An approach for the in-situ specific surface area assessment of aqueous oxide particles

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Abstract:
Ceramic particles tend to exhibit hierarchical surface structures, with measurable surface-area varying with analysis scale, in resemblance to the coastline paradox. Specific surface area for ceramic materials is most often reported as the gas-accessible area, conventionally measured by N_2 adsorption at 77K with BET isotherm interpretation. However, the adsorption of nitrogen at low temperatures may not give a relevant indicator of effective surface area for various applications, particularly those involving aqueous suspensions. Here we examine the use of electrokinetic analysis of ionic adsorption at aqueous particle surfaces to gauge the surface structure of suspended alumina. We establish a numerical framework on the basis of the Grahame equation for modelling the change in electric-potential with Stern layer modification, and the Langmuir model to describe monolayer ligation of ionic species at particle surfaces. This framework is applied for the analysis of surface structure in aluminium oxide. We explore the use of in-situ zeta potential analysis of the adsorption of oxalate anions in aqueous suspension to assess the specific surface area of Al_2O_3 powders with varying morphologies. By parameter fitting of acquired zeta-potential data with a Grahame-Langmuir type relationship it is shown that for a given system, the shift in electrokinetic behaviour with adsorbate concentration can be used for the scalable assessment of available surface area in ceramic powders.

Keywords: Alumina, surface area measurement, adsorption, electrokinetic, electrochemical

INTRODUCTION

We often seek to quantify the specific surface area (SSA) of ceramic materials in powder form, and indeed material specifications for commercial ceramic powders frequently include this parameter alongside particle size and purity as vital material information. The surface structure of ceramic powders, and oxide materials in particular, is of great importance towards properties of sintering behaviour, chemical reactivity, mechanical behaviour, catalytic performance and optical appearance in a range of systems [1-3]. Measurement of SSA facilitates material assessment and process optimisation, with high values being sought after in application requiring high levels of surface activity, such as photocatalysis, and pollutant immobilisation [4, 5]. SSA in ceramic powders is most commonly characterised by the Braun Emmett Teller (BET) method, involving nitrogen adsorption at cryogenic temperatures (77K), although it should be noted that other gases are readily utilisable despite being less commonly employed [6]. This is a widespread method which allows comparative analysis following well known standard procedures.

However this method suffers from limitations that result from its inflexibility with respect to scale and measurement conditions. As with many naturally occurring materials, ceramic particles, tend to exhibit surface fractality with the effective surface area depending on the scale of analysis [7-9]. Thus the adsorption of nitrogen at low temperatures may not give a sufficiently meaningful application-relevant indication of surface area. Additionally the characterisation of SSA by BET methods is a lengthy procedure that necessitates the procurement of dry powder specimens.

As a result of these disadvantages numerous methods have been used that involve characterising the particle surface structure in oxide powders on the basis of interaction with target-application-relevant probe molecules. Such alternative methods have included procedures to examine the adsorption of dyes or other organic compounds to particle surfaces in water, in order to quantitatively gauge particle-fluid interfaces [10-13]. However, this approach has generally involved the assessment of adsorption through lengthy ex-situ analyses on the basis of the assessment of residual adsorbate

molecules in interparticle fluids by spectroscopic or other methods [14, 15].

To enhance the anodic electrophoretic deposition of zirconia and titania ceramic particles onto graphite substrates, the use of carboxylic reagents was recently employed as it was found that the adsorption of carboxylate groups to oxide surface brings about a strong decrease in zeta potential (ζ) without significantly altering suspension properties of pH and conductivity [16-18]. The zeta potential shift with the adsorption of carboxylate reagents depends on both reagent concentration and the available adsorption sites. Hence the use of electrokinetic analysis can be employed to gauge the surface area of particles directly in aqueous suspensions.

Here we present an analytical framework and experimental results to demonstrate the applicability of electrokinetic analysis for surface area assessment in suspended ceramic particles. Essentially we show that zeta potential can be used as an indicative parameter to compare or measure the surface area of particles while they remain in aqueous suspension.

METHODS AND PROCEDURES
Complex ionic adsorbates ligating to the surface of suspended inorganic particles tend towards an effective monolayer formation as further ligation is limited by electrostatic repulsion. This can be described by the Langmuir adsorption isotherm in the form shown in equation 1.

$$\theta = \frac{\varsigma_{occup}}{\varsigma_{total}} = \frac{bC}{1+bC} \qquad (1)$$

The parameter b is the ratio of adsorption to desorption constants (k_{ad}/k_{des}). For a given mass of suspended particles b is proportional to the system volume and inversely proportional to the available surface area of particles (A_{total}) which is the product of specific surface area (α) and solid mass (m). We can thus define a constant b' such that:

$$b = b'VA_s^{-1}$$
$$\theta = \frac{b'CV\alpha^{-1}m^{-1}}{1+b'CV\alpha^{-1}m^{-1}} = \left(\frac{b'^{-1}\alpha}{\kappa}+1\right)^{-1} \qquad (2)$$

Such that κ corresponds to the quantity of reagent per unit mass of particles ($\kappa=CV/m$), measureable in mol g^{-1}.

