THERMOMETRIC TITRIMETRIC DETERMINATION OF REACTIVITY WITH ACIDS AND BASES BY SMELTER GRADE ALUMINA

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Abstract

Novel procedures for the thermometric titrimetric determination of the reactivity with acids and bases by smelter grade alumina are proposed as an adjunct to the traditional BET method for determining specific surface area, an important parameter for evaluating the suitability of the product for use in modern aluminium smelters. The information derived from these new methods is intended to provide workers in the field with additional insight into the chemisorptive performance of smelter grade aluminas in absorbing exhaust gases from the smelting process. Both determinations are conducted in anhydrous, non-aqueous media. The determination of acid reactivity is performed by back-titration of an excess of n-butylamine after reaction of the test alumina, with methanesulfonic acid as titrant. Similarly, reactivity with bases is determined by back-titration of an excess of methanesulfonic acid, using n-butylamine as titrant. Samples of alumina from three different alumina refineries were tested. The BET specific surface areas of the alumina samples under test ranged from 37 to 98 m^2/g, with corresponding acid reactivity ranging from 0.05 to 0.15 mmol/g and reactivity with bases ranging from 0.49 to 0.94 mmol/g. The procedures are robust and reliable, and suitable for routine quality control purposes. The thermometric sensor requires no conditioning, calibration or maintenance.

1. Introduction

Modern alumina smelters are designed to emit very low amounts of particulates and gaseous fluorides. This is accomplished by directing the stream of incoming alumina feedstock counter-current to the exhaust from the smelter pots in very sophisticated, highly efficient "dry scrubbing" units. In order to maximize absorption efficiency, it is important that smelter grade alumina is manufactured with a high specific surface area. The BET surface area method (Brunauer, Emmett and Teller, 1938)[1] is the most widely used and accepted method for determining the specific surface area of smelter grade alumina. The BET procedure measures the adsorption of a mono-molecular layer of a gas (nitrogen), on the principle that one molecule of gas will absorb per active site on the solid. A number of companies manufacture semi-automated equipment which can determine BET surface area on a number of samples at a time. The equipment requires extensive infrastructure in the form of a supply of dry, high purity nitrogen, storage and supply of liquid nitrogen to cool the sample, and vacuum pumps to assist in sweeping the alumina surfaces free of impurities before the determination can commence. It is also demanding of skilled attention and maintenance.

A disadvantage of the BET method is that it reveals little of the chemical nature of the adsorbing sites. The surfaces of smelter grade aluminas contain both acidic and basic sites, which can be expected to offer differing chemical affinities to the gaseous and particulate species present in the smelter exhaust. The chemical nature of alumina surfaces has been of interest to many workers over the years, principally due to the utility of active aluminas in the field of catalysis.

Titration techniques have been used for many years to yield information concerning acidic and basic sites on various surface active solids. Initially, manual titrations using special adsorptive indicators ("Hammett indicators") were devised, but the technique remains controversial due to the interaction of the indicator with the solid surface. Thermometric titrations have also been used since the 1950's, and have yielded interesting results, particularly regarding the relative strength of acidic sites (Sadtler, et al.1991)[2]. However, slow absorption kinetics can lead to poor endpoints and results that are ill-suited for process control purposes.

It was considered that a simple back-titration technique could lead to reproducible results being obtained for the determination of total acidic and basic sites on aluminas, and the results might be considered in conjunction with those yielded from BET analysis to provide more insight into the absorptive capacity of smelter grade aluminas.

2. Experimental

2.1 Apparatus

Thermometric titration system, 859 Titrotherm, Metrohm, Switzerland, comprising

- interface module 859 Titrotherm,
- thermometric sensor Thermoprobe
- 2 x10mL 800 Dosino automatic burettes
- 802 Propeller Stirrer and 804 Titration Stand
- titration vessels 10-90mL
- *tiamo*™ titration software

2.2 Volumetric glassware:

- bulb pipettes, 5mL, 10mL, 15mL, 25mL, 30mL, 50mL capacity

2.3 Reagents:

- toluene, A.R. >0.05% H_2O
- 2-propanol, A.R. >0.05%
- 0.1 mol/L n-butylamine. Dispense 10mL 99.5% n-butylamine (e.g., Aldrich cat. no. 471305, FW=73.08914) into a dry 1000mL volumetric flask, and make to volume with dry toluene.
- 0.1 mol/L methanesulfonic acid. Weigh accurately approximately 9.6g 99.5+% methanesulfonic acid (e.g., Aldrich cat. no. 471356, FW=95.98812) into a dry 1000mL volumetric flask, and make to volume with in 95% toluene, 5% 2-propanol by volume

2.4 Titration system preparation:

Prepare one automatic burette each with 0.1 mol/L n-butylamine and 0.1 mol/L methanesulfonic acid. Protect the 0.1 mol/L n-butylamine solution from carbon dioxide and moisture ingress with a combination soda-lime/3A molecular sieve guard tube. Protect the 0.1 mol/L methanesulfonic acid acid solution with a 3A molecular sieve guard tube.

