CONTROLLED SYNTHESIS AND SURFACE MODIFICATION OF TITANIUM DIOXIDE

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CONTROLLED SYNTHESIS AND SURFACE MODIFICATION OF TITANIUM DIOXIDE

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To my family

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Ayça ABAKAY

MAT, Master of Science Thesis, 2012

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Surface modification, Silane coupling agents

Abstract

TiO_2 nanoparticles were synthesized with simplified sol-gel method using water as solvent and Titanium tetraisopropoxide as precursor. The synthesized materials were characterized by Dynamic Light Scattering (DLS), Simultaneous Thermal Analysis (STA), X-Ray Diffraction (XRD) and C^{13} Nuclear Magnetic Resonance Spectroscopy (NMR). These characterization methods provide valuable information to understand crystal type and size of nanoparticles, effect of synthesis parameters, change in particle size of TiO_2 sols, thermal behavior and pH dependence of particles.

The effects of synthesis conditions such as water:precursor molar ratio, amount of acid catalyst, amount of chelating agent, reaction temperature and time on properties of TiO_2 particles were investigated. High water:precursor molar ratio ensures small particle size and stable particles in aqueous suspension of TiO_2. Additionally, increasing acid amount results in smaller particle size and stable particles with higher surface potential. Results clearly show that acid catalyst has crucial effect on particle synthesis and it is not possible to obtain particles without acid catalyst. In this work acetic acid was used as chelating agent and according to obtained results fine particles can be obtained with higher acetic acid. Reaction temperature and time also serve for smaller size and stable particle. However, effects of these parameters are not significant compared to other parameters.

Isoelectric point of TiO_2 sols was measured between pH 5 and 6. Lower and higher pH values result in stable sols which is needed condition for smooth applications. Additionally, it was observed that significant change in particle size occurs after synthesis reaction TiO_2 sol samples. This change was associated to uncompleted reactions of precursor and C^{13} NMR was used to understand this behavior. XRD patterns of samples showed that anatase crystal particles were obtained for samples on which calcinations process was not applied. Furthermore, it is determined with XRD measurements that water:precursor molar ratio does not have effect on crystal structure of the particles. Phase transition from anatase to rutile crystal phase was determined between 500 and 600^0C. Simultaneous thermal analysis of TiO_2 sample support this phase transition temperature value.

Surface modification of TiO_2 nanoparticles was done with aminopropyl triethoxysilane and modified particles were characterized by Fourier transform infrared spectroscopy (FTIR), STA and Elemental Analysis. Effects of modification conditions such as modifier concentration, TiO_2 concentration and reaction time were investigated. Increasing concentration of modifier has significant effect on amount of surface modification. On the other hand, above certain concentration amount of grafted amino silane is not affected. These results were verified with STA and Elemental Analysis. When TiO_2 concentration increases, reaction between surface OH group and alkoxy group of modifier increases and higher mass loss is observed in thermal analysis due to degradation of grafted organic materials. Moreover, longer reaction time results in higher coverage of modifier on the surface of the particle.

TİTANYUM DİOKSİT'İN KONTROLLÜ SENTEZİ VE YÜZEY MODİFİKASYONU

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Özet

Bu çalışmada TiO_2 nanoparçacıkları basitleştirilmiş sol-gel yöntemi ile solvent olarak su ve precursor olarak Titanyum tetraisopropoksit kullanılarak sentezlenmiştir. Sentezlenen malzemeler DLS, STA, XRD and C^{13} NMR teknikleri kullanılarak karakterize edilmiştir. Bu karakterizasyon teknikleri parçacıkların kristal yapısı ve boyutları, sentez parametrelerinin etkileri, TiO_2 sol örneklerindeki parçacık boyutu değişimi, termal davranışları ve pH'ın örnekler üzerindeki etkilerini anlamak açısından önemli bilgiler sağlamıştır.

Su:prekursör mol oranı, asit katalizör miktarı, şelatlama ajanı miktarı, reaksiyon sıcaklığı ve süresi gibi sentez koşullarının elde edilen parçacıkların özellikleri üzerindeki etkileri incelenmiştir. Elde edilen sonuçlara gore, su:precursor mol oranının yüksek olması küçük boyutta ve sulu süspansiyon içinde kararlı parçacıklar elde edilmesini sağlamaktadır. Ayrıca, asit katalizör miktarındaki artış ile daha küçük boyutta ve yüksek yüzey potansiyeline sahip kararlı parçacıklar elde edilebilmektedir. Asit katalistin parçacık boyutu üzerinde çok önemli etkisi olduğu ve asit katalizör kullanılmadan parçacık sentezinin mümkün olamayacağı elde edilen sonuçlardan açıkça görülebilmektedir. Bu çalışmada asetik asit şelatlama ajanı olarak kullanılıştır. Diğer parametrelerin etkisine benzer olarak kullanılan asetik asit miktarının arttırılması ile daha küçük boyutta parçacıklar elde edilebilmektedir. Reaksiyon sıcaklığı ve süresi de kararlı parçacıklar sentezlenmesine katkı sağlamaktadır fakat bu parametrelerin etkisi diğer parametreler ile karşılaştırıldığında oldukça düşüktür.

TiO_2 sol örneklerinin izolektrik noktası pH 5 ve 6 aralında belirlenmiş olup, daha düşük ve yüksek pH değerlerinde parçacıklar sulu süspansiyon içerisinde herhangi bir çökmeye yol açmayacak şekilde sabit kalabilmektedirler. Bu kararlılığa sahip örnekler uygulamalarda sorunsuzca kullanılabilmektedirler. Bunlara ek olarak, çalışmalar esnasında sentez işlemleri sonrasında örneklerin parçacık boyutlarında önemli değişiklikler olduğu gözlenmiştir. Bu değişimlerin sebebinin prekusörün sonlanmamış reaksiyonları olabileceği düşünülmüş ve örnekler C^{13} NMR kullanılarak karakterize edilmiştir. XRD sonuçlarından 80^0C kurutulmuş fakat kalsinasyon işlemi uygulanmamış TiO_2 örneklerinin anataz kristal yapısına sahip olduğu öğrenilmiştir. Ayrıca Su:prekursör mol oranının parçacıkları kristal yapısı üzerinde herhangi bir etkisi olmadığı gözlenmiştir. Farklı sıcaklıklarda uygulanan kalsinasyon işlemleri sonrasında anataz kristal yapısından rutil kristal yapısına geçişin 500-600^0C arasında gerçekleştiğ belirlenmiştir. Bu sonuçlar parçacıkların termal analiz sonuçları ile de doğrulanmıştır.

TiO_2 nanoparçacıklarını yüzey modifikasyonu aminopropil trietoksisilan ile yapılmış ve örnekler FTIR, STA and Elemental Analiz yöntemleri ile karakterize edilmiştir. Modifikasyon kimyasalının konsantrasyonu, sulu system içerisindeki TiO_2 parçacık konsantrasyonu ve reaksiyon süresi gibi parametrelerin ürün özelliklerini nasıl etkilediği üzerinde çalışılmıştır. Elde edilen sonuçlara göre, aminopropil trietoksisilan konsantrasyonu arttıkça yüzeyde tutunan kimyasal miktarı artmakta fakat belli bir konsantrasyon değerinden sonra bu artışın etkisi görülmemektedir. STA ve elemental analiz yöntemlerinde elde edilen sonuçlar uyumluluk göstermektedir. TiO_2 konsantrasyonundaki artış yüzey OH grupları ile alkoksi grupları arasındaki reaksiyonu arttırmakta ve termal analiz sonuçlarında daha fazla ağırlık kaybı ile belirlenen parçacık yüzeyinde tutunmuş olan organik madde miktarını attırmaktadır. Bunlara ek olarak, uzun reaksiyon süresinin arttırılması daha etkin bir yüzey modifikasyonunun elde edilmesini sağlamaktadır.

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CHAPTER 1

1. Introduction

Titanium dioxide is one of the most studied metal oxides in the literature for its unique properties and wide range of application areas. These areas are paint industry, solar cell applications, gas sensors, ceramics, heterogeneous catalysis and photocatalysis. TiO_2 has attracted a great deal of attention in these areas due to its chemical stability, non-toxicity, low cost, and other advantageous properties.

Industrial production of TiO_2 started in the beginning of the 20th century to replace toxic lead oxides as pigments for white paint. It is used as a white pigment in paints, plastic, paper, food pharmaceuticals [1].

Photocatalytic activity of TiO_2 was discovered by Fujishima and Honda during water splitting process with TiO_2 electrode under ultraviolet light [2]. After this discovery lots of researches were carried out to examine and improve this property of TiO_2.

Many techniques can be used for TiO_2 particle synthesis such as sol–gel method, hydrothermal synthesis, chemical and physical vapor deposition, emulsion method, reactive sputtering, and liquid phase deposition. Among these methods, sol–gel method is the most common technique for TiO_2 nanoparticle synthesis due to its several advantages, such as low processing temperature and homogeneity. Additionally, sol-gel method ensures simple production process which can be applied at larger scales in industry. One of the aims of this work is to be able to synthesize TiO_2 nanoparticles by a simplified method which gives desired product properties such as particle size and stability, crystal phase and surface area. This simplified method has easy processing steps that ensure applications at larger scales and is cost effective.

In all application areas of TiO_2 especially in photocatalysis, size, surface area and crystal structure of the TiO_2 particles are important factors that affect the performance of the materials. Because of this reason, it is crucial to control these properties of the product during synthesis. In this work it is aimed to ensure controlled synthesis of TiO_2

nanoparticles and get better understanding of effects synthesis conditions. To achieve this aim, effects of synthesis parameters such as water:precursor molar ratio, amount of acid catalyst, amount of chelating agent, reaction temperature and time were investigated. Produced TiO_2 sols and powders were analyzed with DLS, STA, XRD and C^{13} NMR to understand crystal type and size of nanoparticles, effect of synthesis parameters, change in particle size of TiO_2 sols, thermal behavior and pH dependence of particles.

Surface modification of TiO_2 particle is used in some of application areas where TiO_2 nanoparticles used as white pigment, polymer filler, UV absorber and photocatalyst. Surface modification enhances proper dispersion in polymer matrix, enhance coating properties, suppressing high photocatalytic activity for UV absorption applications or improve efficiency of Dye Sensitized Solar Cells (DSSCs).

Organosilanes can be used as modifier of TiO_2 surface and aminosilanes are common material which provides better compability with organic mediums. One of the important points in surface modification of TiO_2 nanoparticles is to control amount of grafting/surface modification in order to have optimum surface functionalization and photocatalytic activity. In this work, it is aimed to optimize surface modification by understanding of effects of parameters. Trials were performed by changing concentration of modifier, concentration of TiO_2 nanoparticles in aqueous reaction system and reaction time. Similar with sol-gel synthesis of TiO_2, the main objective is to ensure a simple and effective process for surface modification of nanoparticles. Samples were characterized with FTIR, STA and Elemental Analysis.

CHAPTER 2

2. Literature Review on Titanium Dioxide

2.1. Titanium Dioxide (TiO_2)

Titanium Dioxide is a very well known and commonly used material in industry as a white pigment due to non-toxicity and low cost. After discovery of photocatalytic activity it became much more attractive for different application areas with its unique properties. TiO_2 is cheap, chemically and biologically inert, reusable and has stable chemical structure. Furthermore; it can operate at ambient temperature and pressure, has high catalytic activity and can work with very low concentrations of organic pollutants [3].

2.1.1. Crystal Structures of TiO_2

Crystalline TiO_2 exists in three phases; anatase, rutile and brookite. All three are composed of octahedral groups of oxygen atoms around titanium. As shown in Figure 2.1, anatase and rutile phases have tetragonal structure while brookite phase has orthorhombic structure.

Some synthesis parameters such as synthesis method, starting material, pH and concentration of reaction medium and calcination temperature affect formation of TiO_2 phases. Among three phases, rutile is the most stable phase at high temperatures. Calcination leads amorphous phase transition to anatase and than anatase form is transformed to rutile phase [4].

Anatase has higher photocatalytic activity than rutile phase whereas brookite does not have catalytic activity. Although anatase and rutile form octahedral basic structures and have the same tetragonal crystalline structure; the difference between these two crystal phases is the alignment of octahedrons. In anatase phase octahedrons show higher distortions than rutile phase octahedrons which are also not regular but have slight distortions [5]. This difference results in dissimilarity in electron densities and band structures. Anatase phase shows higher photocatalytic activity than rutile phase in most of the reactions in spite of having higher band energy [6].

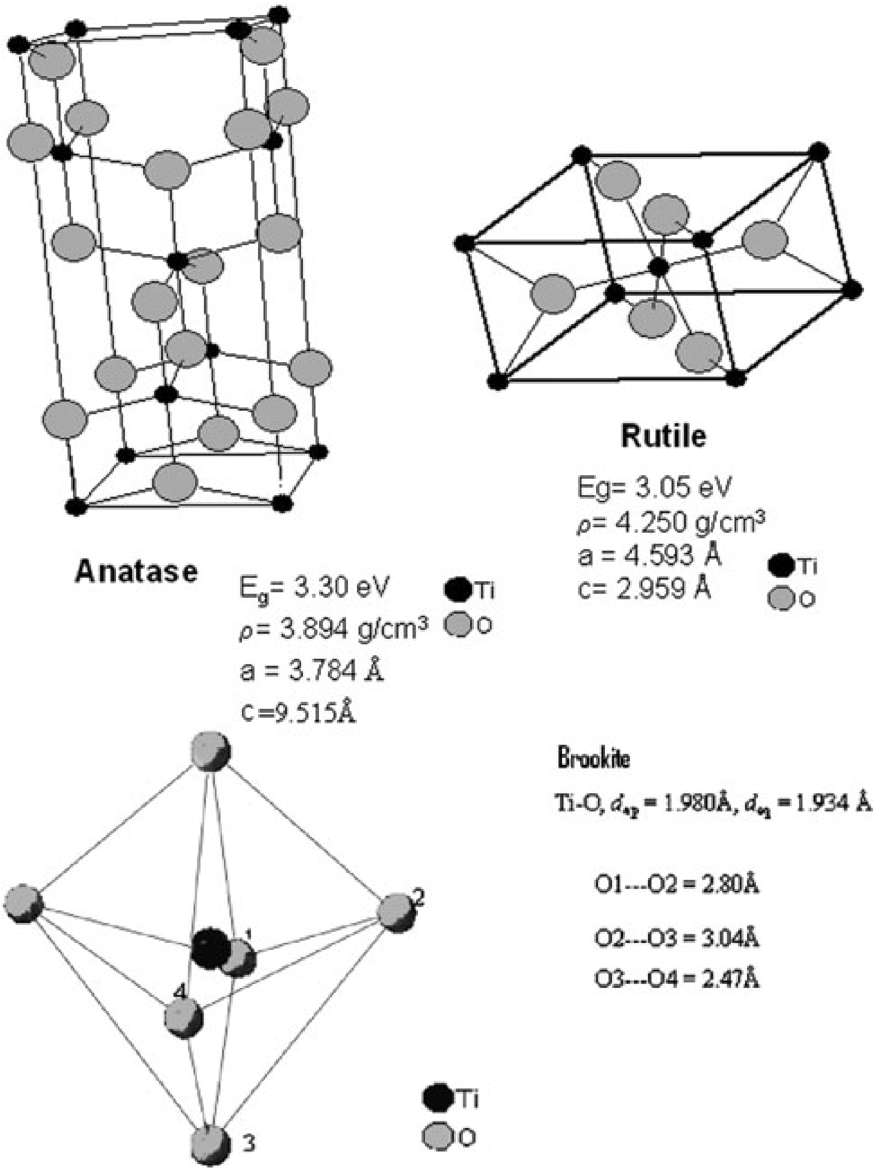


Figure 2.1 Crystal Structures of anatase, rutile and brookite [3]

2.2. Photocatalytic Activity of TiO_2

Catalysis is the change in rate of a chemical reaction due to the participation of a substance called a catalyst. So, photocatalysis is a reaction that uses light to activate a catalyst which changes the rate of a chemical reaction without consumed. TiO_2 is one of the most studied photocatalyst among other semiconductor materials.

Before explaining photocatalytic activity of $TiO_{2,}$ it is better to define band gap. Electrons are allowed to stay in certain energy levels in an atom and these individual levels combine and form bands in materials. The band with the highest energy that an electron can move is valence band. The next energy level, conduction band is the range of electron energies where an electron is free from binding with its individual atom and allowed to move freely within the atomic lattice of the material. The energy difference between valence band and conduction band is called as band gap [7].

A photon with enough energy, which is equal or higher than band gap energy, excites valence band electrons and makes them jump to higher energy conduction band. Moreover, this excited electron generates positive charge hole in valence band. There are two possible routes that electrons and holes can follow. In the first route, electron/hole pairs can diffuse to the surface of the catalyst and react with surface species such as H_2O and O_2 to start photoreduction or photooxidation reactions as shown in Figure 2.2. In the second route, electron/hole pairs can recombine without starting any reaction and this is one of the rate limiting steps of the photocatalytic reactions.

