Journal of Colloid and Interface Science 436 (2014) 204–210

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Determining surface composition of mixed oxides with pH

Jadid E. Samad [a], Safoora Hashim [b], Shuguo Ma [a], John R. Regalbuto [a,*]

[a] Department of Chemical Engineering, University of South Carolina, 301 Main Street, Columbia, SC 29208, United States
[b] Department of Chemical Engineering, University of Illinois at Chicago, 800 S. Clinton St., Chicago, IL, 77840, United States

ARTICLE INFO

Article history:
Received 28 April 2014
Accepted 31 July 2014
Available online 15 August 2014

Keywords:
Mixed oxides
Point of zero charge
Surface charge parameter
Surface characterization
Surface coverage

ABSTRACT

In this study we have developed a 2-surface model with the EPHL ("Equilibrium pH at high oxide loading") method for mixed and composite oxides. Oxide charging parameters, namely the protonation and deprotonation constants and the hydroxyl surface densities, can be established from measurements of the pure oxides and used in the 2-surface model to predict the point of zero charges (PZC) of mixed and composite oxides. The accuracy of these predictions has been demonstrated with diverse control samples of known surface composition (physical mixtures of silica and alumina of high and low surface area). The EPHL method has been extended to composite materials (bound catalysts) and can explain correlations of reactivity with catalyst surface composition. The "apparent surface coverage" (ASC) of a particular mixed or composite oxide sample may then be determined by comparing the PZC of the material to either the 2-surface model results, using parameters of the individual oxides, or a calibration curve of EPHL measurements of physical mixtures of the individual ingredients.

1. Introduction

Composite metal oxides are extensively used in industrially significant catalytic and electrocatalytic processes [1–4] and have demonstrated tremendous potential to replace single metal oxides in metal ion adsorption, separation and photosensitive operations [5–10]. Many of these processes benefit from the unique properties that mixtures of two or more oxide components can develop [5–10].

For a mixed oxide system it is often important to study the electro- and physico-chemical properties based on the fractional surface coverage of each of the oxide components [6,10–14]. Common surface analysis techniques such as X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES) may not be adequately surface sensitive as XPS and AES detect the top ten layers of the surface of light elements. In secondary-ion mass spectroscopy (SIMS), 95% of the detected emitted radiation is from the top 2 layers [Vickerman, 2009 #32]. Ion scattering spectrometry (ISS) is the most surface sensitive technique available, and derives information almost exclusively from the top monolayer [15]. Nevertheless all these techniques are expensive and necessitate considerable expertise and maintenance [3]. Moreover, if one or both of the oxides is porous, as in industrial catalysts, the quantification of composition can be problematic [16].

Studies conducted over the last few years underscore the importance of developing a technique that can be applied to predict surface properties of mixed oxides easily and accurately [1,6,10,11,13,14,17]. In many of these studies the surface under investigation can be characterized in terms of its point of zero charge (PZC). PZC is the pH in solution at which the oxide surface is at net zero charge. It is a surface intensive property that accounts for the proton transfer to and from the surface hydroxyl groups which causes dramatic pH shifts in an aqueous solution [18]. Hence PZC can be regarded as a strictly surface sensitive method; when applied to mixed oxides, the pH measurements of the mixed oxide PZC might offer a simple way to measure surface composition.

Parks utilized the Gouy-Chapman version of electrical double layer theory to show that PZCs of mixed oxides change linearly with the weight fraction of individual components assuming that the components do not interact with one another [19]. Schwarz

---

Abbreviations: EPHL, measurement of "Equilibrium pH at high oxide loading"; PZC, point of zero charge; σ_k, charge on surface k; ε, dielectric constant of solution; ε_o, permittivity of vacuum (8.854×10^{-12} $C^2/N\,m^2$); n_o, number of electrolyte per unit volume; k, Boltzman constant; PZC_{mix}, PZC of mixture; ASC_k, apparent surface coverage of k; N_k, density of OH groups on k; K_1, K_2, ΔpK, ionization constants; T, temperature; Ψ_o, surface potential; F, Faraday constant (9.649×10^4 C/mole); e, electron charge (1.6×10^{-19} C); [H+], equilibrium concentration of H+; HA, HS, high surface area alumina, silica; LA, LS, low surface area alumina, silica; SZ, sulfated zirconia; SAL, sulfated alumina; SA, surface area (m^2/g); SL, surface loading (m^2/l).

* Corresponding author. Address: Room 3C13, 301 Main Street, Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, United States. Fax: +1 803 777 8265.

E-mail address: regalbuj@cec.sc.edu (J.R. Regalbuto).

http://dx.doi.org/10.1016/j.jcis.2014.07.050
0021-9797/

et al. [17] used mixtures of silica and alumina and claimed to have found direct agreement with the results obtained by Parks. However, many experimental values published later disagreed, including one of Schwarz's own later works [14]. Some observed non-linear dependence of PZC of a SiO_2 and Al_2O_3 physical mixture on surface composition which they attributed to the higher sensitivity of alumina to the change of pH [21,22]. Elsewhere, one of the composite oxide models proposed by Schwarz group was based on the premise that PZC of a mixed oxide is the sum of its pure component PZC weighted by surface area [23]. In cases where 2nd oxide is present at a reasonably high concentration they proposed another model utilizing (1) mixed oxide PZC values measured by "mass titration" and (2) a physical mixture calibration curve [24]. Kallay et al. also used mass titration method to predict point of zero charge (PZC) and surface charge density of silica-hematite mixed systems [25]. Zhang et al. used proton equilibrium relations to introduce non-linearity in Parks' model which fit experimental values of TiO_2 and Al_2O_3 mixtures reasonably well [10]. Some have implicated that the surface area effect is the cause of non-linearity, which means Parks' linear model is only valid when components of a mixture share the same surface area [1,26]. Others tried to relate mixture PZC to the surface coverage through a number of equations that are mostly empirical and component specific [24].

