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Surface acidity and basicity: General concepts

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Abstract

A very general definition of acids and basis, following both Brønsted and Lewis theories, is the starting point to introduce the concept of the acid and basic strength of surface sites. The surface of an oxide is described as a bidimensional organization of acid–base pair (AB), whose strength can be measured by probe molecules. It is shown that in order to obtain a reasonable scale of surface acidity and basicity, probe molecules characterized by minimal interaction energy must be used. Among the probe molecules, which can be employed to measure surface acidity, carbon monoxide is the most useful. On the contrary, a probe molecule specific and highly sensitive for basic sites is missing. As case studies, Lewis and Brønsted sites on ZnO and Brønsted acid groups of zeolites are discussed. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Surface acidity; Surface basicity; Probe molecules

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1. Acid and bases in homogeneous phases

1.1. Definitions and methodology problems

Two acid–base theories are utilized today [1]: the Brønsted theory and the Lewis theory. Following the first theory, an acid–base reaction is simply the transfer of a proton from an acid (A_1H) to the base (B)

$$\underset{\text{acid 1}}{\mathrm{AH}} + \mathrm{B} \leftrightarrow \mathrm{A} + \underset{\text{acid 2}}{\mathrm{BH}} \quad K_{\mathrm{a}} \tag{1}$$

Acid strength may be defined as the tendency to give up a proton and *base strength* as the tendency to accept a proton: these definitions have only qualitative character. However, by measuring the position of the equilibrium ($\mathrm{p}K_{\mathrm{a}}$) in water solution or in gas phase, the relative strength of acid 1 and acid 2 can be determined quantitatively so conferring to the concepts of acid and base strength a real physical meaning. In this manner it is possible to construct a table in which acids are listed in order of acid strength. The $\mathrm{p}K_{\mathrm{a}}$ of the various acids is usually reported with respect to water. In the gas phase, [2] where solvation effects are absent, the acidity order can be greatly different. If the bond in HA is fully ionic, Eq. (1) can be formally modified as follows:

$$\mathrm{H}^+ + \mathrm{B} \leftrightarrow \mathrm{BH}^+ \quad (K_{\mathrm{BH}^+}) \tag{1a}$$

If $\mathrm{p}K_{\mathrm{BH}^+}$ is the dissociation constant of BH^+, then

$$\mathrm{p}K_{\mathrm{BH}^+} = \log[a_{\mathrm{BH}^+}/a_{\mathrm{H}^+}\cdot a_{\mathrm{B}}]. \tag{1b}$$

$$\begin{aligned} -\log a_{\mathrm{H}^+} &= \mathrm{p}K_{\mathrm{BH}^+} - \log[a_{\mathrm{BH}^+}/a_{\mathrm{B}}] \\ &= \mathrm{p}K_{\mathrm{BH}^+} - \log[\mathrm{BH}^+]/[\mathrm{B}] - \log f_{\mathrm{BH}^+}/f_{\mathrm{B}}. \end{aligned}$$

From this

$$H_{\mathrm{o}} = -\log a_{\mathrm{H}^+}(f_{\mathrm{B}}/f_{\mathrm{BH}^+}) = \mathrm{p}K_{\mathrm{BH}^+} - \log[\mathrm{BH}^+]/[\mathrm{B}], \tag{1c}$$

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where H_o is the *Hammet acidity function,* [3] which is analogous to pH. In fact in dilute solutions, the activity coefficients become 1 and consequently H_o=pH. The Hammet acidity function is used *in concentrated solutions*, where the pH concept is no longer applicable. In practice when a concentrated acid is involved, the Hammet function is determined by measuring the extent to which an *indicator* (usually a weak or very weak base B) is protonated. The ratio $[BH^+]/[B]$ is usually measured by means of spectroscopic methods (normally UV–vis spectroscopy). To even further simplify the concept, we can say that the method consists in the determination of the weakest base which can be protonated to a significative extent by the concentrated acid. In the Hammet approach the anion A^- formed from the acid HA molecule does not enter explicitly and the acid is considered as a continuum which protonates the probe base without being significantly disturbed or altered by the latter. As we shall briefly discuss in the following, this means that the factors which are favouring the stability of A^- (and hence indirectly of BH^+) are not considered at all, although we know that acidity is greatly influenced by the anion stabilization (often favoured by hydrogen bonding with other acid molecules of the concentrated medium or with the solvent: vide infra). This is a negative aspect of the Hammet approach which limits its extension to heterogeneous systems.

