PRESENTATION ON THE ACTIVITIES OF NCCR
FOR THE YEAR JULY 2008-JUNE 2009

Management and Advisory committee meeting

June 22, 2009

- First MAC meeting on 26th Feb 2007

- Second MAC meeting on July 7th 2008

The Chairman MAC raised several issues during the presentation in the second MAC meeting.

Few of the important ones are:

1. In the area of energy (which is one of the stated areas of research of the centre) the centre should also work on FT synthesis and syn gas production. He was of the opinion that the centre should generate new insights in this area.

2. The Chairman also commented on the carbon materials developed by the centre. He said that uniform quality activated carbon was not available indigenously. The centre should be able to bring out a process for the production of high surface area activated carbon.

3. He also said that the centre should give emphasis on the application of spectroscopy in catalysis.

The actions taken on the three important remarks of the Chairman

Remark 1: In the area of energy (which is one of the stated areas of research of the centre) the centre should also work on FT synthesis and syn gas production. He was of the opinion that the centre should generate new insights in this area

- The centre has attempted the following in the area of energy.

- A project proposal on FT has been evolved with the participation of one of the MAC members Dr Paul Ratnasamy and it has been defended by presentation before CHT committee and it is learnt that it is under consideration by CHT.

- The centre was associated and provided academic input for the development of on board hydrogen generation by a chemical route and this has been directly used as fuel for Maruthi van. This vehicle was demonstrated for public on March, 20 in Hyderabad.

- The centre has obtained a sponsored project from Tata chemcials for the generation of hydrogen from water by photo-electrochemical route.

Remark 2:The Chairman also commented on the carbon materials developed by the centre. He said that uniform quality activated carbon was not available indigenously. The centre should be able to bring out a process for the production of high surface area activated carbon.

- The centre has made considerable progress in the development of carbon materials.
- The Centre has produced three valuable documents in this area which will outline the efforts made in this area. These documents are:
- B. Viswanathan, P. Indra Neel and T. K. Varadarajan , The methods of activation of carbon materials and their specific applications - an e book at the NCCR website http://www.nccr.iitm.ac.in.
- P.Indraneel, B.Viswanathan and T.K.Varadarajan, Submitted to Catalysis Surveys of Asia.
- P.Indraneel, B.Viswanathan and T.K.Varadarajan, submitted to Carbon.
- The centre has also worked on the development of adsorptive desulphurization for treating Narimanam crude and the feasibility of the process is being evaluated by an Australian firm (details will be presented)

Remark 3:He also said that the centre should give emphasis on the application of spectroscopy in catalysis.

- A preschool on applications of electron spectroscopies was conducted prior to the national symposium on catalysis at NCL during January 16 and 17. Prof P Selvam and B.Viswanathan conducted this school in cooperation with Dr C.S.Gopinath of NCL.
- As a consequence of this suggestion NCCR has prepared a book on Surface analytical techniques in Catalysis. This book is now in print by Ms.Narosa Publishing House, New Delhi. This book will be available in 2 months time.
- The orientation course conducted annually by NCCR has been redesigned to have a specific component of this subject being covered in the course. This has been implemented from the programme in 2008.

Points raised by the Secretary, DST in the last MAC meeting on 7th July 2008

Point 1: Capacity building is one of the mandates of the centre and the centre has not made progress in this respect so far. The centre should evolve specific courses and train at least 250 students (both Ph D and Masters) in five years to generate manpower in this important area.

Considering the seriousness and also the implications of this point NCCR has taken the following steps.

1. NCCR is introducing a M Tech Programme in Catalysis Technology from the academic year 2009 offered as part of M Tech in Chemical Engineering (The proposed course contents are given in the next projections for suggestions)

2. NCCR continues handling the catalysis course for M Sc (Applied Chemistry) of the Department of Chemistry, Anna University.

3.They also participate in the M Phil and Ph D courses of Anna University.

4. Research fellows of other institutions like Anna University, Madras University and various sister Institutions have been carrying our their research work in the centre at various levels including spending full time. This number is at present is around 10 and hope to increase in the future. This is in addition to the normal research and project fellows of the centre.

5.NCCR has conducted the course on catalysis (one semester) as part of the M Sc programme in Tezpur, Bharathidasan and Pune Universities. Similar exercises have been done in limited extent in other institutions as well. It is proposed to extend this facility further

Point 2: The centre should also try to involve other institutions (apart from Anna University) in teaching and research. It should also interact with industry and generate projects so that it can function as a self-sustaining unit in five years time.

- For the first part of the remark NCCRs efforts were presented in the previous projection.
- For the second part of the remark the centre has been actively involved in generating projects. Some typical ones are:
- CPCL and IOC (Especially IOC fellowships)
- Shell project has been completed and a second project has been approved.
- A new project with GM has been initiated for auto-exhaust control
- A new project has been approved by Tata Chemicals for the generation of hydrogen through PEC route.
- A project with SRF on development of catalyst is in advanced stage of discussion will be approved soon.
- P and G project has reached a stage for a disclosure which is being considered.
- NMITLI project also is in the stage of yielding some disclosure soon.
- International cooperation with Hungary, Australia and Korea and Taiwan have been progression well.
- Discussions with NISSAN, DOW and others are in progress and they may also join hands for research with NCCR in the future.

Curriculum for the new course
M.Tech. (Catalysis Technology)
I SEMESTER

Course ID	Course Name	L	T	P	C
CA501	Fundamentals of Adsorption and Catalysis	3	0	0	3
CA502	Solids and Surfaces	3	0	0	3
CH501	Chemical Reactor Theory	3	1	0	4
CH502	Experimental and Analytical Methods in Chemical Engineering	3	0	0	3
CA	Elective 1	3	0	0	3
CA	Elective 2	3	0	0	3
	Total Credits	**18**	**1**	**0**	**19**

Semester I - Electives

Course ID	Course Name	L	T	P	C
CA511	Preparation and Properties of Catalysts	3	0	0	3
CA512	Homogeneous Catalysis	3	0	0	3
CA513	BioCatalysis	3	0	0	3
CA514	Computational Methods in Catalysis	3	0	0	3

II SEMESTER

Course ID	**Course Name**	**L**	**T**	**P**	**C**
CA503	Experimental Methods in Catalysis	3	0	0	3
CA504	Introduction to Surface Analysis	3	0	0	3
CH503	Transport Phenomena	3	1	0	4
CA505	Catalyst Preparation and Characterization Laboratory	0	0	3	1
CA	Elective 3	3	0	0	3
CA	Elective 4	3	0	0	3
	Total Credits	**15**	**1**	**3**	**17**

Semester II - Electives

Course ID	**Course Name**	**L**	**T**	**P**	**C**
CA515	Catalysis in Petroleum Technology	3	0	0	3
CA516	Catalysis in Production of Chemicals	3	0	0	3
CA517	Nano-materials in Catalysis	3	0	0	3
CH516	Chemical and Catalytic Reaction Engineering	3	0	0	3

III SEMESTER

Course ID	**Course Name**	**L**	**T**	**P**	**C**
CA651	Project (Stage I)	-	-	-	6*
CA652	Seminar I	-	-	-	1
CA	Elective 5	3	0	0	3
CA	Elective 6	3	0	0	3
	Total Credits	**6**	**0**	**0**	**7**

**Credits to be assigned and added to the IV semester.*

Semester III - Electives

Course ID	**Course Name**	**L**	**T**	**P**	**C**
CA611	Catalysis in Green Chemistry and Environment	3	0	0	3
CA612	Photocatalysis	3	0	0	3
CH604	Chemical Reactor Design for Process Plants	3	0	0	3
CH612	Particle Characterization	3	0	0	3
CH615	Multiphase Reactors	3	0	0	3
CY672	Chemical and Electrochemical Energy Systems	3	0	0	3
CY 676	Principles of Surface Chemistry	3	0	0	3

IV SEMESTER

Course ID	**Course Name**	**L**	**T**	**P**	**C**
CA651	Project (Stage II)	-	-	-	20*
CA653	Seminar II	-	-	-	1
	Total Credits	**-**	**-**	**-**	**21**

- **Inclusive of 6 Credits from III semester.**

Total credits = 19 + 17+7 +21 = 64

PART B
EDUCATION AND CAPACITY BUILDING AT NCCR

Ph D awarded during this year

- The titles of the Ph D theses that have been completed this year are:
- Dr Ch Venkatewara Rao – On the search for efficient catalysts for oxygen reduction reaction.
- Dr L Himakumar – On some challenging avenues in hydrogen storage.
- Dr S Navaladian – Strategies for the synthesis of nano materials and their applications.
- Dr J M Janet – Synthesis and characterization of materials for ammonia formation at atmospheric pressure.
- Dr Satyananda Kishore – Catalytic and electrochemical exploitation of poly oxo metallates
- Dr J Rajeswari – One dimensional nanoarchitectured compounds of Mo/W for electrochemical applications
- Ms M Helen – Development of hybrid membranes for application in Direct Methanol Fuel cells (DMFC)

The Orientation Program in Catalysis

This program is the one of the unique educational endeavors of the Centre, conducted every year for the young research scholars of the country. The last such program (9th in the series) was conducted in the month of November -December 2008 for three weeks (November 25 to 13 December 2008). There were 40 participants from various institutions like IICT, University of Pune, UICT, CUSAT, Anna University, Defence laboratory at Gwaliar and IITM. This program is well structured and conforms to a syllabus, which is evolved and undergoes changes every year, depending on the trends and future scope of research in the area of catalysis. The fundamentals are stressed. The responses of the participants on the conduct of the course are available with Dr. R. Brakaspathy Advisor of DST.

Participation in Anna University Teaching Program

- The faculty of NCCR has handled two courses in the curriculum of the Department of Chemistry, Anna University during the first semester of 2008 (July - November 2008).
- The courses are:
  - AC-086 INDUSTRIAL CATALYSIS for M.Sc. (Applied Chemistry) students (Prof S Sivasanker of NCCR)
  - CY-073 CONCEPTS AND TECHNIQUES IN CATALSYIS for M Phil students.(part only - conducted by B Viswanathan)
- These two courses were conducted by NCCR staff as per the syllabus and the time table provided by the Department of Chemistry, Anna University. Internal tests and final examinations were also conducted by faculty of NCCR. It may be mentioned that Part of the course for the M.Phil students of Anna University was conducted at NCCR.
- **B Viswanathan conducted the course for the M Sc specialization in Catalysis at Tezpur University. Prof A V Ramaswamy conducted similar course in Pune university and also participated the teaching programme of NCL**

Special Training Programmme

- **In addition, the faculty of the centre has participated in various educational and refresher programmes conducted by other institutions like Anna University (International School on Nano Materials, Tezpur University (Greeen Chemistry Summer School), Kalasalingam University, Krishnankovil, and many other schools and some of the details of these are available in the section on presentations.**
- **Special training in catalysis was offered to number students of sister organizations like Christian college, Chennai, Loyola College and University of Madras. Prof S Sivasanker supervised four summer research fellows (two students and two lectures) sponsored by the Indian Academy of Sciences Bangalore for about 2 months. Prof Selvam supervised a summer fellow (under DST INPIRW scheme) from NISER, Bhubaneswar (Mr. Jayanth K Ajay). Also the following persons have been trained for their summer programme at NCCR.**
  - **Mr Abhishek Shiv Kumar MIT, Manipal**
  - **Mr Raghul Raghavan, NIT, Trichirapalli**
  - **Mr K T Vikesh, Thiagarajar college, Madurai**
  - **Mr.R.Shanmugam, Thiagarajar College, Madurai**
  - **S Esskkiammal, Thiagarajar College, Madurai**.

The list of Ph D students jointly registered with other institutions

The list of Ph D students jointly registered with other universities is as follows:

- Ms Banu - Transformation of naturally occurring polyhydric alcohols into value added chemicals (Bharathidasan University).
- Mr Sankaranarayanan - Solid catalysts based on mixed metal oxides for biodiesel (Anna University).
- Ms.Sumathilakshmi - Hydronitrogenation of model compounds over Ni-Mo supported on mesoporous composites (Anna University).
- Mr Suthagar - Conversion of Glycerol to value added chemicals (Anna University).
- Ms Nithya - The role of texture of supports on the catalytic activity (Anna University).

Annual Children’s Club programme

NCCR also conducted this year’s Children’s Club summer programme on Pollution Control Strategies - A Chemists Perspective for two weeks.   This course material is now available as e-book in the NCCR website.

PART C
FACILTIES CREATED AT NCCR

- The following facilities have been added at NCCR during the last one year. All the instruments have been installed tested and are being used.
- XRF facility
- Perkin Elmer GC
- UV Sources
- Thin film (dip) coating unit
- RDE facility
- Parr Auto claves (Three numbers)
- A few other units are under process like GC-MS, NOx, CO and other detectors.
- Few other facilities like GC MS, TEM and other equipments will be procured the process is on.

PART D

Research Activities

Some Highlights of Basic Research at NCCR

- The basic research component of NCCR has various facets. The can be listed as follows:
  - Preparation of various kinds of meso-porous materials including carbon materials both synthetic and natural sources.
  - Exploitation of the synthetic strategies for preparation of new generation nano state materials for possible catalyst applications.
  - Examining the cluster compounds especially poly oxometallates for a variety of organic transformations.
  - Evolving suitable catalyst systems for specific reactions like conversion of glycerol to value added products like 1,2 or 1,3 propandiol or acrolien or esters.
  - Evolving strategies to increase the surface area of carbon with specific application in mind.
  - Fuel cell electro catalysts and membranes are the other areas of research in which the group is contributing considerably. (Some of the salient studies will be considered in subsequent projections)

Industrial sponsored projects at NCCR

Chennai Petroleum Corporation Limited

- There are two on-going projects sponsored by Ms.CPCL, Chennai. Details of these projects have been given in our previous report. In short, these projects are:
- Adsorptive Desulphurization: The aim of the project is to remove sulfur in the SR diesel fraction of Narimanam crude by an adsorptive desulfurization process for which suitable adsorbents have been developed, screened and selected. The process at the laboratory level has been demonstrated and the scale up studies is being pursued at CPCL R and D centre with the participation of NCCR. It is also proposed to convert the removed sulphur compounds into useful products. The process developed by NCCR has also been reproduced by and their results
- End Point Reduction: The objective of this project is to bring down the T95 distillation point of straight run heavy diesel (T95 ~ 380°C) to less than 360°C without substantial yield loss. A number of catalysts have been screened and the most suitable catalyst has been selected and evaluated in detail.

Indian Oil Corporation

- IOC, R and D centre at Faridabad has sponsored two projects:
- Development of alumina of certain specifications for the use of IOC in their catalyst formulations; (and this project has reached the stage, where the methodology for the preparation of alumina with the specified characteristics has been successfully developed)
- Basic understanding of the hydrotreating catalyst systems
- IOC also has this year granted three fellowships for Ph D programme on topics of interest to them.

Procter and Gamble

- This project involves development of specific catalysts for the conversion of long chain hydrocarbons into alcohols. The appropriate catalyst system has been identified and optimization studies are being carried out.

Shell International Pvt. Ltd

The project involves development of high throughput catalyst systems on stainless steel grids. On successful completion of this project, Shell International Private Limited has been considering another sponsored project on developing a specific catalyst system for high through put catalyst for their process

CSIR NMITLI Project

Conversion of glycerol into 1,2 or 1,3 propanediol and acrolein (jointly with NCL, UICT and IICT)

General Motors India Limited

The project envisages the understanding of the kinetics of de -NOX reaction under SCR conditions.

Tata Chemicals Limited

Tata chemicals have sponsored a project for the production of hydrogen through Photo-electrochemical route.

Centre for High Technology

Presented a proposal on “**Monolith-based Fischer-Tropsch Catalysts**” to the Scientific Advisory committee of the Ministry of Petroleum (Centre for High technology, New Delhi) requesting a funding of Rs. 2.27 crores. Project is believed to be under consideration. (proposal with the participation of Dr Paul Ratnasamy)

National Level Tutorial on Electron Spectroscopic Techniques in Catalysis

- NCCR took the initiative of conducting a two-day (16-17 January 2009) Tutorial on Electron Spectroscopic Methods in Catalysis (XPS, UPS,AES, EXAFS, XRF and other techniques for the research scholars from different organizations at the National Chemical Laboratory, Pune, prior to the National symposium on Catalysis (18-21 January 2009). Considering the importance of Electron spectroscopic techniques (Chairman himself has stressed this in his observations in the last year (2008) MAC meeting) in catalysis, the origin, theory and practice of this technique were illustrated with examples, problems and solutions. A practical demonstration and also details on the interpretation of the spectra obtained were also included. The course was conducted by Prof P Selvam and Prof B Viswanathan in coordination with Dr C S Gopinath of NCL.

Part D

Typical examples of high lights of fundamental Research at NCCR

SYNTHESIS OF HIGH SURFACE AREA ANATASE, PHOSPHATED AND SULPHATED TITANIA FOR CATALYTIC APPLICATIONS(Dr.K.Joseph Antony Raj)

- TiO_2 exist in three different polymorphs, namely anatase, rutile and brookite.
- Most of the photocatalytic work use Degussa's P-25 TiO_2 sample, which has a surface area of around 50 m^2/g.
- Till date the only known high surface area titania is P-25 titania (75% anatase and 25% rutile) and this is widely used as a standard for photocatalytic experiments.
- Tioxide (Huntsman) is making the high surface area anatase titania (270 m^2/g) through an unknown process.
- In India high surface area nano titania is not produced. The development of this titania will have a wide application in synthesising supported catalysts and cosmetics.

