

The Acidity of Solid Surfaces and its Determination by Amine Titration and Adsorption of Coloured Indicators

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1 Introduction

Many reactions of both theoretical and practical interest occur on the surface of solid catalysts, and in a considerable number of cases it is the acidic nature of the surface which determines the course of the reaction. Silica-aluminas and, more recently, zeolites with their acidic surfaces play a very important catalytic role in industrial processes, in particular in the petroleum industry. The most useful reactions catalysed by these acidic aluminosilicates, especially zeolites, which by virtue of their crystallinity show a markedly higher catalytic activity, are the catalytic cracking of oils, isomerization of normal alkanes, and also in reforming reactions to yield high-octane gasoline.

For this reason, the dependence of the catalytic properties of solid surfaces, such as silica-aluminas and zeolites, on the presence of acidic centres has been extensively reviewed.¹⁻⁶ The many investigations over the past thirty years have shown that chemical evaluation of surfaces is fundamental in changing the art of catalysis into a science. In describing the acidic nature of a surface it is necessary to take into account the nature of the acid sites (Brønsted or Lewis), their strength, their concentration, their distribution, their location, and their mobility. Several recent reviews on the proposed models for acidity in silica-aluminas⁷ and in zeolites⁸ have been published.

Firstly, the various aspects of the nature of acidity in aluminosilicates, especially zeolites, are summarized. A review of the indicator adsorption method in conjunction with amine titration is then presented together with valuable information in the field of catalysis that has been obtained by its use.

2 Acid Centres on Aluminosilicate Surfaces

Pure silica possesses terminal surface hydroxy-groups, but these are non-acidic,

¹ P. B. Venuto and P. S. Landis, *Adv. Catal.*, 1968, **18**, 259.

² J. A. Rabo and M. L. Poutsma, in 'Molecular Sieve Zeolites II' (Adv. Chem. Ser. No. 102) 1971, p. 284.

³ M. W. Tamele, *Discuss. Faraday Soc.*, 1950, **8**, 270.

⁴ J. Turkevich, *Catal. Rev.*, 1968, **1**, 1.

⁵ P. A. Jacobs, 'Carboniogenic Activity of Zeolites', Elsevier, Amsterdam, 1977.

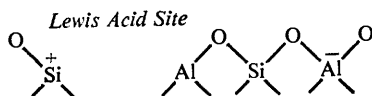
⁶ H. A. Benesi and B. H. C. Winquist, *Adv. Catal.*, 1978, **27**, 97

⁷ J. E. Mapes and R. P. Eischens, *J. Phys. Chem.*, 1954, **58**, 1059.

⁸ D. Barthomeuf in 'Molecular Sieves II', ed. J. R. Katzer, American Chemical Society, Washington, 1977, p. 453.

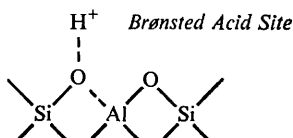
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and this surface is catalytically unimportant. Pure alumina also exhibits non-acidic hydroxy-groups when hydrated. Upon dehydration, exposed aluminium atoms are formed.^{9,10} These exposed atoms, not being fully co-ordinated to surrounding aluminium atoms, are able to receive electron pairs and so are designated as Lewis acid sites, a Lewis acid being defined as an electron pair acceptor (Scheme 1).



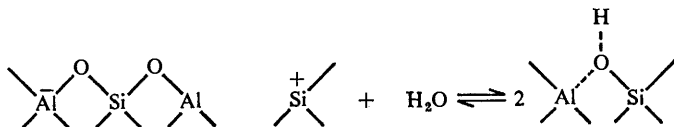
Scheme 1

On the other hand when an aluminosilicate gel, obtained by the coprecipitation of alumina and silica, is dehydrated, the protons of the surface —OH group are found to be acidic in nature, and may react readily with basic substances. These protonic sites are known as Brønsted acid sites, a Brønsted acid being defined as a proton donor (Scheme 2). The Brønsted acid sites formed on de-



Scheme 2

hydrating silica-aluminas may be converted into Lewis acid sites by heating the silica-alumina to over 500 °C, owing to the loss of surface hydroxy-groups and the formation of exposed aluminium atoms. On rehydration, Lewis acid sites may be converted into Brønsted acid sites, OH groups being formed as the surface becomes hydrated (Scheme 3).



Scheme 3

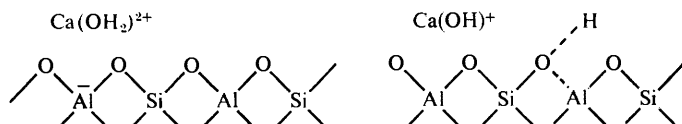
Lewis and Brønsted acid sites may be formed in a similar way in the crystalline aluminosilicates—the catalytically important zeolites.

In zeolites the presence of tetrahedrally co-ordinated aluminium atoms in a

⁹ J. B. Peri and R. B. Hanna, *J. Phys. Chem.*, 1960, **64**, 1526.

¹⁰ J. B. Peri, *J. Phys. Chem.*, 1965, **69**, 220.

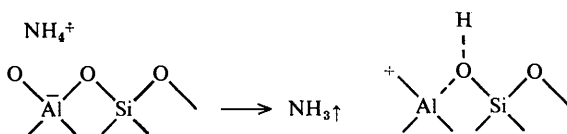
three-dimensional framework results in a negative charge on the lattice. Neutralization of this charge is achieved by exchangeable cations at structural sites within the zeolite channels. The cations in a zeolite, particularly bi- and ter-valent cations, are instrumental in developing acidity in a zeolite; the electrostatic field is increased if multivalent cations are present, owing to the wider charge separation. The result is to polarize existing surface hydroxy-groups, rendering them more acidic.¹¹ Further, during thermal treatment the field strength of the cation polarizes the solvation shell surrounding the cation, resulting in the formation of hydroxy-cations and the attachment of a proton to a lattice oxygen to form acidic structural hydroxy-groups (Scheme 4).^{12,13}



Scheme 4

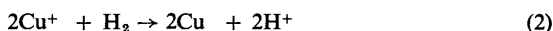
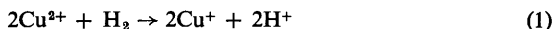
The efficiency of this process and the acid strength of the resultant Brønsted acid site is the greater the larger the polarizing power of the cation. Thus alkali-metal cation forms show little to negligible acidity compared with alkaline-earth or rare-earth cation forms.

An important method for the production of Brønsted acid sites is deammoniation of an ammonium-exchanged zeolite. This results in what is termed a hydrogen zeolite (Scheme 5).



Scheme 5

Brønsted acidity can also be produced in transition-metal cation forms such as Pt^{2+} , Ni^{2+} , and Cu^{2+} by reduction to the metal in the presence of hydrogen or hydrocarbons,^{8,14} e.g. equations (1) and (2).



¹¹ P. E. Pickert, J. A. Rabo, E. Dempsey, and V. Schomaker, in 'Proceedings of 3rd International Congress on Catalysis, Amsterdam, 1964', North Holland, Amsterdam, 1965 p. 714.

¹² A. E. Hirschler, *J. Catal.*, 1963, 2, 428.

¹³ L. Bertsch and H. W. Habgood, *J. Phys. Chem.*, 1963, 67, 1621.

¹⁴ C. M. Naccache and Y. Ben Taarit, *J. Catal.*, 1971, 22, 171.

