An Introduction to Nanomaterials, Sol-Gel Chemistry with
Special Reference to Titania Based Systems and Catalytic /
Photocatalytic / Functional Applications

1.1 An Overview on Nanomaterials

Nanostructured materials have seen an explosion of scientific and industrial interest over the last few years. Nanostructured microstructures have been obtained for ceramic, metallic, diamond, semi conducting, polymer and composite materials. The different forms in which these materials may appear include dry powders, liquid dispersions, coatings, films and bulk solids.

Increased interest in nanomaterials is a result of the unique properties that can be obtained, and the exciting applications that result from these properties. Enhanced electrical, mechanical, magnetic and optical properties have been reported for these materials.

Nanocrystalline materials are three-dimensional solids composed of nanometer sized grains, or crystallites (building blocks). Because of their unique structure, which is characterized by ultrafine grains and a rather high density of crystal lattice defects, these materials have extraordinary
fundamental properties that could be exploited to make next-generation super strong metals, ductile ceramics and wear-free materials. Nanostructured materials have a microstructure, the characteristic length of which is on the order of a few (typically 1-100) nanometers and therefore may be in or far away from thermodynamic equilibrium. Nanostructured materials consisting of nanometer-sized crystallites (e.g., of Au or NaCl) with different crystallographic orientations and/or chemical compositions are far away from thermodynamic equilibrium, while those synthesized by supramolecular chemistry follows thermodynamic equilibrium. The properties of nanomaterials deviate from those of single crystals (or coarse grained polycrystals) and/or glasses with the same average chemical composition. This deviation results from the reduced size and/or dimensionality of the nanometer sized crystallites as well as from the numerous interphases between adjacent crystallites. The reduced size in the nanometric range also characterizes the material to transmit visible light considerably. This feature helps the nanomaterials to act as transparent envelopes over various substrates without affecting their aesthetic/original look. Besides, the extremely high surface to volume ratio possessed by the nanomaterials makes them highly energetic in terms of surface energy, which in turn let the surface to undergo suitable reactions to reduce its surface energy. This possibility can be exploited by using the nanomaterials in catalysis/photocatalysis.
1.2 \textit{Titanium Dioxide}

Titanium oxide has been known for many years as a constituent of naturally occurring mineral ilmenite (FeO.TiO$_2$). Extraction of titanium oxide from the mineral is a chemical process followed through a sulphate route or a chloride route.\textsuperscript{6} Many other processes such as plasma decomposition and direct reduction have also been reported.\textsuperscript{7-10} Presently titanium oxide is well recognized as a valuable material with application as a white pigment in paints,\textsuperscript{11-13} as filler in paper,\textsuperscript{14} textiles and in rubber/plastics.\textsuperscript{15} Applications of titania have further been extended to active as well as passive coatings for electro-optical,\textsuperscript{16-18} optical,\textsuperscript{19-21} electronic\textsuperscript{22} and structural applications.\textsuperscript{23} Titanium dioxide is used in heterogeneous catalysis,\textsuperscript{24-26} as a photocatalyst,\textsuperscript{27-32} in solar cells for the production of hydrogen and electric energy,\textsuperscript{33-39} as gas\textsuperscript{40-41} and/or bio sensor,\textsuperscript{42} as a corrosion-protective coating,\textsuperscript{43-48} as an optical coating,\textsuperscript{49-54} in ceramics, and in electric devices such as varistors.\textsuperscript{55} It is important in earth sciences, plays a role in the biocompatibility of bone implants,\textsuperscript{56-58} is being discussed as a gate insulator for the new generation of MOSFETS\textsuperscript{59} and as a spacer material in magnetic spin-valve systems, and finds applications in nanostructured form in Li-based batteries and electrochromic devices.\textsuperscript{60-62}

Titanium oxide has attractive properties. It has a quite high refractive index (~2.4),\textsuperscript{63} that favour in the field of passive optical coatings\textsuperscript{19-21} and the wide band gap (~3.2 eV) combined with the high UV absorption could be exploited in the field of optically active coatings.\textsuperscript{63} Its photoactive potential and photocatalytic activity are being exploited for practical applications such as
the photocleavage of water, 32,64-67 photocatalytic decomposition of organics, 68-82 and in anti-fogging as well as self-cleaning coatings. 83-85 Further, it finds use in microelectronics 86-87, wastewater purification, 88-89 inorganic membranes 90-95 and as catalyst support. 96 Titania is also a potential ceramic sensor element. 97

Titania has been found to exist in three forms, anatase (tetragonal, D_{4h}^{19}-I_4/mcm, \( a=b=3.782 \, \text{Å}, \ c=9.502 \, \text{Å} \)), rutile (tetragonal, D_{4h}^{14}-P4_2/mnm, \( a=b=4.584 \, \text{Å}, \ c=2.953 \, \text{Å} \)) and brookite (rhombohedral, D_{2h}^{15}-Pbca, \( a=5.436 \, \text{Å}, \ b=9.166 \, \text{Å}, \ c=5.135 \, \text{Å} \)). 98 Anatase and rutile are in tetragonal structure and brookite is orthorhombic. In all the three TiO₂ structures, the stacking of the octahedra results in three-fold coordinated oxygen atoms. 100 Thermodynamically, rutile structure is the stable one. While the rutile and anatase structure have many similarities they also differ in a variety of ways. In both structures, Ti atoms (formally in a +4 oxidation state) are coordinated to six oxygen atoms (formally O²⁻), and the O atoms are linked to three Ti atoms. The octahedron of anatase is somewhat more distorted than that of rutile. The mass density of the anatase phase is lower, and the band gap of anatase is somewhat wider, which affects the photocatalytic activity. 101-102 The nature of chemical bonds in the three titanium oxides studied through ab initio cluster model approach revealed that there is an increasing covalence in TiO, Ti₂O₃ and TiO₂. TiO can nearly be described as an ionic compound, and TiO₂ can nearly be described as covalent. 103
Brookite has an orthorhombic crystal structure and spontaneously transforms to rutile at \(-750^\circ C\).\(^{104\text{-}105}\) Its mechanical properties are very similar to those of rutile, but it is the least common of the three phases and is rarely used commercially. In all the three crystalline forms each of Ti\(^{4+}\) ions are surrounded by an irregular octahedron of oxide ions; but the number of edges shared by the octahedron increases from two in rutile to three in brookite and to four in anatase. Both in rutile and anatase the six oxide ions that surround the Ti\(^{4+}\) ions can be grouped into two. The two oxygen atoms are farthest from Ti\(^{4+}\) and the other four oxide ions are relatively closer to Ti\(^{4+}\). In rutile these distances are 2.01Å and 1.92Å respectively and in anatase they are 1.95Å and 1.91Å (Figure 1). In case of brookite the farthest oxide ions are the only ones, which are equidistant from Ti\(^{4+}\) ions. At room temperature titania exists in the anatase phase and at high temperature it exists as rutile. The anatase to rutile transformation is a metastable to thermodynamically stable phase transformation and therefore there is no unique phase transformation temperature as in the case of equilibrium reversible transformation.\(^{106}\) Anatase transforms irreversibly and exothermically to rutile in the temperature range 600-800\(^\circ\)C.\(^{107}\)

Different crystalline forms of titania are provided in Figures 1a-c. Anatase has a tetragonal crystal structure in which the Ti-O octahedron shares four corners, as shown in Figure 1a.\(^{108}\) Rutile has a crystal structure similar to that of anatase, with the exception that the octahedra share four edges instead of four corners. This leads to the formation of chains, which are subsequently
arranged in four-fold symmetry as shown in Figure 1b. A comparison of Figures 1 and 2 shows that the rutile structure is more densely packed than anatase. As a point of reference, the densities of the anatase and rutile phases are known to be 3.87 \text{ g/cm}^3 and 4.24 \text{ g/cm}^3 respectively. Typical properties of the major two crystal forms of titania are provided in Table 1.

The current research trend to synthesize, characterize, and investigate nanomaterials is also being extended to titanium oxide. This material lends itself quite well to building tiny structures in all sorts of sizes and shapes. Such nano-TiO_2 is typically produced by sol-gel process, where a titanium alkoxide or halide (TiCl_4, TiF_4) is hydrolysed, often in presence of a template such as nano-spheres, nano-rods or anodic porous alumina, but other techniques have been used as well.