Motivation

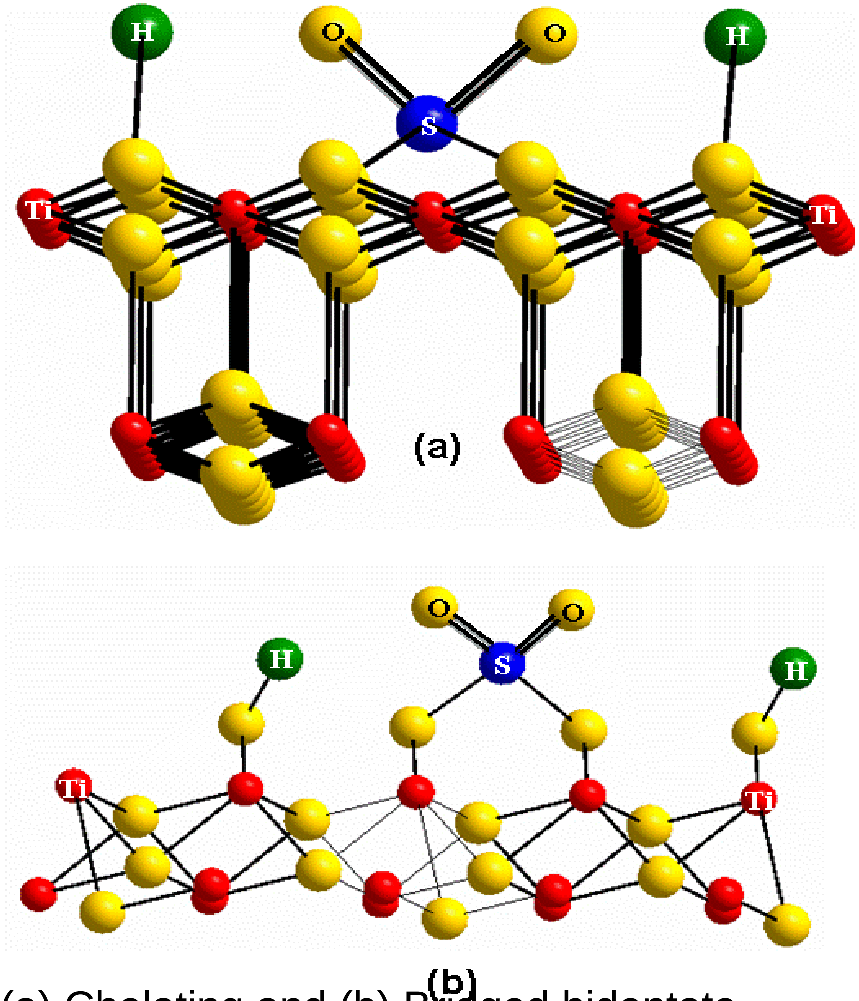
- In India there are three companies producing TiO_2.
  1. Trivangore Titanium Products – Anatase (S.A. = 12 m^2/g)
  2. Kilburn Chemicals Ltd. - Anatase (S.A. = 12 m^2/g)
  3. Kerala Minerals and Metals Ltd. – Rutile (S.A. = 9 m^2/g)

- All the three companies are using ilmenite as the raw material.

- There is a strong potential to develop and commercialise the technology for producing high surface area anatase thro' organic free method using $TiOSO_4$ as the starting material.

- The disadvantages of the existing sol-gel method using alkoxide is that it is expensive because (i) large quantities of water and solvent mixtures are produced which must be disposed of (ii) synthesised titania will have an undesirably elevated carbon content and (iii) there are no chemical methods to remove the carbon from titania.

SINGLE-STEP SYNTHESIS AND STRUCTURAL STUDY OF MESOPOROUS SULPHATED TITANIA NANOPOWDER BY CONTROLLED HYDROLYSIS PROCESS



(a) Chelating and (b) Bridged bidentate

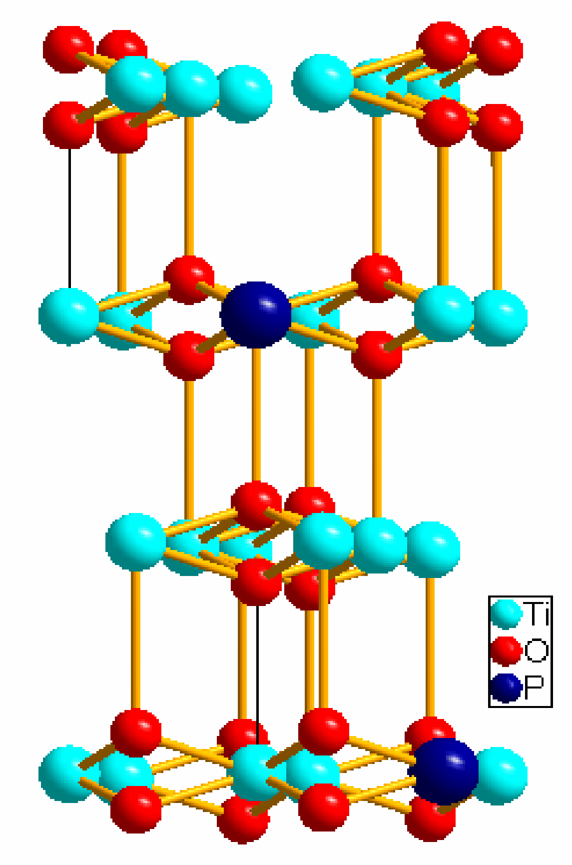
The synthesis of sulphated titania is reported as a **two stage process**. We have attempted a **single step method**.

The reports published so far show a **surface area** of about **100 m^2/g**. The method evolved and reported by us shows that it is possible to produce a mesoporous sulphated titania nanopowder with a surface area of about **275 m^2/g**.

The structural studies using **XPS** and **DRIFT** spectra revealed the presence of sulphate as bridged bidentate and not chelating bidentate on the surface of titania.

The catalytic performance and **NH_3-TPD** studies show the presence of strong acid sites in the material.

SURFACE AREA, PORE SIZE AND PARTICLE SIZE ENGINEERING OF TITANIA WITH SEEDING TECHNIQUE AND PHOSPHATE MODIFICATION



- The environmentally benign route of organic free synthetic method was evolved in precipitating hydrated titania from titanium oxysulphate.
- The thermal stability of the hydrated titania was enhanced by phosphate modification.
- The incorporation of phosphorus in the titania framework was found to inhibit the crystallization and particle growth due to the formation of titanium phosphate.
- The phosphate modified hydrated titania exhibited mesopores with a high surface area (172 m^2/g) after calcining at 500 ^oC.
- The esterification reaction performed on P-TiO_2 samples showed the significance of optimum quantity of *anatase* phase and phosphate content for the catalytic activity.

Sample	% Crystallinity	BET (m^2/g)	% Conversion of propanoic acid at 60 ^oC
0.5P-TiO_2	20	110	0.9
2.5P-TiO_2	10	130	2.8
5P-TiO_2	7	154	3.7
Anatase	100	12	Nil

Catalytic Conversion of Carbohydrates as Renewable Raw Materials to key Platform Chemicals Using Metal Supported Mesoporous Meterials (Dr.S.Anuradha)

Introduction:

As a source of chemicals, biomass has several intrinsic advantages over fossil mass.

Sugars are key intermediates from biomass to chemicals, and conversion of sugars also can be green process.

Glucose would be an important raw material for a variety of chemicals such as sorbitol, glucaric acid, o-isopropylidene and so on.

Objective:

Homogeneous catalyzed process involves multi-steps with several drawbacks such as generation of waste and difficulty in separation of products etc,.

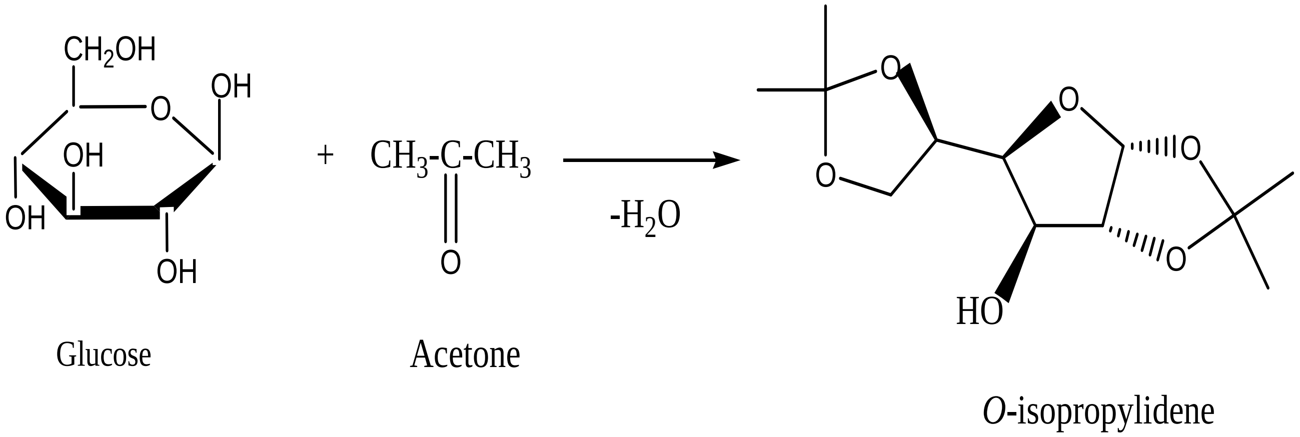
Heterogeneous catalysts may find an opportunity to convert carbohydrates to valuable products in one-step reaction with high catalytic activity and selectivity

Example: To convert D-glucose into o-isopropylidene derivatives using solid acid catalyst

Synthesis of *o*-Isopropylidene sugar Derivatives

Scheme of the reaction:

Monosaccharides which contain two sterically adjacent OH groups in the cis-position can be reacted with aldehydes or ketones



Aldoses, Aldosides and ketoses:

D- Glucose, D-galactose,, Fructose, Sorbose, D-xylose, D-mannose, D-ribose, D-mannitol

Catalyst: Fe_2O_3/SO_4

Catalyst prepared:

Preparation of SO_4/Fe_2O_3

Step 1: Preparation of $Fe(OH)_3$

5g $Fe(NO_3)_3.9H_2O$ + 20ml H_2O + NH_4OH (3ml)

↓

pH8, stand for a day

↓

Decantation, washing

↓

Drying at 100 °C, 24h

Step 2: Sulphate treatment

2g of powdered sample

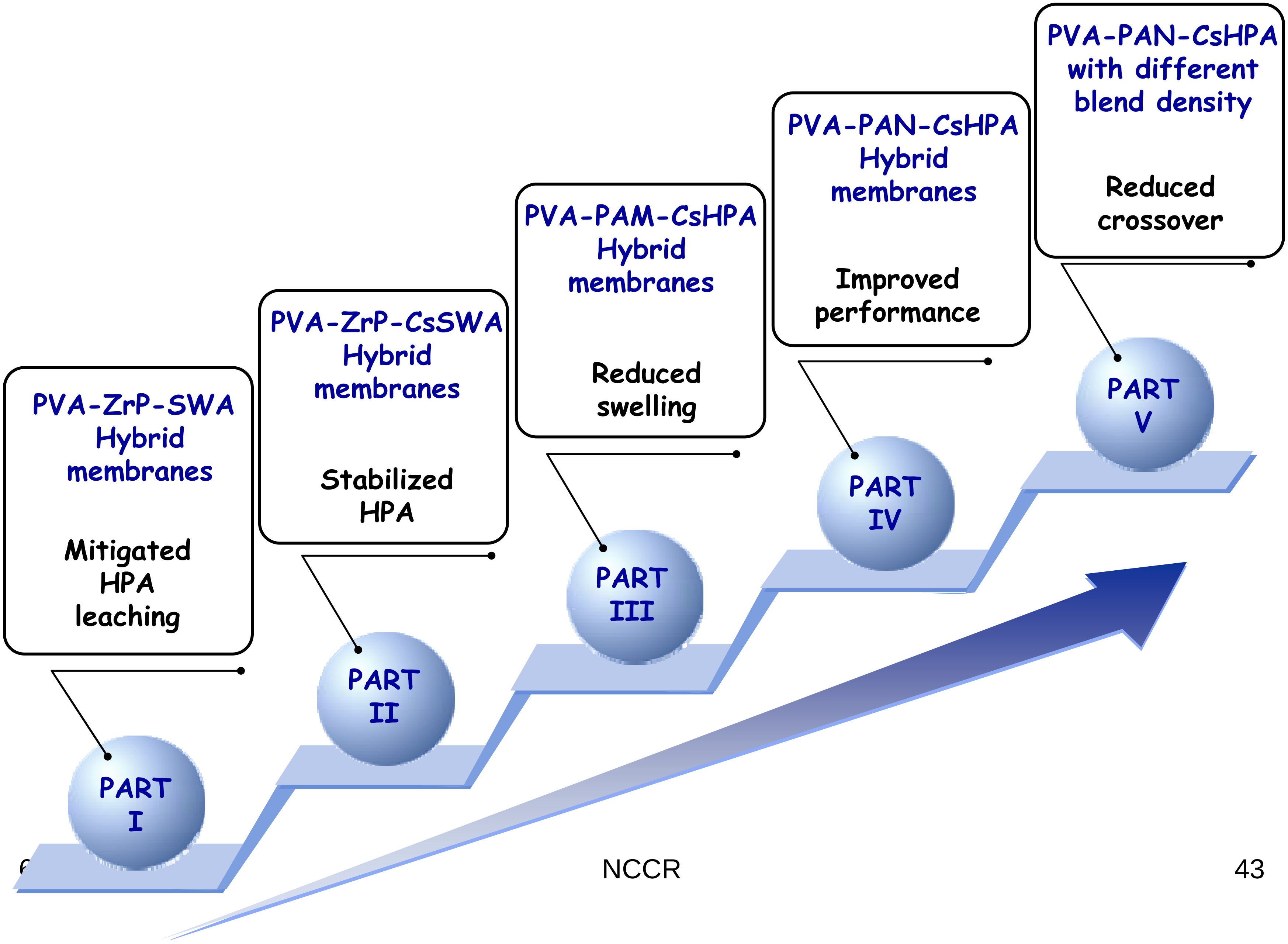
↓ **0.25M H_2SO_4**

dried, powdered

↓

calcined at 550 °C

Development of Hybrid Membranes for Application in Direct Methanol Fuel Cells (DMFC)



PART I

PVA-ZrP-SWA Hybrid membranes

Mitigated HPA leaching

PART II

PVA-ZrP-CsSWA Hybrid membranes

Stabilized HPA

PART III

PVA-PAM-CsHPA Hybrid membranes

Reduced swelling

PART IV

PVA-PAN-CsHPA Hybrid membranes

Improved performance

PART V

PVA-PAN-CsHPA with different blend density

Reduced crossover

Comparison of proton conductivity and permeability for various membranes

Membrane materials	RH (%)	Temperature (°C)	Conductivity (Scm^{-1})	Permeability (cm^2s^{-1})
PVA-ZrP-SWA (10%)	60	RT	2.7×10^{-3}	2×10^{-6}
PVA-ZrP-SWA (20%)	60	RT	4.2×10^{-3}	1.8×10^{-6}
PVA-ZrP-SWA (30%)	60	60	9.7×10^{-3}	5.5×10^{-7}
PVA-Cs_1SWA (30%)	50	90	1×10^{-2}	2.4×10^{-6}
PVA-Cs_2SWA (30%)	50	90	2.4×10^{-2}	1.2×10^{-6}
PVA-ZrP-Cs_1SWA (30%)	50	100	1.3×10^{-2}	2×10^{-6}
PVA-ZrP-Cs_2SWA (30%)	50	100	2×10^{-2}	3×10^{-6}
PVA-PAN-CsSWA-Glu	50	RT	5.3×10^{-3}	9.74×10^{-9}
PVA-PAN-CsPWA-Glu	50	RT	6.8×10^{-3}	2×10^{-8}
PVA-PAN-CsPMA-Glu	50	RT	9.3×10^{-3}	5.95×10^{-8}
PVA-PAM-CsSWA-Glu	50	RT	1.8×10^{-3}	1.38×10^{-8}
PVA-PAM-CsPWA-Glu	50	RT	3×10^{-3}	6.7×10^{-8}
PVA-PAM-CsPMA-Glu	50	RT	3.7×10^{-3}	1.1×10^{-7}
PVA/PWA/SiO_2	-	-	0.004-0.017	10^{-7} to 10^{-8}
PVACO/PMA	-	30-100	10^{-3}	10^{-6}
PEG/SiO_2/SWA	100	80	1×10^{-2}	10^{-5} to 10^{-6}
PEG/SiO_2/PWA	-	-	10^{-5} to 10^{-3}	10^{-6} to 10^{-7}
SPEEK/PWA	100	100	1.7×10^{-2}	-
SPEEK/TPA/MCM-41	-	20	2.75×10^{-3}	10^{-8}
Nafion® 115	100	90	3×10^{-2}	3.5×10^{-6}
CRA-08 [a]	-	60	45×10^{-3}	0.58×10^{-6}
IonClad® R1010 [b]	-	60	146×10^{-3}	0.6×10^{-6}
SPEEK (SD=87 %)	-	60	13×10^{-3}	1.7×10^{-6}

[a] Polyethylene-Tetra-fluoroethylene with sulphonyls in divinyl benzene matrix

[b] Tetra-fluoroethylene with poly(styrene sulfonic acid)

Publications

- M. Helen, B. Viswanathan and S. Srinivasa Murthy, Development of composite membrane materials with cesium salts of various heteropolyacids in PVA-PAN matrix for DMFC application, *J. Membr. Sci.* (Communicated, Mar2008).
- M. Helen, B. Viswanathan and S. Srinivasa Murthy, Cesium salts of heteropolyacid embedded PVA-PAM matrix as electrolytes for DMFC application, (Under Preparation).

