June 2022

CSI Communication

Monthly Newsletter of Catalysis Society of India

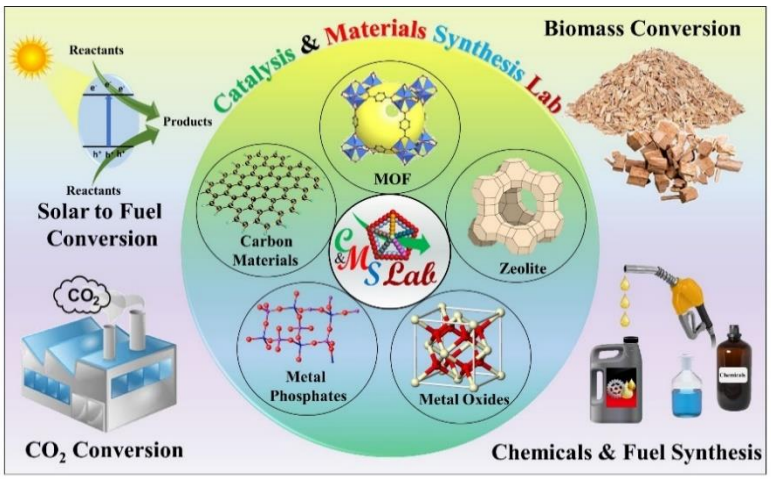
Circulated to all CSI Members

Important Announcement:

CSI newsletter shall be pleased to publish half a page write-up under the title, Centre of Excellence in Catalysis Research in India from any Indian Academics, Research laboratories or Industrial organizations. You may send your brief write-up on your research activities to us which will be published in coming issues of CSI.
You can also share your recent happy moments like publications, granted patents, technology commercialization, fellowship, awards, etc. to highlight in the CSI communication.

Prof. Rajendra Srivastava's Group Research Activities @ Indian Institute of Technology Ropar

Prof. Rajendra Srivastava's research group at the Indian Institute of Technology Ropar is involved in the development of "sustainable" chemical transformation processes that will benefit society in general and, the transportation fuels/chemicals industries/energy sector and develop the corresponding heterogeneous catalytic materials that will accomplish these transformations *without* causing any environmental degradations. His research group develops a wide range of nanoporous materials to produce chemicals/fuels involving all forms of energy sources, thermal energy, solar energy, and electrical energy (Scheme 1). A brief description of some of his research accomplishments is given below.



Scheme 1. Summary of the research work done at CMS lab at IIT Ropar.

1. Development of Mesoporous Zeolites for 21st century

Only selected groups have developed synthesis strategies for the preparation of mesoporous zeolites required for the 21st-century petrochemical/fine-chemical industry. (A) The development

of unique structure-directing agents (SDAs) for the preparation of mesoporous zeolite Beta in just 36-48 h with large surface area and pore volume. In general, conventional zeolite Beta synthesis requires 15 days and zeolite seeds. (B) Mesoporous zeolites are disordered materials. It was a challenge to achieve the order in both length scales (micropore and mesopore) in the mesoporous zeolite. Zeolite ZSM-5 nanosheets were synthesized using specially designed multi-quaternary ammonium surfactants-based SDAs. (C) It was extremely difficult to develop a synthesis strategy for the preparation of mesoporous zeolites of different framework structures using one SDA. A one-step, direct synthesis strategy was developed for the synthesis of mesoporous ZSM-5, MOR, and SOD zeolite nanocrystals using only one SDA under different synthesis conditions. (D) Recently a challenging micro-meso-macroporous tri-level porous ZSM-5 zeolites were synthesized using starch. This work was published and featured on the cover page of the journal ACS Sustainable Chemistry and Engineering. The work was granted Indian Patent in September 2021. Many manuscripts have been published in zeolite synthesis during the past ten years, namely ACS Catalysis, ACS Sustainable Chemistry and Engineering, Catalysis Science and Technology, Chemistry-A European Journal, etc.