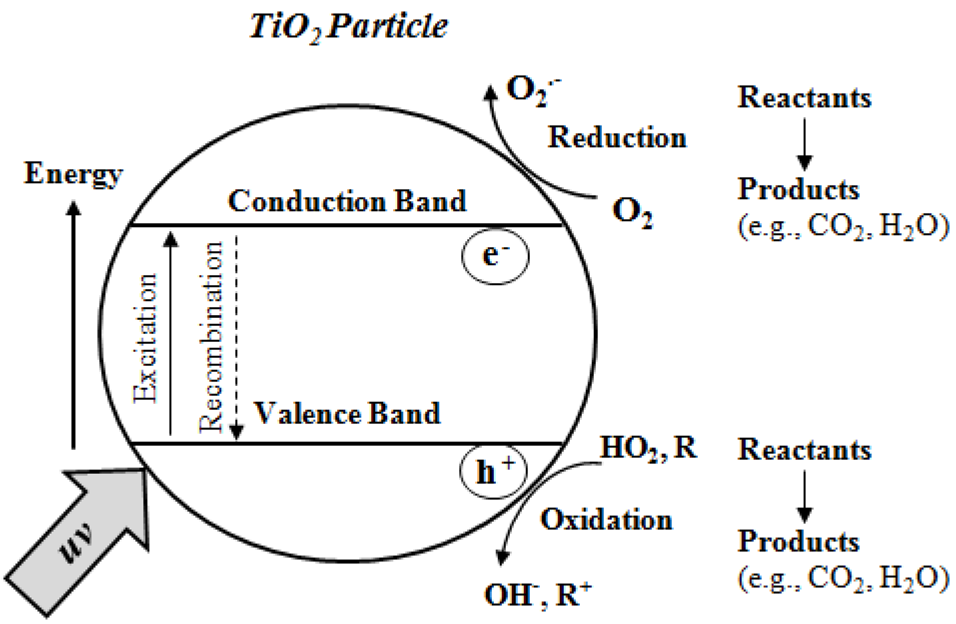


Figure 2.2 Mechanism of photocatalysis

As mentioned above photocatalytic reactions occur at the surface of the catalyst, this brings an important role to surface area of particles on photocatalytic activity. If the surface area of catalyst is high, adsorption of photons become faster. Additionally, as the particle size of the materials decreases surface free energy increases, this means strong interaction between catalyst surface and absorbing species. This increases the possibility of adsorption of charge carriers to the absorbed molecules and finally results in enhancement of catalytic activity [5].

Beside high surface area, mesoporous surface and crystal phase, it is reported in some of the studies that particle size has important effect on photocatalytic activity of TiO_2 [8]. When particle size of the semiconductor material decreases, density of surface defects increases up to a certain value. These surface defects results in delocalization of molecular orbitals on the surface. Since they do not have certain location, these delocalizations create shallow traps near the band edge of its electronic state. Finally, this process brings band gap reduction [9]. If particle size further decreases, charge carriers (electrons and holes) confine in a potential well. This confinement prevents delocalizations that occur at larger particle sizes. This means that when minimum band gap is reached, further decrease in partice size increases band gap. On the other hand, this increase in band gap does not directly result in decrease of photocatalytic activity because at this point surface area of the particle increases which increases photocatalytic activity. These two concepts should be considered together in order to make investigation of photocatalytic activity.

Another property of TiO_2 that affects photocatalytic activity is of course crystal phase. Anatase phase is more advantageous than rutile phase in terms of electron transport from the valence band to the conduction band; separation time in anatase phase is longer which increases electron and hole pairs longevity and finally increases photocatalytic activity. On the other hand, when anatase and rutile phase are close to each other electron transport to the conduction band can be effective in terms of durability and longevity of electron. This interaction between two crystal phases results in better photocatalytic activity for the mixture of anatase and rutile phases. In order to have this enhanced activity ratio of anatase phase should be higher than rutile phase [10,11]. In fact, presence of rutile phase in adjacent to anatase phase in small quantities acts such as a structural defect or impurity and causes high photocatalytic activity [12].

2.3. Synthesis of TiO_2

As mentioned before, TiO_2 is used for different applications as pigment, UV absorber or photocatalyst. In almost all of the application areas, properties of TiO_2 particles such as size, surface area, crystal phase and crystalinity are important factors that affect the performance of the materials. Synthesis method of TiO_2 particles has very important effect on these properties. Therefore, lots of researches have focused on synthesis methods. Many techniques can be used for TiO_2 nanoparticle synthesis such as sol–gel method, chemical vapor deposition, reactive sputtering, emulsion method and liquid phase deposition [13]. However, these methods, other than sol-gel method, need expensive materials and special conditions like high vacuum, magnetic waves; it is not feasible to use these methods for high volume applications. Sol-gel method for TiO_2 synthesis has many advantages over other methods and it is widely used.

2.2.1. Sol-Gel Synthesis

Sol-gel method is a wet-chemical method which is the most common method for synthesis of metal oxides with an intermediate stage including a sol or/and a gel state [14].

Both sol-gel synthesis method itself and the final product have advantages over synthesis methods and their final products. Firstly, simple equipments are needed during sol-gel synthesis. Reactions take place at low temperatures and this allows saving energy and reduces losses due to evaporation. Additionally, process occurs in liquid medium and this prevents pollution caused by dispersion of dust particles. Another advantage of the method is the easy control of reaction parameters which ensures easy control of final product properties. Moreover, the method is very suitable to dope the materials and finally, the solution form enables to coat large and complex surface areas by dip coating, spin coating and simply by spraying. Beside advantages of the method, final product has some advantages as high homogeneity and purity. On the other hand, precursors that are used in sol-gel method are expensive and there is possibility of residual carbon or hydroxyl existence on final product [15].

Sol-gel method synthesis has been commonly used also for TiO_2 nanoparticle synthesis. In this synthesis, some titanium alkoxides and non-alkoxides can be used as titanium precursors. Most commonly used alkoxide precursors are $Ti(i\text{-}OP)_4$ and $Ti(OBu)_4$. Non-alkoxide precursors include inorganic salts such as nitrates, chlorides, acetates, carbonates, acetylacetonates and these precursors require an additional removal of the inorganic anion [16].

Sol-gel method can be used for different type of products and different procedures can be employed in this synthesis method as presented in Figure 2.3. Sol-gel process starts with right type of precursor which leads reactions towards formation of colloidal particles or polymeric gels. When obtained colloidal particles dried and treated by some techniques such as sintering and cold or hot pressing ceramics can be obtained. Moreover, large surface areas can be coated with sol forms of the process and fibers can be obtained after spinning process [15].

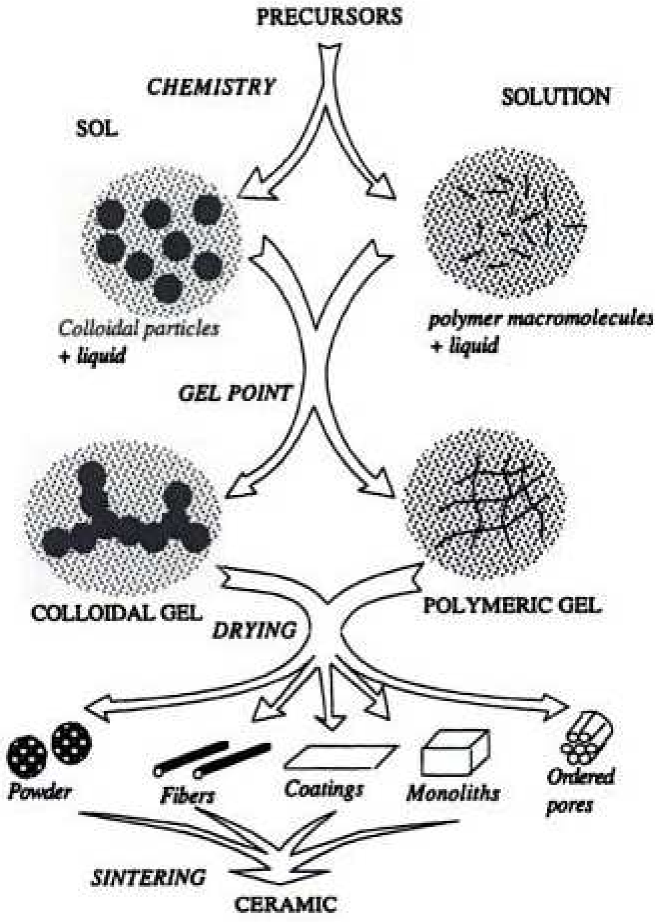


Figure 2.3 Chart of sol-gel synthesis [15]

TiO_2 is usually synthesized by hydrolysis and polycondensation reaction steps. Firstly, titanium alkoxides form oxopolymers in aqueous phase, and then these oxopolymers are transformed into an oxide network. First step of the reactions is hydrolysis reaction of metal alkoxide solution with water as given in Equation 2.1 [17]. During the hydrolysis reaction, alcohol molecules in the structure of metal alkoxides are eliminated with the replacement of water.

$$Ti(OR)_n + H_2O \rightarrow Ti(OR)_{n-1}(OH) + ROH \qquad (2.1)$$

Condensation reactions include two different steps; dehydration and dealcolation. These steps can take place at the same time and can be expressed in Equation 2.2 and 2.3.

Dehydration:

$$Ti(OR)_n + Ti(OR)_{n-1}(HO) \rightarrow Ti_2O(OR)_{2n-2} + ROH \qquad (2.2)$$

Dealcolation:

$$2Ti(OR)_{n-1}(OH) \rightarrow Ti_2O(OR)_{2n-2} + H_2O \qquad (2.3)$$

The overall reaction can be expressed as:

$$Ti(OR)_n + \frac{n}{2}H_2O \rightarrow TiO_{n/2} + nROH \qquad (2.4)$$

2.2.2. Effects of synthesis parameters

As mentioned earlier performance of TiO_2 nanoparticles strongly depend on properties of the particles. Moreover, there are various factors related to synthesis process that can change crystal type, particle size and morphology of TiO_2. These factors are synthesis parameters such as pH, stoichiometry of reactants, reaction time, reaction temperature and calcinations temperature.

One of the important synthesis parameters that have effect on TiO_2 is pH of reaction medium. It has been demonstrated in many studies that acid catalysis increases hydrolysis rates, crystalline and smaller sized powders are formed from fully hydrolyzed precursors [16, 18, 19].

Synthesis of TiO_2 includes two stages of reactions; hydrolysis and condensation. If condensation reaction occurs simultaneously with the hydrolysis, this results in amorphous product. The main reason for this is that alkyl groups inhibit the formation of ordered structures. It is stated that hydrolysis has to be completed before the beginning of the condensation reaction if the objective is to prepare highly ordered crystalline structure [20]. This means that condensation reaction is slow enough. The way to promote hydrolysis reaction versus the condensation reaction is based on low processing pH. The amount of acid added affects the state of the hydrolyzed products in the form of sol, gel, and precipitates. The gelation process is delayed in the synthesis with acid addition and a turbid gel was formed instead of white precipitates [19].

The acid serves not only as an acid catalyst for reactions, but also as an electrolyte to prevent particle growth or agglomeration through electrostatic repulsion. It makes the surface of the precipitates to get positively charged due to the H^+ adsorption. More protons adsorbed onto the surfaces means more repulsion forces between particles. By this way, optically transparent suspensions can be obtained [21].

Beside pH, stoichiometry of reactants such as water:precursor molar ratio affects final TiO_2 product. Effects of this parameter have been investigated in studies where titanium tetra isopropoxide is used as precursor [22-24].

Acid catalysis and pH of the reaction medium affects hydrolysis and condensation rates as stated previously. Moreover, another way to achieve a small particle size and narrow distribution, water:precursor molar ratio is used as a synthesis parameter to control rates of nucleation and growth of particles. In sol-gel process, two regimes are distinguished; synthesis with a low water:precursor molar ratio and synthesis with a high water:precursor molar ratio. Wang et al. investigated effect of water:precursor molar ratio and observed that higher water:precursor molar ratio resulted in reduced crystallite size [19]. Additionally, Yin et al. indicated that the amount of water determined the degree of crystallization [25]. They stated that TiO_2 particles that are synthesized with low water content would require longer calcinations periods for crystallization. According to these studies, low water content allowed ultrafine crystallite size especially for low temperature synthesis processes.

On the other hand, Oskam et al. claimed the opposite [23]. They stated that hydrolysis of titanium alkoxide is very fast and nucleation and growth are completed within seconds. The TiO_2 particles formed with high water content in their process are unstable and a white suspension is immediately formed due to the precipitation of large aggregates.

In literature there are lots of studies which investigate effect of chelating agent on TiO_2 synthesis [26-29]. Metal alkoxides precursors for sol–gel process are generally highly reactive. Because of this, control of the reactivity is necessary in order to obtain sols and gels with desired properties. This control may be achieved with modifiers such as acetylacetone and acetic acid or other complex ligands [28]. Acetylacetone and acetic acid are known as strong chelating ligand and they are used as a stabilizing agent for alkoxides precursors. Presence of these modifier materials serves to control the hydrolysis and condensation reactions and prevents the precipitation of undesired phases. Beside controlling degree of condensation, chelating agents leads to the preferential crystallization of TiO_2 in the anatase phase. Moreover, without the control of the condensation reactions amorphous agglomerated particles may be obtained after hydrolysis reaction [30].

Another important parameter that affects crystal type and size of particles is calcination temperature. After sol-gel process, dried particles are generally amorphous or have low crystallinity. So, powders should be calcined in order to obtain crystallize TiO_2. During calcination, TiO_2 particles experience phase transitions from amorphous to anatase and then from anatase to rutile. Phase transition from amorphous to anatase is known to take place to occur in the temperature range between 623K and 723K while the anatase-rutile transition is known in a wide range of temperature from 873K to 1373K. Exact temperature value of transition depends on the preparation condition of TiO_2 parricles [31]. Ovenstone et al. investigated the effect of particle size on transition temperature from anatase to rutile phase. In their study, small crystal size of anatase results in low temperature of phase transition from anatase to rutile [32].

On the other hand, calcination process should be controlled to avoid high temperatures that result in sintering. Moreover, high temperature calcinations process leads to decrease in surface area, high crystal size and loss of hydroxyl groups. These negative effects should be considered beside advantage of high crystalline particles.

Zeta potential and isoelectric point are also important properties that have direct effect on the product. The particles in a colloidal suspension or emulsion usually carry an electrical charge and have electrical potential. So, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. Zeta potential indicates the degree of repulsion between particles. A value of ±30 mV can be taken as the limit value that separates low charged surfaces from highly charged surfaces. Highly charged surfaces will have strong repulsion and so will have stability and resist aggregation. Moreover, isoelectrical point is the pH value at which there is no net charge on particle. Around this pH value, dispersion has very low even zero zeta potential and so aggregation occurs in the system.

2.2.3. Other Synthesis Method

There are also some other methods that can be used for TiO_2 synthesis rather than sol-gel method. These are hydrothermal synthesis, chemical and physical vapor deposition, emulsion method, reactive sputtering, and liquid phase deposition [33].

Hydrothermal synthesis is other common technique for TiO_2 synthesis after sol-gel method. It is a method that is widely used for the production of small particles in the ceramics industry. Hydrothermal synthesis takes place in steel pressure vessels called autoclaves with or without Teflon liners under controlled temperature and/or pressure with the reaction in aqueous solutions. The temperature can be elevated above the boiling point of water, reaching the pressure of vapor saturation. The temperature and the amount of solution added to the autoclave largely determine the internal pressure produced [34].

Chemical and physical vapor deposition are generally used to form coatings but recently, they have been widely used to produce nanomaterials. In vapor deposition, materials in a vapor state are condensed to form a solid phase material and this process takes place within a vacuum chamber. The process is called as physical vapor deposition (PVD), if no chemical reaction occurs; it is called chemical vapor deposition (CVD) if a chemical reaction occurs. Thick crystalline TiO_2 films can be prepared by pyrolysis of TTIP with using these methods [35].

A microemulsion is a system of water, oil and amphiphile (surfactant). The internal structure of a microemulsion is determined by the ratio of its constituents. The structure consists either of nanospherical monosized droplets or a bicontinuous phase. From a particle-preparation point of view, the microemulsion system is interesting with internal structure consisting of small droplets. Two main ways of preparation are stated in order to obtain nanoparticles from microemulsions. First one is to mix two microemulsions, one containing the precursor and the other the precipitating agent. Other way is to add the precipitating agent directly to the microemulsion containing the metal precursor. It is possible to prepare small particles with this method but it is difficult to obtain a narrow particle size distribution [36].

2.4. Application Areas

TiO_2 has wide range of application areas due to its unique properties. Some of these application areas are self cleaning surfaces, antimicrobial surfaces, water retreatment and purification, solar cells, gas sensor and air purification systems.