Patent

- B.Viswanathan and M. Helen Inorganic-organic hybrid membrane with low methanol permeability characteristics. (Indian Patent Filed, 1016 Che 2009).

Conferences

- M. Helen, "Membrane Catalysis" Presented in 'Joint Research Fellows' Workshop, at IIT Madras, India, on 2nd August 2008
- M. Helen, B. Viswanathan and S. Srinivasa Murthy "Nanocomposite membranes for DMFC applications" Presented in International conference on functional materials' during Nov 27-29, 2008 at Indian Institute of Technology Madras, India (**Best poster award**).
- M. Helen, B. Viswanathan and S. Srinivasa Murthy "Polyoxometalate based membranes for possible DMFC applications" To be presented in the forthcoming international symposium on 'Hybrid Materials 2009' during 15-19 March 2009, Tours, France

SYNTHESIS OF HIGH SURFACE AREA ANATASE, PHOSPHATED AND SULPHATED TITANIA FOR CATALYTIC APPLICATIONS(Dr.K.Joseph Antony Raj)

- TiO_2 exist in three different polymorphs, namely anatase, rutile and brookite.
- Most of the photocatalytic work use Degussa's P-25 TiO_2 sample, which has a surface area of around 50 m^2/g.
- Till date the only known high surface area titania is P-25 titania (75% anatase and 25% rutile) and this is widely used as a standard for photocatalytic experiments.
- Tioxide (Huntsman) is making the high surface area anatase titania (270 m^2/g) through an unknown process.
- In India high surface area nano titania is not produced. The development of this titania will have a wide application in synthesising supported catalysts and cosmetics.

Motivation

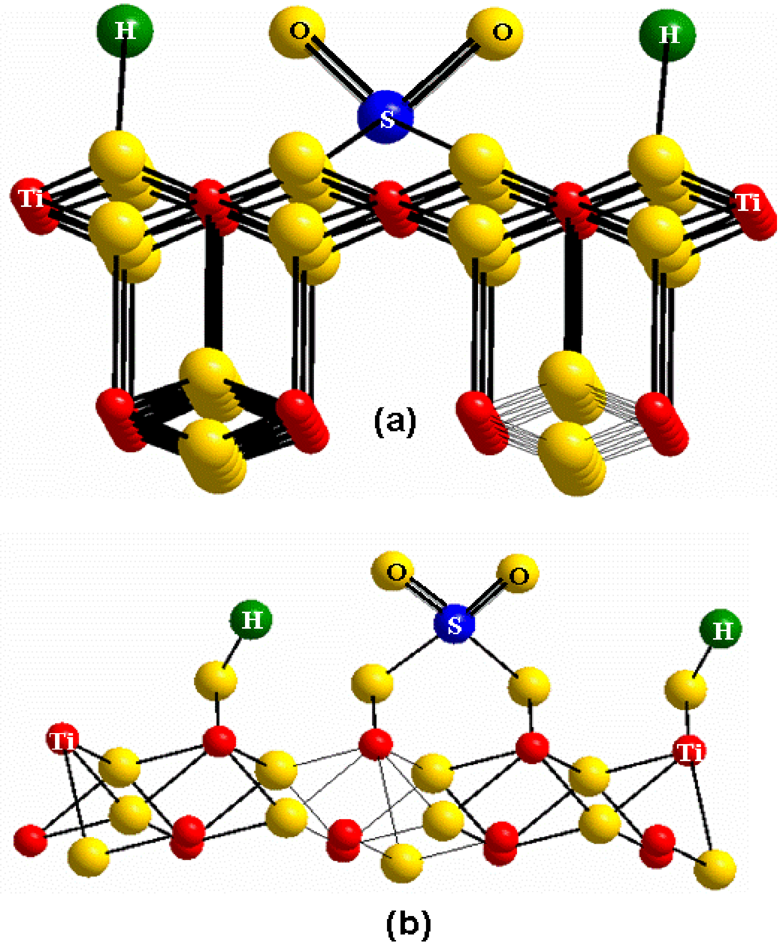
- In India there are three companies producing TiO_2.
  1. Trivangore Titanium Products – Anatase (S.A. = 12 m^2/g)
  2. Kilburn Chemicals Ltd. - Anatase (S.A. = 12 m^2/g)
  3. Kerala Minerals and Metals Ltd. – Rutile (S.A. = 9 m^2/g)

- All the three companies are using ilmenite as the raw material.

- There is a strong potential to develop and commercialise the technology for producing high surface area anatase thro’ organic free method using $TiOSO_4$ as the starting material.

- The disadvantages of the existing sol-gel method using alkoxide is that it is expensive because (i) large quantities of water and solvent mixtures are produced which must be disposed of (ii) synthesised titania will have an undesirably elevated carbon content and (iii) there are no chemical methods to remove the carbon from titania.

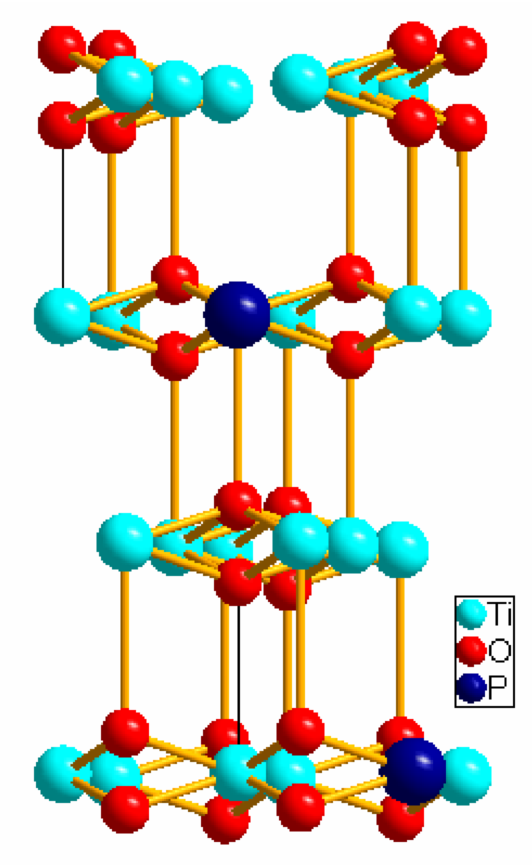
SINGLE-STEP SYNTHESIS AND STRUCTURAL STUDY OF MESOPOROUS SULPHATED TITANIA NANOPOWDER BY CONTROLLED HYDROLYSIS PROCESS



(a) Chelating and (b) Bridged bidentate

- The synthesis of sulphated titania is reported as a **two stage process**. We have attempted a **single step method**.
- The reports published so far show a **surface area** of about **100 m^2/g**. The method evolved and reported by us shows that it is possible to produce a mesoporous sulphated titania nanopowder with a surface area of about **275 m^2/g**.
- The structural studies using **XPS** and **DRIFT** spectra revealed the presence of sulphate as bridged bidentate and not chelating bidentate on the surface of titania.
- The catalytic performance and **NH_3-TPD** studies show the presence of strong acid sites in the material.

SURFACE AREA, PORE SIZE AND PARTICLE SIZE ENGINEERING OF TITANIA WITH SEEDING TECHNIQUE AND PHOSPHATE MODIFICATION



- The environmentally benign route of organic free synthetic method was evolved in precipitating hydrated titania from titanium oxysulphate.
- The thermal stability of the hydrated titania was enhanced by phosphate modification.
- The incorporation of phosphorus in the titania framework was found to inhibit the crystallization and particle growth due to the formation of titanium phosphate.
- The phosphate modified hydrated titania exhibited mesopores with a high surface area (172 m^2/g) after calcining at 500 °C.
- The esterification reaction performed on P-TiO_2 samples showed the significance of optimum quantity of *anatase* phase and phosphate content for the catalytic activity.

Sample	% Crystallinity	BET (m^2/g)	% Conversion of propanoic acid at 60 °C
0.5P-TiO_2	20	110	0.9
2.5P-TiO_2	10	130	2.8
5P-TiO_2	7	154	3.7
Anatase	100	12	Nil

Silico-tungstic Acid based Carbon supported Noble Metal Electrodes for Energy Conversion Applications (J.Phys.Chem (in Press))

Carbon supported noble metal nano particles synthesized by using Keggin type polyoxometalate (POM), silicotunstic acid (STA) were effectively utilized as electrode in an effort to improve the efficiency of electrochemical energy conversion process related to DMFC. The excellent electron transfer and strong adsorption abilities of STA have been exploited for the reduction of metal ions as well as the modification of carbon support to form Pt/STA-C and Pt-Ru/STA-C under microwave irradiation. TEM showed well dispersion. As compared to the commercial Pt/C and PT-Ru/C the systems developed showed lower on set potential, higher activity and better stability. Better tolerance to CO has also been observed.

Mo-amino acid complexes as analogs for molybdoenzyme: A DFT approach

A DFT investigation of hypothesized molybdenum (VI)-amino acid complexes has been considered as a model for xanthine oxidase. All these complexes have been optimized and analyzed by vibrational analysis. The complexes have been subjected to one electron reduction to produce anionic analogs. All complexes and reduced species are optimized in vacuum as well as in water and the associated free energy changes have been estimated. From these changes, the qualitative redox energy has been calculated by thermodynamic cycle which reveals that the complexes are expected to show similar redox behavior. This is also supported by a similar HOMO-LUMO energy gap. The population analysis shows that molybdenum *d*-orbital contributes >50% to LUMO, suggesting that the oxidation is metal-based in these systems. Also, 30% orbital contribution from sulfido center reveals the possible electronic delocalization through sulfur during oxidation of substrate. As a preliminary step for xanthine oxidation, pyrimidin-4-ol has been studied as a model substrate and the reduced sulfhydryl Mo (V) and sulfido Mo (IV)-substrate intermediates have been optimized with molybdenum in distorted square pyramidal geometry. The bond distances clearly show that Mo-S distance is longer in the sulfhydryl analogue than the sulfide intermediate to support the involvement of hydride transfer in the catalytic cycle. The Mo-C2 (carbon flanked between both the nitrogens) distance is 3.237 Å and the C2-O bond distance is 1.28 Å and compared with values reported for the Mo-imidazole intermediate. This study proposes that the hydroxyl oxygen is being inserted in the C-H bond of the substrate to afford pyrimidin-2,4-diol as the product.

[Work done and is under publication]

Synthesis of ordered mesoporous carbon (OMC) from Mesoporous silica, preparation of Pt/OMC and its electrocatalytic application (Mr.B.Kuppan)

OMC (PVP)

5 g PVP + 20 ml DCM

↓ Stirred 30 min at RT

1 g Cal SBA-15

↓ Stirred 6 h at RT

Dried at 70 ^{0}C for 6 h

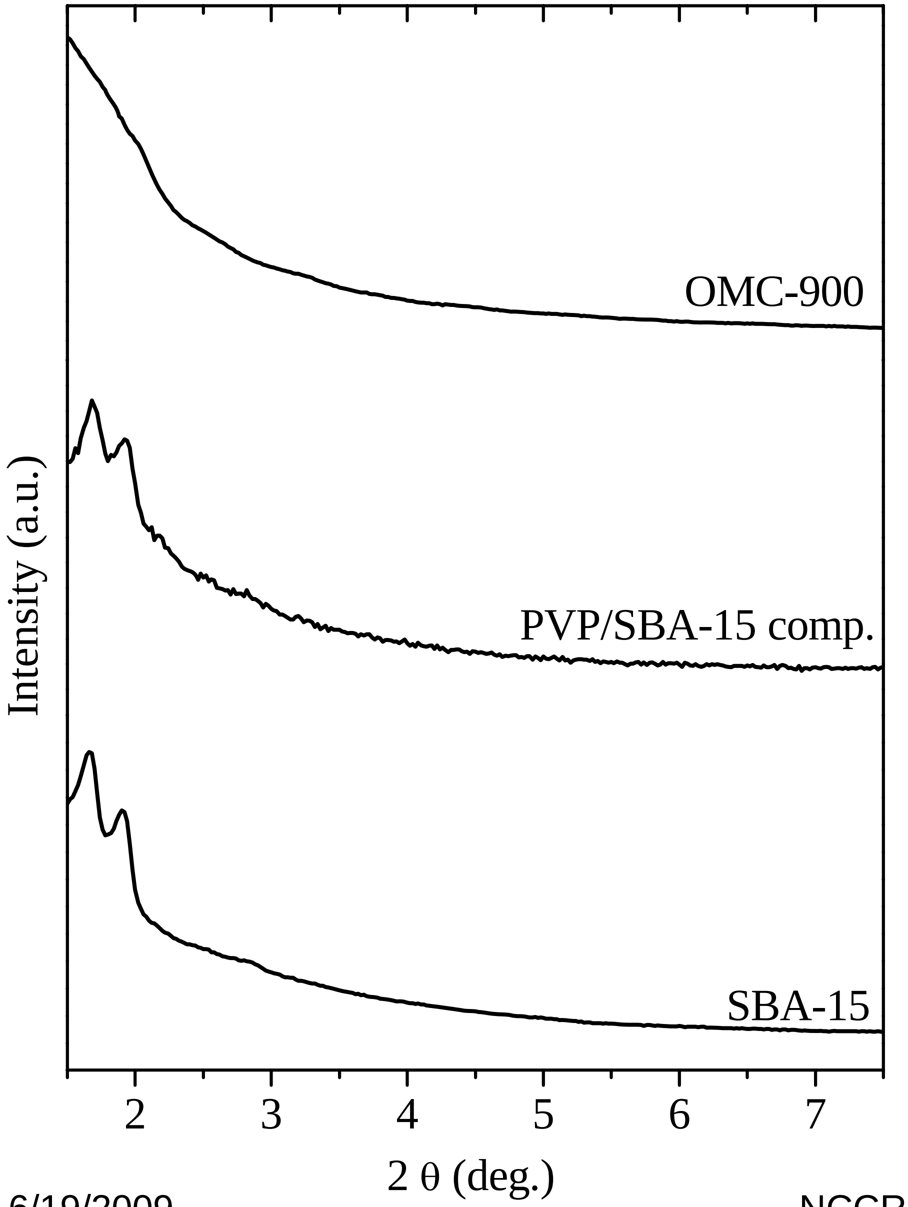
↓

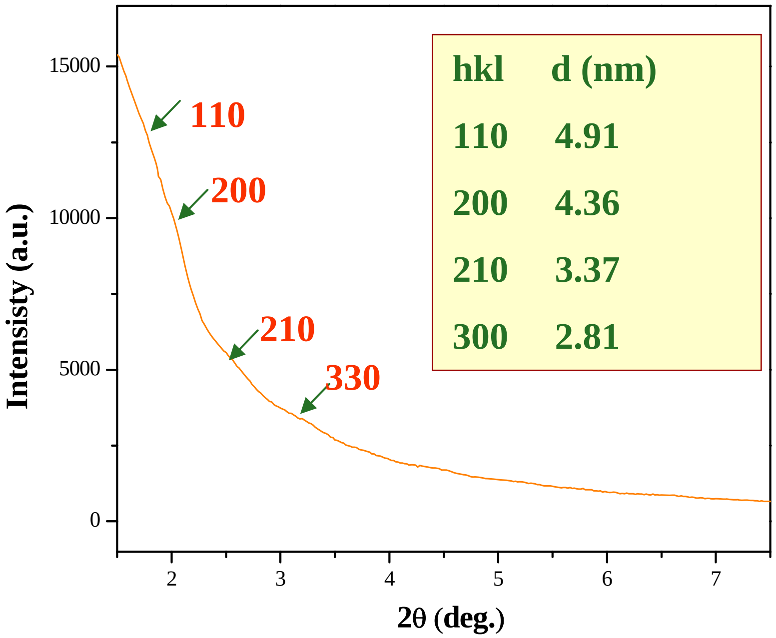
Carbonized at 900 ^{0}C for 6 h under N_2 atm.

