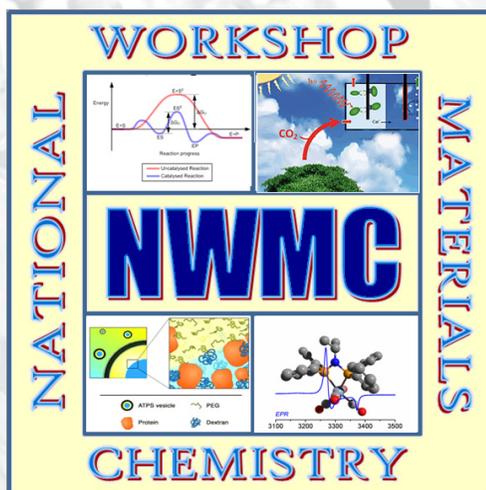




Proceedings of
DAE-BRNS
2ND NATIONAL WORKSHOP ON
MATERIALS CHEMISTRY
(CATALYTIC MATERIALS)
NWMC-2013 (CAT-MAT)



November 22-23, 2013

Bhabha Atomic Research Centre
Trombay, Mumbai-400 085, India

Organised by

Society for Materials Chemistry, India
&
Chemistry Division
Bhabha Atomic Research Centre

Supported by

Board of Research in Nuclear Sciences
Department of Atomic Energy
Government of India



NWMC - 2013

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2nd National Workshop on
Materials Chemistry (Catalytic Materials)**

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November 2013

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Ratan Kumar Sinha



अध्यक्ष, परमाणु ऊर्जा आयोग
व
सचिव, परमाणु ऊर्जा विभाग
Chairman, Atomic Energy Commission
&
Secretary, Department of Atomic Energy

November 13 , 2013



MESSAGE

I am happy to learn that Chemistry Division, BARC, in association with Society for Materials Chemistry (SMC) is organising the DAE-BRNS 2nd National Workshop on Materials Chemistry (NWMC-2013:CAT-MAT), focused on Catalytic Materials, at BARC, during 22-23 November 2013.

Catalytic materials continue to play a dominant role in the economic and sustainable growth of chemical industry catering to the basic needs of the society. Several catalytic materials find applications in DAE programs like mitigation of hydrogen under LOCA conditions, production of H₂ via Sulphur-Iodine thermochemical cycle in the context of CHTR, etc. Designing catalytic materials with specific properties such as activity and selectivity has always been a key challenge to the material chemists.

I understand that NWMC-2013 will cover various scientific and technological aspects of catalytic materials including recent advances. I am also happy to note that the workshop will provide a platform for interaction of academia and industry, and will be quite useful to the young researchers in the field of catalytic materials.

I wish the workshop a grand success.

(R.K. Sinha)



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INTERNATIONAL ADVANCED RESEARCH CENTRE FOR POWDER METALLURGY AND NEW MATERIALS (ARCI)

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(An autonomous R&D Centre of Dept. of Science & Technology, Govt. of India)

Balapur PO, Hyderabad-500 005, India

Lr. No. ARCI/PRR/ASCI/13

November 7, 2013



Message

I am happy to learn that DAE-BRNS 2nd National Workshop on Materials Chemistry (NWMC-2013 : CAT-MAT), a biennial event, focused on Catalytic Materials, is being jointly organized by the Chemistry Division, BARC, and Society for Materials Chemistry (SMC), India at the Bhabha Atomic Research Centre, during November 22-23, 2013.

Catalysis has always been at the core of every chemical process whether in the laboratory or in the industry. Well-known examples include Haber process for ammonia synthesis, contact process for sulfuric acid production, catalysts for petroleum cracking and fine chemical.

The field of catalysis has witnessed a multi-dimensional growth in recent years and currently it encompasses areas such as homogeneous, heterogeneous, photo-catalysis, electro-catalysis and enzyme catalysis. Search for better and low cost catalysts with tailor made properties has kept the researchers busy. I understand that different aspects of catalytic materials including synthesis and characterization will be covered during NWMC-2013, by the experts in the field.

I trust that young researchers working in the area of catalytic materials will utilize this opportunity to enhance their understanding of the subject through scientific deliberations during the workshop.

I wish NWMC-2013 every success in achieving its stated objectives.

P. Rama Rao

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शेखर बसु
Sekhar Basu



निदेशक, भाभा परमाणु अनुसंधान केंद्र
Director, Bhabha Atomic Research Centre
सदस्य, परमाणु ऊर्जा आयोग
Member, Atomic Energy Commission



MESSAGE

I am delighted to know that DAE-BRNS 2nd National Workshop on Materials Chemistry (NWMC-2013 : CAT-MAT), focused on Catalytic Materials, is being organised jointly by Chemistry Division, Bhabha Atomic Research Centre and Society for Materials Chemistry (SMC), India, at BARC, during November 22-23, 2013. I take this opportunity to compliment the organisers for holding these biennial workshops on various themes that are both contemporary and relevant.

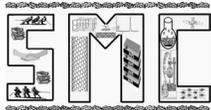
In BARC, there exist substantial expertise in the field of catalysis, which has been gainfully utilised in several of our indigenous R & D programs. Hydrogen mitigation by passive autocatalytic recombiner and catalytic decomposition of sulfuric acid are some such examples. There exist several other avenues particularly in the back end of fuel cycle, where efficient catalysts are a need of the day.

I understand that different aspects of catalytic materials will be covered during NWMC-2013, by the experts in the field. I hope that young participants will be greatly enriched from the deliberations during the workshop.

I extend my best wishes for the success of the workshop.


(Sekhar Basu)

5.11.2013



SOCIETY FOR MATERIALS CHEMISTRY (SMC)
(Reg. No. - Maharashtra, Mumbai/1229/2008/GBBSD)

C/o Chemistry Division

Bhabha Atomic Research Centre, Mumbai-400 085, India

Dr Sisir K. Sarkar
President, SMC



Message

It gives me great pleasure to pen down this special message for DAE-BRNS 2nd National Workshop on Materials Chemistry (NWMC-2013 : CAT-MAT) being organized by Society for Materials Chemistry (SMC) working closely with Chemistry Division, BARC during November 22-23, 2013. This is the first major activity of SMC after the present council has taken over the mantle of showcasing the activity of the Society for the next three years. As you are aware SMC is an organization devoted to promote education, advancement and applications of Material science and technology in India. At the outset let me express my gratitude to each and every members of SMC for their unstinted support and cooperation in the growth of the Society. Formed six years back, SMC today is a well-knit vibrant family with members totaling over 700 with few Corporate members all over the country.

Today Modern Science is poised to take a magical leap forward in our understanding and control of matter, energy, and information at the molecular and atomic levels. The next generation technologies will revolve around new materials and chemical processes that convert energy efficiently among photons, electrons, and chemical bonds for applications in energy, health care, nanoscience, environmental science, and national security.

In this regard, Catalytic materials continue to play important role in enabling development of newer technologies in many areas for the benefit of society and have a great role to play in the economy of the country in general. This workshop will cover both fundamental and applied aspects namely heterogeneous, homogeneous and enzymatic catalysis related to energy, environment, synthesis, sensors, etc. About 200 young researchers working in the field of chemistry, physics and materials science from BARC as well as other units of DAE, National laboratories, and Institutes/Universities, will be immensely benefited.

I hope that NWMC-2013: CAT-MAT will provide a stimulating environment among the peer and the young to open up newer frontiers in material chemistry. Once again, as President of SMC, I extend most warm and hearty welcome to all the delegates and wish the workshop every success in achieving its intended objectives.


(Sisir K. Sarkar)
01/11/2013



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Chemistry Group

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Senior Professor & Dean-Academic
Physical & Mathematical Sciences,
Homi Bhabha National Institute

Distinguished Professor (Adjunct)
Department of Physics,
Indian Institute of Technology Bombay

Ref: CG/BNJ/2013/379

November 07, 2013

MESSAGE

I am happy to note that the Chemistry Division, BARC, in association with the Society for Materials Chemistry, India, is organizing the Second DAE-BRNS National Workshop on Material Chemistry focused on the theme '*Catalytic Materials*' during November 22-23, 2013 at Multipurpose Hall, TSH, Anushaktinagar, Mumbai 400 094.

Catalysis occupies a unique position in the chemistry research owing to its diversified applications in energy, environment, health, and in general in all our endeavors contributing to the better quality of life. For example, over 90% of industrial chemicals are produced with the aid of catalysts and further the growing concerns over the environmental issues in recent times have made catalyst indispensable in pollution mitigation. Catalysis research today encompasses a wide spectrum of issues such as theoretical modeling at the molecular levels, fundamental surface science, and design, synthesis and characterization of novel catalysts for specific applications.

Chemistry Division, BARC has a long tradition of research in catalysis. Some of the notable developments of the recent past include gas recovery catalyst for sealed-off carbon-di-oxide lasers, catalyst for hydrogen and oxygen recombination for nuclear reactors, and low cost non-noble metal catalysts for sulfuric acid decomposition in sulfur-iodine thermo-chemical cycle.

It is quite thoughtful of the organizers to host this thematic workshop which provides a unique platform for discussions on the recent advances in the field of catalysis and also for sharing experience among researchers from national institutes, universities and industries.

I wish the workshop a grand success and look forward to participating in the technical deliberations.

(B.N. Jagatap)

NWMC – 2013 (CAT-MAT)

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PREFACE

Society for Materials Chemistry and Chemistry Division, BARC, are indeed very pleased to jointly organise the DAE-BRNS 2nd National Workshop on Materials Chemistry, focussed on Catalytic Materials (NWMC-2013: CAT-MAT) at BARC. The workshop aims to provide a forum for young researchers to interact with the experts actively working on different aspects of catalysis.

Catalysis is a phenomenon where enhancement in rate of a chemical reaction is achieved by creating a new reaction pathway (characterized by a lower energy barrier) using a relatively small amount of foreign material, called catalyst, and which remains intact at the end of reaction. In addition catalysts also help in achieving chemo-, regio- and stereo- selectivity through an appropriate spatial arrangement of reactants. Catalysis has been a quiet but significant contributor behind the modernization of our chemical industry including petrochemical and pharmaceutical industry, ensuring more efficient use of finite natural resources. It has considerable influence in our day to day life by improving quality of life and environment through products like transportation fuel, paint, cosmetics, wonder drugs, catalytic converters, etc. In nuclear industry it finds applications in processes like production of heavy water, mitigation of hydrogen in nuclear plant under accident scenario, back end processes of the nuclear fuel cycle, etc. Issues like global warming have further enhanced its role in production of alternate energy carrier hydrogen without emission of greenhouse gases.

In past few decades, development of newer synthesis procedures, and ever-increasing sophistication of spectroscopic and computational techniques have contributed in improving our understanding of working of catalyst at atomic scale. These developments have also opened up the possibility of the molecular design of catalysts. It is pertinent to mention here that all biological processes in nature are very precisely and selectively carried out by nature's catalyst called enzyme. This has always been a great inspiration to the catalysis community. Efforts to unify heterogeneous, homogeneous and bio-catalysis under single coherent theory, using molecular modelling techniques appear to be quite promising.

This two-day workshop will cover different facets of catalysis, which will be covered in twenty lectures delivered in seven technical sessions. We hope that the deliberations in this workshop will be quite useful to the participants and will provide them ample opportunity to expand their understanding of the subject.

The workshop organising committee expresses its gratitude to all the invited speakers who wholeheartedly agreed to spare their valuable time and knowledge, in spite of their busy schedule. Financial support from BRNS is gratefully acknowledged. We are grateful to our Patrons and members of the National Advisory Committee and Local Organising Committee for their valuable suggestions and support. We take this opportunity to thank all members of the local organising committee/sub-committees and Chemistry Division staff for their dedicated and untiring efforts towards organising this event.

We wish all the participants a pleasant stay in Anushaktinagar and fruitful interactions during the workshop.

(A. K. Tripathi)
Convener, NWMC-2013

(V. K. Jain)
Chairman, NWMC-2013

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Scientific Programme – NWMC 2013 (CAT-MAT) (November 22-23, 2013)

November 22, 2013 (Day 1)		
08:30 – 09:30		Registration
09:30 – 10:45		Inauguration Key-note address by Prof. M. M. Sharma, ICT, Mumbai An Overview of Catalytic Processes
10:45 – 11:15		High Tea
11:15 – 13:15		Session I – Fundamental and Mechanistic Aspects in Catalysis
11:15 – 11:50	WL-1	Prof. B. Viswanathan, NCCR, IIT, Chennai <i>The Ever Changing Faces of Catalysis</i>
11:50 – 12:25	WL-2	Dr. N. M. Gupta, NCL, Pune <i>Fundamentals of Heterogeneous Catalysis</i>
12:25 – 13:00	WL-3	Dr. C. S. Gopinath, NCL, Pune <i>Fundamental and Mechanistic Aspects in Catalysis – Ertl's Contributions</i>
13:00 – 13:15		Interactive Session
13:15 – 14:00		Lunch
14:00 – 16:00		Session II – Synthesis and Characterization of Catalytic Materials
14:00 – 14:35	WL-4	Dr. Rajiv Kumar, Tata Chemicals, Pune <i>Generation of Clean and Distributed Energy from Waste Biomass through Fuel Cells</i>
14:35 – 15:10	WL-5	Dr. K. Bhattacharyya, BARC, Mumbai <i>Structural Characterization, Catalysis and Intermediates: A Correlation</i>
15:10 – 15:45	WL-6	Dr. Vivek Polshettiwar, TIFR, Mumbai <i>Nanocatalysis: Fibrous Morphology of Catalyst Support makes a Great Difference in Its Activity & Stability</i>
15:45 – 16:00		Interactive Session
16:00 – 16:15		Tea
16:15 – 18:15		Session III- Catalysis for Pollution Abatement
16:15 – 16:50	WL-7	Dr. Giridhar Madras, IISc, Bengaluru <i>Ionic Catalysts for Energy and Environmental Applications</i>
16:50 – 17:25	WL-8	Dr. S. Rayalu, NEERI, Nagpur <i>Engineered Materials for Carbon Neutral Energy</i>
17:25 – 18:00	WL-9	Dr. Raj Pala, IIT-Kanpur <i>Stable Metallic Nanoparticle-Semiconductor Heterostructures via Click Chemistry for Photocatalytic Dye Degradation</i>
18:00 – 18:15		Interactive Session
20:00 onwards		Dinner

*18:45 - 19:45 Annual General Body Meeting of Society for Materials Chemistry

November 23, 2013 (Day 2)		
09:00 - 11:00		Session IV- Hydrogen Production and Storage
09:00 - 09:35	WL-10	A. Shriniwas Rao, BARC, Mumbai <i>Hydrogen Production</i>
09:35 - 10:10	WL-11	Dr. Sahab Dass, DEI, Agra <i>Solar Energy Induced Water Splitting for Hydrogen Generation: Material Related Issues and Challenges</i>
10:10 - 10:45	WL-12	Dr. Rahul Banerjee, NCL, Pune <i>Porous Crystalline Frameworks with/without Metal: Hydrogen Storage, Carbon Capture and Proton Conduction</i>
10:45 - 11:00		Interactive Session
11:00- 11:15		Tea
11:15- 13:15		Session V- C-C Coupling Reactions in Organic Synthesis
11:15 - 11:50	WL-13	Dr. A. K. Sinha, IIP, Dehradun <i>Carbon-Carbon Bond Forming Reactions for Biomass Utilization Processes</i>
11:50 - 12:25	WL-14	Dr. A. T. Biju, NCL, Pune <i>Transition-Metal-Free Carbon-Carbon and Carbon-Heteroatom Bond-Forming Reactions Using Arynes</i>
12:25 - 13:00	WL-15	Prof. S. D. Samant, ICT, Mumbai <i>Modified clays and hydrotalcites as heterogeneous catalysts for C-C bond formation reactions</i>
13:00 - 13:15		Interactive Session
13:15 - 14:00		Lunch
14:00 - 16:00		Session VI- Catalyst Development for DAE and Industrial Applications
14:00 - 14:35	WL-16	Dr. (Mrs) S. R. Bharadwaj , BARC, Mumbai <i>Catalyst Development for DAE Applications</i>
14:35 - 15:10	WL-17	Dr. (Mrs) Tessy Vincent, BARC, Mumbai <i>Catalyst Based Processes at Back End of Nuclear Fuel Cycle</i>
15:10 - 15:45	WL-18	Dr. G. P. Babu, Monarch Catalysts, Mumbai <i>Hydrogenation of Soybean Oil using Silica Supported Basic Mg/Ni and Zn/Ni Carbonates</i>
15:45 - 16:00		Interactive Session
16:00 - 16:15		Tea

16:15 - 17:35	Session VII- Electro- & Enzyme Catalysis	
16:15 - 16:50	WL-19	Dr. S. Ravichandran, CECRI, Karaikudi <i>Design of Electrodes and Electrolytes for Hydrogen Generation via Electrochemical Method</i>
16:50 - 17:25	WL-20	Prof. A. M. Lali, ICT, Mumbai <i>Industrial Enzyme Catalysis: Engineering Protein and Processes</i>
17:25 - 17:35	Interactive Session	
17:35 - 18:05	Concluding Session	
18:05 - 18:30	High Tea	

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The Ever Changing Faces of Catalysis

B.Viswanathan

National Centre for Catalysis Research, Indian Institute of Technology,

Madras, Chennai

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Introduction

Catalysis is essentially a surface Phenomenon. Most of the industrial and natural processes are only taking place at the surface. In this sense, the basis understanding of these processes has to be different from the general science knowledge that one normally acquires in education by studying the bulk processes. Understanding the surface is essentially more difficult than studying the bulk material, since sustaining the surfaces in the same condition for long duration for examination is difficult. There are a variety of surface species that can be present which are usually termed as the “active centres” [1] and many of these centres have characteristics different from that of the similar species in the bulk like the coordination geometry (both number of surrounding species and also the geometrical distance to the neighbours), ad atoms, and vacancy. A simple representation of a possible defect surface is shown in Fig.1. Processes taking place on the surface have many features which are different from the processes taking place in the bulk. Catalysis

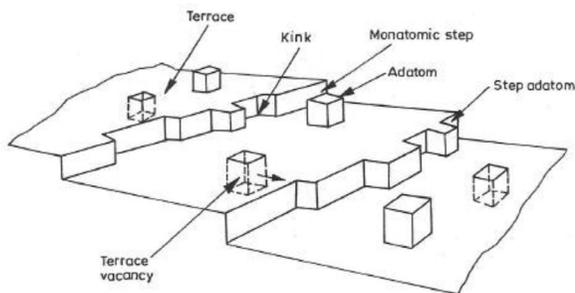


Figure 1: Representative model of a surface with the active species indicated

in its various manifestations accounts for any country's economy and also for the energy needs and to some extent environmental cleanliness. Even though thermal catalysis was predominating till recently, today there are other means of activating and among them both photocatalysis and electrocatalysis seem to be dominating the research efforts.

This situation has arisen due to the fact that reactions like decomposition of water for fuel production, reduction

of carbon dioxide for completing the energy cycle and synthesis of ammonia from reduction of dinitrogen are engaging the attention of catalyst scientists and the efforts have been intensified in the last three to four decades even since Fujishima and Honda [2] demonstrated the possible decomposition of water on TiO_2 surfaces. Historically, heterogeneous catalysis started in identifying the so called active sites, but the situation is complicated since the active sites are not only those that are a priori present on the surface but can also manifest at the call of the reactant molecules (surface reconstruction

or surface segregation) as well normally inactive sites can become active by spill-over phenomenon. Catalyst scientists have spent decades of intense research in identifying these active sites and also to formulate governing principles for the generation of these active sites. Originally, in the absence of experimental tools to directly view these active sites, the identification of these active sites have been attempted in terms of so called structure activity correlation a technique popular in drug manufacture. These correlations can be based on the lattice parameters (geometric factor) or electrical properties (number of charge carriers, density of states and other related parameters) and these correlations have been used to identify the most active surfaces. These correlations mostly identified in the form of volcano shaped and notable contributions have come from the group of Norezskov et al.[3]. They have also proposed three di-mensional correlations diagrams for identifying the optimized catalyst system. These attempts to identify and optimize the active sites led to the development of a host of techniques that could probe surface species at the molecular level. These techniques mostly operate in the mode of employing one of the four particle (electrons, ions, neutrals and photons) or four field (thermal, electrical, magnetic and sonic waves) which induce the emission of particle beams whose analysis in terms of number, chemical identity energy and angular distribution provide the necessary information on the structure, geometry and energy state of the adsorbed state. These techniques have been successfully employed for elucidating the structure and reactivity of adsorbed species which have provided a number of vital information for formulation of active catalyst system[4]. However, these developments have been successful in identifying the possible active sites in a functioning catalyst and the predictive possibility appears to be limited at present.

2. Designing of Catalysts

The designing and fabrication of catalysts with appropriate textural and other surface functions have been important and most challenging till now. The recently developed method, namely Liquid Crystal Templating mechanism has been extensively employed for generating solid surfaces with surface areas of $1000 \text{ m}^2 \text{ g}^{-1}$. This methodology has opened up an avenue for generation of area, surface function modulated solids which can be exploited as active catalyst materials. In general, in this method a surfactant forms a micelle around which the inorganic precursor deposits and subsequently the surfactant is removed to generate architected solid material. In essence the possibilities so far exploited are given in Table 1.

3. Photo-catalysis

According to the glossary of terms used in photo-chemistry [IUPAC 2006 page 384] photo-catalysis is defined as "the change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible or infra red radiation in the presence of a substance the photo-catalyst that absorbs light and is involved in the chemical transformation of the reaction partners." When a semiconductor (or an insulator) is irradiated with light of suitable wavelength corresponding to the energy of the band gap, electrons occupying

Table 1: The possible modes of generating porous solids[5]

	Surfactant	Inorganic precursor	type	Example
Direct pathway (ionic interactions)	Cationic Anionic	Anionic Cationic	S ⁺ I S I ⁺	MCM MCM type materials
Mediated pathways (ionic Interactions)	Cationic Anionic	Cationic Anionic	S ⁺ X I ⁺ S M ⁺ I	Acid Prepared Materials (APM)
Neutral Pathways (Hydrogen bonding)	Neutral Neutral	Neutral Neutral	S ⁰ T ⁰ N ⁰ T ⁰	Hexagonal Mesoporous silica Mesoporous Structural Units
ligand assisted pathways (covalent)	Neutral ,	Neutral ,	S-L ,	Tech Molecular Sieves (TMS) ,

the usually or mostly filled energy levels in the valence band will be transferred to an allowed energy state in the normally empty conduction band thus creating a hole in the valence band. This electron-hole pair is known as exciton. These photo-generated electron-hole pairs promote the so called redox reaction through the adsorbed species on the semiconductor or insulator surface. However, the band gap of the insulators will be usually high and as such generating of such high energy photons will not be comparatively easy and hence insulators are not considered as possible candidates for Photo-catalysis. Generally, metals cannot be employed as photo-catalysts since their occupied and unoccupied energy states are overlapping with respect to energy and hence the recombination of electron-hole pair will be the most preferred process and hence the conversion of photon energy to chemical energy using metals will not be advantageous. However in recent times due to the possibility of making materials in nano state, a new phenomenon is reported which is called plasmonic catalysis caused by the plasmon excitation on metal particles. This aspect will be briefly discussed in a subsequent section.

It is generally considered that the energy position of the top of the valence band of a semiconductor is a measure of its oxidizing power and the bottom of the conduction band is a measure of its reducing capacity. It is therefore necessary one has to know with certain level of certainty the energy positions of the top of the valence band and bottom of the conduction band so that the reactions that these excitons can promote can be understood. Photo-catalytic destruction of organic pollutants in water is based on photo-chemical process involving semi-conductors. When a semiconductor is irradiated with UV (usually but it can be any other radiation as well) light of wavelength appropriate for excitation from valence band to the conduction band of the chosen semiconductor an exciton is created. The photo-chemical oxidation of the organic substrate normally proceeds by the adsorption of the substrate on the surface of the semiconductor

Table 2: comparison of electro-catalytic activities of various electrodes for methanol oxidation

catalyst	EAS (m ² .g ⁻¹)	Onset potential(V)	I _f /I _b	mass activity (mA.g ⁻¹ Pt)	specific activity mA cm ⁻² Pt
Pt/C	23.3	0.41	0.80	191	0.81
Pt/STA-C	33.0	0.31	1.11	37	1.12
Pt-Ru/C	17.2	0.30	0.91	204	1.18
Pt-Ru/STA-C	25.6	0.24	1.05	53	1.96
Pt-Ru(JM)	22.5	0.25	0.95	271	1.20

EAS = Electrochemical Active area; STA = silicotungstic Acid; I_b and I_f are current in backward and forward sweep of voltage.

with transfer of electrons with the hole generated. However other possible oxidation processes can also take place with radicals generated (OH radical if the solvent is water) at the surface of the semiconductor surface. Thus a variety of surface reactions are possible and photocatalysis can thus be in future employed for the generation or production of chemicals as well.

4. Electrocatalysis

Electro-catalysis and bio-catalysis have some common features. Of late electro-catalysis has assumed importance especially for the reduction of carbon dioxide [6]. Keggin type poly oxometallates have been already employed for promoting chemical reactions either in homogeneous or pseudo-liquid phase conditions. Their electro-chemical activity is evaluated for Oxygen Reduction Reaction (relevant for the development of fuel cells and other electrochemical energy conversion devices).

The comparison of electro-catalytic activities of various electrode materials towards methanol oxidation(relevant for Direct Methanol Fuel Cells, DMFC)is given in Table 2.

5. Challenges Still in Catalysis

There are still some challenging aspects to be unravelled in catalysis. Some of them have been already initiated and some of them have to be explored. Let us list some of them at least.

1. Methanol production from methane;
2. syngas production by the oxidation of methane (natural gas);
3. ethylene production from methane;
4. methane to higher hydrocarbons;
5. ethanol from dimethyl ether;

6. Hydrogen peroxide production from molecular hydrogen and oxygen;
7. Nitric acid synthesis from nitrogen water and molecular oxygen.

Some of the reactions that have been already attempted but satisfactory activity levels have not yet been reached. These include (1) asymmetric synthesis; (2) water splitting for fuel production, (3) Carbon dioxide reduction to fuels or to generate useful chemicals and (4) photochemical reforming and (5) photo-catalytic removal of pollutants. It must be remarked that the listing is only indicative and one should not consider the listing to be comprehensive. Efforts are on in each of these to develop appropriate catalyst for making the process economically viable but still there is no word that had been said on any of these processes.

6. Role of Catalysis in Sustainable Development

Sustainable development is generally defined as "Development, which meets the needs of the present without compromising the ability of future generations to meet their own needs". The implication is that human development should be such as to "enable all people to meet their basic needs and improve their quality of life, while ensuring that the natural systems, resources and diversity upon which they depend are maintained and enhanced both for their benefit and for that of future". A major impediment in achieving sustainable development is the environmental damage being caused by rapid population growth and industrialization. It is now believed that catalysis can play a major role in environment protection (if not in reversing the damage already done) and enable sustainable development by a number of ways. Basically, catalysis can help in (i) primary pollution control through non-polluting processes that are atom efficient and produce negligible waste, (ii) secondary pollution control through end-of-pipe solutions, (iii) use of economically attractive alternate feedstocks, (iv) use of renewable feedstocks, (v) producing bio-degradable products, (vi) development of energy efficient processes and (vii) routes to alternate energy. The world catalyst business today is about US dollars

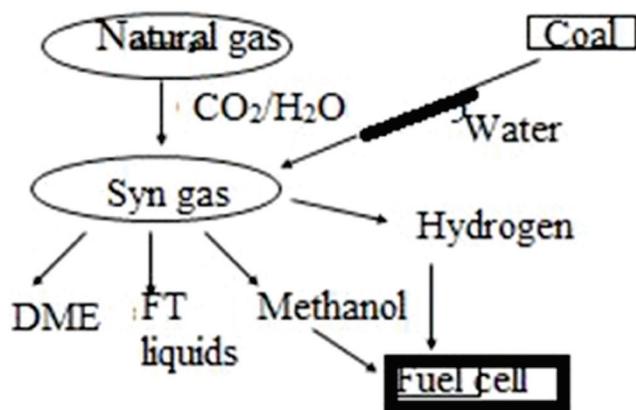


Figure 2: natural gas to syngas and subsequent transformation to fuels and chemicals

11 billion, of which nearly 30 % is in the area of environment catalysts (auto-exhaust, de-NO_x etc). The rest of the business is shared nearly equally between refining, chemical and polymer industries. As stated earlier, one of the challenges lies in the conversion of natural gas to syngas and producing fuel from syngas through a variety of ways as shown in Fig.2. The most preferred source of alternate fuels is biomass, such as cellulosic materials like bagasse, wood chips, straw, and vegetable oils. Effective use of these

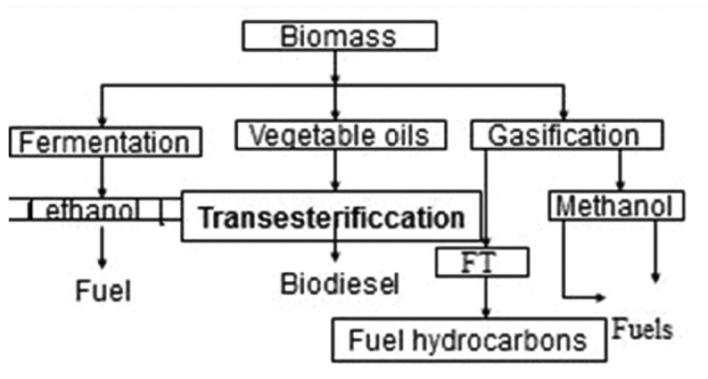


Figure 3: conversion of biodiesel for fuels

production of chemicals (bulk or ne). The route adopted in the catalytic route may be considered to be a green process as compared to other chemical routes. Hence catalysis can play a vital role in a sustainable society.

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materials and discontinuing the use of fossil fuels should decrease the overall CO₂ load in the atmosphere as the production of these raw materials will help in depleting atmospheric CO₂. These raw materials can be converted into fuels and chemicals as shown in Fig. 3.

7. Summary

Catalysis plays a major role either in the conversion to fuels or for the



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Fundamentals of Heterogeneous Catalysis

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Preamble

The subject of catalysis, encompassing reaction mechanism, surface characteristics, kinetics and reactor design, has undergone rapid advancements in the last few decades. The availability of a host of analytical tools has enabled us in understanding the fundamental aspects of catalysis at molecular level. On the other hand, the technological advancements achieved in this area have revolutionized chemical industry, in particular the petroleum, petrochemical and fine chemical industries. As per an estimate, around 27% of GNP and ~90 % of chemical industry world-wide uses the products obtained by involving a catalyst at some stage or other. The recent progresses in the areas of nanoscience and nanotechnology have helped in developing more efficient catalytic materials for application in new energy resources and green chemical processes. With the stringent demand for clean environment, the catalytic devices are now playing a vital role in automotive exhaust control and remediation of environmental pollution.

In this talk, my endeavor will be to introduce the subject of catalysis, heterogeneous catalysis in particular, to the post graduate students of chemistry. Starting with thermodynamic concepts of catalytic processes, my talk will deal with the properties of catalytic surfaces and the molecular transformations involved in a chemical reaction. The details about active surface sites responsible for a catalytic process and the role of catalyst morphology in controlling the overall rate of a chemical reaction will be discussed for some general cases of metal, metal oxide, and supported metal catalysts. Various spectroscopy and microscopy techniques employed for characterization of a catalyst and for *in situ* identification of transient surface species will be deliberated.

Basic Principles

In general, a catalyst can be defined as a substance that accelerates the attainment of the chemical equilibrium between reactants and products without influencing the thermodynamic equilibrium of the reaction. In contrast to the homogeneous catalysis where the reactant and products exist in the same physical state of the reactants, the heterogeneous catalysts are normally solids while the reactants may exist in a gaseous or a liquid phase. In terms of physico-chemical properties, a heterogeneous catalyst may be a metal (normally a group VIII metal or a metal alloy), a semiconductor (metal oxides, such as TiO_2 , V_2O_5 , Mn_2O_3) or an insulator (Al_2O_3 , SiO_2 , zeolites), depending on the nature of the catalyzed reaction. The supported metal catalysts, comprising of nanometer size

metal particle dispersed over a metal oxide surface, in fact find maximum applications in chemical industry.

The catalytic function of a material is due to its ability to chemisorb one or more of the reactant molecules at its surface and to break some of the strong chemical bonds (for example, C-H, C-C, H-H, C=O, N=N etc.). Chemical rearrangement, followed by release of product molecules regenerates the active sites for new reactions. The nature of the bonding between a catalyst and adsorbate molecules and the transient species thus formed are primarily responsible for the activity and selectivity of a metal catalyst. Therefore, the main function of a catalyst is to provide an alternative reaction path that proceeds via lower activation energy requirement, thus helping in accomplishing a reaction at a much lower temperature. The electronic structure, that decides the availability of d- electrons for a chemisorptions process (for instance, % d-character), is one of the important factors that decide the efficacy of a metal to serve as a catalyst and the nature of the transient species formed during a catalyzed reaction. A direct relationship between % d-character of a group-VIII metal and the heat of adsorption has been demonstrated for certain adsorbates.

The surface active sites that help in achieving this goal depend on various factors, such as the chemical composition of the catalyst, particle size and surface area, surface species (such as hydroxyl groups), and the defect states in the bulk or at the surface of a catalyst. For metal and supported metal catalysts, surface structure, crystallographic orientation, assembly of atoms, and surface defects, such as vacancies, dislocations, kinks etc., are known to play an important role. In the case of metal oxides, Lewis and Bronsted acid-base sites and surface oxygen ions serve as active reaction sites.

The product selectivity, i.e. the fraction of the reactants converted into desired products, is an important aspect of heterogeneous catalysis. For instance, the mixture of $\text{CO} + \text{H}_2$ can convert to a variety of the products, viz. alkanes, alkenes, alcohols and aldehydes etc., depending on the catalyst employed and reaction conditions. Moreover, the kinetics of a chemical reaction is of great industrial importance, and is governed by one of the slower steps involved in the catalyzed process, viz: i) diffusion of reactants from the fluid to the surface and their transport through the bulk, ii) adsorption/binding of the reactants at the active sites, iii) formation of transient species and reaction products, iv) desorption of reaction products from the active sites, and v) diffusion of products through the catalyst bulk. Therefore, several physico-chemical characteristics of a catalyst, i.e, the surface area, concentration and morphology of dispersed metal particles, pore structure, chemical reducibility, and acid/base character of support material are some of the prominent factors that collectively govern the progress of a catalytic reaction [1-3].

Supported Metal Catalysts: Role of particle morphology and surface transient species

Recent researches in my laboratory were focused on the role played by textural, morphological and interfacial properties in the catalytic activity of supported metal

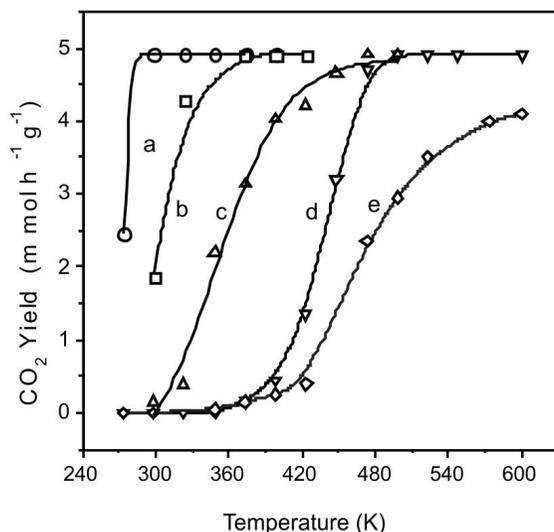


Fig.1 Temperature-dependent CO oxidation activity of different catalysts: a) Au /Fe₂O₃ (670 K), b) metal-free Fe₂O₃; c) polycrystalline gold powder; d) Au/Fe₂O₃ (870 K); e) Au/Fe₂O₃ (970 K). Gold content is 5 at% and the numbers in parentheses represent calcination temperature.

catalysts using adsorption/oxidation of CO and NO as the probe reactions [4-10]. Citing from our previous studies on the nanosize gold particles supported over Fe₂O₃ [4-6], Fig.1 displays the affect of sample calcination temperature on the percentage conversion of CO to CO₂ when CO + O₂ + He (2:1:17) gas mixture was passed over Au (5 at %)/Fe₂O₃ at a flow rate of 1.2 lh⁻¹g⁻¹. Curve (a) in this figure shows representative activity results for a sample calcined at 670 K. When Au/Fe₂O₃ was calcined at a higher temperature, the catalyst activity decreased considerably (curves d, e). Also, a poor activity was observed in for Au-free Fe₂O₃ (curve b) and also for a polycrystalline gold powder sample (curve c). The decrease in catalytic activity on high temperature calcination (Fig. 1, curves a, d, e) is attributed to an increase in the size of gold particles

and also the Fe₂O₃ morphology. We have conducted detailed thermochemical and *in situ* infrared spectroscopy studies on CO adsorption/oxidation over these catalyst surfaces to demonstrate how the nature of the transient species and the heat of CO and CO + O₂ adsorption may depend on the morphology and the Au/Fe₂O₃ interfacial properties [4, 5].

Figure 2 exhibits the affect of calcination temperature on the infrared bands developed on Au/Fe₂O₃ and Fe₂O₃ samples after exposure to 100 Torr CO at 300 K. From the intensity of C-O stretching band appearing at ~2170 cm⁻¹ in Fig. 2 (width

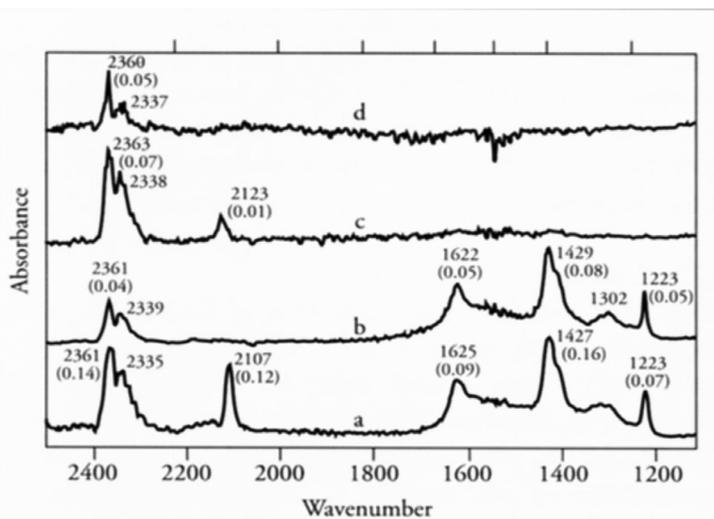


Fig. 2 Infrared bands developed on Au (5 at %)/Fe₂O₃ (curve a) and Fe₂O₃ (curve b) catalysts after exposure to 100 Torr CO at 300 K. Curves (c) and (d) show corresponding IR spectra for Au/Fe₂O₃ samples calcined at 820 and 870 K, respectively. (Numbers in parenthesis represent the absorbance value)

~12.6 cm⁻¹ and no side bands), it is apparent that the CO adsorption is promoted by highly dispersed gold particles (Fig. 2a, b). Moreover, the chemisorptions of CO is controlled by Au particle size and sample morphology (Figs. 2c, d). Similarly the formation of oxygenated species (1100- 1700 cm⁻¹ region bands, arising from carbonate and bicarbonate species) is suppressed considerably on calcination of a sample at high temperatures (Fig. 2, curves c, d), confirming again an important role played by particle morphology. Furthermore, our studies have demonstrated that the binding state of adsorbed molecules and the overall catalytic properties of Au/Fe₂O₃ are governed not only by the morphology but also by the nature of the metal/support interfacial contacts. The effect of the geometry of surface metal clusters in the catalytic properties of metal/oxide systems will be discussed.

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Fundamental and Mechanistic Aspects in Catalysis – Ertl's Contributions

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Introduction

Nobel Laureate Gerhard Ertl was awarded the Nobel Prize on 2007 for having laid the methodological foundations for an entire field of research on surface science and heterogeneous catalysis. The great reliability of Ertl's results is due to the meticulous precision in his work combined with an outstanding capacity to refine problems. He has painstakingly and systematically searched for the best experimental techniques to investigate each separate question. Ertl's contributions are particularly known in the area of ammonia synthesis on iron surfaces as well as catalytic converter reactions on noble metal surfaces, especially carbon monoxide (CO) oxidation on Pt-surfaces. Highlights of his contributions are presented in this extended abstract as well as to be presented in my presentation.