2.4.1. Self Cleaning and Antimicrobial Surfaces

Self cleaning surfaces are one of the first application areas of TiO_2. Photocatalytic activity of TiO_2 enables it to decompose organic contaminations and maintain the surface clean under ultraviolet illumination. This technique has good value, since to obtain self cleaning surfaces TiO_2 coating needs only freely available solar light or ultraviolet emission from fluorescent lamps. By this way, it saves maintenance costs and reduces the use of detergents. Self cleaning surface concept is applied on cover glass for highway tunnel lamps to decompose the contamination from exhaust compounds, windows glasses of homes and especially high towers to maintain cleanness of glass with using photocatalytic activity and its hydrofobic surface. Beside self cleaning property another advantage of TiO_2 coated surfaces is antibacterial activity. Utilization of sol-gel method for TiO_2 nanoparticle synthesis brings additional advantage for this application since sol-gel products are easy to coat large surface areas [37].

2.4.2. Water Treatment

Due to population growth and development of industrialization clean water sources and waste water treatment an important issue. Waste water treatment system should completely eliminate or destroy the pollutants, not generate toxic secondary pollutants and have low operating cost. Conventional methods such as adsorption, sedimentation, filtration, chemical and membrane technologies do not meet these requirements. Advanced Oxidation Processes (AOPs) as the innovative water treatment technologies were started to use in industry with employing semiconductor catalysts such as TiO_2, ZnO, Fe_2O_3, CdS, GaP and ZnS. Among the semiconductor catalysts, TiO_2 has received the greatest interest since it is the most active photocatalyst, remains stable after repeated cycles and has strong mechanical properties. Moreover, TiO_2 is a nontoxic catalyst and so this makes it attractive for cleaning the water environment and even for cleaning drinking water [38].

2.4.3. Air Purification

Another important application area of TiO_2 photocatalysis is air purification systems to decontaminate, deodorize, and disinfect indoor air. Conventional air purification systems use filter components for the cleaning of polluted air. Pollutants are accumulated in filters and they become saturated with adsorbed substances. After a certain period of time they lose their function and treatment of the used air filters may cause the risk of secondary pollution. However, photocatalytic air cleaning filters decompose the organic substances instead of accumulating them and so exhibit better performance than conventional ones. Additionally, photocatalytic filter can kill the bacteria floating in indoor air, which is also important for indoor air purification [39].

2.4.4. Gas Sensors

Another application area of semiconducting metal oxides is gas sensors which is very important in environmental monitoring, domestic safety, public security and automotive applications. Semiconducting metal oxides chance their conductivity upon gas adsorption and this change in electrical signal is used for gas sensing. TiO_2 has advantages in this application such as high dielectric constant, good optical transmittance, high chemical stability and suitable energy band gap. TiO_2 is generally used as gas sensor for H_2, O_2 and CO. In order to improve its sensitivity some catalysts such as Pt and CeO_2 are used [40].

2.4.5. Solar Cells

Dye-sensitized solar cells (DSSCs) became attracted due to their inherent attractive advantages of low cost, less toxic manufacturing and light weight compared to conventional solar cells devices [41]. DSSCs consist of an electrode, TiO_2 film, a sensitizing dye, electrolyte, and a counter electrode. Nanocrystalline porous TiO_2 is preferred because of their physical and chemical properties. Mesoporous TiO_2 has an optical efficiency that is approximately 0.5–1.0% higher than that of the existing nanomaterials, highly porous TiO_2 layers can adsorb much more dye, and it shows high absorption coefficients in the visible spectral region [42-43].

CHAPTER 3

3. Literature Review on Surface Modification of TiO_2

As mentioned in previous section, TiO_2 has wide application areas as white pigment, polymer filler, UV absorber and photocatalyst. Surface modification of TiO_2 particle can be needed in order to have better performances in these application areas. These needs can be to obtain proper dispersion in polymer matrix, enhance coating properties, suppressing high photocatalytic activity for UV absorption applications or improve efficiency of Dye Sensitized Solar Cells (DSSCs). Different surface modification agents and methods can be applied according to desired application or property.

3.1. Surface Modification Agents

The general formula of an alkoxy silane is $R_nSiX_{(4-n)}$. R is a nonhydrolyzable organic part that can be an alkyl, aromatic, organofunctional, or combination of any of these groups. This part provides organic compatibility which allows alkoxy silane to react with organic medium where modified particle is present. X represents alkoxy part, generally methoxy or ethoxy, which reacts with the various forms of hydroxyl groups and forms methanol or ethanol. These groups can provide the linkage with inorganic substrates, pigment, or filler to improve coating integrity and adhesion [44-45].

Reaction of these alkoxy silanes involves four steps. Firstly, hydrolysis of the three alkoxy groups occurs and condensation to oligomers follows secondly. After this point, oligomers hydrogen bond with OH groups of the substrate. Finally, during drying or curing, a covalent linkage is formed with the substrate with loss of water. Instead of following that order, these reactions can occur simultaneously after the initial hydrolysis step [46].

3.2. Reactions between Modification Agents and TiO_2 Surface

As mentioned previously, two different part of alkoxy silane have different functions and it is important to know which one of the parts reacts with particle and which one is free to make contact with medium. Although it is generally stated as alkoxy part reacts with OH groups of oxide particles, there are different claims in literature.

Lin et al. explains the reaction between oxide surface and aminosilane as in Figure 3.1 [47]. As can be seen from the figure, alkoxy part of silane reacts with surface OH groups of oxide particles. There are three possible reactions in this case; one possiblity is reaction of only one alkoxy group with surface OH group. Moreover, two of alkoxy groups or all of them may react surface OH group. These reaction types effect strenght of the bond between alkoxy silane and oxide particle. Additionally, some other reactions can occur with free ends of alkoxy groups.

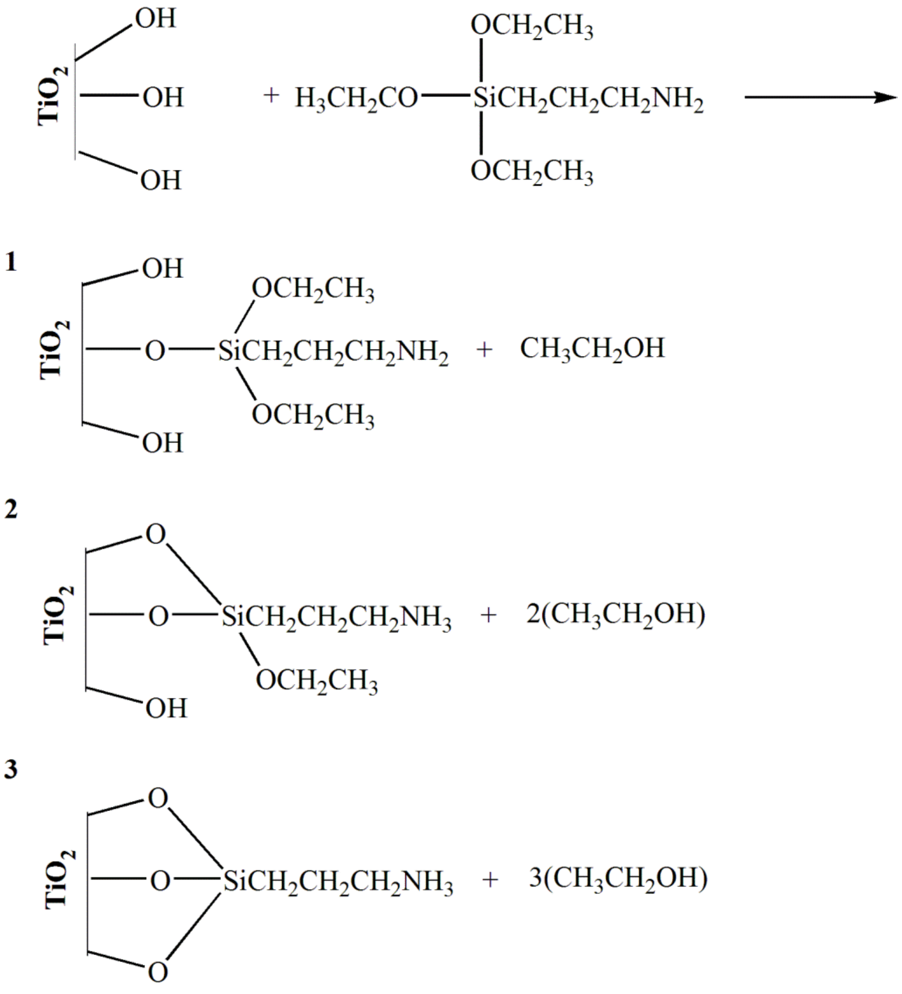


Figure 3.1 Possible reactions between oxide surface and APTES [47]

On the other hand, Jeisonowski et al. proposed another way of reaction between alkoxy silane and oxide particle. As can be seen in Figure 3.2, amine part may enter into a hydrogen bonding interaction with a surface hydroxyl group. Additionally, amine may form ionic bonding with a surface hydroxyl group which leads more stable interaction.

Another possibility is self catalysis of hydrogen bonding which results in covalent siloxane bond.

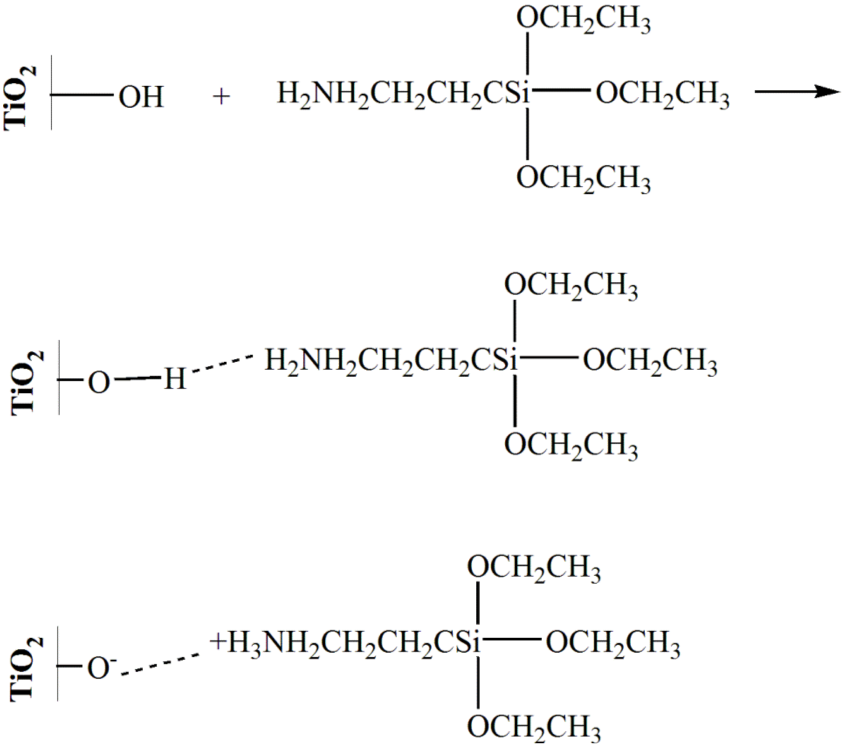


Figure 3.2 Possible reactions between oxide surface and APTES [48]

3.3. Application areas

TiO_2 particles have a potential for UV-ray shielding due to their absorption, scattering and reflecting properties and so TiO_2 can be used in application as a UV filter. On the other hand, TiO_2 has photocatalytic activities [48]. This photocatalytic activity can cause DNA damage if particle has direct contact to skin. In order to suppress this activity but keep UV-shielding ability thin layer of surface modification is needed which can be obtained with surface modification with silane coupling agents. Ukaji et al. modified TiO_2 surface with aminopropyl triethoxysilane (APTES) and obtained 25% suppressed photocatalytic activity and 80% of initial UV-shielding ability. Similar study was performed by Siddiqueya et al. and 72% reduced photocatalytic activity of TiO_2 was observed with methacryloxypropyl trimethoxysilane modification [49].

Ceramic oxides such as Al_2O_3, TiO_2 and ZrO_2 are added to polymers in order to obtain composite materials with better mechanical, thermal, electrical, optical properties. On the other hand, due to their small size and large surface area particles tend to agglomerate. This agglomeration reduces the resultant properties of the nanocomposite materials [50]. To achieve proper dispersion and to yield a better compatibility between the nanoparticles and polymer matrix, the use of different coupling agents such as alkoxy silanes for surface modification of nanoparticles is recommended. Surface modification of TiO_2 nanoparticles were investigated as an additive in a polyurethane clear coat by Sabzi et al. [51]. They determined that amino propyl trimethoxy silane (APS) improves dispersion, mechanical properties and UV protection of urethane clear coating. Similar study was performed by Abboud et al. and in this study desired dispersion was achieved through the grafting of a polymerisable group onto the particle surface and copolymerization was followed with organic monomers. By this process formation of inorganic–organic hybrids and better dispertion properties were achived [52]. This can be obtained by grafting of a polymerisable group onto the oxide surface and it is followed by copolymerisation with organic monomers.

Dye sensitized solar cell DSSCs are another application area of TiO_2 and also surface modification of TiO_2. There are lots of studies are carried out in this topic to improve the photovoltaic parameters such as the short circuit photocurrent Jsc, open circuit photovoltage Voc, and the fill factor FF to increase performance of the DSSCs [53-54]. Chemical and physical methods have been carried out to improve the performance of the DSSCs, such as forming core-shell structure of the photoanode, adding organic coadsorbent and using amines to deprotonate the dye sensitized photoanode [55]. Zhang et. al. uses surface modified TiO_2 by aminosilanes in dye sensitized photoanode and the redox electrolyte interface of the DSSC. According to their results, NH_2 group of aminosilane deprotonates dye sensitized photoanode and changes the TiO_2 conduction band potential negatively. Moreover, $Si\text{-}OC_2H_5$ group blocks the interface recombination of the electrons from the TiO_2 conduction band to the electrolyte. These effects contribute to the improvement of the Voc.

One of the new applications of TiO_2 is nanostructural coatings onto textile substrates where surface modification is also applied in order to improve properties of coating [56]. Ledakowicz et. al. observed in their studies that good UV barrier properties in polyester nonwoven fabrics modified with aminosilane modified TiO_2 and also better photocatalytc activity of coated fabrics with modified TiO_2. Additionally, more uniformly covered fabrics were determined with aminosilane modified TiO_2 compared to unmodified TiO_2 [57].

CHAPTER 4

4. Experimental

This chapter contains experimental processes used in this thesis work. This part covers sol-gel synthesis of TiO_2 nanoparticles and their characterization with Dynamic Light Scattering, X-Ray Diffraction Spectroscopy, Simultaneous Thermal Analysis, C^{13} NMR spectroscopy. Additionally, surface modification process of TiO_2 samples and their characterization with Simultaneous Thermal Analysis, FTIR and Elemental Analysis were covered in this section.

4.1. Materials

For the synthesis of TiO_2 nanoparticles and surface modification components below were required.

- Titanium (IV) isopropoxide (99% pure) from Merck
- Acetic acid (100%) from Merck
- Nitric Acid (65%) from Merck
- Deionized water from Millipore Ultra-Pure Water System
- gamma-Aminopropyl triethoxysilane (Silquest A-1100 Sialne) from Momentive
- Sodium Hydroxide from Merck, diluted aqueous solution

Chemicals were used as received without any further purification.

4.2. TiO_2 Nanoparticles Synthesis

TiO_2 nanoparticles were synthesized with sol-gel method. As a typical procedure, titanium tetraisopropoxide (TTIP) was added dropwise into water which contains acetic acid under vigorous stirring conditions and white suspension was immediately formed. After stirring a few minutes at room temperature, appropriate amount of nitric acid was added. The mixture was heated to 80^0C and continued to stirring for 2 hours. As a final step of synthesis, the mixture was left for cooling for 2 more hours again under stirring.

After these steps, homogeneous and almost transparent sol was obtained. Obtained sol keeps its stability for couple of months.

For characterization and surface modification purposes powder form of TiO_2 nanoparticles were obtained after removal of water in rotary evaporator and drying in oven at 80^0C. Calcination of TiO_2 powders at different temperatures (400^0C – 800^0C) was done with a heating rate of 10^0C/min and samples were kept at desired temperature for 2 hours.

In TiO_2 nanoparticles synthesis one standard sample was determined and reaction parameters of this standard sample were changed in order to understand effects of parameters on product properties. Reaction parameters for this standard sample, TiO_2 sol, are; 200 water:TTIP molar ratio, 0.06M nitric acid, 0.175M acetic acid, 80^0C reaction temperature and 4 hours reaction period. Around this parameter values, none of the reaction parameters block the effects of other parameters. By this way, effects of each parameter can be investigated clearly.

In this work, five control parameters were studied. These are;

1. Water/TTIP moles ratio
2. Acetic acid amount
3. Nitric acid amount
4. Reaction time
5. Reaction temperature

4.2.1. Advantages of Applied Experimental Method

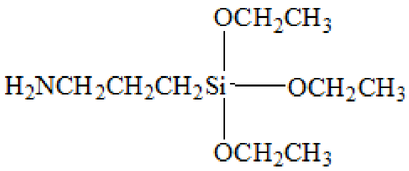
At this point it is important to mention advantages of the experimental method over other common methods in literature. Firstly using alkoxide precursor simplifies experimental method. Since there is no need to have additional process to remove residual components such as nitrates and chlorides as in the method that uses non alkoxide precursors, one extra step is eliminated. In most of the methods, an alcohol generally ethanol or isopropyl alcohol, is used beside water. In experimental methods that use both alcohol and water as solvent, there is requirement to have two different systems. Two different systems are prepared separately and they are combined to have final product. However, in this experimental method only water is used. By this way, cost effective method is achieved and extra work with two different systems are eliminated. Furthermore, there is no need for expensive equipments in sol-gel method as in other methods such as chemical vapour deposition and physical vapour deposition. Additionally, required reaction period in this experimental method is short. It strongly depends on required product properties but approximately two to four hours are enough to have small crystalline particles.

