

HIERARCHICAL ZEOLITES FROM *TOP-DOWN* APPROACH: A SYSTEMATIC INVESTIGATION OF STRUCTURE AND POROSITY EFFECTS ON ACIDITY AND TRANSITION METAL ION UPTAKE

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1. INTRODUCTION

Hierarchical zeolites, characterized by interconnected micro- and mesoporous networks, are versatile materials that can overcome the typical issues related to microporous materials, including poor mass transfer and hindered diffusion. Their application in the removal of transition metal ions from aqueous solutions is of particular interest due to the growing release of metal-containing industrial effluents. While hierarchical zeolites have been extensively characterized, a systematic comparison of how framework topology and controlled hierarchization affect acidity and metal ion uptake is still needed. In this contribution, we investigate the effect of top-down desilication on the structural and adsorption properties of zeolites with different crystalline frameworks (MFI, FAU, and HEU).

2. RESULTS AND DISCUSSION

Three zeolites with different framework structures, topological features, and physicochemical properties—two commercial (HZSM5 and HUSY) and a natural clinoptilolite (HCLI)—were subjected to desilication via post-synthetic *top-down* approach to obtain their corresponding hierarchical variants. In this strategy, the selective dissolution of silicon atoms under alkaline conditions is exploited to introduce secondary porosity within the investigated zeolites.[1,2] Three different treatment pH conditions (8, 9, and 13.3) were investigated and all the samples were thoroughly characterized through a multi-technique approach.

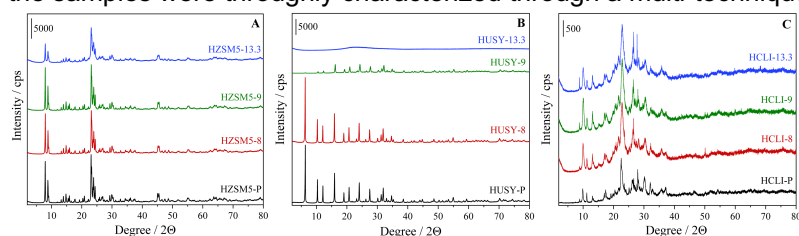


Figure 1 - XRPD patterns of (A) HZSM5, (B) HUSY and (C) HCLI samples desilicated under different pH conditions.

X-ray powder diffraction (XRPD) (Fig. 1) analyses were employed to verify the preservation of the crystalline structure after desilication. In addition, relative crystallinity (RC%) indexes were calculated (Tab. 1), and the response to the treatment was found to be strongly dependent on the zeolite framework and composition. Among the investigated materials, the MFI-type

zeolite (HZSM5) exhibited high resistance to alkaline conditions, enabling the development of significant intracrystalline mesoporosity with only a moderate loss of crystallinity. In contrast, the FAU framework (HUSY) proved to be more sensitive to desilication, as the sample HUSY-13.3 became totally amorphous. The HEU-type natural clinoptilolite showed a non-linear behavior, with mild treatments mainly inducing a purification effect and harsher conditions promoting structural alteration.

From nitrogen physisorption measurements (Tab. 1), a general increase in relative mesopore volume was observed after desilication, confirming the formation of hierarchical porosity in all investigated systems, specifically in the case of HZSM5.

Table 1 - Textural properties of the analyzed zeolitic samples. Relative crystallinity indexes (RC%) and Si/Al ratios of samples are also reported.

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 impact of desilication on zeolite acidity was investigated by FTIR spectroscopy enhanced by the use of basic probe molecules,[3] with particular emphasis on the accessibility of Brønsted acid sites (BAS), which are the main active centers for cation-exchange processes and are therefore useful for cation removal applications. Ammonia (Fig. 2) was used to probe the total BAS concentration (N_{tot}) (Tab. 2), and the Brønsted acidity was estimated semi-quantitatively for all samples before and after desilication using the Lambert–Beer equation adapted for solids:

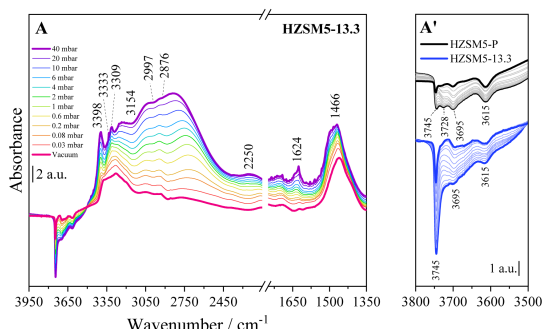


Figure 2 – A) FTIR difference spectra of NH₃ adsorbed on hierarchical HZSM5-13.3 sample at room temperature; A') comparison between the spectra of the desilicated samples and their corresponding parent samples.

in the concentration of accessible BAS for hierarchical samples, as quantified by the accessibility factor values (AF) (Tab. 2). The measurements were carried out using both individual probe molecules and a sequential adsorption approach, in which two basic probes were introduced consecutively within the same experiment, yielding additional insight into this methodology. The results indicate that controlled hierarchization primarily enhances the accessibility of Brønsted acid sites rather than simply increasing their total concentration.

