



Investigation of small molecular weight poly(acrylic acid) adsorption on γ -alumina



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ABSTRACT

The interactions between poly(acrylic acid) (PAA) and alumina have been widely investigated. In this study, the pattern of small molecular weight PAA (M_w 3000) interaction with γ -alumina has been dissected. The alumina/PAA hybrids were prepared at pH 4.0, 5.5, and 7.0, respectively. Nitrogen absorption–desorption analysis, Fourier transform infrared spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, and elemental analysis were conducted to illustrate the characteristics of the hybrids. At pH 4.0, the coiled PAA conformation yielded polymer adsorption primarily on alumina outer surface. At higher pH values, the more stretched PAA molecules were able to infiltrate inside the alumina pores. The phenomenon is explained by the polymer chain reptation motion model. Coiled polymer chains are not oriented enough to penetrate the oxide pore channels. In contrary, stretched polymer chains are more likely to move along the pore channels.

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1. Introduction

Because of its appreciative properties such as high surface area, thermal stability, and mechanical strength, particulate alumina has wide industrial applications including catalyst support, additive for polymer composites, precursor for ceramic composites, formulations for prostheses and implants, paper making, chromatography filler, and adsorbent. Alumina possesses many more valuable properties like surface acid-base centers and mass production status that bestow its frequent use in petrochemical industry processes such as fluid catalytic cracking [1,2]. Alumina itself is made by calcination of aluminum hydroxide and has a point of zero charge pH value ranging from ~ 7 to ~ 10 [3]. A porous material, alumina is classed into several groups, with the α -group and γ -group as the most well known. α -Alumina is the high temperature, more stable transitional type, while γ -alumina is characterized by its high surface area and open porosity, and wide usage as a catalyst support in the chemical industry.

The adsorption properties of alumina in aquatic systems have been actively studied recently. Alumina is widely found in water treatment applications along with active carbon, silica, and zeolites, to remove organic waste from water [2]. Alumina is also a major component in soils, aquifer materials, and sediments, which have

active surface sites for adsorption of metal ions [4]. Abundantly existing in natural environment, alumina particles adsorb organic matter, primarily humic substances, to form a hybrid complex. The hybrid systems have shown distinguished adsorbing properties toward heavy metal ions than that of either pure organic matter or mineral [5]. Yet, the metal ion interaction behavior with the hybrid system cannot be understood by simply superimposing the interaction patterns of metal/mineral and metal/organic matter. The properties of minerals can be significantly changed upon adsorption of humic substances [6]. The coverage of organic matter on mineral surface can render the inorganic phase more hydrophobic thereafter allowing retention of more hydrophobic pollutants in soil. Regarding metal ions, humic substances can either increase metal ion adsorption by offering complexation sites, or decrease adsorption by blocking sorption sites on mineral surface.

To better understand such environmentally imperative processes, one commonly employed method is to use a binary system composed of a surrogate polymer that highly resembles humic substances, and alumina particles. A weakly acidic polyelectrolyte, synthetic poly(acrylic acid) (PAA) has been widely used as such a surrogate [7]. PAA is employed in industry as scale inhibitor, paper-making dispersant, stabilizer, and flocculant. In pure form, it can be used as a heavy metal adsorbent to remove toxic metal ions from industrial effluents. Investigation of the binary PAA/alumina system becomes a valuable tool to illustrate the behavior of the humic substance and mineral hybrid that is extensively present in soil.

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Interactions between PAA and alumina govern the properties of the PAA/alumina hybrid like adsorption and dispersion. Characteristics of the particles, polymer, and the mixing solution, all contribute to the process [8]. The size, morphology, and charge of the inorganic material, the conformation, molecular weight, and concentration of the organic matter, and the ionic strength and pH of the reaction media have been studied to understand the interactions between PAA and alumina.

Because of its superior application properties, especially high surface area, we are particularly interested in better understanding the characteristics of polymer-hybrid of γ -alumina. Regarding the metal adsorption potential of the alumina/PAA hybrid, we assume that a system with polymer chains residing inside the oxide pores may adsorb the most metal ions because of the high metal complexation capability of PAA [7]. Some studies have probed the overall PAA adsorption onto alumina [4–6,8–13]. With a pK_a value of 4.5 [8], PAA chains adapt the coiled conformation when solution pH is lower than 4.5. When the solution pH value is >4.5 , the polymer chains become more stretched due to more ionized carboxylic groups repulsing each other. In the alumina/PAA hybrid, polymer chains tend to adsorb onto the oxide surface in a coiled conformation at lower pH ranges. The polymer layer coated on alumina particles is therefore relatively thick. When the adsorption occurs at higher pH ranges, the stretched polymer chains cover the particles with thin layers. Instead of mixing, PAA has been grafted to alumina through the covalent $-\text{Al}-\text{O}-\text{Si}-\text{O}-\text{C}-$ linkage [14–17]. Usually a hygroscopic organosilane compound with dual functionalities is first reacted with the oxide so the siloxane functional group can be directly attached to the surface. Then the other functional group such as $-\text{C}=\text{C}-$ is utilized to grow polymer chains. Other polymer types than PAA have also been grafted onto alumina [18–22]. The procedure is similar to the grafted PAA, i.e., by using a dual functional organosilane linker followed by polymer chain growth. The composites prepared with covalent linkage demonstrate high mechanical strength compared to non-linked counterparts.

