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**SURFACE STUDIES OF SILANE TREATMENT ON METALLIC ALUMINUM
POWDERS**

A Thesis in
Chemical Engineering
by
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Abstract

This paper describes an investigation of various surface treatment processes that can be applied to bulk aluminum powders to affect the surface chemistry of the aluminum powder particles. The use of silane surface treatment makes it possible to modify the interfacial chemistry of aluminum powder, allowing for improved fluidized powder flow characteristics and tailoring of the hydrophobic properties without compromising the aluminum content. The characterization of the aluminum powders was conducted using Fourier transform infrared spectrophotometer and particle size distribution. The aluminum powder surface was successfully modified with polydimethylsiloxane and the intensities gave qualitative indications of how much was on the surface. The CO dosing on aluminum powder surfaces was observed to be successful but, due to limited time, these experiments warrant further investigation. Additionally, using the PSD analysis for different sections of aluminum powder storage drums, there were no significant signs of segregation. These tasks support aluminum powder processing through improved surface treatment and a better understanding of bulk powder processing.

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List of Abbreviations

Al	Aluminum
CO	Carbon Monoxide
DRIFTS	Diffuse Reflectance Infrared Fourier Transform spectroscopy
FBR	Fluidized Bed Reactor
HCl	Hydrogen Chloride
IR	Infrared
KBr	Potassium Bromide
MTES	Methyltriethoxysilane
PDMS	Polydimethylsiloxane
PTES	Phenyltriethoxysilane
PSD	Particle Size Distribution
ssNMR	solid-state Nuclear Magnetic Resonance
XRD	X-Ray Diffraction

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Chapter 1. Introduction and Literature Review

Introduction

The study of molecular surface chemistry is about understanding and controlling surface chemical reactions. The interface or surface is represented by the boundary between a material and the surrounding environment. There are a variety of applications and developing technologies that constantly drive the increase in understanding surface chemical processes, like heterogeneous catalysis, semiconductor-based technology and silane surface modification. Surface chemistry has developed into a molecular-level science capable of in situ characterization of surface properties and information for large-scale design and chemical processes [1]. The knowledge collected provides a foundation for various aluminum powder applications.

Aluminum and Aluminum Oxides

Aluminum exists in many forms besides pure solids, there are a variety of aluminum oxides. The aluminum can be aged to form aluminum oxides, but bayerite can be formed by neutralizing sodium aluminate solution with carbon dioxide at low temperatures. The formation of bayerite provides a different structure from aluminum oxide and can be used for electrocatalytic applications [2].

Similarly, aluminum (Al) can be aged through a different process to form boehmite, a product occurring through an intermediate stage of the aging sequence of aluminum hydroxide gel. Under an aqueous solution environment and lower temperatures than 350K, the boehmite is made and thermodynamically stable enough to observe and manipulate [2].

The original substrate provides the native oxide layer that can be used for different interface chemistry applications, including adsorption, catalytic activity, and electronic arrangement of the surface molecules [2]. This oxide layer enables the surface treatment of aluminum powder.

Silane Hydrolysis and Surface Treatment

Silanes are utilized as surface modification agents to improve the bonding between molecules on the surface by changing the surface properties. Silanes can be added to lattices to form polymer networks with organic and inorganic properties [3]. The two types of alkoxy silanes are alkyl/aryl and organofunctional. The organofunctional groups have a high surface reactivity with hydrolyzable groups to form silanol groups for bonding to a mineral interface. Additionally, this is beneficial for the organic/inorganic interface due to improved adhesion and durability.

The simplest silane has one single silicon atom with four hydrogen atoms attached. When using an organofunctional silane, the layer formed by the silicon and oxygen provide a layer with hydrophobic properties to be used in different applications such as aluminum powders [4]. Most of the interactions occur on the interface; therefore, this paper focuses on the bonding between substrates, and surface chemistry associated with the treatment of aluminum powders.

These hybrid chemicals react with polymer and mineral components to form durable, covalent bonds across the substrate interface. The silanol groups form once the alkoxy groups in the alkoxy silane are hydrolyzed, creating a source of stress relaxation in the interface [5]. The stress relaxation provides a better flow of the particles, and the hydrophobicity improves the fluid environment of aluminum powders.

