DETERMINATION METHODS FOR THE ACIDITY OF SOLID SURFACES

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ABSTRACT

The acidity of solid surfaces is an important aspect of ion exchange and catalysis. Different techniques have been applied to study the acidity of solid surfaces. Titration methods, the adsorption of basic probe molecules followed volumetrically, gravimetrically, microcalorimetrically, with IR and NMR spectroscopies as well as the desorption of such probe molecules followed by temperature programmed techniques were among the thoroughly applied methods. In this study a brief outline of these studies was made.

INTRODUCTION

The acidic or basic properties of solid surfaces are interesting aspects of surface structure. Especially powders constituted by metal oxides are relevant products of the inorganic chemical industry. These powders find application in the fields of heterogeneous catalysis, pigments technology, adsorption technology and as precursors for sintered ceramics. In all these applications the powder's surface interacts with the environment. The interactions of the oxide surfaces with gases or liquids are mainly governed by acid-base interactions. These type of interactions are also important in particle sintering. Moreover pigment properties partly depend on the interaction of the powder surfaces with the solvents and with water from the environment. The understanding of the acidic nature of a solid surface is of great importance in the fields of ion exchange and catalysis. For these reasons the acidic properties of solid surfaces have been the object of many investigations [1-7]. Different techniques have been used to study the surface acidity of solids. Particularly, the adsorption of water and basic probe molecules followed gravimetrically [8], volumetrically and microcalorimetrically [9,10] and with IR [11-21], Raman and NMR [22] spectroscopies have been applied to investigate surface acidity. Contrarily, the desorption of such probe molecules followed by temperature-programmed techniques have also been applied [23,24]. Titration methods [25-29] and activity measurements in catalytic test reactions [30-32] have also been among the thoroughly applied methods.

The application of these techniques has added greatly to our knowledge about the surface acidity of solid surfaces, however it has also revealed the complexity of predicting the acid strength and number of acid centers on solid surfaces. In order to be able to judge the acidity of solid surfaces, all of these methods have to be kept in mind with their advantages and disadvantages. Therefore, the aim of this study was to make a brief outline of these studies concerning the acidity of solid surfaces.

ACID STRENGTH DETERMINATION METHODS

A complete description of surface acidity requires the determination of an intensive factor which is the acid strength and an extensive factor which is the number of acid centers.

The acid strength of a solid surface is defined as its proton donating ability, quantitatively expressed by Hammett and Deyrup's H_0 function where

$$H_0 = - \log (a_H^+ f_B / f_{BH}^+) \tag{1}$$

Where a_H^+ is the hydrogen ion activity of the surface acid and f_B and f_{BH}^+ are activity coefficients of the basic and acidic forms respectively of the adsorbed indicator [33]. If H_0 has to be used as an acid strength index for solid surfaces then, the f_B / f_{BH}^+ ratio of an adsorbed indicator must be independent of the indicator used. Benesi's work [33] shows that this ratio is either independent of the indicator used or varies in a regular manner with decreasing indicator basicity.

The basis of the acid strength determination is founded on the definition mentioned above. If this definition is applicable to surfaces, the acid strength of any surface should be measurable by observation of the color of suitable indicators adsorbed upon it. The appearance of the color of the acid form of the indicator indicates a value of the H_0 function for the surface lower than the pK_a of the indicator employed.

Walling [34] suggests a similar definition for the acid strength as the ability of the surface to convert an adsorbed neutral base to its conjugate acid where

$$H_0 = - \log (a_A f_B / f_{AB}) \tag{2}$$

Where now, a_A is the activity of the Lewis acid or electron acceptor. The acid strength definitions given by equations (1) and (2) differ from each other in one important aspect. Equation (2) is a more general H_0 function which includes the activity of Lewis acids as well as hydrogen acids. Benesi [33] claims that Equation (2) is not applicable since the relative strengths of generalized Lewis acids depend not only on the solvent medium but also upon the particular base used for reference. Thus even if Lewis acids on a solid surface give rise to indicator color changes the results could not be expressed in terms of a single H_0 function, each Lewis acid