Titanium dioxide has attracted lot of interest from both theoretical and practical point of view as an attractive material for metallic oxide semiconductors. The choice of TiO_2 in the present work was based on its importance in environmental purification and treatment of water, since pollution of water and air is a major concern in the present world. Therefore in the present thesis a systematic study of the synthesis and characterization of photoactive TiO_2 is presented and the study was extended by analyzing the effect of addition of dopants on the photoactivity of titania. Further, TiO_2 films were fabricated out of the various compositions prepared and the photoactivity of the films was analyzed. Finally, the preparation – property correlation is drawn with the help of available experimental results.
<table>
<thead>
<tr>
<th>Crystal form</th>
<th>Anatase</th>
<th>Rutile</th>
</tr>
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<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>3.87</td>
<td>4.24</td>
</tr>
<tr>
<td>Hardness (moh)</td>
<td>5-6</td>
<td>6-7</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Tetragonal, Uniaxial, negative</td>
<td>Tetragonal, Uniaxial, positive</td>
</tr>
<tr>
<td>Compressibility coefficient</td>
<td>--</td>
<td>0.53 – 0.58</td>
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<tr>
<td>(10⁻⁶ cm² Kg⁻¹)</td>
<td></td>
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</tr>
<tr>
<td>Melting point (°C)</td>
<td>In Air</td>
<td>1830 ± 15</td>
</tr>
<tr>
<td></td>
<td>At higher % O₂</td>
<td>1879 ± 15</td>
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<tr>
<td>Specific heat (Cal °C⁻¹ g⁻¹)</td>
<td>0.17</td>
<td>0.17</td>
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<tr>
<td>Dielectric constant</td>
<td>48</td>
<td>114</td>
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Figure 1: Anatase and rutile unit cells and crystals
1.3 **Nanocrystalline Titanium Oxide**

Nano titania has got semiconductor properties owing to the band gap arrangement on clustering.\(^{119-121}\) Fine TiO\(_2\) semiconductor nanoparticles are ideal photocatalysts due to their chemical stability, non-toxicity and high photocatalytic reactivity.\(^{122-125}\) The photocatalysis by titania semiconductors has received considerable attention and has been widely studied after the discovery by Honda and Fujishima in 1972,\(^{27}\) with the final aim of efficiently converting solar light energy into useful chemical energy.\(^{126-133}\) The effective utilization of clean, safe, and abundant solar energy will lead to promising solutions not only for energy issues due to the exhaustion of natural energy sources but also for the many problems caused by environmental pollution. TiO\(_2\) semiconductor photocatalysts have the potential to oxidize a wide range of organic compounds, including chlorinated organic compounds, such as dioxins, into harmless compounds such as CO\(_2\) and H\(_2\)O by irradiation with UV light.\(^{67-74,77}\) High-purity titania powder catalysts are typically made in a flame process from titanium tetrachloride.\(^{134}\) The shapes of the crystallites vary with preparation techniques and procedures. Typically, (1 0 1) and (1 0 0)/(0 1 0) surface planes are found, together with some (0 0 1).\(^{135}\) Several theoretical studies have predicted the stability of different low-index anatase surfaces.\(^{136-137}\) The (1 0 1) face is the thermodynamically most stable surface.\(^{138-139}\) While it is difficult to obtain accurate values for surface energies with density functional theory (DFT) calculations, the relative surface energies are still meaningful. The calculated Wulff shape of an anatase crystal, based on these
numbers, compares well with the shape of naturally grown mineral samples. Interestingly, the average surface energy of an equilibrium-shaped anatase crystal is smaller than the one of rutile, \(^{138-139}\) which might explain the fact that nanoscopic TiO\(_2\) particles are more stable in the anatase phase. \(^{138-139}\)

The most common procedures for preparing the titania powders have been based on the hydrolysis of acidic solutions of Ti(IV) salts, \(^{110-112,140-142}\) or by gas-phase oxidation reaction of TiCl\(_4\) at high temperatures. \(^{143-144}\) Alternative methods like vapour-phase hydrolysis, \(^{145}\) pyrolysis, \(^{146}\) and sol-gel synthesis \(^{147-150}\) of organic precursors (e.g. titanium tetraisopropoxide, TTIP), have been developed to synthesize titania nanoparticles with high purity. Sol-gel synthesis generally refers to a low-temperature method using chemical precursors that can produce ceramics and glasses with better purity and homogeneity \(^{151-156}\) than high temperature conventional processes.

### 1.4 Sol-Gel Process In General

The sol-gel process is a versatile solution process for making ceramic and glass materials. In general, the sol-gel process involves the transition of a system from a liquid sol (mostly colloidal) into a solid gel phase. By applying the sol-gel process, it is possible to fabricate ceramic or glass materials in a wide variety of forms: ultrafine or spherical shaped powders, thin film coatings, \(^{157-160}\) ceramic fibers, microporous inorganic membranes, \(^{90-92,161}\)
monolithic ceramics and glasses, or extremely porous aerogel materials. An overview of the sol-gel process is presented in Figure 2.

The starting materials used in the preparation of the sol are usually inorganic metal salts or metal organic compounds such as metal alkoxides. In a typical sol-gel process, the precursor is subjected to a series of controlled hydrolysis and polymerization reactions to form a colloidal suspension, or a sol. Further processing of the sol enables one to make ceramic materials in different forms. Thin films can be produced on a piece of substrate by spin coating or dip-coating. When the sol is cast into a mold, a wet gel will
form. With further drying and heat-treatment, the gel is converted into dense ceramic or glass articles. If the liquid in a wet gel is removed under supercritical condition, a highly porous and extremely low-density material called aerogel is obtained. If the viscosity of the sol is adjusted to a proper viscosity range, ceramic fibers can be drawn from the sol. Ultrafine and uniform ceramic powders are formed by precipitation, spray pyrolysis, and/or emulsion techniques.

Therefore, the motivation behind selecting the sol-gel process is the higher purity and homogeneity of the product and the lower processing temperatures associated with the method compared to traditional glass melting or ceramic powder methods.

In the sol-gel synthesis, two simultaneous reactions – hydrolysis and polycondensation – take place when metal alkoxide reacts with water. These two reactions are sensitive to many experimental parameters such as water concentration, $\text{pH}$, type and amount of solvent, reaction temperature, and mixing conditions. Therefore, it is essential to understand the hydrolysis and condensation reactions in a sol-gel process since the structure of a gel is established at the time of gelation, drying, stabilization and densification all depend upon the gel structure. The variables of major importance are temperature, nature and concentration of electrolyte (acid, base), nature of the solvent, and type of alkoxide precursor. In fact many studies have reported the variation of the gelation time, viscosity, or
textural characteristics (e.g. specific surface area) of the gel as a function of experimental conditions.\textsuperscript{188-191}

Most of the titanium oxide was prepared by hydrolysis reactions involving salts.\textsuperscript{110-112,140-142} The need for finer particle size and well-defined compositional tolerance along with tailored surface properties lead to adaptation of sol-gel route.\textsuperscript{192} The sol-gel process essentially is the hydrolysis of metal alkoxides by controlled addition of water in presence of alcohol due to the fact that the alcohol with its intermediate polarity makes the apolar alkoxide and polar water compatible.\textsuperscript{193-194} Such hydrolysis produces essentially primary nanoparticles, which may aggregate on aging of the sol.\textsuperscript{195} The pH and temperature also has considerable influence on the sol-gel system. Final drying and calcination of the gel produces the metal oxide.\textsuperscript{196-198}

The parameters such as type of precursors,\textsuperscript{199} pH of the system, ambient temperature, solvents, water/Ti mole ratio, solvent/Ti ratio, (stabilizer/chelating agent)/Ti ratio and electrolyte/Ti ratio\textsuperscript{200} are need to be considered to obtain suitable nanometric building blocks. The influence of building blocks on the microstructure\textsuperscript{201-202} and on the physical, chemical and the mechanical properties need to be understood to tailor the final product.\textsuperscript{152,203} Apart from that, hydrolysis of precursors,\textsuperscript{204-205} the commencement of condensation, its propagation, termination, the nature of polycondensation, effect of solvents on the process and effect of by-products on further reaction are very important parameters and many of these factors have been well studied by many
researchers. Suresh et al.\textsuperscript{206} showed that hydrolysis of titanium tetraisopropoxide at pH 4 resulted in a precursor having an anatase to rutile transformation temperature as high as $\sim 800^\circ$C in place of the usual temperature of $\sim 600^\circ$C. Trace of anatase phase was seen even at $800^\circ$C.

Kallala et al.\textsuperscript{207} identified the structure of inorganic polymers, produced as a result of hydrolysis of sol-gel precursors. The hydrolysis and condensation of titanium alkoxides such as ethoxide, propoxide, butoxide etc. could be selectively controlled by the inhibition of condensation through $\text{H}^+$ ions, which prevents precipitation and provided gelation. Depending on the presence of the inhibitor, the resultant gel could be transparent, turbid or opaque, based on which different properties for the resultant oxides could be obtained. Attempts for obtaining nanosize titanium oxide particles, titania-mixed oxide catalysts and titania for photocatalytic activity is widely investigated. As has been found in the various applications of titania, the characteristics required for the oxide are diverse, but specific to the end use. Since hydrolysis of titanium alkoxide and further condensation of the hydrolysed species can be controlled by manipulating the synthesis conditions, it has been possible to achieve the required oxide with reasonable success. Most of the preparative methods are modifications on the hydrolysis reactions of titanium alkoxides.\textsuperscript{208-210} Titanium ethoxide, propoxide and butoxide are the usual starting alkoxides. The main approaches to synthesis have been the following:

1. Use of acid catalysts ($\text{HCl/\text{HNO}_3}$) on direct hydrolysis
2. Hydrolysis in presence of different alcohol-water ratios.
3. Hydrolysis in presence of chelating agents or intermediates.
4. Hydrolysis involving large polymeric molecules in the medium
5. Hydrolysis involving emulsion templating
6. Hydrolysis of titanium salts (aqueous processing) in place of alkoxides.

