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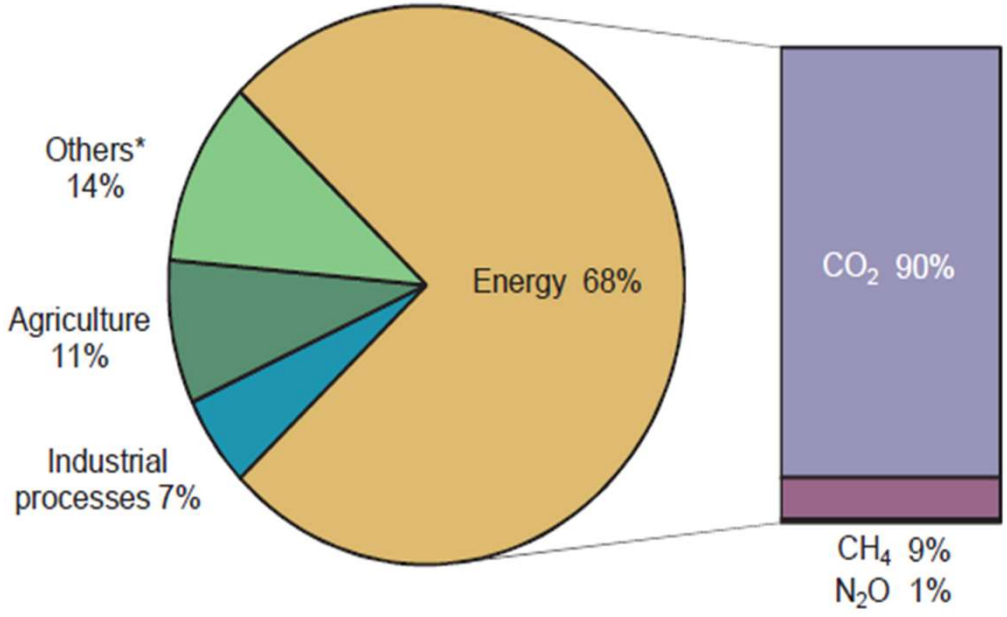
LPA CO_2 Laboratório de Pesquisa em Adsorção e Captura de CO_2

ADSORPTION MICROCALORIMETRY AS A TOOL IN THE CHARACTERIZATION OF MESOPOROUS SILICAS FUNCTIONALIZED FOR CO_2 CAPTURE

Diana Azevedo

INTRODUCTION

- ✓ Climate changes/Greenhouse effect / GHG
- ✓ CO_2 is the second gas with the highest impact in radiation force
- ✓ CCS and CCUS technologies



Source: CO_2 Emissions from fuel combustion. Paris (IEA Stadistical Review of world Energy, *2015*).

INTRODUCTION

(Choi *et al*, 2009)

- What makes a good adsorbent? CO_2 adsorbent

adsorption/desorption kinetics

CO_2 capacity

operating window

Regenerability and multicycle stability

Impact of common flue gas components or contaminants

- Commonly used adsorbents
  - Activated carbons
  - Zeolites
  - MOF'S
  - Supported amines

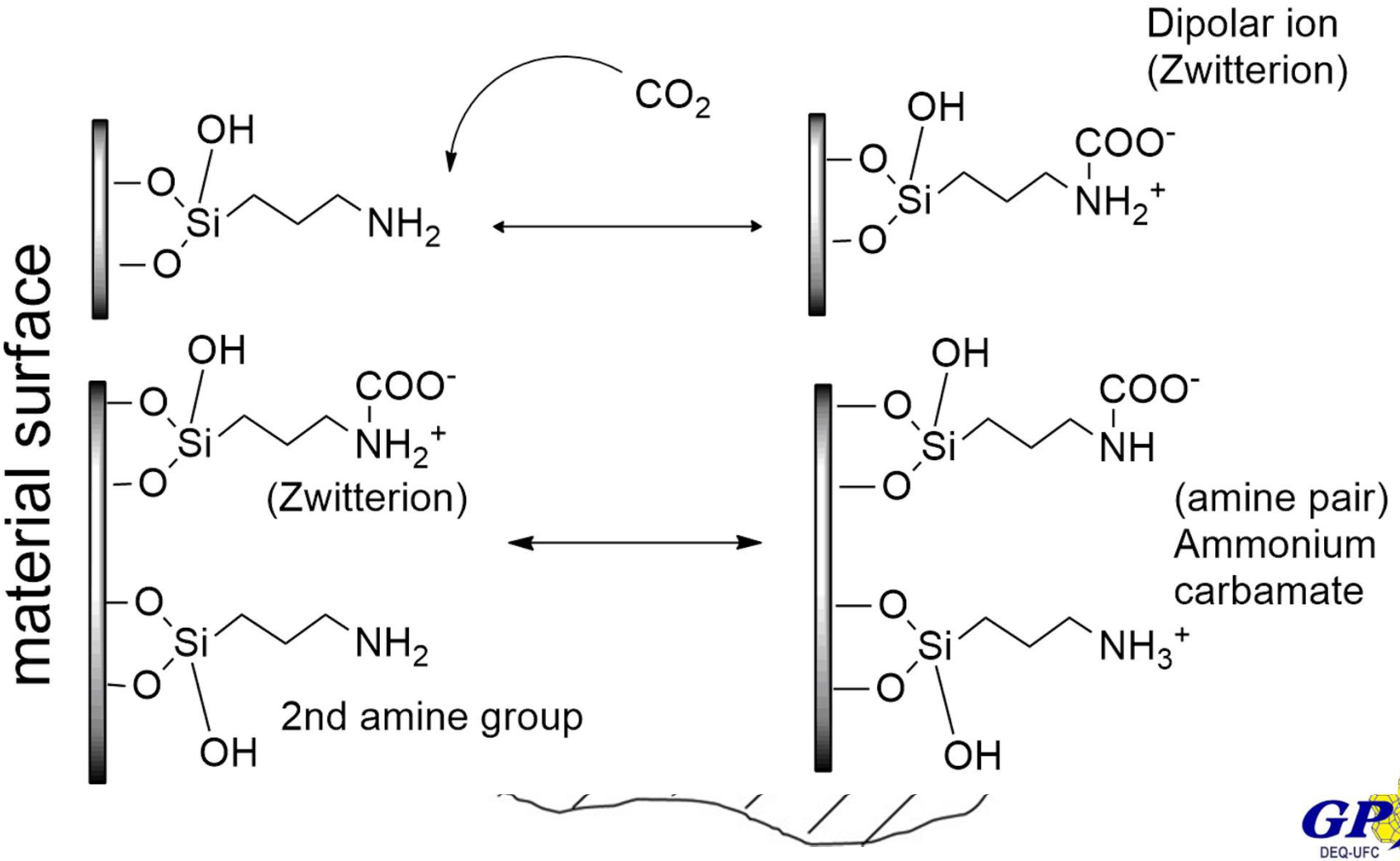
Advantages:

- ✓ High CO_2 selectivity.
- ✓ Low susceptibility to temperature and water vapor
- ✓ Low degradation due to evaporation and vessel corrosion present in aqueous amine configurations.

CHOI, S., DRESE, J. H. AND JONES, C. W. ***ChemSusChem*** *, v.2, p. 796–854 ;2009.*

INTRODUCTION

Generally accepted interaction between CO2 and primary amino group



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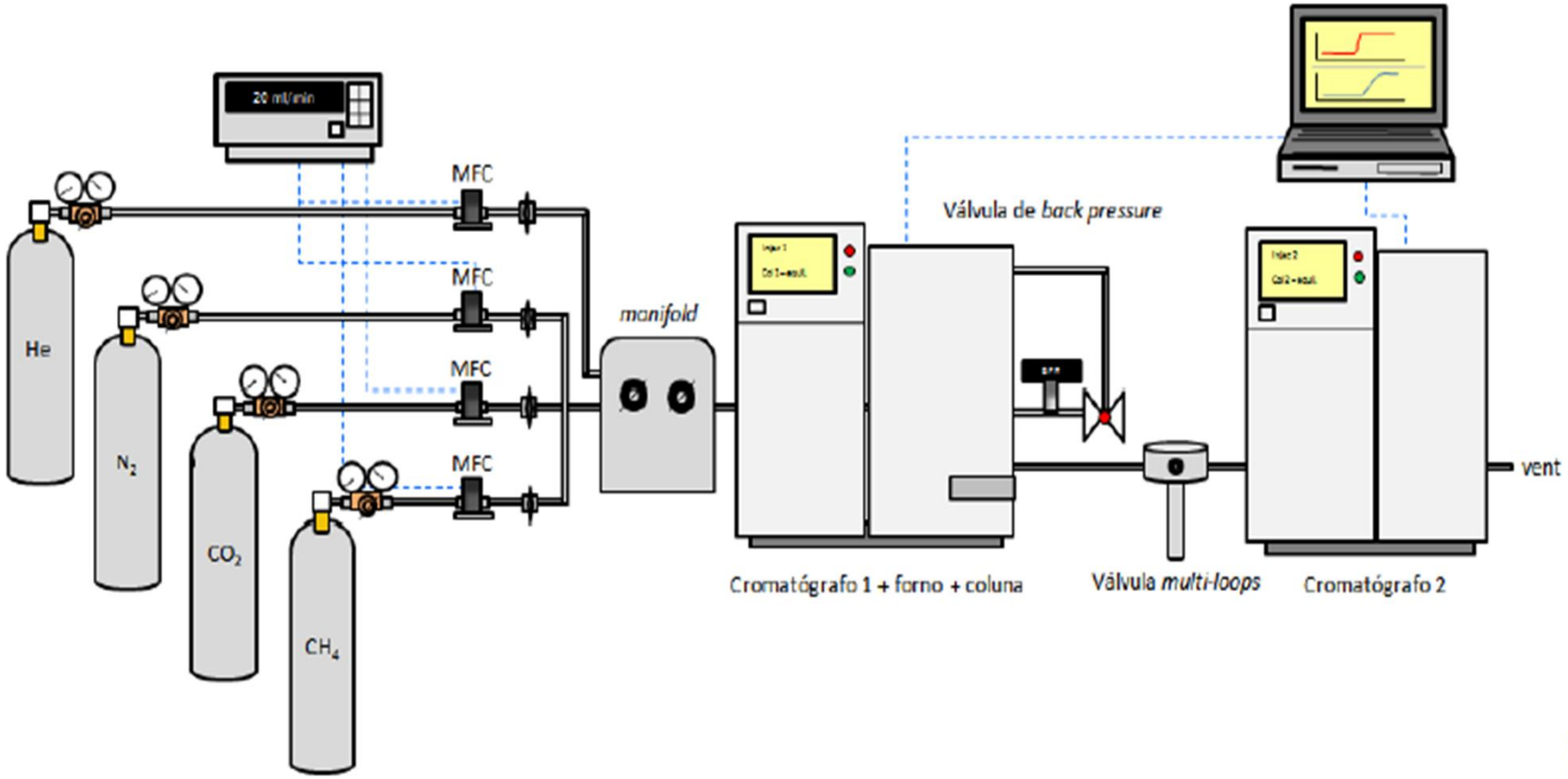
INTRODUCTION

