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This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 720783

Accessible acid sites in hierarchical architectures

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The art of making hierarchical materials is where to put the pores

- ✓ **Top-down vs bottom-up synthetic methods:**

Top down: **cheap & simple but produces a non-ordered mesoporosity**

Bottom-up: **supramolecular templating is in general economically prohibitive but induces an ordered mesoporosity**

- ✓ **A integrated physico-chemical characterization is essential to identify structure-performance relationship.**
- ✓ **Accessibility** of the active sites is the main properties to consider while studying hierarchical materials

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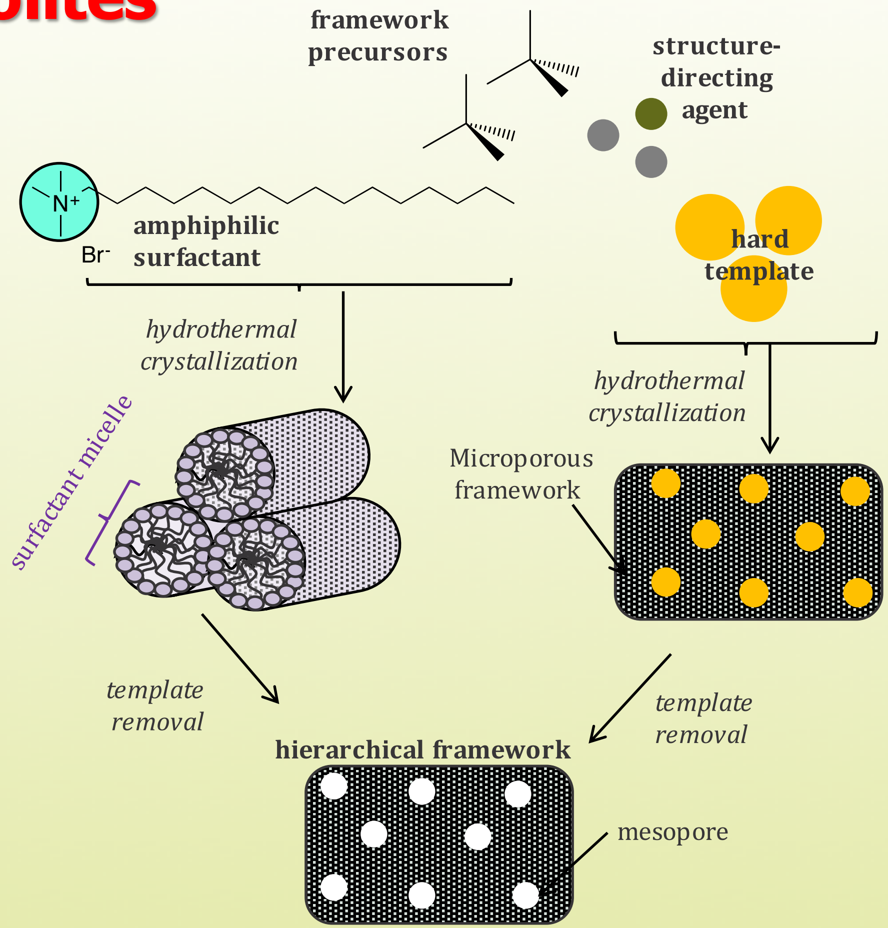
Synthesis of hierarchical zeolites

Bottom-up



Templating methods

- ***Soft templating*:**

  Surfactant molecules self-organized into supramolecular micelles.

- ***Hard templating*:**

  Solid materials such as mesoporous carbons

K. Li et al., *ChemCatChem*, 2014, 6, 46
D.P. Serrano et al., *Chem. Soc. Rev*, 2013, 42, 4004

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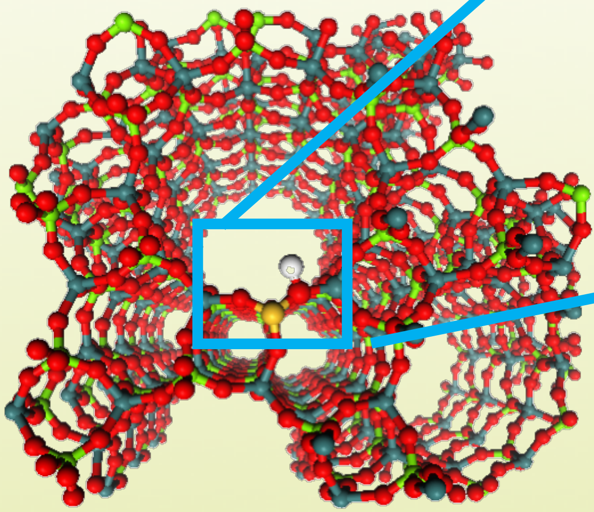
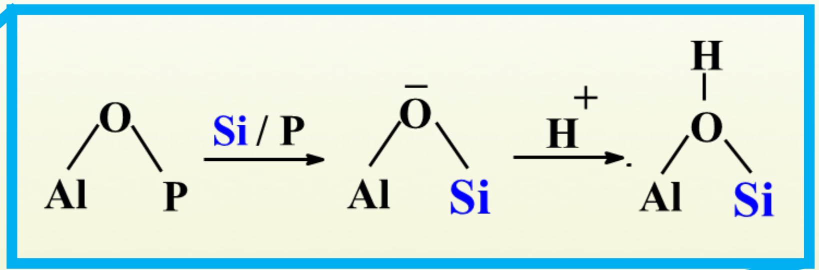
Microporous Silicoaluminophosphates (SAPOs)





SAPO-34

CHA structure

Acid catalyst in methanol-to-olefin (MTO) reactions

The small, 8-ring pore aperture (3.8x3.8 Å) and large CHA cavity (9.4 Å in diameter) *impose severe diffusion limitations* and expedite catalyst deactivation through coke formation/deposition

Aluminophosphates……..