↓ Washed with HF at RT and with EtOH

OMC (PVP)

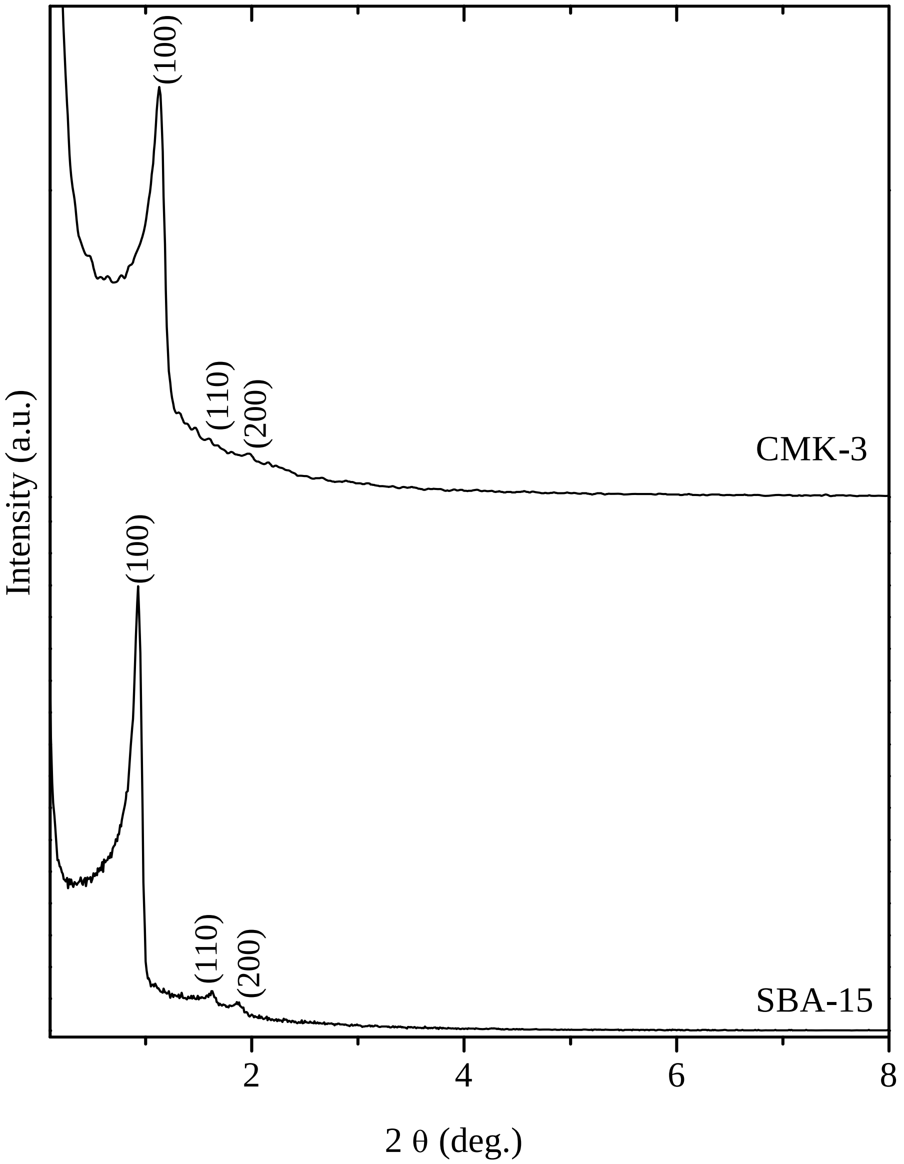
XRD of OMC (PVP)

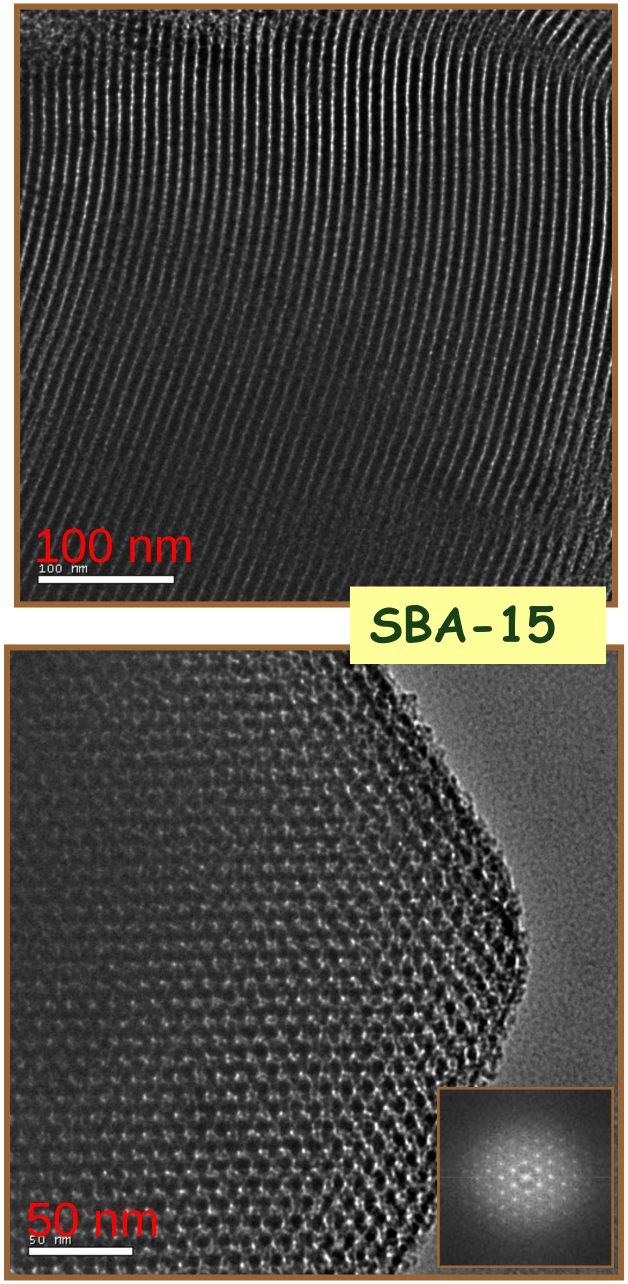




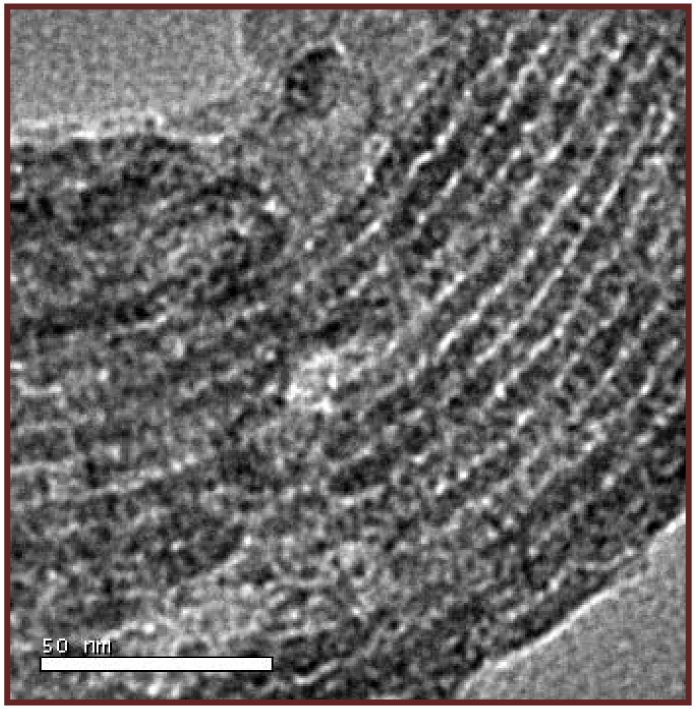
hkl	d (nm)
110	4.91
200	4.36
210	3.37
300	2.81

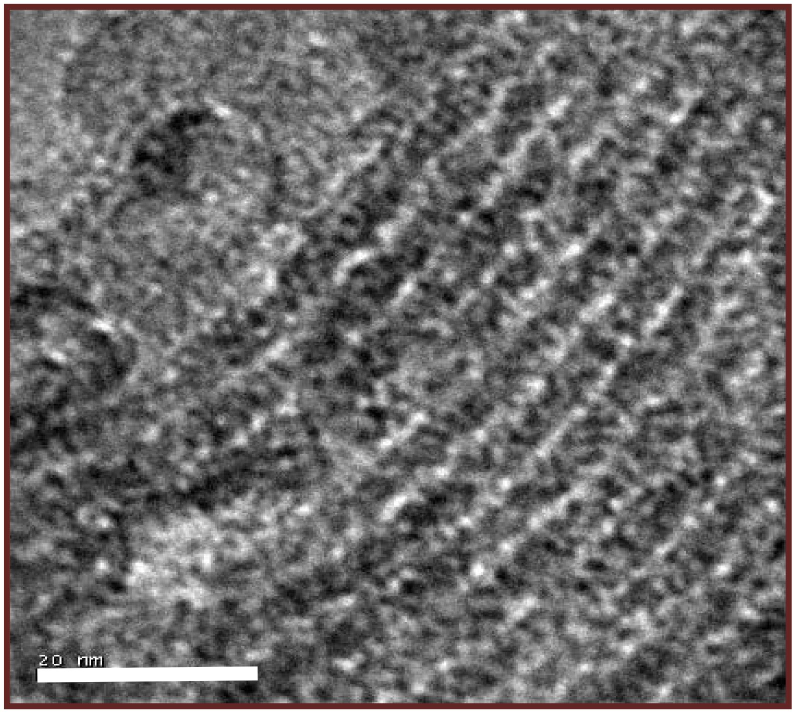
XRD & TEM

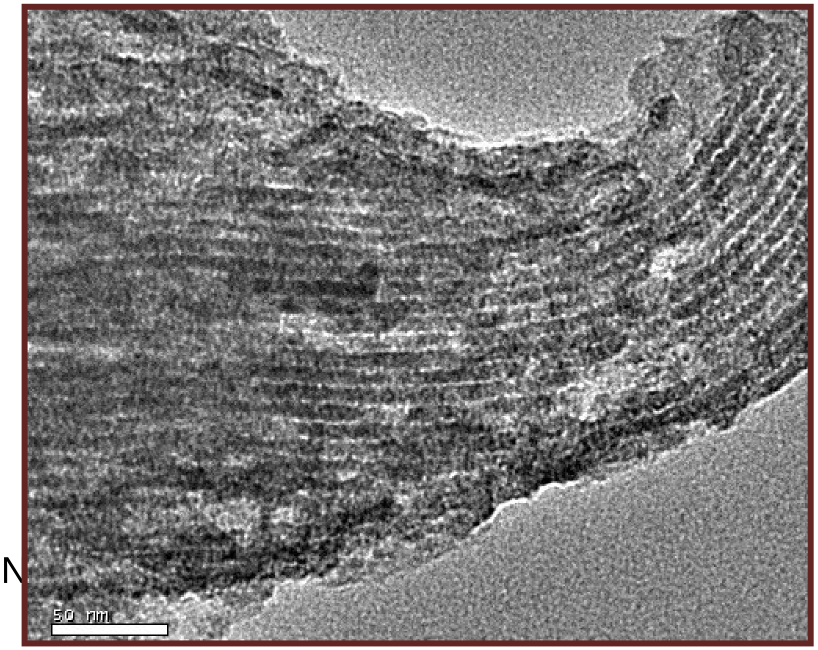

(100)
(110)
(200)
CMK-3
(100)
(110)
(200)
SBA-15
Intensity (a.u.)
2
4
6
8
2 θ (deg.)


100 nm
100 nm
SBA-15
50 nm
50 nm

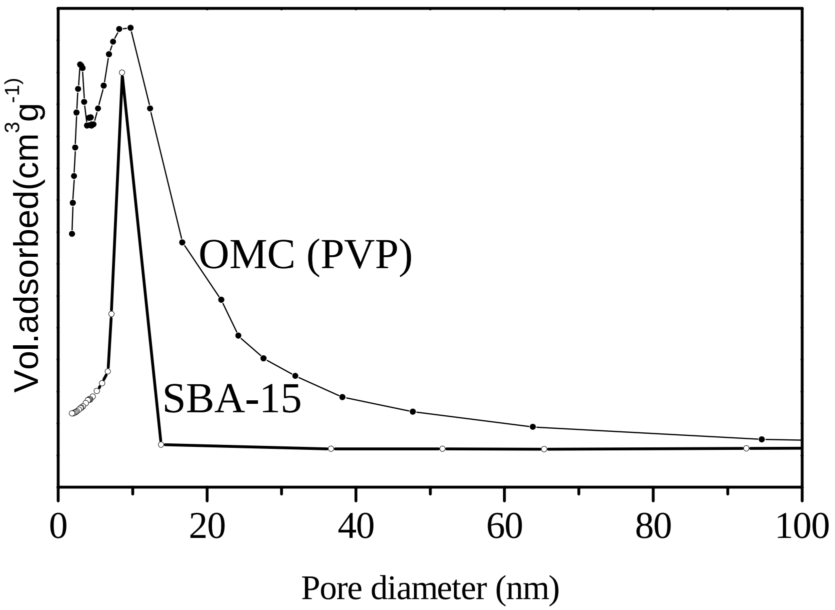
TEM images of OMC (PVP)

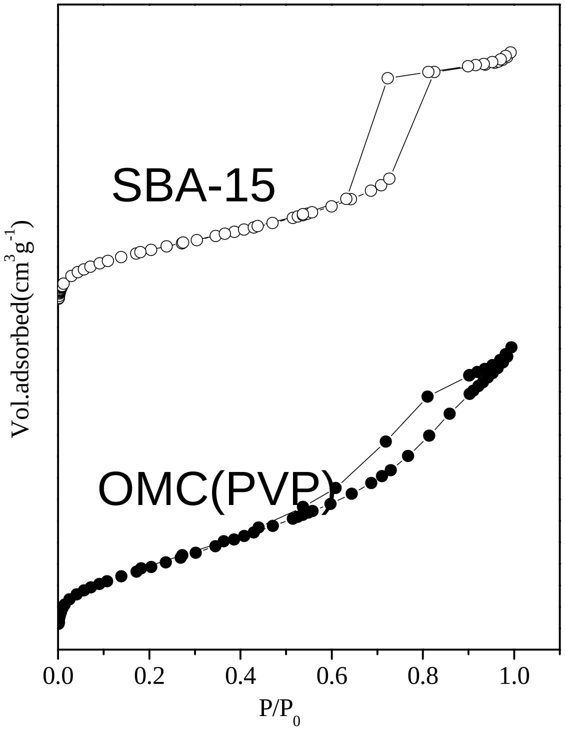






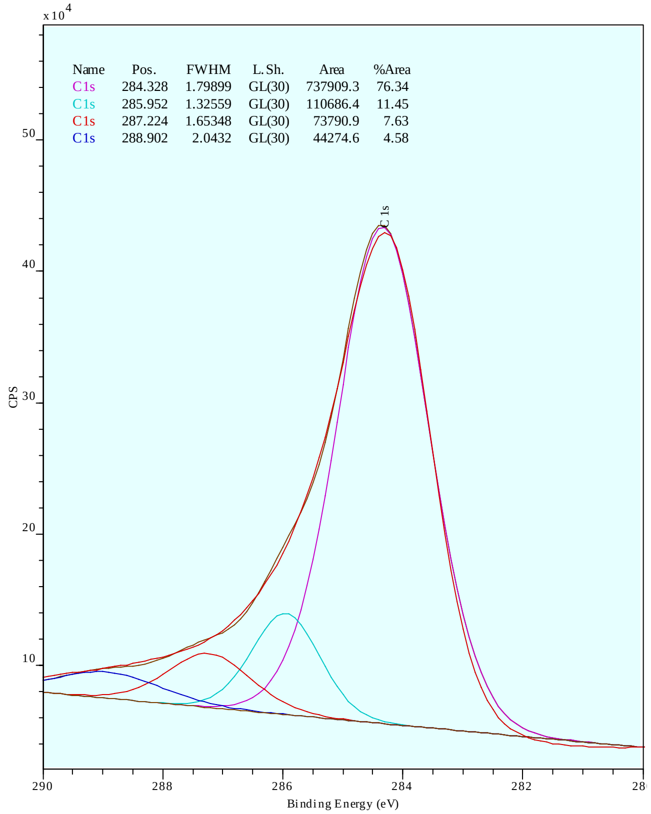
Textural Parameters of SBA-15 and OMC (PVP)





Material	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
SBA-15	680	1.04	8.54
OMC(PVP)	857	1.16	3.0 & 8.9

XPS of OMC (PVP)



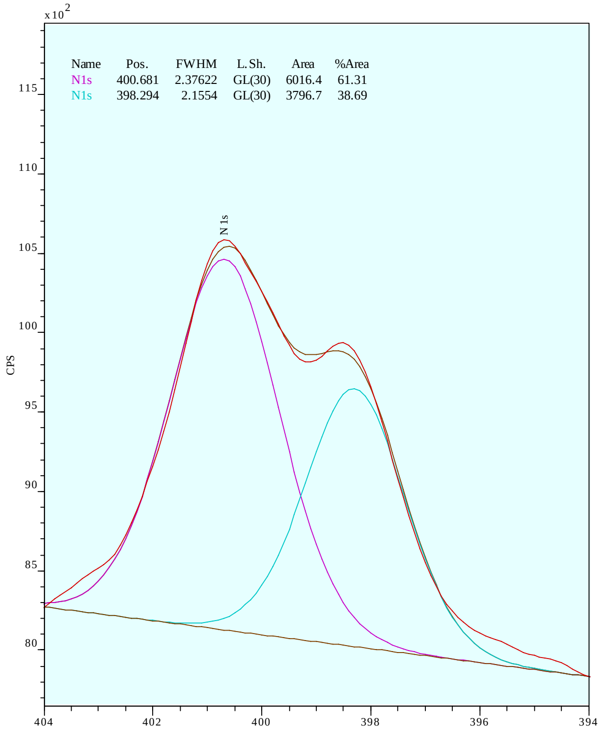
Name	Pos.	FWHM	L. Sh.	Area	%Area
C1s	284.328	1.79899	GL(30)	737909.3	76.34
C1s	285.952	1.32559	GL(30)	110686.4	11.45
C1s	287.224	1.65348	GL(30)	73790.9	7.63
C1s	288.902	2.0432	GL(30)	44274.6	4.58

C1s

284.3 eV – sp^2 gC species

286.0 eV – sp^2 C-N (C-O)

287.2 eV – sp^3 PVP C –N (C=O)



Name	Pos.	FWHM	L. Sh.	Area	%Area
N1s	400.681	2.37622	GL(30)	6016.4	61.31
N1s	398.294	2.1554	GL(30)	3796.7	38.69

