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Additional Information

What is measured when measuring acidity in zeolites with probe molecules?

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ABSTRACT: Based on theoretical calculations of CO, NH₃ and Pyridine adsorption at different sites in MOR and MFI zeolites, we analyze how confinement effects influence the measurement of acidity based on the interaction of probe molecules with Brønsted acid sites. Weak bases like CO form neutral ZH---CO adducts with a linear configuration that can be distorted by spatial restrictions associated to the dimensions of the pore, leading to weaker interaction, but can also be stabilized by dispersion forces if a tighter fitting with the channel void is allowed. Strong bases like NH₃ and Pyridine are readily protonated on Brønsted acid sites, and the experimentally determined adsorption enthalpies include not only the thermochemistry associated to the proton transfer process itself, but also the stabilization of the Z⁻---BH⁺ ion-pair formed upon protonation by multiple interactions with the surrounding framework oxygen atoms, leading in some cases to a heterogeneity of acidities within the same zeolite structure.

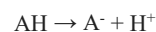
KEYWORDS: Brønsted acid, confinement, DFT, dispersion, microporous structure

Zeolites are inorganic microporous crystalline materials composed by SiO₄ and AlO₄ tetrahedra that link to form channels and cavities of molecular dimensions. Their well-determined topology and microporous structure, the associated high internal surface area, and their notable adsorption and shape-selective properties, are important aspects influencing their successful application as heterogeneous catalysts. Yet, the key factor in most catalytic applications is the presence of single, isolated and well-defined active sites in the framework or in extra-framework positions which can be, most of the times, visualized by means of different physicochemical characterization techniques. Zeolites can be synthesized with a variety of pore dimensions and compositions. It is possible to introduce metal atoms in framework and extra-framework positions, as well as metal or metal oxide clusters within their channels and cavities. The substitution of tetrahedrally coordinated framework Si atoms with a trivalent element such as Al introduces bridging hydroxyl groups in the ordered structure of the solid. The presence of these bridging hydroxyl groups, with their Brønsted acid characteristics, have opened zeolites to a large number of academic and industrial applications, and it is possible to say that zeolites are today the most widely used solid acid catalysts in industry.¹⁻⁸ They are employed in large scale commercial processes in the fields of oil refining and petrochemical industry, and they also find application in the production of fine and speci-

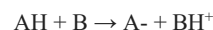
ality chemicals, or in the conversion of methanol to olefins and gasoline (MTO and MTG processes). Moreover, their presence is increasing in emerging fields related with the non-conventional transformation of raw materials, such as the conversion of coal, gas and oil into syngas, olefins, acetylene and aromatics, the potential transformation of alternative sources like biomass, and the valorization of methane or CO₂.⁹⁻¹³

Given that most industrial applications of zeolites are based on their Brønsted acid properties, it is not surprising that, since their introduction as acid catalysts,¹⁴ a large effort has been done to characterize the number, strength and accessibility of the potentially active acid sites, and to correlate these values with their catalytic activity. In addition to theoretical studies,¹⁵⁻²⁰ diverse experimental techniques such as calorimetric measurements, temperature-programmed desorption (TPD) of basic molecules, ¹H, ¹³C and ¹⁷O solid-state NMR as well as IR and Raman vibrational spectroscopies are employed to measure the acidity of zeolites.²¹⁻³⁰ Despite the accuracy of the theoretical and the experimental data obtained nowadays, and the deep understanding of zeolite acidity provided by such techniques, a number of questions are still open related to the heterogeneity of the Brønsted acid sites, either in different zeolites or within the same zeolite structure. This heterogeneity is associated to the location of the acid sites in pores, channels and cavities of different dimensions, with the protons pointing to different environments, and should be taken into consideration when analyzing and comparing the acidity determined by different techniques.

By definition, a Brønsted acid is a species prone to donate a proton according to:



Or, in the presence of a base, a species able to transfer a proton to such base, as described by:



Following the first definition, the intrinsic strength of a Brønsted acid can be quantified by its deprotonation energy E_{DEP} , defined as the energy necessary to separate a proton at an infinite distance from the resulting anion,

$$E_{\text{DEP}} = E(\text{A}^-) + E(\text{H}^+) - E(\text{AH})$$

But in practice Brønsted acidity can only be observed when a proton is transferred to a base, and in this case the feasibility of

the process also depends on the tendency to accept protons, or proton affinity, of the base

$$PA = E(\text{BH}^+) - E(\text{B}) - E(\text{H}^+)$$

And of the stabilization of the resulting $\text{A}^-\text{---BH}^+$ ion-pair by electrostatic and, depending on the system, other types of interactions. In solution, the ionic species A^- and BH^+ are fully surrounded by solvent molecules which provide a different degree of stabilization depending on their polarity, and the dielectric medium decreases the Coulombic attraction between A^- and BH^+ facilitating their separation.^{21, 29}

