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Handbook of Heterogeneous Catalysis

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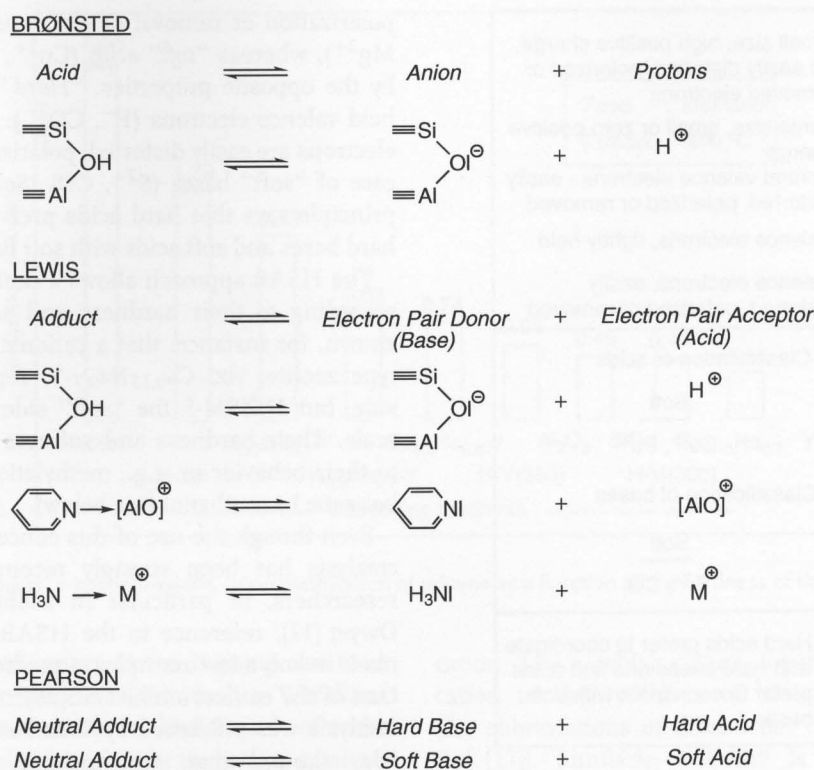
Second, Completely Revised and Enlarged Edition

3.2.4
Acidity and Basicity

3.2.4.1   Concepts and Analysis of Acidity and Basicity

*Hellmut G. Karge**

3.2.4.1.1 Introduction   Many reactions, especially in organic chemistry, are heterogeneously catalyzed by acid or basic solids. Prominent examples are Friedel–Crafts-type reactions such as cracking of paraffins over silica/alumina and zeolites and dehydration of alcohols over alumina. In the case of acid-catalyzed reactions such as paraffin cracking, oxide catalysts have been almost completely displaced by acid zeolites as the essentially active components and oxides or clays, e.g. silica/alumina, only just employed as matrices. Also, basic catalysts may well be derived from zeolites. In this context, it should be mentioned that the term "zeolite" was originally defined in a more restricted meaning: "Zeolites are microporous crystalline, solid and hydrated aluminosilicates of mono- or divalent bases in which the ratio $(M_2^+; M^{2+})O : Al_2O_3$ is unity, which are capable of losing part or the whole of their water without change of crystal structure and of adsorbing other compounds in place of the water removed and which are capable of undergoing base exchange" [1]. Then, a generalized formula of zeolites would be $M_{m/n}[(AlO_2)_m(SiO_2)_q] \cdot pH_2O$, where M stands for a cation of valency n and m, q and p are parameters, with $q/m = Si/Al$, i.e. providing the important ratio of the tetrahedrally coordinated Si and Al atoms in the zeolite framework (e.g. [2]). Today, the term "zeolite" is mostly used in a much broader sense, including also microporous

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BRØNSTED

Acid	Anion	+ Protons

≡Si—OH—Al≡ ⇌ ≡Si—O⁻—Al≡ + H⊕

LEWIS

Adduct	Electron Pair Donor (Base)	+ Electron Pair Acceptor (Acid)

≡Si—OH—Al≡ ⇌ ≡Si—O⁻—Al≡ + H⊕

⟨N→[AlO]⊕⟩ ⇌ ⟨N⟩ + [AlO]⊕

H₃N → M⊕ ⇌ H₃N + M⊕

PEARSON

Neutral Adduct	Hard Base	+ Hard Acid
Neutral Adduct	Soft Base	+ Soft Acid

Scheme 1 Concepts of acidity and basicity.

aluminophosphates (AlPOs), silicoaluminophosphates (SAPOs), metal aluminophosphates (MeAPOs), etc. (cf. the outstanding review article by Flanigen [3]) as well as mesoporous materials such as the members of the M41S family, etc. [4]. In the following section, the focus will be laid on the acidity and basicity of zeolitic solids, and oxide catalysts will be dealt with to a lesser extent. The topic of specifically prepared acid oxide catalysts such as sulfated zirconia will be treated in separate chapters (e.g. Chapter 2.3.9). Earlier review articles on acidity and basicity of zeolites, oxides and related materials are available [5–8].

The terms "acidity" and "basicity" are by no means unequivocal. One has to distinguish between three meanings or aspects of "acidity" and "basicity", viz. (i) *nature*, (ii) *density* (or *concentration*) and (iii) *strength* of the respective acid or basic sites.

Three concepts of acidity and basicity and their application to zeolite or oxide catalysts will be discussed (Scheme 1): (i) the concept of hard and soft acids and bases (HSAB), which in fact has not been very frequently used so far in heterogeneous acid–base catalysis; (ii) the concept of Brønsted acids and bases; and (iii) the concept of Lewis acids and bases. In particular in the case of zeolite catalysis, the role of Brønsted and Lewis acidity has been controversially discussed over a long period and is still not

entirely satisfactorily clarified (cf. Section 3.2.4.1.9). With respect to the acidic and basic behavior of sites of solid catalysts, however, not only their occurrence, generation and nature but also their density (concentration) and strength are important topics of analysis. Therefore, a number of methods and techniques for the characterization of these two parameters will be described, illustrated by examples and critically evaluated in detail.

3.2.4.1.2 Concepts of Acidity and Basicity of Zeolite and Oxide Catalysts

A The Principle of Hard and Soft Acids and Bases The concept of *hardness* and *softness* of acids and bases was advanced by Pearson [9] and successfully applied in organic chemistry. Hardness and softness of acids and bases are characterized as shown in Scheme 2. Pearson's principle of hardness and softness (HSAB-P) is usually expressed as follows: *hard acids* prefer to coordinate with *hard bases* and *soft acids* coordinate preferentially with *soft bases*. According to Klopman's approach [10], "hardness" correlates with a "charge-controlled" interaction, whereas "softness" may be visualized as an "orbital-controlled" interaction.

Hard acid	:	Small size, high positive charge, no easily distorted, polarized or removed electrons
Soft acid	:	Large size, small or zero positive charge; several valence electrons - easily distorted, polarized or removed.
Hard base	:	Valence electrons, tightly held
Soft base	:	Valence electrons, easily distorted, polarized or removed

Examples:	Classification of acids

Hard	Soft
H^+, Mg^{2+}	Cu^{2+}, Pd^{2+}

Examples:	Classification of bases

Hard	Soft
F^-, CO_3^{2-}	S^{2-}, CO

HSAB Principle	:	Hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases

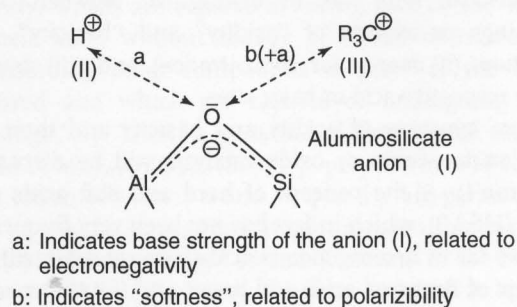**Scheme 2** Pearson's principle of hardness and softness of acids and bases (HSAB principle).

Scheme 2 includes some examples illustrating the principle of hardness (H) and softness (S) of acids (A) and bases (B), (HSAB principle). Figure 1 [11] should give a basic idea of the relevance of the HSAB principle to zeolite chemistry and its relationship to the classic Brønsted site concept.

In this picture, (I) represents the aluminosilicate anion, (II) the proton attached to the anion prior to converting the substrate (e.g. $[CH_3]_2C{=}CH_2$) into a carbocation (III) indicated by R_3C^+. The properties of the final complex, $[\equiv Al \cdots \bar{O} \cdots Si \equiv]^- \leftarrow R_3C^+$, depend mainly on two terms: (i) the intrinsic (base) strength of the oxygen, which is related to the electronegativity and governs the interaction with the proton thus determining the respective classic Brønsted site; and (ii) the polarizability of the $[\equiv Si \cdots (OH) \cdots Al \equiv]$ configuration, which is related to the softness and, additionally, determines the interaction with the carbenium ion, R_3C^+. Both terms, (i) and (ii), are functions of bond lengths and angles of the structure and chemical composition of the zeolite. In the complex of the anion fragment (I) and the carbenium ion (III) in Fig. 1, the character of (III) is modified by the properties of (I), i.e. (III) becomes "softer" if it interacts with a "soft" surface site (I). "*Hard*" *acids* are characterized by a small size of the respective entities, high positive charge and a low propensity to distortion,

polarization or removal of electrons (examples are H^+, Mg^{2+}), whereas "*soft*" *acids* (Cu^{2+}, Pd^{2+}) are described by the opposite properties. "*Hard*" *bases* exhibit tightly held valence electrons (F^-, CO_2^{2-}). By contrast, valence electrons are easily distorted, polarized or removed in the case of "*soft*" *bases* (S^{2-}, CO) (Scheme 2). The HSAB principle says that hard acids prefer to coordinate with hard bases and soft acids with soft bases (cf. Scheme 2).

The HSAB approach allows a ranking of, e.g., zeolites according to their hardness and softness. It could be shown, for instance. that a cationic form of a faujasite-type zeolite, viz. $Ca_{0.15}Na_{0.7}$-Y, represents the "hard" side, but H-ZSM-5 the "soft" side of a corresponding scale. Their hardness and softness could be correlated to their behavior in, e.g., methylation of toluene and/or benzene by methanol (see below).

Even though the use of this concept in heterogeneous catalysis has been strongly recommended by several researchers, in particular in zeolite catalysis, e.g. by Dwyer [12], reference to the HSAB principle has been made in only a few examples of zeolite-catalyzed reactions. One of the earliest studies employing HSAB-P in zeolite catalysis was published by Wendlandt and Bremer [11], who showed that, for example, reactions such as methylation of toluene, methylation of *o*-xylene, nitration and chlorination of toluene, hydrogen transfer and Cannizzaro-type reactions could be understood in terms of hardness and softness. The methylation of toluene was used as a tool for ranking the (acid) solid catalysts according to their hardness, since the electrophilic substitution of toluene with *hard* electrophilic reactants results in *ortho* products (*o*), whereas that with *soft* electrophilic reactants gives rise to *para* products (*p*). Because the hard or soft properties of the electrophilic reactants are modified by the softness or hardness of the surface sites, the *p/o* ratio provides a convenient means of ranking, for instance, the aluminosilicate catalysts according to the HSAB concept. This is illustrated in Fig. 2.

a: Indicates base strength of the anion (I), related to electronegativity

b: Indicates "softness", related to polarizibility

Fig. 1 Example of the interaction of an aluminosilicate anion with a proton or carbenium ion illustrating Pearson's HSAB principle [11].
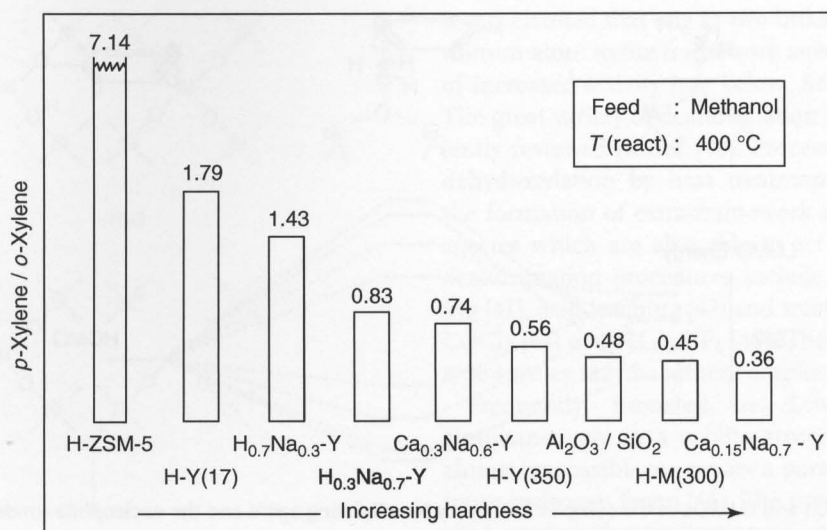
Fig. 2 Ratio of the products, *p*-xylene/*o*-xylene, upon methylation of toluene as a function of the hardness of the catalysts [11].

In a series of related papers, Corma's group also made use of the HSAB concept [13–15]. Similarly to Wendlandt and Bremer [11], these authors studied the role of orbital control in product selectivity during the zeolite-catalyzed electrophilic alkylation of aromatics both theoretically and experimentally, choosing the methylation of toluene and *m*-xylene by methanol as instructive examples. A series of large-pore H-Y zeolites, differing in the Si/Al ratio, were employed as catalysts. The changes in the *p*- to *o*-xylene ratio was observed to change with the Si/Al ratio of the zeolite framework, and this could be related to the LUMO (lowest unoccupied molecular orbital) energies obtained by *ab initio* quantum chemical calculations. Thus, the calculated LUMO energy of the model zeolite clusters interacting with the electrophilic reactant could be used as a measure of acid softness and the effect of the chemical composition of the zeolite rationalized. Similarly, it was established that the "softness" of bases was related to a high energy of the HOMOs (highest occupied molecular orbitals [14]). Figure 3 illustrates qualitatively the effect of the HOMO and LUMO energies of the complexes of alkylating and nucleophilic agents as related to their molecular orbitals formed on zeolites of different Si/Al ratios.

