Annexure III
Syllabi and course structure of
M.Tech Degree Course In Industrial Catalysis

SEMESTER I

Course code	Paper	Credit	C/E	Marks		Total marks
				Tests and Assignments	End Sem Exam	
CHE 3101	Surface Chemistry and Catalysis	4	C	60	40	100
CHE 3102	Catalyst Technology – I	4	C	60	40	100
CHE 3103	Physical Methods In Catalysis	4	C	60	40	100
CHE 3104	Chemical Reaction Engineering	3	E	60	40	100
CHE 3105	Enzyme Catalysis	3	E	60	40	100
CHE 3106	Electrocatalysis	3	E	60	40	100
CHE 3107	Introduction to IPR: Patent Law and Practice (Interdepartmental Elective)	2	E	60	40	100
CHE 3108	Lab course	2	C	100	--	100
CHE 3109	Viva voce (End Semester)	--	C	--	50	50

SEMESTER II

Course code	Paper	Credit	C/E	Marks		Total marks
				Tests and Assig-nments	End Sem	
CHE 3201	Surface Characterization Techniques	4	C	60	40	100
CHE 3202	Catalysis by Metal Complexes	4	C	60	40	100
CHE 3203	Catalyst Technology – II	4	C	60	40	100
CHE 3204	Industrial Catalytic Processes	3	E	60	40	100
CHE 3205	Phase Transfer Catalysis	3	E	60	40	100
CHE 3206	Polymer Supported Catalysis	3	E	60	40	100
CHE 3207	Photocatalysis	3	E	60	40	100
CHE 3208	Lab course	2	C	100	--	100
CHE 3209	Viva voce (End Semester)	--	C	--	50	50

SEMESTER III

Course code	Paper	Credits	C/E	Total marks
CHE 3301	Project progress evaluation	16	C	300

SEMESTER IV

Course code	Paper	Credits	C/E	Total marks
CHE 3401	Project Dissertation evaluation & Viva voce	16	C	300

SEMESTER I

CHE 3101 SURFACE CHEMISTRY& CATALYSIS

4 credits **64 hours**

UNIT I

The solid - liquid interface – surface energy from solubility changes – surface energy from immersion,– contact angle – contact angle hysterisis – experimental methods and measurement of contact angle – theories of contact angle phenomena – adsorption of non-electrolytes from dilute solutions – irreversible adsorption– adsorption in binary liquid systems – adsorption of electrolytes.

UNIT II

The solid - gas interface – surface area of solids – structure and chemical nature of solid surfaces – nature of the solid adsorbate complex – adsorption of gases and vapours on solids – adsorption time – Langmuir adsorption isotherm – the BET and related isotherms – isotherms based on equation of state of the adsorbed films – potential theory – phase transformations in the multiplayer region – thermodynamics of adsorption – critical comparison of various models for adsorption.

UNIT III

Physical adsorption on heterogeneous surfaces – rate of adsorption – adsorption on porous solids: hysterisis – chemisorption and catalysis – chemisorption isotherms – kinetics of chemisorption – surface mobility – chemisorption bond – heterogeneous catalysis – transition state theory – specificity and selectivity in catalysis – catalytic activity and strength of chemisorption – Langmuir-Hinshelwood and Eley-Rideal mechanism – electronic factors in catalysis by metals – geometric factors in heterogeneous catalysis.

UNIT IV

Chemical dynamics at surfaces – inelastic collision and trapping – the sticking coefficient – physisorbed molecules – molecule migration, desorption and transition to chemisorbed state – accommodation coefficients – energy exchange at surface – cube models. Precursor theory of chemisorption – sticking probability curves – their temperature dependence. Desorption – analysis of desorption curves – kinetics of adsorption and desorption.

UNIT V

Dynamics of selective catalysis– catalyst selectivity –kinetic method of estimating selectivity in consecutive reactions – localized and mobile adsorption of the intermediate product – effect of pore size on catalyst selectivity – poly-functional catalysis –inter-particle space and through gas phase – simplified criteria for negligible resistance to mass transfer – selectivity of poly-functional catalysis.

REFERENCE

1. A.W. Adamson & A.P. Gast, "Physical Chemistry of Surfaces", John Wiley and Sons, Canada, 1997.
2. R.H.P. Gasser, "An introduction to chemisorption and catalysis by metals", Oxford, 1985.
3. A. Clark, "Theory of adsorption and catalysis", Academic Press, New York, 1970.
4. D.K. Chakraborthy, "Adsorption and catalysis by solids", Wiley Eastern Ltd. 1990.
5. J.M. Thomas & W.J. Thomas, "Introduction to principles of heterogeneous catalysis", Academic Press, New York, 1967.
6. G. A. Somorjai, "Introduction to Surface Chemistry and Catalysis", Wiley-Black Well, New York, 1994

CHE 3102 CATALYST TECHNOLOGY – I

4 credits **64 hours**

UNIT I

Catalyst preparation methods – precipitation and coprecipitation – sol gel process–Dispersed metal catalysts; support materials; preparation and structure of supports; surface properties – preparation of catalysts – introduction of precursor compound – interaction of metal compound with substrate surface – metal distribution within catalyst pellets – metal cluster compounds as active precursors – pre-activation treatment – drying and calcinations – activation process.

UNIT II

Bulk catalysts and supports – fused catalysts – Skeletal metal catalysts.Heteropoly compounds – Solid superacids. Carbons – structural chemistry of carbon– basic structures – loosely defined structures – formation of carbon materials: catalytic formation of carbon from molecules – carbon on noble metal catalysts – carbon formation in zeolites – graphitization of carbon – reaction of oxygen with carbon – surface chemistry of carbon – non-oxygen hetero elements on carbon surfaces – surface oxygen groups – carbon as catalyst support – carbon as catalyst.