The structure provides a basic understanding of the chemistry of the organofunctional alkoxysilane. The general formula below conveys the rationale behind the chemical properties and benefits of this molecule:



In this general structure, the **R** group can be aromatic, alkyl or a combination. These **R** groups are not hydrolyzable but provide hydrophobic surfaces in applications such as the ability to repel water. To improve flow, mixing time, and hydrophobic properties related to improving pigment dispersion, aryl and alkyl silanes are used [6].

The **X** group can react with various forms of hydroxyl groups, releasing a methoxy or ethoxy group, typically the hydrolysis is caused by minimal amounts of water and is acid catalyzed. These groups provide linkage with inorganic substrates to improve coating integrity and adhesion.

The resulting silanol hydrogen is more electrophilic and, therefore, much more reactive due to the more electropositive atomic structure of silicone. The resulting high dipole moment provides a greater hydrogen bonding between the silanol group hydrogens and the substrate surface [5].

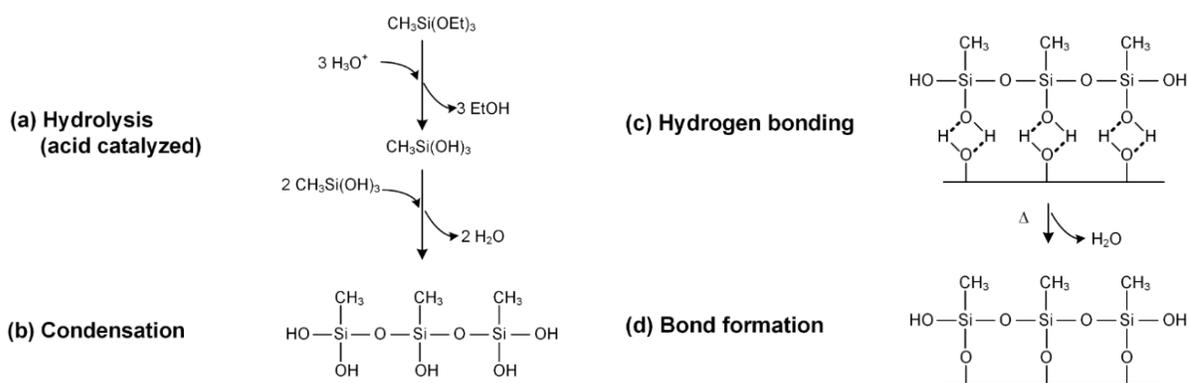


Figure 1. Reaction Process of Alkoxy Silanes (ethoxy released) [6]

The reaction of the silane is seen in Figure 1, which involves the hydrolysis process for methyltriethoxysilane. First, the hydrolysis of the alkoxy (**X**) groups. The reaction occurs by adding water to the molecule and forming a tertiary alcohol. The first and second alkoxy groups are hydrolyzed, in Figure 1a ethanol was released as a byproduct.

Condensation to form oligomers is the second step of the process, Figure 1b. The reaction releases water as a byproduct. It is important to note the pH during this step of the reaction because it will determine if the reaction proceeds with condensation or hydrolysis of the tertiary alcohol. It is the rate determining, or limiting step, of the entire reaction. In general, the condensation is fast, and hydrolysis is slow in an alkaline medium, while the opposite is true for an acidic medium [7]. Figure 2 shows this dependence of the condensation/hydrolysis reaction on the pH value of the environment [7].

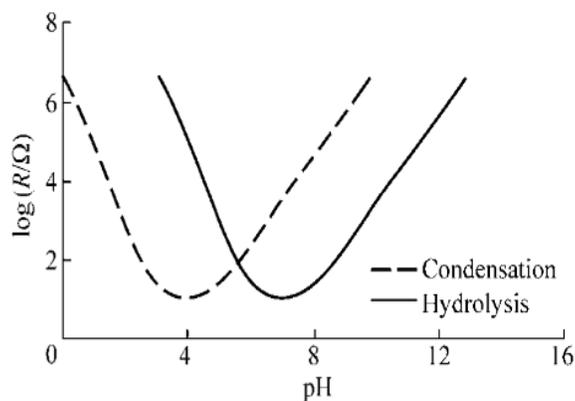


Figure 2. pH Dependence of second step of Reaction of Alkoxy Silanes [3]

Before the organosilane bonds with the substrate surface, hydrogen bonding occurs between the substrate hydroxyls and reactive silanol groups, seen in Figure 1c. The hydrogen of the hydroxyl group closest to the silicone hydrogen bond, while any hydrogens in the **R** group will not contain interactions strong enough to take place in a reaction.

