Chapter 7

Photochemical Degradation of Methylene Blue

Heterogeneous photocatalysis is one of the advanced oxidation processes that has proven to be a promising method for the elimination of toxic and bio-resistant organic and inorganic compounds from waste water by transforming them into innocuous species. Abundant solar energy can be utilized efficiently in the photocatalytic processes for the degradation of organic pollutants. Photochemical degradation of methylene blue, which is an organic pollutant, is described in this chapter under solar illumination that is free and inexhaustible. The percentage degradation of various systems for this reaction is correlated with the band gap energy of the prepared systems.

7.1 INTRODUCTION

Heterogeneous photocatalysis is a promising technology for the removal of toxic organic and inorganic contaminants from water. However, the development of a practical photocatalytic system focuses on the cost effectiveness of the process by the use of renewable solar energy source. Photocatalytic degradation of organic contaminants using solar radiation can be highly economical compared with the processes using artificial UV radiation, which require substantial electrical power input. Voluminous literature is available on photocatalytic destruction of various organic and inorganic pollutants using artificial UV radiation[1-5]. Photocatalytic oxidation of these

pollutants using sunlight has also been reported[6-11]. In recent years, photocatalytic degradation mediated by titania has received considerable attention. Titania is a wide band gap semiconductor with many interesting properties, such as transparency to visible light, high refractive index and low absorption coefficient. Other than these properties, eminent capability of photocatalytic decomposition of organic materials has come to utilization in the environmental business. Development of TiO_2 photocatalytic systems with high efficiency by controlling the nature of TiO_2 is one of the most attractive targets of fundamental studies in this field. The TiO_2 films grown on various substrates promise to have a high commercial potential in the environment applications such as self-cleaning, anti bacterial and waste water purification containment[12].

Heterogeneous photocatalysis is capable of degrading many classes of pollutants, but requires ultraviolet light and thus may be energy intensive. The basic principle of dye sensitization has been demonstrated showing the dependence of sensitization on the intrinsic properties of the support material and the adsorbed dye. The incident photons possessing energies greater than the band gap of the catalyst are absorbed. The absorbed photon then excites valence electrons into the conduction band, creating a positive hole. The resulting electron-hole pair can migrate toward the catalyst surface and initiate redox reactions that oxidize the adsorbed organic molecules[13]. A photocatalyst must posses a large catalytic surface and should also exhibit high proton utilization efficiency. The size of the primary catalyst particles defines the surface area available for adsorption and decomposition of the organic pollutants. When the size of a semiconductor particle is decreased to the extent that the relative proportions of the surface and bulk regions of the particle are comparable, its energy band structure becomes discrete and will exhibit chemical and optical properties different from those of the bulk material[14]. This is known as the quantum size effect and has been observed for nanosized TiO_2 particles[15].

Anatase type TiO_2 have attracted attention of scientists because of its photocatalytic activity for the decomposition of various environmental pollutants, such as NO_x in air and fertilizers in water[5,16-24]. Some problems related to their practical applications, however, have been pointed out; fine particles are desired for high photoactivity without the formation of rutile phase, which has lower photo activity than anatase. A few reports are available on SO_4^{2-}/TiO_2 for photocatalytic degradation of CH_3Br, NO_2^- and textile wastewater[25]. Toyoda and coworkers[26] studied the effect of crystallinity of anatase on photoactivity for methylene blue decomposition in water. Kwon *et al.*[27] reported the photocatalysis of titania prepared via sol-gel process using different alkoxide precursors for the degradation of methylene blue. Degradation rates of various organic dyes such as methylene blue, remazol blue R and orange G under solar irradiation using combustion synthesized nano titania were reported[28]. The photocatalyzed degradation of pyridine in the gas phase was investigated using titanium dioxide semiconductor supported on mordenite[29]. Photocatalytic oxidation of methylene blue and victoria blue in aqueous medium was studied using hydrothermally treated titania pillared clay[30]. In the present case the prepared systems are studied for the decomposition of methylene blue (figure 7.1) in its aqueous solution. Titanium dioxide represents one of the most efficient photocatalyst, however, the effective photo excitation of TiO_2 semiconductor particles requires the application of light with energy higher than the titania band gap energy (E_{bg}). For anatase E_{bg} (anatase) = 3.2 eV and for rutile E_{bg} (rutile) = 3.02 eV, therefore the absorption thresholds corresponding to 380 and 410 nm for the two titania forms respectively[5,31-33]. Consequently, only the ultraviolet fraction of the solar irradiation (about 5%) is active in the photoexcitaiton processes using pure TiO_2 solids. The present interest is to use solar light, which is free and inexhaustible.
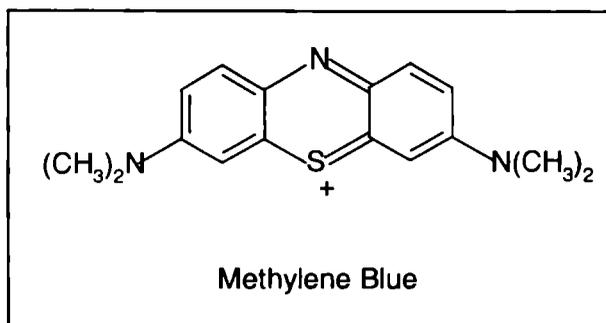
Figure 7.1 The structure of the methylene blue (MB)

