STUDY AND DEVELOPMENT OF PHOTO CATALYSTS FOR ORGANIC TRANSFORMATIONS

Synopsis of the thesis submitted for the degree of Doctor of Philosophy

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Study and development of photo catalysts for organic transformations

Introduction

In today's world due to the increasingly stringent environmental limitations for industrial chemical processes, traditional processes employing harmful chemicals and dangerous oxidation / reduction agents with concomitant formation of large amount of harmful waste must be altered to environmentally benign processes. After the discovery of photoelectrochemical splitting of water on TiO₂ electrodes by Fujishma and Honda a great deal of attention has been devoted in the last decade to photo catalytic processes both in the homogeneous and in heterogeneous systems.

Heterogeneous photo catalytic systems with recyclable catalysts and without the use / emission of harmful chemicals / wastes have significant advantages. This presentation demonstrates that titanium oxide-based photo catalysts have a great potential as a versatile tool in "green" organic synthesis. Several photo catalytic reactions proceed highly efficiently and selectively on the titanium dioxide based photo catalysts. Photo catalytic transformations hold significant promise for the development of economically and environmentally friendly synthesis processes.

Photo catalysis

The term photo catalysis consists of the combination of photochemistry and catalysis and it implies that light and catalysts are necessary to bring out a chemical transformation. When a photo catalyst is illuminated by light with energy equal to or greater than band-gap energy, the valence band electrons can be excited to the conduction band, leaving a positive hole in the valence band (Fig.1). The excited electron-hole pairs can recombine, releasing the input energy as heat, with no chemical effect. However, if the electrons and holes migrate to the surface of the semiconductor without recombination, they can participate in various oxidation and reduction reactions with adsorbed species such as water, oxygen, and other organic or inorganic species.



Fig.1 Photo chemical process under illumination.

The oxidation and reduction reactions are the basic mechanisms of photo catalytic organic transformations and it is a green chemistry application. In the photo catalytic process, the valence band (VB) holes are the important elements that induce the oxidation of substrate. The conduction band (CB) electrons are that induce the reduction reaction of the substrate. The two processes occur simultaneously and are exploited for the synthesis of organic molecules. Several applications of photo catalysis are depicted in Fig.2.



Fig. 2. Photo induced processes of TiO₂

Aim and objectives of the thesis

- To study and improve the efficiency of the synthesis of organic intermediates, by the modifications of photo catalyst surface (i.e., impregnation, photo deposition, solid state dispersion and sol-gel methods) and to understand the effect of surface modification techniques on photo catalytic activity.
- To study the effect of noble metal, transition metal loading, interaction of metal ions with the support and the effect of oxidation state on photo catalytic activity under solar irradiation.
- To study the effect of pretreatment temperatures on the oxidation state of the metal ions and their interactions with the support and its stability under solar and UV irradiations.
- To study the effect of different ion loadings on the surface of photo catalyst, their optimization, characterization and comparing their activities under solar irradiation.
- Synthesis of anion doped nano photo catalysts with high surface area and their characterization and evaluation for photo catalytic organic transformations under solar irradiation.

Outline and plan of the thesis

The thesis covers results of investigations on the surface and structure modifications of TiO_2 photo catalyst and their evaluation for organic transformations under solar and UV irradiations. It consists of eight chapters.

- **Chapter I:** Details the introduction, which highlights the background information available in the literature on TiO₂ based photo catalysis and photo catalytic organic transformations.
- **Chapter II:** Details the experimental preparation of metal ion modified TiO₂ photo catalysts, Synthesis of TiO₂ and C, N and S -doped TiO₂ nano photo catalysts. The basic concepts and characterization by spectroscopic techniques are described.
- **Chapter III:** Highlights the synthesis, characterization and evaluation of TiO₂ and C, N and S -doped TiO₂ nano photo catalysts for ethyl benzene oxidation to actophenone production in acetonitrile medium under solar irradiation.
- **Chapter IV:** Highlights the structure and photo catalytic activity of Ag₂O/TiO₂ photo catalysts for reduction of nitrobenzene to aniline production from methanol as hydrogen source in acetonitrile medium under solar light irradiation and establish a structure- activity correlation.