Previous experiments with amine-loaded silicas

(Santiago et al., submitted to J Envir Chem Eng, 2018)



INTRODUCTION

Previous experiments with amine-loaded silicas

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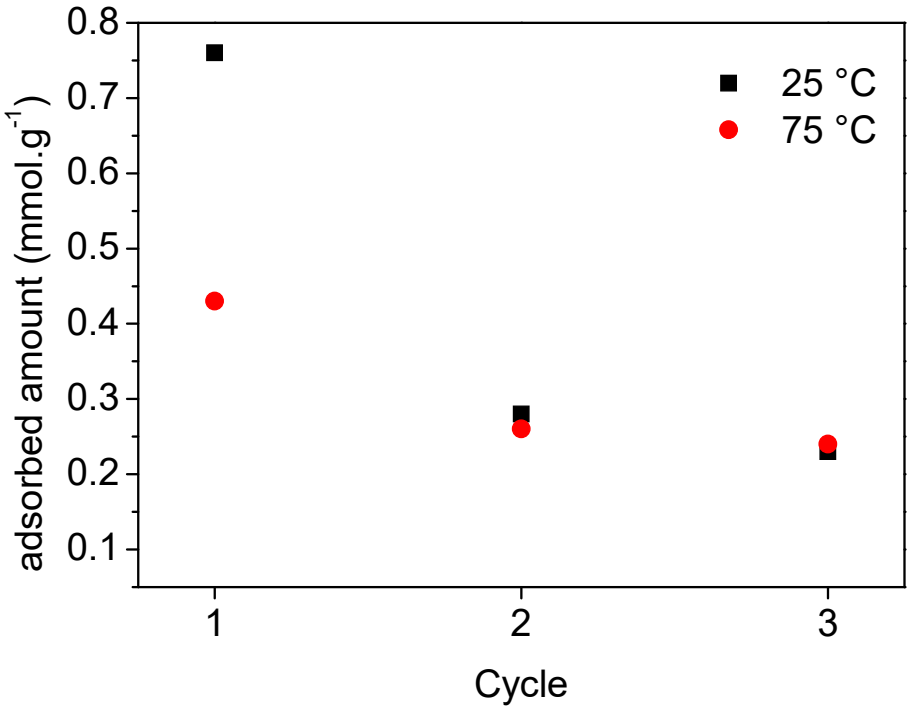
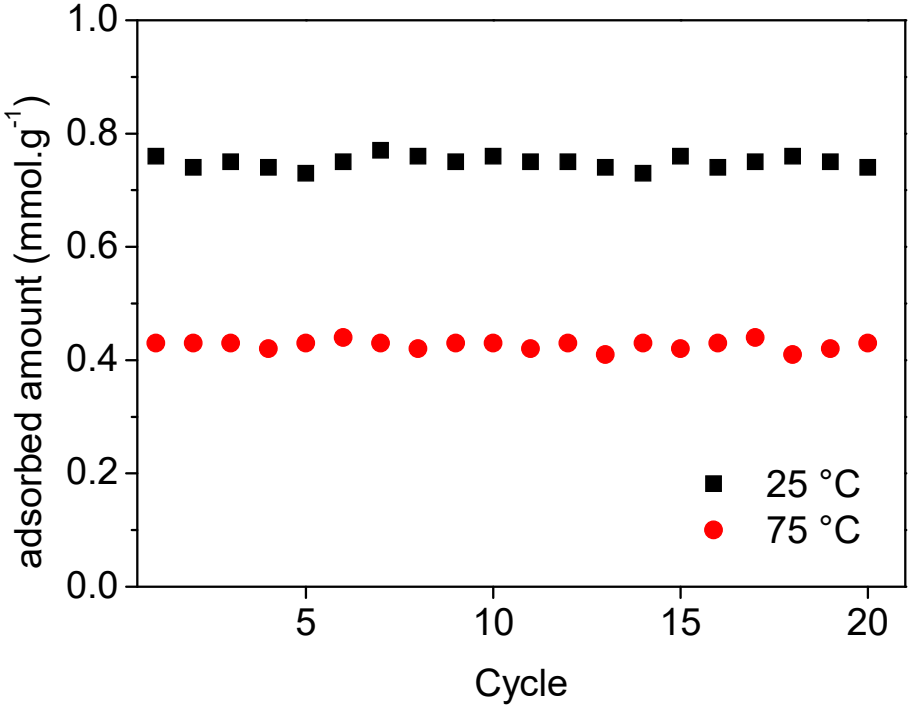




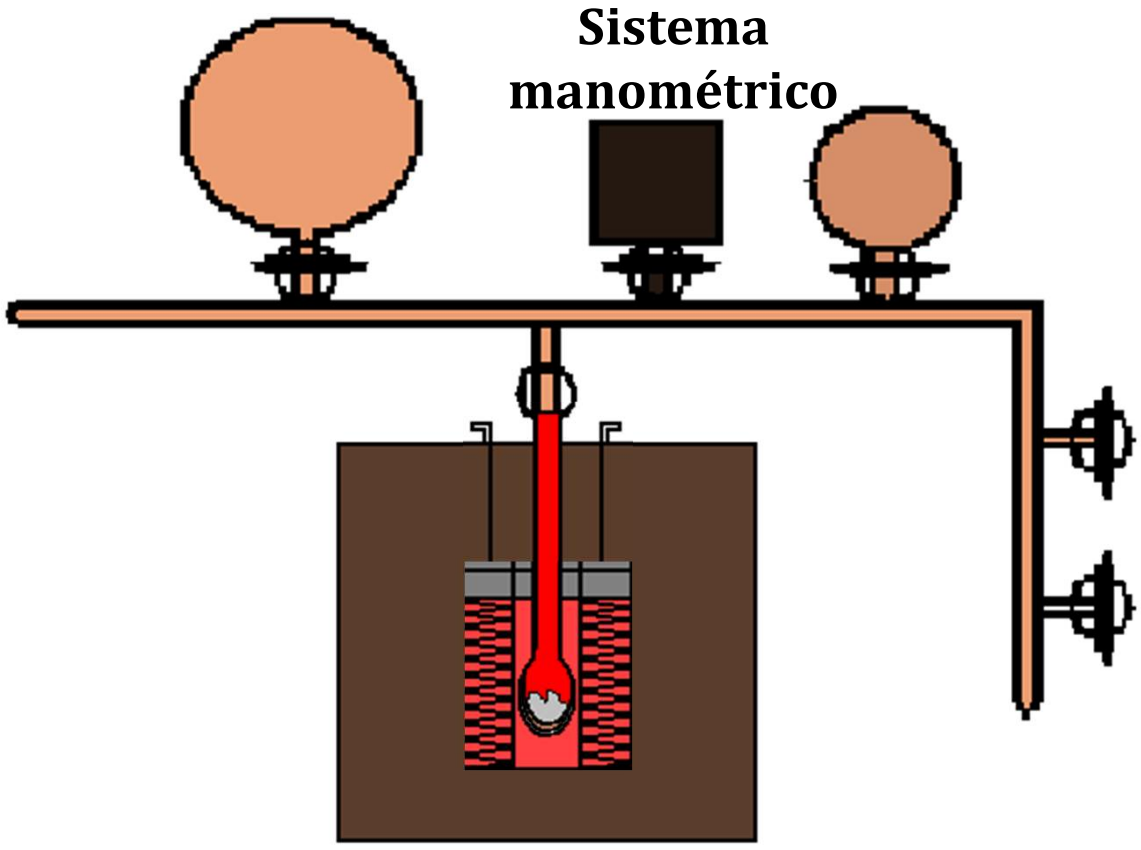
Questions???