In zeolites, the Brønsted acid sites are the so-called bridged hydroxyl groups (Figure 1), formed by a proton directly attached to a framework oxygen atom that is bonded to one Al and one Si atom. The three O-Al, O-Si and O-H bonds are covalent bonds superimposed by small electrostatic interactions, and the O atom has therefore a formal threefold coordination similar to that present in the hydronium cation H_3O^+ . The preferred geometry of an O atom in such non-classical situation is not tetrahedral as in H_3O^+ cation, but tends to be nearly planar with three non-equivalent X-O-X bonds, being X = H, Al and Si. The ordering imposed by the crystalline structure of the zeolite limits the flexibility around this O atom, thus weakening the OH bond and generating acidity. Deprotonation energies E_{DEP} , taken as the most rigorous parameter describing the intrinsic acid strength of a Brønsted acid, cannot be experimentally determined, but they have been estimated from quantum-chemical calculations using isolated clusters,^{31, 32} embedded clusters³³⁻³⁵ and periodic models.^{18, 36} Deprotonation energies calculated using small cluster models show important variations with cluster size that tend to converge for systems containing more than 20 T-atoms. This trend suggests that, at this cluster size, electrostatic interactions already approach those present in real zeolites.³² Polarization of the Si-O bonds, which has been shown to be essential to stabilize the negative charge generated by deprotonation of the Brønsted acid centers, is also a quite local effect that does not extend far beyond the second O-atom coordination sphere from the Al atom.¹⁸ In accordance with this proposal and based on periodic DFT calculations, Grajciar et al. reported that the acidity of Brønsted sites in FER is mostly influenced by their local environment, in particular by the number of Al atoms in the second coordination sphere of the acid site, and not so much by the topology of the site.³⁶ This finding is especially relevant for zeolites with high Al content, and indirectly confirms the similar intrinsic acidity of all isolated Brønsted sites present in high Si/Al ratio zeolites. When the clusters treated with quantum chemical methods are embedded in a periodic system described by interatomic potentials, that is, the QM-Pot approach, the influence of cluster size is much smaller, and all calculated DPE values for FAU and MFI structures stay within 3 and 6 kJ/mol, respectively.³⁷ Deprotonation energy values calculated with the QM-Pot approach for various zeolites with different crystalline structure (CHA, TON, FER, MFI, MOR and FAU) are within a range of less than 30 kJ/mol, indicating that the intrinsic acid strength of zeolites is hardly influenced by the framework structure.^{34, 37} This conclusion was confirmed by Jones et al. in an exhaustive and accurate study of deprotonation energies of isolated Brønsted acid sites in zeolites CHA, BEA, FER, MFI, MOR and FAU. E_{DEP} for the 12 distinct T sites in MFI range from 1655 to 1668 kJ/mol, and from 1622 to 1665 kJ/mol in MOR (see all values in ref. 18). The statistical ensemble averages of E_{DEP} values at each crystallographic position, which reflect the stability of the conjugate anions, are insensitive to the location of the isolated Al atoms, with calculated values of 1201 ± 11 kJ/mol.¹⁸

The wide range of acid and catalytic properties reported for zeolite materials should be therefore related to differences in the stabilization of the protonated BH^+ species by interaction with the negatively charged Z⁻ framework. The net negative charge in the deprotonated zeolite is easily spread out over the oxygen atoms up to two coordination spheres from the Al center,¹⁸ and provides a diffuse electron cloud over the inner surface of the zeolite microporous structure. This indicates that the zeolite anion would be a soft conjugated base, highly adaptable to stabilize soft cationic species confined within the pores.³⁸ The extent of this stabilization by electrostatic and van der Waals interactions depends on the number and strength of contacts between the confined species and the surrounding framework oxygen atoms, that is, on how the size and shape of the guest species fits with those of the zeolite host channels and cavities.^{19, 39}

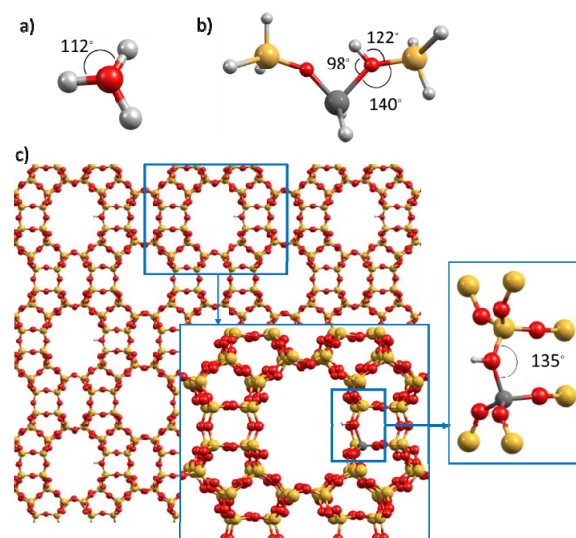


Figure 1. PBE/6-311g(d,p) optimized geometry of a) H_3O^+ cation and b) $\text{SiH}_3\text{-O-AlH}_2\text{-OH-SiOH}_3$ cluster. c) Periodic model of a Brønsted acid site in MOR framework. Si, O, Al and H atoms are depicted as yellow, red, gray and white balls, respectively.

The confinement concept was introduced by Derouane et al., to rationalize some remarkable features of zeolites on the basis of the geometrical curvature of their internal surface.⁴⁰ At difference with shape-selectivity effects, that modify the adsorption and diffusion of reactants and products, or prevents the formation of certain transition states, due to short-range repulsions between the adsorbed molecules and the zeolite microporous structure, confinement effects stem from long-range attractive van der Waals interactions. When the sizes of the host structure and the guest molecule become comparable, the adsorbed molecules and their direct framework environment tend to reciprocally optimize their van der Waals interaction, leading to enhanced adsorption, diffusion, and catalytic properties.⁴¹ A first and simple model to quantify van der Waals interactions in confined spaces considered dispersion forces only, and was based on a dimensionless parameter s defined as $s = d/a$, where d is the distance of the confined molecule to the micropore wall and a is the micropore radius. The magnification of dispersion interactions in a curved environment relative to a flat surface was estimated as proportional to $(1-s/2)^{-3}$, and suggested that physisorption energies could be enhanced by a factor of 8 in the situation of maximum confinement ($s = 1$), and by a factor of ~ 3 in intermediate situations ($0.5 < s < 1$). Further improvement of this model by including pore shape and repulsion

effects led to a maximum magnification of the physisorption energy by a factor of ~ 5 in the optimal tight fit situation.^{40,41}

