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Top-down strategies for tailoring porosity in zeolites: comprehensive evaluation of structural and adsorption properties

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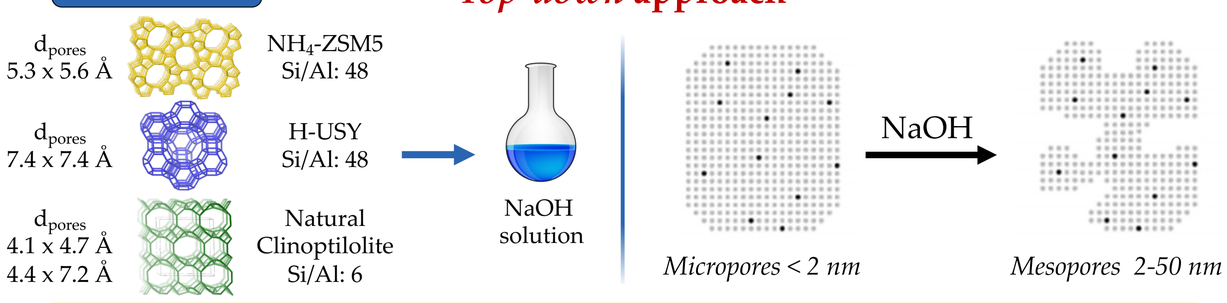
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Introduction

Hierarchical zeolites, characterized by the presence of interconnected micropores and mesopores, are versatile materials capable of overcoming the typical limitations of microporous systems, including poor mass transfer, hindered diffusion, and strict product selectivity[1,2]. One possible route to obtain hierarchical porous materials is through top-down approaches, in which secondary porosity is introduced through post-synthetic modification of a pre-existing microporous matrix. In this study, commercial HZSM5 and HUSY zeolites (SiO_2/Al_2O_3 = 80, MFI and FAU frameworks, respectively) and a natural clinoptilolite (HCLI, Si/Al = 6, HEU framework) were desilicated using NaOH solutions at different concentrations. The resulting hierarchical structures were characterized by XRD, N_2 physisorption at 77 K, TGA and FTIR spectroscopy of adsorbed probe molecules to assess the nature, strength and accessibility of the acid sites. Their performance in Cu^{2+} and Co^{2+} ions removal from aqueous solution was then evaluated by UV–Vis spectroscopy. Selectivity tests were also carried out to determine the materials' affinity for the target ions. The three zeolites exhibited distinct adsorption behaviors: HZSM5 demonstrated the highest adsorption capacity but showed no specific affinity for either metal ion, in contrast to HUSY and HCLI, which displayed a clear preference for Co^{2+}. Notably, the desilication treatment significantly enhanced the adsorption efficiency of the studied materials.

Synthesis

Top-down approach

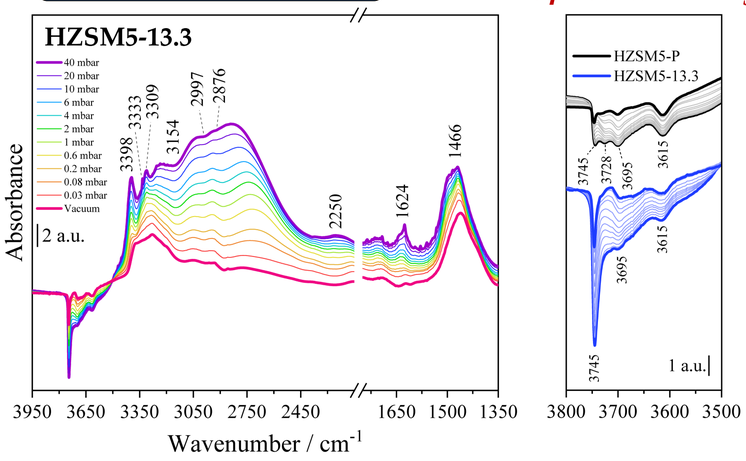


Two commercial HZSM5 and HUSY zeolites (MFI and FAU frameworks respectively) and a natural clinoptilolite (HEU) were employed.