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In amorphous aluminosilicate gels the heterogeneity of the mixed oxide results in many different strengths of acidic centres. Although the crystallinity of the zeolite lattice tends to impart a more homogeneous structure, the large number of possible environments of hydroxy-groups and aluminium atoms, dependent on the proximity of cations and other sites, results in a similarly wide distribution of acid strengths.

Faujasite zeolites, in which the replaceable cations are transition-metal or rare-earth cations, and also in their decationated forms, are extremely important catalysts. The structure of the synthetic faujasites zeolites X and Y is shown in Figure 1. More recently the zeolite mordenite has found wide and increasing

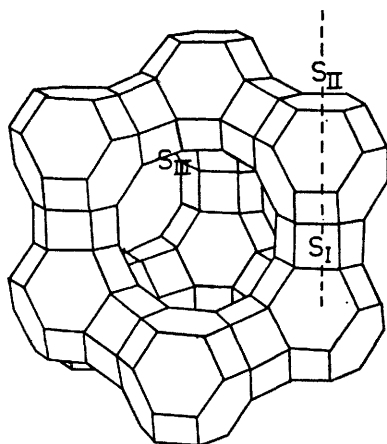


Figure 1 The faujasite zeolite structure showing cation sites

use in a number of catalytic reactions. The high catalytic activity of this zeolite for hydrocarbon cracking and isomerization arises from a low aluminium content, an open pore system, and a high thermal stability associated with the five-membered rings of the structure (Figure 2).

The concept of an acid strength distribution characteristic of a particular sample remains, even though recent models of acidity involve the added concept of cation and proton mobility.^{8,15} Such migration would affect the strength of individual sites but would not alter the overall energy distribution of the system. Modifications to the zeolite structure by processes such as cation exchange, thermal treatment, and aluminium removal do affect this distribution markedly.

The ideal method for measurement of surface acidity should encompass all the above facets and should study the surface as nearly as possible under catalytic conditions. No single method is available that provides all the information and so several approaches must be combined. Many techniques have been described

¹⁵ S. E. Tung and E. McIninch, *J. Catal.*, 1968, **10**, 166.

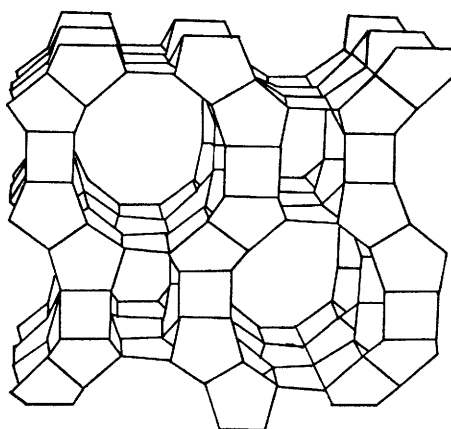


Figure 2 *The mordenite zeolite structure*

in recent publications and reviews,^{16,17} and include infrared,^{18–20} ultraviolet,^{21–23} and n.m.r.²⁴ spectroscopies, gas chromatography,^{25,26} adsorption of coloured indicators,^{21–23} and calorimetry.^{27–29}

Aqueous titrations were used in early surface studies³ but this is not a useful approach because of the modification of acidity in the presence of water. However, titration in a non-aqueous medium does provide very useful information as to the acidity of a surface and this method is described and discussed in some detail.

3 Non-aqueous Titration—Indicator Adsorption Method

The concept of measuring the acid strength of a surface by the observation of the colours of basic indicator molecules adsorbed from a non-aqueous medium was

¹⁶ M. S. Goldstein in 'Experimental Methods in Catalytic Research', ed. R. B. Anderson, Academic Press, New York, 1968, p. 361.

¹⁷ L. Forni, *Catal. Rev.*, 1973, **8**, 65.

¹⁸ P. A. Jacobs, B. K. G. Theng, and J. B. Uytterhoeven, *J. Catal.*, 1972, **26**, 191.

¹⁹ J. W. Ward in 'Zeolite Chemistry and Catalysis', ed J. A. Rabo, American Chemical Society, Washington, 1976, p. 118.

²⁰ A. V. Kiselev and V. I. Lygin, 'Infrared Spectra of Surface Compounds', Keter Publishing House, Jerusalem, 1975.

²¹ H. P. Leftin and M. C. Hobson, *Adv. Catal.*, 1963, **14**, 115.

²² A. Terenin, *Adv. Catal.*, 1964, **15**, 227.

²³ N. S. Kotsarenko, L. G. Karachiev, and V. A. Dzis'ko, *Kinetics and Catalysis*, 1968, **9**, 129.

²⁴ D. Freunde, D. Muller, and H. Schmeidel, *J. Colloid Interface Sci.*, 1971, **36**, 320.

²⁵ M. Misono, Y. Saito, and Y. Yoneda in ref. 11, p. 408.

²⁶ K. V. Topchieva and Kho Shi Tkhoang, *Russ. J. Phys. Chem.*, 1973, **47**, 1185.

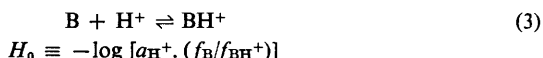
²⁷ K. Tanabe and T. Yamaguchi, *J. Res. Inst. Catal., Hokkaido Univ.*, 1966, **14**, 93.

²⁸ A. C. Zettlemoyer and J. J. Chessick, *J. Phys. Chem.*, 1960, **64**, 1131.

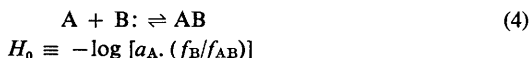
²⁹ K. Tsutsumi and H. Takahashi, *J. Phys. Chem.*, 1972, **76**, 110.

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proposed by Walling, in 1950,³⁰ who applied the Hammett function, H_0 , to surfaces. This function, H_0 , is defined on the basis of the ability of the acid to donate a proton to a non-ionized or neutral substance, *i.e.* a simple basic indicator, equation (3), where f_B , f_{BH^+} are the respective activity coefficients.³¹



It can be seen from equation (3) that H_0 is equivalent to the well known acidity function pH only if dilute aqueous solutions are involved. H_0 may be extended to include the Lewis concept of acidity given in equation (4). This inclusion is



very necessary since colour changes of H_0 indicators are observed in the presence of Lewis acids also.³² The definition of the acidity of a solid surface is given as 'the ability . . . to convert an adsorbed neutral base to its conjugate acid'.³⁰

The acid strength found from indicator adsorption is relative to the pK_a of the indicator, and this provides a sound basis for comparing surface acidities. The pK_a of the basic indicator may be reported relative to sulphuric acid-water mixtures and therefore the acidic strength is often expressed as a weight percentage of H_2SO_4 .³³ To be useful as an indicator a substance should be a neutral base which, when adsorbed on a surface on a 1:1 basis with acid sites, is converted into its conjugate acid, which has a markedly different colour. Properties of many visible H_0 indicators are given in Table 1. The solvent used must not alter or compete with the base for the surface and so it is usually non-polar (*e.g.* iso-octane, benzene).

An indicator will be converted into its conjugate acid only by acid sites which have an acid strength equal to or higher than that of the indicator. Thus, by the use of indicators alone, only the limiting strength for the strongest acid sites on a given surface can be determined, expressed as a range between two indicators of different pK_a , *e.g.* H_0 lies between -5.6 and -8.2 . The limit for the weakest strength of acid sites cannot be found, since indicators of more positive pK_a values will be converted into their conjugate acids by all of the stronger sites.