- **Chapter IV:** Highlights the photo catalytic activity of Cu₂O/TiO₂ and CuO/TiO₂ photo catalysts for selective dehydrogenation cyclohexanol to cyclohexanone in acetonitrile medium under solar irradiation and establishes a structure-activity correlation.
- **Chapter V:** Highlights the photo catalytic activity of Cu loaded TiO₂ and supported on molecular sieve-5A combinate photo catalysts for carbon dioxide reduction to useful chemicals under UV irradiation.
- **Chapter IV:** Describes the TiO₂ and Fe -Titanates (Fe -Ti-O) supported HZSM-5 zeolite photo catalysts and their activity evaluation for synthesis of urea from nitrate ion and isoproponol mixtures under UV irradiation.
- Chapter VIII: Conclusions based on the evaluation of all the results obtained in the thesis program.

Summary of the thesis

Chapter 1: Introduction

One of the fore most challenges currently facing the chemical industry is the need for alternative production technologies that are cleaner, safer and more environmentally friendly. The use of traditional reagents and homogeneous acid catalysts for the synthesis of organic intermediates and fine chemicals are having several disadvantages. They are highly corrosive, demand tedious workup procedure, need stoichiometric quantities non eco-friendly nature and are not reusable. Catalysis in the 20th century was recognized as being multidisciplinary field of science, involving chemists, biologists, physicists and engineers.

The resolution problems and the reaching of targets were usually achieved via the sequential in put and contributions of the disciplines. The 21st century should and will recognize catalysis as an inter- and trans-disciplinary science benefiting from parallel input of many disciplines. Heterogeneous catalysis to the synthesis of fine and specialty chemicals and pharmaceuticals is receiving increased attention as it is the route to the design of safer, cleaner and sustainable process. Goal of organic synthesis is to open the way for highly efficient construction of useful molecules of desired function(s) without unnecessarily wasting resources, energy and generating un-green by-products.

The first chapter details the introduction that highlights background information available in the literature for various organic transformation reactions. Reported studies on structural modifications and photo activity of various catalysts are discussed. For the synthesis of organic compounds and to achieve selectivity, efficient photo catalysts are required. These modifications include composite semiconductor oxide photo catalysts, zeolite supported photo catalysts, nano photo catalysts, metals and non-metal doped photo catalysts.

The back ground literature regarding these modifications is well discussed in this chapter. Among several transformations only a few are discussed in detail, which are useful in organic chemistry.

Chapter II: Experimental

This chapter details the experimental approach viz, the preparation and their characterization techniques. The experimental procedures and spectroscopic techniques used in the present investigation are described.

Preparation and characterization of photo catalysts

Ag₂O/TiO₂, Cu₂O/TiO₂, CuO/TiO₂ and Cu loaded TiO₂ catalysts, Fe -Titanates are prepared by impregnation method. Nano TiO₂ and C, N and Sdoped TiO₂ catalysts are prepared by sol-gel method. Cu -TiO₂, Fe-Titanates supported zeolite catalysts are prepared by solid state dispersion method. Ag/TiO₂ catalyst is prepared by photo deposition method for reference. Nano TiO₂ is synthesized in the laboratory. TiO₂ (P-25) is a commercial catalyst obtained from Degussa corporation, Germany. The commercially available and indigenously synthesized catalysts were characterized by various techniques like XRD, SEM-EDAX, TEM, UV-Vis- DRS, XPS, FT-IR, and BET Surface Area.

Activity evaluation of photo catalysts

The photo catalytic reactions were carried out in a sealed, evacuated and deaerated batch type cylindrical round bottomed reactor of 100 ml capacity. For solar experiments, the reaction was carried out under natural sun light on bright sunny days. The amount of the catalyst in the solution and concentration of substrate in each reaction are optimized. The progresses of reaction in each experiment were monitored by a GC, HPLC.

The intensity of solar light was measured using a LT Lutron LX - 101A digital light meter. The solar light intensity was measured for every hour during experiments.

Chapter III: Ethyl benzene oxidation

This chapter describes ethyl benzene oxidation activity on TiO_2 and C, N and S -doped TiO_2 nano photo catalysts in acetonitrile under solar irradiation.