Table 4.1 Experiments for TiO_2 synthesis with sol-gel method

Sample	Water/ TTIP	Nitric Acid (M)	Acetic Acid (M)	Reaction Temperature (^{0}C)	Reaction Time (h)
TiO_2 sol, 200 w:T	200	0.06	0.175	80	4
TiO_2 sol	300	0.06	0.175	80	4
TiO_2 sol, 400 w:T	400	0.06	0.175	80	4
TiO_2 sol, 0.12M N.A.	300	0.12	0.175	80	4
TiO_2 sol, 0.18M N.A.	300	0.18	0.175	80	4
TiO_2 sol, 0.24M N.A.	300	0.24	0.175	80	4
TiO_2 sol, No A.A.	300	0.06	-	80	4
TiO_2 sol, 0.35M A.A.	300	0.06	0.35	80	4
TiO_2 sol, 0.7M A.A.	300	0.06	0.7	80	4
TiO_2 sol, 0.3M A.A., No N.A.	300	-	0.7	80	4
TiO_2 sol, 60^{0}C	300	0.06	0.175	60	4
TiO_2 sol, 100^{0}C	300	0.06	0.175	100	4
TiO_2 sol, 2h	300	0.06	0.175	80	2
TiO_2 sol, 6h	300	0.06	0.175	80	6
TiO_2 sol, 8h	300	0.06	0.175	80	8

4.3. Surface Modification

TiO_2 powder is dispersed in water and the suspension with desired concentration was sonicated for 30 minutes and mechanically stirred for another 30 minutes. After addition of aminosilanes the mixture was left for stirring for required hours. In this study, aminopropyl triethoxysilane (APTES) was used as modifier and its chemical structure is given in Figure 4.1. Moreover, the amounts of aminosilanes were controlled to be between 0.5 and 2 w which indicates weight ratio of modifier to TiO_2 nanoparticles. The solvent was removed with Eppendorf Centifure 5810 (4000 rpm 10 min) and modified nanoparticles were obtained. In order to extract extra aminosilanes, obtained powder was washed three times with water. Dispersed particles were separated from solvent by centrifuge then redispersed in fresh water for next round of wash. Finally, nanoparticles were dried for 15 hours in oven at 80^0C.



$H_2NCH_2CH_2CH_2Si(OCH_2CH_3)_3$

Figure 4.1 Chemical structure of APTES

Throughout surface modification of TiO_2 nanoparticles three control parameters were studied. These are;

- Modifier concentration
- TiO_2 concentration
- Reaction time

Table 4.2 Experiments for TiO_2 surface modification

Sample	Modifier Concentration (w/w)	TiO_2 Concentration (g/ml)	Reaction Time (h)
W-APTES, 0.5w, 6h, 0.01 g/ml	0.5	0.01	6
W-APTES, 1w, 6h, 0.01 g/ml	1	0.01	6
W-APTES, 1.5w, 6h, 0.01 g/ml	1.5	0.01	6
W-APTES, 2w, 6h, 0.01 g/ml	2	0.01	6
W-APTES, 1.5w, 3h, 0.0075 g/ml	1.5	0.0075	3
W-APTES, 1.5w, 3h, 0.01 g/ml	1.5	0.01	3
W-APTES, 1.5w, 3h, 0.0125 g/ml	1.5	0.0125	3
W-APTES, 1.5w, 3h, 0.015 g/ml	1.5	0.015	3
W-APTES, 1w, 1h, 0.01 g/ml	1	0.01	1
W-APTES, 1w, 3h, 0.01 g/ml	1	0.01	3

4.4. Characterization

Different characterization techniques were carried out to examine the TiO_2 nanoparticles and its surface modification.

X-ray diffraction patterns were recorded with a Bruker AXS advance powder diffractometer equipped with a Siemens X-ray gun and Bruker AXS Diffrac PLUS software, using Cu Ka radiation (k = 1.5418 Angstrom). All samples scanned from $2\theta = 20^o$ to 80^o.

Simultaneous Thermal Analysis was used to determine thermal behavior of nanoparticles and monitor surface modification with amino silane. Measurements were performed on a Netzsch STA 449 C Jupiter differential thermogravimetric analyzer (precision of temperature measurement $\pm 2^oC$, microbalance sensitivity <5 μg) under N_2 atmosphere with a flow rate 50 ml/min, at a linear heating rate of 10^oC/min.

Malvern Instruments Zetasizer Nano-ZS was used for particle size and zeta potential measurements. Measurements were performed at room temperature with quartz cell and 173° backscatter detection was used for all measurements.

The infrared spectra of unmodified and modified TiO_2 were obtained using a Thermoscientific Nicolet IS10 FTIR spectroscopy to observe the surface functional groups of the samples. ATR mode was used with Smart ITR diamond ATR and samples were scan between wavenumbers (cm^{-1}) 4000 and 600.

VISTA PRO-CCD Simultaneous ICP OES was used for Carbon and Nitrogen elemental analysis. Temperature was kept at 1000 K during temperatures and results can be taken at ppm level with this technique.

Structural properties of TiO_2 sol samples were studied with ^{13}C NMR an Inova 500 MHz NMR Varian spectrophotometer.

CHAPTER 5

5. Results and Discussion

5.1. TiO_2 Nanoparticle Synthesis

Properties of TiO_2 nanoparticles as a common material for different types of applications have great importance for performance of the material. Because of this importance, lots of studies were done as in the literature to characterize produced TiO_2 nanoparticles and to achieve well controlled synthesis procedures. TiO_2 sols and powders were analyzed with DLS, STA, XRD and C^{13} NMR. These characterization methods provide valuable information to understand crystal type and size of nanoparticles, effect of synthesis parameters, change in particle size of TiO_2 sols, thermal behavior and pH dependence of particles.

5.1.1. Effects of Synthesis Parameters

As mentioned previously sol-gel method enables to control reaction parameters easily. On the other hand, there are many parameters that have effect on properties of final product. These parameters are precursor and acid catalyst amount, usage of ligand agent such as acetic acid, reaction time and reaction temperature.

Water:precursor molar ratio has effect on rates of nucleation and growth of particles. So, it directly affects particle size of TiO_2. In this study, synthesis with a high water:precursor molar ratio regime was used and it was taken between 200 and 400. TiO_2 sols were synthesized with 200, 300 and 400 water:TIIP ratio and other parameters were kept constant as 0.06M nitric acid, 0.175M acetic acid, 4 hours reaction at 80^0C. Particle size and surface charge results measured with DLS are given in Table 5.1.

Table 5.1 Effect of Water:TTIP molar ratio on particle size and surface potential

Sample	Particle Size (nm)	pH	Zeta Potential (mV)
TiO_2 sol, 400 w:T	130.4	1.47	33.9
TiO_2 sol, 300 w:T	140.2	1.5	30.2
TiO_2 sol, 200 w:T	250.1	1.42	7.9

It is very clear with stated results that water:TTIP ratio has effect on particle size. Increasing water:TTIP ratio results in decrease in particle size since high water content increases hydrolysis reaction of precursor. Additionally, surface potential of particles that synthesized with higher precursor amount is very low and particles tend to precipitate. Even during synthesis reaction precipitates were observed in reaction medium. Since hydrolysis rate is low with higher precursor amount, conversation reaction from precursor to TiO_2 may not be complete and reactants may stay in the medium with some final TiO_2 particles. High water:TTIP ratio serves for small particle size and stable particles in aqueous suspension of TiO_2.

Another factor that affects hydrolysis reaction rates is amount of acid catalyst which is nitric acid in this study. TiO_2 sols were synthesized with 0.06, 0.12, 0.18 and 0.2M nitric acid and other parameters were kept constant as water:TTIP molar ratio 300, 0.175M acetic acid, 4 hours reaction at 80^0C. Particle size and surface charge results measured with DLS are given in Table 5.2.

Table 5.2 Effect of acid catalyst amount on particle size and surface potential

Sample	Particle Size (nm)	pH	Zeta Potential (mV)
TiO_2 sol, 0.06M N.A.	140.2	1.5	30.2
TiO_2 sol, 0.12M N.A.	67.1	1.16	31.5
TiO_2 sol, 0.18M N.A.	63.6	0.96	32.8
TiO_2 sol, 0.24M N.A.	58.0	0.83	34.7

Results are consistent with literature data which states fine particle formation with increasing acid amount [18-19]. As can be seen from results, increasing acid amount results in smaller particle size and stable particles with higher surface charge. On the other hand, change in particle size with amount of acid decreases at higher acid amounts. This means that acid catalyst affects hydrolysis rate but the effect is not directly proportional with amount. Acid catalyst increases reaction up to certain point but after this point other parameters become important to further decrease particle size. Furthermore, effect of acid catalyst on surface charge is not as significant as on particle size. For all sample sols stable particles were obtained with higher zeta potential values while acid amount contributes to higher surface potential.

In this work acetic acid was used as chelating agent and its effects on TiO_2 particle products were investigated. Results are listed in Table 5.4. TiO_2 synthesis without nitric acid with only using acetic acid was tried but result was not successful as can be seen from both particle size and surface potential values. With this trial importance of acid catalyst is reviewed one more time and it is also observed that acidity of acetic acid is not enough for synthesis of TiO_2 nanoparticles. Additionally, trials to produce nanoparticles without acetic acid were performed. Although stable TiO_2 sol was obtained; particle size is larger compared to standard TiO_2 sol sample.

Furthermore, the effect of amount of acetic acid was investigated. As stated in Table 5.3, increasing acetic acid amount results in smaller particle sizes. On the other hand, its effect on surface potential of particles is not significant as particle size.

Table 5.3 Effect of acetic acid amount on particle size and surface potential

Sample	Particle Size (nm)	pH	Zeta Potential (mV)
TiO_2 sol, 0.175M A.A.	140.2	1.5	30.2
TiO_2 sol, No A.A.	221.0	1.52	27.8
TiO_2 sol, 0.35M A.A.	113.3	1.47	30.4
TiO_2 sol, 0.7M A.A.	77.6	1.44	30.7
TiO_2 sol, 0.3M A.A., No N.A.	657.2	2.48	- 0.4

Another reaction parameter that was investigated in this study is reaction temperature. TiO_2 nanoparticle synthesis with sol-gel method is generally done at low temperatures. However, temperature of the reaction again has effect on resultant product. Reaction temperature and so energy consumption of synthesis reaction are important especially for large and commercial applications. For this reasons, TiO_2 sols were synthesized at 60, 80 and 100^0C and other parameters were kept constant as water:TTIP molar ratio 300, 0.175M acetic acid, 0.06M nitric acid and 4 hours reaction period. Particle size and surface charge results measured with DLS are given in Table 5.4.

Table 5.4 Effect of reaction temperature on particle size and surface potential

Sample	Particle Size (nm)	pH	Zeta Potential (mV)
TiO_2 sol, 60^0C	672.1	1.5	15.4
TiO_2 sol, 80^0C	140.2	1.5	30.2
TiO_2 sol, 100^0C	124.7	1.51	30.9

As a standard reaction procedure, 80^0C was used in many of the trials. When reaction temperature was decreased to 60^0C, stable TiO_2 sol could not be observed as can be seen from low zeta potential value and precipitation occurred in reaction medium. Moreover, particle size for this product is very high compared to products that were synthesized at higher temperatures. On the other hand, 100^0C reaction temperature led to smaller particle size and slightly higher surface potential. With these results it can be stated that reaction temperature is an effective parameter on product properties up to a threshold value. After certain temperatures, contribution to fine particle formation become not so significant and optimum reaction temperature should be decided with considering effects of other parameters.

In the scope of the study, effects of reaction time of TiO_2 synthesis were examined. In standard reaction procedure, reaction mixture is kept at 80^0C for 2 hours and then it is left for cooling for another 2 hours while stirring is continued. However, for these trails, cooling process was eliminated and reactants were kept at 80^0C during all reaction period. Reaction time for TiO_2 sols samples were taken as 2, 4, 6, and 8 hours and other parameters were kept constant as water:TTIP molar ratio 300, 0.175M acetic acid, 80^0C reaction temperature. Results are listed in Table 5.5.

Table 5.5 Effect of reaction time on particle size and surface potential

Sample	Particle Size (nm)	pH	Zeta Potential (mV)
TiO_2 sol, 2h	427.1	1.48	24.3
TiO_2 sol, 4h	130.6	1.5	30.2
TiO_2 sol, 6h	112.9	1.51	32.5
TiO_2 sol, 8h	109.3	1.51	34.1

As can be seen from results, 2 hours reaction time is not enough for the formation of fine TiO_2 particles. As in the other products that have very high particle size, resultant sol is not stable. From these results it can be concluded that low acid amount, low reaction temperature and reaction time are not sufficient to have complete hydrolysis and condensation reactions. Intermediate products of TTIP reactions stay in reaction medium without further progress of the reaction. On the other hand, when reaction was carried for longer periods TiO_2 particles can be obtained with lower size. Similar to other investigated parameters, further increase of reaction time does not have significant effect on particle size and surface potential.

Change in particle size during reaction for TiO_2 sols samples that are synthesized with 0.06M, 0.12M and 0.18M nitric acid are shown in Figure 5.1, Figure 5.2 and Figure 5.3 respectively. Other reaction parameters are kept as water:TTIP molar ratio 300, 0.175M acetic acid and 4 hours reaction at 80^0C. DLS results are indicates change of both particle size and polydispersity index (PDI) clearly. As can be seen from Figure 5.1 with lower amount of acid catalyst after 2 hours reaction polydispersity and size of particles are very high. After 2 more hours, particle size decreases and particles have narrower size distribution. In the final 4 hours of the reaction, particle size does not change significantly while particle size distribution becomes narrower.

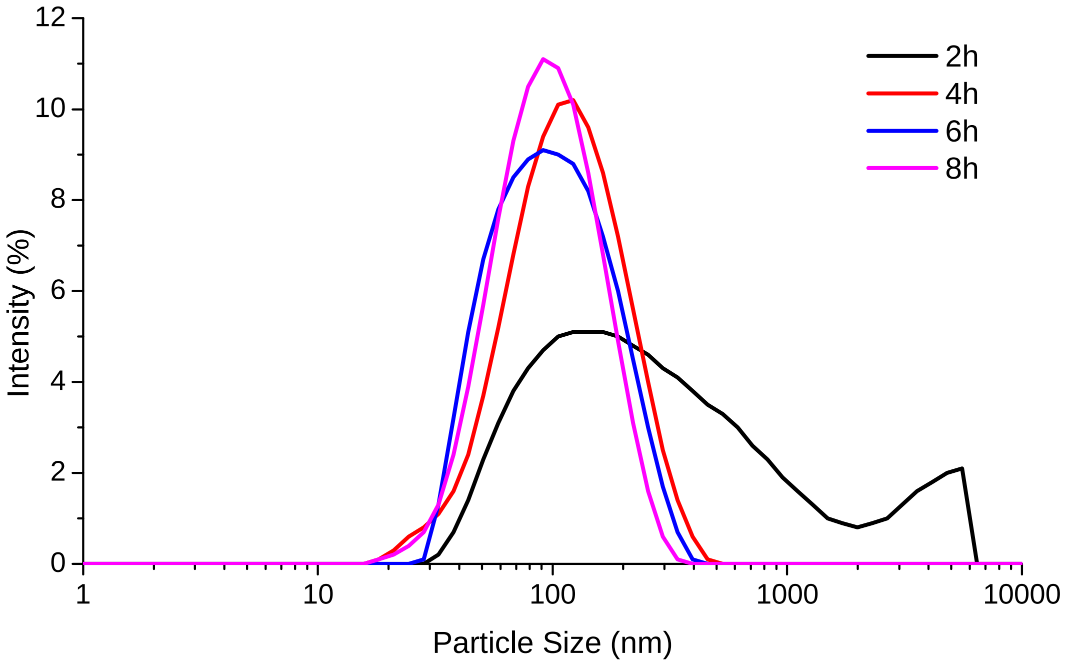


Figure 5.1 Change in particle size during synthesis reaction (Sample-TiO_2 sol)

Similarly, change of particle size and distribution of samples that are synthesized with higher acid amounts are investigated. As can be seen from Figure 5.2 and Figure 5.3, when higher amounts of acid catalyst is used particle sizes around 100nm can be achieved with 2 hours reaction. After further reaction time, narrower particle size distribution of TiO_2 particles is obtained with slightly smaller size. These results again show importance of acid catalysis on particle size, particle size distribution and required reaction time for TiO_2 synthesis with desired properties.

