SYNTHESIS OF NANO ANATASE FOR TITANOSILICATE ETS-10 SYNTHESIS

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Dedicated with much love and gratitude

to my

husband Azard,

Mom, Dad

brother Imran & sister Shanaz
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ABSTRACT

Functionalized textiles present a vast and growing niche in the global textile market at US $400 billion [1, 2]. Engelhard Titanium Silicate 10 (ETS-10), a photocatalytic zeo-type material if coated on textiles, is expected to impart useful properties similar to TiO₂, such as stain-resistant, odor repellant, bactericidal and enhanced UV protection [3, 4]. Typically, small ETS-10 crystals of size ~300-800 nm are synthesized using solid titania (e.g., anatase or P25) sources [5, 6, 7]. However, smaller ETS-10 crystals are required for a uniform surface coating with highly effective surface area. The dissolution of titania particles (i.e., their size) is hypothesized to be important in small ETS-10 crystal formation [5, 6, 7]. Nano anatase was synthesized by modification of two methods: direct precipitation [7] and sol-gel synthesis [3]. Analysis by XRD confirmed that both methods produced nano anatase of crystallite size ~4-5 nm. However, FE-SEM analysis showed that product from direct precipitation, existed as intergrown spheroidal particles with size ~1.0 μm. These particles dispersed poorly in deionized water. Therefore, the best nano anatase samples were from sol-gel synthesis in two forms, dry powder and colloidal anatase.

ETS-10 synthesis was investigated using two methods adopted from literature [6, 7]. The method of Yoon and co-workers [7], with nano anatase in a molar composition of 5.5TEOS: TiO₂: 8.4NaOH: 1.43KF: 350H₂O: 2.2H₂SO₄ produced unknown phase(s) with some ETS-10 and quartz. Using colloidal anatase with molar composition 5.5TEOS:1.0TiO₂:8.4NaOH:1.43KF:400H₂O:2.2H₂SO₄ also produced unknown phase(s). The method of Anderson and co-workers [6] with nano anatase powder in a molar composition of 5.5SiO₂: TiO₂: 5.2Na₂O: 0.5K₂O: 113H₂O produced quartz with ETS-10
impurity. When colloidal anatase was used, with molar composition TiO$_2$:5.5SiO$_2$:5.2Na$_2$O:0.5K$_2$O:332H$_2$O, unreacted anatase and quartz were formed. It was hypothesized that the very low reaction mixture pH of ~4.1 was responsible for the absence of ETS-10. Therefore, pH of this mixture was modified between ~6.55-12.75. At low pH of ~6.55 unreacted anatase was present, while, pH higher than ~11.24 formed ETS-4 crystals. At an “optimum” pH of ~11.24 nearly phase-pure ETS-10 crystals were formed. However, these ETS-10 crystals were not small but ~10-20 µm. This is the first time, that colloidal anatase has been utilized for ETS-10 synthesis.
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1.0 INTRODUCTION

Textile production, properties and its end-use have changed beyond recognition over the last decade thanks to new technological advancements [8]. Hence, ‘functionalized’ textiles present a growing niche in the global textile market [1], which was estimated in 2005 to be worth $400 billion [2]. ‘Functionalized’ textiles are textiles that are modified to impart special properties, for example, flame retardant, deodorizing, antibacterial, soil, stain, oil or water resistance and enhanced UV protection [2].

Engelhard Titanosilicate, also known as ETS-10 is a zeo-type material whose photocatalytic nature, molecular separation and ion-exchange capability has generated much interest since its discovery by Kuznicki in 1989 [9]. The presence of one-dimensional titania chains in the framework has led to the suggestion, that ETS-10 crystals can use the incident light energy to catalyze reactions [10, 11]. Therefore, it is proposed that the ‘photocatalytic’ nature of ETS-10 crystals, similar to that of titanium dioxide, can be utilized to decompose organic molecules into carbon dioxide and water [11, 12]. The photocatalytic property of ETS-10 can also be used to decompose organisms such as bacteria and fungi much like the antibacterial action of photosensitive silver oxide [13]. ETS-10 crystals are also microporous and contain Na and K ions in their pores, allowing them to function in molecular separation or ion-exchange systems.

Therefore, ETS-10 crystals may have potential applications in enhancing the surface properties of materials. Coating textiles with photocatalytic ETS-10, would impart useful functionalities, e.g., stain-resistant or ‘self-cleaning’, odor repellant, bactericidal [3] and enhanced UV protection [4] on the composite material. However, to
produce a uniform coating with a high effective photocatalytic surface area, nanosized ETS-10 crystals are desired. Currently small ETS-10 crystals in the size range of ~300-800 nm are synthesized using solid titania (e.g., anatase or P25- a mixture of anatase and rutile) sources [5, 6, 7]. An increased effective surface area means that more ‘active sites,’ TiOH groups, will be available, therefore improving the activity of the photocatalyst. Synthesis of nanosized crystallites, represents a largely unexplored area of ETS-10 research and little is known about their properties and photocatalytic performance.

Anatase particles are considered to play an important role in ETS-10 crystallization [7]. Dissolution of anatase particles is suggested to be the first step in the ETS-10 formation mechanism, when using a solid source of titania [5, 6, 7]. Therefore, the rate of anatase dissolution is considered to be the rate-determining step in ETS-10 crystallization [5, 6, 7]. It is also believed that the anatase particles may act as nuclei for ETS-10 formation by a direct solid-solid transformation [5, 14]. Thus incorporating nano anatase in the ETS-10 synthesis would increase anatase dissolution rate, generate multiple ETS-10 nucleation points and result in the growth of highly crystalline ETS-10 products with fine and uniform size less than ~300-800 nm. This thesis work is divided into two sections. The first describes synthesis of nano anatase, and the second explores the synthesis of small ETS-10 crystals from nano anatase.

In this work nano anatase have been synthesized using sol-gel synthesis [3, 15, 16] and crystallization by direct precipitation [7, 17]. The synthesized nano anatase has been compared to commercially available sources of anatase such as nano anatase from
Aldrich and bulk anatase from Acros. The synthesized nano anatase in both the dry powder and colloidal forms was used to synthesize ETS-10 crystals using both known [6, 7] and modified compositions. X-ray powder diffraction, particle size distribution analysis and field emission scanning electron microscopy have been used to characterize the synthesized nano anatase and ETS-10 crystals.
2.0 BACKGROUND

It is the aim of this section to lay a solid foundation on the parameters that affect the nucleation and growth of the ETS-10 crystals, the different materials and methods employed in their synthesis, the physical and chemical properties of the material that make it an interesting commercial investment and the mechanism or mechanisms that play a role in the ETS-10 synthesis and photocatalytic activity.

2.1 Introduction to Engelhard Titanosilicate ETS-10

The first zeolite discovered was stilbite in 1756 and since then several natural and synthetic zeolites have been discovered/synthesized [18]. Zeolites have many applications. The physical structure of these materials allows them to perform ion-exchange, shape-selective catalysis, filtering, molecular separation, and gas adsorption tasks [18]. In 1974, Breck [9] hypothesized that perhaps a 1000 different aluminosilicate zeolite framework structures are possible. However, to date, less than 200 have been synthesized [9]. Engelhard titanosilicate ETS-10 is a zeolite-type material that was synthesized in 1989 by Kuznicki working in the laboratories of the Engelhard Corporation [9]. Unlike conventional aluminosilicate zeolites, ETS-10 is composed of TiO$_6$ octahedra and SiO$_4$ tetrahedra and has demonstrated photocatalytic activity [19].

2.2 Framework Structure of ETS-10

ETS-10 has a unique framework structure composed of silica, and titania units as shown by the three different views in Figure 1. ETS-10 can be visualized as stacked sheets composed of octahedral TiO$_6$ units connected by oxygen atoms to tetrahedral SiO$_4$
Each TiO$_6$ octahedron is connected to four SiO$_4$ tetrahedra such that two 3-membered rings are formed. The ETS-10 framework further has 5, 7 and the largest 12 membered rings. The largest pore is of size $\sim$7.6 x 4.9 Å and appears elliptical. Straight non-intersecting Ti-O-Ti-O-Ti... chains, of thickness $\sim$0.67 nm [22], are present which run in two orthogonal dimensions of the ETS-10 crystal. Every titanium atom in this chain is linked to four silicon atoms via oxygen atoms in a plane perpendicular to the direction of the Ti-O-Ti chain. This effectively buffers the Ti-O-Ti chains and studies have hypothesized that these ‘TiO$_2$ rods’ could function as monatomic quantum wires [22, 23].

Every titanium atom in the ETS-10 framework structure carries a net $-2$ charge. This charge is compensated by the sodium and potassium $+1$ charges, which are located within the pores. There is also a high degree of disorder in the stacking of layers in the ETS-10 crystalline structure. This is what delayed a complete structural analysis of the material until 1994 [20, 21]. The disorder in the ETS-10 framework is associated with the presence of two end-member intergrown polymorphs called A and B [20, 21, 24]. Polymorph A, shown in Figure 2a, is built from an ABAB stacking order. It is a tetragonal lattice with chiral symmetry composed of [Ti$_8$Si$_{40}$O$_{104}$]$^{16-}$ units with unit cell parameters of $a= b= 14.84$ Å, $c= 27.08$ Å, and $\alpha= \beta= \gamma= 90^\circ$, and space group P4$_1$ and P4$_3$ with chiral symmetry. Polymorph B, shown in Figure 2b, is built from ABCD stacking order. Polymorph B has a monoclinic achiral lattice arrangement with unit cell parameters of $a= b= 21.00$ Å, $c= 14.51$ Å, $\alpha= 111.12^\circ$, and $\beta= \gamma= 90^\circ$ [20, 21, 24]. Figure 3 shows the high-resolution electron microscopy (HREM) images of ETS-10 crystals,
illustrating clearly the porous nature of the material and the presence of the two polymorphs [25].

Figure 1: Schematic view of the structure of ETS-10 framework a) Top view, b) side view, and c) connection of two TiO$_6$ rods [26].
Figure 2: Shows the two polymorphs of ETS-10 a) polymorph A, and b) polymorph B [27].
Figure 3: HREM image of ETS-10 material [25].
2.3 Synthesis of ETS-10

The original patent filed by Kuznicki described ETS-10 synthesis using TiCl₃ and one other titania source titaniumesquioxide (Ti₂O₃) [9]. Kuznicki also investigated ETS-10 synthesis using three silica sources Ludox (a silica sol), sodium silicate and sodium disilicate. However pure ETS-10 was only obtained using TiCl₃. ETS-10 synthesis is complicated due to formation of titanosilicates ETS-4, AM-1, AM-3 and impurities such as quartz and unreacted anatase. Subsequently other research groups investigated new methods of synthesizing ETS-10 by varying the composition, source of titania or silica, reaction conditions, etc. As a result of these efforts, there has been a considerable improvement to the original synthesis, final product purity and essentially understanding of the parameters that affect ETS-10 crystal formation.

New sources of titania: (NH₄)₂F₆Ti [5, 28, 29], TiF₄ [26], titanium sulfate [30], titanyl sulfate [31] titanium tetraisopropoxide [17], and titanium dioxide [6, 14] were investigated in ETS-10 synthesis. Lv and co-workers [11] demonstrated that of these titania sources, titanium dioxide was the most desirable. Since it produced ETS-10 at a shorter reaction period and the purity of the ETS-10 product was higher than with other sources [29]. Titanium dioxide is also less expensive than TiCl₃, stable and easy to handle. Anderson and co-workers [12] compared TiCl₃ with TiO₂ as a source of titania. Their results showed that different ETS-10 synthesis mechanisms were in play with these two different titania sources. With TiCl₃ ~25 µm ETS-10 crystallites were obtained, while TiO₂ produced small ETS-10 crystallites of ~0.5 µm in size. Anderson and co-workers [12] showed in this work that optimum conditions for ETS-10 crystal growth
were pH ~10.5, silicon to titanium ratio of 5-6, and a synthesis period of over 24 hours was required when crystallizing ETS-10 at ~230 °C.

A typical ETS-10 synthesis involves forming a homogenous reaction mixture with a source of potassium (e.g., KCl or KOH) and sodium (e.g., NaCl or NaOH) ions to a source of titania and silica. The synthesis mixture formed is transferred to a Teflon-lined stainless steel autoclaves. The reaction mixtures in the autoclaves are hydrothermally treated at ~230 °C for ~48 hours. The autoclaves are then removed from the oven and cooled. The products are washed, filtered with deionized water and finally dried in an oven at ~45-100 °C.

2.4 Properties of ETS-10

Thanks to a uniquely large microporous framework with ‘active’ charged sites ETS-10 demonstrates ion exchange, molecular separation, adsorption, and photocatalytic properties. This large pore (7.6 x4.9 Å) microporous material is capable of performing molecular separation of mixtures [32] and has been able to separate ethanol-water mixtures [33]. The ability to exchange a known framework alkali metal cation (Na\(^+\) or K\(^+\)) means that ETS-10 can be used as an ion exchanger. Zhao and co-workers [34, 35] demonstrated that positively charged metal cations Pb\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\) can be successfully exchanged for the Na\(^+\) and K\(^+\) in the framework. Prior work has demonstrated that transition metals such as Fe\(^{3+}\) and Cr\(^{3+}\) [36, 37, 38] have been successfully integrated into the ETS-10 framework by isomorphous substitution. The transition metal incorporated ETS-10 has in some cases (e.g. with Cr\(^{3+}\)) indicated a shift in photocatalytic activity towards the visible region [39]. The Cr\(^{3+}\) substituted ETS-10 was
able to decompose acetaldehyde. It was also reported that ETS-10 was used in dehydrating n-butanol [40].

The framework of ETS-10 crystals, also contain Ti-O-Ti chains which are sandwiched by a silicious matrix. Therefore, it has been suggested that these chains can act as quantum confined wires [41]. The quality of these ‘quantum wires’ in ETS-10 is poor due to disorder in crystals that results in discontinuous chains. However recently Yoon and co-workers [17] synthesized uniform crystals where they claimed the crystals were of high ‘quality’ and they suggested that the band gap of these quantum confined wires are related to the length of the wire.

Recently ETS-10 was used as a support for silver nanoparticles by Lv and co-workers [42]. This work demonstrated that ETS-10 allowed a gradual leaching of the silver nanoparticles into aqueous solution while supporting chemical durability of the silver nanoparticles. The photocatalytic nature of ETS-10, which allows it to break down organic compounds into carbon dioxide and water, opens up several potential applications for this zeo-type material.

2.5 Photocatalysis in ETS-10

Photocatalysis is by definition the acceleration of a chemical reaction by incident photon radiation (not thermal energy) due to the presence of a photocatalyst. Photocatalysis represents a sustainable solution, when currently, limited fossil fuel energy resources are a key issue, and the desire to implement ‘green’ environmentally friendly processes is of high importance. An ideal photocatalyst should be able to absorb most of the visible light in the electromagnetic spectrum, since this constitutes the largest portion
of the radiation from the sun. The absorbed photons would be utilized to promote the
chemical reaction. In the case of ETS-10 there are inherent obstacles that need to be
overcome for this material to be a successful photocatalyst, integrated into commercial
applications.

2.5.1 Mechanism of Photocatalysis in ETS-10

ETS-10 is a semiconductor material having two energy bands, the valence band
and the conduction band. Electrons are typically located in the valence band but if
enough energy is supplied they can be ‘excited’ into the conduction band. The minimum
amount of energy required to excite an electron into the conduction band is called the
band gap energy. When an electron is excited into the conduction band it leaves a
positively charged nucleus referred to as a hole. The creation of these electron-hole pairs
is very important for the photocatalytic reaction. The conduction band electron on the
surface of the photocatalyst can reduce atmospheric oxygen $O_2$ to give superoxide ions
$O^{2-}$. Meanwhile the positively charged holes attract hydroxyl ions (OH$^-$). The hydroxyl
ions can be from water molecules that are typically adsorbed into the external porous
surface of ETS-10. These hydroxyl ions are oxidized to form hydroxyl radicals (OH•). Figure 4 illustrates the electron-hole pair formation. The hydroxyl radicals are very
important as they oxidize the organic material into carbon dioxide and water [43]. In is
also expected that in the case of bacteria and microorganisms, these hydroxyl radicals can
attack the external membranes, reducing them and thereby destroying the
microorganisms.
Figure 4: General mechanism of electron-hole pair formation and subsequent re-doxygen processes on the photocatalyst’s surface [44].