- 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.[3]

Probe Molecules

FTIR Spectra – NH_3 adsorption @ RT

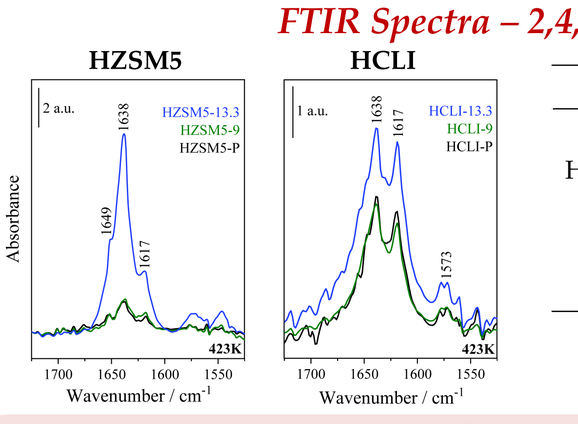


Sample	N_{tot} (µmol g^{-1})[a]
HZSM5-P	218
HZSM5-9	338
HZSM5-13.3	464
HUSY-P	124
HUSY-8	134
HUSY-9	131
HCLI-P	522
HCLI-9	681
HCLI-13.3	552

[a]Calculated using ε = 13.0 cm/µmol

NH_3, with a **kinetic diameter of 2.6 Å**, was adsorbed to quantify the **total Brønsted acid sites (BAS)**, both in micro- and secondary order pores. The number of BAS (N_{tot}) was calculated by means of the band at 1466 cm^{-1} associated with the adsorbed ammonium ion (NH_4^+) using the equation: $A = \varepsilon N \rho$ where A is the integrated area of the specific band, ε is the molar extinction coefficient, N is the number of oscillators and ρ is the density of the material pellet. **HZSM5** showed a **significant increase** in N_{tot} after desilication. **HUSY simply dissolved** during desilication. **HCLI** reflects the **purification effect** of the treatment observed during the XRD analyses.

FTIR Spectra – 2,4,6-TMP adsorption



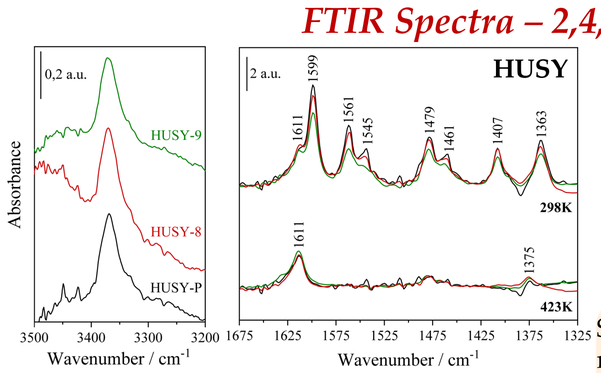
Sample	$N_{2,4,6\text{-}TMPy}$ (µmol g^{-1})[a]	$AF_{2,4,6\text{-}TMPy}$[b]
HZSM5-P	17	0.078
HZSM5-13.3	197	0.425
HCLI-P	32	0.061
HCLI-9	43	0.063
HCLI-13.3	64	0.116

[a]Calculated using ε = 10.1 cm/µmol

[b]$AF_{2,4,6\text{-}TMPy}$ calculated as $AF_{2,4,6\text{-}TMPy} = \frac{N_{2,4,6-TMPy}}{N_{tot}}$

2,4,6-trimethylpyridine (2,4,6-TMPy or Collidine), with a **kinetic diameter of 7.4 Å**, was adsorbed to monitor the **accessibility of BAS in the secondary pores** of hierarchical architectures.
The quantification of BAS was performed by means of the band at 1638 cm^{-1} associated with the protonated form of the probe molecule (2,4,6-$TMPyH^+$ ion) in the outgassed spectra @ 423K. This was done by applying the same equation shown earlier. In addition, **Accessibility Factor ($AF_{2,4,6\text{-}TMPy}$) values are given**. The **desilication process led to a pronounced enhancement in the concentration of Brønsted acid sites accessible to 2,4,6-TMPy in samples treated at pH 13.3**, thereby confirming a higher degree of structural hierarchization.