Bond formation of the substrate is the last reaction in the process. During drying at high temperature, a strong covalent bond is formed with water produced as a by-product. As seen in Figure 1d, a lot of energy is required for the bond formation to occur, therefore it is crucial to heat at a moderate cure cycle (100°C/30 min) [5]. It is important to note that only one bond from each silicone of the organosilane is formed to the substrate surface.

Due to the highly reactive ethoxy sites, organic compatibility, and unique silane hydrolysis chemistry, different alkoxy silanes provide a myriad of straightforward synthesis solutions to high-performance applications, such as treatment of aluminum oxide.

By adding a silane coating to the aluminum particles, it is possible to improve the interfacial chemistry of the aluminum to make the powders flow better and provide hydrophobic properties without compromising the overall metallic aluminum content. The Al powders seen throughout this paper were surface modified which improved the flowability and fluidization properties.

The purpose of this work was to study different facets of the aluminum powder processing methods and gain a better understanding of the molecular-level surface chemistry to aid in the engineering of larger scale processes. The thesis of this work is: if the surface of the aluminum particles can be successfully modified, then surface information specific to the surface coating can be obtained using materials characterization techniques.

Chapter 2. Materials and Methods

Procedure for samples for solution phase treatment [4]

Ethanol (99.5% (w/w), 0.1% water (w/w), KOPTEC, USA), methyltriethoxysilane (MTES, 99.0% (w/w), Gelest, USA), and aluminum powder (99.8% (w/w), Valimet, USA) were all used as received. All powders were sieved using an ultrasonic system (Russell Finex, North Carolina, USA) prior to surface treatment; powders were sieved with a mesh size of 325 (45 μ m). MTES (1 wt%, Gelest) was allowed to hydrolyze in an ethanol:water solution (95/5, w/w, pH adjusted to ~4 with HCl) for 10 min prior to use. The solution and aluminum powder (23 kg, Valimet, California, USA) were loaded into a rotary blender (Gemco) and allowed to tumble for 15 min. The bulk solvent was evaporated under vacuum, followed by trace solvent removal over a period of 4 h. The product was cooled and re-sieved at the above indicated sieve size prior to analysis.

Fluidized Bed Reactor Treatment [8]

PDMS with terminal hydroxyl groups (M_n approximately 550, viscosity approximately 25 cSt; Aldrich, USA) and metallic aluminum powder (d_{50} approximately 20 μ m, Valimet, USA) were used as received. Ultra-high purity nitrogen was employed as the fluidizing gas in conjunction with an inline oxygen/hydrocarbon trap and flow controller. A simple gas-phase deposition apparatus was fabricated in house using two porous gas distributor plates, a glass cylinder with a heating jacket, and a nitrogen gas flow line (flow velocity = 0.2 mm/s) connected to a PDMS reservoir. Prior to each deposition trial, aluminum powder (300 g) was loaded into the cylinder and, to improve the particle-gas-phase interactions. While in the apparatus, the powder was periodically agitated/homogenized. The powder was heated to and held at approximately 100°C for

1 h prior to treatment to remove physisorbed water and also maintained at this same temperature for the duration of the deposition process. The PDMS was heated to approximately 250°C and the resulting vapors were mixed with the nitrogen gas stream over a period of approximately 4 h.

Particle Size Analysis

Using laser diffraction (Mastersizer 3000, Malvern Panalytical Ltd.), the particle size distribution (PSD) was measured and recorded by volume or number distribution of particle sizes. The aluminum samples were dispersed in isopropyl alcohol and sonicated for 1 min before data collection. The sample was loaded into the wet sample dispersion unit until it reached an obscuration value of 11-15%. Measurements of the same sample were collected five times and the average reported. The error associated with the instrument is ± 0.5 microns.

Fourier Transform Infrared Spectroscopy

The diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) data was collected using a Fourier transform infrared spectrophotometer (VertexV70, Bruker, Germany) equipped with a mercury-cadmium-telluride detector. The Praying MantisTM diffuse accessory (Harrick, USA) was used to collect the sample spectra. The reactor was purged with Argon gas, at ambient temperature, continuously throughout the measurements while the spectrum collected had a resolution of 6 cm⁻¹ and 400 scans. Dried powdered potassium bromide (KBr) was used as a reference spectrum, to enable subtraction of atmospheric water and carbon dioxide.

