Surface Treatment of Photocatalyst Metal Supports for VOCs Abatement Applications

DON CHINUNGI
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My God Reigns...So it was and forever shall be!
Abstract

In this work, the preparation of photocatalysts’ metal support for applications in purification of industrial gas emissions has been studied. The supports normally used in literature are ceramics, but they are not suitable for industrial applications. Stainless steel and aluminium are much more common in full-scale reactors and were therefore chosen in this investigation. Chemical etching, anodisation, electrochemical DC etching and AC etching treatment methods were used to modify the surface morphology of aluminium and stainless steel plates in order to improve the mechanical stability of photocatalyst (TiO$_2$) coating. Two-part epoxy-siloxane hybrid (ESH) and sodium silicate adhesives have been evaluated for use as TiO$_2$ binder. Dip and spray coating techniques were employed for preparing TiO$_2$ coatings on blank plates, pretreated plates, ESH and sodium silicate coated plates. Stainless steel electrochemically etched in dilute aqua regia gave the most mechanically stable coating. It was demonstrated that a high microscale surface roughness of the support improves the mechanical stability of TiO$_2$. Additionally, photocatalytic performance of the coating was higher than that coated on ceramic support. The mechanical stability of TiO$_2$ coated on ESH and sodium silicate using dip and spray coating techniques was exceedingly improved. However, Energy Dispersive Spectroscopy (EDS) analysis showed that TiO$_2$ was embedded in the adhesives. Nevertheless, sprinkling of TiO$_2$ powder on sodium silicate presented a very stable coating regardless of high TiO$_2$ loading. It was also shown that coating of sodium silicate on pretreated plates did not affect the mechanical stability of TiO$_2$ coating. A well coated and uniform surface of TiO$_2$ was achieved by spray coating technique.
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1 Introduction

The emission of gasses from industrial processes pose a high risk to human health and the environment. Many of the volatile organic compounds (VOCs) contained in gas emissions are very toxic and some are considered to be carcinogenic and mutagenic. The major problem with VOC emissions is the formation of ozone in the presence of NOx and sunlight \[1\]. Ozone is toxic to humans, damaging to the environment and can result in acid rains \[2\]. Emission of VOCs also contributes to depletion of stratospheric ozone layer, and consequently global warming \[3\]. As a result of such problems as these, the regulations on gaseous emissions are becoming tighter and more stringent.

Today, the main conventional techniques employed to control VOCs emissions from industrial processes includes adsorption, absorption, condensation, membrane separation and thermal incineration \[4\]. However, these techniques are expensive to use because many industrial processes produce low levels of VOCs in large volume flows. Other photochemical degradation techniques exist i.e. UV photolysis, UV photooxidation in the presence of oxidants (ozone, Hydrogen peroxide and hydroxyl radicals) and Photocatalytic Oxidation (PCO) \[4\]. Compared to conventional techniques, PCO has demonstrated to be an efficient VOC abatement technology for the purification of trace amounts of VOCs in gas-phase \[2\]. PCO reaction destroys organic compounds in the presence of air/oxygen and UV-irradiated catalyst. This technique is attractive because of low operation temperature, no addition of chemicals, and oxidation into harmless by-products usually CO\(_2\), H\(_2\)O, and mineral acids.

The application of heterogeneous Photocatalytic Oxidation of VOCs in gas-phase is a relatively new technology which is widely investigated on lab scale \[2\], \[3\]. For a photocatalytic oxidation system to be efficient, the contact between the catalytic active phase and the reactants should be enhanced coupled with efficient irradiation of UV light on the photocatalyst \[5\]. It is therefore important that the specific textural and the catalytic properties of the catalyst coating is retained over longer operation time. Furthermore, the catalyst coating should be durable and stable. The durability and stability of the catalyst coating could be achieved by firmly immobilising the photocatalyst on its support. The catalyst particles should be attached firmly to the deeper sites of the support in order to form durable structures \[5\]. It has been demonstrated that high roughness and porosity of the surface of a solid support material can increase the contact area between the coating and the surface. Subsequently the stability of adhesion and the life of the coatings are improved \[6, 7\]. In this study, the support materials were subjected to different treatment methods in order to increase the surface roughness. The effect of adhesives on the mechanical stability of the coatings was also investigated.
1.1 Aim of Study

The overall objective of this study was to improve the mechanical stability and life of photocatalyst coatings on aluminium and stainless steel as support materials. Aluminium and stainless steel were chosen because they are commonly used in full scale reactors for industrial applications. However, attaining a stable TiO$_2$ coating on metallic supports is challenging as they are not as porous and rough as ceramic supports. The study involved the evaluation of different preparation methods of the support material focussing on increasing the surface area by modifying it’s morphology. Chemical etching, electrochemical etching and anodisation metal preparation methods were employed to achieve a high rough surface morphology. Furthermore, two-part epoxy-siloxane hybrid and sodium silicate adhesives were separately investigated for use as TiO$_2$ coating binder. Different techniques of TiO$_2$ immobilization were also evaluated. These techniques included, spray coating, dip coating and powder sprinkling on wet adhesive coating. The mechanical stability and quality of the coatings were analysed using tape testing method. Additionally the mineralisation of acetaldehyde was tested using the most mechanically stable TiO$_2$ coating as determined by tape testing.
2 Theoretical Background

This chapter presents an overview of photocatalytic oxidation for the purification of organic compounds in gas phase. Suitable semiconductors utilised in photocatalysis and the preferred semiconductor (TiO$_2$) are discussed. An overview of the support materials used to immobilise the photocatalyst is also presented. Methods that could be used to prepare a support material in order to enhance coating stability are herein explained. Additionally, different TiO$_2$ immobilisation techniques on support materials are discussed.

2.1 Photocatalytic Oxidation

Photocatalysis can be defined as the acceleration of a photo chemical reaction by irradiation of a photocatalyst which lowers the activation energy of the reaction [8]. Photocatalytic oxidation also referred to as heterogeneous photocatalysis has been used for purification of water from harmful microorganisms and decontamination of air systems.

Photocatalytic oxidation occurs when a photocatalyst (semiconductor based catalyst) is hit by radiation that has energy which is equal or greater than the band gap energy of the photocatalyst. The irradiation causes the electron to be excited from the valence band (VB) to the conduction band (CB) creating a hole in the valence band (Equation 6). The resultant electron and hole may recombine on the surface of the photocatalyst in the absence of a suitable acceptor and donor for $e_{cb}^-$ and $h_{vb}^+$, respectively. Hydroxyl anions and water molecules adsorbed on the surface of the photocatalyst act as electron donors, while molecular oxygen acts as electron acceptor. The excited electrons interacts with molecular oxygen on the surface of the photocatalyst to produce superoxide (O$_2^-$) radicals. The superoxide radicals reacts with water molecules absorbed on the surface to form hydroxyl (OH$^\cdot$) radicals. On the other hand, the electron holes interacts with absorbed hydroxyl anions and water molecules to produce hydroxyl radicals [9,10]. Formation of hydroxyl and superoxide radicals is represented in Equations 2, 3 and 4.

$$\text{SC} + h\nu \rightarrow e_{cb}^- + h_{vb}^+$$

$$h_{vb}^+ + \text{H}_2\text{O} \rightarrow \text{OH}^\cdot + \text{H}^+$$

$$\text{OH}^- + h_{vb}^+ \rightarrow \text{OH}^\cdot$$

$$\text{O}_2 + e_{cb}^- \rightarrow \text{O}_2^\cdot$$
The hydroxyl radical is a strong oxidant species. Once an organic compound is absorbed onto the surface of the photocatalyst, it reacts with the hydroxyl radical. This results in the structural breakdown of organic compound over several intermediates before complete decomposition.

![Photocatalytic reaction steps in a solid semiconductor particle: Adapted from [11]](image)

Figure 1 shows steps of the photocatalytic reaction in a solid semiconductor. Light photons of energy $h\nu$ equal to or greater than the semiconductor band-gap energy (1); Excited electron ($e_{cb}^{-}$) promotion from valence band to conduction band leaving a hole, ($h_{vb}^{+}$) in the valence band (2); $h_{vb}^{+}$ and $e_{cb}^{-}$ diffuses to the surface and starts the oxidation reactions (3) and reduction reactions (4), respectively.