However the above description is only a simplified version of the complex photocatalysis mechanism that has several elementary reactions in competition with each other [45]. To function as an effective photocatalyst, ETS-10 must be stable against electron-hole recombination process. This is when electron-hole pairs recombine thereby preventing the re-doxygen process at the ETS-10 surface. To avoid the recombination of the electron-hole pairs it is understood that the conduction band electrons must be removed quickly from the photocatalytic material surface. The rate and extent of this electron removal is also very important factor. Gerischer and Heller [45] showed that the electron-scavenging step by oxygen is most likely the rate-limiting step in most photocatalytic oxidation processes. As a result most experiments related to improving photocatalytic
activity has resorted to removal of electrons from the photocatalytic surface and ensure electron-hole recombination does not occur or is reduced.

2.5.2 Comparison of ETS-10 with Anatase Photocatalysis

Anatase is one of three different forms of naturally occurring titanium dioxide. Historically, it has been used as a white pigment in face paint and food coloring due to its brightness and high refractive index of 2.7. It has shown to be non-toxic, stable, less expensive and easy to handle. In 1972, Fujushima discovered the photocatalytic properties of titanium dioxide in the anatase form. This effect was coined as the Honda-Fujishima effect [46]. Anatase is one of the most widely used photocatalysts, and therefore represents, a strong competitor to ETS-10 [47]. Anatase has a lower band gap energy of 3.2 eV [47] compared to the band gap energy of 4.03 eV for ETS-10 [48]. Therefore both anatase and ETS-10 are active in UV light only. However, only 5% of the electromagnetic spectrum is composed of ultraviolet rays. Therefore if either of these two materials are to be effective and efficient photocatalysts then their band gap needs to engineered to a lower value, which would allow activation under visible light. It has been possible to exchange the alkali metal cations in the ETS-10 framework with transition metals to modify the band gap energy of the ETS-10 crystals. Ji [44] demonstrated that V$^{4+}$, Cr$^{3+}$, Mn$^{2+}$, Fe$^{3+}$, and Co$^{2+}$ transition metal modified ETS-10 demonstrated a lower band gap energy between 3.79 eV and 3.89 eV.

Small sized anatase, less than ~250 nm, has a relatively high surface area and therefore a large number of available active sites. Warrier and co-workers [49] reported 5-10 nm anatase particles with a specific surface area of 104 - 375 m$^2$ g$^{-1}$, while Degussa
P25, a mixture of anatase and rutile (another form of titanium dioxide), with particle size of ~30 nm has a surface area of only 50 m$^2$ g$^{-1}$ [50]. The smallest ETS-10 particles, on the other hand, are ~500 nm in size and have a much higher effective surface area of ~350-400 m$^2$ g$^{-1}$ [47]. Therefore, the available hydroxyl free radicals or active sites are hypothesized to be much higher for ETS-10. The uniformly porous nature of this zeotype material give it a much higher effective surface area. Recently ~300 nm [7] ETS-10 crystals were reported, but their effective surface areas were not reported. Losilla et al. [51] reported the use of microwave heating to synthesize ETS-10 crystals of ~200-500 nm using Degussa P25 as the titania source. However, the SEM images provided are not very clear, and it is difficult to verify crystal size. Therefore, future references to small ETS-10 crystals will not include this source. It is also important to keep in mind that smaller particles do not necessarily imply improved photocatalytic efficiency, since the increased surface sites also improve the electron-hole recombination as suggested by Zhang and co-workers [52]. Thus, in the case of nano anatase there appears to be a limitation in improving its photocatalytic activity further. However, there exists no known data for the critical size of ETS-10 crystals where electron-hole recombination would deactivate its photocatalytic nature.

However, the synthesis of small ETS-10 particles less than ~300-800 nm has had limited success to date, and so it has not been possible to explore photocatalytic efficiency in ETS-10 with fine crystal size. ETS-10 due to its ion-exchange ability can be incorporated with transition metals allowing its band gap to be engineered. Thus, in comparison with anatase, small ETS-10 crystals, less than ~300-800 nm, due to their ion
exchange ability compared to TiO₂ could be a more effective photocatalyst with an improved lower band gap energy.
3.0 CRITICAL LITERATURE REVIEW

Since the invention of titanosilicate ETS-10 in 1989 by Kuznicki [9], ETS-10 has attracted much attention as a photocatalyst. Anderson and co-workers [20, 21] solved the structure of this material in 1994. ETS-10 is a large microporous material, which also has potential applications in ion-exchange, adsorption, and molecular separation. ETS-10 is a wide bandgap (4.03 eV) semiconductor; and thus, only photocatalytically active under UV light. Therefore, ETS-10 crystals need to be engineered so that activity is increased and the crystals can absorb radiation in the visible region of the electromagnetic spectrum. Synthesizing nano ETS-10 crystals is one potential method of increasing surface area and hence improving photocatalytic activity. However, ETS-10 crystals smaller than ~300-800 nm have not been synthesized to date using conventional heating.

3.1 ETS-10 Synthesis

ETS-10 is prepared using a source of silica and titania with the presence of alkali metal cations in an aqueous environment. The reaction mixture formed is then homogenized and autoclaved. The time required for ETS-10 synthesis varies depending on the reaction composition, reactant chemicals used, and finally the autoclave temperature. When Kuznicki [9] first introduced ETS-10, it was synthesized using the following composition (Equation 1):

\[ 1.0 \pm 0.25 \ M_{2n}O : TiO_2 : y \ SiO_2 : z \ H_2O \]  

Where z = 0-100; y = 2.5-25; and M= cation with valence of n. Kuznicki produced ETS-10 using six different compositions with TiCl$_3$ and in one instance ETS-4 seeds.
However, of these, the most convenient method was using 126 g sodium silicate (28.7% SiO$_2$, 8.9% Na$_2$O) added to 17.8 g NaOH, 11.0 g NaCl, 8.4 g NaF and 24 ml H$_2$O. This was followed by adding, 81.6 g of 20% TiCl$_3$ solution (also 20% HCl). The synthesis mixture formed had a pH of ~10.16 and was autoclaved for 9 days at ~175 °C. The product formed was identified by XRD analysis as ETS-10. Kuznicki provided the d-spacing for the main peaks of ETS-10, however less distinct peaks are missing from the data he provided. These would be required to successfully compare ETS-10 products from different methods or compositions. No information on crystal shape, size or morphology was provided.

Kuznicki also used several different sources of silica (sodium silicate, sodium disilicate, and Ludox colloidal silica) and titania (TiCl$_3$ and Ti$_2$O$_3$) to synthesize ETS-10 crystals. In his patent, Kuznicki reports that use of either source of titania with sodium silicate in the presence of NaOH, KOH and KF•2H$_2$O, resulted in high reaction mixture pH values of ~12.2±1, which were autoclaved at 125°C for 7-9 days. When using either source of titania a crystalline product was obtained, that was not ETS-10 but identified as ETS-1. Ti$_2$O$_3$ could not form a titanium-silicate gel, since it was insoluble and therefore, took longer to crystallize (7 days). Since TiCl$_3$ is a liquid, it mixes well to form a titanium-silicate gel and crystallizes in 1 day. However, caustic sodium or potassium hydroxide needs to be added, prior to adding the TiCl$_3$, to compensate for the acid used to stabilize TiCl$_3$.

Other research groups soon followed with attempts to optimize synthesis of ETS-10, by using a more straightforward synthesis procedure, less expensive chemicals and a
shorter crystallization time to produce pure ETS-10 products. Investigations also followed to understand how the molar ratios of the reaction components, different titania and silica sources, pH, synthesis temperature and processing conditions influence ETS-10 nucleation and crystal growth, product purity, and properties of the synthesized ETS-10. To keep track of the numerous experiments performed, with sometimes only slight variations in the conditions, experimental compositions will be numbered continuously.

In 1996, Anderson and co-workers [12] compared the synthesis of ETS-10 using bulk anatase (supplied by Merck) and TiCl₃ sources. Their synthesis mixture when using TiCl₃ had the following composition (Equation 2):

\[
\text{TiO}_2 : 5.5 \text{SiO}_2 : 3.4 \text{Na}_2\text{O} : 1.5 \text{K}_2\text{O} : 125 \text{H}_2\text{O} \tag{2}
\]

In this synthesis, an aqueous sodium silicate solution (27 wt% SiO₂, 8 wt% Na₂O) was mixed with distilled water, sodium hydroxide, sodium chloride and potassium chloride. The mixture was homogenized by stirring thoroughly. Titanium chloride (1.9 M in 2.0 M HCl) was added to the mixture while stirring, to form a homogenous gel. The pH of the gel was measured to be ~10.6, before loading it into Teflon-lined stainless steel autoclaves at 230 °C for ~60 hours. The products obtained, were washed with 1 L of distilled water and dried overnight at 110 °C.

The same experiment was repeated but with 0.1 g of ETS-10 seeds, which were added to the synthesis gel and a lower (Na + K)/Si ratio used, such that the composition was as shown by Equation 3.

\[
\text{TiO}_2 : 5.5 \text{SiO}_2 : 4.7 \text{Na}_2\text{O} : 1.5 \text{K}_2\text{O} : 122 \text{H}_2\text{O} \tag{3}
\]
The products were analyzed by XRD, SEM and $^{29}$Si (MAS) NMR. XRD and $^{29}$Si (MAS) NMR data for only the seeded experiment were shown; therefore the two products could not be compared for crystallinity or purity. However, it was reported that both products were pure ETS-10, while SEM images show bipyramidal crystals ~25 µm in size (Figure 5a) from the un-seeded experiment and crystals with size of ~5 µm (Figure 5b) from the seeded experiment. The other difference between these two experiments was the synthesis time which was longer for the unseeded experiment (~60 hours) compared to ~24 hours in the seeded experiment. X-ray fluorescence of the final product gave the ETS-10 material a composition of (Na$_{1.5}$K$_{0.5}$)TiSi$_5$O$_{13}$. Therefore using ETS-10 seeds reduces crystallization time, but produces very large ETS-10 crystals.

![Figure 5: SEM images of ETS-10 crystals synthesized using TiCl$_3$ a) without the presence of ETS-10 seeds and b) with ETS-10 seeds [6].](image)

Nagy and co-workers [53] in 2002 studied the synthesis of ETS-10 using TiCl$_4$ as the source of titania. Using synthesis gels of composition given by Equation 4:

$$y \text{TiO}_2 : 1.49 \text{SiO}_2 : x \text{Na}_2\text{O} : 0.6 \text{KF} : 128x \text{HCl} : 39.5 \text{H}_2\text{O} \quad (4)$$
where $0.5 \leq x \leq 2.5$ and $0.1 \leq y \leq 0.4$. Two precursor solutions, one acidic and the other basic were prepared. The acidic solution was prepared by dissolving HCl, TiCl$_4$ and KF in distilled water. The basic solution was prepared by dissolving sodium silicate (27 wt% SiO$_2$, 8 wt% Na$_2$O) in NaOH. The two solutions were mixed well by stirring until they appeared homogenous. The gel, obtained by adding the acidic solution into the basic solution was stirred for 5 minutes. The pH of the gel was measured as ~11.6 and then loaded into autoclaves and reacted at 190 °C. Autoclaves were removed at fixed time intervals to evaluate the ETS-10 crystallization process. The products were filtered, washed with distilled water, and dried overnight at 100 °C.

XRD, atomic absorption spectroscopy, and Si NMR spectroscopy were used to analyze the products formed, which were utilized to draw a reaction composition diagram (Figure 6). The atomic absorption spectroscopy determined the Si/Ti ratio while Si NMR spectra was used to determine the product composition. The crystallization field for synthesizing pure ETS-10 is clearly small, whereas the crystallization field for pure titanosilicate ETS-4 is much larger. Therefore formation of pure ETS-10 is only possible under very specific conditions. Inspection of this crystallization field shows that the optimal molar amounts of TiO$_2$ and Na$_2$O are ~0.2 and 1.0 mol, respectively. This ratio (i.e. Na$_2$O/TiO$_2$= 5) is in close agreement with the Na$_2$O/ TiO$_2$ ratio shown by Anderson and co-workers [6] in Equation 3.

According to Figure 6 if the amount of TiO$_2$ is fixed at 0.24 moles, and if the amount of Na$_2$O is lowered below 0.8 moles, then the amount of quartz in the product increases until eventually the product is composed of entirely quartz. At higher Na$_2$O
amounts (>1.1 moles), ETS-4 and an unknown titanosilicate starts forming in the product. If the Na$_2$O amounts are fixed at 0.8 moles, then if the TiO$_2$ moles are increased above ~0.24 moles, ETS-4 starts forming and at ~0.33 moles or higher an unidentified titanosilicate is formed.

Figure 6: Crystallization field for gel composition $y$TiO$_2$: 0.49SiO$_2$: $x$Na$_2$O: 0.6KF: 1.28xHCl: 39.5H$_2$O using a reaction temperature of 190 °C for 3 days [53].

XRD patterns of products from selected compositions are shown in Figure 7. At $x$ = 0.75 mole of Na$_2$O, the product obtained is ETS-10 and quartz. The asterisk marks peaks for quartz. When $x$ = 1.0 moles of Na$_2$O, pure ETS-10 is formed. However at higher $x$ values of 1.25 moles of Na$_2$O, ETS-4 appears, and eventually at $x$ =1.5 moles of Na$_2$O, the product consisted of pure ETS-4. The asterisk marks ETS-4 peaks.
Figure 7: XRD patterns of products obtained from the gel composition 0.2TiO$_2$: 1.49SiO$_2$: xNa$_2$O: 0.6KF: 1.28xHCl: 39.5H$_2$O at x = 0.75, 1.0, 1.25, and 1.5. Reaction conditions of 190 °C over 3 days. The asterisks denote quartz and ETS-4 [53].

In this investigation Nagy and co-workers [53] show the importance of the sodium to titanium ratio. However this work is incomplete without accounting for the importance of other parameters such as silicon, potassium and water ratios. TiCl$_4$, though less expensive than TiCl$_3$ is difficult to handle due to its high sensitivity to air and humidity. Both compounds are not very stable and require special handling techniques, as they are very reactive. Therefore, investigations continued to find new titania sources that could be implemented in ETS-10 synthesis to improve the purity of the product formed, and replace TiCl$_3$ as a reagent.
Yang et al. [54] compared P25 with TiF$_4$. P25 is a mixture of 75% anatase and 25% rutile, where the particle size was ~25 nm. In this investigation different compositions were investigated including the effect of using an organic template tetramethyl ammonium chloride (TMACl). The advantage of using TiF$_4$ is that it is more stable in both air and water compared to TiCl$_4$ and TiCl$_3$. However, this investigation showed that a more crystalline material was obtained using the P25 form of TiO$_2$. Synthesis gels were prepared using sodium silicate (27 wt% SiO$_2$, 11 wt% Na$_2$O or 26 wt% SiO$_2$, 8 wt% Na$_2$O), distilled water, NaCl, KOH, and TiF$_4$. The gels were of varying composition as shown in Equation 5:

$$1.0 \text{TiF}_4 : \nu \text{SiO}_2 : \omega \text{Na}_2\text{O} : \chi \text{K}_2\text{O} : \gamma \text{NaCl} : \zeta \text{H}_2\text{O}$$  \hspace{1cm} (5)

where $\nu = 5.3$-$5.6$, $\omega = 1.6$-$2.2$, $\chi = 0.4$-$0.9$, $\gamma = 5.6$-$7.2$, $\zeta = 100$-$110$. The synthesis gel formed was autoclaved at 200 °C for 168 hours. Yang et al. [54] state that the synthesis method used by Anderson and co-workers [6] when using bulk anatase as a source of titania was adopted by Yang et al. [54] for the ETS-10 synthesis using P25. However, on comparison of the composition of the synthesis gels, they were different. The synthesis mixture formed by Anderson and co-workers [6] had the following composition (Equation 6):

$$1.0 \text{TiO}_2 : 5.5 \text{SiO}_2 : 5.2 \text{Na}_2\text{O} : 0.5 \text{K}_2\text{O} : 113 \text{H}_2\text{O}$$  \hspace{1cm} (6)

Whereas the synthesis mixture produced by Yang et al. [54] using P25 had a composition with a much higher Na/ Ti ratio and a lower K/Ti ratio, as shown by Equation 7:

$$1.0 \text{TiO}_2 : 5.3 \text{SiO}_2 : 1.6 \text{Na}_2\text{O} : 1.0 \text{KF} : 7.2 \text{NaCl} : 110 \text{H}_2\text{O}$$  \hspace{1cm} (7)
The pH of synthesis gels using TiF$_4$ were higher ~12.0, while using P25 produced synthesis mixtures of lower pH ~10.5. Both synthesis gels were autoclaved at 200 °C for 14-168 hours. Autoclaves for each synthesis composition were removed at predetermined intervals from the oven to monitor the crystallization process. The products obtained were analyzed by XRD (Figure 8a and Figure 9).