7.2 PROCESS OPTIMIZATION

Photocatalytic degradation of methylene blue was performed taking 50 mL of (0.06 mmol L^{-1}) aqueous solution of methylene blue ($C_{16}H_{18}N_3S$, MB) and 0.1 g of catalyst. The solutions were exposed to sunlight in closed Pyrex flasks at room temperature with stirring. Direct sunlight was used in the present study and all the irradiation was performed during the second half of February 2004 (sunny days), from 11.00 to 14.00 h when solar intensity fluctuations were minimum. The samples were immediately centrifuged and the quantitative determination of methylene blue was performed using *Shimadzu UV-VIS spectrophotometer* (UV-160A) before and after reaction at 660 nm. Experiments were repeated three times to get better results. Control runs were carried out in darkness to monitor the changes in dye concentration due to adsorption. Experiments were also conducted under solar irradiation without catalyst to measure any possible direct photolysis of these organics. The pH variation during the course of reaction was not significant, so all the runs were conducted at natural conditions.

I. Effect of Time

An approximate reaction time is the main assurance for a perfect reaction. MB degradation is conducted and the absorbance measurements are

done at various times and the percentage degradation is calculated. Figure 7.2 illustrates the influence of time on the degradation experiments under solar irradiation. Degradation becomes 78.6% after one hour and increases to 91.6% after four hours of reaction time. As we expected, increase in time favours the percentage degradation. As time increases amount of radiation falling increases and this facilitates the degradation.
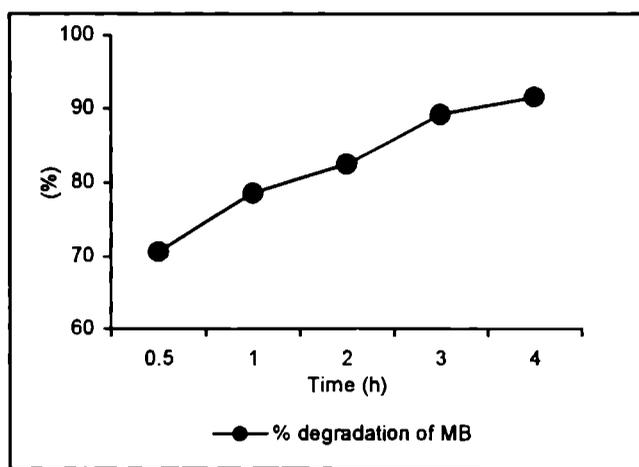

Figure 7.2 Influence of time on degradation of MB

Concentration of MB: 0.06 mmol L^{-1}

II. Effect of catalyst concentration

The effect of catalyst loading on the photocatalytic degradation of MB is studied by varying the amount of titania from 1 to 5 g L^{-1} of methylene blue solution. The percentage degradation of MB for a time period of 60 minutes is calculated and is given in table 7.1. Adsorption of MB by the sample powders is confirmed to be very small in the dark (without solar irradiation). Therefore, the observed decrease in absorbance of the solution is concluded to be due to the decomposition of MB by photocatalytic reaction on anatase samples.