### 2.1.1 Suitable Semiconductors for Photocatalysis

Although there are several different semiconductor materials, metal oxides and metal chalco-genide semiconducting materials are the most used as photacatalysts for mineralisation of organic compounds [11, 12]. In order for a semiconducting material to be suitable as a heterogeneous photocatalyst it must be;

- Possible to activate by visible or UV light.
- Biologically and chemically inert
- Insoluble in water
- Resistant to photo-corrosion
- Cheap
Additionally, for the semiconductor to be photochemically activate, the redox potential of the photogenerated valence band hole must be positive enough to generate OH• radicals in order to oxidize the contaminant and the redox potential of the conductance band electron must be sufficiently negative in order to reduce O₂ to O₂• [12]. Figure 2. illustrates the redox potential of some suitable semiconductor materials for O₂/O₂• and OH•/OH⁻ couples.

Photoanodic corrosion of some highly active semiconductors renders them unacceptable for photocatalytic mineralisation of organic compounds. For example CdS has a sufficient large bandgap that it can be activated using visible light but it’s unstable towards photoanodic corrosion. Mills et al [12] showed that TiO₂ stands out to be the most photoactive semiconductor. It is photostable, insoluble under most conditions and cheap. These features make TiO₂ suitable as a heterogeneous photocatalyst for mineralising organic compounds.

Figure 2: Band positions (top of valence band and bottom of conduction band) for several common semiconductors together with the band-gap energy: Adapted from [13].

### 2.1.2 TiO₂ as Photocatalyst

Titanium dioxide mainly exists in anatase, rutile and brookite crystalline form [14]. Anatase and rutile share tetragonal crystalline system but have different arrangement of the octahedrons and distortion. In both structures, each Ti⁴⁺ is surrounded by six O₂⁻ in its first coordination sphere [11]. The anatase crystalline structure can be formed at temperatures between 400 °C and 500 °C. At temperatures greater than 700 °C anatase is converted to rutile crystalline structures coupled with sintering. Sintering reduces the specific surface area of the formed rutile by a factor of 10 compared to anatase (from which it is formed) [8]. Anatase TiO₂ exhibit higher photocatalytic mineralisation rates of organic compounds due to a longer life time of photogenerated electrons (> few ms). The longer life time in anatase...
TiO$_2$ is attributed to higher amount of surficial OH groups where the holes are trapped resulting in enhanced charge separation [15].

Although TiO$_2$ stand out to be most suitable semiconductor in photocatalytic applications, it presents some limitations. This is because TiO$_2$ has band-gap energy of 3.1 – 3.4 eV, and therefore activated by UV light; Only about 4 – 5 % of sunlight is UV radiation and it is inadequate to trigger a photoreaction [16]. Secondly, the degradation process has a low quantum yield and the fast recombination of the charge carriers is in the order of nanoseconds. The photocatalytic reaction rate can be enhanced by doping metal and non-metal ions into the TiO$_2$ lattice. The modification of TiO$_2$ increases the life time of charge carriers and reduces the band-gap. The increase in life time is attributed to the enhanced transfer and separation of photogenerated charge resulting in increased photocatalytic reaction rate. Furthermore, the reduced band-gap allows activation by longer wavelengths of visible light [11, 16]

2.2 Support for Photocatalyst Immobilization

The treatment of organic pollutants in gas phase requires immobilising the photocatalyst on a substrate due to the challenges of catalyst fluidisation, aggregation of suspended particles and catalyst recovery [17]. The photocatalyst is immobilised in form of a thin film [17]. Glass, cotton, polymer and metal substrates with different configuration has been employed as photocatalyst supports for air purification [5,16,18–20]. An ideal substrate should demonstrate good adhesion, chemical and mechanical resistance, and inert properties. It should promote low pressure drop and provide a high surface area. The substrate should also be cheap and readily available [11]. Therefore, the selection of a suitable support material is dependent on the design of the reactor and aforementioned properties. This is because in an efficient-gas-phase photocatalytic oxidation system, there must be sufficient UV irradiation on the photocatalyst and also good contact between the photocatalyst and gases. In recent research, metals [5,18–22] and glass [16,17] have been employed as support materials for photocatalytic degradation of VOC in gas phase. Aluminium and stainless steel are the common metal supports because they are widely used in industrial structured catalytic reactors [18]. Ceramic supports are used in laboratory studies but metals are preferred in industrial applications because of the mechanical properties and lightness. Additionally, TiO$_2$ could also be coated on the walls of the reactor if metallic supports are used.

2.2.1 Preparation of Support Material

Photocatalytic coatings should be strongly bound to the metal support in order to reduce the probability of failure during operations. Coating adhesion can be improved by increasing the roughness of the metal support [6]; the roughness may be increased by chemical etching [18], electrochemical AC etching [21], electrochemical etching under direct current [7] or
anodization [19]. The increase in surface roughness provides a high surface area onto which the photocatalyst nanoparticles can be anchored [19]. The inner and deeper parts of a rough structure are more protected from erosion caused by high gas flows. Giornelli et al [18] presented the coating of stainless steel plate i.e. a VOx monolayer on TiO$_2$ – anatase coated stainless steel. In their work, the stainless steel plate was chemically treated in sulphuric acid in order to increase the roughness of the surface as can be seen in figure 3. The acidic treatment increased the thickness of the passivation film on the grains. The etchant attacked grain boundaries resulting in pit corrosion only on the surface. In Barati et al research work [20], the steel plate were treated differently before depositing the TiO$_2$ nanoparticles. Plates of 316L were roughened with 80 grit sand papers followed by polishing with 0.3 and 0.05 µm alumina powder.

![Figure 3: SEM images (x5000) of stainless steel surfaces before (a) and after (b) acidic treatment; Reproduced from [18].](image)

Chan Lee et al [7] used electrochemical etching to modify the surface morphology of 304 stainless steel plate. In their work, they etched the plate in dilute aqua regia under direct current. It was found that the plate etched at 10 V and 15 V had high surface roughness. The etched surface had nano-scale, macro pores and bumps as shown in figure 4. Chan Lee et al concluded that electrochemical etching of stainless steel in dilute Aqua regia could be used to provide pretreatments for protective coatings.

![Figure 4: Surface morphology of etched 304 stainless steel at 10 V; Reproduced from [7].](image)
The formation of a porous oxide layer on the surface of the metal support is of great importance for coating TiO$_2$. Aluminium metal can be anodized to achieve a porous oxide layer. In their earlier work, Giornelli *et al* [19] anodised aluminium metal plate before deposition of TiO$_2$-anatase. 1 mm thick aluminium foils were anodized in 400 g/l sulphuric acid for 4 hours with direct current. After anodization, 65µm alumina layers were formed on each side of the plate.

Electrochemical etching process under alternating current can be utilised to obtain homogeneously etched layer with high surface area. It creates a pitted morphology on aluminium surfaces. A square pulse [21] or sinusoidal [23] constant current and HCl as the main etchant mixed with other acids can be used to achieve required morphology. In the anodic half-cycle cubic pits are formed due to dissolution of aluminium which diffuses into the bulk of the electrolyte. During the cathodic half-cycle, the PH is raised due to hydrogen gas evolution. Subsequently, aluminium hydroxide precipitates forming an insoluble etch film. In the preceding anodic half-cycle, at the bottom of the pit, a second pit forms on the weak point in the etch film. A repetition of these processes produces a cluster of pits on the surface [23]. The tendency of the pits to form clusters can be improved by using a H$_2$SO$_4$ in the HCl etchant. The sulphate ions favours pit-to-pit propagation by adsorbing competitively with the chloride ions (etchant) [21,23]. The Effect of sulfuric acid on pit propagation behaviour of aluminium under AC etch process was studied by Ono and Habazaki [21]. The concentration of H$_2$SO$_4$ was varied from 0.001M to 0.1M. A 10 Hz square pulse of 100 mA cm$^{-2}$ was then applied using a Galvanostat. They concluded that the presence of suitable H$_2$SO$_4$ concentration in HCl etchant changed the behaviour of pit propagation. Figure 5 shows etched layer of aluminium foil, deep and homogeneous layer is acheived with 0.01 M H$_2$SO$_4$ in 2M HCl.