UNIT III

Synthesis of aluminosilicate zeolites and related silica based materials – structure, composition, zeolite synthesis, mechanism and chemistry–zeolites obtained from various reaction systems – synthesis of some selected important zeolites – titanosilicates – activation of zeolites. Modification of zeolites – ion exchange – metals supported on zeolites – reduction of metal ions in zeolite – dealumination of zeolites; Shape selective catalysis in zeolites; Phosphate based zeolites and molecular sieves.

UNIT IV

Pillared clays– properties of pillared clays –synthesis and catalytic applications of pillared clays– the use of coordination and organometallic compounds as pillaring agents – the use of polymers and surfactants in pillaring process – pillaring of acid activated clays – enhancement of acidity of PILCs – the use of PILCs as catalyst supports –hydrotalcite like anionic clays in catalytic organic reactions; Mesoporous materials - ordered mesoporous materials – PMOS -synthesis of silica molecular sieve materials - characterization of mesoporous molecular sieves – catalytic properties of mesoporous materials.

UNIT V

Catalyst manufacture– scope and goals – catalysts prepared by precipitation – solution and slurry transfer – filtration – drying: calcining; ion exchange; pulverization, pilling and extrusion; crushing and screening to produce granules; coating (not impregnation); impregnation to orient the coating material to the support – anchor coating or wash coating.

REFERENCE

1. G. Ertl, H. Knozinger and J. Weitkamp (eds), “Preparation of Solid Catalysts”, Wiley-VCH, Verlag, 1999.
2. J.R. Anderson and M. Boudart (Eds), “Catalysis, Science and Technology”, Vol 6, Springer-Verlag, BerlinHeildberg, 1984.
3. J. Weitkamp and L. Puppe (eds), “Catalysis and zeolites – fundamentals and applications”, Springer-Verlag Berlin Heidelberg 1999.

4. A. Corma, Chemical Reviews, 97 (1997) 2373-2419.
5. S. van Donk, A.H. Janssen, J.H. Bitter & K.P. deJong, Catalysis Reviews, 45 (2003) 297-319.
6. A. Gil, L.M. Gandia& M.A. Vincente, Catalysis Reviews Science and Engineering, 42 (2000) 145-212.
7. B.F. Sels, D.E. De Vos & P.A. Jacobs, CatalysisReviews, 43 (2001) 443-488.
8. M. Hartmann & L. Kevan, Chemical Reviews, 99 (1999) 635-663.
9. A.B. Stiles and T.A. Koch, “Catalyst manufacture”, Marcel Dekker Inc., NY, 1995.

CHE 3103 PHYSICAL METHODS IN CATALYSIS

4 credits **64 hours**

UNIT I

Determination of surface area and pore structure of catalysts – physical adsorption methods – mercury intrusion methods – chemisorption methods – X-ray methods – microscopic methods – radioactive isotope method – flow rate and diffusion methods – miscellaneous methods – comparison of methods; Measurement of acidity of surfaces – aqueous methods – nonaqueous liquid phase methods – adsorption from gas phase – hydrogen-deuterium exchange reactions.

UNIT II

Gas chromatography – basic instrumental setup – carriers – columns – detectors – scientific selection of stationary phases – applications in catalytic activity studies – determination of surface area of catalysts – principles and instrumentation of Gas Chromatography–Mass Spectrometry (GC-MS); TG, DTA, DSC – Instrumentation – application in catalysis.

UNIT III

Conventional magnetic methods in catalysis – forms of magnetism – force produced by magnetism – techniques – applications. UV-Vis-NIR spectroscopy – general background – electronic transitions – molecular complexes – non molecular solids – vibrational transitions – DRS – theoretical background – experimental considerations – applications.

UNIT IV

Infrared spectroscopy – experimental techniques – application of infrared spectroscopy to adsorption and catalysis; Raman spectroscopy – theory of Raman Effect – application of Raman spectroscopy to catalysis; Mossbauer spectroscopy – occurrence of the Mossbauer effect – method of measurement – hyperfine interactions – isomer effect – quadrupole splitting – magnetic splitting – applications to adsorption and catalysis.

UNIT V

Electron spin resonance spectroscopy – features of ESR spectra – g value – shifts in g value – tensor properties of g and A parameter – origin of hyperfine interaction – Fermi contact and dipolar terms – identification of catalytic sites by EPR – detection of free radical intermediates – molecular motion on the surface.

Nuclear magnetic resonance spectroscopy – solid state NMR – basic principles and methods of solid state NMR – fundamentals of NMR spectroscopy – nuclear spin interactions in solids – dipolar interaction – chemical shift interaction – quadrupolar interaction – experimental techniques – dipolar decoupling – MAS – DOR – CP – 2D NMR - useful nuclei – important NMR parameters and related structural information – applications.

REFERENCE

1. R.B. Anderson, “Experimental methods in catalysis research”, Vol I, II, Academic press, New York, 1981.
2. W.M.A. Niessen, “Current Practice of Gas Chromatography – Mass Spectrometry”, Marcel Dekker Inc, New York, 2001.
3. W.N. Delgass, G.L. Haller, R. Kellerman and J.H. Lunsford, “Spectroscopy in heterogeneous catalysis”, Academic press, New York, 1979.
4. G. Ertl, H. Knozinger and J. Weitkamp, “Handbook of Heterogeneous Catalysis” Vol 2, Wiley-VCH, Weinheim, 1997.

