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NOTES

Thermometric Titration of Surface Acid Sites of Acid-Modified Silica–Magnesia

The controlled modification of the surface acidity of inorganic solids and its method of determination are subjects of continuing interest in the preparation of support materials and their use as catalysts (*1–4*). Thus, suitable acid treatments of an inorganic solid may bring about the formation of new surface acid sites of different acid strengths (*5, 6*). Many methods and techniques have been used for quantifying and determining the nature and strength of the surface acid sites. These include spectrophotometric methods for the determination of adsorbed bases and the use of indicators (*7, 8*). Calorimetric techniques for the determination of surface acidity were developed by Trambouze *et al.* (*9*), who measured the total heat released in the titration of the solid with an organic base as the sum of the partial heats obtained from the addition of small constant amounts of titrant.

The thermometric method has been successfully applied in the determination of the acidity index of crude oils and petroleum derivatives (*10, 11*), and the method is suitable for the determination of weak acidities in nonaqueous media. Recently, we have optimized the conditions for determining the surface acidity of inorganic solids by thermometric techniques in the continuous titration mode, using thermistors and a constant titrating flow of base. We have determined by this method the acid site content of several acid-modified γ-Al_2O_3 samples, and the results were compared with those obtained by a spectrophotometric method and using Hammett indicators (*12*). We report here results obtained from the characterization of the surface acid sites of several acid-modified silica–magnesia samples by means of the thermometric method.

Amorphous silica–magnesia was prepared by the cogelling at room temperature of 1 *M* magnesium nitrate (R. A. Merck; 200 cm^3) and 1.6 *M* sodium silicate (R. A. Panreac; 500 cm^3) aqueous solutions. After an aging period of 3 days the solid obtained was filtered, washed with bidistilled water, and calcined in air at 673 K for 16 h. Prior to use samples were dried under vacuum at 393 K for 16 h. Several dry samples were treated with different standardized HNO_3 solutions as reported elsewhere (*5*). Suspensions obtained were filtered, washed with bidistilled water, and dried under vacuum at 393 K for 16 h, prior to thermometric titrations. The samples were labeled NSiMg, when silica–magnesia was treated with neutral bidistilled water, and ASiMgx when silica–magnesia was treated with an aqueous HNO_3 solution containing x mmole $H^+ \cdot g^{-1}$ solid (SiMg).

Cyclohexane (R. A. Merck), cyclohexylamine (Scharlau), and pyridine (R. A. Merck) were distilled and stored with molecular sieves under dry argon.

The equipment for thermometric titrations is described in the literature (*13, 14*). It consists of a nylon adiabatic titration cell, a rapid response thermistor of the thermometer type with a nominal resistence value of 100 kΩ at 298 K, a very efficient stirring system, a very stable source, an autoburette Radiometer ABU 12, and a recorder.

We have optimized several variables which affect the thermometric titrations.

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(a) The amount of sample to be titrated should be in the range 0.5–1 g, in order to obtain a suitable suspension and an effective titration of acid centers.

(b) The titrant concentration should be in the range 0.3–0.7 *M* in order to obtain detectable and well-defined slope changes for the thermometric curves and for preventing undesirable errors in the endpoint determination.

(c) The titrant flow rate, the sensitivity, and the recording rate also need to be controlled.

On the basis of (a), (b), and (c) above, the optimum conditions for the thermometric determinations were defined as follows. Each sample (0.8 g) was suspended in 70 cm^3 of cyclohexane. Once the homogeneity and thermal stability were reached in the well-stirred cell, the titrant (0.5 *M*) was added by means of an autoburette at a constant flow rate of 0.28 $cm^3 \cdot min^{-1}$. The thermometric curve was recorded at 2 cm · min^{-1} and at a sensitivity of 50 mV, corresponding to 0.02 K · cm^{-1}.