![Figure 5: SEM images of cross-sections of aluminium foil after AC etching in 2M HCl etchants with and without H$_2$SO$_4$ at 30 °C (a) 0M H$_2$SO$_4$/300 kCm$^{-2}$ (b) 0.01M H$_2$SO$_4$/300 kCm$^{-2}$ (c) 0.1M H$_2$SO$_4$/300 kCm$^{-2}$: Adapted from [21].](image-url)
In this research, electrochemical AC etching and anodisation methods as presented by Ono and Habazaki and Giornelli et al, respectively, were adopted with modifications to prepare the metal support. Additionally, chemical etching and electrochemical etching methods presented by Giornelli et al and Chan Lee et al were used for preparing 304 stainless steel and aluminium before coating TiO$_2$ nanoparticles.

2.3 Photocatalyst Powder Immobilization

Two main routes can be used to immobilise TiO$_2$ on support material. The first route involves synthesis of catalyst during deposition; in this case the Ti - precursor undergo through a series of physical and chemical transformations in suitable solvent and controlled acid-base conditions. The second route involves dispensing photocatalyst powder in a suitable despensing agent [11]. This is a simple route of coating TiO$_2$ on support material; The main techniques used to coat includes dip coating [11,17], spray coating [5], doctor blade [11,16,17], electrophoresis [11] and spin coating [11].

*Dip Coating Technique* - a support material is immersed into a coating material (solution containing TiO$_2$) and then withdrawn at a constant rate. Dip coating produces a thin film on the substrate surface. The thickness of the produced thin film is dependent of the concentration of TiO$_2$ in the solution and the number of times the substrate is immersed into the solution.

*Spray Coating Technique* - The coating material is atomized, dispersed and deposited on the support material. In order to attain the desirable film thickness, the process is repeated allowing drying between the coats.

*Doctor Blade Coating Technique* - the coating material is placed on the edge of the support material. The blade is then moved at a constant speed forming a thin film. The thickness of the thin film is dependent on the distance between the substrate and the blade.

*Electrophoresis Coating Technique* - In this technique the support material and a counter electrode are immersed in coating material and a potential applied. This results in a formation of a thin film on the support material. It’s only suitable for conductive support materials.

*Spin Coating Technique* - In this technique, a small amount of coating material is added on the centre of the support material. It is then rotated at a high speed causing the material to spread by centrifugal force.

In this research, dip coating and spray coating techniques were used to immobilise TiO$_2$
nanoparticles on aluminium and stainless steel supports mainly due to availability of equipment. Two-part-epoxy siloxane and sodium silicate adhesives were also used as binders for improving the adhesion of TiO$_2$ coatings. Inorganic adhesives were utilised due to their ability not to be degraded by UV radiation. Another technique of TiO$_2$ immobilisation was used i.e. sprinkling TiO$_2$ powder on wet adhesive film.
3 Experimental Methods

In this chapter the methods used to prepare the aluminium and stainless steel plates as support material and techniques used to immobilise TiO$_2$ are described. The preparation of two-part epoxy-siloxane is also presented. The characterisation of pretreated support material, the mechanical stability and photocatalytic performance test measurements are reported.

3.1 Treatment of Aluminium and Stainless steel

Aluminium and 304 stainless steel plates were used as support material because of their potential use in the inner walls of photocatalytic reactors for pilot and full scale applications. 20 x 20 x 3 mm plates of aluminium and stainless steel were mechanically prepared for the different pretreatments employed in this study. Before pretreatment, the plates were thoroughly washed with detergent followed by acetone wash. They were then rinsed with deionised water and allowed to dry prior to treatment. After treatment, the plates were gently rinsed with deionised water and allowed to dry at room temperature. A jacketed glass reactor was used for all the treatments. The reactor temperature was maintained by continuously pumping water through the jacketed glass reactor from a water bath; the temperature of the water was controlled from the water bath. For temperatures below 0 °C, the reactor was put in an insulated ice bath and salt was added to further lower the temperature. A magnetic stirrer was used for continuous stirring of the solution in order to improve heat transfer. The equipment arrangement is shown in Figure 6.

![Figure 6: Experimental set-up: (a) Electrochemical DC Etching (b) Insulated Ice bath - Aluminium Anodization](image)
3.1.1 Chemical Treatment

Aluminium and stainless steel plates were chemically treated in sulphuric acid and piranha \((\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2)\) solutions [18, 22]. For sulphuric acid treatment, each metal plate was immersed in 30 wt.% \(\text{H}_2\text{SO}_4\). The plate was treated for 2 hours at 20 °C and 35 °C under continuous stirring. For Piranha treatment, each plate was dipped in a Piranha solution (a mixture of 95 % \(\text{H}_2\text{SO}_4\) and 30 wt.% \(\text{H}_2\text{O}_2\) at 2 : 1 v/v ratio, respectively) for 25 minutes at 50 °C. Stainless steel was also treated at 80 °C. The piranha solution was continuously stirred during treatment.

3.1.2 Anodizing of Aluminium

The aluminium plate was anodised in sulphuric acid solution under direct current [19]. The jacketed glass reactor (cell) was placed in an ice bath and 22 % \(\text{H}_2\text{SO}_4\) solution was added. The aluminium plate to be anodised was pretreated in 1M NaOH for 60 s at 40 °C followed by demutting in 1M HNO\(_3\) for 60s at room temperature [24]. A 26 cm\(^2\) aluminium plate was used as a counter electrode. The aluminium plate to be anodised was kept parallel to the counter electrode at 3 cm distance and then transferred into the cell. A current of 1 A/dm\(^2\) was applied using a DC Laboratory power supply (EA-PS 2342-10B, 0..42 V / 0..10 A) for 4 hours. The pore diameter and interpore distance of the oxide layer decreases with decreasing temperature whilst the surface roughness increases with decreasing temperature [25]. A high surface roughness is desired, as a result the temperature was stabilised at \(-15 < T < -9\) °C during the time of the experiment.

3.1.3 Electrochemical DC Etching

Aluminium and stainless steel plates were separately etched in dilute aqua regia electrolyte; the solution was prepared by slowly adding 1.2 % HNO\(_3\) to 3.6 % HCl at a v/v ratio of 2:1 [7]. The solution was prepared just before using in order to avoid self decomposition. A 10.4 cm\(^2\) aluminium plate was used as a counter electrode. The Aluminium and/or stainless steel to be etched (working electrode) was kept parallel to the counter electrode at 5 cm distance and then transferred into the cell. A constant voltage of 10 V was applied using a DC Laboratory power supply (EA-PS 2342-10B, 0..42 V / 0..10 A). The working electrode and counter electrodes were connected to the positive and negative terminals, respectively. The temperature was controlled at 25 °C and each plate was etched for 10 and 15 minutes.

3.1.4 Electrochemical AC Etching

Both aluminium and stainless steel plates were electrochemically etched under alternating current. An acidic solution containing 2 M HCl and 0.1 M \(\text{H}_2\text{SO}_4\) (1:1 v/v ratio) was used as an electrolyte [21]. Platinum electrode and Ag/AgCl·Sat KCl were used as counter and
reference electrodes, respectively. Before etching, the plate was pretreated in 1 M NaOH at 60 °C for 60 s followed by dipping in 1 M HNO₃ for 180 s at 60 °C. The plate was then rinsed with water prior to immersing in the cell. A constant pulse current of 60 mA/cm² was applied for 1 s using Gamry potentiostat - Chronopotentiometry Test. The etching was run for 100 cycles at room temperature.