2.5 Alumina Samples:

Sample of smelter grade alumina were obtained from three Australian alumina refineries. All samples were treated prior to titration by drying in small glass containers at 200ºC for eight hours. After removal from the oven, the containers were immediately tightly capped and allowed to cool prior to weighing. Representative sub-samples were submitted to Rio Tinto Alcan Gove for specific surface area measurement by BET and determination of the sodium content.

2.6 Method:

2.6.1 Standardization of 0.1 mol/L methanesulfonic acid solution.

For the purpose of the exercise, the stated purity of the n-butylamine was used to calculate the strength of the diluted solution. The strength of the methanesulfonic acid solution was determined by employing an automated titration program. In this program, dispensed volumes of 1, 2, 3, 4 and 4.5mL 0.1 mol/L n-butylamine were titrated with 0.1 mol/L methanesulfonic acid acid in 30mL toluene. The amounts of n-butylamine dispensed (in mmol) were plotted against mL of methanesulfonic acid solution titrated, and the molarity of the methanesulfonic acid solution calculated from the gradient of the line of best fit.

2.6.2 Blank determinations.

The blank determination for basic sites on alumina was commenced by preparing a titration   vessel with 25mL toluene. Using an automated titration program, 5mL 0.1mol/L methanesulfonic acid was dispensed and titrated with 0.1 mol/L n-butylamine. The titration was performed in triplicate, and the mean value stored for calculations. Similarly, a blank determination for acidic sites was performed by titrating a 5mL aliquot of 0.1 mol/L n-butylamine with 0.1mol/L methanesulfonic acid. The blank determinations are made each time new batches of titrant are made up.

2.6.3 Determination of basic sites.

Approximately 1g of alumina was weighed accurately into a freshly oven dried glass bottle of 150-200mL capacity. 75mL of toluene was pipetted into the bottle, followed by 15mL of 0.1 mol/L methanesulfonic acid in 95% toluene, 5% 2-propanol. Add a small magnetic stirrer follower, cap the bottle tightly, and stir gently for 30 minutes on a magnetic stirrer. Allow the suspended solids to settle, and transfer 30mL of solution to a titration vessel. Back-titrate according to an automated program with 0.1 mol/L n-butylamine in toluene to a single exothermic endpoint at a titrant dose rate of 4mL/min. The basic sites are determined as mmol/g alumina by subtracting the back titration volume from the blank volume.

2.6.4 Determination of acidic sites.

Approximately 5g of alumina was weighed accurately into a freshly oven dried glass bottle of 150-200mL capacity. 75mL of toluene was pipetted into the bottle, followed by 15mL of 0.1 mol/L n-butylamine in toluene. Add a small magnetic stirrer follower, cap the bottle tightly, and stir gently for 30 minutes on a magnetic stirrer. Allow the suspended solids to settle, and transfer 30mL of solution to a titration vessel. Back-titrate according to an automated program with 0.1 mol/L methanesulfonic acid to a single exothermic endpoint at a titrant dose rate of 4mL/min. The acidic sites are determined as mmol/g alumina by subtracting the back titration volume from the blank volume.

3. Results and discussion

3.1 Analysis of alumina samples.

Table 1. Determination of acidic and basic sites on smelter grade alumina.

Sample no.	Acidic sites, mmol/g	Basic sites, mmol/g	Specific surface area (BET) m²/g*	Na₂O content % w/w*
1	0.152, 0.155 Av. 0.154	0.942, 0.944 Av. 0.943	98.5	0.38
2	0.052, 0.054 Av. 0.053	0.487, 0.485 Av. 0.486	37.0	0.39
3	0.118, 0.119 Av. 0.119	0.617, 0.602 Av. 0.609	64.7	0.26
4	0.117, 0.118 Av. 0.117	0.732, 0.746 Av. 0.736	71.1	0.32
5	0.106, 0.108 Av. 0.107	0.809, 0.821 Av. 0.815	68.2	0.43
6	0.142, 0.143 Av. 0.143	0.814, 0.823 Av. 0.818	73.0	0.36
7	0.144, 0.145 Av. 0.144	0.799**	74.0	0.37
8	0.142, 0.144 Av. 0.144	0.783, 0.812 Av. 0.798	73.0	0.36

