

SURFACE BASICITY MODIFICATION OF γ -ALUMINA: STUDY BY THERMOMETRIC TITRATION

P. RAMÍREZ DE LA PISCINA *, N. HOMS and F. BORRULL

*Departament de Química, Facultat de Ciències Químiques de Tarragona,
Universitat de Barcelona, Pça. Imperial Tarraco no 1, 43005 Tarragona (Spain)*

(Received 30 March 1988)

ABSTRACT

Surface basicities of various modified γ -aluminas, used as supports in the preparation of metallic catalysts, were measured by a thermometric method. This technique allows the quantification of the modification of basic sites of γ -Al₂O₃ after pretreatment with KOH or HNO₃. For γ -Al₂O₃ pretreated with KOH a change occurred in the characteristics and number of the weaker basic centres, while the stronger basic centres remained unchanged. Some surface basic centres remained in γ -Al₂O₃ pretreated with HNO₃.

INTRODUCTION

Solid acids and bases are extensively used as catalysts or catalyst carriers, and the determination and controlled modification of their surface acidic or basic properties are subjects of continuous interest [1–5]. The determination of basic centres has been described much less frequently than the titration of acidic sites. The study of solid base catalysts has been concerned with the interpretation of their catalytic action in several processes [6–8]. The study of acid–base bifunctional catalysts and, consequently, the simultaneous estimation of their acidic and basic centres is a very interesting subject [3].

In previous investigations we have reported that a suitable acid treatment of inorganic solids may bring about the formation of new surface acid sites of various acid strengths [9,10]. Recently, we have optimized the conditions for thermometric titration of the surface acidity of several acid-modified γ -Al₂O₃ and silica–magnesia samples [11,12]. The thermometric method has successfully been applied in the simultaneous determination of the acidity and basicity indices of crude oil and petroleum derivatives [13,14].

In this paper we report the modification of the surface basic sites of several samples of γ -Al₂O₃ by basic treatment. A quantitative determination

* Author to whom correspondence should be addressed.

of the concentration of basic sites has been achieved using the thermometric method. The concentration of basic sites in several acid-modified γ - Al_2O_3 samples is also discussed.

EXPERIMENTAL

Equipment and reagents

The equipment used for the thermometric titration has been described previously [15]. It consists of a nylon adiabatic cell, a fast response thermistor of the thermometer type with a nominal resistance value of 100 k Ω at 298 K, a very efficient stirrer and a burette entrance to add the titrant. The equipment is completed with an autoburette Radiometer ABU 12, a recorder and a Wheatstone bridge. The e.m.f. for the Wheatstone bridge is supplied by a 9.45 V stabilized source. This temperature monitoring system is a modification of the apparatus of Lumbarres et al. [16].

A stock standard solution of 0.25 M benzoic acid in toluene was prepared as titrant.

Modified γ - Al_2O_3 samples were prepared from Girdler γ - Al_2O_3 with a BET surface area of 188 m² g⁻¹ and a pore volume of 0.39 cm³ g⁻¹.

All the chemicals were of analytical grade and the solvents were distilled and stored with molecular sieves under dry argon.

Procedure

γ - Al_2O_3 samples (4.5 g) were treated with distilled water (60 cm³) at pH 7 for the neutral alumina (NA) sample or with standardized solutions of KOH (60 cm³) at various concentrations for the basic alumina (BA $_x$) samples, where x is the number of mmoles of OH⁻ added to the solution per gram of solid. Suspensions were stirred for 12 h at room temperature, filtered, washed with distilled water and dried in vacuum at 393 K for 16 h prior to thermometric titration.

Acid-modified γ - Al_2O_3 samples (AA $_x$, where x is the number of mmoles of H⁺ per gram of γ - Al_2O_3 added in the pretreatment) were prepared as reported elsewhere [9].

γ - Al_2O_3 samples (about 0.7 g) were suspended in 70 cm³ of toluene and were introduced into the adiabatic titration cell. Once homogeneity and thermal stability had been reached, the titrant was added from the autoburette at a constant flow of 0.575 cm³ min⁻¹. The thermometric curve was registered at 2 cm min⁻¹ and a sensitivity of 50 mV, corresponding to 0.02 K cm⁻¹.

RESULTS AND DISCUSSION

The concentrations of the surface basic sites of the following pretreated γ - Al_2O_3 samples, NA, BA0.25, BA1, BA5, AA0.5, AA2.5 and AA5, were determined from the thermometric curves obtained by titrating the samples with benzoic acid solution as stated in the experimental section.

Figure 1 shows the thermometric curve from titration of the NA sample. Two perfectly defined inflection points (A and C) can be seen, which divide the curve into three portions. The first straight portion OA, corresponding to the titration of basic centres with a higher basic strength, finishes with a well-defined inflection point A. The second zone of the titration curve (AC) corresponds to the titration of the weaker basic centres. The third portion of the curve (CD) corresponds to the endothermic dilution between the benzoic acid and the solvent, and the arrow indicates the end of titrant addition. Thus point B, obtained by extrapolation of the two straight portions on the AD curve, should correspond to the second titration end-point [17].