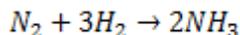
Catalysis is a phenomenon that occurs exclusively on catalyst surfaces. It is neither straightforward nor cheap to investigate how molecules and atoms behave on solid surfaces, in heterogeneous catalysis. So why bother? Simply because, surface reactions play such an important role in both the chemical industry and natural systems. Knowledge of surface chemistry can help explain such diverse processes as why iron rusts, how artificial fertilizers are produced, how the catalyst in an automobile's exhaust pipe works and why the ozone layer is deteriorating. Knowledge about chemical reactions on surfaces will also help us produce renewable fuels more efficiently. In short, understanding the fundamental aspects of catalysis is important to produce better and more active catalysts for various reactions. Ertl's contributions in the area of catalysis of ammonia synthesis and CO oxidation are briefly described.

Catalysis of Ammonia Synthesis – Fundamental Aspects

Heterogeneous catalysis was also the central process behind the award of the Nobel Prize to Fritz Haber (on 1918) "for the synthesis of ammonia from its elements". Even though technical improvements have been made, the same basic concept is used in the modern version of the process. In the Haber-Bosch process, N_2 reacts with H_2 to form NH_3 .

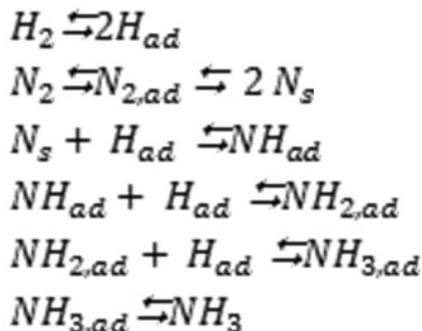
This is the first and most challenging step in the production of artificial fertilizer, such as urea. It is necessary to use a catalyst for this reaction to take place, and this is where surface chemistry plays a role. The catalyst used in the Haber-Bosch process is finely dispersed iron: the reaction takes place using the surface of the grains of iron as support. Nitrogen and hydrogen both attach to the iron surface: in this manner they react more easily with one another. One of the crucial questions which Ertl addressed is which step in the reaction is the slowest. In order to improve the process as a whole it is the slowest step one needs to speed up.

Even though industrial ammonia production was in practice from the First World War days, no one was able to prove the mechanism of ammonia production. This long-standing problem that Ertl attacked concerned the molecular mechanism of the catalytic reaction in the Haber-Bosch process. In the net reaction nitrogen molecules react with hydrogen molecules to form ammonia. To obtain a suitable thermodynamic driving force for the reaction, the industrial process is designed to occur with the reactants at high pressure. The commonly used catalyst consists of iron particles with added potassium



hydroxide on a support of alumina and silica. Due to its economic importance this reaction had been the subject of numerous investigations by the mid-1970s when Ertl initiated his studies. Although it was understood from kinetic studies that the rate-limiting step of the process was the chemisorption of nitrogen, the underlying mechanism was unclear, and even the nature of the reactive species. Alternative reaction mechanisms had been suggested, based on either atomic or molecular nitrogen, and it was clear that it was not possible to discriminate between these on the basis of kinetic data alone. Equipped with the tools of surface science Ertl had the opportunity to investigate aspects of the reaction in model systems. However, these would seemingly be very far from the realities of the Haber-Bosch process.

It was far from obvious that the studies of model surfaces had a clear applicability to the molecular events in the industrial Haber-Bosch process. To demonstrate this Ertl analyzed, using AES (Auger Electron Spectroscopy), the surface composition of a commercial catalyst. They found that at ambient conditions the surface had a complex composition but at the reducing conditions of the process iron and potassium dominate at the surface. Through a characterization of adsorption energies Ertl could also conclude that it is only the adsorbed atomic nitrogen that remains on the surface when the reaction chamber is emptied after a catalytic cycle at high pressures. By using AES to analyze how the surface nitrogen coverage varied with hydrogen pressure during the reaction he was able to demonstrate that the high-pressure data were consistent with those found for model measurements at low pressures. Furthermore, there was a consistency between the observed rates of the elementary processes and the macroscopically measured kinetics. These studies, bridging what is called the pressure gap, were crucial for establishing acceptance of the "surface science" approach to catalysis among the community struggling with the realities of industrial processes involving heterogeneous catalysis.



Having identified the dissociated nitrogen atoms, determined that the formation of this species was slow and demonstrated that the model systems were relevant for the conditions of the Haber-Bosch process it was straightforward to establish the reaction mechanism:

This reaction mechanism was one of those suggested previously, but Ertl did not only show to its correctness but he was also able to provide details of the energetics of the individual steps. To obtain information on the later steps in the reaction Ertl chose to start from ammonia and monitor the steps in the “backward” direction, which is favored at low pressures. Ammonia adsorbs on iron with an energy gain of about 75kJ/mol which is small enough to ensure complete desorption at typical process (ammonia synthesis) conditions (temperature $\geq 400^\circ\text{C}$). According to the reaction scheme the adsorbed ammonia can dissociate on the surface. The presence of the state NH_2 could not be quantified by spectroscopic methods, but instead by co-adsorbing NH_3 and D_2 Ertl could infer dissociation and recombination rates for the reaction

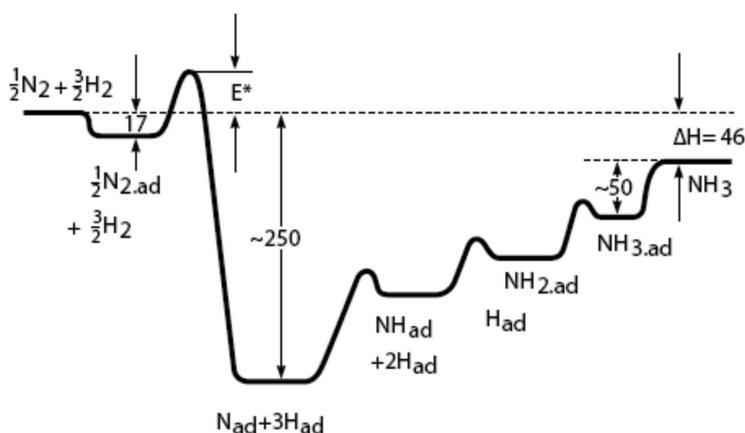
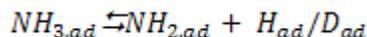


Figure 1: An energy diagram showing the progression of the reaction from the reactants N_2 and H_2 to the product NH_3 . Energies are given in units of kJ/mol.

NH_2 , on the other hand, occurs in large enough quantities to be observable using a number of different methods like UPS (ultraviolet photoelectron spectroscopy), SIMS (secondary ion mass spectrometry), HREELS (High resolution electron energy loss spectroscopy). Thus the reaction mechanism as shown above could be formulated also in energy diagram as shown below:

Although Figure 1 illustrates the reaction in quite some detail, one essential feature of the industrial process remained to be explained. Empirically it had been found that the presence of potassium ions in the catalyst improved the rate of the catalytic cycle. Ertl had also found that the potassium remained on the surface of the catalyst under process conditions. So why does potassium act as a promoter of the reaction? Since the cleaving of the nitrogen molecule is the rate-limiting step in the process, the potassium has to affect this step in order to enhance the rate. It was found that in the presence of potassium the nitrogen molecules adsorbed more readily on the surface and that the adsorption energy increased by 10 to 15 kJ/mol. The effect was attributed to the fact that potassium would donate electrons to neighbouring iron atoms.

Ertl's investigations of the reactions in the Haber-Bosch process serve as a model of how sophisticated experimental methods can be used to study a phenomenon of utmost practical relevance. He started by identifying the crucial features of the reaction in the industrial context. He then demonstrated how, and in what way, studies of model systems were relevant for the understanding of the more complex practical situation. He then isolated a number of elementary steps that were targets of focused studies. These steps were characterized both from a structural, an energetic and a kinetic point of view using the state-of-the-art methodology. This involves the use of many different methods with highly sophisticated equipment. Ertl not only clarified the molecular events of the Haber-Bosch process, but he also demonstrated what it takes to unravel mechanisms of a catalytic process in general. This has had a lasting influence on the field of heterogeneous catalysis.

Catalysis of CO Oxidation on Noble Metal Surfaces- Fundamental and Mechanistic Aspects

In the Haber-Bosch process it turned out to be possible to relate the observed macroscopic kinetics of ammonia production with the kinetics of the individual steps of the reaction as observed under idealized conditions. For some heterogeneously catalyzed reactions it was found at an early stage that the macroscopic kinetics indicated an oscillatory reaction rate, i.e. rate changes even when other reaction conditions (such as pressure, temperature, reactants composition) are constant. This was a clear sign of non-linear dynamic behaviour. Such phenomena have been much studied for chemical reactions in bulk and in 1977, I. Prigogine was awarded the Nobel Prize "for his contributions to non-equilibrium thermodynamics, particularly the theory of dissipative structures". Challenged by observations of oscillatory rates Ertl chose to make an in-depth study of another "classical" catalytic reaction; the oxidation of carbon monoxide by oxygen on platinum. The crucial questions were: What is the molecular mechanism behind the non-linear kinetics? What other phenomena can be inferred in addition to the kinetic oscillations? It turned out that the system can be used to illustrate a range of phenomena typical of systems with non-linear kinetics.

Through a series of imaginative studies, Ertl could establish the microscopic causes of the observed non-linear behaviour. Again, Ertl demonstrated how the full spectrum of

methods of surface physics and surface chemistry could be combined to yield comprehensive understanding of important and complex catalytic processes. High pressure *in-situ* methods include work function measurements that can be used to study changes in adsorbate coverage, FTIR that gives information on adsorbate-surface interaction and X-ray diffraction that yields information on the state of the catalyst itself. These methods are generally much less precise than high vacuum techniques, but they yield invaluable corroborating information to help close the pressure gap. In the study of sensitive oscillatory reactions on surfaces, the energy input must be controlled and minimized, and this is a further constraint. The use of AES that proved such a powerful tool in the studies of the Haber-Bosch process is, for example, not feasible. Instead, low energy methods must be employed, such as LEED that directly monitors structural changes and PEEM (photoelectron emission microscopy) that monitors the local work function with high spatial resolution.

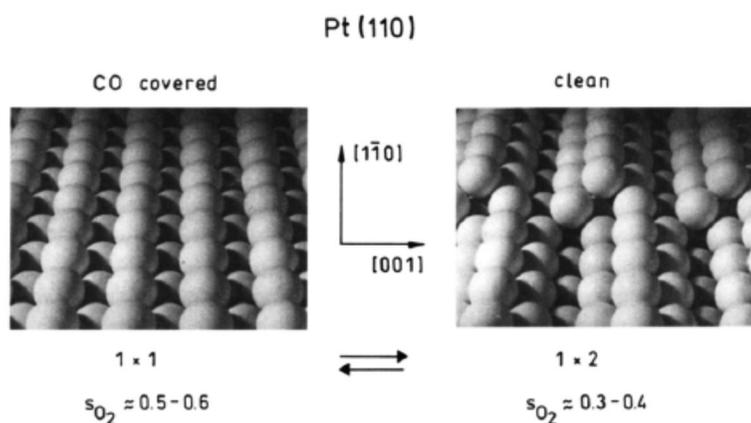


Figure 2: Changes observed in oxygen sticking coefficient (or adsorption capacity) on surfaces on CO-adsorbed and reconstructed Pt(110) surfaces.

For the oxidation of CO on Pt, there are several mechanisms operating but the most spectacular effects were caused by a surface reconstruction. For the bare metal surfaces with (100) and (110) facets, there is a reconstruction to reduce the surface strain. However, CO adsorbs more readily on the unmodified surface and at certain coverage the difference in adsorption energy is sufficient to cause a reversal of the surface reconstruction. Now oxygen is also more chemisorbed on the reverted surfaces. Then the rate of the catalytic process increases leading to a lower coverage and a possibility for a surface reconstruction. This can in addition to an oscillatory kinetics also lead to a spatial organization on the surface with domains rich in CO and O_2 , respectively (Figure 3). Illustrations of variety of adsorption patterns observed by PEEM are shown in the illustrations below. Please refer ref. 1 for detailed discussion on the above aspects.

Through these studies Ertl has demonstrated that his methodology is applicable not only to systems, where the kinetics are dominated by a single rate-limiting step as is the case in the Haber-Bosch process, but also to systems where non-linear dynamics prevail. His methodology sets a standard for how chemical processes on surfaces can be studied and elucidated.

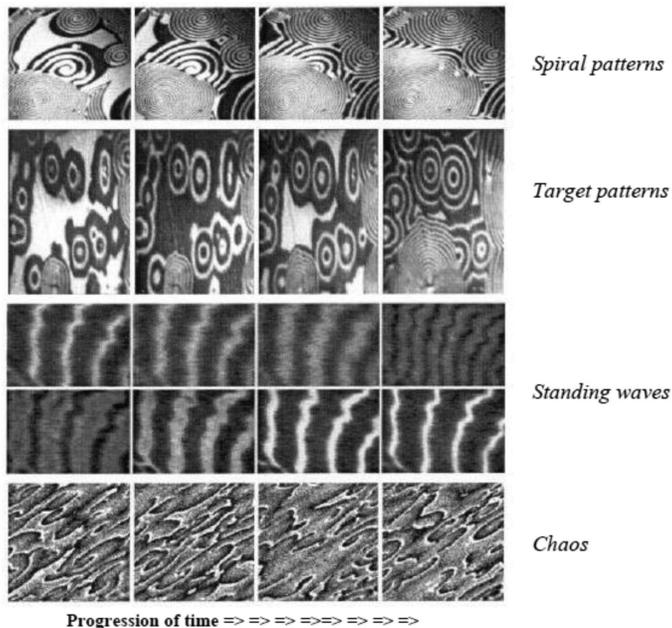


Figure 3: Platinum surface imaged by photo electron emission microscopy. Dark areas are rich in CO while light areas are O_2 rich. Note the oscillatory behaviour of the domain extensions. Time scale $\sim 10s$, length scale $\sim 0.1mm$.

Conclusion

Ertl has developed a general methodology that can be applied to the important problems in molecular surface science. He has applied the methodology to some of the most central previously unanswered questions concerning molecules on surfaces. The investigations have been carried out with the greatest elegance in the experimental approach. His work is characterized by the ambition to always use the method best suited to solve the problem at hand. Ertl is never satisfied with an isolated interesting observation. Instead the studies are brought to their logical conclusions. Through his accurate studies he has provided a firm basis for our thinking about molecular processes at surfaces.

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Awards and Recognitions: 1. Elected fellow of the Indian Academy of Sciences, Bangalore. 2. CNRS Visiting Professor at UCCS Univ. Sci. Technol. @ Lille 1, Lille, France on 2010. 3. Awarded CRSI bronze medal in 11th CRSI-NSC on Feb. 2009 at NCL, Pune. 4. Recipient of the Scientist of the year (2006) Award at National Chemical Lab., Pune. 5. Recipient of the AvH Research Fellowship from AvH Foundation, Germany on 1995. 6. Member, Editorial Board, Journal of Chemical Sciences (From Jan 2012) Research Guidance: Eight students completed PhD, and ten students are currently working towards Ph.D. at different stages.

Generation of Clean and Distributed Energy from Waste Biomass through Fuel Cells

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Abstract

The need for clean and sustainable energy cannot be overemphasized. The solar electromagnetic radiations are the main source of energy whether harnessed directly (PV Cells) or indirectly (via photosynthesis). Although significant improvements have been recently made in the direct use of solar light – a highly desirable option – via silicon based PV or organic solar cells, the efficiency of PV cells needs further efforts to increase the efficiency of, both silicon based or organic PV cells to be of practical use for both large scale as well as distributed power generation. However, the present work deals with harnessing the waste biomass based stored chemical energy through an integrated system of bio based conversion of organic waste to methane (biogas) and PEM fuel cells for distributed localized power generation from locally produced waste like municipal solid waste, animal waste and agro-waste. This aims at solving a major issue of waste generation and power requirements. This presentation shows some recent developments being made in the area of high temperature PEM fuel cells (around 160 °C) to avoid any CO poisoning so that biogas can be used as fuel in a cost effective manner. New organo-inorganic composites for both as electrode catalysts cum proton conductor and membrane where Nafion-free MEA system is developed.

Increasing Energy requirements

World's energy need is expected to increase over 40% by 2030 *cf.* present day. The rapidly exhausting natural fuel reserves have compelled a colossal amount of research to develop technologies for alternate and sustainable energy. Renewable biofuels through green chemical processes have gained considerable attention in the last few decades. Alternate energy through photovoltaics and fuel cells has also gained momentum in the recent past and demands significant improvements in efficiency for viable commercialization.

The technologies to produce electricity from any carbon, hydrocarbon and biomass based sources generates significant amount of CO₂ (Table 1). In India, the majority of the power is generated *via* coal based thermal power plants, where the energy conversion efficiency is ca. 43%. It also produces ca. 0.94 kg of CO₂ per kWh of electricity generated. Considering these factors, elemental hydrogen could be the best source of clean energy.

However, the availability of pure H₂ and infrastructure of H₂ storage is a challenging issue. The next best source of clean energy could be methanol which can produce H₂ through reformer. Among other sources of H₂, bagasse has lowest energy density, since large amount of H₂ combines with the oxygen contained in biomass. Moreover, biomass also produces very high quantities of CO₂ compared to other fuels.

Table 1. Energy density, CO₂ produced and efficiency of available fuel sources

Fuel	Energy Density (kWh/kg)	CO ₂ (kg/kWh)	Efficiency (%)
Coal	9.1	0.94	43
Bagasse	2.2 – 2.5	0.88	43
Methane	15.5	0.35	50
		0.21	85 (incl. co-gen)
Methanol	6.1	0.26	25
Hydrogen	32.9	0.0	

Waste to Energy:

In fact, our nature does not of the concept of any waste generation and disposal, as it is not sustainable in principle itself. Hence, the “use-and-resuse” concept is sustainable eco-system, where the by-product of one activity is the useful raw material for other activity. Humans, on the other hand, have not developed the similar sustainable model and therefore we are facing the climate related issues even threatening our civilization at large. In the following sections some details of our most common waste generation and disposal issue are highlighted. Further some suggestions are also provided to find a suitable solution through using common waste to generate energy and power.

- What is waste?
 - Unused / underused resource.
 - Nature does not have the concept of waste.
 - Waste generation is not sustainable.
- Type of Waste generated from modern human activity:
 - Municipal Solid Waste
 - Kitchen, Mandi, Slaughter House, wet waste
 - Forest / Farm residue and leafy / woody waste.
 - Man made non-biodegradable Polymers /Plastics.
 - Rubber based waste (used tyres , tubes etc)

MSW: Land fills vs. Energy resource

Land Fill:

- Big environmental and climate change problem.
- No more landfill sites available easily,
- Huge waste of precious land resource.
- Increasing cost for disposal
- Land fill is basically Composting
- Foul smell

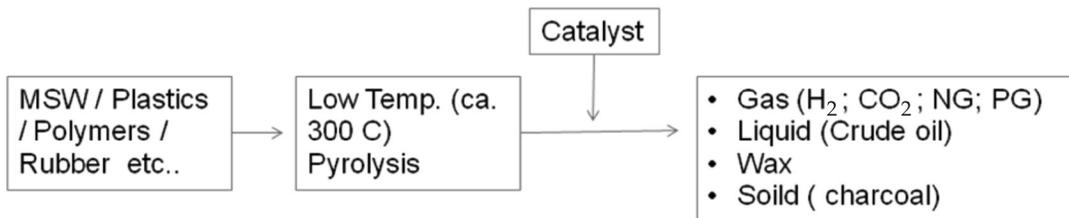
Methane is released in atmosphere (23 times more potent GHE than CO₂ (23 Kg CO₂ = 1 Kg Methane as GHG)

MSW: Generation and as Energy source

- MSW Generation
 - In India: 120 Million Tons/Year
 - In US: 230 Mn Tons /Year
 - **Indian metros / big cities: Daily 0.4-0.5 Kg per person**
 - **Indian Rural / small towns: Daily 0.2 Kg per person day**
- As Energy source
 - Low temperature pyrolysis and catalytic conversion (Poly Crack) to Gas, Water (+small amount of oil) and charcoal: More useful for plastics
 - Bio-digestion to Biogas, water and solid bio-manure
 - **More useful for wet biomass/MSW**

Low temp Pyrolysis / Poly crack

Solid Municipal Waste disposal problem will also have solution.



Status: Early commercial / Pilot Scale

Waste (MSW/WET) to BIO-GAS

- Multi bugs system for efficient wet bio waste with no low residence time and high yields without odour.
- Opportunities for localized, Distributed BIOGAS Supply for Big, Medium & Small Cities and Rural India.

- Solid Municipal Waste and organic waste disposal problem will also have solution.
- Bio-gas and Bio-manure as valuable products.
- Pure CO₂ for beverages are also be produced.

Technologies are available and now being used on large scale also economically.

Biogas to power generation through Fuel Cells.

Fuel cells offer a significant advantage over traditional combustion-based thermal energy conversion. Their efficiency of electricity generation falls in the range of 35–55%; at the same time produce relatively low levels of CO₂. Fuel cells can be constructed in a wide range of power ratings, from a few milliwatts to several megawatts. Depending on the outcome, they can be used in several sectors, from miniaturized portable power through transport to full size power stations. They have significant advantages over batteries with respect to lower weight and instantaneous refueling.

Among the various kinds of fuel cells, solid oxide fuel cell (SOFC) using methane as fuel via reformer, alkaline fuel cell (AFC), molten carbonate fuel cell (MCFC), phosphoric acid fuel cell (PAFC), proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) are being used extensively. Further, the stationary fuel cell market is crowded by DMFC and PEMFC manufacturers due to high power densities unseen in other types of fuel cells. In fact, the storage density of energy conversion of different batteries is several times lower than that of PEMFC and DMFC.

Following section will concentrate on the PEMFC / DMFC and the major issues faced by these. Further an attempt will be made to provide solution to address these issues.

PEMFC and DMFC are best suited for stationary applications as well as transportation and mobile sectors. Commercial exploitation of PEMFC should preferably satisfy the power density of 500 mW/cm² for a platinum loading of <0.5 mg/cm² with a life time of 40,000 hrs. The main components of PEMFC are membrane electrode assembly (MEA) and hardware. MEA is the heart of PEMFC; it consists of a proton conducting electrolyte (membrane) and two electrodes (anode and cathode catalyst layers). These catalyst layers consist of (i) carbon as electron conductor, (ii) Pt catalyst to convert hydrogen into proton (H⁺), and (iii) proton conducting membrane, such as Nafion.

The factors which bar the commercial use of current PEMFC technology are, (i) the combination of two expensive components, namely Pt metal and Nafion, (ii) the availability of CO-free H₂, (iii) a proton conducting membrane which can withstand higher temperatures (>120 °C) under operating condition, even if the feed is contaminated with smaller amounts of CO (>10 ppm), and (iv) flooding of cathode side with water. The CO poisoning of Pt anode is partially taken care of by tailoring of catalyst surfaces at nanoscale by using alloy / bimetallic nanoparticles (such as Pt-Ru) for preferential oxidation (PROX) of CO. Researchers have also developed inorganic-organic hybrid

reinforced membranes having desired proton conductivity and capable of performing optimally up to 120 °C.¹

The membrane requirements are high in the case of DMFC because the fuel cell assembly would be flooded with methanol at the cathode side because of high methanol crossover, which can potentially damage the cell components. Attempts have been made to replace the expensive Pt metal component partially with other metals like Fe, Co, Ni and Cr, which led to prominent new cathode catalyst systems. In addition, platinum free Ru chalcogenides (Ru_xSe_y) are extensively studied as methanol tolerant oxygen reduction reaction (ORR) catalysts.² However, to make DMFC and PEM FC commercial successes, the catalyst and membrane development requires further fine tuning.

In our effort to develop a cheaper fuel cell technology at Tata Chemicals Innovation Center, we have prepared a “2-in-1” electrode catalyst system for cost effective production of MEA.³ The catalyst consists of Pt nanoparticles functionalized with surfactants containing sulfonic acid head groups, e.g., 3-mercaptopropene-1-sulfonic acid (MPSA), further supported on Vulcan XC72 carbon. This single nanocomposite possesses all three characters of an electrode catalyst, viz. H^+ generation by Pt NP, proton conduction by sulfonic acid head group, and electron conduction by carbon support. In this report, we will demonstrate that this catalyst shows better performance than existing (commercial) electrode catalyst system and also has better stability.

Preparation of electrode catalysts

Sulfonic acid ligand coated Pt NPs were synthesized using K_2PtCl_6 , MPSA and NaBH_4 following a patented method.⁴ In a typical synthesis, 100 mg of K_2PtCl_6 (0.2 mmol) and 36 mg of MPSA- Na^+ salt (0.2 mmol) were dissolved in 40 mL of deionized water. The solution was cooled to 0 °C. Thereafter, a solution of 75.6 mg of NaBH_4 (2 mmol) in 20 mL of H_2O was added to it dropwise under ice cold conditions. To disperse the Pt NPs on carbon support (40 wt% Pt/C), the colloidal NP solution was treated with Vulcan XC72 at 0 °C for 1 h. The reaction mixture was filtered, washed with copious amount of water, and dried under vacuum. The terminal SO_3^- head groups were protonated by treatment with 10 mL of 1 M H_2SO_4 (per 100 mg of the solid catalyst) for 4 h at room temperature.

Catalyst Characterization and performance evaluation

The XRD patterns of Pt-MPSA nanocatalysts show characteristic peaks of Pt nanoparticles, indexed as (001), (111), (200), (220) and (222), respectively. The average diameter of the Pt nanoparticles were calculated from the width of the Pt 111 peak at $2\theta = 40^\circ$. The representative TGA scan for a Pt-MPSA/C sample revealed a two stage weight loss; the first at 200–300 °C, and the second at 300–450 °C. The approximate amount of organics was 12–15 wt% for all the samples.

The representative S 2p core level spectrum shows two components at binding energies 163 and 168 eV, which can be attributed to two different oxidation states of sulfur (-2 and +5, respectively) present in the sample.⁴ As expected, the Pt 4f spectrum has two components, namely $4f_{5/2}$ and $4f_{7/2}$ at binding energies 74 and 71 eV, respectively. The representative TEM images (Figure 1) of the Pt-MPSA nanocatalysts and their corresponding size distributions show that the chosen synthesis procedure produces Pt NPs with narrow size distribution (2–5 nm) and standard deviation of ca. 15%. The average diameter from Scherrer equation was found to be 3.5 ± 0.5 nm, which corroborates with that estimated from TEM.

The performance of the Pt-MPSA nanocatalyst (Figure 2) shows >30% increase over that of commercial fuel cell catalysts.⁴ It is important to note that the functionalization of Pt NPs by organic thiol ligands prevents agglomeration of the NPs, thus rendering them durable. The durability of the nanocatalyst was tested for >5000 h. We have observed steady performance of the catalyst so far, and the experiment is ongoing.

The “2-in-1” platinum nanocatalyst developed at Tata Chemicals Innovation Center performs way better than commercial fuel cell catalysts in terms of activity and durability, and provides a cheaper alternative for production of MEA.

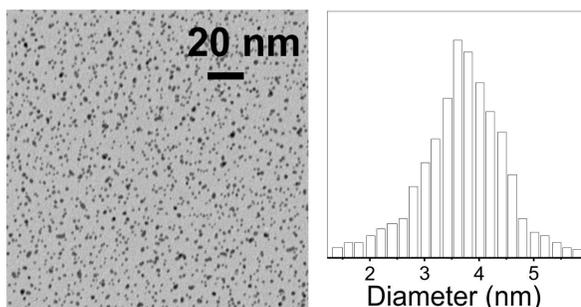


Figure 1. Representative TEM of Pt-MPSA nanocatalyst and its size distribution.

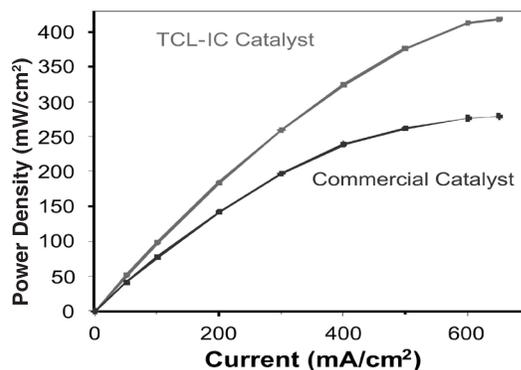


Figure 2. Comparison of fuel cell performance of Pt-MPSA nanocatalyst with commercial catalyst.

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Structural Characterization, Catalysis and Intermediates: A Correlation

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Catalytic technologies have contributed immensely to the growth of chemical industries including refining, petrochemicals, polymers, food manufacturing etc. During the period 1930-1999, there were 85 major product innovations and 40 product innovations of which more than 60% products and 90% processes were catalytic in nature. The word "catalysis" was first used by Berzelius in a published report in 1836 where an account of study and observation of various catalytic substances by Berzelius, Faraday, Thenord, Dobernier and other scientists in the early 1800 was mentioned. Catalysis was said to be concerned with the control of the rate of a chemical reaction by introducing in the reaction path, transient states that as such do not appear in the chemical equation. As a survey study shows that catalysts contribute to one-sixth of the value of all manufactured goods in industrialized countries, for example out of the top 20 synthetic chemicals manufactured industrially worldwide, 13 of them need catalysts of some type [1]. The main three sectors into which industrial catalyst are conventionally divided are chemical (42%), environmental (36%) and refining (22%) [2].

1. Classification of Catalysts

It is convenient to categorize catalytic reactions into three broad classifications depending on catalyst-reactant phases and their nature of applications [3].

- a) *Enzyme catalysis* means reactions catalyzed by complex organometallic compounds generally occurring in nature. Examples are: enzyme hydrolase to obtain products such as alcohols, carboxylic acids, carboxylic esters etc by hydrolysis of esters.
- b) *Homogeneous catalysis* refers to processes where the catalyst is present in the same phase (mostly liquid) as the reactants. These processes are also highly product selective and find application in production of many important chemicals, including many of the vital drugs. A number of soluble organometallic complexes are used as catalyst for industrial processes such as hydro-formylation, oxo-processes, hydrogenation, oxidation, polymerization etc.
- c) *Heterogeneous catalysis* includes those processes in which the reactant (mostly gaseous or liquid) and catalyst (generally solid) are present in different phases. Almost 80% applications of catalysts in chemical industry belong to this class, e. g. use of $\text{Fe-V}_2\text{O}_5$ catalyst in synthesis NH_3 from H_2 and N_2 , the famous Habers process.

2. Heterogeneous Catalysts

Heterogeneous catalysts have gained tremendous importance due to their low cost, easy recovery from reaction system, higher stability, and adaptability to either continuous or batch mode of operation. These catalysts now find wide usage in production of petroleum, petrochemicals, fine chemicals, pharmaceuticals, and also the processes involved in green chemistry for environment control. On the basis of their chemical composition and physico-chemical properties, the heterogeneous catalysts can be classified as:

a. Metals; b. Metal oxides; c. Supported metals; d. Solid / super acids; e. Zeolites and Molecular Sieves; f. Clays and heteropoly acids

Based on their nature and functionality, the above mentioned classes of catalysts, can be logically grouped into mere two types: (i) metals and (ii) non-metals. The former group is largely comprised of transition metals, especially Group VIII, and noble metals of Group IB, the latter of metal oxides and sulphides, salts and acids. The metals are considered to be good catalysts for hydrogen addition or abstraction but are poor catalysts for addition or abstraction of oxygen. Non-metals with differences in electrical/ionic conductivity are further classified as, (i) semiconductors and (ii) insulators. Among them, semiconductors are good for oxidation – reduction processes and insulators work better as dehydration catalysts. Irrespective of the class to which a catalyst belongs, all the catalytic reactions undergo same basic steps:

- (i) Diffusion of reactants to the catalytic sites.
- (ii) Bond formation at the catalytic sites, i.e. chemisorption or primary adsorption of the reactants on the surface of the catalyst.
- (iii) Chemical rearrangements (bond breaking, bond forming, molecular rearrangement) of the adsorbed reaction intermediates leading to the product formation.
- (iv) Desorption of the products.

Since, heterogeneous catalysis finds usage in a widely varied range of technological applications; it cannot be explained by any single theory. Many attempts, however, have been made to generalize such processes. The electronic theory of catalysis, which became popular in the 1950s, attempted to correlate electronic energy levels of the solids (especially semiconductors) and the reactant molecules.

3. Photo-catalysis

Photo-catalysis is a form of heterogeneous catalysis in which the energy, of the light photons, is harvested to undergo suitable red-ox reactions in a semiconductor mediated process. The process of semiconductor photo-catalysis basically involves the following stages. Light energy of a certain wavelength is made to fall onto a semiconductor. If the energy of the incident light is equivalent to the band gap energy (higher than the

work function of the material) of the semiconductor, electrons would be excited from the valence band (V.B) to the conduction band (C.B) of the semiconductor and holes would be left in the valence band. The catalysis is essentially a surface phenomenon. The formation of the h^+ in the V.B and the e^- in the C.B is a bulk phenomenon. These electrons and holes therefore are needed to be transferred to the surface of the photo-catalyst. The electrons and holes present in the surface would undergo subsequent oxidation and reduction reactions with any species, which might be adsorbed on the surface of the semiconductor to give the necessary products. The rule of thumb for the photo-catalyst is that usually the oxidation reaction takes place in the V.B and the reduction reaction occurs in the C.B. The oxidation potential of the V.B should be higher than the oxidation potential of the oxidation reaction being carried out and the reduction potential of the C.B should be higher than the reduction potential of the reductive reaction under contention. However, there is always a competitive reaction of the back electron transfer for the photo-catalysts. Therefore the efficacy of the photo-catalytic catalyst will depend on several factors like:

- a) The band gap of the photo-catalyst which reflects the wavelength of the absorbing light.
- b) The crystal structure of the photo-catalyst: This determines the type of semiconductor it is (viz. direct or indirect), the rate of the transfer of the e^- and h^+ to the surface, kinetics of the back electron transfer and presence of different bulk defect sites.
- c) The surface structure of the photo-catalyst: This decides the different adsorption sites for the reactants and different surface defect sites. The different surface defect sites would lead to trapping of electron or the hole.
- d) The red-ox potential of the V.B and the C.B respectively
- e) The Fermi energy level and it's shape for the particular semiconductor
- f) The shape and size of the semiconductor

The development of effective means to suppress back-electron transfer or (e^- and h^+) recombination process is vital for increasing chemical conversion efficiency. The (e^- and h^+) generated thus can be used to drive chemical reactions provided:

- g) The energy separation (band gap) between (e^- and h^+) is larger than the energy required for desired reaction.
- h) The redox potentials of the (e^- and h^+) (thus the position of CB and VB) are suitable for inducing red-ox processes.
- i) The rates of these red-ox reactions are faster than or at least fast enough to compete with the (e^- and h^+) recombination.

Therefore, development of efficient red-ox catalysts capable of making product formation more competitive against these recombination processes is recognized to be important in this field.

The synthesized photocatalysts (nano-TiO₂, doped TiO₂ and doped - dispersed TiO₂) exhibited enhanced gas phase photo-oxidative activity compared to the commercial bulk anatase TiO₂ and degussa P25. In-depth understanding on the different structural factors of the material which dictates their photocatalytic activity would be understood, and thereby their effect to formalise a better catalyst would be taken. The structure activity correlation of the photo-catalysts were elucidated and the co-relation for factors like particle size, band gap, oxidation state with effective change in the photo-oxidation property of these catalysts were evaluated.[4-5]. The mechanistic studies carried on by photo-oxidation of the Volatile Organic Carbons (VOC's) lead to identification of the intermediate species produced on bare bulk. It was also observed that different intermediates species were formed on the nanoparticles (NP), doped nanoparticles (DNP) and the NP/DNP dispersed in the mesoporous support surface as compared to the bulk surface. Different sources of irradiation (UV and visible) also produced different intermediates leading to different rates. The mechanistic understanding of the surface intermediate species would describe reaction ensemble in totality and would be effective in designing a suitable catalyst for monitoring the kinetics of the degradation process. Host-guest relation of the dispersed nano materials in the mesoporous support was monitored closely [6].

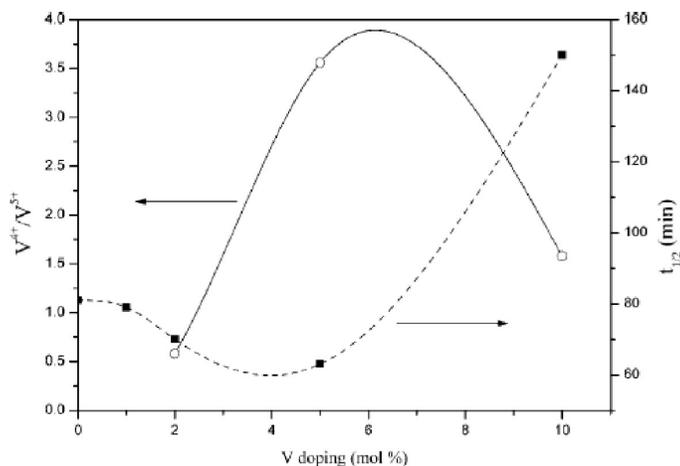


Fig. 1: Comparison of ratio of V^{4+}/V^{5+} states ratio and that of the $t_{1/2}$.

also plays a very important role, the optimum percentage of V^{4+}/V^{5+} is required for the enhancement in the activity of the catalyst. More the amount of the V^{5+} lower is the photocatalytic activity of these catalysts. Among various vanadium-doped titania catalysts evaluated in this study, the 5 mol % vanadium-doped sample shows the

The TiO₂ and doped nano TiO₂ were synthesized by the sol-gel technique, which lead to an increase in the band gap as a function of the vanadium doping in the TiO₂ system. A red shift in the UV-visible spectra of the vanadium-doped titanium materials is observed, which in turn changes the absorbance from the UV region to the visible region. The oxidation of ethylene under ambient conditions was studied, which lead to the conclusion that not only the change in the band gap is required but also the oxidation state of the vanadium

maximum activity for the photocatalytic oxidation of ethylene under ambient pressure and temperature conditions. CO_2 and H_2O are the only products formed suggesting total oxidation of ethylene [7].

The reaction mechanism for ethylene oxidation was elucidated by the *in situ* FT-IR studies. It revealed that in bulk TiO_2 ethylene was transformed to ethoxy group which lead to formation of enolates, which subsequently lead to the formation of aldehydes and then the formic acid as the intermediate species. However, aldehyde, acetic acid, acetates were more stable species in V-doped TiO_2 . The ethylene decomposition occurs via formation of ethoxy, transformed to acetaldehyde or enolates, subsequently to acetates, and then to CO_2 . The enolates are more stabilized on the V-doped TiO_2 than that of Ti of the nano TiO_2 , due to the doped vanadium in the 4+ state. This thereby helps in the adsorption of the stronger nucleophile among all the intermediate nucleophiles formed that is the acetate in the free and the adsorbed and the metal acetates forms, thereby increasing the yield

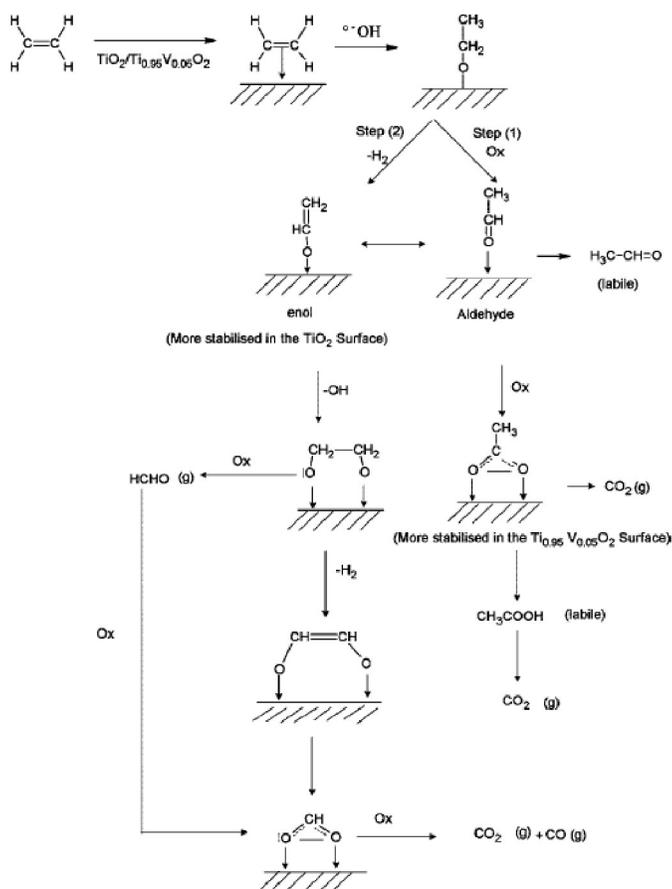


Fig. 2: Scheme showing the route for the different intermediates formed on V-doped TiO_2 and nano TiO_2

of the CO_2 [8]. The host matrix of MCM-41 is synthesized. $\text{Ti}_{0.95}\text{V}_{0.05}\text{O}_2$ nanoparticles were successfully incorporated into the MCM-41 host matrix with a loading up to 20 wt% maintaining the mesoporous structure. We get a positive particle size effect, for the same ethylene oxidation reaction. In spite of the blue shift with a decrease in the particle size, all these catalysts continue to absorb in the visible region. [9]

The FT-IR study reveals a strong interaction between the host matrix and the guest molecules, and conservation of the MCM-41 structure. XPS studies illustrate that there is a strong electronic interaction between $\text{Ti}_{0.95}\text{V}_{0.05}\text{O}_2$ and the host matrix, which increases with increased loading of the guest molecules. The photocatalytic activity of the catalysts varied in the following form: 5 wt% > 15 wt% > 20 wt% ($\text{Ti}_{0.95}\text{V}_{0.05}\text{O}_2/\text{MCM-41}$) > bulk $\text{Ti}_{0.95}\text{V}_{0.05}\text{O}_2$ >

nano- TiO_2 . The strong electronic interaction being a function of the loading percentage of the guest molecules, the interaction between reactant (C_2H_4) and the guest catalytic molecules ($\text{Ti}_{0.95}\text{V}_{0.05}\text{O}_2$ moieties here) was reduced considerably, thus leading to the lower photocatalytic activity of the higher-loaded samples. In the case of $\text{Ti}_{0.95}\text{V}_{0.05}\text{O}_2 / \text{MCM-41}$, the photooxidation of ethylene in air follows different routes under UV and visible irradiation, which can be observed in the scheme shown below [10].

