CHAPTER I

INTRODUCTION

CHAPTER 1 : INTRODUCTION

INTRODUCTION

Catalysis and Catalytic processes are integral parts of modern world. A large part of chemical industry, one of the pillars of the contemporary economic activity, is build on the sound platform of catalytic process.

Catalyst has made giant strides, since Barzelius first explained the phenomenon almost a century back. Catalytic processes have faced many a challenges arising out of continuous changing socio-economic perceptions entailing business compulsions.

Catalysis plays an important role to come up with better and more efficient processes for chemical industries because of serious environmental and ecological[1] concerns. Fresh challenges are being posed for chemical industries, from increasing stringent norms of fuels emission from automobile engines to the reduction of voluminous byproducts in speciality chemical processing. Catalysis hold key to solve many such problems. It is found that most reactions such as oxidation, reduction, hydrolysis, dehydration in living organisms occur at the required rate owing to the participation of biological catalysts which stimulate natural processes. Now for many reactions suitable catalysts are known and readily available in most instances.

Primary factors which govern the choice of useful catalysts in a known process are activity, selectivity and physical suitability. Other important factors such as regenerability and cost of the catalysts are also of importance.

Catalysis contribute, directly or indirectly, to about 25% of gross national product[2]. Catalysis which is a part of the clean technology coupled with precision and elegance into chemical manufacturing makes the research in this area vibrant and interesting (3-4)

Catalysis has normally been classified into two broad categories viz.

1. Homogeneous and
2. Heterogeneous

Homogeneous catalysts have been utilized in many industrial processes (Table 1.1) because of its various advantages(5) such as high activity and selectivity at mild operating conditions and the availability of the entire catalyst molecule to the reacting system. The nature of the active sites could be understood in a better way. It also offers the advantages like stereo specificity, substrate activation and elimination of heat and mass transfer resistance. Their activity and selectivity could be tailored by varying the ligand attached to the metal ions.

However the main disadvantage of homogeneous catalysts is the problem of their separation from the reaction medium. Corrosion, plating out on the reactor wall and product contamination also pose serious problems. The handling and storage of the catalysts are also been found to be very expensive and this hampers the use of homogeneous catalyst for industrial purpose.

On this background heterogeneous catalyst gained a new momentum and research has been turned to heterogeneous catalyst having economical and ecological benefit. It can withstand high temperature and pressure and can also offer easy handling, separation from reaction system, extended catalyst life as well as minimization of the byproducts, which save waste disposal cost. These catalysts could be fixed beds in gas-solid and liquid contact reactors[11]. In this thrust toward transforming homogeneously catalyzed processes to heterogeneous catalytic processes, zeolites are gaining in importance. The experience in the use of such catalysts in the petrochemical industry can be increasingly applied to the selective organic synthesis of chemical intermediates and fine chemicals. Zeolites with their numerous adjustable catalytic properties offer a broad range of possibilities for this purpose. In the Vapour phase

Beckmann rearrangement for the synthesis of αcaprolactum is a good example of this fact. However a large amount of side product was noted which is environmentally unacceptable. The new synthetic route is to use H_2O_2 as an oxidant over a Ti containing MFI-Zeolite TS-I which avoid the use of hazardous and corrosive sulphuric acid and the generation of ammonium sulphate.

Solid acid catalysts have also gained importance due to their high activity. Recently an extremely active solid acid catalyst Nafion resin/silica composite was developed at Dupont R and D for the Friedel Craft Benzylation of benzene and p-xylene with benzyl alcohol. This composite catalyst was found to be nearly two orders of magnitude more active than plain Nafion resin[12]. Catalysis by aerogles have also generated a lot of interest[13]. Neumann et. al[14] have reported metal oxides substitute silicate xerogels as catalysts for oxidation of olefins using H_2O_2 as an oxidant. It was found that kerogles having porous structure with sufficiently large pores for fairly large organic substrates have the important potential as an active oxidation catalyst, valuable for the development of environmentally friendly processes. De Groot et al[15] have investigated the formation of phenol and acetone from cumene hydroperoxide with 100% selectivity using montmorillonite clay F-20 as catalyst. B Juraj et al[16] have studied the peptide bond formation using silica, alumina and clay catalysts and found enhanced efficiency of alumina catalysts. Heterogeneous catalysts have also proved their importance in enantio selective reactions. Cinchona alkaloid modified platinum catalysts have been used for enantioselective hydrogenation of α-keto-ester by Blaster et al[17].