………………a class of highly tuneable, microporous catalysts

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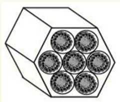
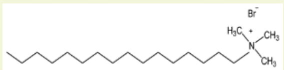
Synthesis of hierarchical SAPO-34 using different bottom-up approach



SAPO-34 from a silica (MCM-41) scaffold

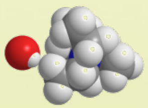
HP-SAPO-34-CTAB

SDA_{meso}



Hexadecyltrimethylammonium bromide (CTAB) encapsulated in MCM-41

SDA_{micro}



Tetraethylammonium hydroxide (TEAOH)

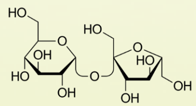
Synthesis gel composition:

1Al: 0.58Si : 1P : 0.066CTAB : 1TEAOH : $50H_2O$

SAPO-34 from saccharide templates

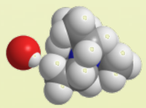
HP- SAPO34-Saccharose

SDA_{meso}



Saccharose

SDA_{micro}



Tetraethylammonium hydroxide (TEAOH)

Synthesis gel composition:

1Al: 0.6Si : 1P : 0.067Saccharose : 1TEAOH : $60H_2O$

Multi-techniques characterization: XRD, SEM, EDX, ICP, ss-NMR, FTIR with probe molecules.

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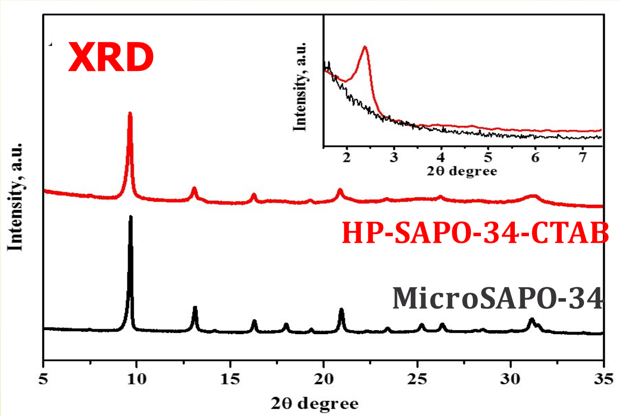
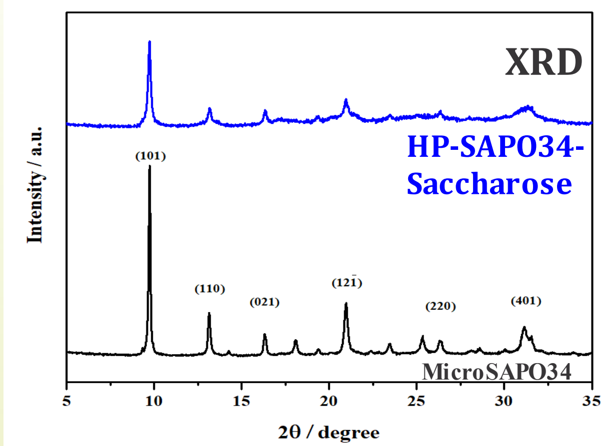
Bottom-up approach to synthesize hierarchical HP- SAPO-34

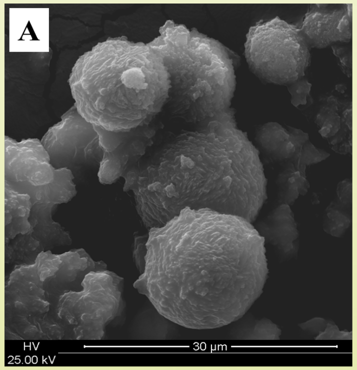
HP-SAPO-34-CTAB



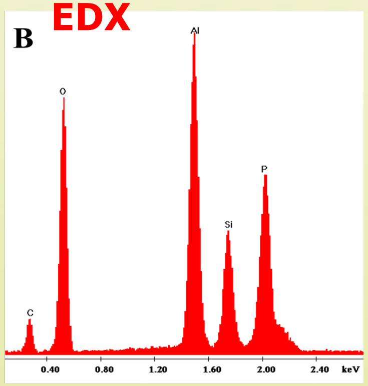
HP- SAPO34-Saccharose



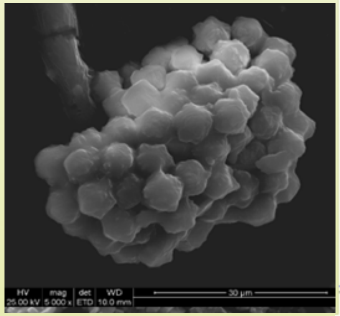
SEM



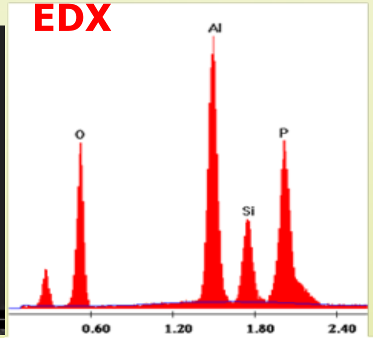
EDX



SEM



EDX



I.Miletto, S. Chapman, G. Paul, L. Marchese, R. Raja, E. Gianotti, *Chem. Eur. J* **2017,** 23, 9952.
I.Miletto, C. Ivaldi, G. Paul S. Chapman, L. Marchese, R. Raja, E. Gianotti, *Chemistry Open* **2018,** 7, 297

