Insights into Adsorption of Linear, Monobranched, and Dibranched Alkanes on Pure Silica STW Zeolite as a Promising Material for Their Separation

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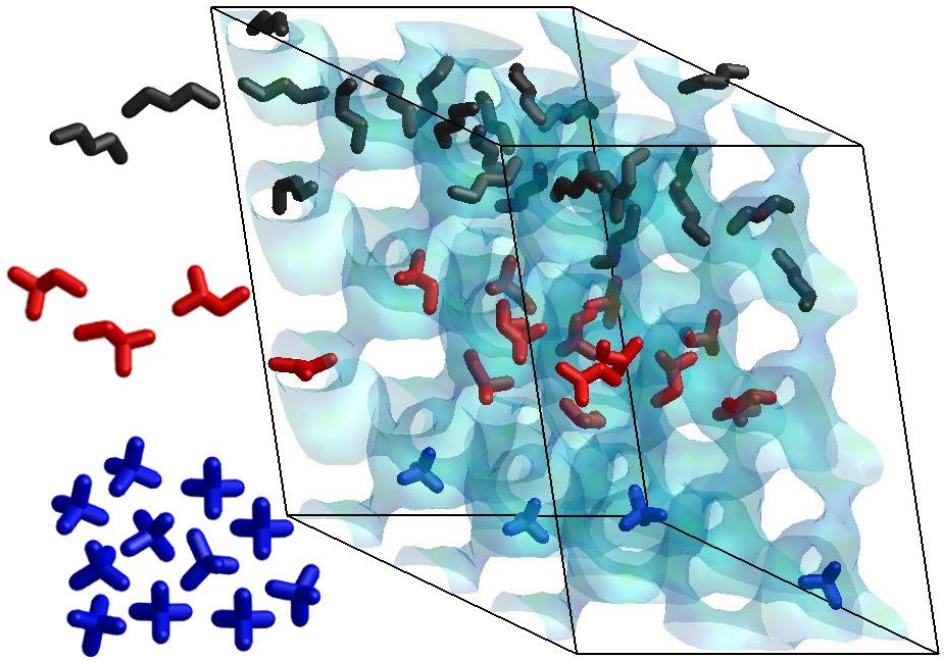
EXCELENCIA SEVERO OCHOA

Outline

- Introduction
  - Gasoline
  - Zeolites
  - Adsorptive separation of hydrocarbons
- Objectives
- Methods
- Results and discussion
- Conclusions



Introduction: Gasoline

- C4 - C12 (contains 4 to 12 carbon atoms)
- Octane number (ON) ≈100
  - branched
  - unsaturated
  - aromatics
- Hydroisomerization of straight run naphta

linear → multibranched + monobranched + linear

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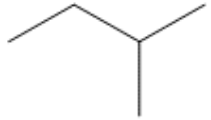
linear → multibranched + monobranched + linear

C5

npentane, n-C5
RON = 61.8, MON = 63.2

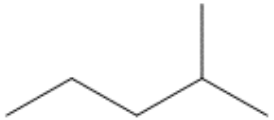


2-methylbutane, 2MB
RON = 93.0, MON = 89.7

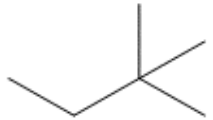
2,2-dimethylpropane, 22DMPr
RON = 85.5, MON = 80.2

C6

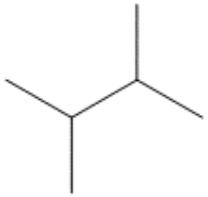
n-hexane, nC6
RON = 24.8, MON = 26.0



2-methylpentane, 2MPe
RON = 73.4, MON = 73.5



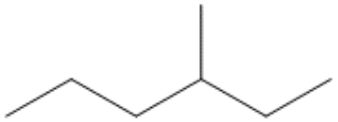
2,2-dimethylbutane, 22DMB
RON = 91.8, MON = 93.4