In their work on isomorphously substituted porous materials, Nagy et al. [16] found that also the propensity to ion exchange or introduction of heteroatoms such as B or Ga in those systems was governed by the HSAB principle, i.e. could be understood in terms of the preferential hard and soft acid–base interaction. The authors refer to the well-known observation that hard acids accompany better hard bases and soft acids link to soft bases. Na^+ is harder than the tetrapropylammonium

cation, TPA^+, which occurs, for instance, as a template cation in the synthesis of boron-containing [B]–MFI (for abbreviations of three letter codes for zeolites, see Ref. [17]). Similarly, $[SiOAl]^-$ is a harder base than $[SiOB]^-$. Thus, the preferential interactions lead to TPA^+ –$[SiOB]^-$ pairs [18], i.e. introduction of boron. However, if the Na^+ cations in the synthesis mixture were replaced with K^+ or Cs^+, which are softer acids than Na^+, the presence of the former cations may also favor the introduction of boron into the MFI structure, since K^+ –$[SiOB]^-$ or Cs^+ –$[SiOB]^-$ pairs will form preferentially.

B Brønsted's Concept of Acidity and Basicity The classical definition of acids by Brønsted [19] visualizes them as proton donors (cf. Scheme 1).

This also applies to zeolite chemistry: the model of a Brønsted acid center in a zeolite structure is that of a bridging [$\equiv Si \cdots (OH) \cdots Al \equiv$] configuration, generally as a part of the microporous aluminosilicate framework, which is able to donate a proton to an acceptor such as pyridine, ammonia or a hydrocarbon. Similarly, proton donors may occur in AlPOs or SAPOs (see above) as P–OH groups, etc. Correspondingly, a species such as M^+ –OH^- donating a negatively charged hydroxyl group, where M^+ may stand, e.g., for a monovalent cation, is regarded as a Brønsted base. However, *Brønsted basic sites* in the form of basic OH groups released from a cationic zeolitic *framework* have to date not been observed. But entities such as M^+ –OH may occur as extra-framework species in zeolites. In any event, the above-described type of acidic sites still plays the dominant role in
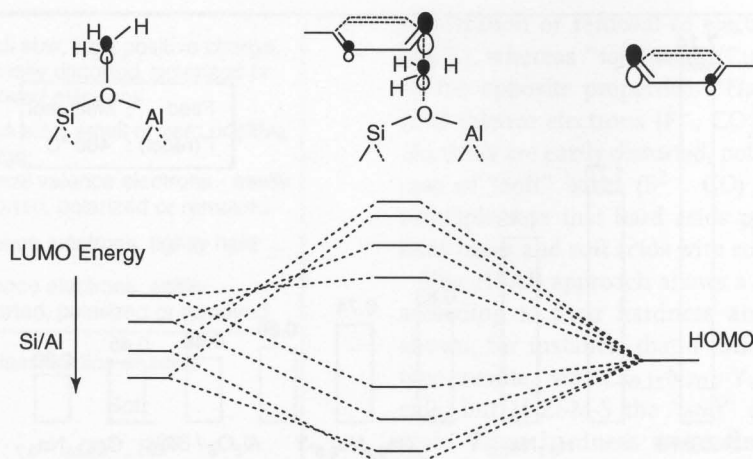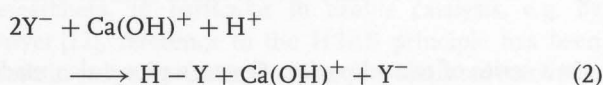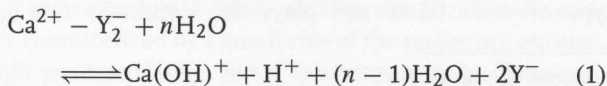
Fig. 3 Qualitative HOMOs and LUMOs of the complex formed by the alkylating agent and the nucleophile (middle) related to the MOs of the alkylating agent (left) and the nucleophile (right) [15].

understanding the catalytic activity of zeolites in many zeolite-catalyzed reactions (see below).

In the most simple cases, acidic (bridging) OH groups may be generated via direct proton exchange of cations such as Na^+ or K^+, which are part of the composition of the respective zeolites due to the chemistry of their natural formation or synthesis in the laboratory or through industrial processes [20, 21]. However, this requires a sufficiently high stability of the zeolite framework against treatment with diluted mineral acids. Examples are silicon-rich zeolites such as mordenite, clinoptilolite and ZSM-5. A more general way to produce Brønsted acid sites is a two-step process, viz. (i) replacement of, e.g., Na^+ or K^+ of the parent zeolite by NH_4^+ via ion exchange with solutions of, for instance, NH_4Cl or NH_4NO_3, and (ii) removal of NH_3 from the thus obtained and dried material through heating it in an inert gas stream or high vacuum, i.e. through deammoniation. Brønsted acid sites are also frequently formed by destruction of the so-called templates used in many syntheses of zeolites [20–23] and by (hydrogen) reduction of noble metal cations residing inside the zeolite structure as charge-balancing species. Also, precipitation of, e.g., Zn^{2+}, Cd^{2+} or Hg^{2+} by H_2S treatment as well as simple interaction of H_2S with, for instance, Na–X [24] leads to the formation of OH groups attached to the framework (besides the corresponding sulfide molecules or clusters of them or SH^- groups). Acid OH groups also form upon hydrolysis of bi- or polyvalent cation-containing zeolites according to the Hirschler–Plank mechanism [25, 26], as indicated by Eqs. (1) and (2) using Ca–Y as an example (cf. also [27]).

$$Ca^{2+} - Y_2^- + nH_2O$$
$$\rightleftharpoons Ca(OH)^+ + H^+ + (n-1)H_2O + 2Y^- \quad (1)$$

$$2Y^- + Ca(OH)^+ + H^+$$
$$\longrightarrow H - Y + Ca(OH)^+ + Y^- \quad (2)$$

with Y^- representing a negatively charged fragment of a Y-type zeolite. Here, residual water molecules are, particularly at higher temperatures, dissociatively split by the action of the Coulomb field of the cations (Ca^{2+}). The resulting proton combines with an oxygen atom of the framework with formation of an acid OH group attached to the zeolite framework forming H-Y, i.e. [≡Si−OH−Al≡] configurations; the remaining (non-acidic) OH^- is attached to the cation giving rise to the $Ca(OH)^+$ complex [cf. Eq. (2)].

The generation of Brønsted acid sites as a side-product of one or the other process (reduction or sulfidation) may sometimes be undesired. The acidic OH groups can be *eliminated* through treatment with NaN_3 [28] or by solid-state ion exchange [29–31] with a suitable salt (NaCl, LiCl, etc.).

The Brønsted acid centers can be also removed through heating of the hydrogen form of the zeolite in an inert stream of gas or vacuum, i.e. via dehydroxylation (cf. Scheme 3), which may sometimes overlap with deammoniation (see above).

C Lewis Concept of Acidity and Basicity *Lewis acid sites* in zeolites are occurring either as electron-pair accepting extra-framework species such as aluminum- and oxygen-containing complexes (e.g. AlO^+, $Al_xO_y^{n+}$, uncharged aluminum oxide particles or aluminum hydroxy oxides), threefold-coordinated (coordinatively unsaturated, "cus" aluminum atoms, cf., e.g., Ref. [32]) or as cations such as alkali metal (M^+), alkaline earth (M^{2+}) or rare earth (M^{3+}) cations counterbalancing the negative charge of a zeolite
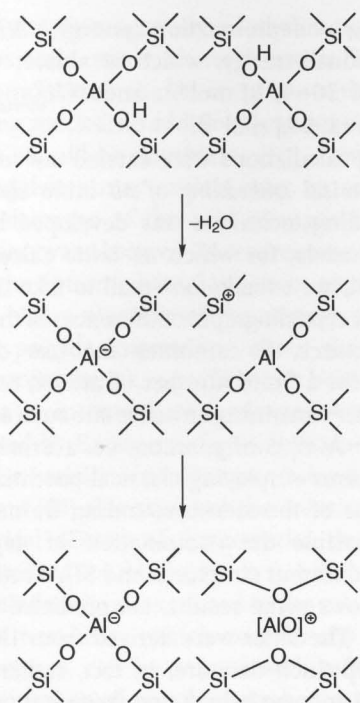
Scheme 3 Schematic representation of the dehydroxylation of a hydrogen form of a zeolite.

framework. Also, complex cations may be encountered, e.g. [La−O−La]$^{4+}$ in a lanthanum-exchanged zeolite, e.g. La−Y. In fact, the nature of "Lewis acid sites" in oxide and zeolite chemistry is not entirely clear. A relatively plausible view of "true" Lewis acid sites containing Al(III) or T(III) species, where "T" stands for another tetrahedrally coordinating framework atom such as B, Ga, Fe, etc., may be that proposed by Kühl [33, 34] and Jacobs and Beyer [35] (cf. Scheme 3 and see below).

Oxygen atoms of the framework or of hydroxyls bearing an excess of negative charge ($\delta-$) may function as *Lewis basic sites*. Zeolitic Lewis basic sites may be ubiquitous. However, to generate Lewis basic sites of higher basic strength than that of those oxygen atoms, usually particular cations with high polarizability (e.g. K$^+$, Rb$^+$, Cs$^+$), basic metal clusters [36, 37] or oxide particles (e.g. Cs$_2$O, CdO) were introduced into the zeolite structure (see below and Refs. [22, 23, 38]).

In the context of Scheme 3, it was already mentioned that dehydroxylation of a hydrogen form of a zeolite containing Brønsted acid OH groups results in the formation of so-called "true" Lewis centers (in contrast to Lewis sites such as Al≡, Si$^+$≡, or metal cations, M^{n+}). This process includes a release of aluminum from the zeolite framework, whereby usually all of the bonds of the aluminum cation to the neighboring framework oxygens are broken (see below; cf. Scheme 4). In some cases, however,

it was claimed that one or two links of the respective aluminum atom to the framework survived, causing centers of increased activity (see below, Scheme 4; cf. Ref. [39]). The great variety of dealumination procedures was excellently reviewed in Ref. [40]. Processes other than simple dehydroxylation by heat treatment also may result in the formation of extra-framework aluminum-containing species which are also able to act as Lewis sites. Such dealumination procedures include, for instance, steaming [41], acid leaching [42] and treatment with SiCl$_4$ [43], COCl$_2$ [44] or (NH$_4$)$_2$SiF$_6$ [45]. The resulting Lewis acid-type species may be rather complex.

Frequently, Brønsted and Lewis acid sites occur simultaneously in a zeolite structure. Sometimes it is almost impossible to prepare a pure Brønsted acid zeolite (pure hydrogen form) [46]. The presence of both types of sites renders the application of certain methods of site determination difficult (see below).

Similarly, in the case of oxides, the surfaces of which are usually covered by OH groups when contacted with (ambient) water vapor, partial dehydroxylation at elevated temperatures leads to the coexistence of Brønsted and Lewis acid and basic sites. Relevant models, especially for aluminas, were developed by Peri [47] and, on the basis of the analysis of partial charges, by Knözinger and Ratnasamy [48]. The validity of these models was well demonstrated by numerous investigations of the surface of, e.g., one of the most prominent oxides used as catalysts or catalyst supports, viz. α- or γ-Al$_2$O$_3$. In pertinent studies, spectroscopic techniques with and without probe molecules were frequently used. Examples will be dealt with in the relevant subsections of Section 3.2.4.1.3.

3.2.4.1.3 Analysis of Acidity and Basicity A large body of methods and techniques for the identification of the *nature* and also for the quantitative determination of acid (and basic) sites in zeolites with respect to their (absolute or relative) *density* and *strength* has been developed. This section will present, even if not exhaustively, the most prominent of them. In many cases, the respective spectroscopic and non-spectroscopic techniques enable us, possibly after some modification, to investigate all of the three above-indicated aspects of zeolite acidity. Nevertheless, depending on the particular circumstances, one or the other method may be preferable. In any event, one should keep in mind that the various techniques are often complementary, and it is usually advisable not to rely on only a single method.

In most cases, methods that were found to be capable of identifying the nature of acid or basic sites are also well suited to determine the concentration and/or the strength

of the sites under study. Therefore, those three aspects of acidity and basicity will be generally jointly discussed but not treated in separate subsections. As an exception, a few remarks regarding particularly the strength of especially Brønsted acid sites in zeolites are made below.

A Strength of Acid Sites in Zeolites

With respect to the above-mentioned three aspects of "acidity", rationalizing the phenomenon of *strength* of acid sites raises particular problems. Because of the importance of the strength of sites in view of the catalytic activity of acid solids, this topic attracted increasing interest during the past two decades. In the frame of Pearson's concept (see above), the ranking in "softness" or "hardness" appear to correspond to the degree of "strength". The ranking then follows from the activity in an appropriate reaction over a series of catalysts of different "softness" or "hardness" under otherwise identical (standardized) conditions (see below, e.g. Fig. 2). Characterization of the nature and concentration of the active sites exhibiting a certain "strength" may be then obtained through analysis of composition and structure of the respective catalysts (cf., e.g., the series of catalysts in Fig. 2).