The hydrolysis of titanium alkoxides results in a polymeric gel or a particulate colloidal gel. Generally, for high surface area powders and membranes, particulate gels are the precursors. The initial step is the hydrolysis of the alkoxides. 147, 170, 177, 204 This is followed by peptization using acid or base, 211-216 which is responsible for the stabilization of sol. Shi et al 208 hydrolysed titanium alkoxide under slow and fast rates in presence of nitric acid and the particle size was observed. It was found that the slow hydrolysis resulted in a large particle size, ~57 nm, while the fast one has ~36 nm. Similarly, when started with titanium butoxide, and isopropoxide, the latter yielded a slow rate of hydrolysis but also a smaller particle size of ~19 nm. This is supposed to be due to the isopropoxide moiety sterically hindering the hydrolysis reaction. Hydrochloric acid catalyst has been widely used in the hydrolysis and peptization of titanium alkoxide for obtaining high surface area oxides often for catalyst applications. 175,217 Such processing route yielded finer crystallite size titania, which had an earlier anatase to rutile transformation temperature. Long aging of such gels, also, raised the anatase to rutile
transformation temperature. Ferreira et al. have had a detailed study on the peptization and the associated structural properties like phase assemblage and anatase to rutile transformation. A detailed study on the peptization of titanium isopropoxide solution using tetraethyl ammonium hydroxide and HCl has been carried out. They reported that peptization is efficient compared to the hydrolysis - peptization in terms of anatase to rutile transformation. The isopropanol derived as a by-product of hydrolysis was described as responsible for the destabilization of the colloidal particles, by enhancing their aggregation. Furthermore, they have suggested a higher ratio of HCl to Ti as responsible for the earlier rutile formation. Polycarboxylic acid was recently used as a peptising agent and the formation of nanoparticles of anatase during the anti-aggregation process was attributed to its chelation effect. A few more reports on acid and base peptization have also been reported.

Another factor influencing the particle size is the amount of hydrolysis water. Hydrolysis with low water content yields smaller grain size for titania and a lower anatase to rutile phase transformation temperature. However, contradicting results have also been reported by Barringer and Bowen (1982). They showed that the average particle size of the titania powders decreased with increasing water concentration or decreasing alkoxide concentration. Heterogeneous mixture of oxides have been prepared based on titania and oxides such as silica, zirconia, alumina, vanadia and minor additives, either by preferentially hydrolysing one alkoxide in a salt solution or peptising suspension of precipitate to nanoparticles. Monophasic alumina-
titania\textsuperscript{224} systems have been prepared by co-hydrolysis of mixed alkoxides, and a comparison with heterogeneous catalysts having similar diphasic counterparts indicated that the monophasic one had much larger efficiencies, and could be an excellent substitute for conventional aluminium trichloride - sulphuric acid systems.

Titanium oxide, synthesized in nanometer range shows excellent magnetic / ferromagnetic,\textsuperscript{225} optical \textsuperscript{19-21} and catalytic properties\textsuperscript{226-227} due to their large surface to volume ratio as well as the quantum size effect\textsuperscript{228-231} associated with them. The important challenges in nanotechnology are, therefore, the real control over its preparative parameters in order to arrive at suitable properties for specific end uses. Hydrolysis of two metal alkoxides needs separate control owing to the differing electropositivity of the metal atoms.\textsuperscript{193} Titanium tetraisopropoxide (TTIP) is highly reactive compared to tetraethylorthosilicate,\textsuperscript{193} which is also used as a dopant in the present system, and hence needs additional control against hydrolysis. Acetic acid is a suitable stabilizer, which effectively stabilizes the titanium tetraisopropoxide moiety by either modifying its coordination sphere to six or by ester formation.\textsuperscript{232-236} However, silica sol was prepared without a chelating agent, but in presence of a solvent and by the controlled addition of water. Temperature has also been found to influence the hydrolysis - condensation process.
1.5 **Effect of Solvents, Catalysts and Complexing Ligands**

Depending on titanium resources and the final target, various solvents have been used to prepare nanometric TiO\(_2\) particles, such as alcohols, carboxylic acids[^237-238] and water[^240-241]. In most cases, some additional reagents have been used together with the solvent either as a peptizer (e.g., inorganic acids),[^237] or as a stabilizer[^242-244] in order to monitor hydrolysis and condensation reactions. The hydrolysis of titanium alkoxides is rather fast, and therefore, chelating agents are incorporated to control the rate of hydrolysis. Common chelating agents reported are acetyl acetone,[^245] acetic acid,[^246-251] tartaric acid,[^252] and certain polymers such as polyvinyl acetate and polyvinyl alcohol.[^253] The influence of ligands on the acceleration of crystallization as well as their effect on two component systems, prepared by sol-gel process, was recently reported by Nishide and Mizukami.[^242-244] Use of chelating intermediates in the development of titania coatings have been reviewed recently, where acetyl acetone, acetic acid and diethanolamine were employed.[^254-256] A complexing agent-assisted sol-gel process using an organic ligand as a modulator can tailor the crystal structure and optical properties of TiO\(_2\) thin films.[^257] Takahashi and Matsuoka reported that control of firing temperature, when diethanolamine is used as a ligand, forms pure anatase and rutile TiO\(_2\) films.[^254] Kato *et al.*[^238,258] reported that the anatase TiO\(_2\) film with preferred orientation is formed when polyethylene glycol is used. Gotić *et al.*[^259] reported a hydroxypropyl cellulose (HPC) stabilized sol-gel preparation of nanosize TiO\(_2\) particles. The particle size and pore distribution in membranes can be
controlled by using polyethylene glycol or glycerol as a gelling agent or a surfactant that is adsorbed on the surface of primary nanoparticles. The use of surfactants and templating agents are attaining great importance in view of the demand for high surface area, meso / macroporous unsupported materials for energy applications. Recently, mixed organic media has also been used for the synthesis of nanocrystalline anatase and rutile titania by Wang et al.

The influence of ligands on the crystal structures and optical properties of TiO₂ was reported by Nishide and Mizukami. The authors have also reported the complexing agent assisted sol-gel process for the preparation of TiO₂-SiO₂ (1: 1) films. Livage and coworkers have studied the role of acetic acid on the molecular level modification of titanium alkoxide precursors. They observed the reproducibility of preparation of monolithic TiO₂ gels in presence of acetic acid, which not only acts as an acid catalyst but also as a ligand and changes the alkoxide precursor at a molecular level and thus modifying the whole hydrolysis condensation process. The bidentate acetate ligand formation by the replacement of OR groups directly bounded to the titanium are reported to be determined by infra-red experiments, which showed the arrangement of both chelating and bridging acetates leading to Ti(OR)₅(Ac)ₖ oligomers. The reaction sequences investigated through infra-red experiments indicated the preferential removal of (OR) groups first and bridging acetates subsequently in the hydrolysis – condensation process, where the chelating acetates were
removed only upon heating above 200°C. Recently, Ivanova et al.\textsuperscript{269} studied the role of acetic acid on the thermal transformations of the sol-gel TiO\textsubscript{2}-MnO system through FTIR technique. The other reports on the chelating agents include the work by Moriguchi et al.\textsuperscript{270} in which they report the role of \textit{n}-octadecylacetate as an amphiphilic chelating agent in the two-dimensional sol-gel synthesis of ultrathin films of titania and zirconia, and that by Trung et al.\textsuperscript{260} They have, recently, reported the effect of glycerol as a new stabilizer in aqueous and non-aqueous media on the preparation of pseudo-spherical TiO\textsubscript{2} nanoparticles of very small size ranging from 4 to 10 nm.

Polyethylene glycol (PEG) is an important gelling, dispersion and filming agent that has been employed many times to prepare the powders and coatings of nanocrystalline TiO\textsubscript{2}.\textsuperscript{271} Polyethylene glycol coordinates to a structure formed by the controlled hydrolysis and polycondensation reactions of titanium tetraisopropoxide chelated with diethanolamine. From the resulting chemically modified precursor solution, anatase coatings consisting of nanometer-sized pores and grains with diameters of ~30 nm and a preferred orientation along the c-axis were prepared on quartz-glass plates by a dip coating method. In contrast, anatase coatings consisting of submicrometer-sized pores and randomly orientated grains were prepared from the solution in which the poly(ethylene glycol) had been isolated.\textsuperscript{272} There is another report on an improved sol-gel method using PEG as a multifunctional agent and
inorganic titanate as a precursor for preparing ultrafine and crystallized TiO$_2$ powders, without a high temperature calcination step.\cite{273}

The effect of HCl and NH$_4$OH catalysts on the control of phase and pore structure was reported by Song et al.\cite{274} According to them, the catalyst concentration has an immense effect on the porosity of powders. Titania powders prepared near the isoelectric point with low concentration of NH$_4$OH showed the highest textural properties and high degree of aggregation. The porosity consists of both intra-aggregate and inter-aggregate pores and the average pore diameter of the intra-aggregate pores decreased with increasing HCl concentration and increased with increasing NH$_4$OH concentration. So, in order to achieve the desirable properties, a variety of synthetic techniques are attempted, where each method highlights certain property. Simple hydrolysis of titanium alkoxide in presence of acid catalysts and controlled hydrolysis by involving stabilizing agents, which may form intermediate compounds on hydrolysis in presence of only water and alcohol, resulted in titanium oxide with different properties. Use of macromolecules in the hydrolysed sol has indicated the possibility of less agglomeration. Use of size specific emulsion droplets on which sol-particles can provide a coating and finally result in mesoporous / macroporous gels has been one of the recent findings.\cite{194} Titania and silica based porous gel systems are also possible candidate materials as high efficiency bio and humidity sensors.\cite{275} Report by Suresh et al\cite{206} showed that hydrolysis of titanium isopropoxide at pH 4 adjusted by the addition of
dilute HNO₃ could produce a precursor having an A > R transformation temperature as high as ~ 800°C in place of the usual phase transformation temperature of ~ 600°C. Recently Bosc et al. proposed a simple route for the low temperature synthesis of mesoporous and nanocrystalline anatase thin films.