CHE 3104(E) CHEMICAL REACTION ENGINEERING

3 credits **48 hours**

UNIT I

Overview of chemical reaction engineering – homogeneous reactions in ideal reactors – kinetics of homogeneous reactions – concentration dependent term – temperature dependent term – searching for a mechanism – predictability of reaction rate from theory – interpretation of batch reactor data – constant volume and varying volume batch reactor – temperature and reaction rate.

UNIT II

Introduction to reactor design – ideal reactors for a single reaction – ideal batch reactor – steady state mixed flow reactor – steady state plug flow reactor; Design for single reactions – size comparison of single reactors – multiple reactor systems – recycle reactor – autocatalytic reactions; design for parallel reactions.

UNIT III

Potpourri of multiple reactions – irreversible first order reactions in series – first order followed by zero order – zero order followed by first order – successive irreversible reactions of different orders – reversible reactions – irreversible series-parallel reactions; Temperature and pressure effects – single reactions – multiple reactions – choosing the right kind of reactor.

UNIT IV

Reactions catalyzed by solids – heterogeneous reactions – solid catalyzed reactions – rate equation for surface kinetics – pore diffusion resistance combined with surface kinetics – porous catalyst particles – heat effects during reaction – performance equations for reactors containing porous catalyst particles – experimental methods for finding rates – product distribution in multiple reactions; the packed bed catalytic reactor; Reactors with suspended solid catalyst-fluidized reactors of various types (mention only); G/L reactions on solid catalyst: trickle beds, slurry reactors, three-phase fluidized beds (mention only).

UNIT V

Biochemical reaction systems – enzyme fermentation – Michaelis-Menten kinetics – inhibition by a foreign substance; Microbial fermentation – introduction and overall picture; substrate-limiting microbial fermentation – batch (or plug-flow) fermentors – mixed flow fermentors – optimum operations of fermentors; product limiting microbial fermentation – batch or plug-flow fermentors – mixed flow fermentors.

REFERENCE

1. O. Levinspeil, “Chemical Reaction Engineering”, IIIrd edition, John Wiley and sons, New York, 1999.
2. J.M. Smith, “Chemical Engineering Kinetics”, IIIrd edition, McGraw Hill Inc. Singapore, 1981.
3. H.S. Fogler, “Elements of Chemical Reaction Engineering”, IInd edition, Prentice Hall of India Pvt. Ltd. New Delhi, 1997.

CHE 3105 (E) ENZYME CATALYSIS

3 credits **48 hours**

UNIT I

Enzymes - classification and nomenclature of enzymes – structure of enzymes – effect on reaction rate – thermodynamic definitions – catalytic power and specificity of enzymes – optimization of weak interactions between enzyme and substrate in the transition state – binding energy, reaction specificity and catalysis – specific catalytic groups contributing to catalysis – enzyme kinetics as an approach to understanding mechanism – substrate concentration and rate of enzyme catalyzed reactions – quantitative relationship between substrate concentration and reaction rate – kinetic parameters used to compare enzyme activities.

UNIT II

Immobilized biocatalysts – definition and classification of immobilized biocatalysts – reasons for immobilization – history of immobilization – economic importance; methods for immobilization – adsorption – ionic binding – covalent binding – cross-linking – matrix entrapment – membrane confinement – combined methods – immobilization on crosslinked polymer supports- immobilization of coenzymes. Synthesis of peptides using immobilized enzymes- triphasic catalysis.

UNIT III

Characteristics of immobilized biocatalysts – activity as a function of temperature – stability as a function of temperature – temperature optimum in the long term process – the influence of pH value – influence of substrate concentration – influence of diffusion – other physical properties; Reactors for immobilized biocatalysts – stirred reactors – loop reactors – bed reactors – membrane reactors – special forms of reactors.

UNIT IV

Lewis acid properties of Zn and its development to phosphotriester detoxifying agents – vanadium haloperoxidases – Mo and W enzymes – catalysis by nitrogenases and synthetic analogs – biological Fe-S clusters with catalytic activity.

UNIT V

Catalysis by Ni in biological systems – oxygen activation at non-heme iron centers – dioxygen activation at heme centers in enzymes and synthetic analogs – biological and biomimetic catalysis of Mn redox enzymes and their inorganic models.

REFERENCE

1. A.L. Lehninger, “Principles of Biochemistry”, Worth Publishers, USA, 1987.
2. W. Hartmeier, “Immobilized Biocatalysts: an introduction”, Springer-Verlag, BerlinHeidelberg, 1986.
3. J. Reedijk and E. Bouwman, “Bioinorganic Catalysis”, Marcel Dekker Inc. New York, 1999.

CHE 3106 (E) ELECTROCATALYSIS

3 credits **48 hours**

UNIT I

Hydrogen adsorption at metal surfaces- importance of surface cleanliness –principles of hydrogen-metal interactions – classification of different cases of hydrogen adsorption – physisorption on metal surfaces – activated and non-activated adsorption of hydrogen on metal surfaces – hydrogen chemisorption including surface restructuring – subsurface, dissolved and hydridic hydrogen; hydrogen on Pt systems as example of importance of hydrogen-metal interaction in catalysis and electrochemistry.

UNIT II

The science of electrocatalysis on bimetallic surfaces – bimetallic surface chemistry – bulk alloys – overlayers and surface alloys– oxidation of adsorbed CO – oxidation of dissolved CO – formic acid oxidation – oxidation of methanol; fundamental aspects of vacuum and electrocatalytic reactions of methanol and formic acid on Pt surfaces.Fuel Cells- different types of Fuel Cells - fuel cell efficiency and technical anode potential – reaction rates by electrical measurements – non-electrical measures of reaction rates – techniques for mechanistic studies – UHV models of electrocatalysis.

