Synopsis

INSTITUTE OF CHEMICAL TECHNOLOGY

(University under Section -3 of the UGC Act 1956)
Maharashtra Govt's Elite Status and Centre of Excellence
Matunga, Mumbai – 400019

A SYNOPSIS OF THE THESIS TO BE SUBMITTED TO

UNIVERSITY OF MUMBAI

FOR THE DEGREE OF PH.D. (SCI.)

DOCTOR OF PHILOSOPHY (SCIENCE) IN CHEMISTRY

TITLE OF THESIS	: HETEROGENEOUS CATALYSIS FOR DEGRADATION OF PESTICIDE AND ORGANIC TRANSFORMATIONS
NAME OF CANDIDATE	: **SANDEEP MAHADEO AGAWANE**
NAME AND DESIGNATION OF RESEARCH GUIDE (and Co-guide)	: DR. (MRS.) JAYASHREE M. NAGARKAR ASSOCIATE PROFESSOR
PLACE OF RESEARCH WORK	: DEPARTMENT OF CHEMISTRY INSTITUTE OF CHEMICAL TECHNOLOGY MUMBAI
DATE OF ADMISSION	: **23-04-2008**
REGISTRATION NUMBER AND DATE	: **11 CHY 4013 / 09-01-2009**
DATE OF SUBMISSION OF SYNOPSIS	: 14-01-2013

SIGNATURE OF RESEARCH GUIDE **SIGNATURE OF CANDIDATE**

INDEX

Introduction:-

Catalytic science has grown as a separate branch of chemistry. The phenomenon of catalyst has been extensively studied for nearly a century and half and subconsciously for a much longer period. The research for newer catalytic transformation and study of one does continue endlessly. Heterogeneous catalyst can be easily separated from the reaction products by simple filtration and quantitatively recovered in the active form. Since they can be recycled, preparation of the some sophisticated fine chemicals can be made less expensive and at the same time the contamination of the product by the trace amount of metal (in case of metal oxide catalyst) can be avoided.

The use of light energy to affect a chemical change has been recognized for many years. Heterogeneous catalyst can also be used for degradation of organic pollutants such as pesticides. In particular TiO_2 is used as a photo-catalyst for the removal of pesticides and dyes. TiO_2 is one of the most promising semiconductor photo-catalyst and lot of research has been carried out regarding application towards environmental clean-up. Charge carrier dynamics on the surface of the metal oxide based catalyst plays a key role in photo-chemical processes.

In the field of heterogeneous catalysis transition metal have provided numerous efficient methods for C-C, C-N, C-O bond formation reactions, oxidation-reduction reactions and photocatalysed reactions. These reactions have a significant impact on academic research and due to this progress, these reactions are increasingly being applied in the chemical industry.

In this context, we have prepared TiO_2 and MgO/ZnO nanocatalysts and explored there photocatalytic activity for degradation of pesticide and dyes. Apart from this we have also focused on the new methodologies for organic transformation by using nanocatalysts.

The various schemes carried out by using synthesized nanocatalyst are as follows:

1. Synthesis of nano TiO_2 and its application to photodegradation of dichlorvos in water
2. Synthesis of nano MgO/ZnO and its application to photodegradation of methyl orange and rhodamine B in water
3. Synthesis and Characterization of Nano CeO_2 for synthesis of α-aminophosphonates under ultrasonication and O, N arylation with 4 nitrochlorobenzene
4. Synthesis and Characterization of nano Pd/CeO_2 for reduction of nitro compounds
5. Synthesis and Characterization of ZnO/Co_3O_4 for synthesis of 5-substituted 1H-Tetrazole

