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SURFACE ACIDITY DETERMINATION OF SEVERAL GAMMA-ALUMINAS USING A THERMOMETRIC METHOD. COMPARISON WITH OTHER METHODS

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ABSTRACT

Surface acidities of different modified gamma-aluminas, often used as supports in the preparation of metallic catalysts, are measured by a thermometric method This technique allows quantification of the acid site content as well as the determination of different types of acid sites, on the solid surface Thermometric determinations with several titrant amines are compared with those obtained from UV-spectrophotometry and indicator titrations The advantages are discussed

INTRODUCTION

It is well known the strong dependence of surface acidity upon the catalytic properties of many inorganic solids [1–3] Nevertheless, the measure of the surface acidity is not always an easy and reliable task, having developed many different methods, up to date Among the most used are titration with amines and indicator adsorption [4,5], electronic spectra of adsorbed Hammett indicators [6], photoacoustic spectroscopy [7], IR spectroscopy [8], etc

The drawbacks in most of the above methods range from the difficulty of titration of coloured samples, when indicators are used in visual methods, to the limited information obtained about types of surface acid sites present on the solid

Recently, a thermometric method was successfully applied in the determination of the acidity index of crude oils and petroleum derivatives [9,10] The thermometric method proved to be more suitable, both for the determination of weak acidities and for non-aqueous media experiments, than other traditional methods such as spectrophotometry, potentiometry, etc Thermometric techniques for titration of the surface acidity of inorganic solids were first introduced by Trambouze et al [11] and developed by Topchieva et al [12] and Tanabe and Yamaguchi [13]

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We report here the quantitative determination of the acid site content of some gamma-alumina samples by means of the thermometric method We compare the results with those obtained from the spectrophotometric [14,15] and Hammett indicator methods

We must emphasize that the acid treatment of a gamma-alumina causes the formation of new surface acid sites of different strengths [14,15] Supports of this type are of interest in the preparation of supported metal catalysts, which influence the final properties of the latter [16]

EXPERIMENTAL

Equipment and reagents

The equipment used for the thermometric titrations is referred to elsewhere [9,10] It consists of a nylon adiabatic cell, a fast response thermistor (of the thermometer type of 100 kΩ at 25 ° C), a conventional stirrer, a recorder and a Radiometer ABU 12 autoburette A double beam Beckman 5260 UV-spectrophotometer was used for the spectrophotometric titrations Standard titration glassware and a shaker were used for the indicator titrations All chemicals were analytical grade Solvents were distilled and dried prior to use

Procedure

Gamma-aluminas were treated as described in the literature [14,15] Samples of gamma-alumina (6 g) were treated either with distilled water at pH = 7 00 (labelled NA) or with a standardized HNO_3 solution by addition of 5 00 mmol H^+ $(g\ Al_2O_3)^{-1}$ (labelled AA5)

Cyclohexane solutions of cyclohexylamine, pyridine, quinoline or benzene solutions of n-butylamine were used as titrants

(a) Thermometric titrations

One gram of the gamma-alumina sample was suspended in 60 ml dried cyclohexane and introduced in a conveniently stirred adiabatic cell Thermal stability and, hence, suspension homogeneity was reached in 10 min, after which the base lines were perfectly horizontal The titrant was added from the autoburette at a constant flow rate of 1 41 ml min^{-1}, upon 60 ml samples The scan rate was 3 cm min^{-1} and the sensitivity, 50 mV, corresponded to 0 02 ° C cm^{-1}

The acidity, A (μmol g^{-1}), of the gamma-aluminas was calculated from

$$A = \frac{DV_b M \times 10^3}{WS_r}$$

where D = distance (cm) from the equivalence point, V_b = burette flow (ml min^{-1}), M = titrant concentration (mol l^{-1}), W = sample weight (g) and S_r = scan rate (cm min^{-1})

(b) Spectrophotometric titrations

As described elsewhere [14,15], the spectrophotometric titrations are based on the addition of a titrant amine solution of low concentration upon a cyclohexane suspension of the solid, following the amine absorption band by UV-spectrophotometry Once adsorption of the titrant remained constant the following assumptions were made (a) the formation of a monolayer of base upon the acid site with pK_a values equal to or lower than that of the base, (b) all of the acid sites are occupied by the titrant By applying the equation of a Langmuir isotherm

$$C/X = 1/(bX_m) + C/X_m$$

where C = concentration of non-adsorbed base in equilibrium with adsorbed base upon solid, X = adsorbed moles of base per gram of solid, X_m = adsorbed moles of base per gram of solid under monolayer conditions and b = constant