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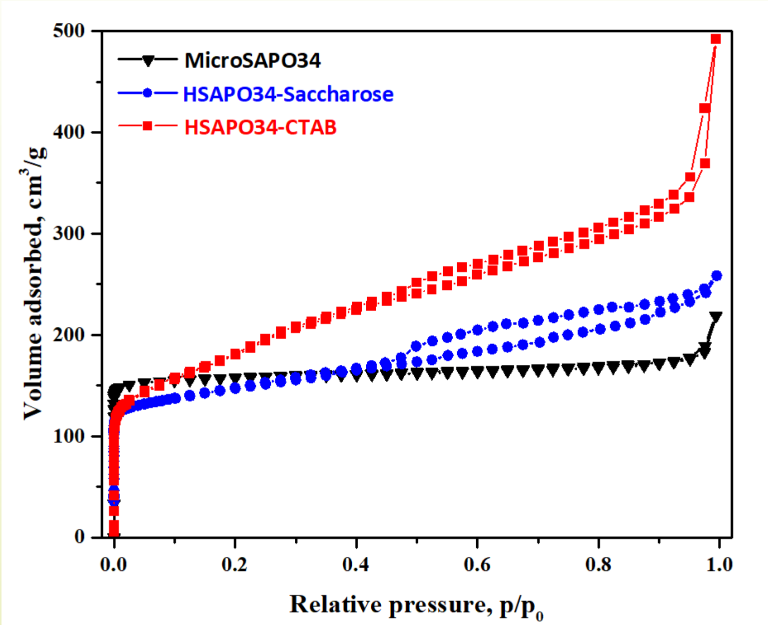
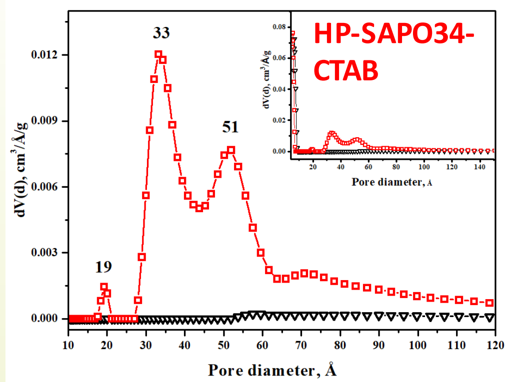
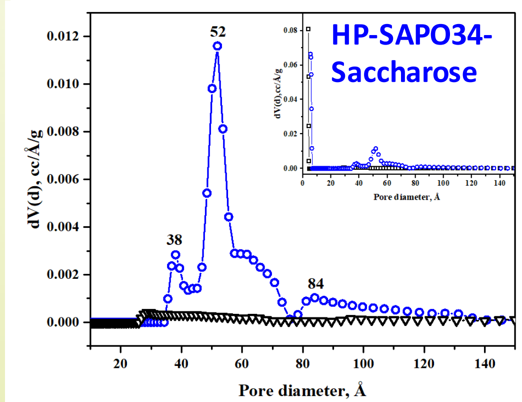
N_2 adsorption/desorption isotherm at 77K







Pore size distributions determined by QSDFT method

Catalyst	S_{BET}	S_{micro} ($m^2 g^{-1}$)	S_{meso} ($m^2 g^{-1}$)	$V_{tot\ DFT}$ ($cm^3 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)	V_{meso} ($cm^3 g^{-1}$)
HP-SAPO34-CTAB	641	511	272	0.58	0.14	0.45
HP-SAPO34-Saccharose	446	690	118	0.36	0.17	0.28
MicroSAPO-34	477	811	8	0.26	0.23	0.03