1.6 Effect of Temperature

Pratsinis and co-workers investigated the effect of hydrolysis temperature on the phase transformation and pore structure of titania in detail. They observed a slight retardation in the phase transformation with increasing hydrolysis temperature, at a small initial water concentration. Recently, Zhang et al. reported the preparation of single-phase nanocrystalline anatase from amorphous titania. Their work addresses the effect of temperature on the tailoring of particle size of nanocrystalline titania.

Gotic et al. investigated the microstructure of TiO₂, synthesized by sol-gel procedure. The aim of their and some other group’s research was to obtain nanosized TiO₂ with improved properties, which was used for development of photoanodes in dye-sensitized solar cells. Liu et al. have proposed and improved sol-gel method for the preparation of ultrafine and crystallized titania powders. In addition, Venz et al. reported the physical properties of chemically modified titania hydrolysates. Again, recently the size-controlled TiO₂ nanoparticles were prepared by Chae et al. in order to use in
the field of optically transparent photocatalytic films. Recent reports also indicate various propositions in the synthesis of nano titania such as by Liu et al., who proposes a photoassisted sol-gel route for the formation of an early rutile phase.

Bacsa and Grätzel (1996) studied the effect of peptization on the phase transformation and found that the anatase-rutile phase transformation was critically dependent on the water / alkoxide molar ratio. Vorkapic and Matsoukas (1998) investigated the effect of temperature and alcohols on the size of the titania particles. Due to the various possibilities of sol-gel process in terms of the variety of products that can be achieved, this process is being used considerably in present days.

1.7 Anatase - Rutile Transformation

Anatase and rutile are the two polymorphs of titania at atmospheric pressure. The room temperature phase is anatase and the high temperature phase is rutile. Anatase transforms irreversibly and exothermically to rutile in the range 400°C to 1200°C depending on parameters such as the method of preparation, grain size, morphology, degree of agglomeration, nature of impurities and reaction atmosphere. At atmospheric pressure, the transformation is time and temperature dependent and is also a function of impurity concentration. The complexity of the transition is typically attributed to the reconstructing nature. The phase
transition is a nucleation-growth process and follows the first order rate law with activation energy of ~90 Kcal/mol.  

The anatase - rutile transformation involves an overall contraction of oxygen and a movement of ions so that a cooperative rearrangement of Ti$^{4+}$ and O$^{2-}$ occur. The transformation implies that two of the six Ti-O bonds of anatase structure break to form a rutile structure. Removal of the oxygen ions, which generate lattice vacancies, accelerate the transformation and inhibit the formation of interstitial titanium.

The impurities that have most pronounce inhibiting action are chloride, sulphate and fluoride ions whereas that accelerates the transformation includes alkaline earth and a few of the transition metal ions. Those ions with valency greater than four reduce the oxygen vacancy concentration and will retard the reaction.

The effect of reaction atmosphere shows that vacuum conditions and atmosphere of hydrogen, static air, flowing air, oxygen, argon, nitrogen and chlorine affect the phase transformation to different extents. Lida and Ozaki as well as Shannon found that the transformation rate in a hydrogen atmosphere is greater than in air and under vacuum decreasing as oxygen partial pressure increases. Oxygen vacancies are formed in hydrogen atmosphere whereas the interstitial Ti$^{3+}$ ions are generated under vacuum. The rate constant of the transformation in hydrogen was 10 times larger than in air.
It has been reported that at 950°C the phase transformation in Ar/Cl\textsubscript{2} atmosphere is about 300 times faster than in air.\textsuperscript{311} The accelerating effect of chlorine atmosphere on the anatase-rutile phase transformation involves two mechanisms that probably occur simultaneously - vapour mass transport and oxygen vacancy formation in which the first generate nucleation and growth in the bulk and the second provide pathways for the diffusion of ions. When the vapour transport is negligible, the primary mechanism is based on oxygen vacancies.

The effect of metal cations such as Li, Na, K, Mg, Ca, Sr, Ba, Al, Y, La, Er, Co, Ni, Cu and Zn on anatase - rutile transformation was studied earlier.\textsuperscript{309} A linear relationship between phase transition temperature and ionic radius, for alkali and alkaline earth metals and group III elements are reported. Transition metals, which entered the matrix interstitially, gave a high transition temperature, whereas those dopants introduced substitutionally did not make any significant change in transition temperature. It was concluded that the oxidation state together with ionic radii of cations and type of sites occupied were the important parameters, which control phase transition temperature.

Depending on the ionic radius of dopant compared with radius of titanium, it can be introduced substitutionally or interstitially or if the size of the dopant is larger than oxygen, it could be intercalated into the matrix, producing a lattice deformation.\textsuperscript{310} The dopants had no effect on the amorphous gel to anatase transformation temperature, but influenced the anatase - rutile transformation. If dopant ion size is less than that of titanium,
anatase phase will be stabilized to a higher temperature. Dopants bigger than oxygen ion produce large local deformation of lattice. Those dopant ions whose size falls in between titanium and oxygen stabilize the anatase phase. Those dopants near to oxygen size can stabilize the titania phase more. The enhancement or inhibiting effect of additives on anatase - rutile transformation depends on their ability to enter the TiO$_2$ lattice, thereby creating oxygen vacancies or interstitial Ti$^{3+}$ ions. Oxides of Cu, Co, Ni, Mn and Fe mixed with anatase TiO$_2$ increases the transformation rate efficiently. Transition metals, which entered the matrix interstitially, gave a high transition temperature, whereas those dopants introduced substitutionally did not give a significant change in transition temperature.

The influence of impurities on the nucleation and growth of rutile from anatase was studied by Shannon and Pask. $^{313}$ They concluded that processes that create oxygen vacancies, such as the addition of acceptor dopants (ions with a lower valence than Ti$^{4+}$) and use of reducing atmospheres accelerate the anatase-rutile transformation. Conversely, processes that increase the concentration of titanium interstitials, such as the addition of donor dopants, inhibit the transformation. Shannon and Pask hypothesized that an increase in the concentration of oxygen vacancies reduces the strain energy that must be overcome before the rearrangement of the Ti-O octahedra can occur, and that cations with a valency less than that of titania (4$^+$) will increase the concentration of oxygen vacancies, due to the necessity for charge balance.
Depero et al.\textsuperscript{314} have studied the anatase - rutile transformation in TiO\textsubscript{2} powders and reported an increase of the crystallites and/or of the lattice perfection accompanied by the transformation on the basis of X-ray microstructural analysis. The studies were carried out on vanadia-treated TiO\textsubscript{2}. The vanadia-treated surface layer was particularly distorted and apparently acted as a restraint to perfecting by thermal treatments. Only the transition to rutile was capable of overcoming that restraint by allowing crystallite growth at the expense of the smaller and distorted anatase crystallites.

Zhang and Banfield\textsuperscript{315} observed that the synthesis of ultrafine titania resulted in anatase and/or brookite, which on coarsening transformed to rutile after reaching a certain particle size. Based on the inferred lower surface energy of nanocrystalline anatase, phase stability reversal is predicted at particle size under 13 nm and supported by coarsening and phase transformation experiments by Gribb and Banfield\textsuperscript{302} as well as by Zhang and Banfield.\textsuperscript{289} Once rutile was formed, it grew much faster than anatase.\textsuperscript{306} They analyzed the phase stability of anatase and rutile thermodynamically to conclude that anatase became more stable than rutile for particle size <14 nm. Hwu \textit{et al}\textsuperscript{316} have reported on the dependence of anatase or rutile formation on the preparation method. Small particle size (<50 nm) anatase seemed more stable and transformed to rutile at \textasciitilde973 K.

Zhang and Banfield\textsuperscript{315} studied the phase transformation behavior of nanocrystalline aggregates during their growth in isothermal and isochronal
reaction by using XRD. They suggested that transformation sequence and thermodynamic phase stability depend on the initial particle sizes of anatase and brookite. They concluded that, for equally sized particles, for particle size <11 nm, anatase was thermodynamically stable, and for particle size between 11 nm and 35 nm, brookite was stable, and for particle size >35 nm, rutile was stable. They cautioned that, for real samples, the particle sizes of different phases were not equal, and this could alter the direction of the initial transformation. They concluded that the energetics of these polymorphs were sufficiently close that they could be reversed by small differences in surface energy.

Ye et al. studied the thermal behavior of nanocrystalline brookite by thermogravimetric analysis, differential thermal analysis, and diffraction. They observed a slow transition from brookite to anatase phase below 1053 K along with grain growth. Between 1053 K and 1123 K, they noticed rapid brookite to anatase and anatase to rutile phase transformations. Above 1123 K, they observed rapid grain growth of rutile, which became the dominant phase. They concluded that brookite couldn’t transform directly to rutile but through anatase phase only. Kominami et al. observed that nanocrystals of brookite directly transformed to rutile above 973 K, in contrast to the observation by Ye et al.