Table 2 - Concentration of total Brønsted sites (N_{tot}) and of BAS accessible to 2,4,6-TMPy molecule ($N_{2,4,6\text{-TMPy}}$) and to 2,4,6-TTBPpy molecule ($N_{2,4,6\text{-TTBPpy}}$), expressed as $\mu\text{mol g}^{-1}$; Accessibility factors (AF) relative to 2,4,6-TMPy and 2,4,6-TTBPpy molecules are also reported.

Sample	N_{tot} ($\mu\text{mol g}^{-1}$)	$N_{2,4,6\text{-TMPy}}$ ($\mu\text{mol g}^{-1}$)	$\text{AF}_{2,4,6\text{-TMPy}}^a$	$N_{2,4,6\text{-TTBPpy}}$ ($\mu\text{mol g}^{-1}$)	$\text{AF}_{2,4,6\text{-TTBPpy}}^b$
HZSM5-P	218	17	0.078	-	-
HZSM5-9	338	-	-	-	-
HZSM5-13.3	464	197	0.425	-	-
HUSY-P	124	-	-	32	0.26
HUSY-8	134	-	-	36	0.27
HUSY-9	131	-	-	47	0.36
HCLI-P	522	32	0.061	-	-
HCLI-9	681	43	0.063	-	-
HCLI-13.3	552	64	0.116	-	-

$$^a \text{AF}_{2,4,6\text{-TMPy}} \text{ calculated as } \text{AF}_{2,4,6\text{-TMPy}} = \frac{N_{2,4,6\text{-TMPy}}}{N_{\text{tot}}}$$

$$^b \text{AF}_{2,4,6\text{-TTBPpy}} \text{ calculated as } \text{AF}_{2,4,6\text{-TTBPpy}} = \frac{N_{2,4,6\text{-TTBPpy}}}{N_{\text{tot}}}$$

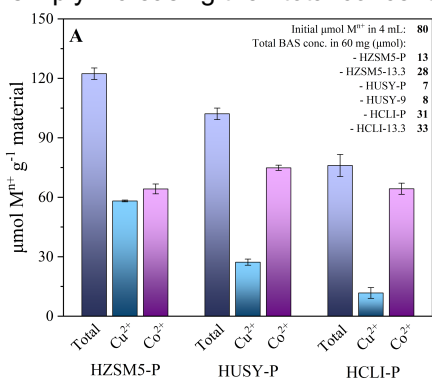


Figure 3 - Amount of Mn²⁺ captured by the studied zeolites from aqueous solution after 24 hours, expressed as $\mu\text{mol g}^{-1}$

Finally, the obtained hierarchical zeolites were evaluated for their ability to recover Cu²⁺ and Co²⁺ ions from aqueous solutions by using UV-Vis spectroscopy. Among the investigated materials, hierarchical HZSM5 exhibited the most pronounced enhancement in metal uptake after desilication (from 57 ± 8 to $84 \pm 9 \mu\text{mol g}^{-1}$ for Cu²⁺ and from 36.3 ± 0.8 to $63 \pm 2 \mu\text{mol g}^{-1}$ for Co²⁺). This behavior is consistent with the observed increase in Brønsted acidity and the improved accessibility of active sites. Selectivity tests were also carried out to determine the materials' affinity for the target ions. The three investigated zeolites exhibited distinct behaviors reflecting their different physicochemical properties (Fig. 3). 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 selectivity toward Co²⁺. These differences are hypothesized to be related to the distinct spatial distribution of aluminum atoms within the respective zeolite frameworks.

3. CONCLUSIONS

This study presents a systematic comparison of hierarchical zeolites derived from different crystalline structures (MFI, FAU, and HEU). The impact of hierarchical porosity on metal ion removal performance extends beyond a simple increase in mesoporosity. Controlled top-down desilication enhances the accessibility of Brønsted acid sites only when structural integrity and pore connectivity are preserved. Among the investigated materials, hierarchical HZSM5 exhibits the most favorable balance between structural stability and acidity, resulting in improved uptake of Cu²⁺ ions from aqueous solutions. These results underline the importance of considering zeolite structure and acid site accessibility in the design of hierarchical zeolites for adsorption and ion-exchange applications, particularly in the context of metal removal from water. Dr. Gioele Ancora holds a PhD career grant supported by Next Generation EU – MUR.

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