Table 7.1 Influence of catalyst concentration on MB degradation

Amount of catalyst (g L^{-1})	-	1	2	3	4	5
% degradation of MB	2.9	65.3	78.6	70.1	55.8	32.6

Catalyst: T, Reaction time: 1 h, Concentration of MB: 0.06 mmol L^{-1}

From the preliminary study a little change in the degradation of MB is observed when the reaction is conducted in the absence of catalyst. Percentage degradation increases as we increase the catalyst concentration upto 2 g L^{-1} and then decreases with increasing catalyst loading. Percentage degradation changes from 78.6 to 32.6 when the catalyst amount increases from 2 to 5 g L^{-1}. This could be attributed to a shadowing effect, wherein the high turbidity due to high TiO_2 concentration decreases the penetration depth of radiation[28]. Hence an optimal catalyst loading of 2 g L^{-1} is enough for the degradation to occur effectively. Similar results were obtained for Nagaveni et al.[28] over Degussa P-25 TiO_2 catalyst under solar irradiation.

III. Effect of Concentration of Methylene blue

The effect of initial concentration of MB on the degradation rate is investigated over the concentration range of 0.04 to 0.07 mmol L^{-1}. It can be seen from the figure 7.3 that the concentration has a significant effect on the degradation rates. Madras and coworkers[4] proposed a model for photocatalytic degradation of dyes by taking into account of various controlling steps and Langmuir-Hinshelwood (L-H) parameters were determined for various dyes under UV irradiation. The degradation decreases from 100% to 64.2% as concentration of MB increases from 0.04 to 0.07 mmol L^{-1}. As the concentration of MB increases the percentage degradation decreases. At high concentration, the irreversible adsorption of the dye may occur on the catalyst surface leading to saturation during degradation[28].
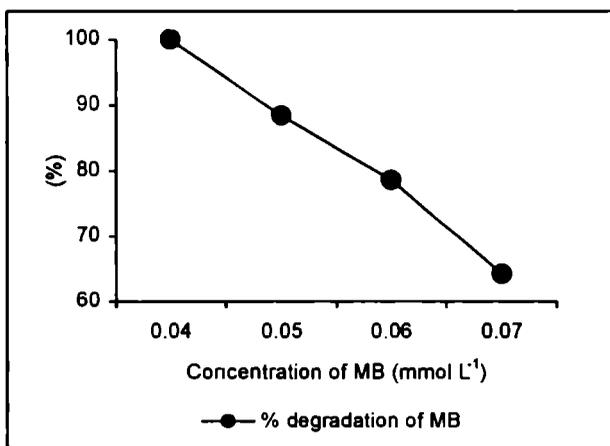
Figure 7.2 Influence of MB concentration on degradation

Reaction time: 1 h, Amount of catalyst: 2 g L^{-1} of T

IV. Catalyst Reusability

In order to understand the catalyst stability the experiments were conducted for one hour and the catalyst is taken at the end of the first cycle and used for the second cycle after activation. The percentage degradation of MB changes from 78.6 to 45.2 as the number of cycle changes from 1 to 4. Degradation rates are comparable in the first two cycles, but from the third cycle onwards a decrease in the percentage degradation is seen (table 7.2). This clearly indicates that the catalyst undergoes deactivation due to blocking of active sites by dye molecules, as the number of cycle increases.

Table 7.2 Catalyst reusability

No. of cycles	1	2	3	4
% degradation of MB	78.6	75.4	65.5	45.2

Amount of catalyst: 2 g L^{-1} of T, Reaction time: 1 h, Concentration of MB: 0.06 mmol L^{-1}

7.3 COMPARISON OF DIFFERENT SYSTEMS

The results obtained for the photo degradation of methylene blue over different systems under the optimized conditions is given in tables 7.3 and 7.4. Pure titania shows good activity. Among the various metal incorporated systems, copper loaded system shows high activity. The high activity may be due to low band gap energy of this catalyst compared to other systems.