N1s

400.6 eV – quaternary N atoms

398.2 eV – pyridine - like N atoms

Electro-catalytic activity

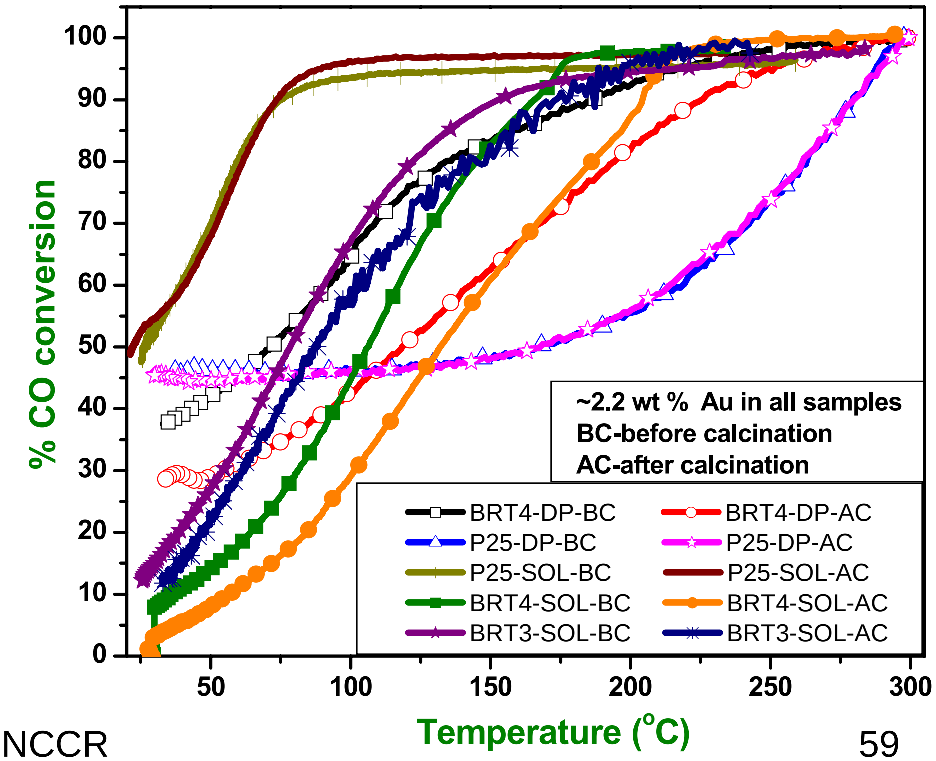
Catalyst (x wt%)	Current density at 0.70 V	Chronamperometric current (initial) mA at 0.7 V	Chronamperometric current (after 3h) mA at 0.7 V	% activity loss after 3h
20Pt/NCCR-1	69.60	63.63	58.56	08.0
20Pt/CMK-3	93.20	86.07	62.00	28.0
20Pt/CMK-1	39.70	31.46	20.60	34.0
20/Pt OMC(PVP)	93.0	80.0	61.5	23.0
10Pt/NCCR-1	29.20	19.17	17.62	08.0
10Pt/CMK-3	25.40	22.74	21.07	07.0
10Pt/CMK-1	25.40	16.23	14.18	13.0

Influence of preparation method on Au/TiO_2 as catalyst for CO oxidation (Mr.G.Magesh)

- Crystalline phase of TiO_2 plays a significant role
- Brookite (BRT4), Anatase + Brookite (BRT3) and Anatase + Rutile (P25) were studied as support for gold
- Method of gold loading also varies the activity
- Sol deposition (Sol) and deposition-precipitation (DP) methods were used to load Au
- In samples prepared by sol method, activity follows the order P25 > BRT3 > BRT4
- BRT4 gives higher activity than P25 in samples prepared by DP method
- In both sol and DP methods, P25 catalysts showed higher thermal stability
- Reasons for the observed trends under different catalyst preparation methods is being studied

Table : Surface area and phases composition of various TiO_2 supports

Catalyst	XRD			Surface area (m^2/g)
	% Anatase	% Rutile	% Brookite	
BRT4	0	0	100	114
BRT3	55	0	45	197
P25	75	25	0	50



60 mg of catalyst studied with 35 ml/min reaction mixture (0.5 vol. % CO, 9.4 % O_2, 51.9 % He and 38.2 % Ar) heating 4 K/min

Visible light activity of coupled CeO_2-TiO_2 system

- TiO_2 active only with UV light
- TiO_2 and CeO_2 have bandgaps of 3.2 eV and 2.7 eV respectively
- TiO_2 and CeO_2 have their CB positions at -0.29 eV and -0.32 eV w.r.to NHE
- Coupling TiO_2 and CeO_2 facilitates visible light activity by coupled semiconductor mechanism
- CeO_2-TiO_2 composite shows visible light activity and higher activity than pure TiO_2 in UV-Visible light
- 1 wt % Ce loading was found to be optimum

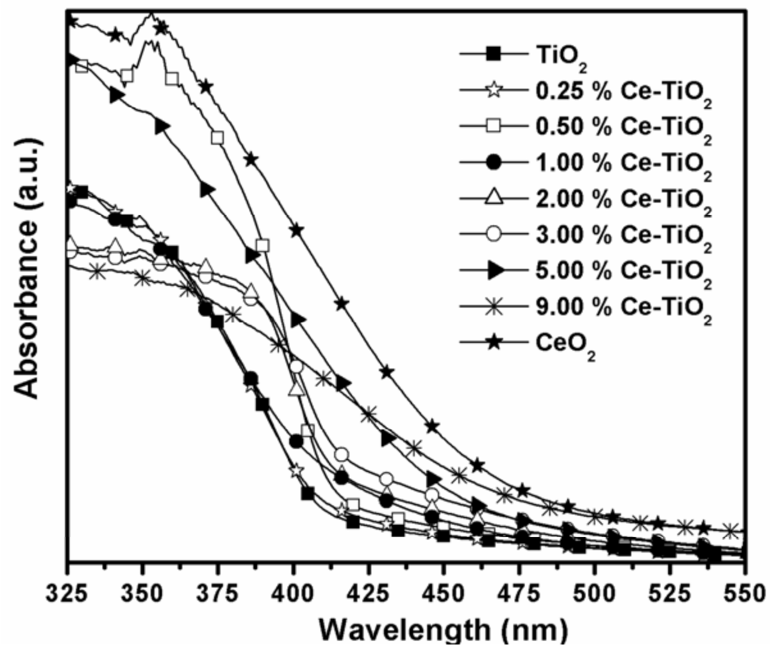


Fig: UV-Visible DR spectra of the various photocatalysts

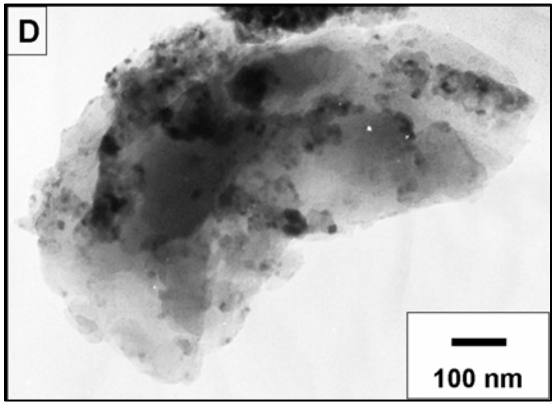
Table: Photocatalytic methylene blue degradation results with 0.1 g catalyst, 80 ml 50 ppm MB (UV) and 20 ppm MB (Visible) using 500 W Hg lamp for 90 mins

Catalyst	Amount decreased (x 10^{-7} mol / 0.1 g catalyst)			
	Visible		UV	
	*Overall	**Net photocatalytic	Overall	Net photocatalytic
TiO_2	9.63	0.53	32.40	23.30
0.25 % Ce-TiO_2	14.65	6.31	34.56	26.22
0.50 % Ce-TiO_2	17.01	9.74	37.28	30.01
1.00 % Ce-TiO_2	16.80	10.27	40.45	33.92
2.00 % Ce-TiO_2	14.65	8.87	39.22	33.44
3.00 % Ce-TiO_2	14.12	8.66	31.61	26.18
5.00 % Ce-TiO_2	11.34	6.74	28.17	23.57
9.00 % Ce-TiO_2	9.73	5.55	26.83	22.65
CeO_2	8.66	5.24	5.18	1.76

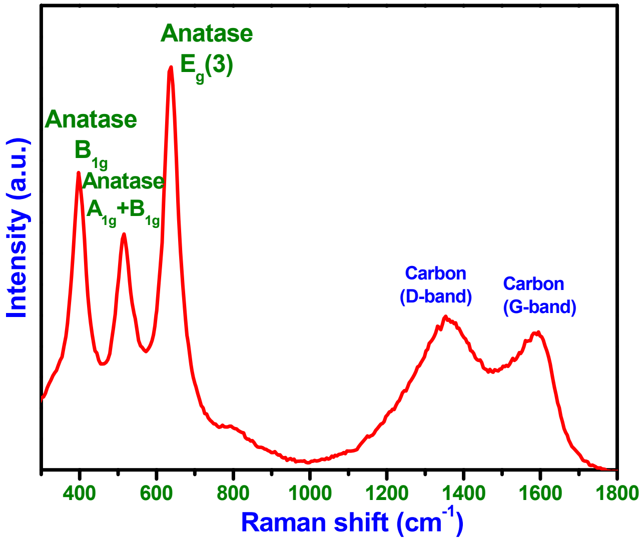
*Overall = Photocatalytic + Adsorbed ; **Net photocatalytic = Overall - Adsorbed

Improved efficiency of carbon-TiO_2 composite photocatalyst

- Photocatalytic efficiency is reduced by recombination
- Recombination can be reduced by improving adsorption of target molecules
- Carbon-TiO_2 composite improves adsorption and there by decreases recombination and increases efficiency
- Results show that upto 35 % increase in photocatalytic efficiency can be achieved by adding 3.0 % of carbon



TEM image of carbon-TiO_2 composite



Raman spectrum of carbon-TiO_2 composite

Table: Photocatalytic degradation results of 80ml of 50 ppm methylene blue degradation using 0.1 g catalyst under 500 W Hg irradiation for 90 mins

Catalyst	% C	% MB concentn. reduced in irradiation	% MB concentn. reduced in dark	% Photocatalytic (Irradiation – Dark)
TiO_2 600 °C	NA	34.0	13.0	21.0
C-TiO_2 300 °C 6h N_2	5.4	88.0	41.3	46.7
C-TiO_2 400 °C 6h N_2	3.0	87.7	31.8	55.9
C-TiO_2 500 °C 6h N_2	2.1	74.5	26.8	47.7
C-TiO_2 600 °C 6h N_2	1.4	72.7	23.8	48.9

Development of Alumina with Defined Physico-chemical properties (T.Nithya)

- To improve the textural properties of alumina without using surfactant, cheaper sources, simple precipitation methods.
- The obtained product must have the combinational pores meso & macropores.
- The look of the materials stability, extrudability for the FCC catalysts.

Preparation

10 ml 5 wt % of $NaAlO_2$

25 ml 2.5 wt % of $Al_2(SO_4)_3.16H_2O$ (~2 ml/min) with stirring at 45 - 50°C heating.

Precipitate obtained (pH = 8)

Aged at 75°C for 6 h. Then filtered, washed with water, dried at 60°C, 12 h.

Boehmite

Calcined at 450°C for 4 h.

γ - Alumina

Results

Crystallite size : 30 Å

Surface Area : 315 (300-350) m^2/g

Pore Volume : 0.81 (>80) cm^3/g

Pore Size : 103 (70–120 = 70-80 %) Å

Conversion of Glycerol (V.Anandha Kiruba)

Introduction

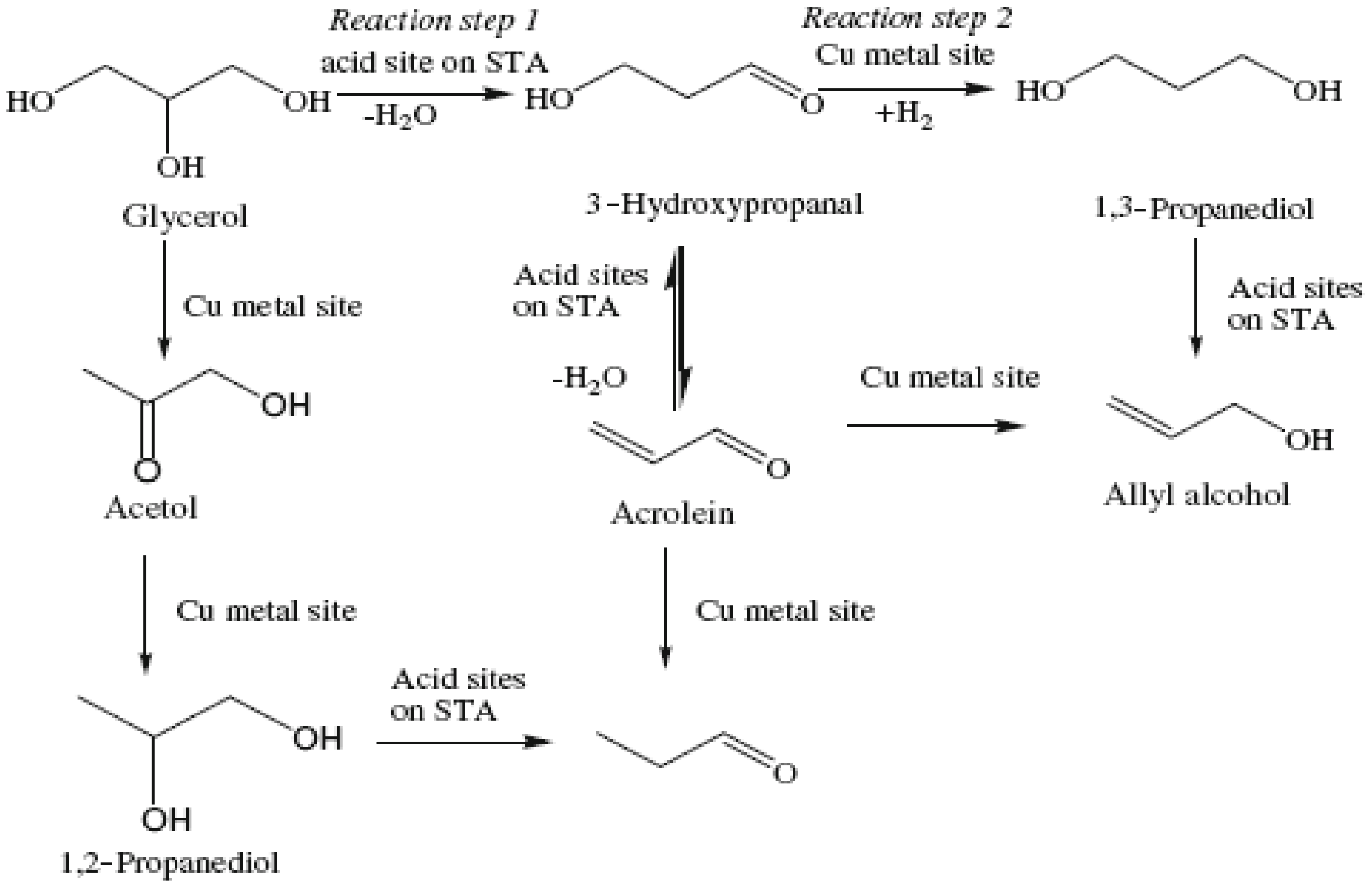
- Glycerol is one of the promising renewable resources. Glycerol is obtained as by-product for ca. 10 mass% of BDF produced.

- Glycerol can be converted into acrolein and hydroxyacetone (HA) through dehydration and further converted into 1,2- and 1,3-propanediol through hydrogenation under hydrogen pressure.

Objective

- To convert glycerol in to Hydroxyacetone and Acrolein by carrying out vapor phase reaction of glycerol over acidic catalysts.