would have to be treated as an individual case. Nevertheless, in the study of Walling[34] it was determined that although alumina and pure silica appeared to have neutral surfaces, silica-alumina and silica-magnesia were strongly acid. Several surfaces containing strongly coordinating metal ions were also strongly acid. In the study of Benesi it was determined that i) the strength of an acid mounted on silica gel tends to increase with increasing acid concentration ii) dried clays and cracking catalysts are strongly acid after they have been neutralized with aqueous sodium hydroxide solution iii) unused silica-alumina catalysts are strongly acid as 98 % sulfuric acid iv) silica-magnesia catalysts are weaker acids than silica-alumina catalysts.

In the above mentioned works the acid strength of solid surfaces was measured based on Hammett and Deyrup's acidity function H_0. The next logical step in determining surface acidity is the measurement of the number of acid centers.

DETERMINATION OF ACID STRENGTH AND THE NUMBER OF ACID CENTERS

In the method which uses Hammett indicators to determine the acid strength, the pK of the indicator is the factor which determines the level of acid strength. In the study by Johnson [25] several Hammett indicators were tried first and no appreciable difference in total acidities was found when different indicators were used therefore, one indicator namely p-dimethylaminoazobenzene was used in the titration of the solid suspended in benzene with n-butylamine to determine the number of acid sites. It was concluded that the amine titration adequately measured the acid sites on a series of silica-alumina catalysts, which were important for polymerization of propylene. It was also shown that for a given number of acid sites, the polymerization activity markedly increased with acid strength. In other studies[26,27] a complete set of adsorbed Hammett indicators were used in titration of benzene suspensions of solids with n-butylamine to yield the number of acid centers as a function of acid strength. This method was useful in characterising the surface acidity of catalyst surfaces which contain acid centers that can be grouped into several acid strength ranges. The same aim was pursued in a study by Frenkel [36] in which the surface acidity of almost homoionic montmorillonites was measured by titrating selected Hammett indicators adsorbed on the clay with n- butylamine by the use of reflectance spectroscopy.

Solely titrations using either indicators or instrumental methods were also used for the determination of surface acidity.

TITRATION METHODS

In a study which aims at determining the surface acidity changes resulting from acid treatment of clays, a volumetric titration method was used [35] among other methods. In this method, 0.5 g of the clay, previously dried was put in a conical

flask to which 15 cm ^{3} of 0.1 N NaOH was added. After stirring the flask for 10 minutes, the clay was titrated with 0.1 N H_2SO_4 acid using phenolphtalein indicator. Acidity was then determined as milliequivalents of NaOH used per 100 g of clay. The concentration of acidic substituent groups in the carbon surface was determined similarly [37]. A titrimetric study about the acidity of H-resin treated nontronite was realized by both potentiometric and conductometric titrations [28]. In such studies the total base combining capacity of the clay as well as data on the nature of the clay acid were determined since each inflection (or break) in the titration curve stands for the neutralization of one acidic principle. Titration of weakly acidic sites on clays is limited in aqueous media by the acidic property of water which prevents sharp end points. Generally it is not possible to obtain sharp end points in aqueous systems for acids with $pK_a > 8$. Therefore, in this study, non aqueous titrations were made in addition to titrations in water and it was observed that the end point in the titration of the weak acid which was masked in the titration in water due to hydrolitic effects came out much sharper in the nonaqueous titrations where such effects were absent. In another study [29] kaolinite with K, H or Al as the saturating cation was titrated in water and acetonitrile using glass-calomel electrode system for potentiometric determination. The application of non aqueous titration procedures for studies of the acidic properties of 2:1 swelling clays was evaluated by the potentiometric titration of montmorillonites saturated with Al^{3+}, H^+-Al^{3+} and K^+ in water, acetonitrile and dimethylformamide [38]. Metal sulfides are abundant in aquatic systems. The formation of metal sulfide precipitates is considered to be an important mechanism controlling the concentration of heavy metals in natural waters. Therefore, the surface acidity of hydrous CdS was determined by both electrokinetic and alkalimetric titration methods [39]. In this study, it was concluded that both alkalimetric titration and zeta potential measurement methods could be used to determine the surface acidity of CdS(s), and from zeta potential measurements it was also possible to characterize the surface Lewis acidity.