However, the advantages of heterogeneous catalysts when compared to homogeneous catalyst are at the expense of activity, selectivity and proper understanding of the nature of the active species. Thus, both homogeneous and heterogeneous catalysts have their own advantages as well as disadvantages. It is ideal, therefore to combine the advantages and simultaneously minimize the disadvantages of each class of catalysts. This could be achieved by heterogenizing homogeneous catalysts i.e. attaching a homogeneous catalyst to heterogenizing homogeneous catalysts i.e. attaching a homogeneous catalyst to a solid insoluble support through covalent bonding. Here the ligand spheres of the metal remains unchanged and the attached complex is bathed by solvent and reactants. Thus, the resultant heterogenised homogeneous catalyst could function mechanistically as if it was in solution but it would operate as a separate immobile phase[17,18]. The ideal catalysts thus obtained would have the specificity and controllability of homogeneous type and seperability of heterogeneous system[19].

The support used for these types of catalyst can be classified into two categories.

1. Inorganic oxides such as silica, alumina, glasses, zeolites, clay etc.,
2. Organic polymers such as polystyrene, polyvinyl pyridines, polyacrylates etc.

Inorganic oxides used as supports, have the advantages of better mechanical and thermal stabilities coupled with reasonable heat transfer properties. A number of studies have been reported using inorganic oxide supported complexes[20] as catalyst for various industrial processes e.g. olefin polymerization using metal oxide supported complexes of Cr, Ti or Zn and synthesis of formaldehyde by methanol oxidation using mixed oxides of Fe and Mo[21] as catalyst. Many reports are available on application of mesoporous molecular sieves(MCM-41) supported catalysts for Hydro sulfarisation (HDS), Hydrodenitrogenation (HDN), Mild Hydrocracking (MHC), Friedel Craft alkylation, olefin oligomerization and many other reactions including environmental studies[22]. Recently Hu et al[23] have reported partial hydrogenation of benzene to cyclohexene using ruthenium catalysts supported on binary oxides La_2O_3-ZnO and a higher yield was obtained.

Kurusu[24] studied the oxidation of organic substrates under mild operating condition using immobilized of Fe(II) and Cu(II) ions on silica gel and montmorillonite clay and a higher catalytic activity was observed. Palladium supported on Spanish sepiolites catalysts were found to be a successful catalyst for the reduction of acetophenone and various other substituted alkenes[25]. A number of studies have been carried out by various workers using supported catalysts. These include the catalysts which were found to be a successful catalysts for the reduction of acetophenone and various other substituted alkenes[25]. A number of studies have been carried out by various workers using supported catalysts for the reduction of acetophenon and various other substituted alkenes[25]. A number of studies have been carried out by various workers using supported catalysts. These include the catalytic oxidation of CO by O_2 using NiO/Al_2O_3 [26].

Malyala and Co-workers[27] carried out the hydrogenation of acetophenone using Ni and bi-metallic Ni-Pt supported on zeolite Y catalysts. Xu et al[28-29] reported reaction of light olefins during Fisher Tropsch synthesis using silicate-2-zeolite supported iron catalyst.