Within the concept of Brønsted and Lewis acidity, the definition of an absolute scale of "acid strength" is indeed difficult. The most promising and reliable way is to use the deprotonation energy as a measure of the strength of (Brønsted) acid sites. Pertinent *ab initio* quantum chemical investigations were particularly conducted by Fleischer et al. [49] and Sauer and coworkers [50–53]. The definition of the strength via the deprotonation energy is achieved as follows:

$$\Delta G_{DP}^{\circ}(T) = \Delta H_{DP}^{\circ}(T) - T\Delta S_{DP}^{\circ}(T) \tag{3}$$

where $\Delta G_{DP}^{\circ}(T)$ = Gibbs free standard enthalpy of deprotonation, $\Delta H_{DP}^{\circ}(T)$ = standard enthalpy of deprotonation, $-\Delta H_{DP}^{\circ}(T) = PA$ = proton affinity of the corresponding anion and $\Delta S_{DP}^{\circ}(T)$ = standard entropy of deprotonation.

$$\Delta H_{DP}^{\circ}(T) = \Delta E_{DP} + \Delta E_{DP}^{ZP} + \Delta H_{therm}^{\circ} \tag{4}$$

where ΔE_{DP} = deprotonation energy, ΔE_{DP}^{ZP} = zero-point vibrational energy, which is almost constant in the range of 30–40 kJ mol^{-1}, and ΔH_{therm}° = thermal correction of ca. 5 kJ mol^{-1}.

Promising calculations were carried out using the so-called *mechanical embedding of ab initio cluster models*. This embedding technique was developed because the molecular models, for which *ab initio* calculations can be conducted, are usually too small to take into account appropriately crystallographic differences of the respective zeolite structures. It combines the use of *ab initio* calculations for a finite number of atoms, representing, e.g., the cluster containing an active site such as a bridging [≡Si−(OH)−Al≡] configuration, i.e. a Brønsted center, with calculations employing classical potential functions for the atoms of the site-surrounding framework. This rendered possible the computation of deprotonation energies for different structures and Si/Al ratios [50].

Table 1 shows some results, i.e. predicted and experimental data. The latter were derived from IR frequency shifts [50, 52]. Such data are, in fact, rather scarce (cf. Refs. [54, 55] and see below) and frequently not very accurate. However, the agreement seems satisfactory; in particular the expected increase with increasing Si/Al ratio is observed: such an increase of the strength of Brønsted acid sites had been frequently reported (cf., e.g., Refs. [56, 57]) and, also, the ranking of the various zeolites with respect to their acidity strength appears to be reasonable.

In several other contexts, the acid strength of zeolites was discussed as a collective phenomenon. Thus, it was related to the intermediate Sanderson electronegativity, $S_{int.}$ [58], for instance by Mortier [59], Jacobs et al. [60], Jacobs [61] and Pfeifer et al. [57]. Jacobs demonstrated that under well-defined conditions the acid strength of a carefully prepared series of H-forms correlated linearly with the intermediate Sanderson electronegativity. As an experimental measure of the acid strength, the shift of the infrared band upon adsorption of benzene was used; always considered was the OH band of the highest wavenumber [62] (see Section 3.2.4.1.3B). However, it was stressed by Jacobs that a prerequisite for this correlation

Tab. 1 Comparison of deprotonation energies in kJ mol^{-1} for surface OH groups

Source	Terminal OH				Bridging ≡Si−(OH)−Al≡ groups					
	Silica	Ref.	H-MOR	Ref.	H-ZSM-5	Si/Al	Ref.	H-Y	Si/Al	Ref.
From spectroscopic data	1390 ± 25	[56]	1140	[56]	1178–1236 H, Na − ZSM − 5	47	[54]	1161–1177 H, Na − Y	2.7	[55]
Calculated	1400 ± 25	[50]	1145 ± 25	[40]	1180–1335 1205	95	[54] [52]	1200 1166	47	[54] [52]

to emerge was homogeneity of the members of the zeolite series under study, i.e. no deviation from the ideal chemical composition should occur (no extra-framework Al-containing species, no additional cations or short-range interactions should be dominant, etc.). Deviations from those prerequisites may explain why, in some cases, a monotonic decrease of the acid strength or $S_{int.}$ upon dealumination was observed. Moreover, one must bear in mind that the intermediate Sanderson electronegativity provides at best a measure of the average acid strength and cannot provide information about the distribution of the acid strengths (as, e.g., TPD; see below). A similar approach via the intermediate Sanderson electronegativity was suggested by Barthomeuf and de Mallman [63] with respect to the basicity of zeolites (see below).

Barthomeuf [64] also analyzed the correlation between the topological density of frameworks, the number of isolated T-atoms (T = Al, Ga, Fe, B, . . .) in tetrahedra and the strength of acidic sites related to the catalytic activity. A density of tetrahedra, which exist for any of the usual zeolite structures, can be defined with reference to the maximum number of possible tetrahedra in a fourfold connected net of atoms [17, 65]. This density can be considered for a given layer or for an ensemble of layers. For instance, the topological density can be calculated for all layers between the second and the fifth. This is expressed as the topological density TD_{2-5} [17, 65, 66]:

$$TD_{2-5} = \frac{\sum \text{number of tetrahedra in layers } 2-5}{480} \quad (5)$$

with 480 as the maximum number of tetrahedra in layers 2–5.

When the numerator in Eq. (5), i.e. the number of Si-containing tetrahedra, decreases, then their topological density, TD_{Si}, decreases. This happens through progressive incorporation of more Al (or other heteroatoms) into the framework. The thus lowered value of the topological density of the SiO_4 tetrahedra may result in a decrease in strong acid sites (see below) and, consequently, in the average acidity of the materials [66, 67].

The topological density TD_{Al} provides, for example, the density of AlO_4^- tetrahedra in a surrounding of a maximum theoretical number of TO_4 tetrahedra. It allows the estimation of the limiting aluminum molar fraction [$m = Al/(Al + Si)$], below which none of the AlO_4^- tetrahedra is in a next-nearest neighbor (NNN) position, i.e. AlO_4^- tetrahedra, which generate the strong proton sites, have to be separated by at least two SiO_4 tetrahedra. The limit value, m_{NNN}, determines the aluminum content below which the acid strength of Brønsted sites should be highest and constant. The m_{NNN} values can be determined for different heteroatoms (T $\neq$ Si, e.g. Al, Ga, Fe, B) and also for SAPOs and various structures. These values are lower

for the topologically denser structures. For instance, in the case of the usual zeolites one finds the ranking of TD_{Al} according to the sequence MFI < MOR < OFF < FAU and, correspondingly, the maximum Si/Al ratios, acid strength and catalytic activity in cracking of *n*-alkanes are ranked as MFI > MOR > OFF > FAU. A maximum of strong acid sites (corresponding to more than 88% H_2SO_4) was expected for the ratio Si/Al $\approx$ 9.4 in H-MOR or 6.8 in H-FAU. A number of reactions are mentioned in Ref. [66] which indeed exhibited a maximum of conversion over, e.g., H-MOR at Si/Al $\approx$ 10 or H-FAU at Si/Al $\approx$ 7.

In another interesting contribution to the elucidation of the phenomenon of acid site strength, Barthomeuf [56, 64] interpreted the increase in acid strength of H-forms of zeolites with decreasing Al content in analogy with the behavior of inorganic oxy acids of the general formula $XO_n(OH)_m$. The strength of such acids increases with increasing *n* or decreasing *m*. An example is the sequence of oxy acids of chlorine: $Cl(OH) < ClO(OH) < ClO_2(OH) < ClO_3(OH)$. The corresponding formula for zeolites is $TO_n(OH)_m$ with T = Al or Si and $n + m = 2$. In the case of Y-type zeolite with Si/Al = 2.42, one obtained $n = 1.71$ and $m = 0.29$, whereas for a dealuminated Y-zeolite with Si/Al = 4.12 the result was $n = 1.81$ and $m = 0.19$. From experiments on the temperature-programmed desorption of pyridine (see below), it was inferred that a material with a higher value of *n* exhibited a higher strength of acidity.

B Utilization of Indicators and Titration in Aprotic Solvents
The utilization of indicators and titration of acidic and basic sites in aprotic solvents such as benzene or hexane was reported relatively early and extensively for surfaces of oxides [68, 69], especially for the classical acidic silica–alumina solids [25, 69, 70], the predecessors of acid zeolites as cracking catalysts. This method and its applications were excellently reviewed by Tanabe [71]. From the color of the appropriate indicators, which in aprotic suspension are simply contacted with the (white) powder of the oxides or zeolites, one may qualitatively estimate the (maximum) *acid* or *basic strength* of the surface sites. Titration with a suitable titrator (in the case of acidity usually butylamine) enables one to determine the *concentration* of the respective sites. The titration cannot be conducted in aqueous suspension, because this would eliminate the differences in acid strength of the various sites. The experimental procedures are described in the literature (see, e.g., Refs. [25, 70–73]).

The use of indicators and titration of the acidic and basic sites [74] are, in fact, the most chemistry-related techniques for zeolite characterization.

A useful basis for a comparison of various *strengths* of acids is the capability of proton transfer to a neutral base. This may be illustrated by the following equilibrium:

$$B + H^+ \rightleftharpoons BH^+ \tag{6}$$

with B = neutral base and BH^+ = conjugated form of the base. Quantitatively, the proton transfer may be described by the acidity function H_0, which was introduced by Hammet and Deyrup [75]:

$$H_0 \equiv -\log\left(\frac{a_{H^+} f_B}{f_{BH^+}}\right) \tag{7}$$

where a_{H^+} = proton activity and f_B and f_{BH^+} = activity coefficients of B and BH^+, respectively.

Similarly, the acid strength of a solid surface may be visualized according to Walling [76] as the capability of an acidic solid surface to transform an adsorbed neutral indicator base, I, into its conjugated form, IH^+:

$$H_0 \equiv -\log\left(\frac{a_{H^+} f_I}{f_{IH^+}}\right) = pK_{IH^+} - \log\left(\frac{c_{IH^+}}{c_I}\right) \tag{8}$$

where pK_{IH^+} is the negative Briggs' logarithm of the thermodynamic equilibrium of the indicator (frequently simply termed pK_a values) and c_{IH^+} and c_I are the concentrations of its acidic and basic form. When c_{IH^+} and c_I become equal (around the color change in the case of titration), it follows that $H_0 = pK_{IH^+}$ or pK_a. Relationships analogous to Eq. (8) can be derived for pure Lewis acids of solid surfaces and also for the use of Hirschler indicators of the arylmethanol type (see Ref. [77], where also preparations of a large number of appropriate Hirschler indicators are described).

However, it turned out that none of the usually used indicators (i.e. neither Hammett [74] nor Hirschler [25, 77] indicators; cf. Table 2) are really selective for either Brønsted or Lewis acid centers. The titration method essentially fails if both types of acid sites are simultaneously present.

Moreover, as mentioned above, the titrations unavoidably have to be conducted in aprotic media (e.g. benzene, hexane), whereas the relevant pK_a values of the indicators, the color change of which indicates the *strength* of a certain fraction of the sites (corresponding to the respective pK_as), are defined for aqueous solutions. Thus, the basis of the applicability of the titration technique remains debatable. On the other hand, the argument frequently advanced against the titration method, namely that the bulky indicator molecules are hindered from diffusing into the interior of the zeolite crystallites, is not relevant, since the visual observation of the indicator molecules and their change upon protonation by acid sites is, at any rate, restricted to the outer surface, except that optical spectroscopy is employed in transmission for determining the end-point of titration. However, in many cases the competition between the adsorption of the molecules of the aprotic solvent and that of the titrator base (e.g. butylamine) impedes the approach to a true chemical equilibrium between the indicator base on the external zeolite surface and the acid sites inside the zeolite structure within a reasonably extended time of the experiment [78]. Neglecting the above-mentioned fundamental limitations of the titration method and taking a phenomenological point of view, one may state, however, that the titration of zeolite acidity has led in several cases to reasonable results, in particular with more open zeolite structures such as faujasite-type materials [25, 77, 79–83]. Thus, the total number of Brønsted acid sites as determined via titration (corresponding to the amount of butylamine consumed with 4-benzeneazodiphenylamine as an indicator, $pK_a = +1.5$) was found to agree very well with the number calculated from the chemical composition of the zeolite [72, 83].

In a few publications, successful titration of zeolite acidity was reported with potentiometric or thermometric determination of the end-point of titration [84].

C IR Spectroscopy of Brønsted Acidity with and without Probe Molecules

IR spectroscopy, as one of the most powerful tools for identifying the *nature* of and quantifying the acidity of solids, was already employed before the advent of acid zeolites as catalysts, viz. in the investigation of amorphous silica/alumina cracking catalysts [85]. The same technique, i.e. the study by diffuse transmission IR spectroscopy of thin wafers, which were pressed from zeolite powders, was then used for characterization of these materials [86, 87]. In the pioneering work by Uytterhoeven et al. [88], the formation of acid OH groups through deammoniation of the ammonium form of faujasite-type zeolite Y was, for the first time, monitored by transmission IR spectroscopy and, also, the subsequent dehydroxylation at higher temperatures (cf. Scheme 3, Fig. 4). The OH groups were easily identified by the typical OH stretching bands at 3640 and 3550 cm^{-1} (Fig. 4).

Similarly, OH groups as Brønsted acid sites were detected in a large number of hydrogen forms of other zeolite types (for the abbreviations, i.e. the three-letter codes, see Ref. [17]), for example in H-MOR (3610 cm^{-1} [89, 90]), H-HEU (heulandite and clinoptilolite structure, 3600 cm^{-1} [90]), H-MFI or H-ZSM-5 (3605 cm^{-1} [91]), H-OFF (3610 and 3550 cm^{-1} [92]), H-BEA (3612 cm^{-1} [93]) and H-FER (3640 and 3600 cm^{-1} [94]), to mention just the most important examples. A more extended list is provided in Table 6 in Ref. [95], in which review the application of IR spectroscopy to zeolites is dealt with in much more detail.