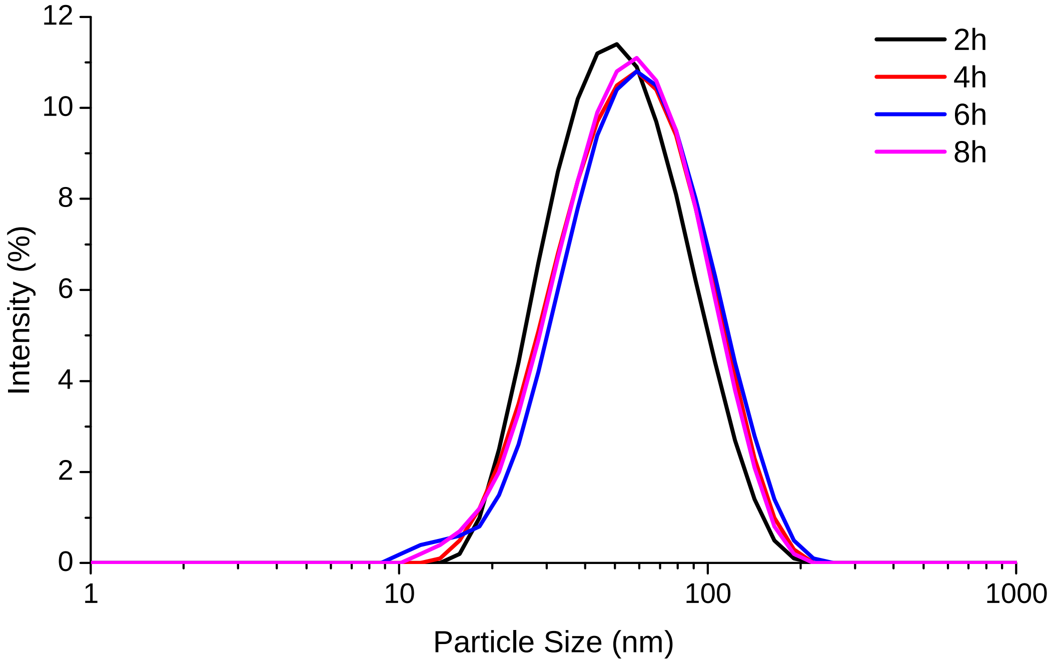


Figure 5.2 Change in particle size during synthesis reaction (Sample-TiO_2 sol, 0.18M N.A.)

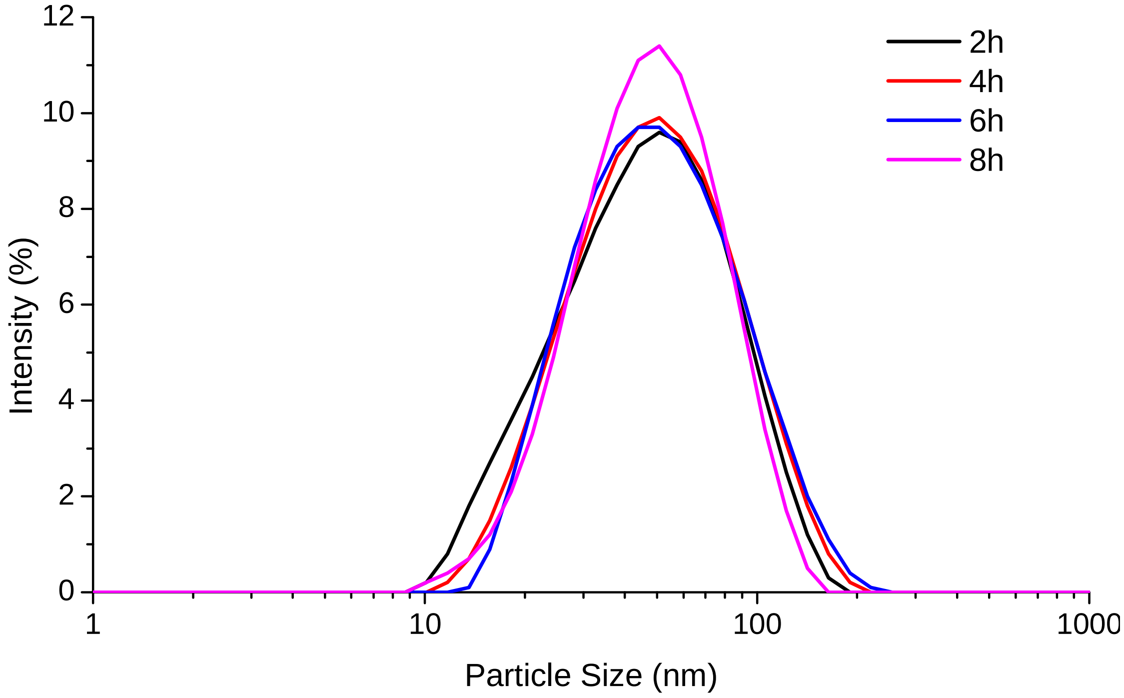


Figure 5.3 Change in particle size during synthesis reaction (Sample-TiO_2 sol, 0.24M N.A.)

5.1.2. pH dependence of TiO_2 Nanoparticles

Stability of TiO_2 nanoparticles in aqueous suspension is very crucial for applications that have long storage period before usage of synthesized material. Nanoparticles should be stable in aqueous suspension and also should preserve their stability for long term in order to maintain appropriate application conditions. Beside stability of the particles, as mentioned previously particle size is also very important for all application areas. For these reasons, pH dependence of particle size and stability of TiO_2 nanoparticles are investigated for full pH range.

Metal oxides nanoparticles in aqueous suspension generally have electrical charge due to the amphoteric dissociation of surface hydroxyl groups because of adsorption of H+/OH ions. The resultant surface charge of nanoparticles is pH dependent [58]. In acidic or basic media surface charges of nanoparticles are high and this surface charge results in strong repulsive force among nanoparticles. Therefore, probability of coalesce of particles decreases and so stable sols can be formed in acidic or basic media.

This study was done with sol-gel synthesized TiO_2 sol with initial particle size and pH 140 nm and 1.5 respectively. The pH was controlled by the addition of HNO_3 and NaOH solutions. As shown in Figure 5.4 the surface potential of TiO_2, which is shown with zeta potential value in the figure, increases when pH value moving away from neutral. Moreover, isoelectric point is measured between pH 5 and 6. This value is consistent with literature data that indicates the isoelectric point of TiO_2 varies within a pH range of 5–7 [17]. It can be clearly stated that pH range of applications of TiO_2 nanoparticle sols should be arranged as to be away from isoelectric range of particles.

Figure 5.5 shows the average size of TiO_2 particle as a function of pH value. As can be seen from the result, particle size increases significantly while pH approaches to isoelectric point pH range. At this range the sol became milky white and precipitation was observed. This is an expected result since probability of coalesce of particles is high due to low surface potential. Moreover, with the same logic it is expected that increasing pH value results in decrease in particle size. However, according to obtained results high surface charge in basic media could not disperse coagulated particles. Therefore, particles stay as coagulated even at very high pH range and surface potentials in basic media. Su et al. observed the same increase in particle size around isoelectric point of TiO_2 nanoparticles. On the other hand, particles with high surface potential in basic media have lower particle size but these sizes are higher than sizes in acidic media.

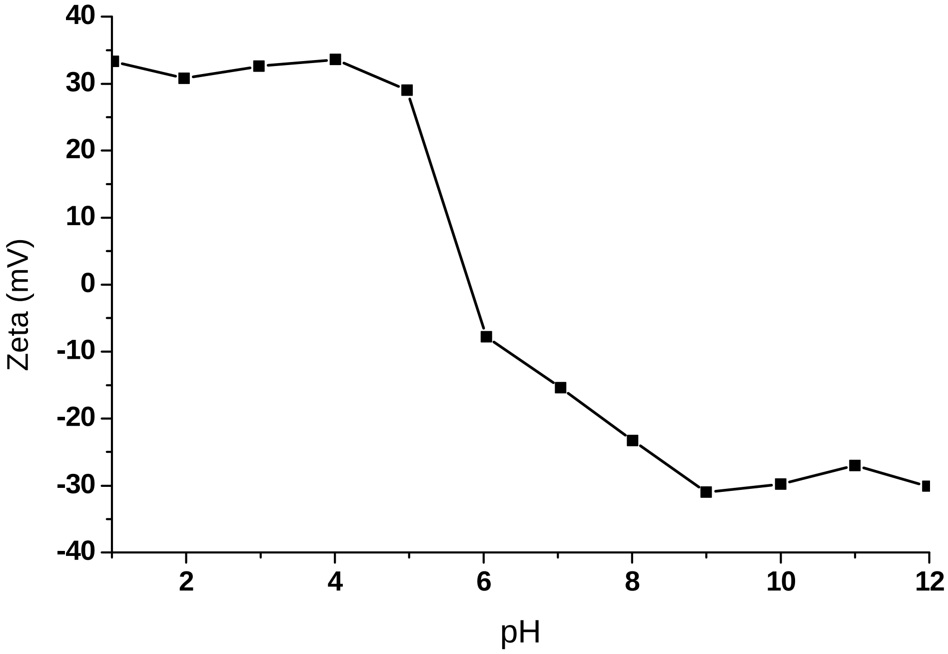


Figure 5.4 pH dependence of TiO_2 surface potentials

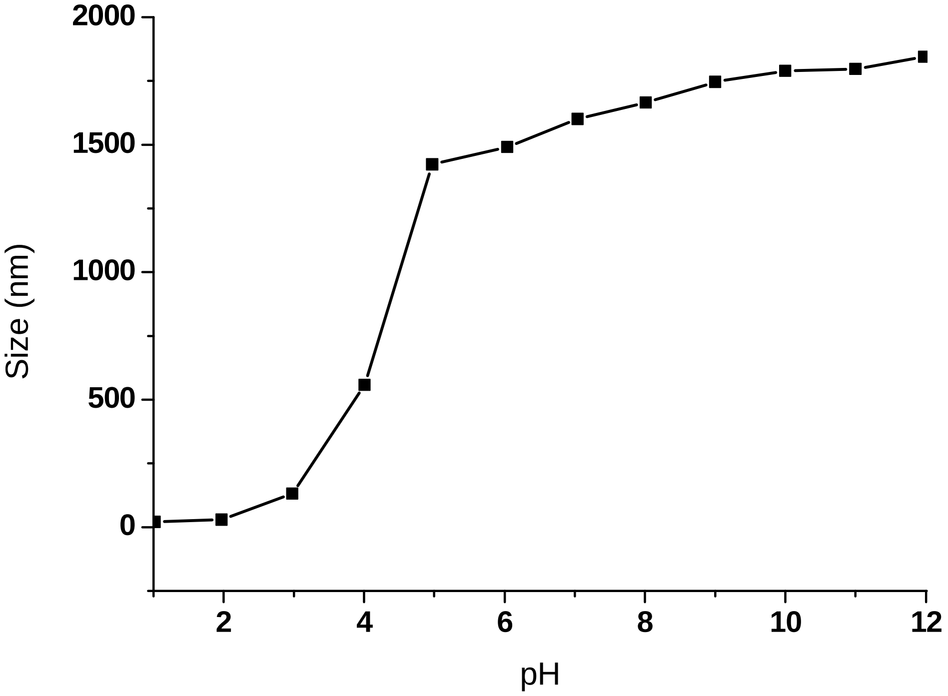


Figure 5.5 pH dependence TiO_2 particle size

5.1.3. Change in Particle Size over Time

As mentioned previously sol-gel synthesized TiO_2 nanoparticles can keep their stability in aqueous suspension for a period longer than six month and this stability is an important property of the product. In order to determine this property, sol samples were observed after synthesis process. During this investigation it is observed that a significant change in color of the sol samples take place. Color of the samples turns from white to transparent over time. Since color of the suspension sample is related with particle size, change in particle size and surface charge was investigated for Sample-TiO_2 sol, 0.12M N.A.

Figure 5.6 shows size change of TiO_2 nanoparticles in aqueous suspension. First day after synthesis particle size and polydispersity index (PDI) were around 70nm and 0.18 respectively. Particle size decreased to 44 nm within five days and to 34 nm in one month period. Moreover, after one month period sample had narrower size distribution with PDI value of 0.15.

On the contrary to particle size, surface charge of TiO_2 nanoparticles had stable trend around 32 mV zeta potential value as can be seen in Figure 5.7. Addition to zeta potential measurements, pH of the sample sol also was measured periodically. In these measurements only very small changes were observed and these changes were not significant to effect surface potential of the particles. Just after synthesis of nanoparticles have high zeta potential value which is not in the range of ±30mV. This means that particles can be pending in aqueous suspension and precipitation is not observed. Within one month period only slight increase was observed in surface charge of nanoparticles.

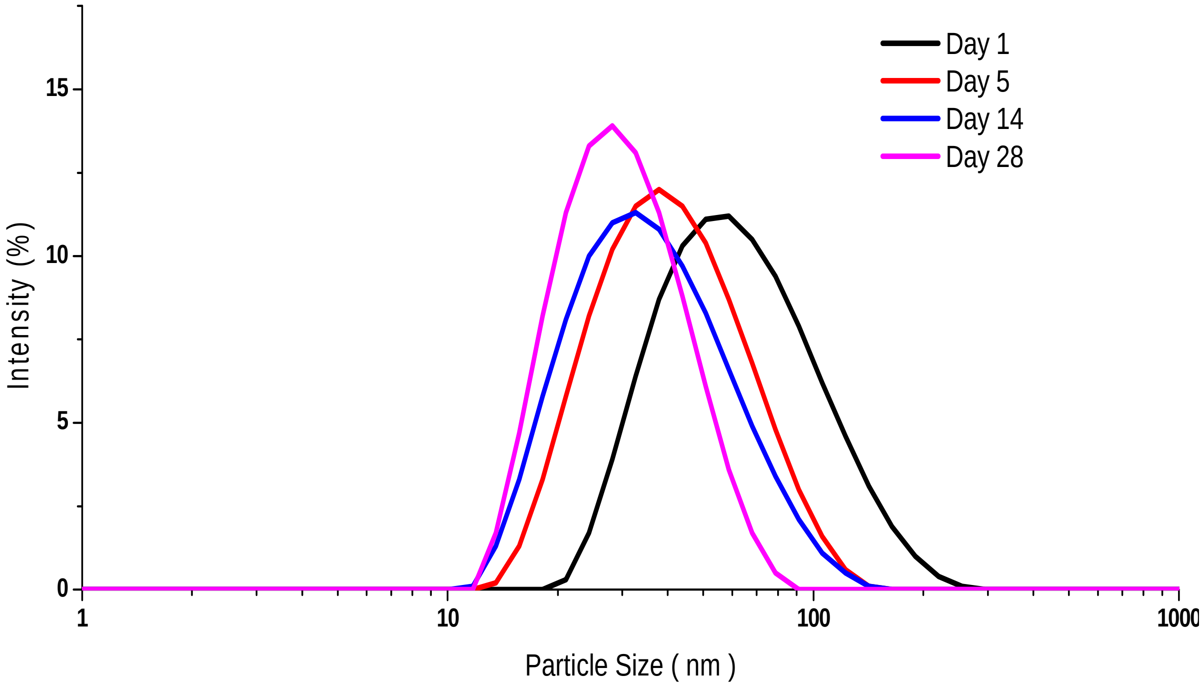


Figure 5.6 Change in particle size after synthesis (Sample-TiO_2 sol)

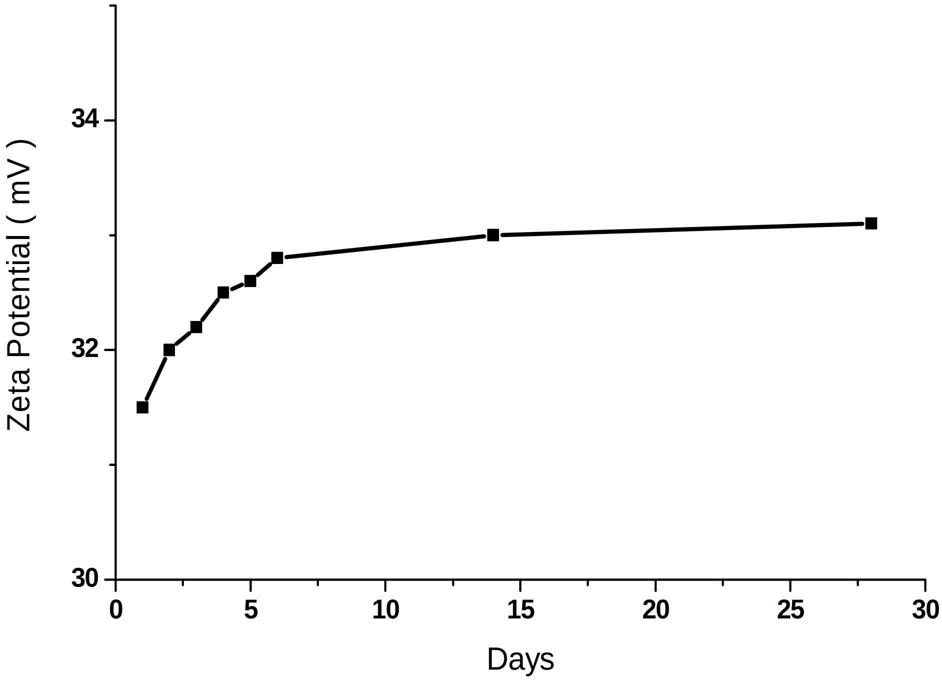


Figure 5.7 Change in zeta potential after synthesis (Sample-TiO_2 sol)

After observation of size change of TiO_2 particles in aqueous suspension over time, reasons for this change was investigated. Possible reason is thought as non complete reaction of isopropoxyl side groups of TTIP. In order to determine whether isopropoxyl groups stay with Ti atom or not, sample sols were characterized with ^{13}C NMR and the results were evaluated with characteristic peaks of C atom listed in Table 5.6.

