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Italiadomani PIANO NAZIONALE DI RIPRESA E RESILIENZA

On the physico-chemical properties of hierarchical zeolites prepared by *top-down* and *bottom-up* approaches

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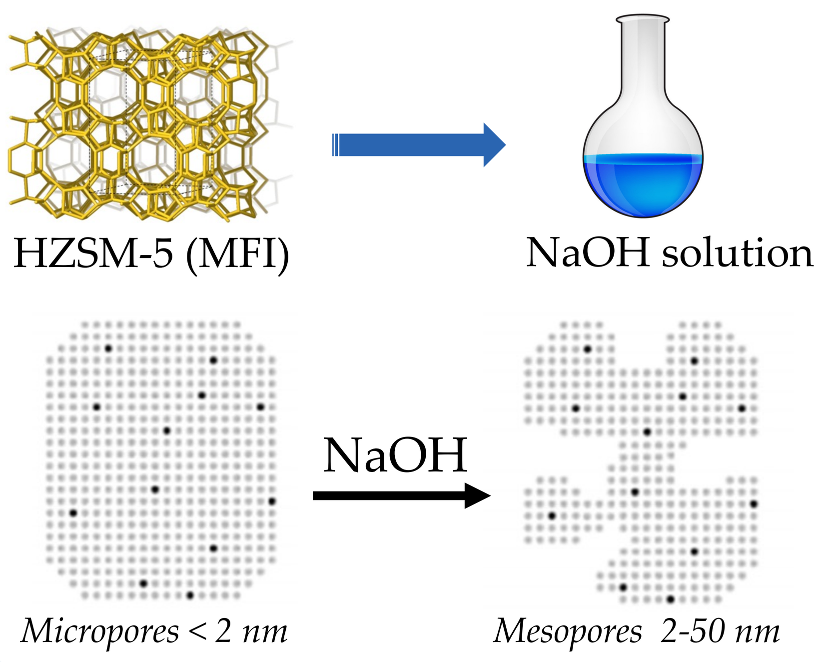
Introduction

Hierarchical zeolites, which exhibit a distinctive structure characterized by interconnected micropores and mesopores, are versatile materials that can overcome the typical issues related to microporous materials, including poor mass transfer, hindered diffusion, and strict selectivity of resulting products. Typically, hierarchical porous materials can be obtained through *bottom-up* or *top-down* approaches. The former introduces dual porosity during synthesis, while the latter employs a post-synthetic step on a pre-existing microporous matrix. [1]

In this contribution, both approaches were applied to synthesize hierarchical porous materials with different properties. In detail: a commercial zeolite (HZSM-5 with SiO_2/Al_2O_3 = 80) with a MFI structure and a natural clinoptilolite (HEU) were desilicated through a *top-down* approach using NaOH solutions at varying concentrations, to evaluate the treatment efficiency. In parallel, two different hierarchical SAPO-34 (CHA) were obtained through a *bottom-up* approach, using either non calcined MCM-41 or SBA-15, which serve as both Si source and mesoporogen. The synthesized hierarchical architectures were characterized by multi-technique approach using XRD, N_2 physisorption at 77K, TGA and FTIR spectroscopy of adsorbed probe molecules, to assess the nature, strength and accessibility of the acid sites.