Following the Lewis theory an acid is any species with a vacant orbital and an acid–base reaction

$$A + B \rightarrow A\text{–}B \qquad (2)$$

is a reaction where the unshared pair of the base B forms a (covalent) bond with the vacant orbital of the acid A. In the Brønsted picture the proton itself is the acid since it has a vacant orbital. The Lewis acid–base theory is more general than the Brønsted theory, because it correlates the behaviour of many more processes. The *Lewis acid strength* concept has been also quantified: however fewer quantitative measurements of acid strength are available compared to that of the Brønsted acids. A simple table of Lewis acidity (for instance corresponding to the pK_a table relative to water) is, however, not feasible because Lewis acidity *depends upon the nature of the base*. Another type of common acid–base reaction which can be described in the framework of the Lewis theory is

$$A\text{–}B + A'\text{–}B' \rightarrow A\text{–}B' + A'\text{–}B \qquad (3)$$

because covalent bonds are formed through one species contributing a filled and the other a vacant orbital (and vice versa).

1.2. The effect of structure on the strength of acids and bases

After having briefly discussed how the acidity and basicity can be quantified, it is worth to spend the minimum number of words in recalling the main factors affecting the acid and basic strength of molecules.

If we compare *the Lewis acid strength* of molecules of the form MX_n the following empirical rules can be extracted: (i) all other things being equal, the acidity of MX_n decreases with the increase of the M radius (because the attraction between the positive nucleus M and the incoming electron pair is decreasing); (ii) all other things remaining equal, the acidity increases with the increase of electronegative character of X; (iii) the maximum acidity is found for the compounds where the n is minimum.

If we limit ourselves to *the Lewis basic strength* of oxygen bases OM_2, the following can be kept in mind: (i) the basicity of O increases with the increase of the electron donating character of M; (ii) when M is a metallic element, the basicity at O increases with the increase of the electropositive character of M (and with the ionic radius as well).

As far as the *acid strength of the Brønsted acid HA* is concerned, it is widely accepted that: (i) the acid strength increases with the increase of the electron withdrawing character of A; (ii) the acid strength increases with the increase of stability of A^- (favoured by hydrogen bonding interactions with the solvent or with other acid molecules); (iii) the acid strength increases with the ability of A^- (conjugated base) to spread the negative charge over the whole moiety. Big size anions (A^-) containing electronegative atoms or anions (A^-) stabilized by resonance, can spread and delocalize efficiently the negative charge: hence they have very small basic character and consequently their conjugated acids, HA, are very strong. Point (i) is well illustrated by the greater acid strength of FSO_3H and CF_3SO_3H with respect to H_2SO_4 [4]; Point (ii) is documented by the FSO_3H–SbF_5 superacid, where the acidity of FSO_3H is exalted by the interaction with the strong SbF_5 Lewis acid which stabilize the FSO_3^- anion through the formation of the FSO_3^-–SbF_5 adduct [4]. Point (iii) is illustrated by the greater acidity of $H(SbF_6)$ ($HF{\cdot}SbF_5$) with respect to HF, because the size of the SbF_6^- anion is larger than that of F^- [4]. Effects (ii) and (iii) cannot always be distinguished.