The parameter B is linearly dependant on specific surface area and is defined as $B = \alpha b'^{-1}$ which allows us to express the Langmuir equation from as shown in equation 3.

$$B = \alpha b'^{-1} \;,\; \theta = \frac{1}{B\kappa^{-1}+1} \qquad (3)$$

In order to relate surface area with electrokinetic behaviour we require a method to describe the zeta potential (ζ) as a function of surface coverage. The variation of zeta potential with surface charge is generally found to follow an inverse hyperbolic sine relationship of the form shown in equation 4. [19-21]

$$\zeta = M_1 \text{arcsinh}\left(M_2\sigma\right) \qquad (4)$$

Where σ corresponds to a value for effective surface charge. The constant M_1 is included to account for system variables of temperature, permittivity and ionic strength of the suspension while M_2 is a constant dependant on shear plane separation and temperature [19-21]. As the adsorption of ionic species can be considered to shift the effective surface charge, we can formulate the expression shown in equation 5, which relates zeta potential to surface coverage and the adsorbate charge. Here σ_0 is the initial surface charge exhibited by suspended in the absence of adsorption, while σ'_m corresponds to the apparent net shift in effective surface charge imparted by monolayer adsorption of a given ionic adsorbate. This can be positive or negative depending on whether anionic or cationic adsorption takes place.

$$\zeta = M_1 \text{arcsinh}\left[M_2\left(\sigma_0 \pm \theta\sigma'_m\right)\right] \qquad (5)$$

The combination of equations 5 and 3 yields the Grahame Langmuir (GL) model shown in equation 6.

$$\zeta' = \zeta_{(\kappa=0)}^{-1}M_1\text{arcsinh}\left[M_2\left(\sigma_0 \pm \frac{\sigma'_m}{\left(1+B\kappa^{-1}\right)}\right)\right] \qquad (6)$$
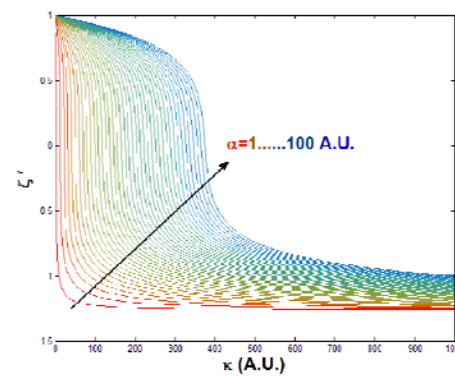

Figure 1. The Grahame Langmuir model relating relative zeta potential to reagent concentration (arbitrary units) for theoretical systems of differing specific surface area.

In the form presented here this model describes the relative shift in zeta potential (ζ'), taken relative to initial zeta potential ($\zeta_{(\theta=0)}$) as a function of proportional reagent addition (relative to powder mass), this relationship is illustrated for a representative system in Figure 1.

To experimentally examine the appropriateness of the Grahame Langmuir model for gauging surface area in ceramic powders we utilised Al_2O_3 powders (Baikowski, >99.9%) of differing morphology and SSA. These powders and their specifications, including the conventionally determined BET specific surface area are listed in Table 1. With representative micrographs shown in Figure 2.

Table 1. Properties of alumina powders utilised

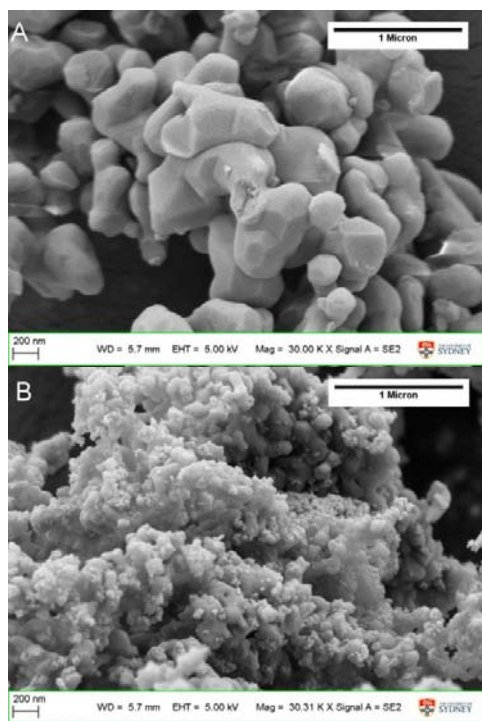| Sample Designation	Supplier name	BET SSA (m^2g^{-1})	Particle size (nm)
A1	CR1	3	1100
A2	CR6	6	600
A3	SMA6	7	300
A4	CR15	15	400
A5	CR30F	26	400
A6	CR125	105	300