Synthesis

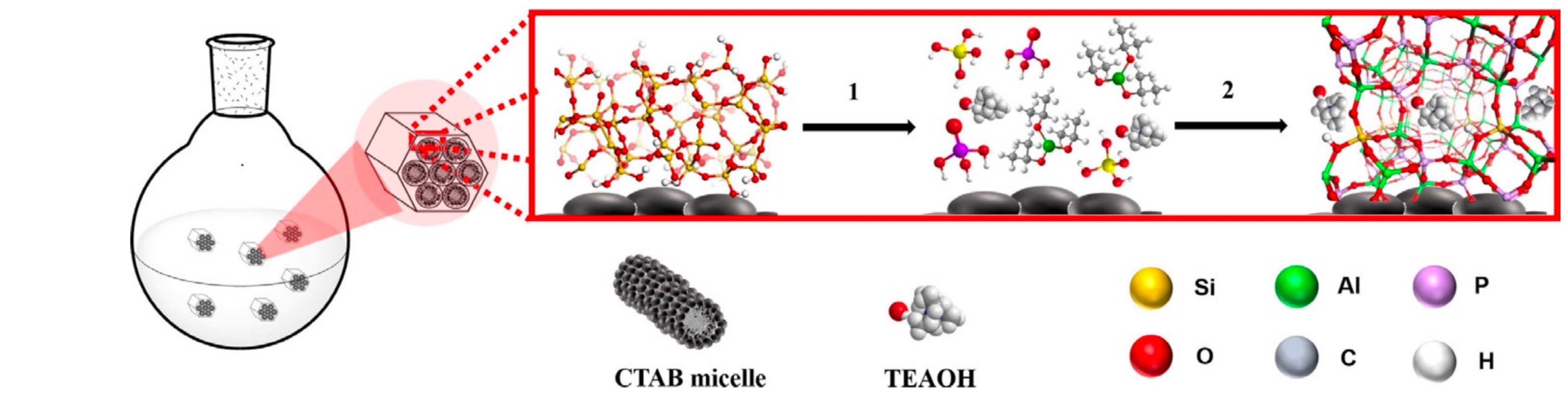
Top-down approach



A commercial HZSM-5 zeolite was employed - CBV 8014 Zeolyst International (Si/Al = 48).

- Desilication treatment was carried out at 3 different pH conditions (13.3, 9 and 8) for 3h.
- After desilication, the samples underwent an exchange treatment with a NH_4NO_3 solution;
- Finally, the materials were calcined at 600 °C for 6h.[2]

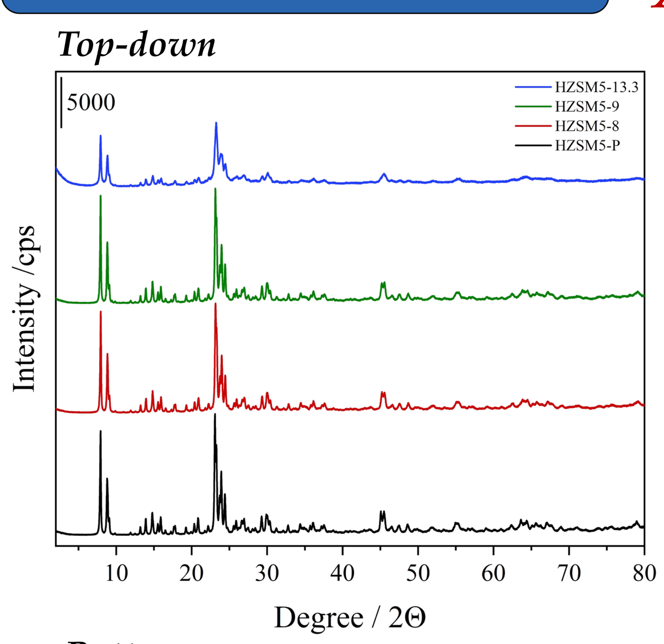
Bottom-up approach



- Two SAPO-34 samples were synthesized through hydrothermal methodology, using either uncalcined MCM-41 or uncalcined SBA-15, containing CTAB or Pluronic P123 respectively, as both Si source and mesoporogen.[3]

Characterization

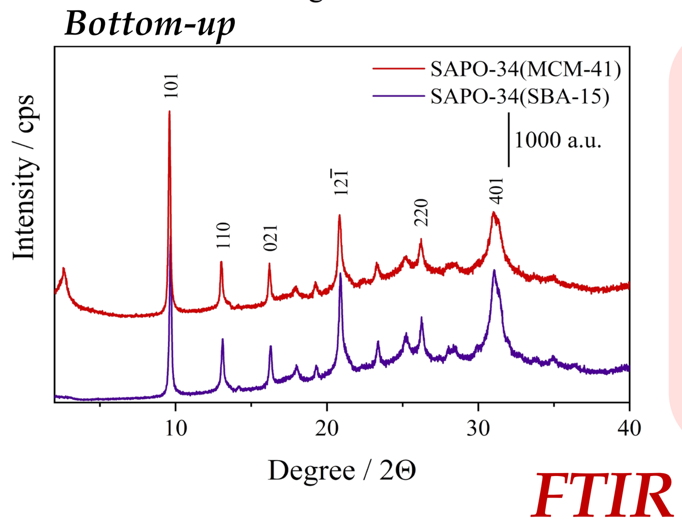
XRD and N_2 adsorption @ 77K



Zeolite	RC %	S_{DFT} m²/g	S_{micro} m²/g	S_{meso} m²/g
HZSM5-P	100	965	946	19
HZSM5-13.3	55	852	653	199