2. Acid and bases at the surface of oxidic systems

The surface of fully dehydroxylated ionic oxides can be considered as a spatially organized distribution of coordinatively unsaturated positively (cations) and negatively (oxides) charged centres. The coordinative unsaturation of the individual centres of this distribution depend upon the type (index) of exposed faces, which in turn is determined by the morphology of the microcrystals [5,6]. On the contrary, the effective charge carried by each surface centre depends primarily upon a bulk property, i.e. the ionicity of the oxide under consideration. The position of the surface cations and anions in vacuo in not simply that deduced on the basis of the crystallographic position occupied in the bulk: in fact any oxide surface is more or less appreciably relaxed, in vacuo, in order to minimize the surface energy. This means that the cations tend to undergo an inward relaxation, while the anions do the opposite [7,8]. This effect, always accompanied by an increase of surface covalency, is small for neutral faces of rock-salt or corundum type structures, both constituted by positive and negative arrays of five coordinated ions (as for instance Mg^{2+} and O^{2-} ions on the (1 0 0) face of MgO or Al^{3+} and O^{2-} of the prismatic (1120) face of α-Al_2O_3 but can be remarkable in many other cases where lower coordinated ions are involved) and is causing a rumpling of the surface and can even lead to reconstruction [7,8]. The relaxation or reconstruction of a surface is a clear example of a *collective* phenomenon, where all involved surface ions modify their position in a concerted way in order to minimize the surface energy. Whatever the extent of the effect of surface relaxation, the positive and the negative centres can behave as Lewis acid (A) and Lewis bases (B): it is so evident that the faces of ionic oxides are regions constituted by bidimensional and ordered arrays of ...ABABAB... acid–base centres where complex acid–base reactions can occur (alternatively they could be described as a bidimensional organization of AB acid–base pairs: $(AB)_n$). Moreover, highly unsaturated positive and negative ions located in edge and corner positions (together with their nearest A, B neighbours located on the intersecting planes forming the edges and the corners) beside being certainly strongly relaxed, can show enhanced Lewis activity and be preferential sites for specific catalytic reactions [5–8].

So far we have spoken of fully dehydrated surfaces where only Lewis acid and Lewis base centres of variable strength are present and whose reactivity can be understood in the frame of the Lewis theory of acid and bases.

However, fully dehydroxylated surfaces are quite exceptional: in fact in the reality oxide surfaces are variably covered by hydroxyl groups. These groups being potential proton donors or acceptors, it is evident that Brønsted acidity and basicity must also be considered as well. Of course Lewis and Brønsted groups are often simultaneously present on the same surfaces where they form densely populated patches: consequently the formulation of a comprehensive ab initio theory of the acid–base properties of the oxide surfaces is practically impossible. In particular, the extension to surfaces of the quantitative concepts outlined for homogeneous phases is extremely problematic. Finally, let us mention that high surface acidity (either of the Lewis or of the Brønsted type) can be induced at the surface of oxides through the introduction of foreign impurities (like for instance sulphates) or by substituting a fraction of atoms.

3. How to probe the surface acid–base properties

3.1. Introductive considerations

The quantitative concepts of acid–base strength outlined in Section 1 are based on the measurement of the equilibrium conditions in acid–base reactions where the reactants are *individual molecules immersed in a homogeneous medium*. This method requires the measurement of the equilibrium concentration (diluted solutions) or activities (concentrated solutions) of the reactants. It cannot be readily extended to surfaces for two obvious reasons: (i) because of the presence of two phases, (ii) because the acid and basic species constituting the surface array (but the same holds for the AB building units) cannot be treated *as separated species*. In other words it is not possible to carry out surface reactions of the Lewis acid–base type

$$\mathrm{A'} + \ldots\mathrm{ABABABA}\ldots \rightarrow \ldots\mathrm{ABA}\overset{\mathrm{A'}}{\mathrm{B}}\mathrm{ABA}\ldots \qquad (4a)$$

$$\mathrm{B'} + \ldots\mathrm{ABABABA}\ldots \rightarrow \ldots\mathrm{AB}\overset{\mathrm{B'}}{\mathrm{A}}\mathrm{BABA}\ldots \qquad (4b)$$

$$\mathrm{A'{-}B'} + \ldots\mathrm{ABABAB}\ldots \rightarrow \ldots\mathrm{ABA}\overset{\mathrm{A'B'}}{\mathrm{B}}\mathrm{ABA}\ldots \qquad (4c)$$

involving only single surface sites (A, B, AB) by using probe molecules with predominant basic (B′), acid (A′) or dual character (A′B′), respectively, without significantly perturbing all the others (it is worth noticing that this limitation is less important for isolated acid groups embedded in a matrix). In fact any adsorption (coordinative) event at a given site is invariably accompanied not only by the formation of new bonds but also by a modification of the surface relaxation around the adsorption site. In other words the adsorption process modifies the structure of the surface. The extent of this very complex effect (usually named lateral interaction and dying away in a few lattice spacings) depends upon the energy involved in the adsorption event.