(c) Indicator titration

To a suspension of gamma-alumina (0 2 g) in benzene (5 ml), a 0 1 N n-butylamine benzenic solution was added till equilibrium, then indicator (neutral red with $pK_a = 6\ 8$ or p-dimethylaminoazobenzene with $pK_a = 3\ 3$) was added, establishing the end-point by successive approximations, varying the amounts of titrant added Consequently, only the acid site with acid strengths equal or lower than the pK_a of the indicator were titrated [2]

RESULTS AND DISCUSSION

The determination of acid sites in gamma-aluminas, particularly, using indicators and UV-spectrophotometry is known [2,14,15,17] However, the former is considered quantitatively imprecise, and the latter is a tedious procedure because of the large number of samples needed

In order to obviate these drawbacks, we extended the study to the thermometric determination of the acid site content of the NA and AA5 samples of gamma-alumina

When cyclohexylamine is used as a titrant, the values are plotted as ΔT (°C) vs t (time, min) in Fig 1, clearly showing the difference between the non-acid modified (NA) and the acid-modified (AA5) gamma-alumina with a higher content of strong acid sites (higher angle α) in the latter

The existence of sites with different acid strengths in the solid accounts for the curved portion of the plot Nevertheless, we can obtain the titration

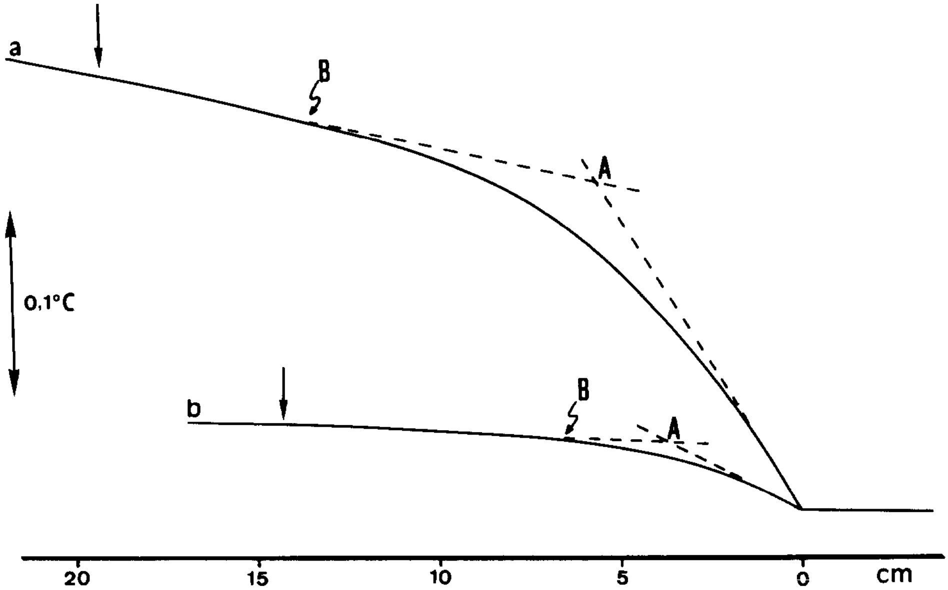

Fig 1 Thermometric titrations of different gamma-aluminas with cyclohexylamine in cyclohexane (burette flow = 1 41 ml min^{-1}, scan rate = 3 cm min^{-1}, sensitivity = 50 mV) (a) 0 8422 g of AA5 sample, (b) 0 9896 g of NA sample The arrow indicates the end of the addition of cyclohexylamine

end-point through intersection of the two straight fragments of the plot, at the beginning and the end of the titration (point A) We must also emphasize the starting point of the second straight portion of the plot (point B), whose thermometric values of acid strengths are fairly coincident with those obtained from the spectrophotometric method (see Table 1)

Thus, points A correspond to values of high acid strengths and points B correspond to total acidities of gamma-aluminas in concordance with the spectrophotometric values, for cyclohexylamine

In order to obtain a more thorough study of the surface acidity of gamma-alumina, we carried out the determination of the acid site content of

TABLE 1

Thermometric titration of surface acidity of some modified gamma-alumina samples (NA, with distilled water pH = 7 00, AA5, with 5 mmol HNO_3 (g Al_2O_3)$^{-1}$) Titrant, 0 1N cyclohexylamine in cyclohexane solution Comparison with other methods