FTIR + ¹H ss-NMR - OH population

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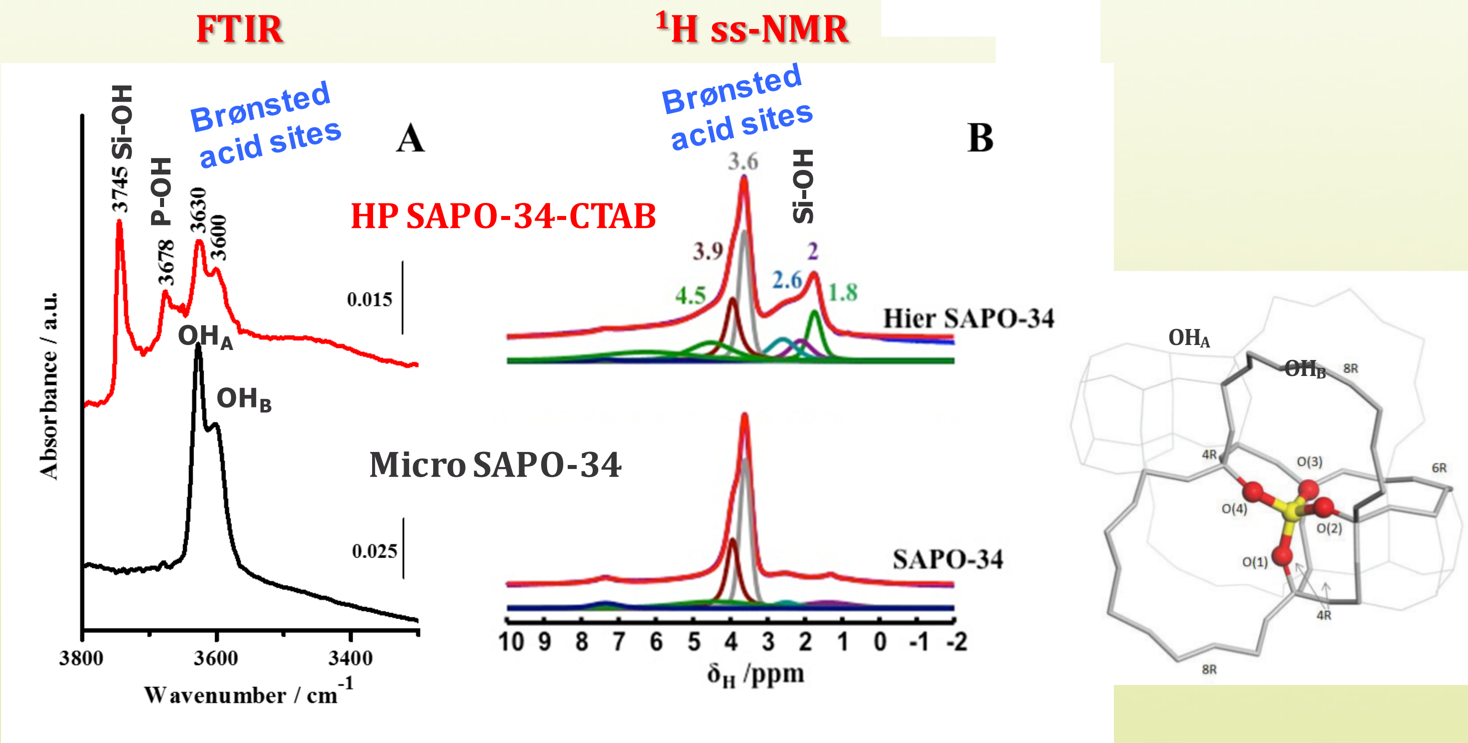
The presence of **Brønsted acid sites** in HP SAPO-34-CTAB typical of microSAPO-34 confirms the dissolution of MCM-41 network and the Si incorporation into the CHA



G. Paul, C. Bisio, I. Braschi, M. Cossi, G. Gatti, E. Gianotti, L. Marchese, *Chem Soc Rev.*, **2018**, 47, 5684-5739

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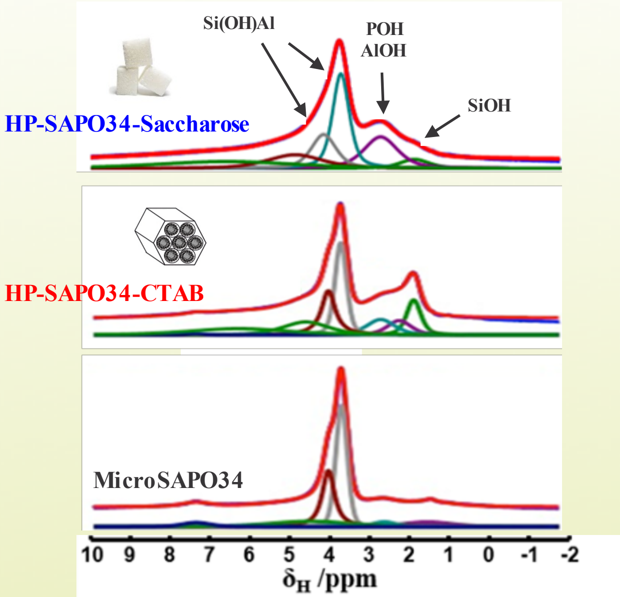
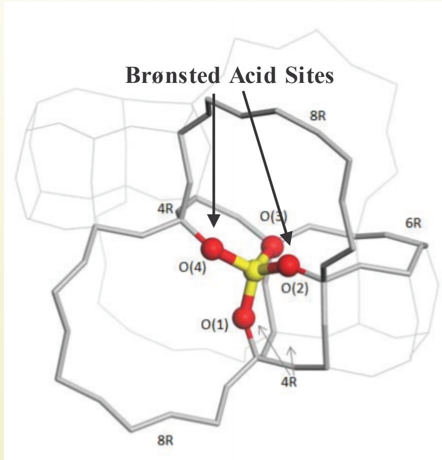
^{1}H ss-NMR - OH population





^{1}H Chemical shift (δ) /ppm	Assignments	^{1}H Species (%)		
		HP- SAPO34-Saccharose	HP-SAPO34-CTAB	MicroSAPO34
1.8-2.0	Si-OH	5	20	-
2.6	P-OH	20	10	4
3.6	Brønsted acid sites (OH_A) **O(4)**	29	23	42
3.9	Brønsted acid sites (OH_B) **O(2)**	16	17	27

All the samples were outgassed at 300°C for 1h 30 min

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How can we discriminate between Brønsted acid sites located inside the micropores and those present on the mesopores surface?

***XRD*: micro and meso structures**

***SEM & EDX*: homogeneous distribution of Al, P and Si, with no evidence of MCM-41-type particles.**

***Volumetric analysis*: the coexistence of multiple levels of porosity within the same material.**

***FTIR + ^{1}H ss NMR*: in hierarchical SAPO-34, the Brønsted acid sites have similar strength and nature of micro SAPO-34.**

.....but where are located the Brønsted acid sites?