While the first obstacle (i) cannot be removed, the second (ii) can be partially surmounted if the probing process fulfils the following conditions:

(a) the probe molecule must be chosen among those showing minimal interaction energy with the surface (and consequently the smallest perturbative effect of the surface structure);

(b) the probing process must involve only a minimum fraction of the surface sites ($\theta\rightarrow 0$, θ being the surface coverage: $0\leq\theta\leq 1$) in order to keep the lateral interactions at the minimum level.

Conditions (a) and (b) must be fulfilled as much as possible if the probing process is intended to give indications on the state of the surface in vacuo, i.e. before the perturbation induced by the probing process.

3.2. *The acidity scale of surface Lewis and Brønsted sites: Problems and proposals*

3.2.1. *Lewis sites*

Following the lines suggested by the previous consideration, it appears that the Lewis acid strength of the surface structures (A) present on the surface of an oxide can be correctly explored only with the help of a *very weakly basic molecule* which is only very weakly adsorbed on Lewis centres. It will be shown that such a molecule is CO, because: (i) it is always adsorbed in end-on (through the carbon) form at the cationic sites; (ii) because its stretching frequency is perturbed in a very specific manner by the electric field at the positive centre [9] and (iii) because the adsorption process is not heavily modifying the surface relaxation. Indeed CO invariably interacts with cationic centres through the 5σ doublet centred at the carbon and the frequency ν of ν(CO) depends upon the electric field strength E sensed at the charged centre following the simple relation $\nu\propto E$ [9]:

$$\mathrm{A}^{(+)}\underset{\underset{(E)}{\longrightarrow}}{\cdots}\mathrm{C{-}O}$$

The $\nu\propto E$ relation is the basis of the spectroscopic scale of surface acidity based on the CO probe. Of course, as this scale suffers from the limitation discussed in point (i) of Section 3.1, it cannot be considered as an absolute scale. Any other physical property simply correlated to the strength of the perturbation induced by the interaction with the surface can be used as well to construct an acidity scale. For instance it has been shown [10] that the adsorption enthalpy of CO increases with the polarizing power of the cation: consequently the adsorption enthalpy can be used as well to establish a *calorimetric scale of surface acidity* (for more details see the contribution of Solinas and Ferino: Catal. Today, this issue).

The CO adducts cannot, in general, be classified as true (inner sphere) Lewis adducts (for instance of the type A: CO), because their formation is not accompanied by full transfer of an electron pair from the molecule to the surface: in this sense they are more similar to outer sphere adducts (following the Mulliken definition). Notwithstanding this difficulty, the obtained *experimental* information is often sufficient to illustrate either the properties determined primarily by the structure of the individual positive sites (for

$\Theta_{CO} \rightarrow 0$) and those determined by their spatial organization (for $\Theta_{CO} \rightarrow 0$). The second information can also be of great interest since, in many surface reactions, positive and negative centres participate simultaneously in the catalytic process.

Another interesting molecule which can be used to test the acid strength of acid sites through the formation of weakly bonded linear adducts is H_2. In fact, like described for CO, the interaction of the dihydrogen molecules with *isolated* cations or positive centres can give, in principle, stable σ-type complexes essentially stabilized by electrostatic forces [11]. Polarization of the single bond and very weak σ-donation from the σ_g orbital are the consequence of this interaction, both causing a decrease of the bond order and of the stretching frequency. Also in this case, the induced shift $\Delta\nu$(HH) (negative) could be used to evaluate the strength of the perturbation and hence to construct an acidity scale (although a linear relation between the shift $\Delta\nu$(HH) of the stretching frequency and the electric field E is not so well documented as for CO). Moreover, unlike CO, the dihydrogen molecule has only one single σ-bond, the effect induced on the force constant, stretching frequency and bond order is (in relative terms) higher than that induced on CO. Due to the small energy involved in the probing process, both molecules fulfil the requirement (a) of Section 3.1.