UNIT III

Electrocatalytic hydrogenation of organic compounds – reaction mechanism – ECH on noble metals – ECH at electrodes made of Raney type materials; Recent advances in kinetics of oxygen reduction – gas phase studies of oxygen- surface structure and reaction kinetics – surfaces modified by foreign metal adatoms – non-noble metals and metal oxides – transition metal and macrocyclic complexes – electrolyte effects – temperature dependence of transfer coefficient for oxygen reduction.

UNIT IV

Studying electrocatalytic oxidations of small organic molecules with in-situ IR spectroscopy – principles and methods of in-situ IR spectroscopy – dissociative adsorption of small organic molecules at the surface of Pt group metals – molecular structure effects in electrocatalytic oxidation of small organic molecules – surface structure effects in electrocatalytic oxidation of small organic molecules – in-situ time resolved IR spectroscopic studies of the kinetics of electrocatalytic oxidation of small organic molecules.

UNIT V

Unified model of electron and ion transfer reactions at metal electrodes – extended Anderson-Newns model – activation barrier and transfer coefficient – pre-exponential factor – double layer effects in the electrode kinetics of electron and ion transfer reactions– electro-reductions of anions – double layer effects at single crystal electrodes – ion transfer reactions – electron transfer to adsorbed reactants – electron and proton transfer at self assembled monolayer.

REFERENCE

1. J. Lipkowski and P.N. Ross, “Electrocatalysis”, Wiley VCH, Canada, 1998.
2. J. O’M. Bockris and S.U.M. Khan, “Surface Electrochemistry”, Plenum press, New York, 1993.
3. J. O’M. Bockris, A.K.N. Reddy and M. G-. Aldeco, “Modern Electrochemistry – fundamentals of electrodics”, IInd edition, Kluwer academic/Plenum press, New York, 2000.

CHE 3107 (E) Introduction to IPR : Patent Law and Practice

2 credits

Inter University Centre for IPR Studies

CUSAT

Introduction to IPR - Patent: Law and Practice

Elective Course on IPR
(For PG Students of CUSAT)
2 Credits

Introduction:

In the era of commodification of knowledge Intellectual property law has great significance. It is believed that Intellectual Property Law, especially Patent Law, is a crucial factor in the promotion of innovation and industrial investment in Research and Development in a market economy. The limited monopoly guaranteed by patent protection could boost industrial and technological development in a congenial atmosphere. A proper understanding of the scope and extent of Patent Law is highly relevant from the consumers' perspective also since another equally important objective of patent protection - apart from protecting inventor's property rights and industrialists' investment - is the dissemination of knowledge and access to the fruits of modern technology at affordable cost. Patents, by providing for the disclosure of technology and permitting research and experimental exceptions open new vistas of knowledge to researchers and thereby promote further research.

PG students of science and technology have a very important role in contributing to innovation. Hence it is highly desirable that they have a minimum understanding of the implications of intellectual property protection, especially patent protection, on research and development and industrial investment. This course, therefore, intends to impart a general awareness of Intellectual Property Law, focusing more on Patent Law. The course shall delve on the scope of property protection and the modalities of its acquisition, management and enforcement, along with its implications on the societal interest.

Objectives:

This course is designed to sensitize the PG students of CUSAT (other than law) the relationship between science, technology, society and IPR. The course is also intended to make the students understand the role patent law plays in promoting creativity and encouraging the products of research reaching the society through industrial production and distribution. The course will surely inform the students the social responsibility of patent law in making the patented products available to the society at an affordable cost.

Name of Centre:	Inter University Centre for IPR Studies
Eligibility:	PG Students of CUSAT registered for any PG Programme other than LL.M
Duration:	One semester – 2 Credits (15 hours of teaching) (2 hours in a week – classes from 4.30 pm to 5.30 pm or from 9.30 to 11.30 on Saturday as per the convince of the students)
Course Teachers:	Prof. N.S. Gopalakrishnan Dr. T.G. Agitha

Course Content:

1. General Introduction to IPR (5 hours)
   a. Meaning of IPR
   b. Relation of IPR to creativity – science, technology and IPR
   c. IP as a tool for technological, economic and industrial development
   d. Various items of IPR – copyright, patent, design, GI, trademark etc.

2. Concept of patent and its justifications (5 hours)
   a. Definition of inventions - meaning of patent and its history
   b. Justifications and role of patent in promoting innovation and industrialization
   c. Concept of novelty, inventive step and commercial utility
   d. Exclusions of inventions from patent and its rational

3. Patent: Procedure (6 hours)
   a. Who can apply and where to make application
   b. Patent application and requirement – disclosure, drawings and claims
   c. Importance of patent documents in finding prior art – patent search - confidentiality and publication
   d. Procedure – examination-notification-opposition- grant of patent – renewal of patent.

4. Patent rights and enjoyment of ownership of patent (4 hours)
   a. Ownership of patent - joint ownership – inventions during employment

b. Assignment of patent – protection of the interest of the inventor
c. Rights recognized and duration of protection
d. Transfer of technology and industrial development

5. International protection of patent (5 hours)
    a. Paris Convention & TRIPS Agreement – over view
    b. Patent Cooperation Treaty – benefits – procedure

6. Patent and public interest (5 hours)
    a. Remedies for abuse of monopoly – compulsory licence & revocation
    b. Promoting innovation – limitations and exceptions to patent rights – research exception - parallel import
    c. Public health, development of pharma industry and access to patented products

Select Suggested Reading:

1. W.R. Cornish, Intellectual Property, (London: Sweet & Maxwell, Latest edn.)
2. WIPO Hand book on Intellectual Property
3. WIPO, Economics of IPR
4. WIPO, Intellectual Property – A powerful tool for economic growth
5. Neil F. Sulivan, Transfer of Technology, (Cambridge University Press)
6. UNCTAD-ICTSD, Resource Book on TRIPS and Development, (Cambridge University Press, 2005)
7. Jaffe Adem & Lerner Josh, Innovation and its Discontent, (Princeton University Press, 2004)
8. Bessen, James, Patent Failure: How judges, bureaucrats, lawyers puts innovations at risk, (Princeton University Press, 2008)