- C, N and S -doped TiO₂ photo catalysts were synthesized on treating titanium isopropoxide with thiourea by sol-gel process.
- The liquid-phase photo oxidation of ethyl benzene (EB) is investigated in solar light with Air/O₂/N₂ at atmospheric pressure, in a batch reactor using acetonitrile medium.
- The photo catalytic oxidation yielded acetophenone (33%) and
 1-phenylethanol (21%) at 56 % conversion of EB during 6 h irradiation time.
- The results conclude that 5 wt% thiourea doped i. e. TCNS5 is an efficient catalyst and the high activity and selectivity may be due to the high surface area, lower electron-hole recombination and the stronger adsorption in visible light region. The substrate concentration of EB of 2.73x10⁻² M, catalyst

amount 3.33 g.L⁻¹ and a neutral pH are found to be favorable conditions for higher oxidation rates. The catalyst activity is found to be sustainable even after the 3rd cycle.

- The XRD studies of all the catalysts showed a single crystalline anatase phase and TEM results confirmed that the particles are highly nano sized with an average size of 3-5 nm.
- N₂ adsorption measurements show that TiO₂ and C, N and S doped TiO₂ catalysts are with high surface area.
- A red shift of around 100 nm in the DRS band of C, N and S -doped TiO₂ compared to bare TiO₂ (P-25) indicates a transition in the band gap towards the visible region and as the content of doped carbon, nitrogen and sulfur increases into the TiO₂ lattice, the band gaps are narrowed from 3.15 to 2.68 eV.
- The formation of oxynitride linkages by thiourea in the synthesis are evidenced from the FTIR results of the air dried sample.
- The formation of Ti-O-N, Ti-O-S and Ti-O-C bonds in C, N and S doped TiO₂ were confirmed by the XPS studies.
- Photo catalytic activity of C, N and S doped TiO₂ was evaluated for ethyl benzene under solar irradiation.
- The enhanced photo catalytic activity on C, N and S -doped TiO₂ compared to TiO₂ (P-25) is due to the incorporation of carbon, nitrogen and sulfur at the surface layers of titania lattice.
- In summary, the application of photo catalytic oxidation of EB offers a step forward in sustainable catalysis. This is advantageous from the standpoint of

low cost, environmental friendliness, and operational simplicity and it may be applicable to large-scale reactions with further fine tuning of the system

Chapter IV: Nitro benzene reduction

This chapter describes the aniline production activity studies over Ag₂O/TiO₂ photo catalysts from nitrobenzene, methanol mixtures under solar light irradiation.

 Aniline (AN) is an industrially important chemical and is prepared by reduction of nitrobenzene (NB).



- Silver loaded TiO₂ catalysts with varying amounts of Ag₂O (wt %) are prepared by impregnation method and are calcined at 450°C for 5 h. Also silver loading on TiO₂ catalyst is attempted by photo deposition method.
- The liquid-phase reduction of nitrobenzene is investigated under solar light in deaerated conditions at atmospheric pressure, room temperature in a batch reactor in acetonitrile as well as in aqueous medium.
- The effects of nitrobenzene concentration, metal content, amount of photo catalyst, sustainability are investigated.
- The advantage of photo catalyzed study is that it occurs at ambient temperature under natural solar light. Moreover greater selectivity and yield of this method is an added advantage. The present study demonstrates

preparation of silver doped TiO_2 photo catalyst and its role in photo catalytic reduction of nitrobenzene to aniline. The results conclude that 1 wt % Ag₂O / TiO_2 is an efficient catalyst for the photo catalytic reduction of nitrobenzene.