Keisk[30] reported catalysts were found to be very effective not only in the industrial processes but in controlling the environmental pollution. Catalytic technologies are helping to protect the ozone layer, reduce the green house effects, create environmentally safer transportation, solve environmental problems of energy production, raise energy efficiency, minimize the use of raw materials and process which renew raw materials.[31] Reformulate fuels which are environmentally more friendly can be produced via new catalytic processes. Catalysts for the oxidation of aqueous organic compounds in waste water treatments have also been developed.[32]

Kasahara and co-workers[33] studied the activity of the mixed components of Pt, Pd and Rh for the conversion of hydrocarbon and CO from the exhaust, so that the efficiency can be improved.

A method was developed by John[34] to restrict the emission of nitrogen oxides as well as of other unwanted vapors emitted from running vehicles and stationary sources.

Wu Shanliange et al[35] developed technology for purifying automobile exhaust gas. CO, hydrocarbons & NO in the exhaust gas were converted into CO_2, H_2O and N_2 by redox reaction using catalytic convertor. Ruby et al[36] reported a classic approach to abate emission at the tail pipe or stock before emitting to atmosphere.

A new technology called prem Air catalyst systems take a different approach and reduces ambient ground level ozone. The new system involves placing a catalytic coating on car's radiator or air conditioner.

Della and co-workers[37] studied the air emissions using driving cycles representatives of different levels of urban traffic.

Gao et al[38] studied the nitration of phenyl methane in liquid phase with HNO_3 phenyl on HM1-MZSM-5. Some other solid acid catalysts have been used and it was found that the nitration reaction proceeds in the pore channel of Zeolites and the paraselectivity for the reaction is closely related to the pore size of the catalysts. During the nitration NO_2 was formed by dissociation of HNO_3 and PhMe was absorbed on catalyst and the catalytic activity depended on both the acidic properties and hydrophobicity of the catalysts.

Agarwal et al[39] have studied the oxidation of toluene in the vapour phase over preovskites viz. La Co CO_3, La Cr CO_3 and La Fe CO_3 and the activity was found to be in the order of La Co CO_3>La Fe O_3 > La Cr O_3.

Recently metal complex catalysts have been used as asymmetric catalysts. Zaohum[40] reported that a siliceous (Si-MCM-41) and alumino-Silicate

Meso-porous molecular sieve (AlMCM-41) with variable frame work Si/Ac ratios have been used as support to immobilize manganese 2,2' – bypyridine (L) complex. Cations $[MnL_2]^{2+}_{,}$ via incipient wetness impregnation of ion exchange with Mn L_2 $(NO_3)_2$ in aceto nitrile.

Organic polymers are found to be popular catalysts support. A brief out line on the emergence, advantages and applications of polymer supported metal complex catalysts is given in the following section.

1.1 : POLYMER SUPPORTED CATALYSTS

The use of polymer supports for catalysts as well as synthetic reagents has grown tremendously since Marrifield demonstrated their use in peptide synthesis.[41]

Attachment of transition metal complexes to organic polymers appeared by the end of 60's as a suitable means to approach two of the main goals[42] of research in catalysis.

1) The formation of suitable catalysts with reproducibility, activity and selectivity as homogeneous systems and separation from reaction products at heterogeneous catalyst.
2) The achievement of a catalyst system where the active sites have known structures which may permit better understanding of the molecular mechanism of catalytic reaction.

The polymer supported catalysts are synthesised by bonding covalently the transition metals to polymeric networks to impart insolubility in the reaction mixture. For this purpose functional polymer support is synthesized either by polymerizing the monomer containing desired functional groups or by functionalizing cross-linked polymers and then incorporating metal complex catalyst precursor on to this functionalized polymer support.

The chief advantage of these type of the support was found in their insolubility, non-volatility, non-toxicity and recyclability.

Most of the polymers are inert and do not interfere in the catalytic processes. These properties are especially attractive in an era of enhanced environmental awareness.[43] These polymers can be synthesized easily with a wide range of physical properties. Their functionalization capacity could be increased by introducing the aryl groups.[44] The degree of functionalizing is significantly different between inorganic oxides and organic polymer supports. Inorganic oxides have an upper limit of monofunctional groups of 1-2 meq., g^{-1} of matrix. Organic matrix can carry up to 10 meq. g^{-1} of matrix.[45]

Thus, compare to inorganic oxides, organic polymer support can offer immense modification possibilities.