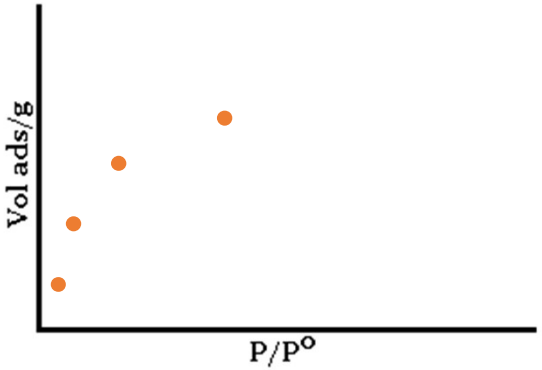
- Is ammonium carbamate the only formed species in anhydrous conditions?
- Is physisorption also important? To which extent?
- How does the load of amine affect chemisorption products, reversibility, adsorption enthalpy and adsorbent stability?
- If several binding mecanisms occur, is there a rate-limiting step?

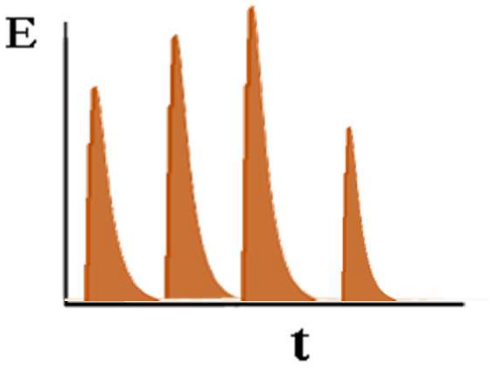
Differential microcalorimetry of adsorption – together with other characterization techniques – may provide insights into some of these questions!

Adsorption microcalorimetry

Soares-Maia, doctoral thesis, UNSL, 2014







EXPERIMENTAL - Materials

- Adsorbent / Pure Material Synthesis (Fulvio *et al,* 2005)

200 mL HCl 1.3 M

5.7 g P123

0.065 g NH_4F

Mixed and strirred at room temperature

12.2 g TEOS

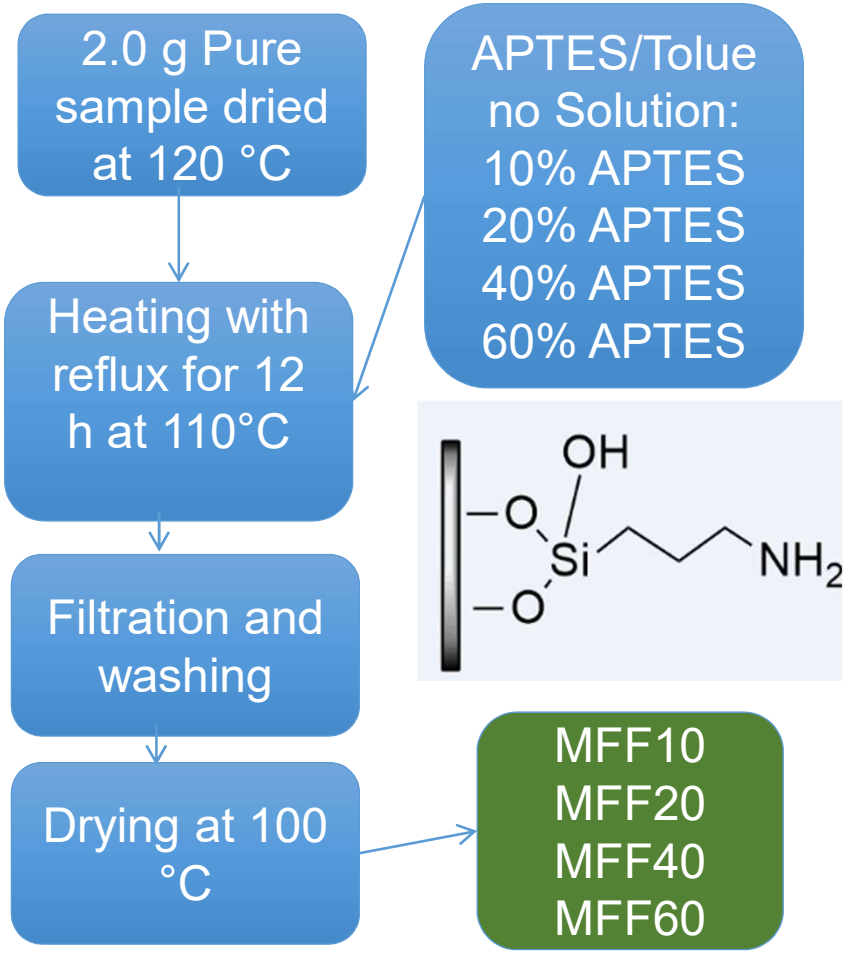
Stirred for 24 h at room temperature → Teflon reactor 100°C 48 h → Filtration and washed → Drying for 24 h at 100°C → Calcination 550 °C 5 h

MFS

FULVIO, P., PIKUS, S. AND JARONIEC, M. ***Journal of Materials Chemistry*** *, v.15, p. 5049 ;2005.*

EXPERIMENTAL - Materials

- Grafting (Hiyoshi *et al*, 2005)



HIYOSHI, N., YOGO, K. AND YASHIMA, T. ***Microporous and Mesoporous Materials*** *, v.84, p. 357–365 ;2005.*

EXPERIMENTAL - Methods

❖ Textural Characterization — Autosorb-iQ3

➢ Nitrogen adsorption at -196 °C

- Specific Surface Area (BET Method)

$$A = n_m N_A \sigma_S$$

- Pore Volume

$$\hat{V}_{po} = n_{ads} \frac{M_{N_2}}{\rho_{N_2(l)}}$$

- Micropore volume (DR method)

$$\hat{V}_{po(mic)} = n_{po(mic)} \frac{M_{N_2}}{\rho_{N_2(l)}}$$

- Pore size distribution (*BJH method)*

❖ Elemental Analysis — CHNS/O Analyzer 2400, Series II

❖ Nuclear magnetic resonance ^{29}Si NMR — Bruker Avance II + 400

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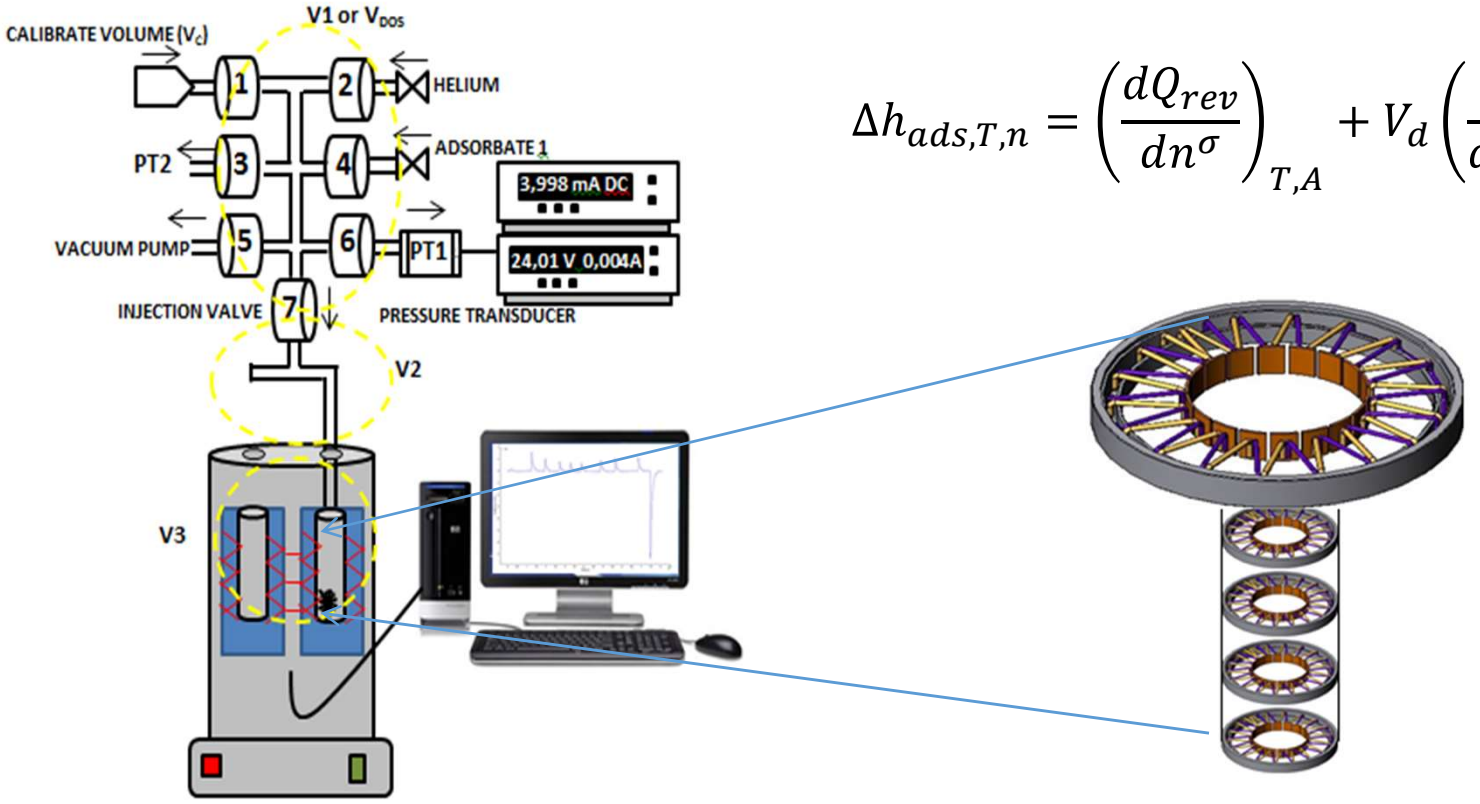
EXPERIMENTAL - Methods

