



Phosphate alteration of chloride behavior at the boehmite–water interface: New insights from ion-probe flow adsorption microcalorimetry



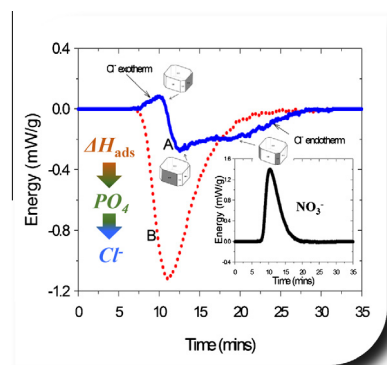
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GRAPHICAL ABSTRACT



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ABSTRACT

Surface complexation of phosphate to aluminum oxyhydroxides can alter surface reactivity depending on the time-scale and mode of attachment. The effects of phosphate adsorption on reactivity of boehmite (γ -AlOOH) particles were investigated using ion-probe flow adsorption microcalorimetry (ipFAMC). Consistent with previous studies on adsorption energetics, probing the surface of pristine γ -AlOOH with chloride ions yielded endothermically unimodal temperature signals with a measured molar heat of exchange (ΔH_{exc}) of -3.1 kJ/mol. However, when the surface of γ -AlOOH was probed with chloride following phosphate complexation, significant changes in surface reactivity resulted. Irrespective of phosphate loading, the typical endothermic response of the chloride-surface hydroxyl interaction was replaced with a multi-modal energy signature consisting of exothermic and endothermic features. These features indicate that in the presence of phosphate, the overall nature of the interaction of chloride with specific surface hydroxyls located on different exposed planes and their subsequent reactivity was transformed to a more complex environment accompanied by two or more short-lived secondary reactions. It was also shown that phosphate-promoted surface alteration of γ -AlOOH was highly selective to probing with chloride since no changes in reactivity were observed when nitrate was employed as the primary ion probe under identical experimental conditions.

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1. Introduction

The reactivity of metal (hydr)oxides in aqueous environments is generally determined by its ability to interact and retain solutes and water at its interface or by its dissolution characteristics in acids or bases. Therefore, unraveling how chemical surface heterogeneity impacts the reactivity of exposed surfaces remains central to the understanding and development of structure–function relationships in metal (hydr)oxide systems. Two perspectives for describing chemical heterogeneity of metal (hydr)oxides can be highlighted. The first viewpoint is heavily examined using laboratory experiments and thus interprets chemical surface heterogeneity on the basis of physicochemical traits (i.e. surface area, particle size, isoelectric point and crystallinity) which are governed largely by the identity and structure of the lattice metal or by molar ratios of individual metal centers in double-hydroxides and mixed-metal oxides. For example, because of their high reactivity at environmental pH values, aluminum (Al) and iron (Fe)-(hydr)oxides can interact strongly with a variety of solutes, including inorganics [1–5], metals [6–8], and organic ions [9–13]. The second interpretation considers physicochemical and catalytic properties (chemical surface heterogeneity) based on morphology of the (hydr)oxide surface, particularly the Lewis (or Brønsted) acidity and basicity of hydroxyl groups. In this respect, surface hydroxyl groups can be distinguished on the basis of the number of surface oxygens attached to lattice metals atoms in singly ($\equiv\text{MeOH}$), doubly ($\equiv\text{Me}_2\text{OH}$), or triply-coordinated ($\equiv\text{Me}_3\text{OH}$) formation [14]. Furthermore, these groups can occur on different exposed crystallographic faces of metal (hydr)oxides with a variety of densities and distributions.

Spectroscopic techniques such as Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR) have been used to compile information pertaining to the densities and distribution of surface hydroxyls on metal (hydr)oxides [15–17], however with the continued advancement in computing, much of what is understood has been to a large extent gathered by a variety of mathematical modeling and chemical computation techniques [17–25]. For example, in a recent study, Motta et al. [24] used first principle molecular dynamic simulation based on density functional theory (MD–DFT) to gain insights into the factors that influence hydroxyl reactivity at the boehmite ($\gamma\text{-AlOOH}$)/water interface. Using this method, the enhanced reactivity of the defective (101) $\gamma\text{-AlOOH}$ surface was shown to be governed by the concentration of singly and doubly-bridged hydroxyls as well as proton transfer between basic groups located on step edges and acidic hydroxyls populated on the terraces of surface defects. Additionally, this study showed that within 6 Å from the surface, acidity of surface groups is pivotal in controlling the orientation of interfacial water molecules.