* analyzed by Rio Tinto Alcan, Gove Alumina Refinery
** duplicate determination failed due to operator error

Duplicate analysis for acidic and basic sites showed the titrations to be reasonably reproducible. The titrations usually take less than a minute to complete, although the 20 minute equilibration time has to be factored in to the total time for the analysis. It should be noted that the equilibration time has not been optimized, with a time of 20 minutes being regarded as highly conservative. Further work could lead to a considerable shortening of the total analysis time.

It will be noted that in all samples, the analysis values acidic sites are much less than those obtained for basic sites. Possible reasons for this could be the blocking of the opening of pores by the n-butylamine molecule (A.K. Ghosh, G. Curthoys, 1983)[3], the nature of the surface structure of the transition aluminas which comprise smelter grade alumina, or the presence of sodium. In this last named instance, sodium is possibly in the form of basic sodium aluminate or similar phases within the alumina matrix and could hence positively bias the apparent magnitude of basic sites. However, there appears to be no obvious correlation between the sodium content of the alumina and the analyzed values for the basic sites.

Approximate correlations between the measured acidic and basic sites and BET specific surface area can be demonstrated, and are illustrated in Figures 1 and 2.
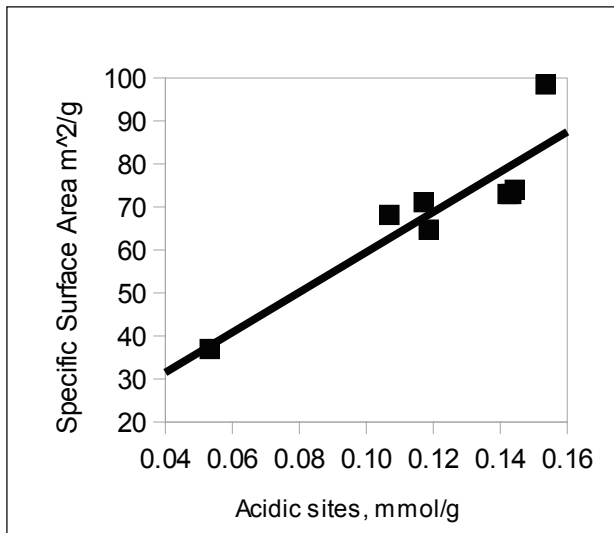
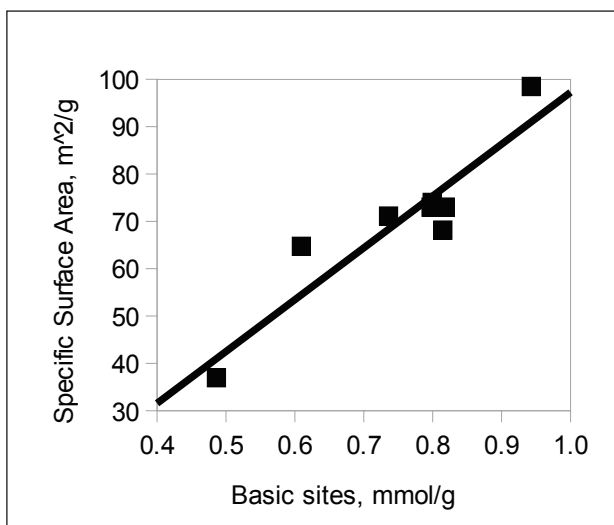Fig. 1. Acidic sites versus BET surface area

Fig. 2. Basic sites versus BET surface area

It should be noted that the samples analyzed were obtained from a number of alumina refineries. Processing conditions including calcination may be assumed to be different, as may have individual conditions of storage and age. Changes in the surface properties of transition aluminas due to rehydroxylation caused by the presence of water vapour can occur (Wefers and Misra, 1987)[4]. The laboratory oven used to dry the alumina samples used in these experiments has a maximum temperature limit of 200ºC, insufficient to obtain a dehydroxylation to a level expected in a freshly calcined alumina. Due to the high affinity of smelter grade alumina for water vapour, some surface change to the samples with age and atmospheric exposure is inevitable.

It is possible that on-site studies using freshly calcined alumina might yield different results to those presented here, and a better correlation between acidic or basic sites and BET surface area could result, especially if the range of samples was restricted to the produce of a single refinery.