2. Biomass Conversion to Renewable Chemicals & Fuel

His group is developing heterogeneous catalysts for cellulose, hemicellulose, and lignin-derived platform chemicals transformations to chemicals and fuels via catalytic oxidation, catalytic reduction, and acid-base catalysis. Fe-Zn double metal cyanide was developed for biodiesel production. His initial fundamental contribution towards catalyst design was later translated into technology for biodiesel production from inedible oils by National Chemical Laboratory, India, and commercialized in the USA. Many manuscripts have been published by his group in the past three years, namely, Green Chemistry, ACS Sustainable Chemistry, and Engg., Journal of Catalysis, etc.

3. Contribution in Photocatalysis

Catalysts were developed for efficient oxidation, cascade reaction, and photoelectrochemical O_2 evolution. Success has been achieved in the visible light-assisted production of H_2O_2 and photocatalytic splitting of water to produce H_2. Success also has been achieved in the photocatalytic reduction of CO_2. Many manuscripts have been published by our group in the past three years, namely, Materials Horizon, Applied Catalysis B, ChemCatChem, ACS Applied Nano Materials, etc

4. Contribution in the Energy Sector

Spinels and CeO_2 decorated mesoporous zeolite were developed for the electrochemical oxidation of methanol for direct methanol fuel cells. Moreover, the usefulness of spinels was explored for the supercapacitor application. Transition metal doped CoMo sulphide catalyst was developed for oxygen and hydrogen evolution reactions. MoS_2 wrapped $MnCO_3$ on graphite paper was designed for electrochemical energy storage application. Many manuscripts have been published by our group in the past three years, namely, ACS Catalysis, ACS Sustainable Chemistry, and Engg, Chemical Engineering Journal, Journal of Physical Chemistry C, ChemElectroChem, etc.

5. Activation & Utilization of CO_2

Eco-friendly catalysts based on silica, zeolites, and MOF materials were developed for the effective utilization of CO_2 in chemical syntheses such as cyclic carbonates, carbamates, and quinazoline-2,4(1H,3H)-dione, and results were published in many reputed journals and USA patents.

6. Unique Catalysts based on MOF COF

His group developed a strategy to prepare mesopore MOF. Later they developed methods to prepare transition metal MOF-derived materials that exhibited unique activity like Pd and noble metals. MOF-COF-derived single metal atoms and metal nanoclusters-based carbon materials were prepared for unique catalysis involving sustainable H_2 and CO sources. The work was published by our group in the past three years, namely, ACS Sustainable Chemistry and Engg, ChemCatChem, ACS Applied Nano Materials, etc.

In conclusion, his group research contributes to the development of new heterogeneous/homogenous catalytic materials for sustainable catalytic processes and energy applications. **His group published 160 research articles in international journals (6 cover page articles) and granted 9 patents**. At present, he is actively involved in executing industrial projects based on zeolites and MOFs.

Group photographs of Prof. Rajendra Srivastava's Catalysis and Materials Synthesis Lab

Professor Rajendra Srivastava is currently working as a Professor at IIT Ropar. He acquired his Ph.D. degree from CSIR-National Chemical Laboratory, Pune, India, where his doctoral work won him the Best Thesis Award of 2006, conferred by the Catalysis Society of India. He is a recipient of JSPS fellowship, Japan. He received the NASI-SCOPUS Young Scientist Award 2017, The Catalysis Society of India Young Scientist Award 2018, and a Midcareer Faculty Research and Innovation Award 2019 by IIT Ropar. His name has been included in the top 2% scientists of the world (5th rank in India and 242 ranks in the world in Physical Chemistry domain) and amongst the top 200 leading Chemistry Scientists of India.