3.2 Coating of Inorganic Adhesive and TiO₂ Catalyst

In order to enhance the adhesion of TiO₂ coating on the support material, a adhesive was coated on the aluminium and stainless steel plates before coating TiO₂ catalyst. The adhesive was coated on both pretreated and untreated plates. Two types of adhesives were used i.e. Sodium silicate solution (SiO₂, ~ 26.5 % and Na₂O, ~ 10.6 %) from Sigma-Aldrich and Two-part epoxy-siloxane hybrid solution (ESH). Two-part epoxy-siloxane hybrid solution was prepared according to [26] with modifications. 25 g of hybrid silicone-epoxide resin (Silikopon EF) was diluted with 4.17 g 1-Methoxy-2-propanol. Diluted Silikopon EF was then mixed with pre-hydrolysed Dynasylan AMEO (3-Aminopropyltriethoxysilane). 6.22 g AMEO was pre-hydrolysed with water for 20 hours; AMEO to water molar ratio of 1:2 was used. AMEO was pre-hydrolysed in order to reduce the reaction time to initiate cross-linking (curing). However, pre-hydrolysing shortens ESH solution pot life. As a result, all the coatings were done within an hour after preparation of the solution. Preliminary adhesive coatings were done to ascertain the % weight drying of the adhesive. The % weight drying of ESH and sodium silicate were found to be 85 % and 48 %, respectively (Table 1). The plate was horizontally dip coated in the adhesive and dried. ESH coated plate was dried for 2 hours at 65 °C in an oven while sodium silicate coated plate was dried for 24 hours at room temperature.

TiO₂ was coated on aluminium and stainless steel plate using three coating techniques in order to ascertain the optimal coating technique for each adhesive; Spray coating, dipping coating and sprinkling of TiO₂ powder. The coating solution was prepared by dispensing TiO₂ in ethanol and/or water at different ratios. Commercially available TiO₂ powder (Aeroxide P25, 85 % Anatase/15 % Rutile) obtained from Evonik was used in this study. The solution was sonicated for 1 hour in order to homogeneously dispense TiO₂ nanoparticles in ethanol. It was then continuously stirred using a magnetic stirrer between the coating of plates.

3.2.1 Coating of P25 with ESH and Sodium Silicate

ESH coated plates were pre-dried at room temperature for 60 minutes before dip coating and spray coating with P25. They were pre-dried in order to prevent ethanol from reducing the viscosity of ESH; in this way a homogeneous layer of TiO₂ was obtained. The coated plate was dried at room temperature for 20 minutes after which it was dried in an oven for 2 hours at 65 °C. P25 powder was also sprinkled on ESH coated plate. In this case the powder was
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</tr>
<tr>
<td></td>
<td>3</td>
<td>0.1985</td>
<td>0.0933</td>
<td>0.470</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>0.48</strong></td>
</tr>
</tbody>
</table>

sprinkled immediately after dip coating with ESH.

Similarly, P25 was dip coated and spray coated on sodium silicate coated plate. After dip coating with sodium silicate, the coating was pre-dried at room temperature for 10 minutes prior to coating P25. The coated plate was dried at room temperature for 24 hours. In a similar way, P25 powder was sprinkled on Sodium silicate coated plate immediately after dip coating. In order to determine the amount of P25 contained in the coating (P25 load), the plate was weighed before and after coating with sodium silicate or ESH and also after complete drying.

In order to effectively analyse the effect of adhesives on the metal support, blank (without adhesive) plate was also coated. The plate was horizontally dip coated and spray coated. The coating was dried in the oven for 30 minutes before applying another coat. The coating was repeated to achieve P25 load of 50 g/m².

### 3.2.2 Coating of P25 on Treated Plates

The coating of aluminium and stainless steel was also repeated for pretreated plates. The pretreated plates were coated with P25 with and without sodium silicate. Spray coating technique was used to coat P25 without the adhesive and powder sprinkling technique was used to coat P25 with sodium silicate. The procedure described in section 3.2.1 was used to coat P25 on treated plates.
3.3 Measurements

3.3.1 Characterisation

The surface morphology of the treated aluminium and stainless steel plates were characterized using scanning electron microscope (SEM, Zeiss Ultra 55). The images were analysed under 300 X, 3000 X, 20000 X and 100000 X magnification; 10 kV and 5kV accelerating voltage was used for aluminium and stainless steel, respectively.

3.3.2 Mechanical Stability of Coating

Tape adhesion testing were carried out to determine the mechanical stability of P25 coating. The tape was applied on the surface and removed at constant speed and consistent angle. The coated plate was weighed before and after applying the tape. Surface uniformity after tape testing was observed. The amount of coating removed from the plate was quantitatively evaluated. The test was repeated 2 times for coatings on untreated plates and 13 times for coatings on pretreated plates.

3.3.3 Photocatalytic Performance of TiO$_2$ Coating

The photocatalytic performance of the TiO$_2$ coatings were evaluated in an already established lab-scale reactor system. The reactor had two parallel fluorescence UV lamps and a volume of 0.615 dm$^3$. The UV lamps used in the reactor are UV-C low-pressure Hg lamps Heraeus GPH135T5L/4. They consumed 5 W each to emit 1.2 W light at 254 nm, the main emitted wavelength. The lamps are integrated in glass quartz sleeves for temperature control.

The tests were carried out with technical air and Acetaldehyde (CH$_3$CHO) at a flow rate of 7 L/min. Technical air contained 15 ppm CO$_2$, < 1 g/m$^3$ humidity and no hydrocarbons. The air was passed through a molecular sieve before feeding the reactor in order to zero CO$_2$ concentration in the air stream. The concentration of CO$_2$ in the reactor outlet stream was used as a measure of photocatalytic performance. The tests were run under dry and humid conditions for 15 hours and 2 hours respectively. Acetaldehyde was maintained at 150 ppm throughout the experiments. The parameters for both conditions are shown in table 2.

<table>
<thead>
<tr>
<th>Feed rate (L/min)</th>
<th>CH$_3$CHO Concentration (PPM)</th>
<th>Relative Humidity (%)</th>
<th>UV lamp Temperature (°C)</th>
<th>Run time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>150</td>
<td>16</td>
<td>48</td>
<td>15</td>
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<tr>
<td>7</td>
<td>150</td>
<td>26</td>
<td>48</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2: Conditions for testing the photocatalytic performance of TiO$_2$ Coatings

The conversion of Acetaldehyde was calculated from the stoichiometry ratios. Two molecules
of CO$_2$ are produced when one molecule of CH$_3$CHO is decomposed (equation 5).

\[
\text{CH}_3\text{CHO} + \frac{5}{2} \text{O}_2 \rightarrow 2 \text{CO}_2 + 2 \text{H}_2\text{O} \quad (5)
\]

Therefore, acetaldehyde conversion, $X_{\text{CH}_3\text{CHO}}$ is given by

\[
X_{\text{CH}_3\text{CHO}} = \frac{C_{\text{CO}_2,\text{out}}}{2C_{\text{CH}_3\text{CHO},\text{in}}} \quad (6)
\]

Where, $C_{\text{CH}_3\text{CHO},\text{in}}$ and $C_{\text{CO}_2,\text{out}}$ are the concentrations of CH$_3$CHO and CO$_2$ in the inlet and outlet streams of the reactor, respectively.
4 Results and Discussion

This chapter reports the results of the study. It presents the characterisation results of aluminium and stainless steel plates subjected to different pretreatment methods. The effect of a rough surface morphology is discussed. Herein, the use of adhesive to enhance adhesion and mechanical stability of P25 coating is also discussed. The impact of coating technique on surface uniformity of P25 coating is presented. The photocatalytic performance of the most mechanical stable TiO$_2$ coating is also discussed.

4.1 Surface Morphology of Treated Plates

4.1.1 Chemical Etching

Chemical etching affected the surface morphology of aluminium and stainless steel plates. The acidic etchant, once in contact with the plate, attacked the iron and aluminium contained in aluminium and stainless steel, respectively. Iron and aluminium are dissolved into Fe$^{2+}$ and Al$^{2+}$, respectively; hydrogen gas is produced in the reaction [6]. The dissolution of stainless steel in H$_2$SO$_4$ is represented in equations 7 (anodic reaction occurring at the collapsed passive points of the surface).

\[
\text{Fe} + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}(\text{SO}_4) + \text{H}_2
\] (7)

The reaction is then complimented by cathodic reaction in the presence of dissolved oxygen.

\[
2\text{Fe}(\text{SO}_4) + 2\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4\text{H}_2\text{SO}_4
\] (8)

The formed Fe$_2$O$_3$ is further dissolved by H$_2$SO$_4$ leaving the etched surface free of Fe$_2$O$_3$ and other impurities.

\[
\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}
\] (9)

Aluminium undergoes through the same steps i.e. dissolution of Al during anodic reaction, formation of Al$_2$O$_3$ during cathodic reaction and pickling of the surface with H$_2$SO$_4$.