Figure 2. SEM micrographs of Al_2O_3 powders with differing SSA: (a) specimen A1 (b) specimen A5

Al_2O_3 suspensions with solids loadings of approximately 1g/litre were prepared in polyethylene tubes, with suspension acidity adjusted to pH=4 by dropwise addition of mild HCl solution to facilitate initial deflocculation and a positive initial ζ value. Suspensions were

magnetically stirred continuously during adsorbate addition to maintain constant dispersion and homogeneity.

As a representative anionic adsorbate, we used dilute oxalic acid (Univar, 99%), which gives rise to the adsorption of oxalate anions at oxide surfaces as seen in earlier work [17, 18]. Using a Malvern nanoZS apparatus in conjunction with an automated peristaltic dispensing system (Malvern Autotitrator), a recirculating suspension under continuous stirring was treated with controlled additions of dilute oxalic acid. The exact quantities of reagent addition were determined on the basis of precise values for suspension volume and solids quantity, in order to yield known levels of relative adsorbate concentration (κ). At each additive increment zeta potential and suspension resistivity were measured in triplicate by the Malvern NanoZS, which relies on Phase Analysis Light Scattering (PALS) to achieve electrokinetic characterisation.

RESULTS AND DISCUSSION

The variation of zeta potential for aqueous suspensions of different Al_2O_3 powders is shown in Figure 3 and follows the inverse hyperbolic sine relationship expected from the GL model. It should be noted that suspension pH exhibited little variation as the result of initial acidification by mild HCl addition, thus a level of pH~4 was maintained throughout reagent addition. Moreover, the low solids loading and reagent concentration meant that little variation in the ionic strength of interparticle fluid was imparted. Thus it is reasonable to assume that the observed decrease in ζ is the result of oxalate anion ligation to suspended particle surfaces.
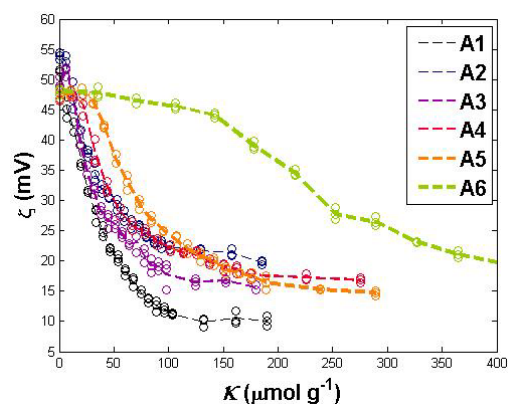

Figure 3. ζ variation with relative oxalic acid additions for powders of differing surface area

As would be expected, for Al_2O_3 materials of higher specific surface area the curve of zeta potential change is shifted to higher relative adsorbate concentration values (κ). This is the natural result of higher surface area meaning a greater number of adsorption sites. The aim of

further interpretation is to examine an analytical framework to utilise this information to gauge surface area by fitting to the Grahame Langmuir form.

The mean relative zeta potential shift (relative to initial conditions in the absence of adsorbate) was subjected to simultaneous multiple parameter optimisation following equation 6 in order to determine the fitted SSA dependant parameter B for each of the six powders and the values $M_2\sigma_0$ and $M_2\sigma'_m$ for the examined system. To achieve this parameter optimisation a parallelised least squares type fitting process was employed using a trust-region reflective algorithm in a Matlab environment.

Results of measured ζ' as a function of relative reagent addition are shown in Figure 4. In this figure we also show the fitted curve (dashed lines) achieved on the basis of parameter optimisation using the Grahame Langmuir model of equation 6.
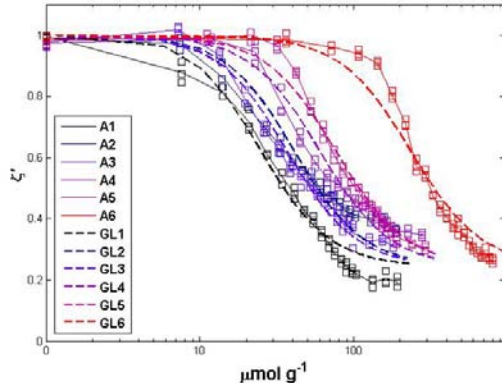

Figure 4. Relative zeta potential shift with parameter optimisation fitting following the Grahame Langmuir model.