In order to stabilize the unstable structure on the surface, it prevents the deactivation of reactive catalytic species. Dimerisation of the catalyst in the reaction could be prevented due to isolation of active sites on the polymer matrix. Thus, supported catalyst can be prepared with high dispersion of metal atoms in polymer matrices, in order to achieve optimum activity and selectivity than the homogeneous counterpart. The polymeric ligands stabilize the reduced metal species, prevent formation of metal aggregates. Polymer support stabilize the reactive and coordinately unsaturated metallic sites, thereby increasing the activity of the catalyst. The presence of metal complexes with vacant ligand sites enhance its activity, such situation rarely occurs in homogenous complex.

Furstner and coworkers[48] formulated a new concept for C-C-bond formation catalyzed by early transition metals in low oxidation states.

Armstrong et al[49] synthesized a chiral catalyst for stereo-selective reductions, epoxidations and hydro-carbozylatins. Eighty three popular chiral reagents were used to synthesise a wide variety of compounds of high enantiomeric purity, Chiral auxiliaries including a variety of oxazolidinones, a wide variety of chiral synthons and chiral resolving agents were studied and found that enantiomeric impurities were found in all reagents. Over half of the chiral reagents tested had enantomeric impurities at levels > 0.1%.

Bala Krishnan and Muragan[50] have prepared surface enriched polymer supported phase transfer catalysts (SE-PSPTC) using vinyl toluene (VT) as a functional monomer.

Recently, metal complex catalysts have been used as asymmetric catalysts.

Brno[51] reported the phenomenon of chirality which is closely associated with diversity of possible structural features and its impact on chemistry. Clark[52] and coworkers[52] synthesised the mesoporous as robust catalyst and used in liquid phase processes, such as Friedel Craft reaction, selective oxidations, nucleophilic substitution and aromatic brominations.

Maxwell[53] reported the innovation of the catalyst for developing the industries and expansion in power generation, which is very crucial due to swell populations.

Blackman[54] studied the non-linear relation between the optical purity of a chiral catalyst and the enantio-selectivity obtained in the catalysed reaction. It is also demonstrated as to how asymmetric application may be exploited for practical strategies in inorganic synthesis.

Xiaomina and co-workers[55] synthesised a catalyst which were found to be useful for enantio-selective silylcination of aldehydes using chiral salen-Te' $(OR)_4$ complexes as catalyst.

Nam et al[56] carried out Salen Mn(II) oxidation of alcohol using sodium hypochloride as an oxidant.

A review was published by Fache et al[57] using nitrogen containing Chiral ligands heterognenising on polymeric support and a large number of reactions were carried out.