Johnson³⁴ has developed the method for the determination of the number of acid sites in which the solid, suspended in a non-aqueous solvent, is titrated with *n*-butylamine, using an adsorbed Hammett indicator to establish the endpoint. The resulting number is only that of the sites whose acid strength is greater than or equal to that of the indicator used. Benesi³⁵ further developed this approach, using a series of indicators, and the result is a distribution of the

³⁰ C. Walling, *J. Amer. Chem. Soc.*, 1950, **72**, 1164.

³¹ L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.

³² G. N. Lewis and J. Bigelstein, *J. Amer. Chem. Soc.*, 1943, **65**, 1144.

³³ K. Tanabe, 'Solid Acids and Bases—Their Catalytic Properties', Academic Press, New York, 1970.

³⁴ O. Johnson, *J. Phys. Chem.*, 1955, **59**, 827.

³⁵ H. A. Benesi, *J. Phys. Chem.*, 1957, **61**, 670.

Table 1 Visible Hammett basic indicators

Compound	Acidity ^c		Colour		Ref.
	H ₀	wt % H ₂ SO ₄	acid	base	
neutral red	6.8	8 × 10 ⁻⁸	red	yellow	—
bromothymol blue ^a	6.8	8 × 10 ⁻⁸	yellow	blue	41
p-ethoxychrysoidin	5.0	—	red	yellow	—
bromocresol green ^a	4.6	—	yellow	green	41
phenylazonaphthylamine	4.0	5 × 10 ⁻⁵	red	brown-yellow	21
benzeneazodimethylamine ^a	3.3	3 × 10 ⁻⁴	red	orange	22,54
2-amino-5-azotoluene	2.0	5 × 10 ⁻³	red	yellow	—
benzeneazodiphenylamine ^a	1.5	2 × 10 ⁻²	purple	brown-yellow	21,40
4-dimethylaminoazo-1-naphthalene	1.2	3 × 10 ⁻²	purple	yellow	—
crystal violet	0.8	0.1	yellow	blue	—
bromothymol blue ^a	-1.5	—	red	brown	41
dichloroacetone	-3.0	48	brick-red	orange	40
bromocresol green ^a	-3.7	—	red	brown	41
benzalacetophenone ^b	-5.6	71	yellow	colourless	23,40
anthraquinone ^b	-8.2	90	light yellow	colourless	23,40,71

^aRecommended for good visible endpoint; ^bnot recommended for visible use; ^c decreasing H₀ is a weaker base and so requires a stronger acid to convert it into its conjugate acid.

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number of acid sites of varying strength. The indicator found to correlate with the total number of acid sites on most surfaces is *p*-dimethylaminoazobenzene (butter yellow, $pK_a + 3.3$). This method of titration is by successive additions of amine to separate samples followed by the addition of the indicator after the acid-base equilibrium has been established. The procedure is best understood by describing a specific example.

About 2 g of the powdered catalyst is pretreated at the appropriate temperature for the desired length of time (usually about 4 h) in air or *in vacuo*. The catalyst is cooled in a desiccator and about 200 mg samples are transferred, in a dry box, to each of about 25 preweighed screw-cap vials of approximate volume 15 cm³. The solid is covered with about 1 cm³ of dry benzene (stored over molecular sieve 4A). Out of the dry box, increasing aliquots of a *n*-butylamine in benzene solution (0.03–0.05 M for a highly acidic surface of about 3 meq acid sites per gram such that titrants up to 10 cm³ are used) are added to the vials from a graduated 10 cm³ burette. The end-points to each indicator, *i.e.* where colour change just becomes visible, are first determined approximately by considering large steps in the addition of titrant over a wide volume range. Near the end-points the difference between aliquots is reduced to be equivalent to about 0.02 meq acid sites per gram (for 0.04 M-*n*-butylamine, steps of 0.05 cm³ are used). The samples are equilibrated overnight in the tightly capped vials, which are shaken vigorously. A modification to shorten equilibration times to within one hour is the use of an ultrasonic mixing tank.³⁶ Small amounts of each suspension are transferred to flat-bottomed vials and separate samples tested with a few drops of a 0.1% solution of each indicator in benzene. After further equilibrium the end-point for each indicator is determined by noting its colour in successive vials near the end-point.

The technique is not limited to white surfaces. Coloured surfaces such as chromic oxide in silica-aluminas, known as the chrome bead catalyst, are titrated in the presence of a known amount of a white solid. The end-point, assumed to occur at the same time on both solids, for a given indicator is observed on the white solid. This solid has a wide range of strengths and so is usually silica-alumina. The titration values for each H_0 of the coloured surface are found by subtraction of the titre at the H_0 involved for the white solid alone, found separately, from that for the combined surfaces.³⁴

The acidity values obtained from a series of indicators are cumulative from the least basic indicator (most negative pK_a), which adsorbs only on the strongest acid sites, to the most basic indicator, which is converted into its conjugate acid by the weak as well as the strong sites. Hence the distribution of strengths of acid sites found by this method yields valuable insight into the heterogeneity of the surface (see Figure 3). The importance in catalysis is that the number of sites possessing a certain range of strength may be the governing influence in a reaction, not the number of all acid sites regardless of strength.

The problem with the Hammett indicators is that both Brønsted and Lewis

³⁶ R. J. Bertolacini, *Analyt. Chem.*, 1963, 35, 599.

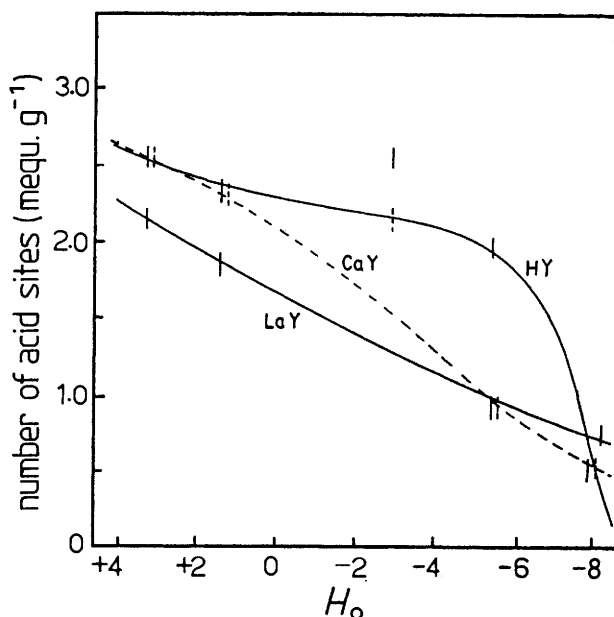
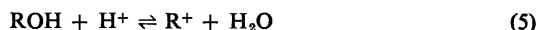


Figure 3 Distribution of acid strength of zeolites *Y*
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acidity is measured without any distinction. Since the catalytic activity of silica-aluminas and zeolites for such reactions as isomerization and cracking of hydrocarbons has been strongly linked to the presence of Brønsted acid sites^{1,4,5} an indicator that is 'proton-specific' would be more useful. Hirschler¹² suggested substances that form stable, coloured carbonium ions by protonation, and established the use of a series of arylmethanols as indicators as given in equation (5).