Figure 7 shows the SEM images of Stainless steel plates immersed in 30 wt.% H$_2$SO$_4$ at 20 °C (a & d) and 35 °C (b & e). The surface morphology of stainless steel and aluminium plates were completely changed after treatment in H$_2$SO$_4$. The stainless steel plates changed from their shiny appearance to black due to changes in chemical surface composition. The H$_2$SO$_4$ solution also changed to green and then brown during etching, an indicative color of
iron ions. Numerous micropores on the surface and corrosion pits running along the grain boundaries were observed. It can be seen that a high rough surface morphology was obtained compared to untreated surface shown in figure 7 (c) and (f). The plates etched at 35 °C had large corrosion pits, consequently a higher rough surface morphology. This is evidenced by the fact that etching rate increases with temperature as pointed out in many papers [6]. The structures at both temperatures did not significantly change at microscale level.

![SEM images of stainless steel surfaces etched in 30 wt.% H₂SO₄ at (a) 20 °C (b) 35 °C (c) Untreated (d) 20 °C (e) 35 °C (f) Untreated.](image)

When commercial aluminium and aluminium alloys are attacked by a corrosive acid, it results in multiple pitting rather than general dissolution. Unlike stainless steel, there is no local breakdown of passivity on aluminium, instead pit initiation occurs around the small particles of intermetallic compounds bulging at the surface of aluminium [27]. Once the pits are initiated, the pit growth is autocatalytic i.e. the growth of the pits occurs due to changes in the pit environment; the dissolution of Al to Al³⁺ ions in solution forces diffusion of SO₄²⁻ ions into the pit to maintain charge neutrality. Al₂(SO₄)₃ then reacts with H₂O to form H⁺ ions. The formation of H⁺ reduces the PH in the pits resulting in a more aggressive environment [27, 28]. This pitting phenomena was observed on the surface of aluminium etched at 35 °C as could be seen in figure 8 (b). The corrosive pits ranged from 190 nm to 30 nm in size and are distributed on the whole surface. The surface morphology was slightly modified at microscale level but it can be said that the surface roughness was not significantly increased. Corrosive pits were not obtained on aluminium plates etched at 20 °C. This could be because of the low dissolution rate of aluminium at 20 °C. Nevertheless, it can be seen from figure 8 (a), with reference to untreated aluminium 8 (c), that a passive layer with many cracks was developed.
Figure 8: SEM images of aluminium surfaces etched in 30 wt.% H$_2$SO$_4$ at (a) 20 °C; 20.0 KX (b) 35 °C; 20.0 KX (c) Untreated 20.0 KX (d) 20 °C; 3.00 KX (e) 35 °C; 3.00 KX (f) Untreated 3.00 KX.

The surface morphology analysis of stainless steel showed corrosion resistance in piranha solution both at 50 °C and 80 °C (figure 10 (a) and (b)). It can be seen that the surface morphology is similar to that of the untreated stainless steel shown in figure 7 (c). The corrosion resistance observed could be attributed to high concentration (95%) of the H$_2$SO$_4$ contained in piranha solution. Generally, most stainless steel types are corrosive resistant at low and high concentration and are attacked at intermediate concentrations of H$_2$SO$_4$ [29,30]. Loto et al [29] observed the corrosion resistance behaviour of 316L stainless steel in 18.2 M H$_2$SO$_4$ concentration. It was found that there was more corrosion resistance of the steel specimen in high concentration. The authors stated that the corrosion resistance observed could have been due to the fact that H$_2$SO$_4$ is oxidising at high concentration and reducing at low and intermediate concentrations. Oxidising acids raise the potential of austenitic stainless steels from the active range into the passive range making them resistant to corrosion attack in oxidising acid medium [27]. Active range is the potential range at which the metal could be dissolved as ions in low oxidation state, while the passive range is the potential range at which the passivity of the metal prevails over dissolution. The transpassive range is the potential range at which the metal could be dissolved as ions in a higher oxidation state. These terms describe the anodic polarisation characteristics and are shown in figure 9.
Aluminium showed a different behaviour when immersed in piranha solution. Unlike many stainless steel types, aluminium is inadequately corrosive resistant in high concentrations of H₂SO₄ [31]. As a result numerous micro corrosion pits were observed on the surface of the plates. Nucleation of pits could also be seen; figure 10 (c) shows the nucleated pits as large as 1.6µm, micro pores can be seen inside the nucleated pits. The nucleation of pits and formation of numerous micro pits could have been affected by the etching conditions i.e. 50 °C and 95 % H₂SO₄ concentration. This is affirmed by the difference in surface morphology with aluminium etched in 30 wt.% H₂SO₄ at 35 °C (figure 8 (b)). As earlier discussed, the growth of nucleated pits occurs due to changes in the pit environment. Subsequently, at more aggressive conditions, pits can grow into shallow depressions or penetrate deeply.

4.1.2 Anodising of Aluminium

Figure 11 (a) and (b) shows SEM images of aluminium plate anodised in 400 g/1 H₂SO₄ at - 15 < T < - 9 °C. It can be seen that a nanoporous anodic aluminum oxide (AAO) layer has been formed on the surface of aluminium. The formed pores are cylindrical and well assembled with 16nm pore diameter and 30nm pore spacing. Mechanically and chemically
stable AAO layer is formed by dissolution of $\text{Al}_2\text{O}_3$ and at the same time formation of $\text{Al}_2\text{O}_3$ by oxidation [32]. The dissolution of $\text{Al}_2\text{O}_3$ at the oxide/electrolyte interface is represented in equation 10.

$$\text{Al}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 3\text{H}_2\text{O} \quad (10)$$

According to [33,34] dissolution of $\text{Al}_2\text{O}_3$ is accompanied by dissociation of $\text{H}_2\text{O}$ in the presence of an electric field. Due to the electric field, $\text{Al}^{3+}$ ions diffuse from aluminium surface into the bulk of the electrolyte while $\text{O}^{2-}$ and $\text{OH}^-$ ions migrate to the metal/oxide interface. Consequently, $\text{Al}_2\text{O}_3$ is formed at the metal/oxide interface which causes the thickness of the oxide layer to increase. The growth of pits around the defects on the surface (grain boundaries, dislocation, nonmetallic inclusions) initiates pore growth on $\text{Al}_2\text{O}_3$ layer; the pits results from the fact that the rate of dissolution of $\text{Al}_2\text{O}_3$ is uneven at nanometre scale. The pore grows in diameter due to the local electric field that increases the dissolution rate at the bottom of the pore. Subsequently, the electric field is increased which forces the diffusion of $\text{O}^{2-}$ ions to the metal/oxide interface for $\text{Al}_2\text{O}_3$ growth.

The surface morphology (figure 11 (b)) obtained is similar to that reported by Sulka & Parkola [25]. Aluminium plates were anodised at constant voltage between 15 V and 25 V in 20 wt.% $\text{H}_2\text{SO}_4$ at -8, 1 and 10 °C. An $\text{Al}_2\text{O}_3$ layer with well-ordered hexagonal arranged nanopores, 35 nm Interpore distance and pore diameter of 14 nm were observed for the plate treated at 15 V and -8 °C. Anodising aluminium plate did not result in a modified surface morphology at microscale level as can be seen in figure 11 (a) for SEM image taken at 20.0 KX.