The acid site contents of the silica–magnesia samples NSiMg, ASiMg0.1, ASiMg0.3, ASiMg0.5, and ASiMg1 were determined from the thermometric curves obtained by titrating the samples with cyclohexylamine and pyridine as stated in the previous paragraph.

Figure 1 shows the thermometric curves from the titration of NSiMg samples with cyclohexylamine and pyridine. When cyclohexylamine is used a a titrant (curve M of Fig. 1) we can see two well-defined portions of the curve, evidencing the existence of two types of acid sites with different acid strengths. The first straight portion of the curve (tan α = 1.6) leads to an inflection point A, which is the first titration endpoint and corresponds to the site titration of higher acid strength. The second portion of the curve, which starts at A, is characterized by slower kinetics, so the second endpoint B is determined by extrapolation and corresponds to the site titration of weaker acid strength (tan β = 1.3) (*15, 16*). Finally, when the titrant addition is stopped (indi-

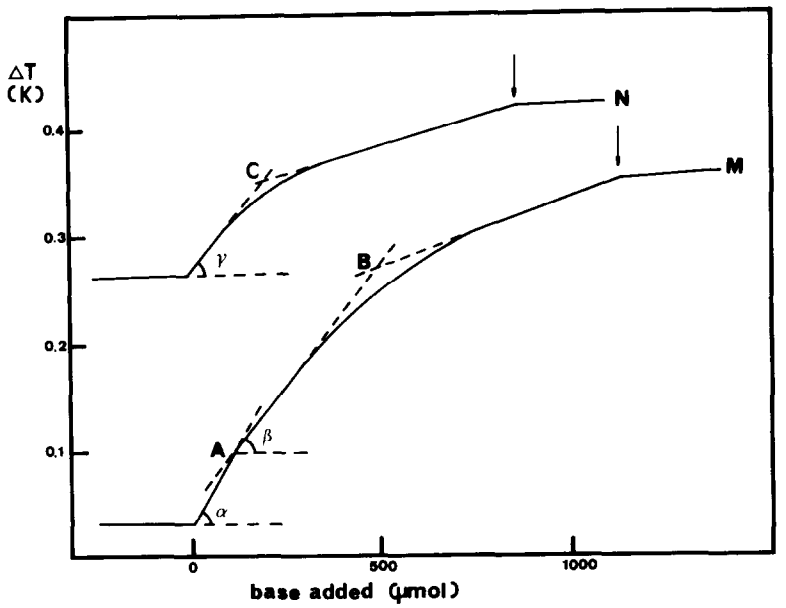

FIG. 1. Thermometric plots of ΔT (K) versus a linear function of the amounts of cyclohexylamine (M) and pyridine (N), added as titrant, upon NSiMg samples. (The arrow indicates the end of the titrant addition.)

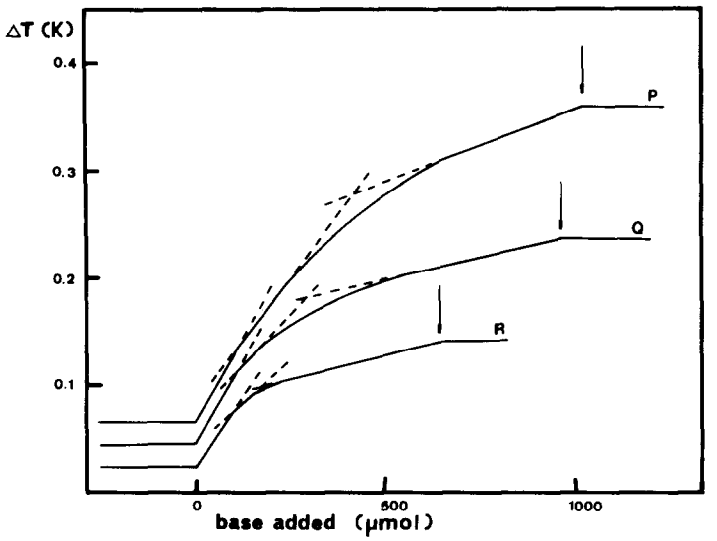

FIG. 2. Thermometric plots of ΔT (K) versus a linear function of the amounts of cyclohexylamine added as a titrant upon several ASiMgx samples. P (x = 0.1), Q (x = 0.3), R (x = 0.5). The arrow indicates the end of the titrant addition.)