❖ Calorimetric experiments

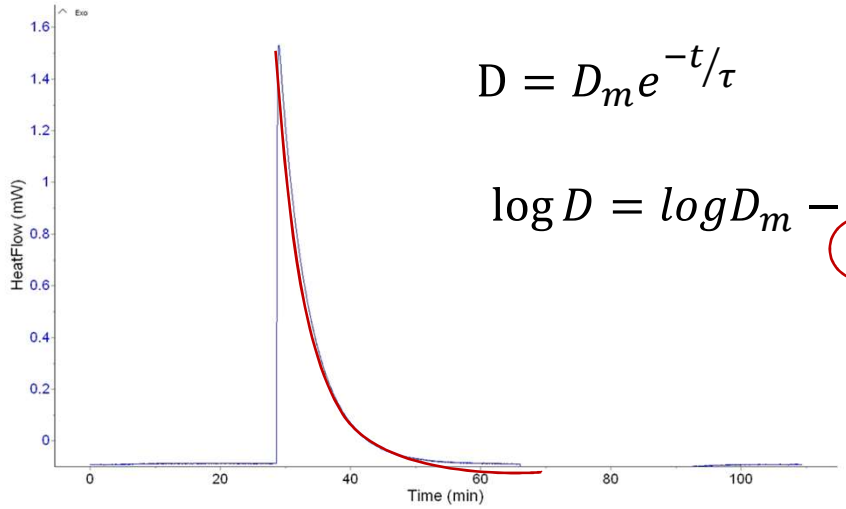


- Tian Calvet calorimeter Setaram C80

$$\Delta h_{ads,T,n} = \left(\frac{dQ_{rev}}{dn^{\sigma}}\right)_{T,A} + V_d \left(\frac{dp}{dn^{\sigma}}\right)_{T,A}$$

EXPERIMENTAL - Methods

- Thermokinetic Parameter

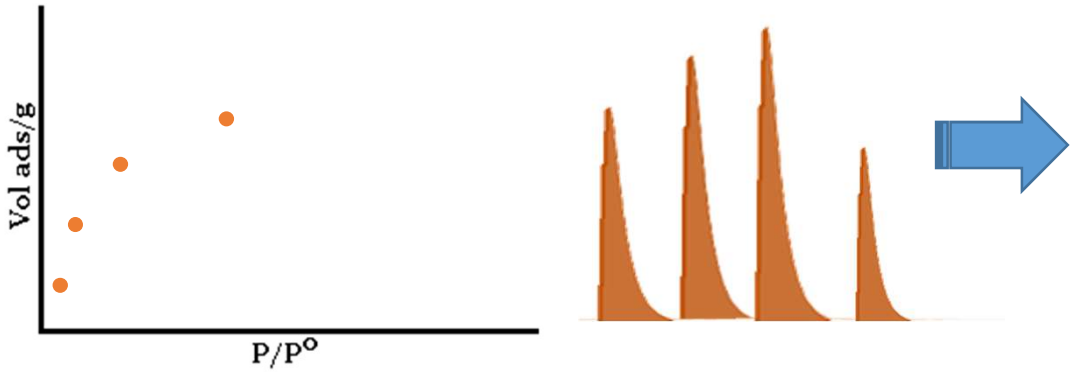


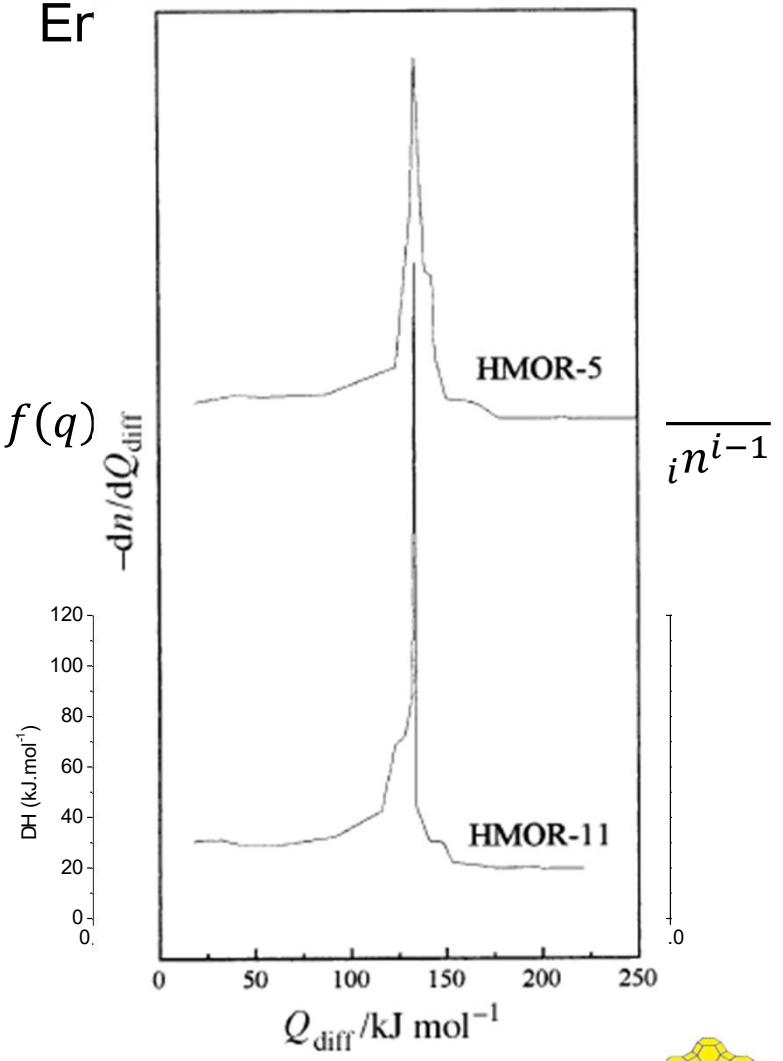
$$D = D_m e^{-t/\tau}$$

$$\log D = log D_m - \frac{t}{\tau}$$

- Er

$$f(q) \quad \overline{{}_i n^{i-1}}$$





FERINO, I., *MONACI*, R., ROMBI, E. AND SOLINAS, V. ***Journal of the Chemical Society,***, v.94, p. 2647–2652 ;1998.

EXPERIMENTAL - Methods

- Equilibrum Data (from manometric system of calorimeter)

$$n_{DOS} = \frac{p_i V_{DOS}}{R T_{DOS}}$$

$$n_e = \frac{p_{eq}(V_{DOS+} V_d)}{R T_{eq}}$$

$$n_i = \frac{p_{eq} V_d}{R T_{eq}}$$

$$n_{ads} = n_{DOS} + n_i - n_e$$

- Equilibrum Models

Duplo-Site Langmuir- Grafted samples

$$q_{CO_2} = \frac{q_{m,CO_2,1} . b_1 P_1}{1 + b_1 P_1} + \frac{q_{m,CO_2,2} . b_2 P_2}{1 + b_2 P_2}$$