1. Nanocrystalline photocatalytic treatment for degradation of dichlorvos by using nano TiO_2

DDVP is chlorinated organophosphate pesticide widely used in agriculture, commercial, domestic and industrial areas. It has high bioactivity and it is cheaper insecticide as compared to other pesticides and hence used in the countries all over the world. Inhalation during exposure to DDVP causes tightness of chest, wheezing, pupil constriction, blurred vision, tearing and headaches. DDVP is also responsible for disorder in the nervous system. So it is classified in the list of Group B 2 by United State Environment Protection Agencies (USEPA), as probable human carcinogen. Minimisation of such pesticides by chemical and catalytic treatment is important for environmental protection. The appropriate irradiation of semiconductor material produces excited, highly energetic electron-hole pairs that can migrate to the surface and act as the photo-catalyst. This leads to complete oxidation (mineralisation) of the organic pollutants. Semiconductor has the property to get excited and can form energetic electron-hole pairs. Hence the attention of semiconductor materials towards the mineralisation of waste water is increased. Among various semiconductor used, TiO_2 has high photocatalytic activity, non-toxic property, chemical stability, and high

oxidation rate [1]. Therefore use of nano sized TiO_2 for the purpose of cleaning the environment from organic matter and a harmful bacterium by photo-catalytic decomposition has been increased [2-7].

In present study, pure anatase nano titanium dioxide is prepared by sol gel method. The powdered $Ti(OH)_4$ is separated from gel by use of spray drier. It was characterised by XRD, IR, TEM and SEM techniques. Photo catalytic activity of TiO_2 was evaluated for degradation of Dichlorvos (DDVP, 2,2-dichlorovinyl O,O-dimethyl phosphate) which acts as an insecticide. The degradation process and the rate of photo-degradation are monitored by noting the increasing concentration of phosphate ion, which is one of the most stable photo-degraded products of the oxidation process. Effect of various parameters such as concentration of pesticide and photo-catalyst, oxidising agent and effect of pH on the extent of photodegradation is studied. It is observed that degradation follows first order kinetics.

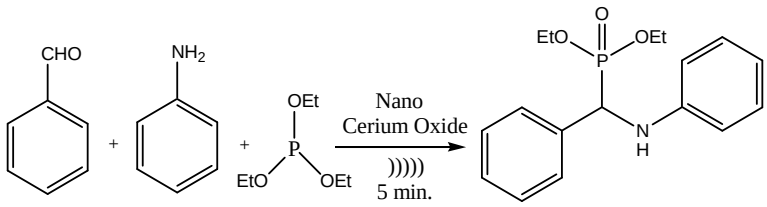
2. Degradation of methyl orange and rhodamine B by using novel nano MgO/ZnO catalyst

Methyl Orange (MO) and Rhodamine B (RB) are water soluble dyes which are widely used in textile, printing, paper, pharmaceutical and food Industries [8,9]. Among all, TiO_2 is the most extensively studied photocatalyst. It showed relatively higher reactivity and is stable to incident photon or chemical corrosion. Next to TiO_2, ZnO is the highly used photocatalyst for degradation of pollutants. The added advantage of ZnO over TiO_2 is that, it absorbs over a larger fraction of the UV spectrum having threshold wavelength of 387 nm. The recombination of electron and hole readily occurs on the surface of the lattice and the rate of degradation depends on the kinetics of recombination. Hence wider charge separation becomes necessary to get high photocatalytic activity. In order to get higher degradation, the rate of recombination of positive hole and valence band electron should be minimized. The use of other semiconductor with TiO_2 improves the charge separation and hinders the charge recombination [10-14]. The 3% MgO on TiO_2 was effectively used for degradation of Eosin Y dye [10]. In this case, the two conduction bands of two different semiconductors come in contact with each other and increasing the photocatalytic activity.

In the present study, a series of MgO/ZnO catalysts were prepared with increased concentration of MgO with ZnO. The prepared MgO/ZnO catalysts were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDAX). Photocatalytic activity of the MgO/ZnO catalyst was evaluated by monitoring the rate of degradation of methyl orange (MO) and rhodamine B (RB) dyes by using ultraviolet light. The extent of degradation of the MO and RB depends upon the concentration of MgO in ZnO photocatalyst. The experimental results suggested that 3% MgO with ZnO was sufficient to increase the photocatalytic activity of ZnO. Various parameters such as concentration of photocatalyst, concentration of dye, temperature, and presence of different anions were optimized for the degradation. It was observed that degradation of MO and RB dyes follows first order kinetics.