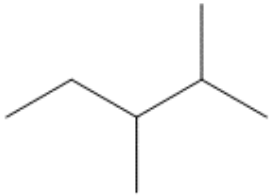
2,3-dimethylbutane, 23DMB
RON = 104.3, MON = 94.2

C7

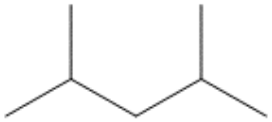
n-heptane, nC7
RON = 0, MON = 0



3-methylhexane, 3MH
RON = 52.0, MON = 55.0



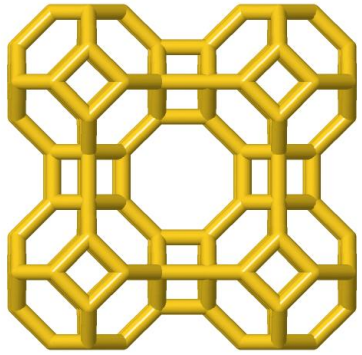
2,3-dimethylpentane, 23DMPe
RON = 91.1, MON = 88.5



2,4-dimethylpentane, 24DMPe
RON = 83.1, MON = 83.8

Introduction: Adsorptive separation of hydrocarbons using zeolites

- Zeolite 5A (LTA) → separation of linear from branched



- Zeolites ZSM-5, silicalite-1 (MFI) and others[1] → separation of mono- and multibranched

We propose a different adsorbent, i.e. Si-STW

[1]Recent Patents on Chemical Engineering, 2012, 5, 153-173

silicalite-1 = Si-MFI

Objectives

- Adsorption of C5-C7 hydrocarbons on Si-STW
  - Thermodynamics
  - Kinetics
- Comparison with Si-MFI
- Experimental and computational work

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Methods

- Adsorption **isotherms 10-60 ºC** and **kinetics 25 ºC**, vapor phase
  - C5, 300 mbar
  - C6, 150 mbar
  - C7, 50 mbar

- **CBMC simulations → adsorption isotherms, enthalpy of adsorption**

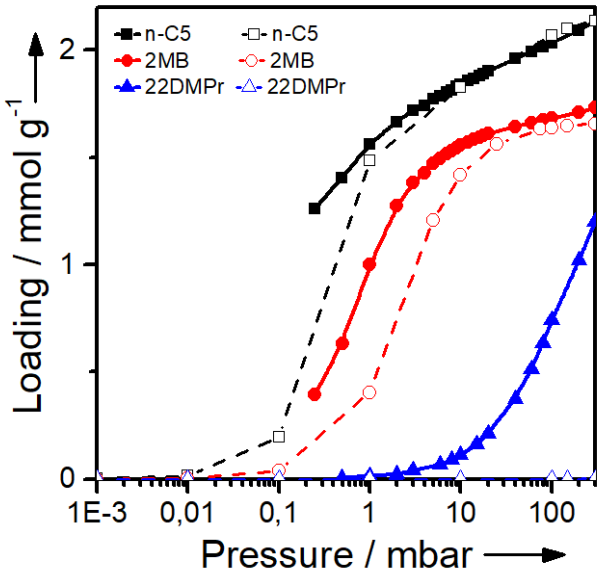
- **MD simulations → mean square displacement**