Zhang et al. measured micro-Raman spectra of nano-sized TiO$_2$ powders prepared by vapour hydrolysis. They obtained amorphous TiO$_2$ at 533 K and predominantly anatase between 873-1173 K. The anatase-rutile
transformation temperature depended on particle size and was complete at ~1323 K. They noted that the phase transformation of amorphous TiO₂ is a two-step process; amorphous to anatase followed by anatase to rutile. They proposed that the rutile formation started at the surface and migrated into the bulk. They also noted that the brookite impurities as detected by Raman spectroscopy but not by XRD, were present on the anatase surface.

Zhang and Banfield proposed that the mechanism of anatase-rutile phase transformation was temperature-dependent. They suggested that this transformation was dominated by interface nucleation below 873 K, by both interface and surface nucleation between 893-1273 K, and by bulk nucleation above 1273 K.

The anatase-rutile transformation depends on impurities, grain size, reaction atmosphere, and synthesis conditions. Zhang and Banfield reported that the anatase-rutile phase transformation occurred at higher temperature with the addition of Al₂O₃. They attributed this to suppression of coarsening caused by surface diffusion. Okada et al. and Yoshinaka et al. found that the anatase-rutile phase transformation occurs at higher temperature with the addition of SiO₂. Ferreira and Yang showed that synthesis conditions (chemicals/peptizing agents) affect the crystallinity and anatase-rutile phase transition temperature. Zaban et al. noted that the surface structure of TiO₂ is affected by the preparation conditions. Ahonen et al. studied the effect of gas atmospheres (nitrogen and air) and temperature on the crystal structure and
transition temperature. Zaban et al.\textsuperscript{324} noted that the surface structure of TiO\textsubscript{2} is affected by the preparation conditions. Ahonen et al.\textsuperscript{325} studied the effect of gas atmospheres (nitrogen and air) and temperature on the crystal structure and specific surface area. They observed that anatase synthesized in air transformed to rutile at 973 K, whereas anatase synthesized in nitrogen persisted to 1,173 K. Gouma and Mills\textsuperscript{326} studied the anatase-rutile phase transformation in commercial TiO\textsubscript{2} powders with an average particle size of 100 nm. Using transmission and scanning electron microscopy, they concentrated on the structural evolution (shape and morphology) of the particles. They proposed that rutile plates are formed initially by a shear force and subsequent coarsening involved interactions between the transforming particles and surrounding anatase particles. Studies by Fransisco et al.\textsuperscript{327} and many others on the anatase to rutile phase transformation illustrate its technical importance in various application fields.

1.8 \textit{TiO\textsubscript{2} Films and Coatings}

The films were prepared/attempted for chemical reactions since conventional powder catalyst suffered from disadvantages in stirring during the reaction and getting it separated after the reaction.\textsuperscript{119,328} When the TiO\textsubscript{2} is used in the powder form, two major difficulties occur. First, ultrafine powders will agglomerate into larger particles, reducing the effective surface area for the
reaction resulting in an adverse effect on catalyst performance. Second, it is very difficult to recover TiO_2 powders from water when they are used in aqueous systems, leading to a potential difficulty in downstream separation. The catalyst coated as thin film was found to be useful in overcoming these disadvantages. Also, industrial applications of TiO_2 thin films, as a basic unit of antibacterial ceramic tile or self-cleaning glass look promising.

The coatings can also be used as passive solar control in architectural windows. For solar control and prevention of superheating of buildings, absorbing glasses (coatings) could be used but a part of the absorbed energy succeeds in infiltrating the buildings by re-emission in the far infrared region. Using reflective coatings attains more efficient reduction of the entering solar radiation, which partially changes the colour characteristics of the transmitted light in the visible region of the spectra. In other words, there must be a decrease of the admitted light energy level, while keeping the colour characteristics of the natural light as good as possible. So, a spectral-neutral transmission is necessary, or if it is possible, a more horizontal spectral transmission curves in the visible spectral region from 0.4 to 0.8 µm need be achieved.

Even though lot of research has carried out in the area of TiO_2 thin films, various approaches are still being reported with respect to basic aspects such as deposition on glass substrates, which emphasize the potentiality of the research on TiO_2 films and coatings. Different photocatalytic titania were
compared recently by Du et al. 129 Bosc et al 171 recently developed a simple route for the preparation of mesoporous and nanocrystalline anatase thin layers. The method consists of templating the acid hydrolysed titanium isopropoxide sol with the poly (ethylene oxide) – poly (propylene oxide) - poly (ethylene oxide) triblock copolymer.

1.9 TiO₂ Nano Catalysts

Traditionally, TiO₂ finds use in mixed vanadia / titania catalysts used for selective oxidation reactions. 333 The surface science of vanadium and vanadia/TiO₂ systems was addressed by several groups. 334-337

In developing novel catalyst systems it is especially critical to develop a powder with the highest possible surface area, or, equivalently, the smallest possible particle size. Non-crystalline TiO₂ powder can be easily obtained at treatment temperatures ≤ 300°C, 338 however, crystallized nanosized TiO₂, e.g. anatase phase, would have better catalysis activity. 339-342

In the past two decades, considerable research has been reported in the synthesis and evaluation of catalytic property of titania based mixed oxides. These oxides have specific surface areas in the range 150-250 m²/g. The various mixed oxides reported are with silica, 322,343-346 alumina, 347 lanthanum oxide, 348-349 cerium oxide 91,327,350 and vanadium oxide. 351-352 Fine metal particles also have been introduced.
One of the studies has been to see any preferential reactivity exists for anatase compared to rutile in reaction with alcohols. The cation coordination environment is the same in anatase and rutile bulk structures where the role of oxygen vacancies (defect states) in titania was investigated by water vapour adsorption and carbon monoxide oxidation. However, the rutile phase showed higher efficiency in the decomposition of \( \text{H}_2\text{S} \) gas than anatase having similar surface areas. In order to keep the phase assemblage at the desired high temperatures, the anatase to rutile transformation temperature has to be controlled, and this is largely achieved, by introducing appropriate dopant oxides in the precursor gel. Benjaram et al. reported the catalytic property of \( \text{V}_2\text{O}_5/\text{La}_2\text{O}_3-\text{TiO}_2 \) mixed oxide systems prepared by co-precipitation route. The anatase form of titania is believed to possess enhanced catalytic activity, probably due to its open structure compared to rutile and its high specific surface area.

### 1.10 Effect of Dopants

Suitably modified titanium oxide has been reported to be efficient catalysts in chemical reactions. A high anatase to rutile transition temperature or otherwise high anatase phase stability is desirable for use of titania in photoreactions at elevated temperatures. The transition temperatures and hence, the transition from one crystalline form of \( \text{TiO}_2 \) to
another can be influenced by chemical doping \(^{363-365}\) or alcohol washing (butanol). \(^{366}\) The catalytic and photocatalytic properties are being investigated widely in the form of bulk powders, films and membranes. \(^{94,367-371}\) Nanocrystalline titania was synthesized by chemical methods involving sol-gel approach. Titania undergoes phase transformation from the low temperature anatase phase to rutile, which is seen to extend to as high as 1000\(^0\) C depending on the method of preparation and in presence of dopant oxides. \(^{372-373}\) The role of a few dopant oxides such as Fe\(_2\)O\(_3\), V\(_2\)O\(_5\) and CuO \(^{374-379}\) on the anatase to rutile transformation is well reported and certain correlation between the ionic radii of the dopants and anatase phase stability was drawn by Ferreira \textit{et al.} \(^{380}\) Anatase-rutile transformation is usually followed by XRD techniques, but impedance spectral analysis was also used to study the transformation. \(^{381}\) Bjorkert \textit{et al.} \(^95\) reported the influence of La\(_2\)O\(_3\) as dopant on the phase development of Al\(_2\)O\(_3\): TiO\(_2\) ceramic membranes. In their work, lanthana was used to stabilize \(\gamma\)-alumina phase in Al\(_2\)O\(_3\): TiO\(_2\) composite ceramic compositions. LaAl\(_2\)O\(_3\) phase is reported to form at the alumina surface, which stabilized the \(\gamma\)-alumina phase. There are reports on the effects of addition of metal ion dopants on the quantum efficiency of heterogeneous photocatalysis of titanium dioxide. \(^{382-385}\) Also Lin \textit{et al.} \(^{386}\) reported the effect of addition of Y\(_2\)O\(_3\), La\(_2\)O\(_3\) and CeO\(_2\) on the photocatalytic activities of titania for the oxidation of acetone. A few other reports on lanthanum oxide doped titania include the work of Gopalan \textit{et al.} \(^{349}\) and LeDuc \textit{et al.} \(^{387}\) The former reports the evolution of pore structure and anatase phase stability as a result of the
addition La$_2$O$_3$. The anatase phase is stable up to 650° C and this is explained by a possible monolayer coverage of lanthana over Titania. Report by LeDuc et al deals also with textural stability La$_2$O$_3$-doped Titania prepared by suspending a commercial titania catalyst in a solution of lanthanum nitrate. A doping level of 5 % La$_2$O$_3$ was recommended for long-term thermal stability up to 650° C. Recently, Francisco et al have studied the effect of ceria on the inhibition of the anatase-rutile phase transformation in the CuO-TiO$_2$ system.