The XRD pattern for ETS-10 synthesized using P25 shows that at shorter time intervals of less than 42 hours, there were peaks at ~25 °2 showing presence of unreacted P25; peaks at ~21 and 27 °2 indicated presence of quartz. As the crystallization time was increased anatase intensity decreased, until at 42 hours no anatase was observed, only pure ETS-10. At longer crystallization times, peaks belonging to another phase began to appear. These peaks were identified as ETS-4. Yang et al. [54] reported that at longer crystallization times, the product was completely transformed to ETS-4. The XRD pattern for the product using TiF$_4$ is almost identical to the product formed by using P25 after 42 hours (Figure 9). However crystallization using TiF$_4$ was longer, taking ~168 hours. In the product synthesized from TiF$_4$, no anatase or quartz impurities were observed.

The two most pure samples from this synthesis were analyzed by SEM (Figure 10). The images show that in the case of P25 derived ETS-10, individual, loosely aggregated ETS-10 crystals of truncated bipyramidal morphology and size ~1µm is formed. There also appears to be some other material around the crystals, which was later identified as possibly amorphous TiO$_2$ using diffuse reflectance UV/VIS spectroscopy. When TiF$_4$ was used, large crystals of ~4 µm were formed, also of truncated bipyramidal
morphology. ETS-10 crystals synthesized by Yang et al. [54] using P25 had size of ~1 µm with no impurities, such as anatase. However, with a similar procedure Anderson and co-workers [6] using bulk anatase produced crystals half the size (i.e. ~0.5 µm), with ~3-5 wt% unreacted anatase. This could be due to the difference in their synthesis mixture compositions (Anderson and co-workers [6] uses the composition given by Equation 6 while Yang et al [54] uses the composition given by Equation 7). This would imply that the proportion of Na and K ions play a significant role in crystal size.

Figure 8: XRD patterns for product synthesized at 200 °C using P25, showing the crystallization progress over 14-168 hours [54].
Figure 9: XRD pattern for product synthesized using TiF$_4$ at 200 °C and 168 hours [54].

Figure 10: SEM images of ETS-10 synthesized using (a, b) P25 and, (c, d) TiF$_4$ at 200 °C [54].
Lv et al. [5] reviewed ETS-10 synthesis using different solid and liquid titania sources. They investigated five different sources of titania: TiF$_4$, TiCl$_3$, (NH$_4$)$_2$F$_6$Ti, bulk anatase from Fisher and Degussa P25, to understand the crystallization mechanism(s). Two precursor solutions A and B were prepared. Precursor solution A was basic and contained sodium silicate, NaOH and KOH. Precursor solution B contained a titania source dissolved in deionized water. The two precursor solutions were mixed under stirring to form a gel, which was then transferred to Teflon-lined autoclaves at 200-230 °C, and removed at predetermined intervals to analyze. The products were then filtered, washed, and dried at 100 °C. The synthesis gel was maintained at a pH of ~10.4-10.5 by using 10M NaOH or 37 wt% HCl solution.

Two different synthesis gel compositions shown by Equations 8 and 9 were used:

\[
1.0 \text{TiO}_2 : 5.5 \text{SiO}_2 : 3.4 \text{Na}_2O : 1.5 \text{K}_2O : 180 \text{H}_2O \quad (8)
\]

\[
1.0 \text{TiO}_2 : 5.7 \text{SiO}_2 : 3.0 \text{Na}_2O : 1.0 \text{K}_2O : 350 \text{H}_2O \quad (9)
\]

The products formed using TiF$_4$, TiCl$_3$, (NH$_4$)$_2$F$_6$Ti, were not pure ETS-10 for either of the two gel compositions, or reaction temperatures. Instead, quartz, titanosilicate phases (AM-3 and ETS-4), and other unidentified titanosilicate phases were formed along with ETS-10. When bulk anatase from Fisher was used, quartz or anatase was present as an impurity. When P25 was used it was possible to obtain a highly crystalline pure ETS-10 product. The XRD patterns (Figure 11) for selected products from each titania source shows the impurities that are present.
Figure 11: XRD patterns for different titania sources TiF₄, (NH₄)₂F₆Ti, TiCl₃, bulk anatase from Fisher, and Degussa P25. *: quartz phase; +: ETS-4; #: an unidentified phase [5].

The products from each synthesis were analyzed by SEM (Figure 12). It is mentioned that the products from solid titania were similar. Lv et al. [5] mention that the product from P25 and bulk anatase was similar, though SEM for bulk anatase have not been provided. The ETS-10 crystals from P25 are of bipyramidal structure and size of ~500 nm. Large particles of ~10 µm and truncated bipyramidal morphology are formed from using TiCl₃. The products from TiF₄ and (NH₄)₂F₆Ti appeared to be unusually
spherically shaped. Lv et al. [5] explained the difference in crystal morphology due to the different titanium sources used.

Figure 12: SEM images of ETS-10 product obtained from titania sources a) P25, b) TiCl$_3$, c) TiF$_4$, and d) (NH$_4$)$_2$F$_6$Ti using synthesis composition of TiO$_2$: 5.5SiO$_2$: 3.4Na$_2$O: 1.5 K$_2$O : 180 H$_2$O [5].
3.2 Influence of pH on ETS-10 Crystallization

Nagy and co-workers [53] studied the effect of pH on ETS-10 crystallinity from different gel compositions. TiCl₄, HCl, KF, sodium silicate, NaOH and distilled water were used to produce a synthesis gel, which was autoclaved at 190 °C and removed at predetermined intervals. The products were cooled, washed with distilled water, filtered and finally dried at 100 °C for 24 hours. The products were analyzed and product crystallinity was compared to the crystallinity of the most crystalline sample. The most crystalline sample was separated of any amorphous phases by sonication, and then compared to the other samples.

Figure 13 shows the crystallinity and pH when synthesis gels were formed from the composition shown by Equation 10:

\[ 0.2 \, \text{TiO}_2 : 1.49 \, \text{SiO}_2 : x \, \text{Na}_2\text{O} : 0.6 \, \text{KF} : 1.28x \, \text{HCl} : 39.5 \, \text{H}_2\text{O} \]  \hspace{1cm} (10)

where \( x \) was varied between 0.5 ! \( x \) ! 2.5 mol. As the amount of Na₂O moles increased, pH also increased. ETS-10 was only formed for \( x = 0.5 \)-1.5 mol. At higher Na₂O amounts \( (x > 1.0 \, \text{mol}) \) ETS-4 and quartz formed. The optimum Na₂O amount required in the gel was 1.0 mol, according to Figure 13, at which 90% ETS-10 crystallinity was achieved and the only impurity was quartz.
Figure 13: Crystallinity and pH for gel composition: 0.2TiO$_2$: 1.49SiO$_2$: xNa$_2$O: 0.6KF: 1.28xHCl: 39.5H$_2$O for 0.5 ≤ x ≤ 2.5 mol at a reaction temperature of 190 °C [53].

According to Nagy and co-workers [53] the crystallization of ETS-10 occurred between pH values of 11.3 and 12.0, and the optimal pH is ~11.7 when 90% ETS-10 crystallinity is achieved. However, since the product is not pure ETS-10, it is possible that the composition has not been optimized. Also, experiments using different sources of titania have yielded optimal pH values that are far lower than the values presented by Nagy and co-workers [53]. Anderson and co-workers [6] showed that an optimal pH of ~10.6 was needed to produce pure, crystalline ETS-10. This suggests that the optimum pH value presented by Nagy and co-workers [53] may apply to this particular synthesis of using TiCl$_4$ in Equation 10.
Figure 14 shows the crystallinity and pH for synthesis gels with composition as shown by Equation 11:

\[
y \text{TiO}_2 : 1.49 \text{SiO}_2 : 1.0 \text{Na}_2\text{O} : 0.6 \text{KF} : 1.28 \text{HCl} : 39.5 \text{H}_2\text{O} \tag{11}
\]

where \( y \) is varied between 0.05 and 0.4 mol. At \( \text{TiO}_2 \) amounts between \(~0.05\) and 0.4 mol ETS-10 is formed. However a pure ETS-10 product, with the highest crystallinity (\(~90\%) is only obtained at an optimum \( \text{TiO}_2 \) amount of 0.2 mol. At this \( \text{TiO}_2 \) value the pH is \(~11.7\). At \( \text{TiO}_2 \) amounts less than 0.2 mol quartz is co-crystallized with ETS-10, while at \( \text{TiO}_2 \) amounts greater than 0.2 mol, ETS-4 is the impurity. The pH of this synthesis gel is still higher than what has been mentioned in ETS-10 work from other investigations where reaction mixture pH was reported to be \(~10.5 \) [5, 6].
Figure 14: Crystallinity and pH for gel composition: $y\mathrm{TiO}_2$: $1.49\mathrm{SiO}_2$: $1.0\mathrm{Na}_2\mathrm{O}$: $0.6\mathrm{KF}$: $1.28\mathrm{HCl}$: $39.5\mathrm{H}_2\mathrm{O}$ for $0.05 \leq x \leq 0.4$ mol at a reaction temperature of $190 \, ^\circ\mathrm{C}$ [53].

3.3 Effect of Fluorine Ions

Kuznicki [9] used potassium fluoride ions in his procedure using TiCl$_3$ as the titania source. Later, Liu and Thomas [14] stated, that the fluoride ions (supplied by KF) were necessary for the formation of ETS-10 when using P25 as the source of titania. Anderson and co-workers [6] investigated the effect of fluoride ions on ETS-10 synthesis. Anderson and co-workers [12] added potassium fluoride to a synthesis mixture of sodium silicate (27 w/w% SiO$_2$, 8 w/wt% Na$_2$O), mixed with distilled water, sodium hydroxide, sodium chloride and potassium chloride with the same composition as shown by Equation 2. The source of titanium in this experiment was either TiCl$_3$ or TiO$_2$ (supplied by Merck). The fluoride ion to titanium molar ratio was varied between 0 and
3. The pH of the gel formed was ~10.6 and was synthesized at ~230 °C. The product formed after 2 days was analyzed and compared to the product from the same synthesis, but without fluoride ions.

Pure ETS-10 using TiCl₃ was only obtained when no fluorine ions are present. The presence of fluoride ions was reported to form other crystalline phases such as AM-3 [59]. When the same experiment was repeated, but using bulk anatase as a source of titania and the fluorine was supplied using KF. The F⁻/Ti molar ratio was varied between 0 and 4. The x in the composition, shown by Equation 12 denotes the amount of KF moles (i.e., moles of fluorine) added.

\[
\text{TiO}_2 : 6.0 \text{ SiO}_2 : 5.0 \text{ Na}_2\text{O} : x \text{ KF} : 122 \text{ H}_2\text{O}
\]  

(12)

The pH of the mixture was ~10.6. On autoclaving at 230 °C, synthesis time was ~30 hours. The presence of fluoride ions did not have an effect on the purity and the crystallinity of the product. This contradicts the reports by Liu and Thomas [14] who reported, fluoride ions were necessary for synthesizing ETS-10 using anatase as the titania source.

Yang et al. [54] also investigated the influence of fluoride ions in ETS-10 synthesis. Their method used gels of composition similar to those used by Anderson and co-workers [6] (Equation 12). Two starting gels were prepared. One used KF as a source of fluorine and potassium ions and the other KCl (the fluoride free gel). All gels were autoclaved at 200 °C for 48 hours. The XRD patterns for the products obtained in these two experiments are shown in Figure 15. On close inspection, there appears to be no unmatched peaks. The XRD patterns are identical and the use of fluorine did not improve
the crystallinity or the purity of products formed. Therefore, contradictory to Liu and Thomas [14], this investigation agrees with Anderson and co-workers [6]. Therefore, it is not a requirement that fluorine ions are present in ETS-10 synthesis using anatase sources P25 and bulk anatase.

Figure 15: XRD patterns for ETS-10 produced using P25 a) with fluorine ions and b) without the presence of fluorine ions, at a temperature of 200 °C and 48 hours. Asterisks indicate ETS-4 impurity [54].

3.4 Mechanism of ETS-10 formation
The mechanism of ETS-10 crystal nucleation and growth is not well understood. It is only by understanding the driving forces of ETS-10 crystallization that it would be possible for scientists to control its growth, size or morphology. In 1996 Liu and Thomas [14], put forward their hypothesis on ETS-10 formation based on their investigation of solid titania sources. They compared different titania sources in ETS-10 synthesis: anatase (particle size ~600 nm), rutile (particle size ~ 1000 nm) and Degussa P25 – a mixture of 25% rutile and 75% anatase, with particle size ~20 nm. Using the same compositions they analyzed the product formed using the different solid titania forms. The synthesis mixtures were autoclaved for predetermined times to evaluate the crystallization time in each case. The pH values of these mixtures were not provided.

Their work showed that the resulting gels from each solid titania source can form ETS-10; however, the rate of ETS-10 crystallization was faster when using Degussa P25. Analysis of the XRD patterns did not show any amorphous phases. However, SEM analysis was not performed to determine crystal size. The faster crystallization in the Degussa P25 case was explained as direct solid-solid transformation. The P25 particles are ~25 nm in size and these act as sites where nutrients start building the ETS-10 crystals directly from crystalline titania. This implies that even smaller solid anatase particles should improve crystallization times. Thus, provided the correct synthesis composition is used, smaller ETS-10 crystals can be synthesized in a shorter time period.

Another mechanism for ETS-10 formation was suggested by Anderson and co-workers [6] in 1998. Their hypothesis was based on an experiment designed to compare the effects of synthesis temperature and pH when using TiCl₃ and anatase as sources of
titania. When TiCl₃ was used as the source of titanium, the synthesis gel formed was of composition as shown by Equation 13:

$$\text{TiO}_2 : 6.0 \text{ SiO}_2 : 4.7 \text{ Na}_2\text{O} : 0.86 \text{ K}_2\text{O} : 122 \text{ H}_2\text{O} \quad (13)$$

Table 1 shows the results of these investigations. These results show that within pH values of 10.3-10.5 and operating temperatures of 175-230 °C, ETS-10 will be obtained. However, pure ETS-10 can only be obtained at high temperatures of 200-230 °C, and at an optimum pH of ~10.5. At low pH, amorphous siliceous material and an unknown material is the impurity, but at higher pH values quartz and AM-1 are the impurities. However, in this investigation only a very narrow pH range (10.3-10.5) was investigated. This does not help to accurately determine the “optimum pH” for pure ETS-10 synthesis. The effects on a synthesis gel of composition as shown by Equation 14:

$$\text{TiO}_2 : 5.6 \text{ SiO}_2 : 4.6 \text{ Na}_2\text{O} : 1.5 \text{ K}_2\text{O} : 130 \text{ H}_2\text{O} \quad (14)$$

using anatase as a source of titania was investigated. In this case pH values of 10.3 and 10.8 were investigated at the same temperature range as with using TiCl₃ (Table 2).

Anderson and co-workers [6] suggested that when using TiCl₃ as the titania source, anatase and amorphous siliceous material is obtained in the product, at low pH values (~10.3) and low temperatures (175 °C), since the formation of the silica-titania gel is the first step in ETS-10 formation. This gel then transforms to give ETS-10. So this explains why at unfavorable reaction conditions a large amount of silica material is found in the product. However, when using a solid source of titania, anatase, at low temperature (175 °C) and pH (~10.3), quartz and anatase are observed as impurity. Anderson and co-
workers [6] suggested that, the dissolution of anatase is the first step, followed by condensation with the silica material.