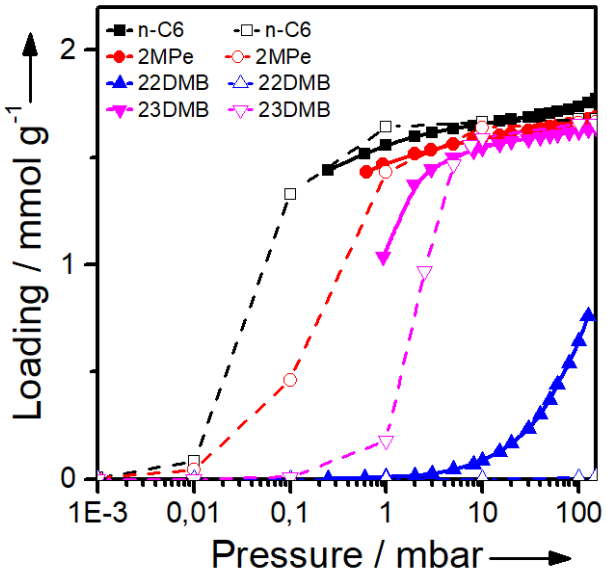
***thermodynamics**
***kinetics**

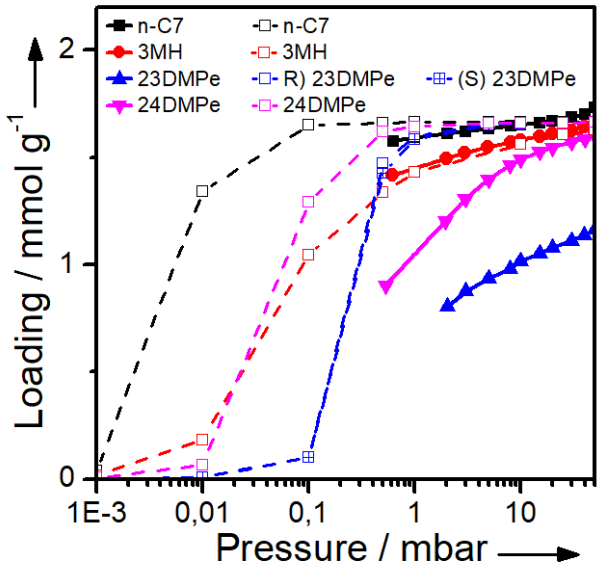
Results and Discussion

Adsorption Isotherms

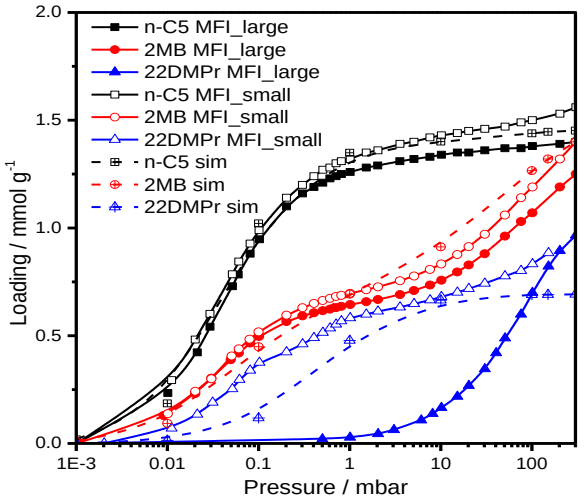
Si-STW







Si-MFI

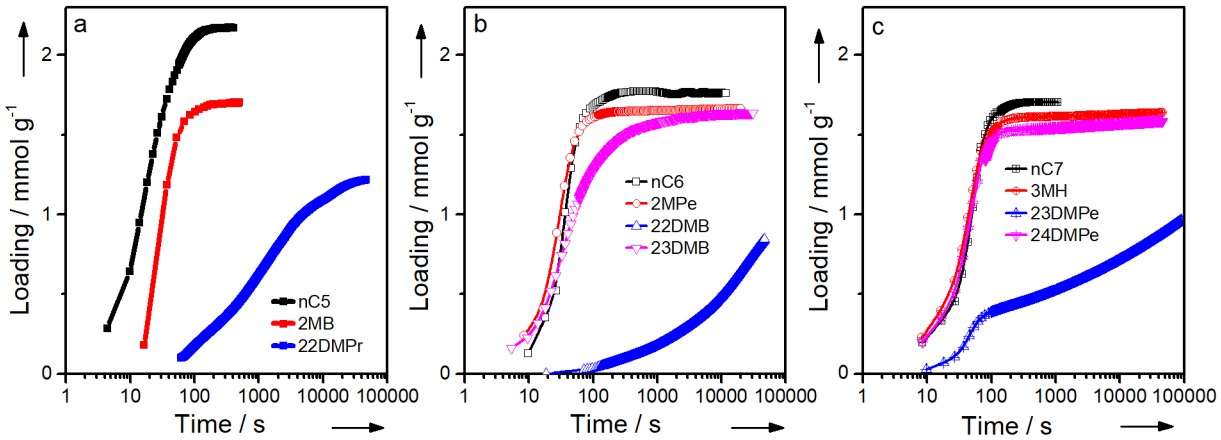


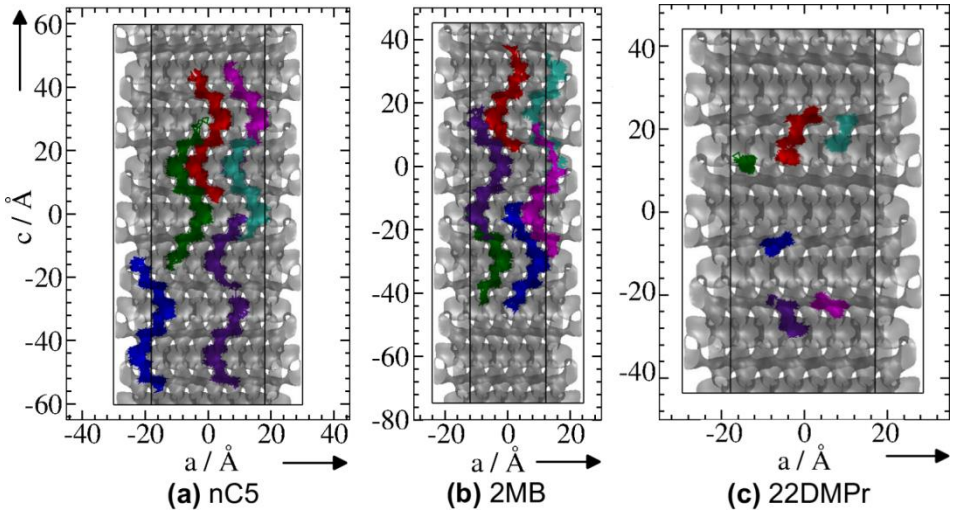
- Larger maximum capacity in Si-STW
- Exp and Sim match for Si-MFI, not as much for Si-STW
- Hydrocarbons with quaternary carbons present kinetic hindrances in both zeolites (more in Si-STW)
- Kinetic hindrances are larger for samples with larger crystals

Adsorption Kinetics in Si-STW

"High" pressure

C5, 300 mbar | C6, 150 mbar | C7, 50 mbar





- Linear and monobranched isomers diffuse fast
- Dibranched isomers diffuse slower
  - Quaternary carbons → diffuse very slowly
  - Relative position of the side chains → the closer, slower the diffusion