Figure 2 shows the thermometric curves corresponding to the titration with benzoic acid of BA0.25, BA1 and BA5 γ - Al_2O_3 samples. These curves are similar to that obtained for the NA sample. For the basic-modified γ - Al_2O_3 samples, stronger and weaker basic sites are also present on the surface and their concentrations are determined from the thermometric curves by the A and B end-points, respectively. Nevertheless, the weaker basic sites of the BA $_x$ samples behave differently to those of the NA sample (a less exothermic reaction was obtained in the titration of these basic centres).

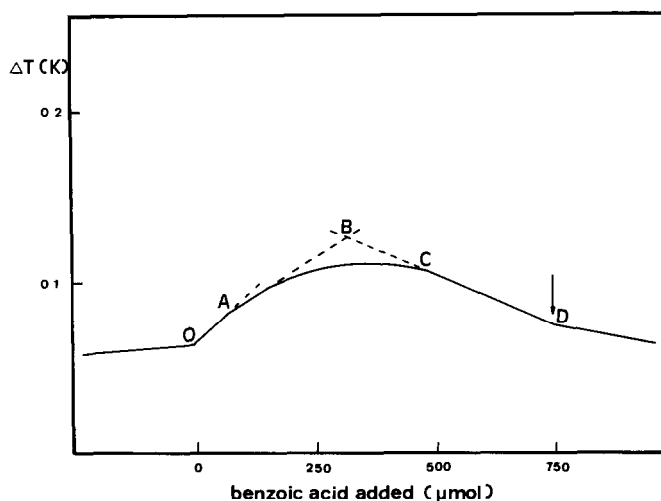


Fig. 1. Thermometric curve of the titration of neutral γ -alumina with benzoic acid (0.25 N) in toluene medium. The arrow indicates the end of titrant addition.

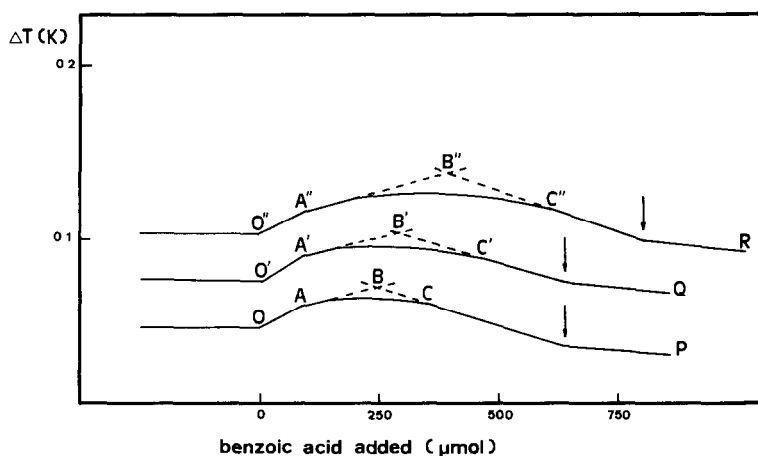


Fig. 2. Thermometric curves of the titration of several basic-modified γ -aluminas with benzoic acid in toluene medium. The arrow indicates the end of titrant addition. P, BA0.25; Q, BA1; R, BA5.

The concentrations of basic centres obtained for the NA and BA x samples are shown in Table 1. We also considered point C as an alternative second thermometric end-point, because it is a very well-defined inflection point, and the error in its determination is smaller than that in the determination of point B. In addition, C values showed a parallel behaviour to B values for NA and BA x samples. Thus, for present purposes, point C is a measure of the total number of weaker basic sites, including those determined previously from point B.

From Fig. 2 and the results in Table 1 we can see that the proposed basic treatment of γ -Al $_2$ O $_3$ does not modify the first portion of the curves, corresponding to the titration of stronger basic centres, and their number remains unchanged. The second portion is progressively affected by this basic treatment; therefore the basic modification mainly affects the weaker basic centres, increasing their number when x is increased for the BA x

TABLE 1

Determination of the concentration of basic centres in several basic-modified γ -aluminas ($\mu\text{mol g}^{-1}$)

Sample	Strong basic sites	Weak basic sites	
	From point A	From point B	From point C
NA	103 \pm 6	300 \pm 15	550 \pm 10
BA0.25	106 \pm 8	212 \pm 14	300 \pm 9
BA1	112 \pm 8	295 \pm 20	480 \pm 9
BA5	111 \pm 10	379 \pm 19	660 \pm 11

Mean of three determinations.