Carbon monoxide dosing procedure

Using the Praying MantisTM diffuse accessory (Harrick, USA) with a dosing chamber accessory was used to collect the sample spectra while adjusting the temperature to avoid buildup of ice on the DRIFTS window from excess water. The sample was prepared normally, then wrapped in

parafilm to ensure there are no holes. The temperature was brought down to 170°C by using a circulating chiller. During the CO dosing, samples were taken every 10 minutes to ensure the CO is adsorbed to the Al surface, then the temperature is increased for the CO to desorb from the surface.

Chapter 3. Research Plan

Hydrophilic and Hydrophobic Silanes

Different silanes can be utilized to find one that is suitable for the desired properties of the powder such as flowability and density. The surface modification can result in hydrophilic, tends to be attracted to water, or hydrophobic, tends to repel water, properties. Typically, silanes are used to modify the interactions that occur on the boundary layer of solids with the water in the bulk of solution [9]. At the interface of the treated Al powders, there is typically one bond to each silicon atom of the organosilane which creates a monolayer where the **R** group of the silane remains available to interact with other phases. To create a successful hydrophobic coating, it must mitigate hydrogen bonding and shielding the polar surfaces from interacting with water [9]. Meanwhile, hydrophilic coatings will have hydrogen bonding sites and allow the formation of tight layers of water [9]. The silanes selected for study in this work and for future research were methyltriethoxysilane (MTES), polydimethylsiloxane (PDMS), and phenyltriethoxysilane (PTES), which create a hydrophobic surface modification. Manipulating the hydrophilicity of the silane during the surface treatment of aluminum powders can improve the fluidization properties for aluminum-water systems.

Segregation in Bulk Aluminum Powders

There was some evidence that segregation may be an issue for powder loading and for long term storage. For a storage drum, samples were taken at the top, bottom and sides to investigate for any segregation over a long-term storage or after loading. The sample data from PSD can be analyzed to understand if segregation occurs in the storage of these Al powders. By understanding more

about this phenomenon, the process, operation, and storage can be changed to provide better material and ensure uniformity in Al powder batches if needed. Similarly, the other samples reviewed in this paper compare the uneven distribution plate of the silane in a fluidized bed reactor before and after it was fixed.

Acid Influence on Silane Coating

The synthesis of silane surface modification can be manipulated to find which acid catalyzes the hydrolysis step better. Although briefly mentioned that the pH ~4 should be used, finding different strong acids can improve the synthesis process and possibly improve fluidization of the Al powders. Experimentally, this could be observed by synthesizing multiple surface treated powders and test the flowability with the acid being the independent variable. The surface can be observed using ssNMR, XRD, and DRIFTS first to see if the surface changes. This was briefly tried with hydrochloric acid and acetic acid, but more experiments were planned, and the flowability can be assessed with a Hall flowmeter. The results would be interesting if they prove there is a relationship between the specific acid, rather than just the pH, and the flowability of the powders.

Carbon Monoxide Dosing on Silane Coated Aluminum Powder Surface

Carbon monoxide dosing has been used to study aluminum oxide surfaces and thus the method was selected for potential research. Although the specific effects are unknown, dosing aluminum powders with CO may show a relationship between the deactivation of metal surfaces because they cover surface sites and block other pores throughout the Al surface [10]. The role of a surface carbon species is yet to be fully understood and possibly differentiate between treated and raw aluminum powders.

Chapter 4. Results and Discussion

Characterization of PDMS Treated Aluminum Powders

The Al powder samples treated with PDMS were characterized using DRIFTs and each peak was given an assignment based on reference data. Looking at the structure of PDMS, seen in Figure 3, the important peaks to look for are observed due to the silicone bonds and the methyl group interactions. The Si-O-Si bond is seen at a broad range of 1100 to 1050 cm^{-1} .