- MD simulations predict the same results (only C5 shown)

Kinetic Selectivity in Si-STW and Si-MFI

Si-STW

	Compounds	Kinetic selectivity at higher pressure
C5	nC5/22DMPr	135
	2MB/22DMPr	88
C6	nC6/22DMB	586
	2MP/22DMB	759
	23DMB/22DMB	328
C7	nC7/23DMPe	567
	3MH/23DMPe	600
	24DMPe/23DMPe	600

Si-MFI large crystals

Compounds	Kinetic selectivity at 300 mbar
nC5/22DMPr	78
2MB/22DMPr	36

Si-MFI small crystals

Compounds	Kinetic selectivity at 300 mbar
nC5/22DMPr	43
2MB/22DMPr	41

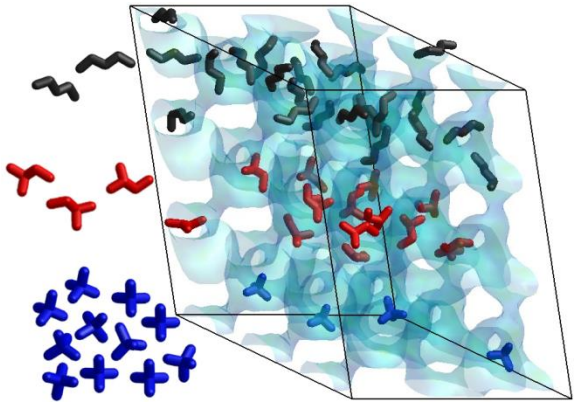
Conclusions

- Si-STW:

linear ≈ monobranched > n,m-dibranched >> n,n-dibranched

- Si-STW presents similar thermodynamic selectivities and superior kinetic selectivities to Si-MFI, as well as a larger adsorption capacity

- Further work: dynamic mixture experiments, improving CBMC force field



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Thanks for your attention!

