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Review

Fourier transform infrared quantification of acid sites in solids: probe molecules in action

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Heterogeneous catalysis plays a crucial role in enabling cleaner and more efficient chemical processes; its performance is largely governed by the nature and strength of active sites. Among these, Brønsted acid sites (BAS) in zeolites are especially important for industrial and emerging sustainable applications. This review discusses recent advances in using Fourier transform infrared spectroscopy with probe molecules to quantitatively assess BAS in zeolites. We highlight a practical and updated workflow emphasizing the determination of reliable molar extinction coefficients for adsorbed probe molecules (carbon monoxide, acetonitrile, ammonia, and pyridine), a key factor often overlooked in acidity measurements. By consolidating methodological developments and best practices, this review provides guidance for improving the accuracy and comparability of acidity quantification in zeolites.

Through the eyes of infrared spectroscopy: a molecular journey into solid acidity

From industrial transformations to environmental remediation, catalysis shapes our modern world. Among the different types of catalysis, heterogeneous catalysis is central to sustainable chemistry, providing solutions to reduce emissions, valorize waste, and design cleaner processes. At the core of this discipline is the nature and strength of active sites, which govern catalytic activity, selectivity, and efficiency. Accurately quantifying the active sites is essential to understanding how solid catalysts operate and to improving catalyst performance [1–3]. As the world moves toward the 2050 environmental goals, mastering this knowledge is essential for driving innovation in catalysis and advancing the principles of green chemistry [4].

Within the landscape of active sites in heterogeneous catalysts, strong acids, such as Brønsted or Lewis sites, are particularly influential, driving many of the key chemical transformations that underpin modern catalytic processes. Their presence and strength often dictate the reactivity and selectivity of a catalyst, making their identification and quantification central to the rational design of next-generation heterogeneous catalysts [5–8].

Among experimental techniques, **Fourier transform infrared (FTIR) spectroscopy** (see Glossary) is a powerful and versatile method for probing surface acidity in heterogeneous catalysts. Upon adsorption of probe molecules such as carbon monoxide (CO), ammonia (NH_3), pyridine (C_5H_5N), or deuterated acetonitrile (CD_3CN), characteristic shifts in their vibrational bands provide molecular-level information on the nature, strength, and distribution of Brønsted and Lewis acid sites [9,10]. For instance, the stretching of CO shifts to a higher frequency with respect to the gas phase upon H-bond coordination with **Brønsted acid sites (referred to as BAS**, see Glossary). Conversely, stronger bases like NH_3 or C_{55} are protonated by the BAS, producing IR bands of ammonium or pyridinium species at different wavenumbers from those of the free molecules.

Highlights

Quantitative Fourier transform infrared assessment of Brønsted acid sites in solids using molecular probes has progressed beyond semiempirical approaches through improved probe selection, spectral analysis, and coupling with quantitative and gravimetric techniques that substantially enhance measurement reliability.

Accurate acidity quantification now relies on the recognition that integrated molar extinction coefficients (ε) are probe-, site-, and framework-dependent, overturning the long-held assumption that ε values are broadly transferable across materials, experimental setups, and analytical protocols.

While recent cross-calibration strategies are enabling more robust and potentially transferable ε benchmarks, their correct determination and use remain intrinsically

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challenging, requiring careful calibration under well-defined experimental conditions to avoid inconsistencies across the literature.

Beyond qualitative identification, the semiquantitative or quantitative evaluation of these diagnostic vibrations, achieved through the integration of specific absorption bands, allows one to discriminate between Brønsted and Lewis acid sites, determine their relative populations, and track their evolution under working conditions.

The ability to accurately characterize and quantify acidity is a crucial parameter for elucidating the catalytic properties of solid catalysts. This is particularly relevant for zeolites, heterogeneous catalysts that inherently contain both Brønsted and Lewis acid sites within their inorganic framework. Zeolites are microporous crystalline aluminosilicates with well-defined pore networks. Their TO_4-based framework units (T = Si, Al) create channels and cavities that host catalytically active sites. Owing to the presence of both Brønsted and Lewis acid sites, zeolites display remarkable activity, selectivity, and stability. The synergy between shape selectivity and framework acidity makes zeolites key catalysts in fluid catalytic cracking (FCC) [11], hydrocarbon isomerization, methanol-to-hydrocarbon (MTH) conversion [12], and NO_x selective catalytic reduction (SCR) [13]. Their tunable composition, porosity, and acidity also enable sustainable applications, including biomass conversion, fuel cells, CO_2 capture and conversion, and water treatment, improving energy efficiency and reducing the environmental impact of chemical processes [11,14,15].

The ability to quantify BAS and their acid strength with probe molecules is crucial to understanding zeolites' structure–property relationships and optimizing their catalytic performance.

In this review, we highlight a practical workflow to guide researchers in the quantitative assessment of BAS in zeolites (Figure 1). Particular emphasis is placed on how to determine and apply molar **extinction coefficients** (see Glossary) for different probe molecules, an essential yet often overlooked step that critically affects the reliability of FTIR-derived acidity measurements. By outlining these methodological considerations, we aim to provide a clearer and more consistent framework for quantifying acidity in zeolites and for interpreting structure–property relationships with greater confidence.

Tools for acid site quantification in solids by probe-molecule adsorption

The BAS quantification in heterogeneous catalysts is a complex procedure, governed by multiple experimental, instrumental, and data-processing variables that determine the accuracy, reliability, and reproducibility of the resulting data.

FTIR quantification of absorbing species in a homogeneous environment is based on the Lambert–Beer law, $A = \varepsilon bC$, which links absorbance (A) to species concentration (C, mol l^{-1}) via the molar extinction coefficient (ε, mol^{-1} l cm^{-2} or mol^{-1} cm 10^3) and path length (b, cm). For solids, however, this relationship must be adapted, since FTIR analysis is typically performed on relatively thick pellets rather than on liquid or gas phases [16]. When probe molecules are adsorbed on the solid surface, the total number of accessible acid sites (BAS or Lewis) can be quantified using a modified Lambert–Beer law, expressed as $A = \varepsilon N\rho$, where A is the integrated area (cm^{-1}) of the IR band formed upon probe interaction, ε is the molar extinction coefficient of the adsorbed species (cm μmol^{-1}), N is the concentration of the vibrating species ($\mu mol\ g^{-1}$), and ρ is the pellet density (mass/area ratio, g cm^{-2}) [17]. The experimental determination of ε is reported in Box 1. In addition, sample preparation, applied pressure during pellet formation, particle size, and all parameters affecting the optical path, diffraction, and scattering within the sample (such as specific surface area and particle morphology) affect the ε values, which can vary significantly among solids [16] Consequently, ε must be determined individually for each sample. Serious concerns have also been raised regarding the general applicability of

Lambert–Beer-type equations in surface chemistry, as well as the transferability of calculated ε between different systems, even when these systems are chemically and/or physically similar [16].