- The ratio of Nitrobenzene: Methanol 5.73 in acetonitrile medium, catalyst amount 3 gL⁻¹ and neutral pH are found to be favorable for higher photo catalytic reduction of nitrobenzene to aniline. The catalyst activity is stable up to 3rd cycle.
- The product aniline showed a maximum yield of 65 %.
- All the catalysts are characterized by XRD, SEM-EDAX, UV-Vis DRS, XPS and TEM techniques to understand the structural changes taking place in TiO₂ photocatalyst with metal ion modification and post-reaction characterization and also carried out to know the oxidation states and stability of the catalyst after usage.
- XRD patterns are showing only the characteristic anatase and rutile phases of TiO₂ and no characteristic peaks corresponding to silver planes are observed in the calcined samples indicating that silver is finely dispersed on the surface of TiO₂.
- EDAX analysis supports the presence of silver species on the surface layers of TiO₂.
- TEM images are showing the fine dispersion of silver particles on TiO₂ surface.
- DRS studies clearly show the expanded photo response of TiO₂ into visible region on impregnation of Ag⁺ ions on the surface layers of TiO₂ due to the

increased number of energy states created by the silver ions in the band gap of TiO_2 .

- XPS of Ag₂O/TiO₂ catalysts showed that silver is in +1 oxidation state and silver ions are in interaction with TiO₂.
- Photo catalytic reduction of nitrobenzene to aniline studies were conducted under solar irradiation over bare TiO₂ and silver modified TiO₂ catalysts in acetonitrile medium and methanol: water mixture used for hydrogen source.
- Aniline production was less observed on bare TiO₂ catalyst used in water and methanol mixture for hydrogen source, whereas aniline production was improved on bare TiO₂ as well as silver modified TiO₂ catalysts when methanol alone was used for hydrogen source.
- Activity studies were also conducted over Ag₂O/TiO₂ reduced, Ag/TiO₂ photo deposited, Ag₂O, Ag₂O/TiO₂ mechanical mixtures to understand the structureactivity correlation.
- Though Ag₂O/TiO₂ reduced and Ag/TiO₂ photo deposited catalysts are showing visible response, these catalysts are not showing any appreciable aniline production activity either in methanol or in methanol: water mixtures for hydrogen source under solar irradiation.
- It is illustrated that interacted Ag⁺ ions on the surface of TiO₂ are responsible for the aniline production activity under solar light irradiation.

Chapter V: Cyclohexanol dehydrogenation

This chapter describes the dehydrogenation of cyclohexanol activity studies over Cu_2O/TiO_2 , CuO/TiO_2 photo catalysts under solar light irradiation.

 Cu loaded TiO₂ catalysts with varying amounts of Cu (wt %) loadings are prepared by impregnation method and these catalysts are calcined at 350°C and 450°C for 5h.



- All the catalysts are characterized by XRD, SEM-EDAX, and UV-Vis- DRS, XPS and TEM techniques before and after the reaction.
- XRD patterns clearly shows only the characteristic peaks of TiO₂. Peaks related to Cu phase are not observed in both the series when Cu is loaded over TiO₂ catalysts.
- EDAX analysis supports the presence of Cu species on the surface layers of TiO₂.
- DRS studies showing the expanded photo response of TiO₂ into visible region on impregnation of Cu on the surface of TiO₂ (in both series) due to the additional energy states created by the copper ions into the band gap of TiO₂.
- XPS studies are showing change in the binding energy values of Ti 2p, O 1s and Cu 2p, indicating that copper ions are in interaction with TiO₂.

- XPS results are also confirming that the oxidation state of copper is +2 in samples calcined at 350°C and it is +1 in samples calcined at 450°C.
- Photo catalytic dehydrogenation of cyclohexanol activity studies are conducted over CuO/TiO₂ and Cu₂O/TiO₂ catalysts in acetonitrile under solar irradiation.
- 40% of maximum cyclohexanone production yielded with 100% selectivity over Cu₂O/TiO₂ catalysts in acetonitrile. No dehydrogenation activity is observed on reduced catalysts under solar irradiation.
- When the catalysts are studied under UV irradiation, 2 to 3 fold decrease in activity is observed on calcined catalysts and the same level of activity is observed on reduced catalysts and the activity is limited (controlled) by the reduction of Cu ions into metallic state.
- Under solar irradiation a stable activity is observed on Cu₂O/TiO₂ catalyst.