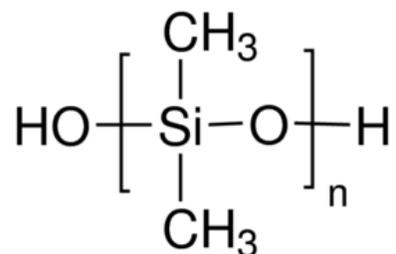


Figure 3. Structure of Polydimethylsiloxane with –OH end groups (PDMS) [11]

Uneven distribution occurred due to the non-uniform PDMS distributor plate, causing more PDMS to one side of the reactor rather than the middle. Samples were taken before and after the distributor plate was fixed. In Figure 4, the side (purple) and bottom samples (green) spectra, before the distributor was repaired, are compared to observe the difference in peak intensity. The side samples have higher intensity absorbance peaks, suggesting higher PDMS surface content than the middle sample (blue).

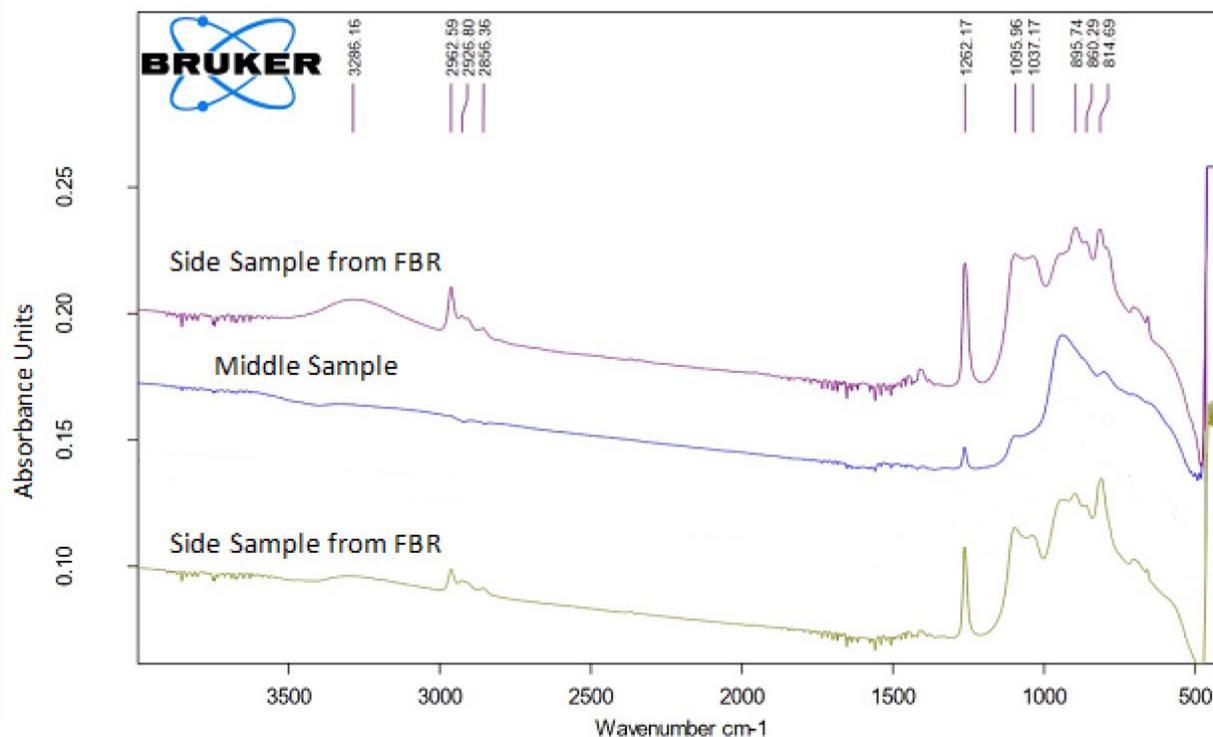


Figure 4. Diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) spectra of PDMS-treated aluminum powder samples from the sides and middle of fluidized bed reactor before PDMS distributor was fixed

Table 1 summarizes the assignments for each peak seen in the side sample from FBR. There are intense peaks around the -CH stretching mode, not seen in the middle samples. The -OH peak around 3286 cm^{-1} is better distinguished in the side sample. Therefore, there is an uneven distribution of PDMS throughout the FBR due to strong OH peaks associated with PDMS, where the buildup is on the sides. The Si-O-Si broad peaks are seen in each sample around 1095 cm^{-1} , but the intensity is strongest in the side samples, further showing the uneven distribution of PDMS during the deposition process of Al powder in an FBR.