Probe molecules in action

Suitable **probe molecules** (see Glossary) to monitor surface acidity in zeolites can be identified by evaluating both their proton affinity and their **kinetic diameter** (see Glossary) with respect to the pore aperture of the zeolite framework. For quantitative analysis, where reliable band integration is required, the vibrational modes of probe molecules upon interaction with BAS should not overlap with the intrinsic vibrational features of the zeolite framework and contributions from weak probe–surface interactions. Furthermore, quantitative analysis strongly benefits from the use of FTIR **difference spectra** (see Glossary), obtained by subtracting the spectrum of the sample under vacuum from that recorded after probe adsorption/desorption. This approach yields bands with well-defined baselines, facilitating the subsequent mathematical integration. **Spectral normalization** (see Glossary) is also a crucial step, as it ultimately determines the integrated band areas and the reproducibility and comparability of the resulting data [22]. Finally, depending on the nature of the interaction between the probe molecule and the surface sites, the adsorption can be performed either at room temperature or under variable-temperature conditions. In the following sections, different probe molecules with progressively increasing proton affinity and kinetic diameters will be presented with their typical spectroscopic features.

Carbon monoxide adsorption

CO, with a proton affinity of 598 kJ mol^{-1}, is among the most versatile and sensitive probe molecules to characterize and quantify acid sites in solids by FTIR spectroscopy. Its linear geometry and small kinetic diameter (3.8 Å) enable access to sterically hindered surface regions, making it particularly suitable to monitor both Brønsted and Lewis acid sites [23,24]. Upon adsorption, the C ≡ O stretching vibration becomes highly sensitive to the local electronic

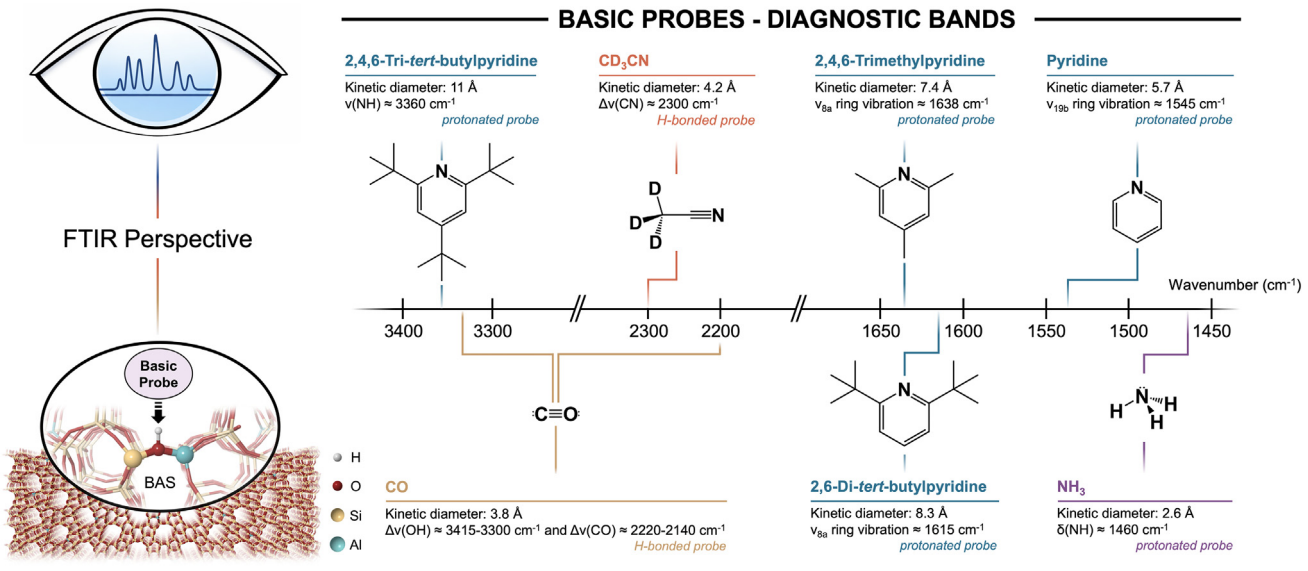

Figure 1. Overview of the most employed basic probe molecules for FTIR characterization of Brønsted acid sites (BAS) in a zeolite framework. The figure highlights the main quantitative diagnostic IR bands of the selected probes after their interaction with BAS as a function of wavenumber, specifying the interaction mechanism (protonation versus hydrogen bonding), together with molecular structures and kinetic diameters. FTIR: Fourier transform infrared.

Box 1. Determination of the molar extinction coefficient ε

Within the use of basic probe molecules as tools for the semiquantitative analysis of Brønsted acidity in materials of different nature, the molar extinction coefficient ε plays a pivotal role. An accurate determination of ε for an appropriate adsorption band of each probe molecule is required, as this value is subsequently introduced into the Lambert–Beer equation adapted for solids. It is therefore necessary to use an IR band that can be employed quantitatively, that is, a band unambiguously associated with the interaction between BAS and the probe molecule (e.g., bands corresponding to the protonated form of the probe, as in the case of NH_3 or C_5H_5N), and located in a spectral region where interfering contributions from other vibrational modes are negligible [16]. Subsequently, a calibration-like relationship must be established by plotting the integrated absorbance of the quantitative band as a function of the probe concentration. The slope of the resulting linear regression is then used as the value of the molar extinction coefficient. In this context, since the early 1990s, the quantitative determination of infrared extinction coefficients has been predominantly based on transmission IR spectroscopy. The seminal work of Emeis introduced the concept of integrated molar extinction coefficient (IMEC) IMECs through C_5H_5N adsorption, assuming that the IMEC does not depend on the material's nature or the strength of the acid site [9]. Subsequent studies refined this approach while highlighting its limitations: Morterra *et al.* [16]. and Jentoft *et al.* [18]. demonstrated the system-specific nature of adsorption coefficients, strong dependencies on particle size, morphology, and scattering effects.

