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

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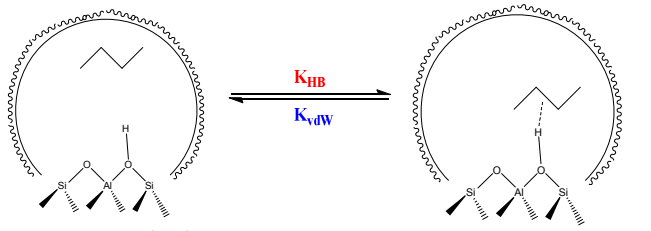
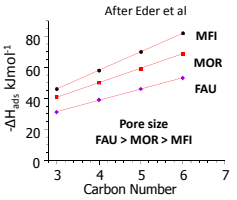
Introduction

• **Adsorption of alkanes in zeolite :** Two energetically different states



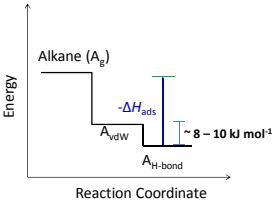
Heat of adsorption (Low T ~ 300K)



• vdW Depends on
- Alkane chain size
- Zeolite pore dimensions

• H-Bonding Independent of
- Alkane chain size
- Zeolite pore dimensions

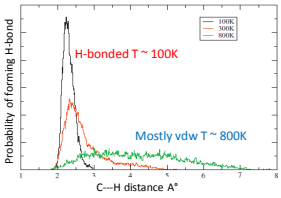
Energetics of alkane adsorption in zeolites



• **Effect of temperature on two adsorbed states:**

A] Adsorption parameters depend on temperature: State-of-art simulations

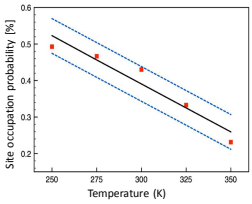
Bučko et al, J. Catal 2011



Tranca et al, J. Phys. Chem. C 2012

Carbon Number	K_{ads} [773K] (Monte Carlo Model)
3	4.02
4	4.87
5	6.00
6	7.61

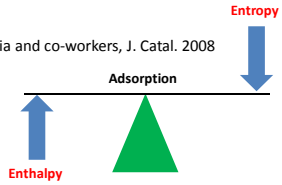
Göltl et al, ACS Catal. 2014



B] Adsorption parameters independent of temperature: Assumption in experiments

Enthalpy - Entropy compensation effect

Iglesia and co-workers, J. Catal. 2008



High temperature extrapolation

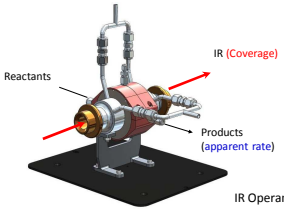
Carbon Number	Extrapolated K_{ads} (773K)
3	0.0055
4	0.0051
5	0.0046
6	0.0046

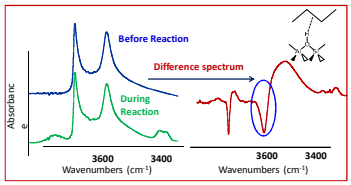
C] Significant differences in theory and experiments !

Temperature dependence	Temperature independence
ΔH_{ads} = -38 kJ mol^{-1}	ΔH_{ads} = -45 kJ mol^{-1}
ΔS_{ads} = -40 J K^{-1} mol^{-1}	ΔS_{ads} = -103 J K^{-1} mol^{-1}

No Experiments to prove this assumption !

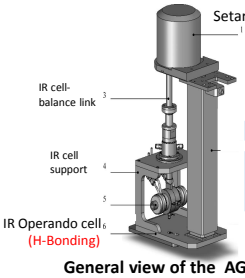
Our Approach : Operando Spectroscopy





Determination of coverage at high temperature (750K)

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



Setaram Gravimetric microbalance B Setsys

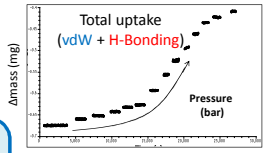
Total uptake
(van der Waals + H-Bonding)

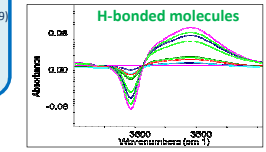
Reactants : Propane, n-Pentane and n-Hexane