Chapter VI: Carbon dioxide reduction to chemicals

- Cu loaded TiO₂ catalysts with varying amounts of metal (wt %) loadings are prepared by impregnation method and these catalysts are calcined at 450°C for 5 h and also supported on molecular sieve - 5A composite systems.
- It is demonstrated that Cu-TiO₂ supported on molecular sieve 5A system acts as a good photo catalyst for CO₂ reduction. Catalysts are evaluated for CO₂ activity in pure water and 0.2N NaOH containing solution under UV light irradiation.
- All the catalysts are characterized by XRD, SEM-EDAX, UV-Vis DRS, XPS and TEM techniques.

 XRD patterns are clearly showing only the characteristic anatase and rutile peaks of TiO₂. No characteristic peaks corresponding to metal ion are observed in all the catalysts indicating that transition metal ions are finely dispersed on the surface of TiO₂.



- EDAX analysis supports the presence of metal ions on the surface layers of TiO₂.
- DRS studies are showing the expanded photo response of TiO₂ into visible region on impregnation of transition metal ions on the surface of TiO₂ due to the additional energy states created by the metal ions in the band gap of TiO₂.
- XPS studies are confirming that metal ions are in interaction with TiO₂.

- The formation of the oxalic acid as the reduced product of carbon dioxide is observed on bare TiO_{2.}
- Cu loaded TiO₂ catalyst is showing comparatively lesser activity than bare TiO₂ in pure water and dissolution of Cu ions into the solution is noticed. Whereas Cu loaded TiO₂ supported on molecular sieve - 5A, dissolution of Cu ions are not seen.
- The increase in the formation of oxalic acid (56 µg /h/g catalyst) is observed on Cu -TiO₂ supported on molecular sieve system, may be because of the copper leached from the TiO₂ surface may be stabilized on the molecular sieve - 5A.
- Highly dispersed Cu -TiO₂ on molecular sieves with increased band gap and good adsorption property of CO₂ enhanced the photo reduction with selective formation of oxalic acid.
- The unsupported Cu -TiO₂ system showed comparatively lesser formation of oxalic acid.
- Methanol and acetic acid were also observed on molecular sieve combinate system. This might be due to shape selectivity of the support and adsorbdesorb shuttle mechanism of CO₂ on the support that plays a crucial role in selective formation of products.
- The yield of oxalic acid, acetic acid and methanol were found to be 65.6, 12.0,
 0.8 (μg / h / g / cat) respectively using 0.2 N NaOH over 10 wt % TC_{2.0} / MS combinate photo catalyst.

 Cu-TiO₂ supported on molecular sieve 5A composite system is showing highest activity compared to the TiO₂ (P-25) catalysts in 0.2 N NaOH solution than in pure water due to the dispersion and stabilization of copper on the large surface area of the support.

Chapter VII: Synthesis of urea

- TiO₂ and Fe -Titanate (Fe-Ti-O) supported on zeolite were prepared by solgel and solid-state dispersion methods.
- Urea was synthesized using photo catalysts under atmospheric pressure and ambient temperature in a batch reactor.
- All the reactions are performed in aqueous medium containing NO₃⁻ and 2-propanol, the latter served as a 'hole, scavenger and as source for CO₂ under UV light Illumination.
- All the catalysts are characterized by XRD, surface area, TEM, SEM and UV-Vis DRS studies
- It is concluded that an optimum of 10 wt % TiO₂ or Fe -Titanate supported on a zeolite provides to achieve 90 % reduction of nitrate to ammonia.
- Using photo catalyst and zeolite combinate system that brings the polymerization reaction of the products which are reduced and the condensation reaction leads to urea formation.



- Urea of 18 ppm was obtained at 90 % conversion of nitrate.
- The optimized reaction conditions at lab scale are scaled-up to five fold with greater success in achieving the important urea product.

Chapter VIII: Summary and Conclusions

This chapter represents the salient features of results obtained in the total thesis work (Table.1).