Tab. 2 Hammett indicators and Hirschler (arylcarbinol) indicators suitable for the visible indication of the end-point in the titration of colorless solid acids[a]

Indicator	Basic color	Acid color	pK_a	Acid strength (wt.% H_2SO_4)
Hammett indicators				
Natural Red	Yellow	Red	+3.3	8×10^{-8}
Phenylazonaphthylamine	Yellow	Red	+4.0	5×10^{-5}
Butter Yellow	Yellow	Red	+3.3	3×10^{-4}
4-Benzeneazodiphenylamine	Yellow	Purple	+1.5	2×10^{-2}
Dicinnamalacetone	Yellow	Red	−3.0	48
Benzalacetophenone	Colorless	Yellow	−5.6	71
Anthraquinone	Colorless	Yellow	−8.2	90
Hirschler (arylcarbinol) indicators				
4,4′,4″-Trimethoxytriphenylmethanol	Colorless	Yellow	+0.82	1.2
4,4′,4″-Trimethyltriphenylmethanol	Colorless	Yellow	−4.02	36
Triphenylmethanol	Colorless	Yellow	−6.63	50
3,3′-Trichlorotriphenylmethanol	Colorless	Yellow	−11.03	68
Diphenylmethanol	Colorless	Yellow	−13.3	77
4,4′,4″-Trinitrotriphenylmethanol	Colorless	Yellow	−16.27	88
2,4,6-Trimethylbenzyl alcohol	Colorless	Yellow	−17.38	92.5

[a]After Benesi and Winquist [7].

The *acidic character* of the above-indicated OH groups was proven also by IR spectroscopy: Contact of the hydrogen form of, e.g., faujasite-type zeolite (H-Y) with basic probe molecules such as NH_3 or pyridine resulted in the elimination of the corresponding OH groups. Simultaneously, the IR bands of ammonium and pyridinium ions developed at 1640 and 1540 cm^{-1}, respectively. Such experiments were also first carried out in Hall's group [88] (cf. also, e.g., Refs. [96, 97]). Ammonia and pyridine still belong to the most popular probes for acidity employed in spectroscopic and non-spectroscopic methods (for the latter, see below, e.g. temperature-programmed desorption and microcalorimetry, Sections 3.2.4.1.3H and I, respectively). Whereas the spectra of ammonia adsorbed on zeolites usually exhibit relative broad bands, the bands of pyridine are rather sharp (cf. Fig. 5) and well-suited for quantitative evaluation of the exact wavenumbers and the band areas.

The *concentration of sites* can be determined from the depths or areas of the IR bands if the intensity (absorbance A) is plotted against wavenumber. For this purpose, use is made of the Lambert–Beer–Bouguer law:

$$A = \varepsilon_{\tilde{v}} c d \qquad (9)$$

where A is the absorbance [see Eq. (10)], $\varepsilon_{\tilde{v}}$ is the extinction coefficient at wavenumber $\tilde{v}$ of a sample with concentration c of centers absorbing at $\tilde{v}$ and a thickness d. If in transmission spectroscopy (see below) the spectrometer does not provide directly the absorbance of the sample but the so-called transmittance, T, then one has to convert T into A according to Eq. (10):

$$A = -\log T = \log(I_0/I)_v \qquad (10)$$

with I_0 being the incident and I the transmitted radiation energy. In principle, Eq. (9) is valid only for dilute systems. For instance, in the case of zeolites populated with OH groups or adsorbate–zeolite systems, one has to be aware of the possibility that $\varepsilon_{\tilde{v}}$ may be dependent on the OH group concentration and adsorbate coverage.

Frequently, it is sufficient to use as a first approximation the maximum absorbance defined by

$$A_{max} = \log T^*(\tilde{v}_{min}) / \log T(\tilde{v}_{min}) \qquad (11)$$

where $T^*(\tilde{v}_{min})$ is the background (baseline) transmittance and $T(\tilde{v}_{min})$ the actual transmittance, both measured at the wavenumber $\tilde{v}_{min}$ of minimal transmittance (cf. Fig. 6 and Ref. [98]).

The integral absorbance, as a more precise measure of the concentration of the absorbing species, is expressed as in Eq. (12):

$$A_{int} = cd \int_{\tilde{v}_b}^{\tilde{v}_e} \log\left[\frac{T'(\tilde{v})}{T''(\tilde{v})}\right] d\tilde{v} = cd \int_{\tilde{v}_b}^{\tilde{v}_e} \varepsilon_{\tilde{v}} d\tilde{v} \qquad (12)$$

where $\tilde{v}_b$ and $\tilde{v}_e$ are the wavenumbers of the beginning and the end of the band, respectively, and $T'(\tilde{v})$ and $T''(\tilde{v})$ are the transmittances along the baseline and the band contour, respectively. Modern instrumentation usually allows routine baseline determination and band integration to evaluate A_{int}. In IR and Raman
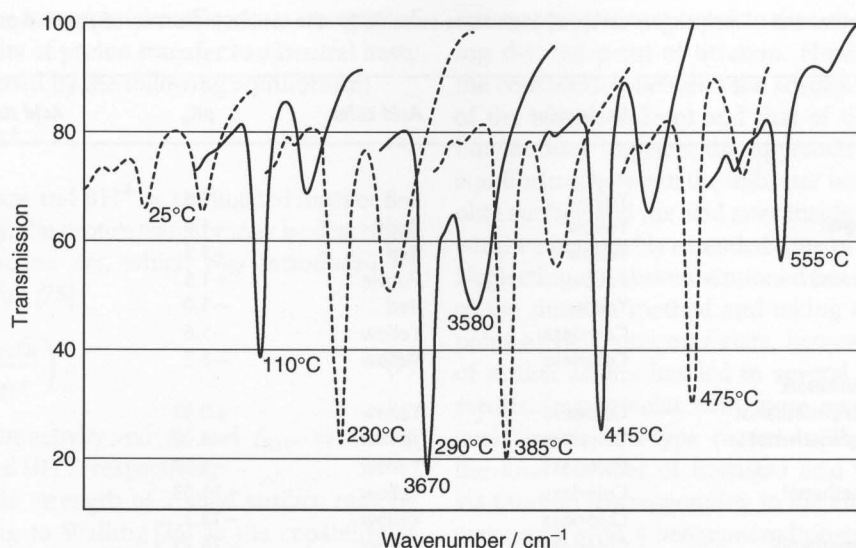
Fig. 4 Development of the stretching bands of acid OH groups of an NH_4,Na-Y zeolite upon deammoniation in high vacuum at increasing temperatures and subsequent dehydroxylation [88].
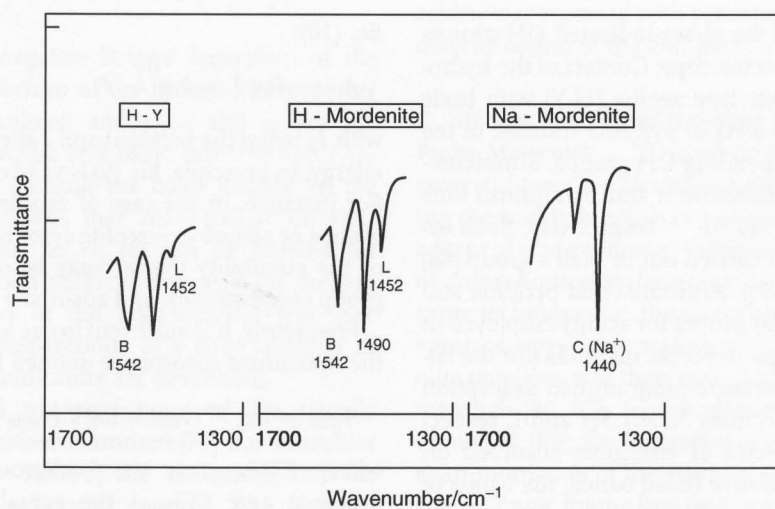

Fig. 5 IR bands of pyridine adsorbed on Brønsted acid sites (B-sites), "true" Lewis acid sites (L-sites) and Lewis acid cations (C-sites, here Na^+) in H-faujasite (H-Y), H-MOR and Na-MOR [31].

spectroscopy of zeolites or oxides and adsorbate-zeolite or adsorbate−oxide samples, the extinction coefficient, $\varepsilon_{\tilde{\nu}}$ or $\varepsilon_{\tilde{\nu}}(c)$, is usually unknown. Therefore, if knowledge of the absolute concentrations is required, $\varepsilon_{\tilde{\nu}}$ has to be determined in separate experiments (cf., e.g., Refs. [99−104]). In such experiments, the absorbance has to be measured of zeolite samples covered with a known number of functional surface groups or loaded with well-defined amounts of adsorbate in order to obtain calibration curves (A_{int} vs. concentration, c).

So far, such determinations of $\varepsilon_{\tilde{\nu}}$ have been carried out for a limited number of systems (cf., e.g., Refs. [105−110]).

Examples of results are collected in Table 2 in Ref. [95]. In some cases, the agreement between the results of different authors is satisfactory. However, frequently significant deviations occur. Therefore, it is advisable not simply to adopt literature data, but to check them or rely on ones own data obtained with ones own range of samples, instrumentation and techniques (for experimental details, compare Refs. [95, 98]). In any event, the (absolute) density of sites is defined as their number per unit cell, N (u.c.)$^{-1}$ or millimoles per gram of dehydrated material (mmol g^{-1}). However, since the distribution of sites over the zeolite crystals is not necessarily homogeneous,
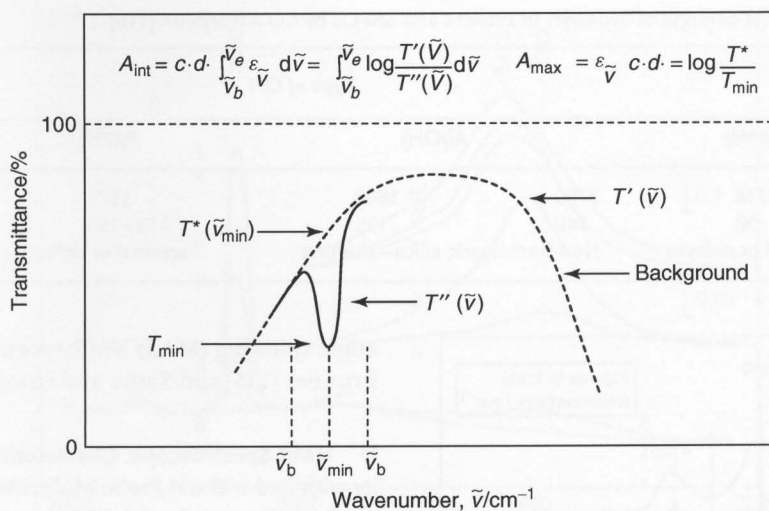
$$A_{\text{int}} = c \cdot d \cdot \int_{\tilde{v}_b}^{\tilde{v}_e} \varepsilon_{\tilde{v}} \, d\tilde{v} = \int_{\tilde{v}_b}^{\tilde{v}_e} \log \frac{T'(\tilde{v})}{T''(\tilde{v})} d\tilde{v} \qquad A_{\text{max}} = \varepsilon_{\tilde{v}} \, c \cdot d \cdot = \log \frac{T^*}{T_{\text{min}}}$$

Fig. 6 Quantitative evaluation of IR spectra – integrated and maximum absorbance (see text) [98].

densities given in N (u.c.)$^{-1}$ or mmol g^{-1} may provide an average value.

In the above-described way, the density of sites may be evaluated from the intensities of the bands of the acid OH groups and also from those of the corresponding ammonium or pyridinium ions (see above). However, both ammonia and pyridine are strong bases and, therefore, rather weak acid sites may be indicated, which in some cases is a disadvantage. Moreover, pyridine molecules are bulky and do not fit into smaller channels or voids of zeolite structures.

In fact, if one wishes to determine the so-called *external* Brønsted (or Lewis) acidity on the outer surfaces of zeolite crystallites, bulky probe molecules such as substituted pyridines (2,6-di-*tert*-butylpyridine, etc.), which cannot penetrate into the zeolitic channels and cavities, may even be very helpful (cf. examples in Refs. [111, 112]). However, in the majority of cases one is interested in the characterization of the *internal* acidity, i.e. inside the zeolite structures. Therefore, many researchers looked, because of the above-mentioned reasons, for other appropriate probe molecules. Examples of adsorbates tested for probing acidity include water [113, 114], amines [115], light hydrocarbons [116], hydrogen [117], carbon monoxide [118, 119], nitrogen monoxide [120, 121] and acetonitrile [122, 123], and carbon dioxide [124] and pyrrole [63] for basicity, to list just a selection of probes and related references (cf., e.g., Ref. [125] and Table 8.6 in Ref. [126]). In many instances, such probes can be employed in attempts to evaluate both the *density* (via the absorbance of the respective bands resulting from the interaction of the probes with the acid sites) and the *strength* of the respective sites (see below).

Kazansky (sometimes transcribed as Kazanskii) and coworkers [127–129] and Beck and Pfeifer [130] undertook pioneering work on the application of light paraffins and dihydrogen as probe molecules. In their experiments, diffuse reflectance IR spectroscopy was employed, which has several advantages: high sensitivity, extension into the region of overtones and combination modes (cf. Table 4.3 in Ref. [131]) and use of zeolite powder instead of pressed wafers. In contrast to diffuse reflectance spectroscopy in the UV-visible range, however, a drawback of this technique lies in the difficulties in obtaining quantitative results. As an example, Fig. 7 (adopted from Ref. [132]) displays the spectrum of H_2 adsorbed on OH groups of H-ZSM-5 and H-Y.