Table 5.6 ^{13}C NMR peak identification

Species and resonating C (*C)	**δ (ppm)**
$\mathbf{Ti(OCH(^*CH_3)_2)_4}$	26
$\mathbf{Ti(O^*CH(CH_3)_2)_4}$	79
$\mathbf{^*CH_3COOH}$	20.5
$\mathbf{CH_3{}^*COOH}$	174
$\mathbf{^*CH_3COO-Ti}$	22-24
$\mathbf{CH_3{}^*COO-Ti}$	178
$\mathbf{(^*CH_3)_2CHOH}$	25
$\mathbf{(CH_3)_2{}^*CHOH}$	64

Firstly, ^{13}C NMR spectrum of pure TTIP was taken in order to be considered as standard for initial of the reaction. The spectrum is given in Figure 5.8. As in stated in literature signals of two different C atoms in TTIP were observed around 26 and 76 ppm [30].

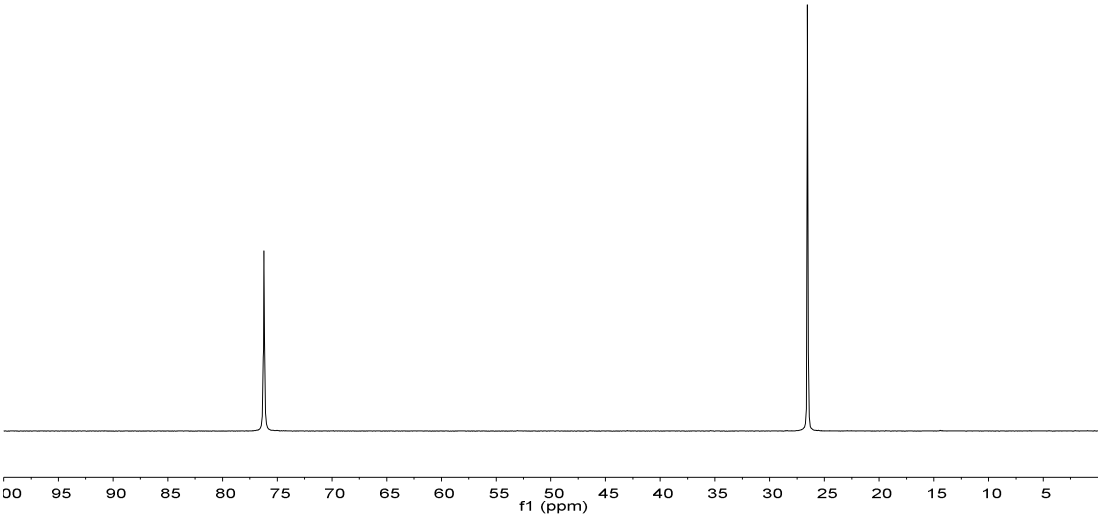


Figure 5.8 ^{13}C NMR Spectra of TTIP

Secondly, TiO_2 sol, Sample-TiO_2 sol, 0.12M N.A., was characterized with ^{13}C NMR and measurement was repeated 4 times to monitor changes in the sample within one week period. ^{13}C NMR spectra of the sample are given in Figure 5.9. Appearance of a band around 64 ppm with resonance of the central CH group indicates the release of isopropoxyl which is previously coordinated to Ti atom. The signals around 26 ppm correspond to the released isopropoxyl. On the other hand, CH_3 groups of isopropoxy bonded to Ti can have signal at very close ppm values. So, it is very difficult to distinguish these two signals. Additionally, the spectra have signals around 21 and 177 ppm which can belong to free acetic acid and acetate groups bonded to Ti atom. Small shifts of the signals in the spectra may change possible outcomes and comments of the results. However, it is very clear that there is no significant difference between spectra that correspond to measurements of different days.

With these results it is not possible to comment on changes in size of TiO_2 particles. These set of measurement were done following TiO_2 synthesis and acid catalyst amount is enough to have high reaction rates. In order to eliminate these effects, another set of measurement was performed with different reaction conditions.

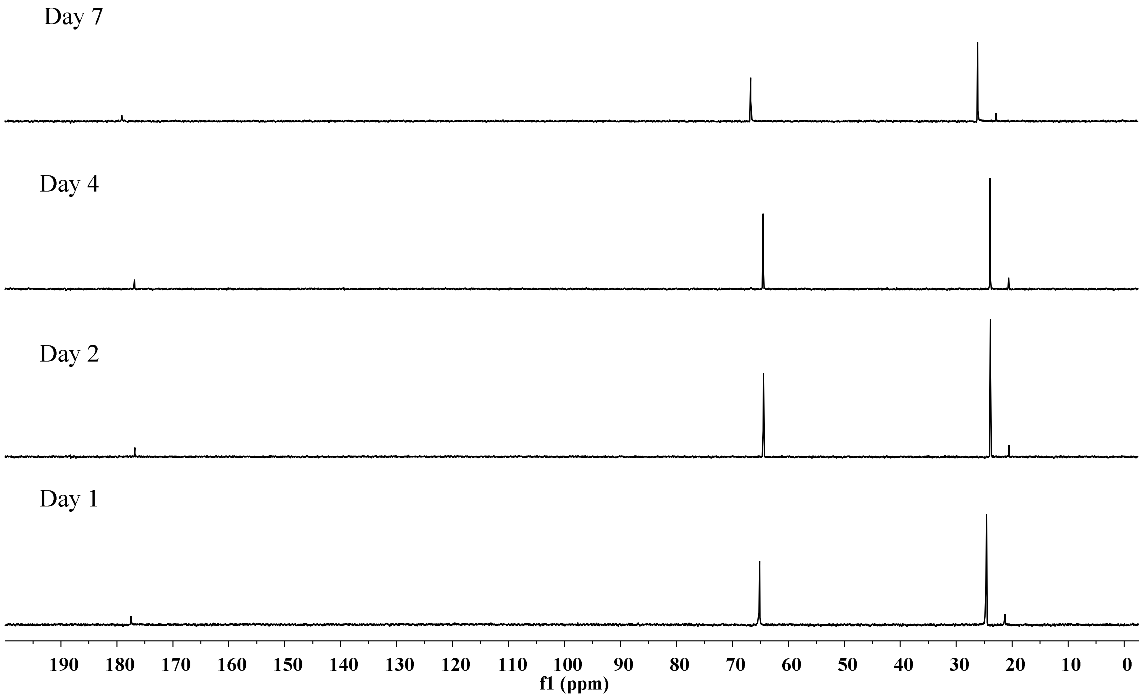


Figure 5.9 ^{13}C NMR spectra of Sample-TiO_2 sol, 0.12M N.A. monitoring one week period after synthesis of the sample

In new set of measurements Sample-TiO_2 sol which has lower amount of acid catalyst was used. By this way it is aimed that slower reaction leads to determine changes in ^{13}C NMR spectrum. Moreover, in order to be able to observe initial stage of the reaction was performed in NMR equipment by adjusting temperature of the reaction medium to desired value. It almost took 10 minutes to place the NMR tube full of prepared reaction mixture and start the measurement. In first 30 minutes of the reaction 6 measurements were taken with 5 minutes intervals. After 30 minutes, 6 more measurements were taken with 15 minutes intervals. Results are given in Figure 5.10 and Figure 5.11.

Very similar to results that are given in Figure 5.9, the spectra have signals around 25 and 64 ppm which corresponds to the released isopropoxyl group of TTIP. Additionally, the spectra have signals around 21 and 177 ppm which can belong to free acetic acid and acetate groups bonded to Ti atom. These signals are not significant in first minutes of the reaction but they become visible as time passes.

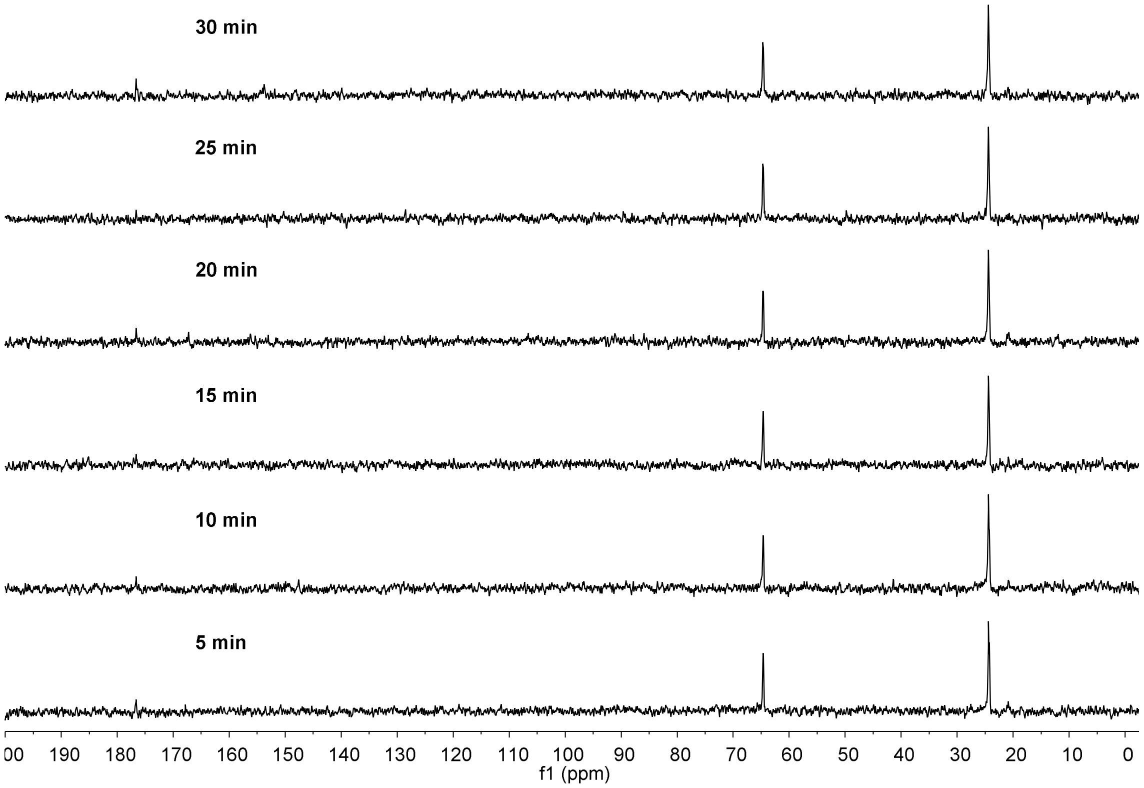


Figure 5.10 ^{13}C NMR spectra of Sample-TiO_2 sol monitoring first 40 minutes of synthesis reaction

Signals around 21 and 177 ppm become more significant after 30 minutes of reaction. Since there is an increase of the signals, these signals should indicate free acetic acid which is bonded Ti previously. This increase in free acetic acid signal indicates function of ligand agent, acetic acid, which previously binds to Ti and prevents undesired reactions and then release from Ti atom. On the other hand, there is no significant change in the signals even in the first 30 minutes of the reaction in which reaction is expected to take place. This means that hydrolysis reaction is very fast and time required for preparation and taking measurement too long to catch up the progress in the reaction. Furthermore, signals that belong to C atoms of related species are very close to each other and these close values make the spectra difficult to analyze.

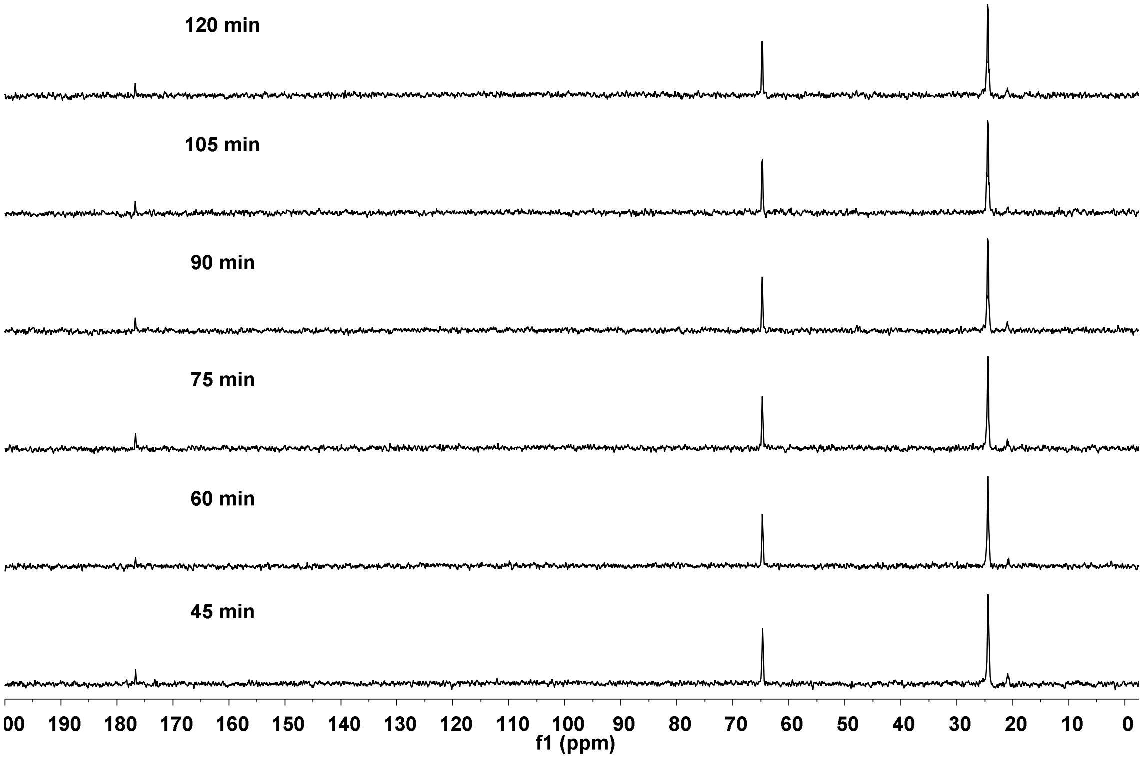


Figure 5.11 ^{13}C NMR spectra of Sample-TiO_2 sol monitoring synthesis reaction between 30 and 120 minutes

5.1.4. XRD Analysis

In order to determine crystal structure of synthesized particles, TiO_2 sols were dried and XRD measurement was done. XRD pattern of Sample-TiO_2 sol is given in Figure 5.12. Characteristic anatase peaks at 25.3, 37.8, 48.0 and 55.0 are observed in XRD result clearly. However, peaks are not sharp but broad. The reason of these broad peaks can be small size and incomplete crystal phase of the particles.

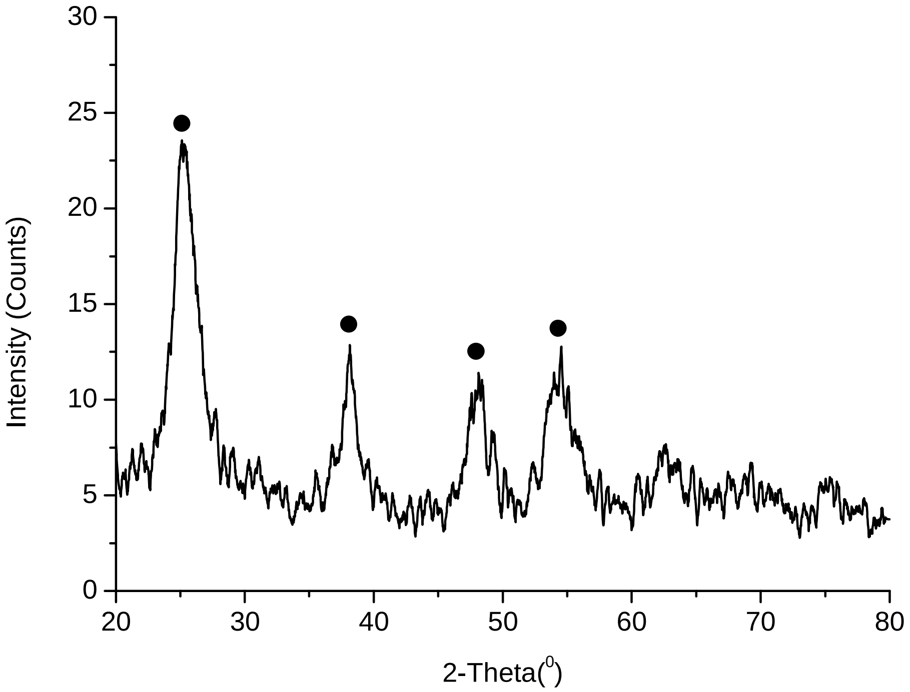


Figure 5.12 XRD pattern of Sample-TiO_2 sol (● indicates characteristic peaks of anatase phase)

Beside effect of water:TTIP molar ratio on particle size and surface potential of TiO_2 particles, its effect on crystal structure is also studied. XRD patterns of samples synthesized with water:TTIP ratio of 200, 300 and 400 are given in Figure 5.13. As can be from XRD patterns, all three samples have characteristic peaks of anatase crystal form of TiO_2 and they are very similar to each other. With this result it can be concluded that although water:TTIP molar ratio affects particle size and surface potential of the particles, it does not have important effect on crystal type of the particles.