Table 7.3 Influence of type of metal loaded in the photo degradation of MB

Catalyst	Percentage degradation of MB	Catalyst	Percentage degradation of MB
T	78.6	STCo(3)	65.2
ST	60.9	STNi(3)	68.4
STCr(3)	50.8	STCu(3)	70.5
STMn(3)	54.7	STZn(3)	52.1
STFe(3)	63.0		

Reaction time: 1 h, Concentration of MB: 0.06 mmol L^{-1}, Amount of catalyst: 2 g L^{-1}

The increase in band gap energy, evident from UV-Vis DRS studies, due to red shift in the λ_{max} leads to decrease in the photoactivity for the modified systems. Polyvalent heterocations negatively affect the photoactivity of TiO_2. It is postulated that the electrons in the d orbitals of these cations act as donors to quench the photogenerated holes by indirect recombination before they can diffuse to the surface. It can create acceptor and donor centers that behave as recombination centers for the photo generated charge carriers[34]. Amount of metal content does not give much difference in the results, because the absorbance maxima vary slightly among these systems and thus their band gap energy. Correlation between the percentage degradation of MB and λ_{max} obtained from UV-Vis DRS is given in figures 7.3 and 7.4.

Table 7.4 Influence of the amount of metal loading in the photo degradation of MB

Catalyst	Percentage degradation of MB	Catalyst	Percentage degradation of MB
STCr(6)	50.3	STCr(9)	49.8
STMn(6)	54.0	STMn(9)	53.5
STFe(6)	62.8	STFe(9)	62.0
STCo(6)	65.0	STCo(9)	64.4
STNi(6)	68.3	STNi(9)	67.8
STCu(6)	69.9	STCu(9)	69.3
STZn(6)	51.6	STZn(9)	51.2

Reaction time: 1 h, Concentration of MB: 0.06 mmol L^{-1}, Amount of catalyst: 2 g L^{-1}

Toyoda *et al.*[26] studied the effects of crystallinity of anatase on the photoactivity for MB decomposition over TiO_2 calcined at different temperature. According to them, both larger full width half maximum (FWHM) of anatase phase and also smaller FWHM obtained by annealing at high temperatures are not desirable for high photoactivity. Decomposition of MB suddenly increases at certain FWHM and then decreases gradually with decreasing FWHM. The degradation is rather low for anatase with small crystallite size and increases suddenly at about 12 nm, but then decreases with further growth of crystallites. In figure 7.5, percentage decomposition of MB against FWHM of 101 plane of anatase is plotted for the sulfated titania systems. Zhang and coworkers[35] reported that improved crystallinity has a beneficial effect on the increasing of photocatalytic degradation of phenol by titania powders. They also reported that mixtures of anatase and rutile are found to be more active than anatase crystallites or rutile crystallites at the same calcination temperatures.
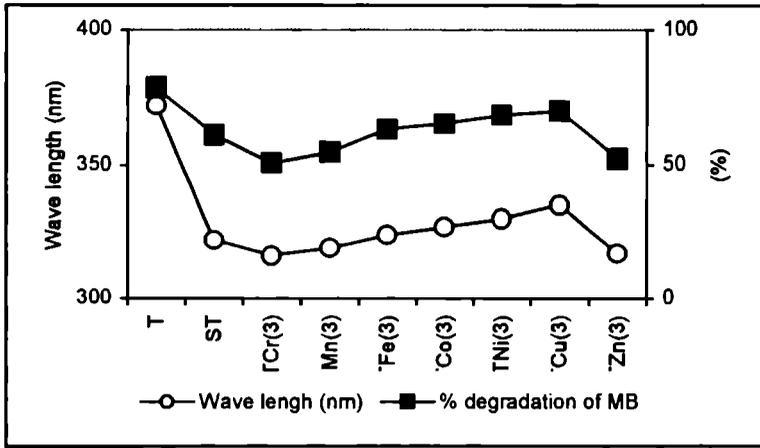
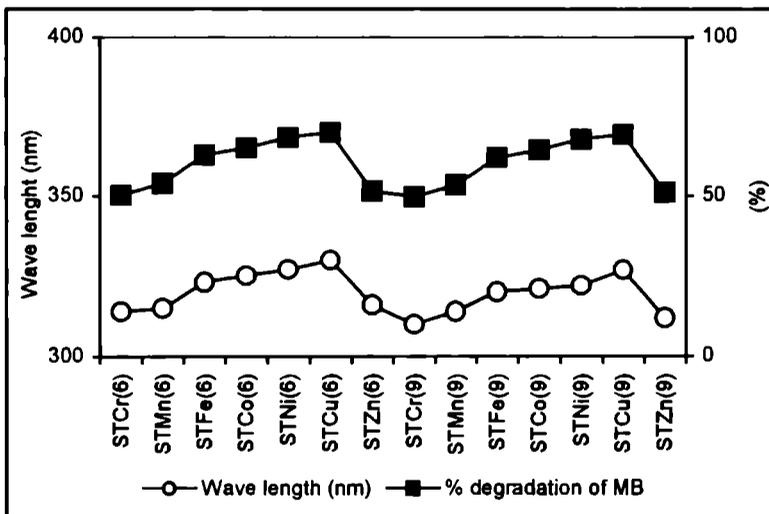Figure 7.3 Correlation between % degradation of MB and λ_{max}