Table 1. Peaks for DRIFTS spectra of PDMS treated Al sample Figure 4.

Wavelength (cm^{-1})	Moiety
3286	-OH
2900-3000	-CH stretching
1100-1050	Si-O-Si deformation
~900	Al-O deformation

Once the PDMS distributor plate was fixed, there should be evidence of a more even composition of PDMS throughout the reactor. Samples were taken from the bottom (green) and side (yellow) again, with the addition of a mixed (blue) sample, seen in Figure 5.

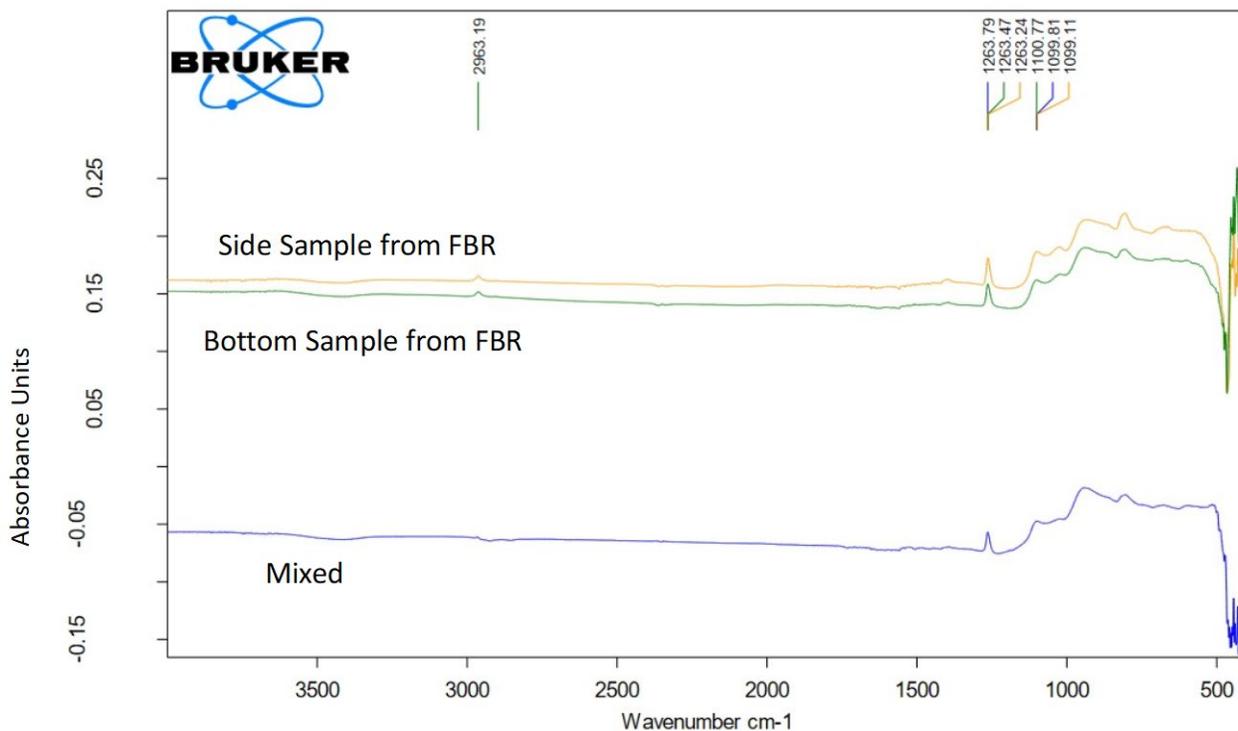


Figure 5. Diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) spectra of PDMS-treated aluminum powder samples from bottom, side, and mixed of fluidized bed reactor after PDMS distributor plate was fixed.

The peaks are present in both of the samples and each assignment is listed in Table 2. The intensities of the peaks observed for both samples are similar, therefore the distributor plate was fixed correctly. The Si-O-Si peaks are observed in all of the samples, which means that each section of the FBR contains amounts of the PDMS. The -CH₃ bending and -CH stretching peaks were observed in each sample.