Based on this hypothesis, at higher temperatures the dissolution of anatase in the synthesis mixture is improved. Therefore, all the nutrients for ETS-10 nucleation are now available readily in the synthesis mixture. As a result the titania species will combine with the readily available silicate species to form highly crystalline, pure ETS-10. This agrees with the results from Table 2 where at high temperature of 230 °C the amount of anatase impurity declined for all the pH (10.3-10.8) values. Comparing the pH values in Table 2, it is also clear that pH of the synthesis gel within the working range of ~10.3-10.8 had no influence on the dissolution of anatase. Therefore dissolution of anatase can be improved by:

1) a higher operating temperature of ~230 °C or greater,

2) using smaller anatase particles. The anatase used in this experiment by Anderson and co-workers [6] was sold by Merck, and was reported to have a particle size of ~600 nm. Thus, using nano anatase would have an improved rate of dissolution and hence, produce pure ETS-10. This would also mean the reaction conditions would be modified so that lower temperature 175 °C or shorter synthesis times (less than 24 hours) can be used.
<table>
<thead>
<tr>
<th>Synthesis gel pH</th>
<th>Synthesis Temperature / °C</th>
<th>Synthesis Time / h</th>
<th>Product (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.3</td>
<td>175</td>
<td>120</td>
<td>ETS-10 present with a high amount of amorphous siliceous material. XRD pattern shows unknown impurity at 21.5 °2.</td>
</tr>
<tr>
<td>10.3</td>
<td>200</td>
<td>36</td>
<td>ETS-10 present with very little amorphous siliceous material. XRD shows peak at 21.5 °2 has almost disappeared.</td>
</tr>
<tr>
<td>10.3</td>
<td>230</td>
<td>24</td>
<td>ETS-10 present with less than 5 wt% quartz</td>
</tr>
<tr>
<td>10.4</td>
<td>175</td>
<td>120</td>
<td>ETS-10 present with less 3 wt% of quartz</td>
</tr>
<tr>
<td>10.4</td>
<td>200</td>
<td>36</td>
<td>ETS-10 present with less than 3 wt% of AM-1</td>
</tr>
<tr>
<td>10.5</td>
<td>175</td>
<td>120</td>
<td>Pure ETS-10 samples obtained.</td>
</tr>
<tr>
<td>10.5</td>
<td>200</td>
<td>36</td>
<td>Pure ETS-10 samples obtained.</td>
</tr>
<tr>
<td>10.5</td>
<td>230</td>
<td>24</td>
<td>Pure ETS-10 samples obtained.</td>
</tr>
</tbody>
</table>

Table 1: Summary of products obtained by using synthesis temperature of 175-230 °C and synthesis gel pH of 10.3- 10.5 [6].
Table 2: Summary of products obtained by using synthesis temperature of 175-230 °C and synthesis gel pH of 10.3-10.8 [6].

Later in 2004, Lv et al. [5] reviewed ETS-10 synthesis using different solid and liquid titania sources. They investigated five different sources of titania: TiF₄, TiCl₃, (NH₄)₂F₆Ti, bulk anatase from Fisher and Degussa P25, to understand the crystallization mechanism(s). This investigation showed that when using a solid source of titania, the impurities formed were mostly anatase and sometimes quartz. However, at certain synthesis gel compositions, they were able to obtain pure ETS-10 using bulk anatase and
P25. Investigations using TiF₄, TiCl₃ and (NH₄)₂F₆Ti, did not produce pure ETS-10 product. The impurities consisted of quartz and other titanosilicates. The morphology of the synthesized ETS-10 product from the solid anatase sources were analyzed by SEM, and showed distinctly different morphology from using TiCl₃ (Figure 12). Based on these observations, they further developed the solid-solid transformation hypothesis that was introduced by Liu and Thomas [14].

Lv et al. [5] hypothesized that when the fine particles of P25 (~25 nm) are well dispersed in the synthesis gel, they readily make contact with the well-dispersed silicate species. A hydrous silica-titania gel is formed which then is directly transformed into ETS-10 crystallites. Lv et al. [5] also hypothesized that alkali cations (Na⁺ and K⁺) particularly Na⁺, plays a structure-directing role in transforming the silica-titania gel into ETS-10 crystals. This hypothesis emphasizes the importance of the concentration of alkali cations, size of the anatase particles, and anatase and silica dispersion in the synthesis mixture (Figure 16). Provided the anatase particles are very fine, they will form multiple ETS-10 nuclei, which by direct solid-solid transformation forms several small perfect ETS-10 crystals of bipyramidal morphology.

When TiCl₃ was used in the synthesis gel, a different mechanism was responsible for ETS-10 crystallization (Figure 17). TiCl₃ in the aqueous solution is hydrolyzed to form a complex ion (Ti(OH)ₙClₘ)²⁻. This complex ion is oxidized by dissolved oxygen in the synthesis mixture to form Ti(IV) oxo species which then form the six coordinated titanium atom. The monosilicate and polysilicate species condense with the six-coordinated Ti atom, to form ETS-10 nuclei. The nutrients around then start growing the
ETS-10 crystals from these nuclei. In this proposed mechanism, nucleation rates and the crystal growth are slow steps. However, the oxidation of the $(\text{Ti(OH)}_n\text{Cl}_m)^{2-}$ species is the slowest, and therefore, the rate-determining step. Therefore, the crystals formed from $\text{TiCl}_3$ grow slowly yielding uniform large crystals of truncated bipyramidal morphology.

Figure 16: Proposed mechanism for ETS-10 crystallization using Degussa P25 [5]

Figure 17: Proposed mechanism for ETS-10 crystallization using $\text{TiCl}_3$ [5].

Recently, Yoon and co-workers [7, 17] reported the synthesis of $\sim 300$ nm ETS-10 crystals of uniform size and shape, synthesized from nano anatase particles of 2-5 nm. In this investigation it was reported that the fine particle size of the nano anatase used,
helped improve the rates of dissolution. Thus, the ETS-10 crystals formed were ~300 nm and were synthesized much more quickly in ~7 hours. The morphology of the crystals formed by Yoon and co-workers [7, 17], showed individual bipyramidal crystals. This agrees with the hypothesis put forward by Anderson and co-workers [12] that, using small anatase crystallites as the source of titanium would produce small ETS-10 crystals.

3.5 Synthesis of Small ETS-10 Crystallites

In 1998 Anderson and co-workers [6] synthesized small ETS-10 crystals of size ~500 nm in their attempt to compare two sources of titania. The synthesis mixture using bulk anatase from Merck was of composition as shown by Equation 15:

$$\text{TiO}_2 : 5.5 \text{SiO}_2 : 5.2 \text{Na}_2\text{O} : 0.5 \text{K}_2\text{O} : 113 \text{H}_2\text{O}$$ (15)

Aqueous sodium silicate (27 w/w% SiO$_2$, 8 w/w% Na$_2$O), distilled water, sodium chloride, potassium chloride was thoroughly stirred. Anatase was added while stirring and the synthesis mixture had a pH of ~10.4. The mixture was loaded into Teflon-lined stainless steel autoclaves at 230 °C for ~24 hours. The products formed were washed, filtered and dried at ~110 °C. XRD analysis showed that the patterns matched that of ETS-10. However, a peak at ~24.5 °2 was observed which did not belong to the ETS-10 pattern. This was identified as anatase. Therefore, ETS-10 formed from using bulk anatase contained ~3-5 wt% unreacted anatase. X-ray fluorescence confirmed that the composition was (Na$_{1.5}$K$_{0.5}$)TiSi$_5$O$_{13}$. This is identical to product obtained, if the source of titania was TiCl$_3$ instead of bulk anatase. SEM images of the synthesized product showed crystals of size ~500-750 nm (Figure 18).
In 2006 Yoon and co-workers [7, 17] synthesized ~300 nm ETS-10 crystallites of uniform size and shape. The technique they described used a reaction temperature of 200 °C over a reaction period of 7 hours. This is of a significant difference in the purity, size and reaction conditions when compared to other ETS-10 synthesis methods. They attributed their success at utilizing ‘nano-anatase’ as a source of titanium in their synthesis procedure. Pure nano anatase of crystallite size ~2-5 nm was prepared using titanium isopropoxide [Ti(PrO)₄] in a hydrothermal precipitation technique. Two solutions were prepared, one of nano anatase in acidified water and the second a hydrolyzed tetraethyl orthosilicate (TEOS) solution with NaOH and KF. The two solutions were mixed while stirring and then placed in an autoclave at 200 °C for 7 hours. The reaction mixture formed was of composition as shown by Equation 16:
Yoon and co-workers [7] also demonstrated in this method of synthesis, that at 6 hours no ETS-10 was present and leaving the autoclave in the oven for longer periods of ~24 hours, produced small amounts of ETS-4 (Figure 19). SEM images for the ETS-10 crystals of size ~300 nm are shown in Figure 20.

**Figure 19:** XRD patterns for products obtained at fixed intervals from ETS-10 synthesis [7].
Figure 20: SEM of ETS-10 crystals synthesized using nano anatase [17].

Yoon and co-workers [7] attributed the ‘spontaneous’ crystallization observed at 7 hours to be due to the nanosized anatase particles. However, XRD and TEM images have not been provided for the synthesized nano anatase. If nano anatase is indeed formed via hydrolysis and condensation of titanium isopropoxide then it appears to agglomerate, which explains the precipitation observed [7]. Therefore, even though XRD patterns would have suggested small anatase crystallites of 2-5 nm, TEM images if supplied would have helped in ascertaining if the anatase crystals are individual particles or form larger agglomerates. Agglomeration of the nano-anatase would have a negative effect on the rate of dissolution of the anatase particles. Titanium dioxide is a material that has garnered a wide interest owing to its photocatalytic properties. It is questionable whether the method used by Yoon and co-workers [7] that resulted in precipitate formation is possibly the best option, since there appears to be several documented
methods of synthesizing nano-anatase colloids [3, 15, 16]. These methods are discussed in the next section.

3.6 Synthesis of Anatase

Titanium dioxide exists in eleven different forms: naturally occurring rutile, anatase, and brookite; three synthetic metastable forms: monoclinic TiO$_2$(B) [56], tetragonal TiO$_2$(H) [57], and orthorhombic TiO$_2$(R) [58]; and five high-pressure forms. Investigation of ETS-10 synthesis using all the different forms of titanium dioxide has not been explored. Investigation of ETS-10 synthesis using different titania sources has shown that anatase is the most suitable choice for ETS-10 synthesis [5]. The anatase used in this instance was bulk anatase form Merck with particle size of ~600 nm. However, recently, it has been shown that utilization of nano anatase particles, forms ETS-10 crystallites ~300 nm in size [7, 17].

3.6.1 Methods of Nano Anatase Preparation

There are several methods of nano anatase synthesis. Some of these techniques for anatase synthesis are more expensive, such as chemical vapor deposition [59, 60], flame spray pyrolysis [61] pulsed laser deposition [62], ion-assisted electron beam evaporation [63] and atomic layer deposition [64, 65]. Wet chemical methods such as hydrothermal crystallization [66, 67], direct precipitation [68], co-precipitation method [69], and sol-gel synthesis [3, 15, 70, 71], are more popular as they are relatively simpler and less expensive techniques. The properties of the synthesized TiO$_2$ nano particles are strongly dependent on the particle size, crystal structure and morphology [72, 73]. Therefore, the method of synthesis plays a major role in the synthesized TiO$_2$ properties.
Work by Oskam and co-workers [74] has shown that while rutile is the more stable solid phase of TiO$_2$, solution-phase preparation methods favor the formation of the anatase.

### 3.6.2 Direct Precipitation of Nano Anatase

Direct deposition from an aqueous solution of TiF$_4$, was used by Tsukuma and co-workers [68] to synthesize nano anatase. The concentration of the TiF$_4$ solution was $\sim$0.03-0.1 mol/L at a pH of $\sim$1.0-3.1 at 40-70 °C. At pH values below 1.0 and solution concentrations above 0.03 mol/L a large amount of precipitation occurred. In this investigation Tsukuma and co-workers [68] deposited the anatase particles onto cotton fibers. SEM of the deposited particles shows agglomerates of size less than $\sim$100 nm [Figure 21]. However, no initiatives were taken to analyze the crystallite size of the anatase particles before deposition on the cotton fiber.

![SEM of cotton fiber coated with anatase particles deposited directly by precipitation from an aqueous solution of TiF$_4$ [68].](image)

**Figure 21:** SEM of cotton fiber coated with anatase particles deposited directly by precipitation from an aqueous solution of TiF$_4$ [68].
Yu et al. [70] used a hydrothermal technique to synthesize nano anatase particles of ~4 nm. In this method two solutions were prepared, one containing titanium n-butoxide and ethanol. The other solution consisted of distilled water, nitric acid and PEG6000. When the two solutions were mixed, precipitates form. This mixture is loaded into a Teflon-lined autoclave, tightly closed and placed in an oven at 160 °C for 5 hours. The product was then cooled, centrifuged and the recovered powder washed with distilled water and dried at room temperature. Contradictory to what was reported by the authors, XRD analysis showed some unknown peaks (Figure 22), which indicate that the product obtained contains a second unknown phase besides anatase. Figure 22 shows the XRD patterns from both a pure anatase product (Figure 22a) and the product from hydrothermal synthesis (Figure 22b). The asterisks mark the occurrence of the unknown peaks. TEM analysis confirmed product contained particles of ~5 nm [Figure 23].
Sol-gel synthesis is a wet-chemical technique where a precursor solution undergoes various forms of hydrolysis and polycondensation to form a two-phase (solid and liquid) system. This can either be in the form of a gel or a colloid. When the solid phase consisting of discrete nanoparticles forms a network, a gel is formed. A colloid is formed when there is a large amount of fluid. Sol-gel synthesis of nano anatase has been reported with varying experimental conditions and precursor mixtures. Daoud and co-workers [16, 75] described preparing a TiO$_2$ colloid using titanium tetraisopropoxide as the source of titanium.

3.6.3 Sol-Gel Synthesis of Nano Anatase

Figure 22: XRD of a) pure anatase product and b) product from hydrothermal synthesis at 160 °C. Asterisks identify peaks due to the second unknown phase [70].

Figure 23: SEM of product obtained by hydrothermal synthesis of titanium n-butoxide [70].
Titanium tetraisopropoxide was added to a mixture of acidified water, ethanol, and acetic acid at room temperature. The mixture was heated under vigorous stirring for 16 hours until a TiO$_2$ colloid was formed. Experiments were conducted under three different temperatures 23 °C, 38 °C, and 58 °C. The colloid formed was then treated with 10% sodium carbonate solution to precipitate the TiO$_2$ particles. This was centrifuged at 2000 rpm for 3 minutes and the top liquid phase was removed. The precipitates were washed with water twice, then ethanol, followed by acetone, and then dried in an oven for 12 hours at 38 °C.

XRD analysis of the solid powder obtained from all the samples are shown in Figure 24. The XRD patterns confirm the product is phase pure anatase when operating at a temperature of 38 °C and 58 °C. Significant line broadening is observed at 25.3 °2 indicating the presence of nanoparticles. However, the full-width-half-maximum value for the two XRD patterns, Figures 24a and 24b, are 2.2 ° and 1.6 °, respectively. So the nano anatase sample obtained at lower temperature of 38 °C has a smaller average crystallite size compared to the sample synthesized at 58 °C. The XRD pattern of the sample obtained from synthesizing at room temperature shows amorphous material.

Figure 25 shows an AFM micrograph for the sample synthesized at 38 °C. Daoud and co-workers [16] reported these particles to be ~2-3 nm. However, the AFM images show larger particles of ~5 and 8 nm as well. Also, it was stated that the particles from synthesis at 58 °C were larger at ~4-5 nm. However, on inspecting the AFM micrographs of this sample, the particles appear to be uniformly sized at ~2-3 nm. Thus, nano anatase of ~2-8 nm can be produced using the sol-gel method and operating at higher
temperatures of ~58 °C gives small uniformly sized particles. Daoud and co-workers [16] did not analyze the effects of treating the colloid with carbonate to obtain dry anatase powder nor did they analyze the colloid.

Figure 24: XRD patterns for anatase synthesized at a) room temperature 23 °C, b) 38 °C, and c) 58 °C [16].

Figure 25: AFM micrograph of thin anatase film from synthesis at 38 °C [16].
TiO$_2$ colloidal synthesis in the absence of ethanol has also been reported [15]. Analysis of the powder extracted from the colloid confirm phase pure nano anatase crystallites of size ~4-5 nm. The investigators, however, did not mention how the powder was extracted from the colloid. SEM analysis of the nano anatase shows a film composed of nano particles. However at the resolution used, the size of these nano particles cannot be estimated accurately [Figure 26].