Figure 7.4 Correlation between % degradation of MB and λ_{max}

It was reported[36,37] that the pore structure, pore size, particle size and activation temperature of TiO_2 affect the photocatalytic activity of organic pollutants in wastewater. The effects of sizes of primary particles (crystal) and secondary particles (aggregates) of anatase were examined in detail on the decomposition of trichloroethylene gas[13,38]. Chromia loaded samples having

low crystallite size show low photoactivity. In practice narrow range of FWHM, is found to be effective for high photoactivity. Reaction depends strongly on primary particle size, a maximum degradation rate at around 12 nm size and then there is a gradual decrease with increasing size. The decrease in photoactivity due to increase in crystallite size may be due to the cooperative effects of partial transformation of rutile.
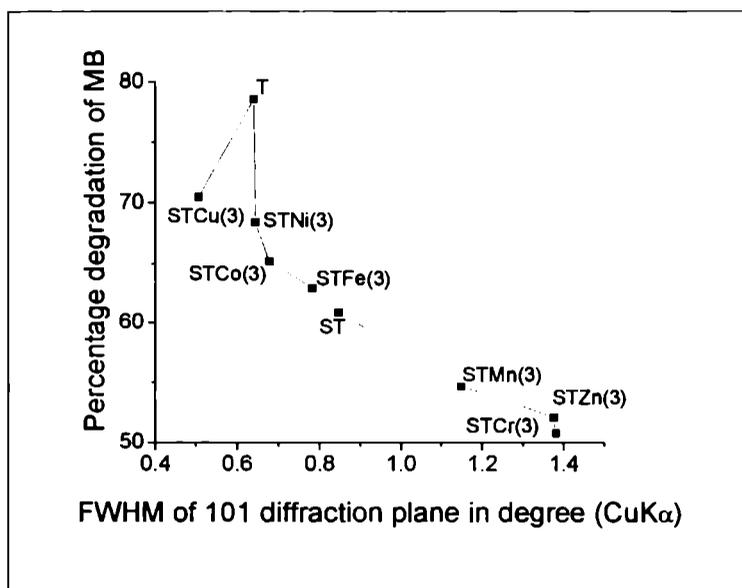

Figure 7.5 Relation between % degradation of MB and FWHM of 101 diffraction line of anatase phase on the sulfated titania samples

The influence of the particle size of TiO_2 nanostructured catalyst on its reactivity for trichloroethylene (TCE) photo-oxidation has been studied[13]. The TCE degradation over TiO_2 exhibits a maximum at a primary particle size of 7 nm. For the TiO_2 catalysts with a crystal size larger than 7 nm, the smaller crystals afford a larger surface area and exhibit higher TCE degradation. When TiO_2 is smaller than 7 nm, the catalyst activity decreases with smaller particle size. A blue shift in the band gap was observed for these smaller catalysts

resulting in a lower photon utilization and a different reactivity for the generated e^-/h^+ depending on the redox potential of the adsorbed molecules. However, it is difficult to attribute the decrease in TiO_2 catalyst activity solely to the structural or electronic effects. Anpo[39] observed an increase in the TiO_2 photocatalytic activity for the hydrogenation of CH_3COH with decreasing particle size. They associated the pronounced activity enhancement for particles smaller than 10 nm with the combined effects of larger surface area and size quantization. A similar observation was also made for the photocatalytic degradation of methylene blue in aqueous suspension for a series of TiO_2 particles larger than 30 nm[36]. However, other reports[40-42] showed that the photocatalytic efficiency does not monotonically increase with decreasing particle size. An optimal particle size of about 10 nm was observed for nanocrystalline TiO_2 photocatalysts in the liquid-phase decomposition of chloroform[40,41].