Many efforts have been done since then to quantitatively evaluate confinement effects in zeolites, considering not only the average size of molecules and channels, but also molecular shape and local framework geometry within the pores. Methods based on classical force fields have been widely used to simulate molecular adsorption and diffusion in zeolites, due to their computational efficiency and accuracy.⁴² But they are not suited to describe chemical reactions involving bond breaking and formation, and therefore quantum mechanical (QM) methods, despite being computationally more expensive, have been applied to the study of reactivity in zeolites. QM methods are applied to cluster models in which a portion of the zeolite is taken into account, to hybrid schemes combining clusters treated at QM level inserted in a periodic system described with force fields, or to fully periodic systems.^{15,16,19} In the case of periodic calculations based on Density Functional Theory (DFT), one of the main challenges is the description of the dispersion interactions, which are not accounted for by local density functionals. Several approaches have emerged in recent years to overcome this limitation, and encouraging results have been reported for instance for adsorption of alkanes in zeolites using computationally accessible techniques.⁴³⁻⁴⁵ Among them, the DFT-D methodology proposed by Grimme combines an excellent computational efficiency with reasonable accuracy, with average deviation from experimental values of about 5 kJ/mol.^{46,47}

To illustrate the effect of confinement associated to the curvature of the zeolites microporous structure, four molecules of increasing size and polarity, CO, CH₄, NH₃ and Pyridine, have been placed within the channels of pure siliceous models of mordenite (MOR) and ZSM-5 (MFI), and their position optimized without restrictions at DFT level (Figures 2, 3). The channel system of MFI is composed by interconnected straight and sinusoidal 10-ring (10R) channels of ~ 5.0 Å diameter, that intersect forming larger void spaces of ~ 7.0 Å diameter, while MOR contains large 12R channels of ~ 7.0 Å interconnected via small 8R side pockets of ~ 4.0 Å. Two initial positions were considered for each molecule in each zeolite: in the 12R channels and 8R side pockets in MOR, and in the 10R channels and at the channels intersections in MFI.

Table 1. Interaction energies (in kJ/mol) calculated for CO, CH₄, NH₃ and Py within the channels system of pure silica mordenite.

| molecule | position | E_{int} PBE | E_{int} D3 | E_{int} PBE-D3 |
|-----------------|---------------------|----------------------|---------------------|-------------------------|
| CO | MOR-12R | -13 | -8 | -21 |
| CO | MOR-8R | -13 | -25 | -38 |
| CO | MFI-int | -1 | -19 | -20 |
| CO | MFI-10R | -1 | -24 | -25 |
| CH ₄ | MOR-12R | -13 | -11 | -24 |
| CH ₄ | MOR-8R | -11 | -30 | -41 |
| CH ₄ | MFI-int | -2 | -22 | -24 |
| CH ₄ | MFI-10R | 1 | -29 | -28 |
| NH ₃ | MOR-12R | -4 | -16 | -19 |
| NH ₃ | MOR-8R | -26 | -25 | -52 |
| NH ₃ | MFI-int | -6 | -18 | -24 |
| NH ₃ | MFI-10R | -9 | -25 | -34 |
| Py | MOR-12R \parallel | -17 | -49 | -67 |
| Py | MOR-12R \perp | -21 | -54 | -75 |
| Py | MFI-int | -6 | -70 | -76 |
| Py | MFI-10R | -3 | -69 | -72 |

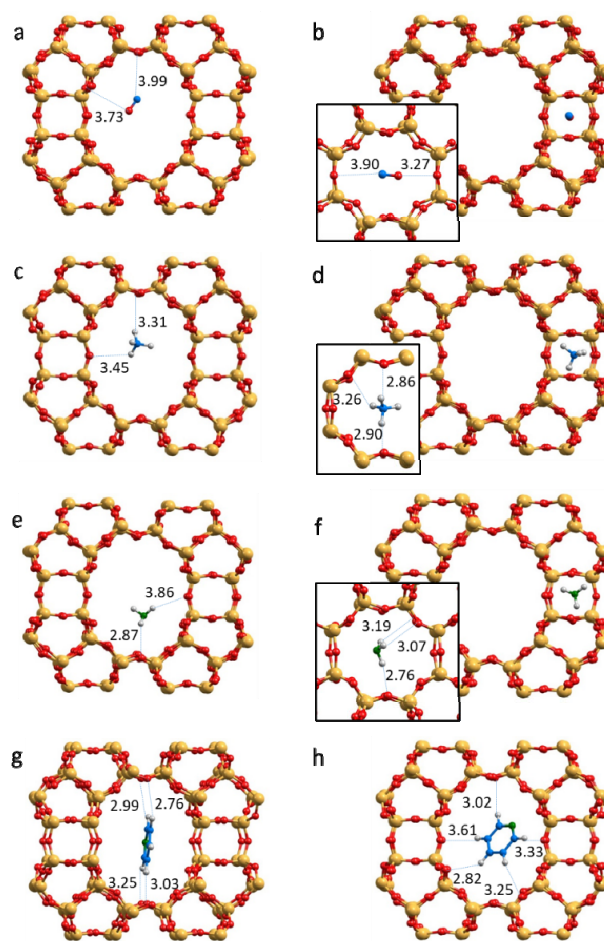


Figure 2. Optimized structures of CO (a,b), CH₄ (c,d) NH₃ (e,f) and Pyridine (g,h) placed in the main channel and side-pockets of a pure siliceous model of MOR zeolite.

The main contribution to the calculated interaction energies corresponds to dispersion forces (E_{intD3} in Table 1), in agreement with previous work.⁴⁴ In general, along the series of guest molecules and host zeolites, this term becomes larger as the size of the molecule increases, $\text{CO} < \text{NH}_3 \sim \text{CH}_4 < \text{Py}$, and as the diameter of the channel decreases, $\text{MOR-12R} < \text{MFI-int} < \text{MFI-10R} < \text{MOR-8R}$, with the calculated values ranging from -20 to -70 kJ/mol. Only for NH₃ in the side-pockets of MOR, the presence of some local hydrogen bonding between the slightly positive H atoms and three close O atoms in the ring, results in a comparable contribution of the pure DFT and the D3 values to the calculated interaction energy. The orientation of Py within the 12R channels of MOR results in a non-negligible difference in dispersion effects of 6 kJ/mol favoring the perpendicular orientation. In the narrower channels of MFI, however, Py moves slightly towards the wider region at the intersection, so that the global confinement in the two positions initially considered is similar, and larger than in MOR. These stabilizing interactions associated only to confinement in curved environments have been generally taken into account to study adsorption of hydrocarbons in zeolites,⁴⁸ and more recently have been included in reactivity studies.³⁹ We analyze now how these confinement effects influence the measurements of acidity based on interaction of probe molecules with Brønsted acid sites.