CHE 3108 PRACTICAL – I

3 credits **9 hours / week**

1. Preparation of supports for catalysts – alumina, silica, amorphous silica-alumina, zeolites, chromia, titania.
2. Comparison of different preparation techniques – precipitation, precipitation from homogeneous solution, polymer pyrrolysis, template synthesis, sol-gel method etc.
3. Shaping of support materials to extrudates and spheres.
4. Preparation of dispersed metal oxide catalysts – co precipitation, impregnation techniques.
5. Conversion of active phase into metal form – reduction.
6. Determination of surface area of the catalysts using BET method, total and micro pore volume and evaluation of pore size and particle size distribution.
7. Thermal studies of catalysts using TG and DTA/DSC.
8. Measurement of acidity of catalysts – Temperature Programmed Desorption of ammonia, adsorbed ammonia IR spectra, TG of pyridine, 2,6 DMP adsorbed samples.
9. Characterization of surface functional groups using IR spectroscopy.
10. Fabrication of reactors.

SEMESTER II

CHE 3201 SURFACE CHARACTERIZATION TECHNIQUES

4 credits **64 hours**

UNIT I

Surface crystallography and electron diffraction – surface symmetry – description of over-layer structures – reciprocal net and electron diffraction – surface structure determination using low energy electron diffraction (LEED)– reflection high energy electron diffraction (RHEED) – powder XRD – principles of powder diffraction – phase identification – quantitative analysis – determination of atomic structure of crystalline catalysts – determination of local atomic arrangement of amorphous catalysts – extended X-ray absorption fine structure spectroscopy (EXAFS).

UNIT II

X-ray photoelectron spectroscopy (XPS) – photon sources – shapes and shifts – XPS as core level spectroscopy – synchrotron radiation studies – structural effects in XPS – Auger electron spectroscopy (AES) – basic processes – energy levels – shifts and shapes – AES for surface composition analysis – comparison of AES and XPS. Ultraviolet photoelectron spectroscopy (UPS) – UPS in the study of adsorbed molecules.

UNIT III

Incident ion techniques – charge exchange between ions and surfaces – applications in ion scattering techniques – low energy ion scattering (LEIS) – application of LEIS in catalysis – secondary neutral mass spectrometry (SNMS) - secondary ion mass spectrometry (SIMS) – theory of SIMS – electron and photon emission under ion bombardment – energy distribution of secondary ions – ionization probability – emission of molecular clusters – conditions for static SIMS – charging of insulating samples – applications in catalysts – model catalysts.

UNIT IV

Desorption spectroscopies – thermal desorption techniques – qualitative analysis of pressure-time curves – experimental arrangements for flash desorption and TPD, FD and TPD spectra – temperature programmed reduction – thermodynamics of reduction – reduction mechanisms – applications; temperature programmed sulphidation; electronically stimulated desorption – basic mechanisms, instrumentation and applications.

UNIT V

High field techniques – field emission – field emission microscope – factors governing operation – practical microscope configurations – applications of field emission microscopy (FEM);Scanning tunneling and atomic force microscopy (STM, AFM); Work function techniques – single crystal surfaces – polycrystalline surfaces – work function measurements based on diode method – field emission measurements – photoelectric measurements; Electron microscopy (SEM, TEM) – instrumentation – applications on catalysts – element analysis in the electron microscope.

REFERENCE

1. D.P. Woodruff and T.A. Delchar, "Modern techniques of surface science", CambridgeUniversity press, 1990.
2. J.W. Niemantsverdriet, "Spectroscopy in Catalysis: an introduction", VCH, NY, 1995.
3. G. Ertl, H. Knozinger and J. Weitkamp, "Handbook of Heterogeneous Catalysis" Vol 2 & 3, Wiley-VCH, Weinheim, 1997.

CHE 3202 CATALYSIS BY METAL COMPLEXES

4 credits **64 hours**

UNIT I

Coordinative unsaturation– Oxidative addition- Addition reactions of hydrogen, halogens, organic halides- Addition reactions of Si-H and C-C bonds- C-H activation – Reductive elimination reactions- Migration (insertion reaction)- Insertion of CO, isocyanide, carbon dioxide, alkene and alkynes- nucleophilic and electrophilic attack on coordinated ligands- Ligand cone angles– catalytic cycles – hard and soft catalysis.

UNIT II

Hydrogenation reactions- Reversible cis-dihydrido catalysts- asymmetric hydrogenation- alkene isomerisation, hydrosilylation and hydroboration reaction- Reactions of Co and hydrogen- watergas shift reaction- Fischer –Tropsch reaction- hydroformylation of unsaturated compounds carbonylation reactions- Oxo synthesis – production of acetic acid by carbonylation of methanol – selective ethylene oxidation by the Wacker process – oxidation of cyclohexane- Monsanto L-Dopa process

UNIT III

Oligomerization of ethylene (SHOP); Cluster compounds as homogeneous catalysts and catalyst precursors – classification of catalyst precursors based on structure. homogeneous and heterogeneous Zeigler-Natta catalysts – supported metal complex catalysts – Phillips process for ethylene polymerization; Late-metal catalysts for ethylene homo and copolymerization – effect of nature of metallocene complexes of group IV metals on their performance in catalytic ethylene and propylene polymerization – carbocationic alkene polymerizations initiated by organo transition metal complexes.