Adsorption of bulky probe molecules is required

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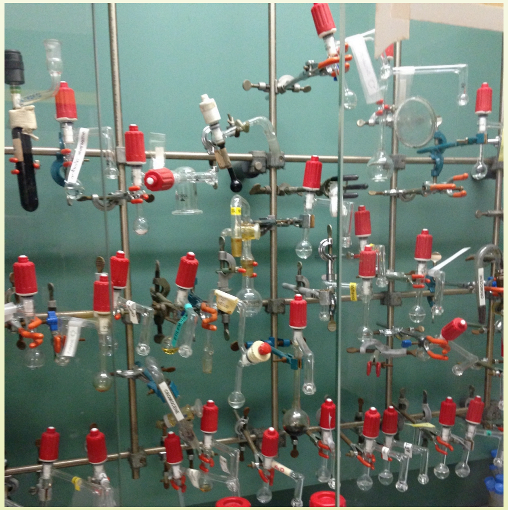
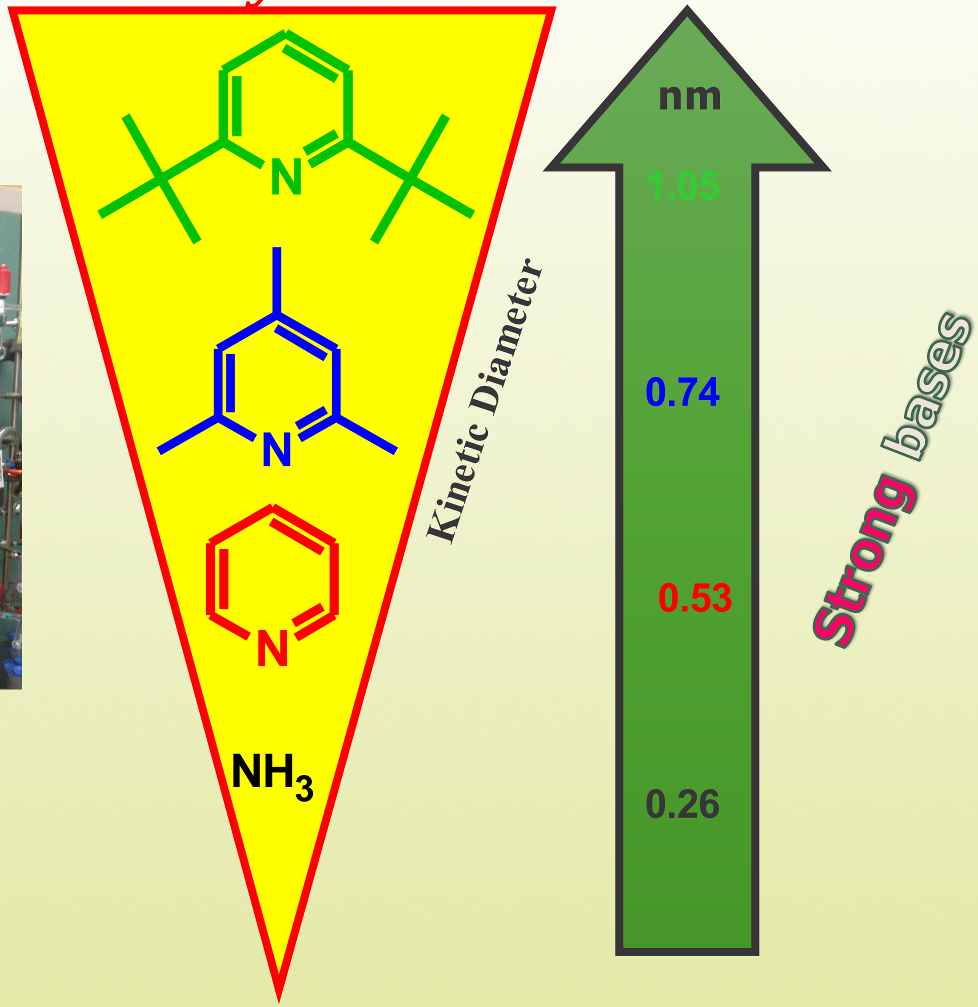
Adsorption of probe molecules to elucidate *strength* and *accessibility* of acid sites