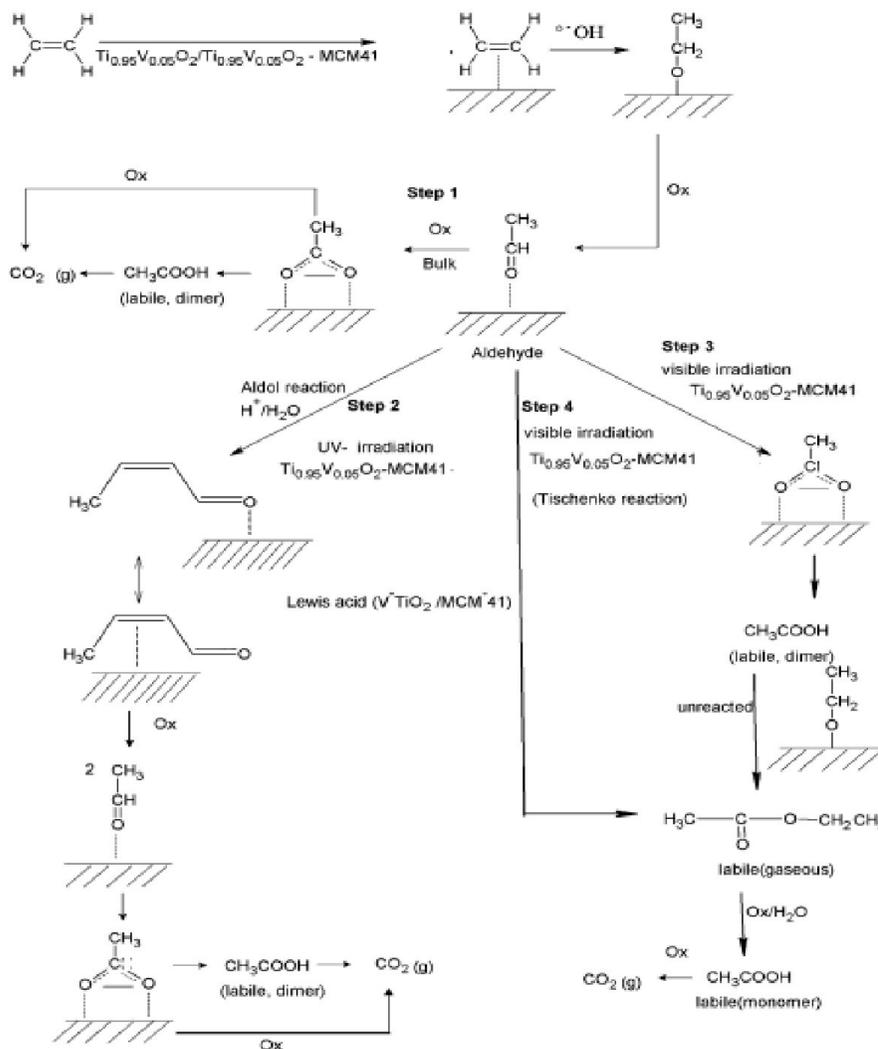


Fig.3 Schematic representation of photooxidation of ethylene in air.

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(i) Material Science: Synthesis, characterization and Catalytic property measurements of several nano, mesoporous materials. (ii) Catalysis mainly photocatalytic (oxidation/reduction) reactions for environmental and energy applications. (iii) Mechanistic studies for surface reactions (in situ FTIR, in situ EPR, in situ Raman, studies). (iv) First Principle calculations for understanding the surface reactions. (v) Understanding the surface behavior for catalytic reactions (using XPS, EXAFS, AR-XPS, AES, ISS SEM, SAM like techniques) and establishing the structure activity correlation. Membership: (i) Society for Material Chemistry. (ii) Material Research Society of India. (iii) ACS-(2011) Awards: 1) DAE Young Scientist Award-2012. Dr. Bhattacharyya has got 27 publications in the journals of international repute and is working on the field of Catalysis and Surface Science presently in BARC.

Nanocatalysis: Fibrous Morphology of Catalyst Support Makes a Great Difference in Its Activity and Stability

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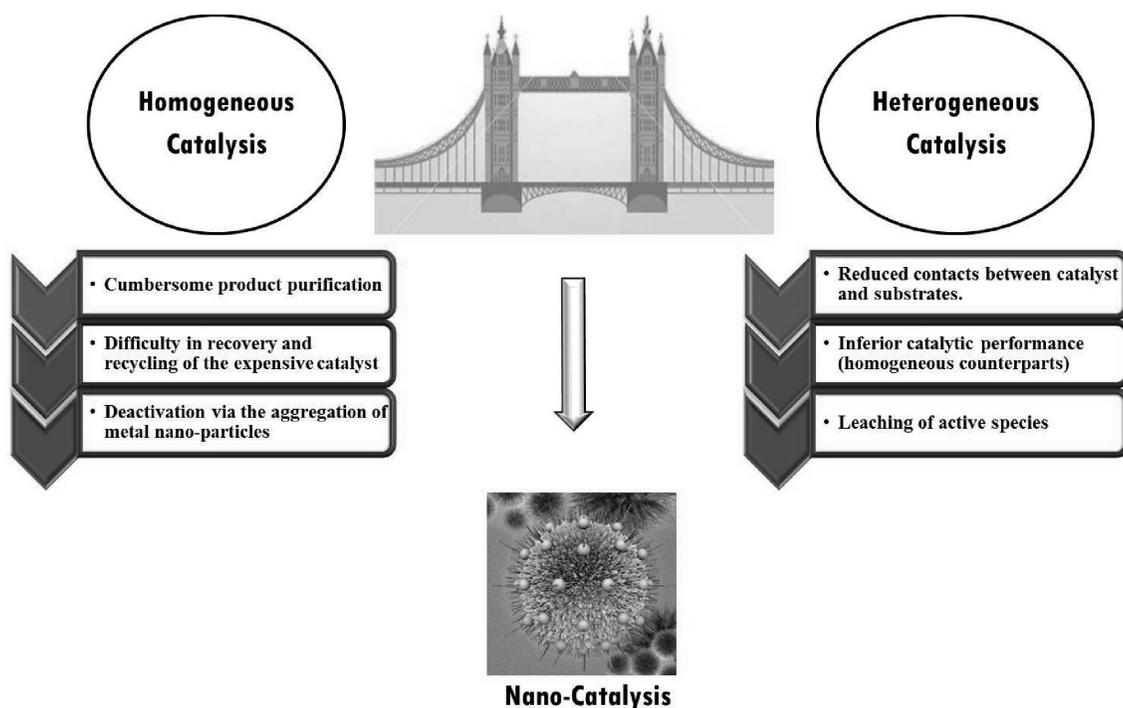
Abstract

Advanced nanomaterials, such as high surface area nano-silica, have wide applications in a range of fields, such as catalysts, energy generation (solar cells, water splitting, bio fuels), environment remediation (CO₂ capture, water purification), and drug delivery. Recently, we have developed high-surface-area silica with a unique fibrous morphology (KCC-1). High surface area of KCC-1 is attributable to fibres and not to pores, which dramatically increase its accessibility compared to well-known SBA-15 or MCM-41 mesoporous silicas. This unique property was found to be useful in the design of silica-supported nanocatalysts and CO₂ capture sorbents. We are exploring applications of KCC-1 and surface modified KCC-1 in a range of nanocatalytic protocols. In particular, nitridated KCC-1 demonstrated excellent CO₂ capture and catalysis capabilities. Use of KCC-1 could help develop green and sustainable technologies.

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Catalysis is becoming a strategic field of science since it represents a new way to meet the challenges of energy and sustainability. These challenges are becoming the main concerns of the global vision of the societal challenges and world economy. The societal pressure has been at the origin of the concept of sustainable chemistry which is becoming a leitmotiv in any important project dealing with this strategic domain of science. Catalysts are chemical

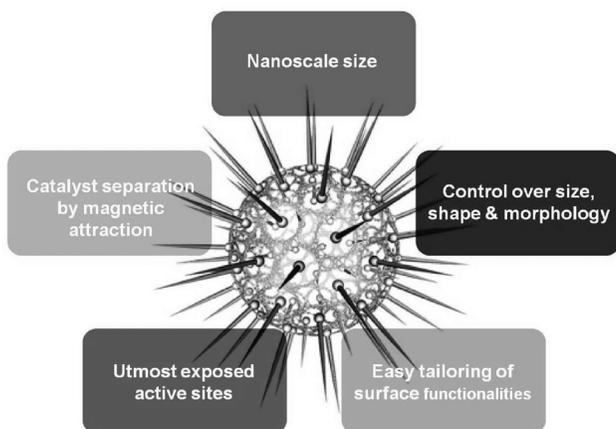
substances that enable the transformation of fine chemicals into value-added chemical products or synthetic materials. Catalysts are traditionally divided into two major groups based on the type of phase of the catalyst is in relative to the catalytic reaction mixtures, *i.e.*, homogeneous and heterogeneous catalysts. Homogeneous catalysts are those that exist in the same phase as the reactants. They are generally soluble organic or organometallic complexes and often give chemo-, regio- and stereo-selective products. However, they are relatively difficult to separate from reaction mixtures for reuse at the end of reactions. On the other hand, there are solid or insoluble catalysts, also called heterogeneous catalysts. In many instances, the solid catalysts contain homogeneous catalysts supported on neutral or catalytic-active solid support materials such as porous silica or alumina. These types of catalysts are easily separable and reusable at the end of reactions; however, they often give relatively poor reaction yields, compared to many of their homogeneous counterparts. Thus, the catalyst which can bridge homogeneous and heterogeneous system is needed (Figure 1).



(Figure 1)

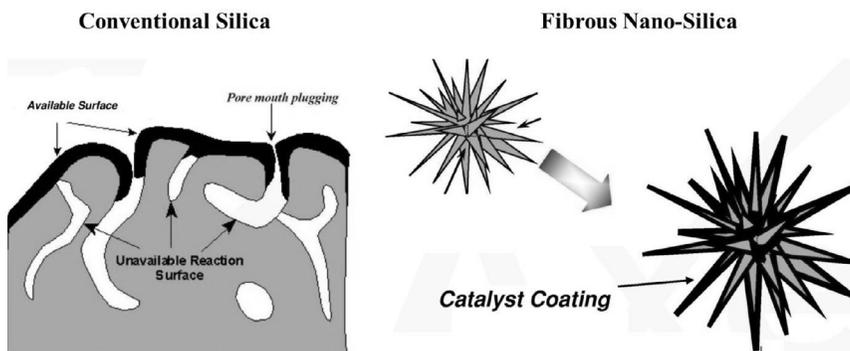
The fields of nanotechnology have been unquestionably thriving over the last few decades. One of the most stimulating features of nanotechnology is its potential use in almost any field. The discovery of nanoparticles with varied size, shape and composition has stretched the limits of technology in ways that scientists would never have dreamt of a century ago.⁵ Nature makes and chemistry re-shapes; huge varieties of nanoparticles have emerged in our daily life, in every field from drugs and electronics to paints and beauty care, and they are now emerging in the field of catalysis, nanocatalysis.

Nanocatalysis can thus be simply defined as the use of nanoscale materials in catalysis. Nanocatalysts are highly active (like homogeneous system) and also easy to recover/reuse (like heterogeneous system). In other words, nanocatalysts exhibit quasi-homogeneous or quasi-heterogeneous catalytic properties, and thus allow for rapid and selective chemical transformations, with excellent product yield and ease of catalyst separation and recovery. It has also made the greening of chemistry possible. In addition to the size, nanocatalysts are extremely shape sensitive and their catalytic efficiency and selectivity dramatically depend on their shape and morphology (Figure 2). The concept of nano-catalysis, which makes the catalysis science even more creative, has become integral part of sustainability.^{1,4}



(Figure 2)

Accessibility of surface area plays the major role in nano-catalysis, and generally this surface area is due to pores and not easily accessible. Silica's like SBA-15 or MCM-41 are generally used as a support and the effectiveness of these materials as catalyst supports is mainly due to their microstructures, which allow active catalytic sites to disperse on the large internal surfaces and pores, which in turn improve the activity of the catalyst system. However, high surface areas of these materials are due to the pores, which are not always accessible and can also get blocked during catalysts preparation (Figure 3). Poor accessibility to the active sites inside these pores sometimes limits their applications for which significant mass transport is essential. Therefore, to design better nanocatalysts, with higher accessibility and thus higher activity, we need a new support material which could have high surface area and also which could preserve its accessible surface area even after coating or functionalization during catalyst preparations.

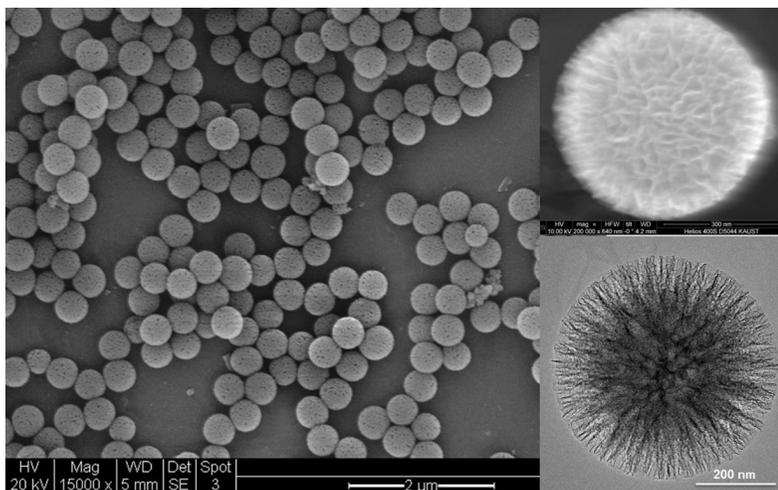


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fibers and their respective channels and not due to the pores. It is clear from their SEM and TEM images (Figure 4), that these fibers are easily accessible from all the side and hence any active sites on them will also be accessible. Notably, this material exhibits excellent physical properties, including a high surface area, a fibrous surface morphology, a good thermal and hydrothermal stabilities and a high mechanical stability.



(Figure 4)

KCC-1 can be very useful as catalysts support, wherein accessibility of active sites can be increased significantly. In order to prove this, KCC-1 has been tested as support in a variety of catalytic systems, particularly TaH/KCC-1,⁷ Pd/KCC-1,⁸ and Ru/KCC-1.⁹ In all these systems we did observed that use of KCC-1 support is advantageous in terms of activity and stability of

catalysts, as compared to SBA-15 or MCM-41 support. However, these results indicates that the better catalytic activity is not only due to fibrous nature of KCC-1, but also due to other parameters such as shape and size of active metal nanoparticles supported on KCC-1 or use of hydrogen gas (in TaH system) during the reaction. Thus, there was a need to prove that fibrous nature of KCC-1 alone could increase the catalytic activity, due to its highly accessible surface area. Thus, there was a need to prove this concept by conducting the reaction which fully depends on surface area accessibility only.

We developed novel solid base by ammonolysis of KCC-1 and showed the advantages of its fibrous morphology and highly accessible surface area. Ammoniated KCC-1 was found to be very active and robust base, for Knoevenagel condensation of challenging substrates, which is not possible using most of the the nitridated bases. It even showed multifold better activity than recently reported active base, Me-NSBA. This enhancement in activity was explained on the basis of accessibility of amines, which is excellent in KCC-1 due to its open and flexible fibrous structure (unlike MCM-41 or SBA-15) which helps substrates to easily penetrate and interact with basic amine sites, which in turn accelerate the overall reaction.¹⁰

These materials were also evaluated for the first time as sorbents for CO₂ capture. They exhibit the following advantages over conventional amine-grafted silica: 1) good CO₂ capture capacity; 2) faster kinetics; 3) easy regeneration and efficient reuse of sorbents; 4)

excellent mechanical strength; 5) high thermal stability in inert and oxidative environment and 6) clean and green material synthesis and less expensive production costs, which allow the overall process to be sustainable.¹¹

In my presentation, I will be discussing above mentioned results in more details.

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Dr. Vivek Polshettiwar is Reader in the Division of Chemical Sciences at TIFR Mumbai. Before joining TIFR, he obtained his Ph.D. (2005) under the supervision of Prof. M. P. Kaushik from Jiwaji University and DRDO, Gwalior. He then investigated nano-structured silica-catalysts, with Prof. J. J. E. Moreau in 2006 during his postdoctoral research at École Nationale Supérieure de Chimie de Montpellier (ENSCM), France. He then moved to

United State Environmental Protection Agency (US EPA) (2007-2009) as ORISE research associate to research nano-catalysis for green chemistry with Prof. R. S. Varma. Then, he started his independent group of nanocatalysis at KAUST (2009-2013). During this period, he also worked as visiting scientist at CPE, Lyon, France with Dr. Jean Thivolle.

He has published nearly 75 articles with h-index 34 and more than 2900 citations; in high-impact journals such as Angewandte Chemie, ACS Nano, RSC Chemical Science, ChemComm, Chemistry-A European Journal, ACS Catalysis, ChemSusChem, Journal of Organic Chemistry, Green Chemistry etc, including reviews in journals such as Chemical Reviews, ACS Accounts and Chemical Society Reviews, book chapters, patents (US, PCT, GCC). He has also edited one book from the RSC green chemistry series and another one for Wiley on nanocatalysis. Several of his articles are rated as Top-10, Top-5, Hot article and appeared on journal's front covers.

He is recipient of prestigious Oak Ridge Institute for Science and Education (ORISE) Research Fellowship (2007) at US-EPA and the eminent Scientific and Technology Achievement Award by US Environmental Protection Agency, Special Mention (2009). He has also been awarded other esteemed fellowships like Humboldt, Marie Curie in 2009 (not accepted due to prior commitment to KAUST) and French government fellowship in 2005. He was also awarded as Top-25 cited author in 2011 by Tetrahedron and Young Scientist Award at DSL-2012. Recently, he also received Asian Rising Stars award from Nobel Laureate Professor Ei-ichi Negishi, during 15th ACC Congress, Singapore by Federation of Asian Chemical Society.

Dr. Polshettiwar's research interests are in the area of advanced nano-materials, nanocatalysis and green chemistry. He believes that next generation catalysts can be developed by shape and morphological control of nano-materials which will allow preferential exposure of active site. His nano-catalysis group is working in the area of nano-materials (metals, metal oxides, silica, titania, MOFs) synthesis with controlled shape and morphology and their application as nano-catalysts (CH activation, metathesis, hydrogenolysis, organocatalysis, etc) and environmental applications (e.g. CO₂ capture, water purification etc) that allow for more sustainable and green production processes.

Ionic Catalysts for Energy and Environmental Applications

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Noble metals have shown exceptional properties for catalyzing a large variety of reactions especially redox reactions studied in this thesis. High cost of noble metals necessitates their effective use and synthesis. Therefore, lower amounts and smaller particle sizes are becoming the key for the development and application of any catalytic system. Supported catalysis was developed with the intention of achieving high dispersion of noble metals over high surface area compounds. However, it was realized that interactive supports can actually further enhance the activity of the catalyst. Although it was not the primary goal, ionic dispersion of metals in an oxide matrix proved to be a good strategy for achieving a high dispersion. The ionic nature of the metal in the compounds resulted in lack of tendency of agglomeration of metal, a phenomenon which has been reported for the loss of catalytic activity for several systems.

The ionic substitution of noble metal ions in the oxide supports was carried out with an intention of harnessing the enhanced electronic interactions in the catalysts, which is vital for the redox reactions. This indeed could be accomplished, as observed from the results on the water-gas shift reaction and catalytic hydrogen combustion. Thus, the catalysts with noble metals in ionic state were found to be superior compared to impregnated catalysts in which the metal was dispersed in metallic state. In case of catalytic hydrogen combustion, ionic dispersions resulted in lower working temperature of the catalysts, while the water-gas shift reaction resulted in higher equilibrium CO conversions owing to lower temperatures.

Three different supports were tested in the studies, viz., CeO_2 , ZrO_2 , and TiO_2 . Whereas the ionic nature of the compound was indeed found to be maintained on exposure to reaction conditions for CeO_2 and TiO_2 -based compounds, reduction of the metal ion to metallic state was observed during the water-gas shift reaction on ZrO_2 -based catalysts, as determined by the XPS of Pt4f after the reaction. Therefore, two different classes of compounds and, hence, two different mechanisms for the water-gas shift reaction were proposed. The first class of the compounds was the reducible oxides in which lattice oxygen utilization was possible and this was proposed to constitute a very important step in the mechanism of the reaction. For both water-gas shift reaction as well as catalytic hydrogen combustion, lattice oxygen utilization and the formation of anionic vacancies was proposed. This was supported by the spectroscopic evidence that the reduction of Ce^{4+} to Ce^{3+} was observed in XPS spectra. Two different sites for the reaction were proposed. Whereas the adsorption of CO/H_2 was proposed to take place over the metal

ion, dissociative adsorption of $\text{H}_2\text{O}/\text{O}_2$ was proposed to take place over the anionic vacancies. The elementary steps, proposed on the basis of spectroscopic observations, were found to describe the mechanism of the reaction. This was confirmed by deriving the rate expression corresponding to the proposed elementary steps and determining the rate constants in the rate expressions. Physically feasible rate parameters could make the proposed mechanism acceptable. At the same time, certain other mechanisms, which were also tested for the reactions including the Langmuir-Hinshelwood mechanism and Eley-Rideal mechanism were rejected owing to the unrealistic rate parameters.

Irreducible oxides can be considered as the second class of compounds. Noble metal ion-substituted ZrO_2 was considered in this category of the compounds. From the XPS of Pt 4f in the compound after the reaction, it could be concluded that the ionic dispersion of the metal in the matrix could not be maintained for a long time and the utilization of oxygen from the support was not possible. Therefore, a different mechanism was proposed for ZrO_2 -based compounds. Acidic sites in ZrO_2 and the presence of surface hydroxyl groups in such compounds is known. The mechanism for the reaction over ZrO_2 -based compounds was proposed to take place utilizing the surface hydroxyl groups. The rate parameters for the rate expression obtained from the elementary steps proposed for the reaction over this class of compounds could satisfactorily describe the reaction. Therefore, it can be said that it is important to understand the effect of the support on the kinetics and mechanism of the reaction as the identity of the support indeed governs the surface processes during the reaction.

Solution combustion is a novel technique for synthesizing oxide materials. Superior catalytic activity of combustion synthesized materials compared to those synthesized by conventional techniques has been reported for photocatalytic reactions. This method also proved to be an excellent way of achieving substitution of noble metal ions in nanocrystalline oxides. Certain other systems were also synthesized using the solution combustion technique which showed high activity for CO oxidation. Smaller crystallite size of the material can result in superior catalytic properties and we had observed this with CeO_2 for CO oxidation. Combustion synthesis provides an attractive advantage of tuning the crystallite size and phase by suitably adjusting the fuel. 2-3 nm CeO_2 particles could be successfully synthesized using mixture of fuel approach and the compound showed higher activity for CO oxidation compared to CeO_2 synthesized using a single fuel which had crystallite sizes in the range of 30-40 nm. Therefore, by the use of conventional single fuel itself, it was possible to achieve nanocrystalline CeO_2 . But even further modifications are possible by exploring the different fuels and their combinations.

Following the principles of ionic catalysis explored in this study, it can be possible to extend the study to other reactions, especially those involving oxidation and dehydrogenation reactions. Apart from the reactions like steam reforming and preferential oxidation, numerous organic reactions requiring Pd ions can be carried out. In this manner, this study provides a whole new class of compounds for a large variety of reactions.



Giridhar Madras received his chemical engineering degree from Indian Institute of Technology at Madras in 1990. He subsequently obtained his Ph.D. degree in chemical engineering from Texas A&M University, USA, in 1994. Subsequently, he worked in the University of California at Davis, USA. He returned to India as an Assistant Professor of chemical engineering at the Indian Institute of Science, Bangalore in 1998. Since 2007, he has been a Full Professor at the Chemical Engineering Department. He is also an associate faculty in Solid State and Structural Chemistry and the center for nanotechnology.

He received the Scopus Young Scientist Award from Elsevier for being the most cited young author in engineering. He was awarded the Presidential Swarnajayanthi fellowship by the Department of Science and Technology, India, in 2006 and the S.S. Bhatnagar prize from CSIR, India in 2009 from the Prime minister of India for his contributions to the field of engineering. He has published more than 300 international journal articles, which have more than 7000 citations with a h-index of 45 and is among the most cited engineering scientists in India. He is listed by Web of Science as among the top 1% of all scientists in the world.

He is currently the associate editor of several journals including *Advanced powder technology*, *Current Science* and *International journal of polymer science*. His research interests are in the area of reaction engineering applied to polymers, supercritical fluids, and catalysis.

Engineered Materials for Carbon Neutral Energy

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Abstract

Catalytic chemistry is proving to be an essential prime requisite for making cleaner environment a reality and enhancing sustainability and carbon balance. In order to meet the challenges of carbon neutral energy through catalysis engineered materials are being developed for solar energy to chemical energy conversions and hybrid energy systems with novel cross-disciplinary paradigm. The engineered materials are being developed by designing synthetic analogues of natural materials and by tailoring the properties of the conventional and natural materials for targeted applications including i) carbon capture, valorization and sequestration (CCVS) and ii) solar energy to chemical energy conversion. The details are as follows:

1.0 Plasmonic photocatalysts for photocatalytic generation of hydrogen:

In order to maximize photocatalytic activity, it is required that the photocatalyst should not only resist recombination reaction but also should have a high specific surface area and, in addition to it, the material has to be active in the visible range (Sinha et al. Sathish et al. Abe et al.). In our previous work we synthesized composite photocatalysts which showed significant photocatalytic activity in the visible range wherein the hydrogen evolution rate of 2730 $\mu\text{mol/h/g}$ of TiO_2 has been achieved (Dubey et al.). New metal nanoparticles (Polishettiwar et al) have been tested for hydrogen evolution reactions. The metal nano particles investigated have shown great potential in photocatalytic hydrogen generation with hydrogen evolution rate in the range of 90-300 $\mu\text{mol/h}$ of photocatalyst.

Plasmonic photocatalysts are showing a significant edge over the conventional photocatalysts in terms of their visible light absorption properties. 1- 5 wt% of Au and TiO_2 , CeO_2 , Cu_2O and Fe_3O_4 composites have been synthesised via the photo deposition method to illustrate the influence of SPR (Surface Plasmon Resonance) on photocatalytic hydrogen generation. Au/ TiO_2 shows hydrogen evolution rate of 920 $\mu\text{mol h}^{-1}$ and 32.4 $\mu\text{mol h}^{-1}$ under UV-visible and visible radiation, respectively followed by Au/ CeO_2 , Au/ Cu_2O and Au/ Fe_3O_4 for SED (Sacrificial Electron Donor) assisted water splitting under UV-vis radiation.

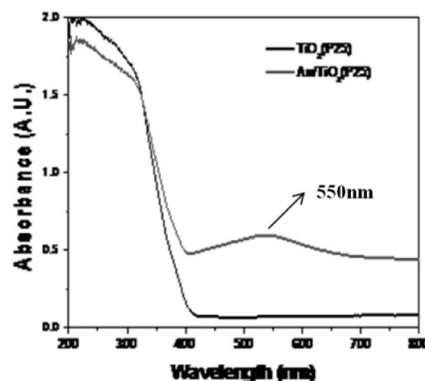
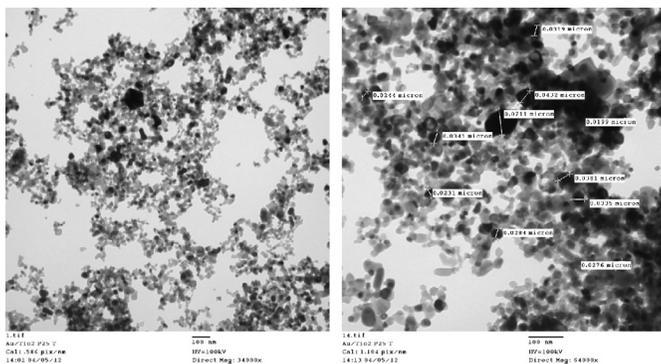
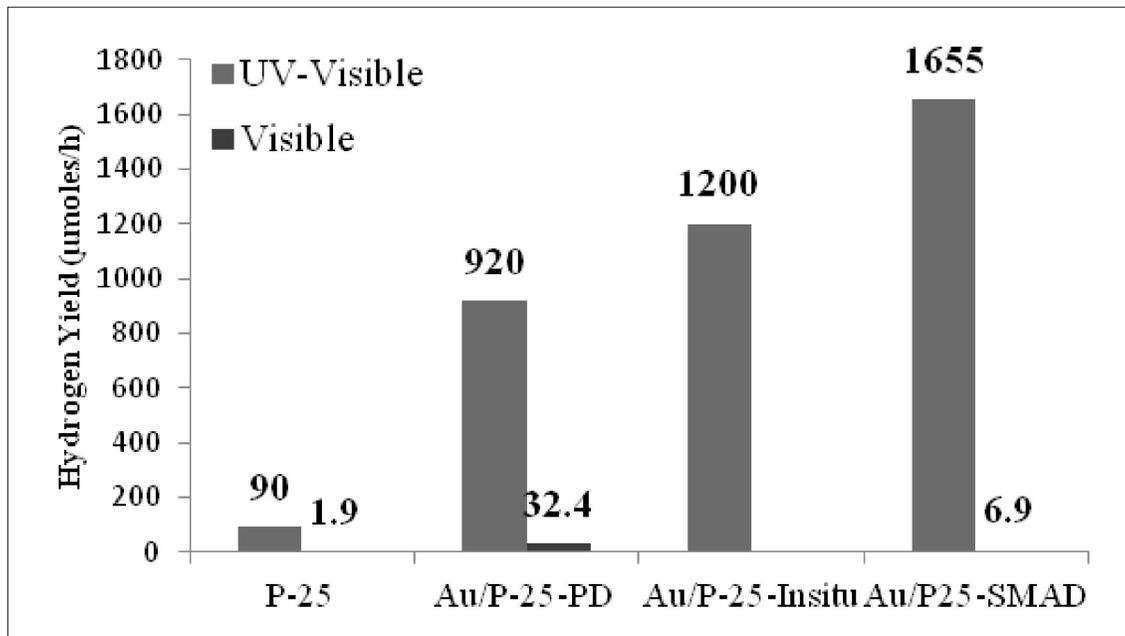


Fig 1: TEM images of Au /TiO₂ composites

Fig 2: UV DRS of Au/TiO₂ composites

2.0 Biomimetic materials for solar hydrogen:

In-situ nanostructured Titania and other plasmonic photocatalysts have been developed using algae as nanoreactor. The photocatalyst shows exceptionally high hydrogen evolution to the tune of about 17.50 mmoles/h/g of photocatalyst (sensitized algae) as compared to 0.0906 mmoles/h/g of photocatalyst (algae as such) establishing its superior photocatalytic activity especially in the visible light region under solar energy irradiation.

3.0 Carbon capture, valorization and sequestration:

New molecule and functionalized materials are being developed for capture of carbon dioxide with sorption capacity in the range of 100-200 mg of CO₂/g of material or

molecule. A new mimic of chitosan like absorbent has been developed for capturing CO₂ with high Carbon capture capacity of 16 mmol/g on materials.

4.0 Immobilised and stabilised enzyme nanoparticles for biomimetic carbon capture, sequestration and valorisation (CCVS):

Efforts are being made worldwide to mimic the reaction for fixation of anthropogenic CO₂ into calcium carbonate using carbonic anhydrase (CA) as a biocatalyst. Efforts are also being made to mimic the reaction for fixation of anthropogenic CO₂ into bi-carbonate using carbonic anhydrase (CA) as a biocatalyst. CA is being employed to accelerate the rate of hydration of CO₂ to form carbonate ions and proton. Presently carbonate is being precipitated from aqueous solution as calcium carbonate given a suitable saturation of calcium and carbonate ions by addition of appropriate buffer. The generation of chemicals and cleaner energy resources/fuel in addition to carbonates as end products during biomimetic carbonation may make the process commercially viable to be adopted by industries emitting carbon dioxide. CA has been immobilised on different matrices and tested for reuse and recyclability. Also a unique protocol for the synthesis of stabilized enzyme nanoparticles (SENs) has been developed for carbonic anhydrase to stabilize the enzyme activity by encapsulating each enzyme molecule with a hybrid organic/inorganic polymer network. The Km and Vmax of free SEN is 6.143 mM and 0.02857 mmole/min/mg as compared to Km and Vmax of 1.252 mM and 0.02029 mmole/min/mg respectively for free enzyme. CA is being employed to accelerate the rate of hydration of CO₂ to form carbonate ions and proton.

Efforts are being made to couple biomimetic carbonation with photocatalysis to generate high value added products including formic acid, hydrogen, syngas etc.. This approach may prove to be a revolutionary technical advancement required for hydrogen economy demanding carbon neutral hydrogen production.

Engineered materials and processes ensures cleaner and greener and sustainable environment.

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Stable Metallic Nanoparticle-Semiconductor Heterostructures via Click Chemistry for Photocatalytic Dye Degradation

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Sri Sivakumar and Raj Ganesh S Pala**

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Introduction

Metallic nanoparticles (MNP) are utilized as electrocatalysts, co-catalysts and photon absorbers in heterostructures that harvest solar energy. In such systems, the interface formed should be stable over a wide range of pH values and electrolytes. Recently, metal-semiconductor heterostructures have gained considerable attention as the incorporation of noble metals (such as Au and Ag) on semiconductors surfaces offered new prospects for enhancing photocatalytic activity due to the surface plasmon resonance (SPR) effect of noble metals¹. However, most metallic-semiconductor heterostructures are fabricated through physical mixing, electrochemical deposition, non-covalent interactions, spin coating, Langmuir Blodgett, Doctor Blade and sputtering². However, these heterostructures are stable only under certain chemical conditions due to relatively weak interactions between the metal and semiconductor surfaces; it is thus expected that covalently bound interfaces would enhance the stability of such heterostructures. In this work, we demonstrate a generic “chemical” approach for fabricating highly stable electrochemically/photocatalytically active monolayer of azide/alkyne modified gold nanoparticle on alkyne/azide modified silicon and indium tin oxide via click chemistry. The stability and photocatalytic properties of the interface are shown via photocatalytic degradation of Rhodamine B (RhB) dye. The results suggest that the proposed approach can be extended for large-scale fabrication of highly stable heterostructure materials for electrochemical and photoelectrocatalytic devices.

Experimental Section

1. Synthesis and azide functionalization of gold nanoparticles

Gold nanoparticles were prepared using the citrate method³ in which a deep red color solution confirms the formation of approximately 20-nm gold nanoparticles after adding 1% sodium citrate solution to heated 1mM aq. solution of chloroauric acid (HAuCl_4) salt under continuous stirring. Gold nanoparticles were then precipitated by centrifugation at 10000 rpm for 50 min. Ligand exchange with 3-chloro-1-propanethiol was performed by dispersing the gold nanoparticles in dichloromethane (DCM) and stirring the solution at room temperature for 60 h; the resulting nanoparticles were precipitated using centrifugation, and finally, the particles were washed with ethanol to remove any

unreacted thiol. Particles were redispersed in DCM, and an equal volume of sodium azide (0.25 M) in DMSO was added to the solution and stirred for 48 h, after which the particles were recovered by centrifugation and washed with water to remove unreacted sodium azide⁴.

2. Alkyne functionalization of silicon wafer

Silicon wafers (100) were cut into approximately 5 x 5 mm² pieces and washed with piranha solution (H₂SO₄:H₂O₂:: 3:1)(*caution: Piranha solution is very dangerous, handle with care*) at 100 °C for 30min to introduced more hydroxyl groups onto the silicon wafer substrate. After piranha washing, the pieces of silicon wafers were transferred to 2.5% solutions of hydrofluoric acid (HF) (*caution: HF solution is very dangerous, handle with care*) for 90 sec under inert atmosphere to generate hydrogen terminated silicon surface. Immediately after HF etching, hydrogen terminated silicon wafer pieces were transferred to a three neck flask containing a 0.9 mM solution of 1,8-nonadiyne under an inert atmosphere to prevent the formation of an oxide layer on the surface. Next, the flask was heated in an oil bath at 170 °C for 3 h to form the hydrophobic layer of the alkyne group on the silicon surface. Finally, the silicon wafers were washed with acetone (twice), ethanol (twice) and water (twice) to remove any unreacted chemicals⁵.

Result and Discussion

Monolayer of Nanoparticles

Scanning electron microscopy (SEM) images in Figure 1a and 1b clearly show the formation of densely packed monolayers of gold nanoparticles (~ 20 nm) on a silicon and indium tin oxide (ITO) substrates via click chemistry. This result clearly shows that the proposed approach can be applied to the fabrication of monolayers of different sized nanoparticles over large areas of various substrates with minimal aggregation.

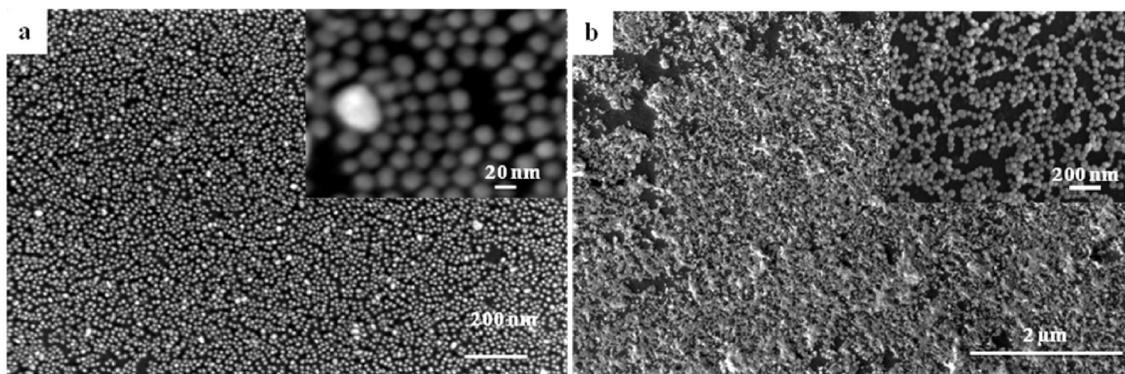


Fig 1: SEM images of a monolayer of azide-functionalized gold nanoparticles on alkyne-functionalized substrates (a) silicon and (b) ITO via click chemistry.