![SEM of anatase film prepared by sol-gel synthesis at 60 °C [16].](image)

Fray and co-workers [76] investigated the effect of changing the process parameters in sol-gel synthesis. The TiO$_2$ sols were prepared using titanium tetraisopropoxide of 0.1, 0.2 and 0.4 molar concentrations in acidified deionized water. Acetic acid was not used as a reagent in this method. Each sol was within the pH range ~1-2. The influence of temperature on sol-gel synthesis was investigated by running experiments at two different temperature points of 50 °C and 70 °C. However, in this
investigation the solution was heated for only 2 hours to form a clear solution, which was characterized using a DLS particle size distribution (PSD) analyzer.

This investigation showed that lower titanium tetraisopropoxide concentration and temperature favored the formation of smaller anatase particles in the colloid. A temperature of 50 °C and 0.1 molar concentration of titanium tetraisopropoxide produced a colloid with an anatase hydrodynamic diameter of ~13 nm. The anatase particles with the largest hydrodynamic diameter (28 nm) were formed at a 0.2 molar concentration of titanium tetraisopropoxide of 70 °C. It has been reported that TiO$_2$ molecules have an isoelectric pH of ~5.9 ±0.3, this is the pH at which TiO$_2$ molecules carry a net zero electrical charge [77]. Therefore at the pH of the TiO$_2$ sols, which are at a pH of ~ 1-2, the TiO2 molecules have a highly positive surface charge. It is the repulsion between these positively charged TiO$_2$ particles that maintain stability of the colloid. The charged TiO$_2$ particles polarize the water molecules, which form a double layer around the TiO$_2$ particles. The PSD measurement cannot differentiate between the double layer and the actual particle size and measures the total size or hydrodynamic diameter. Hence, the actual particle size would be less than the measured hydrodynamic diameter.

The clear solution formed at 50 °C and 0.1 molar concentration of titanium tetraisopropoxide was dried at room temperature to form a dry powder. Analysis of this powder, showed the presence of another phase besides anatase. This was identified as brookite. Crystallite size of the anatase was reported as ~1.3 nm. Fray and co-workers [76] reported that annealing the powder at 800 °C, resulted in complete phase transformation to rutile, with a reported average crystallite size of ~ 6.5 nm.
There have been investigations using other titanium sources to prepare nanoanatase such as TiCl$_4$ [78] and titanium n-butoxide [79]. Zhang et al. [78] prepared a precipitate by adding TiCl$_4$ solution to a 10% NH$_4$OH. Nitric acid (1.6 M) was added to this precipitate. The mixture was then stirred vigorously for 24 hours at 70 °C to produce a stable highly dispersed titania sol, with mean particle hydrodynamic diameter of ~14 nm. However, the dry nano anatase powder from this method was not analyzed to determine average crystallite size or morphology.

Yu et al. [79] hydrolyzed titanium n-butoxide in a mixture of anhydrous ethanol, nitric acid and water. Stirring the mixture vigorously for ~2 hours produced precipitates. These precipitates were calcined (at ~450 °C) or hydrothermally treated to produce anatase powder. In the case of hydrothermal treatment, the mixture containing the precipitate was loaded into a Teflon-lined stainless steel autoclave at 160 °C for 5 hours to produce nano anatase crystallites of size ~5 nm. However, calcination produced nano anatase particles of ~40 nm. Similarly, Ito et al. [80] used a modified hydrothermal sol-gel synthesis method utilizing Ti(OCH(CH$_3$)$_3$)$_2$$_4$ in a mixture of 2-propanol and water [80]. The mixture is autoclaved at 235 °C for 12 hours and added to HNO$_3$. The mixture formed was heated at 80 °C for 8 hours, dried in a rotary evaporator and the precipitate formed is dispersed in water to form a colloid. PSD measurement of the colloid indicated a hydrodynamic diameter of ~100 nm while XRD analysis of the dried powder showed an average crystallite size of ~37 nm. The XRD patterns indicated the presence of brookite with anatase. Oskam and co-workers [81] suggested that precursor chemistry, i.e., the reagents used and surface energy effects determine the type of TiO$_2$ polymorph formed. However, due to use of different methods of TiO$_2$ synthesis, it has not been
possible to compare the reaction mechanisms that lead to the formation of the TiO₂ polymorphs.

Compared to the hydrothermal methods, and other sol-gel synthesis methods, the method described by Daoud and co-workers [16] is the most suitable for ETS-10 synthesis since phase pure anatase can be synthesized. This technique also yields nano anatase in two forms: colloidal and powder. The colloidal form has its advantages in that it can be easily implemented to create homogenous precursors for ETS-10 synthesis. Also, both the powder and colloidal form may provide a nano anatase sol with a faster dissolution rate. This would imply possibly a faster ETS-10 crystallization and result in small ETS-crystals of uniform size and purity.

4.0 EXPERIMENTAL
The goal of this work has been to synthesize very small, less than \( \sim 300\text{--}800 \text{ nm} \) in size ETS-10 crystals for producing uniform, effective photocatalytic surfaces on textiles. In order to achieve this goal two key objectives have been identified. The first objective was to synthesize phase pure nano anatase crystallites. These nano anatase would then be used in synthesizing small ETS-10 crystallites. This approach has originated from a hypothesis developed by Anderson and co-workers [6] who suggested, that when nano anatase particles are used as a source of titania, they promote the formation of multiple ETS-10 nuclei and hence give rise to small, uniformly sized ETS-10 crystallites.

4.1 Preparation of Nano Anatase

In this investigation two methods of nano anatase preparation have been utilized. Both methods are solution phase preparation techniques, but use different synthesis procedures. The first is a direct precipitation of nano anatase that was introduced by Yoon and co-workers [7] in their attempt to synthesize nano anatase for utilization in ETS-10 synthesis. The second is a well-documented method of sol-gel synthesis [3, 15, 16]

4.1.1 Nano Anatase by Direct Precipitation

The following steps were used to produce nano anatase from a mixture of titanium isopropoxide in concentrated sulfuric acid with ample amounts of deionized water.

a. Add 4.92 g of titanium isopropoxide (98\% liquid, \( \text{Ti(iPrO)}_4 \), Acros) to a clean reflux glass vessel of volume 250 ml. Titanium isopropoxide is a liquid, with
color varying from a clear to a light yellow and appears to vaporize slightly at room temperature.

b. Add 3.8842 g of concentrated sulfuric acid (96.5%, H₂SO₄, Fisher) drop-wise to the titanium isopropoxide. On addition of the sulfuric acid a solid yellowish pink precipitate is formed.

c. Add 30.2105 g of deionized water (resistivity > 18 MΩ cm) to the above sulfuric acid and titanium isopropoxide. White precipitates are observed at certain points where the titanium isopropoxide is in direct contact with the water.

d. The contents are refluxed in a set-up shown in Figure 27 for approximately an hour.

e. On refluxing the contents, the white and other colored precipitates will gradually dissolve and eventually a turbid solution is formed. This suddenly transforms to a white suspension with some white deposit at the bottom.

f. Cool the white suspension and dry in a watch glass at an oven temperature of ~45 °C.

g. On drying, a fine white powder is formed, which is then analyzed and used in further ETS-10 synthesis experiments.
4.1.2 Nano Anatase by Sol-gel Synthesis

There are several methods of sol-gel synthesis that yield nano anatase crystallites. Each of these methods uses slightly different conditions or different chemicals and their quantities. The following steps describing the sol-gel procedure were adopted from work published by Daoud and co-workers [15, 16].

a. Weigh 133.95 g of deionized water onto a clean conical flask of volume 250 ml.

b. To this add 2.13 g of concentrated nitric acid (Certified A.C.S. Plus, 69.9%, HNO₃, Fisher), 15.75g of acetic acid (Glacial, < than 80wt%, CH₃COOH, Mallinckrodt), and finally 7.125 g of titanium isopropoxide (98% liquid, Ti(iPrO)₄, Acros).
c. On addition of nitric acid followed by acetic acid the mixture remains colorless. But on adding the titanium isopropoxide white precipitates are formed.

d. Heat the mixture on a hot plate under constant stirring, with the top of the flask covered securely by parafilm as shown in Figure 28. A thermometer is fixed securely to ensure that the temperature remains at ~60 °C.

e. Heat the mixture for 16 hours, during which the white precipitates dissolve (after ~30 minutes) and a clear solution is formed. Eventually a bluish colored solution is formed which is normally indicative of a colloidal suspension. Allow the colloidal suspension to cool.

f. There are three possible ways to use the nano anatase from this method.

I. Using the anatase as is in the colloidal suspension.

II. Drying the colloidal suspension in an oven at ~38 °C yields a fine white powder of anatase.

III. Treatment of the colloidal suspension with adequate amounts of sodium carbonate solution (10 wt%, Na₂CO₃, Aldrich) yields a white precipitate [15]. The contents are centrifuged for 6 minutes. Two phases are formed; the colorless phase on top is removed by pipetting. Next the precipitates are washed with deionized water twice to remove any remaining carbonate. Again the contents are centrifuged for 6 minutes and the top colorless phase is removed by pipette. The same process is repeated with ethanol (absolute 200 proof, ACS reagent, 99.5+%, C₂H₂O, Acros). Finally the precipitates are washed with acetone (Certified ACS, 99.6%, C₃H₆O,
Fisher) centrifuged for 6 minutes and then the top liquid is decanted. Finally the precipitates are dried in an oven at 38°C. This yields a white powder, which is then ready to be analyzed or used in the ETS-10 synthesis.

Figure 28: Equipment set-up for nano anatase production by sol-gel synthesis.

4.2 Preparation of ETS-10 from Synthesized Nano Anatase

In preparing ETS-10 from nano anatase two different synthesis procedures were investigated. The first is a method published by Yoon and co-workers [7], which has been developed specifically for the nano anatase synthesized by these authors. This method produced uniform ETS-10 crystallites as small as ~300 nm. The second method is an ETS-10 synthesis procedure, which was first put forward by Anderson and co-workers [6] when using bulk anatase as a source of titania. This composition has shown yielded fine ETS-10 crystals of ~500 nm in size.
4.2.1 ETS-10 Synthesis Using Yoon’s Procedure

This method was used to compare the influence of using five different anatase sources on ETS-10 synthesis: commercially available bulk anatase (99%, TiO$_2$, Acros, particle size ~25-250 nm), nano anatase (99.7%, TiO$_2$, Aldrich), nano anatase from direct precipitation, nano anatase from sol-gel synthesis, and the colloidal form of nano anatase. This method requires the preparation of two precursor solutions, a nano anatase suspension and a tetraethyl orthosilicate (TEOS) solution are prepared using the following steps:

a. To prepare the nano anatase solution, add 2.9355 g of concentrated sulfuric acid (96.5%, H$_2$SO$_4$, Fisher) drop by drop to 11.2903 g of deionized water. To this weigh 1.0 g of the synthesized nano anatase. Sonicate or stir the suspension with a magnetic stirrer.

b. The TEOS solution can be prepared by weighing 4.3871 g of sodium hydroxide (97% beads, NaOH, Aldrich) and 1.1298 g of potassium fluoride (99%, KF, ACROS) into a 125 ml high density polyethylene (HDPE) bottle. Dissolve the salts in 70.9678 g of deionized water. Shake the contents for five minutes until the salts dissolve. Next weigh 15.0977 g of tetraethyl orthosilicate solution (98% liquid, C$_8$H$_{20}$O$_4$Si, Aldrich) into the HDPE bottle. Shake the contents for 20 minutes.

c. The TEOS and dissolved salts tend to form two phases, hence the need to shake vigorously. Add the nano anatase suspension to the TEOS solution and shake vigorously for 15 minutes. A white homogenous mixture is formed.
d. The white mixture is transferred (with good mixing to ensure homogeneity) into clean Teflon-lined stainless steel autoclaves.

e. The autoclaves are placed in an oven set at 200 °C and are removed at fixed time intervals to analyze the product formed.

When using the colloidal form of the anatase, experiments were conducted by accounting for the excess water in the colloid. Yoon and his co-workers [7] have reported that in using this particular procedure ETS-10 crystallites form at 7 hours and at 24 hours impurities of ETS-4 begin to form.

4.2.2 ETS-10 Synthesis Using Anderson’s Procedure

In this method of ETS-10 preparation the following steps need to be followed:

a. Weigh 0.9239 g of potassium chloride (Certified ACS 99.4%, KCl, Fisher) into a clean 125 ml HDPE bottle.

b. Weigh 5.1852 g of sodium chloride (99.0%, NaCl, Sigma) into the HDPE bottle, followed by 16.2127 g of deionized water.

c. Close and secure the HDPE bottle. Then shake the contents until the salts dissolve.

d. Using a pipette add 14.3232 g of sodium silicate marketed as N-brand (28.89% SiO₂, 8.89% Na₂O, PQ Corp.). Shake the contents well for 5 minutes.

e. Finally add 1.0 g of the synthesized nano anatase into the HDPE bottle. Close the lid and shake well for 5 minutes. A white homogenous mixture is formed.
f. Decant the white mixture into clean Teflon-lined stainless steel autoclaves. Place the autoclaves in an oven set at a temperature of 230 °C. Remove the autoclaves at predetermined intervals. In Anderson’s synthesis procedure reaction time to produce very pure highly crystalline samples is typically 48 -84 hours. Therefore, as new sources of titania are used in this work, it is important to remove autoclaves at intervals determined from the results of the previous autoclave.

4.3 Characterization Techniques

Several characterization techniques were used to analyze both the synthesized nano anatase (in both powder and colloidal form) as well as the ETS-10 product. Measurement of the synthesized colloid and ETS-10 reaction mixture pH proved to be very useful in identifying any early errors in the synthesis procedure. Size, purity, crystallinity, and morphology of the synthesized nano anatase as well as the ETS-10 crystallites were determined using a field emission scanning electron microscope (FE-SEM) and X-ray powder diffraction (XRD). Particle size distributions (PSDs) for the dry anatase or colloidal anatase, were analyzed using a dynamic light scattering (DLS) analyzer, while an Aero-disperser dry powder dispersion system was used to analyze PSD’s of ETS-10 samples. The synthesized nano anatase will be compared with commercially available sources of titanium dioxide; while the synthesized ETS-10 will be compared with a typical ETS-10 sample synthesized using bulk anatase (99%, TiO₂, Acros) in the Anderson’s procedure.
4.3.1 pH Measurement

A Denver pH meter, model 215 was utilized in measuring the pH of colloidal products and the ETS-10 synthesis mixtures. In both instances the equipment was calibrated and a known solution of pH 10.0 was used to check the accuracy of the calibration. The pH of the colloidal nano anatase was measured after the synthesized sol was cooled. On the other hand, ETS-10 reaction mixtures had their pH readings performed immediately after mixing the titania (section 4.2.1 step c. Yoon’s procedure and section 4.2.2 step e. Anderson’s procedure). During the course of this investigation it also became useful to assess the pH of the different titania sources suspended in constant amount of deionized water.

4.3.2 X-Ray Powder Diffraction

Nano anatase and ETS-10 powder samples were analyzed using a Bruker D5005 : 2 Bragg-Brentano diffractometer with CuKα radiation. This instrument has a curved graphite crystal diffracted beam monochromator and a NaI scintillation detector. Operational conditions were set at 40 kV and 30 mA and a delay time of 60 seconds. When anatase powder samples were being analyzed, diffraction data was collected from 20 to 80 °2 with a step size of 0.02 °2 and a count time of 3 seconds per step. ETS-10 samples were analyzed using a diffraction data collection range between 5 and 37.5 °2 with a step size of 0.02 °2 and a count time of 3 seconds per step. The total scan time was 2 hours, 31 minutes and 1 hour and 22 minutes for the anatase and ETS-10 samples respectively. In all analysis runs a receiving slit of 1 mm, divergence slit of 1°, and an anti-scattering slit of 1° were in use. Samples were prepared for analysis by grinding a
small quantity of the crystals into a fine white powder and pressing it into the sample space of the aluminium holder. Depending on the nano anatase yield, a 6 mm as well as a 20 mm aluminum holder was utilized for XRD analysis. The 6 mm sample holder was preferred in the case of the ETS-10 samples.