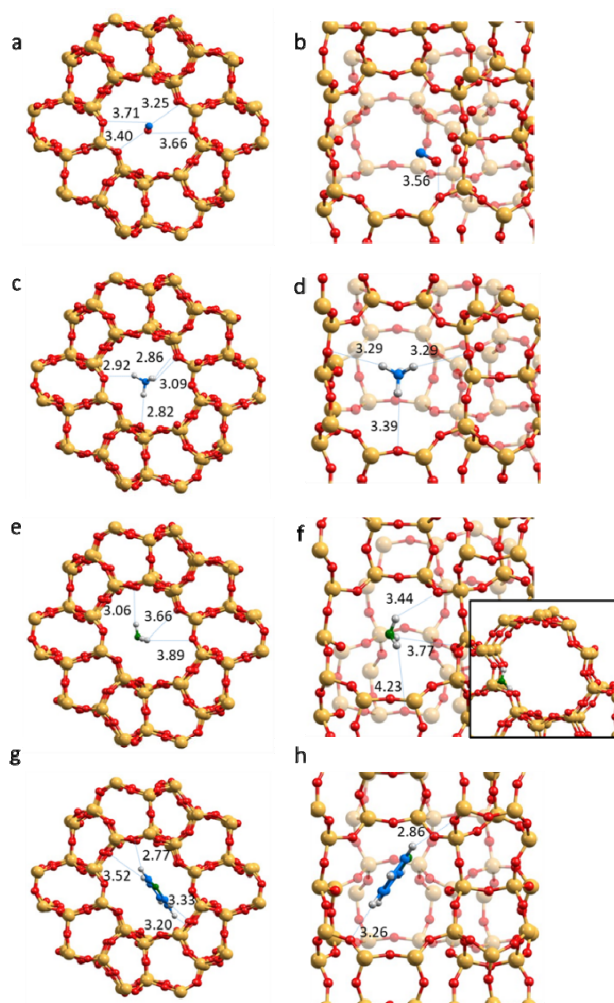


Figure 3. Optimized structures of CO (a,b), CH₄ (c,d) NH₃ (e,f) and Pyridine (g,h) placed in the 10R channel and at the channels intersection of a pure siliceous model of MFI zeolite.

The adsorption of probe molecules of weak basicity such as N₂, CO, ethene, propane, CH₃CN or methanol, and the measurement of the perturbation of the $\nu(\text{OH})$ frequency by formation of a ZH--B adduct between the Brønsted acid site and the weak base, have been widely used to quantify acid strength in zeolites.^{21,25,28} Upon formation of a weak hydrogen bond with a base like CO, the $\nu(\text{OH})$ stretching frequency of different zeolites undergoes a red shift of up to 400 cm⁻¹, while the $\nu(\text{CO})$ vibrational frequency is blue-shifted by 30-40 cm⁻¹, with the magnitude of the shifts being assumed to be proportional to the acidity of the OH group and, therefore, to the strength of the interaction.^{24,49,50}

Indeed, accurate measurements of enthalpy changes associated to CO bonding to Brønsted acid sites in H-Y, H-ZSM-5 and H-FER zeolites were found to correlate with the shift in the $\nu(\text{OH})$ frequency. However, the trend did not apply for H-MCM-22 and H-MCM-56 zeolites.⁵¹ Using surface science techniques in a UHV environment, Boscoboinik et al. characterized the acidity of a bidimensional zeolite model system consisting of a bilayer aluminosilicate film supported on Ru(0001) surface. The red-shift in the $\nu(\text{OH})$ frequency induced by CO and ethene adsorption on the bridged hydroxyl groups present in the 2D model was in the order of the most acidic OH groups reported for zeolites, indicating that the aluminosilicate film is more acidic than 3D zeolites. But the

calculated adsorption energies were larger in the zeolite cavities than in the flat surface, because of the larger contribution of dispersion interactions in the curved surfaces of 3D zeolites.^{52,53} It seems therefore that a number of factors can influence the measured shifts apart from the intrinsic acidity of the Brønsted site, at least some of them being associated to the confinement effect. In order to gain a deeper insight into how the confinement effect associated to micropores of different diameter affects the characterization of acidity by means of CO adsorption, the interaction of CO with ten Brønsted acid sites located in the 12R channels and 8R pockets of MOR, and in the 10R channels and channels intersections of MFI, with the protons pointing to different environments, has been investigated using the DFT-D3 approach.

There are four non-equivalent tetrahedral sites in the MOR unit cell, T1 in the 12R main channel, T2 and T4 at the intersection between the 12R channel and the 8R side-pockets, and T3 inside the 8R pockets. To cover different environments of the acid centers, an Al atom was introduced at T1, T3 and T4 positions and, in each case, two different Brønsted acid sites were generated by attaching a proton to two out of the four different O atoms directly bonded to Al, labelled O_a and O_b (Figure 4). Among the twelve non-equivalent tetrahedral sites present in the orthorhombic structure of MFI, T4 and T10 are located in the sinusoidal 10R channel, T8 and T11 are in the straight 10R channel, and the rest (T1, T2, T3, T5, T6, T7, T9 and T12) are at the intersection between the sinusoidal and straight 10R channels. We studied two different environments, one within the straight 10R channels by placing an Al at T11 site, and another one at the wider void at the channels intersection with Al located at T1. And again, in each case, two possible orientations of the Brønsted acid site were considered depending on the oxygen atom, O_a or O_b, to which the proton was attached (Figure 5). Interaction energies with and without dispersion corrections are summarized in Table 2, together with the shifts in the $\nu(\text{OH})$ vibrational frequencies obtained using the accurate ω/r correlation method described by Nachtigall et al.⁵⁴

The optimized geometry of the adducts formed by interaction of CO with a Brønsted acid site is linear, with optimized ZH--CO distances close to ~ 2 Å, and with the CO molecule occupying the void space to which the proton in the isolated site was pointing to. But if the dimensions of the pore do not allow a linear configuration or there are spatial restrictions forcing a too short/too long hydrogen bond, the acid-base interaction is weaker and the system is slightly destabilized. On the other hand, depending on the architecture of the microporous system, some configurations allow a tighter fitting of CO within the channel void, leading to a larger stabilization by dispersion interactions. Both effects are independent and can contribute to the final geometry and stability of the system.