UNIT IV

Polymer bound transition metal complex catalysts – synthesis of supports and catalysts – characterization by physical methods – catalysis – stability of polymer supported catalysts – comparison of polymers with inorganic catalyst supports; Specific features of catalysis by immobilized metal complexes – ligand exchange in metal-polymeric systems – characteristics of electron-transfer reactions – macromolecular effects – main factors regulating activity – effects of cluster formation and cooperative stabilization – outlook for polyfunctional catalysis – technological aspects.

UNIT V

Zeolite entrapped metal complexes – synthesis – flexible ligand method – ship in a bottle method – zeolite synthesis method – characterization – stability analysis – oxygen adsorption – cyclovoltametry – catalysis by zeolite entrapped transition metal complexes – ordered mesoporous and microporous molecular sieves functionalized with transition metal complexes as catalysts for selective organic transformations – propene polymerization with silica supported metallocene/MAO catalysts.

REFERENCE

1. F.A. Cotton, G. Wilkinson, C.A. Murillo & M. Bochmann, “Advanced inorganic chemistry”, VI edition, John Wiley and sons, Singapore, 1999.
2. J.E. Huheey, “Inorganic chemistry: principles of structure and reactivity”, Harper and Row publishers, Singapore.

3. J. Hagen, "Industrial catalysis: A practical approach", Wiley VCH, Weinheim, Germany, 1999.
4. D.C. Sherrington & P. Hodge, "Synthesis and separations using functional polymers", John Wiley and Sons, 1988.
5. A.D. Pomogailo, "Catalysis by polymer-immobilized metal complexes", Gordon & Breach Science Publishers, Amsterdam, 1998.
6. G. Ertl, H. Knozinger and J. Weitkamp, "Handbook of Heterogeneous Catalysis" Vol 3 and 5, Wiley-VCH, Weinheim, 1997.

CHE 3203 CATALYST TECHNOLOGY – II

4 credits **64 hours**

UNIT I

Deactivation of catalysts – classification of catalyst deactivation processes; general aspects of catalyst deactivation – poisoning of catalysts – poisoning of metallic catalysts – poisoning of non metallic catalysts – poisoning of bifunctional catalysts – coke formation on catalysts – metal deposition on catalysts – sintering of catalysts; diffusion and deactivation of catalysts – analogy between selectivity and deactivation mechanisms – catalyst deactivation – correlations for activity decay – separable and non separable kinetics; Optimization of deactivated reactor systems – comparison of various reactor types under deactivating conditions – optimization of deactivating reactors – optimal temperature policies – other optimal policies.

UNIT II

Regeneration of deactivated catalysts – feasibility of regeneration – description of coke deposit and kinetics of regeneration – regeneration of fluidized bed reactors – regeneration of coked catalyst pellets – regeneration of fixed beds containing coked catalysts; Technological economics – cost of producing a chemical – variable costs – fixed costs – direct costs – indirect charges – capital dependent charges – effect of scale of operation – effect of low plant operation – contribution of catalyst to production cost; Catalytic processes in an integrated system – effect of catalyst on plant equipment – catalyst life – effect of improvement in catalyst performance on process and economics – prospects for new catalytic process

UNIT III

Design of industrial catalysts; design procedure; the overall design of catalysts – overall development of an industrial catalyst – scientific basis of design – the idea – preliminary checking – the description of the idea – theoretical design: primary components of the catalyst – catalyst deactivation – secondary components of a catalyst – selection of the preferred form of a catalyst – the overall design; design of the primary constituent of the catalyst – theories of chemical bonding – theories of bonding and adsorption – bond theories and catalysis – theories of bonds and catalyst design – activity patterns and catalyst design.

UNIT IV

Design of the secondary components of a catalyst – secondary component design via mechanistic studies – alloy catalysts – metal cluster catalysts – metal oxide solid solutions – specific examples of oxide solid solution catalysts applied to design; choice of support materials – texture and strength of support – chemical interaction – deactivation; experimental testing – preliminary testing – testing of the effect of secondary components – measurement of reaction kinetics – tubular reactors – plug reactors – stirred reactors – long term catalyst testing.

UNIT V

Specific examples of catalyst design; design of a catalyst for conversion of olefins to aromatics – description of the idea – design of primary constituents – experimental testing – design of secondary components; design of a catalyst for selective hydrogenation of acetylene in presence of ethylene – the idea – the description of the idea – the design of the primary components; design of a catalyst for reduction of nitrogen oxides to nitrogen – the idea – description of the idea – co-ordination and geometric considerations and design – catalysis by metals – conclusions – comments.

REFERENCE

1. R. Hughes, “Deactivation of catalysts”, Academic press, London, 1984.

2. R. Pearce and W.R. Patterson, “Catalysis and chemical processes”, Academic press, Leonard Hill, London, 1981.
3. C.A. Heaton (ed), “An Introduction to Industrial Chemistry”, Leonard Hill, London, 1984.
4. D.L. Trimm, “Design of industrial catalysts”, Elsevier scientific, NY, 1980.

CHE 3204 (E) INDUSTRIAL CATALYTIC PROCESSES

3 credits **48 hours**

UNIT I

Environmental catalysis – Mobilesources – Stationary sources –Catalytic routes to hydro (chloro) fluoro carbons –Inorganic reactions – Ammoniasynthesis –Ammonia oxidation.

UNIT II

Energy related catalysis – Perspectivesin oil refining – Steam reforming – Water gas shift and COS removal – Methanol synthesis – CO and CO_2 hydrogenation – Methanol to hydrocarbons – Hydrotreating reactions – Catalytic reforming – Catalytic cracking

UNIT III

Hydrocracking and catalytic dewaxing –Aromatization of light alkanes – Catalytic coal gasification – Catalysis in coal liquefaction – Fuel cells – Heterogeneous photocatalysis.