This equilibrium is defined by another acidity function, H_R , given by Deno *et al.*³⁷⁻³⁹ as shown in equation (6), and hence the two surface acidity functions

$$H_R = -\log a_{\text{H}^+} + \log a_{\text{H}_2\text{O}} + \log (f_{\text{R}^+}/f_{\text{ROH}}) \quad (6)$$

are related by equation (7). Both functions are shown against acid strength in

$$H_R = H_0 + \log a_{\text{H}_2\text{O}} - \log \left(\frac{f_{\text{ROH}} f_{\text{BH}^+}}{f_{\text{R}^+} f_{\text{H}^+}} \right) \quad (7)$$

³⁷ M. S. Newman and N. C. Deno, *J. Amer. Chem. Soc.*, 1951, **73**, 3644.

³⁸ N. C. Deno, H. E. Berkheimer, W. L. Evans, and H. J. Peterson, *J. Amer. Chem. Soc.*, 1959, **81**, 2344.

³⁹ N. C. Deno, J. J. Jaruzelski, and A. Schreisheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044.

terms of wt % H_2SO_4 in Figure 4.¹⁶ The properties of useful arylmethanols and references to their syntheses are given in Table 2.

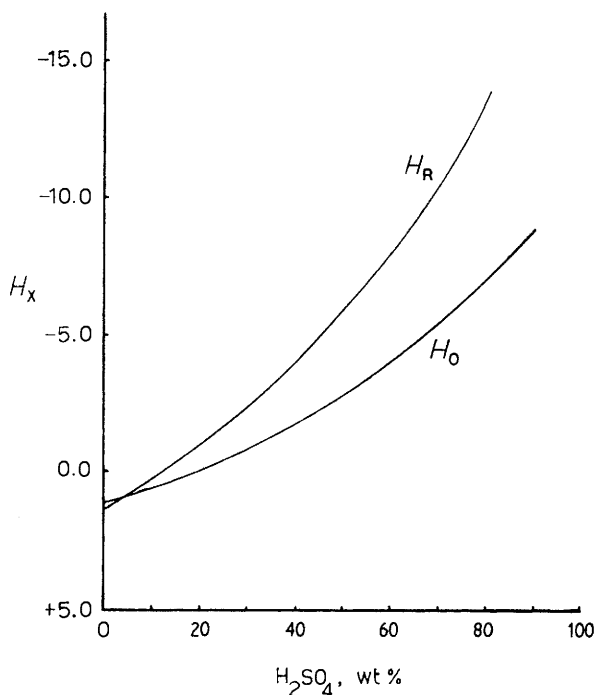


Figure 4 H_0 - H_R relationship

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Table 2 Arylmethanol indicators

Compound	Acidity		Ref.
	H_R	wt % H_2SO_4	
4-dimethylaminotriphenylmethanol	4.75	—	—
4,4',4''-trimethoxytriphenylmethanol	0.82	1.2	52
4,4',4''-trimethyltriphenylmethanol	-4.04	36	37
triphenylmethanol	-6.63	50	23, 72
3,3',3''-trichlorotriphenylmethanol	-11.6	68	—
diphenylmethanol	-13.3	77	23
4,4',4''-trinitrotriphenylmethanol	-16.3	88	52
2,4,6-trimethylbenzyl alcohol	-17.4	92.5	23, 37

A complicating factor in the accuracy of the *n*-butylamine titration with the use of visible indicators may be the effect of physical adsorption alone on the electronic character of the indicator molecule. Reservations as to this effect had been expressed in early reviews on the electronic spectra of adsorbed molecules.^{21,22} Physical adsorption may cause a spectral shift to longer wavelengths (a bathochromic shift) and it has been proposed that visible indicators for which the base form is colourless but has a strong absorption band just below 400 nm should be used only if the titration is followed spectrophotometrically; this happens to be the case with those Hammett indicators with a pK_a more negative than -5.6 (the frequently used benzalacetophenone and anthraquinone).⁴⁰⁻⁴² Physical adsorption of the base may produce a yellow colour which is easily confused visibly with the protonated species. Titration to the loss of this colour would be a significant overestimation of the number of acid sites of this strength. The magnitude of the spectral shift depends also on the field strength of the surface so this limitation on the choice of visible indicator would be most critical for the highly active silica-alumina and zeolite surfaces. The lack of heterogeneity observed in some studies on silica-alumina^{12,35} and zeolites²⁶ may be attributed to the use of these unsuitable indicators (*i.e.* benzalacetophenone and anthraquinone). Drushel and Sommers⁴⁰ recommend, for visible determination of the end-point, indicators which are coloured in both base and acid forms, *e.g.* bromothymol blue and bromocresol green. Ultraviolet indicators, given in Table 3, may be used if the end-point is determined spectrophotometrically.¹⁷

Table 3 Ultraviolet spectrophotometric Hammett indicators

Compound ¹⁷	Acidity H_0	Wavelength/nm		Ref.
		acid	base	
aminoazobenzene	2.8	—	—	—
<i>p</i> -nitroaniline	1.1	380	323	73,74
<i>o</i> -nitroaniline	-0.2	410 (water) 270 (H ₂ SO ₄)	378	21,23
<i>p</i> -nitrodiphenylamine	-2.4	440 (water) 265 (H ₂ SO ₄)	350	21,74
2,4-dichloro-6-nitroaniline	-3.2	—	—	—
<i>p</i> -nitroazobenzene	-3.3	—	—	—
2,4-dinitroaniline	-4.4	235	225,250 310,365	23
<i>p</i> -benzoyldiphenyl	-6.2	—	—	—
2,4,6-trinitroaniline	-9.3	340,420	302,390	23
3-chloro-2,4,6-trinitroaniline	-9.7	—	—	—
<i>p</i> -nitrotoluene	-10.3	350—380	265	23,41
nitrobenzene	-11.3	280	252	73,74,75
2,4-dinitrotoluene	-12.8	—	—	—

⁴⁰ A. V. Drushel and A. L. Sommers, *Analyt. Chem.*, 1966, **38**, 1723.

⁴¹ M. Frenkel, *Clays Clay Miner.*, 1974, **22**, 435.

⁴² M. Frenkel, *Analyt. Chem.*, 1975, **47**, 598.

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These may provide further information as to the strongest sites, since most have very negative pK_a values.

Other methods for the determination of acidity of solid surfaces, namely, chemisorption of ammonia on the stronger acid centres,²⁶ gas chromatography,²⁵ infrared spectra of adsorbed pyridine,^{5,43-46} and ammonium acetate base exchange,⁴⁸ have given results comparable to those obtained by the amine titration procedure outlined above.

Amine titration and adsorption of basic indicators has proven itself a simple, versatile method for the determination of many important aspects of the acidity of solid surfaces, provided the experimenter has full realization of its few limitations.

The adaptability of this method is shown in the wide variety of solid surfaces on which it has found application; simple chemicals,^{30,47,48} mounted acids,^{34,35,49} oxides,^{35,49-52} clays,^{35,41,49,51} and the catalytically important surfaces of silica-alumina^{12,30,35,51-57} and recently zeolites.^{12,26,43,58-63}

4 Acidic Properties of Aluminosilicates and their Correlation with Catalytic Activity

Over the past ten years zeolites have extensively replaced amorphous aluminosilicates as catalysts in the petroleum refining industry. Although the active centres on both catalysts are of similar nature, their number and effectiveness are greater on a zeolite surface, and the crystalline nature of zeolites provides a nearly model structure for the investigation of active centres. More importantly, the ability to modify the structure by cation exchange, pretreatment variation, and dealumination may lead to catalysts with a greater selectivity for a given reaction. To assist in the understanding as to why zeolites are such efficient catalysts, the effects of such modifications on the structure must be evaluated.