More recent studies have explored alternative methodologies for the determination of ε. Glorius *et al*. proposed an approach based on *in situ* diffuse reflectance infrared Fourier transformed (DRIFT) spectroscopy, yielding extinction coefficients in very good agreement with literature values and providing a valuable starting point for further methodological developments [19]. Other contributions, notably by F. Thibault-Starzyk *et al*. [20,21], significantly improved the accuracy of ε by employing coupled IR/thermogravimetric setups (AGIR), which enable the simultaneous acquisition of both qualitative and quantitative information through the combined use of thermogravimetric analysis and operando IR spectroscopy, complemented by online mass spectrometry. Regardless of the specific methodology, a common and unavoidable requirement remains the determination of ε on a material-by-material basis, as the transferability of extinction coefficients is intrinsically limited [16].

environment, resulting in characteristic frequency shifts (typically in the range of 2140–2220 cm^{-1}) that directly reflect the strength and nature of the adsorption site [25]. The adsorbed CO bands are well separated from the gas-phase vibration at 2143 cm^{-1}, which facilitates unambiguous spectral deconvolution and quantitative analysis. When coordinated to Lewis acid sites, such as exposed metal cations in oxides or zeolites, CO donates electron density from its filled 5σ orbital to the empty orbitals of the cation. Simultaneously, π-back donation from metal d orbitals to the CO π* antibonding orbital weakens the C ≡ O bond, producing a redshift or blueshift depending on the cation's oxidation state and electrophilicity [23]. In oxides containing highly electrophilic centers (e.g., Al^{3+}, Zn^{2+}, and Fe^{3+}), the interaction is dominated by σ-donation and yields blue-shifted bands up to 2220 cm^{-1}, while transition metals capable of significant back-donation (e.g., Cu^{+} and Ni^{2+}) cause redshifts below 2140 cm^{-1} [26]. The magnitude of this shift ($\Delta\nu_{(CO)} = \nu_{ads} - \nu_{gas}$) provides a quantitative descriptor of Lewis acidity, correlating with the polarization strength of the metal center. This principle was elegantly demonstrated by Maleki and Pacchioni [27], who showed through density functional theory (DFT) calculations that CO adsorption on undercoordinated Zr^{4+} sites on monoclinic and tetragonal ZrO_2 produces blueshifts between + 12 and + 29 cm^{-1} relative to CO gas phase, consistent with experimental results near + 31–51 cm^{-1}. Such correlation validates the direct link between $\Delta\nu_{(CO)}$ and the local electron-acceptor ability of surface cations. In mesoporous [Al]-SBA-15, upon CO adsorption at 100 K, multiple bands corresponding to distinct families of Brønsted and Lewis sites are observed [23]. Blue-shifted bands at 2160–2175 cm^{-1} were attributed to CO bound to framework Al^{3+} centers, while lower-frequency bands reflected interactions with surface hydroxyls.

Although CO interacts preferentially with Lewis acid sites, it can also serve as a sensitive probe for Brønsted acidity at cryogenic temperatures. In the seminal FTIR study by Chakarova and Hadjiivanov [24], adsorption of CO at 100 K on H-ZSM-5 led to the formation of H-bonded CO–BAS complexes, giving rise to two red-shifted O–H stretching components at 3306 and 3415 cm^{-1} with respect to the free BAS at 3616 cm^{-1}, accompanied by a $\nu_{(C \equiv O)}$ band at

Glossary

Brønsted acid site (referred as BAS): framework hydroxyl group (e.g., Si–O(H)–Al) that acts as a proton donor upon interaction with an adsorbed base. In FTIR spectroscopy, BAS are quantified through characteristic vibrational bands of hydrogen-bonded or protonated probe molecules.
Difference spectra: infrared spectra obtained by subtracting the spectrum of the activated material from that recorded after probe adsorption/desorption. This procedure suppresses framework contributions, improves baseline quality, and isolates probe-induced vibrational features.
Extinction coefficients (ε): integrated molar absorption coefficient correlating the integrated area of a vibrational band to the amount of adsorbed species. In solid-state FTIR, ε is required for quantitative analysis via the modified Lambert–Beer law and is probe-, site-, and material-dependent.
Fourier transform infrared (FTIR) spectroscopy: Fourier transform infrared spectroscopy, a vibrational technique used to identify and quantify surface species through their characteristic absorption bands. In acidity measurements, FTIR monitors interactions between molecular probes and acid sites.
Kinetic diameter: effective molecular size governing diffusion through porous materials. In zeolites, the kinetic diameter of a probe determines whether it can access internal cavities or selectively interact with external acid sites.
Probe molecules: molecules intentionally adsorbed to investigate surface acidity. Common probes (e.g., CO, CD_3CN, NH_3, and C_5H_5N) cover a broad range of basicity and molecular size, enabling selective interaction with different types of acid sites.
Spectral normalization: data-processing step in which spectra are scaled to a reference signal, such as pellet thickness or a framework vibration. Normalization affects integrated band areas and must be explicitly reported in quantitative analyses.
Zeolite framework codes: three-letter code (e.g., MFI, FAU, MOR, BEA, and CHA) assigned by the International Zeolite Association to describe framework topology and pore architecture, which strongly influence

probe accessibility and measured extinction coefficients.

2175 cm^{-1}. The larger shift ($\Delta\nu_{(OH)} \approx 310\ cm^{-1}$), observed between the free BAS (3616 cm^{-1}) and the strongly H-bonded species (3306 cm^{-1}), was shown to scale with the BAS strength. Notably, the 3415 cm^{-1} band was assigned not to less acidic hydroxyls but to different H-bonded configurations of CO on chemically equivalent BAS, as no intrinsic heterogeneity of the acidic OH groups was observed. The authors also clarified that earlier overestimations of $\Delta\nu_{(OH)}$ were caused by Fermi resonance effects, emphasizing that CO provides an accurate probe when analyzed with care. CO adsorption at 80 K on SAPO-34 provides unambiguous spectroscopic evidence of CO–BAS interactions (Figure 2). The O–H stretching modes of the BAS are red shifted from 3630 and 3610 cm^{-1} to approximately 3350 cm^{-1}, indicating H-bonded CO–BAS adducts. Concomitantly, the CO stretching mode is blue shifted by 32 cm^{-1} from CO liquid-like (2138 cm^{-1}) [28].

Although the interaction of CO with BAS via H-bonding is weaker than the proton transfer observed with stronger bases (e.g., NH_3 or C_5H_5N), it nevertheless enables a sensitive assessment of BAS heterogeneity. The low basicity of CO limits site perturbation and minimizes competitive adsorption, making it suitable for probing subtle variations in hydroxyl acidity within zeolites, as reflected by the $\nu_{(CO)}$ and $\Delta\nu_{(OH)}$ values in Table 1 where **zeolite framework codes** (see Glossary) are reported [24].