Reports show that the interface between anatase and rutile enhances the photoactivity of titania, in which anatase phase is directly exposed to UV rays[43]. In the case of pure titania, the interface between rutile and anatase might be formed, so that both phases can be exposed to sunlight and give high activity. The photocatalytic reaction on the TiO_2 surface is very sensitive to its surface structure because the photocatalytic reaction is a surface reaction. Samples that show low crystallite size have various structural defects. These defects were reasonably supposed to act as scattering centers for electrons and holes formed as a result of UV irradiation and consequently, promote the recombination of these couples. This seems to be the reason for low photoactivity for methylene blue in the case of metal incorporated systems.

Nagaveni et al.[28] showed that surface hydroxyl groups play an important role in determining photocatalytic activity. Since OH^- and H_2O groups are the most abundant adsorbates, these groups accept holes generated by solar or

UV illumination to form hydroxyl radicals thus preventing electron-hole recombination. Thus the high photocatalytic activity of pure titania can be attributed to high crystallinity as seen from XRD, nano size distribution (10-12 nm) as seen from the line width in XRD as well as SEM, large amount of surface hydroxyl groups evident from FTIR spectra and lower band gap energy of 3.2 eV as seen from the UV-Vis DR spectra.

7.4 MECHANISM OF PHOTOCHEMICAL REACTION

Photo irradiation of TiO_2 with photon energy greater than the band gap energy creates electrons and holes. Consequently following the irradiation, TiO_2 acts as either electron or hole donor to reduce or oxidize the materials present in the surrounding media.

$$TiO_2 \xrightarrow{h\nu} \bar{e}_{C.B.}(TiO_2) + h^+_{V.B.}(TiO_2)$$
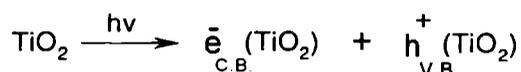
These electrons and holes are responsible for the photochemical reactions taking place on the surface of TiO_2. It is well known that photocatalytic activity strongly depends on bulk and surface physicochemical properties of the titania powder, such as the kind of crystal structure[44,45], surface area and particle size[46,47] and surface hydroxyls[48,49]. The mechanism of photocatalysis is discussed in recent reviews by Hoffmann *et al.*[5], Fox and Dulay[23]. Fewer recombination sites on the surface lead to slower recombination of electrons and holes, thus a higher photocatalytic activity[50]. The small crystal size also gave rise to quantum size effects[51]. This results in a net shift in the semiconductors band-gap energies. A blue shift in the TiO_2 band gap occurred for the modified samples. This means that for the same light source, there are fewer photons with the required energy to generate the e^-/h^+ pairs needed for the reaction. This results in a lower utilization of photons.

Titanium dioxide in the form of anatase is widely used mainly because of its high photocatalytic activity. Anatase is a wide bandgap semiconductor with bandgap energy of 3.2 eV, so only solar radiation with wavelengths below 387 nm is absorbed to form the e^-/h^+ pairs. At the ground level, however, solar irradiation starts at about 300 nm; thus approximately 4% of the total spectrum can activate TiO_2. During photocatalytic process, light activates a photocatalyst and establishes a redox environment in the aqueous solution. The semiconductor photocatalyst absorbs impinging photons with energies higher than the bandgap or threshold energy and generates oxidation sites on its surface. These oxidation sites react with adsorbed water molecules or hydroxyl to produce hydroxyl radicals, very strong oxidants capable of oxidizing virtually any organic compounds. When the TiO_2 surface is exposed to UV light, negatively charged particles-electrons-are released, just as the same way as the electron released when sunlight hits the surface of the solar power cells. Simultaneously, positively charged holes are formed on the surface of the catalyst and an electron is released. These electrons and holes create very strong oxidizers, called the hydroxide radical, even stronger than hypochlorous acid and ozone. When harmful substance sticks to the positive holes, they are completely broken down to harmless compounds. The hydroxide radical also can inhibit the growth of bacteria and mold.

7.5 CONCLUSIONS

The following conclusions can be drawn from the present study

- Photo degradation of methylene blue occurs effectively confirming that the prepared systems are photochemically active.

- Crystallite size of anatase was shown to be an important factor in order to get high photocatalytic activity for the decomposition of MB in water.

✍ Among the different systems pure titania shows the highest activity. The activity could be well correlated to their band gap energy.