FTIR Spectra – 2,4,6-TTBPy adsorption



Sample	$N_{2,4,6\text{-}TTBPy}$ (µmol g^{-1})[a]	$AF_{2,4,6\text{-}TTBPy}$[b]
HUSY-P	32	0.26
HUSY-8	36	0.27
HUSY-9	47	0.36

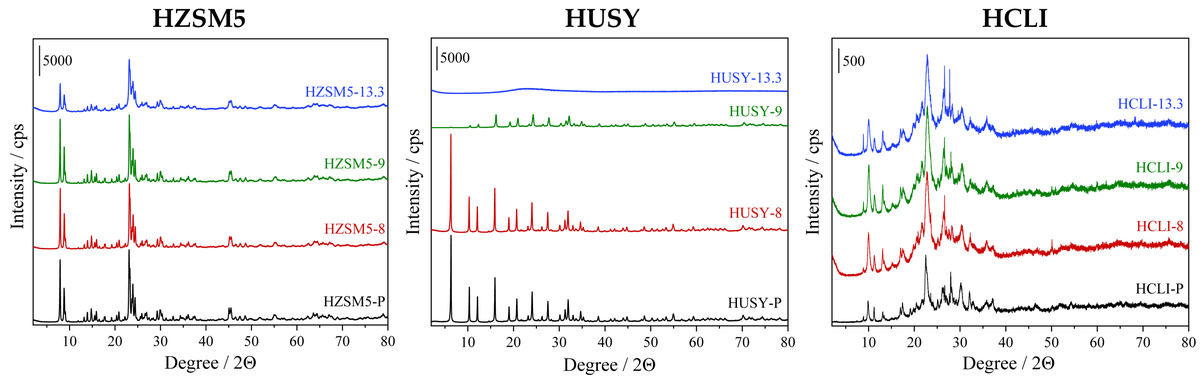
[a]Calculated using ε = 5.74 cm/µmol

[b]$AF_{2,4,6\text{-}TTBPy}$ calculated as $AF_{2,4,6\text{-}TTBPy} = \frac{N_{2,4,6-TTBPy}}{N_{tot}}$

Since 2,4,6-TMPy molecule can enter the 12-membered ring openings of the faujasitic supercages of HUSY, it does not exclusively probe BAS located in secondary porosities. Consequently, the bulkier **2,4,6-tri-*tert*-butylpyridine** (2,4,6-TTBPy, **kinetic diameter of 11 Å**) was employed in the case of HUSY zeolite.
A quantification of BAS was performed by means of the band at 3364 cm^{-1} associated with the 2,4,6-$TMPyH^+$ ion, in the outgassed spectra @ 423K. The resulting **Accessibility Factor ($AF_{2,4,6\text{-}TTBPy}$) values confirmed an enhanced population of BAS accessible to 2,4,6-TTBPy following desilication.**

Characterization

XRD and N_2 adsorption @ 77K



Sample	RC %	SSA_{BET} (m^2 g^{-1})	$V_{tot\ DFT}$ (cm^3 g^{-1})	V_{micro} (cm^3 g^{-1})	V_{meso} (cm^3 g^{-1})	Relative mesoporous volume %	Si/Al ratio[a]
HZSM5-P	100	397	0.24	0.13	0.11	46	42
HZSM5-13.3	74	435	0.49	0.11	0.38	78	19
HUSY-P	100	684	0.44	0.19	0.25	57	57
HUSY-9	38	705	0.47	0.19	0.28	60	46
HCLI-P	72	120	0.21	-	0.18	86	6
HCLI-13.3	93	91	0.16	-	0.16	100	4

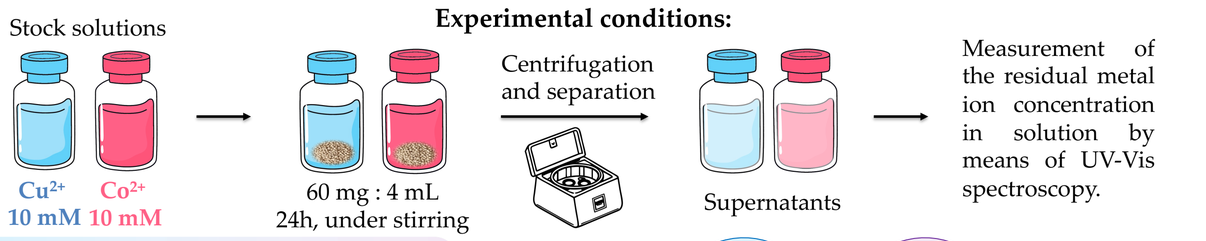
[a] Calculated using FESEM-EDX analyses

The **relative cristallinity RC%** values, calculated from XRD patterns, indicate a **partial loss of crystallinity following desilication**. HUSY is the most sensitive to basic treatment, while a "purification" effect was observed for HCLI samples.
From N_2 physisorption analyses, a **general increase in relative mesoporous volume** was observed, confirming the effective introduction of mesoporosity.