In principle, the quantification of acid site concentration by CO-FTIR spectra is based on the integrated absorbance of the $\nu_{(C \equiv O)}$ band and the knowledge of its ε. However, **reliable and**

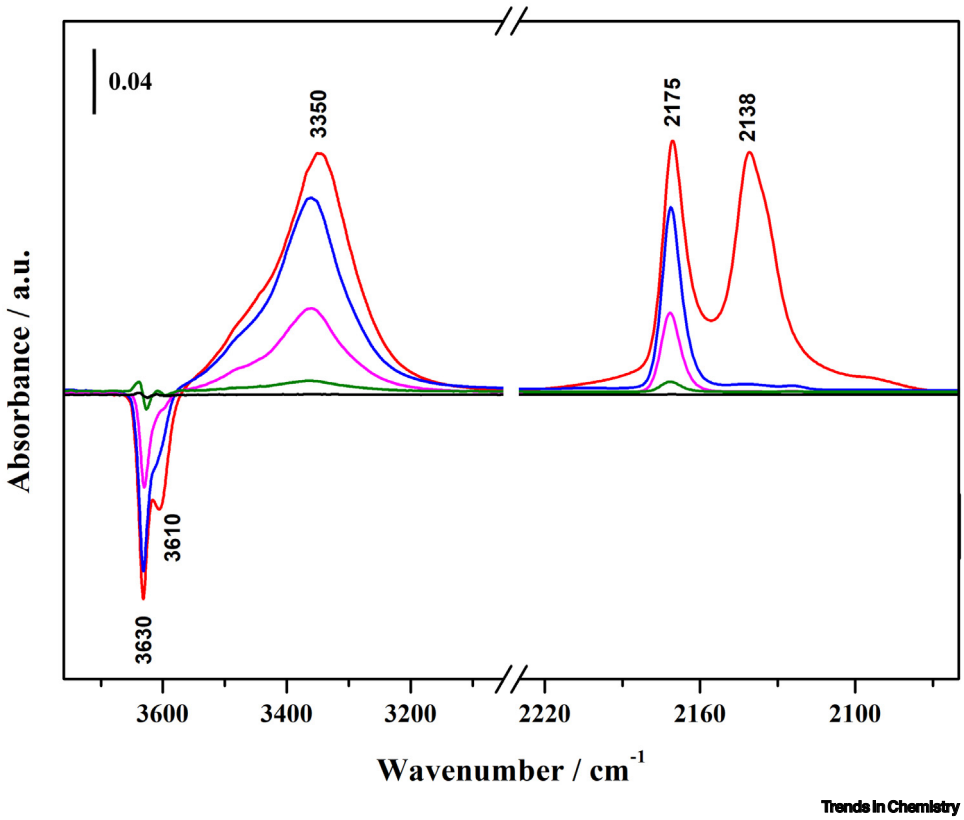

Figure 2. FTIR difference spectra in the O–H (high frequency, 3800–3100 cm^{-1}) and in C–O (low frequency, 2220–2040 cm^{-1}) stretching region of CO adsorbed at 80 K on SAPO-34 (unpublished data). FTIR: Fourier transform infrared; SAPO-34: a silicoaluminophosphate with CHA structure.

Table 1. Literature FTIR data for CO adsorption on Brønsted and Lewis acid sites of selected zeolites, including $\nu_{(CO)}$ (or $\Delta\nu_{(CO)}$) and $\Delta\nu_{(OH)}$

Material	Acid site type	$N_{(CO)}$ or $\Delta\nu_{(CO)}$/cm^{-1}	$\Delta\nu_{(OH)}$/cm^{-1}	Refs
MFI	BAS	2175 (+32)	≈ –310	[24,29]
MTT	BAS	2173 (+30)	≈ –305	[30]
BEA/MOR	BAS	2165–2178	–290 to –320	[30]
[Al]-SBA-15	Lewis + BAS	2160–2175 (+20–30)	–250 to –280	[23]
FAU	BAS	2171 (+28)	–234	[31]

[Al]-SBA-15: mesoporous ordered silica containing Al; BAS: Brønsted acid sites.

universally accepted ε values for CO adsorbed on BAS of zeolites are not available, as $\underline{\varepsilon}_{(CO)}$ strongly depends on surface composition, framework topology, temperature, and surface coverage. Reported values span a broad range for CO adsorbed on solids, reflecting the strong sensitivity of the CO vibrational intensity to the local environment and adsorbate–adsorbate interactions [25,28,30]. At sub-monolayer coverages, CO predominantly interacts with isolated acid sites, and the IR response is approximately linear, whereas at higher loadings, dipole–dipole coupling among adjacent CO molecules induces nonlinear absorption behavior and band shifts. Consequently, CO-FTIR is mainly employed for qualitative or semiquantitative analysis of acid strength and site heterogeneity, rather than for absolute quantification of BAS, and careful control of adsorption temperature (typically 77–120 K) and CO pressure is required to remain within the linear regime [23,26]. A reliable quantitative calibration of acid site densities in zeolites has instead been achieved by combining solid-state ^{1}H magic-angle spinning nuclear magnetic resonance (MAS NMR) and FTIR spectroscopy. In this approach, Gabrienko *et al.* [30] determined **an ε** value of 3.06 ± 0.04 cm μmol^{-1} for BAS and 1.50 ± 0.06 cm μmol^{-1} for terminal silanols (Si-OH) in H-ZSM-5 and H-ZSM-23. These values refer to the OH stretching modes and not to the CO vibrations and therefore provide quantitative benchmarks for BAS densities from hydroxyl IR bands. Despite its high sensitivity, CO is not a universal probe. On strongly basic oxides, it may undergo chemical transformations (e.g., carbonate or formyl formation) above ~150 K, compromising quantitative interpretation [32]. Moreover, multilayer adsorption or co-adsorption on adjacent acid pairs can result in complex band envelopes requiring careful spectral deconvolution. For this reason, modern studies increasingly combine CO-FTIR with DFT modeling, temperature-programmed desorption (TPD), microcalorimetry, and solid-state NMR to achieve a robust and cross-validated description of acid site density, strength, and heterogeneity [23,27,30,33].

Overall, CO remains a powerful and selective probe of surface acidity owing to its low basicity, molecular simplicity, and well-defined spectroscopic response. Under controlled conditions and alongside complementary methods, CO-FTIR provides reproducible insights into acid strength and site heterogeneity in zeolites and oxides, remaining a benchmark tool for probing acidity in catalysts.

Deuterated acetonitrile adsorption

Acetonitrile is a small, linear nitrile with a proton affinity of 788 kJ mol^{-1}and a kinetic diameter of about 4.2 Å [34], which allows it to access most microporous channels in zeolites [35]. Its proton affinity enables strong interaction with BAS without causing irreversible chemisorption. The polarizable CN produces an intense, well-isolated stretching vibration highly sensitive to H-bonding, making acetonitrile an excellent spectroscopic probe of Brønsted and Lewis acidity [17,35–38].

The detailed interaction of acetonitrile with Brønsted and Lewis acid sites in zeolites was described and interpreted in a study of CD_3CN on HZSM-5 and HY [35]. CD_3CN adsorption on BAS produces a characteristic CN band near 2300 cm^{-1}, whereas adsorption on Lewis sites yields bands at higher frequencies (2332–2320 cm^{-1}), while interaction with terminal Si-OH gives rise to bands around 2275 cm^{-1} and gas-phase CD_3CN appears at ≈ 2265 cm^{-1}. At low coverage, CD_3CN adsorption on bridging OH groups also generates the classical A–B–C trio of OH-related bands at ≈ 2890, 2400, and 1700 cm^{-1}, well known for strong hydrogen-bonded complexes, whose positions and intensities can be correlated with hydrogen-bond strength and, hence, absolute Brønsted acidity [39].