Masanori et al[58] succeeded in getting a homoallylic alcohol derivatives in a regio and sterio selective manner where 1, 3 dienes is reacted with aldehydes in the presence of EtSiH using a catalytic amont of Ni $(Cod)_2$ and PPh_3. Ram et al[59] synthesised Ru (III) complex, by sequential attachment of $H_2N-CH_2-CH_2-NH_2$ and $RuCl_3$ to chloromethylated styrene – divinyl benzene co-polymer with 8% cross linking. The activity of this catalyst was tested for $Ph-CH_2OH$ oxidation by varying the parameters such as temperature of the system, and also by varying the concentration of substrate and catalysts. The activation energy and entropy were calculated from the kinetic data and probable reaction mechanism was proposed. Ram et al[60-61] synthesised the polymer supported palladium (II) complex catalyst for oxidation of toluene. They also synthesised Ru(III) complex as catalyst and the activity of this catalyst was also tested for oxidation, and thoroughly studied. Lei ziging et al[62] studied the oxidation of alkylbenzene to aryl alcohol and ketones. This was accomplished with high selectivity and activity using linear poly (styrene) (PS) and styrene divinyl benzene co polymers (DVB) as support for copper (II) complex catalysts. The reaction was carried out in presence of molecular oxygen at 110^{0}C. Groves John T and co-workers[63] studied the novel oxidative processes for substrate such as olefins, alkenes aromatic and alcohols, using, metallic porphyrins or salen. The complex is having axial ligands and electron-withdrawing peripheral substitutions are preferred. Weiner et al[64] reported that polyoxo anion supported from (II) complex is significant as well as enroute to the goal of achieving a long 6-lived, catalytic dioxygenase system without the need to worry about catalyst lifetime-limiting ligand oxidation side reactions. Skarias and co-workers[65] synthesized novel polymer supported vanadium (V) and chromium (VI) ions as oxidation catalysts. A variety of oxidation reaction were carried out. Gu and co-workers[66] reported that N N' bis (Salicylidence) – 1, 3, propy lenediiminato Cobalt (II) as catalysts which can co ordinate and make active the molecular oxygen. It is utilized in synthesis of fine chemicals. The kinetic study was carried out by changing the parameters such as concentration of catalyst, the temperature of the system, the time and the velocity of air flow and the solvents. The possible mechanism was discussed. Zhang et al[67] reported the oxidation of toluene to benzoic acid and oxidation of other aromatic hydrocarbons in presence of cobaltrchloroacetate, manganese trichloroacetate and ammonium bromide as catalyst.

1.2 : AIM AND OBJECTIVE OF THE WORK

1. The main aim of the present work is to heterogenize the homogenous transition metal complex catalysts and to probe their catalytic activity for oxidation and other industrially important reactions. The work is focused on oxidation of toluene using manganese (II) and Nickel (II) complexes of O-phenylenediamine and salicyladehyde-p-phenylenediamine anchored on to various cross-linked styrene-divinylbenzene co-polymer. Many polymer bound non-chelated complexes are reported to be less stable and leached out into the solvent under the reaction conditions. Chelated complexes are more stable and less liable than non-chelated ones. Chelated complexes are polymer matrix and alternatively, use of commercially available chloromethylated styene-divinylbenzene as support. It is believed that highly functionalized co-polymer will give rise to strongly bonded metal complexes to prevent or reduced metal leaching.
2. Synthesis of the chelated metal complex similar to the polymer-anchored metal complexes to study the catalytic activity in homogeneous system.
3. Characterisation of synthesized catalysts using different techniques such as infrared; uv-vis reflectance, electron spin resonance spectroscopy (ESR). Thermo-gravemetric analysis (TGA). scanning electron microscopy (SEM), swelling studies using different solvents, surface area measurement using BET method at liquid N_2 temperature and the other physico-chemical studies like moisture content, bulk density etc. Attempt has been made to propose possible structure of catalysts on the basis of modern spectroscopic techniques.
4. Investigation of catalytic activity of the synthesized catalyst for oxidation of toluene under mild operating conditions.
5. Comparison of catalytic activity of homogenous and heterogenised homogeneous catalysts.
6. Life cycle studies of heterogenised catalysts.
7. Elucidation of probable reaction mechanism for both the systems.

1.3 : THE PRESENT STUDY INCLUDES :

1. Functionalization of styrene divinyl benzene co-polymer of different cross linking by chloromethylation, treatment with multi-dentate ligands with N and O as donor atoms and finally attachment of Mn(II) and Ni(II) metal ions to form appropriate metal complexes on the area measurement using BET polymer matrix and alternatively, use of commercially available chloromethylated styrene-divinylbenzene as support. It is believed that highly functionalized co-polymer will give rise to strongly bonded metal complexes to prevent or reduced metal leaching.
2. Synthesis of chelated metal complex similar to the polymer-anchored metal complexes to study the catalytic activity in homogeneous system.
3. Characterization of synthesized catalysts using different techniques such as infra-red, UV-vis reflectance, Electron spin resonance spectroscopy, theremogravimetric analysis (TGA), scanning election microscopy (SEM), swelling studies using different solvents; surface area measurement using BET method at liquid N_2 temperature and other physico-chemical studies like moisture content, bulk density etc. Attempt has been made to propose possible structure of catalysts on the basis of the modern spectroscopic techniques.
4. Investigation of catalytic activity of the synthesized catalyst for oxidation of toluene under mild operating conditions.
5. Comparison of catalytic activity of homogenous and heterogenised homogeneous catalysts.
6. Life cycle studies of heterogenised catalysts.
7. Elucidation of probable reaction mechanism for both the systems.