The utilization of two other frequently used probes, benzene and carbon monoxide, for the characterization of the Brønsted acid strength by IR spectroscopy is illustrated in Fig. 8, Table 3 and Fig. 9. In both cases the wavenumber shift, $\Delta\tilde{v}_{\text{OH}}$, of the original OH band, which indicated the Brønsted acid sites, was adopted as an approximate measure of the acid strength.

More recently, Kazansky and coworkers [133, 134] suggested characterizing the strength of acid (active) sites not through the shift upon interaction with probe molecules but by the intensities of the correlated bands.

Note, however, that the use of probes can hardly provide more than a ranking of members of a homologous series of acid solids, since the interaction of the probe molecules with the acid sites is a dynamic phenomenon which probably modifies the original acid strength and its distribution. Thus, when probes are involved one cannot expect to determine the *"intrinsic"* acid (or basic) strength.

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Tab. 3 Characterization of the strength of hydroxyls in zeolites and SAPOs by CO adsorption [118]

Parameter	Type of OH				
	Si(OH)	*Al(OH)*		*P(OH)*	*Si(OH)Al*
$\bar{\nu}_{OH}/cm^{-1}$	3748	3700	3660	3677	3650–3615
$\Delta\bar{\nu}_{OH}/cm^{-1}$	90	140	195	175–195	237–332
Origin	Terminal or defects	Non-framework; silica–alumina		Terminal or defects	Framework; bridging
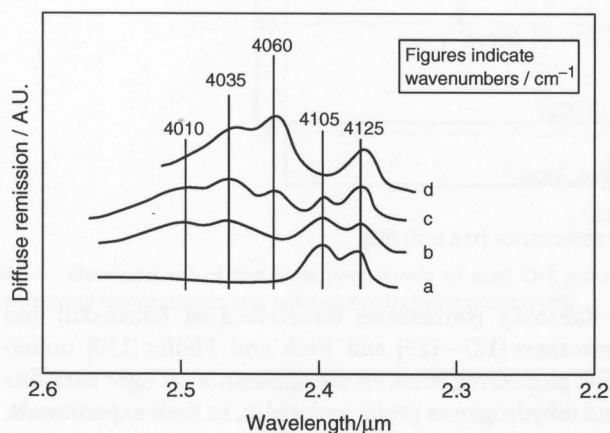
Fig. 7 Diffuse reflectance spectra of hydrogen adsorbed on H-ZSM-5 at 77 K: a, b and c, after heat-pretreatment in high vacuum at 770, 970 and 1220 K, respectively; d, on H-Y after "deep-bed treatment" at 770 K. Abscissa linear in wavelength; important bands indicated in wavenumbers (cm⁻¹) [132].
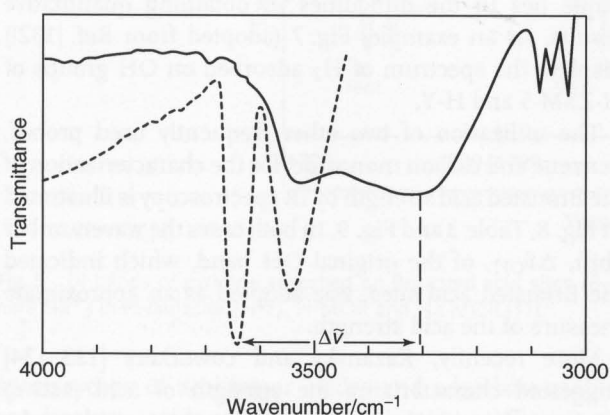

Fig. 8 Wavenumber shift, $\Delta\bar{\nu}$, of the high-frequency OH band (at 3640 cm⁻¹) of H-Y zeolite on adsorption of benzene: dotted curve, spectrum before adsorption; solid curve, spectrum after adsorption of benzene.

A more reliable measure of the strength of Brønsted acid sites is provided by the deprotonation energy, E_p (see above), which may be calculated via quantum chemical methods (cf. the work of Sauer and coworkers, e.g. Refs. [50, 51]) or experimentally determined by magic

angle spinning (MAS) NMR spectroscopy (cf. the work of Brunner [135] and Sauer and coworkers [136]).

D NMR Spectroscopic Characterization of Brønsted Acidity with and without Probe Molecules Similarly to the IR method, Brønsted acid sites may be easily identified as such, i.e. without probe molecules, through ¹H MAS NMR spectroscopy. In their classical papers, Pfeifer and coworkers [57, 137, 138] (see also Ref. [139]) detected that acidic OH groups give rise to characteristic chemical shifts, e.g. of $\delta = 1.8$ (line a), 3.9–4.6 (line b), 4.8–5.6 (line c) and 7.0–7.5 (line d) ppm [referenced to tetramethylsilane, TMS, therefore usually indicated as δ(TMS)] for the non-acidic OHs (silanol groups, corresponding to IR bands at about 3740 cm⁻¹), so-called high-frequency (HF) OH groups in the large cavities of H-Y (corresponding to the IR band at 3640 cm⁻¹), low-frequency (LF) OH groups in the smaller β-cages (corresponding to the IR band at 3550 cm⁻¹) and to residual NH_4^+ cations (cf. also Ref. [99] and Fig. 10).

The OH groups in H-ZSM-5 give rise to chemical shifts of $\delta = 2.0$, 4.2 and 7.0 ppm (cf. Fig. 11), corresponding to IR bands of silanol groups, Si—OH, at 3740 cm⁻¹, bridging OH groups, [≡Si—OH—Al≡], at ca. 3614 cm⁻¹ and bridging OH groups with an additional electrostatic interaction to the framework at 3250 cm⁻¹, respectively [139, 141]. The weakly acidic or non-acidic silanol groups (corresponding to IR bands around 3740–3720 cm⁻¹) generally produce a signal at about $\delta = 2.0$ ppm [135, 139–141]. A more detailed list with lines and corresponding IR bands of various species is given in Ref. [141] (see also below, Fig. 13).

With respect to the quantitative spectroscopic characterization of zeolitic systems, MAS NMR [98] is usually in a better situation than IR, because the former technique provides more directly quantitative results in that only a comparison with a standard is required. Unlike quantitative IR determinations, no extinction coefficients (see above) need to be determined in separate experiments. However, when reliable IR extinction coefficients were available and the pretreatment of the samples was identical, good agreement between the results obtained by IR and ¹H MAS NMR spectroscopy was observed (Fig. 12).
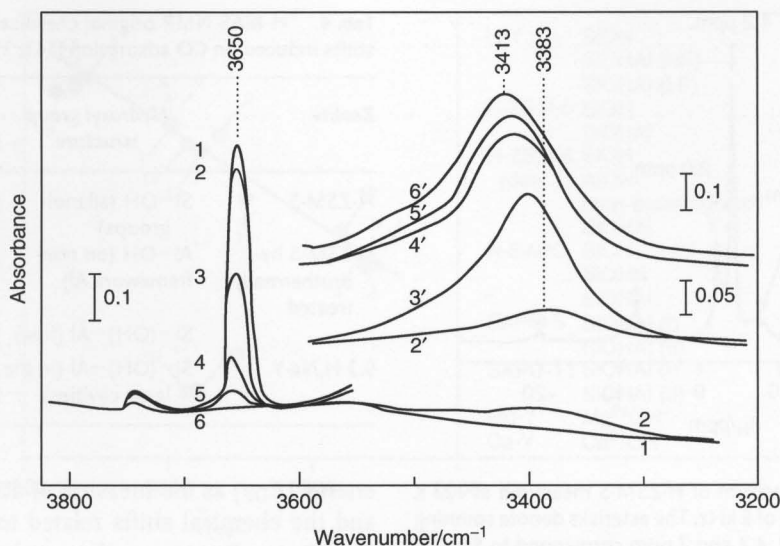
Fig. 9 IR spectra of OH groups of H,Na-Y zeolite before (1) and, after (2–6) adsorption of increasing amounts of CO and, at lower wavenumbers, the bands shifted according to the strength of the OH groups involved, viz. to 3383 → 3413 cm^{-1}, which indicates a decrease from 2 to 6 [118].
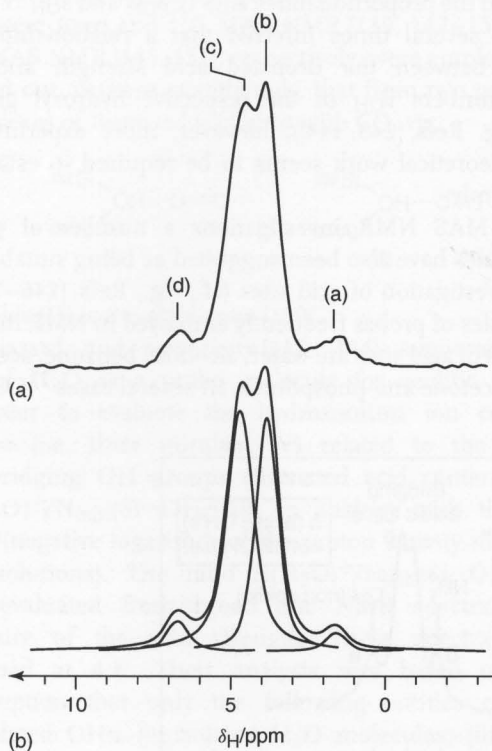
Fig. 10 (a) ^{1}H MAS NMR spectrum of H-Y. (b) Decomposition into the four lines a, b, c and d, corresponding to non-acid OHs (silanol groups, IR bands at 3740 cm^{-1}), acid OH groups in the supercages (HF IR band at 3640 cm^{-1}), acid OH groups in the small cages (β-cages, LF IR band at 3550 cm^{-1}) and OH groups with additional electrostatic interaction with oxygen atoms of the framework (IR band around 3250 cm^{-1}), respectively (see text and Ref. [135]).

Moreover, in the hydrogen form of a classical zeolite, i.e. in an aluminosilicate, a ^{27}Al MAS NMR signal at $\delta = 60$ ppm [referenced to Al(H$_2$O)$_6^{3+}$, i.e. aqueous solution of Al(NO$_3$)$_3$] indicates the presence of Brønsted acid sites (cf., e.g., Ref. [139]). This signal is due to tetrahedrally coordinated framework aluminum and, therefore, corresponds to structural acid OH groups (see top of Scheme 3). Thus, from the area of the signal at $\delta = 60$ ppm the number of Brønsted sites can also be determined.

Pfeifer and coworkers suggested using the chemical shifts of the OH group directly as a measure of Brønsted acid strength [57, 137, 138]. Basically, the shifts should increase with increasing strength. Exceptions are the shifts of OH groups, which are affected by additional electrostatic interactions with adjacent oxygen atoms of the framework (see e.g., the above-mentioned lines c and d of H-Y or the OH groups located in channels of ferrierite (FER) formed by eight-membered rings compared with those in the wider channels built by 10-membered rings [94]; see also below).

The accuracy of the method could be significantly improved by increasing the differences in the chemical shifts by adsorption of CO or halogenated hydrocarbons such as C$_2$Cl$_4$, which induced additional chemical shifts ($\Delta\delta_{OH}$) and thus increased the resolution (see e.g. Table 4). Both the total chemical shifts ($\delta_{OH} + \Delta\delta_{OH}$) and the induced chemical shifts ($\Delta\delta_{OH}$) were suggested as an appropriate measure of acidity strength, since they correlate well with the induced wavenumber shifts,
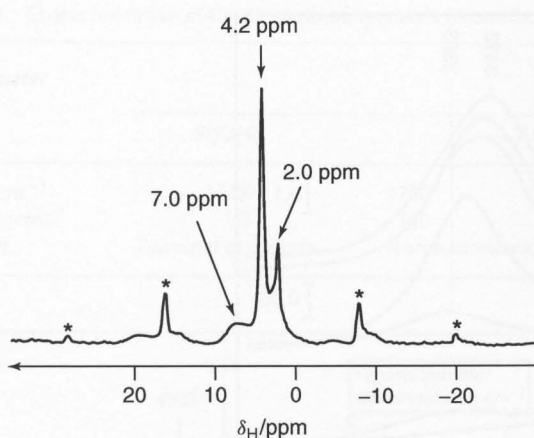
Fig. 11 ^{1}H MAS NMR spectrum of H-ZSM-5 measured at 123 K with a sample spinning rate of 6 kHz. The asterisks denote spinning sidebands. The lines at 2.0, 4.2 and 7 ppm correspond to Si–OH groups at the external surface of the crystallites or framework defect sites (IR band at 3740 cm^{-1}), bridging hydroxyl groups (Brønsted centers, IR band at 3614 cm^{-1}) and OH groups affected by additional interaction with the zeolite framework (broad IR band at about 3250 cm^{-1}) [141].

Tab. 4 ^{1}H MAS NMR original chemical shifts of OH groups and shifts induced on CO adsorption [141, 150]

Zeolite	Hydroxyl group structure	δ_H/ ppm	$\delta_{H\cdots CO}$/ ppm	$\Delta\delta$/ ppm
H-ZSM-5	Si–OH (silanol groups)	2.0	2.0	0.0
H-ZSM-5 hydrothermally treated	Al–OH (on non-framework Al)	2.9	3.9	1.0
	Si–(OH)–Al (free)	4.2	6.2	2.0
0.3 H,Na-Y	Si–(OH)–Al (in the large cavities)	3.9	4.8	0.9

$\Delta\tilde{\nu}_{OH}$ (see above; cf., e.g., Refs. [118, 119] and, for $\Delta\delta_{OH}$, Ref. [141]). Simultaneously, it turned out that upon loading with the adsorbates the OH groups indicated by the line at about $\delta_{OH} = 7$ ppm behaved like free bridging OH groups, i.e. the action of, for instance, CO molecules on those OH groups annihilated their electrostatic interaction with adjacent framework oxygen atoms [141].