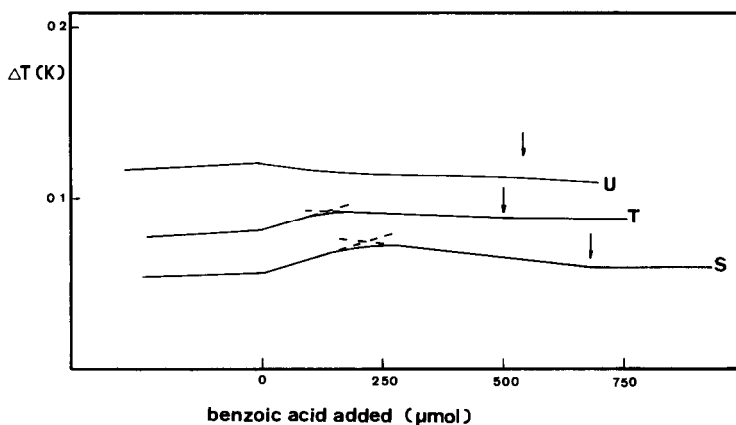


Fig. 3. Thermometric curves of the titration of several acid-modified γ -aluminas with benzoic acid in toluene medium. The arrow indicates the end of titrant addition. S, AA0.5 (0.6488 g); T, AA2.5 (0.7924 g); U, AA5 (0.4678 g).

samples.

Determinations of the number of basic sites of several acid-modified γ - Al_2O_3 samples were also carried out. In Fig. 3 the thermometric curves for AA0.5, AA2.5 and AA5 samples, with benzoic acid as titrant, show only a slight exothermic reaction. In this case the titration end-point is determined by extrapolation with a high experimental error. Nevertheless, it can be seen that these acid pretreated γ -alumina samples have a relatively important surface basicity, which decreases as expected with increasing x in the AA x samples. Acid-modified γ - Al_2O_3 can be regarded as an acid–basic bifunctional solid and its possibilities as a bifunctional catalyst must be explored. It has been used as a very appropriate support in the preparation of metal catalysts from coordination compounds, where it influences the surface characteristics of the active phase and thus its catalytic activities in the ammonia synthesis of iron or ruthenium catalysts [18,19].

The thermometric method is a reliable technique which allows the accurate determination (by simple procedures) of acid [11,12] and basic sites on inorganic solids. Work is in progress to optimize the experimental conditions for surface basicity determination of acid-modified samples.

REFERENCES

- 1 K. Tanabe, *Solid Acids and Bases*, Academic Press, New York, 1970.
- 2 H.A. Benesi and B.H.C. Winquist, *Adv. Catal.*, 27 (1978) 97.
- 3 K. Tanabe, in J.R. Anderson and M. Boudard (Eds.), *Catalysis, Science and Technology*, Vol. 2, Springer-Verlag, Berlin, 1981, Chapter 5.
- 4 K. Jiráťová and L. Beránek, *Appl. Catal.*, 2 (1982) 125.

- 5 E.A. Paukshtis and E.N. Yurchenko, *Russ. Chem. Rev.*, 52 (1983) 242.
- 6 H.P. Boehm and H. Knözinger, in J.R. Anderson and M. Boudard (Eds.), *Catalysis, Science and Technology*, Vol. 4, Springer-Verlag, Berlin, 1983, Chapter 2.
- 7 L. Mondek and Z. Vit, *Appl. Catal.*, 2 (1982) 269.
- 8 Z. Vit, J. Vala and J. Málek, *Appl. Catal.*, 7 (1983) 159.
- 9 N. Homs, P. Ramírez de la Piscina and J.E. Sueiras, *J. Catal.*, 89 (1984) 531.
- 10 N. Homs, P. Ramírez de la Piscina, J.L.G. Fierro and J.E. Sueiras, *Z. Anorg. Allg. Chem.*, 518 (1984) 227.
- 11 F. Borrull, N. Homs and P. Ramírez de la Piscina, *Thermochim. Acta*, 127 (1988) 355.
- 12 N. Homs, P. Ramírez de la Piscina, F. Borrull and J.E. Sueiras, *J. Catal.*, 111 (1988) 227.
- 13 F. Borrull, V. Cerdà, J. Guasch and J. Torres, *Thermochim. Acta*, 98 (1986) 9.
- 14 F. Borrull, V. Cerdà, J. Guasch and J. Torres, *Thermochim. Acta*, 98 (1986) 1.
- 15 J. Lumbarres, C. Mongay and V. Cerdà, *Analisis*, 8 (1980) 62.
- 16 J. Lumbarres, C. Mongay and V. Cerdà, *J. Therm. Anal.*, 22 (1985) 275.
- 17 D. Rosenthal, J.L. Jones, Jr. and R. Megargle, *Anal. Chim. Acta*, 53 (1971) 141.
- 18 J.E. Sueiras, N. Homs, P. Ramírez de la Piscina, M. Gracia and J.L.G. Fierro, *J. Catal.*, 98 (1986) 264.
- 19 P. Ramírez de la Piscina, N. Homs, J.L.G. Fierro and J.E. Sueiras, *Z. Anorg. Allg. Chem.*, 528 (1985) 195.