Langmuir- Pure sample

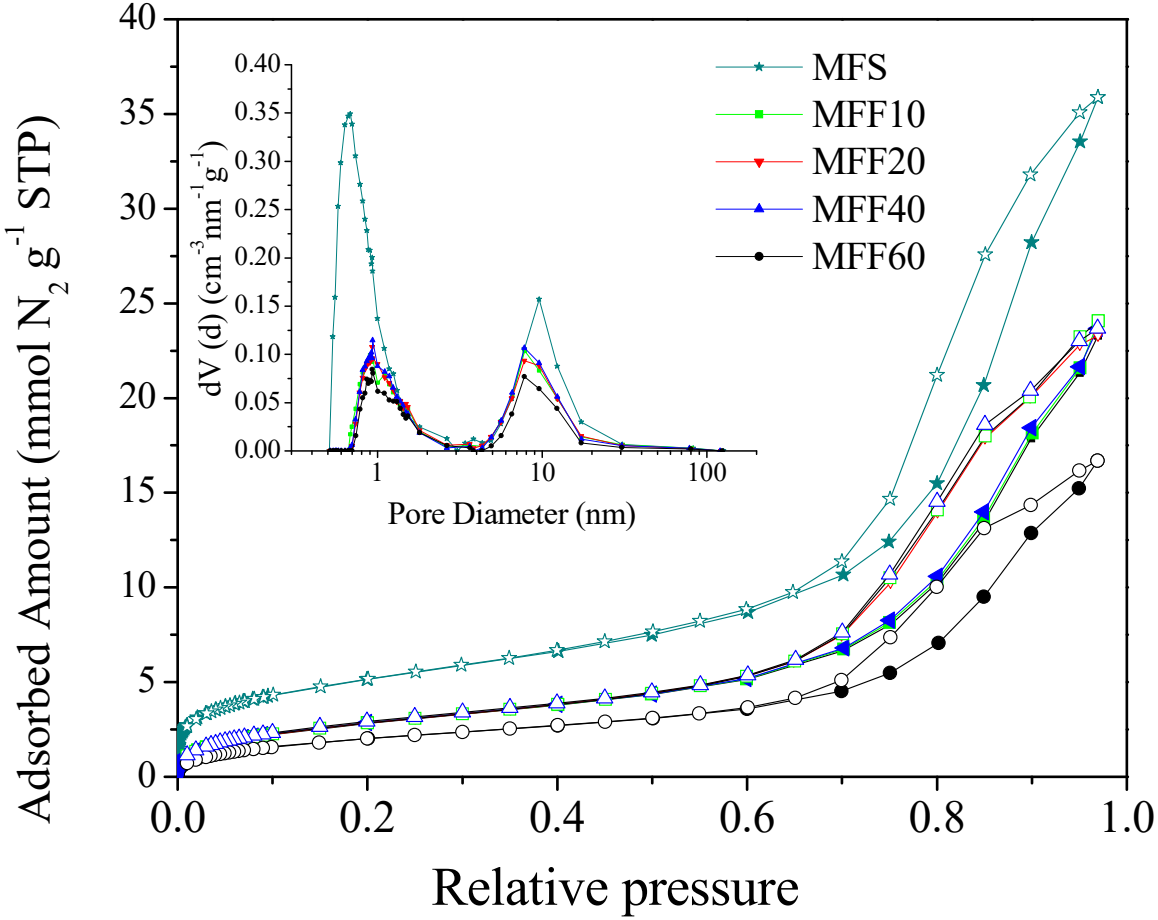
$$q_{CO_2} = \frac{q_m . bp}{1 + bp}$$

RESULTS AND DISCUSSION

❖ Textural Characterization

Nitrogen isotherms -196°C

Samples were outgassed at 120°C for 4 h, under vacuum of 10^{-6} bar before the experiment.



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RESULTS AND DISCUSSION

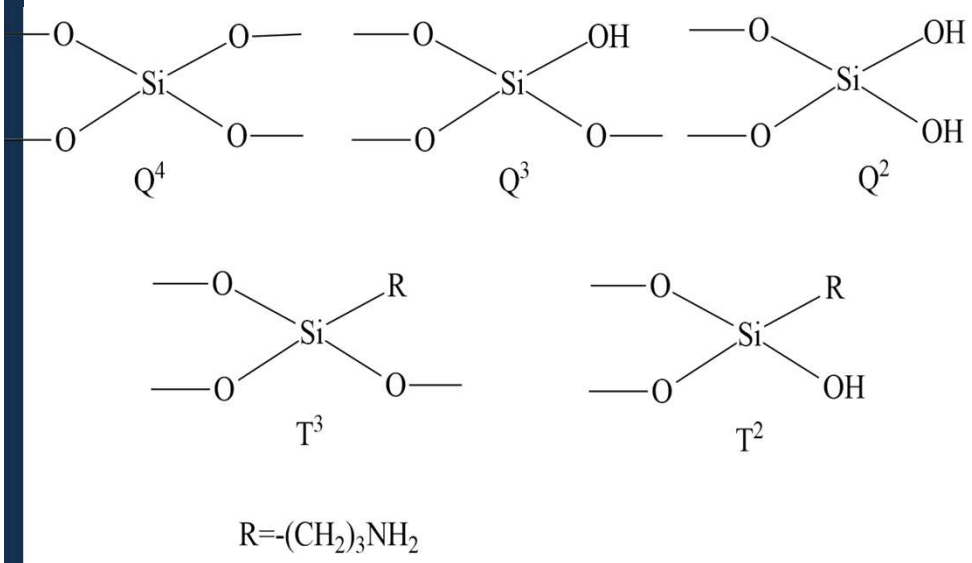
Table 1 Textural properties calculated from N_2 isotherms and nitrogen content.

Samples	A_{BET} ($m^2.g^{-1}$)	Pore Vol ($cm^3.g^{-1}$)	Pore Size (nm)	Micro pore Vol ($cm^3.g^{-1}$)	N_C ($mmol.g^{-1}$)
MFS	392	1.43	9.57	0.125	0.03
MFF10	213	1.02	7.81	0.057	1.57
MFF20	211	0.96	7.80	0.056	1.76
MFF40	215	0.98	7.80	0.056	1.95
MFF60	151	0.55	7.79	0.045	2.64

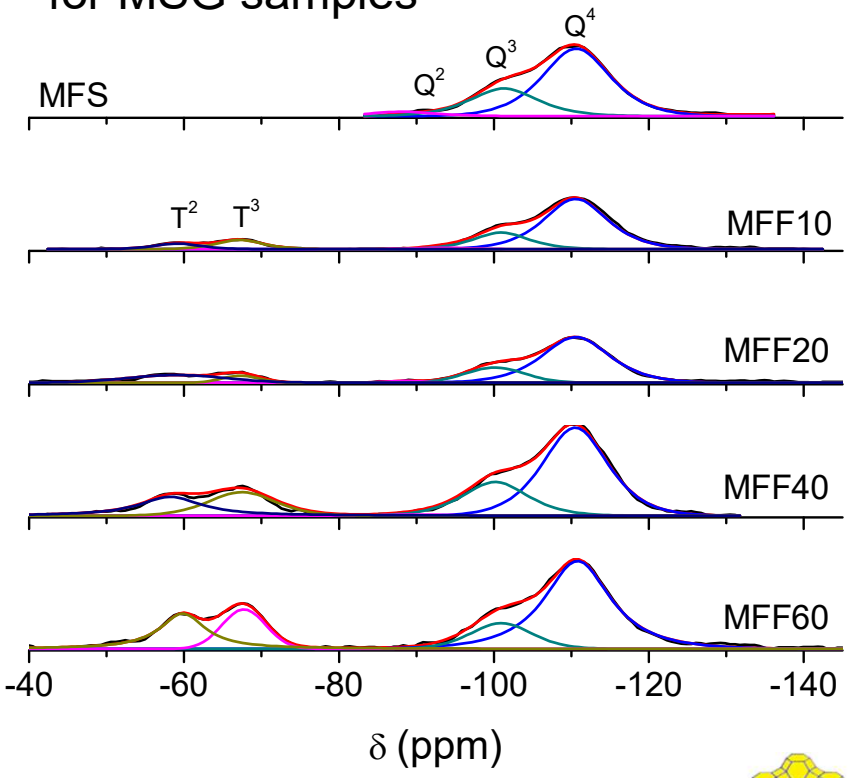
RESULTS AND DISCUSSION

❖ Nuclear Magnetic Resonance (NMR ^{29}Si)

Chemical composition of chemical surface



Deconvolution 29Si chemical shift signal for MSG samples



RESULTS AND DISCUSSION

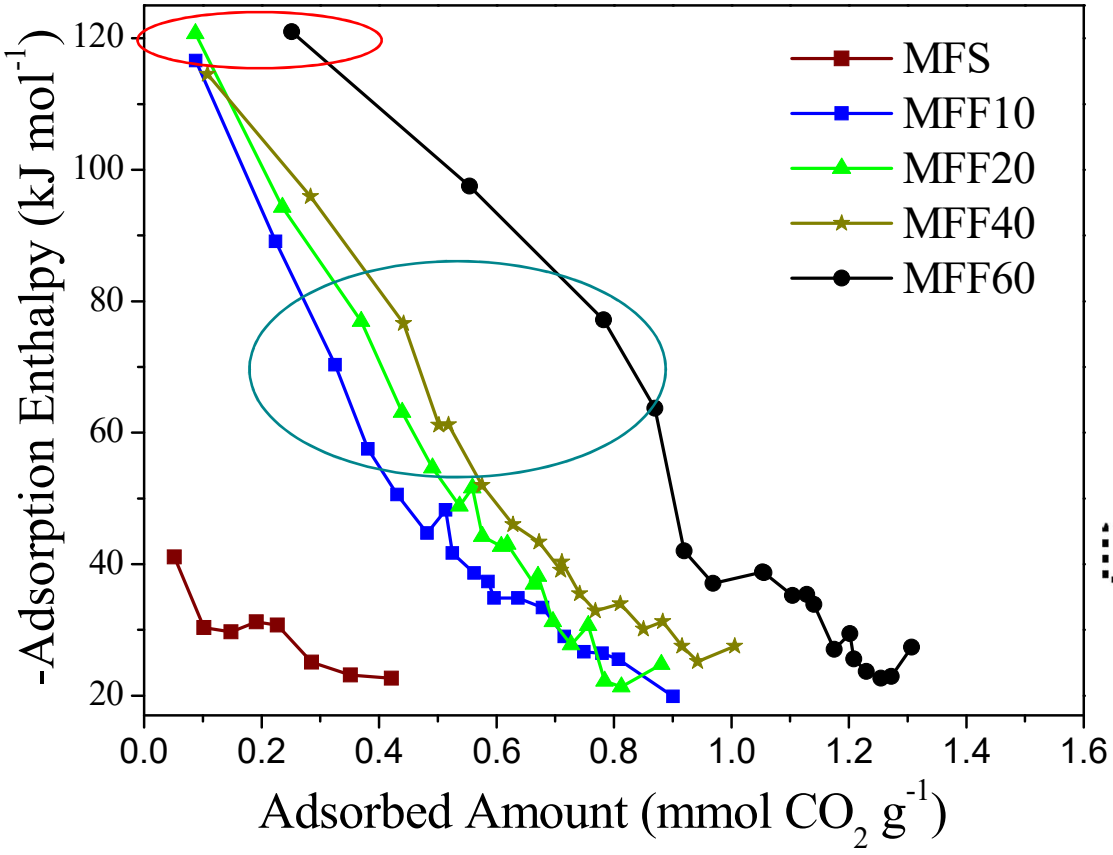
Table 2 ^{29}Si MAS NMR peak integration for mesoporous silica studied