Table 2. Interaction of CO with Brønsted acid sites in MOR and MFI. Distances $r(\text{H--CO})$ in Å, interaction energies E_{int} in kJ/mol.

| zeolite | site | location | $r(\text{H--CO})$ | E_{int} DFT | E_{int} D3 | E_{int} DFT-D3 | $\Delta\nu(\text{OH})$ |
|---------|--------------------|----------|-------------------|-------------------------|------------------------|----------------------------|------------------------|
| MOR | T1-O _a | 12R | 1,897 | -25 | -18 | -43 | -368 |
| MOR | T1-O _b | 12R | 1,915 | -38 | -16 | -53 | -278 |
| MOR | T3-O _a | 8R | 1,819 | -17 | -35 | -52 | -426 |
| MOR | T3-O _b | 8R | 1,896 | -14 | -33 | -47 | -419 |
| MOR | T4-O _a | 8R | 1,911 | -27 | -16 | -42 | -346 |
| MOR | T4-O _b | 12R | 1,901 | -24 | -15 | -39 | -345 |
| MFI | T1-O _a | int | 1,891 | -25 | -24 | -49 | -366 |
| MFI | T1-O _b | int | 1,893 | -24 | -26 | -50 | -378 |
| MFI | T11-O _a | 10R | 1,905 | -33 | -17 | -50 | -357 |
| MFI | T11-O _b | 10R | 1,895 | -33 | -16 | -49 | -358 |

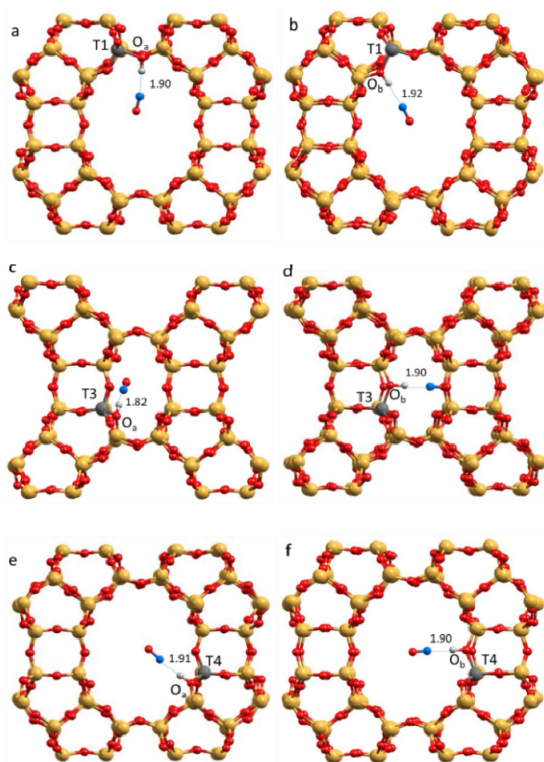


Figure 4. Optimized structures of CO interacting with Brønsted acid sites placed in the main channel (a,b,e,f) and side-pockets (c,d) of MOR zeolite.

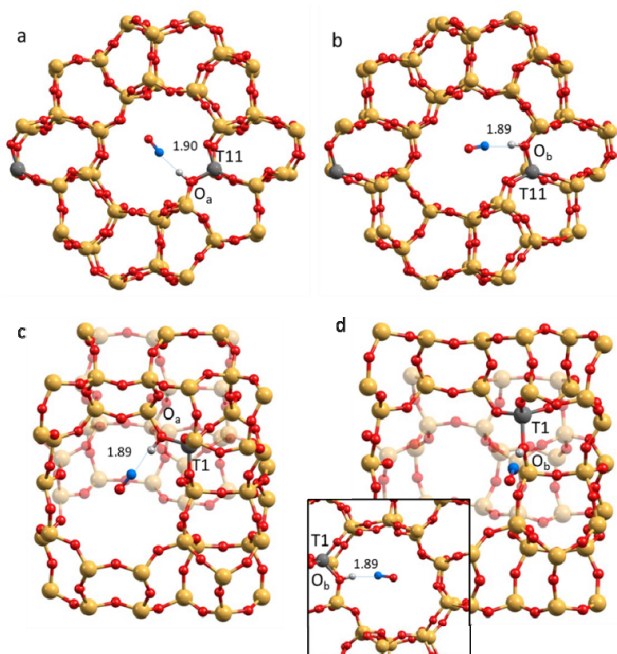


Figure 5. Optimized structures of CO interacting with Brønsted acid sites placed in the 10R channel (a,b) and at the channels intersection (c,d) of MFI zeolite.