Photocatalytic RhB Dye Degradation

Figure 4a shows the absorbance at 553 nm vs time curve for an RhB dye solution in contact with the different samples. The decrease in the absorbance peak at 553nm with time suggests faster degradation of the RhB dye in the presence of Au@silicon (48% degradation efficiency) and Au@ITO (40% degradation efficiency) than under illumination without the catalyst. A plot of $\ln C_0/C$ (where C_0 is the initial concentration of the dye and C is the concentration of the dye at different time intervals) vs time is shown in Figure 4b, clearly suggesting that, in the presence of gold nanoparticle monolayer samples, RhB dye degradation follows pseudo-first order reaction kinetics. Figure 4c shows a schematic representation of a possible mechanism for the degradation of RhB dyes. During the photocatalytic degradation of the RhB dye, both the SPR effect of the gold nanoparticles and the electronic transition in the gold nanoparticles play roles (Figure 4c). Upon illumination, the gold nanoparticles absorb resonant photons and excite electrons from the band below the Fermi level to higher energy states. The excited electrons are transferred to the conduction band of the semiconductors, where the electrons are further transferred to adsorbed O_2 molecules to generate $\bullet O^{-2}$ species. Simultaneously, photogenerated holes react with water molecules to generate hydroxyl ($\bullet OH$) radicals,

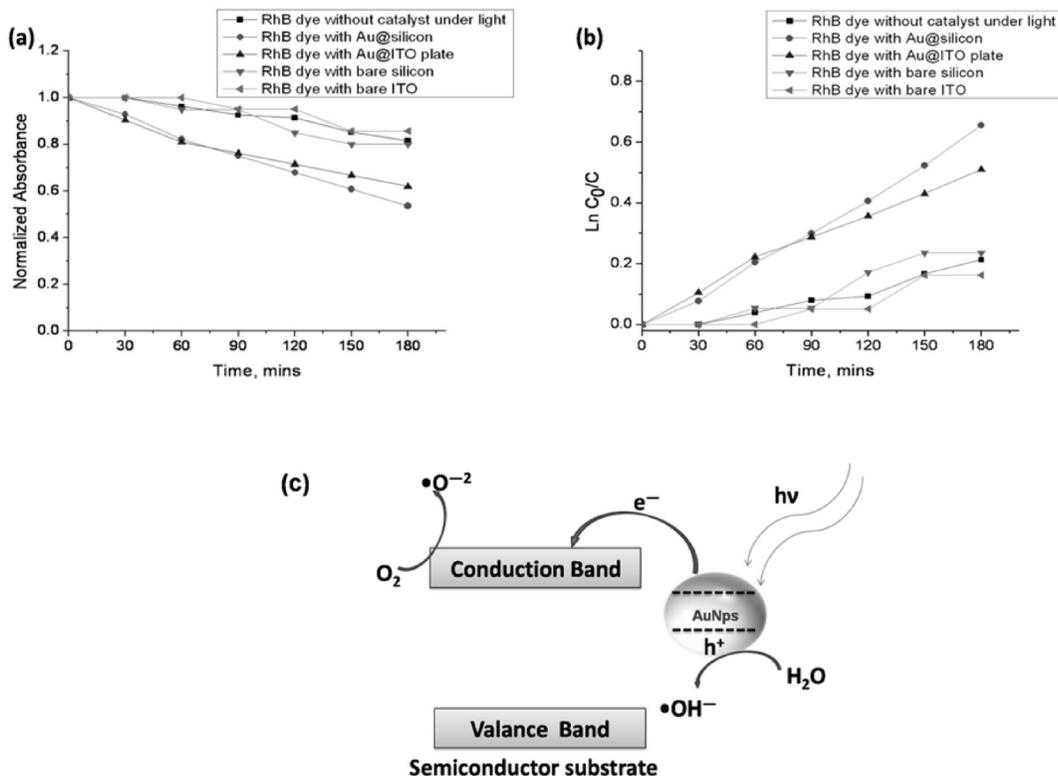


Fig 2: (a) Absorbance vs time curve for RhB dye under light illumination, (b) rate constant curves for RhB dye degradation and (c) schematic diagram for the proposed dye degradation mechanism.

which are mainly responsible for the degradation of the RhB dye. Therefore, we believe that the SPR effect cannot be decoupled from the electronic transitions, and both play significant roles in RhB dye degradation^{1,6}.

Conclusion

Our results demonstrate a generic approach for processing metallic monolayer on different substrates (silicon and ITO) via click chemistry. We observed enhancement in the photocatalytic activity and stability of heterostructures towards photocatalytic degradation of RhB dye. The enhancement in the stability of the heterostructures is because of the stable triazole linkage formed between the azide and alkyne groups present on the gold nanoparticles and substrates surfaces, respectively.

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Raj Ganesh S. Pala is presently working in the department of chemical engineering, Indian Institute of Technology at Kanpur. He works in the area of chemical, electrochemical and photoelectrochemical approaches for conversion of solar energy. The research focus of the group is on the elucidation of concepts that aid in designing functional materials that are useful in converting various forms of energy and also in reducing environmental pollution. Elucidation of these underlying principles often involves a semi-quantitative description of phenomena that span a wide range of length and time scales. In this context, analysis is made using a wide variety of computational and theoretical tools like quantum chemical density functional theory, molecular dynamics, lattice based Monte Carlo methods and continuum transport equations. These studies are closely work coupled with experiments performed in the group as a combined experimental and theoretical analysis is often imperative in addressing systems as complex as a typical industrial catalyst.

Hydrogen Production

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The realization of the hydrogen as an energy carrier for future power sources relies on a practical method of producing hydrogen in large scale with no emission of green house gases. Combustion of fossil fuels currently provides about 86% of the world's energy. The conventional fossil fuel produces a great deal of greenhouse gas which was assumed to be responsible for the global warming. Hydrogen is an environmentally attractive alternative to replace fossil fuels, but current hydrogen production uses fossil fuels as a raw material. Hydrogen production by thermo chemical water splitting, a process that accomplishes the decomposition of water into hydrogen and oxygen, is an environmentally attractive way to produce hydrogen without using fossil fuels.

Hydrogen is considered as an excellent candidate for the future energy system with its many advantages. Hydrogen can be transported for long distance; it can be stored in the form of compressed gas, liquids or hydrogenated compounds. It is clean, as water is the only product after burning. Therefore hydrogen is a promising candidate of alternate energy carrier in our future energy system.

Electrolysis and thermo-chemical cycles are the two leading processes for the massive hydrogen production from water. Since direct thermolysis of water which requires temperatures of $>2500^{\circ}\text{C}$, is not practicable under normal circumstances. One of the promising approaches to produce large quantities of hydrogen from nuclear energy efficiently is the Iodine-Sulfur (I-S) thermo-chemical water-splitting cycle, driven by high temperature heat from a helium Gas-Cooled Reactor. Nuclear energy that emits no carbon dioxide and that can supply a huge amount of energy is a promising candidate for the massive hydrogen production. The goal of nuclear hydrogen initiative is to demonstrate the economic, commercial scale production of hydrogen using nuclear energy. However, given the prospect of increasing energy demand, of a shortage of fossil resources and of greenhouse gases release limitations, water could be the only viable and long term candidate raw material for hydrogen production.

Hydrogen Production Technologies are:

- **Steam Methane Reforming**

- Mature technology, used primarily in the fertilizer industry
- Highly efficient if CO_2 disposal not considered

- **Advanced Steam Methane Reforming**
 - Hybrid process, with non-fossil source for process heat
 - Less CO₂ production than standard reforming
- **Electrolysis**
 - Mature technology
 - Opportunity for distributed production
- **Thermo chemical Water-Splitting**
 - Potentially most efficient process
 - Not yet demonstrated on a commercial scale

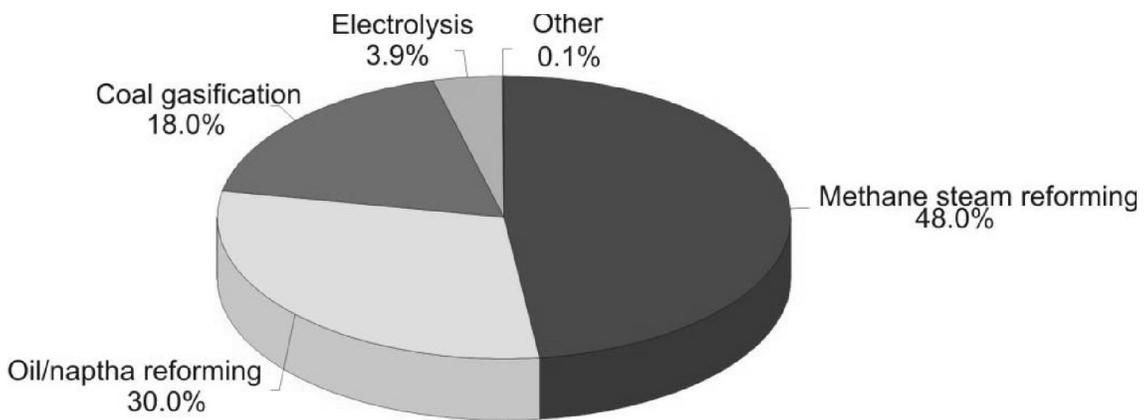


Fig 1 Hydrogen production

Importance of thermo-chemical processes

Thermo-chemical water splitting cycles have attracted interest. It has capability to be coupled to a high temperature nuclear (HTGR) or solar heat source or by hybrid solutions including both. Here the heat can be directly used (better efficiency than alkaline electrolysis). These are promising methods for efficient, CO₂ free and mass hydrogen production.

Importance of I-S (Iodine-Sulfur) thermo-chemical process

Compared to other approaches, IS process has apparent advantages. Firstly, IS cycle is a pure thermal process which indicates an economy of scale; therefore, it is suitable for large-scale hydrogen production. Secondly, IS process has high predicted thermal efficiency of ~ 50%. Thirdly, IS process is an all fluid process, which is easy to be scaled up and achieve continuous operation. Among hundreds of possible cycles, the IS cycle is a promising one, in combination with high temperature heat, having no solid phase, within the process operating conditions. With these merits, IS process is being comprehensively

studied as one of the best thermo-chemical cycle for nuclear hydrogen production. Thermo-chemical water splitting cycle offers a method for the large scale production of hydrogen. The cycle is composed of plural chemical reactions and the net chemical change of the cycle is water decomposition. The cycle works like a chemical engine to produce hydrogen by absorbing high temperature heat through endothermic chemical reactions. By utilizing high temperature nuclear heat supplied by high temperature gas cooled reactors, the cycle works as an energy converter from nuclear energy to chemical energy of hydrogen.

I-S Thermochemical Cycle

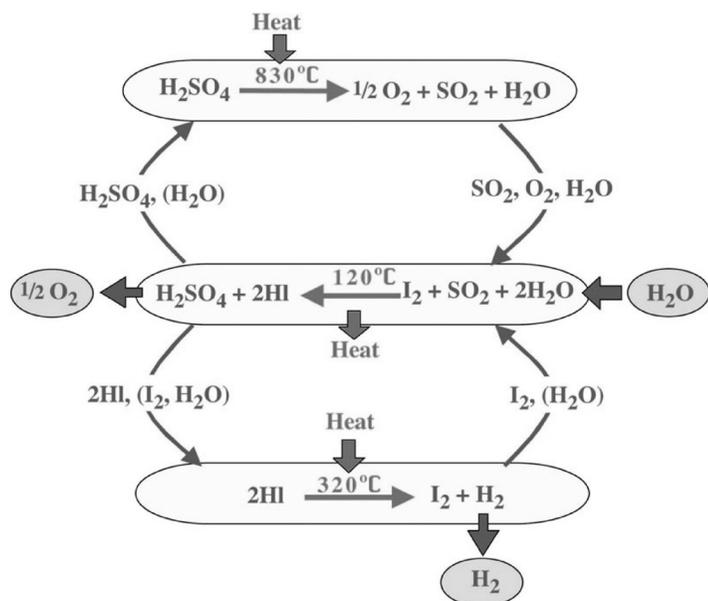


Fig. 2 Iodine-Sulfur thermo-chemical cycle

exothermically in liquid phase and produces two immiscible acid phases (sulfuric acid and hydriodic acid) in the presence of excess of iodine.

Hydrogen Iodide Decomposition

HIx phase is first concentrated by distillation and the HI-H₂O distillate at azeotropic composition (16% molar in HI) is decomposed in the vapour phase to iodine and hydrogen. It is a catalytic and equilibrium limited reaction with endothermic heat of reaction. The catalyst used in the closed loop were activated carbon as well as platinum on activated carbon.

Sulfuric Acid Decomposition

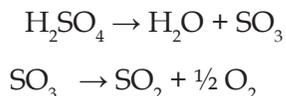
The sulfuric acid decomposition step is an endothermic 2-stage reaction: first sulfuric acid dehydration, then the sulfur trioxide catalytic decomposition.

In IS thermo-chemical cycle, water is decomposed into hydrogen and oxygen via chemical reactions using intermediate compounds/elements which are recycled. Thermo-chemical IS process is composed of following three chemical reactions.

The IS cycle is characterized by the three basic reactions shown in the Figure 1.2. In principle, the only input is water and heat; the products are hydrogen and oxygen.

Bunsen Reaction

Bunsen reaction, proceeds



The first stage decomposition occurs at temperature of 673-773K, whereas the second stage decomposition occurs at 1073K in the presence of a solid catalyst. Various catalysts have been tried out for sulfur trioxide decomposition. Iron oxide and chromium doped iron oxide catalyst have been prepared and tested in closed loop IS process operation. The results are tabulated as follows (Table-1):

Table-1 Decomposer performance at different operating conditions

Sr. NO.	H ₂ SO ₄ Conc ⁿ in vaporiser reboiler (Wt %)	Wt. of Cr doped iron oxide Catalyst in decomposer (gm)	Vaporiser bath temp °C	Decomposer Bed Temp (°C)	Evaporation rate (ml/hr)	Convesion (%)
1	98	NIL	330	850	364	16.5
2	98	930	330	850	80	60
3	98	740	330	870	48.57	66
4	98	740	330	870	23.33	84

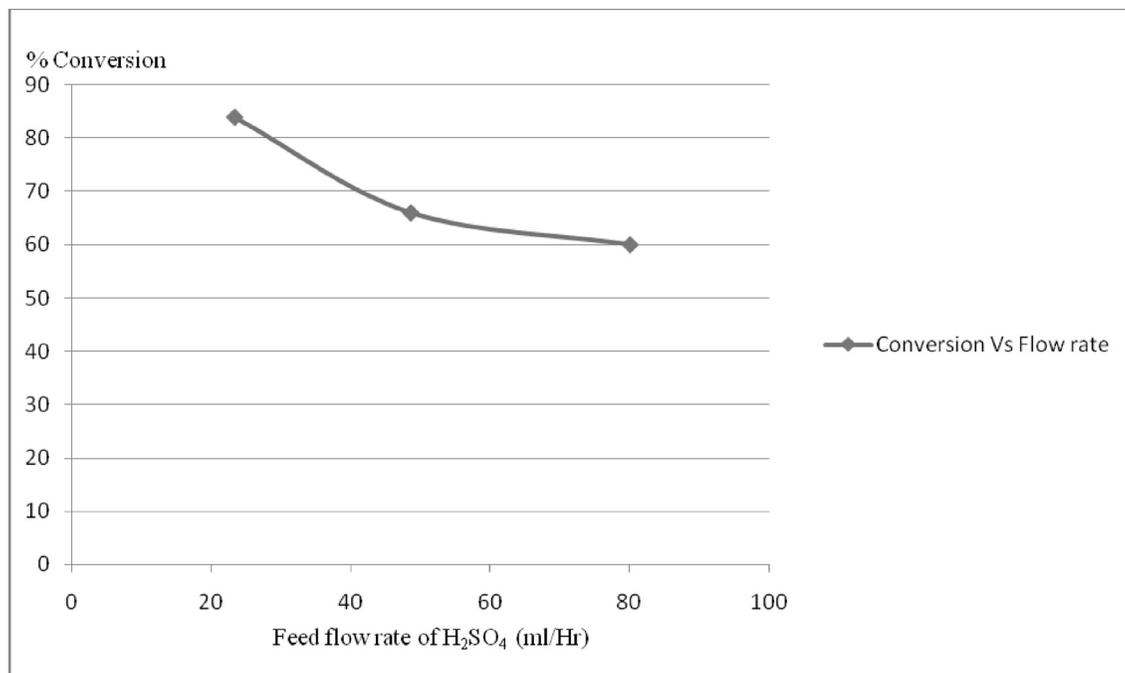


Fig 3: H₂SO₄ conversion Vs H₂SO₄ flow rate, Decomposer at 870°C & 740 g catalyst mass.

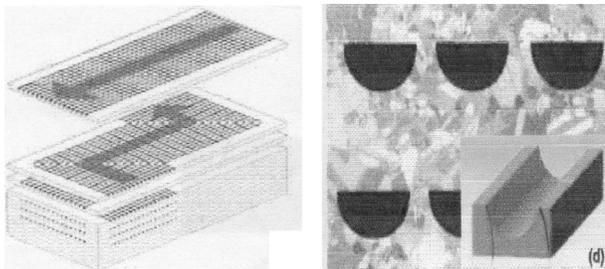


Fig 4: Printed circuit Heat Exchanger

Heat Exchanger (PCHE) as shown below also can be a good choice.

3 mm flow channels are etched on plates

Platinum catalyst thin layer

Above figure shows that conversion of SO_2 production increases as the evaporation rate decreases.

Further catalyst is being worked on to improve weight hourly space velocity to match the industry requirement.

For effective heat transfer & Sulfuric Acid Decomposition, Printed Circuit



A. Shriniwas Rao, Head, MDS, ChTD, joined DAE on 01/01/2003 after successful completion of B. Tech (Chemical Engineering) from LIT, Nagpur. He contributed in the development of PFD and P&ID of Dry reduction of uranium hexafluoride to uranium fluoride/oxide, Sulfur hexafluoride production and Iodine-Sulfur Thermochemical process-Bunsen Section. The activities such as closed loop glass system of Iodine-Sulfur thermochemical cycle for Hydrogen production and Sulfur hexafluoride production were accomplished successfully under his guidance. He gained expertise in areas such as process development, planning & execution of experimental set up and operational trouble shooting of experiments. His current interests are process simulation and process development for up-gradation of Fluorine technology and Hydrogen Energy projects. He is also faculty in Homi Bhabha National Institute and imparts training to CAT-1 trainees.

Solar Energy Induced Water Splitting for Hydrogen Generation: Material Related Issues and Challenges

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Owing to the rising standards of living and the fast growth of the world population, the future energy demand is expected to increase significantly. It is estimated that the global energy consumption rate would grow, by 2.3 % per year, from 13.5 TW (in 2001) to 27 TW by 2050 and become triple *i.e.* 43 TW by 2100 [Hoffert *et al*, 1998; Lewis *et al*, 2006]. Our dependence on the fast depleting fossil fuels that are also implicated in causing the global warming have led the scientific community at large to look for alternative energy sources/carriers.

Among various alternatives, hydrogen as fuel offers the highest potential benefits in terms of diversified supply and reduced emission of pollutants. While using hydrogen, unlike fossil fuel reactions, no carbon dioxide, carbon monoxide, sulphur dioxide or particulates are produced [Kreith *et al*, 2004]. The attractive features associated with hydrogen can be listed as:

- The combustion of hydrogen generates only steam and liquid water; hence, it is completely environmentally benign.
- Heat of combustion of hydrogen is 34.18 Kcal/g, which is almost three times to heat of combustion of petroleum.
- Energy storage capacity of hydrogen is 119 kJ/g, which is very high.
- It is non toxic.
- It is easily assimilated into the biosphere as its combustion products are recycled by plants to make carbohydrates.
- The hydrogen can be used as a feed stock for the chemical industry, enabling the production of chemicals and conventional petrochemicals.
- It is the most suitable fuel used in the fuel cells.
- Transmission of energy in the form of hydrogen is more economical than transmitting electricity through high voltage grid lines at large distances.

Realizing the importance of hydrogen as a fuel in the coming years, the Ministry of New and Renewable Energy, Government of India prepared a National Hydrogen Energy Road Map for the country to have one million hydrogen-fuelled vehicles – combustion-

engine as well as fuel-cell vehicles – on Indian roads by 2020 and to generate 1,000 MW of power through hydrogen-fuelled plants [National Hydrogen Energy Road Map, Govt. of India, 2007].

Hydrogen can be produced by a number of processes, such as electrolysis (using electricity), steam reforming (converting natural gas into hydrogen), and biomass conversion (using micro-organisms to convert organic waste products into hydrogen) [Wilhelm *et al*, 2006]. The current global hydrogen production is 48 % from natural gas, 30 % from petroleum, 18 % from coal, and 4 % from electrolysis [Air Products and Chemicals, 2003]. While all these methods are based on use of fossil fuels the challenge before the scientific community is to generate hydrogen from renewable energy sources.

Out of various renewable methods of generating hydrogen using solar energy, Photoelectrochemical (PEC) Splitting of Water is considered to be the most promising and is discussed here.

Solar Hydrogen Production: Photoelectrochemical (PEC) Splitting of Water

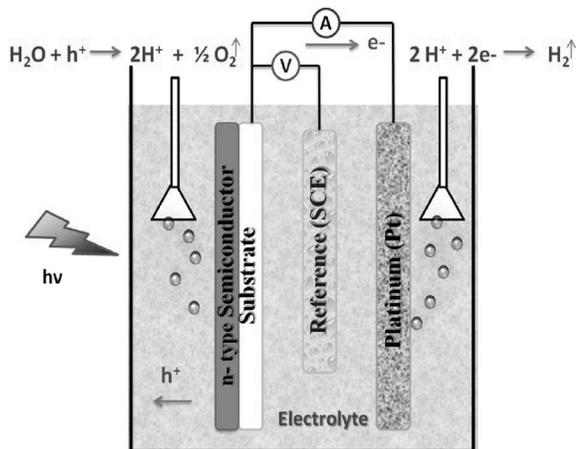
Photoelectrolysis is an elegant method towards the truly sustainable production of hydrogen. Photoelectrochemical (PEC) splitting of water is an environmental friendly method of hydrogen generation based on renewable and apparently unlimited natural resources such as water and solar energy. Assisted by solar radiation, direct splitting of water into molecular hydrogen and oxygen was demonstrated for the first time in 1972 by Fujishima and Honda in a PEC cell with *n*-type semiconductor (TiO_2) as photoanode.

PEC water splitting method offers several crucial advantages:

- (i) the ability to produce hydrogen and oxygen in separate compartments,
- (ii) the higher solar-to-hydrogen conversion efficiencies, and
- (iii) the ease of removing the photoactive material from water.

Photoelectrochemical hydrogen production system consists of a light-sensitive semiconductor as working electrode and a platinum counter electrode, both immersed in an aqueous electrolyte [Gratzel, 2001]. With exposure to sunlight, photons create photogenerated electron-hole pairs in the semiconductor; interact electrochemically with ionic species in solution at the solid/liquid interfaces. In case of *n*-type semiconductor photoelectrode, photoexcited holes drive the oxygen evolution reaction at the anode surface, while photoexcited electrons drive the hydrogen evolution reaction at the cathode surface.

The groundbreaking work of Fujishima and Honda in 1972 showed that hydrogen generation *via* splitting of water with visible light was possible at a semiconductor electrode. An explosion of scientific research soon followed in this area. However, 40 years later, a visible light-driven water-splitting system that is efficient and stable still



Photoelectrochemical based solar hydrogen production system

et al, 1998; Khaselev *et al*, 2001; Licht *et al*, 2001].

Material Related Issues

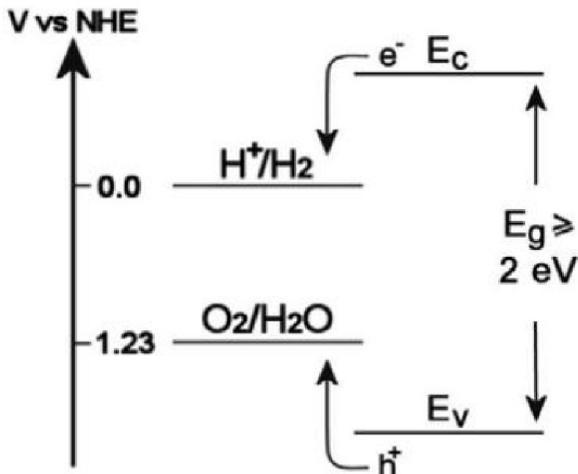
There are various material related issues that need addressing before the desired goal of developing the most efficient material is achieved for taking this technology to the commercial level. These include band gap, electronic energies, chemical stability, charge transfer kinetics etc. to be efficiently used in PEC cell. Although these properties have been identified, it has so far not been possible to have a material which satisfies all these requirements simultaneously.

Band gap

The spectral region in which the semiconductor absorbs light is determined by the band gap of the material. The maximum value of the band gap is determined by the solar spectrum. Below 400 nm the intensity of sunlight drops rapidly, imposing an upper limit of ~ 3.1 eV on the band gap. Hence, the optimum value of the band gap should be somewhere between 1.9 and 2.1 eV, which is within the visible range of the solar spectrum. Theoretically thermodynamic potential of the order of 1.23 eV ($\Delta G = 237$ kJ/mol) is required for the spontaneous generation of hydrogen and oxygen by water splitting but taking into account the energy losses (~ 0.8 eV) caused by the recombination of the photogenerated charge carriers, resistance of the electrodes and electrical connections and voltage losses at the contacts etc., a voltage of ~ 1.8 eV is needed for spontaneous water splitting which corresponds to a wavelength of ~ 650 nm. Accordingly, minimum band gap of any semiconductor is determined by the energy required to split water (1.23 eV) plus the thermodynamic losses (~ 0.4 eV) and the overpotentials that are required at various points in the system to ensure sufficiently fast reaction kinetics (~ 0.3 - 0.4 eV) [Bolton *et al*, 1985; Bak *et al*, 2002; Murphy *et al*, 2006]. Thus, a semiconductor with optimum band gap (1.8-2.2 eV) is considered more suitable in PEC water splitting.

remains an elusive goal. The main work in PEC splitting of water still concern for increasing the efficiency and stability of the photoactive materials [Nowotny *et al*, 2005; Meng *et al*, 2007] to achieve the required efficiency target of 10 % that will be viable for commercialization [U.S. Department of Energy, 2009]. At the moment stable metal oxide based PEC semiconductor materials have quite low efficiency [Fujishima *et al*, 1972; Gratzel, 2001; Cesar *et al*, 2006] while high efficiency (above 10%) can be achieved by the materials based on multijunction conventional semiconductors but they are degraded within a short time [Kocha

Position of Band edges

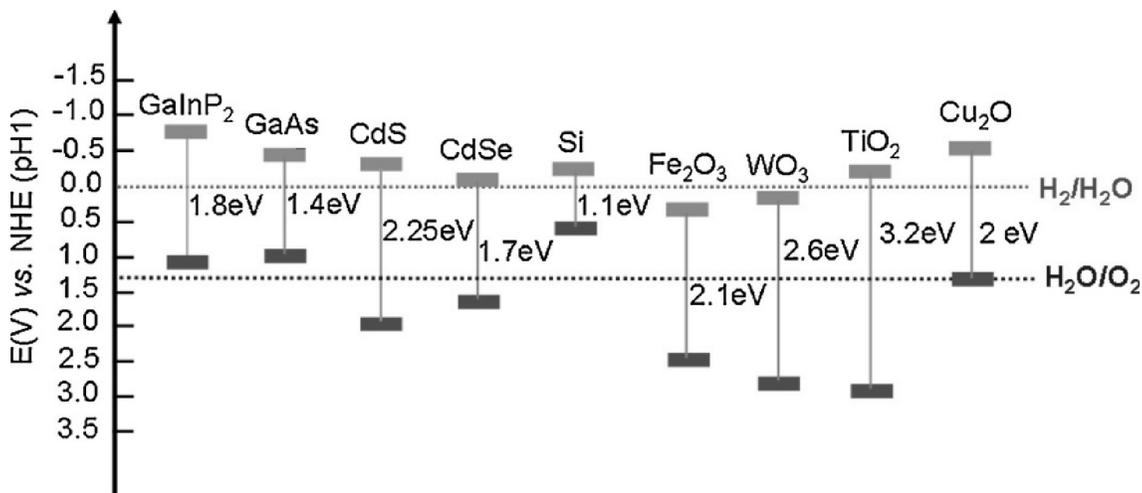


Ideal straddling condition of conduction and valence band edges of a semiconductor with reduction and oxidation potentials of water.

The positions of the conduction and valence band edges of the semiconductor is important in determining the spontaneous water splitting and also the stability of material in the PEC cell. A semiconductor capable of spontaneous water splitting must have band gap of ~ 2 eV with conduction band energy (E_c) higher and valence band energy (E_v) lower than that of reduction E_{red} (H_2/H^+) and oxidation potential E_{ox} (OH^-/O_2) of water respectively [Maeda *et al*, 2011]. These conditions are energetically favourable for efficient transfer of charge carriers between semiconductor and electrolyte. Most non-oxide semiconductors are able to reduce, but not oxidise water. Conversely, most oxide

semiconductors are able to oxidise, but not reduce water. Since the stability criterion favours oxide semiconductors, the reduction of water appears to be challenging.

An alternative and exciting possibility to overcome the limitations imposed by the band energies is by exploiting quantum-size effects. When reducing the size of a semiconducting particle to values that approach the characteristic wavelength of the



Band positions of several semiconductor materials in contact with aqueous electrolyte at pH 1 (green lines represent the upper edge of the valenceband whereas the red ones represent the lower edge of the conduction band). The visible spectrum corresponds to energies from 1.56 eV (800 nm) to 3.12 eV(400 nm).

electrons and holes, the band gap of the material increases. Hence, EC and EV increase and decrease, respectively, the amount of which is determined by the effective masses of the electrons and holes [Brus, 1986]. For instance, by decreasing the particle size of Fe₂O₃ it might be possible to raise the conduction band to a level just above the reduction potential of water [Vayssieres *et al*, 2005]. Since metal oxide semiconductors usually have comparatively large effective electron and hole masses, the particle size needs to be reduced to less than ~10 nm before quantum-size effects become noticeable. The consequence of using quantum-confined structures is the blue-shift of the absorption spectrum due to the increased band gap value. This should be taken into account when aiming for an optimal match with the solar spectrum. Moreover, the positions of the energy bands with respect to the water redox potentials may also shift during illumination (*i.e.* band edge “unpinning”) [Memming, 2000].

Resistance

In photoelectrochemical cell, semiconductor metal oxides have been recognized for their potential as high performance photoanodes as they satisfy several criteria *viz.* the appropriate bandgap, high stability and elevated values of flat band potential. The other key factors considered for high performance in PEC water splitting process are low electrical resistance and good corrosion resistance in aqueous solution [Bak *et al*, 2002; Khan *et al*, 1993]. In PEC water splitting process, electron mobility in semiconductor leads to reduced electrical resistance and enhanced electron transfer efficiency. Improvement of conversion efficiency in the semiconductor could potentially be achieved by minimizing the resistance between material and the substrate.

The major sources of energy losses derived from the ohmic resistances of the external and internal circuits of the PEC include:

- electrodes
- electrolyte
- electrical leads (wires)
- electrical connections
- measuring and control equipment

In order to achieve the maximum conversion efficiency, the electrical resistances of all of the above said items must be minimized.

Charge transfer kinetics

Transfer of holes across the *n*-type semiconductor/electrolyte interface should be sufficiently fast in order to compete with the anodic oxidative photocorrosion. Furthermore, it should also be sufficiently fast in order to avoid the accumulation of holes at the surface, as this would lead to a decrease in the electric field and associated increase in electron-hole recombination. This is especially important for very small

(*viz.* quantum-confined) structures, since they cannot sustain an electric field that is large enough to effectively separate the photo-generated electrons and holes. For such systems, the interfacial charge transfer kinetics need to be sufficiently fast in order to avoid recombination. To improve the kinetics of hole transfer, catalytically active surface species can be added. A known example of effective oxygen evolution catalyst is RuO_2 , whereas Pt is usually employed as a catalyst for hydrogen evolution [Memming, 2000].

Stability

The stability of photoelectrode against (photo) corrosion is a severe issue that limits the usefulness of many photo-active materials. Most non-oxide semiconductors, such as Si, GaAs, GaP, CdS, etc., either dissolve or form a thin oxide film which prevents electron transfer across the semiconductor/electrolyte interface. Almost all metal oxide photo-anodes are thermodynamically unstable, which means that the photo-generated holes are able to oxidise the semiconductor [Memming, 2000]. However, if the kinetics of charge transfer across the interface (oxidation of water) is faster than the anodic decomposition reaction, photo-corrosion is inhibited, although it can remain as a side-reaction. For example, TiO_2 and SnO_2 show excellent stability over a wide range of pH values and applied potentials, while ZnO always decomposes in aqueous environments upon illumination. Fe_2O_3 represents an intermediate case, for which the stability appears to depend on the presence of dopants, pH and oxygen stoichiometry [Shinar *et al*, 1983]. The general trend is that wide-band gap metal oxide semiconductors are stable against photo-corrosion, while small-band gap metal oxide and non-oxide semiconductors are not. While this is in obvious conflict with the requirement of visible light absorption, it does not represent a fundamental limitation.

Targets to be achieved in PEC Water Splitting

The aim of solar hydrogen production research is to split water into hydrogen and oxygen using solar energy as the energy source, with efficiencies high enough to allow production of hydrogen on a commercial scale. While the research efforts in the PEC splitting of water for hydrogen have come a long way but we are still far from the commercial viability. In PEC experiments to date, solar-to-hydrogen (STH) efficiencies between 12-16 % have been demonstrated in $\text{GaInP}_2/\text{GaAs}$ hybrid tandem photocathodes [Honda *et al*, 1979; Khaselev *et al*, 2001] while photocurrent of 15 mA cm^{-2} at 0.82 V versus SHE has been obtained in case of iodine-doped iron-oxide thin-film electrodes [Khan *et al*, 1993]. Both these systems suffer from high cost and limited durability which are the key barriers to practical PEC hydrogen production, and breakthroughs in synthesis and in surface stabilization are needed. It is well accepted that the system to be commercially viable should be able to demonstrate [Bak *et al*, 2002]:

- i) conversion efficiency > 10%
- ii) current density (J_p):- 10-15 mA/cm^2
- iii) production cost cut down by 3-4 times, and
- iv) durability of more than 2000 hrs.

These goals are based on current fuel and infrastructure costs and are likely to change depending on future economic and political conditions. Hydrogen can prove to be an environmentally clean energy fuel for which a complete infrastructure has to be in place for storing, transporting and distributing hydrogen before it can be viable commercially.

Strategies for Improvement of Semiconductor Performance in PEC Water Splitting

Various techniques such as, reduction in particle size (nanomaterial), addition of electron donors, anion and cation doping, swift heavy ion irradiation, dye sensitization, layering of other metal oxides etc., have been reported in the literature for improving the photoelectrochemical response of semiconducting material. A brief description of various strategies is given below:

Doping

Doping may be a useful strategy in order to improve the absorption of wide band gap semiconductors such as TiO_2 , SrTiO_3 , SnO_2 , ZnO etc. in the visible range of the solar spectrum. Doping is the standard procedure to reduce the band gap and tune the band edge characteristics of the semiconductors. When applied to semiconductors, the term doping refers to the intentional introduction of impurities to the material for the purpose of modifying electrical characteristics. An ideal dopant must increase the valence band edge, thus reducing the band gap without lowering the conduction band and either improve or at least minimize electron-hole recombination, so as to minimize any loss in quantum yield [Lee *et al*, 2004; Huang, 2008].

It was observed that the chemical composition of metal oxides can be altered by doping which may lead to change in optical and electrical property of the material [Huang, 2008]. Specifically, the metal or the non-metal (oxygen) component can be replaced in order to alter the material's optical properties. It is desirable to maintain the integrity of the crystal structure of the photocatalytic host material and to produce favorable changes in electronic structure.

Swift Heavy Ion Irradiation

The irradiation of semiconductors with swift heavy ions (SHI) leads to creation of a wide variety of defect states in the material. Hence, it can be exploited as a method to reduce the band gap energies of high band gap semiconductors. As the energetic ions pass through the material, they lose the energy and materials gain the energy, which results in modifications of material properties. The interaction of the ion with material is the deciding factor in the ion beam-induced material modification. These energetic beams can induce structural and morphological changes depending upon ion energy, fluence and ion species, which can be attributed to grain fragmentation or defects. Upon SHI irradiation of nanocrystalline semiconductor materials, the possibilities that exist

are: (i) creation of amorphous band in the lattice, (ii) development of subnanoparticles on account of grain fragmentation due to confinement of energy in the small volume of nanoparticles, and (iii) impurity segregation on grain boundaries. Such modifications, occurring at atomic and grain level, would lead to alteration in properties *viz.* bandgap, resistance and structural defects, which are expected to modify the photoelectrochemical response of the material [Chaudhary *et al*, 2006; Solanki *et al*, 2013].

Our group in D.E.I. has pioneered effects of SHI irradiation on α -Fe₂O₃, CuO, Cu₂O, ZnO, BaTiO₃ and TiO₂ for the development of more efficient PEC photoelectrode [Chaudhary *et al*, 2006; Satsangi *et al*, 2008; Gupta *et al*, 2009; Singh *et al*, 2010; Solanki *et al*, 2011; Solanki *et al*, 2013].

Dye-Sensitization

Sensitizing semiconductors by dyes to achieve a better use of solar light has been intensely investigated in the fields of photovoltaics, photocatalysis and photoelectrochemistry [Nazeeruddin *et al*, 1993]. Most of the dye sensitized solar cells operate in a fashion that first, the dye is adsorbed on the surface of nanocrystalline metal oxide semiconductor which absorbs the photon and an electron is excited to the LUMO (lowest unoccupied molecular orbital) from the HOMO (highest occupied molecular orbital) in the dye. The photoinjected electron then migrates to the conduction band of the semiconductor and moves through the nanocrystalline semiconductor network to the external circuit. The hole created after the excitation at the HOMO of the dye is recovered by transfer of an electron from the redox electrolyte. The success of a dye-sensitized cell depends upon the collection of photogenerated electrons at the external circuit without any disturbance. For such electron transfer, the electrode should fulfil the following conditions: (i) possess good transport property in the semiconductor matrix, (ii) fast recovery of the electron to the oxidized dye (an electron supply from the redox electrolyte), and (iii) a good electron separation (charge injection from the sensitizer to the semiconductor). So it can be seen that overall process is limited by the electron transport in the semiconductor. An injected electron might recombine with the redox electrolyte, the oxidized dye, traps in the semiconductor or the valence band of the semiconductors. The recombination with the oxidized dyes takes tens of nanoseconds to a millisecond, depending on the density of electrons in the metal oxide semiconductor [Haque *et al*, 2000]. The instability of dye-sensitized photoelectrodes, limits its application in PEC water splitting process.

Bilayered Systems

Bilayered systems are the most exciting and recent strategy to achieve absorption of large part of the solar spectrum for increasing the efficiency of the process. Bilayered systems comprises of two semiconductors possessing different energy levels for their corresponding conduction and valence bands. Various studies with respect to PEC water splitting have shown improved visible-light photoactivity with bilayered semiconductors, *viz.* CdSe/CdS [Martirosyan *et al*, 2001], SnO₂/CdSe [Nasr *et al*, 1997], TiO₂/CdS [Yin *et*

al, 2007; Chi *et al*, 2008], TiO₂/CdSe [Liu *et al*, 1993], CuO/Cu₂O [Wijesundera, 2010; Zhang *et al*, 2012], ZnO/CdS [Dang *et al*, 2010], ZnO/NiO [Ajuba *et al*, 2010], SrTiO₃/Fe₂O₃ [Wang *et al*, 2007] and WO₃/Fe₂O₃ [Luo *et al*, 2007]. In a bilayered system, the small band gap semiconductor is primarily responsible for visible light absorption and sensitizing the large band gap semiconductor through electron and/or hole injection. Efficient electron injection requires that the bottom of the CB of the small band gap semiconductor be above the bottom of the CB of the large band gap semiconductor [Kamat, 2007; Hao *et al*, 1999]. The electron transfer between the two semiconductors could also enhance the charge separation and inhibit the recombination rate by forming a potential gradient at the interface. These composite heterostructures combine the properties of two semiconductors in unique architecture to address the shortcomings of individual semiconductors as photoanode, representing a new and promising approach for PEC and other applications.

Some of the significant features of bilayered modification strategy in PEC cell are listed as:

- Absorbance of large band gap material shifts towards visible region *i.e.* red shift.
- Improvement in charge separation of both the material resulting in decrease of recombination of charge carriers.
- Increase in lifetime of charge carriers.
- These systems shows synergistic behaviour and are capable of satisfying at least one energetic requirement *i.e.* matching the conduction band minimum (CBM) or (VBM) with either the H₂ reduction or O₂ oxidation potential.
- Possess different band bending properties compared to single semiconductor material near the heterojunction and have shown more promising performance in PEC cell.

The details on all the above said aspects with reference to Photoelectrochemical Splitting of Water for Hydrogen Generation would be discussed.