Deuterated, rather than protonated, acetonitrile is preferred in FTIR studies because the CN region of CH_3CN is complicated by Fermi resonances and combination bands, which obscure and distort the CN fundamental band and complicate baseline definition and band integration [35,40,41]. In CD_3CN, the deuteration of the methyl group shifts CH-related modes sufficiently so that the CN stretching band becomes isolated and narrower, eliminating Fermi resonance with combination bands and greatly simplifying quantitative analysis. Furthermore, the CD stretching/deformation modes appear at lower wavenumbers and with reduced overlap with framework and OH overtones, improving the robustness of deconvolution in the 2300–2260 cm^{-1} window, where CN bands associated with distinct site types are found [42]. These spectral advantages are crucial when CD_3CN is used to resolve closely spaced contributions from different acid sites in zeolites (Figure 3).

For the quantitative use of acetonitrile as a Brønsted probe, the key parameter is the ε of the CN band associated with CD_3CN interacting with BAS. Early work on ferrierite [43] and other zeolites established measured coefficients for hydrogen-bonded CD_3CN in the range of 2.0 to 2.1 cm μmol^{-1} for the CN band at ≈ 2297–2300 cm^{-1} [42]. This value was widely adopted as a framework-independent constant for Brønsted sites, without recalibration, in subsequent studies on zeolite acidity and site heterogeneity, sometimes in combination with higher values

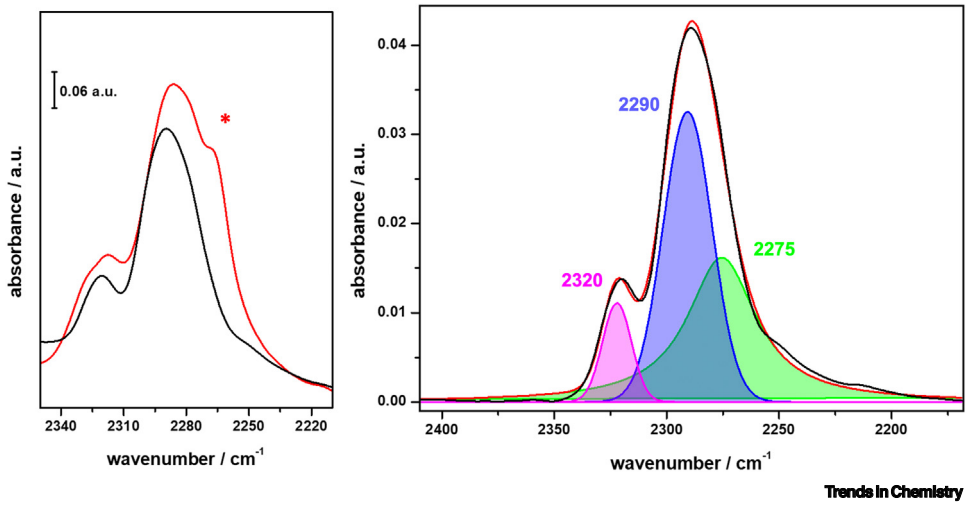

Figure 3. FTIR difference spectra of HFER zeolite at maximum d_3-acetonitrile coverage and after desorption of the probe molecules at room temperature (red and black curves, respectively; *marks the contribution from CD_3CN gas phase). On the right panel, the deconvolution of the irreversible fraction at room temperature is reported, highlighting the different contributions form CD_3CN interacting with Brønsted and Lewis sites; adapted from [42]. FTIR: Fourier transform infrared.; HFER: protonated ferrierite zeolite.

(≈3–4 cm μmol^{-1}) for CD_3CN coordinated to Lewis sites [42–48]. In this 'first-generation' approach, then, acetonitrile-based Brønsted site densities were often reported with limited attention to framework dependence or to the stoichiometry linking parent Brønsted sites and newly formed Lewis centers upon partial hydrolysis [17,49].

A recent work has highlighted that ε values are neither strictly universal nor strictly framework independent; Lebrón-Rodríguez *et al*. proposed a framework-specific recalibration of the CD_3CN ε for BAS in MFI, when partially hydrolyzed and extraframework species have to be precisely accounted [49]. This framework-specific redefinition of ε represents a significant advancement toward a more accurate determination of molar extinction coefficients and a more quantitatively reliable use of acetonitrile as a Brønsted acid probe. It recognizes that integrated molar coefficients depend on both framework and site identity and that they must be anchored to independent structural metrics by other quantitative methods [ion exchange, inductively coupled plasma (ICP), and NMR].

Ammonia adsorption

NH_3, a basic molecule with a proton affinity of 854 kJ mol^{-1}, is widely used as an effective probe molecule for the characterization and quantification of acid sites in porous solids by FTIR spectroscopy. Owing to its small kinetic diameter (2.6 Å), NH_3 readily accesses and diffuses through even the narrowest micropores of crystalline frameworks [13]. Beyond its established qualitative use for discriminating acid sites of different strengths, NH_3 also serves as a semiquantitative tool for determining the concentration of BAS on zeolites. Upon adsorption, NH_3 interacts with surface species, generating characteristic vibrational features in FTIR spectra [50,51]. Due to NH_3's basicity, in the presence of BAS, a proton transfer mechanism occurs, leading to the formation of the ammonium ion (NH_4^+), which generates a distinctive band at ≈ 1460 cm^{-1} (δ_{as} N–H) [22,51]. This band is quantitative and can be exploited to estimate BAS concentration via the Lambert–Beer equation adapted for solids [52]. To avoid the contribution of weak probe–surface interactions, it is necessary to carry out the measurements at sufficiently high temperatures (≈150°C) [53,54] to prevent NH_3 physisorption or, alternatively, at room temperature through variable-pressure desorption experiments [22,55]. Upon NH_3 desorption, bands related to weak acidic site interactions with the probe are completely restored, whereas those associated with BAS remain essentially unchanged due to proton transfer and the NH_4^+ ions (Figure 4) [55]. Consequently, the characteristic NH_4^+ band (1460 cm^{-1}) can be unambiguously identified, integrated, and employed for BAS quantification.

The initial NH_3 pressure strongly affects adsorption equilibrium, influencing both interaction kinetics and diffusion, and should be chosen to maximize interaction with all accessible BAS.

As with other probe molecules, the critical parameter for BAS quantification is the ε of the ammonium band, which is highly sensitive to the material type, the experimental conditions, and spectral processing, accounting for the variability in reported literature values (Table 2) [56].