3. Nano ceria catalyzed synthesis of α-aminophosphonates under ultrasonication (Tetrahedron Lett., 52 (2011) 3499-3504)

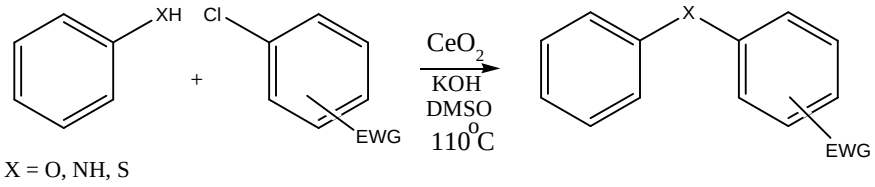
α-Aminophosphonates have been the focus of attention in recent years because of their structural analogy to the corresponding α-amino acids as well as heterocyclic phosphonates. These molecules have found a wide range of applications in the areas of industrial, biological, and medicinal chemistry, as inhibitors of synthase, HIV protease, antibiotics, enzyme inhibitors, anti-thrombotic agents, herbicides, fungicides, insecticides, plant growth regulators and as substrates in the synthesis of phosphonopeptides. The use of acidic catalysts has attracted considerable attention. Amberlyst-15, CdI_2 and $BF_3 \cdot OEt_2$ have been used as catalyst by various researchers for the synthesis of α-aminophosphonates [15-17]. Various perchlorates and various zirconium precursors were used for synthesis of α-aminophosphonates [18,19]. Potassium carbonate also used for synthesis of chiral α-aminophosphonates at room temperature [20,21].



A simple, efficient and general method has been developed for the one-pot three component syntheses of α-aminophosphonates. The condensation of aldehyde, amine and triethyl phosphite by employing CeO_2 nanoparticles as catalyst gave α-aminophosphonates. The catalyst showed good recyclability. Nano CeO_2 has been found to be an excellent catalyst for the green synthesis of α-aminophosphonates under ultrasound irradiation and solvent-free condition. The α-aminophosphonates are obtained in good to excellent yield. This catalyst provides cleaner conversion, short reaction time and high selectivity which makes the protocol feasible and economically attractive.

4. Nano ceria catalysed O, N arylation with 4 nitrochlorobenzene
   (Tetrahedron Lett., 52 (2011) 5220-5223.)

Aryl ethers and N-arylated compounds are widely used in organic synthesis, pharmaceutical and biological applications. Polyaromatics have exclusive characteristics which make their use as organic conductors or semiconductors. Various reactions are reported to carry out the synthesis of aryl ethers and N-arylated compounds. Such compounds are obtained by employing intermolecular reaction between aryl halide and phenol or amine using Cu or Pd as a catalyst. Many copper catalyzed C-O, C-N and C-S bond formation reactions have been carried out with or without ligand to form carbon-heteroatom bond [22-27].

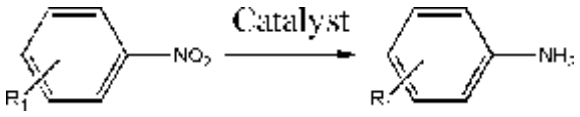


We report a robust and novel method which provides an efficient and economic route for synthesis of O, N and S arylation by using nano cerium oxide (Ceria, CeO_2). CeO_2 is therelatively cheaper catalyst than reported copper and other copper based catalyst. This method provides wide range of substrate applicability in case of phenol and amine. Less reactive chlorobenzene substituted with strong electron withdrawing groups such as 4-nitrochlorobenzene and 4-

cyanochlorobenzene favor the reaction. This protocol avoids the use of ligand and gives arylated product in satisfactory yields.