After carefully reviewing the literature on characteristic studies of the alumina/PAA hybrid system, we find that the high porosity aspect of γ -alumina has not been directly addressed. γ -Alumina usually has a pore diameter of a few nanometers. When discussing the likelihood of polymer chains infiltrating the alumina pores, a prerequisite is that the chain size in solution is small enough [23–25]. The average size of polymer chains in solution can be represented in radius of gyration R_g or hydrodynamic radius R_h , while the two are similar numerically. For a polyelectrolyte such as PAA, its radius is dependent on the polymer molecular weight M_w , charge density, solution pH, and ionic strength. The calculated R_g for PAA with an M_w of 5000 is 0.85 nm [10], while in 1 M NaCl solution, the R_g value for PAA with an M_w of 1656 is 1.25 nm [26].

In this study, we select PAA with a small M_w value of 3000. According to the aforementioned data, these PAA chains should have an average radius of gyration around 1 nm. Considering the γ -alumina particles we use have pores with an average diameter of ~ 9 nm (vide infra), we assume there is a good chance that some PAA chains may infiltrate the alumina pores. After we adsorb PAA onto γ -alumina in aqueous solution, we apply a series of analytical techniques to dissect the alumina/PAA hybrid at the microscopic level. The isolated hybrids are analyzed with the nitrogen adsorption/desorption isotherms, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and elemental analysis (EA). Our results indicate that at higher pH values, more PAA chains are able to infiltrate the oxide pores efficiently. Based on the experimental findings, the physical meaning of such a phenomenon is interpreted.

2. Experimental

2.1. Materials

Poly(acrylic acid) ($(\text{C}_3\text{H}_4\text{O}_2)_n$, PAA) with a molecular weight of 3000 was supplied by Aladdin Chemicals Co. Ltd. (Shanghai, China). The commercial PAA was directly used to prepare aqueous solutions. In a typical procedure, 0.24 g PAA was dissolved in 100 ml water. A 3-ml aliquot was transferred to a 100-ml flask and added with water. 0.1 M NaOH or 0.1 M HCl was used to adjust the solution pH, followed by topping up with water to 100 ml. In this way, 1.0 mM PAA solutions were prepared with pH values of 4.0, 5.5, and 7.0, respectively. γ -Alumina was acquired from Kelong Chemicals Co. Ltd. (Chengdu, China). The grinded powders in 40–60 mesh range were activated at 500 °C for 3 h prior to use.

2.2. Methods

2.2.1. Sample preparation

100-ml PAA solution was added with 3.0 g freshly activated γ -alumina. The mixture was gently stirred at room temperature for ≥ 12 h, then filtered and rinsed with small portions of water. The solid was collected and dried at 110 °C in air for ≥ 12 h. The samples prepared with PAA pH at 4.0, 5.5, and 7.0, were denoted by numbers **2**, **3**, **4**, respectively, while the control γ -alumina was number **1**.

2.2.2. Characterization

Room temperature Fourier transform infrared (FT-IR) was performed on a Bruker Tensor 27 Fourier transform spectrometer. X-ray diffraction (XRD) analysis was carried out using Philips X'pert PRO with Cu K α (45 kV, 50 mA) radiation. X-ray photoelectron spectroscopy (XPS) was conducted on XSAM800 spectrometer with an Al K α ($h\nu = 1486.6$ eV) X-ray source. The charging effects were corrected by adjusting the binding energy of C 1s peak from carbon contamination to 284.6 eV. The morphologies of the samples were determined using a Hitachi S-4800 field emission scanning electron microscope (SEM), operated at 5 kV. The specific surface areas, total pore volumes, and average pore diameters were determined from the nitrogen adsorption-desorption isotherms at -196 °C, which were measured using an automated surface area and pore size analyzer (Quadrasorb SI apparatus). Before each measurement, the samples were degassed in vacuum at 300 °C for 3 h. Specific surface areas of samples were calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution and average pore diameter were determined according to the Barrett-Joyner-Halenda (BJH) method applied to desorption isotherms. Sample chemical compositions were determined by elemental analysis (EA) on a Euro EA3000.

3. Results

PAA incorporation into alumina has been well reported in the last two decades. The literature studies normally describe the overall adsorption of polymers onto particle surface. Our current investigation is focused on the likelihood of small PAA molecules (M_w 3000) infiltrating γ -alumina pores. The oxide powders have a pore diameter of ~ 9 nm, greater enough than the estimated ~ 2 nm diameter of PAA polymer used in this study. When placed in aqueous solution with gentle stirring, polymer chains and oxide particles can form hybrids controlled by a diffusion process. The hybrid formation may be established fairly quickly, usually within a few seconds [8–10]. However, the polymer chain infiltration inside the oxide pores follows a very different process (vide infra). We let the particle/polymer mixture stir for over 12 h so that the infiltration process has adequate time to take effect. A series of characterizations were conducted to dissect the results from the infiltration process.

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