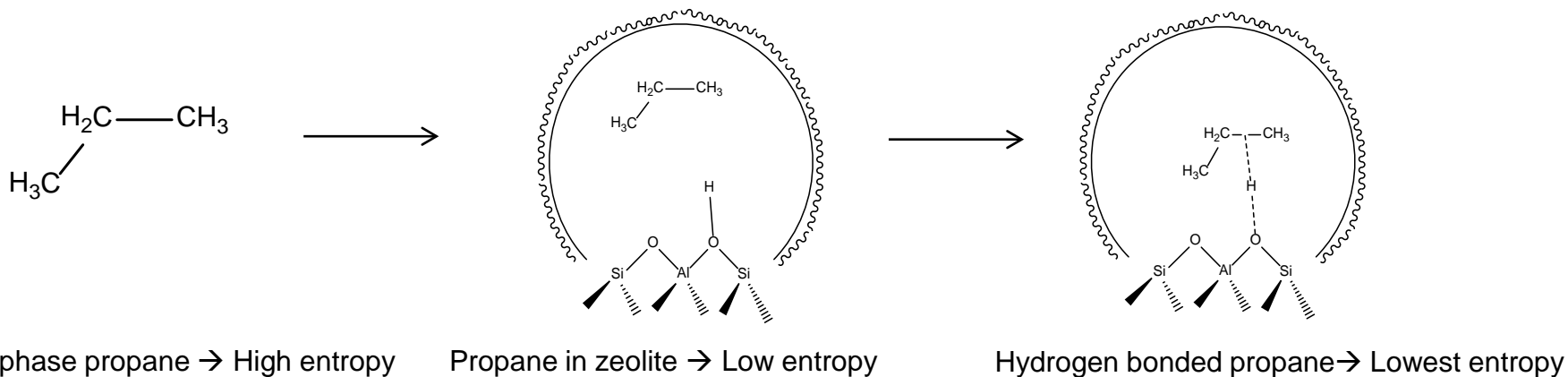


Molecular Entropy



Increase in disorder from solid state to gaseous state

Increase in entropy from solid state to gaseous state





Does temperature really affects the hydrogen bonding ?

Using **IR spectroscopy** we capture **hydrogen bonded** molecules at **LOW** (398K) and **HIGH** temperature (773K)

Alkanes	Zeolite	Hydrogen bonded Entropy	
		At Low T 398 K	At High T 773K
Propane	H-MFI	-92 (2)	-91 (3)
Propane	H-FER	-112 (3)	-111 (4)
n-Pentane	H-MFI	-117 (3)	-118 (3)
n-Hexane	H-MFI	-139 (2)	-138 (3)

No Effect of Temperature on Hydrogen Bonding !



Conclusions

- Zeolites are important catalysts which can react like enzymes
- The formation of hydrogen bond is the KEY step
- Temperature has no effect on hydrogen bonding
- The loss in entropy due to hydrogen bond formation helps to form selective transition state during reaction

Discriminating weak interactions of alkanes in zeolites (vdW vs. H-Bonding)

Shashikant Kadam,^a Haoguang Li,^a Richard F. Wormsbecher^{Ab*} and Arnaud Travert^{a*}

^a Laboratoire Catalyse et Spectrochimie, Université de Caen – ENSICAEN – CNRS, 6, Bd du Maréchal Juin, 14050 Caen, France
^b Department of Chemistry and Biochemistry, University of Maryland Baltimore County, MD, 21250 USA
^c W. R. Grace and Co., Columbia, MD 21044 USA
 * arnaud.travert@ensicaen.fr

Introduction

• Adsorption of alkanes in zeolite: Two energetically different states

Heat of adsorption (Low T = 200K)

Heat of adsorption (High T = 300K)

Energy

Reaction Coordinate

• ΔH_{ads} depends on:

- Alkane chain size
- Zeolite pore dimensions

• H-Bonding independent of:

- Alkane chain size
- Zeolite pore dimensions

• $\Delta H_{ads} \approx -10 \text{ kJ mol}^{-1}$

Results

• Discriminating vdW and H-Bonding:

A) Isotherms

B) van't Hoff plots

C) Adsorption parameters

Alkanes	Zeolite	ΔH_{vdW}	$\Delta H_{H-bonding}$	ΔS_{vdW}	$\Delta S_{H-bonding}$
Propane	H-MFI	44 (1)	-33 (1)	97 (2)	-75 (1)
Propane	H-FER	-53 (1)	-112 (1)	105 (2)	-
n-Pentane	H-MFI	-66 (2)	-54 (2)	-117 (1)	-94 (1)
n-Hexane	H-MFI	-83 (1)	-66 (1)	143 (2)	-114(1)

D) Significant differences in theory and experiments I

Temperature dependence: $\Delta H_{vdW} = -38 \text{ kJ mol}^{-1}$, $\Delta S_{vdW} = -40 \text{ J K}^{-1} \text{ mol}^{-1}$

Temperature independence: $\Delta H_{H-bonding} = -45 \text{ kJ mol}^{-1}$, $\Delta S_{H-bonding} = -103 \text{ J K}^{-1} \text{ mol}^{-1}$

Our Approach: AGIR (Analysis by Gravimetry and InfraRed spectroscopy)

General view of the AGIR system. (Bazin et al Dalton Trans., 2020, 39, 8432-8436)

Enthalpy-Entropy compensation effect: H-Bonding vs. vdW

• A very good correlation is obtained for compensation effect due to hydrogen bonding
 • Compensation effect in zeolites is an intrinsic property of H-Bonding like enzymes!

Conclusions

- Two weak interactions of alkanes within zeolites (vdW and H bonding) are experimentally discriminated for the first time
- Adsorption parameters (ΔH_{ads} and ΔS_{ads}) were determined for both interactions
- Negligible influence of temperature on hydrogen bonding
- Strong compensation effect is observed for n bonded molecules compared to vdW
- Hydrogen bonded molecules may be considered as immobile adsorbate

To learn more

Please visit my poster !

Thank you !!