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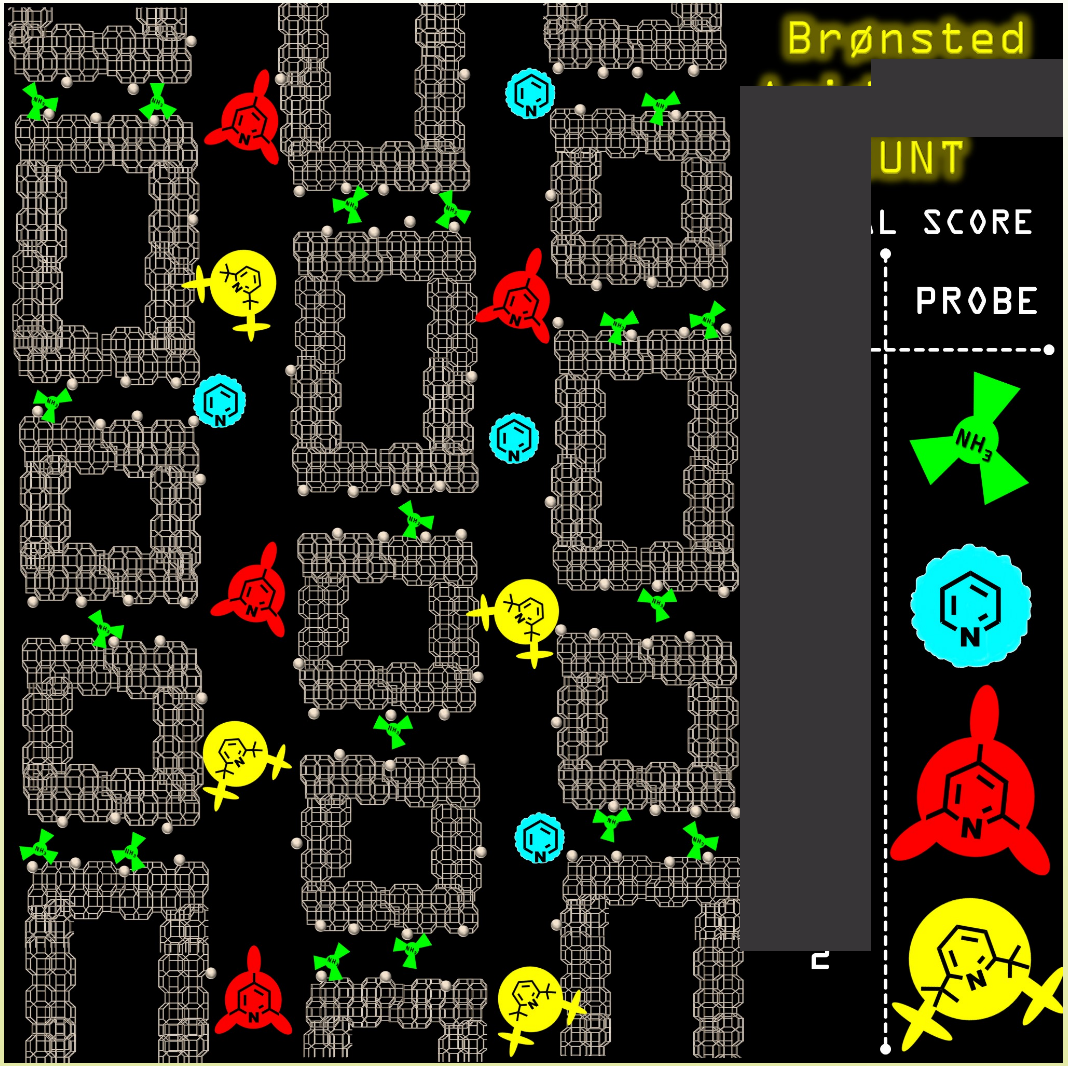

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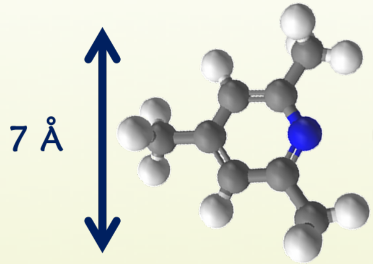
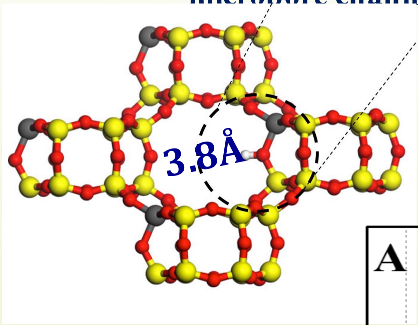
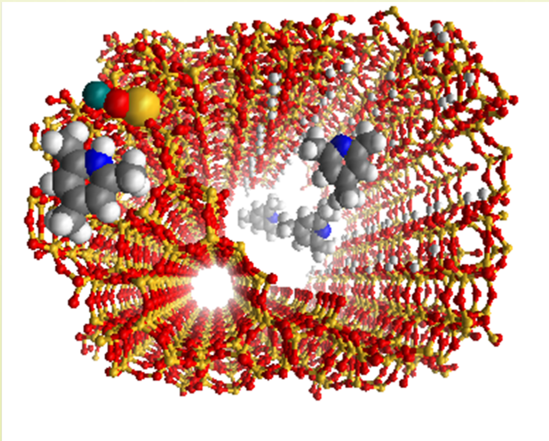
Collidine adsorption at 298K - FTIR

SAPO-34
micropore channel

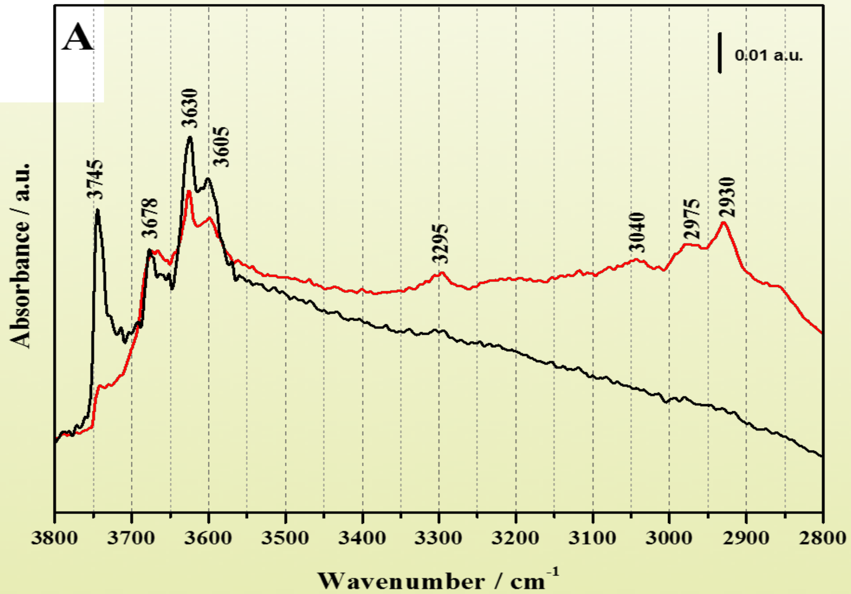




Collidine
2,4,6-trimethylpyridine (2,4,6-TMP)