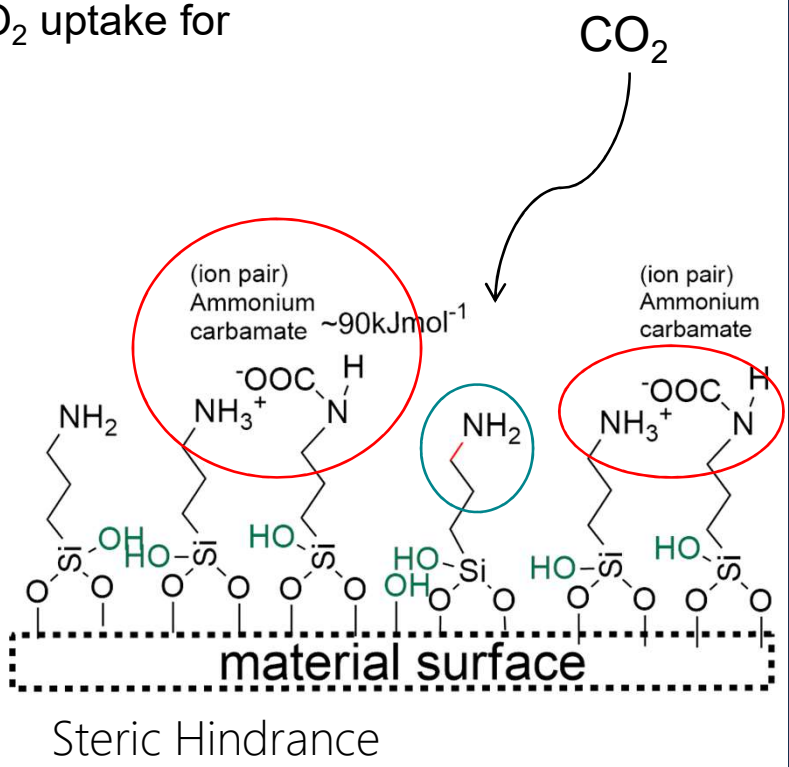
Samples	T^2 (int%)	T^3 (int%)	Q^2 (int%)	Q^3 (int%)	Q^4 (int%)
MFS			3.8	28.0	68.2
MFF10	5.4	4.8	1.8	18.9	65.1
MFF20	11.2	8.8	1.2	17.0	62.7
MFF40	14.2	12.5	0.9	11.7	63.7
MFF60	20.0	12.2	—	6.7	61.2

RESULTS AND DISCUSSION

❖ Calorimetric Characterization

Differential enthalpy of adsorption in function of CO_2 uptake for mesoporous silica