5. Reduction of nitro compound by using nano Pd/CeO_2 catalyst at room temperature

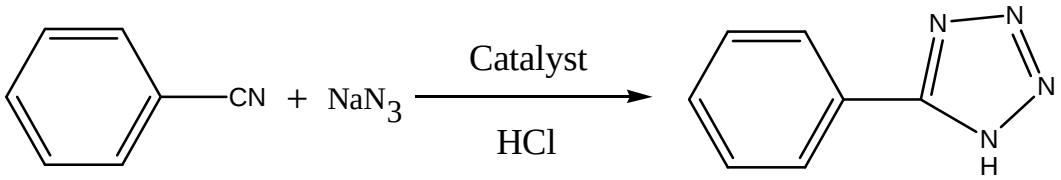
Amines and their derivatives are useful in various fields of everyday life. The reduction of nitro aromatic compounds to the corresponding amines is an important step in many industrial processes. Aromatic amines are found in biologically active compounds, pharmaceuticals and agrochemicals. They are widely used as dye intermediates for azo-dyes, pigments and optical brighteners, as intermediate for photographic chemicals, in polymers via isocyanates for polyurethanes and as oxidants. They have been listed as corrosion inhibitors for mild steel in the pickling process. The largest share of aniline consumption is used for the manufacture of isocyanates, primarily for DMI [4,4′-methylenebis(phenylisocyanate)] to make polyurethanes. Many herbicides, fungicides, insecticides and repellents are made from aniline and its derivatives. Rh, Pd, Ni and Fe are prominently used catalysts for the reduction of the nitro compounds to their corresponding amines. These catalysts are used in combination with other catalyst or on some support. This makes the catalyst heterogeneous and thus increases the reusability of the catalyst [28-31].



Nano Pd/CeO_2 catalyst was prepared and used for reduction reaction of nitro aromatic compounds. Palladium was doped on cerium oxide. The catalyst was well characterized by various analytical techniques. It show good activity by using water as solvent at ambient temperature in presence of KOH. The catalyst shows excellent catalytic activity and recyclability.

6. Synthesis and Characterization of nano ZnO/Co_3O_4 for synthesis of 5-substituted 1H-Tetrazole (Catalysis Science and Technology, 2 (2012) 1324-1327.)

Tetrazoles are a class of nitrogen containing heterocyclic compounds which are studied extensively due to their wide range of applications. Application of tetrazole involves their use in pharmaceuticals, in speciality explosives and as precursors of a variety of nitrogen containing heterocyclic compounds like imidoylazides. Synthesis of 5-substituted 1H-tetrazole involve [3+2] cycloaddition of azide (NaN_3/$TMSN_3$) to the corresponding nitrile. Several methods are reported for the preparation of 5-substituted 1H-tetrazoles. Zinc salts proved themselves as a potential catalyst in the synthesis of tetrazoles [32-34].



Zinc salts have catalytically active sites suitable for synthesis of substituted 1H-tetrazoles. Herein we report synthesis of 5-substituted 1H-tetrazoles catalyzed by using nano ZnO/Co_3O_4. This is a novel heterogeneous catalyst which showed excellent efficiency, affording good to excellent yield of products.

Presentation of the thesis:-

The thesis comprises of six chapters. The first chapter gives the introduction of the research project. The second chapter contains synthesis and characterization of nanocrystalline TiO_2 for photocatalytic degradation of dichlorvos. The third chapter includes novel synthesis of nano MgO/ZnO and its characterization. The photocatalytic activity of nano MgO/ZnO is tested on degradation of methyl orange and rhodamine B. The fourth chapter comprises the synthesis and characterization of nano CeO_2 and its catalytic application for synthesis of α-aminophosphonates under ultrasonication and O, N arylation with 4 nitrochlorobenzene. Fifth chapter deals with applications of nano CeO_2 as support for Pd. This chapter includes the synthesis and characterization of Pd/CeO_2. This catalyst was explored for room

temperature synthesis of aniline from nitrobenzene. Sixth chapter reports the synthesis and characterization of nano ZnO/Co_3O_4. This catalyst was used for synthesis of 5-substituted 1H-Tetrazole.