![Figure 11: SEM images of anodised aluminium surfaces in 400 g/l $\text{H}_2\text{SO}_4$ (a) 20.0 KX (b) 100 KX (c) anodised aluminium by Sulka & Parkola [25]](image)

### 4.1.3 Electrochemical DC Etching

It can be seen from Figure 12 (a) and (b) that a rough surface structure was achieved on stainless steel etched in dilute aqua regia under direct current. Uniformly distributed nanoscale and microscale bumps were developed on the surface. The mico structure was completely changed to a hierarchical structure with bumps. The observed surface morphology is similar
to one obtained by Lee et al [7]; the method used in this study. The authors reported the presence of nanoscale, microscale pores and microscale bumps on the surface of the specimen etched at 10 V. The average surface roughness increased to 15.02 µm compared to 2.64 µm for a sandblasted specimen. It was also observed that hierarchical structure formed on the surface improved the wettability; the drop of a liquid was unable to roll but got stuck on the surface. The authors attributed the phenomena to the presence of microscale bumps. The drop could easily be soaked into the bumps and firmly stick on the surface.

It is worth mentioning that neither nanopores nor micropores were observed in this study which is not the case for Lee et al observations. The authors suggested that formation of a porous surface morphology was as a result of anodic oxidation (formation of an oxide layer). According to Fujimoto et al [35], the growth of a porous oxide layer is due to recurrence of dissolution of Fe and Cr at lower potential ($E_L$) and re-oxidation of Cr$^{2+}$ at higher potential ($E_H$). Fe and Cr are dissolved into Fe$^{2+}$ and Cr$^{2+}$ ions at $E_L$ in the active range of Fe and Cr. The Cr$^{2+}$ ions are re-oxidised at $E_H$ in the passive range into Cr$^{3+}$ ions to form a continuous passive oxide layer if $E_H$ is kept constant. The anodic process is summarised as shown below.

Anodic Oxidation Process:

\[
E_L: \text{Fe} - \text{Cr} - \text{Ni} \rightarrow \text{Cr}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}
\]
\[
E_H: \text{Cr}^{2+} \rightarrow \text{Cr}^{3+}
\]

When the applied potential is switched from the higher potential to the lower potential in the active range, dissolution of Fe and Cr reoccurs on the entire surface under the oxide particles formed at $E_H$. The H$_2$O molecules and ions are able to penetrate through the pathways of the preformed oxide layer. Repetition of this process yields a thick porous oxide layer on the surface of stainless steel. Fujimoto et al formed a thick porous oxide layer on type 304 stainless steel by applying a square wave potential in H$_2$SO$_4$ at 50 - 80 °C.

No significant difference in surface morphology was observed between the plate etched for 10 minutes and 15 minutes (figure 12 (a) and (b)); this observation affirms the reproducibility of obtained results in this treatment method. However the weight loss was high for the plate etched for 15 minutes especially on the edges. The presence of nanoscale and microscale bumps on the surface of stainless steel could be very useful in achieving a stable coating. On the other hand, irregular nanoscale pits were observed on aluminium plates etched for 10 minutes and 15 minutes as shown in figure 12 (c) and (d). High weight loss was also observed as evidenced by large (in millimetre scale) etch pits on the surface and size reduction of the plates. Aqua regia turned out to be a very strong etchant for aluminium in this treatment.
method. However, the micro structure of aluminium surface was not changed as can be seen in figure 12 (d) at 3.0 KX and figure 8 (a) (untreated aluminium).

![SEM images of stainless steel etched for (a) 10 min(b) 15 min and Aluminium for (c) 10 min (d) 15 min at 25 °C.](image)

**Figure 12: SEM images of stainless steel etched for (a) 10 min(b) 15 min and Aluminium for (c) 10 min (d) 15 min at 25 °C.**

### 4.1.4 Electrochemical AC Etching

Electrochemical AC etching of aluminium in HCl produces cubic etch pits covered by an amorphous film of oxide/hydroxide [23]. Addition of H₂SO₄ to the HCl etchant increases the tendency of the pits to form clusters [21]. Figure 13 (a, b and c) shows the etched surface of aluminium after 100 cycles. It can be seen that a rough surface morphology with a high surface area was achieved due to formation of deep pits. As earlier discussed in section 2.2.1, addition of sulphate ions in the etchant favours pit-on-pit propagation. The pit clusters formed are deep and localised around the surface of the plate. This surface morphology is analogous to the observations made by Ono and Habazaki [21]. The authors reported from SEM analysis, that the formation of localised deep etched regions for the specimen etched in 2 M HCl and 0.1 M H₂SO₄ was due to excess clustering of pits.
Figure 13: SEM images of Stainless steel and Aluminium surfaces etched in H$_2$SO$_4$ at 20 °C

The surface morphology of stainless steel etched in HCl : H$_2$SO$_4$ solution under alternating current developed many nanopores and nanoscale bumps and a few microscale bumps (figure 13 (d)). Some precipitate was also observed on the surface. The nanoscale and microscale bumps are similar to that observed for etching in aqua regia (figure 12). Even if the bumps may be similar, there are large regions where the bumps were not developed. It can therefore be said that an inhomogeneous oxide layer was grown on the surface of stainless steel. The localised porous oxide layer is a mirror of inhomogeneous etched layer on aluminium plate treated under the same conditions.

4.2 Coating of Inorganic Adhesive and P25

Preliminary TiO$_2$ coatings were carried out to optimise TiO$_2$ to ethanol ratio, to give a stable coating. Coating solutions comprising ratios of TiO$_2$ to ethanol at 1:5 and 1:10 by weight were formulated. It was found that ethanol had an effect on sodium silicate. Ethanol reacted with sodium silicate to form sticky and soft polymers. This resulted in agglomeration of TiO$_2$ nanoparticles on the surface of the plate. Consequently, TiO$_2$ was dispersed in water for coating on sodium silicate coating. Ethanol had also an affect on the viscosity of ESH coating. It was found that with high ethanol content in coating solution, the viscosity of ESH was drastically reduced. Ethanol is a good solvent for silikopon EF, the main component of ESH. As a result a homogeneous TiO$_2$ layer on ESH coat could not be obtained; with 1:5 ratio, the coating showed improved appearance with a more homogeneous layer of TiO$_2$. Therefore, a TiO$_2$ to ethanol and TiO$_2$ to H$_2$O ratio of 1:5 was used to coat TiO$_2$ on ESH and sodium silicate, respectively. TiO$_2$ to ethanol ratio of 1:20 was used to coat TiO$_2$ on treated and untreated plates (blank) without adhesive pre-coating. With a high ratio (1:20) a crack free and uniform coating was achieved [36].
4.2.1 Coating on Untreated Plates

The first set of samples were coated in order to find a suitable coating technique and adhesive to give a uniform and mechanically stable coating. Different TiO$_2$ coatings were prepared by different coating techniques on ESH, sodium silicate and blank samples. Coating of TiO$_2$ on both ESH and sodium silicate using dip coating technique resulted in small buildup of coating on one side of the surface. The coating buildup was more prominent with increased number of dipping in the coating solution. This could be because of the increased amount of ethanol on the surface with the number of dipping. The coating solution could not flow steadily across the whole surface resulting in accumulation of TiO$_2$ nanoparticles near and on the edges. On the other hand, the samples coated using spray coating technique showed good surface uniformity of TiO$_2$. This is attributed to consistent and even spreading of coating solution on the adhesive surface. However, it was observed that in both coating techniques the TiO$_2$ nanoparticles appeared to be embedded in the ESH and sodium silicate coatings. This is evidenced by Energy Dispersive Spectroscopy (EDS) analysis on SEM. Figure 15 shows the EDS spectrum and the corresponding elemental analysis and SEM images of TiO$_2$ coated on ESH and sodium silicate. There was no trace of TiO$_2$ on the surface of ESH coated samples. It can be seen from EDS spectra and elemental analysis that only C, O and Si were detected (figure 15 (a)). Similar results were observed for sodium silicate samples coated using spray coating technique (figure 15 (b)). But Traces of TiO$_2$ were detected for sodium silicate samples coated using dip coating technique as shown in figure 15 (c) and (d). Figure 15 (d) shows the spectra and corresponding SEM image directed on the exposed TiO$_2$. The low Ti atomic % exemplify the absence of TiO$_2$ on the surfaces of ESH and sodium silicate coated samples. The elements and their atomic % presented in figure 15 are that of sodium silicate and epoxy siloxane resin. The calculated weight % and molecular structures of sodium silicate and Epoxy siloxane resin are shown in figure 14 below. The weight % of the elements are qualitatively comparable.