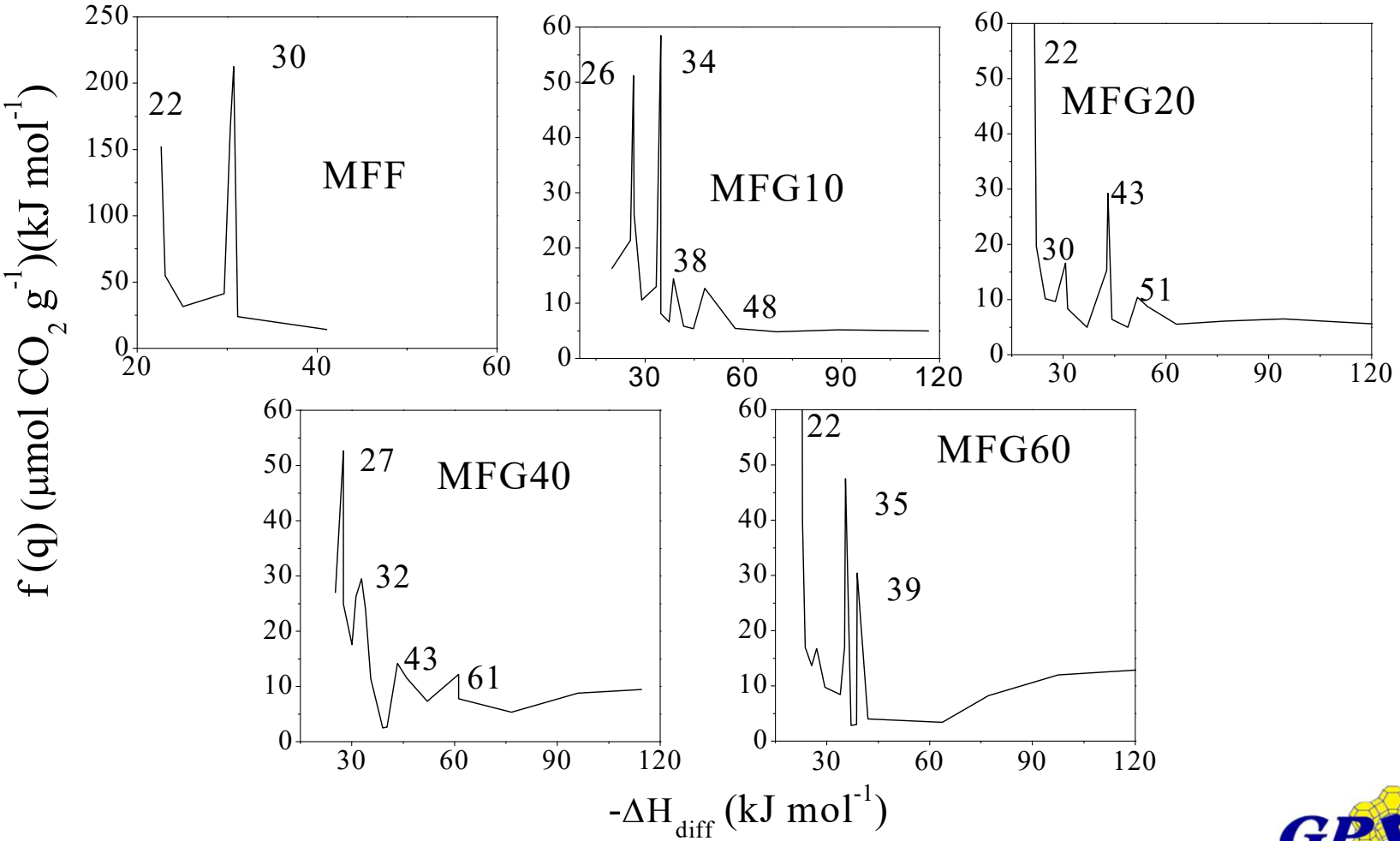




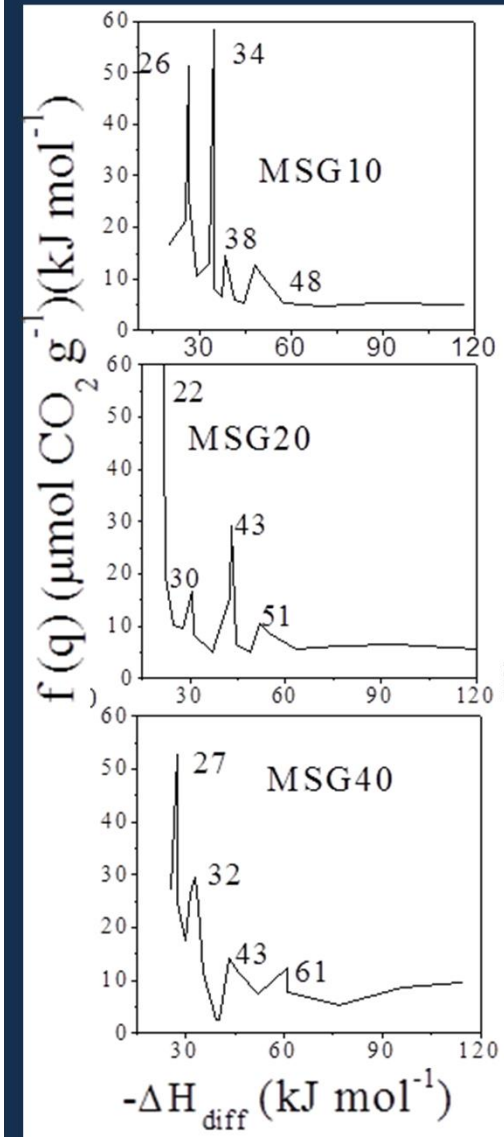
Steric Hindrance

RESULTS AND DISCUSSION

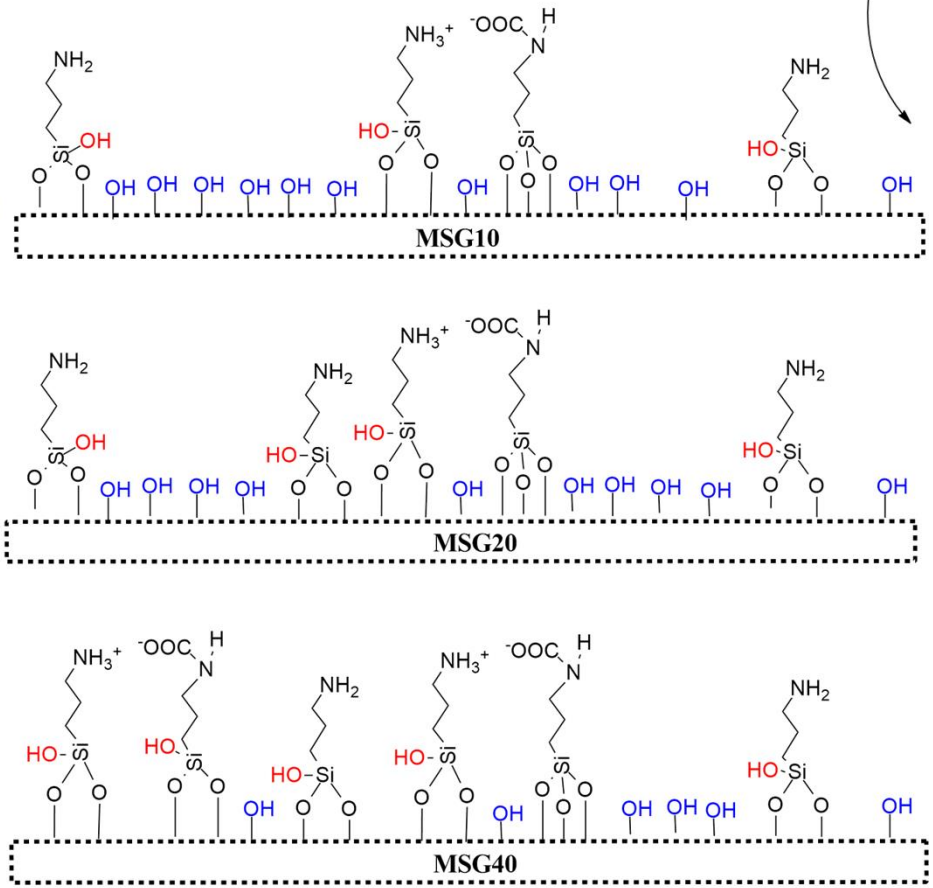
Energy site distribution

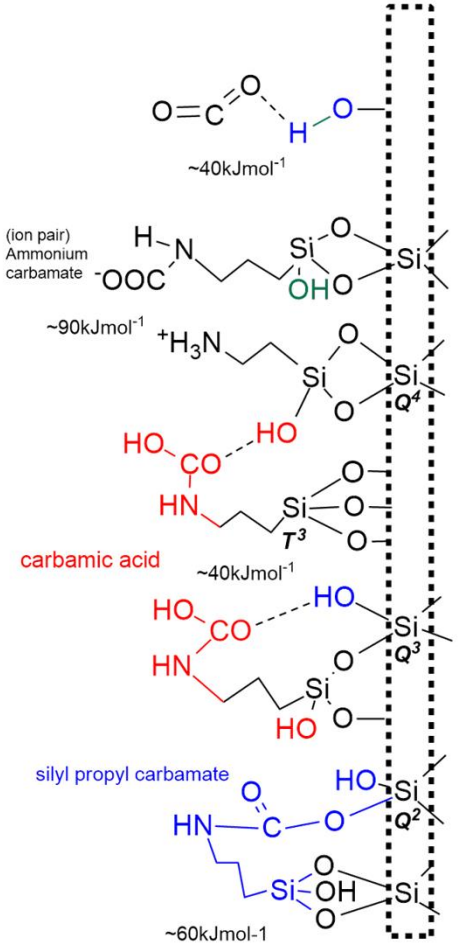


RESULTS AND DISCUSSION



Hypothetical amine and silanols distribution based in the elemental analysis and NMR





MEDIUM AMINE DENSITY

~4-5 molecules per nm^2

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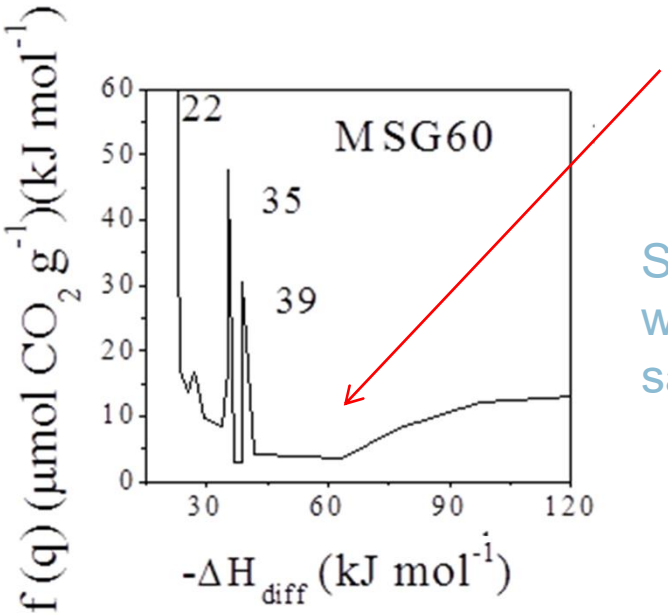
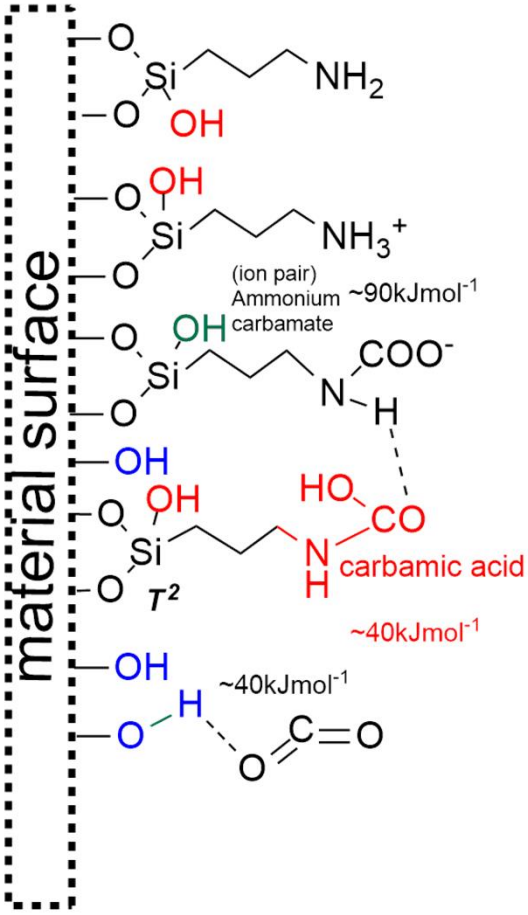
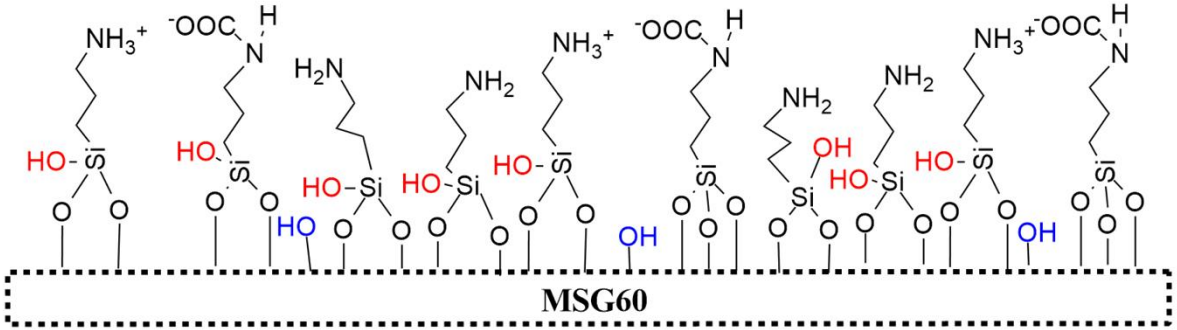
RESULTS AND DISCUSSION