The software EVA in the Bruker XRD package was used to assess the XRD pattern. Using this software it was possible to compare XRD patterns of different samples with each other as well as reference samples. In Figure 29 a typical ETS-10 sample synthesized via the Anderson procedure using bulk anatase (99%, TiO₂, Acros) is shown. If there are reflections at ~7.6, 12.5, 16.5, 19.86, 24.6, 25.8, 26.2, 29.0, 30.0, 30.7, 32.3, 34.5 and 35.8 °2, then this indicates that the product contains some titanosilicate ETS-4. Reflections at ~25.26 and 36.98 °2 show the presence of anatase. If the peak intensity at ~25.26 and 36.98 °2 is high then it usually means that the sample needs a longer reaction time as it has been unable to convert all the anatase into ETS-10. Finally if peaks are present at 21.0 and 26.5 °2, this shows the presence of quartz. The XRD pattern in Figure 29, shows that the product contains ETS-10 with some anatase impurity. The black bars on top represent the positions at which ETS-10 peaks are present. The red and blue bars indicate presence of anatase and quartz respectively. There are no peaks at the points represented by the blue bars, therefore quartz is not present in this sample. Other impurities such as ETS-4 are not observed. This pattern is the same as that obtained by Anderson and co-workers in their investigation [6].
Figure 29: XRD pattern of ETS-10 sample synthesized via the Anderson procedure showing presence of anatase. Black, red and blue bars indicate the positions for peaks due to presence of ETS-10, anatase and quartz, respectively.

Another Bruker XRD software, Profile Plus, was used to calculate the average crystallite size of the anatase samples. In the software the Modified Lorentz Model was selected to determine the full-width-at-half-maximum (FWHM) of anatase peak at 25.3 °2 [16], which is one of the major peaks for phase-pure anatase. Figure 30 illustrates the XRD pattern from a commercially available anatase (99%, TiO₂, Acros). This will serve as a reference pattern for comparison with the synthesized nano-anatase samples. The
major anatase peaks are observed at 25.26, 36.98, 37.76, 38.53, 48.02, 53.88, 55.17, 62.07, 62.7, 68.8, 70.3, 74.95, 75.0 and 76.03 °2.

Figure 30: XRD pattern of bulk anatase (99%, TiO₂, Acros).

4.3.3 Field Emission Scanning Electron Microscopy

A Hitachi S-4700 field emission scanning electron microscope (FE-SEM) was used for the visual inspection and identification of both the anatase and ETS-10 samples. Using the FE-SEM, crystal shape, size, and particle agglomeration can be evaluated and compared. Small quantities of the sample are dispersed by diluting with appropriate amounts of deionized water and sonicated using a Branson Model 2200 for half an hour. Drops of the sonicated sample are then pipetted onto the SEM sample holder, which has been cleaned, coated with carbon paint and dried in the oven. The sample holder with the wet sample is placed in the oven to evaporate the suspension and leave a layer of crystallites on the carbon painted holder.
The microscope is operated at a 2 kV accelerating voltage and a 10 µA electron beam current. Ultra high-resolution settings where the imaging distance from the holder surface is at 6mm was selected to analyze the samples. Anatase samples were imaged at typically 20 kX magnification to identify particle agglomeration, while magnifications of ~40 to 80 kX were used for close-up analysis of particle size and shape. In ETS-10 samples, magnification of ~10 kX yielded clear images of ETS-10 crystallite size, shape and morphology. Figures 31 and 32 show the typical FE-SEM images of bulk anatase and ETS-10 crystallites that will be compared with the nano anatase and ETS-10 synthesized from this work, respectively. The FE-SEM image of bulk anatase (Figure 31) verifies that this source contains particles that have agglomerated resulting in clumps of ~300 nm. The ETS-10 sample (Figure 32) shows crystallites of size ~0.5-1.8 µm.

Figure 31: FE-SEM image of bulk anatase (99%, TiO₂, Acros).
4.3.4 Particle Size Distribution Analysis

The Brookhaven 90 Plus Particle Analyzer that uses a quasi elastic light scattering (QELS) technique was used to analyze the particle size distribution (PSD) in anatase samples. When analyzing submicron size samples this instrument poses several advantages. The device is versatile, non-destructive, allows the use of small sample size, with fast processing and a measurement time that is independent of the sample particle density. There are several aspects of the scattered light that has over the years been used to measure particle size. They are:

a) changes in the average intensity as a function of the angle,
b) changes in polarization,

c) changes in the wavelength, and

d) fluctuations about the average intensity.

This device implements the final property d) to generate the sample particle size distribution pattern. A 15 mW solid state laser is passed through the sample, which is then scattered by the particles and received by a detector. Since the particles undergo Brownian motion it is assumed that despite the detector being located at a fixed distance from the sample, the distance travelled by the scattered waves is a function of time. Depending on the distance to the detector the waves may interfere either constructively or destructively and therefore results in an average intensity. The fluctuations in intensity are as a result of the particle diffusion, which in turn is a function of particle size. Hence the measured fluctuation intensity is correlated to the particle size by the device software, using Equation (17).

Since the anatase sources that would be visited in this investigation are within the submicron range, the particles can be assumed to be spherical in shape. Equation (17) given below is for a spherical particle and therefore the distribution pattern developed from this device should be very nearly accurate. However, this equation assumes monodispersity, i.e. the particles are moving independently of each other.

\[ D = \frac{K_B T}{3 \pi \eta(t)d} \]  

(17)

Where:
$K_B$ is Boltzmann’s constant ($1.38054 \times 10^{-16}$ ergs/deg)

$T$ is temperature ($°K$)

$\eta(t)$ is viscosity of the liquid in which the particle is suspended. In our case this is water. (cP)

d is particle diameter (nm)

$D$ is the translational diffusion coefficient ($\text{cm}^2/\text{s}$)

The sample to be analyzed must be in the suspension form and concentration should be within a 50 to 500 kilo count per second (kcps). Dry anatase powder is prepared for analysis by dispersing in deionized water and sonicating for 15 minutes. When analyzing the colloidal form of anatase it is diluted with excess deionized water. Typical colloidal concentrations are $\sim 1.25 \times 10^{-3}$ g/ml. All analysis runs are performed on 3 ml samples, which are measured using an Eppendorf pipette into a clean four clear-sided methyl methacrylate cuvette.

The pertinent settings on the Brookhaven PSD are: 2 batches for each sample, with 5 runs per sample, and 20 seconds per run. This allows the detection of any serious errors in a single run, such as the presence of large particles or dust that would lead to a huge difference in the two runs. The solvent selected is water in this investigation and the sample dust cut off point is about 30 sec. Operating temperature is always at 25 °C, while the scattering angle is set at 90°. The Brookhaven Particle Sizing software presents data in a variety of ways. The simplest and most useful for this work is the lognormal distribution of the particle sizes. In this PSD plot the x-axis is the hydrodynamic diameter
in nm and the y-axis is the number of particles of a particular size. The software yields other useful data such as the normalized plots of intensity, volume and surface area of the particles against the x-axis hydrodynamic diameter. Figure 33 shows a lognormal plot of the hydrodynamic diameter for the commercially available bulk anatase (99%, TiO$_2$, Acros) dispersed in deionized water using a Brookhaven 90 Plus Particle Size Analyzer.

![Particle Size Distribution of Bulk Anatase (Acros)](image)

**Figure 33: PSD of bulk anatase (99%, TiO$_2$, Acros) dispersed in deionized water.**

ETS-10 samples were analyzed using an API Aerosizer LD equipped with an API Aero-Disperser dry powder dispersion system (TSI, Inc., Particle Instruments/Amherst). In the case of ETS-10 dry powder samples are used. The sample is dispersed in an air stream before the particle size measurement. The Brookhaven PSD device can analyze particles between 2 nm to 3 µm whereas the API Aero-Disperser can only handle analysis of particles between 0.2 µm to 700 µm.
4.3.5 Dispersion of Nano Anatase Crystallites

The main objective of this investigation is based on the hypothesis that the rate of dissolution of the source of solid titania is the rate determining step in ETS-10 formation. Since it is has already been shown by Yoon and co-workers [7, 17] that the synthesized nano anatase yielded smaller ETS-10 crystallites compared to their larger counterparts such as bulk anatase. This implies that the commercially available anatase forms such as Degussa P25, bulk anatase, nano anatase and the synthesized nano anatase formed via sol-gel synthesis and direct precipitation could differ in their properties, specifically the rate of dissolution. Therefore it is important to identify any physical variance in these samples of anatase and characterize their dispersion in deionized water. Five different sources of anatase were investigated: Bulk anatase (99%, TiO$_2$, Acros), commercially available nano anatase (99.7%, TiO$_2$, Aldrich), nano anatase synthesized from direct precipitation dried nano anatase powder from sol gel synthesis and nano anatase powder obtained from sol gel synthesis by precipitation using carbonate treatment.

First, 0.01 g of each dry anatase sample was dispersed in 5.0 g of deionized water. Each sample was observed to note its mixing in the deionized water at both light mixing and heavy mixing (using a sonicator). Samples were further observed to note their behavior on standing and appearance. Finally, 3 ml of each sample was pipetted into a four sided, clear methyl methacrylate cuvette and the particle size distribution of each sample was measured using the Brookhaven 90 Plus Particle Analyzer.
5.0 RESULTS AND DISCUSSION

Nano anatase synthesis via two different methods was investigated. The products obtained were characterized and compared with commercially available bulk and nano anatase. The nano anatase produced was used in ETS-10 synthesis. Using new sources of titania required modification of the existing ETS-10 synthesis procedures until the optimal conditions for ETS-10 crystallization were found. As a result, existing ETS-10 synthesis compositions and conditions were adjusted to obtain a pure ETS-10 product.

5.1 Nano Anatase Synthesis

There are several methods for preparing nano anatase [59, 60, 61, 62, 64, 67, 69, 82, 83]. However, the following two techniques were investigated as they best suited the interests of this work. The first is direct precipitation reported by Yoon and co-workers [7, 17], where the nano anatase produced was utilized to form ETS-10 crystallites ~300 nm in size. This was deemed a good starting point in efforts to synthesize ETS-10 crystallites smaller than ~300 nm. The second technique, sol-gel method, has been used extensively to prepare nano anatase by slight modifications to the starting materials and operating conditions [3, 15, 16, 76]. Qi et al [3, 16] used a starting mixture of titanium isopropoxide, ethanol, acetic acid, nitric acid and deionized water, which was then heated to ~40 °C. Later work by Qi et al. [15] showed that nano anatase could be synthesized in the absence of ethanol. Mohammadi et al [76] used hydrochloric acid and water with titanium isopropoxide to synthesize nano anatase. However, this product contained some brookite.
5.1.1 Method of Direct Precipitation

In this method, the sulfuric acid was added to titanium isopropoxide directly to form a solid yellowish sludge. When deionized water is added, some white precipitates are observed. The white precipitates formed are titanium dioxide, which are produced by the reaction shown in Equation 18.

$$Ti\{OCH(CH_3)_2\}_{4} + 2H_2O \rightarrow TiO_2 + 4(CH_3)_2CHOH$$  \hspace{1cm} (18)

The mixture is not stirred. On refluxing, the white precipitates gradually dissolved and formed a turbid solution. This solution was refluxed for one hour after which a white suspension was obtained. There was some white deposit at the bottom of the reaction vessel. The contents were allowed to cool before eventually drying in a glass dish at \(\sim 45\) °C. The dried product had a brilliant white powder appearance. This experiment showed several contradictions between results described by Yoon and co-workers [7] and what was actually observed when performing the experiment:

a. Yoon and co-workers [7] reported the formation of a pink colored solution that gradually became turbid. However from this investigation it is believed that the color of titanium isopropoxide, which varies from colorless to yellow, is responsible for the pink color observed. Therefore, the color changes cannot be used to accurately describe stages of the reaction.

b. The turbidity of the solution and the subsequent white deposit at the bottom of the flask suggests that if indeed nano anatase particles are formed, they tend to agglomerate.
Figure 34 shows the XRD pattern obtained for the product. The analysis of this pattern showed: 1) significant line broadening observed for the two main peaks for anatase, which are at ~25.3 and ~48.0 °2θ and 2) the presence of additional peaks which appeared at ~25.4, 33.0, 44.0, and 58 °2θ. The presence of significant line broadening indicated that the anatase formed consisted of very small, possibly nanoscale crystals. The additional peaks indicated the presence of impure phase(s).

The impurity in the anatase product was identified as TiO₂ beta phase (PDF No. 35-0088, JCPDS). The black bars in Figure 33 indicate the peaks for the crystalline anatase material. The measured TiO₂ beta phase, (shown by the red bars in Figure 34), which has some peaks coinciding with the major peaks of the anatase product, makes it impossible to evaluate the crystallite size of anatase using the Scherrer Equation.

![XRD pattern of nano anatase powder synthesized by direct precipitation.](image)

**Figure 34:** XRD pattern of nano anatase powder synthesized by direct precipitation.

Black bars show anatase peaks (PDF No. 21-1272, JCPDS) and red bars show TiO₂ beta phase (PDF No. 35-0088, JCPDS).
In order to produce a phase pure anatase product, the experimental procedure was modified to include continuous stirring and heating of the reaction mixture. The same reagents were added to a conical flask. In this case, as before, a yellowish sludge formed on adding the sulfuric acid to titanium isopropoxide, and some white precipitates formed on adding deionized water to the yellowish sludge. On heating and stirring, all the precipitates dissolved giving way to an opaque solution. Eventually, this solution changed into a turbid solution, and a white deposit formed as before. This suspension was allowed to cool and dried in an oven at ~45 °C to yield a white powder. The XRD pattern for this product is shown in Figure 35b and compared with the product from un-modified direct precipitation method (Figure 35a). Controlling the temperature and stirring speed led to optimum conditions where phase pure anatase was form (Figure 35c).
Figure 35: XRD patterns of products obtained using a) direct precipitation, b) modified to include continuous stirring, and c) modified to include both stirring and heating. The black and red bars on top denote the anatase (PDF No. 21-1272, JCPDS) and TiO₂ beta peaks (PDF No. 35-0088, JCPDS) respectively.

Figure 35b shows that the product from the modified direct precipitation technique does not show very prominent beta phase peaks at ~29.1, 33.0 and 44.0 °2\& when compared to product from direct precipitation without modification (Figure 35a). Eventually, under optimum conditions of ~70-80 °C and a stirrer speed of ~1000 rpm, the XRD pattern does not show any TiO₂ beta peaks, only pure anatase product is formed (Figure 35c). Applying the Scherrer Equation to the main anatase peak at ~25.3 °2\&[15] gave an average crystallite size of 4-5 nm. This is consistent with the anatase particles obtained by Daoud and co-workers [16], where the particle size was ~4-5 nm. However
FE-SEM images of this product showed much larger particle (Figure 36). This product consisted of ~1.0 µm particles which appeared to form spheroidal larger intergrowths. Under higher magnification these larger particles appeared to be formed of smaller constituents of size less than ~50 nm (inset in Figure 36). Therefore, despite crystallite size of ~4-5 nm, these nano anatase crystallites pack together to form large clusters of ~50 nm, which are observed by SEM.

![Figure 36](image)

**Figure 36:** FE-SEM image of anatase product from the direct precipitation method modified to include continuous stirring and heating. Inset image shows a higher magnification image of the individual anatase particles.

### 5.1.2 Sol-gel Synthesis of Nano Anatase

Deionized water, nitric acid, acetic acid and finally titanium isopropoxide were added consecutively under continuous mixing. The mixture was then heated at ~60 °C for
16 hours. The mixture cleared up gradually as the white precipitates dissolved under the constant stirring and heating. After ~30 minutes a clear solution was formed, which under further heating and stirring took a light bluish hue. This was visually identifiable as a colloid or an anatase sol.

The anatase obtained using this technique was of three forms:

1) Anatase powder obtained from sol evaporated in an oven at ~38 °C.

2) Anatase powder obtained from sol by treatment with 10% sodium carbonate, deionized water, ethanol and then followed by acetone. The final product was dried at ~38°C.

3) Colloidal suspension of nano anatase.

