SUMMARY AND GENERAL CONCLUSIONS

1. Introduction

Titanium dioxide is a versatile material with a number of applications associated with its optical, semiconductor and chemical properties. It exists in crystalline as well as amorphous forms. The three crystalline forms of TiO_2 are anatase, rutile and brookite. It is the most widely used white pigment in paints and cosmetics because of its brightness and high refractive index. It is also used as a coating for metals, sensor technology, adhesion, microelectronics etc. After Fujishima and Honda used titania for the first time for photoelectrolysis of water, TiO_2 chemistry has come a long way. It is widely investigated for environmental applications as a photocatalyst, for degradation of VOCs etc. Titania supported catalysts are also found to be more efficient and interesting as a catalyst as well as a support for numerous reactions. In recent years an exponential growth has been seen in the synthesis of TiO_2 nanomaterials owing to its applications ranging from photocatalysis to photovoltaic to sensors. Since TiO_2 is a versatile material, its synthesis is a subject of hot pursuit.

2. Objectives of the present work

Each application of titania requires a specific structure and also a specific size, hence it is important to develop synthesis methods in which the size and structure can be controlled.

The objectives of the present work were:

- To prepare nanocrystalline titania using $TiCl_3$ as a convenient precursor
- To prepare TiO_2 and its composites with ZnO
- To investigate the prepared titania for photocatalytic degradation of dyes
- To study the catalytic activity of prepared titania and its composites towards the liquid phase epoxidation and benzoylation reactions

3. Contents of the Thesis:

The present work has been described in 5 chapters

Chapter I: Introduction and Literature Status

This chapter deals with the following aspects

1. Introduction to TiO_2 with respect to crystalline modifications and phase formation.
2. Anatase to rutile phase transformation in relation to temperature, pressure, additives and dopants.
3. A brief literature review discussing the several precursors of TiO_2 and methods used for the synthesis of the same.
4. Techniques used for surface characterization of titania.
5. Titania as a catalyst and catalyst support.
6. A brief review discussing the activity – selectivity profiles of various catalysts used for epoxidation and benzoylation reactions.
7. Objectives of the present work in relation to epoxidation and benzoylation reactions

Chapter II: Experimental

This chapter describes

1. Synthesis by thiourea precursor method: Synthesis of rutile and anatase TiO_2 by a simple method involving use of acidified $TiCl_3$ and thiourea in different concentrations with or without use of oxalic acid.
2. Synthesis by hydrolysis method: Synthesis of TiO_2 by hydrolysis of $TiCl_3$ in presence of small amount of seed/nitric acid at room temperature or elevated temperatures.

Characterization of the catalysts is carried out by using instrumental techniques such as XRD, Raman spectroscopy, TG-DTA, XPS, TPD studies using ammonia, pzc, FTIR, insitu FTIR using pyridine, SEM and TEM.

Following observations were made:

(i) Use of oxalic acid resulted in the formation of pure anatase phase.
(ii) Increase in thiourea resulted in increase in surface area, lower crystallite size and increased pore volume.
(iii) TiO_2 can be rapidly synthesized at room temperature from aqueous solutions of $TiCl_3$ in presence of a small amount of 'seed'.
(iv) The rate of the $TiCl_3$ hydrolysis precipitation reaction was further enhanced in nitric acid medium or at elevated temperatures ~ 60 ^{o}C.
(v) Surface areas obtained by addition of HNO_3 in the synthesis are comparatively higher.
(vi) Pure rutile phase can be easily prepared by rapid hydrolysis of $TiCl_3$.