The A centres can also be probed by means of a variety of other probe molecules (B′), with stronger Lewis base character, through the formation of surface AB′ surface species (following reaction (2)). Py, with its electron pair at the nitrogen atom, is one of these molecules (but also acetonitrile should be mentioned). Indeed, when the Py is allowed to contact a surface containing coordinatively unsaturated cations, Lewis adducts are invariably formed whose number equals that of the adsorbing centres. The Py–A bond is quite strong and the perturbation induced on the surface structures so important that the surface vibrational modes of the surface centres (different from those of the bulk because of relaxation) are irreversibly perturbed. Due to the strong basic character of Py, practically all the acid centres of the surface (whatever their acid strength) react with Py: this means that the Py probe does not discriminate between sites of slightly different acidity. Moreover (unlike CO and H_2) the vibrational properties of these adducts do not depend selectively enough upon the acid strength of the adsorbing centres (this happens at all the times the interaction energy is large) to allow a use similar to that of CO and H_2. In other words Py does not completely fulfil the conditions required for being an innocent probe: it is consequently more useful as titrant of the number of surface centres than to establish a sensitive spectroscopic scale of Lewis acidity.

3.2.2. *Brønsted sites*

The use of CO and H_2 as surface probes retains its validity also for hydroxylated surfaces. In fact acidic OH groups form very weak *hydrogen bonded adducts* with both CO and H_2 probes and the shift of the stretching frequency induced by the perturbation is proportional to the charge present on the hydrogen (and hence indirectly upon its Brønsted acidity) [12,13]. On the contrary, basic OH do not show any tendency to interact with CO and H_2. This allows to extend the application of the $\Delta\nu \propto E$ relation to the construction of a general spectroscopic scale of the acid strength valid for both Lewis and Brønsted acids. In the Brønsted adducts

$$AH \cdots CO$$

not only the ν(CO) mode is perturbed by the electrostatic interaction with the positively charged hydrogen atom, but also the ν(AH) stretching undergoes a shift to lower frequency, indicating how the formation of the hydrogen bonded adduct is perturbing the adsorbing centre. The same is found when the $AH \cdots H_2$ adducts are considered. The negative shift of the ν(AH) mode observed in the CO adduct is (in absolute terms) about 10 times the positive shift of the corresponding ν(CO) mode. Moreover, as the two shifts are roughly proportional: it is so suggested that, when AH Brønsted groups are involved, the shift $\Delta\nu$ of the ν(AH) mode can be also used to construct a sensitive scale of Brønsted acidity.

In many publications, the acidity of surface Brønsted acid sites on oxide surfaces (for instance zirconia containing sulphate groups, which is considered to have superacidic character), is often defined in terms of the Hammet acidity function, by using weak or very weak bases as indicators. However, for all the reasons outlined in the previous sections, the extension of the Hammet approach to solid surfaces (where, for instance the interaction of BH^+ with A^- surface ions is intrinsically different from that encountered in solution) is highly debatable: consequently the figures appearing in the literature for some acid species commonly encountered on solid surfaces, must be considered with great caution. I shall illustrate this problem in one of the case studies.

All acid Brønsted groups characterized by an acid strength larger than a minimum value (in terms of proton affinity, lower than that of silanols, which are the most common weak acid groups of siliceous surfaces) can be selectively titrated with Py with formation of PyH^+. The associated process can be easily followed by IR spectroscopy, because PyH^+ has a vibrational spectrum which can be easily distinguished from that of the Py-Lewis acid adducts [14].