<table>
<thead>
<tr>
<th>Element</th>
<th>weight (g/mol)</th>
<th>weight %</th>
</tr>
</thead>
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<tr>
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<td>46.23</td>
</tr>
<tr>
<td>Si</td>
<td>84.28</td>
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<tr>
<td>Total</td>
<td>400.33</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Figure 14: Calculated elemental composition of sodium silicate and epoxy resin.
Figure 15: EDS spectra and corresponding elemental analysis and SEM images of TiO$_2$ coated on (a) ESH using spray coating (b) Sodium silicate using spray coating (c) and (d) Sodium silicate using dip coating.

Tape testing results showed that no TiO$_2$ was removed on the surface of both ESH and sodium silicate. No weight loss was recorded after conducting mechanical stability tape testing on the surface of sodium silicate for both spray coating and dip coating techniques (figure 16 (b)). Similarly, no weight loss was recorded for ESH samples coated using dip coating technique. This illustrates that the force with which the coating was adhered to the surface of the plate was more than the force with which the tape adhered to the coating surface. It can be said that the coating is mechanically stable. However, photocatalyst activity could be negatively affected due to the fact that TiO$_2$ is embedded in the adhesive coating. There were small amounts of TiO$_2$ on the surface of ESH samples coated using spray coating. The TiO$_2$ layer present on the surface was completely removed with scotch tape.

In order to avoid the embedding of TiO$_2$ into the adhesive, TiO$_2$ powder was sprinkled on freshly coated ESH and sodium silicate. The samples coated using this technique had very poor surface uniformity and very high TiO$_2$ loading. The amount of TiO$_2$ loaded on the surface was difficult to control since powder was manually sprinkled. A uniform coating could be achieved with a powder spray coating system. Additionally, blank samples coated using spray coating technique showed good surface uniformity.
Figure 16 shows the tape testing results for the first set of coated samples. The tape test was repeated 2 times. The TiO$_2$ coating was mechanically stable on Sodium silicate coated samples than ESH coated samples for powder coating technique. TiO$_2$ powder was firmly attached to the surface of sodium silicate; less than 5 wt.% of TiO$_2$ was removed with scotch tape on both aluminium and stainless steel samples. On the other hand, more than 50 wt.% of TiO$_2$ was removed on ESH coated samples. This could be due to the fact that ESH was viscous and quickly formed a very thin top layer hence preventing TiO$_2$ from sticking onto the surface. In comparison with TiO$_2$ coating on ESH and sodium silicate, the mechanical stability of TiO$_2$ coatings on blank plates for spray and dip coating techniques was poor (figure 16 (d)); Over 28 wt.% of TiO$_2$ was removed with scotch tape. A high wt.% was recorded for sample SS.B.1 due to high loading of TiO$_2$. It was observed that more TiO$_2$ remained on the tape with a high TiO$_2$ loading. Therefore, for the proceeding coatings, the tape testing was repeated until there was no more TiO$_2$ remaining on the tape. It was repeated 13 times for TiO$_2$ coated on blank pretreated plates and 6 times for TiO$_2$ coated on sodium silicate.

4.2.2 Coating on Pretreated Plates

In the second set of coating, TiO$_2$ was coated on pretreated aluminium and stainless steel plates using spray coating technique. Spray coating technique was used because it gave a uniform surface of TiO$_2$ coating. Powder coating technique was also employed to coat TiO$_2$ on sodium silicate; sodium silicate was coated on pretreated plates. Sodium silicate was used because of its ability to firmly bond with TiO$_2$. Based on the surface morphology from SEM analysis, five pretreated plates were selected for coating TiO$_2$. The treatment methods and
A high rough surface morphology of a support material is useful in improving mechanical stability of the coating. The surface roughness was not quantitatively measured but the observed modified surface morphology indicated improved surface roughness. This observation agrees with the surface roughness recorded for plates modified with the above (table ??) treatment methods [7,18]. In order to quantitatively determine the surface morphology that would give a stable coating, the mechanical stability was evaluated using tape testing. As earlier discussed, the test was repeated until no weight loss of TiO$_2$ was recorded. The results are shown in Figure 17; % weight loss of TiO$_2$ after tape testing 13 times (the loading of TiO$_2$ for the different plates as a function of number of tape testing can be seen in appendix).

![Tape Testing on Pretreated Plates](image)

**Figure 17:** % weight of TiO$_2$ removed after tape testing thirteen times

For TiO$_2$ coated on blank pretreated plates, the lowest weight loss was recorded for stainless
steel (SS_2) electrochemically etched in dilute aqua regia. It can therefore be said that the coating on sample SS_2 was the most mechanically stable. The difference in mechanical stability of the coating could be caused by the characteristic surface morphology at microscale level. According to characterisation results as shown in figure 4 (a) and (b), the surface of SS_2 had numerous nanoscale and microscale bumps; the bumps were evenly distributed on the whole plate surface. However, there was no significant change in surface morphology at microscale level upon treatment for SS_1, AL_1 and AL_2. It can also be seen that the performance of AL_3 was better than SS_1, AL_1 and AL_2. The surface of AL_3 had localised microscale clustered pits. This result further affirm the impact of a microscale modified surface morphology on TiO_2 coating stability.

The performance of TiO_2 coating on sodium silicate was far much better than TiO_2 coating without sodium silicate. Less than 8 wt.% of TiO_2 was recorded on all the plates regardless of the high TiO_2 loading. As earlier discussed in section 4.2.1, TiO_2 strongly bonded to sodium silicate. Sodium silicate solution has physical and chemical properties such that when a thin layer is applied between two surfaces, a tough and tightly adhering inorganic film is formed [37]. On the other hand, there was no significance difference in performance between TiO_2 coating on sodium silicate coated on pretreated and untreated plates. In both cases the average weight loss was less than 5 %. These results suggest that the pretreated plates had no effect on the mechanical stability of the TiO_2 coated on sodium silicate.

### 4.3 Photocatalytic Performance of TiO_2 Coating

The photocatalytic performance of TiO_2 coating on pretreated stainless steel (SS_2) and sodium silicate coated aluminium supports were investigated. As earlier discussed, TiO_2 coated on SS_2 and sodium silicate gave the most mechanically stable coating. Table 4 shows the concentration of CO_2 in the reactor outlet stream at different humidity. The concentration of CO_2 rapidly increased when the UV lamps were switched on and acetaldehyde introduced. This shows that some of the acetaldehyde was decomposed into CO_2 due to photocatalytic reaction of TiO_2. Furthermore, the concentration of CO_2 decreased with increasing humidity. The concentration dropped from 26 ppm at 0.008 g/m² absolute humidity to 22 ppm at 0.013 g/m² absolute humidity. This could be because of the competitive adsorption of acetaldehyde molecules and water molecules on the same sites. The water molecules could have been adsorbed on the surface hence blocking the active sites for acetaldehyde adsorption [38]. It can also be seen from table 4 that very low concentration of CO_2 was recorded for P25 on sodium silicate coated plate. It is speculated that the low concentration could be due to reduced surface area of TiO_2 exposed to UV light. Sodium silicate could have reduced the amount of TiO_2 available for photocatalytic reaction by ingnaling part of TiO_2.
Table 4: Concentration of CO\textsubscript{2} at different absolute humidity

<table>
<thead>
<tr>
<th>Absolute Humidity (g/m\textsuperscript{2})</th>
<th>P25 on SS\textsubscript{2}</th>
<th>P25 on Sodium silicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.008</td>
<td>0.013</td>
<td>0.009</td>
</tr>
<tr>
<td>Run time (hours)</td>
<td>15</td>
<td>2</td>
</tr>
<tr>
<td>CO\textsubscript{2} Concentration (ppm)</td>
<td>26.0</td>
<td>22.0</td>
</tr>
</tbody>
</table>

Figure 18: % weight of TiO\textsubscript{2} removed after tape testing thirteen times

