

A SEQUENTIAL PROBE ADSORPTION APPROACH FOR THE CHARACTERIZATION OF ACID SITES IN HIERARCHICAL ZEOLITES

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Hierarchical zeolites, featuring a distinctive architecture of interconnected micro- and mesopores, are widely studied for their tunable acidic properties, whose nature and accessibility play a key role in determining their performance in adsorption and catalytic processes.[1,2] These systems can be obtained either via post-synthetic *top-down* approaches or through *bottom-up* synthesis strategies, and the nature and spatial distribution of Brønsted acid sites (BAS) are crucial for understanding structure–property relationships. FTIR spectroscopy coupled with the adsorption of basic probe molecules is a well-established approach for this purpose. In particular, probes with different kinetic diameters are commonly employed to selectively access BAS located in distinct pore environments. However, conventional methodologies rely on separate single-probe experiments, which are time- and resource-intensive. In this contribution, two *top-down* desilicated commercial zeolites (HZSM5 and natural clinoptilolite, HCLI, with MFI and HEU structures, respectively) and a *bottom-up* synthesized SAPO-34 (CHA structure) were investigated. Their hierarchical architectures were characterized through a multi-technique approach, including XRD, N₂ physisorption at 77K, TGA and FTIR spectroscopy of adsorbed probe molecules, to assess the nature, strength and accessibility of the acid sites. Conventional single-probe adsorption experiments (NH₃ and bulkier probes such as 2,4,6-trimethylpyridine 2,4,6-TMPy and 2,4,6-tri-tert-butylpyridine 2,4,6-TTBP) were performed to assess total BAS concentration in different pore domains. To gain deeper insight into the accessibility of acid sites, a sequential adsorption approach was explored, involving the adsorption of bulky probes

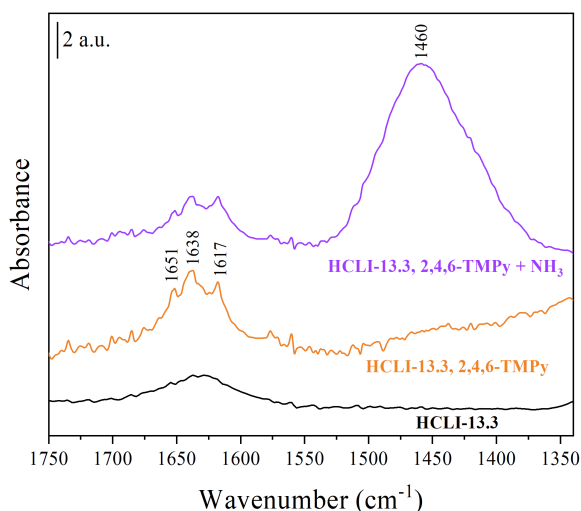


Figure 1. FTIR difference spectra of 2,4,6-TMPy and NH₃ probes sequentially adsorbed on HCLI-13.3 sample in the low wavenumber region.

and NH₃ under identical conditions, yielding promising results. FTIR difference spectra collected after sequential adsorption show the simultaneous presence of characteristic bands of both probe molecules, confirming the feasibility of the approach (Figure 1). This strategy offers the prospect of determining, within a single experiment, both the total BAS concentration and their spatial distribution across the pore system, thereby substantially reducing experimental time and energy consumption. Moreover, it may provide insights into the interactions between the different basic probe molecules.

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[1] S. Mitchell et al. Nat. Commun. 6 (2015) 8633-8647.

[2] I. Miletto et al. Chem. Eur. J. 23 (2017) 9700-9968.