✍ Activity difference among different metal incorporated systems is due to the combined effect of surface area, pore volume, crystallite size, pore structure and band gap energy.

✍ Abundant solar energy can be utilized efficiently in the photocatalytic processes for the degradation of organic pollutants. This is highly economical compared with the processes using artificial UV radiation which require substantial electrical power input.

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Chapter 8

Summary And Conclusions

To meet the challenges related to the industry, development of new generation of catalysts is necessary. In this connection, sulfated titania catalysts play an important role. The fundamental aspects, with focus on the preparation of heterogeneous catalysts by sol-gel method, its characterization, acidity determination and some industrially important reactions are briefly reviewed in this thesis. Systematic investigation of the physico-chemical properties and catalytic activity of some transition metal loaded sulfated titania catalysts are given in the previous chapters. A number of trends were found in the catalytic activity from the present study. This chapter deals with the summary and conclusions of the results described in the preceding chapters of the thesis.

8.1 SUMMARY

The present work is devoted to the synthesis of titania, sulfated titania and transition metal loaded sulfated titania catalysts. Its characterization and acidity determination using various methods are also discussed in detail. Titania has gained much attention in catalyst industry due to its application as a catalyst or catalyst support for metal or metal oxide catalysts used in heterogeneous catalysis including photocatalysis of industrially important and environment friendly reactions. Sulfated titania catalysts are prepared by sol-gel method, which is a homogeneous process resulting in a continuous transformation of a solution into a hydrated solid precursor. The nanochemistry

involved in the sol-gel method is a direct way to prepare highly divided materials. Sulfate modification is done using sulfuric acid to enhance the surface acidity so that they can replace the environmentally unfriendly catalyst in acid catalyzed reactions. Various characterization techniques have been used to evaluate the structural and textural properties of these solids. Finally, the catalytic activities of these materials in various industrially important reactions are investigated. Sulfation and incorporation of transition metals have positive influence on the acidity and catalytic activity. The characterization and catalytic activity results are compared with that of pure titania and sulfated titania. The present thesis comprises of eight chapters expounding the introduction, experimental and results and discussion parts. The chapter-wise depiction of the thesis is as follows.

Chapter 1 covers a brief literature review on titania and sulfated titania systems. The effect of sulfate doping on the physico-chemical characteristics and catalytic properties are included in this chapter. This chapter also includes literature survey on heterogeneous Friedel-Crafts alkylation, *tert*-butylation of phenol, nitration of phenol, photo degradation of methylene blue and Beckmann rearrangement reaction.

Chapter 2 deals with the various materials and experimental methods adopted for the synthesis and characterization of the catalyst systems. It also gives a brief account of the relevant theory of each method of characterization employed. Surface acidity determination by different techniques, including the test reactions like cumene conversion and cyclohexanol decomposition are the additional features of the chapter. The experimental procedures used to evaluate the catalytic activity are also incorporated in this chapter.

Chapter 3 discusses the physico-chemical characteristics of the catalyst systems. The catalyst systems are characterized by XRD analysis, surface area and pore volume measurements, EDX analysis, Scanning Electron

Microscopy, thermal studies, UV-Vis DRS, ^{1}H NMR and FTIR spectroscopy. Surface acidic properties are examined by three independent techniques namely ammonia TPD, perylene adsorption and thermodesorption studies using 2,6-dimethylpyridine as probe molecule. Cumene conversion reaction served as a test reaction for acidity. Cyclohexanol decomposition is performed to know the acid base properties of the catalysts.

Chapter 4 focuses on the application of the catalytic systems for Friedel-Crafts reactions. Benzylation of aromatics is achieved using benzyl chloride in liquid phase and *tert*-butylation of phenol in vapour phase. The influence of different reaction parameters on the catalytic activity and selectivity is subjected to investigation. The reusability of the catalytic systems is also checked. Attempt has been made to correlate the catalytic activity with the surface acidic properties of the catalyst systems and plausible mechanisms have been drawn out in each case based on the experimental observations.

Chapter 5 illuminates the application of sulfated titania systems towards the Beckmann rearrangement of cyclohexanone oxime. Influence of various reaction parameters like temperature, flow rate, concentration of oxime, influence of solvent etc. are discussed.

Chapter 6 narrates the nitration reaction of phenol over sulfated titania systems under different reaction conditions. It is found that certain optimum parameters are required for the better performance of the catalysts in the reaction.