REFERENCES:-

1. Agency for Toxic Substances and Disease Registrar Toxfaqs September 1997; U.S. Environmental Protection Agency, Integrated Risk Information System (IRIS) on Dichlorvos (CASRN 62-73-7), Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Cincinnati, OH, 1994.
2. Z. Mengyue, C. Shifu, T. Yaowu, J. Chem. Technol. Biotechnol., 64 (1995) 339.
3. K. Harad, T. Hisanga, K. Tanaka, Water Res., 24 (1990) 1415.
4. S. A. Naman, Z. A. –A. Khammas, F. M. Hussain, J. Photochem. Photobiol. A: Chem. 153 (2002) 229.
5. E. Engenidou, K. Fytianos, I. Poulios, Appl. Catal. B: Environ. 59 (2005) 81.
6. P.K. Mishra, B.B. Nayak, B.K. Mishra, Powder Technology, 196 (2009) 272.
7. Std. Vogel Method for determination of phosphate ion as phosphomolybdic acid, Vogel textbook of quantitative inorganic analysis, fourth edition, pp. 756.
8. A. Mittal, A. Malviya, D. Kaur, J. Mittal, L. Kurup, J. Hazard. Mater. 148 (2007) 229.
9. S. D. Richardson, C. S. Wilson, K. A. Rusch, Ground Water, 42 (2004) 678.
10. J. Bandara, S. S. Kuruppu, U. W. Pradeep, Colloids and Surfaces A: Physicochem. Eng. Aspects. 276 (2006) 197.
11. J. Bandara, K. Tennakone, P. Jayatilaka, Chemosphere, 49 (2002) 439.
12. A. Hattori, Y. Tokihisa, H. Tada, S. Ito, J. Electrochem. Soc. 147 (2000) 2279.
13. K. Vinodgopal, P. V. Kamat, Environ. Sci. Technol. 29 (1995) 841.

14. K. Tennakone, J. Bandara, O. Ileperuma, W. Kiridena, Semicond. Sci. Technol. 7 (1992) 432.
15. A. Tajbakhsh, A. Heydari, H. Alinezhad, M. Ghanei, S. Khaksarb, Synthesis, 3 (2008) 352.
16. M. M. Kabachnik, L. I. Minaeva, I. P. Beletskaya, Synthesis, 14 (2009) 2357.
17. I. L. Odinets, O. I. Artyushin, N. Shevchenko, P. V. Petrovskii, V. G. Nenajdenko, G.V. Roschenthaler, Synthesis, 4 (2009) 577.
18. S. Bhagat, A. K. Chakraborti, J. Org. Chem. 72 (2007) 1263.
19. S. Bhagat, A. K. Chakraborti, J. Org. Chem. 73 (2008) 6029.
20. Q. Chen, C. Yuan, Synthesis 24 (2007) 3779.
21. Q.Chen, J.Li, C. Yuan, Synthesis, 18 (2008) 2986.
22. Z. Liu, Y. Chen, Tetrahedron Lett. 50 (2009) 3790.
23. J. Y. Kim, J. C. Park, A. Kim, A. Y. Kim, H. J. Lee, H. Song, K. H. Park, Eur. J. Inorg. Chem. 28 (2009) 4219.
24. G. Shen, X. Lv, W. Qian, W. Bao, Tetrahedron Lett. 49 (2008) 4556.
25. B. Sreedhar, R. Arundhathi, P. L. Reddy, M. L. Kantam, J. Org. Chem. 74 (2009) 7951.
26. M. C. Bagley, M. C. Dix, V. Fusillo, Tetrahedron Lett. 50 (2009) 3661.
27. D. J. C. Prasad, A. B. Naidu, G. Sekar, Tetrahedron Lett. 50 (2009) 1411.
28. Q. Shi, R. Lu, K. Jin, Z. Zhang and D. Zhao, Green Chem., 8 (2006) 868.
29. R. J. Kalbasi, A. A. Nourbakhsh, F. B., Catal. Commun., 12 (2011) 955.
30. P. Selvam, S. K. Mohapatra, S. U. Sonavane and R. V. Jayaram, Tetrahedron Lett. 45 (2004) 3071.
31. P. Luo, K. Xu, R. Zhang, L. Huang, J. Wang, W. Xing and Jun Huang, Catal. Sci. Tech., 2 (2012) 301.
32. Z.P. Demko, K.B. Sharpless, J. Org. Chem., 66 (2001) 7945.
33. Z.P. Demko, K.B. Sharpless, Org. Lett., 4 (2002) 2525.
34. O. G. Manchen O, C. Bolm, Org. Lett., 9 (2007) 2551.