3.3. *A basicity scale for surface* O^{2-} *sites: Problems and proposals*

Always following the considerations outlined before, a probe molecule specific for the basic (O^{2-}) sites should also be searched. This molecule must have prevailing acid character. To my knowledge a weak Lewis probe with such character has never been found and extensively experimented (BF_3 has been proposed: but a sufficient experimental evidence is lacking). The acid CO_2 molecule has also been proposed: however its utilization suffers from the same limitations outlined for Py because, due to its high acidic character, it forms stable adducts with a large variety of surface O^{2-} sites characterized by basic strengths comprised in a large interval: consequently it does not possess the ability to discriminate sites of slightly different basicity.

In the absence of reversible and handy aprotic probes, weak protic acids can be proposed instead. In order to discriminate between sites of slightly different basicity (which is the ultimate scope when a precise basicity scale is needed), a series of probe molecules with very weak to weak Brønsted acid strength (B′H) should be used: the expected result of this interaction is the selective protonation of the B (O^{2-}) site with appropriate basicity, with formation of $(OH)^-$ groups, following the scheme

$$B'H + \ldots ABABAB \ldots \rightarrow \ldots AB\overset{B'H}{A}BAB \ldots \qquad (5)$$

This reaction, although guided primarily by the protonation step and hence by the basic character of B, is, strictly speaking, of type (3) and necessarily involves the participation of AB pairs. To this scope a variety of acidic molecules with acid strength comprised in large interval have to be used: among all we mention in order of acid strength: ethene, propene, acetylene, alkylacetylenes, etc. By observing the behaviour of the basic sites upon the interaction with a series of probes of increasing acid strength, the basic strength of surface sites can be classified in terms of the minimum acid strength which must be possessed by the probing molecule in order to give reaction (5)). In this way it is possible, in principle, to construct a qualitative basicity scale not having spectroscopic character. Of course, as any oxide surface can possess families of basic sites of different strength (for instance located on different faces or at defects), their full classification in terms of the protic molecules which have just enough acid strength to protonate only one of them (and of course the stronger ones) can be very laborious. Of course, any basicity scale derived with this method suffers from all ambiguities derived from the choice of the proper acid strength (solution or gas-phase) adopted for the titrating acids. To our knowledge this classification of the basic sites has never been attempted systematically for oxides, even if there is probably a sufficient quantity of data in the current literature which could be organized in order to allow such an attempt.

When highly basic O^{2-} surface species on ionic oxide surfaces are involved, hydrogen can also behave as a very weak protic acid and hence be very informative about the basic strength of these sites. The behaviour of H_2 is not surprising since it can be considered as the simplest protic acid. An even weaker probe which can be proposed for superbasic structures is CH_4.

4. Case studies

To check the validity of the concepts outlined in the previous sections, a few case studies will be briefly illustrated in the following.

4.1. *Lewis acid sites at the* ZnO *surface*

The morphology of ZnO microcrystals obtained by combustion of Zn (Kadox) [7,16] are represented in

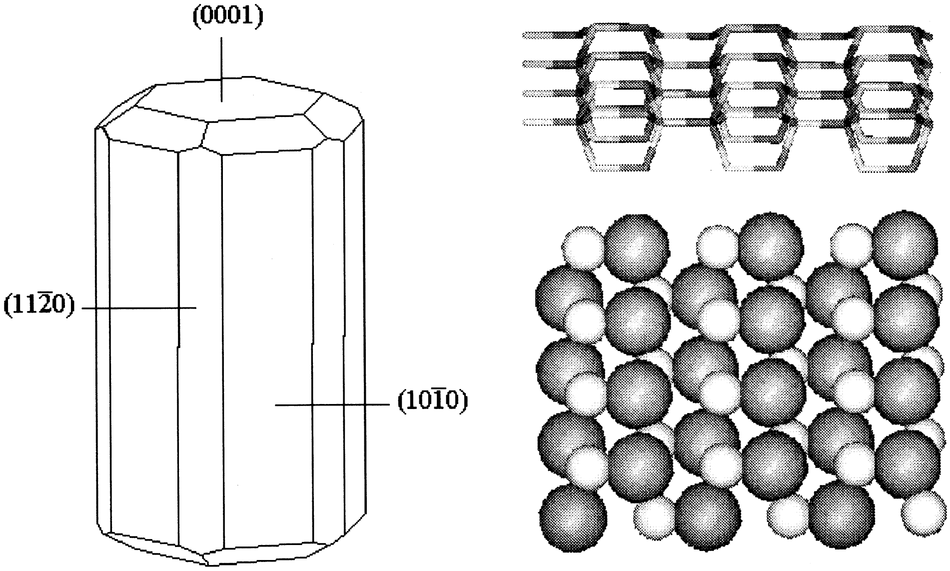
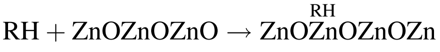