Catalyst : H-MFI (Si/Al = 29) and H-FER (Si/Al = 9)

Experimental conditions :
T = 398 – 473K
P = 0.0002 – 0.32 bar

General view of the AGIR system.
(Bazin et al *Dalton Trans., 2010, 39, 8432–8436)*





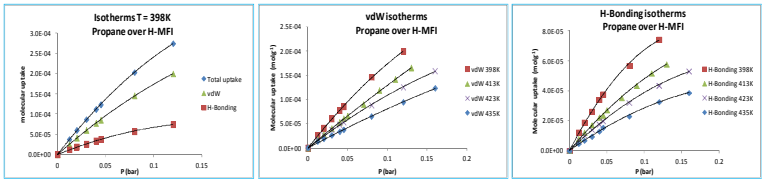
$N_{vdW} = N_{total\ uptake} - N_{H\text{-}bonded}$

Results

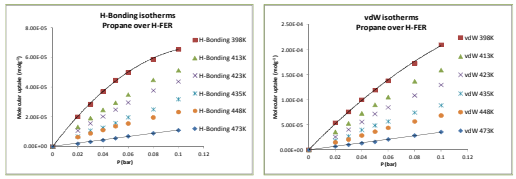
• **Discriminating vdW and H-Bonding:**

A] Isotherms

- Propane over H-MFI

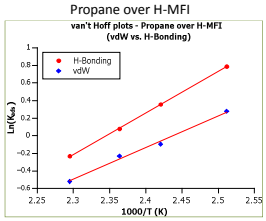


- Propane over H-FER

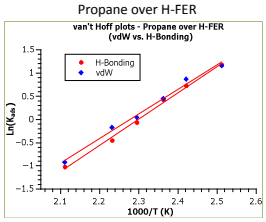


B] van't Hoff plots

Propane over H-MFI



Propane over H-FER

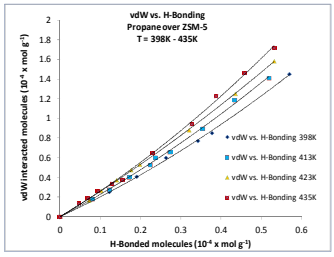


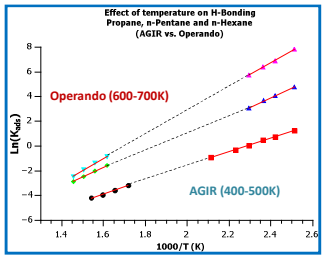
C] Adsorption parameters

Alkanes	Zeolite	ΔH_{ads} AGIR H-Bonding	ΔH_{ads} Operando (HB-750K)	ΔH_{ads} AGIR vdW	ΔS_{ads} AGIR H-Bonding	ΔS_{ads} Operando (HB-750K)	ΔS_{ads} AGIR vdW
Propane	H-MFI	-43 (1)	-39 (2)	-33 (1)	-97 (2)	-91 (3)	-75 (1)
Propane	H-FER	-52 (1)	-49 (2)	-46 (1)	-112 (3)	-111 (4)	105 (2)
n-Pentane	H-MFI	-66 (2)	-66 (2)	-54 (2)	-117 (3)	-119 (3)	-94 (3)
n-Hexane	H-MFI	-83 (1)	-81 (2)	-66 (1)	-143 (2)	-138 (3)	-114(1)

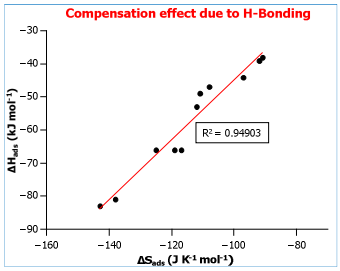
ΔH_{ads} and ΔS_{ads} in kJ mol^{-1} and J K^{-1} mol^{-1}. Standard errors are reported in parenthesis

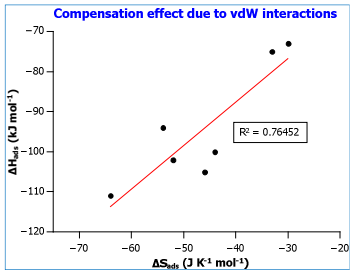
• **Effect of temperature on two adsorbed states: AGIR Approach**





• **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

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