Source: Prof. Rajendra Srivastava, Catalysis and Materials Synthesis Lab, Indian Institute of Technology, Ropar, India

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Commercial & Policies

- **GAIL to set up one of India's largest PEM based Green Hydrogen project**

GAIL (India) Limited is to set up one of the largest Proton Exchange Membrane (PEM) Electrolyser in India. The project would be installed at GAIL's Vijaipur Complex, in Guna District of Madhya Pradesh, and would be based on renewable power. The Project has been designed to produce around 4.3 Metric Tons of Hydrogen per day (approx. 10 MW capacity) with a purity of about 99.999 Volume %. It is scheduled to be commissioned by November 2023.
Source: https://www.pib.gov.in/PressReleasePage.aspx?PRID=1824727

- **National Metallurgical Lab collaborates with Pune-based Recy Energy for recycling of used Lithium-Ion batteries**

CSIR-National Metallurgical Laboratory (NML) entered into an agreement with Recy Energy Pvt Ltd of Pune to transfer a breakthrough technology for the recycling of scrap, waste, and used Lithium-Ion Batteries (LIB). India generates over 50,000 tonnes of Lithium battery waste every year, which is expected to increase three-fold by 2025.
Source: https://avenuemail.in/jamshedpur-csir-nml-mou-with-recy-energy-pvt-ltd-for-recycling-scrap-used-lib/

- **Clariant and Lummus Awarded Contract for One of the World's Largest PDH Units**

Clariant and its process partner Lummus was awarded a major contract by Fujian Meide to supply CATOFIN technology and catalysts for a new, world-scale propane dehydrogenation (PDH) unit in Fuzhou, China. Already operating one PDH unit at its Fuzhou petrochemical complex, Fujian Meide is now building one of the largest PDH units in the world and has selected the CATOFIN process and catalysts for the project's second phase. The new unit will produce 900,000 metric tons of propylene annually and is scheduled to commence operation in 2023.
Source: Clariant, 5/25/2022.

- **Evonik Catalysts opens its First Zero Liquid Discharge Plant in India**

Evonik Catalysts opened a new Zero Liquid Discharge (ZLD) plant at its facility in Dombivli, India. The new plant reduces the amount of fresh water required for production processes and turns material that was previously considered waste into saleable products. ZLD purifies and recycles wastewater at the end of an industrial process, leaving little to no effluent remaining when it is completed. The main ambition with the Dombivli ZLD plant is to improve the treatment of process water. In addition, processing leads to the production of 15-20 metric tons of sodium sulphate and certain mixed salts which can be resold as a commercial product. Source: Evonik, 5/26/2022.

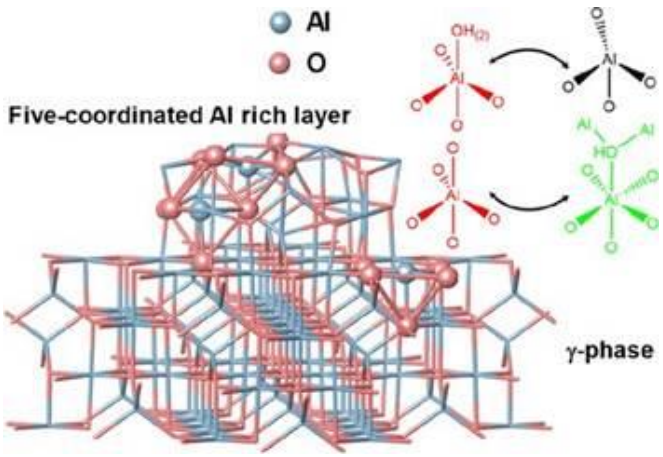
- **IIT Kanpur, MIT Secure Joint Patent for a Water Purification Device**

IIT Kanpur (IIT-K) and MIT USA have jointly secured an Indian patent for a water purification device. The invention titled "A Vessel and A Method for Purifying Water and Monitoring Quality of Water" is expected to be quite a cost-effective apparatus to check water quality.