UNIT IV

Alkylationof aromatics – Isomerization and trans-isomerization – Dehydrogenation reactions – Hydrogenation reactions – Hydroformylation – Selective oxidations.Carbon-carbon bond forming reactions- coupling reactions- Ni, Cu, Pd catalysts in C-C bond forming reactions. Heck, Suzuki, Sonogashira, Stille Coupling reactions.

UNIT V

Amination reactions –Acylation of aromatics – Nucleophilic Aromatic Substitution reactions – Elimination and addition reactions – Oligomerization and metathesis.

REFERENCE

1. G. Ertl, H. Knozinger and J. Weitkamp, "Handbook of Heterogeneous Catalysis" Vol 4 and 5, Wiley-VCH, Weinheim, 1997.
2. R.J. Farrauto and C.H. Bartholomew, "Fundamentals of Industrial Catalytic Processes", Blackie Academic and Professional – Chapman and Hall, 1997.
3. R. Pearce and W.R. Patterson, "Catalysis and chemical processes", Academic press, Leonard Hill, London, 1981.
4. J. Weitkamp and L. Puppe (eds), "Catalysis and zeolites – fundamentals and applications", Springer-Verlag Berlin Heidelberg 1999.

CHE 3205 (E) PHASE TRANSFER CATALYSIS

3 credits **48 hours**

UNIT I

Basic concepts in phase transfer catalysis – phase transfer catalyzed reactions – basic steps of phase transfer catalysis – effect of reaction variables on transfer and intrinsic rates – outline of compounds used as phase transfer catalysts; Phase transfer catalysts – use of quaternary salts – macrocyclic and macrobicyclic ligands – PEG's and related compounds – other soluble polymers – use of dual phase transfer catalyst or co-catalyst in phase transfer systems – catalysts for transfer of species other than anions – separation and recovery of phase transfer catalysts.

UNIT II

Insoluble phase transfer catalysts –PTC catalysts bound to resins – phase transfer catalysts bound to inorganic solid supports – phase transfer catalysts contained in separate liquid phase (third liquid phase catalyst); Variables in reactor design for application of PTC – choice of catalyst – structure activity relationships – catalyst stability – separation and recycle – choice of solvent and nature of chemical reaction – stabilization of transition state – solubility of complex in organic phase – rate of transfer – solvent free PTC – presence of water – agitation – choice of anion, leaving group and counter anion – choice of base – guidelines for exploring new PTC applications;

UNIT III

PTC displacement reactions with simple anions – general considerations – important factors – characteristics of various anions – PTC catalysts for displacement reactions – behaviour of various anions in PTC displacement reactions – cyanide, halide, carboxylates, azide, sulphide and disulphide, thiocyanate, sulphite, nitrite, hydroxide, carbonate and bicarbonate, peroxide and superoxide, phosphide and phosphinite, cyanate; PTC reactions with strong bases – C alkylation – N alkylation – O alkylation: etherification – S alkylation: thioetherification – dehydrohalogenation – carbene reactions – condensation reactions – deuterium exchange, isomerization etc.

UNIT IV

Phase transfer catalyzed oxidations – permanganate oxidations – oxidations with hypochlorite and hypobromite, hydrogen peroxide, air or oxygen,persulphate, nitric acid, CCl_4/NaOH, periodate and related anions,perborate, ferrate and ferricyanide, superoxide – PTC electrochemical oxidations – PTC oxidations with other oxidants;PTC reductions – $NaBH_4$ reductions – $LiAlH_4$ reductions – reductions with sodium formate, sulphur containing anions – hydrogenations – reductions with formaldehyde – electrochemical reductions – photochemical reductions – Wolff-Kishner reduction – reduction by dodecarbonyl tri iron and related species

UNIT V

PTC: Chiral phase transfer catalyzed formation of C-C bonds – alkylation reactions – methylation and alkylation – asymmetric alkylation of oxindoles – synthesis of chiral amino acids – Michael addition reactions; PTC: transition metal co-catalyzed reactions – carbonylation and reactions with CO – formation of metal carbonyl anions – carbonylation of alkyl and aryl halides, olefins, acetylenes, aziridines and azobenzenes, thiiaranes, phenol – reduction and hydrogenation with metal co-catalysts – coupling reactions of alkenes, alkynes and alkyl halides – other reactions

REFERENCE

1. C.M. Starks, C.L. Liotta and M. Halpern, "Phase Transfer Catalysis – fundamentals, applications and industrial perspectives", Chapman&Hall, New York, 1994.
2. Y. Sasson and R. Neumann (eds), "Handbook of Phase Transfer Catalysis", Chapman & Hall, Great Britan, 1997.

CHE 3206 (E) POLYMER SUPPORTED CATALYSIS

3 credits **48 hours**

UNIT I

Preparation of functionalized polymers – polymerization – condensation polymerization – addition polymerization – copolymerization – chemical functionalization of synthetic organic polymers – functionalization of polystyrene – functionalization of condensation polymers – chemical modification under phase transfer catalysis – functionalization by grafting – functionalization of membranes – functionalization of biopolymers – functionalization of inorganic supports.

UNIT II

Organic reactions using polymer supported catalysts – monitoring of polymer supported reactions – some general features of polymer supported reactions – selected polymer supported catalysts – Design and industrial application of polymeric acid catalysis – homogeneous versus heterogeneous catalysis – industrial applications – new developments in catalyst design- polymer supported dendrimers and dendrigraft polymers as catalysts in organic reactions- organo catalysts.