It is not suggested at this stage that determination of acidic and basic sites could or should supplant the determination of BET surface area as a routine procedure for evaluation of smelter grade aluminas. The purpose of this work principally has been to demonstrate that relatively simple procedures with modest equipment requirements can yield interesting results which can add to analyses from existing methods to give increased insight into the surface properties of the alumina. A thermometric titration system to analyse both acidic and basic sites on smelter

grade alumina by the methods described here has a modest bench footprint of approximately 300mm x 300mm, is robust and reliable, and has no infrastructure requirements other than a source of electric power. The thermometric sensor requires no calibration or maintenance.

Unlike direct titration of alumina surfaces, thermometric back-titrations yield sharp, reproducible endpoints. Figures 3 and 4 illustrate thermometric titration plots for the back-titrations in the determination of acidic and basic sites respectively. The solid lines represent the solution temperature as a function of added titrant. The reaction of n-butylamine with methanesulfonic acid is exothermic, and the temperature rises until no more analyte remains, at which point a break in the curve occurs as cooling of the solution commences due to environmental influences. The titration takes place in uninsulated glass vessels. The broken line represents the second derivative of the temperature curve, and is used to precisely determine the endpoint of the titration. Because the endpoint is determined from the rate of change of temperature, an accurate indication of temperature is unnecessary. This makes the technique particularly suitable for routine analytical applications.
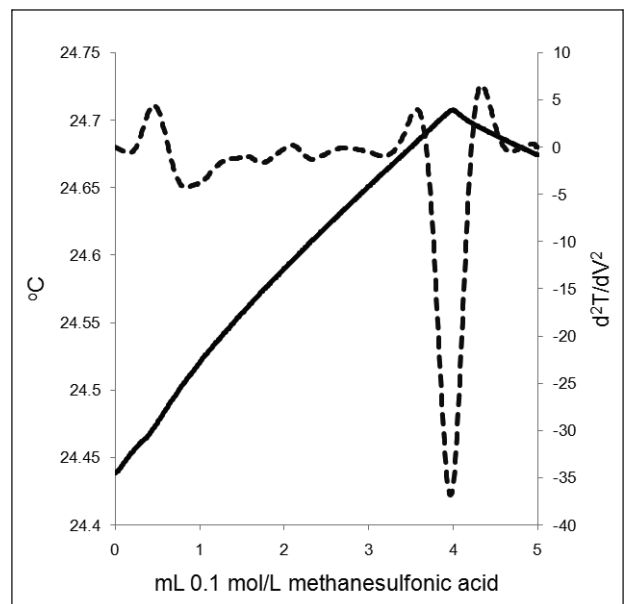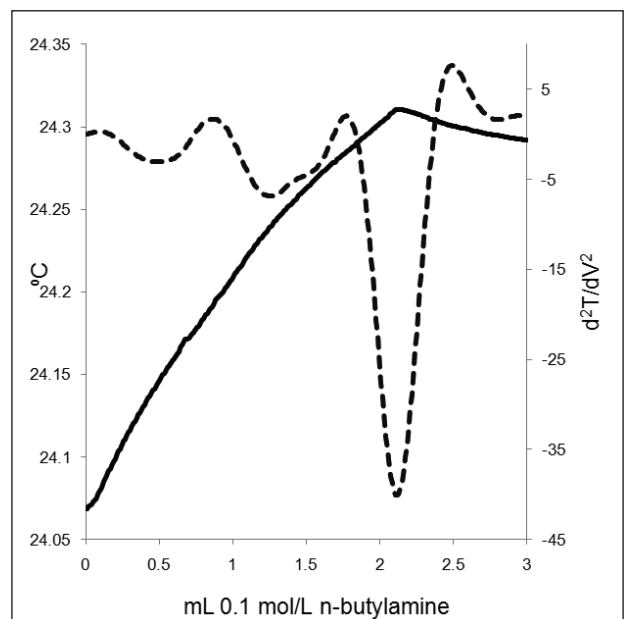

Fig. 3. Back-titration plot for acidic sites .

Fig. 4. Back-titration plot for basic sites

4. Conclusions

A simple, robust and reliable technique for the determination of acidic and basic sites on smelter grade alumina has been demonstrated. The technique is suitable for routine laboratory analysis, and requires little infrastructure. Reasonable correlations between acidic and basic sites and BET surface area have been determined, but it is considered that further work should be undertaken on freshly calcined and sampled aluminas.

5. Acknowledgements

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