This is clearly observed, for example, when comparing the adsorption of CO at T3 and T4 sites in MOR. The geometry of the adduct formed at T3-O_a site should be equivalent to that obtained at T4-O_a site (Figure 4c,e), but the proximity of other framework oxygen atoms belonging to the narrow sinusoidal 8R channel restricts the free space available for CO, so that the optimized H-CO distance, 1.82 Å, is the shortest among all the computed values, and the DFT interaction energy is 10 kJ/mol lower than at T4-O_a. The local geometry of the adducts formed at T3-O_b and T4-O_b sites in MOR seems similar (Figure 4d,f) but CO adsorption at T3-O_b provokes a distortion of the dihedral angle $d(\text{H-O-Al-O})$ from 13° to 69° which results in a low interaction energy at the DFT level, while on T4-O_b the $d(\text{H-O-Al-O})$ dihedral angle only changes from 11° to 29° due to interaction with CO. Counteracting this effect, we observe that while in T3-O_a and T3-O_b the CO molecule is closely surrounded by the O atoms of the 8R, in T4-O_a and T4-O_b it is placed at the center of the large 12R channel, which results in differences in stabilization by dispersion forces of nearly 20 kJ/mol (Table 2). Altogether, the total adsorption energies are larger at T3 than at T4, which correlates with larger $\Delta\nu(\text{OH})$ frequency shifts at T3. However, this trend is lost when T1 is included in the comparison. The largest total interaction energy in MOR is obtained for T1-O_b site with CO crossing the main 12R channel, but the calculated $\Delta\nu(\text{OH})$ shift in this position is the lowest, -278 cm⁻¹. In contrast, for the environments considered within MFI structure, both the Brønsted sites associated to Al atoms placed at the 10R channels and those placed at the channels intersections are able to form ZH-CO adducts with the proton and CO oriented towards the void space at the intersections (Figure 5), without any geometrical constraint associated to the presence of too close framework atoms. The differences in the DFT and D3 contributions between sites are lower than 10 kJ/mol, the total interaction energies are within 1 kJ/mol, and the shifts in the $\nu(\text{OH})$ vibrational frequencies are in a narrow range of 20 cm⁻¹.

These results show that there are several independent factors contributing to the optimized geometry, $\nu(\text{OH})$ frequency and stability of ZH-CO adsorption complexes, which explain the lack of correlation between CO adsorption energies and induced $\Delta\nu(\text{OH})$ shifts in some cases,^{51,53} and questions the use of these shifts to evaluate the acid strength of zeolites and its influence on reactivity.

At difference with weak bases like CO, strong bases like NH₃ and Pyridine are protonated by Brønsted acid sites, and the resulting cationic species, NH₄⁺ and Pyridinium⁺ cations, interact strongly with the negatively charged zeolite framework. Temperature-programmed desorption (TPD) of NH₃, Py and other amines with different degree of substitution, is one of the most widely used methods for quantifying Brønsted acidity in zeolites.^{1,21,29,55-57} It is based on an initial saturation of the catalyst surface with chemisorbed NH₃ or amine followed by a linear increase in the temperature, with the amount of NH₃ or amine desorbed at different temperatures providing information about the concentration and strength of the acid sites present. Adsorption enthalpies obtained from TPD measurements include not only the thermochemistry associated to the proton transfer process itself, but also the stabilization of the Z---BH⁺ ion-pair formed upon protonation by multiple interactions with the surrounding framework oxygen atoms. A simple thermochemical cycle was proposed by Gorte and collaborators to understand the acidity of zeolites, as depicted in Figure 6.^{29,55,58,59}

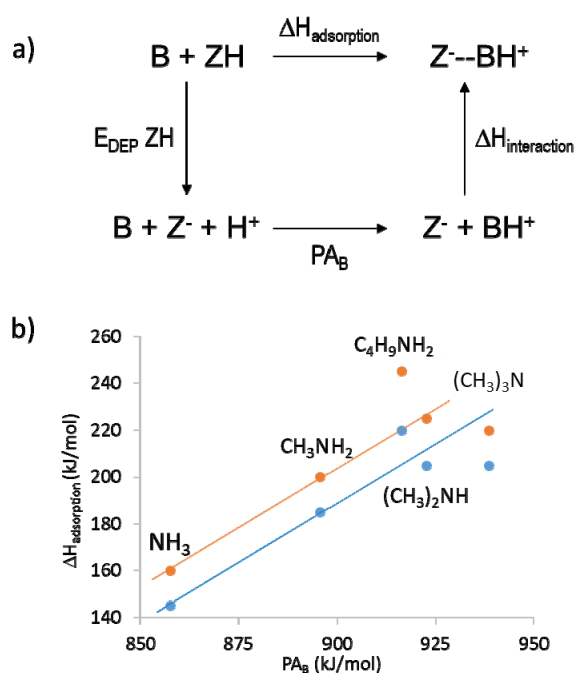


Figure 6. Thermochemical cycle for acidity in zeolites (a) and correlation between heats of adsorption ($\Delta H_{\text{adsorption}}$) and proton affinities (PA_{B}) of alkylamines in H-MOR (orange) and H-ZSM-5 (blue) (b). Adapted from reference 59. Copyright 1996 American Chemical Society.

According to this scheme, the experimentally measured heat of adsorption ($\Delta H_{\text{adsorption}}$) of a strong base B in a zeolite ZH includes the deprotonation energy of the zeolite (E_{DEP}), the proton affinity of the base (PA_{B}) and the specific stabilization of the $\text{Z}^{\ominus}\text{---}\text{BH}^{\oplus}$ ion-pair within the zeolite void where it is formed ($\Delta H_{\text{interaction}}$) or, in other words, the confinement effect of a particular zeolite on a given molecule. Since the deprotonation energies of all sites in all zeolites are similar,^{18,34,37} the measured adsorption enthalpies for one base in different zeolites are indicative of the different confinement effects exerted by these zeolites on this base. Thus, for instance, the larger experimental enthalpies of adsorption of NH_3 in H-MOR, 160 kJ/mol, as compared to H-ZSM-5, 145 kJ/mol, indicate a larger ion-pair stabilization or confinement effect in the voids of mordenite.⁵⁹ On the other hand, the existence of a correlation between the heats of adsorption and the proton affinities of a series of alkyl amines in H-MOR and H-ZSM-5 (Figure 6b) suggests that confinement effects within a given zeolite structure are in principle similar for a series of structurally related bases. The negative deviation from the correlation found for trimethylamine was attributed to the loss of one hydrogen bond with the framework in $(\text{CH}_3)_3\text{NH}^{\oplus}$ cation as compared to NH_4^{\oplus} or the other protonated primary or secondary amines, while the higher than expected adsorption enthalpies obtained for butylamine were explained on the basis of an enhanced stabilization by dispersion interactions between the alkyl chain and the pore walls.⁵⁹ While these and similar results reported for substituted pyridines provide a clear picture of the role of confinement in stabilizing protonated bases in different zeolite structures, they do not reflect however the possibility of having a heterogeneous distribution of Brønsted acid sites within a particular zeolite associated to their location in