Chapter III: Photocatalysis

This chapter deals with the photocatalytic activity of synthesized titania for degradation of methylene blue and congo red dye. The experiment was carried out simultaneously for all the catalysts, by exposing aqueous dye solution and catalyst to sunlight. The photocatalytic behaviour of the catalyst was observed to depend largely on phase formation, pzc (point of zero charge) and band gap.
The results of photocatalytic degradation can be summarized as follows:

(i) Both rutile as well as anatase samples synthesized by thiourea precursor method showed higher photocatalytic activity as compared to the undoped TiO_2 sample.
(ii) The relatively lower activity of S-doped rutile sample as compared to S-doped anatase is attributed to higher rate of electron hole recombination.
(iii) All samples synthesized by hydrolysis of $TiCl_3$ were active for the photodegradation of methylene blue.
(iv) Rutile TiO_2 synthesized by hydrolysis of $TiCl_3$ in nitric acid medium at room temperature showed excellent efficacy for degradation of cationic dye methylene blue as well as anionic dye congo red.

Chapter IV: Epoxidation reactions

This chapter deals with the epoxidation of cyclohexene and cis-cyclooctene in presence of TiO_2 synthesised by thiourea precursor method. The use of pure TiO_2 in epoxidation reactions has been hardly investigated. Epoxidation reactions are indispensable for the chemical industry because of the ease with which they can be used to convert olefins to epoxides. Epoxides are valuable and versatile chemical intermediates used as key raw materials for wide variety of products owing to the numerous reactions they undergo. Epoxidation reactions require the presence of catalyst with greater porosity and good amount of acidic sites. We investigated the epoxidation of cyclohexene and cis-cylooctene using the synthesized catalysts.

The results of can be summarized as follows:

(i) Pure phase anatase catalysts having mesoporous structure are better suited for epoxidation reaction.

(ii) The higher activity in case of R3a (anatase TiO_2) could be due to favourable porosity which gave only one distinct porosity peak, unlike others.

(iii) The higher activity of the S-doped catalysts in comparison to the undoped sample may be due to the favourable effect of Sulphur and much lower particle size of the synthesized samples.

(iv) The significantly poor activity of the Degussa P-25 could be due to absence of mesopore structure, low surface area as well as presence of rutile phase that resulted in low catalytic performance.

(v) It was seen that all the catalysts showed higher activity for cyclooctene conversion than cyclohexene conversion.

Chapter V: Benzoylation reactions

Benzoylation constitutes a very important class among acylation reactions due to the commercial importance of benzophenones in agrochemical industries. $ZnO-TiO_2$ nanocomposites synthesized by a simple method were used as catalysts for benzoylation reactions for the first time.

The catalysts were highly active and selective for benzoylation of toluene and anisole in presence of p-toluoyl chloride as the acylating agent.

The results of benzoylation reactions can be summarized as follows:

(i) Describes synthesis of ZnO-TiO_2 nanocomposite catalysts in various proportions of active components.

(ii) The catalysts were investigated for benzoylation of toluene, anisole and o-xylene at preoptimised reaction conditions.

(iii) A catalyst of composition 70 % $ZnO(TiO_2)$ showed highest benzoylation activity for all three substrates as well as best selectivity to the desired *para* benzophenones.

(iv) Z4 catalyst 70 % $ZnO(TiO_2)$ nanocomposite showed good activity for the benzoylation of toluene, anisole and o-xylene as compared to pure ZnO or pure TiO_2.

(v) The high conversion and *para* selectivity using the above catalysts is attributed to the synergistic effect of ZnO and TiO_2 or the formation of new phase $ZnTiO_3$.

(vi) The high *para* - selectivity could also be attributed to the presence of Lewis acid sites of moderate strength.

4. Conclusions

(i) A nanocrystalline S-doped TiO_2 of high photocatalytic activity has been synthesized by a simple process involving $TiCl_3$, HNO_3, thiourea and oxalic acid.

(ii) Developed a rapid synthesis of TiO_2 from aqueous solutions of $TiCl_3$ in presence of small amount of “seed” for the first time.

(iii) Rutile TiO_2 having excellent efficacy for degradation of methylene blue as well as congo red dye was synthesized by hydrolysis of $TiCl_3$ in nitric acid medium at room temperature.

(iv) Highly active and selective ZnO-TiO_2 catalysts have been developed for benzoylation of toluene and anisole.