Material Performance

Metal Ion Adsorption Experiments

Experimental conditions:



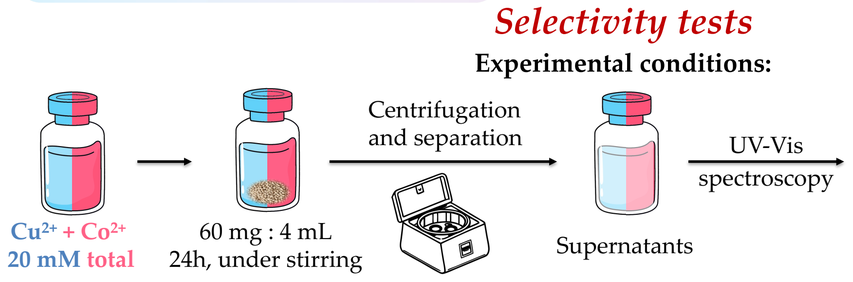
The developed materials were tested for the uptake of transition metal ions from aqueous solution, focusing on Cu^{2+} and Co^{2+}. The amount of metal adsorbed by each sample was then calculated from the difference between the initial and residual concentrations in solution. **Desilication generally enhances the metal-uptake performance of the treated zeolites**. This improvement is especially pronounced for HZSM5, in agreement with previous observations showing that HZSM5 is the only material exhibiting a substantial increase in BAS concentration upon desilication.

29 Cu Copper 63.546
27 Co Cobalt 58.933

Sample	µmol Cu^{2+} g^{-1} material	µmol Co^{2+} g^{-1} material	[BAS] (µmol g^{-1})
HZSM5-P	57 ± 8	36.3 ± 0.8	218
HZSM5-13.3	84 ± 9	63 ± 2	464
HUSY-P	53 ± 3	70.2 ± 0.2	124
HUSY-9	56.5 ± 0.7	70.7 ± 0.4	131
HCLI-P	22 ± 1	39.1 ± 0.6	522
HCLI-13.3	26.0 ± 0.8	48 ± 3	552

Selectivity tests

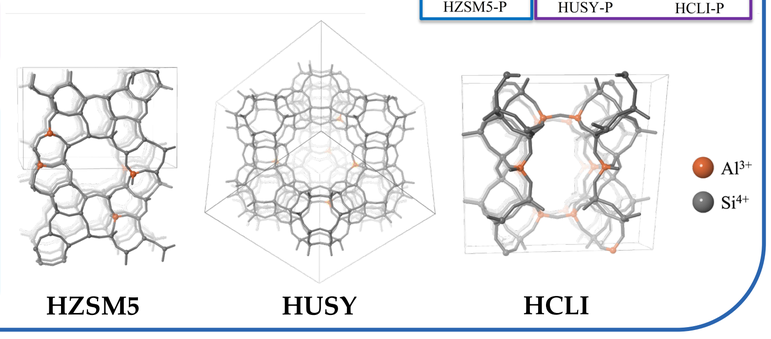
Experimental conditions:



Different selectivity: why?

HUSY and **HCLI**: The Al^{3+} atoms are located in more accessible positions in their frameworks.

HZSM5: The Al^{3+} atoms are located in sterically constrained regions (channel intersections/ narrow microporous cavities). In this context, HZSM5 framework may stabilize the geometrically distorted species of Cu^{2+} aqua complexes (Jahn-Teller effect).



Conclusions

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This systematic investigation revealed how the **desilication treatment** applied to different zeolite frameworks can **modify their physico-chemical and structural properties**. Moreover, the obtained results indicate that **the interplay between the porosity evolution and the enhanced accessibility of BAS** in the production of hierarchical zeolites **strongly affects the removal efficiency of metal ions** from aqueous solutions. Dr. Gioele Ancora acknowledges financial support from the Next Generation EU – MUR PhD career grant.

References

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[2] S. Mitchell, A.B. Pinar, J. Kenvin, P. Crivelli, J. Kärger, J. Pérez-Ramírez, *Nat. Commun.* **2015**, 6, 8633-8647.
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