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Prof Sahab Dass after completing his education from Dayalbagh institutions obtained Ph.D. in Chemistry in 1985 from Agra University and was awarded the ISCA Young Scientist Award the same year. He joined the Dayalbagh Educational Institute (Deemed University) as Lecturer in the Dept. of Chemistry in the year 1986 where he is currently serving as Professor. Prof Dass is committed to research in renewable energy and is presently involved in the production of hydrogen by solar energy induced splitting of water using nanostructured semiconductors by photo-electrochemical route. He has completed number of research projects funded by Dept of Science and Technology, University Grants Commission, World Bank etc . He was the co-ordinator of recently completed prestigious DST-NSF (MWN) collaborative project with University of Maryland, USA on Solar Hydrogen Production. Prof Dass has published about 90 papers in International and national journals, supervised 10 PhD students, delivered invited talks and chaired sessions in National and International Conferences in India and abroad. He has recently been appointed as visiting Professor in the University of Malaya, Kuala Lumpur, Malaysia.

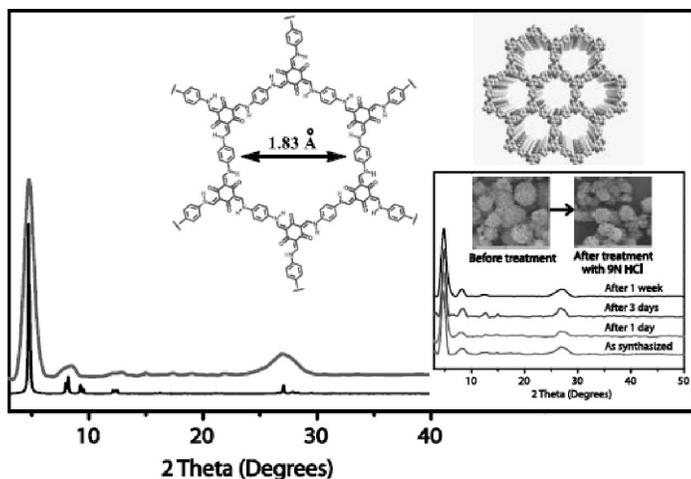
Porous Crystalline Frameworks with/without Metal: Hydrogen Storage, Carbon Capture and Proton Conduction

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Covalent Organic Frameworks (COFs) are lightweight porous crystalline material, constructed via strong covalent bonds between elements like C, B, O, N, Si. It is believed that reversibility in covalent bond formation during synthesis is required for the successful crystallization COFs, which is necessary to identify their specific structural details precisely. Irreversible organic reactions always lead to the formation of amorphous porous polymeric materials, separately categorized as Porous Organic Polymers (POPs) or Porous Aromatic Frameworks (PAFs). Little improvement in water stability was achieved by pyridine doping and alkylation of COF pore walls. However these modifications always lead to decrease in the gas adsorption properties even though it enhances the hydrolytic stability to a small extent. Hence, stability problem in COFs still remain a



challenge which prevents the usage of COFs for diverse practical applications. Here we report the first time synthesis of new COFs by a combination of reversible and irreversible organic reaction. These COFs are stable and remain crystalline in acid (9N HCl), base (9N NaOH) and water.

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Research Interest

- Hydrogen Storage and Carbon dioxide sequestration in Metal Organic Frameworks (MOFs) and Covalent Organic Frameworks (COFs).
- High throughput synthesis of MOFs and COFs.
- Crystal Engineering in Metal Organic Gels.
- Solid State Proton Conducting Materials.

Carbon-Carbon Bond Forming Reactions for Biomass Utilization Processes

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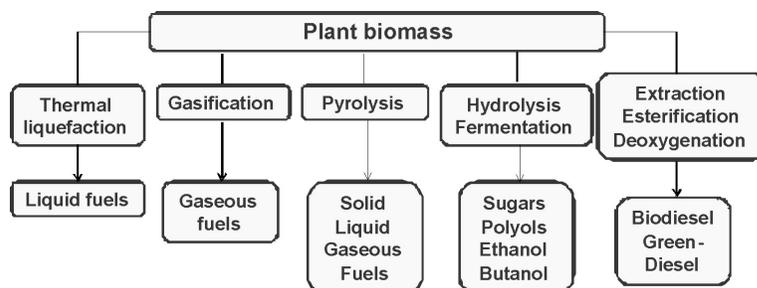
1.1 Introduction

Development of a renewable liquid transportation fuel, specifically for air-transport is one of the major challenges faced by scientists. As biomass provides a renewable source of carbon it is a suitable alternative and supplement to the traditional petroleum derived feedstocks. There is need to develop technologies that do not require significant infrastructure changes and can easily convert a variety of biomass types to drop-in liquid fuels.

While there have been a number of different techniques used to convert biomass to liquid fuels, those which can quite efficiently break down biomass directly into a liquid, such as, pyrolysis and hydrolysis [1] are particularly promising. The resulting liquids, such as, bio-oil and platform chemicals from sugars and polyols, are a complex mixture containing a large number of oxygen functionalized compounds. Unfortunately, these liquids have a number of issues that must be resolved before they can be effectively utilized as a liquid transportation fuel including acidity, reactivity, and low energy density. With this in mind, heterogeneously catalyzed C-C bond forming reactions are potentially valuable for the upgrading of bio-oil and biofuel platform chemicals such as sugars and polyols.

1.2 Biomass conversion processes

There have been a number of different processes developed for biomass to fuel conversions. These are primarily biochemical and thermochemical processes. Common thermochemical processes are liquefaction, combustion, gasification, and pyrolysis while typical biochemical processes are digestion and fermentation [2]. While combustion and digestion are used more for electricity and methane production, some of these processes can still allow production of desirable liquid fuels.



For example, gasification creates a syngas mixture that could be subsequently upgraded via Fisher-Tropsch synthesis to make transportation-length hydrocarbons [3].

Liquefaction can also create liquid fuels, but is largely ignored as an option due to its high costs [2]. Fermentation is primarily used for the production of ethanol and butanol, but is not likely a good option in development of a widely transportable and inexpensive drop-in fuel due to limitations on feedstock as well as its different chemical properties in comparison to more common hydrocarbons. However, the products of pyrolysis, plant-oil deoxygenation and lignocellulose hydrolysis are especially well suited for the creation of liquid drop-in fuels. This is due to reasons such as their low costs, simple process, use of existing infrastructures, and feedstock flexibility.

1.3 Bio-oil, lipids, sugars, polyols - composition

The oil derived from the pyrolysis of biomass is an extremely complex mixture of oxygenated compounds that varies widely based on the type of biomass used as well as process variables. Lignin fraction of biomass gives a high content of phenolic compounds on pyrolysis, while the breakdown of the cellulose and hemicellulose components results in smaller oxygenated molecules. These can be upgraded into desirable fuels by C-C coupling reactions. Due to the complexity of the feedstock, the resulting bio-oil has a diverse range of chemical species - over 300 different compounds [4]. Organics such as

esters, ketones, sugars, phenols, guaiacols, syringols, furans, acids, alcohols, aldehydes, along with other molecules containing multiple functional groups are prevalent in the oil, along with 15-30 wt% water [4]. Energy density of the bio-oil is low (less than 50 % of fuel oils) due to the prevalence of oxygenated compounds (oxygen makes up 35-40 wt% of the oil).

Lipids are triglycerides of long chain fatty acids present in plant oils, animal fats, algal oils and microbial oils. These triglycerides can be trans-esterified to produce biodiesel, or they may be hydroprocessed to produce petroleum-like drop-in biofuels for road and air transport [5-12]. C-C coupling reactions are undesirable here, as they produce longer chain waxy compounds which tend to choke the reactor and rapidly deactivate the catalyst [10]

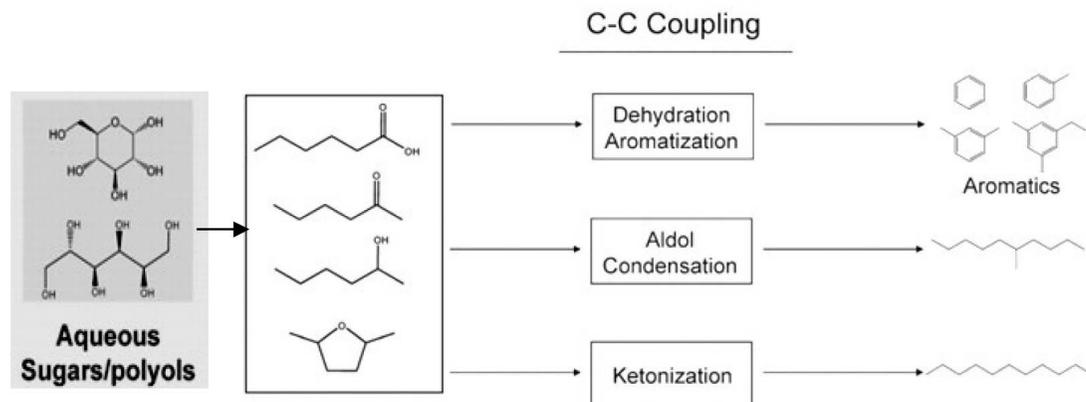
Hydrolysis (either using acids or enzymes) into sugar, polyols (from cellulose and hemicellulose) and lignin fractions provides platform chemicals. Strategies for converting these platform chemicals (carbohydrates and polyols) into liquid transportation fuels, involves the combination of various processes including catalytic reforming, reduction, dehydration, alkylation, aromatization, C-C coupling (aldol condensation, ketonization), hydrogenation, and hydrodeoxygenation.

1.4 C-C coupling reactions for bio-oils, lipids, sugars, polyols

There are a couple of different processes that can help alleviate some of the aforementioned problems in the use of above-discussed feedstocks to make hydrocarbon type liquids.

These operations consist of both pre-treatments of the biomass as well as post-catalytic conversions. The treatments could then be tailored to create an oil product modified for particular applications. Post-catalytic treatments have been found to be extremely beneficial to upgrading of biomass-derived liquid feedstocks to fuel. One common technique is to perform hydrodeoxygenation (HDO) of the oil. It is easy to see how this would create a better fuel as oxygen is removed, ridding the oil of carboxylic acids as well as other reactive molecules, while increasing energy density. This method has been the topic of a number of recent publications by us [5-8, 10-12]. However, with the large amount of oxygen contained in the oil, massive quantities of hydrogen will be needed for this process to be successful. A downside to HDO of bio-oil is that the many low molecular weight molecules in the bio-oil will be unusable as liquid fuel sources after hydrogenation. This will result in the loss of significant amounts of renewable carbon that could have been used for our desired applications. Therefore hydrodeoxygenation as the primary upgrading step is not preferred for bio-oils, but is required for upgrading biomass derived lipids.

Another upgrading option would be to perform catalytically controlled reactions that could remove oxygen and carboxylic acids as well as increase carbon chain lengths of the small molecules in bio-oils, sugars and polyols, before a final hydrodeoxygenation step. Here, the low molecular weight organic acids first undergo decarboxylative coupling to form small ketones. These ketones are then reacted with the prevalent low molecular weight aldehydes present in the oil using the aldol condensation. *Ketonization* and *aldol condensation* reactions are ideal for the bio-oil and biomass derived platform chemicals (from sugars and polyols), upgrading process as they can efficiently create carbon-carbon bonds between the low molecular weight acids, ketones, and aldehydes so that they are not eliminated as potential liquid fuels during hydrodeoxygenation. The two reactions are also beneficial in that they remove oxygen in the form of water and CO₂ as well as ridding the oil of the acidic carboxyl groups.



Scheme of the process for the catalytic conversion of sugars and polyols derived platform chemicals into liquid hydrocarbon fuels via C-C coupling reactions.

Dumesic and his team are intensively working on catalytic conversion of sugars and polyols to liquid hydrocarbon fuels [13]. First step of this process is to convert sugars and polyols into a mixture of monofunctional compounds for example alcohols, ketons, aldehydes, carboxylic acids and other over Pt-Re catalyst. The oxygen is removed in reaction called hydrogenolysis and hydrogen needed for this reaction is produced from water-gas shift reaction. Most of the remaining oxygen is removed in the following step to upgrade intermediate into fuel, that involves aldol condensation, ketonization, and oligomerization reactions. These reactions eventually lead to formation of various types of fuel-like hydrocarbons.

In case of deoxygenation of lipids [5-8, 10-12] such C-C coupling condensation reactions are counter-productive as they result in waxy long chain oxygenated products which tend to accumulate on the catalyst surface, choke the reactor and cause rapid catalyst deactivation. The reaction conditions have to be optimized to minimize condensation reaction during this process [10].

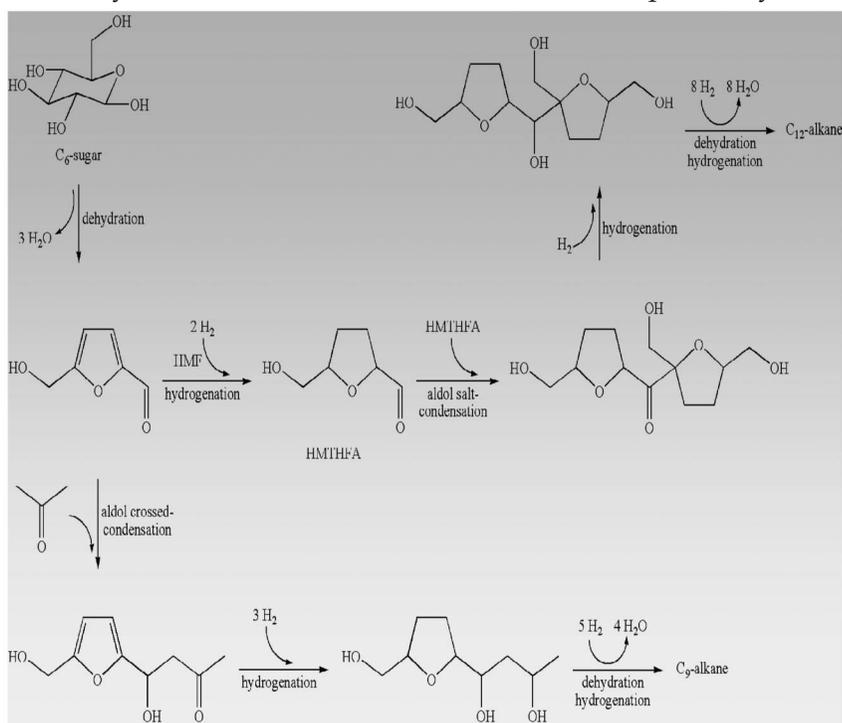
1.4.1 Aldol condensations

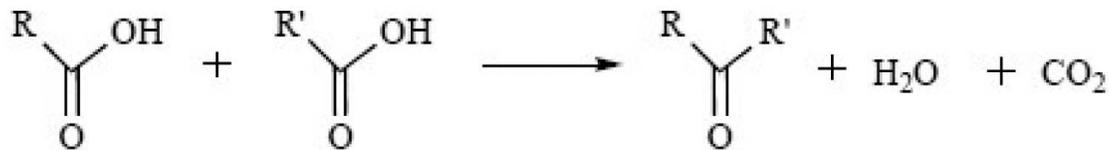
The aldol condensation is a well known reaction in organic chemistry usually promoted through the use of strong acid or bases. However, uses of these types of catalysts will likely cause undesirable side reactions. Ideally cooperative

catalysis allows for weaker acids and bases to work in tandem to promote the reaction. Use of aluminum phosphate catalysts allowed for the tuning of the acidity and basicity of the materials through a nitridation process. Through performing aldol condensations using model bio-oil compounds acetaldehyde, acetone, and MEK, it was found that acid and base sites were both needed to efficiently promote the cross condensation of the aldehyde and ketone.

1.4.2 Ketonization

Ketonization of carboxylic acids is also an ideal reaction for bio-oil and biomass derived





platform chemicals (from sugars and polyols) upgrading as it removes acidity and oxygen as well as creates C-C bonds. However, this reaction is almost always performed in the vapor phase due to the high temperatures necessary to achieve significant conversions. In order to try to engineer a more active catalyst able to perform the reaction at lower temperatures, more must be understood about ketonization. Condensed phase ketonization was examined using ceria catalysts calcined at different temperatures. It was found that the reaction proceeded either through the formation of carboxylates in the bulk or on the surface of the catalyst depending on the temperature of calcination. Kinetic studies found that the mechanism for both these routes was likely the same. It was found that the temperature of ketonization greatly influenced the reaction pathway with intermediate temperature reactions resulting in metal carboxylate formation in the bulk and high temperatures promoting the reaction on the surface. Metal carboxylate formation and decomposition are of supreme importance for ketonization and are influenced by mixing of oxides. Research into ketonization is a significant step forward into understanding of the reaction and how it can be applied to the upgrading of biomass derived liquids.

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Qualification

Publications:

Papers:

~70 (Peer Reviewed)

**Conferences/
Presentations**

30

Patents:

18 (International: 7 Indian: 11)

Previous Affiliations

Toyota Central R & D Labs Inc., JAPAN (2003 -2007)

NI-AIST, Osaka, JAPAN (2000-2003) – JSPS-STA Fellow

Academia Sinica, Taiwan (1999-2000)

National Chemical Laboratory, JRF-SRF(1995-1999)

**Current Research
Areas**

Nanostructured Catalyst designing for petroleum refining, biomass conversion to fuels for road and air transport.

Dye Sensitized Solar Cells.

**Awards/
Fellowships:**

JSPS-STA Fellowship (Japan). AIST Postdoctoral Fellow (Japan).

Lise Meitner Postdoctoral Fellowship (Austria). Postdoctoral Fellowship - Academia Sinica & National Taiwan University, Taiwan. CSIR, India Research Fellowships.

PhD Students

5 (current), working on nanoporous oxides based catalysts for organic transformations, biomass conversion, refining

Transition-Metal-Free Carbon-Carbon and Carbon-Heteroatom Bond-Forming Reactions Using Arynes

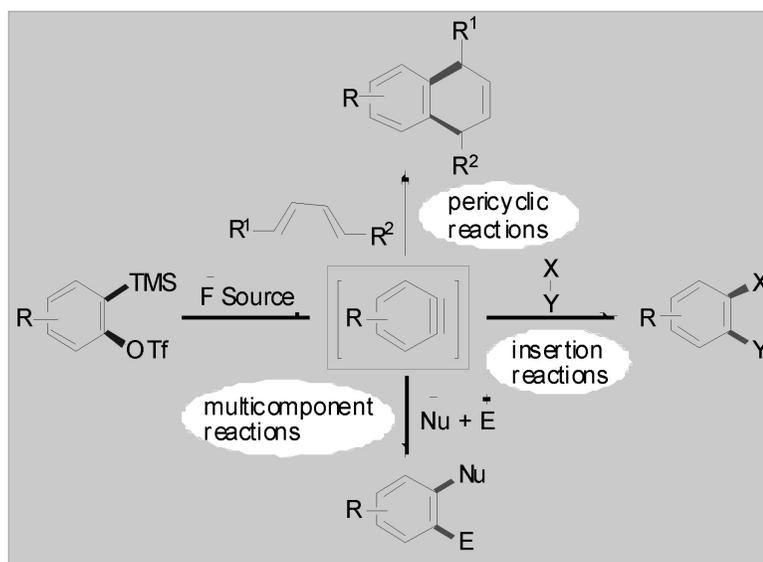
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Abstract

Arynes are highly reactive intermediates poised to offer numerous applications in organic synthesis. They are uncharged transient intermediates derived from aromatic systems by the formal abstraction of two hydrogen atoms from adjacent positions. A concise account of the major developments that occurred in the transition metal-free carbon-carbon and carbon-heteroatom bond-forming reactions employing arynes forms the subject matter of this presentation.

This presentation is aimed at highlighting recent developments in transition-metal-free carbon-carbon and carbon-heteroatom bond-forming reactions utilizing a versatile class of reactive intermediates, *viz.*, arynes, which hold the potential for numerous applications in organic synthesis.¹ Key to success of the resurgence of interest in the rich chemistry of arynes is primarily the mild condition for their generation by the fluoride-

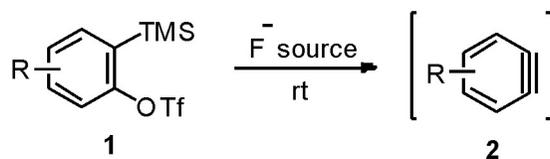


Scheme 1. The versatile transition-metal-free applications of arynes

induced 1,2-elimination of 2-(trimethylsilyl) aryl triflates.² Consequently, arynes have been employed for the construction of multisubstituted arenes of structural diversity and complexity. The versatile transition-metal-free applications of arynes include cycloaddition reactions, insertion reactions and multicomponent reactions (Scheme 1). In addition, arynes have been found applications in natural product synthesis. A concise ac-

count of the major developments that occurred in this field during the past eight years forms the subject matter of this presentation.

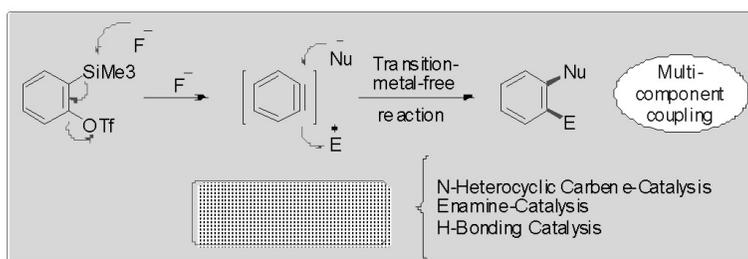
In view of the extreme reactivity of arynes, they have to be generated in situ. Traditionally, arynes have been generated by the treatment of aromatic halides with strong bases like sodium amide. The highly basic reaction condition is however unfavourable in the case where the molecule contains base-sensitive functional groups. In 1983, Kobayashi and co-workers developed a facile method for the generation of arynes **2** by the fluoride-induced 1,2-elimination of 2-(trimethylsilyl) aryl triflates **1** (Scheme 2).² The mild reaction conditions involved in this procedure are compatible with a variety of reagents, substrates, functional groups and even transition metal catalysts are well tolerated. Because of these reasons, today, this approach is the most widely used and the most efficient one for the generation of arynes.



Scheme 2. Mild method for the generation of arynes

Pericyclic Reactions

Due to the high electrophilicity of their C-C triple bond, arynes act as excellent dienophiles in various pericyclic reactions. Consequently, pericyclic reactions are used both as a method for the detection of arynes and as a valuable tool for the synthesis of various benzene derivatives. The different aspects of pericyclic reactions of arynes have received a lot of attention and a number of reviews have addressed various aspects of this reaction.

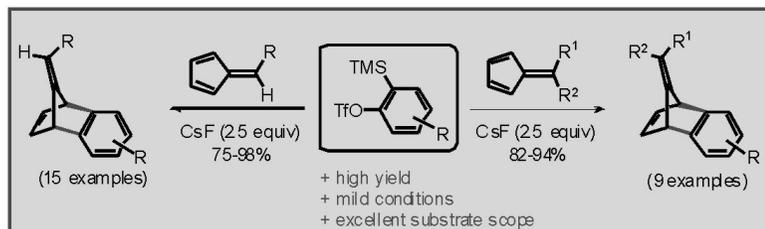


Angew. Chem., Int. Ed. **2012**, *51*, 1520.

Chem. Soc. Rev. **2012**, *41*, 3140.

At CSIR-NCL, our current research is focusing on transition-metal-free carbon-carbon and carbon heteroatom bond-forming reactions using arynes. This one-pot construction of molecular complexity has been applied to the synthesis of various heterocyclic scaffolds and 1,2-disubstituted arenes. The application of arynes in transition-metal-free

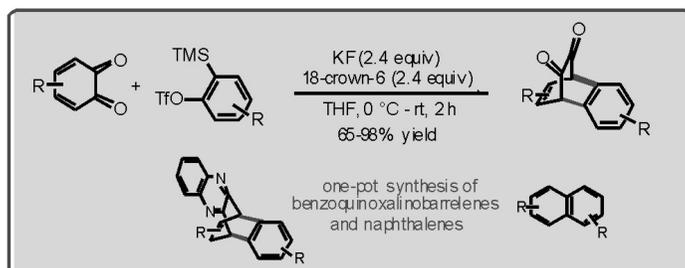
multicomponent coupling reactions, pericyclic reactions and insertion reactions has been recently reviewed. Presently, the research group is focusing on expanding the scope of multicomponent reactions using arynes by the catalytic generation of nucleophiles (by NHC-catalysis, enamine catalysis and H-bonding catalysis).



Org. Lett. **2012**, *14*, 4098.

of 2-(trimethylsilyl) aryl triflates undergoes efficient cycloaddition with 6-substituted and 6,6-disubstituted pentafulvenes leading to the formation of benzonorbornadiene derivatives. The benzonorbornadienes have potential applications in organic chemistry. Ring opening metathesis polymerization (ROMP) of using Mo carbene initiators afforded highly stereoregular polymers. In addition, the addition of benzonorbornadienes to 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) resulted in a convenient entry to polycyclic azoalkanes, which are valuable target molecules.

Very recently, a new protocol for the efficient Diels-Alder reaction of 1,2-benzoquinones with arynes is reported. The aryne generated by the fluoride induced 1,2-elimination of 2-(trimethylsilyl) aryl triflates undergoes a facile Diels-Alder reaction with 1,2-benzoquinones affording the dioxobenzobicyclooctadienes



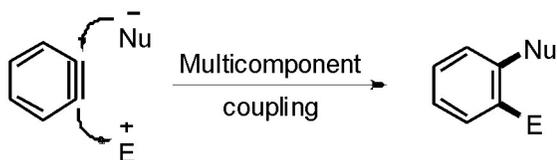
Org. Lett. **2012**, *14*, 6238.

in moderate to excellent yields. In addition, this methodology has been applied to the one-pot synthesis of benzoquinoxalinobarrelene and naphthalene derivatives. The dioxobenzobicyclooctadiene derivatives are potentially amenable to a number of synthetic transformations including various photochemical reactions of the bicyclo [2.2.2] octadiene moiety as well as the reaction of 1,2-diketo group.

Multicomponent Reactions (MCRs)

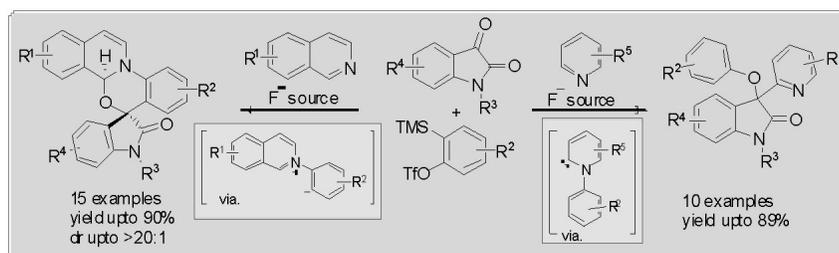
Another important aspect of aryne chemistry that received much attention recently is multicomponent reactions, which mainly include the initial addition of nucleophiles to arynes and subsequent trapping of the aryl anion intermediate with electrophiles. If the nucleophile and electrophile do not belong to the same molecule, the overall process is

a unique three-component coupling, where the aryne is inserted between the other two coupling partners (Scheme 3). This versatile transition-metal-free methodology has been applied to the synthesis of valuable heterocycles and in natural product synthesis.



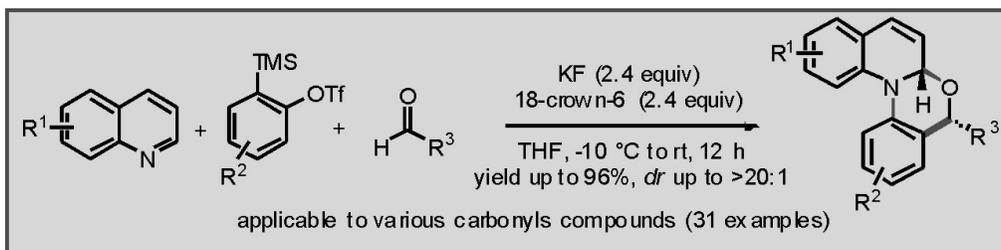
Scheme 3. Aryne MCRs

In the context of our interest in aryne MCRs, we have demonstrated the conceptually new multicomponent reactions involving arynes, N-Heterocycles and isatins. With isoquinoline as the nucleophilic trigger, the reaction afforded the spirooxazino isoquinoline derivatives proceeding via 1,4-dipolar intermediates. Interestingly, the utility of pyridine as nucleophile furnished indolin 2-one derivatives and the reaction is likely to proceed through a pyridylidene intermediate.



Angew. Chem. Int. Ed. **2013**, *52*, 10040.

We have also developed the MCR involving arynes, quinolines and aldehydes leading to the diastereoselective synthesis of benzoxazino quinoline derivatives in good yields proceeding via 1,4-zwitterionic intermediates is reported. In addition, the synthetic potential of various carbonyl compounds in this reaction as well as the utility of isoquinoline as the nucleophilic trigger has been examined.

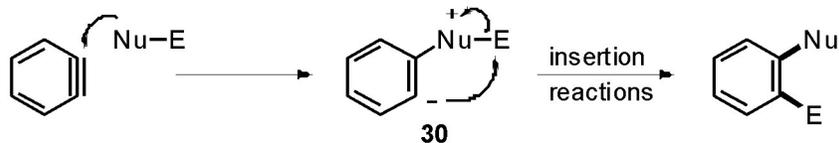


Org. Lett. **2013**, *15*, 4620.

Insertion Reactions

Due to the pronounced electrophilicity and highly strained carbon-carbon triple bond, arynes undergo facile insertion to element-element bonds. Even neutral nucleophiles that are inert towards activated alkynes can add to arynes. If the nucleophilic and

electrophilic sites of a molecule are connected (Nu-E), then the initially formed zwitterion **30** undergoes nucleophilic attack on the electrophilic site of Nu-E to form the insertion product (Scheme 4). This mode of action of aryne has found numerous applications in carbon-carbon and carbon-heteroatom bond-forming reactions.



Scheme 4. Insertion Reactions of Arynes

In conclusion, this *presentation* is expected to expose the rich and fascinating chemistry of arynes, especially from the standpoint of transition-metal-free carbon-carbon and carbon-heteroatom bond-forming reactions. Arynes have found multitude of applications in pericyclic reactions, insertion reactions and multicomponent reactions. Some of these reactions result in the formation of valuable heterocycles with interesting biological activity. Thus, arynes have developed from being laboratory curiosities to efficient synthetic tools in organic chemistry. However, many aspects of the chemistry of these reactive intermediates are not well understood yet. It is reasonable to believe that the aryne chemistry will continue to flourish and lead to surprising developments in the years to come.

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Modified Clays and Hydrotalcites as Heterogeneous Catalysts for C-C Bond Formation Reactions

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Abstract

Solid acids and bases serve as important heterogeneous catalysts for C-C bond formation in aliphatic and aromatic chemistry. Clays are naturally occurring aluminosilicates, which optionally contain other elements, and have layered structure. Cationic clays are acidic, while anionic clays are basic. A cationic clay, like Montmorillonite, can be modified in a number of ways, like heat, acid treatment, cation exchange, pillaring, intercalation, etc. and a variety of acidic catalysts can be prepared for acid catalysed C-C bond formation reactions. Mg-Al Hydrotalcite (HT), is a hydrated magnesium aluminium hydroxycarbonate, and is a typical anionic basic clay. It can be modified in a number of ways and these catalysts are used as solid heterogeneous basic catalysts in many base catalyzed C-C bond formation reactions, such as Aldol condensation, Knoevenagel condensation, Michael reaction, Claisen-Schmidt reaction, cyanoethylation, and heterocyclic synthesis.

The formation of carbon-carbon single bonds is of vital importance in organic synthesis. A number of methods have been developed for carbon-carbon bond formation and the efforts are continuously being made to improvise the methods. Classically, in aliphatic chemistry most of the C-C bond formation reactions are base catalyzed; while in aromatic chemistry they are acid catalyzed.

In the area of catalysis replacement of homogeneous catalysts by the corresponding heterogeneous solid catalysts is a frontier area¹. Heterogeneous catalysts have many advantages particularly on the background of environmental concerns. They have distinct advantages over homogeneous catalysts viz. recyclability, easy separation of catalyst/product, catalyst selectivity, reusability of catalyst, etc². With this in view many solid acids and bases have been developed³. Among the solid acid-base catalysts, acidic catalysts have been developed to a great extent, while the development on basic catalysts side is slow³. This is mainly due to following reasons- deactivation of catalysts, some catalysts may not interact with the solid support, stability of support material can be poor under harsh reaction conditions⁴.

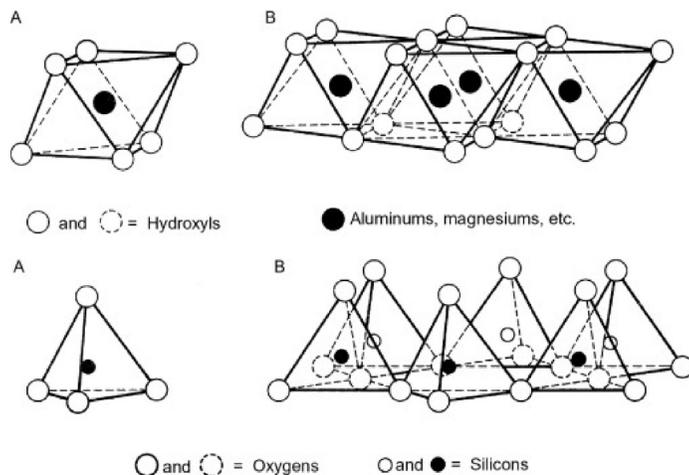


Fig. 1 Basic units of clays and T and O layers

clays. The former are acidic, while the latter are basic. Clays are layered aluminosilicates and contain two basic units – silicon tetrahedra and aluminium octahedral (Fig. 1). These units join each other to form layers of tetrahedral (T) and octahedral (O). These layers stack one over the other (TO, TOT etc) to give the basic structure of clays.

Clays have the following structural features:

Primary structure: Arrangement of T and O sheets to give the *Layered structure*

Secondary structure: Replacement of Si or Al by Mg, Fe, Cr, Zn, Li, etc. with lower valency to give negative charge

Tertiary structure: Na^+ , K^+ , Ca^{2+} ions are trapped in the interlayer space as free moving ions. These ions are exchangeable cations

In addition to this there is water in the interlamellar space.

Clays have a great potential in catalysis due to - easy availability, large surface area, surface acidity (Bronsted and Lewis), possibility of activation through acid treatment and dehydration, presence of electrical double layer on the surface, and a number of modifications possible.

Bentonite is a commonly available clay consisting mostly of mineral montmorillonite, $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot (\text{H}_2\text{O})_n$. Montmorillonite is a TOT type expansive clay (SiO_2 66.7%, Al_2O_3 28.3%, H_2O 5.0%). When it is heated its lamellar structure gradually collapses and at $>700^\circ\text{C}$ it is completely destroyed. It can be treated with an acid during the heating to induce desired acidity. During the combined heat and acid treatment following processes take place - extraction of Mg and Al, partial collapse of the structure, ion exchange of Na, Mg by H, great increase in surface area. Montmorillonite thus gives commercial varieties K0, K10, KSF, KSF0, KP10. K10 is the most popular acidic clay

There are various types of solid acids used in organic synthesis such as, clay minerals, aluminosilicates like zeolites, ion exchange resins, metal oxides and mixed oxides, heteropoly acids, etc. Further these can be modified in a variety of ways.

Clays are naturally occurring aluminosilicates, which optionally contain other elements, and have layered structure. Clays are classified in a variety of ways. In one classification they can be classified as Cationic and Anionic

and is used for a number of reactions^{5,6}. In K10, 25-50% structure of the clay is retained, remaining is quartz and crystoballite. It has surface area 230 m²/g and cec 35 meq/100g. Replaceable cations in it can be exchanged with desired cations which we intend to use for catalysis. The catalytic activity depends on nature and loading of the reagent, activation temperature, nature of solvent used and anion. Thus, there is a great scope for the manipulation of the activity. Catalytic clays such as Clayfen (Clay + Ferric salt), Clayzic (Clay + Zinc salt), and Claycop (Clay + Copper salt) can be thus prepared. These cation exchanged clays can be used for C-C bond formation reactions like Friedel-Crafts alkylation using alkyl halide or alcohol⁷, aromatic electrophilic substituted reactions, Diels-Alder reaction⁸, esterification⁹, cyclization reactions, dehydration reaction, oligomerization, acid catalyzed rearrangement like Beckmann rearrangement, etc. Clays containing oxidizing species like clayfen can be used for oxidation reactions.

Clays can be treated with polyoxo metal cations and then calcined to obtain pillard clays (fig 2).

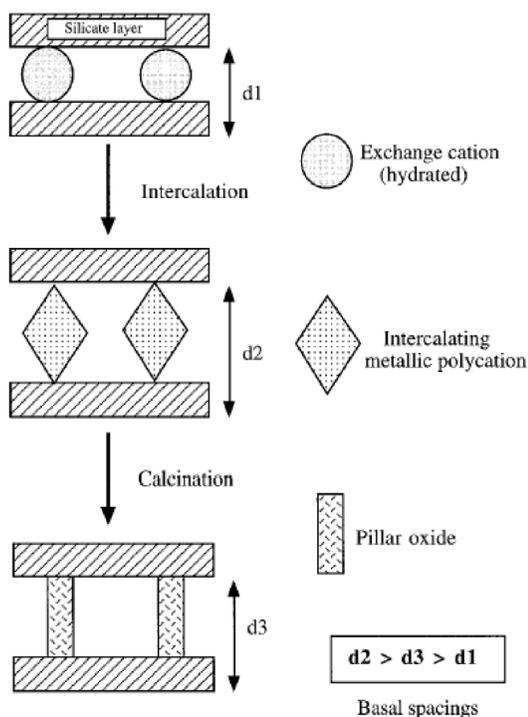


Fig. 2 Schematic representation of formation of pillard clay

and A^{n-} is the interlayer anion with charge n (Fig. 3). The space between the stacked brucite-like cation layers is filled with charge compensating anions (e.g., CO_3^{2-} , Cl^- , NO_3^- , SO_4^{2-} , OH^- and many others) and water molecules. For example, magnesium aluminium hydrotalcite $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}]$ is hydrated magnesium aluminium

Pillaring induces more surface area, more porosity, greater thermal stability, more open structure, and extra reacting centres. Thus, d can be increased from 9 Å to 15 Å, surface area from 40-50m²/g to 200-500m²/g, and thermal stability from 700°C to 1000°C. Pillared clays are used as catalysts for organic transformations¹⁰.

Various molecules and polymers can be intercalated in clays to modify their properties. Clays can be treated with surfactants to obtain organoclays, which swell in organic solvents. Organoclays find applications in paint, pharmaceutical, ink and cosmetic industries.

Hydrotalcites (HTs) are anionic clays and are used as solid heterogeneous basic catalysts¹¹⁻¹⁴. HTs have general formula $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}[\text{A}^{n-}_{x/n}m\text{H}_2\text{O}]^{x-}$, where M^{2+} are divalent cations (e.g., Mg^{2+} , Zn^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+}), M^{3+} are trivalent cations (e.g., Al^{3+} , Cr^{3+} , Fe^{3+} , Co^{3+} , Ga^{3+}),

hydroxycarbonate. They have brucite-like ($\text{Mg}(\text{OH})_2$) structure, where Mg^{2+} ion in Brucite is replaced by a trivalent ion of similar size, such as Al^{3+} or / and Fe^{3+} ion. The layers acquire positive charge with water and anions in the interlayer region. HTs are basic clays and have tunable basicity and high surface area.

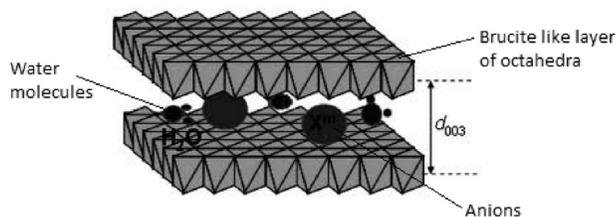


Fig. 3: Structure of hydrotalcites

HTlcs containing the following anions are known

- (i) Inorganic anions: F^- , Cl^- , Br^- , I^- , $(\text{ClO}_4)^-$, $(\text{NO}_3)^-$, $(\text{ClO}_3)^-$, $(\text{IO}_3)^-$, OH^- , $(\text{CO}_3)^{2-}$, $(\text{SO}_4)^{2-}$, $(\text{S}_2\text{O}_3)^{2-}$, $(\text{WO}_4)^{2-}$, $(\text{CrO}_4)^{2-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{SiO}(\text{OH})_3]^-$
- (ii) Heteropolyacids: $(\text{PMo}_{12}\text{O}_{40})^{3-}$, $(\text{PW}_{12}\text{O}_{40})^{3-}$
- (iii) Organic acids: adipic, oxalic, succinic, malonic, sebacic, 1,12-dodecane dicarboxylic acid, acyl and arylsulphonates, chlorocinnamic acid.