Fig. 1. Polyhedron with the indexed faces mimicking the shape of the ZnO particles and the arrangement of Zn^{2+} (white balls) and O^{2-} (grey balls) species on one of the most commonly exposed $(10\bar{1}0)$ face.

Fig. 1. In the same figure the structure at the atomic level of the most commonly exposed $(10\bar{1}0)$ face is reported. In the following we shall limit our considerations to this face, because it is very well studied (the reactivity of edges and corner sites will not be considered in detail, also because these sites cannot be "cleaned" from adsorbed hydroxyls at reasonable temperatures).

Due to the tetrahedral coordination of Zn and O in the bulk, the $(10\bar{1}0)$ face exposes 3-fold coordinated Zn and oxygen ions which form potential Lewis acid–base pairs. In agreement with the tetrahedral structure, the ionicity of the ZnO crystal is smaller than that of MgO and on the basis of the accepted ionicity values the charge on the Zn and oxygen sites is estimated to be more near to $+1$ and -1 than to $+2$ and -2, respectively. The surface cations (Lewis acids) form with CO, reversible end-on adducts already at RT. If a purely electrostatic interaction is assumed, the electric field centred at the 3-fold coordinated Zn sites can be estimated (on the basis of usual $\Delta\nu \propto E$ relation of the CO stretching [9]) to be only slightly lower than that measured for Mg^{2+}_{3c} sites on corner positions of MgO microcrystals [15]. This result is in rough agreement with the more screened position and lower effective charge of Zn^{2+} ions on the $(10\bar{1}0)$ face. However, there is a definite problem here: in fact a purely electrostatic interaction cannot explain the superior stability of the $Zn^{2+}_{3c}\cdots CO$ adducts with respect to the analogous $Mg^{2+}_{3c}\cdots CO$ [15]. Moreover, UPS results show definitely that a genuine σ-bond has been formed. The activity of surface oxygen ions in abstracting the proton from weak and very weak protic acids is also similar to that found for the oxygen sites on the corners of MgO cubelets [15]: in fact it readily interacts with hydrogen and propene following the scheme (charges omitted):



$$RH + ZnOZnOZnO \rightarrow ZnO\overset{RH}{Zn}OZnOZn$$

$$(R = H,\ C_3H_5)$$

In conclusion: the interaction with CO and H_2/propene proves that on the surface of ZnO Lewis acid–Lewis base pairs are present and that coordination state is playing a very decisive role in determining the acid and basic properties of positive and negative sites at the surface of oxides.

4.2. Brønsted acid groups in zeolites

For the sake of simplicity we shall use the H-ZSM5 zeolite as case study. The local structure of the zeolite