In Table 2, all ε values originate from calibration procedures based on linear correlations between the intensity of the ≈ 1460 cm^{-1} band and the amount of adsorbed NH_3, and the corresponding slopes were used to derive ε. Most studies rely on reference materials containing exclusively BAS, calculating ε values upon NH_3 adsorption [51,53,54,56,57]. Conversely, Bortnovsky *et al.* [58] derived ε from a linear regression of ≈ 1460 cm^{-1} band intensities on several zeolites (FER, MOR, MFI, and BEA), obtaining an average coefficient. However, this value was obtained by using NH_4-exchanged zeolites. Similarly, Suzuki *et al.* [59] reported an ε value averaged over multiple zeolite frameworks (MWW, BEA, HY, USY, FER, MFI, and MOR), derived from the

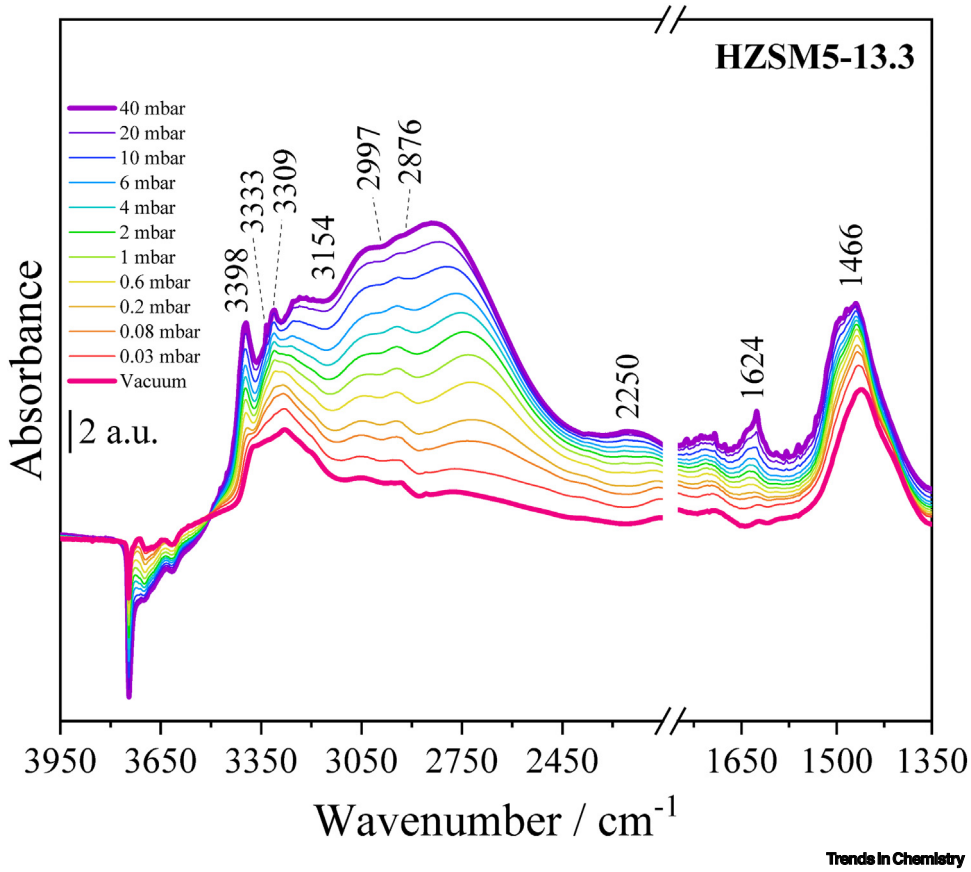

Figure 4. FTIR difference spectra of NH_3 adsorbed (max pressure 40 mbar) on hierarchical HZSM5-13.3 sample (HZSM5 desilicated at pH 13.3) at room temperature. The intermediate pressures at which spectra are collected during desorption are reported in the figure; adapted from [55]. FTIR: Fourier transform infrared; HZSM5: protonated ZSM-5 zeolite with MFI structure.

number of BAS and the integrated IR absorption intensity, based on the Lambert–Beer equation, within a combined infrared-mass spectroscopy and temperature-programmed desorption (IRMS–TPD) approach [59]. In addition, sample pretreatment (activation temperature and time) also strongly influences ε determination, as it affects the removal of residual surface species. In this respect, the literature exhibits a certain degree of inconsistency in the description of activation

Table 2. Selected ε values for NH_3 adsorbed on different types of porous materials

Material	ε NH_3-BAS/cm μmol^{-1}	Refs
FAU	0.130	[51]
MOR	0.11	[54]
FER	14.8	[56]
MCM-41 and modified MCM-41	3.03	[57]
MCM-41	1.47	[53]
NH_4-zeolites (FER, MOR, MFI, and BEA)	13.0	[58]
NH_4-zeolites (MWW, BEA, HY, USY, FER, MFI, and MOR)	9.4	[59]

procedures, which constitutes a significant limitation for data comparability. All these considerations indicate that NH_3-based quantification of BAS sites in zeolites is governed by the concomitant contribution of experimental and methodological factors. These variables act concomitantly and synergistically in defining the uncertainty and heterogeneity of the reported ε values, suggesting the presence of a nonnegligible arbitrary component in quantitative measurements.

Consequently, NH_3-based BAS probing in zeolites should be regarded as a semiquantitative rather than a strictly quantitative method. Its utility is maximized in comparative studies of the same material under strictly identical experimental conditions, where relative changes and trends can be discerned, and ε-related uncertainties mitigated. By contrast, quantitative comparisons across different materials or independent studies remain intrinsically challenging unless all experimental, analytical, and sample-related parameters are rigorously matched. From this perspective, the use of basic probe molecules for acidity characterization constitutes a particularly powerful approach when combined with bulkier probes, as it allows discrimination of BAS accessibility across distinct pore environments, which cannot be resolved by strictly quantitative techniques (Box 2).

Pyridine adsorption

C_5H_5N, a strong organic base (proton affinity of 930 kJ mol^{-1}), serves as a well-established infrared probe for investigating surface acidity in zeolites [38,65]. Due to its relatively large kinetic diameter (5.7 Å), C_5H_5N is sterically hindered from accessing the internal architecture of small-pore zeolites (e.g., CHA, LTA, and ERI), where narrow apertures (~3.8 Å) restrict adsorption to the external surface and pore mouths. While C_5H_5N effectively distinguishes Brønsted and

Box 2. Probing and quantifying accessibility of acidic sites

Accessibility, and not only the number and strength of BAS, is crucial for the catalytic effectiveness of zeolites. Due to their microporous structure, many internal sites are inaccessible to bulky molecules, limiting the catalytic performances, especially in terms of reusability. Enhancing accessibility, for example, through mesopores generation, can improve accessibility and extend the applicability of zeolites to the catalytic processing of bulky reactants.