cated by the arrow) a good thermal stability is again reached in the system (final straight portion). When pyridine is used as a titrant (curve N of Fig. 1), the thermometric curves show only one titrating zone, with an endpoint C, corresponding to the titration of stronger acid sites, in accord with the smaller pK_a value of pyridine (5.25) versus that of cyclohexylamine (10.6).

All thermometric curves for the acid-modified samples using cyclohexylamine as a titrant (Fig. 2, curves P, Q, R) are of the type of the NSiMg curve (curve M, Fig. 1), and from them one can see the differences between the acid-modified and nonmodified silica–magnesia samples.

Table 1 compiles the results obtained according to their different acid strengths for the different samples and titrating amines. it must be pointed out that acid pretreatments less than 0.3 mmole $H^+ \cdot g^{-1}$SiMg bring about an increase in the number of stronger acid sites, when compared to the NSiMg samples, as shown by the first portion of the thermometric curves, with both cyclohexylamine (tan α = 1.6) and pyridine (tan γ = 1). As far as the weaker acid sites ($0.9 \leq \tan \beta \leq 1.3$) are concerned, a slight decrease in their number is observed for acid pretreatments up to 0.3 mmole $H^+ \cdot g^{-1}$SiMg, and a dramatic decrease in the number of acid sites is found for higher acid pretreatments.

We should emphasize that when using either cyclohexylamine or pyridine as titrant the values of tan α and tan γ assigned to the titration of stronger acid sites remain almost unchanged. Conversely, the values of

TABLE 1

Determination of Surface Acid Sites of Acid-Modified Silica–Magnesia Samples

Sample	Titrant					
	Cyclohexylamine acid sites (μmole · g^{-1})				Pyridine acid sites (μmole · g^{-1})	
	Strong (tan α)		Weak (tan β)		Strong (tan γ)	
NSiMg	97	(1.6)	600	(1.3)	140	(1)
ASiMg0.1	147	(1.6)	588	(1.3)	175	(1)
ASiMg0.3	155	(1.6)	571	(1.1)	175	(1)
ASiMg0.5	124	(1.5)	172	(0.9)	134	(1)
ASiMg1	—	—	160	(0.6)	—	—

Note. All values are the means of three determinations.

tan β assigned to the titration of weaker acid sites change significantly for acid treatments ≥ 0.3 mmole $H^+ \cdot g^{-1}$SiMg, denoting the weaker acid sites having a higher sensitivity to the acid pretreatment. More markedly, the results obtained for a ASiMg1 sample show that acid pretreatments higher than 0.5 mmole $H^+ \cdot g^{-1}$SiMg drastically decrease the number of acid sites.

We conclude that the thermometric technique used in this work for the titration of silica–magnesia acid sites allows the differentiation and quantification of two types of acid sites. Also, acid pretreatment of the samples shows an increase in the stronger acid sites and a slow decrease in the weaker ones for small amounts of H^+ added (<0.5 mmole $H^+ \cdot g^{-1}$ SiMg). However, the two types of acid sites progressively vanish when higher acid pretreatments (≥ 0.5 mmole $H^+ \cdot g^{-1}$SiMg) are carried out, probably by removing surface magnesium cations; in this situation only a few acid sites of weak type should remain on the surface.

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N. HOMS
P. RAMIREZ DE LA PISCINA
F. BORRULL
J. E. SUEIRAS

Departament de Química
Facultat de Ciències Químiques
Universitat de Barcelona
Plaça Imperial Tarraco No. 1, 43005 Tarragona, Spain

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