Fleischer et al. [136] have shown that under restricted conditions [only oxygen atoms surrounding the T atom (T = Al, Si, P, etc.) bearing the bridging OH group], a linear relationship exists between the deprotonation energy (E_{DP}) as the measure of acid strength (see above) and the chemical shifts related to the acid OH groups, δ_{OH}. Later, Brunner and coworkers [141, 142] provided evidence for a corresponding linear relationship between the wavenumbers of Brønsted acid OH groups, $\tilde{\nu}_{OH}$, and the chemical shifts, δ_{OH} (TMS) (cf. Fig. 13 and Refs. [141, 142]).

From the proportionalities $E_{DP} \propto \delta_{OH}$ and $\delta_{OH} \propto \tilde{\nu}_{OH}$, it was several times inferred that a relationship also exists between the Brønsted acid strength and the wavenumbers $\tilde{\nu}_{OH}$ of the respective hydroxyl groups (cf., e.g. Refs. [143, 144]); however, more experimental and theoretical work seems to be required to establish this firmly.

For MAS NMR investigations a number of probe molecules have also been suggested as being suitable for the investigation of acid sites (cf., e.g., Refs. [146–148]). Examples of probes frequently employed in NMR investigations of acid sites are water, alcohols, benzene, acetone, acetylacetone and phosphines. In several cases ^{13}CO and
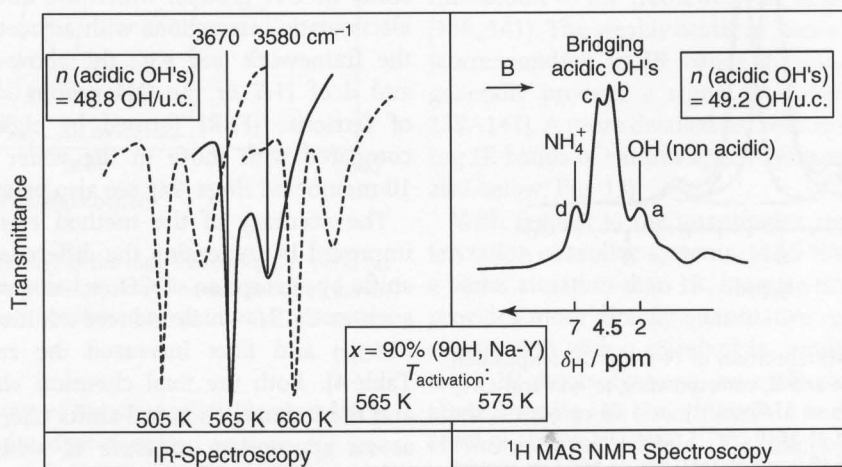

Fig. 12 Comparison of the determination of the density of acid OHs in H-Y (degree of exchange: $x = 90\%$) by IR spectroscopy and ^{1}H MAS NMR spectroscopy under almost identical conditions [88, 137].
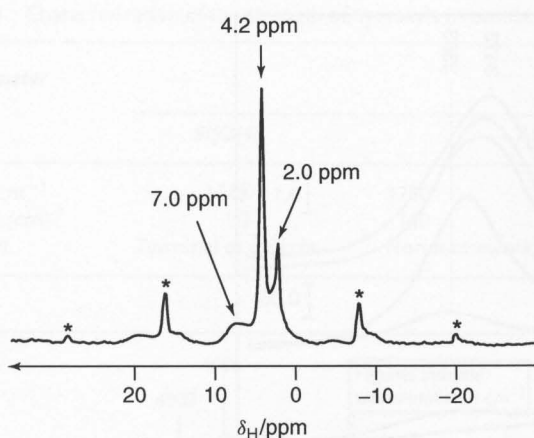
Fig. 11 ^{1}H MAS NMR spectrum of H-ZSM-5 measured at 123 K with a sample spinning rate of 6 kHz. The asterisks denote spinning sidebands. The lines at 2.0, 4.2 and 7 ppm correspond to Si—OH groups at the external surface of the crystallites or framework defect sites (IR band at 3740 cm^{-1}), bridging hydroxyl groups (Brønsted centers, IR band at 3614 cm^{-1}) and OH groups affected by additional interaction with the zeolite framework (broad IR band at about 3250 cm^{-1}) [141].

Tab. 4 ^{1}H MAS NMR original chemical shifts of OH groups and shifts induced on CO adsorption [141, 150]

Zeolite	Hydroxyl group structure	δ_H/ ppm	$\delta_{H...CO}$/ ppm	$\Delta\delta$/ ppm
H-ZSM-5	Si—OH (silanol groups)	2.0	2.0	0.0
H-ZSM-5 hydrothermally treated	Al—OH (on non-framework Al)	2.9	3.9	1.0
	Si—(OH)—Al (free)	4.2	6.2	2.0
0.3 H,Na-Y	Si—(OH)—Al (in the large cavities)	3.9	4.8	0.9

$\Delta\tilde{\nu}_{OH}$ (see above; cf., e.g., Refs. [118, 119] and, for $\Delta\delta_{OH}$, Ref. [141]). Simultaneously, it turned out that upon loading with the adsorbates the OH groups indicated by the line at about $\delta_{OH} = 7$ ppm behaved like free bridging OH groups, i.e. the action of, for instance, CO molecules on those OH groups annihilated their electrostatic interaction with adjacent framework oxygen atoms [141].

Fleischer et al. [136] have shown that under restricted conditions [only oxygen atoms surrounding the T atom (T = Al, Si, P, etc.) bearing the bridging OH group], a linear relationship exists between the deprotonation

energy (E_{DP}) as the measure of acid strength (see above) and the chemical shifts related to the acid OH groups, δ_{OH}. Later, Brunner and coworkers [141, 142] provided evidence for a corresponding linear relationship between the wavenumbers of Brønsted acid OH groups, $\tilde{\nu}_{OH}$, and the chemical shifts, δ_{OH} (TMS) (cf. Fig. 13 and Refs. [141, 142]).

From the proportionalities $E_{DP} \propto \delta_{OH}$ and $\delta_{OH} \propto \tilde{\nu}_{OH}$, it was several times inferred that a relationship also exists between the Brønsted acid strength and the wavenumbers $\tilde{\nu}_{OH}$ of the respective hydroxyl groups (cf., e.g. Refs. [143, 144]); however, more experimental and theoretical work seems to be required to establish this firmly.

For MAS NMR investigations a number of probe molecules have also been suggested as being suitable for the investigation of acid sites (cf., e.g., Refs. [146–148]). Examples of probes frequently employed in NMR investigations of acid sites are water, alcohols, benzene, acetone, acetylacetone and phosphines. In several cases ^{13}CO and
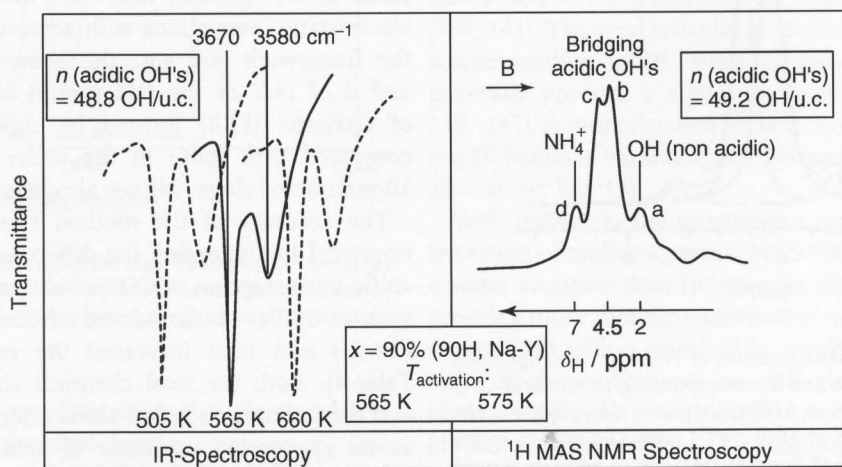

Fig. 12 Comparison of the determination of the density of acid OHs in H-Y (degree of exchange: $x = 90\%$) by IR spectroscopy and ^{1}H MAS NMR spectroscopy under almost identical conditions [88, 137].
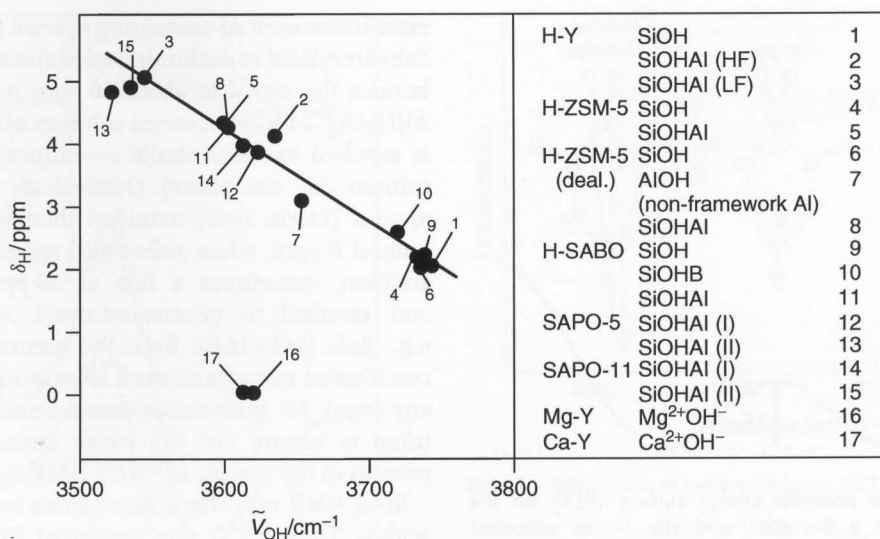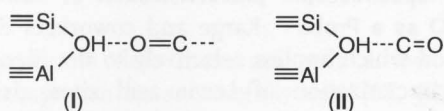
H-Y	SiOH	1
	SiOHAl (HF)	2
	SiOHAl (LF)	3
H-ZSM-5	SiOH	4
	SiOHAl	5
H-ZSM-5	SiOH	6
(deal.)	AlOH	7
	(non-framework Al)	
	SiOHAl	8
H-SABO	SiOH	9
	SiOHB	10
	SiOHAl	11
SAPO-5	SiOHAl (I)	12
	SiOHAl (II)	13
SAPO-11	SiOHAl (I)	14
	SiOHAl (II)	15
Mg-Y	$Mg^{2+}OH^-$	16
Ca-Y	$Ca^{2+}OH^-$	17

Fig. 13 Dependence of the ^1H chemical shift, δ_H, of surface hydroxyls in zeolites on the wavenumber of OH stretching vibrations, $\tilde{v}_{OH}$ [142].

^{15}N-containing ammonia, pyridine, amines or acetonitrile were used and ^{13}C MAS NMR [139, 147–150] and ^{15}N MAS NMR [145, 151], respectively, were employed. It turned out, perhaps surprisingly, that from two possible complexes of Brønsted acid sites with CO, viz.

$$\begin{array}{cc} \equiv Si \\ \quad\quad OH\cdots O=C\cdots \\ \equiv Al \\ \textbf{(I)} \end{array} \qquad \begin{array}{cc} \equiv Si \\ \quad\quad OH\cdots C=O \\ \equiv Al \\ \textbf{(II)} \end{array}$$

complex (II) is the stable one [150].

Fraissard and coworkers [113, 114] suggested the use of H_2O as a probe molecule for zeolitic acidity in order to evaluate the hydroxonium ion concentration (i.e. their number, N) related to the original bridging OH groups (Brønsted acid centers), i.e. $N(H_3O)^+/N_{init.}(Si-OH-Al)$, in analogy with the pH scale (negative logarithm of the proton activity in aqueous solutions). The ratio $N(H_3O)^+/N_{init.}(Si-OH-Al)$ was evaluated from broad line NMR spectra as a measure of the acid strength. These spectra were obtained at 4 K. Their analysis was based on the assumption that only the following entities coexist: (i) isolated OHs; (ii) isolated H_2O molecules; (iii) H_2O molecules attached to OH groups via hydrogen bonds; and (iv) hydroxonium ions, H_3O^+. Evidence was offered that, up to room temperature, the temperature effect on the equilibrium is negligible. In the case of non-dealuminated H-Y, it was claimed that an equilibrium, i.e. $N(H_3O^+)/N_{init.}(Si-OH-Al) =$ constant, was reached for one H_2O molecule per initial $(Si-OH-Al)$. With dealuminated H-Y, a second
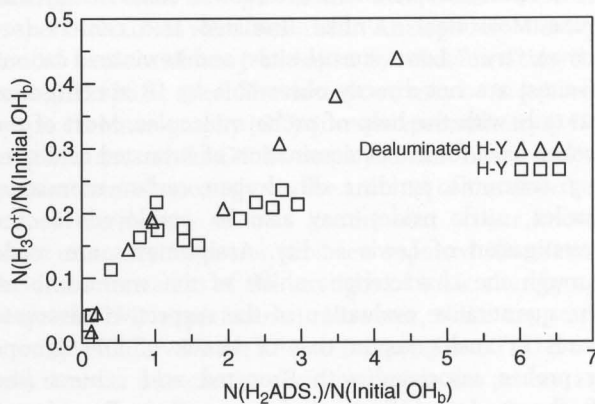

Fig. 14 Formation of hydroxonium ions, H_3O^+, as a function of loading of non-dealuminated H-Y zeolite ($\triangle$) and dealuminated H-Y ($\square$) with H_2O [113, 114].

increase in $N(H_3O)^+/N_{init.}(Si-OH-Al)$ was observed for $N(H_2O)/N_{init.}(Si-OH-Al) > 2$ (Fig. 14).