The results conclude that 5 wt% thiourea doped i. e. TCNS5 is an efficient catalyst and the high activity and selectivity may be due to the high surface area, lower electron-hole recombination and the stronger adsorption in visible light region. The substrate concentration of EB of 2.73x10⁻² M, catalyst

SI. No.	Photo catalysts	Reactions Studied	Publications
1	C,N and S-doped TiO ₂	(Conv = 56%) Solar light H ₃ C C=0 H ₃ C OH + CH ₃ CN + (Yield = 33 %) (Yield = 22 %)	Res. Chem. Intermed 37 (2011) 901 - 918
2	Ag ₂ O/TiO ₂	(Hold - CO + 3) (Hold - 22 + 3) $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - CO + 3) (Hold - 22 + 3)$ $(Hold - 22 + 3) (Hold - 22 + 3)$ $(Hold - 22 + 3) (Hold - 22 + 3)$ $(Hold - 22 + 3) (Hold - 22 + 3)$ $(Hold - 22 + 3) (Hold - 22 + 3)$ $(Hold - 22 + 3) (Hold - 22 + 3)$ $(Hold - 22 + 3) (Hold - 22 + 3)$ $(Hold - 22 + 3) (Hold - 22 + 3)$ $(Hold - 22 + 3) (Hold - 22 + 3)$ $(Hold - 22 + 3) (Hold - 22 + 3)$ $(Hold - 22 + 3) (Hold - 22 + 3) (Hold - 22 + 3)$ $(Hold - 22 + 3) (Hold - 22 + 3) (Hold - 22 + 3)$ $(Hold - 22 + 3) (Hold - 23 + 3$	Indian J. Environ. Prot . 31 (2011) 1-15
3	Cu ₂ O/TiO ₂	$(Conv = 40 \%) \xrightarrow{OH} \frac{Solar light}{CH_3CN} \xrightarrow{O} + H_2$	Res. Chem. Intermed 37 (2011)1069 -1086
4	Cu-TiO ₂ / Zeolite	$CO_{2} + H_{2}O \xrightarrow{\text{Reduction}}_{\text{UV illumination}} + COOH + CH_{3}COOH + CH_{3}OH$ (Yield = 56 micro g / h / cat)	Photochem. Photobiol. 87 (2011) 995-1001
5	TiO ₂ / Zeolite Fe-Ti-O / Zeolite	H_2O+NO_3 H_2 NH_3 $H_2N_2C=O$ (CH ₃) ₂ CHOH (CH ₃) ₂ CO CO ₂ + H ₂ O (Yield = 18 ppm)	Photochem. Photobiol. In press (2011)

Table 1. Salient features of photo catalysts prepared and evaluated for organic transformations

amount 3.33 g.L⁻¹ and a neutral pH are found to be favorable conditions for higher oxidation rates. The catalyst activity is found to be sustainable even after the 3rd cycle. The photo catalytic oxidation yielded acetophenone (33%) and 1-Phenylethanol (21%) at 56 % conversion of EB during 6 h irradiation time. This product distribution is indicating that C-H bond activation has occurred only at the alkyl chain.

- Ag₂O/TiO₂ catalysts are prepared by impregnation method and by photo deposition method. Activity tests were conducted over Ag₂O/TiO₂ calcined and reduced sample as well as Ag/TiO₂ photo deposited catalysts. Only Ag₂O/TiO₂ calcined catalysts are showing nitrobenzene reduction for production of aniline activity under solar irradiation and reduced and photo deposited catalysts are not showing any activity. Interacted Ag⁺ ions on the surface layers of TiO₂ are responsible for continuous hydrogen production activity under solar irradiation. The results conclude that 1 wt % Ag₂O / TiO₂ is an efficient catalyst for the photo catalytic reduction of nitrobenzene. The ratio of Nitrobenzene: Methanol of 5.73 in acetonitrile medium, catalyst amount 3 gL⁻¹ and neutral pH are found to be favorable for higher photo catalytic reduction of nitrobenzene to aniline. The catalyst activity is stable up to 3rd cycle.
- Cu₂O/TiO₂ and CuO/TiO₂ catalysts are prepared by impregnation method. The activity on Cu₂O/TiO₂ is stable and is high compared to CuO/TiO₂ as well as reduced catalysts which are not showing any hydrogen production under

solar irradiation. The optimum cyclohexanol is 3.20×10^{-3} M concentration and catalyst amount is 3.33 g.L^{-1} which are found to be the required amounts. It is note worthy that cyclohexanol dehydrogenation is giving rise to 40 % yield of cyclohexanone in mild conditions like temperature or pressures compared to thermal catalytic processes. This study provides for further exploration of an efficient and low cost viable method for cyclohexanone production from cyclohexanol using solar energy. Also the present results hold a great promise in the industrial preparation of steps needed to improve the cyclohexanol / cyclohexanone ratio.