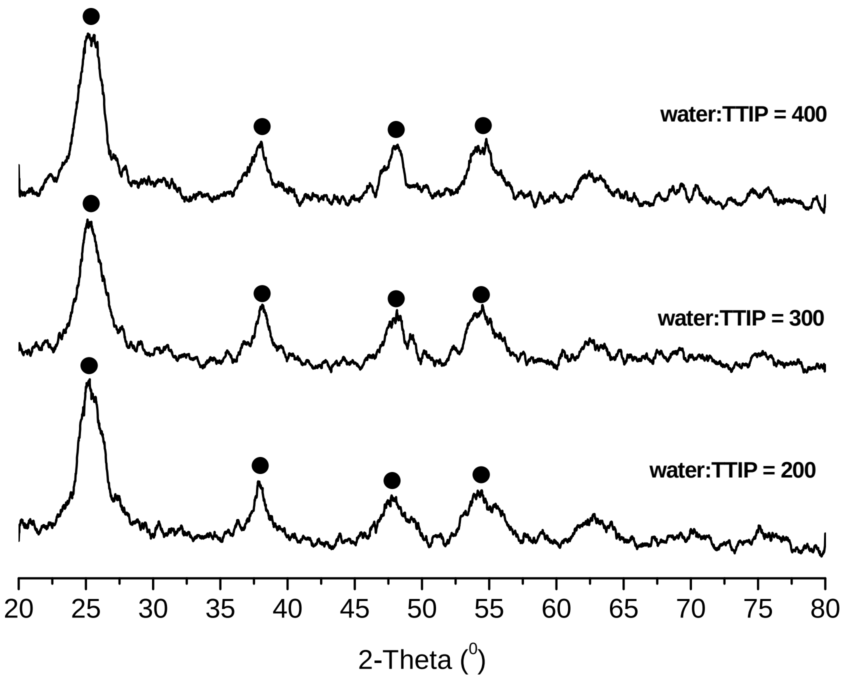


Figure 5.13 XRD patterns of samples with water:TTIP molar ratio of 200, 300 and 400 (● indicates characteristic peaks of anatase phase)

Additionally, effect of calcination temperature of dried TiO_2 particles on crystal structure was examined. XRD patterns of the TiO_2 samples after heat treatment at 400, 500, 600, 700 and 800^0C for 2 h are shown in Figure 5.14. Even non calcined TiO_2 sample exhibits peaks of anatase but the peaks are much more significant for calcined samples. As mentioned previously, with heat treatment phase transition from anatase to rutile phase takes place. However, the sample calcined at 400^0C still has characteristic anatase peaks and after 500^0C calcination process both indicates anatase peak at 25.3 and rutile peak at 27.7^0. Moreover, 600^0C calcinations temperature leads to increase in intensity of anatase peak which shows increase of particle size and increase in intensity of rutile peak which shows increase of rutile phase in the sample. For higher calcinations temperatures, 700^0C and 800^0C, main peak of anatase at 25.3^0 leaves its place to main rutile peak at 27.7^0. Additionally, another peak of rutile at 36^0 is also observed in these samples. These results show that anatase to rutile phase transition takes place between 500 and 600^0C. This conclusion also consists with STA results that indicate phase transition at similar temperatures.

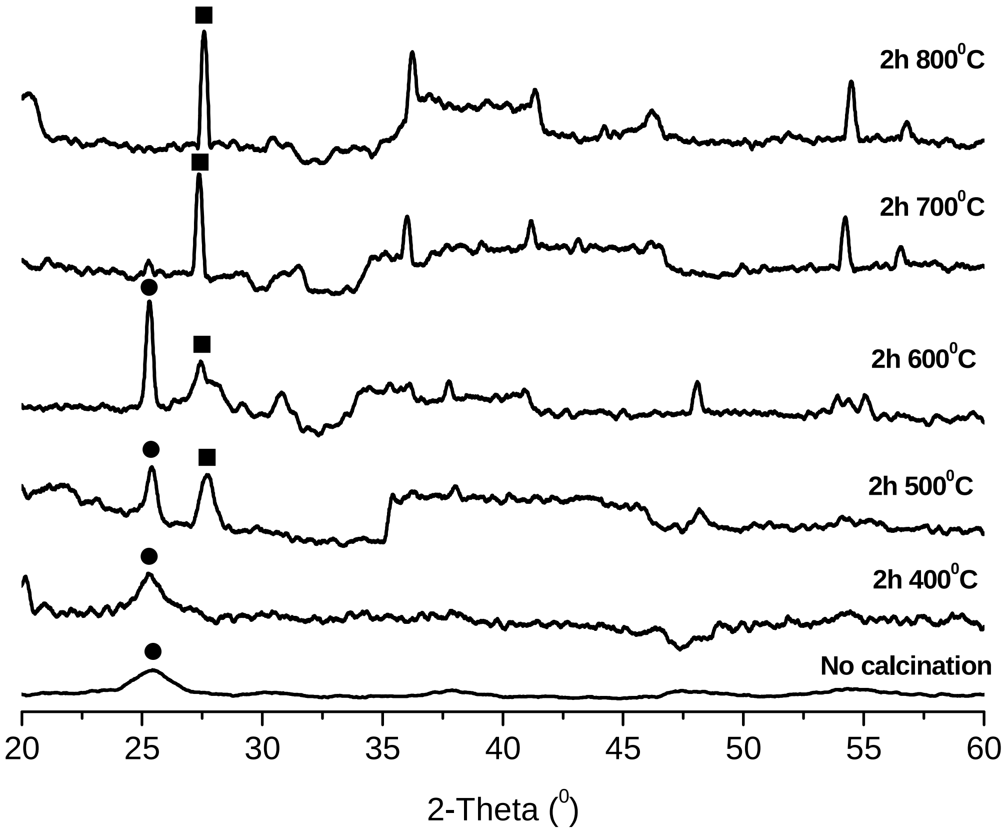


Figure 5.14 XRD patterns of TiO_2 samples (Sample-TiO_2 sol) with different calcination temperatures (● and ■ indicates main characteristic peaks of anatase and rutile phases respectively)

5.1.5. Thermal Analysis

The simultaneous TGA and DTA curves of TiO_2 powders after drying but without calcination are shown in Figure 5.15. There is almost no mass change up to 100^0C and at around 100^0C there is a significant endothermic peak which is related to mass loss of adsorbed water. Additionally, evaporation of acetic acid and nitric acid has effect on 15% mass loss up to 400^0C. Small endothermic peak around 350^0C indicates crystallization peak of amorphous TiO_2 particles to anatase phase according to Viana et al. [59]. No weight loss is observed above 400^0C related to the other DTA events. However, very wide exothermic peak is observed starting from 550^0C to 750^0C. This important peak is related to phase transition of TiO_2 particles from anatase to rutile crystal phase [59-60].

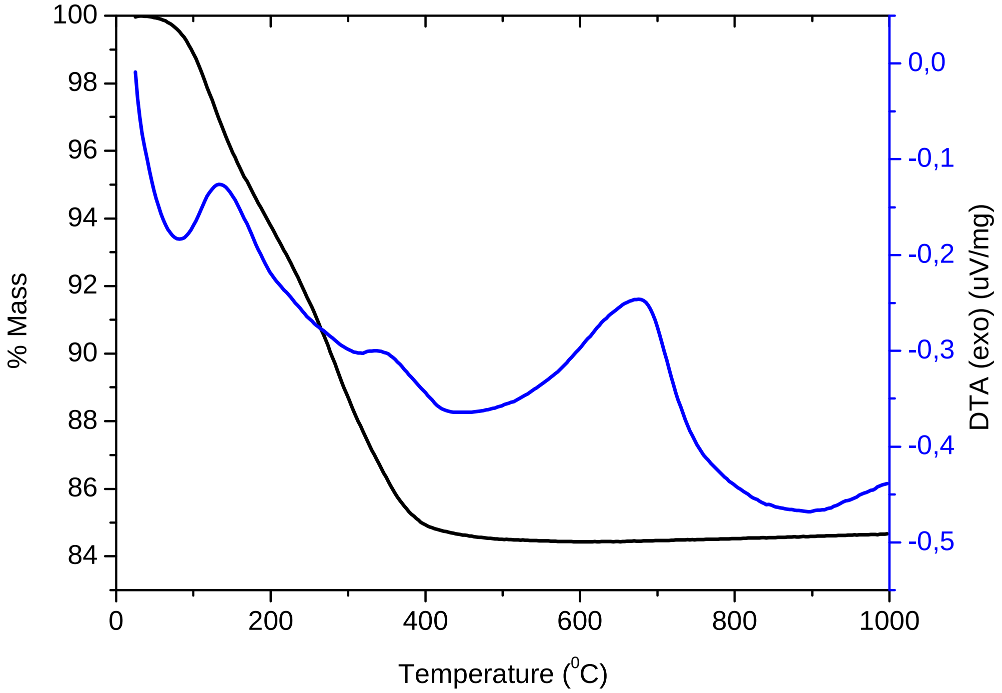


Figure 5.15 TGA curve of TiO_2 nanoparticle (Sample-TiO_2 sol)

Figure 5.16 shows TGA curves of TiO_2 samples calcined at different temperatures. The difference between non calcined and calcined samples is very clear. Non calcined sample has significant mass loss due to adsorbed water and combustion of organic residues remained on TiO_2 particles. The sample calcined at 400^0C has almost 4% mass loss mostly in the region of 300-600^0C which corresponds to mass loss due to organic content. However, the samples calcined at 600 and 800^0C have negligible mass loss that means there is no absorbed water and organic residue within the sample.

Besides TGA curves, DTA curves of the samples are given in Figure 5.17. As can be seen from the results, there is no significant peak in energy curve and this means that there is no energy chance during heating in 600 and 800^0C curves. This means adsorbed water and combustion of organic residues remained as concluded with TGA results. Moreover, there is no crystallization and phase transition peak since the crystal type have already turned to rutile. On the other hand, there is a broad peak in the curve of 400^0C calcined sample which could not be identified.

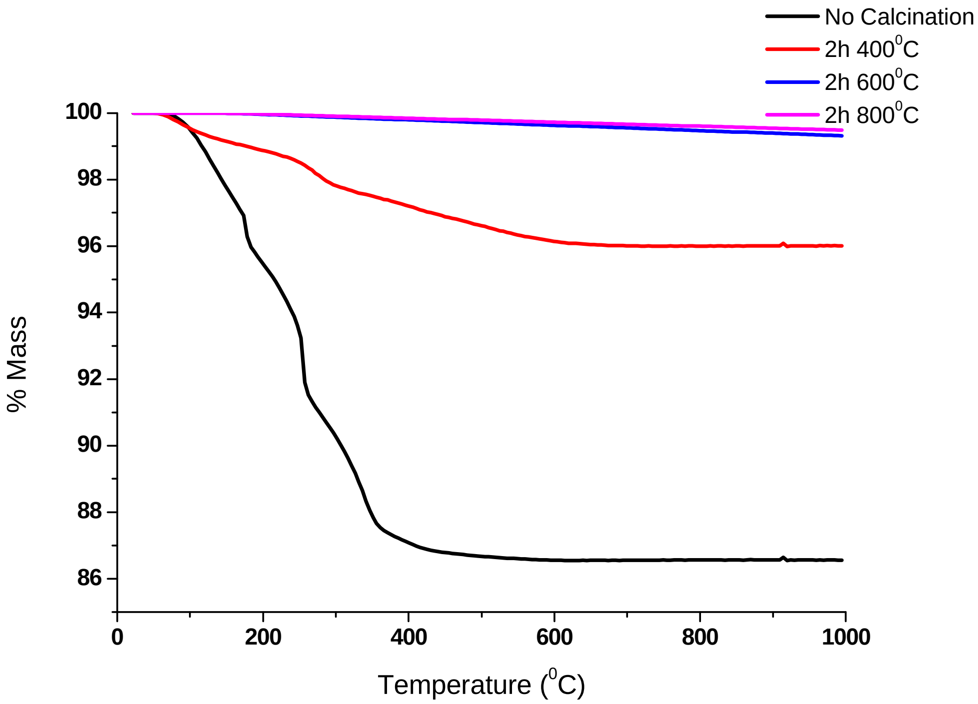


Figure 5.16 TGA curve of TiO_2 nanoparticle (Sample-TiO_2 sol) with different calcination temperatures

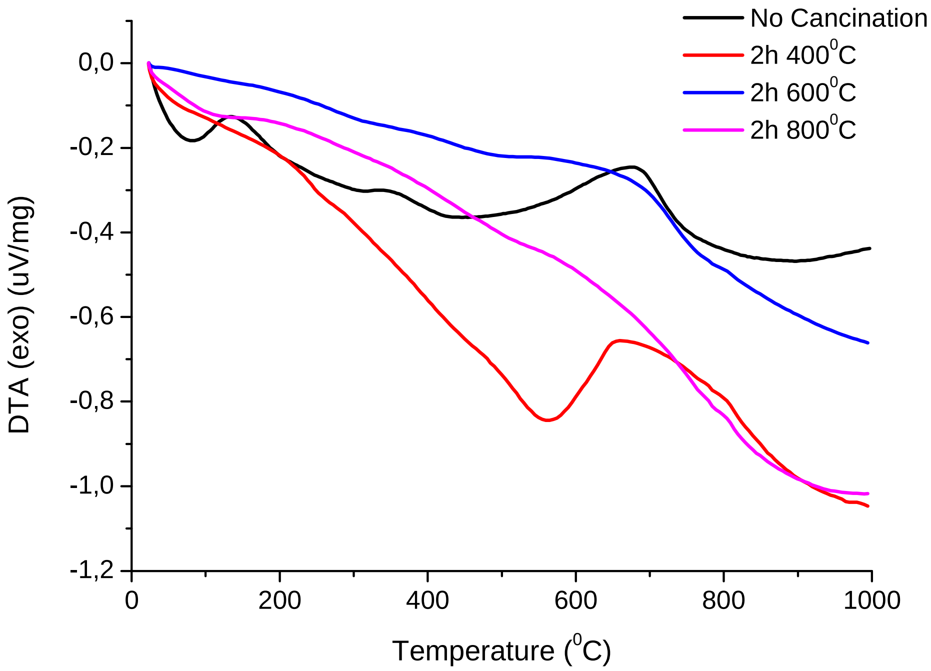


Figure 5.17 DTA curve of TiO_2 nanoparticle (Sample-TiO_2 sol) with different calcination temperatures

5.1.6. Photocatalytic activity of TiO_2 nanoparticles

Photocatalytic activity of TiO_2 nanoparticles is not in the scope of this thesis work. However, in order to obtain general information about photocatalytic activity of synthesized particles, degradation of methylene blue sample was observed under UV irradiation. This experiment was done with four sol samples that have different particle sizes and results are given in Figure 5.18.

As can be seen from the graph, for all particle sizes there is decrease in concentration of methylene blue compared to initial concentration after 2 hours UV irradiation. Degradation of methylene blue results in color change of the sample, which can be clearly seen by eyes, and this change was determined by UV spectrometer.

The lowest color change and so lowest photocatalytic activity belongs to the sample with 75nm particle size. With decrease in particle size, photocatalytic activity of particles increases. On the other hand, further decrease in particle size affects catalytic activity negatively because of confinement of charge carriers (electrons and holes) in a potential well at low particle sizes. This confinement results in higher band gaps of particles and so decrease in photocatalytic activity of the particles. As shown in the results, an optimum particle size, which is 43nm particle in our study, can be achieved with balancing contribution from high surface area and negative effects from band gap increase.