The latter finding was explained by a reaction of H_2O with defect sites. Note, however, that according to quantum chemical calculations by Sauer and coworkers [152, 153], an isolated, i.e. non-hydrated, hydroxonium ion as the cation participating in an ion pair such as $[\equiv Si-O-Al^-\equiv(O_3)-Si]^-\cdots H_3O^+$ is in aqueous solutions not a stable but a transition structure. Its energy corresponds to a saddle point separating two stable hydrogen-bonded neutral structures, $[\equiv Si-OH-Al\equiv(O_3)-Si]\cdots H_2O$, by only 10 kJ mol^{-1} (see Fig. 15).
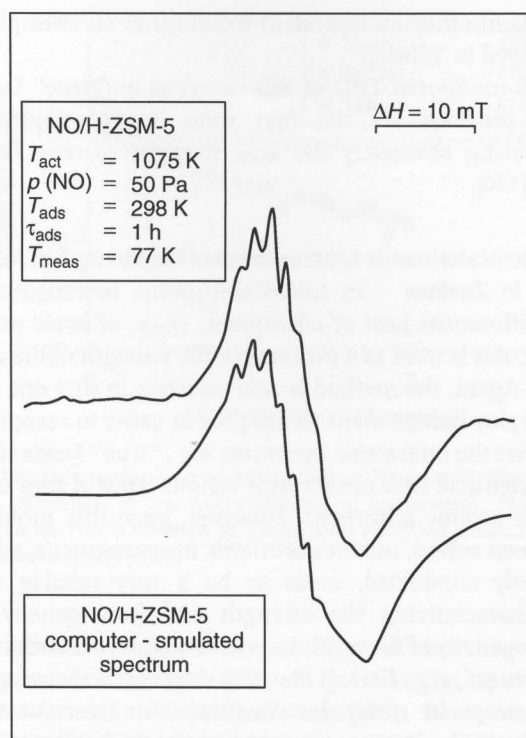
Fig. 16 ESR spectrum of NO adsorbed on H-ZSM-5 containing "true" Lewis sites and comparison with the computer-simulated spectrum [170].

Fig. 17 Adsorption of pyrrole on basic K-LTL zeolite [63].

Unfortunately, to date there are only a few probes which perhaps can be successfully used [63, 172–175]. Carbon dioxide has been employed several times, but it may suffer from the drawback that it can form various carbonates when interacting with zeolites. Other probes suggested for the characterization are acetic acid, boric acid trimethyl ester, acetylene derivatives, halogenated paraffins (e.g. deuterochloroform, Cl_3CD [173]) benzene and pyrrole [172]. In some instances, benzene was used for probing basic oxygen sites in the 12-membered ring windows of faujasite-type zeolites, where a benzene molecule can weakly interact with basic oxygen atoms through its hydrogen atoms. It was suggested that the shift of the CH deformation band provides a measure of the basic strength [173]. Similarly, the shift of the IR band due to the NH vibration of the amphoteric probe molecule pyrrole was used for characterizing the basicity of, e.g., zeolites containing cations of alkali metals. Figure 17 shows as an example the spectrum and the shift $\Delta \tilde{v}$ after adsorption of pyrrole on K-LTL [63, 174, 175]. This approach, advanced by de Mallman and Barthomeuf, was supported by the finding that the thus determined basicity parallels the value of the partial negative charges on the basic oxygen sites.
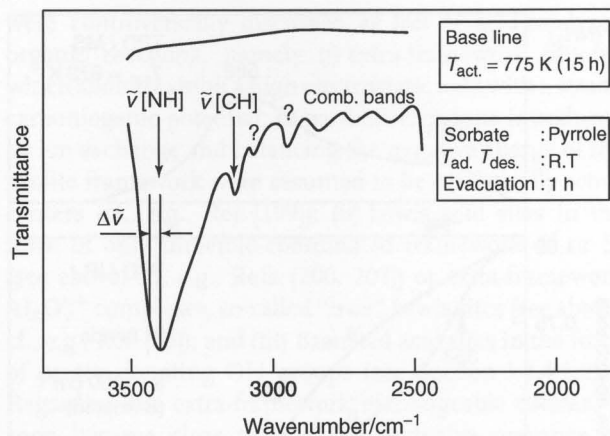
H   Temperature-programmed Desorption (TPD) of Probe Molecules from Acidic (or Basic) Sites   Temperature-programmed desorption of bases such as ammonia, amines and pyridine is a popular method for characterizing the acid strength of the sites from which the probe molecules were desorbed. Analogously, desorption of weak acids may be tested for characterizing the strength of basic sites. The desorption may be monitored by gas chromatography (GC) or mass spectrometry (MS). In particular, when GC is employed one has a tool to measure simultaneously via the amount of the desorbed probes the density of sites (to the best of our knowledge, examples have not been reported illustrating the characterization of the strength of basic sites by appropriate TPD experiments). However, there are some possible pitfalls with the TPD technique. First, TPD is not selective, i.e. one cannot decide whether the probes are desorbing from Brønsted or Lewis acid sites when both types are present. Therefore, in order to characterize the strength of acidic sites, it is advisable to combine TPD with an independent technique, e.g. simultaneous *in-situ* IR spectroscopy. Observation of the developing TPD peaks and the simultaneous decrease in the IR bands indicating the Brønsted and/or Lewis acid sites permits an assignment of the TPD peaks to the respective types of sites [154, 155]. Figure 18 shows the desorption of NH_3 from mordenite monitored simultaneously by MS and IR spectroscopy.

Second, the TPD results may be corrupted by re-adsorption of the species desorbed from acid sites. Here, the use of thin samples or sample layers may be helpful [176, 177]. Models have been developed that take into account the kinetics of the desorption and the possibility of a distribution of acid strength. They enable one to derive the number, n, of types of sites and evaluate
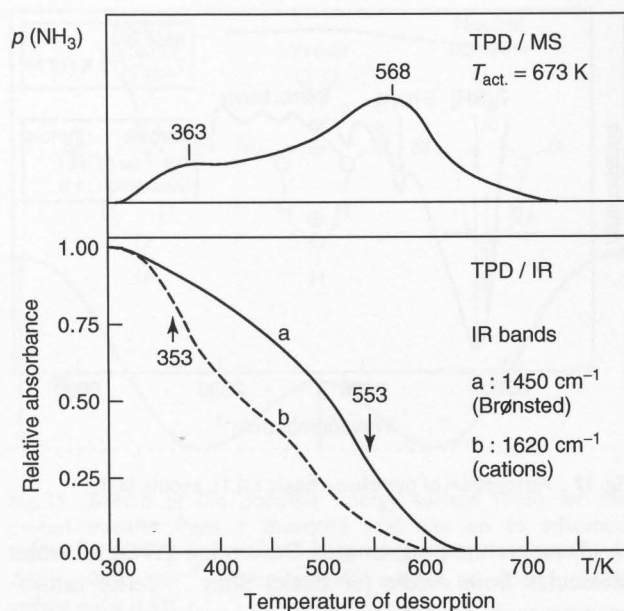
Fig. 18 Temperature-programmed desorption of NH_3 from Be-MOR simultaneously measured by MS [increase in $p(NH_3)$] and IR spectroscopy (decrease in the absorbances at 1450 and 1620 cm^{-1}), due to desorption from Brønsted acid sites and Be cations, respectively. The maxima in the upper part of the figure correspond to the steepest decrease in the respective absorbance [154, 155].

the activation energies of desorption, E_n. The latter may provide a quantitative measure of the acid strength and at least lead to a reliable ranking of the members of a sample series with respect to their acidity strength [177, 178] (see Table 5). Even though TPD is a method the application of which must often be treated with caution, there are many instances where it led to a ranking of acid zeolites with respect to acid strength in good agreement with the

results of other, independent techniques; an example is displayed in Table 5.

ESR-monitored TPD of NO adsorbed on "true" Lewis sites provided for the first time the possibility of measuring selectively the acid strength of true Lewis sites [170].

I Microcalorimetric Measurement of the Strength of Acidic Sites in Zeolites In microcalorimetric investigations, the differential heat of adsorption, Q_{diff}, of basic probe molecules is used as a measure of the strength of the acid sites. Again, the method is non-selective in that one has to employ independent techniques in order to recognize whether the interaction occurs on, e.g., "true" Lewis sites, Brønsted acid sites or cations if various types of sites exist in the zeolitic adsorbent. However, once this problem has been solved, microcalorimetric measurements, when properly conducted, seem to be a very reliable tool for characterizing the strength and homogeneity or heterogeneity of the acidic internal and external surface of zeolites (cf., e.g., Refs. [179–182]). Moreover, the amount of basic probe molecules consumed for neutralization of the acid sites measures directly their density in the adsorbent sample. Figure 19 compares the results of microcalorimetric measurements of NH_3 adsorption on a heteropoly acid, which was used as a standard and exhibited a high degree of homogeneity (constant Q_{diff} until complete neutralization), with an almost homogeneous sample of H-ZSM-5 and an La,Na-Y zeolite with a rather broad distribution of acid strength.

J Catalysis and Test Reactions Since the advent of zeolites in research on and application of heterogeneous [183, 184] catalysis by about 1960, a huge body

Tab. 5 Ranking of the acid strength of Brønsted sites of three H-ZSM samples through various techniques[a]

H-ZSM-5 $T_{act} = 673$ K	TPD/MS (NH_3)		C_6H_6 adsorption IR spectroscopy	Microcalorimetry NH_3 adsorption
	T_{des}(max.)/K	$\bar{E}_{des}$/kJ mol^{-1}	$\Delta\bar{v}_{OH}$/cm^{-1}	Q_{diff}/kJ mol^{-1}
Sample A	655	110	359	157
Sample B	619	104	337	147
Sample C	620	103	340	145

[a]T_{act}, activation temperature; T_{des}(max.), maximum temperature of desorption; $\bar{E}_{des}$, most frequently occurring energy of desorption; $\Delta\bar{v}_{OH}$, wavenumber shift upon adsorption of benzene; Q_{diff}, differential heat of NH_3 adsorption (see text).
Sample A: $H_{4.0}Na_{0.4}[Al_{4.4}Si_{91.6}O_{192}]$; Si/Al (total) = 21; Al^F = 2.5; Al^{NF} = 1.9.
Sample B: $H_{2.4}Na_{0.4}[Al_{2.8}Si_{93.2}O_{192}]$; Si/Al (total) = 33; Al^F = 2.1; Al^{NF} = 0.7.
Sample C: $H_{2.6}Na_{0.2}[Al_{2.8}Si_{93.2}O_{192}]$; Si/Al (total) = 33; Al^F = 2.8; Al^{NF} = none.
Al^F = framework Al; Al^{NF} = non-framework Al.
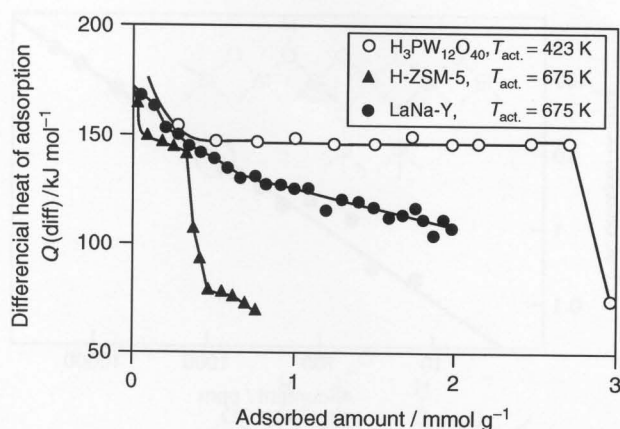
Fig. 19 Differential heat of adsorption of NH_3 on $H_3[PW_{12}O_{40}]$ (for calibration of the microcalorimetric equipment), H-ZSM-5 and La,Na-Y as a function of the amount adsorbed measured via microcalorimetry [182].

of literature has been accumulated in this field. Very informative reviews were provided by, *inter alia*, Venuto and Landis [185], Venuto [186], Poutsma [187], Csicsery [188], Hölderich [189], Haag [190] and Weitkamp and Puppe [191]. With respect to catalysis of inorganic reactions, there was and still is remarkable research activity on zeolites in environmental catalysis (for example, in decomposition of NO, selective reduction of NO by NH_3, etc.) where, however, the catalytically relevant centers are formed by exchange cations such as Cu^{2+}, Cu^+ and Co^{2+} (cf., e.g., Refs. [192, 193]). For the Claus reaction (reaction of SO_2 with H_2S to form water and elemental sulfur [194]) aluminas or bauxites are still the dominant catalysts [195] and in this catalysis basic Lewis sites are strongly involved, as has been shown by gas-phase titration with BF_3 and monitored by IR spectroscopy [196]. The IR spectroscopic observations in the latter study [196] are in agreement with the model proposed by Knözinger and Ratnasamy [48]. Zeolites also catalyze the Claus reaction but are usually rapidly deactivated through deposition and pore blocking by sulfur [197]. Thus, the main domain of zeolite catalysis lies in the area of hydrocarbon reactions.