PZCs of oxide materials can be accurately determined via simple pH measurements as described in an earlier work of Park and Regalbuto [18]. They simulated the strong buffering effect of oxide surfaces immersed in thick aqueous slurries with a model that solves a proton balance, a simple electric double layer (Gouy-Chapman model) theory and an oxide charging model simultaneously for the determination of PZC. This technique, known as "Equilibrium pH at High Loading" (EpHL), has several advantages over others commonly used, such as acid-base titration, electrophoresis, potentiometric titration, pH drift technique and mass titration [18].

While EPHL was originally developed for pure oxides [18], the current paper demonstrates how it can be extended to provide estimates of surface composition for mixed and composite oxide surfaces. Oxide charging parameters, namely the protonation and deprotonation constants and the hydroxyl surface densities, can be established from measurements of the pure oxides and then used in the 2-surface model to predict the PZCs of mixed and composite oxides. The charge over each surface fraction is quantified to account for the nonlinearity of the surface charge – pH relationship; this quantification allows for the calculation of surface composition from the PZC data, even for composite oxides of widely disparate PZCs.

Various types of interaction between component oxides can potentially complicate the characterization of mixed oxide surfaces. Such interactions, as have been widely reported in literature, include heterocoagulation, co-precipitation and dissolution from one solid and adsorption onto another [27]. Various models have been proposed to account for such interactions [28,29]. In this study we developed out 2-surface model for a series of mixed oxides (predominantly physical mixtures of solid powders) for which such interactions were assumed to be negligible. Nevertheless, the accuracy of this method has been demonstrated with control samples of known and diverse surface composition (for example, physical mixtures of silica and alumina of high and low surface area) as well as with data from the literature. The EPHL surface composition measurements of a set of bound catalysts (composite oxides) are seen to correlate well with catalyst reactivity which verified our justification of neglecting interactions between components.

2. Theory

The charging mechanism applied in this study stems from the original work of Park and Regalbuto [18]. In short, simple mineral oxides contain terminal hydroxyl groups which accumulate charge as they come into contact with aqueous solutions. The nature of hydroxyl groups dictates the charging mechanism. For 2-component mixed oxides, two different OH groups will populate the surface and thereby create 2 different sites for aqueous medium to interact (Fig. 1). Furthermore if it is a physical mixture it can safely be assumed that one type of hydroxyl group will not affect the functionality of the other and vice versa. For such a system the net charge at a given pH can be predicted as the sum of negatively charged (more acidic) and positively charged (more basic) sites weighted by mole fraction (Eq. (1))

$$\sigma_{net} = f_1\sigma_1 + f_2\sigma_2 \tag{1}$$

where

$$f_k = \frac{\text{moles of OH groups on surface } k}{\text{total moles of OH groups}} = \frac{A_k N_k}{\sum A_k N_k} \tag{2}$$

σ_k is surface charge of k, A_k is surface area of k, N_k is density of OH groups on k (mol/m^2)

When pH is near the PZC of the oxide surface the Nernstian approximation accurately estimates surface charge in terms of pH of solution and PZC of individual oxides (Eq. (3)).

$$\sigma_k = K(\text{pH} - \text{PZC}_k) \tag{3}$$

where, PZC_k is point of zero charge (PZC) of k, K is a constant = $\frac{\varepsilon k}{4\pi}$

However, this approximation is no longer valid when pH values are considerably different from the PZC of individual component. Hence a new term (y_k) has to be introduced to the equation to account for the deviation (Eq. (4)).

$$\sigma_k = y_k K(\text{pH} - \text{PZC}_k) \tag{4}$$

At the PZC the net charge of a mixed oxide will be zero i.e., negatively charged sites will effectively cancel out positively charged sites. Thus Eq. (1) transforms to:

$$0 = K[y_1 f_1(\text{PZC}_{mix} - \text{PZC}_1) + y_2 f_2(\text{PZC}_{mix} - \text{PZC}_2)] \tag{5}$$

ASC can be defined as the fraction of surface area occupied by one component (Eq. (6)).

$$\text{ASC}_k = \frac{A_k}{\sum A_k} \tag{6}$$

Combination of Eq. (5) and (6) with 2 yields the 2-surface model,

$$\text{ASC} = \left[Z\left(\frac{\text{PZC}_{mix} - \text{PZC}_2}{\text{PZC}_1 - \text{PZC}_{mix}}\right) + 1\right]^{-1} \tag{7}$$

where

Z is $\left(\frac{y_2}{y_1}\right)\left(\frac{N_2}{N_1}\right)$

Z values can be obtained by solving, for each component, the oxide charging equation (Eq. (8)) and Gouy-Chapman model equation (Eq. (9)) at the pH of the mixed or composite oxide [18].

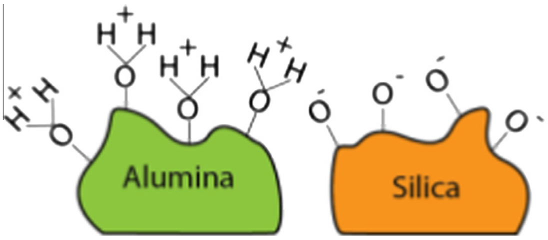

Fig. 1. Schematics of a physical mixture of alumina and silica immersed in an aqueous solution where $\text{PZC}_{silica} < \text{pH} < \text{PZC}_{alumina}$.