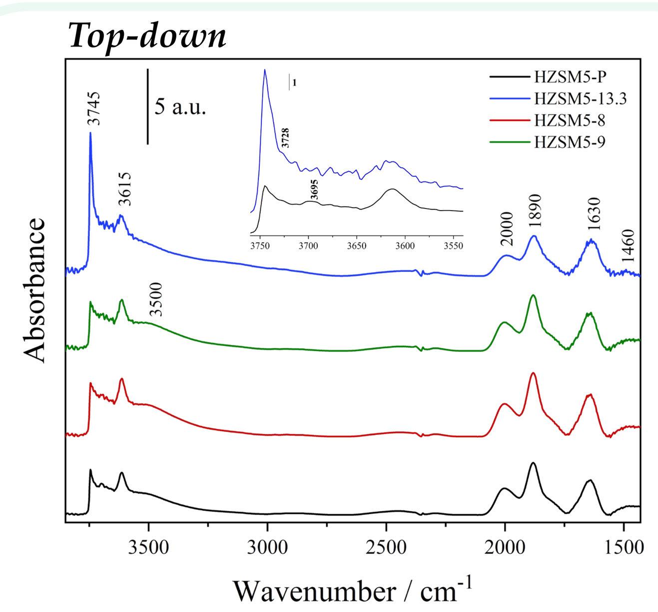
RC% = Relative Cristallinity %

The crystal lattice structure is maintained during the desilication process; only HZSM5-13.3 sample shows less intense diffraction peaks.

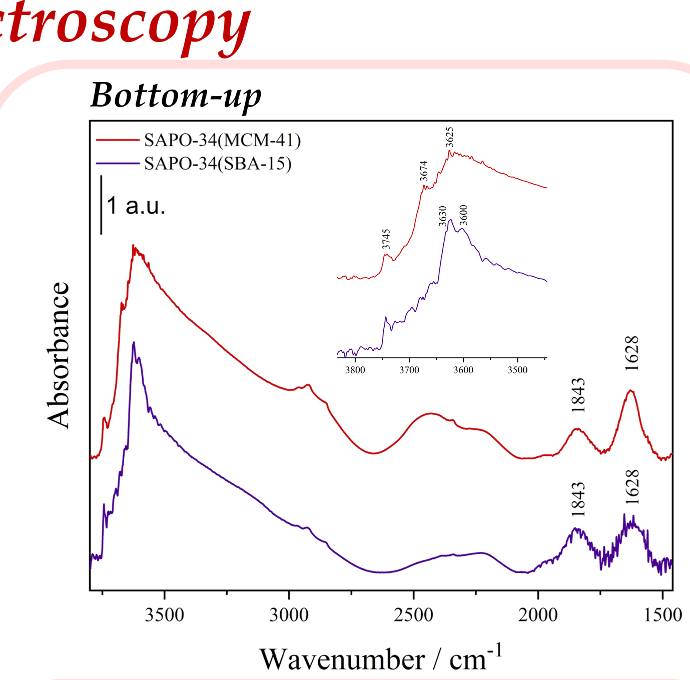


In the XRD patterns of both samples, the characteristic diffraction peaks of the CHA structure are present; in the low angle range, SAPO-34(MCM-41) exhibits also a diffraction peak at ca. 2° that is indicative of ordered mesoporosity.

FTIR Spectroscopy



The peak at 3745 cm^{-1}, related to the isolated silanols, shows higher intensity for the sample treated at pH 13.3; this is due to a higher mesoporous character of the latter.