⁴³ M. Ikemoto, K. Tsutsumi, and H. Takahashi, *Bull. Chem. Soc. Japan*, 1972, **45**, 1330.

⁴⁴ J. W. Ward, *J. Catal.*, 1970, **17**, 355.

⁴⁵ J. P. Damon, B. Delmon, and J. M. Bonnier, *J. C. S., Faraday I*, 1977, **73**, 372.

⁴⁶ P.O. Skokart, F. D. Declerck, R. E. Sempels, and P. G. Rouxhet, *J. C. S., Faraday, I*, 1977, **73**, 359.

⁴⁷ K. Tanabe and M. Katayama, *J. Res. Inst. Catal., Hokkaido Univ.*, 1959, **7**, 106.

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⁵³ V. C. F. Holm, G. C. Bailey, and A. Clark, *J. Phys. Chem.*, 1959, **63**, 129.

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⁵⁵ J. Kobayashi, *Nippon Kagaku Zasshi*, 1963, **84**, 21, 26.

⁵⁶ I. Matsuzaki and Y. Fukuda, *J. Res. Inst. Catal., Hokkaido Univ.*, 1969, **17**, 192.

⁵⁷ J. P. Damon and J. M. Bonnier, *J. Colloid Interface Sci.*, 1976, **55**, 381.

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⁵⁹ L. Moscou and R. Moné, *J. Catal.*, 1973, **30**, 417.

⁶⁰ W. Kladnig, *J. Phys. Chem.*, 1976, **80**, 262.

⁶¹ R. Beaumont, D. Barthomeuf, and Y. Trambouze, in 'Molecular Sieves II' (Adv. Chem. Ser. No. 102) 1971, 327.

⁶² R. Beaumont and D. Barthomeuf, *J. Catal.*, 1972, **26**, 218.

⁶³ R. Beaumont and D. Barthomeuf, *J. Catal.*, 1972, **27**, 45.

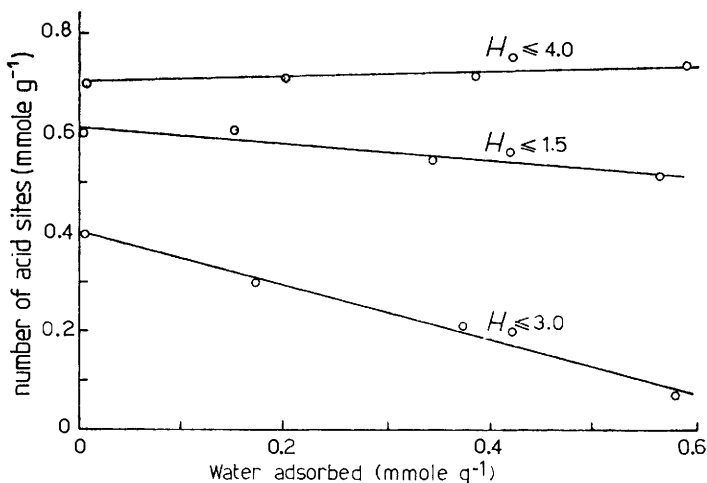


Figure 5 The effect of water adsorption on the acidity of a silica-alumina catalyst (Reproduced by permission from *J. Res. Inst. Catal., Hokkaido Univ.*, 1969, 17, 192)

of the X zeolites, with their higher Al content. In the hydrogen forms the total number of acid sites was quite constant with pretreatment above 300 °C, indicating a high thermal stability for this cationic form.

The strong acidity at $H_0 \leq 5.6$ of bi- and ter-valent cation forms of zeolite Y as a function of pretreatment temperature is shown in Figure 6. The CaY and SrY zeolites showed a maximum number of strong acid sites ($H_0 \leq -5.6$) at 450 °C and 470 °C respectively, which correlated well with the i.r. observations by Ward⁴⁴ for maximum Brønsted acidity. Hence these surfaces possess strong acid sites of a predominantly Brønsted nature. For the rare-earth forms LaY and GdY, maximum strong acidity ($H_0 \leq -5.6$) was observed for a 350 °C pretreatment but many strong acid sites were still evident at 650 °C. In these cationic forms Lewis acid sites (either dehydroxylated Al atoms or the La³⁺ and Gd³⁺ cations themselves) are present also, and contribute to the titration of strong acid sites when H_0 indicators are used.^{60,64}

A strong Brønsted acid site (one in which the proton is weakly bound to the surface) arises from a strong interaction between the lattice oxygen atom to which the hydrogen atom is attached and a cation of high polarizing power. If the cation is shielded by water molecules within the zeolite channels, the proton of the hydroxy-group will be more strongly bound to the lattice oxygen atom. The protons of the water adsorbed on Brønsted sites may or may not be exchanged with the proton of the hydroxy-groups (Scheme 7).

B. The Effect of Cation Exchange.—The many investigations into the effect of

⁴⁴ K. Tsutsumi and H. Takahashi, *J. Catal.*, 1972, 24, 1.

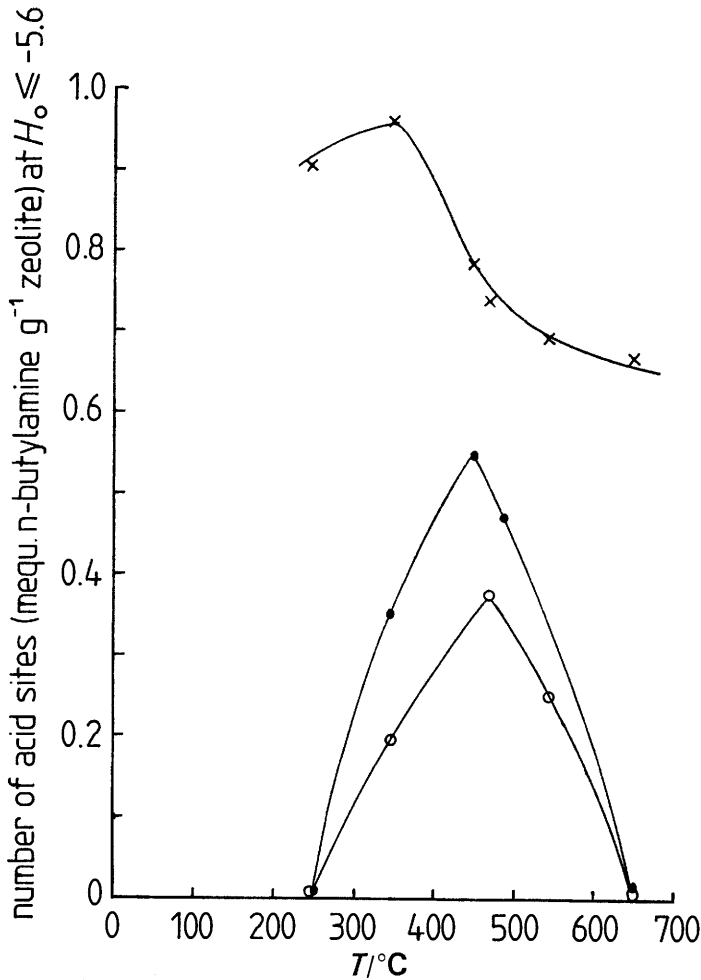
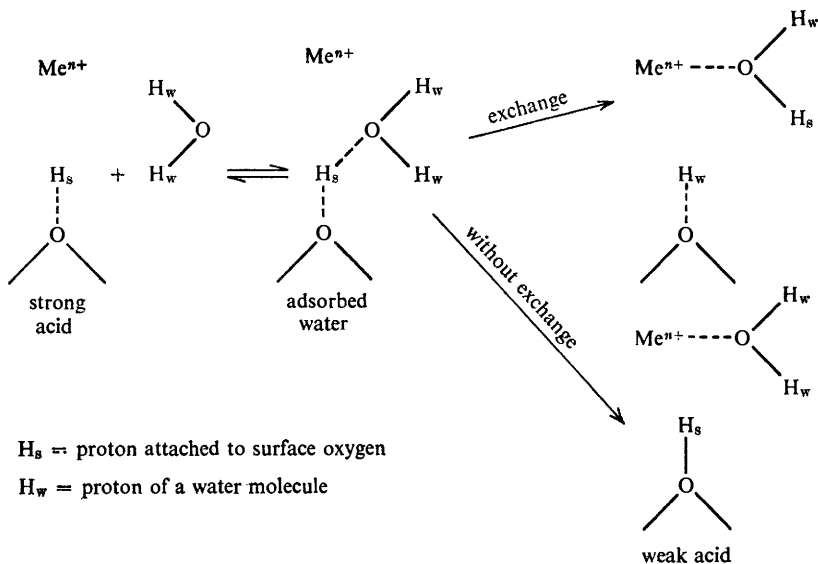