Hydrotalcites can be easily synthesized by the following methods-

- 1) Precipitation method, 2) Anion exchange method, 3) sol-gel method, 4) urea hydrolysis method and 5) Microwave irradiation method.

HTs can be modified by taking different metals in combination and also by varying their molar ratio. They can be modified by calcination, calcination followed by hydration, anion exchange and intercalation. Further they serve as precursors to mixed oxide, which are obtained by strongly heating HTs.

In the area of catalysis, hydrotalcites (HTs) and related materials can be used in different ways like (i) basic catalysts, (ii) as supports for active catalytic species, (iii) as precursors of mixed oxides.

HT shows basic sites with pKa values up to 16.5, most of them begin in the range of $10.7 < \text{pKa} < 13.3$ ⁷. Hydrotalcites have been used in many base catalyzed C-C bond formation reactions, such as Aldol condensation¹⁵, Knoevenagel condensation, Michael reaction, Claisen-Schmidt reaction¹⁶, Cyanoethylation¹⁷, and heterocyclic synthesis¹⁸.

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Catalyst Development for DAE Applications

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1. Introduction

It was around the year 1974 that a modest beginning was made in the erstwhile Chemistry Division to take up the research and development activities in the areas of heterogeneous catalysis. The catalysis research carried out in Chemistry Division is a combination of applied and fundamental aspects of heterogeneous catalysis and significant contributions have been made for several projects of interest to the Department of Atomic Energy. Notable among these contributions during 1990 to 2000 are: (i) catalysts for isotopic exchange between hydrogen and water, (ii) a gas recombiner catalyst for sealed-off continuous wave (cw) CO₂ lasers and (iii) catalysts for mitigation of hydrogen in nuclear power plants under severe accident conditions. Recently, Chemistry Division is involved in the development of catalysts for the two important steps in the sulfur-iodine (S-I) thermochemical cycle for large scale hydrogen generation by water splitting and also for mitigation of hydrogen in nuclear reactors under LOCA conditions. In this lecture, the focus will be on the catalyst development for S-I thermochemical cycle and for the mitigation of hydrogen.

2. Sulfur-Iodine Thermochemical Cycle

Thermochemical cycles produce hydrogen from water through a number of chemical reactions involving intermediates that are fully recyclable [1-3]. Among various thermochemical cycles proposed for hydrogen generation, Sulfur – Iodine (S-I) process due to its attractive features such as higher energy efficiency (~47%), all fluids process and adaptability with a high temperature nuclear reactor (~950°C), is widely considered as a potential choice to produce hydrogen on industrial scale [3]. S-I thermochemical cycle, originally proposed by General Atomics, is schematically presented in Fig.1.

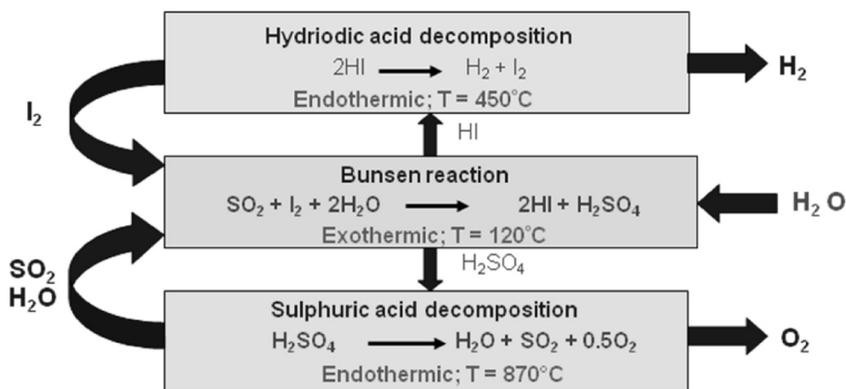


Fig. 1: Schematics of S-I thermochemical cycle.

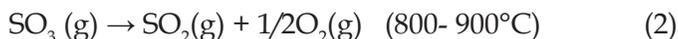
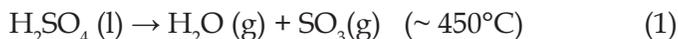
potential choice to produce hydrogen on industrial scale [3]. S-I thermochemical cycle, originally proposed by General Atomics, is schematically presented in Fig.1.

In view of the availability of high-grade heat from

the proposed Compact High Temperature Reactor (CHTR), work on S-I cycle started at BARC in 2006 with an aim to demonstrate this process with a hydrogen generation rate of ~ 150 Normal Litres per hour. Various Divisions of BARC are participating in this activity which is coordinated by Chemical Technology Division, BARC.

2.1 Catalytic decomposition of sulfuric acid

The intense heat flux from the high temperature nuclear reactor can be effectively utilized for the most energy demanding step of this cycle namely, sulfuric acid decomposition. Thermal decomposition of sulfuric acid involves two steps, namely, non-catalytic decomposition of sulfuric acid into sulphur trioxide (Eqn.1) and water at temperatures above 350°C and the catalytic decomposition of sulphur trioxide resulting in formation of sulphur dioxide and oxygen at temperatures above 700°C (Eqn.2).



Efficiency of S-I thermochemical cycle largely depends on the kinetics of the catalytic decomposition of sulfuric acid.

Studies on catalytic decomposition of sulfuric acid were initiated in 2006 in Chemistry Division with an objective to develop non-noble metal catalysts which are both active and stable under harsh reaction conditions existing over the long hours of operation of reactor heat extraction cum acid decomposition step of the sulfur iodine thermochemical cycle. For this purpose various oxides/mixed oxides and ferrites were evaluated to develop a suitable catalyst with better chemical, thermal stability and catalytic properties. Out of these systems, iron oxide based catalysts (Fe_2O_3 & $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{O}_3$) [4, 5] and copper, nickel and cobalt ferrites [6] were found to be quite active for the high temperature decomposition of sulfuric acid. Iron oxide based systems were investigated in detail for their large-scale deployment in an integrated glass setup for S-I process at Chemical Technology Division. Necessary setups required for high temperature decomposition of sulfuric acid at lab scale were developed indigenously. Synthesis of catalytic materials involved different routes like solid state, precipitation/co-precipitation, gel-combustion etc. while characterization of both synthesized and spent catalysts was carried out using various techniques such as N_2 -BET surface area evaluation, and XRD, IR, SEM/EDX, XPS, EXAFS, etc.

Two glass setups developed in-house [5, 6] to study the catalytic decomposition of sulfuric acid in temperature range of 600 – 850°C are shown in Fig. 2. The decomposition setup shown in Fig. 2 A, was used to evaluate catalytic activity (primarily used for screening of the developed catalysts) employing small amount (200-500 mg) of powder sample (200-300 mesh) in a fixed bed reactor while that shown in Fig. 2B, was utilized to evaluate the long-term performance of the selected catalysts in granular form (4-6 mm diameter nearly spherical granules) using about 20 g sample. Whereas nitrogen (40 ml/

min) carried the sulfuric acid vapours (produced in the pre-heater where injection of concentrated sulfuric acid is made through a syringe pump at a rate of 0.05 ml/min) to the powder catalyst in the decomposition setup as shown in Fig. 2 A, no carrier gas is used in the setup employed for the granular catalysts (Fig. 2 B). Herein the boiler, pre-heater and the acid decomposer were integrated into one. Sulfuric acid flux in this setup could be varied in the range 0-2 ml/min by varying the temperature of boiling zone (from 250 to 330°C) while acid flux beyond 2 ml/min were achieved by using a water pump at the outlet of the iodine trap.

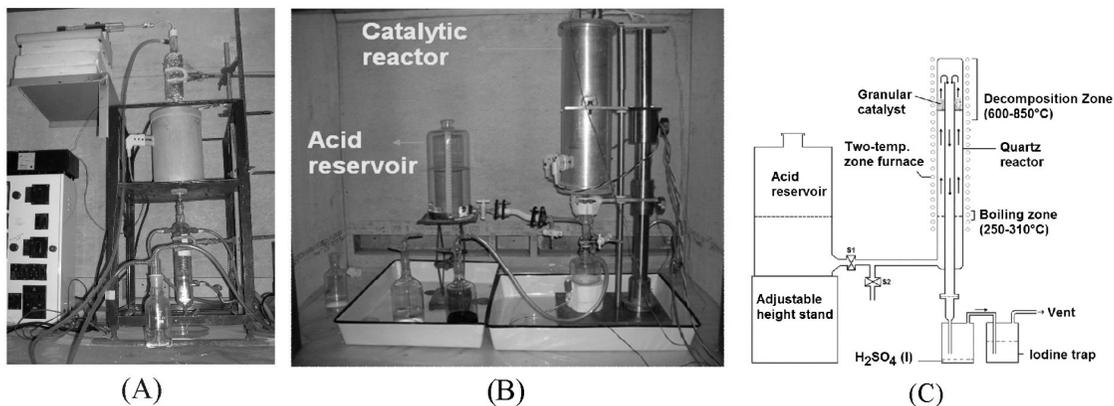


Fig. 2: Photograph of sulfuric acid decomposition setups: (A) For powder catalyst, (B) For granular catalyst, and (C) Schematic of setup (B).

Various analytical methods like iodimetry, acidimetry, gas chromatography, IR spectroscopy, mass spectrometry were explored for ex-situ product analysis. At each temperature measurements were made after about 45 min of equilibration. Percentage SO_2 yield was calculated from the number of moles of SO_2 produced out of the total number of sulfuric acid moles used as given below:

$$\text{Percentage } \text{SO}_2 \text{ Yield} = \frac{\text{No. of moles } \text{SO}_2 \text{ produced}}{\text{Total moles of Sulfuric acid used}} \times 100$$

Fig. 3 presents the temperature dependent activity of various catalyst systems that were screened for catalytic decomposition of sulfuric acid using powder sample in a decomposition setup shown in Fig.2 A. As can be seen here that iron oxide based catalysts show higher activity than the ferrite ones and were therefore subjected to detailed investigations and comparison with a commercial Pt/ Al_2O_3 catalyst in a decomposition setup shown in Fig.2 B, for their possible deployment in an integrated glass setup of S-I process at Chemical Technology Division.

Owing to their higher activity iron oxide based catalysts (Fe_2O_3 and $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{O}_3$) were evaluated in detail. Their performance during prolonged use was compared with a commercial Pt/ Al_2O_3 catalyst for possible deployment in an integrated glass setup of

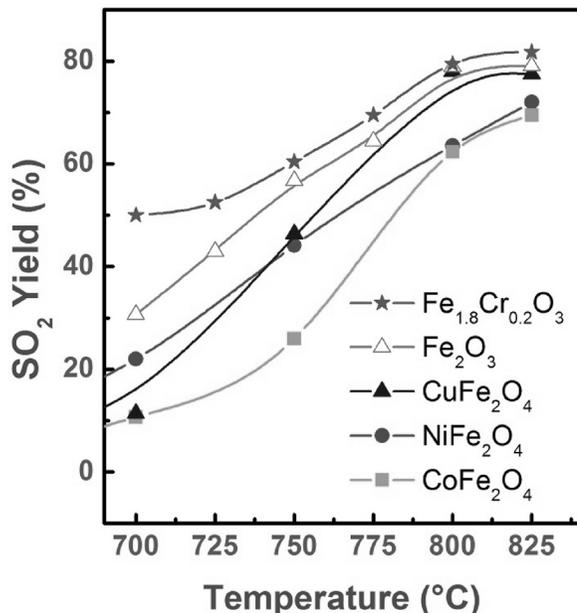


Fig. 3: Temperature dependent SO_2 yield during decomposition of sulfuric acid over different powder samples. Catalysts amount: 0.2 g; Acid (liquid) feed rate: 0.05 ml min^{-1} in N_2 carrier gas (flow rate: 40 cc/min).

loading of platinum. These catalysts have been characterised using XRD, SEM and N_2 adsorption and have been evaluated for their activity and stability under the HI reflux conditions. The conversion of HI to hydrogen has been assessed from this reflux.

The catalysts prepared were evaluated for their activity for HI decomposition reaction using setup as shown in Fig. 4. The zirconium oxide supported platinum catalysts considerably increased the conversion of HI to hydrogen as compared to that for without catalyst. Also, catalyst showed significant increase in conversion levels as compared to use of the zirconia support alone (without Pt metal). The results of XRD, EDS and SEM show that the loading of platinum metal over zirconia enhances the sintering resistance of the noble metal thereby increasing life of the catalyst and also the dispersion of Pt over the supports is found to be uniform. The catalyst was found to be stable under the liquid phase HI decomposition reaction conditions. From this study, it could be concluded that these catalysts have a potential to be used in HI decomposition reaction of Sulphur-Iodine cycle for hydrogen production.

S-I process at Chemical Technology Division, for which about a kilogram each of the granular catalysts has been made available. The results have shown that iron oxide based catalysts can be a suitable substitute for noble metal catalysts at temperatures above 750°C and may play an effective role in utilization of intense heat flux from the high temperature nuclear reactor for decomposition of sulfuric acid towards realization of the goal of S-I process for large scale hydrogen generation.

2.2 Catalyst for hydroiodic decomposition

HI decomposition reaction as such is thermodynamically limited with very low thermodynamic conversions and it requires a catalyst to achieve workable reaction rates [7]. In Chemistry Division, we have synthesised platinum supported on zirconia catalysts with different

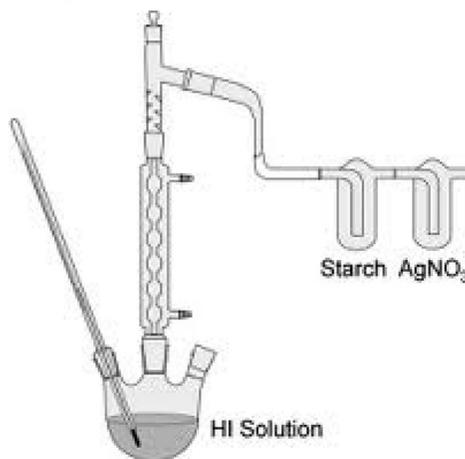


Fig.4- Reactor Setup used for liquid phase HI decomposition reaction

3. Development of catalyst for hydrogen mitigation under LOCA conditions

Hydrogen generated in nuclear power plant during accidental condition poses threat to reactor containment once it exceeds flammability limit in air, which endangers the environment in form of radioactivity fall out. Passive autocatalytic recombiner (PAR) is one of the best suitable devices to deal with this scenario. For this purpose we have recently developed stainless steel (SS) wire gauze supported Pt-Ru nanoparticles as catalysts. Simultaneous electroless deposition has been used for their synthesis. Pt-Ru based bimetallic catalysts were characterized for their rate of coating kinetics, noble metal loading, phase purity by XRD and surface morphology by SEM and TEM. Catalytic activities were evaluated for H₂ and O₂ recombination in air as well in presence of various types of prospective poisons like CO₂, CH₄, CO and relative humidity. Pt-Ru



Fig. 5 Catalyst Bearing Panel consisting of Pt + Pd on SS wire-gauze catalysts, for hydrogen mitigation.

based bimetallic catalyst with 0.9 % optimum loading found to be active for CO poisoning up to 400 ppm of CO.

Catalyst Bearing Panels, (80 Nos) consisting of Pt + Pd on SS wiregauze catalysts, as shown in Fig. 5, have been supplied to Hydrogen Recombination Test Facility (HRTF), Tarapur for testing and evaluation.

4. Conclusions

In this article, just a glimpse of development of catalysts for DAE applications has been highlighted. There are numerous other examples, where catalysts have played crucial role for DAE applications. Especially, catalysts development is important in solving various problems at the back end of the fuel cycle. Our colleague from Nuclear Recycle Group will discuss this aspect.

Acknowledgements

All my colleagues of Fuel Cell Materials & Catalysis Section have contributed immensely to the various activities discussed in this article. I thank all of them and I am confident that they will continue to contribute to the DAE programs in future as well.

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Catalyst Based Processes at Back End of Nuclear Fuel Cycle

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Heterogeneous catalysts occupy a pivotal position in chemical industry. Their advanced preparation technology allows us to employ these catalysts for wide range of application. But the deployment of catalyst based radiochemical technology has to address the particular features like aggressive nitric acid media and intensive radiation fields. This put forward the rigid requirements to a choice of catalysts: high chemical and radiation stability of the catalyst and support, mechanical durability, catalytic activity and simplicity of preparation. Hydrogenation process with Pt/SiO₂ has been adopted industrially for making uranous nitrate (U⁴⁺) from uranyl nitrate (U⁶⁺) in PUREX process at commercial reprocessing plants. Bimetallic catalysts are being explored for the destruction of nitrates generated during nuclear fuel cycle operations.

Process Development for Making Uranous Nitrate by Catalytic Processes:

Reprocessing of nuclear materials is carried by the conventional solvent extraction process called PUREX. Uranium and plutonium are together extracted by employing TBP-dodecane and are separated from each other by uranous nitrate, the partitioning agent. Small quantities of hydrazine are added along with uranous as a nitrous acid trap. The production of uranous nitrate from the uranyl nitrate solution is an important step since it is an input to PUREX process. Uranous nitrate can be generated either by electrolytic, photolytic, hydrazine catalytic or catalytic hydrogenation process.

In our Indian reprocessing plants, uranous nitrate is produced by electrolytic method using TSIA (Titanium Substrate Insoluble Anode) with hydrazine nitrate as uranous nitrate stabilizer. In this method, the conversion attainable is only 50 to 60%. In addition, it is a kinetically slow process and leads to fouling of the platinised anodes. In order to achieve higher conversion of uranyl nitrate to uranous nitrate, a heterogeneous catalysis route has been initiated using hydrazine nitrate as reducing agent in presence of Adams' catalyst (PtO₂) at laboratory scale. Though this method could produce uranous nitrate at ease and faster rate with higher yield, higher attrition rate was observed during the reduction process.

Subsequently, an alternate catalyst form i.e., Pt supported on alumina was tried and extensive bench scale studies were carried out for the reduction reaction to optimise the catalyst to uranium weight ratio. With Pt loaded alumina substrate as the catalyst, reduction in conversion time was observed due to the nanosized particles compared to Adams' catalyst of 37µm size. However, the developed process with hydrazine as

reductant appeared to be difficult to be deployed for continuous production of uranous nitrate due to slow kinetics.

Since it has been reported that catalytic reduction process using hydrogen leads near total conversion with enhanced reaction rates, conversion of uranium (VI) to (IV) was tried with H_2 as reducing agent. Bench scale hydrogenation studies using 99.9% H_2 and hydrazine were carried out using Adams' catalyst and kinetics was observed to be fast compared to hydrazine alone and it was found to enhance with hydrogen pressure and concentration of hydrazine. But the utilization of catalyst in terms of catalyst to uranium ratio was very high due to low pore volume and surface area of Adams' catalyst. In order to reduce the platinum consumption, Pt loaded on alumina beads have been tried. Studies with Pt loaded on alumina imply that the reduction performance using nano sized Pt (102 nm) with a C/U of 1:55 is comparable with the micron sized Adams' catalyst (20 μ) with a C/U ratio of 1:10.

As the catalyst supported on alumina was found to be unstable in acidic environment, Pt loaded on silica powder was developed in association with industry. Based on bench scale experiments, the process parameters for near total conversion of U (VI) to U(IV) using 2 wt% Pt on silica were established. U(VI) at a concentration of 200 g/L has been converted into uranous nitrate in 100 minutes at optimized process parameters viz C/U

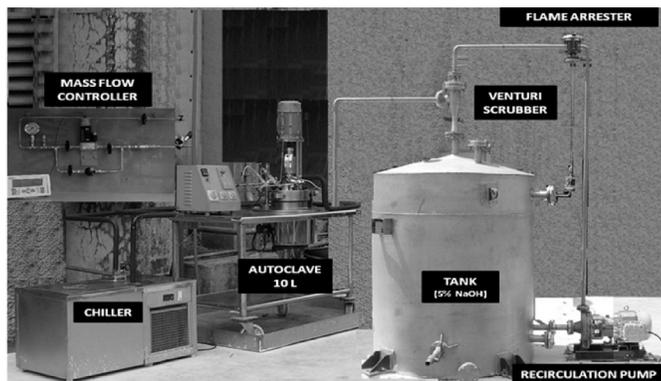


Fig.1 Catalytic hydrogenation loop at OTF

of 1:100, H_2 pressure of 3.5 MPa, temperature of 299 K, acidity of 2.56 M and hydrazine concentration of 1.0 M. Under optimized conditions, free acidity of 1.0 M and hydrazine concentration of 0.6 M in the product uranous could be achieved confirming the stability in terms of acidity & hydrazine concentration. The developed process has been demonstrated to produce 5 L of uranous nitrate per batch as shown Fig.1

Process Parameters:

U (VI) = 200g/l

Pressure: 35 Kg/cm²(g) ; 99.9% H_2

Temp: 26°C

H_2 Flow : 50 NLPH

H^+ =2.56M, $N_2H_5^+$ = 1.0M

Catalyst: 2wt% Pt loaded on Silica

Catalyst to uranium ratio: 1:200

RPM:400

More than 99.8% conversion was achieved in 25 minutes with product acidity: > 1.0M & $N_2H_5^+$ > 0.5M

60 litres of uranous nitrate solution containing 200g/L of U has been prepared and was introduced in the partitioning column of HA cycle at PP, Trombay and plutonium reduction performance was found to be satisfactory.

Though the catalyst - platinum supported on spherical silica gel bead was chosen, silica may not be the support of choice due to low mechanical strength and low abrasion resistance leading to mechanical degradation of the catalyst upon long term utilisation. In order to address this, platinum supported on zirconia beads are being developed and synthesised on laboratory scale by Chemistry Group and its reduction performance are being evaluated.

Process Development for Catalytic Denitration of Alkaline Wastes:

PUREX technology based on aqueous reprocessing method, starting from chemical de-cladding using sodium hydroxide and sodium nitrite followed by dissolution and solvent extraction in nitric acid media generate significant amount of nitrate bearing wastes. Alkaline wastes generated during the reprocessing operations of spent nuclear fuel contain nitrates in the range of 10000 – 150000 ppm. Release of nitrates into the environment can cause eutrophication of water bodies leading to serious human health problems like cancer and blue baby syndrome.

Regulatory standards in India specify that concentration of nitrate in the treated effluents should be below 100 ppm before such effluents can be discharged into the environment. Nitrate removal can be performed by physicochemical treatments. However, these methods remove nitrate from raw water and concentrate it in reject water or brine. Disposal of reject water is both expensive and an environmental issue. Biodegradation processes are also being tried to destruct nitrates but it is an inherently slow process.

Catalytic denitration is a promising approach for nitrate removal as it allows rapid conversion of nitrate to harmless nitrogen gas. Pd bimetallic catalysts, especially Pd-Cu supported on metal oxides, have proved to be the most effective for nitrate reduction. Use of hydrogen or hydrazine as a reducing agent in catalytic denitration generates large amount of ammonia as a by-product. Formalin over comes this problem as it allows reduction of nitrate to nitrogen with negligible release of ammonia. It is also cheap and easy to handle unlike hydrogen. Therefore, formalin has been considered as a reducing agent.

Column studies were performed using $NaNO_3$ containing 1,00,000 ppm of nitrate at a pH of 12.5 on 1litre scale in a batch recycle mode. Bimetallic catalyst used was Pd (2wt%) Cu (0.6wt%) loaded on 2-3 mm alumina beads. Temperature was maintained at 45°C. After 240 min, nitrate was reduced to 5262 ppm whereas build up of nitrite ~ 23,934 ppm was noted. Afterwards, experiments were carried out with simulated alkaline waste

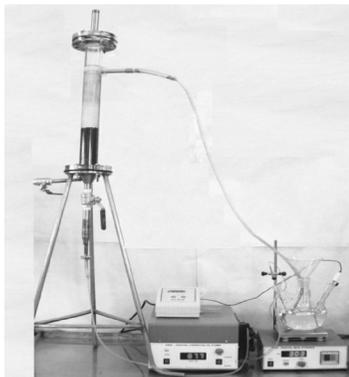


Fig.2 Set up with bi-metallic catalyst

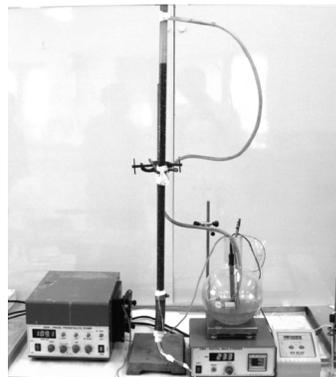


Fig.3 Set up with mono metallic catalyst

containing 1,50,000 ppm of nitrate and 5000 ppm of nitrite. After 300 min, nitrate was reduced to 4700 ppm whereas build up of nitrite ~ 42000 ppm was observed.

To reduce the nitrites generated during the reduction process, the product obtained from Pd-Cu bed was subjected to another catalyst 0.5 wt% Pd/alumina bed at a pH of 3.5 which is specific for nitrites. In case of

sodium nitrate stream, nitrite was reduced to 355 ppm and for simulated waste stream, nitrite was reduced to 4300 ppm.

By adopting a two step reduction process i.e., by converting nitrates to nitrites by Pd-Cu catalyst followed by Pd catalyst to convert nitrites to nitrogen, it was demonstrated that alkaline wastes having 150000 ppm of nitrates can be reduced to 4300 ppm level. Both the catalysts, Pd-Cu and Pd are being modified in terms of BET surface area and porosity and its performance are being tested in close coordination with Chemistry Group.

Conclusion:

So far in the uranous making facility (5 L per batch), natural uranium was used for its conversion to uranous. Now efforts are being made to demonstrate the process using plant uranyl nitrate solution which is generated from PUREX itself. Based on the performance of this catalytic hydrogenation loop, two reactors one in batch mode and other for continuous production of uranous are being designed.

The developed process based on catalytic denitration for the treatment of alkaline waste is a pH dependent one. The conversion from nitrate to nitrite is favoured at a pH of 12 and conversion from nitrite to nitrogen is favoured at a pH of 3. Since, the actual intermediate alkaline waste is having a pH of 12, no pretreatment is needed before feeding to the bi-metallic catalyst column. However, pH is to be maintained at 12. Alkaline waste contains sodium aluminates and gets precipitated in the pH range of 10.7-4.0. As the second column operates at 3.5 pH, precipitation is avoided. Now the process is being scaled up to treat 10 L of waste.



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Hydrogenation of Soybean Oil using Silica Supported Basic Mg/Ni and Zn/Ni Carbonates

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Hydrogenation of vegetable oil was first discovered in the beginning of 20th Century and quickly became a major processing step in the fats and oils industry. Refined oils used in foods are generally pale in color, free from disagreeable odor and contain < 0.2% free fatty acids and susceptible for becoming rancid upon storage due to presence of large number of double bonds. Therefore, the partially hydrogenated oils with less number of double bonds are reported to be much more stable and resistant to rancidity.

The products thus obtained from partial hydrogenation of oils are regularly used in various food applications such as Vanaspati, Margarine and Shortenings (change in consistency of oil), ice cream coatings (hard coating but not brittle), bakery coatings, cream filling between wafers (melts in the mouth giving a cool sensation on the palate), toffees, coffee whiteners (milk substitutes), whipped toppings (whipping gives stiffness to the foam) and chocolate (about 15% of the cocoa butter in chocolate is replaced by a vegetable fat)

The vegetable oils contain double bonds only in cis form however during the partial hydrogenation the residual double bonds present in oil are known to be present in *trans form*. Research in medical sciences revealed that “saturated fats” and “trans fats” are detrimental to health and it is necessary to control their intake in our daily diets for better health.

The present study focuses on the use of different catalysts for partial hydrogenation of soybean oil and analysis of trans isomer formation at different levels of hydrogenation. Also the emphasis is given on identification and recommendation of the catalyst and hydrogenation conditions that minimizes / eliminates formation of trans isomer in the partially hydrogenated oils.

The first step is preparation of silica supported basic nickel carbonate by co-precipitation of nickel sulphate and sodium carbonate solutions. Basic metal carbonate samples (supported or unsupported) obtained from the above procedure are listed in the following Table 1. In the second step, above mentioned basic carbonate samples were reduced to metal (Ni, Mg or Zn as the case may be) which acts as a catalyst for hydrogenation.

Table 1: Different types of basic metal carbonates prepared for this study

Sr. No.	Sample Description
1	Basic Ni carbonate
2	Basic Ni carbonate supported on silica
3	Basic Mg carbonate
4	Basic Mg carbonate supported on silica
5	Basic Ni carbonate supported on silica with Mg (in different concentration) (such that, Mg/Ni molar ratios are :0.15, 0.30, 0.45 & 0.60)
6	Basic Zn carbonate
7	Basic Zn carbonate supported on silica
8	Basic Ni carbonate supported on silica with Zn (in different concentration) (such that, Zn/Ni molar ratios are: 0.15, 0.30, 0.45 & 0.60)

The reduction of basic metal carbonates were carried out at different temperatures showing that reduction of Ni^{2+} to Ni^0 is complete (Degree of Reduction = 99%) at 320 °C and further increase in reduction temperature had no effect on reduction. In case of silica supported basic nickel carbonate the reducibility of nickel was very low (DR = 12.47%) at 320 °C. The Degree of Reduction was found to increase by increase in reduction temperature (DR = 67.02 % at 450 °C). The silica reacts with a definite fraction of nickel to form nickel silicate ($-\text{Ni}-\text{O}-\text{Si}-$) which is not reducible to Ni^0 even at 450 °C.

In basic Mg/Ni carbonate-silica, the decrease in degree of reduction of nickel with increase in Mg/Ni mole ratio from 0.15 to 0.45 indicates that Mg participates in the structure of basic nickel carbonate and modifies the reduction property of the nickel. It has been reported that the nickel is difficult to reduce if it is linked to Mg through oxygen as $-\text{Ni}-\text{O}-\text{Mg}-$. Therefore with increase in Mg/Ni mole ratio from 0.15 to 0.45, the formation of higher number of $-\text{Ni}-\text{O}-\text{Mg}-$ linkages decrease the reducibility of nickel. This was attributed to the shift in electron density in $-\text{Ni}-\text{O}-\text{Mg}-$ towards Mg and Ni becomes more electron deficient, which is difficult to reduce as compared to that of $-\text{Ni}-\text{O}-\text{Ni}-$ linkages. Possibly beyond Mg/Ni mole ratio of 0.45 the excess Mg might not be participating in the structure of basic nickel carbonate and might be precipitating separately as basic magnesium carbonate.

The addition of Zn as a promoter shows no influence on degree of reduction of nickel in silica supported basic nickel carbonate. It is possible that most of the added Zn might not be participating in the structure of basic nickel carbonate (i.e. it does not form $-\text{Zn}-\text{O}-\text{Ni}-$ linkages) and resulting into no influence on the degree of reduction of nickel. Therefore with increase in Zn content (Zn/Ni from 0.15 to 0.60) shows negligible decrease in degree of reduction of nickel. The XRD and IR data confirmed the above hypothesis made on the role of Mg and Zn in basic nickel carbonate precipitate.

All the catalysts were tested for the partial hydrogenation of soybean oil. The results show that the decrease in Iodine Value is negligible i.e. from 127.48 to 126.22 (Delta Iodine Value = 1.26) with the unsupported nickel catalyst even if it contains > 98% reduced nickel metal. Whereas, the silica supported nickel catalyst (Ni-SiO₂) containing 67.02% reduced nickel metal (32.98% unreduced nickel) shows sharp decrease in Iodine Value from 127.48 to 41.71 (Delta Iodine Value = 85.77). Thus, we can conclude that the silica support decreases the reduction of nickel but it has beneficial role in improving metal dispersion therefore giving better (higher) hydrogenation activity.

The results with Mg/Ni-SiO₂ catalysts show that Mg at Mg/Ni mole ratio of 0.15 and 0.30 has beneficial effect in hydrogenation of soybean oil. That is, the Delta Iodine Value of 113.78 and 98.12 was obtained respectively as compared to the Delta Iodine Value of 85.77 obtained with Ni-SiO₂ catalyst. However, higher concentration of Mg in Mg/Ni-SiO₂ catalyst i.e. mole ratio of Mg/Ni = 0.45 and 0.60 show no benefit but gave similar activity (Delta Iodine Value) as that of Ni-silica catalyst.

The results from incorporation of Zn at wide range of mole ratios (Zn/Ni = 0.15 – 0.60) in Ni-SiO₂ catalyst showed negative effect in hydrogenation of soybean oil. That is, the Delta Iodine Values are very low (27.85, 20.86, 14.35 and 19.11) as compared the Delta Iodine Value obtained with Ni-silica catalyst (85.77) without Zn incorporation. The phenomenon is explained by XRD analysis i.e., most of the added Zn not participating in the structure of basic nickel carbonate and therefore has no beneficial role in hydrogenation activity.

The results also show that at given constant Delta Iodine Value, the trans content in the product is almost similar with un-promoted Ni-SiO₂ as well as Mg and Zn promoted Ni-SiO₂ catalysts at same temperature. However, it is interesting to observe that the decrease in hydrogenation temperature has shown drastic decrease in trans content at similar Delta Iodine Values. Thus, trans fatty acid (elaidic) formation was found to be dependent upon hydrogenation temperature and not on the catalyst used for the reaction.

But it is very difficult to achieve 'zero trans' in the partially hydrogenated product even at very low temperatures. Therefore, a popular method "Interesterification" is adopted to manufacture edible fat with zero trans fatty acid content (European Margarines). A partially hydrogenated oil composition is simulated by mixing fresh oil (with large number of double bonds in "cis" form) with fully hydrogenated oil (no double bonds) in different ratios, followed by the solidification or "interesterification" using sodium methoxide as catalyst. The interesterified mixture was further cooled and allowed to stand for longer duration. These homogenous semi-solid (soft solid = vanaspati) samples were found to contain the desired fatty acid composition, melting property as that of partially hydrogenated oil but with zero trans content.

**Dr. G. P. Babu**

At Present (from 2005) Dr. G. P. Babu is working for Monarch catalyst Pvt Ltd as General Manager R&D. The work involved is development of new solid acid and base catalysts for non-hazardous and environmentally clean process (i.e. O-alkylation and C-alkylation of phenolic compounds using methanol as alkylation agent, etherification of alcohols using reusable solid base catalysts, nitration of aromatics without sulphuric acid, and selective reduction of keto/ ester group using copper silica/copper chromite catalysts).

In 1983 – 2001, worked for Hindustan Lever Ltd (presently HUL and transferred to ICI/JM during 2002-2004) in catalysts division at different levels. During that time catalysts were developed for up-gradation of sal-fat, dipentene to p-cymene and converting isoamyl alcohol selectively to 2M2B. Preparation of nickel/silica catalyst was modified in the laboratory and plant to match the catalyst quality of international grades. Silica and alumina nanoparticles were developed for protecting the fabric from soiling.

During PhD program (1980 - 83) under the guidance of Dr. P. Ratnasamy a commercially important zeolite “ZSM5” type catalyst was prepared for vapour phase xylene isomerisation reaction and participated in the team of NCL-ACC-IPCL for the implementation of xylene process at IPCL.

Publications: Research papers: 20

Catalyst and process Patents: 14

Design of Electrodes and Electrolytes for Hydrogen Generation via Electrochemical Method.

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Hydrogen as an energy carrier is the attractive option, because it is flexible, affordable, safe and used in all sectors of the economy. In addition, it has the long term potential to reduce our dependence on foreign oil and lower carbon emission from the transportation sectors. Hydrogen generation from water splitting represents a holy grail in energy technology as water is the most abundant hydrogen source. Among different methods, hydrogen generation via electrochemical (EC) method is a viable approach to generate hydrogen in association with renewable energy sources. Therefore, we present some of the progress towards developing suitable electrodes /electrolyte materials for water electrolysis to generate hydrogen. Based on these materials, a prototype electrolyser was assembled and demonstrated.

(A) An alternative approach to selective sea water oxidation for hydrogen production

Sea water electrolysis is one of the promising ways to produce hydrogen since it is available in plenty on the earth. However, in sea water electrolysis toxic chlorine evolution is the most preferred reaction than oxygen evolution at the anode. In this work, study has been focused on the development of electrode materials with high selectivity for oxygen evolution reaction than chlorine evolution. A selective oxidation in sea water electrolysis has been demonstrated by using cation selective polymer. We employed perm selective membrane (Nafion®) which electrostatically repels the chloride ion (Cl⁻) to the electrode surface and thereby enhances the oxygen evolution at the anode.

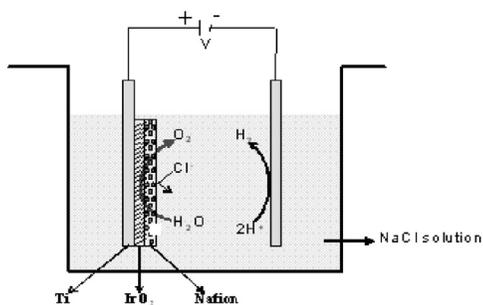
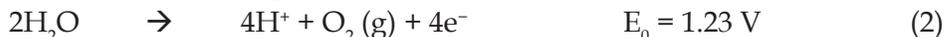


Fig.1 Schematic presentation of sea water electrolysis

However, in sea water electrolysis, toxic chlorine evolution is the preferred reaction over oxygen evolution at the anode for the following reasons:

- (i) The pH at the electrode surface becomes acidic during electrolysis, which favours chlorine evolution as it is independent of pH.

- (ii) Although oxygen evolution should be the preferred reaction over chlorine evolution according to the thermodynamic potentials [1] (Eqs. 1 & 2), this is only valid at zero current.



- (iii) The oxygen evolution reaction is associated with a higher overpotential than the chlorine evolution reaction.

Nevertheless, oxygen evolution dominates under certain conditions [2], which may be summarized as follows:

- (i) Sea water electrolysis at very low current density ($< 1 \text{ mA/cm}^2$).
- (ii) Operating the cell at far in excess of the limiting current for chlorine evolution.

However, the above two circumstances are impractical because sea water oxidation at low current density would require a very large electrode area, and electrolysis at above the limiting current would lead to IR heating and high power consumption, which would be uneconomical.

Therefore, we speculated that if we could prevent chloride anions from accessing the electrode surface by electrostatic repulsive forces, this might be effective in enhancing oxygen evolution and suppressing chlorine evolution. We assumed that this might be

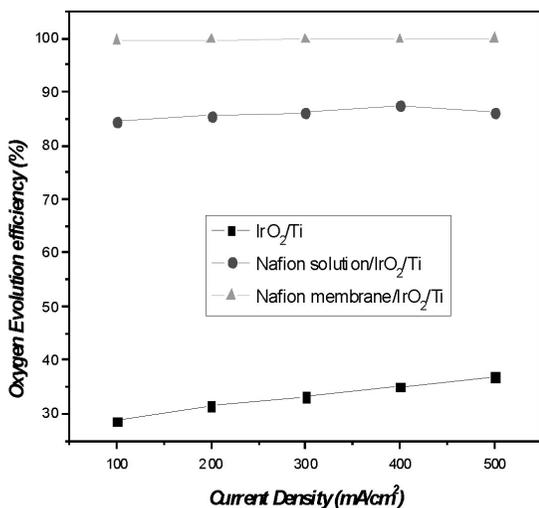


Fig. 2. Oxygen evolution current efficiency of various electrodes as a function of current density in 0.5 M NaCl and pH 8.3, at 30°C. IrO₂/Ti-IrO₂ coated Ti electrode: NS/ IrO₂/Ti-Nafion solution coated IrO₂/Ti electrode: NM/IrO₂/Ti-Nafion membrane coated IrO₂/Ti electrode.

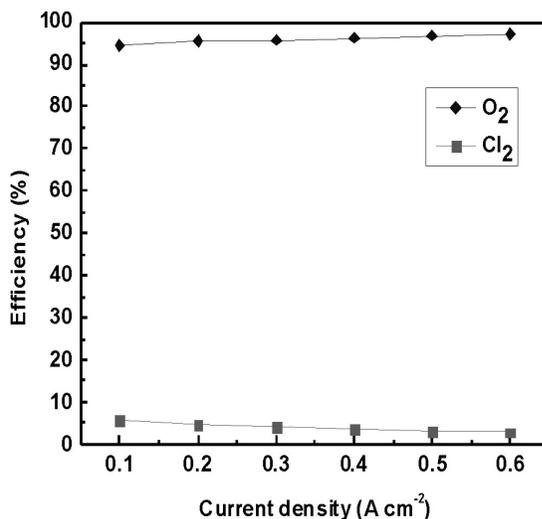


Fig. 3. Oxygen and chlorine evolution current efficiency of S-PSEBS/IrO₂/Ti electrode as a function of current density in 0.5 M NaCl and pH 8.3, at 30°C.

possible by applying a cation-selective coating on the electrode surface. To the best of our knowledge, there have not hitherto been any reports based on this idea. Hence, after thinking of some cation-exchange materials, we resolved to use a perfluorosulfonic acid membrane (Nafion[®]) and S-PSEBS as a cation-selective layer on an IrO₂ electrode [3,4].