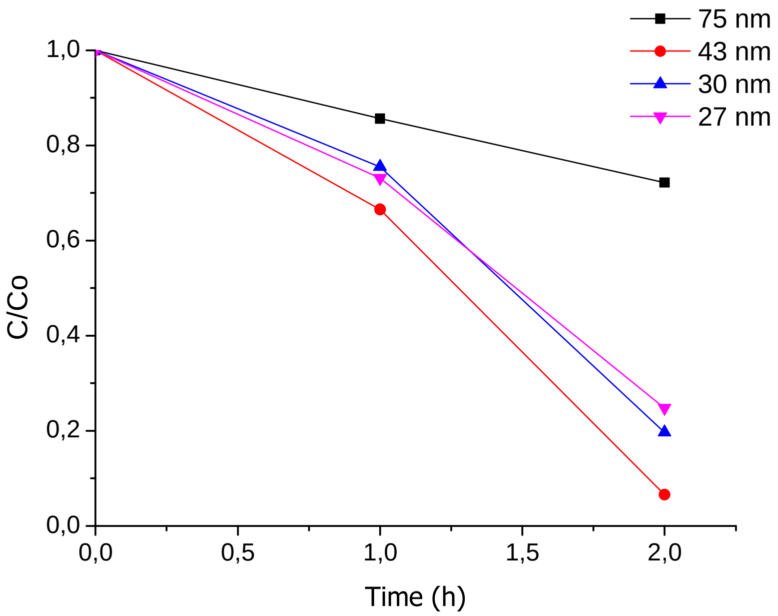


Figure 5.18 Photocatalytic activity test results of TiO_2 nanoparticles

5.2. Surface Modification of TiO_2 Nanoparticles

Surfaces of TiO_2 nanoparticles were modified with APTES and modified particles are characterized to determine amount of surface modification. For characterizations of surface modified TiO_2 nanoparticles FTIR, STA and Elemental Analysis were used.

As explained previously surface modification of TiO_2 nanoparticles are used in many different applications. In all these applications amount of surface modifier on the surface is very important since surface modification has effect on performance of the material. To determine effects of experimental parameters on surface modification, experiments were performed with changing modifier concentration, TiO_2 concentration and reaction time.

Amino silane concentration in the system is an important parameter that has direct effect on surface modification. Concentration was changed between 0.5 and 2 w which indicates weight ratio of amino silane to TiO_2 particles. TGA results of trials are given in Figure 5.19. Difference between modified and unmodified samples is very clear. Unmodified TiO_2 sample has significant mass loss up to 400^0C due to elimination of water. As can be seen from the figure, for modified nanoparticles there is a loss up to 300^0C which is due to desorption of water. However, the significant decrease in mass starts around 350^0C which can be attributed to thermal decomposition of aminosilane chains. Additionally, increasing concentration from 0.5 to 1 w does not have significant effect on amount of surface modification. On the other hand, when concentration further increases to 1.5 w; mass change due to decomposition of amino silane increases. Similar to relation between 0.5 and 1 w, there is significant increase in surface modification when concentration increases from 1.5 to 2w. According to these results, 0.5 w or 1.5 w amino silane concentrations can be used according to desired surface modification level.

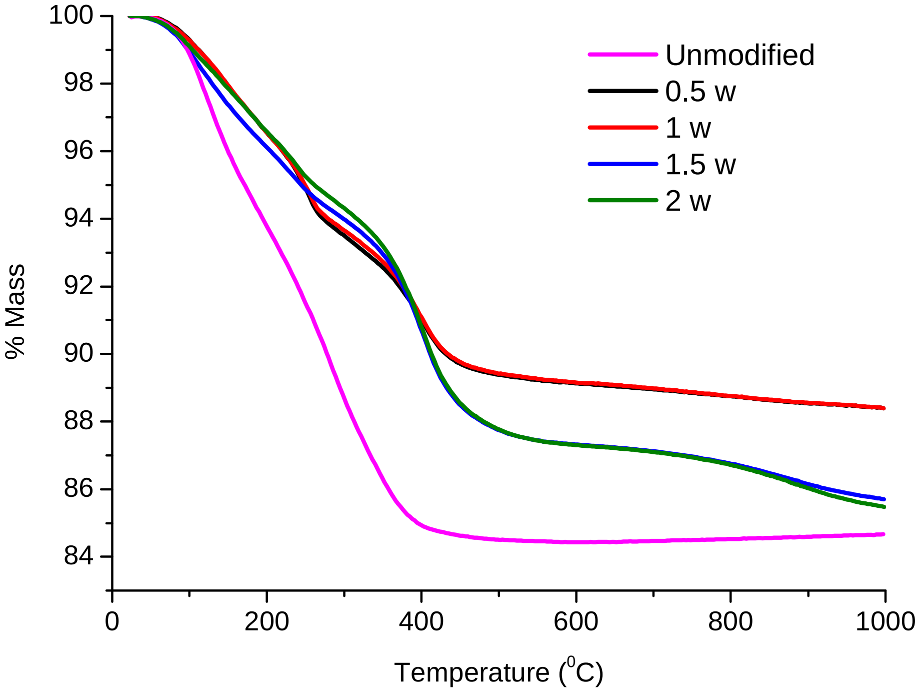


Figure 5.19 TGA curve of modified TiO_2 nanoparticles (W-APTES, 6h, 0.01 g/ml, w=AS/TiO_2)

TGA results of surface modification were supported with Elemental Analysis and results are listed in Table 5.7. Nitrogen and Carbon contents of the samples coincide with TGA results. Unmodified TiO_2 sample has low amount of Nitrogen and Carbon due to usage of nitric acid as acid catalyst and organic content of alkoxide precursor. As listed below, there is important increase in Carbon content of the samples after surface modification. On the other hand, Carbon content of 0.5 and 1 w, 1.5 and 2 w are very close to each other. Additionally, as in TGA results a significant increase is observed in amount of surface modification when concentration increases from 1 to 1.5 w. these results shows that TGA gives reliable results for surface modification amount.

Table 5.7 Effect of amino silane concentration on Nitrogen and Carbon content of modified TiO_2 samples

Sample Name	%N	%C
Pure TiO_2	1.10	1.04
W-APTES, 0.5w, 6h, 0.01 g/ml	0.97	2.92
W-APTES, 1w, 6h, 0.01 g/ml	1.07	3.30
W-APTES, 1.5w, 6h, 0.01 g/ml	1.74	5.04
W-APTES, 2w, 6h, 0.01 g/ml	1.79	5.24

Another parameter that is investigated in this work is TiO_2 concentration in aqueous solution. TiO_2 concentration was changed between 0.0075 g/ml and 0.015 g/ml. TGA curves of the samples are given in Figure 5.20. Increase in TiO_2 concentration in the system results in more efficient surface modification. When TiO_2 concentration increases, possibility of reaction between surface OH group and alkoxy group of modifier increases. Otherwise, modifier directly contacts with water and hydrolysis of alkoxy group occurs. This decreases surface modification. On the other hand, if TiO_2 concentration is further increased, surface modification decreases. The reason of this decrease may be insufficient amount of modifier.

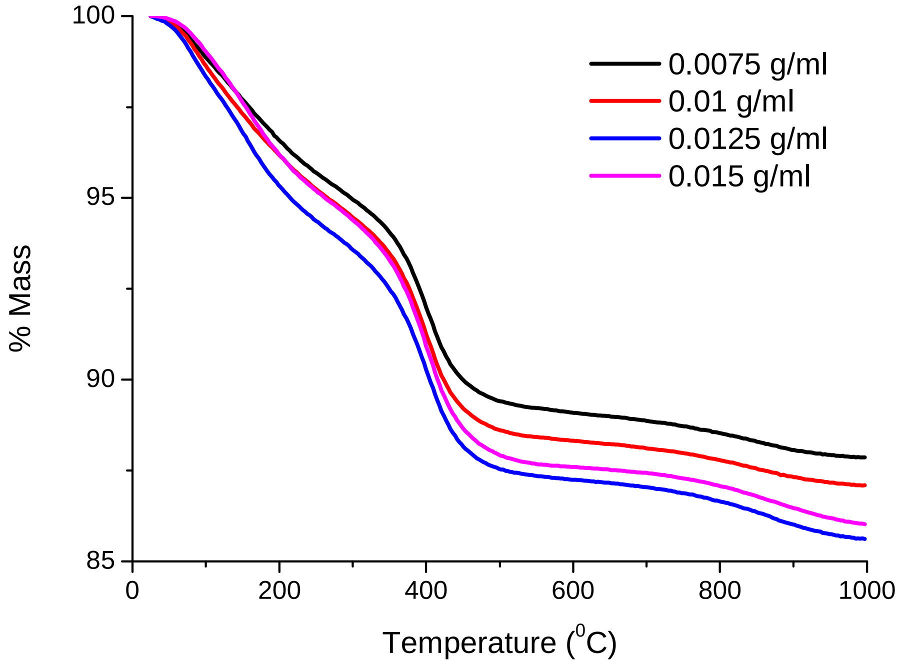


Figure 5.20 TGA curve of modified TiO_2 nanoparticles (W-APTES, 1.5w, 3h)

The last investigated parameter is reaction time. Reaction time between modifier and TiO_2 particles was changed between 1 hour and 6 hours. TGA results are shown in Figure 5.21. When reaction time increases from 1 hour to 3 hours, mass loss and so surface modification amount increases. On the contrary, surface modification with 6 hours reaction results in lower surface modification compared to 3 hour reaction. This is an interesting result and it was repeated three times to verify the result. Longer reaction time may somehow affect the bond between modifier and particle which results in lower coverage of modifier on the surface of the particle.

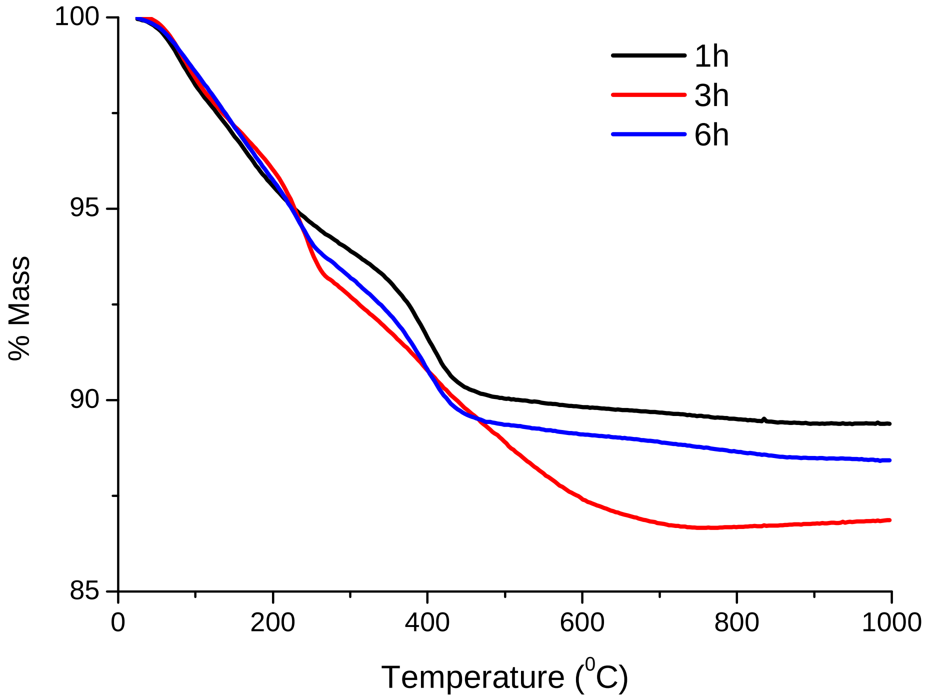


Figure 5.21 TGA curve of modified TiO_2 nanoparticles (W-APTES, 1w, 0.01 g/ml)

FTIR spectrum of unmodified and modified TiO_2 nanoparticles is given in Figure 5.22. In spectrum of unmodified TiO_2, the over saturated peak below 700 cm^{-1} is assigned to Ti–O and Ti–O–Ti bonding of titania [61]. The weak peak at 1300 cm^{-1} in unmodified sample can be considered as carbonate contamination. Although according to STA results it is known that there are significant amount of physisorbed water in unmodified sample, there is no distinct peak of adsorbed water which should be between 3500 and 3000 cm^{-1} as a broad peak. On the other hand, all modified samples have this adsorbed water peak in their spectra.

It is very clear that after surface modification with amino silanes additional peaks appear which belong to grafted amino silane. Both of the samples which are modified with different concentrations have the peak around 1560 cm^{-1} which belongs bending of $–NH_2$ at the functional amino group. The small peaks around 2950 cm^{-1} are proofs that the nanoparticle surface is modified by an organic modifier. Since these peaks shows the existence of $–CH_2–$. When 1 and 2 w samples are compared a slight increase in $–CH_2–$ signal can be seen. This indicates that with higher amine concentration amount of grafting amino silane is increasing as observed in TGA results also. According to these spectra, it is clear that the surface of TiO_2 nanoparticles is modified with amino silanes.

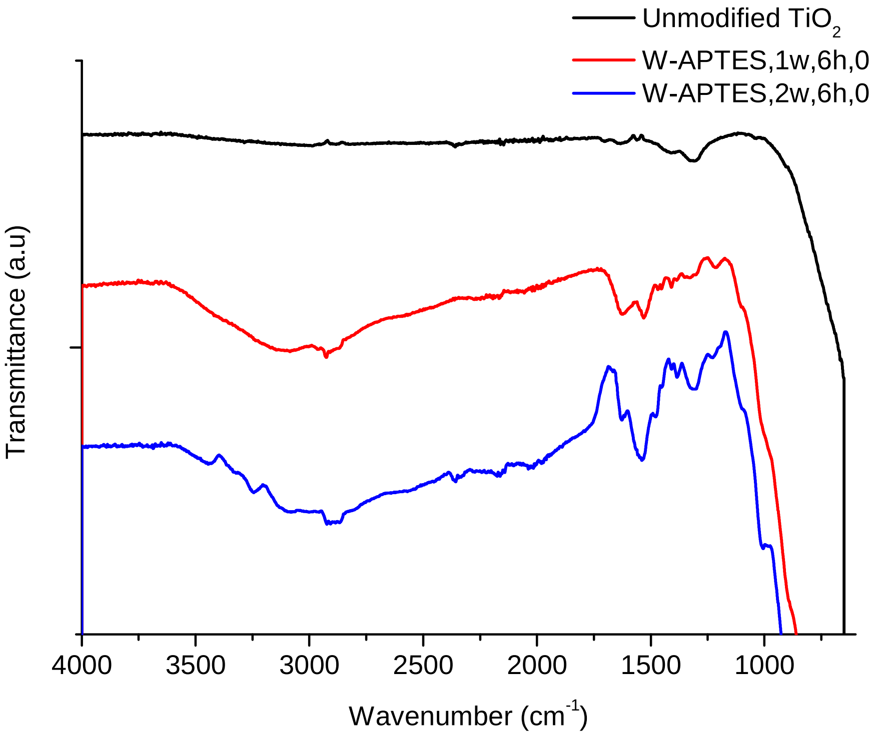


Figure 5.22 FTIR spectrum of unmodified and modified TiO_2 samples

CHAPTER 6

6. Conclusion

The main aim of the study is to ensure controlled synthesis of TiO_2 nanoparticles and this aim was achieved by simplified and cost effective sol-gel method. Effects of synthesis conditions on product properties were investigated by an experimental set which includes trials with different synthesis parameters. These parameters are water:precursor molar ratio, amount of acid catalyst, amount of chelating agent, reaction temperature and reaction time.

- Applied experimental method was very successful, simple, easy to apply larger scales and effective to obtain small and stable particles. Firstly, there is no need to have additional steps to remove residual components. Additionally, elimination of alcohol usage as a solvent results in cost effective and one stage process. Furthermore, production can be done with simple and inexpensive equipments and TiO_2 sol product can be obtained in relatively short reaction periods.

- Increasing values of all reaction parameters result in better product qualities with small particle size and higher surface potential. Within these parameters amount of acid catalyst is the most effective parameter and it is not possible to obtain particles without acid catalyst. Water:precursor molar ratio and amount of chelating agent have significant effects especially on particle size. On the other hand, effects of reaction temperature and reaction time are smaller compared to other parameters. Particles with size of 20nm and 35mV zeta potential value can be obtained with this method by arranging optimum reaction parameters.

- Isoelectric point of TiO_2 sols was measured between pH 5 and 6. Lower and higher pH ranges are suitable for applications of the product. Additionally, lower ph values should be sustained in order to have smaller particle sizes.

- One of the interesting results that was observed in this work is significant change in particle size during resting of the sol sample after synthesis reaction. Particle size changed from 70nm to 35nm within one month period. In order to examine progress of reaction and understand this particle size change C^{13} NMR was used and changes in the sample within one week were monitored. However, any significant data could not be obtained since hydrolysis reaction of precursor is very fast. On the other hand, there is no significant change in pH value and surface potential of particles. In order to understand this change, further studies are needed.

- With applied experimental method anatase crystal particles were obtained without any calcinations process. When samples were treated at high temperatures phase transition from anatase to rutile crystal phase was determined around 500^0C. Furthermore, it is determined with XRD measurements that water:precursor molar ratio do not have effect on crystal structure of the particles.

Another aim of this project is to ensure conditions for effective surface modification. Aminopropyl triethoxysilane was used as modifier and modifier concentration, TiO_2 concentration and reaction time were investigated.

- Increasing concentration of modifier has significant effect up to certain values, after certain concentration amount of grafted amino silane was not affected. When TiO_2 concentration increases, grafted organic material increases due to higher reaction possibility of surface OH groups and alkoxy group of modifier. Furthermore, longer reaction time results in higher coverage of modifier on the surface of the particle.

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