Table 2. Assignments of absorbance peaks from DRIFTS spectra of PDMS sample in Figure 5

Wavelength (cm⁻¹)	Moiety
2963	-CH stretch
1264	-CH ₃ deformation
1100-1050	Si-O-Si deformation
~900	Al-O deformation

Segregation Results

Due to the fine Al powder's ability to generate electrostatic charging, particle segregation can occur in the bulk solid material [12]. This affects the uniformity of the Al powders and could cause difficulties in processing and handling the material. Therefore, particle segregation of Al powders is observed through particle size distribution and how particles of one size will be in a different area than particles of another size. Various Al powders were analyzed to observe any segregation that could have occurred during the process and storage of the silane treatment on Al powder. In Figure 6, the volume density for top and bottom sample of the storage drum were compared.

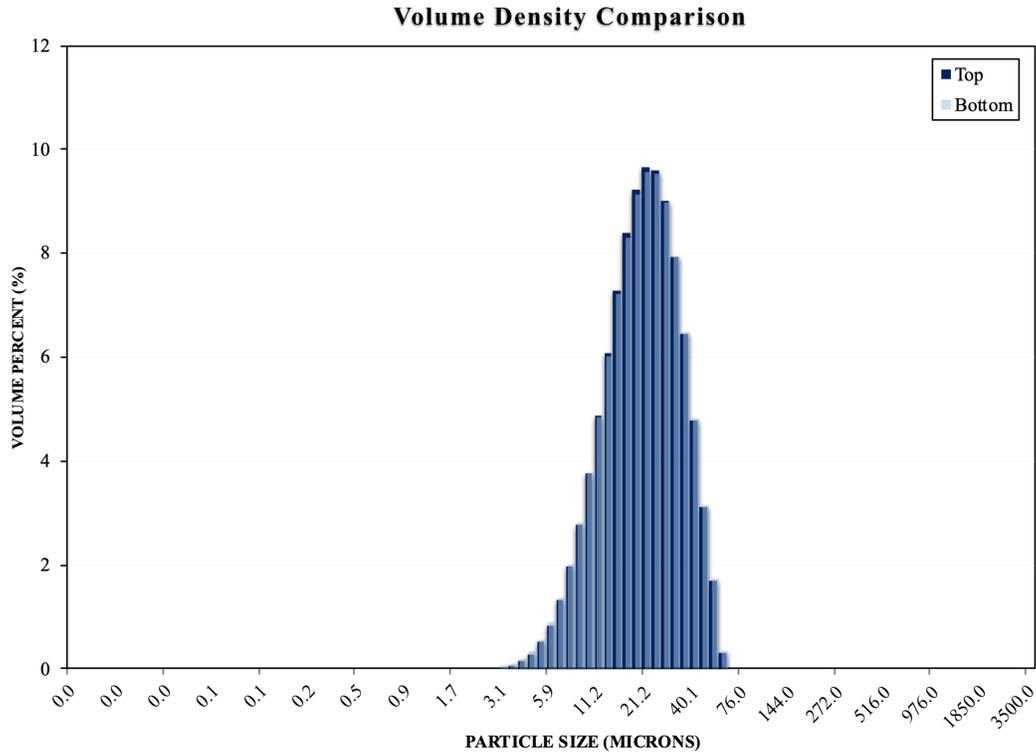


Figure 6. PSD data for top and bottom samples from storage drum.

The difference in volume density between the top and bottom should be small if there is no segregation observed. Since the differences are miniscule, then there was no significant amount of segregation in the large storage drums.

Carbon Monoxide Dosing Aluminum Surface

Although the effects of CO dosing are unknown for aluminum powder surfaces, the experiment suggests that at very low temperatures it is possible to absorb CO as seen in Figure 5. The increase in the integrated area during dosing represents more CO being adsorbed to the surface.

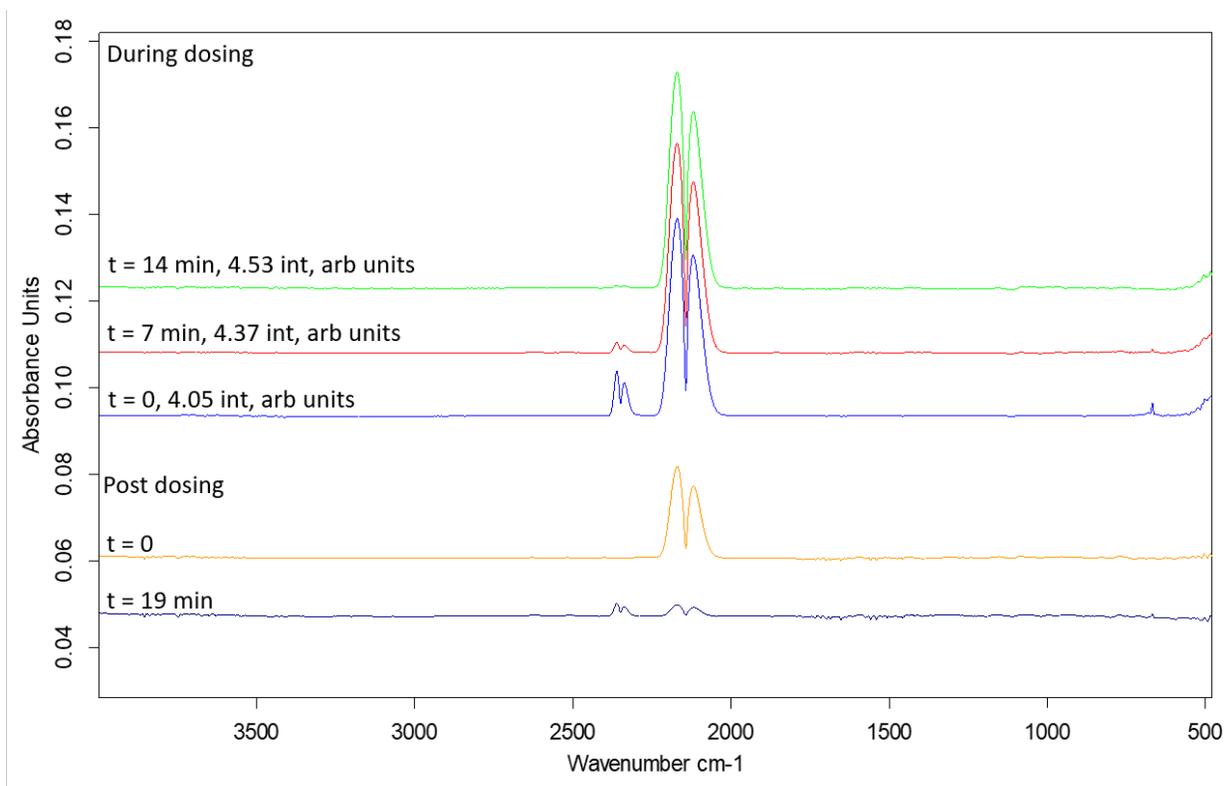


Figure 7. Diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) spectra of PDMS-treated aluminum powder sample during CO dosing.

The peaks around 2100 cm^{-1} , of the DRIFTS spectra, increase in intensity as the time of CO dosing increases. Meaning the CO is adsorbed on the surface at low temperatures. Once dosing is completed, the post dosing peaks begin to decrease in intensity as the CO is no longer observed on the surface.

This experiment was only completed once, which is the data shown above, but there are plans to continue work on the effects of CO dosing.

Chapter 5. Summary and Conclusions

This paper gathered a range of data to support silane surface treatment processes for Al powders. The observations of the DRIFTS for FBR samples showed that the process needed to improve to minimize the uneven PDMS through the gas distributor plate. Specifically, the FBR setup was changed to improve the heat transfer to allow for better distribution of PDMS in the gas flow. As shown in the IR data.

As explained previously, the Al powder's ability to segregate could be minimized based on the particle's characteristics that relate to the segregation process [12]. For example, reducing the number of steps of the process will decrease the segregation because the powder mixture will not need to be transferred constantly. After collecting PSD data from the storage drum, the differences between the top and bottom of the drum show there is no significant amount of segregation in the stored aluminum powders.

The effects of CO dosing warrant further investigation. There is potential for the silane surface treated Al powder samples to be dosed with CO and examine if it interacts with the silane treatment or with the aluminum oxide surface. It also possibly could be used to test if the silane treatment is truly hydrophobic or hydrophilic depending on the preference in a specific application. It would also be interesting to be able to differentiate between the treated and raw Al powder, which can provide further insight on how the CO dosing could affect the silane surface modification of Al powder.

Overall, there are areas to improve and test, but also observe new techniques on the surface of Al powders. These studies can be continued to assess the possibilities of improving Al powder silane surface modification and minimizing of segregation.

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