The high surface area TiO$_2$, which is a necessity for good catalysts, were also prepared by many researchers. Titanium oxides prepared via sol-gel method exhibit comparatively high surface areas and hence have an advantage over conventional materials for potential applications as catalysts, sorbents, or electrodes. The rutile form of Titania, which has a lower surface area and high refractive index as well as high opacity is used for cosmetics and pigment applications. On the other hand, the anatase form of titania is believed to possess enhanced catalytic activity, compared to rutile. However, a drastic reduction in surface area of titania is reported to occur on heating to higher temperatures. It has been suggested that the enhanced sintering rate during the phase change from anatase to rutile is responsible for this drastic reduction in surface area. Suitable doping can retard the rate of reduction in surface area at higher temperatures. Kumar et al have earlier reported the effect of second phases such as yttria and lanthana on the textural properties of anatase phase. Kumar et al have also studied the pore structure stability of
ceria doped structured alumina. Ozawa et al \cite{391} reported the thermal stability of γ-alumina modified with lanthanum or cerium. Koebrugge et al \cite{350} reported the thermal-stability of nanostructured titania and titania ceria ceramic powders prepared by the sol-gel process. We have reported the influence of lanthana on the structural and textural properties of titania. Report by Kasuga et al \cite{392} points toward a silica doping-and-subsequent leaching out to be a possible method to synthesize high surface area titania. However, the maximum surface area obtained by them was 150 m²/g at 600°C. Further, Sang et al \cite{393} reported the preparation of mesoporous titania by selective dissolving of titania-silica binary oxides. The material showed enhanced photoactivity compared to the untreated titania. High surface area obtained as a result of the treatment was reported to be major reason for the enhanced photoactivity. High surface area titania have also been synthesized by many methods by many researchers. \cite{175,210,217}

1.11 Effect of Additives

Titania-silica sol-gel systems have been subjected to studies related to catalysis \cite{394-396} in various chemical environments. In fact, addition of titania to a silica gel matrix had synergistic effects. The crystal sizes vary and spherical titania was dispersed in disc shaped silica matrix. The particle size was in the range 10-5 nm. The presence of Si-O-Ti bond has been identified. \cite{397}
Titania-silica sol-gel systems exhibit significant changes in the surface acidities. Certain results from temperature programmed desorption (TPD) and infra red spectral data indicated that the total acidity and relative acid strength of silica decreased as silica was introduced to titania. All the acid sites on pure titania were originally Lewis type whereas more than 80% on the mixed oxides were of Bronsted type. The enrichment in reactivity with respect to Brønsted acid was present in the titania in mixed oxide, while it is not present in pure titania. This should be due to the local charge imbalance associated with tetrahedrally coordinated silica, chemically mixing with octahedral titania matrix. On the other hand, in silica rich mixed oxides, titanium substituted isomorphously for Si in tetrahedral silica matrix, eliminating the local charge imbalance carrying Brønsted acidity. Evidence for the decrease for the Ti-O bond distances by incorporation of Si into mixed oxide was observed through EXAFS and thus disruption of usual octahedral coordination of pure titania. This is also associated with formation of Ti-O-Si linkages in the mixed oxides. Diffuse reflectance UV-VIS spectroscopy (DRS) has been used to identify the presence of isolated Ti sites in titania-silica mixed oxides which are understood to be the primary reason for the extraordinary catalytic activity of titania-silica mixed oxides. Further, it has also been shown that there should be a high Titania dispersion in the silica matrix, in addition to the site isolated Titania. The existence of Ti-O-Si bond in such titania-silica xerogels calcined in the range 400-800°C was also confirmed by infra red and Raman spectral data. Hydrophilicity of titania
dispersed silica containing monomodal pore size distribution of about 0.7 nm has been accounted for the size selective epoxidation reactions of olefins. In a matrix of silica, titanium oxide along with other oxides such as MoO$_3$ and WO$_3$ were also substituted in a sol-gel medium and enhanced catalytic properties were observed. The IR spectral data indicate Si-OH vibrations and MAS NMR data indicate that the molecular dispersion of the metal oxide takes place in xerogels. These gels have a microporous nature with average pore diameter of 1.5 nm and specific surface area as high as 750 m$^2$/g. Recently, Warrier et al. reported on the effect of silica addition on the high temperature stabilization of pores compared to the undoped titania. The homogeneously distributed silica particles in titania matrix, prepared through sol-gel route, helped the matrix to retain its microporosity considerably even after tempering for 32 hours.

In order to achieve the high efficiency titania-silica catalysts, a variety of techniques are reported. The drying method was investigated with respect to TiO$_2$-SiO$_2$ catalyst system. A comparative evaluation of drying of a titania-silica precursor sol under high temperature supercritical drying, low temperature supercritical drying and evaporative drying adopted for xerogels are reported. Low temperature supercritical drying was shown to be the most ideal. High epoxide selectivity is reported in titania-silica gels. Partial hydrolysis of Ti-O-Si bonds was observed which had a sort of correlation
between oxidation rate and Ti-O-Si connectivity, which is a characteristic of the Ti dispersion in silica. 403

Alumina-titania systems are reported to be potential solid acid catalysts and a range of compositions with varying Al/Ti are synthesized as well as characterized. 404-407 These compounds have been found to have high specific surface areas and enhanced acidity than comparable mixed oxides. The strength and density of the acid sites have been found to be proportional to the Ti content. Effect of addition of other oxides such as WO₃ to alumina-titania was investigated. 408 The tungsten species is present largely as mono oxo wolframyl species and are strong Lewis acid sites. By absorption of water, the overall coordination of tungsten grows and it behaves as a strong Brønsted acid site. There appeared W-O- (Ti, Al) bonds without significant W-O-W bridges. Vanadium oxide has been loaded on to alumina-silica-titania composite oxide and the alumina rich or silica rich catalysts are found to have comparable properties. 336 In such catalysts, specific surface area appears to play a major role.

Vanadium-titanium oxide catalysts showed presence of Brønsted acid sites associated with [V⁵⁺] –OH surface sites 409 as was revealed by temperature programmed desorption study. Catalytic reduction of nitric oxide by ammonia over vanadia-titania mixed oxide catalysts has indicated that the concentration of Brønsted acid groups on the catalyst determines the efficiency. 410 Comparative studies of temperature programmed desorption between titania
and titania-vanadia mixed oxide catalysts for NO reduction showed that the mixed oxides were more efficient. Further, mechanism of the vanadia-titania catalyst indicated a catalyst cycle that consisted of both acid and redox reactions involving surface V-OH (Brönsted acid sites) and VO species. Many other mixed oxides with titanium oxide were prepared and tested for various catalytic reactions. Sol-gel mixtures of silica or zirconia with titania have shown enhanced catalytic property when compared to individual oxides. Other mixed oxides, which are less reported, but may be, potential candidates are, chromia-titania and ceria-titania. Chromia-titania was found to be efficient as selective catalytic reduction of NO by ammonia and the Brönsted acid site bound ammonia enhances absorption of NO and is responsible for selective catalytic reduction of NO to NO₂. Chromium ion doped polycrystalline titania catalysts were further characterized by FTIR and XPS. Two identical compositions prepared by co-precipitation and impregnation on analysis showed that irrespective of the method of preparation, there are two types of acid sites, Lewis and Brönsted. The latter is characteristic of chromium since pure titania does not show any Brönsted acid site. The one prepared by co-precipitation containing upto 2% Cr has given better results. Ruiz et al. reported that Cr-doped TiO₂ p-type semiconductor thin film could be used for gas sensor applications. Table 2 presents various titania compositions and the major chemical conversions reported for catalytic reactions.
Table 2: Titania aerogels and xerogels and various catalytic systems reported

<table>
<thead>
<tr>
<th>Titania system</th>
<th>Reaction system</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>Gamma-Ray Destruction of EDTA</td>
<td>412</td>
</tr>
<tr>
<td></td>
<td>Water vapour chemisorption and</td>
<td></td>
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<tr>
<td></td>
<td>CO oxidation</td>
<td>354</td>
</tr>
<tr>
<td>TiO₂ Anatase &amp; Rutile</td>
<td>Adsorption of alcohols</td>
<td>353</td>
</tr>
<tr>
<td>TiO₂-based oxide catalysts</td>
<td>Selective catalytic reduction of NO</td>
<td>413</td>
</tr>
<tr>
<td>WO₃/TiO₂</td>
<td>Adsorption of alcohols</td>
<td>414</td>
</tr>
<tr>
<td>Halogen Ions-Modified</td>
<td>Selective Catalytic Reduction</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃, ZrO₂, and TiO₂ as Catalysts</td>
<td>(SCR) of NO with NH₃ at Low</td>
<td>415</td>
</tr>
<tr>
<td>V₂O₅/TiO₂ aerogel</td>
<td>Reduction of NO</td>
<td>416-418</td>
</tr>
<tr>
<td>V₂O₅/TiO₂ xerogel</td>
<td>Reduction of NO by NH₃</td>
<td>408-409</td>
</tr>
<tr>
<td>V₂O₅/TiO₂ and Cr₂O₇/TiO₂</td>
<td>Catalytic Removal of Nitrogen Oxides</td>
<td>419</td>
</tr>
<tr>
<td>Vanadium Oxide Incorporated into</td>
<td>Catalytic Oxidation</td>
<td></td>
</tr>
<tr>
<td>Mesoporous Titania</td>
<td></td>
<td>420</td>
</tr>
<tr>
<td>Chromia/TiO₂</td>
<td>Reduction of NO by NH₃</td>
<td>379</td>
</tr>
</tbody>
</table>
The photoelectric and photochemical properties of TiO$_2$ are in the focus of active research for the last one-decade. The initial work by Fujishima and Honda [27] on the photolysis of water on TiO$_2$ electrodes without an external bias, and the thought that surface defect states may play a role in the decomposition of water into H$_2$ and O$_2$, has stimulated much of the early work on TiO$_2$. Unfortunately, TiO$_2$ has a low quantum yield for the photochemical conversion of solar energy. The use of colloidal suspensions with the addition of dye molecules has been shown to improve efficiency of solar cells, [35,36,424] and has moved TiO$_2$-based photoelectrochemical converters into the realm of economic competitiveness. [425] Another method to improve the quantum yield is the manipulation of band gap, [119,426] which necessitates an active research and
the researchers all over the world are looking at it. The huge number of research papers getting published in this aspect shows its technological importance.