The Reaction pathways of 1,3-PD and 1,2-PD formation and their dehydration reactions over Cu-STA/SiO$_2$



L. Huang et al.,Catalysis Letters, 2009

Catalyst Preparation

0.05 mol $Zn(NO_3)_2 .6H_20$ + 0.025 mol $Al(NO_3)_3.9H_20$

↓ To this NaOH and Na_2CO_3 were added (pH = 11)

Precipitate

Zn:Al=2

↓ Precipitate kept at 65°C for 18 h (hydrothermal treatment)

↓ Obtained gel is dried at 110°C over night

↓ Calcined at 500°C for 18 h

Calcined Zn-Al Hydrotalcite (ZnO)

Future Work

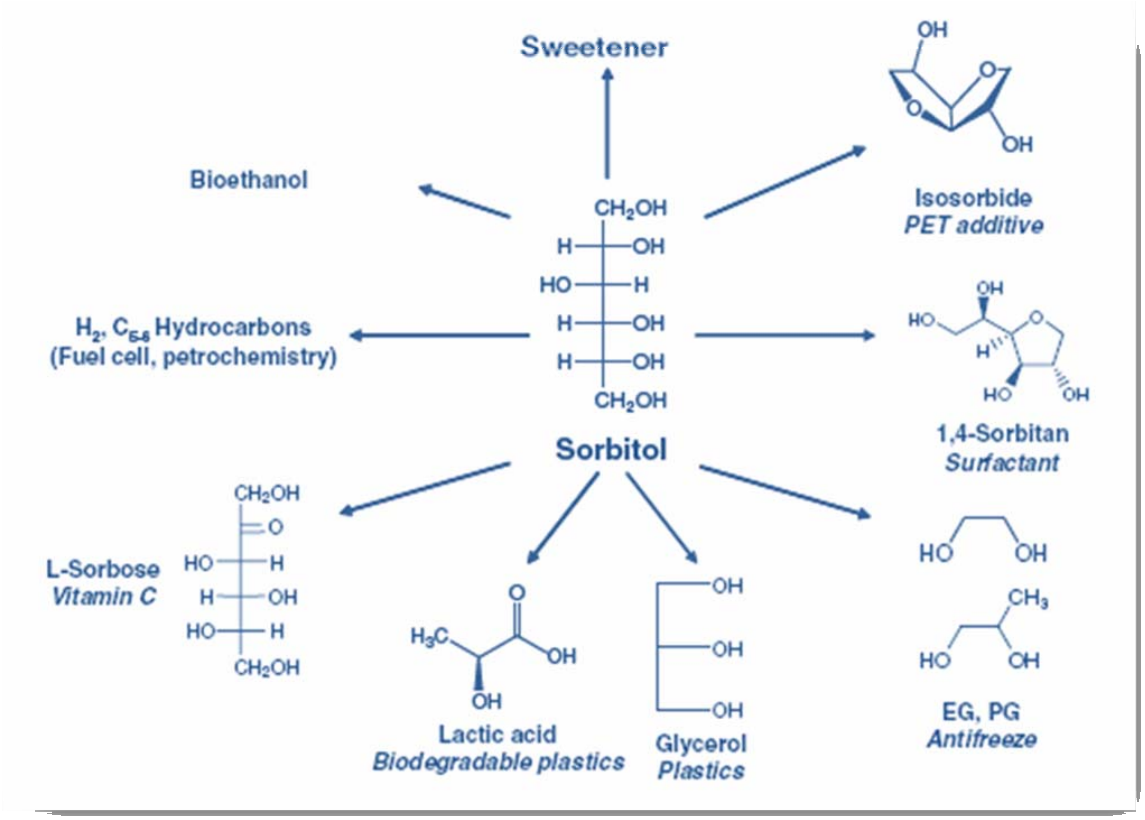
- Characterisation of the Catalyst.
- To carry out vapor phase reaction of glycerol over Calcined Zn-Al Hydrotalcite and analyze the products using GC.
- To optimise the reaction conditions.
- Regeneration of the Catalyst.

Biomass Conversion And Utilization of Polyhydric Alcohols From Natural Sources(Ms.Banu)

- We are now in the century when it is widely accepted that hydrocarbon resources will become very short supply.
- It is vital that we develop chemical processes and chemical products on alternative feedstock's and especially renewable crops.
- The production of biobased organic chemicals has been identified as the most promising platform for the utilization of renewable biomass as an alternative to petroleum.
- Cellulosic biomass, like carbohydrates is considered to be the most abundant organic material on earth and is therefore an ideal feedstock for the production of biobased chemicals.
- In some precising schemes , conversion of carbohydrates can involve the initial hydrogenation of a simple sugar, such as glucose to the sugar alcohol sorbitol.
- Therefore sorbitol was used as the starting feedstock for the hydrogenolysis studies on metal catalysts.

Objectives

- The subsequent catalytic hydrogenolysis of sorbitol yields lower molecular weight polyols such as glycerol, ethylene glycol and propylene glycol.



Catalyst Preparation

0.5wt% of Ru^{3+}(0.65 ml of 1 wt % solution $RuCl_3$) + 0.4975g H-Zeolite

↓

Then dried at 120°C, 12h.

↓

Reduced at 400 °C with H2 Flow, 3h

↓

Ru/H-Zeolite Catalyst

Reaction Condition

Reactant: 15% Sorbitol

Catalyst: 0.5g Catalyst

Parr Reactor: 300 ml Reactor

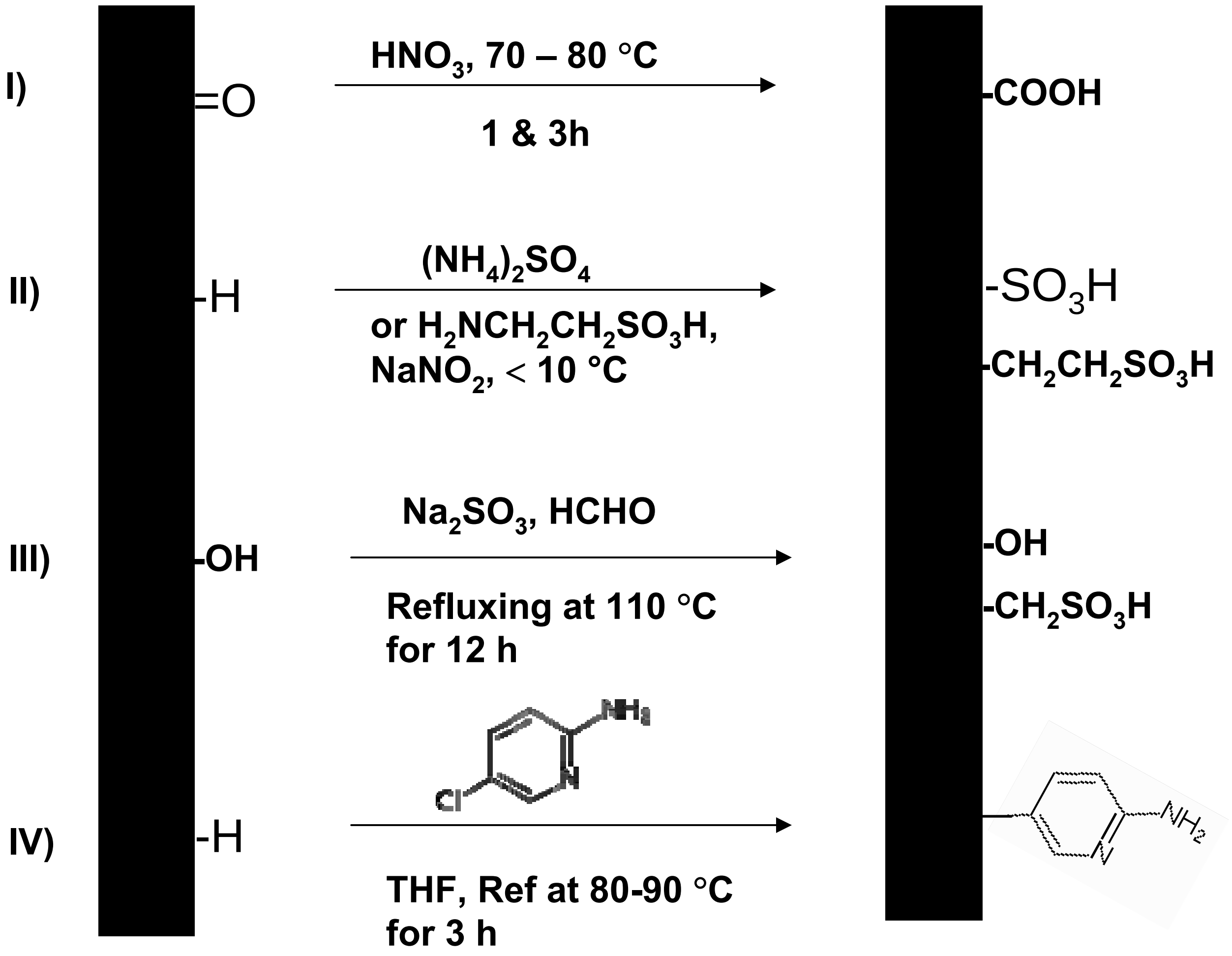
Temperature: 220 °C

Pressure: 60 bar H_2

Reaction Time: 6 h

Products will be analyzed by GC and HPLC

Chemical modification of CDX975 carbon black (Ms.Chandravathanam



I) =O $\xrightarrow[\text{1 \& 3h}]{HNO_3\text{, 70 – 80 °C}}$ -COOH

II) -H $\xrightarrow{(NH_4)_2SO_4}$ or $H_2NCH_2CH_2SO_3H$, $NaNO_2$, < 10 °C -SO_3H -$CH_2CH_2SO_3H$

III) -OH $\xrightarrow{Na_2SO_3\text{, HCHO}}$ Refluxing at 110 °C for 12 h -OH -CH_2SO_3H

IV) -H $\longrightarrow$ THF, Ref at 80-90 °C for 3 h

Table-1 Comparative results of HNO_3 treated CDX975

					10% Pt loaded on acid treated catalyst	
S.no.	Sample	pH	BET surface area (m^2/g)	Pore volume-BJH desorptive (cm^3/g)	Crystallite size XRD (nm)	Mass specific methanol oxidation activity (A/g)
1	Untreated CDX	6.1	211	0.54	13.5	214
2	1N HNO_3 treated CDX - 60 min	5.0	194	0.44	21.2	311
3	conc. HNO_3 treated CDX - 60 min	4.5	136	0.42	6.6	406
4	1N HNO_3 treated CDX - 95 min	4.1			12.9	269
5	conc. HNO_3 treated CDX – 95 min	3.7	139	0.4	13.4	265

Table-2 Comparative results of sulphonic acid modified 10% Pt/ CDX975

S.No	Sample	pH	Mass specific methanol oxidation activity (A/g of Pt)
1	0 % 2aesa / 10% Pt / CDX	6.0	125
2	10 % 2aesa / 10% Pt / CDX	4.4	275
3	20 % 2aesa / 10% Pt / CDX	4.2	290
5	10 % am. sul. / 10% Pt / CDX	5.1	225
6	20 % am. sul. / 10% Pt / CDX	4.9	170

Table-3 Comparative results of sulphomethyl group modified 10% Pt/ CDX975

S.No.	Sample	XRD crystallite size (nm)	EAS (m^2/g)	Mass specific methanol oxidation activity (A/g)
1	No sulphomethylated 10% Pt/ CDX975	13.5	17.9	214
2	Sulphomethylated 10% Pt/ CDX975	5.5	41.5	484

Table-4 Comparative results of 2-amino-5-chloro pyridine(acp) modified CDX975

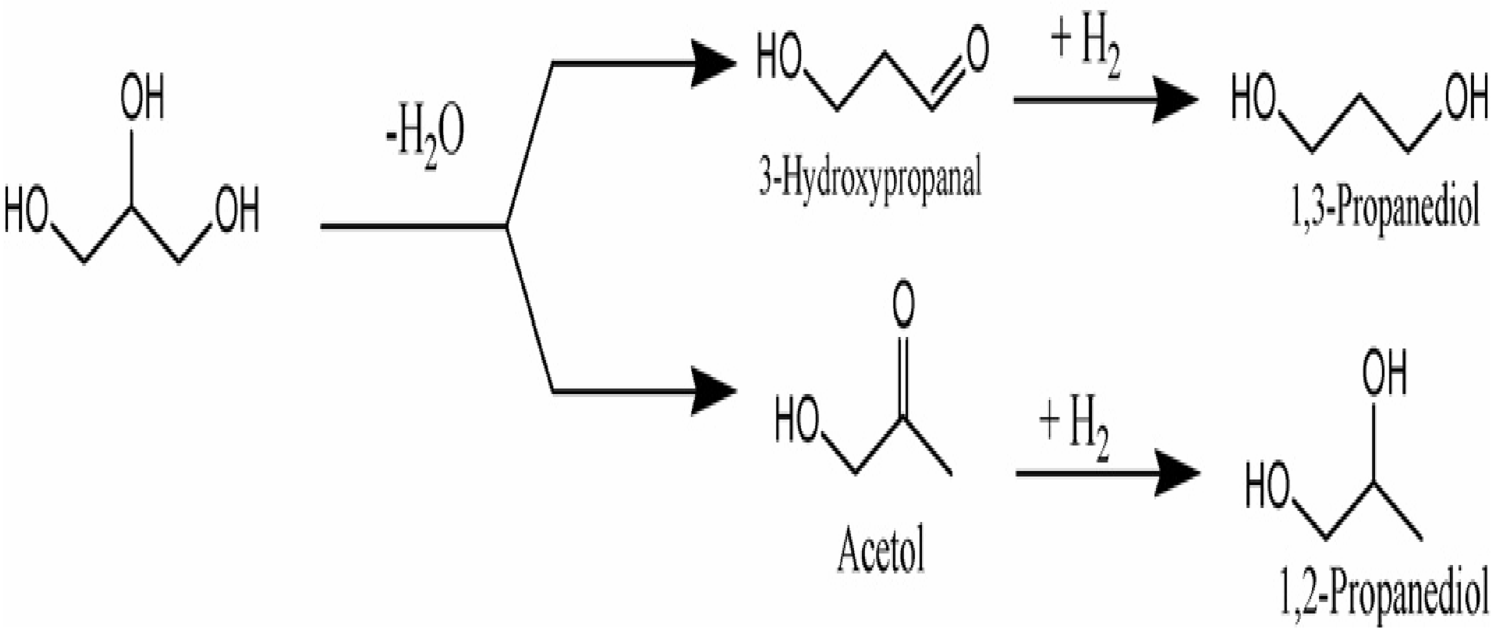
S.No.	Sample	C %	H %	N %
1	0% acp/ cdx	95.33	0.6	0.15
2	1% acp/ cdx	96.02	0.96	0.23
3	5% acp/ cdx	94.96	0.45	0.84

S.No.	Sample	XRD crystallite size (nm)	EAS (m^2/g)	Mass specific methanol oxidation activity (A/g)
1	10% Pt/ 0% acp/ cdx	18.5	19.3	155
2	10% Pt/ 1% acp/ cdx	13.4	38.7	270
3	10% Pt/ 5% acp/ cdx	9.4	60.0	415

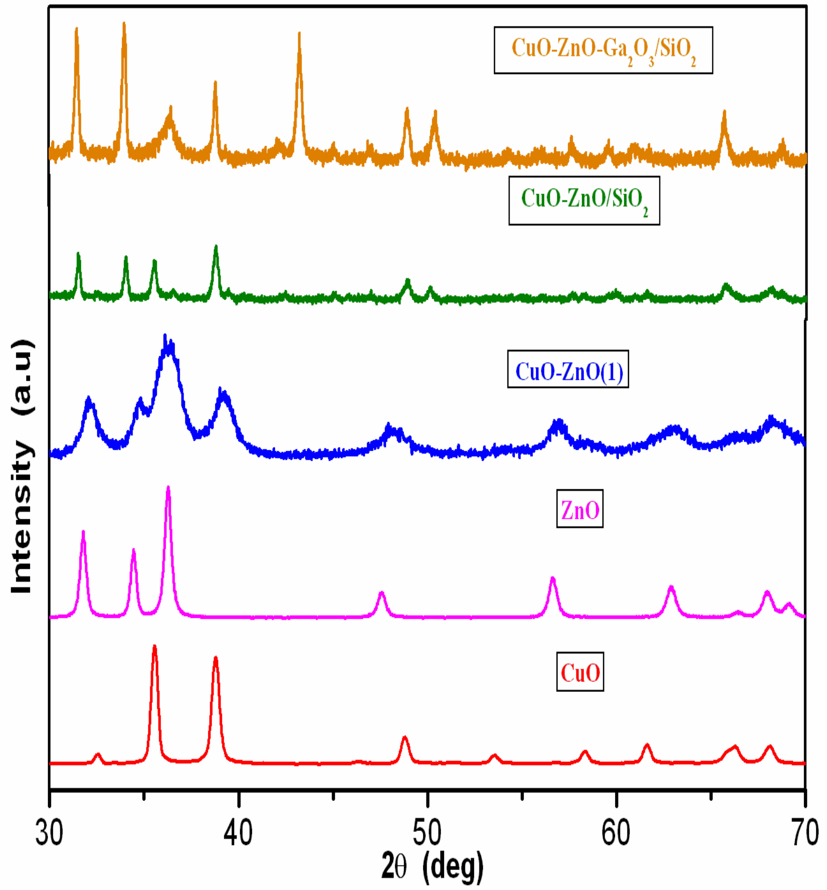
Conversion of glycerol to 1,2 / 1,3 propane diols

K.Suthagar

Reaction Mechanism



- Hydrogenolysis of glycerol reaction has to follow two steps
- First step dehydration and second step hydrogenolysis
- Metel oxide and silica supported metal oxide catalyst were prepared by co-precipitation and impregnation method respectively



XRD patterns of MO$_x$/SiO$_2$ catalysts

TPR spectra

Hydrogenolysis of glycerol

Catalyst	Temp (ºC)	H_2 Pressure (bar)	Weight of the catalyst (g)	Time (h)	Conversion (%)	Selectivity (%)		
						1,2 - Propane diol	1,3 propane diol	EG
CuO-ZnO	**180**	**42**	**0.5**	**12**	**8**	**91**	**-**	**-**
5 wt.% CuO - 5 wt. % ZnO / Fumed-SiO_2	**18.0**	**42**	**0.5**	**12**	**18**	**92**	**-**	**-**
4 wt. % CuO - 4 wt % ZnO- 2 wt Ga_2O_3 / Fumed-SiO_2	**180**	**42**	**1**	**12**	**2.5**	**80**	**2**	**-**
2 wt.% Ru / 2 wt % Cu on Fumed SiO_2	**180**	**42**	**0.5**	**12**	**5**	**33**	**-**	**-**
5 wt% Cu – 5 wt % Ni on activated carbon	**180**	**42**	**0.5**	**12**	**2**	**81**	**-**	**-**

<u>Reaction Conditions</u>: Glycerol: 15 g ; Solvent : Isopropyl alcohol (65 ml), RPM : 300,