voids of different size. To add some information regarding this possibility, we have now calculated the energetics of adsorption and protonation of NH_3 and pyridine at different sites in MOR and MFI structures, so that the role of confinement in different regions of the same zeolite can be estimated and compared.

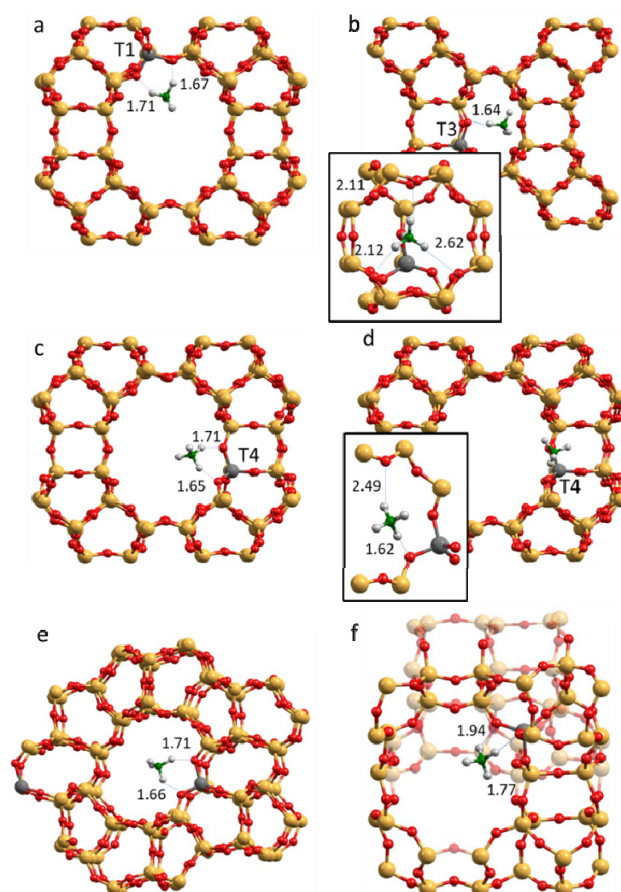


Figure 7. Optimized structures of NH_3 protonated by Brønsted acid sites placed in the main channel (a,c) and side-pockets (b,d) of MOR, and in the straight channel (e) and channels intersection (f) of MFI zeolites.

Table 3. Interaction of NH_3 and Pyridine with Brønsted acid sites placed in the main channels and side-pockets of MOR and in the 10R channels and channels intersections of MFI. Interaction energies E_{int} in kJ/mol.

| molecule | site | location | E_{intDFT} | E_{intD3} | E_{int} |
|---------------|---------|----------|---------------------|--------------------|------------------|
| | | | | | DFT-D3 |
| NH_3 | MOR-T1 | 12R | -127 | -20 | -148 |
| NH_3 | MOR-T3 | 8R | -135 | -34 | -169 |
| NH_3 | MOR-T4a | 12R | -124 | -16 | -140 |
| NH_3 | MOR-T4b | 8R | -124 | -27 | -151 |
| NH_3 | MFI-T1 | int | -114 | -21 | -135 |
| NH_3 | MFI-T11 | 10R | -138 | -17 | -155 |
| Pyridine | MOR-T1 | 12R | -147 | -63 | -210 |
| Pyridine | MOR-T4a | 12R | -143 | -62 | -205 |
| Pyridine | MFI-T1 | int | -142 | -69 | -211 |
| Pyridine | MFI-T11 | 10R | -154 | -68 | -222 |

All Brønsted acid sites in MOR and MFI structures are accessible to NH_3 , which upon interaction with a bridged hydroxyl group is spontaneously protonated forming a Z---NH_4^+ ion-pair. The interaction energies calculated for the process $\text{Z-H} + \text{NH}_3 \rightarrow \text{Z---NH}_4^+$ at pure DFT level are significantly higher than those obtained for CO adsorption, reflecting the much stronger interaction between charged species, while the contribution of dispersion interactions included in the D3 term is in this case less relevant. In all cases, NH_4^+ remains close to the Al atom, forming two strong hydrogen bonds with the two most accessible oxygen atoms directly attached to Al. The optimized H-O distances in the ion-pair complexes in which NH_4^+ is occupying the free space in the straight 12R of MOR or 10R channels in MFI are quite similar, ~ 1.65 and ~ 1.71 Å (Figure 7a, c, e). But the presence of other close oxygen atoms in the pockets of MOR or at the channels intersection in MFI readily distort this geometry. Thus, when NH_3 is protonated at T3 inside the MOR pockets, the NH_4^+ cation is stabilized by one short bond with the oxygen attached to Al and by three weaker hydrogen bonds with the framework oxygen atoms of the 8R (Figure 7b). Moreover, the contribution of dispersion forces in this position is larger than in the main channel, and altogether the calculated interaction energy at T3 is the largest of all values in Table 3. A similar conformation was explored at T4, with NH_3 initially placed within the 8R, but in this case only one extra hydrogen bond was formed to stabilize NH_4^+ (Figure 7d). Finally, the relative orientation of the four oxygen atoms directly bonded to Al in T1 site in MFI (Figure 7e) does not allow the formation of a clear bidentate complex, and consequently the adsorption energy of NH_3 at the channels intersection in MFI is 20 kJ/mol weaker than within the channels. The average of the calculated values for NH_3 chemisorption in MFI are in very good agreement with the experimental data obtained by Lee et al., 145 kJ/mol,⁵⁹ who also reported a higher value for the adsorption energy of NH_3 in MOR, 160 kJ/mol. In this case, the measured data agrees with the adsorption energy calculated at the most stable site in MOR, inside the 8R pockets, but does not reflect the heterogeneity of sites in MOR regarding the stabilization of the Z---NH_4^+ ion-pair.