Only a fraction of Brønsted acid sites are accessible to the 2,4,6-TMP molecules



Collidine will not enter in the micropores and can interact with active sites located in mesopores or in the pore mouth

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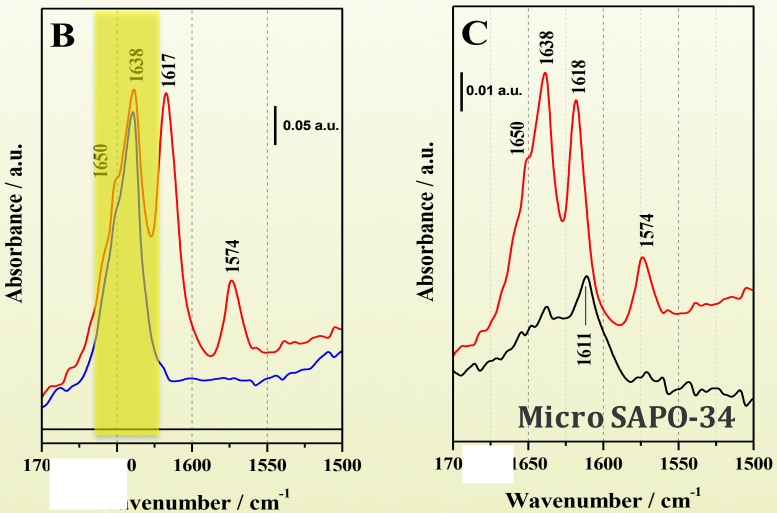
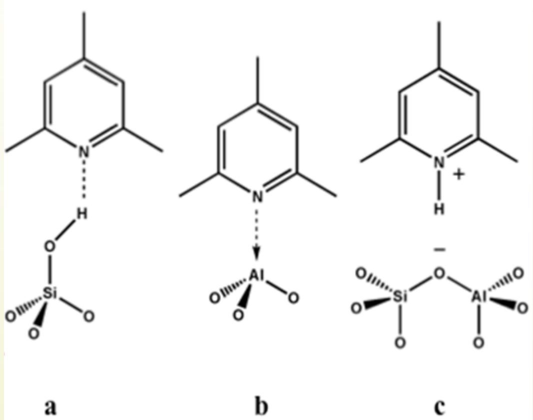
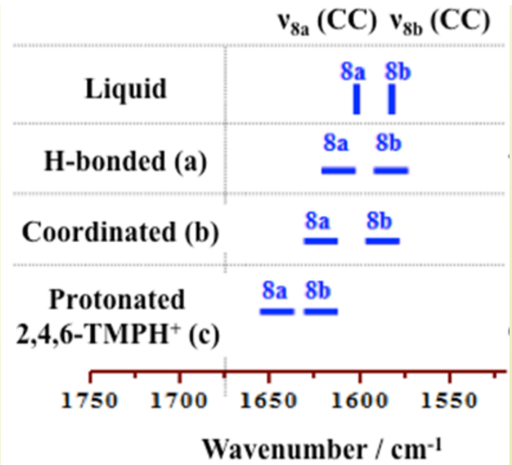
Collidine adsorption at 298K - FTIR

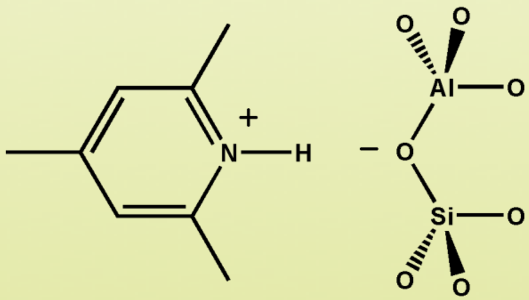
HP SAPO-34-CTAB







ν C-C ring modes



Lambert-Beer law $A = \varepsilon N \rho$

A= integrated area of $\nu_{C\text{-}C}$ band, ε= molar extinction coefficient (cm mmol^{-1}), N= concentration of the oscillators (mmol g^{-1}), ρ= density of the disk (mg cm^{-2})

*K. Mlekodaj *et al.*, *Micropor. Mesopor. Mater.* **2014**, 183, 54.