Any questions?

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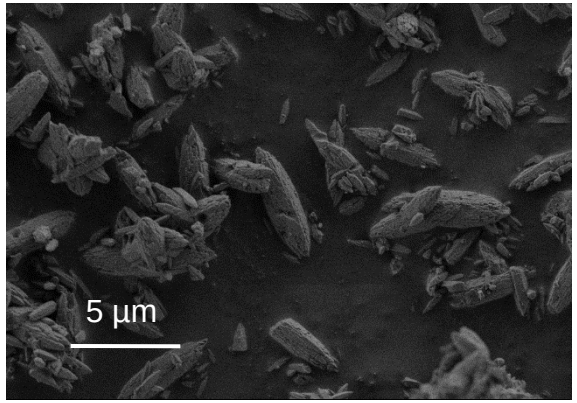
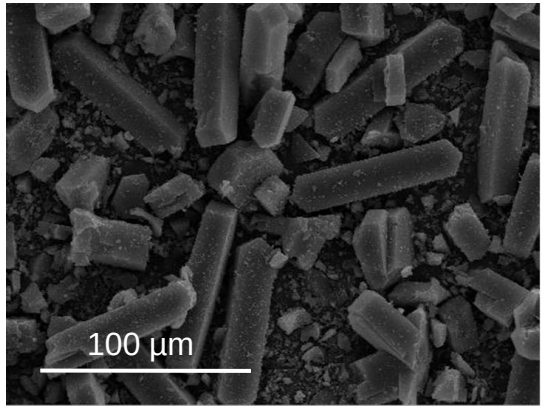
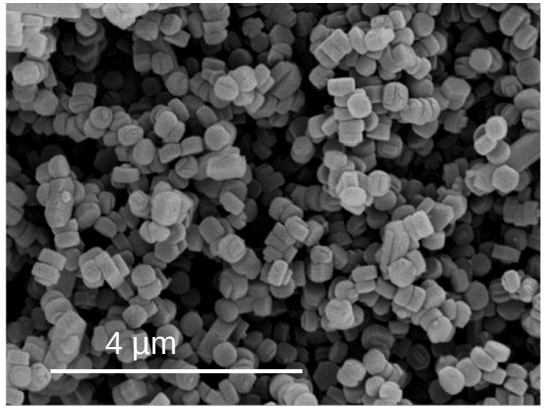
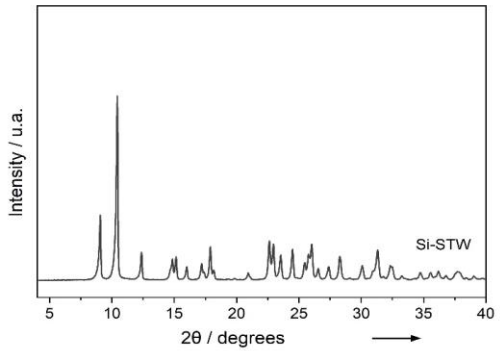
Si-STW

