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CSI Communication

Monthly Newsletter of Catalysis Society of India

Circulated to all CSI Members

Important Announcement:

Wishing all Catalysis Society of India Members, A Very Happy & Colorful Holi!!!

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.

- **Development of Catalytic and Adsorptive Systems for CO_2 Capture and Utilization @CSIR-CSMCRI, Bhavnagar**

Emissions from fossil fuel use and deforestation are the main contributor to the increased atmospheric CO_2 levels. This large quantities of CO_2 in the atmosphere are also obtained as a by-product from industrial processes such as steam reforming, ammonia synthesis, oil- and gas industry and fermentation. Particularly, the ever-increasing emission of CO_2 in the earth's atmosphere (>415 ppm) and its associated problems urges global control measures. In view of these concerns, efforts have been made to reduce the atmospheric CO_2 level through approaches such as shift to non-fossil energy sources, CCS (carbon capture and storage) and CCU (carbon capture and utilization), valorization of CO_2 has attracted among the researchers. With this understanding the national research laboratory CSIR-CSMCRI, Bhavnagar under CSIR is working intensively in various diverse catalytic process for the CO_2 product and its capture through porous materials in last two decade. