

ATOMIC LAYER DEPOSITION AS A METHOD OF FINE TUNING THE SURFACE CHEMISTRY OF OXIDE MATERIALS

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List of Symbols and Abbreviations

ALD: Atomic Layer Deposition

SiO₂: Silicon oxide

TiO₂: Titanium oxide

TiCl₄: Titanium tetrachloride

TMA: Trimethyl aluminum

RPM: Revolutions per minute

SEM-EDX: Scanning electron microscopy – energy dispersive x-ray spectroscopy

XPS: X-ray photoelectron spectroscopy

MW: Molecular weight

N_A: Avogadro's Number

r₁: Inner radius

r₂: Outer radius

χ : Titanium/silicon ratio

At. %: Atomic Percent

α : Atomic percent of surface sites of substrate

Summary

Atomic layer deposition (ALD) is a vapor-phase synthesis method in which a material is deposited onto a surface with precise atomic thickness. Through ALD, ultra-thin monolayers of oxide materials can be deposited onto powders, creating mixed oxide surfaces with tunable surface chemistries, enabling their usefulness towards catalytic processes in the petrochemical and fine chemical industries. ALD holds an advantage over typical solution-phase methods of creating mixed oxide materials due to the latter's difficulty in controlling the surface composition, making analysis difficult. However, if we can better understand the interactions of the surface in solution, it can be used to design more effective catalysts. One way to observe this is by studying the zeta potential of the surface, which is directly correlated with surface charge and is a product of these acid-base interactions at the interface. Each material can be identified using the isoelectric point, which is the point at which the zeta potential/net surface charge is zero. For mixed metal oxides, their isoelectric points were calculated in the literature to be the summation of each individual component's isoelectric point multiplied by its surface coverage. However, this calculation assumes that the components do not interact with each other when mixed. In order to investigate this discrepancy, we used ALD to deposit thin layers of titanium oxide onto silicon oxide powders. If we were to assume the equation used in the literature, we can assume that one single monolayer over the surface would be sufficient to convert the isoelectric point from that of silicon oxide to that of titanium oxide. However, our results have indicated that the isoelectric point did not reach that of titanium oxide until multiple monolayers were deposited, indicating that a different model/equation must be utilized to better elucidate the surface behavior. Additionally, during these studies of the isoelectric point, we have formulated an equation that can correlate the thickness of ALD-deposited films with the material's relative atomic percent. This equation was created by assuming that the shape of the particle + film

retains its shape, and therefore its volume formula, allowing it to work for ultra-thin films, but not for much thicker films. Finally, this thesis highlights the importance of being mindful of the precursor used for powder ALD: precursors like TiCl_4 can create byproducts like HCl from the reactor walls and the powder itself. These byproducts can then adsorb onto the powder surface, which can block film growth or affect the pH of the resulting solution when the powder is dispersed in water. Extra measures, such as a double dose or a post-process washing step, were implemented, and should be used when performing powder ALD.

1. Introduction

1.1 Catalysis

1.1.1 Overview

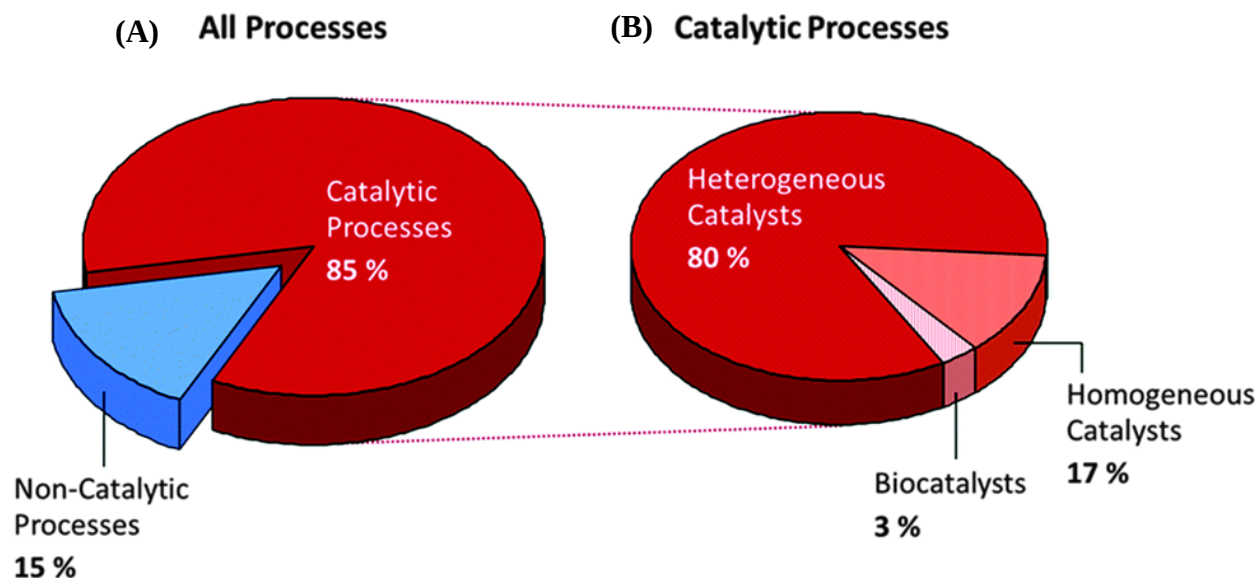


Figure 1: Pie charts showing (A) the relative percentages of all processes that require catalysts and (B) catalytic processes that require the use of heterogeneous, homogeneous, and biocatalysts.

Simply put, catalysts are facilitators: they are able to reduce the activation energy required to progress a reaction without being consumed in the process.¹ They are an essential part of our world: more than 80% of all manufactured products involve a catalyst at some point, highlighting its importance in today's economy (**Figure 1**).^{2,3} The Haber-Bosch process, considered to be one of the world's most important inventions of the 20th century, uses iron oxide catalysts to produce ammonia from nitrogen and hydrogen gas, and is responsible for the production of food all around the world.⁴ The polymerization of olefins, which is responsible for the production of plastics worldwide, is catalyzed by a titanium based catalyst known as the Ziegler-Natta catalyst.⁵ Hydrodesulfurization, in which sulfur is removed from fuel in order to prevent the emissions of toxic sulfur (IV) oxide, requires the use of molybdenum-cobalt mixed catalysts. Without catalysts,

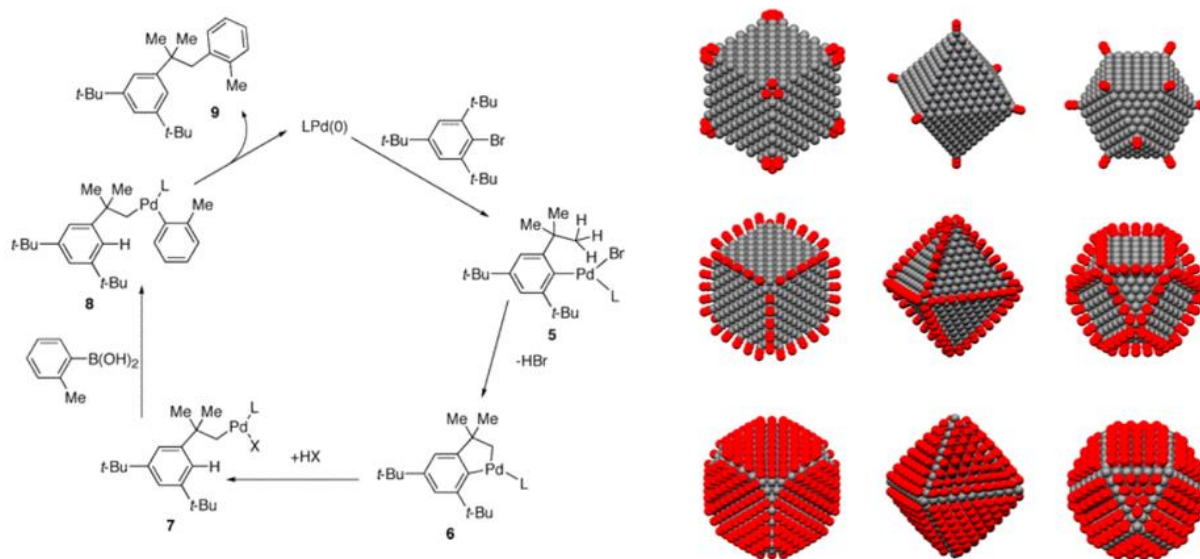


Figure 2 Homogeneous (left) vs heterogeneous (right) catalysts. Homogeneous catalysts have high selectivity due to their iteratively studied molecular structure. Heterogeneous catalysts have lower selectivity due to the multiple different active sites (red) present.

these processes that make up a huge part of our lives would not be possible, and improving these catalysts is an ever-important topic in chemistry research.

To improve catalysis, we must look at the properties of a catalyst that make it work for a reaction. A catalyst's performance is defined by three parameters: activity, selectivity, and recoverability.⁶ The activity of a catalyst is described by its yield, or how much of the reactants are converted into products. The selectivity of a catalyst is its ability to preferentially yield one product over another. Finally, the recovery of a catalyst is the ease with which the catalysts can be separated from the products.

Catalysts can be divided into homogeneous catalysts, which have high activity and selectivity but low recovery, and heterogeneous catalysts, which have high activity, low selectivity, and high recovery (**Figure 2**). Homogeneous catalysts are usually molecular catalysts that are in the same phase as the products. Due to their molecular nature, it is very easy to identify

and tune the active sites of these catalysts to adjust their reactivity, enabling them to have high activity and selectivity.⁷ However, recovering these catalysts can require energy-intensive methods such as distillation or liquid-phase separation. Examples of homogeneous catalysts are the Ziegler-Natta catalyst and the Suzuki-Miyaura catalyst. On the other hand, heterogeneous catalysts are in a separate phase from the products, such as nanoparticles and catalyst powders. This separated phase allows the catalysts to be recovered more easily with methods such as centrifugation and filtration.⁸ But the active site of these catalysts are difficult to isolate, such as the many different facets present in polyhedral nanoparticles, and selectivity and sometimes yield is low as a result.⁶ Examples of heterogeneous catalysts include the Haber-Bosch catalyst and the hydrodesulfurization catalyst. Despite their drawbacks, heterogeneous catalysts are significantly more used than homogeneous catalysts and biocatalysts as it accounts for 80% of all catalyzed processes in the chemical industry.³

1.1.2 Acid Catalysis

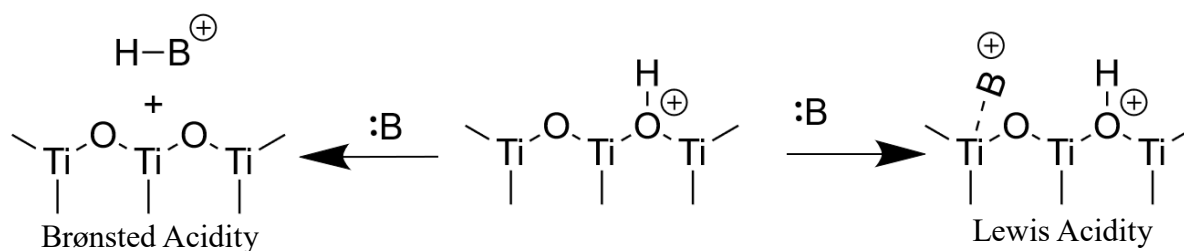


Figure 3: Brønsted vs Lewis acid: Brønsted acids donate a proton to a base, such as an OH group donating its proton to a base B, while Lewis acids accept an electron pair from a base, such as the titanium cation accepting an electron pair from a base B

One of the most important areas within this catalysis industry is acid catalysis, which is the use of a proton donor or electron acceptor to catalyze a chemical reaction. These types of acids can be further categorized into Brønsted acids, which are characterized by proton donors like H₂SO₄ or HF, and Lewis acids, which are characterized by electron acceptors such as AlCl₃ and

BF₃ (**Figure 3**) . These acid catalysts are some of the major catalysts used in these industries and are homogeneous catalysts.

1.1.3 Brønsted Acid Catalysts

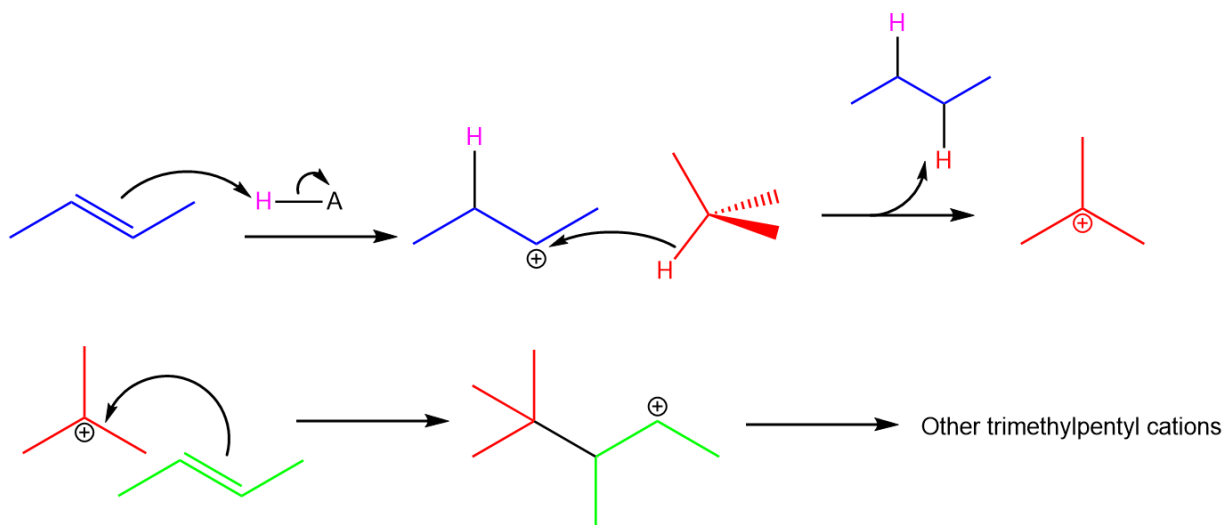


Figure 4: Mechanism of Brønsted acid catalyzed alkylation of isobutane with light olefins.

As one of the most industrially important processes used in the petrochemical industry, alkylation using light olefins is an example of a reaction that uses Brønsted acid catalysts.⁹⁻¹³ In this reaction, an addition reaction is performed on the double bond of an olefin via a strong proton (H⁺) donor, creating a carbocation. This carbocation is located on a secondary carbon, and abstracts a hydride (H⁻) from isobutane (red), as the tertiary carbon of the isobutane can better stabilize the carbocation than the secondary carbon. This isobutane carbocation then performs an addition reaction onto another olefin, re-creating a secondary carbocation which then abstracts a hydrogen from another isobutane molecule, continuing the reaction.¹³ Finally, the acid regenerates by abstracting a proton from the carbon neighboring the carbocation, performing an elimination reaction and recreating an olefin (**Figure 4**).

1.1.4 Lewis Acid Catalysts

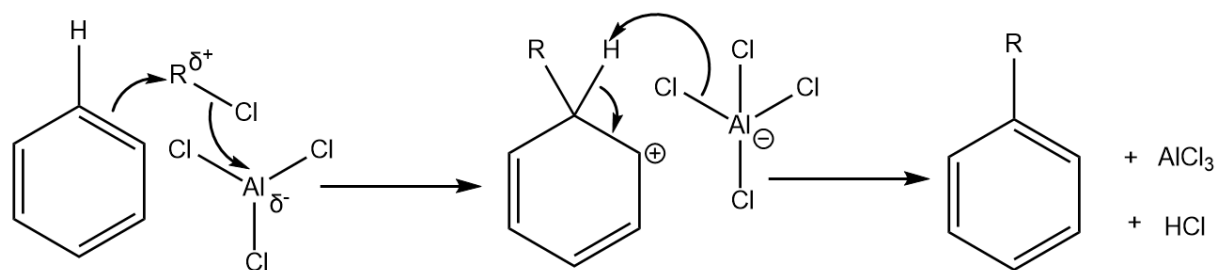


Figure 5: Mechanism of Friedel-Crafts alkylation of a benzene ring using an alkyl halide and a Lewis acid such as $AlCl_3$.

Lewis acids also play a large role in the chemical industry: Friedel-Crafts catalysis is one of the most industrially important processes in the production of low and high volume chemicals. In Friedel-Crafts catalysis, Lewis acid catalysts are used to add substituents to benzene such as acyls, benzoyls, alkyls, and sulphonyl groups. As seen in **Figure 5**, a Lewis acid catalyst such as $AlCl_3$ activates an alkyl halide (chloride), allowing a benzene ring to attack the alkyl portion of the halide and creating a carbocation which is resonance stabilized throughout the ring. The unfilled orbital in $AlCl_3$ allows for it to take in an electron pair, so it is able to take in an electron pair from the negatively charged chloride, becoming $AlCl_4^-$. The $AlCl_4^-$ molecule then has one of the chlorine ions abstract the proton adjacent to the alkyl group, restoring the aromaticity of the benzene ring, creating HCl byproduct, and restoring the $AlCl_3$ catalyst. Most batch processes use $AlCl_3$ due to its low cost and strong Lewis acidity. However, this high reactivity also means that $AlCl_3$ and other similar metal halide catalysts can be readily hydrolyzed and would be difficult to handle. Consequently, these catalysts must be employed in stoichiometric quantities, posing health and safety hazards for a large inventory.¹²

Many of these acid catalyzed processes require strong acid catalysts, so sulfuric acid and other mineral acids are often used.¹² However, as many of these acids are toxic and corrosive, they must be separated from the product, adding process difficulties and leading to high costs and large

volumes of waste.¹⁴ Following the trend of green chemistry, it is necessary to utilize materials more efficiently, use less toxic solvents, and generate significantly less waste into the environment.¹⁵

1.2 Acid Properties

Before continuing on this thesis, there are some important concepts about acids that must be clarified: acid strength, acid amount, and acid hardness. It is important to differentiate these three parameters as each of these plays a distinct role in an acid's ability to catalyze a reaction.

1.2.1 Acid Strength and the Hammett Acidity Function

Acid strength is defined for Brønsted acids as the ability for a chemical species to donate its proton. Inversely, it can be interpreted as the stability of an acid's conjugate base after it dissociates or is deprotonated, which can be done if the electron density of the acid site is shifted away from the acid site.

The extreme end of Brønsted acidity – that is, acids that have an extremely strong proton donating power – is known as superacidity and is defined as having a proton donating strength greater than that of pure 100% sulfuric acid. Typically, the strength of an acid solution would be determined using the Henderson Hasselbalch equation, where the pH (concentration of H⁺ ions, or protons) would be determined by the acid dissociation constant, pKa, and the relative amounts of acid and conjugate base (**Equation 1**). However, this equation only applies to dilute acid solutions,

$$pH = pKa + \log\left(\frac{[A^-]}{[HA]}\right)$$

Equation 1: The Henderson Hasselbalch equation, in which the concentration of protons in solution is determined by the pKa and the concentrations of the acid and its conjugate base.

$$H_0 = pKa + \log \left(\frac{[A^-]}{[HA]} \right), \quad H_0 = -\log a_{H^+} \frac{\gamma_{A^-}}{\gamma_{HA}}$$

Equation 2: The Hammett acidity equation, in which the activity of the protons (a_{H^+}) and the activities of the acid/conjugate base species (γ_{A^-}) and (γ_{HA}) are now factored into account.

in which the thermodynamic activity of the protons can be largely ignored, and their predicted concentrations would match the measured concentration of protons. However, for concentrated acid solutions, this activity begins to change much more quickly than the concentration, making pH an inaccurate measure of the true acidity of a solution. In order to compensate for this error, the idea of pH was replaced with the Hammett acidity parameter, H_0 , which takes into account the activity of the protons and the activity coefficients of the acid and conjugate species (**Equation 2**). In fact, the Henderson Hasselbalch equation is an approximation of the Hammett acidity equation, except that the activity coefficients are near unity, allowing pH and H_0 to be nearly identical.^{16, 17}

Using Hammett acidity parameters, the H_0 of pure 100% sulfuric acid would be -12, meaning any acid that has an H_0 below -12 would be classified as a superacid.¹⁸ In many cases, a superacid solution can be created by mixing a strong Lewis acid with a strong Brønsted acid. Once the Brønsted acid gives its proton up, the Lewis acid can then stabilize the conjugate base and reduce its proton accepting ability, becoming even more acidic.¹⁹ One well known example of a superacid behaving in this manner is fluoroantimonic acid, which is a mixture of HF and HSbF₅. As two HF molecules ($H_0 = -15$) are mixed with SbF₅ ($H_0 = -21$), when one HF molecule dissociates into H⁺ and F⁻, the F⁻ ion is stabilized by the SbF₅, creating SbF₆⁻ which is an extremely weak base. The remaining H⁺ ends up binding to HF, as it is the strongest Brønsted base in the mixture, creating H₂F⁺ which has an H_0 of about -28.²⁰

The Hammett acidity function is used to define a Brønsted acid's strength and can be experimentally determined using titration techniques with indicators of known pKa. The indicator starts at its base form, and if it is protonated into its acid form, then the acid has a lower H_0 than the indicator's pKa. For example, from **Figure 6**, an acid that can change the color of 2,4-Dinitrofluorobenzene from colorless to yellow, but not the color of 1,3,5-trinitrotoluene will have an H_0 between -14.52 and -16.04. Any acid that cannot change the color of the base-form of any of these indicators would have an H_0 greater than 6.8.²¹

Another method of determining the acid strength is through the gaseous base adsorption method. When gaseous bases adsorb onto acid sites, the adsorption binding strength of the base depends on the acid strength: a stronger acid would bind more strongly to the base than a weaker one. At elevated temperatures, the more weakly-bound base would leave first, followed by the more strongly bound base as the temperature increases. The temperature-programmed desorption profile of base molecules such as pyridine or ammonia can then be taken to determine the relative strength of acid sites.²¹

1.2.2 Acid Amount

The amount of acid is the concentration of acid sites in an acid; for Brønsted acids specifically, it is the number of sites that can donate a proton. The acid amount is not necessarily dependent on the electron density of the site, but rather on the surface area of the solid acid.

Indicators	Color		pK_a ^{†1}	$[H_2SO_4]^{†2}/\%$
	Base – form	Acid – form	pK_a	
Neutral red	yellow	red	+ 6.8	8×10^{-8}
Methyl red	yellow	red	+ 4.8	—
Phenylazonaphthylamine	yellow	red	+ 4.0	5×10^{-5}
<i>p</i> -Dimethylaminoazobenzene	yellow	red	+ 3.3	3×10^{-4}
2-Amino-5-azotoluene	yellow	red	+ 2.0	5×10^{-3}
Benzeneazodiphenylamine	yellow	purple	+ 1.5	2×10^{-2}
Crystal violet	blue	yellow	+ 0.8	0.1
<i>p</i> -Nitrobenzeneazo- (<i>p'</i> -nitro-diphenylamine)	orange	purple	+ 0.43	—
Dicinnamalacetone	yellow	red	— 3.0	48
Benzalacetophenone	colorless	yellow	— 5.6	71
Anthraquinone	colorless	yellow	— 8.2	90
2,4,6-Trinitroaniline	colorless	yellow	— 10.10	98
<i>p</i> -Nitrotoluene	colorless	yellow	— 11.35	^{†3}
<i>m</i> -Nitrotoluene	colorless	yellow	— 11.99	^{†3}
<i>p</i> -Nitrofluorobenzene	colorless	yellow	— 12.44	^{†3}
<i>p</i> -Nitrochlorobenzene	colorless	yellow	— 12.70	^{†3}
<i>m</i> -Nitrochlorobenzene	colorless	yellow	— 13.16	^{†3}
2,4-Dinitrotoluene	colorless	yellow	— 13.75	^{†3}
2,4-Dinitrofluorobenzene	colorless	yellow	— 14.52	^{†3}
1,3,5-Trinitrotoluene	colorless	yellow	— 16.04	^{†3}

Figure 6: Table of basic indicators used to determine the H_0 of Brønsted acids.

Materials with higher specific surface areas such as smaller powders or porous materials will have higher acid amounts.

The acid amount can also be determined using amine/pyridine adsorption. By placing a sample placed onto a quartz spring balance, then evacuated, the mass of the sample is determined. Then, the base is introduced, adsorbing onto the sample, and then is evacuated as well until the sample mass does not decrease. The increased mass can be used to calculate the total mass of base, and subsequently the number of acid sites.

1.2.3 Acid Hardness/Softness

Acid hardness/softness is primarily used in the context of Lewis acids/bases and is not a measure of a chemical species' acidic/basic strength but rather on its polarizability. Small, relatively nonpolarizable species are considered hard while large, relatively polarizable species are considered soft. Following this definition, Pearson put a simple rule: hard acids preferably bind to hard bases, while soft acids preferably bind to soft bases. Examples of hard acids would be Ti^{4+} or Al^{3+} , which are cations of electropositive metals with high charge-to-radius ratios, which would result in a smaller electron shell and therefore lower polarizability. These hard acids would bind to bases with donor atoms such as N, O, or F which are highly nonpolarizable due to their high electronegativities reducing their ionic radii. Due to the nature of these species, hard acid/base interactions tend to be more electrostatic. Soft acids like Au^+ , or Pd^{2+} would preferably bind to bases like CO or H^- , with a more covalent bonding nature.

While the hard/soft acid-base theory applies mostly to Lewis acids, it is also worth noting that H^+ has no electrons to polarize and is therefore classified as a hard acid, and will bind preferentially to hard bases. This does not mean that the proton necessarily will bind to a *strong* base, simply that it would prefer to bind to a strong hard base rather than a strong soft base, if given the opportunity.²²

1.2.4 Solid Acid Catalysts and Surface Acidity

Yet another class of acid catalysts that exists in the realm of acid catalysis are solid acids. These catalysts are heterogeneous catalysts and can have the advantage of easy separation via filtration and can be reused without any significant losses in activity.¹⁴ Solid acids, notably metal oxides, can have both Brønsted acid sites and Lewis acid sites in the form of its hydroxide groups

and its non-proton surface cations, respectively, but for the purpose of this thesis, only Brønsted acid sites, or its ability to donate/accept protons, will be the primary focus.²³

The ability for a solid acid catalyst to donate its proton can also be seen as the stability of its conjugate base, which in the case of oxides refers to the deprotonated oxygen. If the electron density is primarily concentrated within this oxygen, then its alkalinity, or its ability to abstract a proton from a proton source, increases accordingly. If a neighboring atom shifts some of this electron density away from the oxygen, then the negative charge becomes delocalized, stabilizing the conjugate base and increasing the acidity of the oxygen. Therefore, oxides with stronger surface acidities will tend to have higher cation electronegativity, which is dependent on the material factor.²⁴ The nature of an oxide material in solution depends on the nature of the bond, which in turn is effected by the electronegativity as well. If the difference in electronegativity between the metal and the oxygen is significantly high enough, then the oxide is held together via primarily ionic forces. If the electronegativity difference between the metal and the oxygen are much closer, then the oxide is considered to be a more covalently bonded solid. Under the context of a surface acidity, covalently bonded solids are the main focus because these shifts in electron density would not occur in ionic solids, which are held together via electrostatic forces rather than through electron delocalization.

These solid acids can also be further described in terms of the strength and number of these acid sites, and in terms of their morphology with regards to surface area and porosity.¹⁴ Furthermore, the acid strength and amount of the metal oxide generally increases with decreasing cationic radius, increasing cation charge, and increasing cation electronegativity.²⁴ In other words, this also means that in many cases, alongside the proton, the cation will often serve as a Lewis acid.

1.2.5 Surface Acidity and Mixed Oxides

The surface acidity of an oxide material can be further modified or even significantly enhanced by mixing it with another oxide.²⁵ In many cases, mixing oxides can not only add extra acid sites onto the surface, but it can increase the strength of those acid sites compared to their individual counterparts. For example, some combinations of oxides, such as titania-silica, silica-zirconia, also exhibit an increased number of acid sites with increased strength.²⁶

Shibata et. al noted that the acid strength of mixed oxides is correlated with their combined average electronegativities (**Figure 7**). The reason why the averaged electronegativity values correlate with acid strength has not been fully elucidated, but we believe that the phenomenon involves synergistic behavior between Lewis and Brønsted acidity. Much like how the Brønsted conjugate base of a superacid is stabilized by a Lewis acid, the Brønsted conjugate acid of an oxide surface may be stabilized by a nearby Lewis acid site. By having two high but dissimilar electronegativity values, the oxide moiety with the higher electronegativity can pull electrons towards itself more strongly, leaving the less electronegative oxide moiety with lower electron density, and thus have a higher Lewis acidity, which can then influence the stability of nearby conjugate base sites in the form of -O^- groups. For example, at the Ti-O-Si interface in titania-silica gels, the higher electronegativity of the silicon ion relative to the titanium ion causes the former to be more electron accepting, shifting the electron cloud from the titanium onto the oxygen atom and further onto the silicon ion. While this would increase the Brønsted base character of the bridging oxygen ion, it would also the titanium ion would gain stronger Lewis acid character, allowing it to influence any free hydroxyl groups.²⁷

This change in electron density is similar to the inductive effect in organic chemistry, in which electron-donating or electron-withdrawing groups can affect the acidity of organic acids by

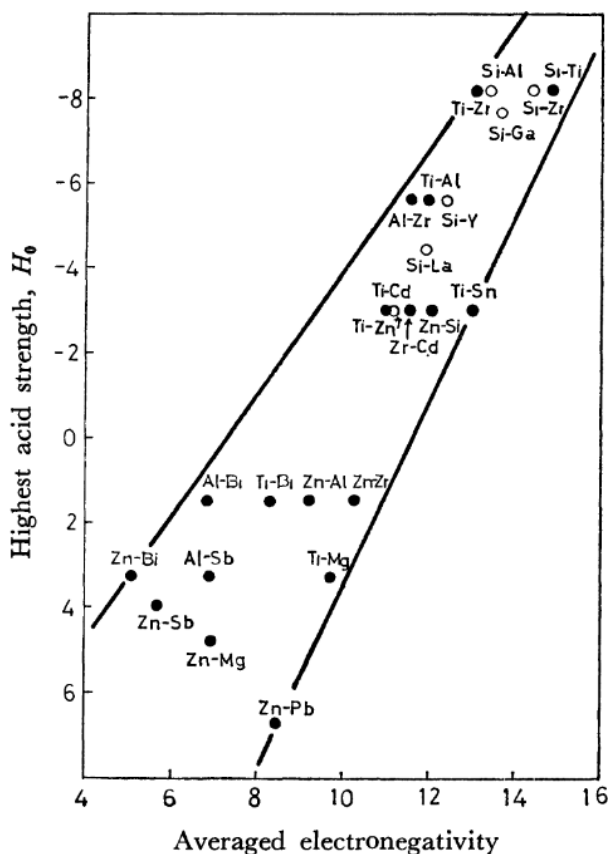


Figure 7: Highest acid strength of mixed oxides compared with their averaged electronegativity values.

affecting the stability of neighboring acid sites.²⁸ This phenomenon is also directly related to the electronegativity of the substituents, in which higher-electronegativity substituents can pull electron density from the conjugate base site, stabilizing it and increasing the acid strength. Studies on amorphous silica-alumina suggests that the Brønsted acidity of silanol groups (Si-OH) can be enhanced when they are in close proximity to less coordinated aluminum cation sites.^{29, 30} Another example of a mixed oxide superacid would be sulfated zirconia, in which the surface sites of zirconium oxide is filled with sulfate groups. Though sulfated zirconia is not strictly a mixture of two solid oxides, the nature of stabilization should still be the same as mentioned before: the zirconium cation acts as a Lewis acid for the oxygen groups in sulfate, stabilizing the general structure.³¹

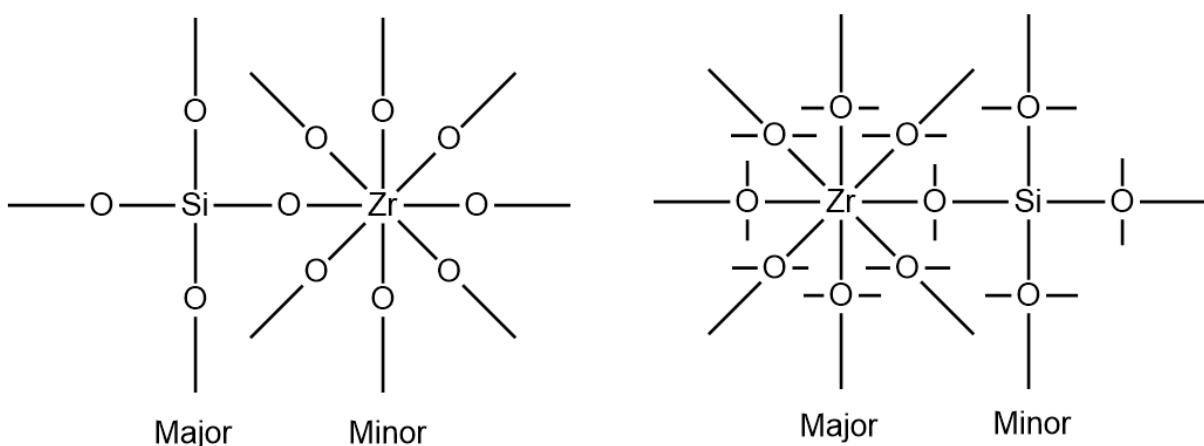


Figure 8: Coordination numbers of each ion of SiO₂-ZrO₂ mixed oxide. When SiO₂ is the major component, oxygen has a coordination number of 2. When ZrO₂ is the major component, oxygen has a coordination of 4.

This phenomenon may extend to the general case of any combination of mixed oxide, in which the acidity of a hydroxide group attached to one oxide cation may be enhanced by the Lewis acidity of the other oxide cation.

In many cases, mixing oxides not only increases the acid strength, but it also increases the number of acid sites. Tanabe proposed a model of a binary mixed oxide which uses two assumptions. The first assumption is that the coordination of the cation of each component oxide is retained even when mixed. The second assumption is that the coordination of the oxygen anion is that of the major component oxide. Then, the oxygen anion and the minor component cation's valence is divided by their respective coordination numbers, and then added together. Any excess charges can be compensated by protons or by the presence of Lewis acidity. For example, on a SiO₂-ZrO₂ mixed oxide material, Si⁴⁺ has a coordination number of 4 while Zr⁴⁺ has a coordination number of 8. If the oxide is Si-rich, the oxygen has a coordination number of 2, and Zr⁴⁺ cation has a +4 valence that is spread out over 8 bonds ($+4/8$), while the oxygen has a -2 valence that is spread out over two bonds ($-2/2$). Therefore, at the Zr-O bond, the net charge is $+\frac{4}{8} - \frac{2}{2} = -\frac{1}{2}$.

Since there are 8 Zr-O bonds, the total net charge at the Zr moiety is -4, which can be compensated by adding four H^+ ions. From Si-rich SiO_2 - ZrO_2 , Brønsted acidity is expected. In the case of a Zr-rich SiO_2 - ZrO_2 oxide, the Si cation has +4 valence spread over 4 bonds (+4/4) while the O anion has -2 valence spread over 4 bonds (-2/4), giving the net charge of $+\frac{4}{4} - \frac{2}{4} = +\frac{1}{2}$ at the Si-O bond. Since Si has four bonds, this equates to a total net charge of +2 on the Si, indicating Lewis acidity (**Figure 8**).³² This method of determining acidity has been effective for a large number of binary oxides tested, but this model is not useful for scientific discussion as it cannot take into account any changes that may be needed to balance the stoichiometry in the matrix.²⁵

Kung et. al introduced a different theory with the assumption that there is a dilute solid solution of cations A with stoichiometry AO_y substituting into an oxide B with stoichiometry BO_z , leading to two possible outcomes:

1. y equals z, substitution occurs with little effect on the matrix, and new acidity would be associated with the only electrostatic potential of the A site.
2. y does not equal z, substitution causes changes to the matrix, and new acidity would be associated with both this change and the electrostatic potential of the A site.

The difference in electrostatic potential of the substituting cation A can be determined by

Equation 3:

$$\Delta V = \sum \left(\frac{q_i}{r_i} \right)_{BO_z} - \sum \left(\frac{q_i}{r_i} \right)_{AO_y}$$

Equation 3: Difference in electrostatic potential when a cation A from oxide AO_y is substituted into oxide BO_z

In which q_i is the charge of ion i located at a distance r_i from the A site. Essentially, **Equation 3** compares the electrostatic potential felt by cation A in an infinite 3D matrix of AO_y with that felt

Formation of new acid sites when substituting oxide AO_y in matrix BO_z according to the model of Kung (4).

Case	Formation of new acid site		
	At substituting ion	In matrix	
	Lewis acid	Brønsted acid	Lewis acid
$y < z$	Yes	Yes	May be
$y = z$	Yes if BO_z more covalent	No	No
$y > z$	No	No	May be

Figure 9: Result of Kung's model for the formation of new acid sites when adding oxide AO_y moieties to matrix BO_z

by cation A in an infinite matrix of BO_z . If ΔV is negative, then the cation feels a more negative potential in B than in A and is thus electrostatically more stable and can accept electrons more easily. This would make the A site act as a Lewis acid site.

When there is a stoichiometry mismatch, the matrix will change so as to restore stoichiometry. When $y < z$, the formal oxidation state of A in AO_y will be less than that of B in BO_z and there will be an excess of oxygen in the matrix. To restore the charge caused by this imbalance, substitution can develop in anion vacancies or proton adsorption onto the surface, which is just Brønsted acidity. When $y > z$, the formal oxidation state of A will be higher than that of B, and there will be an oxygen deficiency in the matrix. Then, substitution can result in adsorption of negative anions like oxygen or OH^- on the A cation. A summary of the results can be viewed in **Figure 9**.³³

Kung's model is also limited in that it assumes that the substituting ion A is surrounded by an infinitely large BO_z matrix, and that other AO_y moieties would not contribute to any change in the electrostatic potential that the A ion would feel. However, it has been shown to be still very effective at predicting binary oxide behavior while being more scientifically intuitive.

1.2.6 Zeolites

One of the most well studied examples of mixed oxide acid catalysts is zeolites, which are silica-alumina mixed oxides with microporosity (pore diameter < 2 nm).³⁴ While silica or alumina alone do not have the necessary acidity to perform reactions such as hydrocracking or dehydrogenation, mixing them into these zeolites creates a significant number of Brønsted sites with the necessary strength to do so.³⁵ Viewing **Figure 7**, Si-Al oxide mixtures have one of the highest possible acid strengths for binary mixed oxides, as well as one of the highest possible combined electronegativities. In zeolites, the active acid site was well established to be the bridging oxygen in the Al-O-Si groups. This high acidity as well as the small pore size allows zeolites to be selective with its substrate size, allowing for high activity and selectivity.³⁶

However, there may also be other factors that can contribute to high acidity: Al-O-Si bridging groups in non-microporous silica-alumina composites do not exhibit the same kind of acidity. Instead, the acid sites are the silanol (Si-OH) groups that are near unsaturated Al centers. While this is similar to the bridging Al-O-Si sites, these silanol groups are much more mobile compared to the more rigid sites of the former. The most likely reason for this discrepancy is due to the porosity of zeolites: the small pore size prevents solvent molecules from moving freely, reducing the stabilizing effect that solvation can have on the donated protons.³⁷

1.3 *Surface Charge*

Surface acidity can manifest itself via another surface-related phenomenon: surface charge. Proton transfers between the surface and the solution will inevitably lead to surface charge: from the exchange of protons between the surface and the solution, charged species will form from these sites. Starting from a neutral metal oxide surface with neutrally charged hydroxide groups on the

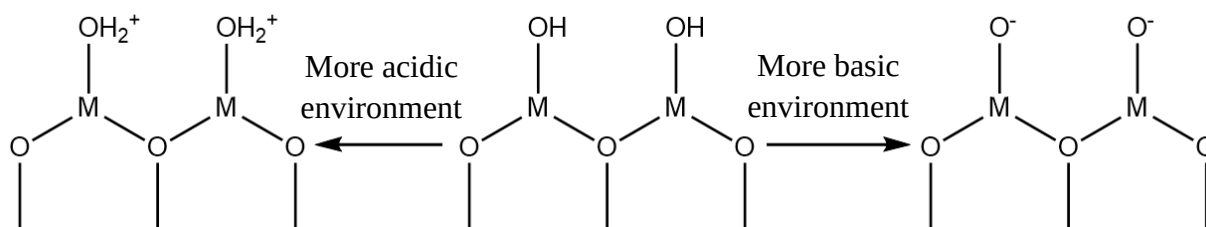


Figure 10: Oxide surface charges as a function of pH. The solution can exchange its protons to the oxide surface, creating $-\text{OH}_2^+$ or OH^- moieties that give the surface a positive or negative charge, respectively.

surface, an sufficiently acidic environment around the surface would impart protons onto the OH groups, creating $-\text{OH}_2^+$ groups and creating a positively charge surface. A sufficiently basic environment around the surface would abstract protons from the OH groups, creating $-\text{O}^-$ groups that would give the surface a more negative charge (**Figure 10**).

1.3.1 Surface Charge Models

As these charges begin to build onto the particle surface, ions of opposite charge, known as counterions, are attracted to the surface while ions of the same charge, known as coions are repelled from it. This combination of the surface and the excess of neutralizing counterions surrounding the surface creates what is known as an electric double layer.^{24, 38} In order to explain the electrokinetic phenomena that result from this electric double layer, Helmholtz likened this electric double layer to a parallel plate capacitor with surface electric potential ψ_0 , in which the counterions are arranged parallel to the surface. The distance between plates is given by δ , which was estimated to be roughly the radius of a counterion, and the surface potential decreases linearly across δ (**Figure 11**). But the Helmholtz model is limited: for instance, later research uncovered a layer of water molecules that remains bounded to the surface which moves as the particle does,

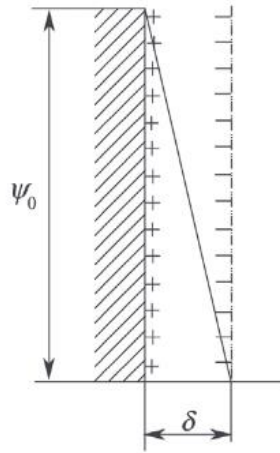
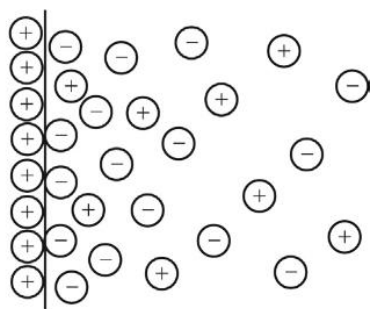


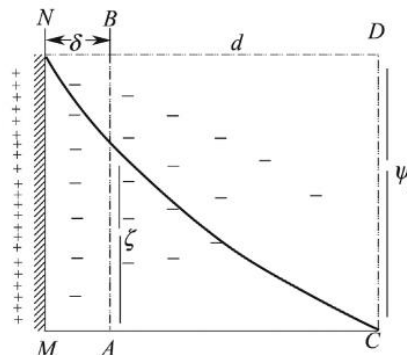
Figure 11: Helmholtz model of the electric double layer. Based off of a parallel plate capacitor, the surface electric potential ψ_0 decreases with distance δ

and is thicker than the Helmholtz double layer. With the Helmholtz model, this bound water layer should not exist due to the neutrality of the proposed double layer.

To address the unresolved problems in the Helmholtz model, Gouy and Chapman added an assumption that the counterions are influenced by electrostatic forces and thermal motion. As a result, the counterions are distributed more diffusely, rather than in a parallel manner. Consequently, the concentration of excess counterions decreases with distance from the surface, and the electric surface potential decreases more gradually instead of linearly (**Figure 12**). This allows room for water molecules to solvate the counterions, which is what creates this bound water layer on the surface of the particle. The boundary between this water layer and the rest of the solution is called the shear plane, and the electric potential at the surface of the shear plane is known as the zeta potential, ζ .³⁹



Gouy-Chapman model of diffuse double layer.



Change of the electric potential of diffuse double layer.

Figure 12: Gouy-Chapman model of the electric double layer. Unlike the Helmholtz layer, the counterion concentration is more dispersed, with a higher concentration and electric surface potential near the surface.

1.3.2 Isoelectric Point

The magnitude of the zeta potential is dependent on the pH of the solution, as the acidity of the solution relative to the surface can change the surface hydroxyl groups into negative -O^- moieties, neutral -OH moieties, or positive -OH_2^+ moieties.⁴⁰ Additionally, the pH of the solution can then be adjusted such the zeta potential can reach zero from the positive charges and negative charges balancing out. This pH level is called the isoelectric point and due to its dependence on the acid-base sites, varies with the material factor and can be indicative of the acidic properties of the surface. The zeta potential of a surface can be measured using electrophoretic light scattering methods. Charged particles are dispersed in water and inserted into specialized bent capillary tubes with electrodes. When a voltage is applied, these charged particles will move towards the electrode with opposite charge: a particle with a net positive surface charge will drift towards a negatively charged electrode. As this electric field is applied, a laser beam is split, one of which is shined through the cuvette and the other of which is used as a reference beam. The mobile particles will scatter this light at a different frequency than the original laser which is proportional to the speed of the particles (Doppler Effect). This scattered light will then be recombined with the other split

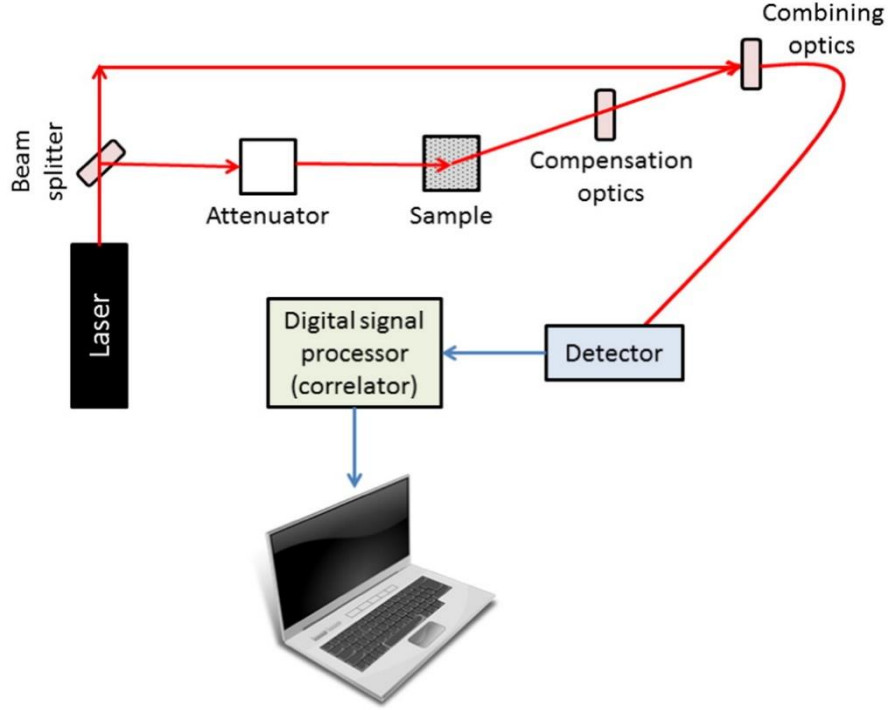


Figure 13: Schematic of the zeta potential measuring process. The split light beam entering the sample has its frequency changed due to the mobility of the particles scattering the light.

beam to determine the Doppler shift, which is used to calculate the magnitude of the particle velocity. From this particle velocity, the zeta potential of the particles can be determined (**Figure 13**).⁴¹

1.3.3 Mixed Oxides and Isoelectric Point

Additionally, when different oxide materials are mixed, it appears that the isoelectric point of the new material lies somewhere between the isoelectric point of the two pure oxide materials. This new isoelectric point can be expressed as a function of the isoelectric points of the pure materials and their relative surface coverages (**Equation 4**).⁴²⁻⁴⁴ Given a mixed oxide material composed of oxides A and B, the isoelectric point of the mixed material is the linear combination

$$IEP = IEP_A * X_A + IEP_B * X_B = \sum_n IEP_n * X_n$$

Equation 4: Isoelectric point of binary oxide materials, given oxide materials A and B

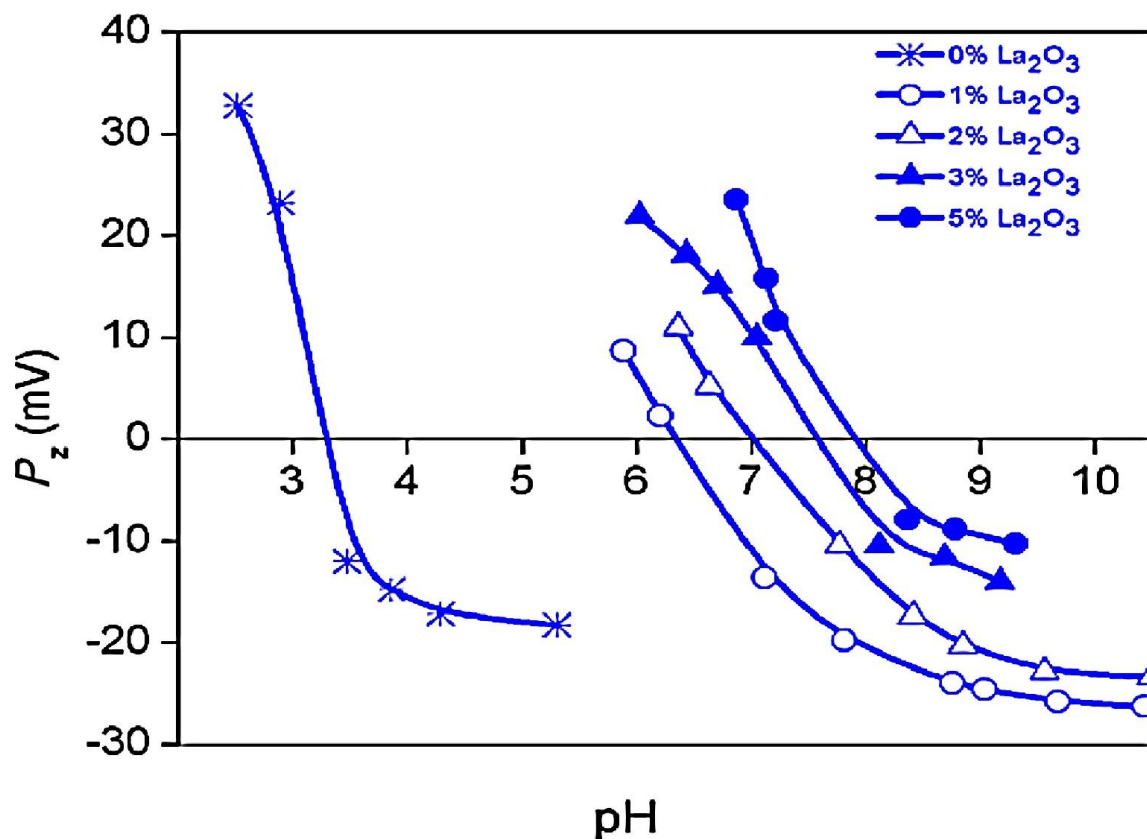


Figure 14: Isoelectric point changes of ZrO₂ mixed with increasing amounts of La₂O₃. The La₂O₃ is assumed to be covering the ZrO₂ as a monolayer up to 3% La₂O₃, and then forms multilayer agglomerates beyond that.

of each material's isoelectric point multiplied by the fraction of the surface covered by that material. This equation can also be extended to materials that are composed of more than two oxides.⁴² For example, Salinas et. al mixed ZrO₂ with increasing amounts of La₂O₃ to investigate the latter's influence on the mixed oxide's ability to produce biodiesel from canola oil. For pure ZrO₂, the isoelectric point was determined to be around 3.4, and the isoelectric point increases with increasing amounts of La₂O₃. Using **Equation 4**, Salinas assumed that the surface is composed of a La₂O₃ monolayer covering a ZrO₂ surface up to 3% La₂O₃ loading, which contributes to the change in isoelectric point as seen in **Figure 14**.

Equation 4 implies that the surface acid sites of material A operate independently from those of material B. In the case where there are significantly large surface “patches” of A or B (as

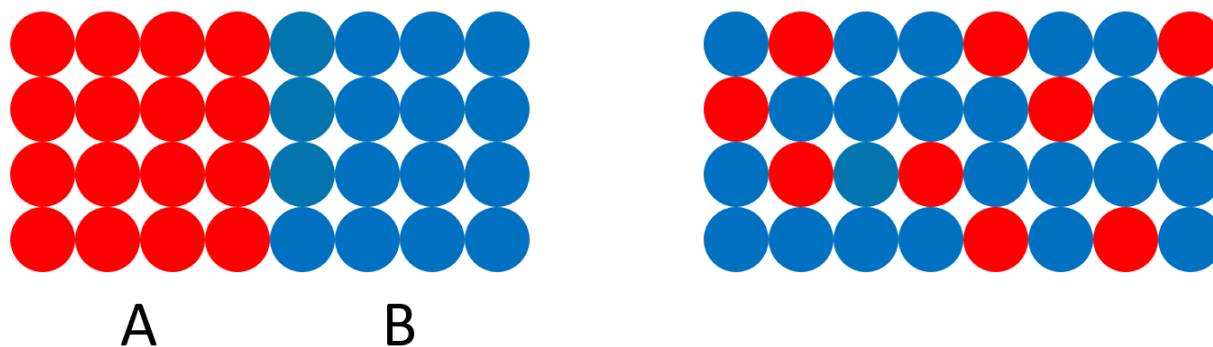


Figure 15: Different structures of oxides A and B mixed: (Left) regions of unmixed oxide, allowing for surface regions of only A and only B. Interfacial effects are more negligible. (Right) Homogeneously mixed oxide surface. Interfacial effects are more significant.

in Salinas's work), that may be more accurate, as a surface site of oxide A is more likely to be surrounded by other A oxide moieties while the acid sites located at the interface of A and B can be largely ignored. But in the case of a more homogeneously mixed oxide, the number of interfacial acid sites can be significantly higher, and so they may play a much larger role in affecting the surface chemistry (**Figure 15**). I believe that **Equation 4** is therefore insufficient to fully describe the surface of a mixed oxide and may need to be modified in the future.

1.4 Surface Acidity and Isoelectric Point of Mixed Oxides

The surface acidity and the isoelectric point of a material are two properties that manifest from the interactions between a material surface and the solution phase, yet experimentally, it seems unclear as to how these properties are connected. In mixed oxides, the isoelectric point of a mixed oxide is an intermediate value between its two pure component materials, depending on the relative concentrations of each at the surface. As mentioned before, **Equation 4** assumes that the oxide components do not interact with each other, and consequently that the Brønsted acidity of each respective acid site does not change. However, a mixed oxide will inevitably have some sort of interaction at the interface between oxide species. This is demonstrated by the earlier discussion of increased acidity/superacidity with mixed oxides: if mixed oxides are assumed to not interact,

then their acid strengths should exist somewhere in between the respective oxides. Yet many mixed oxides exhibit acid strength greater than their individual counterparts, implying some sort of interaction between the materials.

The difficulty in characterizing these mixed oxide acid sites comes from the synthetic methods involved in their fabrication. In these prior studies regarding the surface chemistry of mixed oxides, the oxides are often synthesized into homogeneously mixed oxides using liquid-phase reactions, or in some cases, uncontrolled vapor phase deposition methods.^{26, 30} These traditional methods, combined with the inherent disorder present on the surface of nanoparticles, result in poor control over the condensation of the oxide sites.⁹ In zeolites, for example, the zeta potential behavior is very complex due to the non-uniformity of surface sites, in both morphology and acid strength.

1.5 Atomic Layer Deposition

Atomic layer deposition (ALD) can be used to address this issue of poor control over the synthesis process. ALD is a vapor phase deposition technique which introduces precursor gases sequentially to a surface (**Figure 16**). The process begins by introducing a precursor which binds only onto a substrate surface. As the precursor only reacts to the surface and not itself, this process is self-limiting, theoretically coating up to a single monolayer onto the surface. This step is then followed by an initial purge to remove any unreacted precursor and byproduct. Afterwards, the substrate is exposed to a co-reactant precursor, which also reacts only with the newly covered surface, depositing another self-limited layer of material and priming the surface to react with the first precursor. The reactor chamber is purged again to remove the second coreactant, and the first precursor is reintroduced to restart the ALD cycle.⁴⁵ The self-limiting chemistry of the precursor

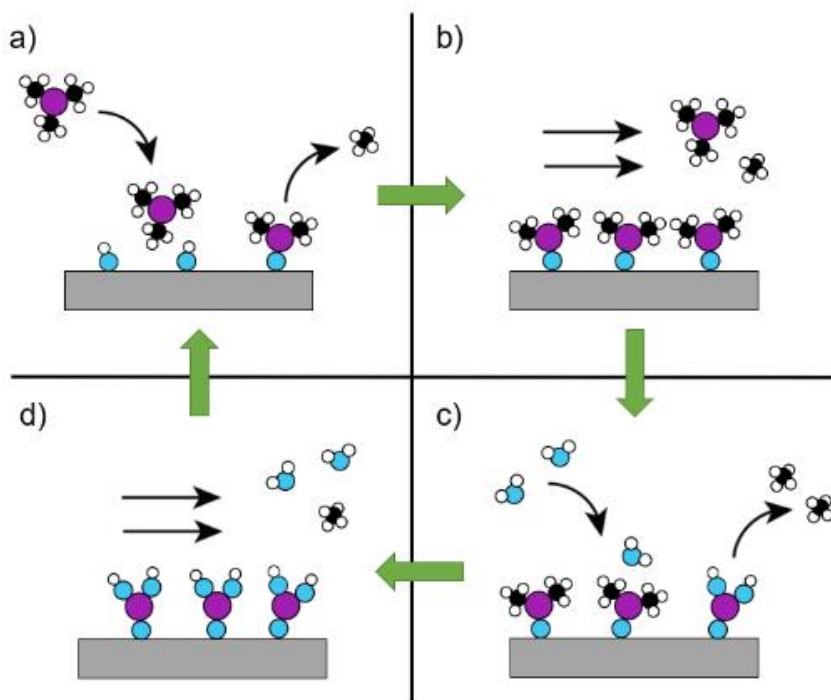


Figure 16: Schematic of the ALD process. a) the precursor molecules react with active sites on the surface. b) a purge step removes unreacted precursor and by-products of the reaction. c) a co-reactant is introduced, reacting with the new active surface sites. d) another purge step removes the unreacted precursor and by-products.

enables excellent control of the thickness, while allowing for conformal coating onto irregular surfaces.

Xia et. al investigated the isoelectric point of thin film oxides deposited via ALD. In his work, he deposited a comprehensive variety of oxide materials onto silicon wafers and examined their zeta potentials. From that work, he demonstrated that the isoelectric point of each deposited oxide film matches that of the pure oxide material, with a few justified exceptions. However, the thin films in work are over 5 nm thick, and the interface between the native oxide and the deposited ALD layer would not be investigated.⁴⁶ Additionally, these depositions were done on flat silicon wafers, but heterogeneous catalysis is often done with high surface area powders rather than large flat surfaces.

1.5.1 Powder ALD

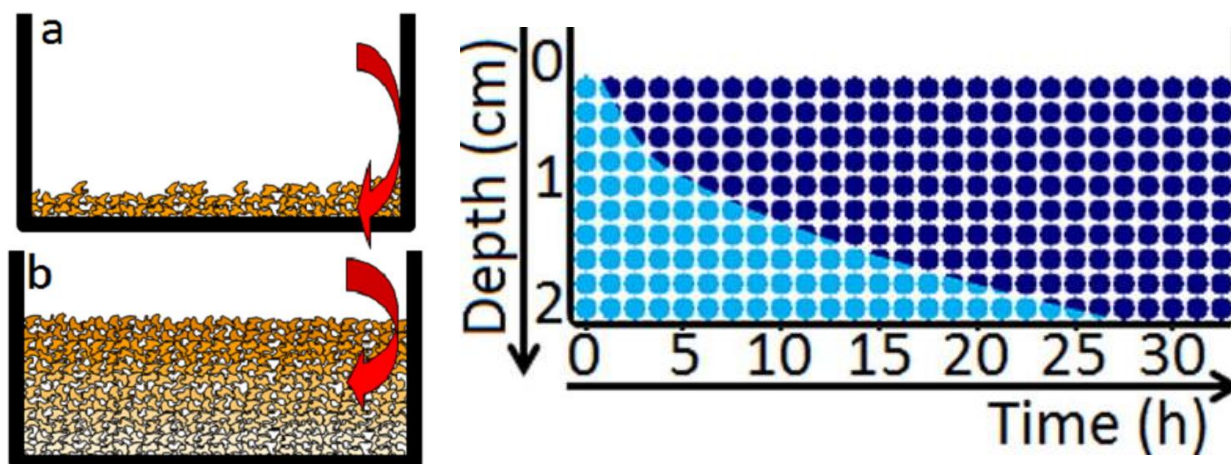


Figure 17: Representation of a 2 cm deep crucible filled with uncoated powder arranged in a simple cubic arrangement. The depth of particles that becomes coated (dark blue) is displayed as a function of time. The entire bed of powder becomes coated after about 27 hours under 10 mbar of trimethyl aluminum precursor.

Due to the reliability of ALD to coat ultrathin films on conformal surfaces, it is a potential option to evenly coat films onto nanoparticles as well. However, many lab-scale reactors are usually fixed-bed reactors, in which the powder remains static.⁴⁷ In these types of reactors, hold steps must be added to the ALD process to allow time for the precursor to diffuse between the interstitial spaces between the powders. **Figure 17** shows that for 10 mbar of trimethylaluminum above a crucible holding a 2 cm tall pile of powder arranged in a simple cubic manner, it will take 27 hours for the precursor to fully coat the powder. Decreasing the powder thickness to 1 mm will decrease this hold time to 4 min, showing that conformal powder coatings can be done at least in a laboratory setting.⁴⁸

Of course, for industrial purposes, fluidized or rotary bed reactors are the reactors of choice for powder ALD, as they can agitate the powders and allow unreacted surfaces to be exposed to the precursor.⁴⁸ However, in porous materials such as zeolites or mesoporous materials such as

SBA-15 or A300 silica, hold times would still have to be employed to allow the precursor to diffuse through the pore length.

A few experiments for powder ALD and surface acidity have been done before with studies of ALD-deposited silica and alumina to investigate their acidic properties for catalysis.^{9, 49} In one notable study, Canlas et. al showed that when silica was functionalized with one cycle of alumina followed by multiple cycles of silica, the Lewis acidity of the surface increased and the Brønsted acidity decreased when the number of silica ALD cycles increased. Additionally, the Brønsted acidity was determined to be caused by the interaction between the silanol present on the silica and an adjacent uncoordinated alumina ion was responsible for stronger acidity of the silanol.⁹

1.6 Statement of Purpose

Powder ALD used directly to prepare catalytic materials is still an application that remains fairly unexplored. Due to the excellent control over the thickness of the films, a single monolayer of oxide material can be deposited and analyzed, such that the active sites of acid catalysis can be isolated and identified.⁴⁹ Therefore, with ALD, we should be able to isolate and expose the interface between the base substrate and the deposited material. But there can still be issues when it comes to the deposition process, and this thesis will first talk about these complications that can arise when performing powder ALD on a fixed bed reactor. The results of these findings are primarily applied for laboratory scale fixed bed ALD systems and are not necessarily useful for fluidized/rotary bed reactors when applied to solid nonporous powders. However, these results can also be applied to any type of reactor when using high surface area porous powders, as particle agitation does not affect pore diffusion as much.

Furthermore, this thesis will demonstrate the changes in the surface charge of oxide materials as a function of sub-nanometer thickness of ALD-deposited material. According to the literature, the atomic interface of two different oxide materials is assumed to have a negligible effect on the zeta potential. However, the existence of mixed oxides seems to indicate that some sort of interaction does indeed exist at this interface.^{42, 50-53} The work in this thesis will be work to resolve this discrepancy, and is possible due to the ability for ALD to controllably deposit material onto the surface.

2. Experimental Methods

2.1 Atomic Layer Deposition Recipe

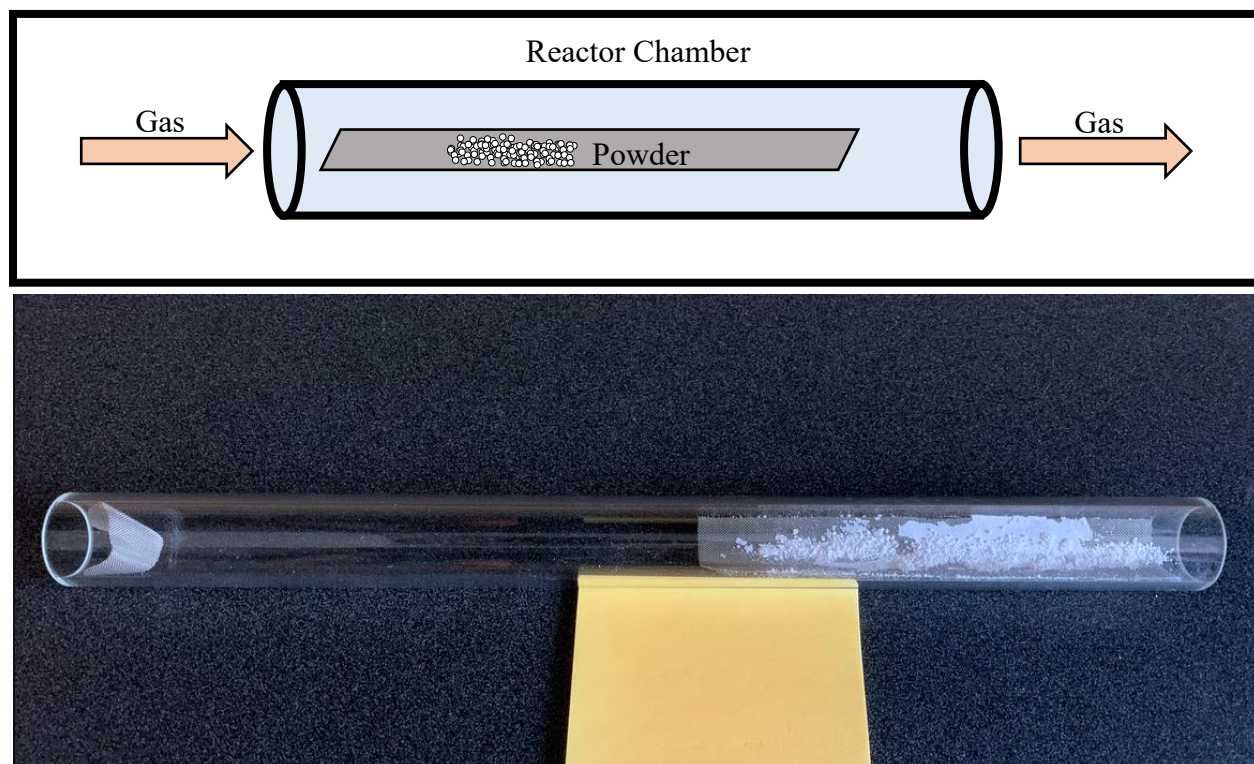


Figure 18: Schematic of the ALD setup within the reactor tube. The powder is on top of a mesh within a glass cylinder.

ALD was conducted in a horizontal flow tube hot-walled reactor chamber. The powder was placed on a fine steel mesh, which was then placed inside a 0.81 in. inner diameter glass cylinder and placed horizontally in the reactor (**Figure 18**). The purpose of the steel mesh was to allow the precursor gas to come into contact with the powder pile from underneath, essentially halving the powder “height” and allowing the gas to penetrate into the powder bulk more quickly.

When the powder was in the reactor tube, the chamber was then purged with ultrahigh purity nitrogen for 1 hour to remove remnant moisture in the chamber and on the powder surface. The chamber was subsequently pumped down and isolated. Titanium tetrachloride (TiCl_4) was

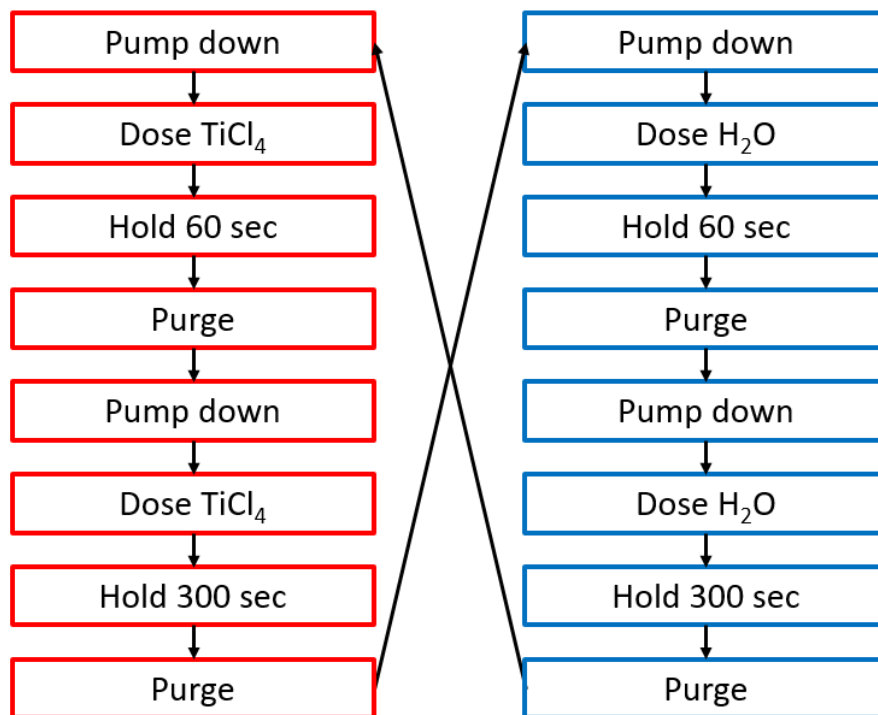


Figure 19: Two-dose recipe for coating powders via ALD

then dosed into the chamber for five seconds, and the chamber was isolated again for 60 seconds. This was then followed up with a purge and pump down step, and a second TiCl_4 dose with a 300 second isolation time. This same process was repeated but with a 1-second dose of water instead of a 5-second dose of TiCl_4 (**Figure 19**). This double precursor dose step was performed due to the formation of HCl byproducts created from the reactor walls, the glass cylinder, and to a lesser extent, the powder. By performing an initial dose step, the bulk of the HCl byproduct can be removed from the chamber, preventing it from hampering film growth onto the powders. Additionally, the chamber wall and the glass cylinder become passivated, allowing the second dose of precursor to react with the powder rather than the walls and the glass.

Once the powder was removed from the reactor, it was washed in distilled water and centrifuged at 14,000 rpm for 3 minutes. Powders that aggregated in water were sonicated to break down the aggregates. This step is repeated for a total of three times before the powder is dried in

a furnace. Samples were then allocated for surface charge/chemistry analysis and elemental analysis such as Scanning Electron Microscopy – Electron Dispersive X-ray Spectroscopy (SEM-EDX) and X-ray Photoelectron Spectroscopy (XPS).

2.2 *Mass Titration*

After the powder is washed, it is then redispersed in a 0.01M KNO₃ solution at pH 7. To produce this solution, KNO₃ salt was dissolved in distilled water to produce a stock 0.01M KNO₃ solution. A portion of this stock solution was taken, and its pH was adjusted using HNO₃ and KOH salt until the desired pH was achieved. The pH was measured using an Orion pH electrode from Thermo-Fischer, calibrated with pH 4, 7, and 10 buffers.

2.3 *Zeta Potential Analysis*

To make samples for zeta potential analysis, solutions of varying pH must be prepared first. As with the KNO₃ solution at pH 7, 0.01M KNO₃ solution was made first, and then portions were separated to create solutions of a desired pH. For this experiment, KNO₃ solutions of pH 2, 4, 6, 8, and 10 were produced.

5 mg of powder was dispersed into 10 mL of the solution of the desired pH and sonicated for 30 minutes to break down aggregates. These samples were then injected into specialized Malvern DTS1070 cuvettes and inserted into the Malvern Zetasizer Nano ZS to be analyzed. The temperature was set to 25°C, and three distinct measurements were taken, with a 10 second delay between each measurement. After analysis of each sample, the dispersion was removed and the cuvette was rinsed to remove any particles and acid/base remnants.

3. Modeling Thickness and Ti Atomic Percent

3.1 Particle ALD and Hold Time

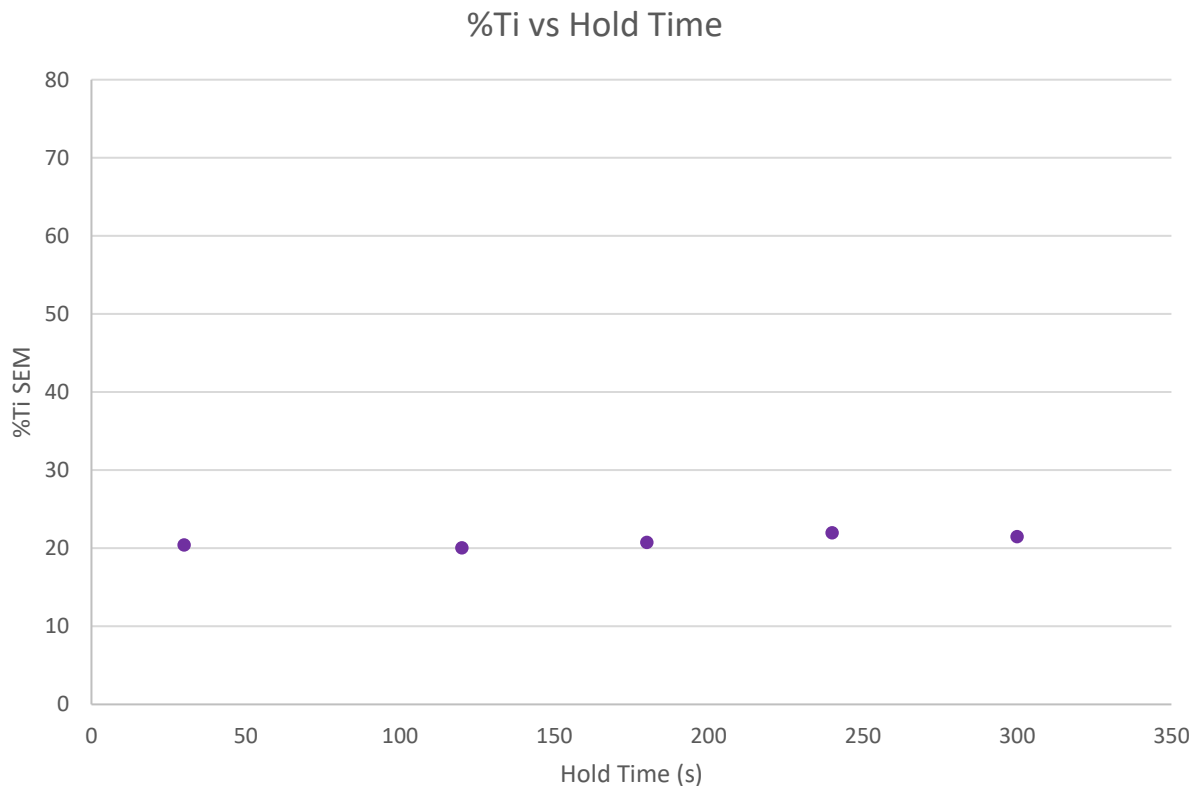


Figure 20: Ti atomic percent as a function of hold time as measured using SEM-EDX. The amount of Ti doesn't change significantly with increasing hold time

When powder is exposed to precursor, it should take time for the powder to be able to diffuse through the interstitial spaces between the particles. In order to ensure powders were sufficiently coated per step, we varied TiCl_4 hold times on silicon oxide powder and determined their relative Ti atomic percents. As seen in **Figure 20**, the amount of titanium as detected by SEM-EDX has not changed significantly. XPS was not employed for this step due to the relatively shallow depth of analysis (~ 5 nm) whereas SEM-EDX can analyze samples at a much lower depth (up to 2 microns).⁵⁴

3.2 Monolayer Thickness and Relative Atomic Percent

$$t_m = \left[\frac{MW}{(N_A * \rho)} \right]^{\frac{1}{3}}$$

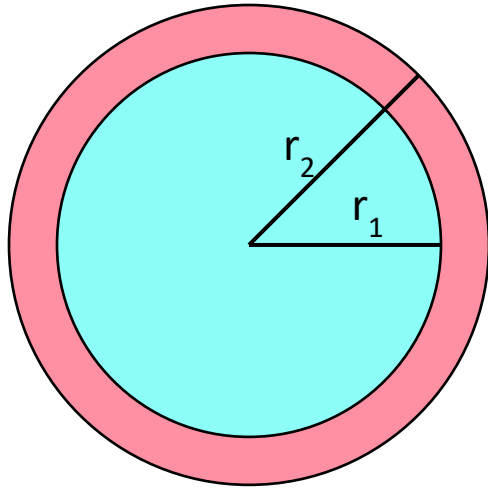
Equation 5: Estimated thickness of one monolayer of material given the density (ρ), molecular weight (MW), and Avogadro's number (N_A)

The thickness of one monolayer of TiO_2 , t_m , can be estimated using **Equation 5**, where MW is the molecular weight (79.87 g/mol for TiO_2), N_A is Avogadro's number, and ρ is the density of the material (2.9-3.9 g/cm³ for TiO_2). With these parameters, the thickness of one monolayer of TiO_2 is estimated to be ~0.32-0.35 nm. Since the growth per cycle (GPC) of TiCl_4 is estimated to be about 0.5Å per cycle, TiCl_4 and H_2O based ALD should achieve full surface coverage in seven cycles.

Given the thickness of one monolayer of TiO_2 , it is then possible to approximate the atomic percent of titanium relative to the silica. Assuming a core-shell spherical geometry for the nanopowders and that the titanium coats evenly onto the powders, we can calculate the volume of the titanium oxide shell and the silicon oxide core given the radius of the latter.

At first, calculating the volume alone may not appear to be sufficient to determine the atomic concentrations of Ti and Si relative to each other, due to their differences in density and molar mass. However, given these values, we can calculate the molar volumes of titanium oxide and silicon oxide:

$$\text{Molar Volume} = \frac{\text{Molar mass}}{\text{Density}}$$



Relevant Constants and Equations:

- Density of amorphous TiO₂: 3.7 g/cm³
- Density of amorphous SiO₂: 2.65 g/cm³
- Molar mass of TiO₂: 60.08 g/mol
- Molar mass of SiO₂: 79.87 g/mol

$$\text{Volume of Sphere: } \frac{4}{3}\pi r^3$$

Figure 21: Spherical growth model and formulas required to calculate the relative atomic percentages of Ti and Si given the thickness of a vapor deposited layer.

From the relevant constants and equations given in **Figure 21**, the molar volume of TiO₂ is 21.58 cm³/mol and the molar volume of SiO₂ is 22.67 cm³/mol. These values are close enough to each other such that we could assume that the use of volume to approximate the relative atomic amounts of Ti and Si is a fairly accurate method.

We can then determine the volume of the shell by subtracting the volume of the entire core-shell sphere (radius r_2) from that of the core itself (radius r_1). Additionally, we now introduce a proportionality constant χ , which represents the atomic ratio of titanium to silicon. This χ is multiplied by the volume of the silicon oxide to also yield the volume of the titanium oxide shell. In other words, by knowing the radius of the silicon oxide core and the thickness of one monolayer of TiO₂, we can determine how much Ti is in the latter. This yields **Equation 6**:

$$\frac{4}{3}\pi r_2^3 - \frac{4}{3}\pi r_1^3 = Vol_{TiO_2} = \chi * \frac{4}{3}\pi r_1^3$$

Equation 6: Volume of TiO₂ based on a spherical nanoparticle geometry

$$(A): r_2^3 = (1 + \chi)r_1^3$$

$$(B): (a' * b' * c') = (1 + \chi)(a * b * c)$$

Equation 7: (A) Simplified form of **Equation 6**. (B) Generalized form of (A), in which a, b, and c are volume-related parameters of the SiO₂ while a', b', and c' are the volume-related parameters of the TiO₂ coated SiO₂

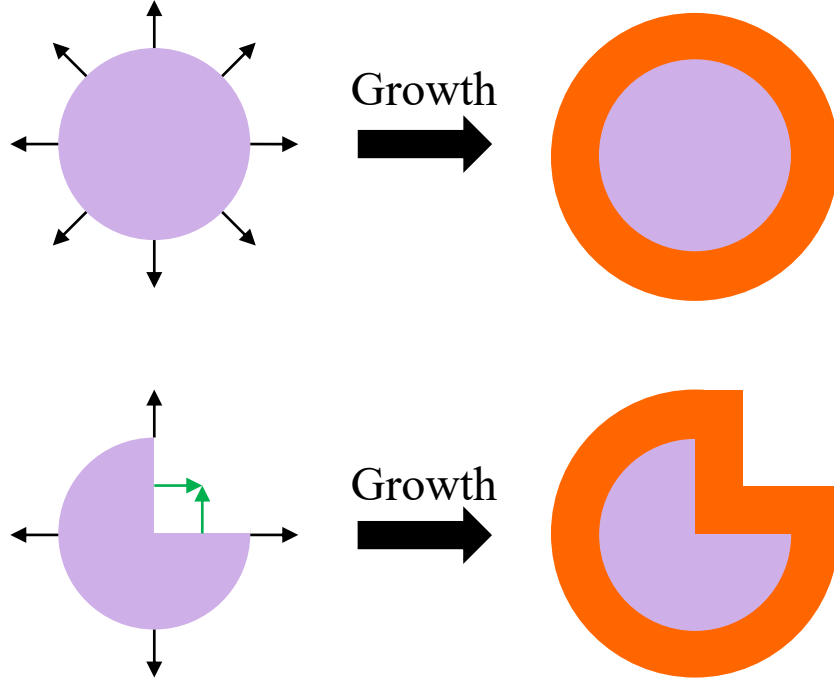


Figure 22: Growth on convex vs concave shapes. In the former, the shape is retained due to growth vectors (arrowed) not intersecting. In concave geometries, the intersecting growth directions can significantly change the final shape.

Removing the common terms, **Equation 6** can then be simplified into **Equation 7A**.

Furthermore, assuming that the particle retains its shape before and after deposition, **Equation 7A** can be generalized for many convex shapes, yielding **Equation 7B**.

However, in layer-by-layer growth on convex shapes, the growth direction vectors as seen in **Figure 22** do not intersect with each other. In concave structures, the growth directions do intersect with each other, complicating growth and rendering the structure unable to retain its exact shape. For ultra-thin layers (relative to the original particle shape), **Equation 7B** can still be used

as a good approximation because the difference in shape can be considered negligible. But as more layers are deposited onto the surface, the shape becomes distorted, and **Equation 7** cannot be applied. As seen in **Figure 22**, a concave figure such as a three quarters circle does not stay as such upon a thick deposited layer, and the formula for the new volume must be different as well. In the case of the three-quarters circle, the estimated amount of Ti should be much higher than from **Equation 7**. This discrepancy in Ti content is also inconsistent: other geometries may result in a lower estimated amount of Ti than is suggested from **Equation 7**. In short, if the growth direction vectors do not intersect with each other, then the particle maintains its shape and its volume equation during growth, making **Equation 7** valid; if the growth directions do intersect, then the particle cannot maintain its shape and volume equation, making **Equation 7** insufficient to determine the Ti atomic percent.

Applying this logic to this thesis, while many of our silicon oxide powders may be convex in shape, the particles are packed and piled together, which would give the powder as a whole a “concave” geometry during ALD growth. For thin layers of TiO_2 , we anticipated that the calculated Ti atomic percent would be very close to that of our measured Ti atomic percent. For high-thickness films (within the same magnitude as the radius of the particle or greater), the Ti content is expected to be less than what was calculated.

The silicon oxide powder has an average diameter of 20 nm, so the core radius is 10 nm. One monolayer of TiO_2 is assumed to be about 0.35 nm, so the radius of the entire shell is 10.35 nm. Solving for χ , we get a 0.108 Ti to Si fraction, which translates to about 9.8% Ti and 91.2% Si (ignoring oxygen). The assumptions used to calculate this fraction were based on a layer-by-layer growth model and may not represent exactly what is happening on this powder surface.

3.3 Elemental Analysis: SEM-EDX and XPS

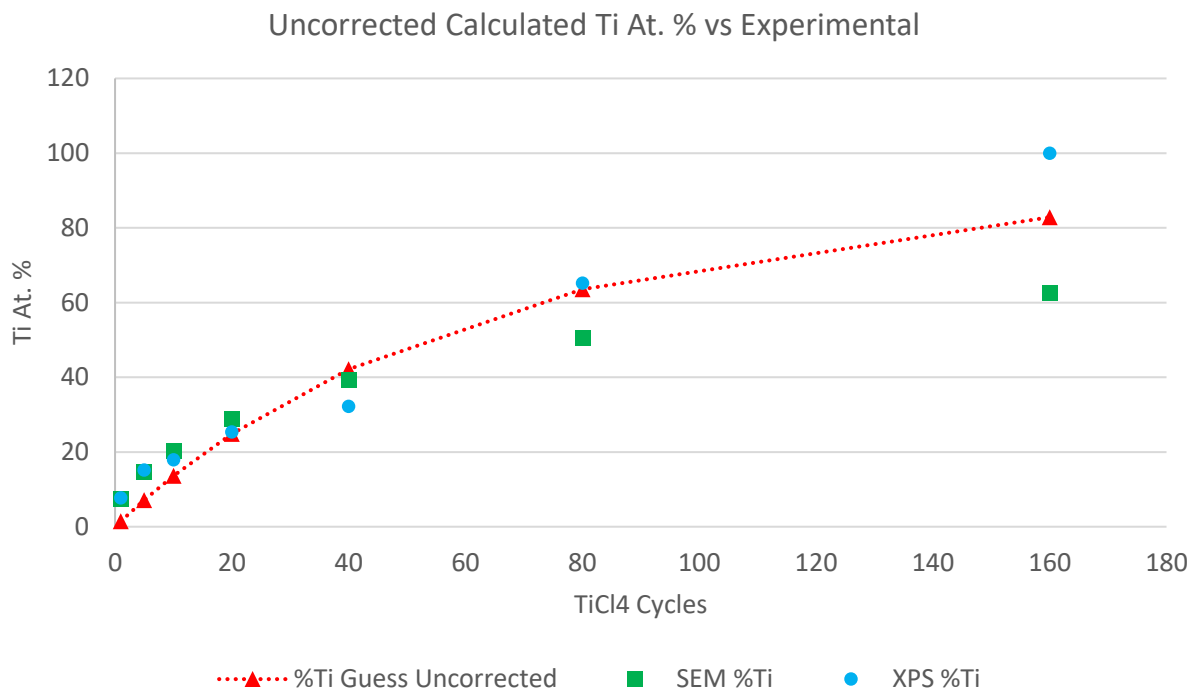


Figure 23: Calculated Ti atomic percent (red triangle) compared to experimentally determined values.

Through SEM-EDX, we can see that the titanium concentration increases with increasing TiCl_4 cycle numbers (**Figure 23**). The threshold of a single monolayer appears to be achieved at less than 5 TiCl_4 cycles, which has an atomic percent of 14.5%. Through quantitative analysis via XPS, we have also seen a similar trend for the Ti atomic percent up until 80 cycles, upon which the amount of Ti detected via XPS becomes significantly higher than that detected via SEM. Finally at 160 cycles, XPS detected no silicon in the sample (100% Ti) whereas the SEM detected some silica. This result is expected to some degree because the probing depth of XPS only goes down to about 5 nm, and with a growth rate of $0.5\text{\AA}$ per cycle and at 160 cycles, we would reach a TiO_2 film thickness of about 8 nm, burying the silicon oxide layer underneath.

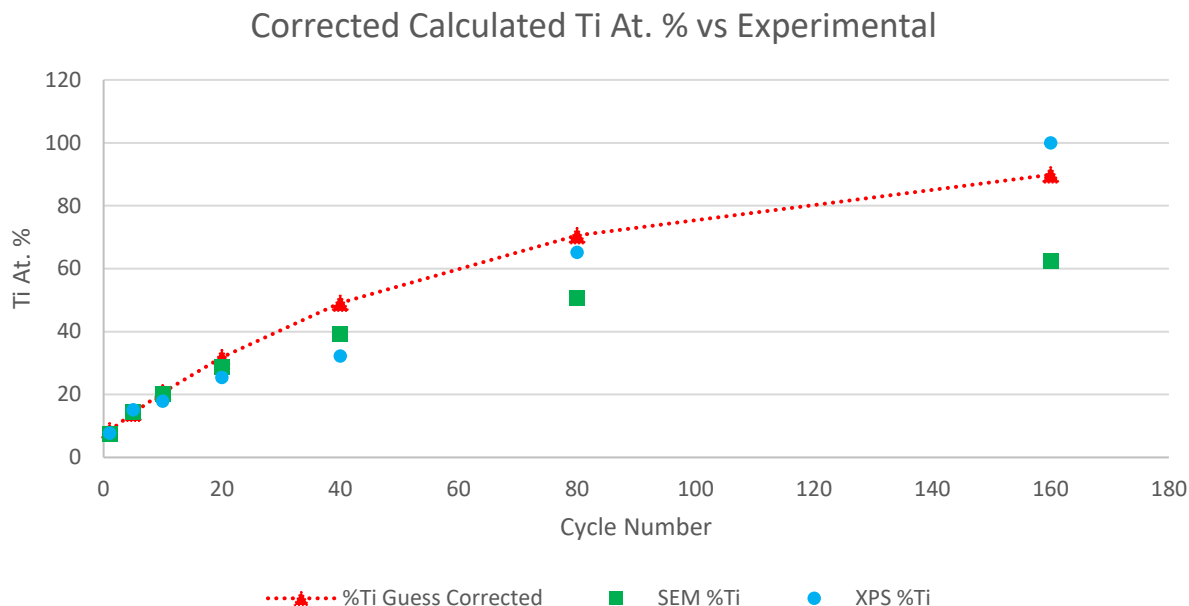


Figure 24: Corrected calculated Ti atomic percent (red triangle) compared to experimentally determined values.

The nominal Ti atomic percent was calculated as a function of the number of TiCl_4 cycles based on the previously created model. Compared to this function, the actual Ti atomic percent as determined via SEM shows an abrupt spike at 1 TiCl_4 , and then parallels the curve well at low cycle numbers but begins to diverge at higher cycle numbers (**Figure 24**). This initial spike at 1 TiCl_4 may be attributed to the fact that the silica surface has many hydroxyl surface groups onto which the TiCl_4 can easily react with. Because hydroxyl group formation on titanium oxide surfaces is less thermodynamically favorable, fewer hydroxide surface sites will form on new surfaces, which can slow growth significantly beyond the first step.⁵⁵ In other words, the first monolayer is easily formed, but subsequently layers will not deposit as easily. Taking this into account, we arbitrarily added 7 Ti at. % to all points in the calculation curve, simulating the formation of a near-complete monolayer of TiO_2 on the SiO_2 surface. Doing so allows the calculated Ti atomic percent to align much more precisely with the SEM-EDX analyzed data at low cycle numbers.

$$Atomic\ Ti\% = \left(\frac{\chi}{\chi + 1} + \alpha \right) * 100$$

or

$$Atomic\ Ti\% = \left(1 - \frac{r_1^3}{r_2^3} + \alpha \right) * 100$$

$$\chi = Ti/Si\ ratio$$

$$\alpha = Atomic\ \% \ surface\ sites\ of\ substrate$$

Equation 8: Ti atomic percent calculated based on current data. α is the number of surface sites and is dependent on the material factor.

The divergence in trend from the calculated Ti atomic percent is also consistent with our predictions: the amount of Ti detected would be less than what was calculated due to the concavity in the powder interstitial spaces interfering with the growth. At low cycle numbers, in which the thicknesses of the films are significantly less than that of the silica particle radius ($r_2 - r_1 \ll r_1$) we can still accurately approximate the volume of the coated particle using the same volume formulas. At high cycle numbers, the film thicknesses become comparable, if not greater than that of the silica particle radius ($r_2 - r_1 \approx r_1$) and the formulas used to determine the volume of the original silica particle cannot be used to determine the coated particle. Looking at **Figure 24**, the model fits the experimental data well up to 20 cycles, which is about equivalent to a 1 nm thick layer. Ultimately, the model that can establish the relationship between the titanium atomic percent and the relative thickness of the film can be determined for ultrathin films by using **Equation 8**.

3.4 Elemental Analysis: Chlorine

In addition, on **Figure 25**, we see that chlorine has been identified on pre-washed samples (except for 5-cycle $TiCl_4$), but not on washed samples. The chlorine source can either be $TiCl_4$ or HCl, but $TiCl_4$ would not be the source of the chlorine, due to its reactivity with the water vapor in

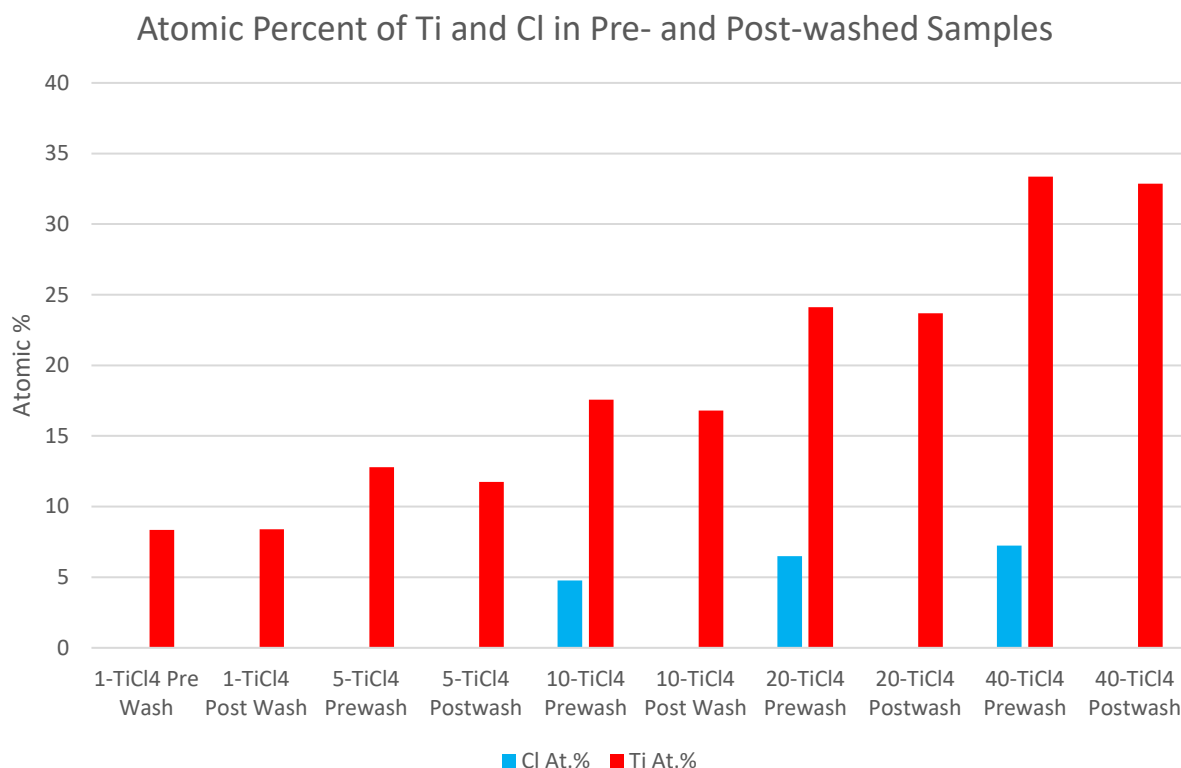


Figure 25: Elemental analysis of TiCl_4 deposited powders before and after washing cycles.

air. This leaves HCl to be the most likely candidate for this chlorine peak, as HCl was most likely physisorbed onto the sample surface and was easily washed away after three washing cycles.

Even with washing steps, however, chlorine is still detected to significant amounts (> 1 at. %) at high cycle numbers. While the chlorine percent did decrease after washing, chlorine was still retained to some degree. While it is unclear what or where this chlorine is, it seems unlikely that this chlorine is from any surface HCl, as low-cycle powders had their chlorine signals removed after washing. It is possible that this chlorine signal came from unreacted chlorine groups that are trapped within the TiO_2 layers and are unexposed to the surface.

The presence of chlorine after ALD highlights the importance of considering the reagents used as well as the side products that develop during the ALD process. Precursors such as trimethyl

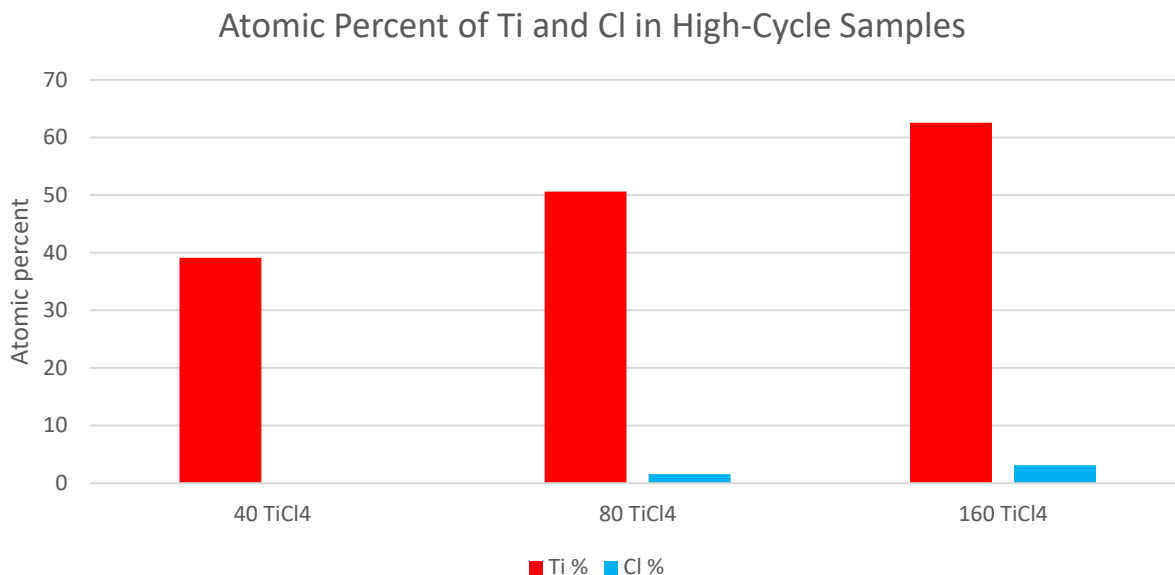


Figure 26: Elemental analysis of higher cycle post-washed samples. Chlorine is still retained after washing

aluminum (TMA), whose byproducts are stable and volatile, are not problematic as the byproducts will not adsorb onto the surface. However, ALD with TiCl_4 and water as the co-reactants creates HCl as a byproduct, which can additionally severely affect film growth during the reaction process by adsorbing on reaction sites, blocking them from further interaction with new precursor.⁵⁶ As a result, precautions and post-treatment steps must be employed in order to ensure that the presence of HCl does not negatively affect the state of the final product. More specifically, the partial pressure of this HCl vapor is increased significantly when precursor is added to the chamber, again due to the chamber walls, glass cylinder, and from the sample itself. It is for this reason that we performed a two-dose step as mentioned in the experimental section: the first precursor dose step would be used primarily to react with the easy-to-access walls and glass cylinder, leaving behind a passivated layer. The second dose step would then be employed, with the majority of the reactions happening within the bulk of the sample powder, without concerns of externally produced HCl affecting film growth rate. Because of this two-dose ALD setup, we can conclude

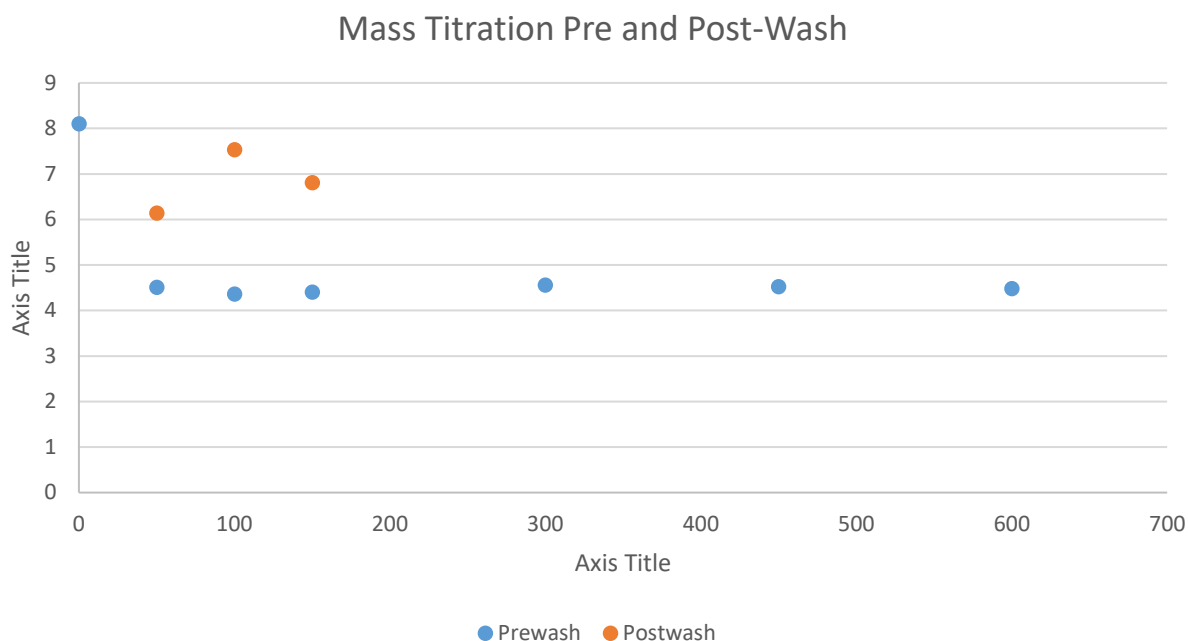


Figure 27: Mass titration curves of TiCl_4 deposited alumina particles before and after washing in water

that the HCl seen in SEM-EDX is primarily from the byproducts of the precursor reacting with the powder.

Mass titration experiments were briefly performed early on, and alumina was chosen as the sample due to its isoelectric point being in the relatively basic range (over pH 7), and any changes in its isoelectric point. During these initial experiments, a faulty valve caused TiCl_4 precursor to be released at significantly lower pressures than was expected, and therefore very little titanium was observed through spectroscopic methods. As titanium was not present with the initial batch of powders, it should be expected that the isoelectric point of the alumina surface from mass titration (at around 8-9) should not be near that of titania (around 4-5). However, pre-washed powders have been observed to have a significantly lower pH compared to its post-washed counterparts, with a pH of roughly 4.5. The reduction in pH cannot be attributed to an ALD deposited TiO_2 surface, due to the lack of titanium observed on the powders, but rather to the HCl byproducts that remained

on the surface and dissociated upon dispersion in water (**Figure 26**). We hypothesized that what little TiCl_4 that did enter the reactor chamber reacted with the chamber walls first, releasing HCl that then adsorbed onto the powder surface. The increase upon washing is associated with the removal of these HCl groups in solution.

4. Zeta Potential as a Function of Film Thickness

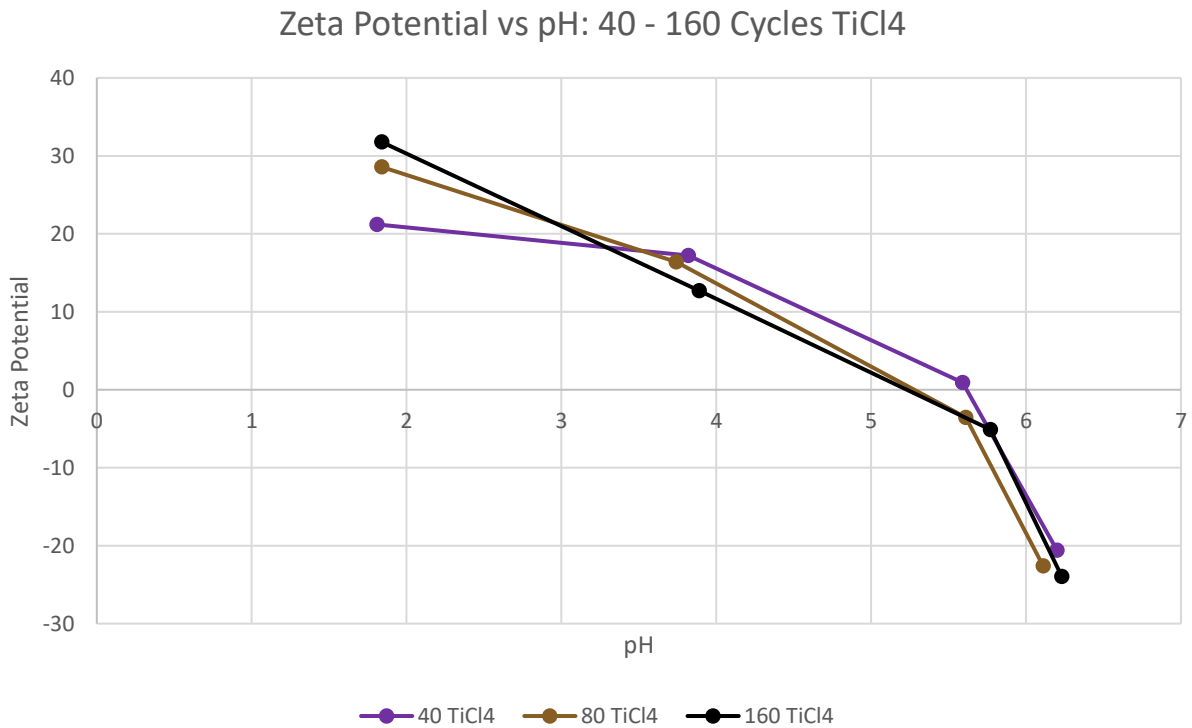
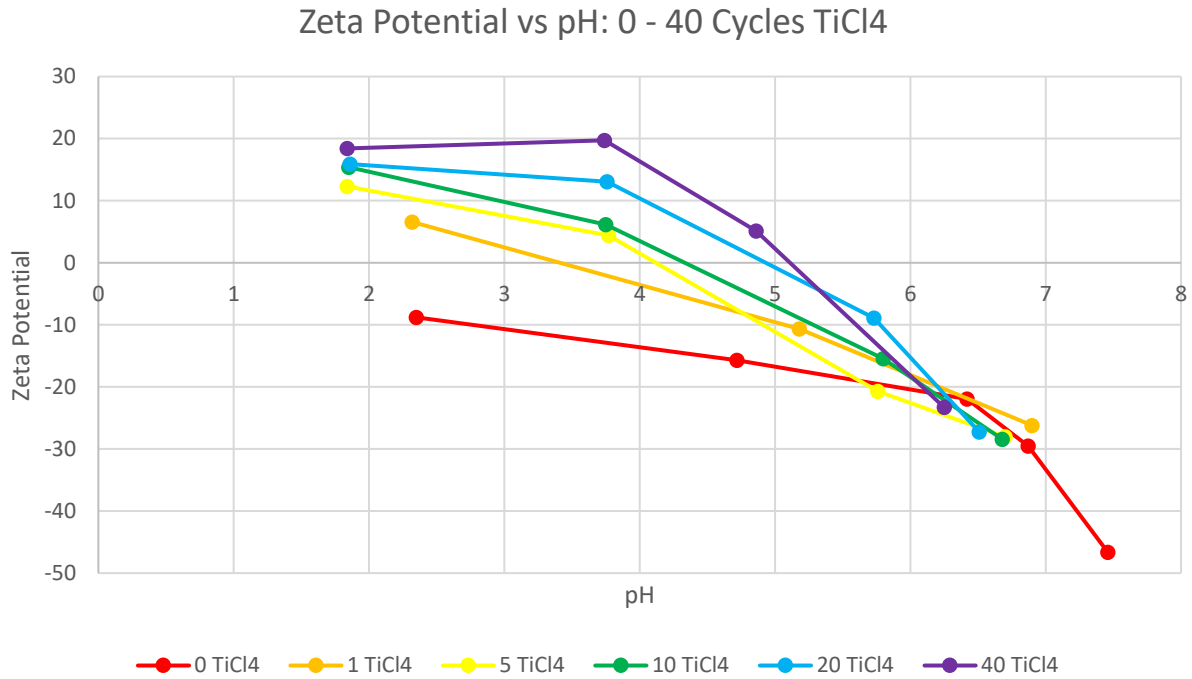


Figure 28: Zeta potential with different layers of TiCl_4 on SiO_2 , from 0 – 160 cycles

4.1 Zeta Potential

The isoelectric of mixed oxides has been previously determined as the average of the isoelectric points weighted by their apparent surface coverage (**Equation 4**).¹⁸ However, this equation assumes that the individual oxide moieties act independently from one another. From this equation, we should then predict that a single layer of material deposited over a substrate via ALD should have complete apparent surface coverage of the former rather than the latter. Therefore, upon depositing a single monolayer, the isoelectric point should immediately switch from that of the substrate surface to that of the deposited material.

If there is no interaction between the titania and the native oxide, it should be expected that the isoelectric point of the powders should first change gradually from the native surface to a titania surface up the first monolayer. Then at one monolayer of TiCl_4 , the isoelectric point should have reached that of a titanium oxide surface and should not change with the addition of more layers.

First, we can see that in **Figure 27**, the curves shift upwards as the number of layers increases. While SiO_2 (0 TiCl_4 sample) appears to have an isoelectric point below 2 since it does not intersect at all with the x axis in this graph, it is stated in literature to be almost impossible to be able to achieve a positive zeta potential silica and that its true isoelectric point hovers at a pH of around 2-3.^{57, 58}

Figure 28 shows the isoelectric point as a function of the Ti atomic percent as determined via SEM- EDX. The graph has additional vertical dashed red lines that represent one monolayer: at 9.8 at.% the first monolayer is completely deposited, while the second monolayer is deposited at 18.3 at.%, etc. Some variation in the measurement of the isoelectric point is expected, due to the sensitivity of zeta potential to surface impurities and other imperfections. Nevertheless, it reaffirms

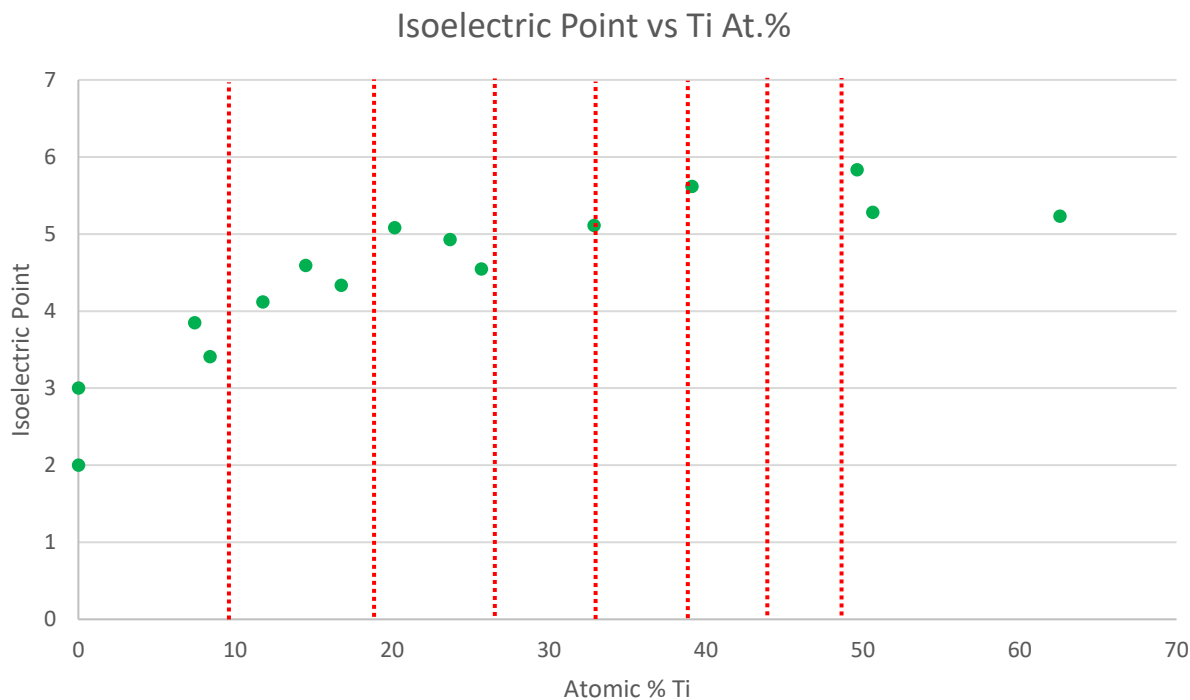


Figure 29: Isoelectric point as a function of Ti at. %. The vertical red dashed lines represent one monolayer each.

that is still an upward trend of the isoelectric point as the Ti atomic percent increases. Contrary to the hypothesis that a single monolayer will completely change the isoelectric point and will not do so upon the deposition of further layers, we can see that the isoelectric point tends to stabilize after about three monolayers of TiO_2 have been added. This phenomenon appears to be like the inductive effect, in that the SiO_2 moiety acts as the “heteroatom” to the TiO_2 surface, drawing electron density away from the Ti cation and affecting its acid properties due to the former’s higher electronegativity. Moreover, the effects of the SiO_2 moiety on the TiO_2 moiety disappears after a few monolayers have been deposited, paralleling the behavior of inductive effect which becomes less pronounced with increasing distance from the heteroatom.

4.2 Potential Active Sites

To identify the possible acid sites responsible for creating the charged surface, we must first look at all the possible sites for proton exchange. In **Figure 29**, we have identified the following: pure Si-OH, bridging Si-O-Si, interfacial Si-OH, bridging Si-O-Ti, interfacial Ti-OH, and pure Ti-OH. The bridging oxygen groups are unlikely to be acid sites, since they are formed by consuming the hydrogen during ALD and would not likely be protonated unless the surface is in very acidic conditions. This leaves us with the pure oxide-OH groups and the interfacial oxide-OH groups. As the number of cycles increases, the contribution of each type of oxide-OH will change. Prior to deposition, the surface would only be composed of pure Si-OH groups. As the first layer of TiO₂ is deposited, the surface acidity is then a mix of pure Si-OH, interfacial Si-OH, and interfacial Ti-OH. Once the first monolayer is deposited, only the interfacial Ti-OH groups remain. More TiO₂ deposits onto the surface, shifting the surface more towards a TiO₂-like surface.

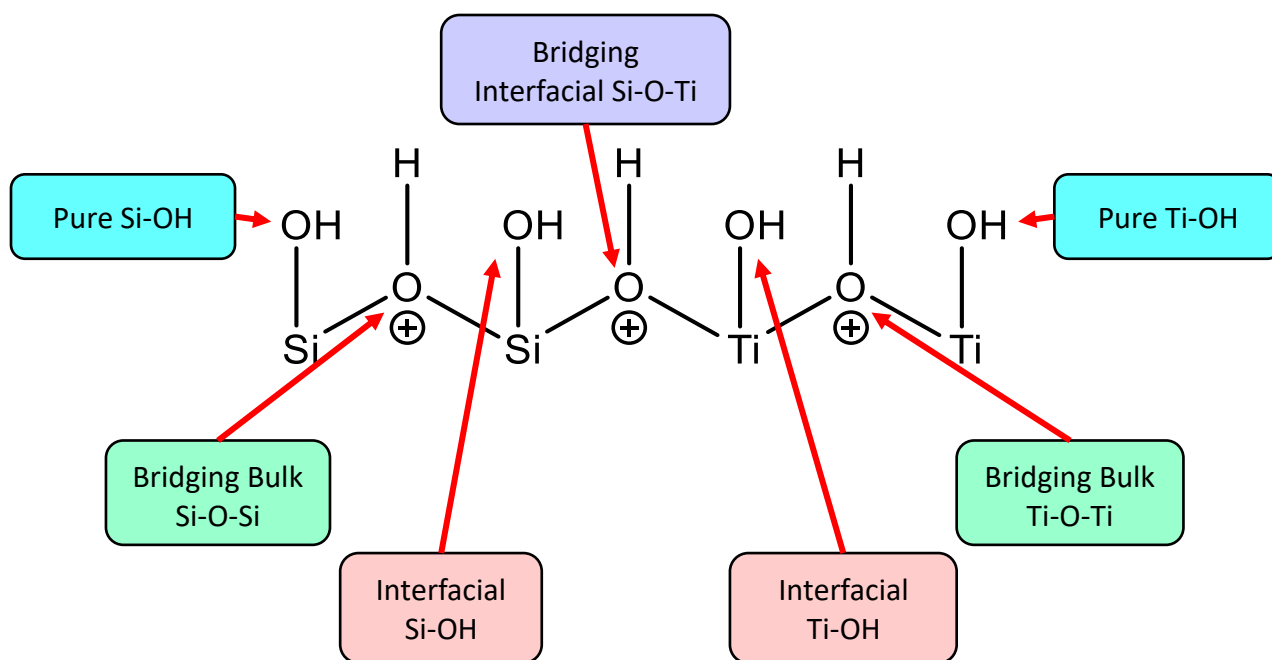


Figure 30: Possible acid sites that can exchange protons with the solution to create surface charges. Bridging oxygen sites are unlikely to be acid sites.

Eventually, there should be enough TiO_2 piling onto the surface to create a “pure” TiO_2 surface with a corresponding isoelectric point.

Given the current behavior of the isoelectric point of ultrathin ALD-deposited films of varying thickness, it is clear that the underlying substrate can have a profound effect on the chemistry of the newly deposited layers. Therefore, **Equation 4**, which assumes that mixed binary oxides do not interfere with each other, must be changed upon in order to compensate for these mixing interactions.

5. Conclusions and Future Work

5.1 Conclusions

The first aim of this thesis was to highlight the complications that arise when performing fixed-bed powder ALD. The most notable problem was the adsorbed byproducts (HCl) from TiCl_4 deposition on the surface of the silica powder. On a flat surface such as a silicon wafer, adsorbed HCl can easily desorb given proper purging procedures and therefore is not an issue in semiconductor wafer applications. However, for the direct synthesis of catalysts with high surface area, adsorption of byproducts can affect the surface chemistry or even prevent film growth. In the case with our experiments, this HCl has directly affected the measurements of the isoelectric point when we were performing mass titrations.

Another complication which is related to the first was the reaction of the precursor with the reactor chamber itself. Since the precursor can react to the walls, it can produce an even higher concentration of byproducts, which further increases the likelihood of adsorbed products onto the substrate surface. To address these problems, we first implemented a two-dose step for each precursor per cycle. The first dose is a quick step that has the precursor react with the reactor chamber walls and can purge the byproducts of that reaction. The second dose is a long hold step that allows the precursor to infiltrate into the powder sample without concerns about HCl byproducts from the walls.

Even with the two-dose step, HCl will still be present due to the reaction of TiCl_4 with the powder, albeit at significantly lower concentrations. While the solution is not perfect as it cannot prevent adsorbed HCl from stunting further growth, we have added a post-processing washing step that can at least remove any HCl remaining on the surface after deposition. All in all, not every ALD precursor will necessarily produce byproducts that adsorb strongly to the surface –

Trimethylaluminum (TMA) produces methane gas which would never adsorb onto the silica surface – but this issue should be considered when using any ALD precursor, especially when depositing on powders.

In addition, we have created a geometry-independent equation that models the growth of thin films onto convex powder via ALD. Using this equation, we may be able to calculate film thicknesses via their respective atomic percentages in SEM-EDX, which is facile and noninvasive. This model can correlate thickness with atomic percent well for films that are significantly thinner than the diameter of the particle. For films that are comparable to the powder thicknesses (at least within an order of magnitude), this equation falls off, and will overestimate the actual Ti amount due to concavity present from the powders packing together.

The second aim of this thesis was to observe the changes in the isoelectric point of SiO_2 powder as a function of the number of ALD cycles of TiCl_4 .

Our initial hypothesis was that the isoelectric point would reach that of pure TiO_2 upon reaching 20 cycles, or two monolayers. This hypothesis runs counter to the literature-based formula of the isoelectric point of mixed oxides, which would assume that a full monolayer of TiCl_4 would result in the isoelectric point completely shifting to that of pure TiO_2 . However, based on the currently established models, the isoelectric point still transitions even after 80 cycles, or equivalent of four monolayers.

5.2 *Future Work*

This work represents the first step in understanding the surface properties of ultra-thin oxide films deposited onto powders through ALD. The titania-silica interface is just one combination of materials that can exhibit increased acidity; other systems like binary Al-Ti oxide

systems or even ternary systems like Al-Zr-Si systems can be produced using ALD systems, and provide an excellent potential to be explored.

Additionally, the chemistry of the outermost layer of multi-precursor ALD may differ depending on the last cycle. In an Al-Ti oxide system, in which Al_2O_3 layers can be alternately deposited with TiO_2 layers, the chemistry of the surface may depend on which layer is the final layer.

In this thesis, the zeta potential was the sole characterization technique used to probe the surface acidity of ALD-deposited oxide surfaces. Other techniques, such as elemental NMR (Si NMR, Al NMR), acid-base titrations, and amine-based FTIR are available, and should be explored in order to better understand the acidity of these new combinations of ALD films.

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