Catalyst	Temp (ºC)	H_2 Pressure (bar)	Weight of the catalyst (g)	Time (h)	Conversion (%)	Selectivity (%)		
						1,2 - Propane diol	1,3 propane diol	EG
2 wt.% Ru / MCM-41	180	42	0.250	12	16	94	2.4	-
Fe-SBA-15	180	42	0.5	12	21	88	-	8
Cr-SBA-15	180	42	0.5	12	23	91	-	8.2
Cu-MCM-41	180	42	0.5	12	6	30	-	30

<u>Reaction Conditions</u>: Glycerol: 15 g ; Solvent : Isopropyl alcohol (65 ml), RPM : 300,

Activated Carbon Materials from Natural Sources

Multi-dimensional utility of Activated Carbon Materials

- Molecular sieving – High pure oxygen production
- Filtration – Nuclear, Chemical and Biological filters
- Energy storage media – Hydrogen, electric charge
- Electrode fabrication – Batteries, Fuel cells and Super capacitors
- Sorbent – CO_2 capturing, desulphurization, mercury sorption, HCN sorption
- Reinforcing filler – Fabrication of composite materials
- Multifunctional building Blocks – Fabricating electro mechanical nanodevices

Interesting properties of Activated carbon Materials

- Stable physical and chemical properties
- High specific surface area
- Good electrical conductivity
- Biocompatibility
- Dielectric in nature
- Relatively low cost
- Production from diverse sources and ways

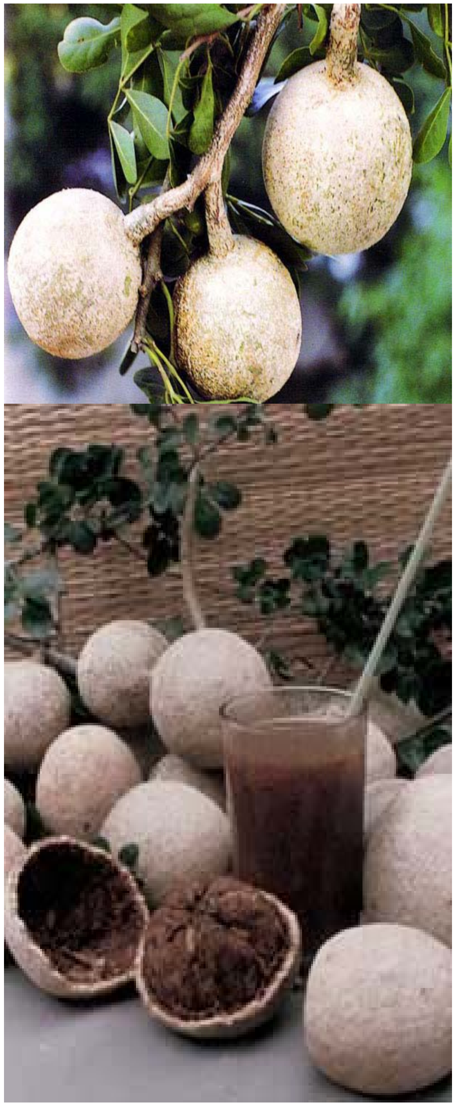
Andrei et al., Carbon 47 (2009) 2372
Mykola Seredych et al., Carbon 47 (2009) 2491
Glenn O Rubel et al., Carbon 47 (2009) 2442
Huanlei Wang et al., Carbon 47 (2009) 2259
Lara – Marie Barnes et al., Carbon 47 (2009) 1887

Natural sources for Activated Carbon

Calotropis gigantea
Support for HPA's
Etherification Catalyst
Hydrogenation Catalyst

Borassus Flabellifera
Support for HPA's
Etherification Catalyst (MTBE synthesis)
Out performed SBA 1 as support

Lemonia Acidissima
Support for Pt
Oxidation Catalyst
(Fuel Cell electrocatalyst)
Out performed Vulcan carbon as suppo



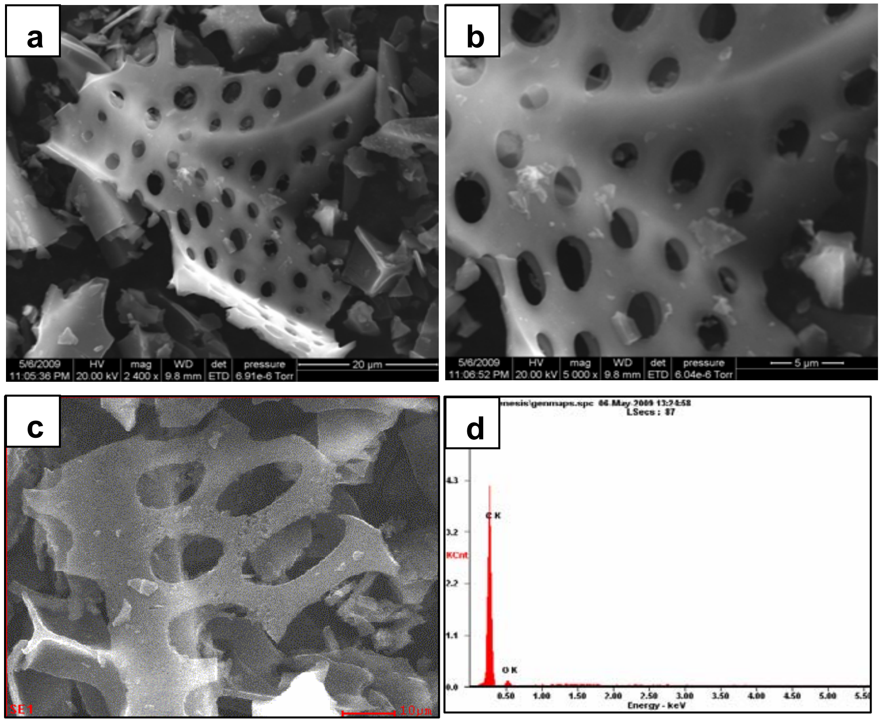
Some other promising precursors for Activated Carbon

Ipomoea Carnea

Mercury sorption

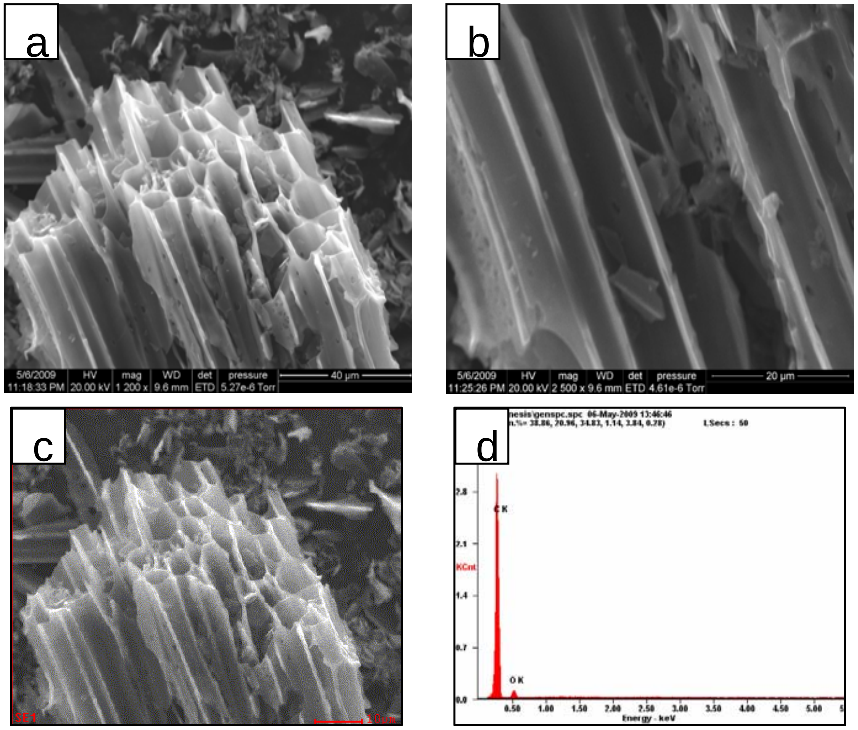
Special Features of Carbon Materials from Natural Sources

- Unusual morphologies
- High specific surface area values
- Both morphologies and surface area values are tunable depending on the activation



Activation with potassium carbonate

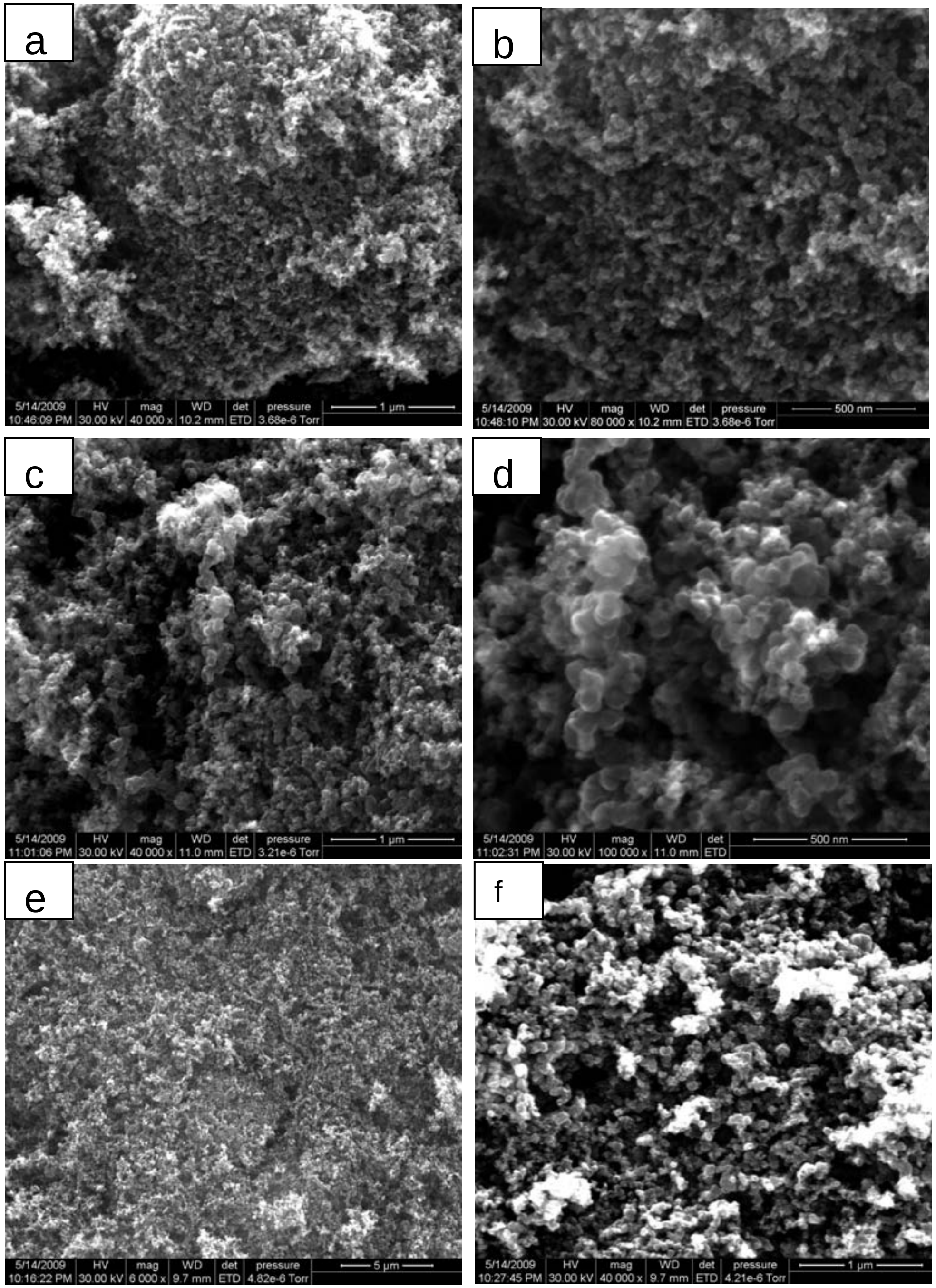
1296 m^2/g



Activation with sodium oxalate

785 m^2/g

SEM images of Black Pearl 2000, Vulcan XC 72 R and CDX 975 carbon materials

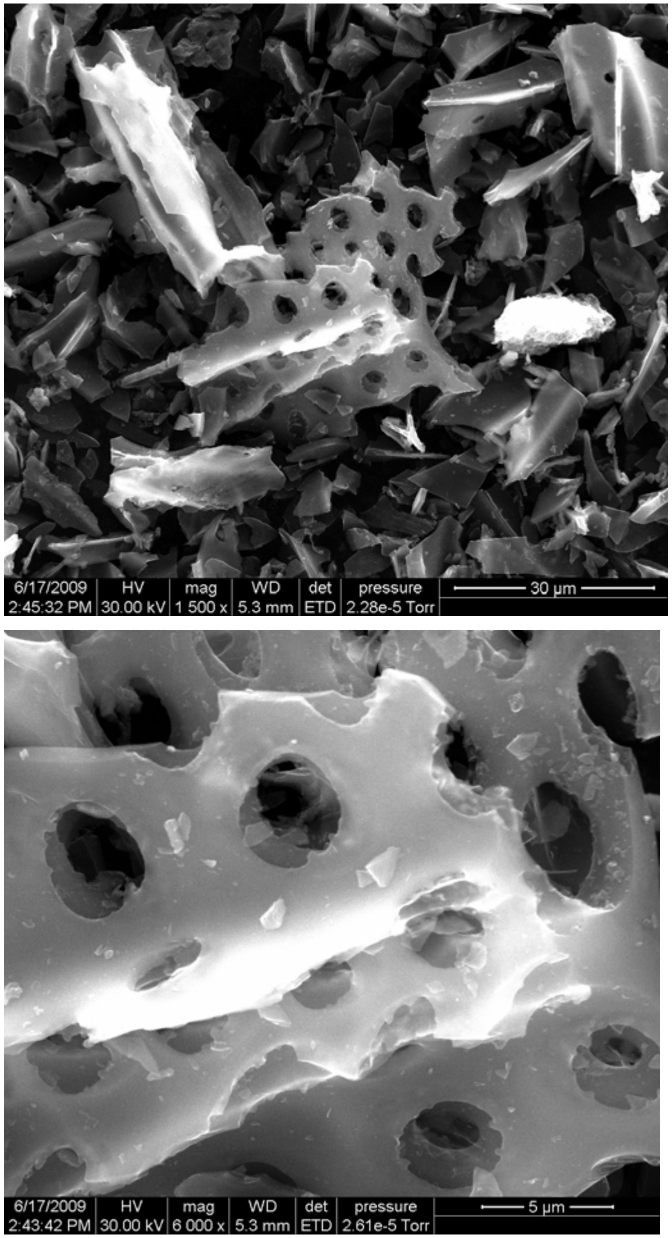


FEG SEM images (at different magnifications) of commercial activated carbon material:
(a & b) Black Pearl 2000 (40, 000 X, 80, 000 X),
(c & b) Vulcan XC 72 R (40, 000 X, 1,00, 000 X)
and (e & f) CDX 975 (6000 X, 40, 000 X)

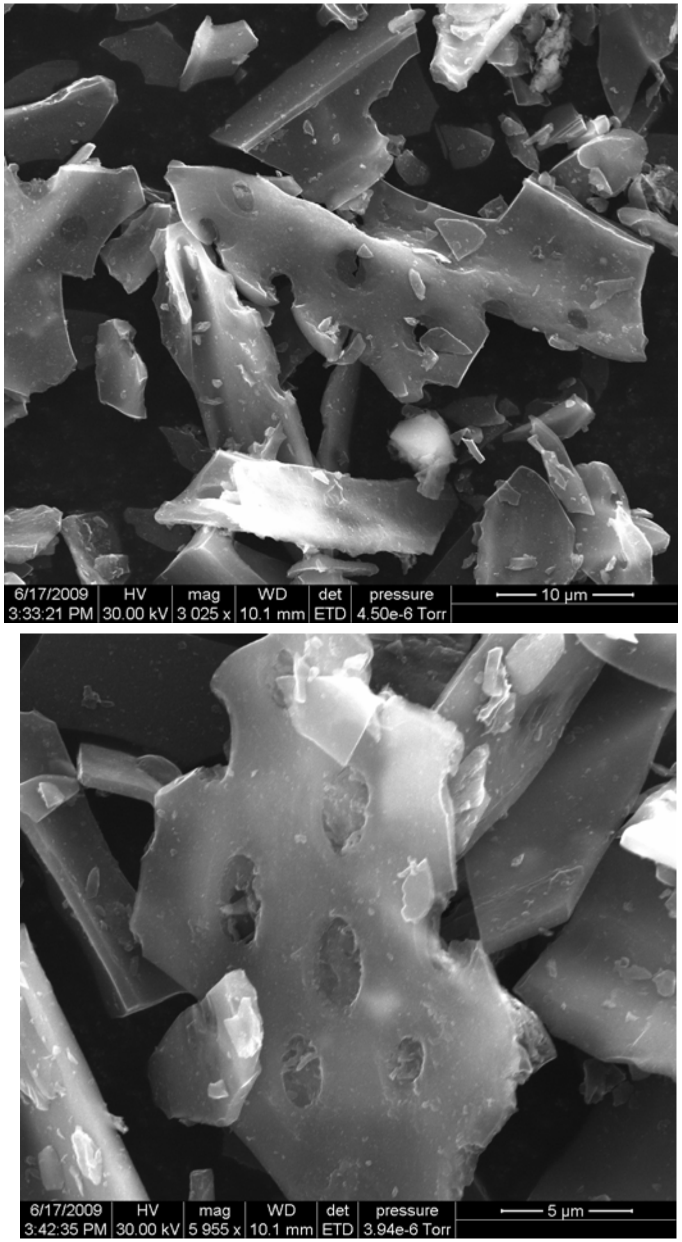
Commercial carbon materials showed only spherical carbon particles