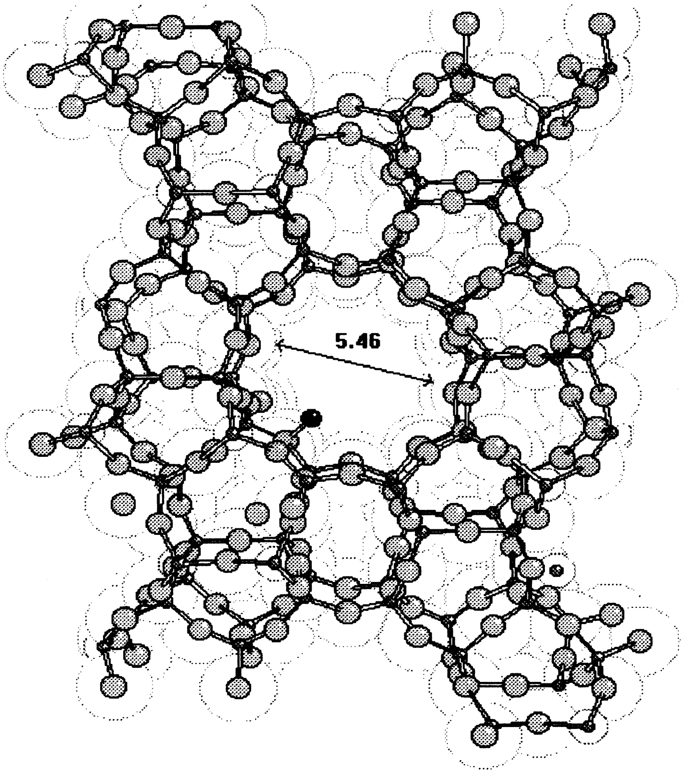
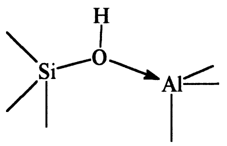


Fig. 2. Schematic representation of a portion of zeolitic framework (MFI view along the [0 1 0] direction) showing a Brønsted group protruding in the zeolite channel. The zeolitic atoms are represented by grey balls, while the proton is reported in black. Dotted spheres show the framework atom hindrance.

channel where the Brønsted group is located, is shown in Fig. 2.

The Brønsted group itself (ν(OH)=3610 cm^{-1}) can be seen as a silanol group whose acidity is enhanced by the interaction with a strong Lewis centre (Al^{3+}) following one of the general rules already illustrated in one the previous sections.



When probed with CO, the bridged OH groups show a distinct propensity to form OH$\cdots$CO hydrogen bonded adducts which are characterized by a ν(CO) at 2171 cm^{-1} ($\Delta\nu$: +33 cm^{-1}) and by a ν(OH) at about 3275 cm^{-1} ($\Delta\nu$: ~350 cm^{-1}) [12]. These figures are among the highest ones observed for all zeolitic structures: this allows us to conclude that H-ZSM5 is one of the most acidic zeolitic structures synthesized so far, in agreement with its well-known catalytic properties. Similar results are obtained when the Brønsted groups are probed with other extremely weak bases like H_2 or N_2. I am not aware of parallel calorimetric investigation on the formation of these adducts. When probed with the strong Py base, PyH$^+$ is readily formed as well documented by its characteristic IR spectrum. Unfortunately PyH$^+$ is also invariably formed when Py is used to test the Brønsted acidity of many other different zeolites [14] like HX and HY which are known (when probed with CO, H_2 and N_2) to have definitely lower acid strength: this shows once again that Py can be better used to count the number of protic sites than to establish an acidity scale. The Hammet approach has been extensively applied to establish the relative strength of the acid sites present in the channels of the various zeolites. To this scope the interaction of very weak indicators like 4-nitrotoluene and 4-nitrofluorobenzene with various zeolites has been studied spectroscopically [17]. For the reasons outlined in Section 1, the published figures must be considered with some caution. To illustrate this point let us simply recall that zeolites containing acid AH groups *of the same strength* can show different propensity to react with the same indicator B. In fact, depending upon the dimension of the channel where the Brønsted group is located and upon the negative charge carried by the framework, the BH^+ is more or less stabilized by the interaction with the channel walls, and hence the equilibrium is more or less shifted to the right. This is plausibly the reason differentiating H-ZSM5 from H-MORD, which contain nearly the identical Si(OH)Al structures. In other words, the effective acidity does not depend only upon the chemical properties of the Brønsted acid centre but also upon the supramolecular organization of the zeolite. For several acidic zeolites it has been shown that, in absence of proton transfer, a linear correlation exists between $\Delta\nu$(OH) of internal Brønsted sites and $\Delta\nu$(OH) of external silanols [18–20]. The slope of this line can be used to establish a spectroscopic scale of Brønsted acidity for protonic zeolites: H-X<H-Y<H-MORD≈H-β≈H-ZSM5.

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