As was mentioned earlier the adsorption of basic probe molecules were widely used for the investigation of the surface acidity of solids.

BASE ADSORPTION METHODS

These methods can be broadly classified into two groups i) those which measure the number of acid sites, ii) those which differentiate between the Bronsted and Lewis centers.

i) Base adsorption methods to measure the number of acid sites:

In order to determine the number of acid sites on various clays, amine adsorption method was used [27]. In this method air dried samples of known weight (10-20 mg) were taken into test tubes. Different amounts of 0.01 M n-butylamine solution in benzene ranging from 2 to 5 cm^3 were added to each tube. The tubes were tightly stoppered and stored. One cm^3 portions of the supernatants were taken

from the equilibrated suspensions, and the amounts of n-butylamine remained were obtained by titrating them with 0.016 M trichloroacetic acid solution in benzene using 2,4-dinitrophenol as an indicator. The amount of n-butylamine adsorbed was calculated by subtraction of its amount remained in the supernatant from that added.

A method for the determination of the concentration of acid sites on the surface of alkali promoted $AlPO_4$ catalysts by the adsorption of appropriate substances, using a spectrophotometric method was described by Campelo et. al. [40]. In this method, a freshly prepared titrant agent solution (10 cm^3) is pipetted into a cylindrical glass tube which was previously loaded with the solid (0.1g). The tube is fitted with a glass stopper, shaken for one hour at constant temperature and the concentration of substrate in solution in equilibrium with the adsorbed substrate is determined spectrophotometrically. Sorption experiments are developed at the wavelength of the maximum absorption (λ_{max}, nm) and between the titrant concentrations where the Lambert-Beer Law is fitted. The experiment is carried out from cyclohexane solutions. The chemical interaction between the adsorbate and surface is consistent with the Langmuir adsorption isotherm equation

$$(c / X) = (1 / b X_m) + (c / X_m) \qquad (3)$$

where c is the concentration of the substrate in solution in equilibrium with the adsorbed substrate, b is a constant which characterizes the adsorption energy, X is the amount of adsorbed substrate per gram of solid and X_m is the monolayer coverage, which corresponds to the theoretical amount of solute by 1.0 g of solid system if all sites are covered. The method is capable of providing useful data on the total concentration of sites as well as their strength and the relative number of sites accessible to adsorbed molecules, by the use of compounds with different pK_a and steric hindrance.

In the study of Campelo et. al. [40] the basic probe molecules used were cyclohexylamine ($pK_a = 10.6$), 2,6-di-t-butyl-4-methylpyridine (pK_a 7.5) and pyridine ($pK_a = 5.3$). The amount required to cover the surface of the solid with a monolayer was assumed as the acidity of the sample, corresponding to a specific pK_a of the titrant used. It was noted that the chemisorption of cyclohexylamine was greater than the other two bases since by definition it measured the total acidity of these surfaces.

The same method was used for the determination of the acidity of i) manganese nodules [41], ii) transition metal promoted $AlPO_4$ catalysts [42] iii) manganese (III) pillared montmorillonite and pillared acid-activated montmorillonite[43] and iv) sepiolite [44]. In the studies of i) the basic probe molecules used were 2,6-dimethylpyridine, 2,6-dimethyl piperidine, and 2,6-dimethylmorpholine, ii) they were pyridine, morpholine and piperidine iii) pyridine, piperidine and 2,6-dimethylpyridine and in iv) n-butylamine.

Also, surface acidity of montmorillonites was studied directly by using calorimetric measurements of ammonia adsorption [14,23]. The study of Brown et.al. [14]

was made using a modified combined thermobalance / differential scanning calorimeter. The principle of the method is that the sample is thermally activated in situ under flowing helium. The temperature is then set at a suitable level to permit chemisorption of ammonia on the solid surface but prevent physisorption. A controlled series of ammonia pulses is then introduced into the helium stream. Sample weight and enthalpy changes are monitored as ammonia is adsorbed and assuming one ammonia molecule is adsorbed on each acid site these are interpreted in terms of the abundance of acid sites on the catalyst surface and their strength expressed as enthalpies of adsorption of ammonia.