UNIT III

Hydrogenation processes catalyzed by metal containing polymers – principal information concerning the mechanism – relationships between preparation conditions and catalytic properties – composition, structure and activity, influence of solvent properties – influence of reaction temperature – dependence of rate on concentration ratios – catalysis by dispersed colloidal particles and transition metal clusters – selectivity – enantioselective hydrogenation – catalytic hydrogenation by heterometallic polymers – H-H activation and hydrogen transfer – hydrosilylation – reduction of macromolecules.

UNIT IV

Oxidation reactions catalyzed by immobilized metal complexes – basic laws – activation and binding of dioxygen – hydrocarbon oxidation – polymeric metalloporphyrin catalyzed olefin oxidation – catalase type activity – metal polymer catalyzed olefin epoxidation by alkyl hydroperoxides – macromolecular complexes for oxidation – oxidation of sulphur containing compounds – asymmetric induction in oxidationreactions – catalytic oxidation of polymers.

UNIT V

Activation of small stable molecules and stimulation of catalytic reactions through participation of immobilized metal complexes – Fischer-Tropsch synthesis – carbonylation – water gas shift reaction – hydroformylation – catalytic hydrolysis and dehydration – acid catalysis – binding and activation of molecular hydrogen – photochemical decomposition of water – electrochemical stimulation of catalytic processes; Polymeric phase transfer catalysts – synthesis of catalysts – analysis of catalysts – mechanism of catalysis – experimental design – synthetic applications.

REFERENCE

1. A. Akelah& A Moet, “Functionalized polymers and their applications”, Chapman and Hall, 1990.
2. D.C. Sherrington & P. Hodge, “Synthesis and separations using functional polymers”, John Wiley and Sons, 1988.
3. A.D. Pomogailo, “Catalysis by polymer-immobilized metal complexes”, Gordon & Breach Science Publishers, Amsterdam, 1998.

CHE 3207 (E) PHOTOCATALYSIS

3 credits **48 hours**

UNIT I

Fundamentals of Photochemical and Photophysical processes. Photochemistry in Practice – Radiometry and Actinometry – Priciples of Radiometry and radiometers – Actinometry – Quantum Yields – Light Sources – Optical Materials and Filters – Photochemical Reactors
Photoinduced Electron Transfer – Theory of Electron transfer – Advanced Oxidation Process– Reactive species in photocatalysis, generation and reactivity: trapped electron and hole– superoxide radical anion– hydrogen peroxide– hydroxyl radical– singlet molecular oxygen. Homogeneous photocatalysis – Mechanism of Fenton reaction and Photo Fenton Reaction – applications of Fenton and Photo – Fenton Reaction

UNIT II

Semiconductor Photocatalysis: Photoelectrochemical process in semiconductors. – Thermodynamics of photocatalysis– Photocatalytic rate and kinetic models– Effects of surface area and crystal structure on the efficiency of photocatalysis– Modified Photocatalysts– surface modifications–doping with metal ions and oxides– Sensitization of semiconductors– Mass transfer in photocatalysis– Preparation of TiO_2 powers: Sulphate route, chloride route and alkoxide route. – Activities of TiO_2 photocatalysts other photocatalytic oxides– Photocatalytic thin films.

UNIT III

Photo electrochemistry (PEC) - Semiconductor electrodes for solar energy conversion, comparison of photosynthesis - photovoltaics and photoelectrochemistry - Dye sensitized solar cells (DSSC) - Configuration, sensitizers, electrolytes, hole transporting materials, packaging, current voltage characterization, Dye characteristics.

UNIT IV

Applications of semiconductor photocatalysis in environmental remediation - Air purification, sterilization - antifouling. Oxidation of air pollutants - volatile hydrocarbons and halogenated hydrocarbons.

Water purification: Degradation of pollutants (Volatile organic compounds, pesticides, endocrine disruptors, waterborne microbes *Escherichia Coli* etc) Types of solar reactors for water treatment.

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UNIT V

Photocatalysis in chemical transformations: Photoredcution of CO_2 - Photolysis of water – semiconductors in organic synthesis - Applications of Titanium Dioxide in oxidations, reductions and coupling reactions - Applications of polyoxotungstates, Highly dispersed oxides of Ti, V and Cr.

REFERENCE

1. Photocatalysis – Science & Technology Ed.by Masco kaneko & Ichiro Okura. (Springer) 2002.
2. Helerogeneous photocatalysis Ed. By Mario Schiavello (wiley) (1995)
3. Photoelectrochemistry, Principles & Practices, B. Viswanathan & Aulice Sabioh, (Narosa) (2010)
4. Photocatalysis and water purification: from fundamentals to recent applications. Ed. G. Q. Max Lu, (Wiley –VCH) 2013
5. Photocatalysis Vol 303 in Topics in Current Chemistry, Ed. C.A. Bignozzi, (Springer) 2011.

CHE 3208 PRACTICAL – II

3 credits **9 hours / week**

1. Phase characterization-using XRD.
2. Activity studies for hydrogenation reactions using pulsed micro-catalytic reactors and continuous flow reactors.
3. Activity studies of cracking and oxidation reactions.
4. Activity studies for FC Alkylation and acylation reactions.
5. Product analysis using Gas Chromatography.
6. Comparison of activity for different types of reactors – STR, FBR.
7. Synthesis and characterization of some transition metal complex catalysts using conductance, magnetic susceptibility, IR and TG measurements.
8. Oxidation of p-xylene to tere-phthalic acid using Co(II)Br_2.
9. Hydrogenation of buta-1,3-diene using pentacyamocobaltate(II)
10. Oxidation of ethylene to acetaldehyde using palladium chloride.

Cochin University of Science and Technology (CUSAT)

Department of Applied Chemistry

Syllabus for
M. Tech. Industrial Catalysis
(With Effect From 2015-16)