1.4 : REFERENCES

1. W.F. Hoderih, Roseler, G. Heifmann A.T. Liebeng, Catalysis Today, 37, 353.
2. Ian. E Marwell CATTECH, March 1997, P5
3. J.H Cleark and D.J. macquanrrie, Chew, Soc. Review, 1996, 303.
4. R.A. Sheldon, CHEM TECH, March 1994, P 38
5. R. Ugo,Aspects of Homogeneous catalysis, Reidel Boston 1974.
6. Japanj Kokai Patents 1989 2577 1.
7. M. Otake, CHEMTECH 1995, P 36
8. S.P. Gupta and R.V. Chaudari J. Catal 1984, 24, 197.
9. S. B. Dake, D.S. Koble and R.V. Chaudari J. Mol. Catal 1984, 24, 99
10. R.V. Chaudari, Y.T. Shah, N.R. Foster Catal Rev. Sci. Eng. 1986, 28, 431.
11. C. U. Pitmann, Jr. in P Hodge and D.C. Sherrington (eds) Polymer Suported reactiosn in organic synthesis, John wiley chichestev 1980, P 249-79.
12. Q, Sun, M.A. Harmer, W.E. Farnet Ind. Eng. Chem. Res, 36 (12), 1997, 5541.
13. M. Scheneider and A. Baiker Catal.Rev. Sci. Eng. 1995, 37 (4), 515.
14. R. Neumann and M. Levin-Elad J. Catal 1997, 166-206.
15. W.A. de Groot, E.L. Coenen, B.F.M. Kuster and G B. marin in J.W. High tower, W. Nicholas Delgass 101B, Elseviev, Amsterdam, 1996, P-75.
16. B Juraj, R.M. Bernd Origen life Eval. Bio Sphere, 1999. 29, 451 (C.A. 132 194637a, 2000)
17. H. Blaster, H. Jalett, M. Muller and M. Studer Catalysis Today, 19977, 37, 441.
18. D. Chatterjee and Halligudi Bull, Catal Soc., India 1996, 6(4), 10.
19. K Venkataswamy, D. Thomas Sadananad, R. Ramesh and P Saui Prakash, I. J. Chem, 1997, 36 A, 98.
20. Y.I. Waswa, Tailored Metal Catalyts Reidel, Dordecht.
21. R.R. Hartely, Supported Metal complexes D. Reidel, Dordrech 1985, P-10