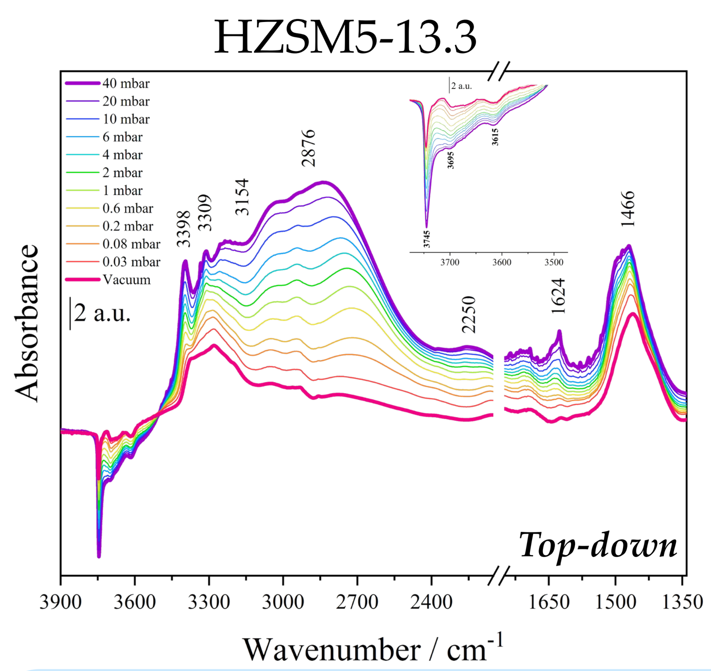
Both synthesized materials show the signals of free silanols (3745 cm^{-1}) and Brønsted acid sites (3630, 3625 and 3600 cm^{-1}).

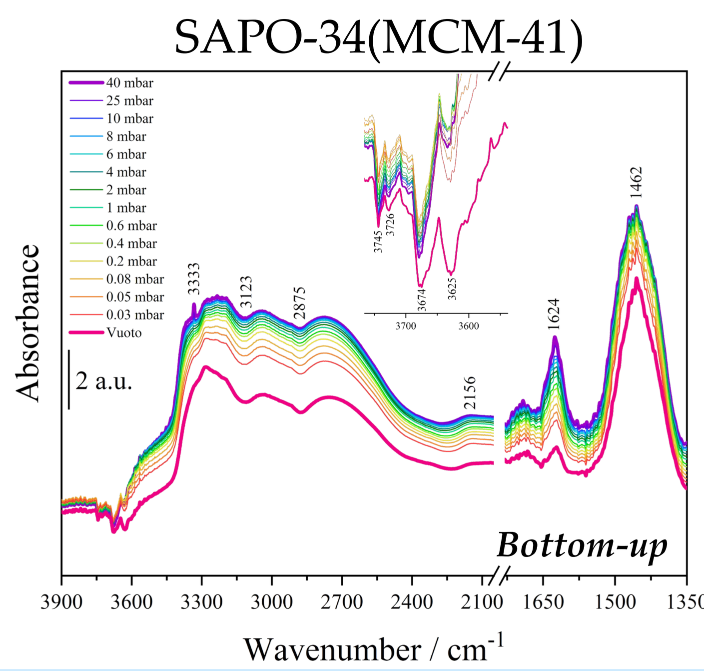
Potential Applications

The synthesized hierarchical zeolites possess applications in various fields, such as heterogeneous catalysis and as adsorbents toward cationic species in solution (i.e. metal ions), either individually or in combination, depending on the quantity of captured metal and its coordination state. Future analyses will investigate their potential properties and focus on optimizing synthesis and desilication procedures.

Probe molecules

FTIR Spectra – NH_3 adsorption @ RT





Sample	N_{tot}[a] µmol g^{-1}
HZSM5-P	218
HZSM5-13.3	464
SAPO-34(MCM-41)	478
SAPO-34(SBA-15)	453