By far, the most actively pursued applied research on titania is its use for photo-assisted degradation of organic molecules. TiO$_2$ is a semiconductor and the electron-hole pair that is created upon irradiation with sunlight may separate and the resulting charge carriers might migrate to the surface where they react with adsorbed water and oxygen to produce radical species. These attack any adsorbed organic molecule and can, ultimately, lead to complete

Figure 3: Energy scheme of a semiconductor particle in which an electron is excited by light absorption. Located now in the conduction band it is capable of reducing species A (in most cases just oxygen from air). When excited by absorbing a photon hv there remains a positive charge (defect electron or hole) in the valence band capable of oxidizing species D. In TiO$_2$ the oxidizing power of such a hole is very high.
decomposition into CO$_2$ and H$_2$O. A schematic representation of photoassisted reaction is provided in Figure 3. The applications of this process range from purification of wastewaters;$^{89}$ disinfections based on the bactericidal properties of TiO$_2$$^{85,329-330,427-430}$ (for example, in operating rooms in hospitals); use of self-cleaning coatings on car windshields,$^{431}$ to protective coatings of marble (for preservation of ancient Greek statues against environmental damage.$^{432}$ It was even shown that subcutaneous injection of TiO$_2$ slurry in rats, and subsequent near-UV illumination, could slow or halt the development of tumour cells.$^{29,433-435}$ Several review papers discuss the technical and scientific aspects of TiO$_2$ photocatalysis.$^{436-439}$ An extensive review of the surface science aspects of TiO$_2$ photocatalysis has been given by Linsebigler et al.$^{120}$ and some of these more recent results are discussed.

Other oxides of similar behaviour are, ZnO, iron oxide, cadmium sulphide and ZnS. ZnO, which is also a reasonable substitute for titania, except for its property of undergoing incongruent dissolution resulting in formation of zinc hydroxide coating on the ZnO particles leading to slow catalyst inactivation. Among the photocatalysts, titania is believed to be the most promising material due to its superior photoreactivity, nontoxicity, long-term stability and low price. Titania crystallizes mostly in two polymorphic forms: anatase and rutile, whose band gaps are 3.23 and 3.02 eV, respectively (Figure 4). It is generally accepted that anatase titania is more efficient as photocatalyst than rutile titania.$^{257,389-390}$ Some researchers showed that catalysts with mixed
phases possessed a significantly higher catalytic activity than the pure anatase phase. Degussa P-25, a standard industrial photocatalyst, which is composed of 70% anatase and 30% rutile, is a good example. The main reason is ascribed to better charge carrier separation in the mixed phase. Ohtani et al proposed that a high photocatalytic activity of titania can be achieved when two requirements are satisfied, namely, a large surface area to absorb substrates and high crystallinity to minimize the photoexcited electron-hole recombination rate. However, these requirements are in general conflict with each other, because the crystallinity increases with calcination temperature while the surface area decreases. Photoactivity of amorphous titania is negligible compared to that of nanocrystalline anatase, which is greater than that of rutile. The activity of nanocrystalline rutile increases with decreasing particle size.

\[
\begin{array}{c}
\text{CB} \\
3020 \text{ mV} \\
\text{VB} \\
3230 \text{ mV}
\end{array}
\quad
\begin{array}{c}
\text{CB} \\
\text{VB}
\end{array}
\]

Figure 4: Schematic representation of band gaps of anatase and rutile

Conduction band edges of anatase and rutile are nearly at the same level of electron energy, whereas the edge of the valence band of anatase lays 140-
210 mV lower than rutile. Therefore the photoreduction power of anatase and rutile is equal but the oxidation power of anatase is significantly higher than rutile. This makes anatase attractive as species for photocatalytic oxidation reactions. In addition, its nature as a solid acid with adjustable surface properties and active H\(^+\) and Ti\(^{4+}\) centers make anatase attractive for a wide range of organic reactions. E.g., the synthesis of α-pinene.

However, the band gap of titania, 3.2 eV is too large to absorb in the visible region, which contains the largest amount (~40%) of solar energy. Hence, efforts have been made to dope titania with impurities and introduce states in the band structure about 2 eV below the conduction band minimum of titania so that the band gap of resultant material would be optimum for the photo production of hydrogen. Doping of transition metals into TiO\(_2\) has been tried.\(^{357,445-448}\) However, doped materials suffer from thermal instability, increase in the number of carrier recombination centers and require expensive ion implantation facility. Also, it has been argued that creation of oxygen deficiency introduces localized oxygen vacancy states located at 0.75 to 1.18 eV below the conduction band minimum of TiO\(_2\), so that the energy levels of the optically excited electrons are lower than the redox potential of the hydrogen evolution (H\(_2\)/H\(_2\)O) located just below the conduction band minimum of TiO\(_2\) and that the electron mobility in the bulk region will be small because of the localization.\(^21\)
Photocatalytic decomposition of trichloroethylene in water was investigated \(^4\) in which anatase form was found to be better compared with rutile form. \(^2\) Titania prepared by sol-gel route was porous, having high specific surface area of \(~ 600 \text{ m}^2/\text{g}\) containing anatase microcrystallites of the size of \(~50 \text{ Å}\) and was highly photoactive. \(^4\) Chloroform was subjected to photo degradation in a medium containing suspended particles of titania. \(^4\) Similarly, phenol photodecomposition has been reported using fine titanium oxide. \(^4\) Photocatalytic reactions involving NO were conducted in presence of Titania. \(^4\) Silica as support and titania as the active catalyst were tested for photoreactions and compared with the precursor characteristics. \(^4\) Titania supported on alumina and silica was used for photocatalytic decomposition of salicylic acid and the titania-alumina system showed improved performance. \(^3\) On analysis, it has been found that titania-silica consisted of matrix isolated titania quantum particles while the \(\text{TiO}_2-\text{Al}_2\text{O}_3\) did not have such particles. Pt/Pd metal particle carrying Titania was also prepared and tested. Titania film containing well dispersed Au or Ag metal particles were prepared by sol-gel method, the effect of the dispersed metal particles on the photo-electrochemical properties of the titania electrodes has been reported. \(^4\) The photo responsive formation of gold particles dispersed silica-titania composite gels was further investigated recently. \(^4\) Photoreduction of such systems containing Au (III) ions yielded gold particles and this principle was used to produce micro patterns of gold particles on silica-titania films.
There are reports on the effects of addition of metal ion dopants on quantum efficiency of heterogeneous photocatalysis of titanium dioxide. The enhanced photoactivity of titania doped by rare-earth oxides such as Europium, Praseodymium and Ytterbium oxides was recently reported by Ranjit et al. The high activity of oxide/TiO₂ photocatalysts is attributed to the enhanced electron density imparted to titania surface by the dopant oxides. Table 3 presents various titania compositions and the major chemical conversions reported for photocatalytic reactions.