The amounts of pyridine and ammonia adsorbed on montmorillonites were also determined by thermogravimetric analysis using a Mettler TA 3000 system [45-47].

ii) Base adsorption methods which differentiate between Brønsted and Lewis acidity

The term acidity mostly discriminates between sites of Brønsted character and Lewis character. Here, we should give a reminder of the Brønsted and Lewis definitions of acidity and basicity.

According to the concepts independently proposed by J. M. Brønsted and T. M. Lowry in 1923, an acid is any hydrogen containing species which can release a proton and a base is any species which can accept a proton. This definition does not exclusively imply water as the reaction medium. In this regard, acid-base interactions consist in the equilibrium exchange of a proton from an acid HA to a base B giving rise to the conjugated base of HA, A⁻, plus the conjugated acid of B, HB^+:

$$HA + B \Leftrightarrow A^- + HB^+ \tag{4}$$

In the same year a different approach was proposed by G. N. Lewis. In this view an acid is defined as any species (which has an incomplete electronic grouping) that can accept an electron pair to give rise to a coordination bond. Conversely, a base is any species that posseses a non bonding electron-pair that can be donated to form a coordination bond. Thus, Lewis type acid base interaction can be defined as follows:

$$B: + A \Leftrightarrow {}^{\delta+}B \quad A^{\delta} \tag{5}$$

The adsorption of basic probe molecules such as CO, ammonia, n-butylamine, pyridine and piperidine was investigated by IR or FTIR spectroscopy techniques in order to determine the Brønsted and Lewis acidities on solid surfaces [12-21,48-58]. The IR spectroscopic detection of surface acid centers is based on observation of the vibrational perturbation undergone when they adsorb on solid surfaces. Certain absorbtion bands observed in the spectra are used to distinguish

between Lewis and Brønsted acidity. Data on some useful basic probe molecules are reported in Table 1.

Table 1. Basic probes, their pK_a values and the position of their diagnostic vibrational bands.

Base	Conjugated acid	Basic Strength pK_a	Sensitive bands(base) Lewis acidity Mode	Position	Diagnostic band Bronsted acidity Mode	Position
Piperidine $C_5H_{10}NH$	$C_5H_{10}NH_2$	11.1			δNH_2^+	1650
n-Butylamine $n\text{-}C_4H_9\text{-}NH_2$	$n\text{-}C_4H_9\text{-}NH_3^+$	10.9			$\delta_{sym} NH_3^+$	1540
Ammonia NH_3	NH_4^+	9.2	$\delta_{sym} NH_3^+$	1300-1000	$\delta_{as} NH_4^+$	1440
Pyridine C_5H_5N	$C_5H_5NH^+$	5.2	v_{8a}	1632-1580	v_{8a}	1640
			v_{19b}	1455-1438	v_{19b}	1540
			$v_{(ring)}$	1020-990		
Acetone $(CH_3)_2C=O$	$(CH_3)_2C=OH^+$	-7.2	$v_{C=O}$	1730-1650		
Carbonmonoxide CO	$(HCO)^+$		$v_{C\,O}$	2240-2150		

In this method it is possible to delineate the acid strengths of surfaces by the use of basic probe molecules having different pK_b values and also to obtain a semi quantitative idea about Lewis and Brønsted acidity from the integrated intensities of the corresponding sensitive bands in the spectra.

A different method which uses NMR spectroscopy to characterise Lewis and Brønsted acid sites in dealuminated H-zeolites which uses NH_3 as a surface probe was described by Blumenfeld et. al. [22]. The method is founded on the quantitative comparison of the rotational echo double-resonance (REDOR) evolution curves obtained by one pulse and CP excitation as well as the spin –echo editing technique.

OTHER METHODS

Contrarily to base adsorption methods, the surface acidity of solid surface was also determined by temperature programmed desorption of a pre-adsorbed base, in which the rate of desorption of the base is monitored as a function of temperature[24,56,59].