The purification vessel contains a regenerable sorbent material capable of binding the impurities and preserving it in a moist or dry format, thus producing inorganic contaminant-free water at a cost as low as ₹2 per liter.
Source: https://www.techcircle.in/2022/05/06/iit-kanpur-mit-secure-joint-patent-for-a-water-purification-device

Scientific Updates

- **Nature of Five-coordinated Aluminum on γ-Al_2O_3 Surface**

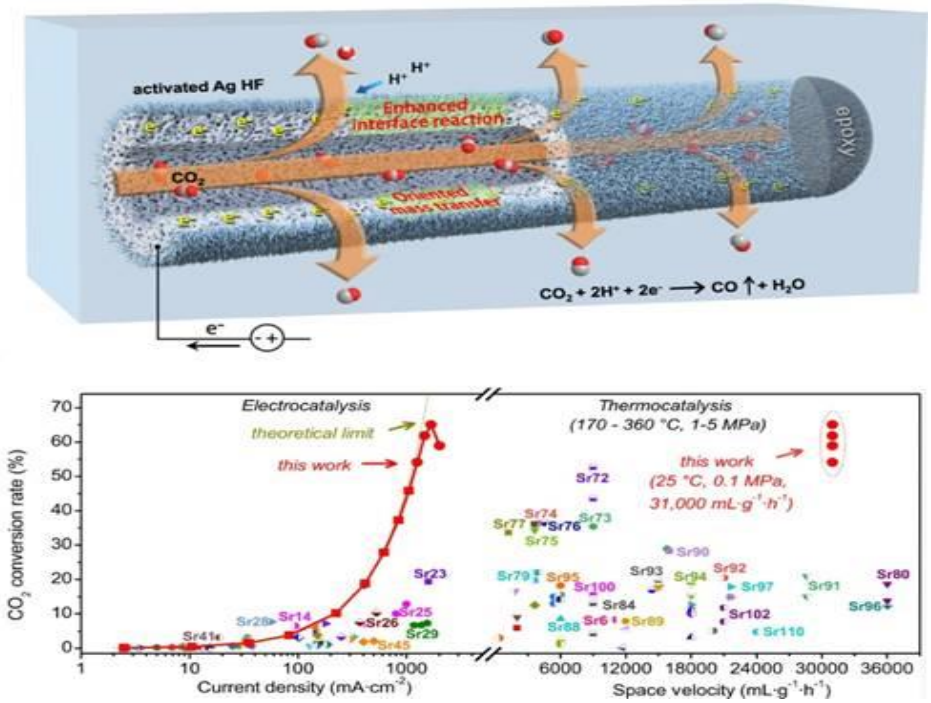


γ-Al_2O_3, an important catalyst and catalyst support, is widely used in various industrial applications. The five-coordinated aluminum, or Al(V), on the surface of γ-Al_2O_3 can affect the catalytic performances of γ-Al_2O_3.
The researchers investigated the structural properties of commercial γ-Al_2O_3 and amorphous alumina nanosheets (Al_2O_3-NS) rich in Al(V) by ultrahigh-field multinuclear and multi-dimensional Magic Angle Spinning (MAS) NMR. They analyzed the aluminum species in both aluminas and found the flexible structural features on the surface of Al_2O_3-NS. They demonstrated the hydroxyl groups on the surface of γ-Al_2O_3 with close spatial proximity that were able to be removed under high-temperature dehydration, resulting in surface structure reconstruction. Moreover, by using ultrahigh-field ^{27}Al-^{27}Al double-quantum NMR, the researchers for the first time revealed that most Al(V) species tended to aggregate into Al(V) domains on the surface of γ-Al_2O_3 like Al_2O_3-NS, rather than tetragonal pyramid coordination on (100) surface previously predicted from theoretical models. Source: phys.org, 6/1/2022.

- **Novel Silver Hollow Fiber Boosts CO_2 Electroreduction**

A research team led by Profs. Wei Wei and Chen Wei have reported a hierarchical micro/nanostructured silver hollow-fiber electrode to boost CO_2 electroreduction. The electrode reduces CO_2 to CO with CO_2 conversions exceeding 54% at a high space velocity of 31,000 mL $gcat^{-1}{\cdot}h^{-1}$ under ambient conditions, maintaining stable large current densities (~1.26 $A{\cdot}cm^{-2}$) and high CO faradaic efficiencies (~93%).
The electrochemical conversion of CO_2 into carbon-based fuels and valuable feedstocks by renewable electricity is an attractive strategy for CO_2 abatement and renewable energy consumption that can help achieve the goal of carbon neutrality. CO_2 electroreduction to CO is considered one of the most promising means of obtaining cost-competitive products.