Figure 6 The effect of the pretreatment temperature on strong acid sites in zeolites Y (Reproduced by permission from *J. Phys. Chem.*, 1976, **80**, 262)

different cations on the number, strength, and distribution of acid sites on zeolites as determined by amine titration agree satisfactorily.

The number of acid sites on the surface of zeolites X and Y is increased when Na^+ ions are replaced by Ca^{2+} and La^{3+} ions. However, this increase occurs only after the exchange has reached a certain level. In the case of La^{3+} ions a 20% degree of exchange was required before an increase in the number of acid sites was produced.^{43,58} In the case of CaNaY and SrNaY an abrupt increase in the number of acid sites occurred at 50% exchange.^{43,60} Bivalent cations prefer the fully octahedral co-ordination of the S_1 cation positions within the hexagonal

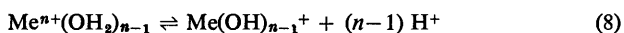


Scheme 7

prisms of the faujasite structure and during the calcination treatment migrate to these positions and replace any Na^+ ions remaining there. The cations in these positions, being fully shielded by the oxygen lattice atoms, do not produce acid sites. When locations S_I are fully occupied by bivalent cations, locations $S_{II'}$ and $S_{III'}$ in the sodalite cage are occupied but the acid sites formed in the sodalite cage, due to the presence of cations in locations S_I and $S_{II'}$, are inaccessible to the titrant. Hence only when bivalent cations are present at locations S_{II} and S_{III} in the supercage (at about 50% exchange) are acid sites available to the titrant, and indeed to reactants involved in catalytic reactions.

It has been demonstrated by Kladnig⁶⁰ that there is a linear dependence of the number of acid sites on the polarizing power of the cation for samples of the same degree of exchange and pretreatment (Figure 7). This correlates well with the model for the formation of Brønsted sites involving the polarizing of water by cations.¹³

An innovative approach by Beaumont *et al.*⁶¹ involving a semiquantitative description of the 'acidic efficiency' of a cation to produce acid sites [equation (8)] further confirms such a model. The number of acid sites in metallic cation



zeolites Y when exchanged with protons was found to bear a linear relationship to the number of metallic cations present (Figure 6).⁶² The exchange of Na^+ ions by protons is on a 1:1 basis but the amount of acidity is increased by only 0.6 equivalents per unit cell for the exchange of one equivalent of Na^+ ions per

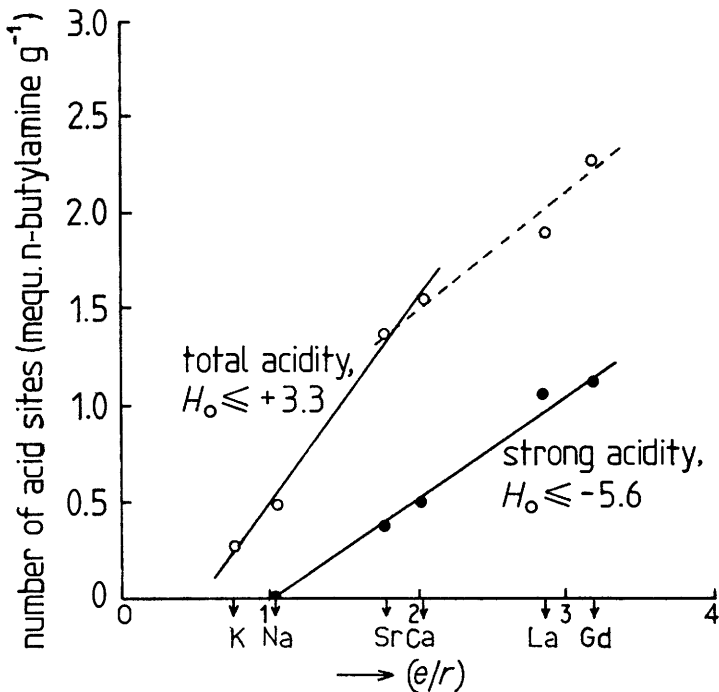


Figure 7 Correlation between the polarizing power of the cation and acidity in zeolites Y (86% exchange, 500 °C pretreatment)

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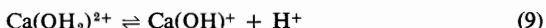
unit cell. This fraction is denoted by the parameter α_0 , characteristic of a sample of a given aluminium content.⁶¹ It implies that, in a zeolite, only a fraction of the theoretical charge of one $(\text{AlO}_4)^-$ tetrahedron is capable of producing acid sites (in zeolite Y this fraction is 0.6). More important to this discussion on the effect of cation exchange is the ratio of the slope of the above linear relationship for the multivalent cation forms of the same zeolite Y, α , to the α_0 parameter found from NaHY forms, given in Table 4. According to the model

Table 4 The relationship between cation valency and the acidic efficiency ratio, α/α_0 ⁶¹

Zeolite	Cation Valency	N^a	$N/\text{Cation Valency}$	α/α_0
NaHY	1	1	1	1
KHY	1	1	1	1.09
CaHY	2	1	1/2	0.48
LaHY (300 °C)	3	1	1/3	0.33
LaHY (500 °C)	3	2	2/3	0.65

N^a is the effective number of aluminium atoms neutralized by one metallic ion.

proposed [equation (8)], the ionization of a water molecule attached to a bivalent cation would produce one proton which associates with one of the two $(\text{AlO}_4)^-$ tetrahedra involved, as shown in equation (9). Beaumont *et al.*⁶² refer to this as



neutralization of equivalent to one of the two possible acid sites, which are based on the $(\text{AlO}_4)^-$ tetrahedra since these are the origin of the acid sites. The univalent hydroxy-cation is then associated with the other $(\text{AlO}_4)^-$ tetrahedron but this does not result directly in the formation of an acid site. It is the electrostatic interaction between this hydroxy-cation and the $(\text{AlO}_4)^-$ tetrahedron that renders acidic the one structural hydroxy-group produced nearby by the exchange of a bivalent cation. Thus as one Ca^{2+} ion may replace two Na^+ ions, only one of the two $(\text{AlO}_4)^-$ charges associated with Na^+ ions is neutralized by a proton, and a slope of $\alpha_0/2$ is observed for CaHY in Figure 8.