The method to obtain anatase powder from sol evaporated at ~38 °C takes a long time, since evaporation at this temperature is very slow and the average yield is ~1.49 ±0.03 % based on the mass of the original reactant chemicals and 3 experimental trials. The second method of obtaining anatase powder from the sol, required treatment with a dilute sodium carbonate salt, to allow the colloidal suspension to agglomerate. The subsequent treatment with water, ethanol and acetone are to wash it. This technique had an average yield of 0.92 ± 0.09 %. nano anatase, based on the results of three experiments. The lower yield in this process could be due to some product being lost in the subsequent treatment with carbonate, ethanol, acetone and water. The dry anatase obtained from drying the sol directly has a shiny white powder like appearance, whereas, the dry anatase powder obtained from sol by chemical treatment with sodium carbonate,
was a hard solid with a yellowish color (Figure 37). The yellow color observed in sample labeled A5 could be due to some carbonate, acetone or ethanol being adsorbed by the nano anatase particles.

![Figure 37](image)

**Figure 37**: Nano anatase samples of obtained by drying sol directly at ~38 °C (A4) and from chemical treatment with sodium carbonate, water, ethanol and acetone at ~38 °C (A5).

The XRD patterns for these samples (anatase from drying sol directly and anatase from drying sol treated with carbonate) were identical and showed only phase pure nano anatase with considerable line broadening (Figure 38). The black bars indicate positions where anatase peaks occur. Due to line broadening some peaks merge and are seen as a
single broad peak. XRD analysis in this case was carried out in a 20 mm sample holder. Applying the Scherrer Equation, for the main anatase peak at ~25.3 °2\& showed that the average anatase crystallite size was ~4-5 nm. Based on these observations the time spent on treating the sol with chemicals to obtain dry anatase was not beneficial. So drying the sol directly to obtain dry anatase was the preferred choice for ETS-10 synthesis.

**Figure 38:** XRD pattern of nano anatase samples obtained by a) chemical treatment of sol with sodium carbonate water, ethanol and acetone at ~38 °C and b) drying sol directly at ~38 °C. Black bars indicate anatase peaks (PDF No. 21-1272, JCPDS).

Figure 39 shows the FE-SEM images of the anatase from drying the sol directly. But the product appeared to be composed of fine particles forming a film (Figure 39a). At high resolution with a dilute sample of this same anatase product, it was possible to
identify particles of ~6 nm and in instances of agglomeration particles of ~10 nm. This is consistent with the average crystallite size calculated from the XRD.

Figure 39: FE-SEM image of a) TiO$_2$ film deposited from nano anatase powder re-dispersed in deionized water, and b) TiO$_2$ nanoparticles deposited from a very diluted aqueous anatase dispersion on a carbon paint.

The anatase in the colloidal form was also a potential new source of titania that could be used in ETS-10 synthesis. However it is important to evaluate the stability of the colloid and also determine the particle size distribution (PSD) of TiO$_2$ in the colloidal form. The PSD data is important to confirm that the nano anatase exists as separate individual particles in the colloidal form and that these particles do not agglomerate and form sediments. If the particle size measured by the PSD is close enough to XRD and SEM measurements, then we can confirm that the colloid contains individual nano anatase crystallites. The pH of the colloid was measured soon after it cooled from the 16-hour heating, and the results showed a consistent pH value of ~0.8-1.0. This matches the reported pH value of ~1.0 from Daoud and co-workers [15]. Figure 40 shows the PSD distribution obtained using a quasi elastic light scattering (QELS) technique on for
colloidal anatase. The colloid contained particles within the size range of ~3-40 nm with the mean hydrodynamic diameter as ~12.1 nm.

![Figure 40: PSD for colloidal anatase measured by QELS.](image)

The difference between the sizes of anatase nanoparticles determined by QELS, the FE-SEM and XRD, can be readily explained. TiO$_2$ nanoparticles have been reported to have an isoelectric point at a pH of ~5.9 ±0.3 [84, 85, and 87]. Since the prepared colloidal sample for the PSD determination is acidic (pH of ~1.6), the TiO$_2$ nanoparticles have a high positive charge. This positive charge would polarize water molecules and hence a double layer formed of water molecules will surround the charged nano anatase particles. The QELS cannot differentiate between the double layer and the nano particles. Thus, the measured value is the overall diameter, i.e. the sum of the particle diameter and the double layer, also known as the ‘hydrodynamic’ diameter.
Particle size distribution measurements of the mean nano anatase were carried out over a 77-day period to check for sol stability (Figure 41). No significant changes in the hydrodynamic diameter of the sol were observed using the QELS, nor were they observed visually. The PSD measurements showed that the particle size fluctuated at ~11 nm for up to 55 days. Subsequent readings show that particle size has increased. No visible changes in the colloid such as deposition were observed. Therefore, it is concluded that the colloid is stable for at least ~55 days.

![Figure 41: Mean hydrodynamic diameter of colloidal anatase measured over a 77-day period.](image-url)
5.1.3 Comparison of Anatase Sources

Figure 42 compares the XRD patterns for bulk anatase (Acros), nano anatase (Aldrich) and nano anatase from sol-gel synthesis (obtained by drying the sol directly). Bulk anatase shows no discernible line broadening. Line broadening was observed for the nano anatase sample from Aldrich as well as the sol-gel derived samples. Applying the Scherrer Equation resulted in the average crystallite size of ~18 nm for the nano anatase from Aldrich and ~4-6 nm for the nano anatase derived from sol-gel synthesis. Therefore, the nano anatase obtained in this investigation has a much smaller crystallite size than the commercially available anatase sources. Figure 43a shows that bulk anatase from Acros has large particles of ~25-300 nm, while nano anatase from Aldrich is made of very small particles of size less than ~50 nm but appear to be agglomerated (Figure 43b). However, FE-SEM shows that agglomeration is high with all the samples, excluding that of the sol-gel derived anatase samples which was not treated with carbonate.
Figure 42: XRD patterns for a) bulk anatase from Acros, b) nano anatase from Aldrich, and c) anatase from drying sol directly.

Figure 43: FE-SEM images for a) bulk anatase from Acros, b) nano anatase from Aldrich.

Since the XRD determined average crystallite size for nano anatase from Aldrich and sol-gel derived anatase is not too different, it would be expected that ETS-10
synthesis from the two sources would be similar. Since the commercially available nano anatase from Aldrich has crystallites of the average size ~18 nm, it would be expected that it’s rate of dissolution would be higher than that of bulk anatase and it would produce smaller ETS-10 crystallites. However, attempts to use nano anatase to synthesize ETS-10 have not been successful. This question can be solved by looking at the FE-SEM of nano anatase (Aldrich). Despite the small crystallite size, anatase exists as a clumpy powder, which forms agglomerates (Figure 43b). It is possible that these agglomerates do not dissolve readily and hence do not form ETS-10 crystallites.

To check this hypothesis dispersion of each anatase source (bulk anatase from Acros, nano anatase from Aldrich, nano anatase from direct precipitation, nano anatase from direct drying of colloid and nano anatase from carbonate treatment of colloid) were compared. The concentration of anatase in water was identical in each case (2x10^{-3} \text{ gmL}^{-1}) to match the concentration of anatase in the colloidal sol (1.5 wt%). Each nano anatase sample was mixed, then sonicated for ~15 minutes and left to stand for 30 minutes.

Each anatase source was observed to behave differently (Figure 44a). Upon mixing bulk anatase (sample labeled A1) and nano anatase from Aldrich (sample labeled A2) dispersed quickly forming white suspensions. Nano anatase prepared by direct precipitation (sample labeled A3) appeared only slightly turbid. Nano anatase prepared by drying carbonate treated sol (sample labeled A5) did not appear to disperse well in deionized water and therefore, took a clear appearance. This can be explained by the immediate sedimentation observed in this sample. Anatase from sol dried directly
(sample labeled A4) took a bluish appearance, and appeared to disperse very well in deionized water. No immediate sedimentation was observed with this sample.

Figure 44: a) Initial appearance of each anatase source A1, A2, A3, A4, and A5, after sonicking for ~15 minutes. b) Inset image shows the appearance of the anatase sources after standing for ~30 minutes.
The inset image Figure 44b shows the effect of leaving the samples stand for approximately 30 minutes. All samples showed slight sedimentation probably due to the presence of large particles. Bulk anatase (A1) and nano anatase from Aldrich (A2) settles slowly. However, sedimentation was the highest in the nano anatase obtained from the carbonate treatment of sol (A5), which explains its clear water like appearance. However, it is also possible that the observed lack of dispersion may be as a result of achieving equilibrium in the liquid. The least amount of settling was observed in the nano anatase sample dried directly (A4), which maintained a stable colloidal appearance. Therefore, the sol-gel derived anatase sample is most likely the better solid anatase source since it does not have large agglomerates to form sediments and forms a well-dispersed suspension. These results suggest that the sample obtained by drying sol directly (A4) will result in a more homogenous ETS-10 synthesis mixture would aid the dissolution rate of the anatase particle and achieve a more homogenous mixture compared to other dry anatase powder sources.

5.2 ETS-10 Synthesis

The solid nano anatase powders were used in two different ETS-10 compositions shown by Equations 18 and 19.

5.5 TEOS : TiO$_2$ : 8.4 NaOH : 1.43 KF : 350 H$_2$O : 2.2 H$_2$SO$_4$ \[18\] \[7\]

5.5 SiO$_2$ : TiO$_2$ : 5.2 Na$_2$O : 0.5 K$_2$O : 113 H$_2$O \[19\] \[6\]

The use of nano anatase in the colloidal form was also investigated. In this case, however, the compositions were modified since the anatase colloidal form contained excess water.

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Experiments were performed using the bulk anatase (A1), nano anatase from Aldrich (A2), nano anatase from direct precipitation (A3), nano anatase from sol-gel synthesis (A4), and colloidal nano anatase (labeled C1).

5.2.1 Using ETS-10 composition developed by Jeong et al. [7]

In this method ETS-10 was synthesized by preparing two precursor solutions, one containing anatase and the other tetraethyl orthosilicate (TEOS) solution. The dry anatase product was added to acidic water and sonicated, to disperse the anatase particles. The TEOS containing solution was prepared by dissolving KF and NaOH in deionized water and then adding TEOS. It was necessary to mix this solution by shaking, as using a magnetic stirrer was found to be ineffective. When using the magnetic stirring TEOS was not mixed thoroughly with the KF and NaOH solution. Therefore, TEOS solution was shaken for 20 minutes by hand, in an HDPE bottle. After addition of the anatase solution to the TEOS, the resulting mixture was vigorously shaken for 15 minutes. The reaction mixture was loaded into Teflon-lined stainless steel autoclaves and heated at 200 °C. When colloidal anatase was used in this method, the water content in the reaction mixture was much higher because of high water content in the anatase sol. The new composition given by Equation 20 has a new Ti:H2O ratio of 1:400, which is a slightly higher amount of water than when using anatase powder.

5.5 TEOS : 1.0 TiO₂ : 2.2 H₂SO₄ : 8.4 NaOH : 1.43 KF : 400 H₂O  

(20)

When using the composition developed by Yoon and co-workers [7] all solid anatase samples formed reaction mixtures with pH greater than ~11.5. Table 3 summarizes the reaction mixture pH values and the results of XRD analysis of the
products using each anatase source. Figure 45 shows the XRD patterns of all products obtained from different anatase sources using the composition and procedure developed by Yoon and co-workers [7]. The black, red and blue bars on top indicate the positions of ETS-4, anatase and quartz peaks, respectively.

The bulk anatase sample pattern (Figure 45a) shows presence of quartz and unreacted anatase. There are also some unidentified peaks occurring between 20.4 and 23.2 °2& and also at 36.0 °2& There is some ETS-10 present but this appears to be dwarfed by the amount of quartz in the sample. The XRD patterns for nano anatase from Aldrich (Figure 45b) and direct precipitation (Figure 45c) does not show the presence of ETS-10, instead the XRD pattern is identified with that of ETS-4. In the case of the sample utilizing nano anatase from Aldrich as the titania source, there appears to be two unidentified peaks occurring at 15.31 and 23.00 °2& There is also a small peak occurring at 25.4 °2&indicating the presence of unreacted nano anatase. The pH of the mixtures from the Aldrich anatase and direct precipitation samples, are high at 12.25 and 12.41 respectively. High pH values have been shown to favor ETS-4 formation [6]. When nano anatase from sol-gel synthesis (Figure 45d) was used some ETS-10 was obtained after. However, there were also some quartz and unknown phases occurring at 6.65 and 31.5 °2&and also between 20.6 and 20.9 °2& When using the colloidal form of nano anatase (Figure 45e) no ETS-10 or ETS-4 was observed. Instead unidentified product(s) were obtained.

The procedure developed by Yoon and co-workers [7] uses TEOS and it is mentioned in their work, that extensive stirring of the TEOS solution results in its
hydrolysis and the crystallization of unknown products. The excessive hydrolysis of TEOS could be a possible explanation for the formation of the unknown product(s). The reaction mixture pH values were also much higher than what has been observed in ETS-10 synthesis [5, 6]. However, Yoon and co-workers [7] did not mention their reaction mixture pH. Thus, it is difficult to ascertain if they indeed synthesize ETS-10 from a reaction mixture with a high pH.

<table>
<thead>
<tr>
<th>Anatase Sample</th>
<th>pH</th>
<th>XRD Analysis of Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 – Bulk anatase</td>
<td>11.54</td>
<td>Quartz, unreacted anatase, unknown product(s) and some ETS-10 present.</td>
</tr>
<tr>
<td>A2 – Nano anatase (Aldrich)</td>
<td>12.25</td>
<td>ETS-4, unreacted anatase and some unknown product(s).</td>
</tr>
<tr>
<td>A3 – Nano anatase from direct precipitation</td>
<td>12.41</td>
<td>ETS-4 and some unreacted nano anatase.</td>
</tr>
<tr>
<td>A4 – Nano anatase from sol-gel synthesis</td>
<td>11.47</td>
<td>Some ETS-10, quartz and unknown product(s)</td>
</tr>
<tr>
<td>C1- Colloidal anatase</td>
<td>13.33</td>
<td>Unknown product(s)</td>
</tr>
</tbody>
</table>

Table 3: Reaction mixture pH and products obtained using different anatase sources for the synthesis of ETS-10 using composition developed by Yoon et al. [7]
Figure 45: XRD patterns for products obtained using different anatase sources a) bulk anatase, b) nano anatase from Aldrich, c) nano anatase from direct precipitation, d) nano anatase from sol-gel synthesis, and e) colloidal nano anatase, in ETS-10 synthesis using Yoon’s procedure [7]. Black, red and blue bars indicate peaks from ETS-4, anatase and quartz respectively.

5.2.2 Using ETS-10 Composition developed by Rocha et al. [6]

The salts used in this case were, NaCl and KCl, which were dissolved in deionized water. Next N-brand sodium silicate followed by the anatase powder was added. The reaction mixture was vigorously shaken, loaded into a Teflon-lined stainless steel autoclave and placed in an oven at 230 °C. Table 4 summarizes the results of these experiments. The XRD patterns for the products obtained are shown in Figure 46. When using the colloidal anatase the synthesis method was modified due to excess water in the
colloid. The new composition (Equation 21) has more than twice the water as the composition for anatase powder, given by Equation 19.

\[ \text{TiO}_2 : 5.5 \text{ SiO}_2 : 5.2 \text{ Na}_2\text{O} : 0.5 \text{ K}_2\text{O} : 332 \text{ H}_2\text{O} \]  

(21)

<table>
<thead>
<tr>
<th>Anatase Sample</th>
<th>pH</th>
<th>XRD Analysis of Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 – Bulk anatase (Acros)</td>
<td>10.86</td>
<td>ETS-10 product with a small amount of unreacted anatase impurity.</td>
</tr>
<tr>
<td>A2 – Nano anatase (Aldrich)</td>
<td>10.75</td>
<td>Presence of quartz with very little ETS-10</td>
</tr>
<tr>
<td>A3- Nano anatase from direct precipitation</td>
<td>10.9</td>
<td>Mostly quartz with some ETS-10</td>
</tr>
<tr>
<td>A4- Nano anatase from sol-gel synthesis</td>
<td>10.6</td>
<td>Mostly quartz and some ETS-10.</td>
</tr>
<tr>
<td>C1- Colloidal anatase</td>
<td>4.1</td>
<td>Mostly unreacted anatase and some quartz.</td>
</tr>
</tbody>
</table>

Table 4: Reaction mixture pH and products obtained using different anatase sources for the synthesis of ETS-10 using composition developed by Anderson et al. [6].
Figure 46: XRD patterns for product obtained using different anatase sources a) bulk anatase, b) nano anatase from Aldrich, c) nano anatase from direct precipitation, d) nano anatase from sol-gel synthesis, and e) colloidal nano anatase, in ETS-10 synthesis using Anderson’s procedure [6]. The black, blue and red bars indicate the positions at which ETS-4, quartz and anatase peaks respectively, would be visible.