	NA		AA5	
	Point A	Point B	Point A	Point B
Therm method [a]	184 ± 5	284 ± 6	282 ± 4	663 ± 8
Spectr method	–	301	–	698

[a] Mean of three determinations

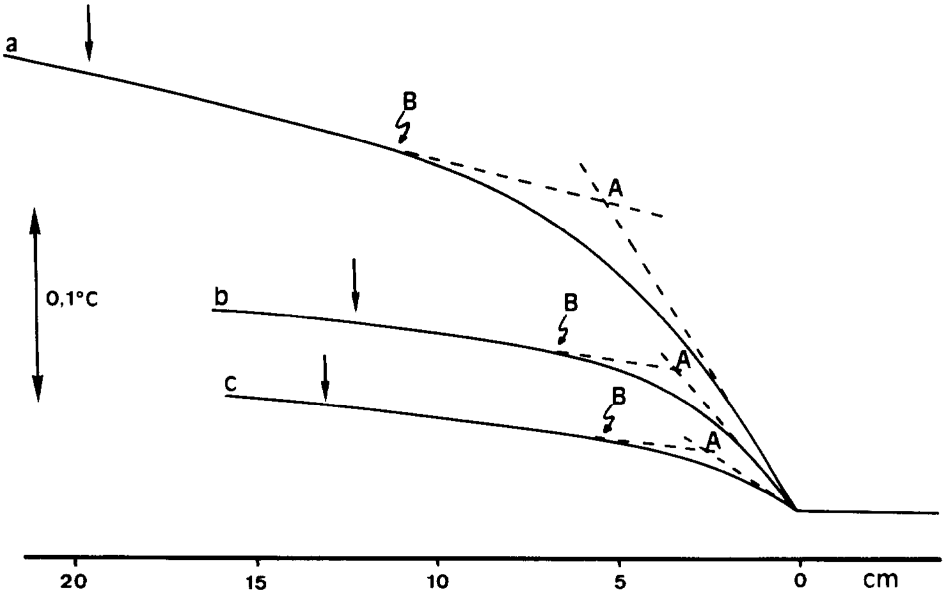

Fig 2 Thermometric titrations of an acid-modified gamma-alumina (AA5) with different bases 0 1 N cyclohexane solution (a) 0 8422 g of AA5 sample with cyclohexylamine, (b) 0 8887 g of AA5 sample with pyridine, (c) 1 0517 g of AA5 sample with quinoline (burette flow = 1 41 ml min^{-1}, scan rate = 3 cm min^{-1}, sensitivity = 50 mV (0 02° C cm^{-1})) The arrow indicates the end of the addition of different bases

the AA5 sample using pyridine and quinoline as titrants Figure 2 shows the titration curves obtained from the three bases used As expected, the values obtained from cyclohexylamine are higher than those obtained from pyridine, which are higher than those from quinoline in concordance with their different sizes and donor strengths

Table 2 shows the results obtained thermometrically compared with those obtained spectrophotometrically [15] for the three amines Again, points B are fairly concordant with those total acidities obtained from the spectrophotometric method Points A correspond to values of higher acid strength for these aluminas

TABLE 2

Thermometric titration of the surface acidity of some modified gamma-alumina samples (see text) Titrants used cyclohexylamine, pyridine, quinoline Comparison with other methods

	Cyclohexylamine		Pyridine		Quinoline	
	A	B	A	B	A	B
Therm method [a]	282 ± 6	664 ± 8	189 ± 4	321 ± 5	131 ± 3	225 ± 4
Spectr method	–	698	–	440	–	309

[a] Mean of three determinations

TABLE 3

n-Butylamine titration of gamma-aluminas acid sites using basic indicators

Solid	Acid site concentration (μmol (g Al_2O_3)$^{-1}$)	Indicator	pK_a
NA	0– 25	Neutral red	6 8
AA5	300–350	p-dimethylaminoazobenzene	3 3

Table 3, shows our results of acid-site titration of the NA and AA5 aluminas using the indicator method [4] As shown in Table 3, this method does not give acidity values, but acidity intervals clearly showing the uncertainty of the indicator method

CONCLUSIONS

The thermometric technique gave us more information about the sites of acid-modified gamma-aluminas than the spectrophotometric and Hammett indicator methods Total acidity values (points B) were in accordance with those from the spectrophotometric method, and new acidity values, corresponding to the strong acid sites (points A) were uniquely obtained by the thermometric technique, giving also a measure of the acid modification of the solid

Other advantages of the method are fast analyses, better precision than indicator methods, and low cost of the equipment

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