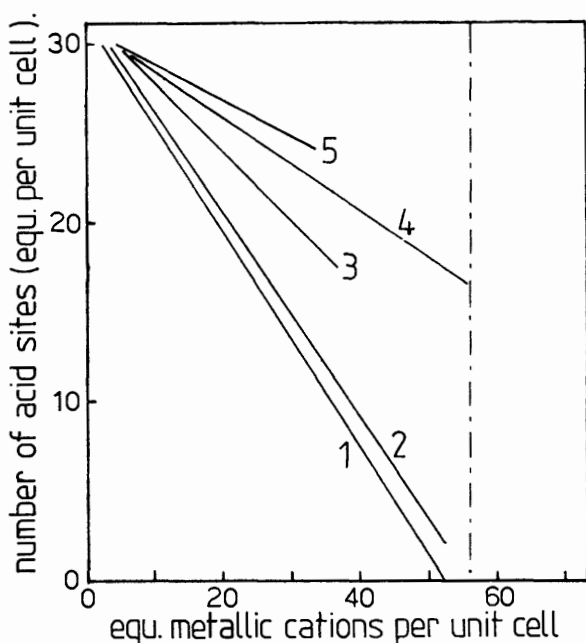
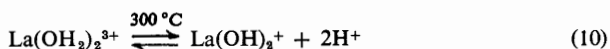
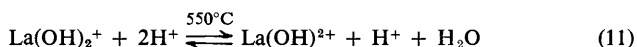


Figure 8 Acidity of zeolites Y as a function of the metallic cation content—acidic efficiency; (1) KHY; (2) NaHY; (3) LaHY (550 °C); (4) CaHY; (5) LaHY (300 °C) (Reproduced by permission from *J. Catalysis*, 1972, 26, 218)

Similarly for the exchange of three Na^+ ions by one La^{3+} ion and subsequent heating at 300 °C, the equation is as given in (10). Two of the three $(\text{AlO}_4)^-$



tetrahedra involved are neutralized by protons, and so the remaining tetrahedron which is associated with the univalent hydroxy-cation renders these two hydroxy-groups acidic. This results in a ratio for the 'acid site efficiency' for LaHY (300 °C) of $\alpha_0/3$, as observed. With LaHY, further heating at 550 °C results in partial dehydroxylation of the lattice as given in equation (11). That is, under a



high pretreatment temperature, one hydroxy-group is formed per tervalent cation and the remaining two $(\text{AlO}_4)^-$ tetrahedra are associated with a bivalent hydroxy-cation.

Thus these observations^{61,62} are in accord with the model of acidity which involves the formation of Brønsted acid sites, their number and strength depending on the polarizing power of the cations in the zeolite.

C. The Effect of the Si/Al Ratio.—Several investigators using amine titration and adsorbed indicator molecules have noted a higher acidity, both in number and strength of acid sites, for zeolite samples with a higher Si/Al ratio.^{26,43,62,63}

Beaumont *et al.*^{62,63} have also shown this effect quantitatively in their concept of 'acid site efficiency'. Their parameter α_0 is a specific property of the $(\text{AlO}_4)^-$ sites, namely their proximity to each other. The variation in α_0 has been observed for a series of faujasite zeolites that were progressively aluminium-deficient, achieved by either 'deep-bed calcination' to give ultrastable zeolites^{65,66} or by extraction of Al with chelating agents such as acetylacetone and EDTA.⁶⁷ A linear relationship between the number of Al atoms per unit cell and the acidic efficiency, α_0 , was found for each NaH-form (Figure 9). For NaHX with 86 Al atoms per unit cell, an α_0 value of 0.16 equivalents per unit cell was found, compared to 0.60 equivalents per unit cell for NaHY with 56 Al atoms per unit cell. The limiting values coincide with limits on the stability of the crystalline structure: $\alpha_0 = 1.0$ for 28 Al atoms per unit cell and $\alpha_0 = 0$ for the minimum Si/Al value of 1 at 96 Al atoms per unit cell. This acidic efficiency parameter behaves like an activity coefficient, decreasing as the concentration of aluminium sites increases.⁶⁸ The slope of the relationship between the acidic efficiency and its aluminium content, *ca.* 1.45×10^{-2} , is a characteristic acidity parameter of the faujasite structure. It means that 'the introduction of one aluminium more in the unit cell of a faujasite zeolite leads to a decrease of the efficiency of all pre-existing aluminium atoms of $\simeq 1.45 \times 10^{-2}$ equivalents (or 1.45%) per site'.⁶² That is, as the aluminium content decreases and the $(\text{AlO}_4)^-$ tetrahedra are separated farther from each other, the influence of each on the formation of acidity is perturbed less by its neighbours and so acts more as a whole (higher α_0) in reactions of an acid-base nature. This means an increase in the 'effective

⁶⁵ J. B. Peri in 'Catalysis', ed. J. W. Hightower, North Holland, Amsterdam, 1973, Vol. 1, p. 329.

⁶⁶ G. T. Kerr in 'Molecular Sieves' (Adv. Chem. Ser. No. 121), 1973, p. 219.

⁶⁷ R. Beaumont, P. Pichat, D. Barthomeuf, and Y. Trambouze in ref. 65, p. 343.

⁶⁸ D. Barthomeuf, *Acta. Phys. Chem.*, 1978, **24**, 71.

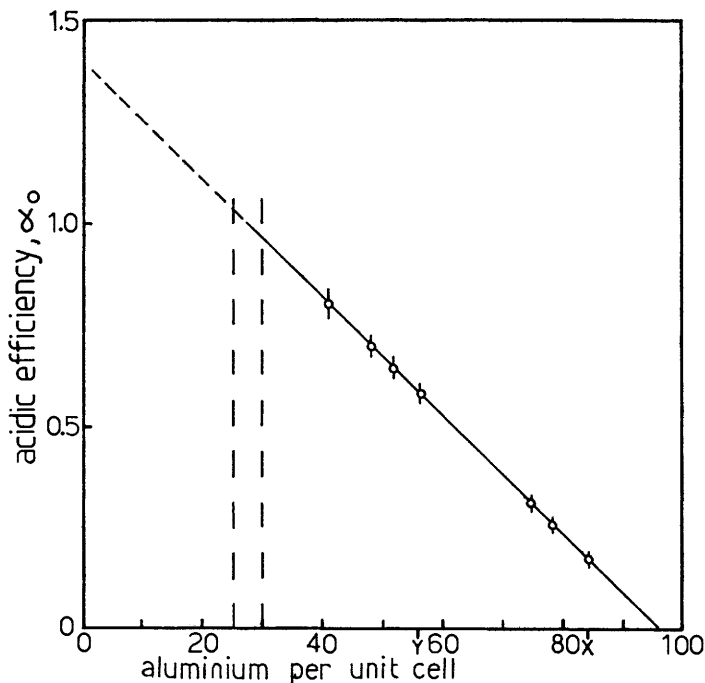


Figure 9 The relationship between the acidic efficiency of the faujasite structure and the aluminium content

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acidity' of each Brønsted acid site as it is separated farther from another site. This would explain the fact that dealumination results in an increased acid strength of sites on a zeolite surface. Since, on dealumination, the more weakly bound Al atoms would be selectively removed, a more homogeneous distribution of acid strengths results from a lower Si/Al ratio. There is an analogy between this situation and the effective acidities of the acid sites of $\alpha\omega$ -dicarboxylic acids $\text{HOOC}-(\text{CH}_2)_x-\text{COOH}$.⁶⁶

Hence this concept of acid site efficiency can explain the observation of a larger number of acid sites, especially a larger number of stronger sites, in zeolites Y compared to zeolites X. This relationship between acid site density and their 'effective acidity' may account for the greater catalytic ability known for zeolites with higher Si/Al ratios.