(B) Development and performance evaluation of Proton Exchange Membrane (PEM) based hydrogen generator for portable applications

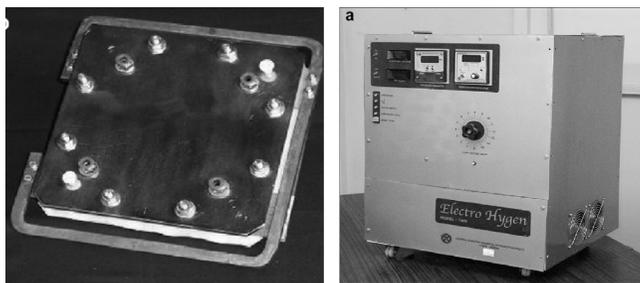


Fig. 4. Components of PEM water electrolyzer (a) assembled electrolyzer stack (b) 80 l/h hydrogen generator.

The development of key components, specifications, configuration and operation characteristics of an 80 l/h Proton Exchange Membrane (PEM) water electrolyzer system for portable applications [5, 6]. The reliability in operation of developed PEM water electrolyzer system is tested for running the stack about 3000 h with 100 A current. The results indicate the reasonable stability of

MEA fabrication and cell design method.

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Dr.S .Ravichandran is presently Sr.Scientist at Central Electrochemical Research Institute Karaikudi, India. He obtained his Ph.D (1997) from Madurai Kamaraj University, Taminadu. He did his Post-doctoral work on conducting polymers at IIT, Chennai and later on in Li Batteries at National Taiwan University of Science and Technology, Taipei, Taiwan. After a brief period in fuel cell and super capacitor R &D, currently he is focussing in the area of electrodes/electrolytes interfaces for hydrogen generation via electrochemical and photoelectrochemical methods. With over a decade of experience in the area of electrochemical hydrogen generation, he has transferred three technologies to industry. He has published about 25 papers in a journals of repute and filed 5 patents.

Industrial Enzyme Catalysis: Engineering Protein and Processes

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Of the thousands of enzymes known to catalyze variety of reactions in relatively efficient and specific manner, the number of enzymes actually used on industrial scale to facilitate chemical synthesis remains significantly smaller than expected. The reasons are many and can be matter of many a debate. Broadly speaking, wider and large scale exploitation of enzymes for industrial catalysis has not been witnessed thus far due to an absence of confluence of two very different areas of expertise namely, protein biochemistry and reaction engineering. Understanding the structural issues associated with protein activity and stability, and coupling this with the knowledge domains of thermodynamics of reactions and fluid dynamics of reactors is the key factor that only can ensure that enzymes work in manner that is both scalable and cost effective especially for low price-large volume product molecules.

On the other hand, given the nature and spectrum of products mankind has become used to, every product cannot be made through enzyme catalysis. Further, the substrate specificity of enzymes greatly limits their diverse applications. It is a fact that nature produces only those enzymes that have a role in cellular metabolisms and are surely not intended for the reactions mankind wants to conduct as large scale chemical synthesis. Modern biology holds out some hope in this matter. Tools of modern biology today facilitate design of enzymes that can be produced cheaply and used on 'unnatural' substrates and for 'unnatural' reactions. However, despite this promise, the number of enzymes used industrially has not grown to projected proportions for reasons mentioned above.

A handful number of example however can demonstrate that this dismal picture can be transformed to an extent if basic chemical reaction engineering principles are innovatively employed in designing enzyme catalyzed processes. Further, rational design can also provide enzymes with far better stability and efficacies than provided by native enzymes. Our group at ICT has undertaken the task of attempting to carry out design of enzymes and design & scale up enzymatic processes in a manner very differently than known in published literature. A combination of insights into structure-activity relationships, and reaction mechanisms & rates has resulted in successful industrial use of many enzymes in ways traditionally not considered possible. Lipase catalyzed hydrolysis and

esterification; peroxidase catalyzed oxidation; and cellulase catalyzed hydrolysis are three of the success stories resulting from the holistic approach to industrial enzyme technology that has involved changing the enzyme structure and designing of processes that do justice to their mechanistic actions. The underlying philosophy that emerges from the work is that while protein engineering is able to provide novel enzymes and enzyme activities, it is the intervention of smart reaction engineering that will prove to be the enabling feature of the next generation industrial enzyme technologies.



Arvind Lali has developed expertise in the area of bioseparations and biotransformations having provided technical support and solutions to many Pharma, Biopharma and Food companies (Biocon, Dr. Reddys, Merck, Cadila, Strides-Acrolab, Unisankyo, Resindion SRL, Italy, Bio-Rad Laboratories India/USA, Pepsico India/USA, General Mills Inc, USA etc.). He heads India's first Centre for Energy Biosciences funded by the Department of Biotechnology with objectives to create a sustainable R&D platform for biofuels. He has developed technologies that have been and are being implemented at pilot and larger scale by Indian or foreign industries. Major research achievements include affinity adsorbent for antibody purification. He is granted with many national and international patents for his major research achievements on Fractionation of biomass and enzymatic hydrolysis Novel extraction for natural product extraction. Working currently in a major way in development of viable and scalable technologies for conversion of unutilized or low-utilized agricultural and agri-industry waste to wealth, Arvind Lali is involved in turning a number of potentially impacting technologies into demonstration plants for subsequent scale up and multiplication across agricultural economies.

**Activities of Chemistry Division
&
Society for Materials Chemistry**

R & D Highlights of Chemistry Division

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Chemistry Division is one of the oldest Divisions which came into being at the early stages of the Indian Atomic Energy programme. Since its inception, the Division has served to nucleate research and development activities relevant to the programmes of atomic energy. As several of these programmes blossomed with time, the Division underwent re-organizational changes from time to time. Chemistry Division has six sections, viz., Synthesis & Pure Materials Section (SPMS), Fuel Cell Materials & Catalysis Section (FCMCS), Solid State Chemistry Section (SSCS), Structural Chemistry Section (SCS), Thermal & Interfacial Section (TICS) and Materials Chemistry Section (MCS).

The Division has rich traditions of taking up research programmes in frontier areas of contemporary chemical research. The research output of the Division is manifested in terms of developing know-how for various products (*e.g.*, ultra-purification of strategic materials; catalysts, development of sorbents for recovery of important radio-isotopes, *etc.*) and solutions to chemical problems relevant to our programmes. Divisional current research activities encompasses broad areas like nuclear materials, hydrogen energy, chemistry of nano-materials, organometallic chemistry, catalysis, high purity materials, functional materials, fuel cells, *etc.* Various research activities are executed primarily through 5-Year plan projects with existing scientific and technical (~75) staff and additional manpower of KSKRA and doctoral students. Additionally there are some ongoing collaborative projects with other research groups in BARC (*e.g.*, Nuclear Recycle Group, Analytical Chemistry Division, Radiation Biology & Health Sciences Division (RB & HSD), Product Development Division (PDD), Process Development Division (PSDD), Chemical Technology Division (CTD), Reactor Engineering Division (RED), *etc.*) and DAE units (IGCAR, TIFR, RRCAT, DAE-UGC-CSR), Universities and national institutes through BRNS and DST schemes and also with other countries (Russia, Italy, USA, *etc.*). The major activities can be clubbed as follows:

1. Nuclear Materials

The Division is involved in research activities on nuclear materials from the point of view of front end as well as back end applications.

1.1 Studies on thorium based metallic fuels and alloys

One of the activities of the Division on nuclear materials is to generate experimental database on thermo-physical, thermodynamic and transport properties of thorium and uranium-based metallic fuels and related materials. Indigenous generation of

such data is one of the important activities of the Division. Thermophysical studies have been carried out on few alloys (Th, U, Th-10wt.% U, Th-20 wt.% U and U-10 wt.% Zr). Specific heat measurements on these samples were made using Temperature Modulated DSC (RT - 773 K) in flowing N₂ atmosphere. The results were comparable to the earlier reports.

Heat capacity of thorium-based alloys such as Th-Rh₅ was measured in the temperature range 323-773 K employing drop calorimeter. The temperature dependant heat capacity of the alloys in this range could be expressed as $C_{p_{\text{ThRh}_5}} = 0.141 + 5.12 \times 10^{-5} T$ kJ/mol. Efforts have also been made to augment the instrumental facilities for thermodynamic research using in-house design and fabrication of accessories which includes a resistance furnace with tungsten heating element for Knudsen effusion mass spectrometer, an air tight stainless steel cylindrical sample drop assembly for Calvet calorimeter and a top loading water cooled and high vacuum quartz assembly for induction melting (in collaboration with Product Development Division (PDD), BARC).

Thermodynamic investigations of inter-metallic phases belonging to Mo-Te, Zr-Sb, Fe-Ge, Ge-Te, Si-Te, systems were carried out. The inter-metallic phases of these binary systems were synthesized by heating the samples in evacuated ampoules and characterized by XRD, SEM-EDX techniques. Thermodynamic stability of the compound was determined by measuring the partial pressures of volatile components employing Knudsen effusion mass loss technique. The standard enthalpy of formation of the compounds was determined using high temperature Calvet calorimeter.

1.2 Phase distribution study on SIMFUEL

The successful performance of alloy fuel (10-15 atom% burn up) is known to be achieved with somewhat porous matrix. The porosity and micro-structure of these alloys are strongly dependent on their composition and phases present. Porosity also influences the extent of fuel swelling and gas release. Thus to assess fuel performance and fuel integrity under high burn-up conditions it is essential to know about the new phases formed and their redistribution that occurs as a result of inter-diffusion and temperature gradient. These issues were addressed by using the base alloy U-10 wt% Zr. The partially simulated fuel (corresponding to 10 atom% burn-up) containing Rh, Ru, Pd and Mo along with calculated amounts of the rare earths (Ce and Nd) were annealed at 1000 °C for 30 days under vacuum. SEM and EDX studies revealed that there are prominent U and Zr rich regions in the alloy containing only noble metals. The noble metals aggregated more in the Zr-rich regions which appeared as light-grey patches. A small amount of third phase (whitish grains with some amount of oxygen coming from the contaminated base metal U) was observed which was distributed sporadically as particles in the matrix. On addition of rare earths the light-grey Zr-rich patches and the U-rich whitish granules ceased to exist, although U-rich and Zr-rich grains of smaller sizes were still present. In the presence

of rare-earths three different phases were present: i) U-rich, ii) Zr-rich with noble metals Rh, Ru and Mo, and iii) Pd rich with Ce and Nd. The phase segregation could be due to the difference in crystal structures and inter-diffusion coefficients of the precipitating phases. Insoluble phase precipitations of Pd with rare-earths and Zr with noble metals corroborate their immiscibility as revealed by the respective equilibrium binary phase diagrams.

1.3 Separation technology in nuclear processing

Nanomaterials have promising potential as sorbents for separation of radio-nuclides from nuclear waste. In this direction, nano-crystalline MnO_2 was synthesized by a simple chemical method and its potential as a sorbent for plutonium in low level liquid waste (LLW) solutions was investigated. The kinetic studies on the sorption of Pu by MnO_2 revealed that equilibrium sorption is obtained in 15 hours; however 90% of sorption could be achieved within an hour. The sorption was nearly independent of the ionic strength (0.01 – 1.0 M) of the aqueous solutions maintained using NaClO_4 , indicating the inner sphere complexation between the Pu^{4+} ions and the surface sites on MnO_2 . Interference studies with different fission products, *viz.*, Cs^+ , Sr^{2+} and Nd^{3+} , revealed a decrease in the percentage sorption with increasing pH of the suspension indicating the competition between the metal ions. However, at the metal ion concentrations prevalent in the low level liquid waste solutions, Pu sorption was only marginally decreased to 90% at pH = 3. This study shows that nano-crystalline MnO_2 can be used as a sorbent for separation of Pu from LLW solutions (In collaboration with Waste Management Division (WMD) and Radioanalytical Chemistry Division (RACD), BARC).

Hydrogen titanate nan-otubes (HTNT) were prepared by hydrothermal method and characterized by SEM, TEM, XRD. The sorption efficiencies for α -emitting radio-nuclides ^{239}Pu , ^{233}U and ^{241}Am were investigated. All three radionuclides were completely taken up by HTNT between pH 1.00 and 6.00 from their mCi/L or mg/L feed concentration. The sorption process was sufficiently fast and complete uptake was within an hour (In collaboration with Nuclear Recycle Group)

Laser desorption/ ionization- Time of Flight Mass Spectrometry (LDI-TOFMS) has been applied to identify and characterize the organic species formed during the extraction of thorium nitrate by 1.1 M tri-*n*-butyl phosphate (TBP) and *N,N*-dihexyl octanamide (DHOA) solutions in *n*-dodecane. Thorium concentrations (at 4 M HNO_3) in aqueous phase have been suitably chosen to load organic phases with or without a third-phase. The extracted species have been characterized for the first time using LDI-TOFMS. The results show feasibility of the use of this technique for understanding extraction mechanisms and third-phase formation behavior of different extractants. Different chemical species observed using this technique is consistent with those observed by small angle neutron scattering (SANS) (in collaboration with Radiochemistry Division (RCD) and Applied Spectroscopy Division, BARC).

1.4 Studies on ceramic waste form

In the interest of possible ceramic host materials for nuclear waste immobilization, a compound of composition $\text{CaZrTi}_2\text{O}_7\text{-Nd}_2\text{Ti}_2\text{O}_7$ has been prepared by multi-step solid state reaction of constituent oxides. The products were characterized by XRD, SEM and EDX. Four different phases, namely, i) monoclinic zirconolite, ii) cubic perovskite, iii) cubic pyrochlore, and iv) monoclinic $\text{Nd}_2\text{Ti}_2\text{O}_7$ -type were identified in this system. All the phases, being components of synroc, may be potential matrices for nuclear waste immobilization. Moreover in the system $(\text{Ca,Zr})_{1-x}\text{Nd}_{2x}\text{Ti}_2\text{O}_7$ ($0.00 < x < 1.00$) the phases fields in the region $0.20 < x < 0.40$ shows co-existence of zirconolite, perovskite and cubic pyrochlore phases as composites. On the other hand phase fields in between $0.50 < x < 0.70$ shows co-existence of perovskite and cubic pyrochlore. All the phases show inter-diffusion of atoms as evident from the unit cell parameters and compositional analysis by EDX. It has been inferred that that the system is very stable towards cationic order-disorder and therefore has a potential for immobilization of other radioactive ions.

1.5 Optimization of UF_6 to UF_4 dry reduction process

For high yield synthesis of UF_4 , a convenient process is being developed by Chemical Technology Division (CTD) employing reduction of UF_6 by hydrogen. For optimization of the process, identification of various products in the reaction is essential. Thus the samples produced by dry reduction of UF_6 were analyzed by XRD. The samples showed well crystalline UF_4 in most of batches. Detectable amounts of $\beta\text{-UF}_5$ and U_2F_9 in sample batches were also observed. Further, hydration products of UF_4 obtained during dry reduction process, followed by heating at several temperatures were also investigated by XRD. Three different types of hydrated samples, namely cubic, orthorhombic and monoclinic, were identified. The monoclinic phase of hydrated sample could be assigned to $(\text{UO}_2)_2\text{F}_2 \cdot 1.57(\text{H}_2\text{O})$. These inputs are crucial in increasing the yield of UF_4 (in collaboration of Chemical Technology Division (CTD) BARC).

2. Hydrogen Energy: Generation, Storage and Mitigation

2.1 Hydrogen generation

Thermo-chemical cycle

Various aspects of S-I cycle, such as catalyst development, effect of possible reactants on the catalytic activity, iodine speciation during the reaction, etc. have been investigated. The evaluation of catalytic activity of $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{O}_3$ for sulfuric acid decomposition in the presence of I_2 and HI in the feed stream in addition to sulfuric acid as the major component was carried out. The % SO_2 conversion for sulfuric acid decomposition reaction with 0.2 g of powder sample of $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{O}_3$ catalyst, as a function of time at 800 °C for 20 h with WHSV of 27.6 g acid g^{-1} catalyst h^{-1} (acid flux 0.05 ml min^{-1}) with three different feed compositions were evaluated. No decrease in SO_2 yield was observed at 800 °C for 20 hours. Subsequently, the XRD patterns of the spent catalysts revealed that

there was no change in phase due to use for sulfuric acid decomposition reaction for 20 h even in the presence of impurities like HI and I₂. Post characterization results over spent samples support the temperature, time dependent catalytic activity data that the Fe_{1.8}Cr_{0.2}O₃ catalyst is active and stable for sulfuric acid decomposition reaction in the presence of I₂ and HI in feed as impurities.

Evolved gas analysis by TG-mass spectrometry of the spent Pt/Al₂O₃ catalyst (used for sulfuric acid decomposition for 100 h) was carried out in the temperature range of 40 to 1100 °C. The TG exhibited a two-step decomposition pattern of aluminum sulfates (present on the catalyst) with the evolution of SO₂. This type of decomposition was also observed earlier in the TG-IR of the spent Pt/Al₂O₃ catalyst, whereas bulk aluminum sulfate exhibited single step decomposition at a much higher temperature. The above thermal studies of the spent catalyst suggest that metal-support synergism facilitates decomposition of sulfate species at lower temperatures in dispersed samples. The sulfate species present on support (in the presence of dispersed Pt-particles) can play an important role in decomposition mechanism in contrast to the reported SO₃ adsorption-decomposition mechanism on noble metal particles.

In order to identify the polyiodide species present in the HI phase coming out of the Bunsen reaction due to excess iodine, electro analytical techniques were applied. Solutions containing of HI and I₂ in varying ratios were made in the range of [HI:I₂ ratios 10:1 to 1:10]. Experiments carried out using DME (Dropping Mercury Electrode), showed a distinct shift in peak current and voltage with increasing iodine concentration. Shift in peak current position and voltage indicate the change in concentration of polyiodic species.

Photo-catalytic methods

In pursuance of our approach for hydrogen generation, photo-catalytic methods for splitting of water have been explored. Several photo-catalysts were developed and their catalytic activity for water splitting reaction was evaluated. Ultrathin PdO-TiO₂ composite films have been prepared by thermal decomposition of the multilayer Langmuir-Blodgett (LB) films of octadecyl amine-metal (Ti and/or Pd) ion complexes and have been used as a photocatalyst for hydrogen generation from methanol-water mixture. Enhanced H₂ production has been observed in the composite film as compared to pure TiO₂ film.

Photo-catalytic activity of CdS-ZnO and indium doped CdS-ZnO composites was studied for hydrogen generation from an aqueous solution of Na₂S and Na₂SO₃ using sunlight. Indium doped CdS-ZnO showed the highest activity for hydrogen generation. In the presence of Pd co-catalyst, higher activity was also noted. Hydrogen evolution rate of 48 μ mole per hour was obtained when 50 mg of Pd-CdInS-ZnO was suspended in 25 ml of the solution and irradiated using fluorescent lamp as source of light.

Various CuO:TiO₂ composite samples in the ratio 2:8, 5:5 and 7.5:2.5 were prepared by sol-gel method. Biphasic nature of samples (CuO and TiO₂ anatase phase) was revealed by powder XRD. These samples were tested in sunlight for photo-catalytic activity for hydrogen generation from water-methanol mixture. All samples showed photo-catalytic activity. There was no increase in H₂ yield during dark period. Maximum hydrogen yield of ~306 μmole in 12 h was observed with 0.1 g of the CuO:TiO₂ (2:8) catalyst (rate of H₂ evolution = 255 μmole/ g/ hr). The effect of doping of CuO in TiO₂ was also investigated. Ti_{1-x}Cu_xO₂ oxides (x = 0.0, 0.02, 0.06) were prepared by sol-gel route. Samples were single phasic (TiO₂ anatase phase) solid solutions as revealed by powder XRD. These samples showed photo-catalytic activity and generated hydrogen when a water-methanol mixture was exposed to sunlight. There was no increase in H₂ yield during dark period. Maximum Hydrogen yield was ~430 μmole in 12 h with 0.1 g of the Ti_{0.98}Cu_{0.02}O₂ oxide. The rate of H₂ evolution over this sample was calculated to be 360 μmoles/g/hr equivalent to 8.06 ml/g/hr.

Theoretical studies

The decomposition of SO₃ is energetically the most demanding step for producing hydrogen through the sulfur-iodine thermo-chemical cycle. Using first principles density functional theory, a comparative study of SO₃ interaction with three tetramer clusters (Ag₄, Pd₄, and Ag₂Pd₂) deposited on the alumina surface has been carried out. All calculations were performed using the plane wave based pseudo-potential approach under the spin-polarized density functional theory. The results revealed that the supported Ag-Pd bimetallic clusters are more efficient to weaken the S-O bond in the SO₃ molecule. A comparison of the SO₃ interaction with Ag₄, Pd₄, and Ag₂Pd₂ tetramers showed that while Ag₄ elongates the S-O bond by 7%, Ag₂Pd₂@Al₂O₃ can stretch the S-O bond up to 14%. The higher efficiency of the Ag₂Pd₂@Al₂O₃ system is attributed to both excess charge transfers from the oxide surface and the combination of acceptor-donor properties of Pd and Ag, respectively, which makes a better catalyst for weakening the S-O bond in the SO₃ molecule.

2.2 Hydrogen storage

Both experimental and theoretical investigations were performed with reference to hydrogen storage in different materials. The systems investigated includes, Zr_{2-x}Ti_xNi (x = 0, 0.5, 1.0) alloys and annealed Ti₂CrV + x ZrFe_{1.8}V_{0.2} (x = 0, 5, 10, 20 %) composite systems. Detailed hydrogen absorption kinetics was done on Ti₂Nb_{0.4}Fe_{0.6} alloy and activation energy for hydrogen absorption was calculated. Different hydrogen absorption sites have been identified by room temperature Mössbauer measurements on Ti₂Nb_{1-x}Fe_x and Ti₂Nb_{1-x}Fe_xH_y (x = 0.4, 0.6; y = 3.65, 4.47).

Hydrogen adsorption behavior of two SiC nanostructures, a planar sheet and a nanotube (10, 0) of 1 nm diameter decorated by Ti atoms has been investigated. All calculations have been performed using a plane-wave based pseudo-potential method. The lowest energy structure of the Ti adsorbed SiC sheet shows that Ti atom distorts the sheet in such

a way that one of the Si atoms goes down the plane and the Ti atom binds with nearest three carbon atoms. The interaction of this Ti decorated sheet with hydrogen suggests that each Ti atom can bind up to four hydrogen molecules (all hydrogens are adsorbed in the molecular form) with an average binding energy of 0.37 eV. For SiC nanotube, the adsorption of Ti favors the hexagonal hollow site. Moreover, on interaction of this Ti decorated tube with hydrogen leads to dissociation of the first hydrogen molecule in the atomic form and thereafter adsorbs hydrogen in the molecular form. The average binding energy of hydrogen molecules on this Ti decorated tube is estimated to be 0.65 eV. Based on these results it was inferred that the Ti decorated SiC nanostructures moderately bind with hydrogen molecules (within the energy window for hydrogen storage materials) and therefore, can be considered as one of the potential hydrogen storage material.

In the present day's scenario, there is a strong need of an irreversible hydrogen sink inside the reactor containment which can effectively absorb/adsorb hydrogen under severe accident condition and carbon nano-tubes (CNTs) have been chosen as one of the promising material. To overcome the challenges in using carbon nano-tubes for actual reactor condition, it was decided to undertake a systematic study on this subject. The initial results show that multi-walled carbon nano-tubes (MWCNT) can absorb a maximum of 0.056 wt% of hydrogen at room temperature and up to 50 bar of hydrogen pressure. The hydrogen storage capacity decreases with increase in temperature and at 323 K the hydrogen storage capacity was found to be 0.03 wt% for the bare multi-walled carbon nano-tubes. No structural change was observed in the hydrogenated carbon nano-tubes under the experimental conditions which indicate the interaction of hydrogen is physisorption in nature and hydrogen molecules do not interact chemically with the nano-tubes. (Work in collaboration with Materials Group and Reactor Design & Development Group)

2.3 Hydrogen mitigation

Hydrogen mitigation in nuclear reactors/ submarines is an important problem. Several approaches have been adopted for this. Among them, catalytic conversion of hydrogen to water and adsorption of liberated hydrogen on carbon nano-tubes, are perused. In the former approach several catalysts have been developed and evaluated. Hydrogen - air recombination reaction for two initial hydrogen concentrations of 4 % and 1.5 % in air were tested. All the catalysts were active for this reaction with $t_{1/2}$ of 2.7 minutes for 4.0% initial hydrogen concentration while for 1.5 % initial hydrogen concentration it was 3.4 minutes indicating high performance of our catalyst. In the latter approach carbon nano-tubes both bare and doped with palladium have been prepared. Their possible application for hydrogen mitigation is being evaluated (in collaboration with Reactor Engineering Division (RED), BARC).

3. Chemistry of Nano-materials and Composites

3.1 Oxide based nano-materials

Luminescent materials based on lanthanide ion (Ln^{3+}) emission have many applications in phosphor lamps, display devices, cathode ray tubes and components of telecommunication as well as active laser materials. Recently there has been great interest in incorporation of these luminescent materials in several host lattices including polymer based materials because of easy processing of polymers and ease of integrating different components.

GdVO_4 nanoparticles doped with Ln^{3+} ($\text{Ln}^{3+} = 1, 3, 5, 7, 10, 15$ at.%) have been prepared by the wet chemical method using polyethylene glycol (PEG) and ethylene glycol (EG) as capping agent and solvent medium. In a typical synthesis a solution containing Gd^{3+} was treated with a solution containing VO_4^{3-} hydrolyzed by addition of NaOH solution. The luminescence study showed an efficient energy transfer from vanadate absorption of GdVO_4 to Ln^{3+} and thereby enhanced emissions were obtained. As prepared samples were well dispersed in ethanol, methanol and water and were incorporated into polymer films of polyvinyl alcohol (PVA) and borax. These showed blue, green, orange and red colors depending on different Ln^{3+} ions ($\text{Ln}^{3+} = \text{Dy}^{3+}, \text{Eu}^{3+}, \text{Sm}^{3+}, \text{Tm}^{3+}$) doped in GdVO_4 .

Both metastable orthorhombic and stable monoclinic forms of Y_2GeO_5 were prepared by urea hydrolysis of $\text{Y}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ (dissolved in conc. HCl) and $\text{Ge}(\text{OPr}^i)_4$ in ethylene glycol. Both phases were doped with optically active trivalent lanthanide ions such as europium and terbium for their potential applications as phosphor materials.

Luminescent nanomaterials of BaSnO_3 , SrSnO_3 , $\text{Y}_2\text{Sn}_2\text{O}_7$ etc., doped with lanthanide ions (Eu^{3+} , Tb^{3+} and Dy^{3+}) with different shapes like spheres and rods were synthesized at relatively low temperatures and their luminescence properties were investigated by both steady state and time resolved luminescence techniques combined with electron paramagnetic resonance spectroscopy. Dual emission has been observed from $\text{BaSnO}_3:\text{Eu}$ nanomaterials upon single wavelength excitation, which has been attributed to the co-existence of both Eu^{3+} and Eu^{2+} in the BaSnO_3 lattice. In several cases solubility limit of lanthanide ions in the lattice has been estimated by recording the emission spectrum of compounds doped with Eu^{3+} ions. Some of the lanthanide doped nanomaterials have been incorporated in polymers like PMMA/PVA. These composites have improved luminescence properties.

Sono-chemically synthesized rare - earth doped Bi_2O_3 nano-rods, a bifunctional material, exhibits both photo-catalytic properties and white light emission. Normally "phosphor is complementary to photo-catalyst" as long as both originate from the same set of two optical levels. However, in this case, the emission is primarily from the dopant levels. The novelty of the work lies in striking a balance, where one is able to get emission from the rare-earth dopant ions while still preserving the photo-catalytic activity of the host material. Zinc phosphate based, $\text{Zn}_3(\text{PO}_4)_2:\text{RE}$ ($\text{RE} = \text{Eu}, \text{Tb}, \text{Ce}$), nano-phosphors

have been synthesized sono-chemically and a white light emitting composition could be achieved. The synthesis has been carried out in the absence of any capping agent and it is also a surfactant free and template free technique which ensures easy recovery of the final product. The presence of capping agents is known to partially quench the luminescence due to unfavorable energy transfer and hence it is undesirable.

Nano-crystalline BaWO_4 was prepared by a sono-chemical route and investigated for sorption of rhodamine B and methylene blue. Complete removal of these dyes was possible within a short time of 10-15 minutes. The adsorbed dyes could be desorbed completely from nanoparticle surfaces by annealing at moderate temperature and were efficient for multi-cyclic use. The adsorbent capacity of the tungstate is much higher than that reported for other nanomaterials like Fe_2O_3 , MnO_2 , WO_3 , etc.

Nano-sorbents are being developed for environmental remediation and separation of radio-nuclides. As part of this work, zinc oxide nanoparticles were synthesized by two different routes namely pyrolytic and gel combustion methods and characterized using different techniques like XRD, TGA/DSC and diffuse reflectance spectrophotometry, Zeta potential, NMR and IR. The efficiency of the nanoparticles with respect to sorption of different toxic species like chromate and rhodamine 6G was evaluated. The studies showed that the synthesis route adopted affects the characteristics of the nanoparticles, thus leading to the difference in the sorption efficiency. The mechanism of sorption was proposed was based on the different characterization studies and it was found that the sorption was not only an electrostatic interaction but can occur due to the presence of pores or some binding groups.

3.2 Metal chalcogenides nano-materials

Unlike metal oxides, the chalcogenides materials are delicate structures and readily undergo composition and phase changes, and hence a softer route for their synthesis is desirable. Single source molecular precursors (SSMP) have emerged as promising synthons for the preparation of delicate composition and phase of metal chalcogenides nano-materials and thin films and success of the process relies on the availability of desired precursor. In our approach in developing SSMPs, synthesis of Groups 11, 12, 14 and 15 metal complexes have been undertaken and the utility of these complexes for the preparation of metal chalcogenides nano-structures has been demonstrated. Metal chalcogenide materials were prepared using pyrimidyl selenolates of group 11, 12 and 15 metals of the type, $[\text{M}\{\text{SeC}_4\text{H}(4,6\text{-Me})_2\text{N}_2\}]_n$ ($\text{M} = \text{Cu}$ or Ag), $[\text{Cd}\{\text{SeC}_4\text{H}(4,6\text{-Me})\text{N}_2\}_2(\text{tmeda})]$, $[\text{Hg}\{\text{SeC}_4\text{H}(4,6\text{-Me})_2\text{N}_2\}_2]$, $[\text{M}(\text{SepymMe}_2)_3]$ ($\text{M} = \text{Sb}$, Bi). Nanoparticles of Cu_2Se_4 and Ag_2Se have been prepared in dodecanthiol by decomposition of $[\text{M}\{\text{SeC}_4\text{H}(4,6\text{-Me})_2\text{N}_2\}]_n$ ($\text{M} = \text{Cu}$ or Ag) while copper selenide thin film has been deposited on glass substrate by AACVD of $[\{\text{Cu-SeC}_4\text{H}(4,6\text{-Me})\text{N}_2\}_4]$. The complexes, $[\text{Cd}\{\text{SeC}_4\text{H}(4,6\text{-Me})_2\text{N}_2\}_2\text{tmeda}]$ and $[\text{Hg}\{\text{SeC}_4\text{H}(4,6\text{-Me})_2\text{N}_2\}_2]$ either alone or in combination on pyrolysis in OA/OA, OA/TOPO and TOP/TOPO afforded CdSe, HgSe or CdHgSe nano-particles. Thermolysis of $[\text{In}\{\text{SeC}_4\text{H}(3\text{-Me})\text{N}_2\}_3]$ in TOPO, OA, HDA in the temperature range

of 230-330 °C yield indium selenide nanomaterials of different morphologies while thermolysis of both the complexes, $[\text{In}\{\text{SeC}_5\text{H}_3(3\text{-Me})\text{N}_2\}_3]$ and $[\text{Cu}\{\text{SeC}_5\text{H}_3(3\text{-Me})\text{N}_2\}_3]$ in the same coordinating solvents afforded tetragonal phase of CuInSe_2 nanomaterials. Nanomaterials of tin selenide have been prepared by injecting $[\text{Et}_2\text{Sn}\{\text{SeC}_5\text{H}_3\text{N}(3\text{-Me})\}_2]$ ($\text{R} = \text{H}, \text{Me}$) and $[\text{Bu}_2\text{Sn}(\text{SeC}_5\text{H}_4\text{N})_2]$ in hot oleyl amine while thin films of tin selenide have been deposited by AACVD of $[\text{Bu}_2\text{Sn}(\text{SeC}_5\text{H}_4\text{N})_2]$ on glass and silicon substrates at different temperatures.

4. Organometallic Chemistry

4.1 Organometallic chemistry of platinum group metals

In pursuance of our investigations on organometallic chemistry of platinum group metal complexes with reference to antitumor activity, catalysts in homogeneous catalysis and supra-molecular assemblies various systems have been designed and synthesized. Platinum complexes of the general formula $[\text{Pt}(\text{N}^{\text{O}}\text{N})(\text{dmpzCH}_2\text{CH}_2\text{Se}(\text{CH}_2)_n\text{COOH})][\text{NO}_3]_2$ ($\text{N}^{\text{O}}\text{N} = \text{en}$ or 2NH_2 , tmeda; $n = 1, 2$) and $[\text{Pt}(\text{N}^{\text{O}}\text{N})(\text{dmpzC}_6\text{H}_4\text{Se}(\text{CH}_2)_n\text{COOH})][\text{NO}_3]_2$ ($\text{N}^{\text{O}}\text{N} = \text{en}$ or 2NH_3 and $n = 1, 2$) have been synthesized by the reactions of $[\text{Pt}(\text{N}^{\text{O}}\text{N})(\text{NO}_3)_2]$ with one equivalent of either $\text{dmpzCH}_2\text{CH}_2\text{Se}(\text{CH}_2)_n\text{COOH}$ or $\text{dmpzC}_6\text{H}_4\text{Se}(\text{CH}_2)_n\text{COOH}$ in the presence of a base. Similarly, the reaction of $[\text{PtCl}_2(\text{PhCN})_2]$ with $\text{dmpzCH}_2\text{CH}_2\text{SeCH}_2\text{COOH}$ in CH_2Cl_2 yielded $[\text{Pt}(\text{dmpzCH}_2\text{CH}_2\text{SeCH}_2\text{CH}_2\text{COOH})_2] \cdot (\text{Cl})_2$ as revealed from crystal structural analysis. These complexes were characterized by microanalyses, NMR (^1H , ^{13}C , ^{77}Se and ^{195}Pt) and IR spectroscopy. The complex $[\text{Pt}(\text{en})(\text{dmpzCH}_2\text{CH}_2\text{SeCH}_2\text{COOH})][\text{NO}_3]_2$ is stable in water for several days as evaluated by ^{195}Pt NMR spectroscopy (δ -3348 ppm). It's binding with 5'-GMP was studied by ^{195}Pt NMR to understand its biological activity.

The ligating behavior of $\text{dmpzC}_6\text{H}_4\text{SeX}$ towards palladium and platinum has been examined. The complexes $[\text{M}(\text{SeC}_6\text{H}_4\text{-dmpz})_2]$ have been synthesized and their reactivity has been studied. The molecular structures of palladium selenolate complexes, $[\text{Pd}(\text{SeC}_6\text{H}_4\text{-dmpz})_2]$ and $[\text{Pd}_2\text{Cl}_2(\text{SeC}_6\text{H}_4\text{-dmpz})_2]$ ($\text{dmpz} = 3,5\text{-dimethyl pyrazole}$) have been structurally characterized. The former exhibits two six-membered rings joined to Pd through Se and N atoms of the ligand. The selenium atoms are in mutually *cis* position. The complex, $[\text{Pd}_2\text{Cl}_2(\text{SeC}_6\text{H}_4\text{-dmpz})_2]$ is a binuclear palladium derivative with two bridged selenolate group forming a $\text{Pd}_1\text{Se}_1\text{Pd}_2\text{Se}_2$ four-membered ring. Each of the nitrogen atoms from dmpz ring coordinates to palladium to form a *trans* isomer. The bis-complex, $[\text{M}(\text{SeC}_6\text{H}_4\text{-dmpz})_2]$, showed a strong interaction towards solvent molecules such as ethyl acetate, diethyl ether, toluene, etc. as revealed by ^1H NMR spectroscopy. The complex $[\text{Pt}(\text{SeC}_6\text{H}_4\text{-dmpz})_2]$ when treated with $[\text{Pt}(\text{PEt}_3)_2(\text{OTf})_2]$ (1:1 mole ratio) in toluene to yielded $[\text{Pt}_2(\text{SeC}_6\text{H}_4\text{-dmpz})_2(\text{PEt}_3)_2](\text{OTf})_2$ (^{31}P NMR 15.9 ($^1J_{\text{Pt-P}} = 2868 \text{ Hz}$); ^{77}Se NMR t -290 (d, $^2J_{\text{P-Se}} = 85 \text{ Hz}$ and $^1J_{\text{Pt-Se}} = 495 \text{ Hz}$). The bis complexes, $[\text{M}(\text{SeC}_6\text{H}_4\text{dmpz})_2]$ readily react with Ag ions. Reaction of $[\text{M}(\text{SeC}_6\text{H}_4\text{dmpz})_2]$ with AgOTf (2:1 mole ratio) in acetonitrile yielded a complex of molecular formula $[\{\text{M}(\text{SeC}_6\text{H}_4\text{dmpz})_2\}_2\text{Ag}]\text{OTf}$. The ^{77}Se NMR spectrum of this complex showed a signal at -27.0 ppm which is shifted upfield by 42 ppm from platinum bis complex.

The allyl palladium selenolate-complexes, $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{Se}^\text{n}\text{N})]_n$ and $[\text{Pd}(\eta^3\text{-C}_4\text{H}_7)(\text{Se}^\text{n}\text{N})]_n$ ($\text{Se}^\text{n}\text{N} = \text{dmpzC}_6\text{H}_4\text{Se}$) exist in a dynamic equilibrium between dimer and trimer as revealed by variable temperature $^1\text{H-NMR}$ spectroscopy. On lowering the temperature signals for dimer ($n = 2$) and trimer ($n = 3$) could be separated. In the trimeric molecule all the three ligand moieties are disposed differently as revealed by low temperature NMR spectral analysis. Pyrolysis of selenolato-bridged allyl palladium complex, $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{Se}^\text{n}\text{N})]$ ($\text{Se}^\text{n}\text{N} = 2\text{-SeC}_6\text{H}_4\text{dmpz}$) gave Pd_7Se_4 (when heated in a furnace at 365°C) or $\text{Pd}_{17}\text{Se}_{15}$ (in oleylamine at 265°C) depending pyrolytic conditions.

Keeping in mind the interest and importance of cyclometalated palladium complexes (or palladacycle) due to their outstanding applications as catalyst in organic synthesis and their rich reaction chemistry, cyclopalladation reaction of organochalcogen ligands and its mechanism has been investigated. Accordingly, palladacycles derived from organoselenium and organotellurium ligands have been prepared. The C-H (sp^3) activated metallated complex $[\text{Pd}_2(\mu\text{-Cl})_2\{\text{MesSeC}_6\text{H}_2(\text{Me}_2)\text{CH}_2\}_2]$, $[\text{Pd}(\mu\text{-Cl})\{\text{MesSeC}_6\text{H}_2(\text{Me}_2)\text{CH}_2\}]_n$ and the intermediate $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{Mes}_2\text{Se})_2]$ were prepared and characterized by NMR (^1H and $^{77}\text{Se}\{^1\text{H}\}$) and microanalysis. The molecular arrangements were revealed by single crystal XRD analysis. From the molecular geometry and other experimental evidences it was noticed that the strong intra-molecular C-H...Pd interaction is the key factor for activation of the C-H sp^3 bond.