Knowledge of fundamental energetic information, particularly the enthalpy of adsorption at the metal oxide/water interface is a useful prerequisite for gaining additional insights into complex reaction phenomena on chemically heterogeneous surfaces, especially in situations when selected –OH groups undergo reversible modification at shorter times relative to other surface reactions. Observing these subtle and short-lived alterations in hydroxyl reactivity creates a challenge both for experimental and mathematical methods. In order to overcome this challenge, ion-probe flow adsorption microcalorimetry (ipFAMC) has been applied to examine reversible and short-term modification to surface hydroxyls. Flow adsorption microcalorimetry offers a direct quantitative assessment of the reactivity of –OH groups at the metal oxide/water interface and is well suited for distinguishing chemical surface heterogeneity governed by interactions of solutes in solution with surface –OH of various reactivity. Additionally, ipFAMC

is capable of resolving the energies of multiple solute/surface reactions when they occur at different rates [26].

The main objective of this study was to examine how surface heterogeneity from the viewpoint of hydroxyl reactivity of $\gamma\text{-AlOOH}$, was influenced by the presence of phosphate in solution. Our approach entailed employing mainly chloride (Cl^-) as the target and nitrate (NO_3^-) as the reference probe to monitor changes in hydroxyl reactivity before and immediately following phosphate exposure to elucidate the nature of permanent versus reversible (or short-term) surface modifications imposed by ligand exchange of phosphate. Subsequently, this approach provided better insights into the nature of the $\text{Cl}^-/\gamma\text{-AlOOH}$ interaction in the presence of phosphate. Boehmite was chosen as the model surface because of (i) its importance as a catalytic support and precursor of γ -alumina ($\gamma\text{-Al}_2\text{O}_3$); which is one of the most common catalyst used in industrial heterogeneous catalysis [27,28], (ii) its structure and surface properties are known to be stable between pH 5–9 at room temperature [29,30], (iii) its adsorption properties [31–33], and (iv) its crystallography as well as hydroxyl groups that populate the exposed faces have been characterized extensively by various experimental [34–37] and mathematical modeling techniques [21,34,38–40].

2. Materials and methods

2.1. Chemicals and mineral phase

All chemicals were reagent grade and were used without further purification. Sodium salts in the form of NaCl, NaNO_3 , NaOH, phosphate (NaH_2PO_4), and concentrated ($\sim 12.1\text{ M}$) HCl were obtained from Fisher Scientific (Fairlawn, NJ). Boehmite ($\gamma\text{-AlOOH}$) was obtained from Sasol North America Inc. (Houston, TX) in the powdered form under the trade name Catapal-D and contained no impurities distinguishable by powder XRD analysis (Fig. SI-1, Supporting Information). The $\gamma\text{-AlOOH}$ surface has an iso-electric point (IEP) of 9.1 based on electrophoretic mobility (EM) measurements and a specific surface area (SSA) of $220\text{ m}^2\text{ g}^{-1}$ determined by the 6-point N_2 Brunauer–Emmett–Teller ($\text{N}_2\text{-BET}$) gas adsorption isotherm method. Prior to use in microcalorimetry studies, the $\gamma\text{-AlOOH}$ was washed with nanopure water ($18.2\text{ M}\Omega\text{ cm}$; Barnstead), dried to constant weight at $60\text{ }^\circ\text{C}$, and gently crushed to facilitate homogenous packing into the microcalorimeter. Based on Cl^- adsorption measurements at 5.8 ± 0.05 , the washed $\gamma\text{-AlOOH}$ was determined to have an anion exchange capacity (AEC) of $29.2 \pm 2.1\text{ cmol}_{(+)}\text{ kg}^{-1}$.

2.2. Ion probe microcalorimetric measurements

The flow microcalorimeter used in this study was custom-designed and fabricated in our laboratory. Details of the basic design and operation were presented previously [41,42]. Therefore, only a brief description outlining our experimental approach, data acquisition and data utilization pertaining to this study is provided here. The instrument consists of a calorimetric micro-cell with a calibrating resistor and two thermistors hermetically sealed inside a glass housing and submerged in an insulated water bath which is maintained at room temperature. Experiments were conducted using 25.0–57.0 mg of $\gamma\text{-AlOOH}$ packed inside the micro-cell which was flanked by the reference thermistor and calibrating resistor on the leading/influent end, and the column thermistors on the downstream/effluent end. Solutions containing the ion-probe molecule (Cl^-) as well as NO_3^- and phosphate were advanced through the cell at a solution flow rate of $0.29 - 0.34\text{ mL min}^{-1}$. The reference thermistor senses the temperature

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