

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

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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 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$, MFI and FAU frameworks, respectively) and a natural clinoptilolite (HCLI, $\text{Si}/\text{Al} = 5$, 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 (Figure 1A,A'). 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+} (Figure 1B). Notably, the desilication treatment significantly enhanced the adsorption efficiency of the studied materials. Dr. Gioele Ancora acknowledges financial support from the Next Generation EU – MUR PhD career grant.

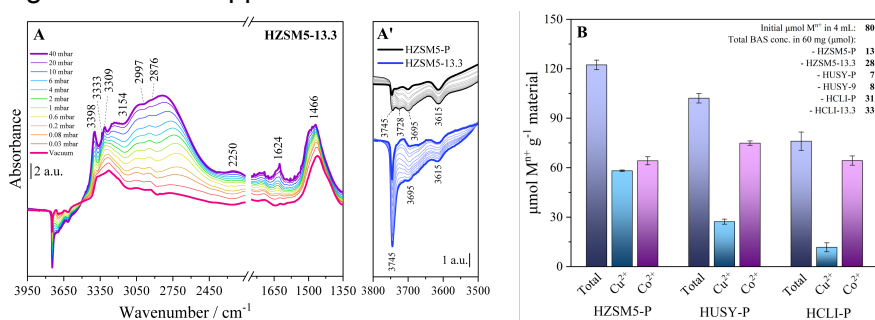


Figure 1: FTIR difference spectra of NH_3 adsorbed on hierarchical HZSM5 at room temperature (A); comparison of HZSM5 spectra before and after desilication in the OH stretching region (A'); Amount of M^{n+} captured by the studied zeolites from aqueous solution after 24 hours, expressed as $\mu\text{mol g}^{-1}$ (B).

[1] M. Hartmann, Angew. Chem. Int. Ed. 43 (2004) 5880–5882.

[2] S. Mitchell et al. Nat. Commun. 6 (2015) 8633–8647.