4.2 Oxidative addition reactions of diorganodichalcogenides to Pd(0) and Pt(0) precursors

Oxidative addition reactions of organochalcogen ligands with low valent palladium complexes are of relevance in C-chalcogen bond formation catalyzed by palladium compounds. Thus oxidative addition reactions of diselenides and ditellurides with $[\text{M}(\text{PPh}_3)_4]$ ($\text{M} = \text{Pt}$ or Pd) have been investigated. The reactions of $(4,6\text{-R}_2\text{C}_4\text{HN}_2)_2\text{Se}_2$ with $[\text{M}(\text{PPh}_3)_4]$ ($\text{M} = \text{Pt}$ or Pd) in benzene afforded complexes of composition, $[\text{Pt}\{2\text{-Se-C}_4\text{H}(4,6\text{-R})_2\text{N}_2\}_2(\text{PPh}_3)_2]$ and $[\text{Pd}\{\text{Se-C}_4\text{H}(4,6\text{-R})_2\text{N}_2\}\{\eta^2\text{-Se-C}_4\text{H}(4,6\text{-R})_2\text{N}_2\}(\text{PPh}_3)]$ ($\text{R} = \text{H}$ or Me). The former when left in solution dissociated to $[\text{Pt}\{\text{Se-C}_4\text{H}(4,6\text{-R})_2\text{N}_2\}\{\eta^2\text{-Se-C}_4\text{H}(4,6\text{-R})_2\text{N}_2\}(\text{PPh}_3)]$ and PPh_3 . Treatment of $[\text{PtCl}_2(\text{P}^\text{n}\text{P})]$ ($\text{P}^\text{n}\text{P} = \text{dppe}$ or dppp) and $\text{NaEC}_4\text{H}(4,6\text{-R})_2\text{N}_2$ (for $\text{E/R} = \text{Se/H/Me}$ or Te/Me) gave mono-nuclear complexes $[\text{Pt}\{2\text{-E-C}_4\text{H}(4,6\text{-R})_2\text{N}_2\}_2(\text{P}^\text{n}\text{P})]$ ($\text{R} = \text{H}$ or Me , $\text{P}^\text{n}\text{P} = \text{dppe}$ or dppp) which on leaving for recrystallization in dichloromethane/ CDCl_3 solution resulted in tri-nuclear chalcogenido-bridged complexes $[\text{Pt}_3(\mu\text{-E})_2(\text{P}^\text{n}\text{P})_3]2\text{Cl}$. The latter were also formed when $[\text{PtCl}_2(\text{P}^\text{n}\text{P})]$ ($\text{P}^\text{n}\text{P} = \text{dppe}$ or dppp) was treated with sodium salts of 2-pyrimidyltelluroate. The substitution reactions between $[\text{PdCl}_2(\text{P}^\text{n}\text{P})]$ ($\text{P}^\text{n}\text{P} = \text{dppe}$ or dppp) and $\text{NaEC}_4\text{H}(4,6\text{-R})_2\text{N}_2$ ($\text{E} = \text{Se}$ or Te ; $\text{R} = \text{H}$ or Me) afforded chalcogenido-bridged tri-nuclear complexes, $[\text{Pd}_3(\mu\text{-E})_2(\text{P}^\text{n}\text{P})_3]2\text{Cl}$ ($\text{P}^\text{n}\text{P} = \text{dppe}$ or dppp).

Oxidative addition reactions between $[\text{M}(\text{PPh}_3)_4]$ ($\text{M} = \text{Pt}$, Pd) and nicotinamide diselenide have been performed to obtain chelated complexes of general formula, $[\text{M}\{\eta^2\text{-Se-C}_5\text{H}_3(3\text{-COR})\text{N}\}\{2\text{-Se-C}_5\text{H}_3(3\text{-COR})\text{N}\}(\text{PPh}_3)]$ ($\text{R} = \text{NH}_2$, NHPh , NHpym) while a similar reaction of $[\text{M}(\text{PPh}_3)_4]$ ($\text{M} = \text{Pt}$, Pd) with $[2\text{-NC}_5\text{H}_3(3\text{-CONHPh})\text{SeI}]$ yielded

the expected oxidative addition products, $[M(I)\{2\text{-Se-C}_5\text{H}_3(3\text{-CONHPh)N}\}(\text{PPh}_3)_2]$ which on prolonged standing in dichloromethane gave several products such as $[M(I)\{\eta^2\text{-Se-C}_5\text{H}_3(3\text{-CONHPh)N}\}(\text{PPh}_3)]$, $[M(I)(\text{Ph})(\text{PPh}_3)_2]$ and $[2\text{-NC}_5\text{H}_3(3\text{-CO)Se-NH}]$. Few of them have been structurally characterized. Substitution reactions between $[M\text{Cl}_2(\text{P}^n\text{P})]$ ($M = \text{Pt}$ or Pd ; $\text{P}^n\text{P} = \text{dppm}$, dppe or dppp) and NaEAr ($\text{Ar} = \text{Mes}$, Ph or tolyl ; $\text{E} = \text{Se}$ or Te) afforded mononuclear complexes of the type, $[M(\text{EAr})_2(\text{P}^n\text{P})]$.

4.3 Supra-molecular chemistry

Supra-molecular assemblies based on weak secondary interactions have received considerable recent attention. Three different families of non-chelating bidentate chalcogen ligands, viz., $\text{dmpzC}_6\text{H}_4\text{SeX}$, 4-mercaptobenzoic, 4-pyridylselenolate, have been employed. The reactions of $\text{dmpzC}_6\text{H}_4\text{SeX}$ ($\text{X} = \text{CH}_2\text{COOH}$, $\text{CH}_2\text{CH}_2\text{COOH}$, $\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_2\text{CH}_2\text{NH}_2$) with $\text{PdCl}_2/\text{PtCl}_2$ in acetonitrile gave complexes of composition, $[M\text{Cl}_2(\text{dmpzC}_6\text{H}_4\text{SeX})]$ ($M = \text{Pd}$ or Pt) as yellow to orange crystalline solids. The structures of four such complexes were established by single crystal X-ray analyses which exhibit hydrogen bonded chain structures.

The metal building blocks $\text{Pt}(\text{P}^n\text{P})(\text{OTf})_2$ ($\text{P}^n\text{P} = 2\text{PEt}_3$, dppe) on treatment with 4-mercaptobenzoic acid yielded a product in which two phosphines are *cis* oriented as predicted from NMR spectra which is confirmed by X-ray structural analysis. The S atom bridges between two Pt centers whereas the carboxylic acid group is H-bonded with another molecule both sides thus making a linear chain via extended intermolecular H-bonding in the solid state. The same reaction with Na-salt of the ligand, however, yielded a monomeric complex $[\text{Pt}(\text{PEt}_3)_2(\text{SC}_6\text{H}_4\text{COOH})_2]$ in which phosphines are *trans* oriented as confirmed by the structural analysis. The reaction of $[\text{Pd}(\text{dppe})(\text{OTf})_2]$ with two eqv. of 4-mercapto benzoic acid and one eqv. of 3-mercapto benzoic acid yield products of composition $[\text{Pd}(\text{dppe})(\text{SC}_6\text{H}_4\text{COOH})_2](\text{OTf})_2$. The molecular structure of the latter, is isomorphous to $[\text{Pt}_2(\text{PEt}_3)_2(\text{SC}_6\text{H}_4\text{COOH})_2](\text{OTf})_2$. In these complexes the thiolate group bridges two metal centers. The free carboxylate groups are inter-molecularly H-bonded via water molecule and triflate ions forming an infinite linear chain.

The reactions of 4,4'-dipyridylselenide or 4-pyridylselenolate ion with palladium and platinum compounds have been explored and several mono-, bi- and trinuclear complexes have been isolated and several of them have been structurally characterized. The reaction of $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ with one and two eqv. of 4-NaSepy yielded a mixture of products, like *trans*- $[\text{Pd}(\text{PPh}_3)_2\text{Cl}(4\text{-Sepy})]$, $[\text{Pd}(\text{PPh}_3)\text{Cl}(4\text{-Sepy})]_n$ and *trans*- $[\text{Pd}(\text{PPh}_3)_2(4\text{-Sepy})_2]$ as observed in ^{31}P NMR spectra. The reaction of 4,4'-py₂Se₂ with $\text{Pt}(\text{PPh}_3)_4$ exclusively yielded *trans*- $[\text{Pt}(\text{PPh}_3)_2(\text{Sepy})_2]$ whereas the reaction of *cis*- $[\text{Pt}(\text{PPh}_3)_2\text{Cl}_2]$ with two eqv. of 4-NaSepy gave *trans*- $[\text{Pt}(\text{PPh}_3)_2(\text{Sepy})_2]$. The reaction of $[M_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PR}_3)_2]$ with two eqv. of 4-NaSepy exclusively yielded orange products of composition $[M\text{Cl}(4\text{-Sepy})(\text{PR}_3)]_n$, except triphenyl phosphine palladium complex, which exist as a selenolato bridged dimer, all other are trimeric.

4.4 Organometallic chemistry of gallium and indium

The remarkable photo-physical properties of AlQ_3 have stimulated R & D activities on group 13 organometallic compounds. We have synthesized organo-gallium /-indium complexes to study their stereochemistry, photo-physical properties. The dialkylmetal complexes were prepared by treatment of triorgano-gallium and -indium etherates with protic ligands like 2-(2'-hydroxyphenyl)benzoxazole, 2-(2'-hydroxyphenyl)benzimidazole, 2-(2-hydroxyphenyl)benzothiazole and Schiff bases [prepared using carbonyl compounds (such as 3, 5-di-tert.butyl-2-hydroxy benzaldehyde or 2-hydroxy acetophenone) and amines (such as 1, 4-diaminobenzene and 4,4'-diaminodiphenylmethane)] and characterized. The gallium complexes derived from benzoazole ligands are monomeric while the corresponding indium derivatives are dimeric. The photoluminescence studies have revealed that the quantum yields from the complexes are always higher than the corresponding free ligands.

4.5 Organoselenium compounds as antioxidant and radio-protector

Ever since selenium is recognized as an essential micronutrient extensive work on synthetic organoselenium compounds with reference to their biological aspects has been carried out by several research groups. In our efforts to develop low molecular weight water soluble organoselenium compounds, design and synthesis of three different classes of derivatives have been undertaken. These include synthesis of peptide based $PhSeCH_2CONHCHRCOOH$ ($R = H, CH_3, CH_2Ph, \text{proline}$), $\{PhC(OCH_2CH_2O)CH_2Se\}_2$ and $PhC(OCH_2CH_2O)CH_2Se(CH_2)_nNH_2$ ($n = 2, 3$).

Antioxidant, glutathione peroxidase (GPx) and radio-protector activities of several organoselenium compounds have been investigated by 1H NMR spectroscopy and HPLC methods. The *in vitro* GPx-like catalytic activity of pyridyl (py) and pyrimidyl (pym) selenides, $(Ar-Se)_2$ and $Ar-Se-(CH_2)_nX$ [$Ar = \text{py or pym}; n = 1-3, X = -COOH; n = 2-3, X = -NH_2, -OH$] is dependent on electron density around selenium atom as is reflected from $^{77}Se\{^1H\}$ NMR chemical shifts. Based on HPLC data it was observed that the diselenides, $(Ar-Se)_2$ ($Ar = \text{py, pym}$) exhibited higher activity followed by monoselenides having $-COOH, -OH$ and $-NH_2$ groups. Radio-protector activity of a water soluble nicotinamide diselenide $[2-NC_5H_3(3-CONH_2)Se]_2$ at 2.5 mM, evaluated by γ -ray induced DNA damage assay, was 55 % protection of DNA. The mechanism of GPx catalytic activity of $[2-NC_5H_3(3-CONHR)Se]_2$ ($R = H, Ph$) was investigated by ^{77}Se NMR spectroscopy and various species, like selenenic acid ($\delta \sim 1050$ ppm), selenenyl sulfide ($\delta \sim 600$ ppm), involved in the catalytic cycle have been identified. The compounds $Se\{(CH_2)_nCONHR\}_2$ exhibited higher radical scavenging capacity as compared to a standard antioxidant butyl hydroxy toluene (BHT). Among all the selenides of this series, $Se\{(CH_2)_nCONHR\}_2$ ($R = \text{o- and p-aminophenol}$) showed highest activity (in collaboration with Radiation and Photochemistry Division (RPCD), BARC).

5. Cluster Chemistry

Xenon clusters in gas phase are one of the most explored systems in laser-matter interaction studies. Most of the studies deal with interaction of xenon cluster with highly intense laser pulses of ultra short duration. Generation of multiply charged ions of xenon (up to +40 state) with kinetic energy as high as 1 MeV under laser intensity of 2×10^{16} W/cm² for clusters consisting of $\sim <2500>$ atoms has been reported. Observation of such highly energetic multiply charged xenon ions was explained based on field ionization, followed by efficient electron heating of the micro-plasma by the laser pulse. Over the last few years, we have reported formation of multiply charged atomic ions from molecular cluster such as methyl iodide, carbon disulfide, acetone, etc.

Both experimental and theoretical investigations on clusters have been carried out to understand laser matter interaction in the giga-watt regime. We have previously shown that multiply charged atomic ions are produced during the interaction of atomic and molecular clusters with nanosecond laser pulses. In order to understand the mechanism of the above mentioned phenomenon, different studies were carried. In one of the studies, inert gas clusters (Ar_n , Kr_n , Xe_n) were doped with low ionization energy molecules such as $\text{Fe}(\text{CO})_5$ (Ionization energy = 7.8 eV). It was postulated that the presence of dopant species having lower ionization energy would lead to facile ionization of doped inert gas clusters, resulting in efficient ionization of the cluster system, at 266,355 and 532 nm. However, the highest observed charge states were lower for doped inert gas clusters, as compared to those obtained for pure inert gas clusters, for all laser wavelengths. Inefficient coupling of laser energy in case of doped inert gas clusters compared with pure inert gas clusters has been rationalized on the basis of accelerated disintegration of the cluster due to facile initial ionization of dopant molecules having low ionization energy. The results suggest that longer laser wavelength and slower rate of cluster expansion facilitate efficient transfer of optical energy to the cluster systems. Efforts were made to detect negative ions, if formed, upon laser excitation of different cluster systems (Xe_n , $(\text{Fe}(\text{CO})_5)_n$, $(\text{CH}_3\text{I})_n$). For these studies the time-of-flight mass spectrometer was operated in negative ion mode by modifying the detector/ acceleration circuit of the mass spectrometer. For studies carried out on $(\text{CH}_3\text{I})_n$ negative ions I^- , $(\text{CH}_3\text{I})\text{I}^-$ and $(\text{CH}_3\text{I})_2\text{I}^-$ were detected in the time-of-flight mass spectrum. While for studies carried out on Xe_n and $(\text{Fe}(\text{CO})_5)_n$ cluster systems, very weak negative ion signals were observed in the time-of-flight mass spectra, which could not be assigned unambiguously due to their low S/N ratio. These results suggest that for formation of negative ions in laser-cluster interaction studies, electron affinity of the cluster species as well as the energy of photo-generated electron are crucial parameters.

Clusters assemblies and CO oxidation study of $\text{M}@\text{Au}_6$ clusters (M = Ni, Pd, and Pt)

Based on the first-principles approach, this study reports that the ground state geometry of the $\text{Ni}@\text{Au}_6$ cluster forms chair-like conformation, which is distinctly different than the $\text{Pd}@\text{Au}_6$ and $\text{Pt}@\text{Au}_6$ clusters, where hexagonal planar structure is favored over non-

planar isomers. The higher stability of the chair-like conformation has been verified through various complementary basis sets and methodologies. Further investigations were carried out to show the stability of a cluster assembled material (CAM) based on these small clusters and the CO oxidation reaction was carried out to establish their uses as an industrial catalyst.

5.2 Structure of Au_n and Pt_n clusters on α -Al₂O₃(0001) surface

The structural and electronic properties of Au_n and Pt_n (n =1-6) clusters on a clean α -Al₂O₃ (001) surface is investigated using DFT approach and the geometries of the deposited Au clusters are compared with their gas-phase counterparts. The nature of chemical bonding at the interface is established by the charge difference analysis, which suggests an overall charge transfer from the surface to the metal cluster. The additional negative charge on the deposited cluster resulted in the red shift of the energy levels in comparison to the free clusters. In order to verify the enhanced catalytic activity of the negatively charged deposited Au clusters, further investigations were carried out by interacting oxygen molecule with the Au₂@Al₂O₃ system, a prototype to study oxidation mechanism. The results reveal that the interaction of O₂ with Au₂@Al₂O₃ leads to activate the O-O bond by the transfer of electronic charge into anti-bonding orbital. On the basis of these results it is inferred that the Au clusters deposited on the clean Al₂O₃ surface are more effective for oxidative catalysis.

6. Catalysis

The Division has been involved with the design and development of both homogeneous and heterogeneous catalysts for various applications.

6.1 Homogeneous Catalysis

Palladium chalcogenolate complexes, [PdCl₂(PhSeCH₂CH₂NMe₂)], [PdCl(SCH₂CH₂CH₂NMe₂)₂], [PdCl(SeCH₂CH₂NMe₂)₃], corresponding acetate complexes and trans-[PdCl(4-Septy)(PPh₃)₂] have been synthesized, characterized and evaluated for their catalytic activity in C-C coupling reactions between an aryl halide and arylboronic acid. The aryl iodides and activated aryl bromides yielded more than 92% of product within 10 hrs reaction time in 1,4-dioxane as solvent and Na₂CO₃ as base. Similar reactions between tolyl iodide and phenyl boronic acid were performed. The catalytic activity of Pd complexes for the similar systems follows a trend: S > Se; propyl > ethyl; acetate > chloride. It was found that methyl, methoxy, trifluoro or without substituent at para position give high yield ($\geq 90\%$).

6.2 Heterogeneous catalysis

Numerous catalysts for sulfur-iodine cycle and photo-catalytic reaction for hydrogen generation and hydrogen mitigation have been developed and evaluated. Several other catalysts for de-nitration and U(VI) to U(IV) reduction which are relevant to DAE

programs have been developed (in collaboration with Process Development Division (PSDD), BARC).

7. Fuel cell materials

Studies related to the development of materials for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs) based on both oxide ion conductors and proton conductors were continued. Anode supported single cell for proton conducting SOFC, comprising of BSCF ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ cathode)| BCY ($\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ electrolyte)| NiO-BCY (anode) has been fabricated. BCY powder synthesized by sol-gel route heated at 1200 °C was used for cell fabrication. Anode powder was prepared by mixing BCY and commercially available NiO powder in 50:50 wt%, respectively and 10% starch was added as a pore former. Half cell of BCY| NiO-BCY was prepared by co-pressing and co-firing at 1400 °C for about 4 h. Over the electrolyte layer BSCF cathode layer was painted in the form of slurry with terpineol binder which was then sintered at 900 °C. The diameter of anode supported cell is ~12 mm where electrolyte, cathode and anode thickness are ~0.05, ~0.02 and ~0.12 mm, respectively. This cell could generate an OCV of 0.91 V and a maximum power density of 35 mW/cm² at 873 K.

8. High purity materials

High purity gallium (5-6 N), indium (5 N), germanium (~ 6 N) and cesium iodide (~5N) have been purified and supplied to different Divisions in BARC.

9. Functional materials

9.1 Electro-ceramic and multi-ferroic materials

In continuation of our research activities on electro-ceramic, multi-ferroic, magneto-electric and dielectric materials, several systems have been prepared and studied. Low temperature measurements on relaxor dielectric materials, like FeTiMO_6 (M = Ta, Nb and Sb) have been carried out. Polaronic relaxations with variable range hopping conduction have been observed in all the compounds. By XAFS study near the iron edge, the valence state of the iron is predominantly Fe^{3+} with a partial presence of Fe^{2+} . Dielectric and electrical conductivity of orthorhombic InVO_4 have been measured in the temperature range RT to 973 K. Appreciable conductivity was observed at higher temperature, while almost no conduction was noticed below 723 K. Ionic conductivity of Bi_2O_3 - Dy_2O_3 and Bi_2O_3 - Yb_2O_3 composite systems in rare-earth oxide region has been investigated. In Bi_2O_3 - Dy_2O_3 system, a new rhombohedral phase with composition $\text{Dy}_{0.56}\text{Bi}_{0.44}\text{O}_{1.50}$ is observed. Appreciable ionic conduction has been observed by addition of about 5 % of Bi_2O_3 to almost non-conducting Dy_2O_3 or Yb_2O_3 . Activation energies of the composites were in the range of 1.1 to 1.2 eV. The phase evolution study and the effect of phase transition on oxide ion conductivity were also investigated in $\text{Nd}_{2-x}\text{Ho}_x\text{Zr}_2\text{O}_7$ system. It was established that an optimum degree of disorder in structure is required for getting an enhanced value of ionic conductivity.

Low temperature magnetic and dielectric properties of complex vanadate, namely $Zn_3Fe_4V_6O_{24}$ have been investigated. The compound showed anti-ferromagnetic like behavior around 20 K. In search of metastable phases, a new high pressure polymorph of $Ce_2Zr_2O_8$, an anion filled pyrochlore lattice has been identified by *in-situ* high pressure XRD and Raman measurements in a diamond anvil cell. The compound adopts a rhombohedral super-structure of the cubic pyrochlore lattice.

Electrical conductivity and dielectric properties of several oxide systems, such as yttrium doped $SrCeO_4$, rare earth uranates (RE_6UO_{12} , RE = Nd, Gd, Dy, Tb), $Bi_{2-x}La_xSn_2O_7$, $Nd_{2-x}Ho_xZr_2O_7$ pyrochlores, *etc.* have been investigated using impedance spectroscopy in the temperature range 300 - 1000 K. Few oxide systems have been studied for their bulk thermal expansion behavior as a function of temperature. Proton conductors ($Ba_{1-x}Ce_{0.8}Y_{0.2}O_{3-\delta}$) and rare earth uranates (RE_6UO_{12} , RE = Nd, Gd, Dy, Tb) have been studied. In addition to this, temperature modulated DSC has been successfully used for rapid and reliable measurement of specific heats of various substituted scandates namely, $La_{1-x}Ba_xScO_{3\pm\delta}$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$), $La_{1-x}Ba_xSc_{1-x}Mg_xO_{3\pm\delta}$ ($x = 0.0, 0.05, 0.10, 0.15$) and $LaSc_{1-y}Mg_yO_{3\pm\delta}$ ($y = 0.0, 0.1$) in the temperature range 300 - 773 K.

Multi-ferroic materials are the materials which exhibits spontaneous magnetization (M_s) with ferroelectric polarization (P_s) and eventual mutual coupling of these two properties. In this context, Sc doped $Bi_2Fe_4O_9$ nanoparticles were prepared by sono-chemical method. Substitution of Sc ions for Bi enhances ferromagnetic as well as ferroelectric properties of this system, which is mainly attributed to the antiferromagnetic core and ferromagnetic surface of the nanoparticles, together with the mild structural distortion. Among composite based multi-ferroics, fabrication of a single nanowire multi-ferroic system, a new geometry, exhibiting room temperature magneto-dielectric coupling were demonstrated. A coaxial nanotube/ nanowire hetero-structure of barium titanate and cobalt has been synthesized using a template-assisted method. Room temperature ferromagnetism and ferro-electricity were exhibited by this coaxial system, indicating the coexistence of more than one ferroic interaction in this composite system. In another attempt, nanohybrid structures of FePt and $BaTiO_3$ with bifunctional properties were synthesized by a two-step synthesis procedure including solid state and solvothermal methods. The hybrid composite, having the lower FePt concentration, exhibited bifunctionality including super-paramagnetism and ferro-electricity at ambient conditions. Magneto-capacitive measurements of this bifunctional FePt- $BaTiO_3$ sample showed behavior typical of weak magneto-electric coupling. The ferroelectric behavior of pure and lanthanum doped $Bi_2Sn_2O_7$ was also studied.

9.2 Materials for drug delivery

Surface functionalized materials and thin films that are relevant to chemical or bio-molecular sensing and drug delivery applications have been investigated. The research on surface functionalized materials for biomedical applications has seen an upsurge in recent years. By using soft chemical approach, we have developed a water dispersible,

pH-responsive peptide mimic shell cross-linked Fe_3O_4 magnetic nano-carriers (PMNCs) for combination of chemotherapy and hyperthermia. They show good colloidal stability, super-paramagnetism, self-heating capacity under external AC magnetic field (AMF) and cyto-compatibility with cell lines. These nano-carriers transformed from a negatively charged to a positively charged form in an acidic environment and promoted anticancer drug (DOX) release, specifically in tumor environment. Moreover, the enhanced toxicity to tumor cells by DOX loaded PMNCs under AMF suggest their potential for combination therapy involving hyperthermia and chemotherapy (In collaboration with RB&HSD, BARC and IITB, Mumbai).

In recent years, magnetic nanoparticles (MNPs) have attracted much interest because of their extensive biomedical applications. Different physical and chemical methods for the synthesis of functionalized MNPs are known. Co-precipitation method has been widely used for the synthesis of Fe_3O_4 MNPs from aqueous medium because of its simplicity. There are many reports on the different heating ability values from same amount of Fe_3O_4 under same conditions of induction heating. We have observed that the difference in heating ability is related to different contents of water molecules in as prepared Fe_3O_4 samples. Usually, as prepared Fe_3O_4 MNPs contain unexpectedly large amounts of water molecules. The average weight of five different wet MNPs samples decreased by 80% on washing with acetone or allowing it to dry. The wet samples having particle surface functionalized with different amount of oleic acid (OA) did not show the trend of heating temperature with increase of sample amount due to different Fe_3O_4 contents per volume, whereas dry samples showed an increase of heating temperature with increase of sample. These samples achieved hyperthermia temperature (43 °C) for cancer therapy. Intracellular localization of MNPs-OA was studied in mouse fibrosarcoma cells (Wehi 164). MNPs-OA was interacting mainly with the cell membrane. Cells treated with MNPs-OA in combination with induction heating showed decrease of viability as compared to respective induction heating controls. These results were supported by the altered cellular morphology after treatment of MNPs-OA in combination with induction heating.

Glycine passivated Fe_3O_4 nanoparticles and super-paramagnetic $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) nanoparticles with excellent specific absorption rate have been fabricated, which can be used as effective heating sources for hyperthermia treatment of cancer. To explore self assembled nanostructures for drug delivery applications, block copolymer assemblies for solubilisation of various drug molecules such as DOX, methylparaben or model hydrophobic compounds such as phenol have been investigated. Understanding structural evolution in self-assembled materials upon dilution is important for its *in-vivo* application as drug delivery system. Dilution induced structural changes in surfactant-hydrotrope mixed assemblies were investigated by light scattering, neutron scattering and rheology. To mimic biomineralisation of natural bone and explore its potential as drug delivery material, mesoporous hydroxyapatite particles were prepared using fibrous surfactant assemblies as a template.

9.3 Bio-sensors

In the area of biosensor research, attempts were made to develop polyaniline based electrochemical sensor for detection of carcinoma. Polyaniline was deposited on gold interdigitated electrodes by electro-polymerization using potentiodynamic method. The polymer film was suitably modified to obtain sensor film for recognition of the tumor cells. Response of the sensor to various tumor cells such as lung cancer cells, human fibrosarcoma cells, prostate cancer cells and breast cancer cells were studied. The electrochemical response could help to differentiate cancerous cells from non cancerous cells (in collaboration with RB&HSD).

Thin film materials useful for photovoltaic, photo-catalytic and gas sensing applications were prepared by various routes. The high surface area and improved charge separation kinetics of porous silicon- metal oxide (TiO_2/ZnO) hetero-junctions resulted in enhanced photocurrent upon visible light illumination. The efficiency of porous silicon-nitrided TiO_2 hetero structure was estimated as 0.87% (under light) whereas for porous silicon-ZnO it was 9.5%. However, for porous silicon-ZnO hetero structure the photocurrent decreased drastically on exposure to light due to photocorrosion. Photoresponse and impedance studies of ultrathin films of $\text{SnO}_2/\text{TiO}_2$, SnSe films and dye sensitized solar cells consisting nano-coral-titania films loaded with different dyes, *etc.* were also carried out. DC and AC electrical measurements on ultrathin SnO_2 films were carried out under various H_2S gas concentrations to understand the kinetics of gas response and recovery as a function of temperature. Photocurrent behavior of hetero-structured $\text{SnO}_2/\text{TiO}_2$ thin films prepared by LB technique was also investigated. The photo response shows about 10 times increase in the current with fast switching characteristics.

9.4 Materials for detectors

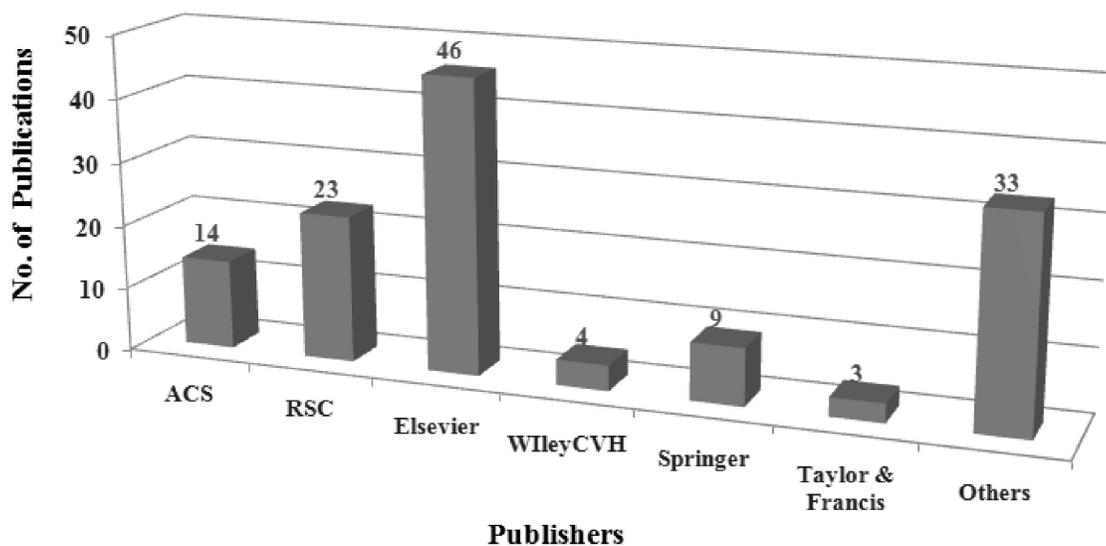
Development of CVD grown diamond thin film-based alpha particle detectors for online monitoring of alpha activity of highly corrosive and radioactive liquids (such as spent fuel reprocessing streams containing U, Pu and minor actinides (MA) in concentrated nitric acid) is another important activity of the Division. In a major step towards achieving our objective, we had demonstrated the alpha sensing capability of few indigenously made detectors in acidic liquids (3M HNO_3 having dissolved ^{239}Pu , activity: 1.7×10^7 dpm/ μg). These detectors were prepared by using high quality polycrystalline diamond films deposited by MPCVD. Initial testing experiments brought out some challenges pertaining to (i) non-wetting of diamond film due to air bubble formation, (ii) acid compatible sealing of diamond films in the detector shell for prolonged use, (iii) enhancing the sensitivity, and (iv) improvement in electronics. The issue of air bubble formation and non-wetting of diamond surface has been successfully resolved by suitable design modification. Further improvisation of these devices is in progress.

Surface conductivity (SC) of hydrogenated diamond (HD) films has been exploited to detect H_2S at room temperature. Additionally, gas sensing properties of HD films have been investigated for various oxidizing and reducing gases. Up to 25% decrease in

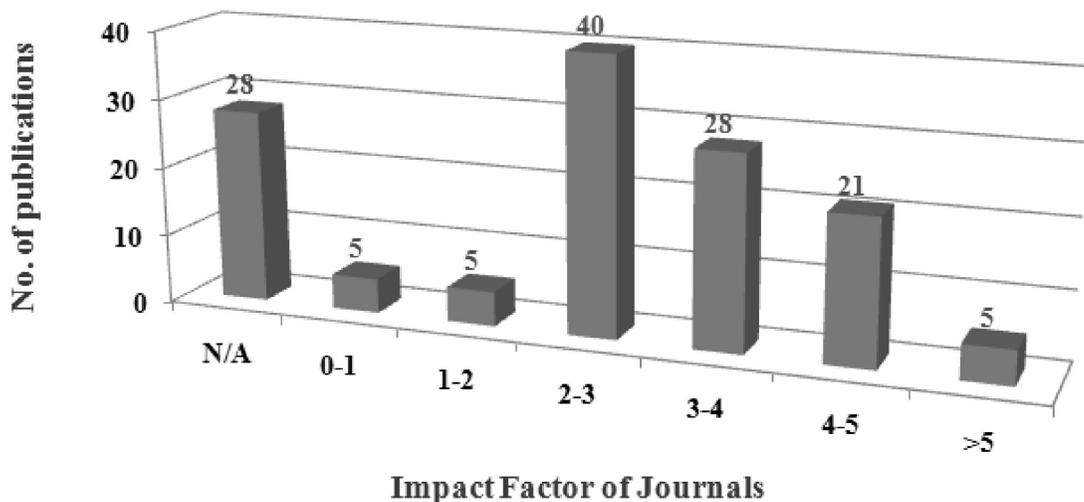
conductivity was observed for trace levels of H_2S , compared to other common reducing gases. The sensitivity was found to be linear as a function of H_2S concentration. The sensing mechanism has been explained based on the 'transfer doping model'. Gas sensors have also been fabricated using PVA- In_2O_3 nano-composite films which showed a repeatable and good response towards H_2S with short response and recovery times at room temperature. The composites also showed superior thermal stability as compared to pristine polymers.

10. Human resource development activity

Human resource development is an essential and an integral part of organizational growth. Several members of Chemistry Division were actively involved in human resource development program carried out by HRDD, BARC. The activities cover preparation of question bank, conducting written test examinations and interviews for selections of trainee officers and CAT-I and CAT-II trainees, coordinating and delivering lectures and conducting laboratory practical in the training courses in chemistry discipline, for OCES, HBNI PhD students and CAT-I trainees, and evaluations of their performances at different stages. The division has been actively involved in training and mentoring Ph.D. thesis work of several students, guiding short term research students from different parts of country under various schemes. Many of our senior colleagues are invited as specialists, and core committee members in promotional cases at different levels. We organize/ participate in symposium/ workshop/ theme meeting/ scientific forums for strengthening the cause of materials chemistry research in DAE and outside DAE. Chemistry Division is also contributing to the education and research program of



Papers published with various publishers during 2012



General impact factor trend of publications in 2012

UM-DAE Centre for Excellence in Basic Sciences. The division has been sustaining high output in the form of publishing papers in international peer reviewed journals (fig. 1). The work has been appreciated and recognized various forms such awards to our several staff members by different agencies.

Chemistry Division organized the DAE-BRNS 4th Interdisciplinary Symposium on Materials Chemistry (ISMC-2012) during 11-15 December 2012, at BARC, Mumbai where more than 500 scientists participated including 15 from abroad. The Society for Materials Chemistry (SMC) is being run from Chemistry Division as its Head Quarter.



Dr. Vimal K. Jain is currently working at Bhabha Atomic Research Centre, Mumbai as Outstanding Scientist (OS) and Head, Chemistry Division. He is an honorary Professor of Chemistry at Homi Bhabha National Institute (deemed University). He obtained his M.Sc. degree in organic chemistry from Agra University (1976) and Ph.D. from Rajasthan University, Jaipur in 1981 under the guidance of Prof. R. C. Mehrotra. After his Ph.D. he moved to Canada in 1981 where he was a post-doctoral fellow at the University of Guelph, Ontario with Prof. H. C. Clark. In 1984, he was appointed as Scientific Officer (SD) in Chemistry Division, BARC.

His research interests include: organometallic and metalloorganic chemistry of platinum group metals and main group elements, design and synthesis of molecular precursors for inorganic materials (like semiconductor nanoparticles), and multinuclear NMR spectroscopy. He is author/ co-author of about 300 research papers and review articles published in international peer reviewed Journals. He has supervised the thesis work of 19 Ph.D. and 7 masters' degree students. He has received several awards in recognition of his work, including:

- (i) "Bruker NMR Award for the Young Scientist (1989)".
- (ii) "International Scientific Exchange Award" (1993) of NSERC, Canada.
- (iii) "Homi Bhabha Science and Technology Award (1996)" of Department of Atomic Energy.
- (iv) "Royal Society of Chemistry Journals Grants" (1999) for International Authors to visit Oxford University.
- (v) "Prof. S. S. Sandhu Award (1999)" of the Indian Chemical Society.
- (vi) "Chemical Research Society of India Medal (2001)".
- (vii) "Prof. Priyadarajan Ray Memorial Award (2006)" of the Indian Chemical Society.
- (viii) "Group Achievement Award (2009)" of Department of Atomic Energy as a group leader for Process development of high purity strategic materials.
- (ix) Prof. W. U. Malik Memorial Award (2012) of Indian Council of Chemists
- (x) The Dharamsi Morarji Chemical Co. Visiting Fellowship (2013) of Institute of Chemical Technology, Mumbai

In 1995, he was elected **Fellow of the National Academy of Sciences, India** and was the Young Associate of the Indian Academy of Sciences (1988-1991). He was a National representative of IUPAC, a member of Project Advisory Committees of DST and is member of Editorial boards of a number of scientific journals and a Fellow of IUPAC and Royal Society of Chemistry (U.K.).

Society for Materials Chemistry

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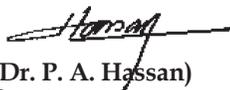
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Materials Chemistry has emerged as an important area in Chemistry cutting across the traditional boundaries of Inorganic, Organic and Physical Chemistry. Chemists have been making remarkable contributions to the development of materials for applications in areas as microelectronics, energy technologies, polymer science, catalysis, nanotechnology etc. With ever increasing demand for improved quality of life and depleting natural resources, there is a growing need to develop advanced materials for alternative energy sources such as hydrogen generation and storage, photovoltaic materials, fuel cells, sensor materials, super capacitors, optical materials etc. Some other important materials are in the field of drug delivery systems, soft-matter, biomaterials, multi-ferroics, spintronics and high purity materials. The advent of nanomaterials has brought the new concepts of size and shape dependent functionalities of materials. Likewise, there is a need to develop new materials for Nuclear Technologies as well, in particular from the point of view of new generation reactors such as Advanced Heavy Water Reactor, Compact High Temperature Reactor, Accelerator Driven sub-critical systems and Fast Reactors with shorter doubling time.

Materials Chemistry has been playing significant role in search of novel materials for advanced applications. Novel functional materials emerge as a result of concerted effort of chemists, physicist and materials scientists in general using the basic information in optimization of the structure through compositional as well as particle size variation for improved characteristics for a particular application. The latest trend in Chemistry is to use soft-chemical methods instead of conventional high temperature methods. Nature has been synthesizing a large number of compounds at ambient or very close to ambient conditions using self-assembly.

In view of this, it was felt since long that there is a need to form a society primarily dedicated to Materials Chemistry, but encompassing other disciplines also such as Condensed Matter Physics and Life Sciences. The idea of Society for Materials Chemistry was first germinated during National Workshop on Materials Characterization (NWMC) organized by Chemistry Division, BARC in Sept, 2004. This was further strengthened during 1st DAE-BRNS International Symposium on Materials Chemistry (December, 2006) organized by Chemistry Division BARC. In the valedictory function of ISMC-2006, several delegates supported the need of such scientific interactions for augmenting materials chemistry research in India. With these initial efforts, SMC was founded in 2007. We are happy to inform you that through our persistent efforts the "Society for Materials Chemistry (SMC)" has been registered under the Mumbai registration act. This society hopes to provide a common platform to young researchers and active scientists in the area of material chemistry to exchange their ideas, develop interdisciplinary collaborations and share costly instruments / techniques available at premier institutes. SMC will also provide linkages with university researchers and other national laboratories with Department of Atomic Energy. The 2nd, 3rd and 4th DAE-BRNS International Symposia on Materials Chemistry (December 2008, 2010 and 2012 respectively) were organized by Chemistry Division, BARC in association with SMC. The Department of Atomic Energy has kindly approved the organization of ISMC series biennially. The next ISMC will be held in Dec. 2014. It was also decided to organize biennial National Workshops on Materials Chemistry (NWMC) under the auspices of SMC. The first NWMC workshop is being held during 7-8 Dec. 2011 at BARC under the theme "functional materials" and the present one is being organized under "Catalytic Materials". SMC also arranges series of lectures on various contemporary topics by eminent scientists across the globe.

The current life membership of the society stands at about 720 researchers from different institutes of India. We do hope for further enrichment of the strength and activities of this society and look forward for your active participation to take the society to greater heights.



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Society for Materials Chemistry

Society for Materials Chemistry was mooted in 2007 with following aims and objectives:

- to help the advancement, dissemination and application of the knowledge in the field of materials chemistry,
- to promote active interaction among all material scientists, bodies, institutions and industries interested in achieving the advancement, dissemination and application of the knowledge of materials chemistry,
- to disseminate information in the field of materials chemistry by publication of bulletins, reports, newsletters, journals.
- to provide a common platform to young researchers and active scientists by arranging seminars, lectures, workshops, conferences on current research topics in the area of materials chemistry,
- to provide financial and other assistance to needy deserving researchers for participation to present their work in symposia, conference, etc.
- to provide an incentive by way of cash awards to researchers for best thesis, best paper published in journal/national/international conferences for the advancement of materials chemistry,
- to undertake and execute all other acts as mentioned in the constitution of SMC.

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