From the good degree of fit, we can conclude that the Grahame Langmuir model is appropriate for the description of zeta potential variation with ionic adsorbate addition. This model does not perfectly describe the electrokinetic variation of particles in suspension as it relies on numerous simplifications inherent in the individual components of the Langmuir adsorption model and the Grahame function. To account for specific system behaviour or the limitations of analytical techniques it may be necessary to adopt particular variations to the model.

Despite the simplifications implicit in the GL model, this description captures well the surface area dependence of adsorbate driven electrokinetic variation. Figure 5 shows the comparison of B_{Fit}, the optimised parameter for the variable B for each alumina type, which is linearly correlated to the SSA following equation 3 with the BET determined values of SSA for powders A1 to A6.

The clearly evident linearity between fitted values for B and the conventionally determined SSA suggests that the electrokinetic behaviour of ceramic particles in aqueous suspension, in conjunction with the addition of an ionic adsorbate, can be used to glean meaningful information regarding the specific available surface area of the material.
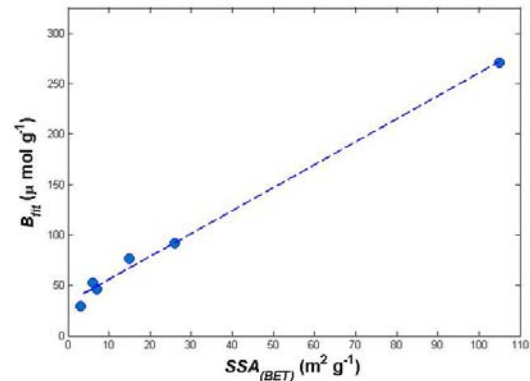

Figure 5. Comparison of the surface area normalised adsorption coefficient B, extracted from parameter optimisation following the GL model, with BET measured surface area

The use of conventionally determined BET surface area data to assess the validity of the current methods is unideal as the result of the aforementioned scale limitations of gas adsorption methodologies. Nonetheless it is necessary to compare the currently developed methods with conventional procedures. The use of electrokinetic measurements to qualitatively compare SSA between different oxide powders is readily achievable as suggested by these results. The use of these methods for the quantitative analysis of oxide surface would necessitate the use of a calibration process, using a specimen of known surface area at a relevant analysis scale.

The approach developed here has numerous benefits relative to the use of nitrogen adsorption methods typically employed for SSA characterisation. Firstly, for each of the six powders assessed, the methods used were applied to a single recirculating aqueous suspension. This method is thus *in-situ* in the sense that suspended oxide powders are maintained in their aqueous environment at room temperature, rather than being used in dried form at 77 K. The results of ex-situ analytical procedures may in some cases not yield sufficiently meaningful data with respect to certain aqueous applications as particle structure may be altered by drying or by low temperatures. It is likely that substituting PALS methods with alternative electrokinetic analysis tools, such as streaming current or electrosmosis [22], may be appropriate for denser systems involving higher levels of solids loadings as required. A further notable advantage of the present approach is its scalability, that is to say

by use of ionic adsorbates of varied molecular size the effective analysis scale can be modified to yield more meaningful results with respect to target applications. The use of N_2 molecules as surface probes is associated with certain limitations owing to the scale variance of naturally occurring ceramic materials' surface structures (surface fractality). The current method allows for SSA to be determined across multiple scales, potentially allowing the determination of surface fractality. Finally in terms of rapidity and simplicity the current approach is advantageous relative to BET with results obtainable within a time from of one or two hours and a significantly shorter equilibration time for each measurement.

CONCLUSIONS

A model was constructed to describe the variation of zeta potential in suspended oxide particles with increasing concentration of an ionic adsorbate. This model was built on the Langmuir model to describe effective-monolayer adsorption and the Grahame model to describe the variation of potential with changing surface charge. It was found that using this GL model to interpret, using parameter optimisation, the oxalate modified zeta potential exhibited by different alumina suspensions facilitated specific surface area characterisation of powders with differing surface structures on the basis of electrokinetic variation in conjunction with reagent addition.

It is envisaged that by appropriate modification of the adsorption model and/or the Grahame equation, the use of alternative electrokinetic of electrochemical methods can be developed with a view towards scalable surface characterisation in a range of granular materials, ceramics and soils by relying on the principal established here of measuring and interpreting parameters indicative of adsorbate interactions.

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