The photocatalytic performance of TiO\textsubscript{2} coated on pretreated SS\textsubscript{2} and sodium silicate were compared to TiO\textsubscript{2} coated on ceramic support. The results are shown in figure 18. The conversion of acetaldehyde was slightly higher for TiO\textsubscript{2} coated on pretreated stainless steel. This is affirmed by the high conversion obtained at 0.013 g/m\textsuperscript{2} absolute humidity. The high conversion is attributed to the high surface area of the pretreated stainless steel support. With a high surface area of the support material, more TiO\textsubscript{2} nanoparticles are exposed to UV light irradiation resulting in increased photocatalytic reaction. Furthermore, the concentration of CO\textsubscript{2} in the outlet stream of the reactor at 0.008 g/m\textsuperscript{2} absolute humidity did not change with time. The test was run for 15 hours. It can be seen in figure 19 that the photocatalytic performance of the TiO\textsubscript{2} coating on SS\textsubscript{2} was very stable. This implies that TiO\textsubscript{2} was not deactivated for the time of the experiment.
Figure 19: Change in CO$_2$ concentration at 16 % relative humidity as a function of UV irradiation time
5 Conclusions

Chemical etching, anodisation, electrochemical DC etching and AC etching treatment methods have been used to modify the surface morphology of stainless steel and aluminium; A high rough surface was obtained for both plates. Electrochemical DC etching using dilute aqua regia has shown to be the most effective method for preparation of stainless steel support. The surface morphology of etched stainless steel was completely changed to a hierarchical structure with nanoscale and microscale bumps. As a result, a more mechanically stable TiO$_2$ coating was obtained. It can therefore be concluded that a high micro surface roughness of a support material improves the mechanical stability of TiO$_2$ coating. Subsequently, stainless steel electrochemically etched in dilute aqua regia was scaled up for photocatalytic performance testing. The coating showed a high conversion of acetaldehyde in relation to TiO$_2$ coated on ceramic support. It also showed a stable photocatalytic performance for 15 hours run time.

The use of two-part epoxy-siloxane hybrid and sodium silicate adhesives was presented for enhancing the mechanical stability of TiO$_2$ coating. Mechanical stability was remarkably improved but TiO$_2$ was embedded inside the adhesive coatings when coated using dip and spray coating techniques. Additionally, there is no significant improvement in mechanical stability of TiO$_2$ coating when sodium silicate is coated on pretreated plates. TiO$_2$ coating on sodium silicate presented a mechanically stable coating using powder technique. It has therefore been demonstrated that the powder coating technique using sodium silicate is a useful method for coating of TiO$_2$ on aluminium and stainless steel plates. However, very low acetaldehyde conversion of 0.7 % was recorded.

Spray coating was found to be a more effective coating technique than dip coating as it resulted in a more uniform surface. Effective and consistent spreading of colloidal suspension and quick evaporation of solvent in the spray could have lead to a well coated uniform surface.
6 References


Appendices

A  TiO₂ Coating on Untreated Plates

A.1 Loading of TiO₂ on ESH coated plates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt. of ESH (g)</th>
<th>Wt. of TiO₂ (g)</th>
<th>TiO₂ Load (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS_U_1</td>
<td>0.10552</td>
<td>0.0087</td>
<td>21.8</td>
</tr>
<tr>
<td>AL_U_1</td>
<td>0.10156</td>
<td>0.0116</td>
<td>28.9</td>
</tr>
<tr>
<td>SS_U_2</td>
<td>0.09505</td>
<td>0.0120</td>
<td>30</td>
</tr>
<tr>
<td>AL_U_2</td>
<td>0.10530</td>
<td>0.0100</td>
<td>24.9</td>
</tr>
<tr>
<td>SS_U_3</td>
<td>0.13667</td>
<td>0.0007</td>
<td>1.7</td>
</tr>
<tr>
<td>AL_U_3</td>
<td>0.14445</td>
<td>0.0006</td>
<td>1.4</td>
</tr>
</tbody>
</table>

*SS_U and AL_U are untreated stainless steel and aluminium plates, respectively

*1 - spray coating, 2 - dip coating, 3 - powder sprinkling

A.2 Loading of TiO₂ on sodium silicate coated plates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt. of sodium silicate (g)</th>
<th>Wt. of TiO₂ (g)</th>
<th>TiO₂ Load (g/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS_U_1</td>
<td>0.14596</td>
<td>0.0385</td>
<td>96.2</td>
</tr>
<tr>
<td>AL_U_1</td>
<td>0.12626</td>
<td>0.0323</td>
<td>80.7</td>
</tr>
<tr>
<td>SS_U_2</td>
<td>0.07913</td>
<td>0.0127</td>
<td>31.6</td>
</tr>
<tr>
<td>AL_U_2</td>
<td>0.07677</td>
<td>0.0175</td>
<td>43.7</td>
</tr>
<tr>
<td>SS_U_3</td>
<td>0.20711</td>
<td>0.1070</td>
<td>267.4</td>
</tr>
<tr>
<td>AL_U_3</td>
<td>0.19926</td>
<td>0.0900</td>
<td>225.1</td>
</tr>
</tbody>
</table>

*SS_U and AL_U are untreated stainless steel and aluminium plates, respectively

*1 - spray coating, 2 - dip coating, 3 - powder sprinkling
A.3 Loading of TiO$_2$ on blank plates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt. of TiO$_2$ (g)</th>
<th>TiO$_2$ Load (g/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS_U.1</td>
<td>0.01309</td>
<td>22.57</td>
</tr>
<tr>
<td>AL_U.1</td>
<td>0.0105</td>
<td>18.10</td>
</tr>
<tr>
<td>SS_U.2</td>
<td>0.00878</td>
<td>15.14</td>
</tr>
<tr>
<td>AL_U.2</td>
<td>0.00795</td>
<td>13.71</td>
</tr>
</tbody>
</table>

*SS$_U$ and AL$_U$ are untreated stainless steel and aluminium plates, respectively

*1 - spray coating, 2 - dip coating

B TiO$_2$ Coating on Pretreated Plates

B.1 Loading of TiO$_2$ on sodium silicate coated pretreated plates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt. of sodium silicate (g)</th>
<th>Wt. of TiO$_2$ (g)</th>
<th>TiO$_2$ Load (g/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS.1</td>
<td>0.09</td>
<td>0.1463</td>
<td>365.72</td>
</tr>
<tr>
<td>SS.2</td>
<td>0.08</td>
<td>0.1791</td>
<td>447.68</td>
</tr>
<tr>
<td>AL.1</td>
<td>0.15</td>
<td>0.1908</td>
<td>476.88</td>
</tr>
<tr>
<td>AL.2</td>
<td>0.09</td>
<td>0.1399</td>
<td>349.76</td>
</tr>
<tr>
<td>AL.3</td>
<td>0.13</td>
<td>0.1922</td>
<td>480.62</td>
</tr>
</tbody>
</table>

*SS: 1 - Chemically etched, 2 - Electrochemically etched (DC)

*AL: 1 - Chemically etched, 2 - Anodised 3 - Electrochemically etched (AC)
B.2 Loading of TiO$_2$ on blank pretreated plates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt. of TiO$_2$ (g)</th>
<th>TiO$_2$ Load (g/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS.1</td>
<td>0.02681</td>
<td>53.62</td>
</tr>
<tr>
<td>SS.2</td>
<td>0.02598</td>
<td>51.96</td>
</tr>
<tr>
<td>AL.1</td>
<td>0.02812</td>
<td>61.78</td>
</tr>
<tr>
<td>AL.2</td>
<td>0.03089</td>
<td>51.2</td>
</tr>
<tr>
<td>AL.3</td>
<td>0.0221</td>
<td>44.2</td>
</tr>
</tbody>
</table>

*SS: 1 - Chemically etched, 2 - Electrochemically etched (DC)

*AL: 1 - Chemically etched, 2 - Anodised 3 - Electrochemically etched (AC)

C Tape testing of TiO$_2$ coating on pretreated plates

C.1 TiO$_2$ loading on sodium silicate coated plates as a function of number of tape testing
C.2 TiO\textsubscript{2} loading on blank pretreated plates as a function of number of tape testing