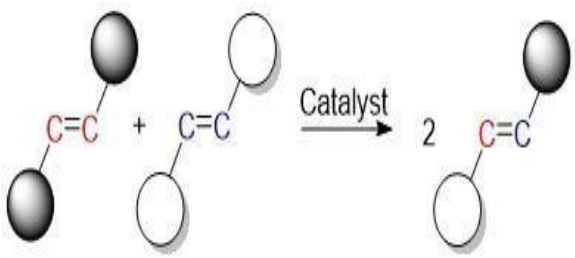
However, highly efficient CO_2 conversion with high space velocity under mild conditions remains a challenge.



Schematic illustration of hollow fiber electrode for boosting CO_2 reduction to CO. Credit: SARI

Source: phys.org, 6/6/2022.

- **New Research Shows Iron Catalyst to Make Chemical Reactions Cheaper and Sustainable**



The olefin metathesis reaction produces new carbon-carbon double bonds by breaking the original double bonds and regenerating new ones. Image Credit: Okinawa Institute of Science and Technology Graduate University.

The olefin metathesis reaction produces new carbon-carbon double bonds by breaking the original double bonds and regenerating new ones. Researchers have now developed a catalyst made of iron, a much more abundant element, to speed up an important chemical reaction known as olefin metathesis. The olefin metathesis reaction is among the most widely applicable catalytic reactions for carbon-carbon double bond formation. By switching the carbon atoms in olefins, the olefin metathesis reaction creates new carbon-carbon double bonds. By disrupting the initial double bonds and forcing new ones to form, the catalyst enables this swapping. The valuable metal ruthenium is currently one of the most preferred catalysts for this reaction. The researchers created a novel iron complex and showed that it could be utilized as a catalyst in the olefin metathesis

reaction in this work. They demonstrated it by making a polymer, which is a long-chain molecule made up of many smaller chemical units. Source: AZO Materials, 6/6/2022.

- **New Light-powered Catalysts Could Aid in Manufacturing**

MIT chemists have designed a new type of photoredox catalyst, which can absorb light and transfer the energy to a chemical reaction, that could make it easier to incorporate light-driven reactions into manufacturing processes. Unlike most existing photoredox catalysts, the new class of materials is insoluble, so it can be used repeatedly. Such catalysts could be used to coat tubing and perform chemical transformations on reactants as they flow through the tube.

To combine the benefits of heterogeneous and homogeneous catalysts, the researchers decided to embed the dyes that make up homogeneous catalysts into a solid polymer. For this application, the researchers adapted a plastic-like polymer with tiny pores that they had previously developed for performing gas separations. In this study, the researchers demonstrated that they could incorporate about a dozen different homogeneous catalysts into their new hybrid material, but they believe it could work with many more. Source: MIT, 5/27/2022.

- **Catalyst Technology for Mobile Use of Liquid Hydrogen Storage Systems**

LOHC technology has been researched well for several years. However, there have not yet been any so-called 'hydrogen releasers' that could perform the process efficiently for mobile applications. The joint research team from Fraunhofer HHI and HI ERN has now developed an apparatus that elevates the hydrogen release process to a reproducible and scalable level. Additionally, a significant increase in power density is achieved compared to conventional hydrogen releasers. The core of the apparatus is a so-called surface catalyst. Catalysts need as much surface area as possible to release hydrogen efficiently. Previous processes work with porous pellets for this purpose. Unfortunately, these pellet catalysts wear off quickly in mobile applications because the mechanical stability of the pellets is not high enough. Source: ChemEurope, 6/7/2022.

- **Heterogeneous Ethylene Hydroformylation Enables Highly Efficient Industrial Production of Propanal/n-propanol**

A research team led by Prof. Ding Yunjie and Prof. Yan Li has realized the highly efficient industrial production of propanal/n-propanol via heterogeneous ethylene hydroformylation.