21. R.R. Hartely, Supported Metal complexes D. Reidel, Dordrech 1985, P-10
22. X.S. Zhao, G.Q Lu and G.J. Miller, Ind. Eng. Chem. Res. 1996, 35, 2075.
23. S. Hu. Y Che., Ind. Eng. Chem. Res., 1997, 36 (12), 5153.
24. Y. Kurusu, Rective polymers, 1995, 25, 63.
25. M.A. AraMedia, V. Borah C. Jimenez, J.M. Marinas A Porras, F.J. Urbano and L. Villar, J. Mol Catal, 1994, 94, 131.
26. G.El. Schobaky, M. Hassan A Ahmed, Afinidad, 1997, 54, 382. (C.A. 127; 323233P)
27. R.V. Malyala, V. Rodec M. Arai S.g. Hegde, R.V. Chaudary Appl. Cataly, 2000, 193, 71.
28. Xu Longya – Wang; Qingxia, Xu, Yide, Lin, Liwwer, Am. Chem. Soc. Div. Pet, Pet, Chem., 2000, 45, 225.
29. N.H. Lee, S.J. Baik, S.B. han, Korean Chemical Society, 1998, 19, 726.
30. Catalysis in Environmental Tech. Keiski, Ritta Column, Yilopisto, Oulo, Finaland Kem-Kemi, 1998, 25(1) 18-25 (Fernish), Kemian Kustannus Oy.
31. S. Siebig and R Eldik, Inorg. Chem 1997, 36, 4115.
32. Y.H. Lin, I.D. Williams, P Li Appl. Catal A General, 1997, 150(2), 221.
33. Kasahara, G.G. mogli mykh, Yu I Shuvshinow D.G. Zaikovsmil, (ISK. RAN, Nonvosibirsk Russia) Khim Prom Sf. (moscoud 1997, (4) 270-273 (Russ).
34. Moffat, John B. (Department of Chemistry university of wwaterloo (an, NZL, 3G-1) Spec. Publication R. Soc. Chem 1998, 217 (Chemistry Energy and Environment) 167-174 (Eng.) Royal Society of Chemistry.
35. Wu Shemliang (East China University of Science and technology, Shaghai, People Rep. China 200237). Shangai Huarae gong 1997, 22(4), 1-3, (Ch).
36. Ruby Wamer, Ober Raymond Durilla Michel Anderson, Dennis, Hokio, Jeffery Heck Ronadl (Engle Hard) Corporation J Selin, NJ USA proe. Annu. Meot, Air Waste Mange Assoc. (Computer optical dist. () 1996 (Eng.)

37. Ragiane, Livia, Della, ,Prati, Maria vittoria, Repone, Mariao (Inst. Motori) (N.R. USA) Soc. Automet Eng. (Spec. Pub) J. Sp. 1997-SP 1275. (Factory influencing Emissions and Emission Formation processes) 23-32 (Eng.) Society of Automotive Engineers.

38. Gao Yang, Xiao-bo, Gao, Guang (Dept. Chem, Fudan Univ) Shangiha Xue-hao 1994, 15(6) 474-B (Ch)

39. Agarwal D.D. Goswami H.S. (School Studies Chemistry Ji Wais Univ. Gwalior 474011, India) Rect. Kinetic Catla left. 1994, 5 360 441-9 (Eng.)

40. Zhaohua 'L, Xu, Jie, Kanen Lary (Dept. of Chemistry), University of Hirston Huston TX 77204-5641 USA) Cjem Mater 1998, 10(11) 3699-3706 (Eng) American Chemical Society.

41. R.B. Merrifield J. Am. Chem. Soc. 1963, 85, 2149.

42. F. Giardellia, G. Braca Carlini, G. Sbrana, G. Valentim. J. Mol. Catal. 1980, P-14;1.

43. S. Schlick, E Bortel and Dyrek. Acta Polymer, 2996, 47, 1.

44. J Lito, D Milstein, R.L. Abright J.v. Minkie cold and B.C. Gales, Chemitech Jan. 1983, P-46.

45. F.R. Hartely Supported metal complexes D. Reidal, Dord recht 1985, P10.

46. C.V. Pittman, Jr. L.R. Smith and S.E. Jacobson in B-Delmon and G. Jannes (Eds) catalyses Heterogeneous and Homogenous Elsvier, Amsterdam, 2975, P-393.

47. C.V. Pittman, Jr. and L.R. Smith in Y Ishil and M.T. Sutsui (Eds.) Organic Transcription metal chemistry Plenum press New-York, 1975, P 143.

48. Fustney, Alols. (Max-Plank iInstitute for Kahienfors Chung, D. 45470).

49. Arm-Strong, Danial W Lee Jauht, Chang, Lisa W. (Department of Chem.) University of missourse, Rolla, Rolla MO 65401, USA). Tetrahedron Asymmetry 2998 9(12), 2043-2046 (Eng.) Elsevier Science Ltd.