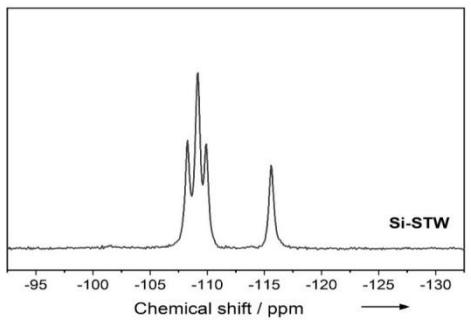


Si-MFI

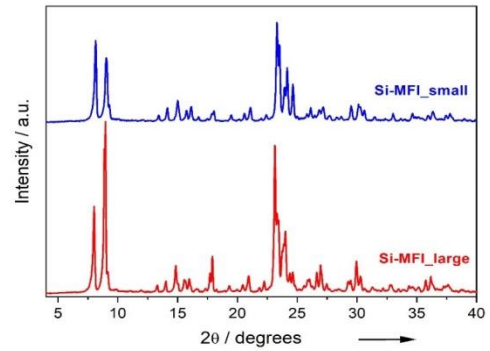


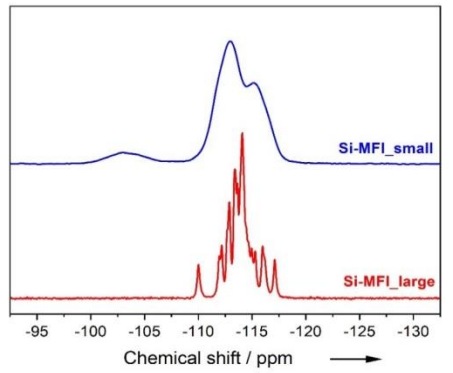






Sample	BET surface area (m^2/g)	Micropore volume (cm^3/g)	Average pore size (Å)	Approximate crystal size (µm)
Si-STW	630	0.24	5.3	0.5 - 5
Si-MFI_large	386	0.17	5.1	5 - 100
Si_MFI_small	451	0.18	5.1	0.5