Based on heterogeneous ethylene hydroformylation technology, the facility with propanal/n-propanol yield of 50 kt/year was put into operation in August 2020 in Ningbo, China. So far, it has been in stable operation for 22 months. The heterogeneous hydroformylation technology adopts porous organic polymers with large specific surface area and hierarchical porous structure as both carrier and ligand. It metalates rhodium ions to form single-Rh-sites catalyst with good performance and high stability using multiple Rh-P coordination bonds. The reaction system is solvent-free, and the products have high purity. Moreover, a large amount of low-grade reaction heat can be efficiently used in the hydroformylation and hydrogenation reaction," phys.org, 5/16/2022.

Catalysis Research out of India

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2. Sandip K. Singh, Paresh L. Dhepe, "Alpha-, Beta- and Gamma-Cellulose Quantification and Two-Stage Concentrated-Dilute Acid Lignin Recovery from Three Rice Husks: Lignin Characterization and Depolymerization", **Waste and Biomass Valorization,** 2022, DOI: https://doi.org/10.1007/s12649-022-01704-1.
3. S Kondawar, C Rode, "Ionic liquids for the sustainable transformation of levulinic acid to gamma-valerolactone (GVL)" **Current Opinion in Green and Sustainable Chemistry**, 2022, 100607
4. RD Parate, MS Dharne, CV Rode, "Integrated chemo, and bio-catalyzed synthesis of 2, 5-furandicarboxylic acid from fructose derived 5-hydroxymethylfurfural", **Biomass and Bioenergy,** 2022, 161, 106474
5. NS Date, CV Rode, KW Huang, AM Hengne, "Role of noble metal catalysts for transformation of bio-based platform molecules" **Biomass, Biofuels, Biochemicals**, 2022, 641-672
6. Izabela S Pieta, Barbara Gieroba, Grzegorz Kalisz, Piotr Pieta, Robert Nowakowski, Mu Naushad, Anuj Rathi, Manoj B Gawande, Anna Sroka-Bartnicka, Radek Zboril, "Developing Benign Ni/g-C3N4 Catalysts for CO_2 Hydrogenation: Activity and Toxicity Study", **Industrial & Engineering Chemistry Research, 2022, https://doi.org/10.1021/acs.iecr.2c00452**
7. Xinzhu Pang, Varaha P Sarvothaman, Nathan Skillen, Zhe Wang, David W Rooney, Vivek V Ranade, Peter KJ Robertson, "Kinetic modelling of the photocatalytic degradation of Diisobutyl phthalate and coupling with acoustic cavitation", **Chemical Engineering Journal,** 2022, ,444,136494
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9. Umesh Gaikwad, G.D. Yadav, "Synergism of Novel Mesoporous Solid Acid Catalyst and Microwave Irradiation in Claisen-Schmidt Condensation of Benzaldehyde with Acetophenone

to Chalcone," **Catalysis in Green Chemistry and Engineering,** 2022, DOI: 10.1615/CatalGreenChemEng.2022039079

Upcoming Symposium/ Conferences/Seminars

1. June 19-24, 2022-Gordon Research Conference-Catalysis, Colby-Sawyer College, New London, United States.
2. June 28 to July 01, 2022- 22nd Tetrahedron Symposium - Catalysis for a Sustainable World, Lisbon, Portugal
   https://www.thescientistt.com/nanotechnology-nanomaterials/2022/speakers.php
3. The 12th International Conference on Environmental Catalysis (ICEC2022) will be held during July 30-August 2, 2022, in Osaka, Japan.
4. International Online Conference on Nano Material [ICN 2022] 12-14 August 2022 Mahatma Gandhi University, Kottayam, Kerala, India.
5. June 15-16, 2022-Chemical Recycling – 2022- Exploring the potential of chemical or advanced recycling to turn waste plastics into new materials, Cologne, Germany

Editorial Team

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Quote of the Month

"Each work has to pass through three stages: Ridicule, Opposition, and then Acceptance".
— Swami Vivekanand