Silyl propyl carbamate was not formed on this sample





HIGH AMINE DENSITY

~10 molecules per nm²

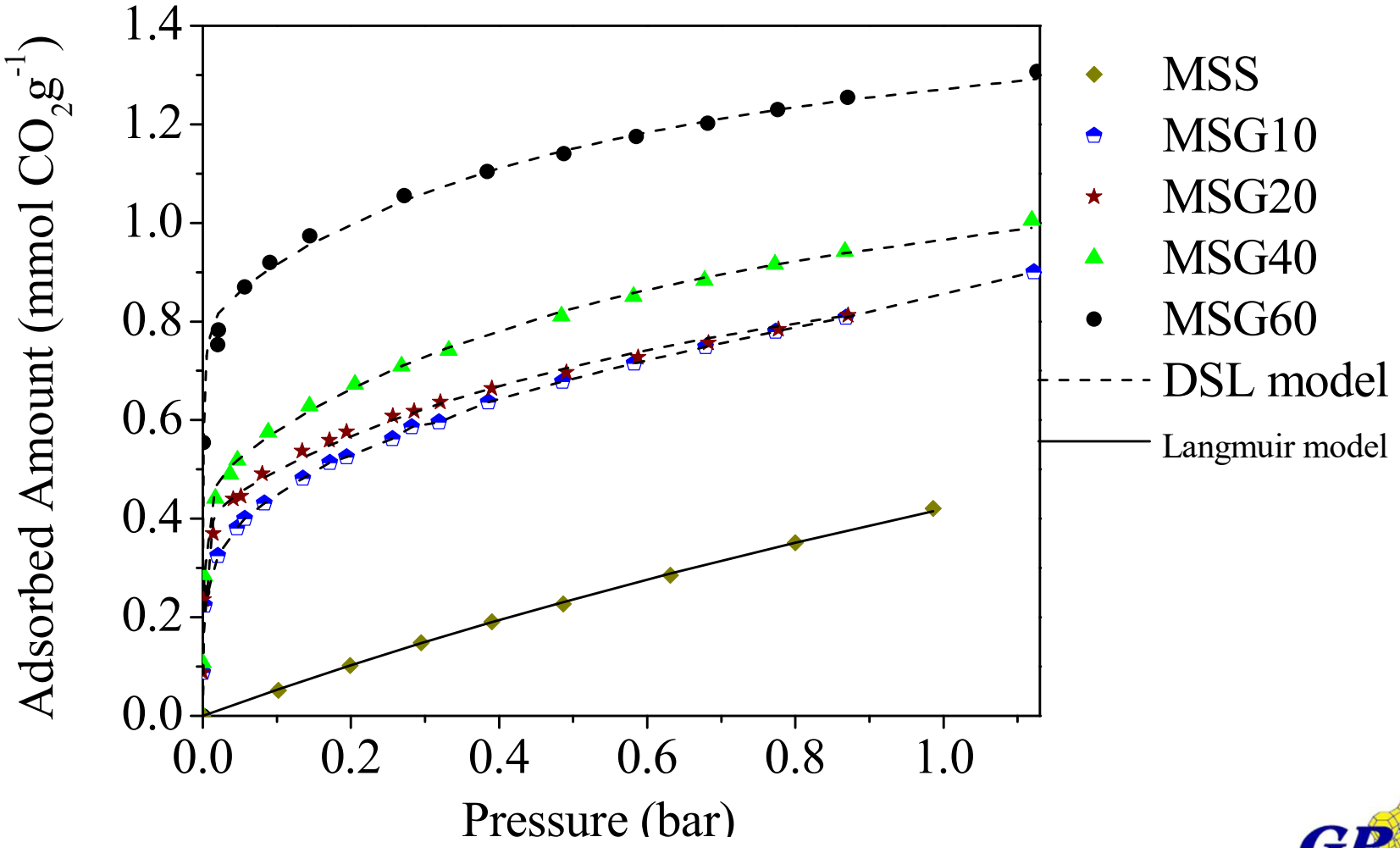
RESULTS AND DISCUSSION

Table 3. Maximum thermokinetic parameter (τ_{max}) and its corresponding enthalpy

Sample	$\varnothing_{-NH2}$, Amine molecule. nm^{-2}	Maximum thermokinetic parameter (τ_{max})	
		τ_{max}, s	ΔH_{ads}, $kJ.mol^{-1}$
MFS	-	397	30
MFF10	4.43	447	43
MFF20	5.02	354	43
MFF40	5.46	489	40
MFF60	10.53	613	64

RESULTS AND DISCUSSION

- CO_2 isotherms at 25 °C for mesoporous materials



RESULTS AND DISCUSSION

Table 4 DSL fitting parameters to the experimental data at 25 ° C

Parameter	MFS	MFF10	MFF20	MFF40	MFF60
qm_1, $mmolCO_2g^{-1}$	0	0.34	0.42	0.47	0.79
b_1, bar^{-1}	0	671.1	795	823.7	2159
qm_2 $mmolCO_2g^{-1}$	1.84	0.93	0.76	0.81	0.67
b_2, bar^{-1}	0.29	1.17	1.24	1.50	2.53
R^2	0.99	0.99	0.99	0.99	0.97

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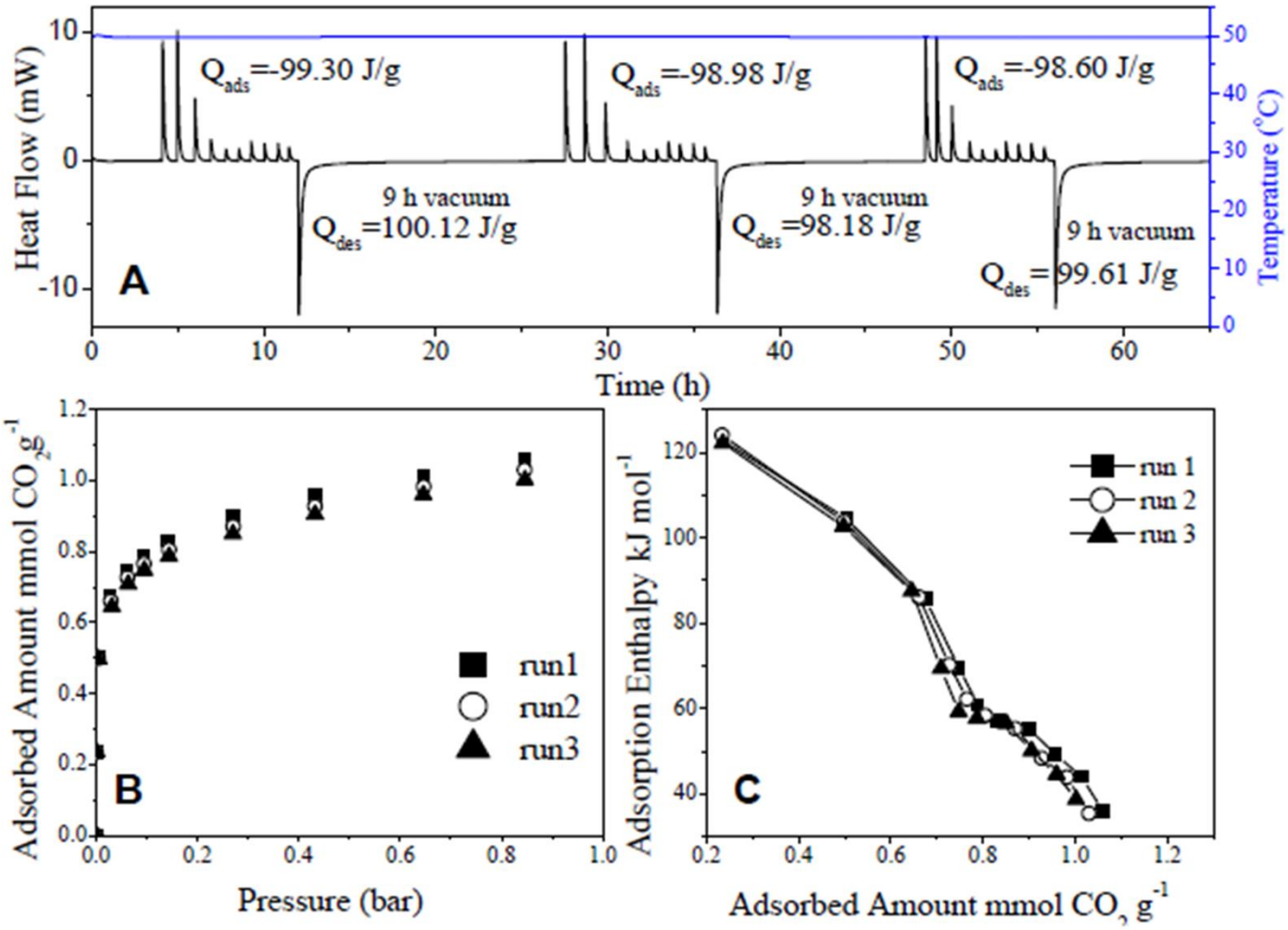
CONCLUSIONS

- This work aimed to understand how grafted amine density on silica supports having a direct impact on adsorbed CO_2 and on the strength of binding.
- The distribution of silanol groups was found to have key importance. Adsorption microcalorimetry together with ^{29}Si NMR and textural analysis were helpful tools to infer on CO_2 chemisorption products and the relative importance of physisorption.
- Thus we concluded that physisorption is the dominant binding mechanism for the support (MFS) whereas for MFF samples, in addition to physisorption, there is chemisorption leading to the formation of propyl ammonium carbamate, silyl propyl carbamate and propylcarbamic acid.
- The samples that present values of amine density around 5 molecules per nm^2 presented kinetic restrictions to stabilize carbamic acid as a product of CO_2 interaction with isolated amines. In contrast, functionalized materials having around 10 molecules per nm^2, the formation of silyl propyl carbamate is suppressed and acts as the limiting step to reach the equilibrium.
- Limited formation of silyl propyl carbamate may be advantageous because this species is irreversibly bound and cannot be removed only with vacuum.

Cycling adsorption-desorption for MFF60



Check oral presentation by Débora Maia (196) 24/04, 15:15

ACKNOWLEDGEMENTS

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Célio Cavalcante Jr.

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1890 citations
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Undergrad Students (10)







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