Catalytic test reactions to measure the acidity of catalyst surfaces were also among the methods used [14].

CONCLUSION

Numerous methods have been applied for the determination of the acidity of solid surfaces, yet it seems that most of these methods are somewhat insufficient by themselves to determine the surface acidity of solid surfaces in its every respect.

Of course each method can be used separately or in combination according to the specific information needed about the acidity of solid surfaces as was frequently done in more recent studies[13-15,23].

REFERENCES

[1] Benesi, H. A.; Winquist, B. H. C. *Adv. Catal.,* 1978, 27, 97.
[2] Jacobs, P. A. *Characterization of heterogeneous catalysts,* Ed.: Delannay, F., Dekker, NewYork, 1984.
[3] Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. *New Solid Acids and Bases, Their Catalytic Properties,* Elsevier, Amsterdam, 1989.
[4] *Acidity and basicity of solids: Theory, assessment and utility,* Ed.: Fraissard, J.; Petrakis, L., NATO ASI Series, Kluwer Academic, Dordrecht, 1994.
[5] Corma, A. *Chem. Rev.,* 1995, 95, 559.
[6] Sommer, J.; Jost, R.; Hachoumy, M. *Catal. Today,* 1997, 38, 309.
[7] Zecchina, A.; Lamberti, C.; Bordiga, S. *Catal. Today,* 1998, 41,169.
[8] Deeba, M.; Hall, W. K. *Z. Phys. Chem. Neue Folge,* 1985,144,85.
[9] Cardona-Martinez, N.; Dumesic, J. A. *Adv. Catal.,* 1992, 38, 149.
[10] Solinas, V.; Ferino, I. *Catal. Today,* 1998, 41, 179.
[11] Mishra, T.; Parida, K. *J. Mater. Chem.,* 1997, 7(1), 147.
[12] Morterra, C.; Cerrato, G. *Phys. Chem. Chem. Phys.,* 1999, 1, 2825.
[13] Mortland, M. M.; Raman, K. V. *Clays Clay Miner.,* 1968, 16, 393.
[14] Brown, D. R.; Rhodes, C. N. *Catal. Letters,* 1997, 45, 35.
[15] Parry, E. P. *J. Catal.,* 1963, 2, 371.
[16] Basila, M. R.; Kantner, T. R.; Rhee, K. H. *J. Phys. Chem.,* 1964, 68(11), 3197.
[17] Morimoto, T.; Imai, J.; Nagao, M. *J. Phys. Chem.,* 1974, 78(7), 704.
[18] Miyata, H.; Nakagawa, Y.; Ono, T.; Kubokawa, Y. *J. Chem. Soc., Faraday Trans.1,* 1983, 79, 2343.
[19] Corma, A.; Perez-Pariente, J.; Fornes, V.; Mifsud, A. *Clay Miner.,* 1984, 19, 673.
[20] Miyata, H.; Mukai, T.; Ono, T.; Kubokawa, Y. *J. Chem. Soc., Faraday Trans. 1,* 1988, 84(11), 4137.
[21] Blanco, C.; Herrero,J.; Mendioroz, S.; Pajares, J. A. *Clays clay Miner.,* 1988, 36(4), 364.
[22] Blumenfeld, A. L.; Fripiat, J. J. *J. Phys. Chem. B,* 1997, 101, 6670.
[23] Brown, D. R.; Rhodes, C. N. *Thermochim. Acta,* 1997, 294, 33.
[24] Richter, M.; Parlitz, B.; Eckelt, R.; Fricke, R. *Chem. Commun.* 1997, 383.
[25] Johnson, O. *J. Phys. Chem.,* 1955, 59, 827.
[26] Benesi, H. A. *J. Phys. Chem.,* 1957, 61, 970.
[27] Henmi, T.; Wada, K. *Clay Miner.,* 1974, 10, 231.
[28] Kapoor, B. S. *Clay Miner.,* 1972, 9, 425.