IR investigation with probe molecules of different kinetic diameter is a powerful tool to assess accessibility. Small probes such as NH_3 (~ 0.26 nm) access almost all acid sites, whereas larger probes, such as 2,4,6-trimethylpyridine (~ 0.74 nm), 2,6-di-tert-butylpyridine (~ 0.83 nm), 2,4,6-tri-tert-butylpyridine (~ 1.1 nm), and trihexylamine (~1.4 nm), cannot enter most micropores and thus selectively probe acid sites on external surfaces [60,61] or in mesopores [62]. In 2009, Thibault-Starzyk *et al.* [63] introduced a key method to quantify acid site accessibility in hierarchical zeolites. At the time, such materials, combining zeolitic microporosity (0.25–1 nm) with a secondary mesopore network (2–50 nm), were recognized for overcoming the diffusion limits of purely microporous zeolites. However, evidence of improved site accessibility was mostly indirect, and no standardized quantitative protocol existed to directly assess it across materials prepared by different routes. This gap hindered rational catalyst design by preventing correlation between structure, transport, and catalytic performance. To address it, the authors proposed the accessibility index (AI) or accessibility factor (AF), defined as the ratio of acid sites titrated by a bulky probe to those detected by a small one (e.g., NH_3).

When evaluating Lewis acid sites, this approach is generally reliable, whereas for Brønsted sites, additional caution is required. Protons from Brønsted hydroxyl groups may be drawn toward strong bases even from sterically protected regions, allowing interaction with hydroxyl groups in regions considered virtually inaccessible and complicating accessibility assessment [10].

Ideally, reactant molecules themselves should be used to probe accessibility; nevertheless, this is often not possible, so careful probe selection is essential. The use of too bulky probes can underestimate accessibility, while, for correlating accessibility with catalytic outcomes, the probe must be chosen considering both size and chemical properties of reactants [64]. The size of the chosen probe molecule, in fact, should be comparable to the steric hindrance of the reactant, to specifically probe the fraction of acid sites relevant for a given reaction.

Lewis acid sites, its molecular sieving effect can underestimate total acidity in small-pore zeolites compared to smaller probes like NH_3. This limitation is often used to differentiate external from internal acidity. Whereas small molecules assess total acidity in zeolites, C_5H_5N provides a specific map of the acid sites available for bulkier catalytic reactants, which are subject to the same diffusion constraints (Box 2).

C_5H_5N can be adsorbed on surface sites of solids through different interaction modes, depending on the nature and strength of these sites. This effect is clearly reflected in the vibrational ring modes of the molecule (ν_{8a}, ν_{8b}, ν_{19a}, and ν_{19b}), which occur in the 1700–1400 cm^{-1} IR region. C_5H_5N can be weakly physisorbed or H-bonded to surface Si-OH, giving rise to bands at 1595 and 1580 cm^{-1} (ν_{8a} and ν_{8b}) and 1445 and 1438 cm^{-1} (ν_{19a} and ν_{19b}). In contrast, C_5H_5N coordination to Lewis sites leads to typical bands at 1456 cm^{-1} (ν_{19b}) and 1622 cm^{-1} (ν_{8a}). Finally, when C_5H_5N is adsorbed on BAS in zeolites (Figure 5), proton transfer occurs, leading to the formation of pyridinium ions (PyH^+), which exhibit characteristic ring modes at 1635 and 1623 cm^{-1} (ν_{8a} and ν_{8b}) and at 1545 and 1488 cm^{-1} (ν_{19b} and ν_{19a}) [20,66].

To specifically monitor the formation of pyridinium ions, which reflect the BAS concentration, the zeolite is outgassed at approximately 150°C to remove weakly adsorbed C_5H_5N from the FTIR spectra. Subsequently, the BAS quantification is commonly performed by integrating the 1545 cm^{-1} band, as it does not overlap with other ring vibrational bands. However, accurate quantification of the ε remains challenging, as the literature reports a wide range of ε values for $C_5H_5N_N$ adsorbed on BAS (Py-BAS) in FAU, MOR, MFI, and BEA zeolites (Table 3) [20,70].

An accurate determination of the ε of C_5H_5N adsorbed on BAS in zeolites has recently been reported by combining FTIR spectroscopy with high-precision thermogravimetric analysis

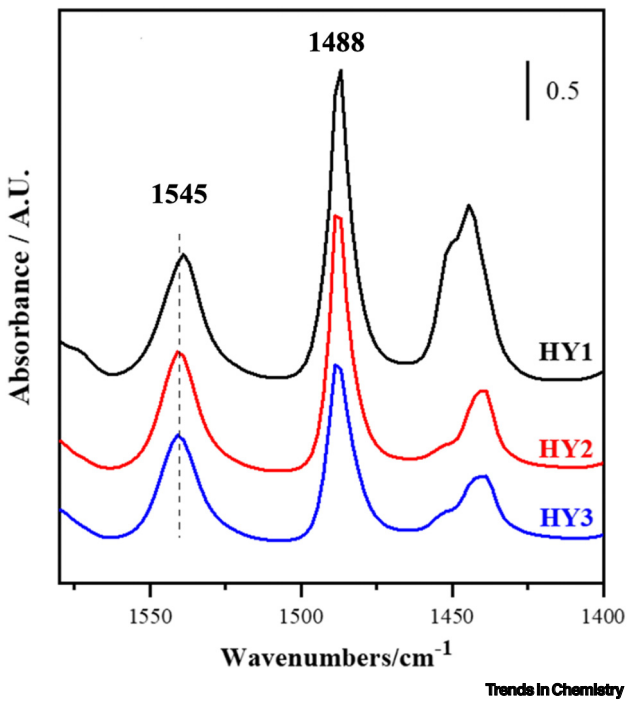

Figure 5. FTIR difference spectra of adsorbed C_5H_5N on HY zeolites with different porous distribution upon outgassing the sample at 150°C; adapted from [64]. FTIR: Fourier transform infrared.