Table 3: TiO₂ compositions for photocatalysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction / remark</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>Photocatalytic Transformation of 2,4,5-Trichlorophenol</td>
<td>461</td>
</tr>
<tr>
<td>Titanium Dioxide</td>
<td>Photocatalytic Oxidation of Cadmium-EDTA</td>
<td>462</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Stearic Acid</td>
<td>463</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Degradation of Bisphenol A in Water</td>
<td>464</td>
</tr>
<tr>
<td>Titanium Oxide</td>
<td>Decomposition of NO</td>
<td>465</td>
</tr>
<tr>
<td>TiO₂ Thin Film</td>
<td>Microbial sterilisation</td>
<td>466</td>
</tr>
<tr>
<td>TiO₂ films</td>
<td>Trichloroethylene</td>
<td>467</td>
</tr>
<tr>
<td>TiO₂ Microsphere</td>
<td>Water and Wastewater Treatment</td>
<td>468</td>
</tr>
<tr>
<td>Material</td>
<td>Application</td>
<td>Page</td>
</tr>
<tr>
<td>----------</td>
<td>--------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>TiO₂ aerogel</td>
<td>Aquatic decontamination</td>
<td>450</td>
</tr>
<tr>
<td>TiO₂ suspension</td>
<td>Chloroform</td>
<td>451</td>
</tr>
<tr>
<td>TiO₂ in zeolite</td>
<td>Phenol</td>
<td>452</td>
</tr>
<tr>
<td>structure</td>
<td>Reactions of NO</td>
<td>453</td>
</tr>
<tr>
<td>TiO₂-WO₃</td>
<td>Energy storage in the gas phase</td>
<td>469</td>
</tr>
<tr>
<td>TiO₂-SiO₂</td>
<td>Oxidation of 2-Chloroethyl Ethyl Sulfide</td>
<td>470</td>
</tr>
<tr>
<td>TiO₂-SiO₂ Binary</td>
<td>Photocatalytic Epoxidation of Oxides</td>
<td>471</td>
</tr>
<tr>
<td>Titanium Silicalite</td>
<td>Decomposition of Acetic Acid</td>
<td>472</td>
</tr>
<tr>
<td>Titanium Dioxide-Coated Surfaces</td>
<td>Photocatalytic Oxidation of Bacteria, Bacterial and Fungal Spores, and Model Biofilm Components to Carbon Dioxide</td>
<td>473</td>
</tr>
<tr>
<td>Silver-Coated TiO₂</td>
<td>Bactericidal Activities</td>
<td>474</td>
</tr>
<tr>
<td>TiO₂-Supported Gold Nanoclusters</td>
<td>Cryogenic CO Oxidation</td>
<td>475</td>
</tr>
<tr>
<td>Defective TiO₂ (110) Surfaces</td>
<td>DCOOD Decomposition</td>
<td>476</td>
</tr>
<tr>
<td>Cu-deposited TiO₂</td>
<td>Bactericidal Activity</td>
<td>477</td>
</tr>
<tr>
<td>Pt/TiO₂</td>
<td>CO Photooxidation</td>
<td>478</td>
</tr>
<tr>
<td>Au/Au (III)-TiO₂</td>
<td>Visible Photooxidation for Water</td>
<td>479</td>
</tr>
</tbody>
</table>
1.13 High Temperature Catalysts

Most of the applications of titania ceramics at high temperature require pure rutile phase, which is usually formed by heating the titanium salts above 600°C. However, with the expanding applications in the area of catalysts, photocatalysts, membranes and active humidity sensors, the need for obtaining anatase phase stable at elevated temperatures become significant. Earlier work indicates that even as a surface modifier for anatase titania pigments, alumina was used as a coating in order to improve gloss property as well as to prevent degradation. Recent identification of 'self-cleaning' surfaces by transparent anatase coatings on glass, ceramic tiles and bricks necessitates the anatase phase to be retained at the processing temperature above 1000°C.

The anatase-rutile transformation temperatures are fairly dependent on the history of the sample. Further, the low temperature densification in titania could be associated with the phase formation temperature. Early indicative reports on the incorporation of aluminum oxide, copper oxide, manganese oxide, iron oxide and zinc oxide postulated that the mechanism for modification of anatase-rutile transformation is related to oxygen vacancies on titania. This was also explained that the dispersion of alumina on titania stabilizes its surface and increases the apparent activation energy for the rutile
nucleation at titania-alumina interfaces. By using copper chloride as a dopant solution, a modified titania having nanocrystalline brookite stable at 400°C and having a narrow band gap than normal titania, could be produced through sol-gel route.\textsuperscript{19} However, a detailed investigation using thermal analysis and XRD techniques on the role of alumina in increasing the anatase-rutile transformation indicate\textsuperscript{481} that a metastable anatase solid solution containing alumina is formed at relatively low temperatures, and alumina is formed from exsolution process of the as formed anatase solid solution, in which rutile is formed at higher temperature. This argument is further supported by the fact that θ-alumina is formed at as early as 900°C in presence of titania while the usual α-alumina formation is above 1100°C. The influence of addition of zirconia in the raising of transformation temperature of anatase to rutile is also reported. Since zirconia is not expected to involve in any oxygen vacancy change in Titania, the role of zirconia was identified to be due to incorporation of Zr ions into anatase lattice. The formation of a limited solid solution\textsuperscript{482} of zirconia in anatase at low temperature increased the strain energy and thus leads to a higher anatase to rutile transformation temperature. An investigation on the effect of several cations of lanthanum, zinc, aluminum, potassium, sodium, calcium, barium and cobalt on the anatase-rutile transformation has been reported.\textsuperscript{483} The dopants were introduced into the Titania gel in the form of nitrates, heat-treated in the range 350-1100°C and was characterized by wide angle X-ray diffraction (WAXS) and thermogravimetry. Depending on the ionic radius of the dopant compared with titanium, can be introduced
substitutionally or interstitially or if the size of dopant is larger than oxygen it could be intercalated into the matrix, producing a large lattice deformation. The conclusion of the study is while the dopants have no effect on the amorphous gel to anatase transformation temperature, the anatase-rutile transformation is influenced considerably. Anatase phase is stabilized to a higher temperature when the dopant ion size is less than that of titania. Similarly, dopants bigger than oxygen ion produce large local deformation of the lattice. Those dopant ions whose size is falling between titanium and oxygen will stabilize the anatase phase. Those dopants near to oxygen size can stabilize the titania phase more. Similarly there is a correlation between the anatase phase stabilization temperature and charge of the ion times the cation volume.

Lanthanum oxide was doped in Titania membrane precursors in order to study the thermal stability and it was seen that there was an increase of 150°C in the anatase to rutile transformation in the doped composition. $\text{SnO}_2$, $\text{Al}_2\text{O}_3$, and $\text{Fe}_2\text{O}_3$ were doped in nanocrystalline Titania precursors and found that while $\text{SnO}_2$ and $\text{Fe}_2\text{O}_3$ decrease the transformation temperature, $\text{Al}_2\text{O}_3$ increased the same. However, the interesting fact is that these oxides were successful in controlling grain growth, which normally occurs in rutile as a result of the transformation. As is known in the case of nanocrystalline materials, the grain growth can be regarded as coalescence of smaller neighbouring grains, where grain boundary motion is mainly involved, and the role of these dopant oxides would be to restrict the movement of these grain
boundaries thus lowering the grain growth. The transformation kinetics in presence of Fe$_2$O$_3$ has been reported, where Fe$_2$O$_3$-TiO$_2$ mixture was heated in air and in argon atmosphere to different temperatures and the phases formed were analyzed for using XRD techniques. As found in the earlier study, the Fe$_2$O$_3$ primarily decreases the anatase to rutile transformation temperature.

Platinum was incorporated in titania prepared through titanium butoxide and platinum acetyl acetonate. Platinum promoted the formation of rutile probably through metal catalyzed dehydroxylation of anatase precursor or through the presence of PtO$_2$, which has the rutile structure, as an intermediate phase. Platinum atoms, however, did not go into crystalline structure of rutile.

In another study, chromium (III) was incorporated in anatase titania catalyst in different concentrations and analysis of the cell parameters indicated that there is a stability limit for the system at ~1.4 atomic percentage. Acceleration in the rate of anatase to rutile phase transition was also reported. Further, nanosize silver was incorporated in titania precursor gel and its effect of A$\rightarrow$R transformation was investigated using impedance spectral measurements. The transformation was delayed in presence of silver.

1.14 Definition of The Research Problem

Titanium dioxide is used in heterogeneous catalysis and as a photocatalyst for the decomposition of organics, in the treatment of industrial wastewater, for elimination of harmful bacteria and in the photocleavage of
water, in solar cells for the production of hydrogen and electric energy and in antifogging and self-cleaning coatings. Even though, lots of studies are reported on the synthesis and on various properties of titania, there exist many gaps in the understanding of the various parameters, which control the effectiveness of titania as photocatalysts. Further, methods of synthesis for nano crystalline titania and doped titania with general reference to effectiveness, to high temperature and on phase stability, reactivity and pore stability in bulk as well as in transparent nano coatings are still a very potential field of research. Sol-gel method is one of the most effective methods for synthesis of such active nano titania. The present study is an investigation into synthesis of nano size titania by sol-gel process involving an intermediate such as acetic acid, during hydrolysis-condensation reaction of titanium alkoxide. The role of acetic acid in modifying the hydrolysis-condensation reactions of titanium tetraisopropoxide in presence of dopants such as lanthana and/or ceria, which has been chosen based on the Hard and Soft Acids and Bases (HSAB) principle. Further, the HSAB principle helps in utilizing the heterodentating effect of acetate moiety to the fullest. Due to the specific reaction mechanism, the process is found to be repeatable, which is a concern in the sol-gel process.

Therefore, in the present work an attempt is made to
1. Study the synthesis of nanocrystalline titania and lanthanum and or cerium oxide doped titania through a modified polymeric sol-gel route.
2. Study the effect of acetic acid (stabilizing agent) and lanthanum and/or cerium (III) nitrate (dopant precursors) on the texturing of
nanocrystalline doped-titania and to correlate its chemical sequences with the structural and textural (surface area, porosity and pore volume) properties.

3. Modify the textural features by a co-doping-chemical leaching process, where silica was employed as the co-dopant.

4. Study the chemical interaction between titania and lanthana and/or ceria based on the HSAB principle.

5. Investigate the A>R transformation as well as photocatalytic efficiency in detail.

6. Fabrication and detailed morphological investigation of transparent, photoactive, self-cleaning, nanocrystalline titania coatings on glass surfaces.