Protonation of Pyridine according to $\text{Z-H} + \text{Py} \rightarrow \text{Z---Py}^+$ generates a planar Pyridinium cation that can only form mono-dentate adducts with one of the O atoms directly bonded to Al and that, due to the different size and bonding geometry as compared to NH_3 , tends to occupy in all cases the void spaces in the large 12R channels in MOR or at the channels intersections in MFI (Figure 8). Thus, while neutral Py adsorbed parallel to the channels axis in pure siliceous models of MOR and MFI (Figures 2 and 3), once it is protonated stronger hydrogen bonds between the five H atoms attached to C and framework oxygen atoms are formed, which change the orientation of the molecule to maximize such hydrogen bond interactions. As a consequence, only adducts with Py^+ cation perpendicular to the 12R channel axis in MOR and occupying the space at the channels intersections in MFI are obtained. In this situation, both the electrostatic interactions correctly reproduced at the DFT level and the dispersion contributions included in the D3 term are comparable in all adducts (Table 3). The total interaction energies are independent of the zeolite framework and location of Al, and are in excellent agreement with the experimental values reported for Pyridine adsorption in H-ZSM-5 and H-MOR, 200 kJ/mol.⁵⁹

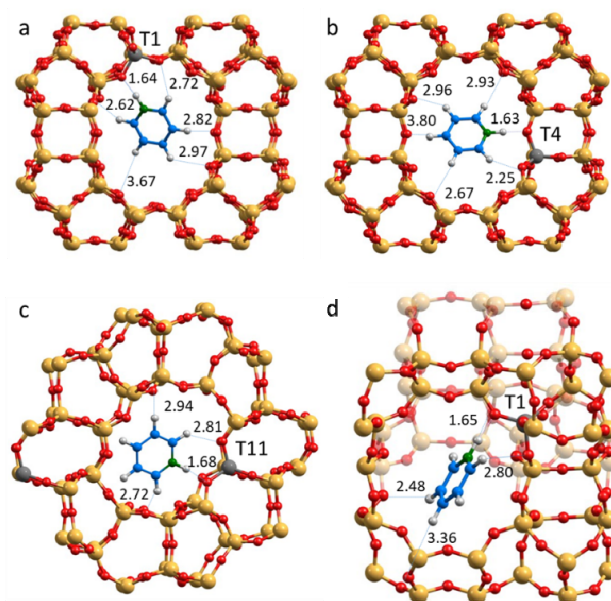


Figure 8. Optimized structures of Pyridinium cation formed by protonation of Pyridine by Brønsted acid sites placed in the main channel of MOR (a,b) and in the straight channel (c) and channels intersection (d) of MFI zeolites,

In summary, while it is accepted today that the intrinsic acidity of bridged hydroxyl groups in high Si/Al ratio zeolites determined by their deprotonation energy is independent of zeolite structure or site location within the framework, a more complex situation is found when acidity is measured by means of adsorption of probe molecules. Weak bases interacting with Brønsted acid sites form neutral ZH---B adducts whose preferred geometry can be distorted by spatial restrictions associated to the pore dimensions and to the relative orientation of the adduct within the microporous structure. On the other hand, and depending on the location of the Brønsted acid sites within the microporous system, i.e. in channels, cavities or pockets, a larger stabilization by dispersion forces can be obtained when there is a tight fitting of the probe molecule with the confining void. Strong bases interacting with Brønsted acid sites become protonated, and the adsorption enthalpies obtained with calorimetric or TPD techniques go beyond the thermochemistry of the proton transfer process and, therefore, beyond the measurement of “acidity”, because they also include the stabilization of the Z---BH^+ ion-pair formed upon protonation by multiple interactions with the surrounding framework oxygen atoms. Therefore, unless all these factors are uncoupled, the conventional methods based on adsorption of probe molecules cannot determine the intrinsic acidity of the acid sites of zeolites. Nevertheless, since different probe molecules form adducts whose size, geometry and location within the confining voids results in different destabilizing constraints and stabilizing dispersion interactions, the use of series of probe molecules can still be informative. Indeed, by combining theoretical results as exemplified here with adequate adsorption experiments, it should be possible, with a structurally known zeolite, to determine the degree of heterogeneity of the acid sites present depending on the synthesis or post-

synthesis conditions. Finally, if the zeolite is to be applied in a particular reaction, the combination of the theoretical work outlined before with adsorption and kinetic studies should give information about the acid sites interacting, their geometries and energetic implications, and about where to locate the acid sites within the zeolite structure to maximize activity and selectivity.

Computational Details. All calculations are based on periodic density functional theory (DFT) and were performed using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within the generalized gradient approach (GGA)^{60,61} as implemented in the Vienna Ab-initio Simulation Package (VASP) code.⁶² The valence density was expanded in a plane wave basis set with a kinetic energy cutoff of 500 eV, and the effect of the core electrons in the valence density was taken into account by means of the projected augmented wave (PAW) formalism.⁶³ Integration in the reciprocal space was carried out at the Γ k-point of the Brillouin zone. During geometry minimizations, the positions of all atoms in the systems were fully relaxed without any restriction. Dispersion corrections to the energies were evaluated using the D3 Grimme's method.^{46,47}

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Notes

The authors declare no competing financial interest.

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What is measured when measuring acidity in zeolites with probe molecules?

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