Table 3. Selected ε values for C_5H_5N adsorbed on different zeolites

Material	ε (Py-BAS)	Units	Temperature/°C	Refs
FAU	0.73	cm μmol^{-1}	200	[67]
	1.67±0.12	cm μmol^{-1}	150	[9]
	1.8±0.1	cm μmol^{-1}	-	[68]
	0.078 ±0.004	cm^2 μmol^{-1}	145	[69]
	1.36±0.03	cm μmol^{-1}	200	[21]
	1.95 ±0.13	cm μmol^{-1}	150	[40]
	1.54 ±0.15	cm μmol^{-1}	150	[20]
	1.46 ±0.15	cm μmol^{-1}	200	[20]
MOR	1.67±0.12	cm μmol^{-1}	150	[9]
	1.8	cm μmol^{-1}	30	[70]
	0.078 ±0.004	cm^2 μmol^{-1}	145	[69]
	1.29 ±0.04	cm μmol^{-1}	150	[20]
	1.23 ±0.04	cm μmol^{-1}	200	[20]
MFI	1.67±0.12	cm μmol^{-1}	150	[9]
	0.07	cm^2 μmol^{-1}	170	[71]
	1.3 10^{-6}	cm μmol^{-1}	150	[72]
	1.09 ±0.08	cm μmol^{-1}	150	[20]
	1.05 ±0.08	cm μmol^{-1}	200	[20]
	1.38	cm $mmol^{-1}$	150	[73]
BEA	1.3 10^{-6}	cm μmol^{-1}	30	[74]
	0.070	cm μmol^{-1}	150	[75]
	1.12 ±0.16	cm μmol^{-1}	150	[20]
	1.07 ±0.15	cm μmol^{-1}	200	[20]

Py-BAS: pyridine adsorbed on BAS

(AGIR), enabling the simultaneous measurement of sample mass (corresponding to adsorbed C_5H_5N) and IR band intensities [20]. This methodology significantly reduces the uncertainties commonly associated with conventional quantification approaches. The calculated ε values depend systematically on multiple parameters, including the zeolite framework, C_5H_5N desorption temperature, IR spectral resolution, and pellet density. As a result, reliable and comparable quantification critically requires the standardization of experimental protocols. Complete removal of physisorbed C_5H_5N is essential, as residual weakly bound species can induce solvent-like effects that attenuate the Py–BAS vibrational band. The framework-dependent nature of the response further emphasizes the need for structure-specific calibration coefficients rather than reliance on nominally universal literature values. In addition, because ε is temperature sensitive, sample temperature must be controlled and clearly reported to allow reliable comparison between studies. Notably, ε values increase in the order ZSM-5/BEA < MOR < FAU, a trend attributed to differences in Si/Al ratio, acid strength, and confinement effects within the zeolite micropores. The experimental ε values for the various zeolite frameworks, obtained in this reference study and highlighted in bold in Table 3, provide a robust and transferable benchmark for the quantitative assessment of Brønsted acidity in zeolites using C_5H_5N as a probe molecule. Their reliability is further reinforced by recent literature reports that have applied these ε values to the quantitative determination of BAS in zeolite Y [60].

How the choice of extinction coefficient shapes BAS quantification

To better illustrate the implications arising from the use of different molar extinction coefficients, even when considering the same material, a representative experimental dataset can be reprocessed using alternative ε values. In the case of BAS quantification using C_5H_5N as a probe molecule, Zholobenko *et al.* [20] reported BAS concentrations of 325 and 450 μmol g^{-1} for ZSM-5-40 and ZSM-5-27 (MFI framework), respectively. In that work, the molar extinction coefficient (ε) was determined through an advanced methodology combining gravimetric analysis with FTIR spectroscopy, yielding a value of 1.09 cm μmol^{-1}. If, instead, the same integrated absorbances were reprocessed—under identical assumptions regarding material and experimental conditions—using the value proposed by Emeis [9] (ε = 1.67 cm μmol^{-1}), a substantial variation in the calculated BAS concentration would be obtained. Notably, Emeis originally reported no evidence for a dependence of the integrated molar extinction coefficients (IMECs) on either catalyst structure or strength of the acid site. Under this alternative assumption, the BAS concentrations would decrease to 212 and 294 μmol g^{-1} for ZSM-5-40 and ZSM-5-27, respectively, corresponding to a reduction of approximately 35%.

An analogous approach can be applied to NH_3-based quantification. Suzuki *et al.* [59] reported a BAS concentration of 420 μmol g^{-1} for an MFI zeolite (Si/Al = 46), employing an averaged extinction coefficient of 9.4 cm μmol^{-1} (Table 2). Reprocessing the same data using an alternative averaged value of ε = 13.0 cm μmol^{-1}, as proposed by Bortnovsky *et al.* [58], would lead to a recalculated BAS concentration of 304 μmol g^{-1}, that is, approximately 28% lower.

These examples represent illustrative recalculations based on hypothetical reprocessing of the same experimental data using different ε values, aimed at highlighting the strong impact of the chosen extinction coefficient on the derived BAS concentration.

Concluding remarks

FTIR spectroscopy combined with probe-molecule adsorption is a powerful and versatile tool for investigating acidity in solid catalysts, especially zeolites, as it allows the identification and characterization of BAS, which are crucial for understanding their catalytic behavior.

Beyond qualitative identification, the quantitative analysis of BAS in zeolites critically depends on methodological rigor, with particular emphasis on the determination of reliable molar extinction coefficients and strict control of experimental parameters such as sample preparation, adsorption conditions, temperature, and spectral normalization.

The wide variability of ε values in the literature complicates comparisons across solids, making careful evaluation of how these coefficients were obtained key to the realistic quantification of acid sites. Combining small probes (e.g., CO and NH_3) for total site mapping with bulkier probes (e.g., C_5H_5N) for pore-specific assessment enables a comprehensive understanding of site accessibility and heterogeneity. When coupled with standardized protocols and rigorously calibrated ε values, probe-molecule FTIR studies provide robust structure–property relationships, guiding the rational design of selective, efficient, and sustainable catalysts. Importantly, the technique becomes truly quantitative when integrated with temperature-programmed studies or solid-state NMR, providing robust structure–property correlations and guiding the rational design of next-generation catalysts for sustainable and green chemistry applications (see Outstanding questions).

Outstanding questions

Is there a reliable strategy to standardize ε values across different laboratories while explicitly accounting for differences in pellet preparation, scattering effects, spectral resolution, and temperature-dependent band intensities?

Can unified cross-calibration workflows, combining Fourier transform infrared with quantitative techniques (e.g., magic-angle spinning nuclear magnetic resonance, gravimetry, or infrared-mass spectroscopy and temperature-programmed desorption), be translated into standardized and widely adoptable protocols for framework- and site-specific ε determination?

How should mixed Brønsted/Lewis acidity populations and the possible formation of extra-framework Al species be accounted for in the overall acidity quantification when using basic probes for zeolite characterization?

How can probe-size-dependent Fourier transform infrared approaches be made more robust and standardized to reliably discriminate between internal and external Brønsted acid sites in hierarchical and small-pore zeolites?

Can operando and variable-temperature Fourier transform infrared measurements under reactive gas feeds deliver quantitative, time-resolved acidity information without losing comparability with established vacuum-based reference protocols?

Can Brønsted acid site quantification, based on different molecular probes, be organized into a common quantitative scale through well-defined conversion or normalization procedures to enable consistent comparison of materials?

Can differences in Brønsted acid site concentrations, derived from different basic probes, be rationalized by integrating information on pore size distributions obtained from porosimetric analyses with the aid of the most suitable density functional theory models?

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Declaration of interests

The authors declare no competing interests.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this manuscript, the authors used ChatGPT (Open AI) to reduce the number of words as required by the guidelines. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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