MULTI2HYCAT **FTIR**

HP-SAPO-34-CTAB

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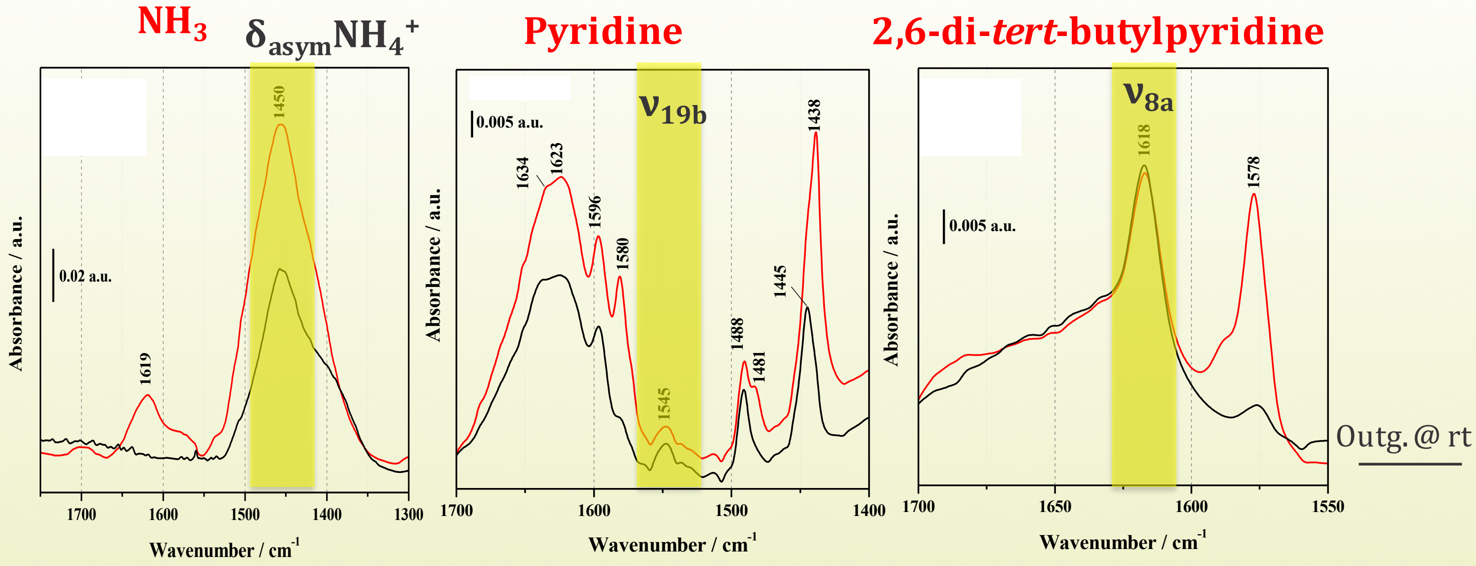

Probe molecule	Protonated species	IR band of protonated species	N (μmol g^{-1})	AF
NH_3	NH_4^+	1450 (δ_{asym})	59	1
Pyridine	PyH^+	1545 (ν_{19b})	6.3	0.107
2,4,6-TMP	2,4,6-TMPH$^+$	1638 (ν_{8a})	2.2	0.038
2,6-dTBP	2,6-dTBPH$^+$	1618 (ν_{8a})	2.1	0.037

AF = accessibility factor $N_{alkylpyridineH+} / N_{NH4+}$

FTIR

HP-SAPO34-Saccharose

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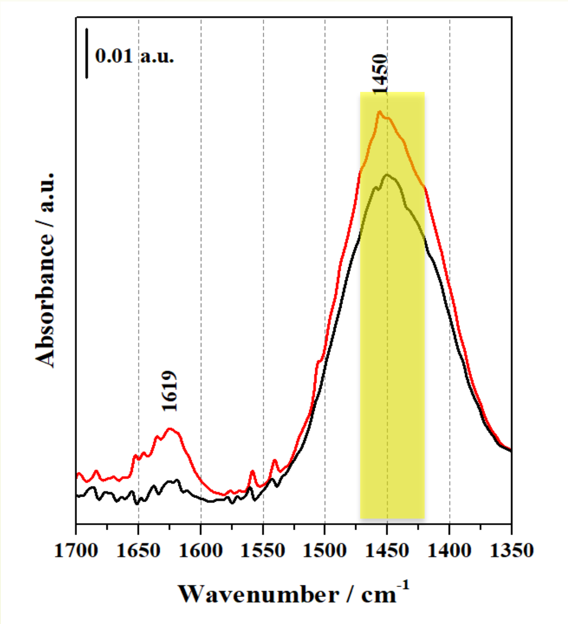
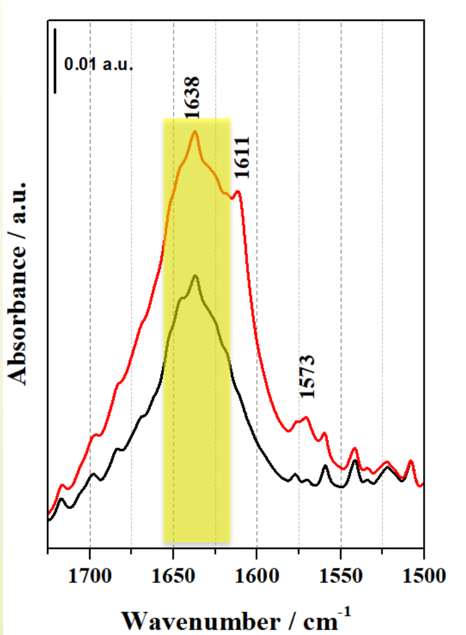
NH_3



Collidine



Outg. @ rt

	Probe molecule	Protonated species	IR band of protonated species	N µmol g^{-1}	AF
HP-SAPO34-CTAB	NH_3	NH_4^+	1450 (δ_{asym})	59	1
	2,4,6-TMP	2,4,6-TMPH$^+$	1638 (ν_{8a})	2	0.038
HP-SAPO34-Saccharose	NH_3	NH_4^+	1450 (δ_{asym})	41	1
	2,4,6-TMP	2,4,6-TMPH$^+$	1638 (ν_{8a})	3	0.072

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Conclusions

- **Mesoporous ordered silica (MCM-41) containing CTAB and saccarose have been used as precursor to drive the synthesis of hierarchical acid SAPO-34 catalyst, *avoiding the use of sophisticated surfactants.***

- **This method benefits from superior retention of the desirable acid properties of the microporous parent framework, whilst simultaneously enhancing its mass transport capabilities.**

- **An integrated physico-chemical characterization is essential to elucidate the *nature*, the *strength* and the *accessibility* of the active acid sites and to identify structure-properties relationship**

- **The superior catalytic activity can be rationalized on the basis of the *enhanced diffusion*, through the interconnected hierarchical network, and to a *higher accessibility of a fraction of the Brønsted acid sites* with respect the microporous catalysts.**