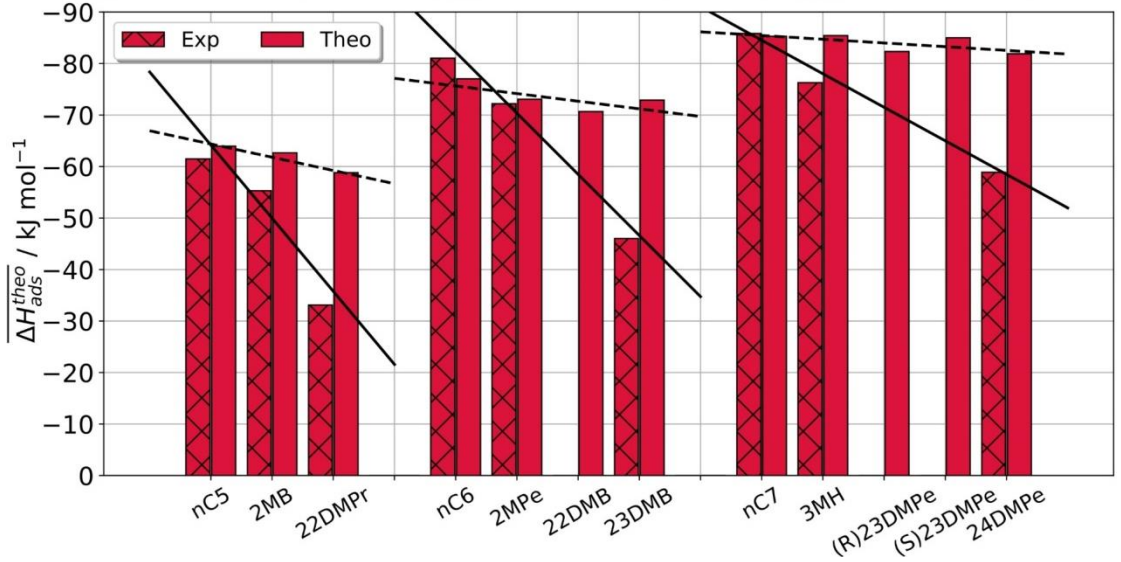




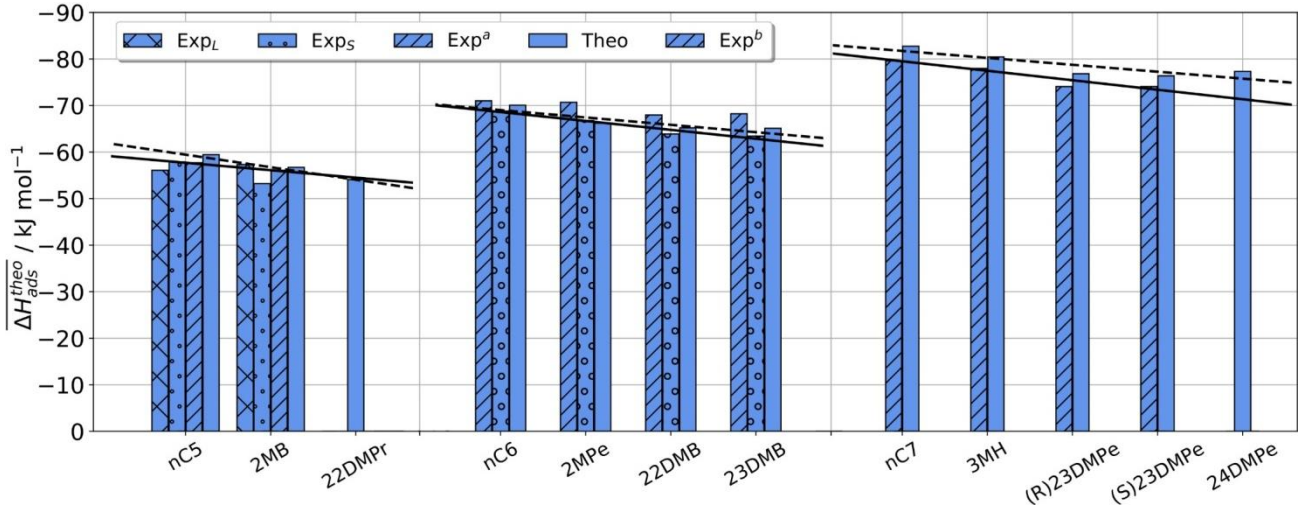
Isosteric Heat of Adsorption*

* negative value of the enthalpy of adsorption

Si-STW



Si-MFI



- High heats of adsorption in both materials, increasing with chain length
- Mismatch between Exp and Sim in Si-STW, especially for branched isomers

[a] J. Phys. Chem. B 1998, 102, 4588-4597

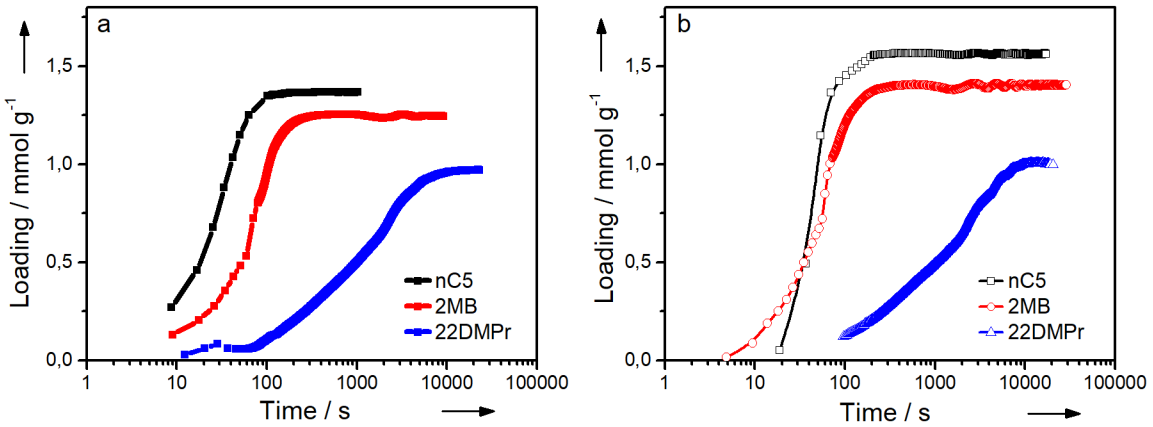
[b] Adsorption (2007) 13: 105–114

Adsorption Kinetics of C5 in Si-MFI

"High" pressure, 300 mbar

Large crystals

Small crystals



- Similar qualitative observations to Si-STW