- Cu-TiO₂ supported on molecular sieve 5A composite system is showing highest activity compared to the TiO₂ (P-25) catalysts in 0.2 N NaOH solution than in pure water due to the dispersion and stabilization of copper on the large surface area of the support. The yield of oxalic acid, acetic acid and methanol were found to be 65.6, 12.0 and 0.8 (µg / h / g / cat) respectively using 0.2 N NaOH over 10 wt % TC_{2.0} / MS combinate photo catalyst.
- Urea of 18 ppm was obtained at 90 % conversion of nitrate. By utilizing photo catalyst and zeolite combinate system the polymerization reaction of the products are reduced and the condensation reaction leads to urea formation.

List of publications from thesis work

- Selective solar photo catalytic oxidation of ethyl benzene on C, N and S doped TiO₂
 B.Srinivas, P.Anil Kumar Reddy, M.Rajesh, V. Durga Kumari, M. Subrahmanyam and B.R.De Research on Chemical Intermediates 37 (2011) 901 918.
- Photo catalytic reduction of nitrobenzene over silver doped TiO₂ under solar light
 B.Srinivas, K. Lalitha, P.Anil kumar Reddy, S.Malyadri,
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 Indian Journal of Environmental Protection 31 (2011) 1- 15.
- Cyclohexanol dehydrogenation over Cu loaded TiO₂ photocatalyst under solar illumination
 B.Srinivas, K. Lalitha, P.Anil Kumar Reddy, G.Rajesh, V. Durga Kumari, M. Subrahmanyam and B.R.De.
 Research on Chemical Intermediates 37 (2011) 1069 - 1086.
- 4. Photo catalytic reduction of CO₂ over Cu-TiO₂/Molecular Sieve-5A Composite. **B. Srinivas**, B.Shubhamangala, K.Lalitha, P.Anil Kumar Reddy, V. Durga Kumari, M. Subrahmanyam and B. R. De Photochemistry and Photobiology 87 (2011) 995 -1001.
- Photo catalytic synthesis of urea from in-situ generated ammonia and carbon dioxide
 B. Srinivas, V. Durga Kumari, G. Sadanamdam, Ch.Hymavathi, M. Subrahmanyam and B. R. De Photochemistry and Photobiology (2011) In press.

Other Publications of the candidate

- Preparation and characterization of Bi-doped TiO₂ and its solar photocatalytic activity for the degradation of isoproturon herbicide
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- 9. A comparative and mechanistic study on regioselective photooxidative demethylation of N-heterocyclics using TiO₂ and molecular oxygen,
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1. Patent No. India [185482]

Title: An improved process for the production of 2-methyl pyrazine (2-MP) from ethylene diamine and propylene glycol using promoted zinc chromate based catalysts. Inventors: M.Subrahmanyam, G.Muralidhar, S.J.Kulkarni, V.Viswanadhan, B.Srinivas, J.S.Yadav, A.V.Rama Rao.

2. Patent No. India [185150]

Title: A novel promoted zinc-chromate based catalysts for the production of 2-methyl pyrazine (2-MP) from ethylene diamine and propylene glycol Inventors: M.Subrahmanyam, V.Viswanathan, S.J.Kulkarni, G.Muralidhar, B.Srinivas, A.V.Rama Rao, J.S.Yadav, K.V.Rami Reddy.

3. Patent No. India [1102/DEL/95] **Title:** A process for the modification of zinc chromite catalyst for the preparation of γ - butyrolactone selectively

Inventors: M.Subrahmanyam, B.Srinivas, S.J.Kulkarni, Y.V.Subba Rao, P.K.Rao, A.R.Prasad.

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- 1. "Preparation and characterization and photocatalytic activity of structured TiO₂ based photo catalyst for disinfection of crude water for drinking water production", Indo-Italian Research project, DST, New Delhi, in S & T between India and University of Palermo, Palermo, Italy for ten days, June 2007.
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