No peculiar morphology is seen analogous to those seen in the carbon materials from natural sources

Activation with $ZnCO_3$ Vs $ZnCl_2$



Zinc Carbonate activation is better than Zinc chloride activation



$ZnCO_3$ activation (pores evolved well)
626 m^2/g

$ZnCl_2$ activation (pores in incipient state)
356 m^2/g

Tuning the porosity – Method of activation

S. No.	Activating agent	S_{BET} (m^2/g)	V_p cm^3/g	Type of isotherm/porosity
1	Li_2CO_3	478	0.26	Type I (Microporous)
2	Na_2CO_3	811	0.40	Type I (Microporous)
3	K_2CO_3	892	0.50	Type I (Microporous)
4	$Ca(CO_3)_2$	524	0.33	Type I (Microporous)
5	$Ba(CO_3)_2$	170	0.10	Type I (Microporous)
6	$Zn(CO_3)_2$	626	0.30	Type I (Microporous)
7	NaCl	400	0.20	Type I (Microporous)
8	NaBr	319	0.16	Type I (Microporous)
9	KBr	275	0.10	Type I (Microporous)
10	NaI	58	0.04	Type I (Microporous)
11	CaO	521	0.25	Type I (Microporous)
12	$Ca(OH)_2$	189	0.11	Type I (Microporous)
13	$CaCl_2$	156	0.09	Type I (Microporous)
14	$Ba(OH)_2$	152	0.08	Type I (Microporous)
15	Al_2O_3	174	0.17	Type IV (Mesoporous)
16	$Al(NO)_3$	253	0.19	Type I (Microporous)
17	Urea	439	0.21	Type I (Microporous)
18	Sodium acetate	548	0.26	Type I (Microporous)
19	Sodium oxalate	707	0.33	Type I (Microporous)
20	Sodium potassium tartarate	394	0.20	Type I (Microporous)
21	Sodium citrate	419	0.20	Type I (Microporous)
22	Sodium tartarate	394	0.20	Type I (Microporous)
23	Citric acid	127	0.07	Type I (Microporous)
24	Tartaric acid	42	0.04	Type I (Microporous)
25	Oxalic acid	317	0.14	Type I (Microporous)

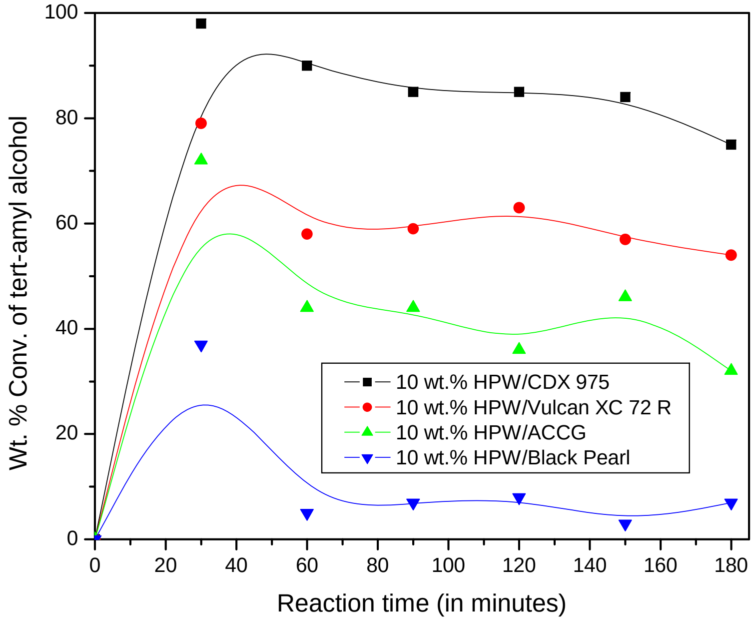
HPW/C for the Synthesis of TAME (t-amyl methyl ether)

Catalyst	**10 wt% HPW/CDX 975**			**10 wt% HPW/Vulcan XC72R**			**10 wt% HPW/Carbon from Calotropis Gigantea**			**10 wt% HPW/Black pearl**		
		% selectivity			**% selectivity**			**% selectivity**			**% selectivity**	
Reaction Time in min	**Wt% conv. of TAA**	**TAME**	**olefins**	**Wt% conv. of TAA**	**TAME**	**olefins**	**Wt% conv. of TAA**	**TAME**	**olefins**	**Wt% conv. of TAA**	**TAME**	**olefins**
30	98	60	40	79	84	16	72	52	48	37	45	55
60	90	50	40	58	94	6	44	57	43	5	19	81
90	85	51	49	59	86	15	44	47	53	7	41	59
120	85	60	40	63	75	25	36	64	36	8	61	39
150	84	41	59	57	95	5	46	60	40	3	44	56
180	75	65	35	54	87	13	32	73	37	7	47	53

Reaction temperature	= 100 ºC
Mole ratio of the feed, MeOH : TAA	= 10:1
Flow rate of the feed	= 10 ml/h
Flow rate of carrier gas (N_2)	= 30 ml/min
GC Column used	= OV 101Packed column

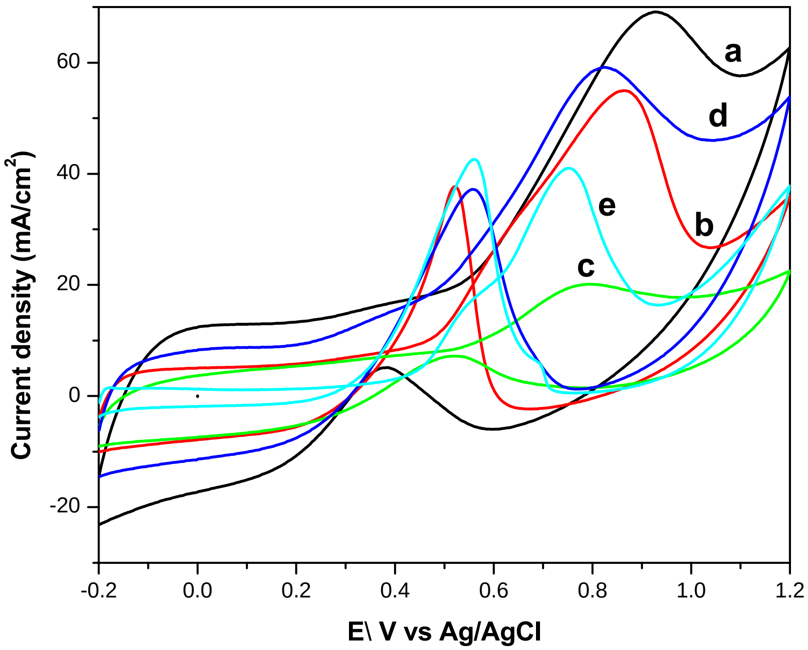
Activity Order:

- ❑ HPW/CDX 975 (215 m^2/g) > HPW/Vulcan XC 72 R (224 m^2/g) > HPW/ACCG (1012 m^2/g)) > HPW/Black Pearl (1091 m^2/g))
- ❑ High activity of the catalyst is derived from the support (CDX 975) with the least specific surface area
- ❑ CDX 975 support offers optimum dispersion and thereby resulting in mild acidity needed for etherification reaction because of the relatively low specific surface area value



Plot of wt. % conversion of t- amyl alcohol Vs reaction time (in min)

MeOH Electro-oxidation Activity of Pt/C catalysts



Cyclic Voltammetric response of

(a) GC/C_{WA} - 5 wt.% Pt - Nafion electrode

(b) GC/C_{WA} - 10 wt.% Pt - Nafion electrode

(c) GC/C_{WA} - 15 wt.% Pt - Nafion electrode

(d) GC/C_{WA} - 20 wt.% Pt - Nafion electrode and

(e) GC/Vulcan XC 72 R - 20 wt.% Pt - Nafion

in 0.5 M H_2SO_4 and 1 M MeOH

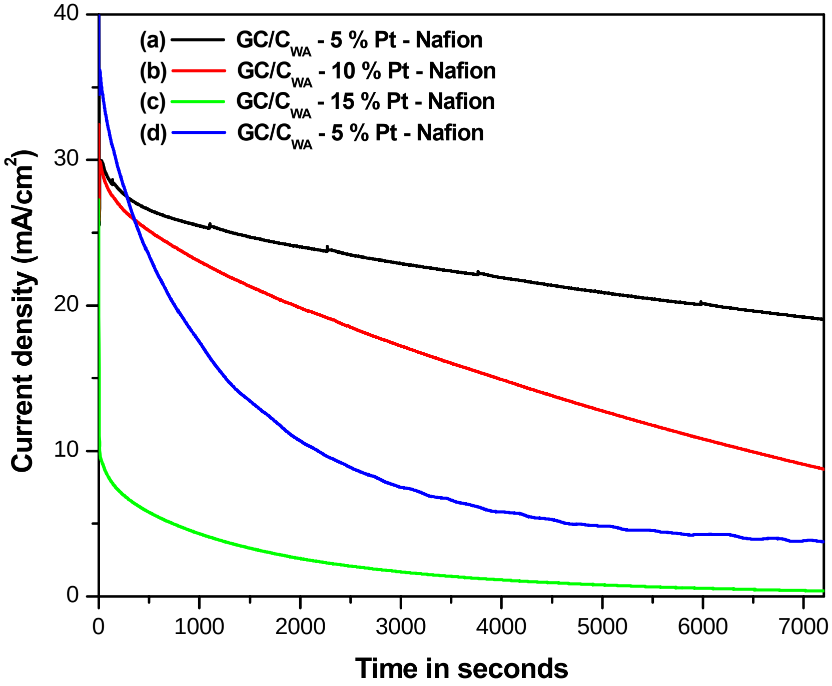
Scan rate : 25 mV/s

Potential window: -0.2 to 1.2 V

Comparison of Electrocatalytic Activity – Pt/C_{WA} and Pt/Vulcan XC 72 R

S. No.	Electrode	Onset Potential V	i_f/i_b	Activity*			
				Forward sweep		Reverse sweep	
				I (mA/cm^2)	E (V)	I (mA/cm^2)	E (V)
1	GC/C_{WA}-5 % Pt-Nafion	0.21	14.4	69.0	0.92	4.97	0.37
2	GC/C_{WA}-10 % Pt-Nafion	0.18	1.45	55.0	0.86	37.6	0.52
3	GC/C_{WA}-15 % Pt-Nafion	0.30	2.76	20.0	0.79	7.2	0.51
4	GC/C_{WA}-20 % Pt-Nafion	0.18	1.60	58.9	0.82	37.28	0.51
5	GC/Vulcan XC 72 R-20 % Pt-Nafion	0.25	0.96	40.9	0.75	42.6	0.56

Electrochemical Stability of Pt/C catalysts - Chronoamperometry



Chromoamperometric response of :

(a) GC/C_{WA} - 5 wt.% Pt - Nafion electrode

(b) GC/C_{WA} - 10 wt.% Pt - Nafion electrode

(c) GC/C_{WA} - 15 wt.% Pt - Nafion electrode

(d) GC/C_{WA} - 20 wt.% Pt – Nafion electrode

polarized at + 0.6 V Vs Ag/AgCl

in 0.5 M H_2SO_4/ 1 M MeOH for 3 h

S. No.	Electrode	Activity*		% Decrease in activity after 3 h at + 0.6 V
		Initial (I), $mAcm^{-2}$	Final (I), $mAcm^{-2}$	
1	GC/C_{WA}-5 % Pt-Nafion	25.2	19.1	24
2	GC/C_{WA}-10 % Pt-Nafion	29.7	19.0	36
3	GC/C_{WA}-15 % Pt-Nafion	10.0	0.4	96
4	GC/C_{WA}-20 % Pt-Nafion	36.1	3.7	89

*Stability evaluated in 0.5 M H_2SO_4 and 1 M CH_3OH for 3 h with the electrode being polarized at + 0.6 V Vs Ag/AgCl

PART E
INTERNATIONAL COLLABORATION

Indo- Hungarian Program

- Visits by Hungarian professors and technical officer
- Visit by NCCR faculty and research scholar
- Research in nano gold catalysis on brookite support.

Indo-Australian Program

- This program has just been approved by DST, New Delhi
- The collaborative research involves strategies for conversion of bio-sources into valued chemicals.
- The Australian team (Dr Jorge Beltramini and Dr Akshat Tanksale; ARC Centre for Functional Nanomaterials, The University of Queensland, Brisbane) visited NCCR and held discussions and the project is taking shape for production for platform chemicals from carbohydrates.
- .

Other International collaborations

- A project for the development electrodes and hydrogen storage material has been approved and the development of materials already has been completed and evaluation is going on.
- A MOU has been signed between NCCR and the New Chemistry Research Division, Korea Research Institute of Chemical Technology, for joint collaboration and exchange of research students.
- Catalysis Research Centre, Technical University, Munich and NCCR has signed an MOU for mutual cooperation and also for joint research projects
- A Confidentiality Agreement between Nissan Motor Company and NCCR has been entered for work on dry reforming and other aspects.
- A MOU has been signed between International Centre for Materials, Nanoarchitectures, National Institute of Materials Science (NIMS), Japan for mutual cooperation and collaboration.
- Efforts are being made to have MOU with Prof Sung Hwa Jhung, Department of Chemistry, Kyungpook National University, Daegu 702-701, Korea.

PART F
RESEARCH OUTPUT OF THE CENTRE FOR 2008-2009

Publications & Presentations

- A total of 36 papers have been published by the members of NCCR during this year
- About 10 other papers have been submitted and at various stages of revision and processing.
- The staff and students of NCCR have made over 50 presentations during this year under review

Books & ebooks published by faculty of NCCR

1. **Catalysis some selected Applications(contributed mainly by Prof S.Sivasaner, Prof A V Ramaswamy and B.Viswanathan) (Narosa publishing House) .**
2. **Nano materials (Narosa Publishing House)**
3. **D.K.Chakrabarty and B.Viswanathan, Heterogeneous catalysis, International edition New Age Science Limited Kent TN1 1YS UK November 2008.**
4. Surface characterization techniques (Submitted to Narosa Publishing house and in preparation..

- **e-books ((at the site** http://www.nccr.iitm.ac.in)

1. **Methods of activation and specific applications of carbon materials.**
2. **Pollution control – A chemists Perspective**

PATENTS

- R P Viswanath and B.Viswanathan, water purification system (filed)
- B.Viswanathan and M Helen, Membranes based on Heteropoly acid embedded polymer matrix
- **P.** .Selvam, B. Viswantahan, and K. Suthagar, “Selective formation of 1,3 propane diol from gycerol” Submitted to our Dean IC and SR (To be filled).

PART G
THE CATALYSIS SOCIETY ACTIVITIES

Catalysis Society Activities

- The Catalysis society of India brings out a quarterly bulletin. For the year 2008 this bulletin had four issues with a total of 176 pages. **The Bulletin of the catalysis Society of India is fully available in electronic form.**
- 2. In addition, the catalysis Society conducted its National symposium in NCL, Pune.
- 3. B. Viswanathan is one of the editors for a special issue of Catalysis Today.
- 4. In January 2009, the catalysis society conducted a tutorial on electron spectroscopy techniques in catalysis during the national symposium on catalysis, This has been mentioned already in this report.
- On behalf of the Catalysis society of India on open access Catalysis Data base has been continued to be maintained by NCCR. In this year, the data base has over **1300 full length** articles uploaded. More than30 Ph D theses have also been uploaded. **The server was maintained without any down time during this year.**

PART H

Other Activities

- **(Only a few activities are only listed)**
- **Date Activity**
- **January 16 and 17 -Pre-school on Electron Spectroscopy conducted by P.Selvam and B.Viswanathan with others at NCL.January 18-2119th National Symposium on Catalysis**
- **January 31- IOC hydrogen initiative meeting**
- **Feb 5 to 8 - Visit of Prof N Roesch and also signing of MOU for cooperation with CRC of the Technical University Munchen Prof N Rosch of CRC Technical university , Munich gave a seminar on Hydrogen Activation by Transition Metal Species in Zeolites: A Density Functional Study**
- **Feb 17 -**Prof.Ogura visited the centre and gave a seminar on 'Synthesis of new functional zeolites from mesoporous silica‘
- **March 20 -Demonstration of car by hydrogen fuel at Hyderabad**
- **April 11-NCCR Anna university RS meet**
- **April 29-Prof selvam submitted the indo Chinese research programme**
- **May 15-Seminar by Dr Raghuram Chetty on Flexible fuel cells.**

PART I

Strengthening the collaboration with the Department of Chemistry, Anna University

- **NCCR conducted two Joint research scholars meet in august 2008 and April 2009. Third one is planned for August 2009.**
- **M SC (course of Anna University) one full course was conducted by Prof S Sivasanker during the odd semester of 2008.**
- **M Phil/Ph D course was conducted by NCCR partially during the odd semester of 2008.**
- **Ph D guidance is being strengthened. NCCR has been guiding some (5) students jointly with Anna University**
- **NCCR has provided laboratory and other facilities for work by Anna University students in NCCR (two of them are working at NCCR at present)**
- **Visits by scientists from other countries are mutually coordinated.**

Thank you all