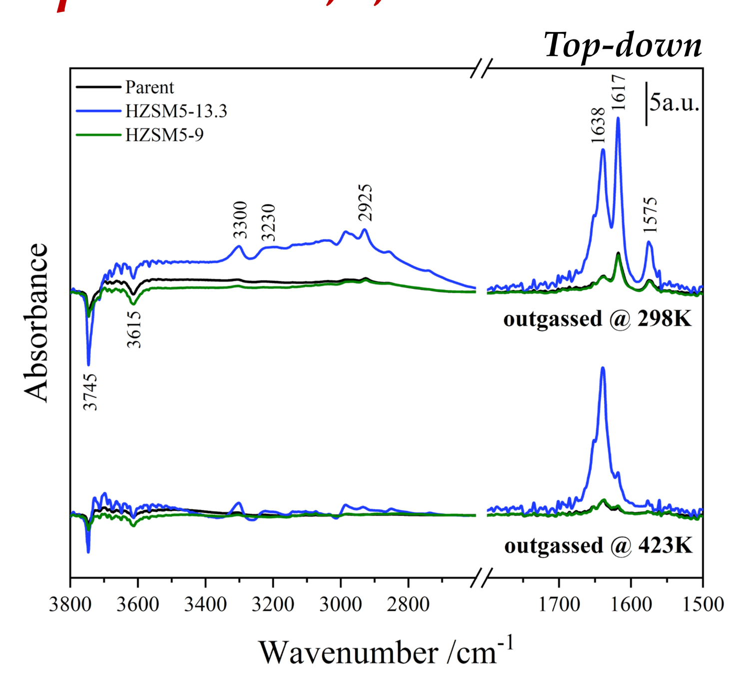
[a]Calculated using ε_v = 13,0 cm/µmol

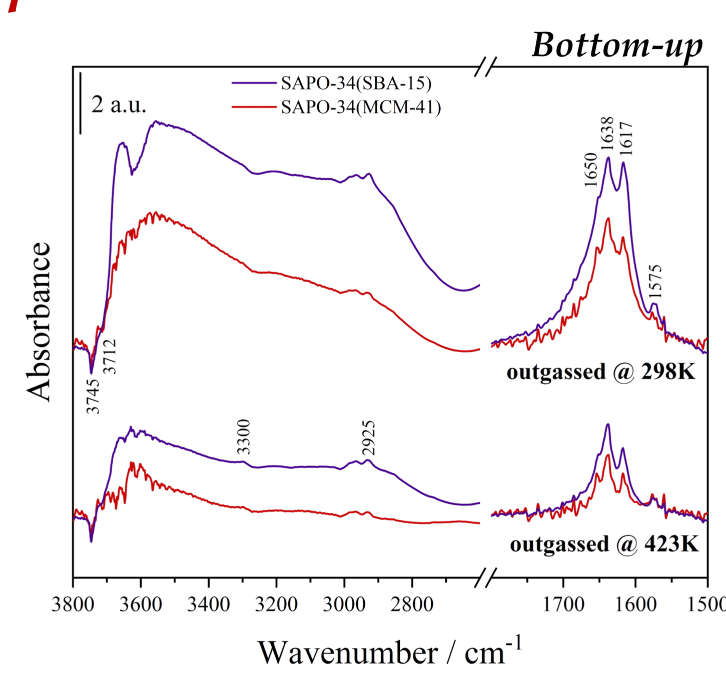
NH_3, with a diameter of 2.6 Å, was adsorbed to quantify the total Brønsted acid sites (BAS), both in micro- and mesopores. The number of BAS (N_{tot}) was calculated by means of the band at ca. 1460 cm^{-1} associated with the adsorbed ammonium ion (NH_4^+) using the equation: $A_V = \varepsilon_V N \rho$ where A_V is the integrated area of the specific band, ε_V is the molar extinction coefficient, N is the number of oscillators and ρ is the density of the material pellet.

FTIR Spectra – 2,4,6-TMP adsorption

2,4,6-trimethylpyridine (2,4,6-TMP or Collidine), with a diameter of 7.4 Å, was adsorbed to monitor the accessibility of BAS in the mesopores of hierarchical architectures.

Among all samples, HZSM5-13.3 and SAPO-34(SBA-15) showed greater mesoporous character.





A quantification of BAS was performed by means of the band at 1638 cm^{-1} associated with the protonated 2,4,6-TMP molecule (2,4,6-TMPH$^+$ ion) in the outgassed spectra @ 423K.

The quantification was done by applying the same equation shown earlier. In addition, Accessibility Factor (AF_{Col}) values are given; the basic treatment increased the accessibility of the zeolitic framework, while among the SAPO-34 samples, the SBA-15 generated one showed a better diffusion capacity toward the collidine molecule.

Sample	N_{Col}[b] µmol g^{-1}	AF_{Col}[c]
HZSM5-P	32	0.15
HZSM5-13.3	311	0.67
HZSM5-9	41	-
SAPO-34(MCM-41)	21	0.044
SAPO-34(SBA-15)	58	0.13

[b]Calculated using ε_v = 10,1 cm/µmol, [c]Calculated as N_{Col}/N_{tot}

References

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