50. T. Balakrishanan, & E. Murugan I.J. Chem 1997 36A 697, J.S. Do & T.C. Choll. J. Appl. Electrochem 1992, 22(10) 966.

51. Brno, (zech., Rep., GZ 61137) Chem. Pap. 1997, 51(9) 167-182 (Eng) Slovak Academy of Science Institute Chemistry.

52. Clark James H. Bufferworth Andrew J, Towener Stewart, Teasdale Andrew I. (Department of Chemistry University York, York, UK YOI 500) J. Chem. Techny, Biotech 1997, 68(4), 367-376 (Eng.)

53. Naxwell, San E (Shell Research and Technology Centre, 1031, C.M. Amsterdam neth). Cat Tech. 1997 1(1) 6-14 (Eng.) Batzer Science Publisher.

54. Blckman, Donna G. (Max-Plank Institution for konlenforschung Muheim an der Ruhr. D. 45470 Germany) 1998 (Catalysis of organic reactions 455-465.)

55. Feng Xiaomina,Gang, Lia-Zhu (Union Lab – Asymmetric Synthesis chender Inst. Organic chem.., Chinese Academy Sci-Chengdu. Peop. Rep. China (10041) Guodang Xuexi Huaxe Huebck, 1998, 10(9), 1416-1421 (Chongaodeng Jeaoyu Chubansbe).

56. Lee Nam, Ho Baik, Jong Seok, Hansung (Department of Chemistry Cheju National University Chejil 690-756 S. Korea) Bull. Morean Chemical Soc. 1998 19(7), 726-728 (Eng.) Korean Chemical Society.

57. Feche, F, Dunjick, GarneZP Lomaine M. (Institute de-Rec-perochessur La Catalyse et Laboratine de catalse et Synthese organic USBL- CPE 69 622 Vil euroanne, Fr. Top Catal 1998).

58. Masanon, Hiranga, Mosi, Miwako (Graduate School of Pharmaceutical Sciences, Hokaido uni Sapporo – Japan 060-0812) Tetrahecdron Letter 1998.

59. Dalai Mahesh, KJ. Upadhyay M. Ram R.N., J. Moi Catal, A. Chem 142(3), 325-322 (Eng.) Elsevier Science B.V.

60. Dilip Patel, Dalal Mahesh K; Ram R.N., Stud. Surf Sai Catal 113, 1998.

61. John Jacob; Dalal Mahesh K; RamR.N., Stud. Surf, Sci. Catal 1997 110 (3rd coorld congress on oxidation catalysis, 1997) 1165-1171 (Eng.) Elsevier Science B.V.

62. Lei, Zigiang, Han, Xiangen; Zhang, yan; Wang Rengmin, Cao; Yong heng; Wang, Yunpu, Polym plast Technol Eng. 38(1); 159-169, 1999 (Eng.) Marcel Dekker, Inc.

63. Groves john. T; Carofiglio Tommaso Banchlo, Mercella; Sawye, Antony, PCT. Int Appl. W.O. 98 04, 538 (Ci C07 D 301/06) 5 Feb. 1998, US Appl. 760, 849, 5 Dec, 1996, 48 PP. (Eng.)

64. Weiner, Heiko; Hoyashi Yoshinito; Finake, Richard G, Inorg. Chim. Ata 291 (1-2), 426-437; 1999 (Eng.) Elsevier Science.

65. Suresh, S; Skaria, S; Ponarathnam S., Stud. Surf. Sci Catal 1998 113 (Recent Advance in Basic and Applied Aspect of Industrial Catalysis) 915-919 (Eng.)

66. Gu, Fengcal, Wang Jinming, Liu, Yinfan; Ye, Wengiang, Sun, Shumer, Daxuie, xuebao Bianjibel 31 (5), 666-670, 1998.

67. Zhang Xiang-Fushi; Xiao-Tian Hechang Huaxue (4); 433-437 (Ch) 1998