[29] Loeppert Jr., R. H.; Zelazny, L. W.; Volk, B. G. *Soil Sci. Soc. Am. J.,* 1977, 41,

1101.
[30] Guisnet, M. *Catalysis by acids and bases,* Ed.: Imelick, B., Elsevier, Amsterdam, 1985.
[31] Gervasini, A.; Auroux, A. *J. Catal.,* 1990,131,190.
[32] Corma, A.; Garcia, H. *Catal. Today,* 1997, 38, 257.
[33] Benesi, H. A. *J. Am. Chem. Soc.,*1956, 78, 5490.
[34] Walling, C. *J. Am. Chem. Soc.,* 1950, 72, 1164.
[35] Kumar, P.; Jashra, R. V.; Bhat, T. S. G. *Ind. Eng. Chem. Res.,* 1995, 34, 1440.
[36] Frenkel, M. *Clays Cay Miner.,* 1974, 22, 435.
[37] Graham, D. *J. Phys. Chem.,* 1955, 59, 896.
[38] Loeppert, R. H.; Zelazny, L. W.; Volk, B. G. *Clays Clay Miner.,* 1986, 34(1), 87.
[39] Park, S. W.; Huang, C. P. *J. Coll. Interf. Sci.,* 1987, 117(2), 431.
[40] Campelo, J. M.; Garcia, A.; Gutierrez, J. M.; Luna, D.; Marinas, J. M. *J. Coll. Interf. Sci.,* 1983, 95(2), 544.
[41] Parida, K.; Satapathy, P. K.; Sahoo, A. K.; Das, N. *J. Coll. Interf. Sci.,* 1995, 173, 112.
[42] Parida, K.; Mishra, T. *J. Coll. Interf. Sci.,* 1996, 179, 233.
[43] Mishra, T.; Parida, K. *J. Mater. Chem.,* 1997, 7(1), 147.
[44] Ceylan, H.; Sarıkaya, Y. *Tr.J. Chem.* 1989, 13(2),130.
[45] Soled, S. L.; Mc.Vicker, G. B.; Murrell, L. L.; Sherman, L. G., Dispenziere Jr., N. C.; Hsu, S. L.; Waldman, D. *J Catal.* 1988, 111, 286.
[46] Ravichandran, J.; Lakshmanan, C. M.; Sivasankar, B. *React. Kinet. Catal. Lett.,* 1996, 59(2), 301.
[47] Ravichandran, J.; Sivasankar, B. *Clays Clay Miner.,* 1997, 45(6), 854.
[48] Herrero, J.; Pajares, J.; Blanco, C. *Clays Clay Miner.,* 1991, 39(6), 651.
[49] Pesquera, C.; Gonzales, F.; Benito, I.; Blanco, C.; Mendioroz, S. *Spec. Letters,* 1992, 25(1), 23.
[50] Akbaş, A.; Mitzel, H.; Hönice, D. *Tr. J. Chem.,* 1995, 19, 284.
[51] Akbaş, A. *Tr. J. Chem.,* 1995, 19, 211.
[52] Akbaş, A.; Mitzel, H.; Hönice, D. *Tr. J. Chem.,* 1996, 20, 38.
[53] Billingham, J.; Breen, C.; Yarwood, J. *Clay Miner.,* 1996, 31, 513.
[54] Hess, A.; Kemnitz, E. *Applied Catal.: General,* 1997, 149, 373.
[55] Amores, J. M. G.; Escribano, V. S.; Ramis, G.; Busca, G. *Applied Catal. B: Environ.,* 1997, 13, 45.
[56] Kooli, F.; Jones, W. *Clay Miner.,* 1997, 32, 633.
[57] Morterra, C.; Cerrato, G.; Bolis, V.; Di Ciero, S.; Signoretto, M. *J. Chem. Soc. Faraday Trans.,* 1997, 93, 1179.
[58] Yurdakoç, M.; Akçay, M.; Tonbul, Y.; Yurdakoç, K. *Tr. J. Chem.,* 1999, 23, 319.
[59] Biaglow, A. I.; Adamo, A. T.; Kokotailo, G. T.; Gorte, J. *J. Catal.,* 1991, 131, 252.