Similarly to catalysis by other solids, e.g. oxides and metals, the question soon arose as to which type of sites are the catalytically relevant centers. In the case of oxides, it was found that Lewis acid sites, i.e. coordinatively unsaturated cations, play the most important role. As an example, the dehydration of alcohols over alumina should be mentioned (cf., e.g., Ref. [198]). Regarding metal catalysts, frequently certain surface positions of the metal atoms, for example in so-called kinks (Halbkristall-Lagen), on steps or corners were claimed to be active centers. With respect to zeolites, three types of sites

were controversially discussed as *loci* of acid-catalyzed organic reactions, namely (i) extra-framework cations, which should exhibit a high electrostatic field with a strong carboniogenic potential; in particular, cations introduced by ion exchange and balancing the negative charge of the zeolite framework were assumed to be catalytically active centers (cf., e.g., Ref. [199]); (ii) Lewis acid sites in the form of only threefold-coordinated framework Al or Si (see above; cf., e.g., Refs. [200, 201]) or extra-framework $Al_xO_y^{n+}$ complexes, so-called "true" Lewis sites (see above; cf., e.g., Ref. [35]); and (iii) Brønsted acid sites in the form of proton-donating OH groups (see Section 3.2.4.1.2B). Regarding the extra-framework exchangeable cations, it soon became clear that in the exclusive presence of monovalent cations, i.e. when even traces of multivalent cations were carefully avoided, the respective zeolites did not catalyze hydrocarbon reactions such as cracking, alkylation, dealkylation and isomerization. In cases where multivalent cations were not excluded, acid OH groups form according to the Hirschler–Plank mechanism [see above; cf. Refs. [25, 26] and Eqs. (1) and (2)]. Correspondingly, when Karge and coworkers prepared lanthanum-containing zeolite catalysts via solid-state ion exchange and also carefully excluded even traces of water during the pretreatment and admission of the reactant (ethylbenzene), no catalytic activity was observed. Only when small doses of water vapor were intermittently admitted (1 min contact with 10^2 Pa water vapor), the reaction started to occur, because now the Hirschler–Plank mechanism became operative; simultaneously, on the zeolite in the IR transmittant flow-reactor cell, the typical OH bands at 3616 and 3518 cm^{-1} were observed [31]. Furthermore, the alternative "Lewis acid sites vs. Brønsted acid sites" was clarified in favor of the latter, since a close correlation was found between the catalytic activity and the density of Brønsted centers in, for instance, the alkylation of benzene by ethene or propene (cf. Ref. [89] and Fig. 20). Here, the decrease in the activity (measured via the conversion of benzene) upon dehydroxylation (see above; see, for instance, Scheme 3) followed exactly the decrease in the density of the acid OH groups as determined by IR spectroscopy with and without the probe pyridine.

At higher dehydroxylation temperatures, the density of Lewis sites as determined via IR spectroscopy with pyridine as a probe is still high but the activity is zero. It is not yet entirely clear why the density of Lewis sites decreases at all when the pretreatment temperature is above 450 °C. Most likely this is due to an agglomeration of AlO^+ to bulkier $Al_xO_y^{n+}$ complexes. Similar relations between the concentration of Brønsted centers and catalytic activity have been observed in many other cases of acid-catalyzed hydrocarbon reactions.
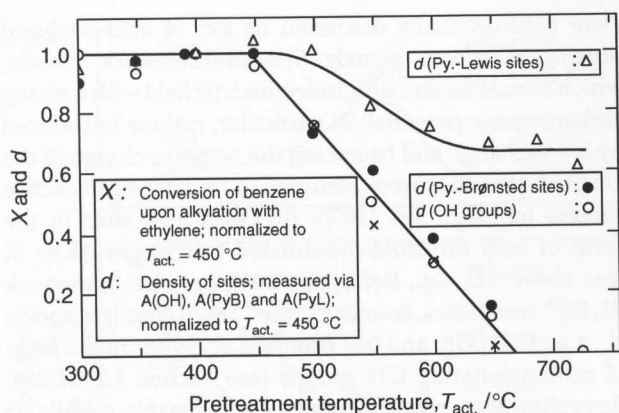
Fig. 20 Comparison of activity in benzene alkylation by ethylene and acid site density of H-mordenite as a function of pretreatment temperature [89].

Fig. 21 Linear relationship between the *n*-hexane cracking activity over and the Al content (measuring the density of acid OH groups) in H-ZSM-5 [190].

It is not definitively clarified whether or not the Lewis sites play any role in heterogeneous catalysis on zeolites. Several authors claim that they are relevant in coke formation (cf., e.g., Ref. [202]) and it seems very likely, however, that Lewis sites are able to increase the acid strength of adjacent Brønsted OH centers through a quasi-inductive effect, which lowers the deprotonation energy of the OH groups. Moreover, it was shown that Lewis acid sites are able to form carbenium ions such as triphenylmethyl cations (CPh_3^+) [123] and catalyze the Meerwein–Ponndorf–Verley reaction and its reverse, the Oppenauer oxidation [203].

Several times it has been reported that such correlations between the density of acid sites of a zeolite sample and the conversion or rate of a reaction catalyzed by these sites may be used as tests and means of determination of the site density. A very impressive example was provided by the work of Haag and coworkers [39, 190], who used *n*-hexane cracking (alpha test) over H-ZSM-5 as a test reaction (cf. Fig. 21).

However, "mild steaming" (up to 13.3 kPa for 2.5 h at 813 K) increased the activity to values much above the linear correlation curve [190]. The authors proposed that mild steaming creates sites of enhanced activity and that these sites are formed only from Al atoms in close proximity, such as paired Al centers, which explains the strong dependence of the effect on the Al content [190]. A scheme for the formation of this type of site was proposed [39, 190] (see also Ref. [204] and Scheme 4, where state IV represents a site of enhanced activity). On more severe treatment this site is transformed to a conventional "true" Lewis site (see above; cf. Refs. [33, 34]).

Similarly, a linear relationship was measured between the conversion in the disproportionation of ethylbenzene and the density of Brønsted acid sites in a series of
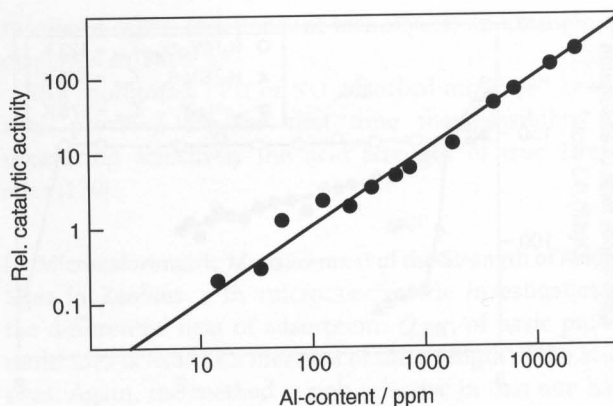
mordenites or Y-type samples as measured through the absorbance of the respective IR bands of the acid OH groups or pyridinium ion bands (cf. Fig. 22 and Refs. [72, 143, 205]).

This reaction, when properly conducted, does not suffer from deactivation through coke formation [72]. The fact that the straight line in Fig. 22 does not go through the origin indicates that a minimum strength of the Brønsted acid site is required to operate as catalytically active centers, which is not fulfilled in the case of the barium-modified mordenites. Sigl et al. [206] employed the same reaction to check the acid strength of [Al]-, [Ga]- and [Fe]-H-ZSM-5 samples with almost exactly identical Si/Al ratios (about 25) under standardized conditions. In agreement with the results of various other tests, it turned out that the level of quasi-stationary conversion
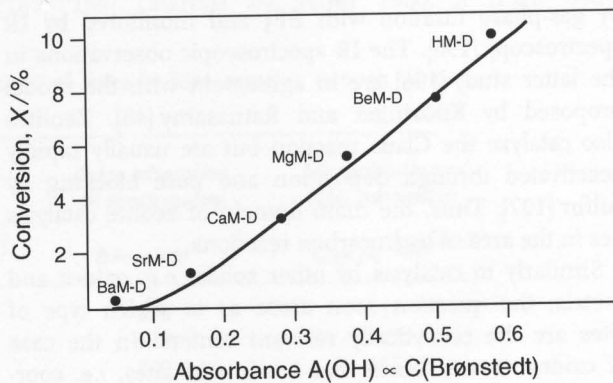
Fig. 22 Steady-state conversion of ethylbenzene disproportionation over dealuminated mordenites as a function of the density of acidic OH groups as measured by the absorbance of the OH stretching band around 3600 cm^{-1}. Conditions: $T_{activ.} = 673$ K, $p_{activ.} = 10^{-4}$ Pa, $T_{react.} = 448$ K, $p(EB) = 1.33 \times 10^3$ Pa, mass of catalyst, $m = 0.25$ g, absorbances $A(OH)$ normalized to equal sample thickness of 10 mg cm^{-2} [143].
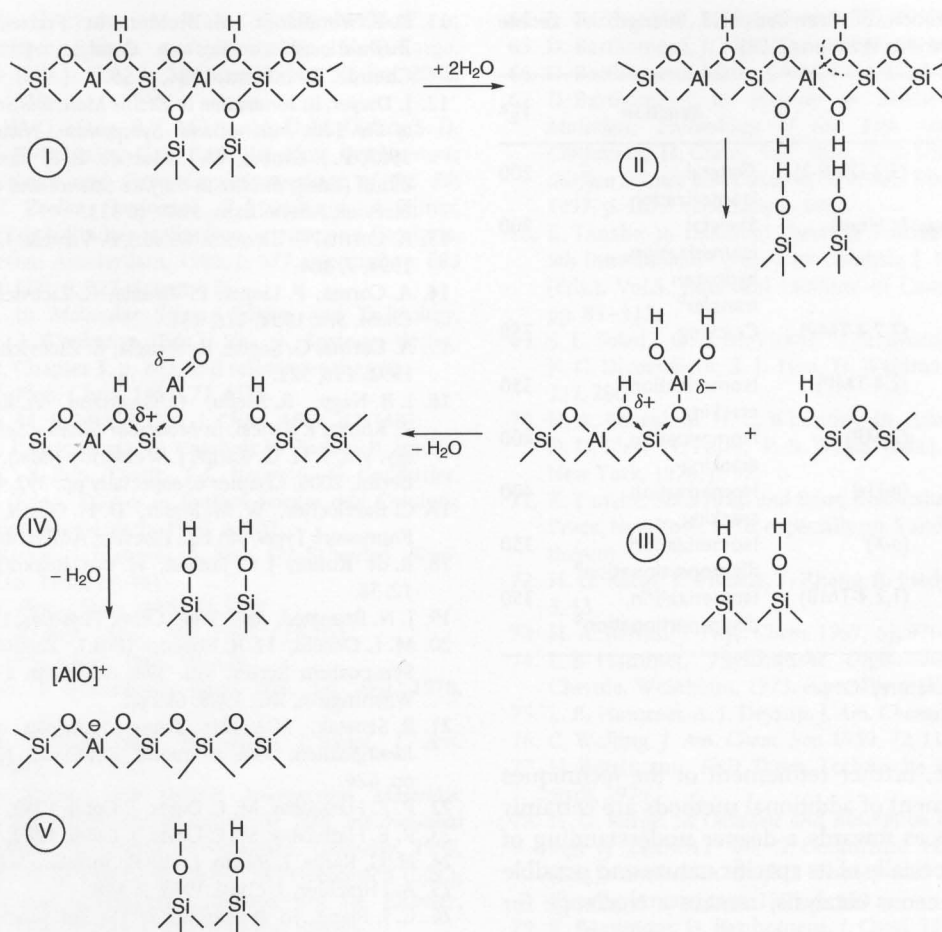
Scheme 4 Formation of acid sites of enhanced activity in H-ZSM-5 after mild steaming.

reflected the acid strength decreasing in the sequence [Al]-H-ZSM-5 > [Ga]-H-ZSM-5 > [Fe]-H-ZSM-5.

Several other test reactions have been proposed, such as conversion of toluene, xylene isomerization [207] and dehydration of cyclohexanol. The last reaction was studied by Karge et al. [111] *inter alia* over mordenites and clinoptilolites as catalysts with different acid strength, which was systematically varied by appropriate cation exchange. Using 2,6-di-*tert*-butylpyridine as a probe for IR spectroscopic investigation, it was demonstrated that the reaction occurred in the case of the clinoptilolites only on the external surface. Similarly to what was observed with the disproportionation of ethylbenzene, the reaction rate depended linearly on the density of the Brønsted acid sites. Also, series of test reactions (cf. Table 6) requiring different activation energies or reaction temperatures under otherwise standardized conditions were suggested by Guisnet and coworkers [208] in order to measure the different acid strengths of the zeolites employed to catalyze these reactions (Table 6).

As test reactions for the basicity of zeolites, *inter alia* the already mentioned Knoevenagel condensation of benzaldehyde with malononitrile [173], side-chain alkylation of alkylbenzenes, conversion of 2-propanol with formation of acetone and of methanol to carbon monoxide have been suggested and to some extent successfully employed.

3.2.4.1.4 Conclusion The Brønsted acidity of oxides and, in particular, of zeolites and its role in heterogeneous catalysis has been extensively studied and seems to be relatively well understood. Its qualitative identification is largely routine work and in most cases reliable. Also, a large number of techniques for the quantitative determination of the density of Brønsted and Lewis acid sites and their strength is available. However, the methods for characterization of Brønsted and Lewis acid sites usually allow only a ranking of the strengths within a series of similar acid materials under standardized

Tab. 6 Characterization of Brønsted acid strength of zeolite catalysts through various reactions [208]

Reactant		Reaction	T_R[a]
3,3-Dimethyl-1-butene	(3,3-DMB-1)	Skeletal isomerization	200
Cyclohexene	(c Hexe)	Skeletal isomerization, hydrogen transfer[b]	200
2,2,4-Trimethylpentane	(2,2,4-TMP)	Cracking	350
2,4-Dimethylpentane	(2,4-TMP)	Isomerization, cracking	350
2-Methylpentane	(2-MP)	Isomerization, cracking	400
n-Hexane	(n-Hx)	Isomerization, cracking	400
o-Xylene	(o-X)	Isomerization, disproportionation[b]	350
1,2,4-Trimethylbenzene	(1,2,4-TMB)	Isomerization, disproportionation[b]	350

[a] T_R: reaction temperature/°C.
[b] Bimolecular reaction.

conditions. Here, further refinement of the techniques and the development of additional methods are certainly desirable. Advances towards a deeper understanding of Lewis acidity, especially of its specific nature and possible role in heterogeneous catalysis, remain a challenge for further research.

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