Since the pH of all reaction mixtures were less than ~11.0, the absence of ETS-4 in any of the products is not surprising. When bulk anatase was used, ETS-10 was the main product, with some unreacted anatase present (Figure 46a). However quartz was formed, with ETS-10 as impurity, in the nano anatase samples from Aldrich (Figure 46b), direct precipitation (Figure 46c) and nano anatase powder from sol-gel synthesis (Figure 46d). When using colloidal anatase (Figure 46e) a significant peak at 25.4 °2& indicated the presence of unreacted anatase.
Table 3 and Figure 45 showed that when using the composition of Yoon and co-workers [7] (Section 5.2.1), ETS-10 is formed in the product only when using bulk anatase from Acros and nano anatase from sol-gel synthesis as the sources of titania. However, in both cases unknown phase(s) were present as well as quartz. Using the colloidal form of anatase resulted in unknown product(s). ETS-4 was formed in the product when using nano anatase from direct precipitation or nano anatase from Aldrich. Previous work by Anderson and co-workers [6] has shown that reaction mixture pH values greater than ~10.7 produced ETS-4 in the product. However, despite high pH of ~11.47 when using nano anatase from sol-gel synthesis (Table 3), no ETS-4 was observed.

Table 4 and Figure 46 showed that using the composition by Anderson and co-workers (Section 5.2.2) ETS-10 was obtained with all dry anatase powders that were investigated. However, quartz was present in all these samples except the bulk anatase sample. This implies that the compositions need to be modified to obtain pure ETS-10 as the product. The product obtained by using the colloidal form of nano anatase appeared to consist of unreacted nano anatase and quartz. This could be due to the low reaction mixture pH (~4.10), which does not favor ETS-10 formation. Therefore, it is possible that if the pH of the reaction mixture using colloidal nano anatase is modified to ~10.60, ETS-10 could be formed.
5.2.3 Influence of pH

When using colloidal anatase in a mixture with the composition, given by Equation 21, the pH is very low at ~4.10. Substitution of NaOH in place of NaCl in this composition increased pH to ~10.60. This is the pH at which ETS-10 growth is expected [6]. Therefore by changing the amount of NaOH, the pH of reaction mixture can be controlled. However, studies by Ji et al. [86] have shown that the Na$_2$O to K$_2$O ratio plays an important role in the size and morphology of the crystals. Therefore the following Equation 22, showing the mass ratios of each reagent, was used to vary the pH of the mixture:

$$8.33 \text{ (colloidal) TiO}_2 : 1.79 \text{ Sodium Silicate} : 0.44y \text{ NaOH} : 0.11y \text{ KCl} \quad (22)$$

Here $y$ is changed from 1.0 to 2.0 to increase reaction mixture pH.

In this series of experiments, KCl is weighed in a plastic HDPE bottle, followed by NaOH. Next, the colloidal anatase is added and then shaken by hand for 5 minutes to form a white homogenous suspension. Finally, the sodium silicate is added and shaken by hand for 5 minutes until the mixture is homogenous. The pH of the mixture is measured, and the mixture is loaded into Teflon-lined autoclaves, which are kept at 230 °C for 48 hours. The pH of the reaction mixtures formed and the products obtained are listed in Table 5.
Table 5: Products formed by using the composition 8.33 (colloidal) TiO₂: 1.79 Sodium Silicate : 0.44 y NaOH : 0.11 y KCl, where y is increased from 1.0 to 2.0.

The XRD patterns for the products obtained from this series experiments are shown in Figure 47. At low reaction mixture pH of ~6.55 no ETS-10 is formed (Figure 47a). The XRD pattern appeared to show mostly amorphous material. The small hump observed at 25.4 °2& corresponds to the broad peak of nano anatase from sol-gel synthesis. This would imply that unreacted nano anatase is present in the product, and low pH values are unfavorable for the formation of ETS-10. Small peaks at 20.82 °2& and 26.54 °2& correspond to those of quartz, indicating the onset of quartz formation.

Increasing the pH from 6.55 to 11.24 (Table 5 and Figures 47a-f) gradually increased the relative amounts of ETS-10 in the product. The relative amount of quartz in the product decreased with increasing pH. XRD analysis also showed that colloidal

<table>
<thead>
<tr>
<th>y/ g</th>
<th>pH</th>
<th>XRD Analysis of Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>6.55</td>
<td>Amorphous material possibly unreacted nano anatase and some quartz.</td>
</tr>
<tr>
<td>1.2</td>
<td>8.85</td>
<td>Quartz, some unreacted nano anatase and ETS-10</td>
</tr>
<tr>
<td>1.3</td>
<td>9.96</td>
<td>Quartz with some ETS-10 and nano anatase.</td>
</tr>
<tr>
<td>1.35</td>
<td>10.6</td>
<td>ETS-10 and some quartz</td>
</tr>
<tr>
<td>1.4</td>
<td>11.02</td>
<td>ETS-10 and some quartz</td>
</tr>
<tr>
<td>1.5</td>
<td>11.24</td>
<td>ETS-10 and some quartz</td>
</tr>
<tr>
<td>1.7</td>
<td>11.75</td>
<td>ETS-4 with some ETS-10 and quartz</td>
</tr>
<tr>
<td>2.0</td>
<td>12.75</td>
<td>ETS-4 with some quartz and ETS-10</td>
</tr>
</tbody>
</table>
anatase is present in the products formed by reaction mixtures with pH lower than ~9.96 (Figure 47a-c). This is indicated by a small hump occurring at 25.4 °2& Increasing the pH above ~11.24 resulted in the formation of ETS-4 (Figure 47g and h). At pH values increasing above ~11.24 the amount of ETS-10 appeared to decrease while, that of ETS-4 increased. At very high pH values of ~12.75, ETS-4 was obtained with only a trace amount of ETS-10 as impurity (Figure 47h). Based on the XRD patterns, ETS-10 synthesis is possible at higher pH values of ~11.24 when using colloidal anatase as the titania source. This is the first time that an anatase sol has been utilized in ETS-10 synthesis. However, if pure ETS-10 is to be synthesized then the composition needs to be further modified to remove quartz.

Figure 47: XRD patterns for product obtained by using colloidal anatase at different pH values of a) 6.55, b) 8.85, c) 9.96, d) 10.60, e) 11.02, f) 11.24, g) 11.75, and h) 12.75. The black, red and blue bars indicate peaks of ETS-4, anatase and quartz respectively.
All the samples from this series of experiments were analyzed by FE-SEM to evaluate ETS-10 crystal size and morphology. In all the samples some amorphous material was observed. The amount of this amorphous material is considerably high with low pH of ~6.65 (Figure 48) and declined as the pH increased (Figures 49-51). This is in agreement with the results of XRD analysis (Figure 47a-f). In addition, in these products, quartz detected by XRD, (Figure 47) was also observed by FE-SEM (inset Figure 49).

Figure 48: FE-SEM image of amorphous product obtained when using colloidal anatase in a reaction mixture pH of ~6.55. Inset image shows a higher magnification image of the amorphous product.

The ETS-10 crystals formed at pH of ~11.02-11.24 are well-formed and large with size of ~10-20 µm (Figure 49-50). Reaction mixtures with pH greater than ~11.75, produced ETS-4 (Figure 51)
Figure 49: FE-SEM image of product obtained when using colloidal anatase in a reaction mixture pH of ~11.02. Inset image shows the quartz crystals present in this product.

Figure 50: FE-SEM image of product obtained, when colloidal anatase is used in a reaction mixture pH of ~11.24.
Therefore, FE-SEM analysis confirms the observations from XRD analysis:

a) Nearly phase-pure ETS-10 product was obtained at pH of ~11.24. This “optimum pH” value differs from those of other ETS-10 synthesis investigations, which showed “optimum pH” value of ~10.7 was necessary for ETS-10 formation, while pH values greater than 10.7, favored ETS-4 formation [6, 54]. This could be due to the unique composition consisting of colloidal anatase.

b) The formation of quartz and ETS-10 can be seen as two competitive reactions. It is possible that at a pH of ~11.24 the formation of ETS-10 is favored. Hence the product contains quartz only as an impurity. Whereas at pH values less than ~9.96, quartz is formed with ETS-10 as the impurity.
c) At pH values greater than ~11.24, ETS-4 formation is favored but not ETS-10 or quartz. This explains why quartz and ETS-10 are obtained only as an impurity at this pH.

Based on this series of experiments, a reaction mixture pH of ~11.24 favors the formation of ETS-10 crystals. Therefore colloidal anatase has been successfully utilized to synthesize ETS-10 crystals using a modified Anderson composition as shown by Equation 22. Well-formed ETS-10 crystals are obtained after 48 hours. However, the product contains some quartz impurity. Therefore further investigation is required to remove this quartz impurity. The composition shown in Equation 21, TiO$_2$ : 5.5 SiO$_2$ : 5.2 Na$_2$O : 0.5 K$_2$O : 332 H$_2$O, can investigated further to remove the quartz impurity and modify the ETS-10 crystal size.

Based on the results of this investigation, it is not possible to confirm the hypothesis put forward by Lv et al. [5]. It was expected that using colloidal anatase would produce multiple nuclei and hence generate small ETS-10 crystals by solid-solid transformation. Therefore, it is not very clear why large ETS-10 crystals were obtained in this investigation. It is possible that the suggested solid-solid transformation requires other conditions such as temperature or composition to allow for small ETS-10 crystal formation. These conditions would need to be investigated in future work. Finally, despite supplying well dispersed nano anatase, these particles could agglomerate in the reaction mixture and thereby prevent the formation of separate nuclei.
6.0 CONCLUSIONS

In this investigation two different methods of nano anatase synthesis were investigated: direct precipitation [7] and sol-gel synthesis [3]. The method of direct precipitation formed nano anatase but with TiO$_2$ beta phase as an impurity. Therefore, this method was modified, by heating the mixture under continuous stirring to generate a homogenous reaction mixture. This eliminated the TiO$_2$ beta phase in the final anatase product. The sol-gel synthesis method yielded a colloidal form of anatase, which was treated by a carbonate solution or dried directly at 38 °C to form the anatase powder. The anatase powder from carbonate treatment consisted of solid chunks while the direct drying formed a fine white powder of nano anatase. The nano anatase powder from carbonate treatment of the colloid is a hard solid with a yellowish appearance, which is believed, to be due to impurities from the carbonate treatment.

The dry powders formed by either (i) modified direct precipitation or (ii) drying the TiO$_2$ colloid, were shown by XRD to consist of pure nano anatase crystallites of size ~4-5 nm. However, despite similar crystallite size FE-SEM analysis showed that these products contained particles with different morphology. The nano anatase from direct precipitation appeared to form large spheroidal aggregates with size of ~1.0 µm, whereas the nano anatase powder from sol-gel synthesis formed uniform films composed of particles with size of ~4-10 nm. The larger 10 nm particles observed could be as a result of agglomeration. Compared with commercially available nano anatase from Aldrich, which contains agglomerates of 50 nm, the sol-gel derived nano anatase particles are much smaller.
Comparison of the synthesized dry anatase forms with commercially available anatase sources showed that each anatase source dispersed differently in deionized water. The nano anatase from carbonate treatment appeared to form sediments due to the presence of large agglomerates. This suggests that it might fail to form the required homogeneity in the ETS-10 synthesis mixture. The nano anatase from direct precipitation also formed sediments. The nano anatase obtained by direct drying of the colloid appeared to disperse well. The dispersion of commercially available bulk anatase (Acros) and nano anatase (Aldrich) were compared with the synthesized nano anatase samples. It was observed that these two commercially available sources formed a brilliant white mixture which appeared to slowly settle on standing. Based on these observations, it was hypothesized that since the directly dried anatase from sol-gel synthesis demonstrated good dispersion, it is the most suitable for small ETS-10 crystal synthesis.

Nano anatase in the colloidal form could also be used in ETS-10 synthesis. Particle size distribution analysis of the colloidal anatase over a 55-day period showed that the colloid was stable and no sedimentation was observed. Particle size distribution measurement of the colloid showed that the mean particle size was ~12.1 nm. This value is higher than the XRD and FE-SEM determined values due to the charged nature of the nano anatase particles, which results in a “double layer” increasing the apparent particle dimension.

Two different methods of ETS-10 synthesis were investigated in this work. These were ETS-10 synthesis methods developed by Anderson and co-workers [6] and Yoon and co-workers [5]. When using colloidal anatase these methods were
modified, due to the excess water that is present in this titania source. Yoon’s method of ETS-10 synthesis formed a reaction mixture with a pH greater than 11.5, for all mixtures with nano anatase. With the nano anatase from direct precipitation only ETS-4 and some unreacted anatase were obtained. The pH of this mixture was high at ~12.41 which is believed to favor ETS-4 formation. Using nano anatase powder from sol-gel synthesis produced some ETS-10 with quartz and some unknown phase(s). Using the colloidal form of anatase produced a mixture with a very high pH of ~13.33 which yielded unknown phase(s) in the product.

The method developed by Anderson and co-workers [6] formed quartz with ETS-10 as impurity when all dry nano anatase samples were used. In these instances, all the reaction mixtures had a pH of ~10.6-10.9, which should have favored ETS-10 formation. The colloidal form of anatase was the most promising as it has well dispersed titania particles. However, the reaction pH was ~4.1 and the product contained unreacted nano anatase and quartz. Therefore, the low pH of ~4.1 may be responsible for the inability to form ETS-10 crystals. Hence, it was hypothesized that modification of the pH of this reaction mixture may allow ETS-10 crystallization.

Substitution of NaOH in place of NaCl in the method developed by Anderson and co-workers [6] satisfies the requirement of sodium ions in the composition using colloidal nano anatase, while also allowing the pH of the mixture to be adjusted in a wide range of ~6.65-12.75. Increasing the pH up to ~11.24, nearly phase-pure ETS-10 was crystallized with traces of quartz. This pH is unusually high to produce ETS-10. However, this can be explained by the unique reaction mixture, consisting of the colloidal form of nano
anatase. FE-SEM analysis of the products obtained using colloidal anatase showed large ETS-10 crystals (~10-20 µm). The other interesting aspect of this investigation is that by altering the pH to ~12.75, nearly phase-pure ETS-4 can be formed with some quartz impurity.

If the hypothesis put forward by Lv et al. is correct, then the colloidal form of anatase which contains very well dispersed nano anatase particles, would be expected, to form very small ETS-10 crystals. Instead the ETS-10 crystals obtained are very large (~10-20 µm). Therefore, it is possible that conditions suitable for small ETS-10 formation using colloidal anatase need to be further investigated. In conclusion, a synthesis method, including the reaction mixture composition and starting pH, were developed for synthesis of ETS-10 using a colloidal anatase suspension. This is the first report of using colloidal anatase as a titania source, to produce ETS-10 crystals.
7.0 RECOMMENDATIONS

Sol-gel synthesis yields nano anatase in two useful forms: nano anatase powder and the colloidal TiO$_2$ suspension. The anatase crystallites in the powder produced are of size ~4-5 nm, as shown by XRD analysis. In the colloidal form, PSD measurements have shown that the average hydrodynamic diameters of these particles are ~12.1 nm. Further investigations can be carried out to investigate synthesis of ETS-10 using both colloidal anatase and dry anatase form. Some suggestions are:

(i) The silica to titania ratio can be varied to confirm that the silica present is not in excess. This might help eliminate quartz formation.

(ii) Investigate the effect of varying ratios of other components in the composition, such as water, or the Na$_2$O to K$_2$O ratio on the ETS-10 product purity and crystallite size [86].

(iii) Anatase sols with higher concentrations of anatase (3-5.2 wt%) have been prepared [87]. These colloids contain anatase with the average particle size diameter that varies from 12-30 nm. It would be useful to investigate the effect of anatase particle size on the ETS-10 crystal size.

(iv) Investigate ETS-10 synthesis using nano anatase powder from sol-gel synthesis.
8.0 REFERENCES


[87] J. Warzywoda, Triton Reports, 2009