D. Correlations with Catalytic Activity.—Amorphous silica-aluminas and zeolites catalyse similar hydrocarbon transformations, for example cracking reactions, polymerization, isomerization, and hydrogen transfer, since both surfaces possess similar types of acid centres. However, greater efficiency

and scope are found for zeolites because of their highly polar surface which possesses a high area, crystalline uniformity, and a thermal stability that result in a larger number of acid sites. Not only is the number of acid sites important but the strength of the acid sites is fundamental to the type of reaction catalysed, since the activation energy required for different reactions varies. Major evidence for the role of acid centres in catalysis by aluminosilicates is the parallel trends observed for the effect of structure modifications on both the acidic character of the surface and its ability to convert hydrocarbons in catalytic reactions.

Both the number of acid sites and the catalytic activity of zeolites have been observed to increase with the degree of multivalent cation exchange and an increase in the Si/Al ratio, the maximum activity being dependent also on the pretreatment temperature.^{58,64}

The order of catalytic activity for the cracking reactions over various cation-exchanged zeolites X or Y was observed to be $\text{La}^{3+} > \text{H}^+ > \text{Ca}^{2+} \gg \text{Na}^+$, dependent on both the number of acid sites and their acid strength, provided the degree of exchange of multivalent cations is sufficient for them to be in exposed positions in the supercage. Zeolite Y forms exhibited a higher activity than the corresponding cation form of zeolite X, in accord with a greater number of acid sites and their effective acidity associated with a lower Si/Al ratio. Maximum conversion in cracking reactions occurs on dealuminated zeolites that possess a majority of strong acid sites.⁶⁹ The importance of the presence of strong acid sites in cracking reactions is evidenced by the occurrence of sites of strength $H_0 \leq -12.8$ only on the La^{3+} -exchanged zeolite that had shown the greatest activity.⁴³

Thus a rare-earth-exchanged Y zeolite appears a most effective cracking catalyst, except that the presence of very strong acid sites also results in side reactions that form carbon and polymeric residues that quickly poison the acid sites. However, because of the high-thermal stability of the zeolite structure, regeneration is possible by high-temperature oxygen treatment and rehydration, followed by recalcination. Hydrothermal (or steaming) treatment has been observed to decrease only the number of very strong acid sites without diminishing cracking conversion factors, but with a decrease in coke formation. Such a catalyst fits satisfactorily many of the criteria described by Jacobs⁵ for a good cracking catalyst.

By comparison of the acidity distributions and the catalytic activities of widely different acidic surfaces the relationship between acid strength and selectivity to many reactions has been observed.^{57,70} For surfaces with only very weak acidity (*e.g.* ThO_2) the only reaction of 2-methylpentan-2-ol that was observed to occur on the surface was dehydration to form 2-methylpent-1-ene. On the

⁶⁹ R. Beaumont and D. Barthomeuf, *J. Catal.*, 1973, **30**, 288.

⁷⁰ J. P. Damon, J. M. Bonnier, and B. Delmon, *Bull. Soc. chim. France*, 1975, 449.

⁷¹ A. V. Kiselev, D. G. Kitiashvili, and V. I. Lygin, *Kinetika i Kataliz*, 1971, **12**, 1075.

⁷² H. P. Leftin, *J. Phys. Chem.*, 1960, **64**, 1174.

⁷³ M. Robin and K. N. Trueblood, *J. Amer. Chem. Soc.*, 1957, **79**, 5138.

⁷⁴ J. C. D. Brand, *J. Chem. Soc.*, 1950, 997.

⁷⁵ A. V. Kiselev, L. A. Kupcha, and V. I. Lygin, *Kinetika i Kataliz*, 1968, **9**, 1183.

The Acidity of Solid Surfaces

other surfaces with strong acidity the various isomerization reactions of this alkene product also occurred. These reactions were found to be catalysed by surfaces of increasing acid strength in the order: *cis-trans* isomerization, 1,2-double-bond migration, further double-bond migration, and lastly skeletal isomerization. The overall parallelism between catalytic activity-selectivity and the acidic strength distribution is shown in Table 5.

Table 5 Correlation of catalytic activity with acid strength⁴⁵

Acid Strength, H_R	(1)—(2) Dehydration	Isomerization			
		<i>cis-trans</i>	(1)—(2)	double- bond migration	skeletal
$H_R > 0.82$	+	—	—	—	—
$0.82 \geq H_R > -4.04$	+	+	+	—	—
$-4.04 \geq H_R > -6.63$	+	+	+	+	—
$-6.63 \geq H_R > -11.63$	+	+	+	+	+

A comprehensive list of hydrocarbon transformations catalysed by surfaces exhibiting acidic carboniogenic activity has been arranged by Jacobs⁵ in a sequence requiring increasing acid strength (Table 6). Higher pretreatment temperatures are required to produce the strong sites required for cracking, and so this reaction would occur on relatively few sites compared to, say, polymerization.

Table 6 Correlation of carboniogenic activity of zeolites with acid site strength⁵

Reaction	Increasing Strength Required	
	wt % H_2SO_4	
(1) dehydration of alcohols	3	$\times 10^{-4}$
(2) isomerization of alkenes	3	$\times 10^{-4}$
(3) alkylation of aromatics	—	—
(4) isomerization of alkylaromatics	—	—
(5) transalkylation of alkylaromatics	—	—
(6) cracking of alkylaromatics	70	—
(7) cracking of alkanes	88	—

5 Conclusion

The amine titration coupled with the adsorption of indicator molecules in a non-aqueous medium is a very useful technique for the determination of the number and strength of acid sites on surfaces, especially for the elucidation of changes in the distribution of acid strengths caused by modification to the structure of silica-aluminas and zeolites. Such observations provide a valuable

insight into the relationship between acidity (number, strength, and location of acid sites) and the catalytic ability of these aluminosilicate surfaces.

The trends in acidity variations with the zeolite cation and the formulation by Beaumont *et al.*⁶³ of the acid site efficiency parameter α_0 obtained by the use of this analytical approach support the model generally proposed for the formation of Brønsted acid sites which involves the polarization of water molecules associated with the zeolite cation.

Thus this method provides information on many aspects of surface acidity and, when used in conjunction with, in particular, infrared spectroscopy and gas chromatography, results in an efficient characterization of the surface acid sites.