Chapter 7 explains the photocatalytic activity of the prepared systems towards methylene blue degradation under solar irradiation.

Chapter 8 presents the summary and important conclusions of the present work.

8.2 CONCLUSIONS

The following conclusions are drawn from the present investigation.

➢ Titania, sulfated titania and transition metal loaded sulfated titania systems can be successfully prepared by sol-gel method. In all the catalysts, predominant phase is anatase. Sulfate modification retards the transformation from anatase to rutile.

➢ Incorporation of transition metals and sulfate modification improve the physico-chemical characteristics and surface properties of pure titania. Increase in surface area and decrease in crystallite size have been observed after sulfate modification, which is clear from XRD and SEM pictures.

➢ An optimum metal loading of 6% is found to be active in all the cases. High loading leads to the blockage of the active sites. Different characterization techniques like FTIR, ^{1}H NMR, and UV-Vis DRS show the presence of tetrahedrally coordinated Ti^{4+} ions.

➢ The surface acidity increases upon modification. Good correlation is obtained among the surface acidities measured by three independent methods. Vapour phase cumene conversion reaction works out as a test reaction for acidity. Good correlation is obtained between cumene conversion and the amount of total acid sites. Cracking and dehydrogenation product selectivity could be correlated with the Brönsted acidity and Lewis acidity of the systems respectively. Cyclohexanol decomposition reaction confirms the acidic character of the prepared systems.

➢ The systems are very active towards the Friedel-Crafts benzylation of toluene and *o*-xylene using benzyl chloride. High selectivity towards monoalkylated product is obtained in all the cases. Activities could be well

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correlated with the Lewis acidity of the samples. *Tert*-butylation of phenol gives 4-TBP as the major product, which is catalyzed by medium acid sites.

🔊 Beckmann rearrangement of cyclohexanone oxime proceeds effectively on the prepared systems. The conversion and selectivity depends greatly on the reaction conditions. ε-caprolactam selectivity could be correlated to the medium acid sites of the samples obtained from NH_3-TPD.

🔊 Nitration of phenol is achieved over the different systems and the conversion could be correlated with the Brönsted acidity of the samples. The product selectivity remained the same for different catalytic systems while a slight alteration is observed with variation in the reaction conditions.

🔊 Photochemical degradation of methylene blue occurs effectively, confirming that the prepared systems are photochemically active. The activity could be correlated with their band gap energy. Abundant solar energy can be utilized efficiently in the photocatalytic processes for the degradation of organic pollutants, which is highly economical compared with the processes using artificial UV radiation which require substantial electrical power input.

Future Outlook

Goal of both academic and industrial researchers is to obtain new catalytic systems having an enhanced activity and high selectivity towards the required product. Titania has created strong foundations in today's industrial and manufacturing world. A great deal of effort has been devoted in recent years to develop oxide catalysts by sol-gel process using metal alkoxides as precursors at room temperature. The results of present investigations reveal that sulfated titania systems are excellent catalysts for various industrially

important reactions such as Friedel Crafts benzylation of aromatic compounds, *tert*-butylation of phenol, Beckmann rearrangement of cyclohexanone oxime and nitration of phenol. The reason for selecting these reactions is that, metal oxides have long been known as favorable catalyst for these reactions but there is still plenty of room for improvement, particularly in the selectivity to a particular product as well as in catalyst life in view of practical application. The work can be extended to the development of environmentally friendly sulfated titania catalysts for the alkylation of various aromatic compounds using different alkylating agents. Since the prepared systems are acidic in nature, studies can be extended for various industrially important acid catalyzed reactions and rearrangements.

Huge improvements towards the development of environmentally friendly processes have been achieved in the nitration reactions. Nitration of other aromatics can be done over these catalysts to give better results under mild reaction conditions. Degradation of methylene blue occurs effectively over the prepared catalytic systems under solar irradiation. A great deal of attention has been directed towards various applications of photocatalyst for achieving a better environment. These catalysts can be used as photocatalysts to reduce toxic pollutants in the atmosphere and water, especially CO_2 and other volatile organic compounds in the atmosphere. Currently, the photocatalytic processes for the reduction of global air pollution have been focused due to the lower energy consumption, lower operating cost, lower operation temperature and utilization of solar energy for environmental protection.

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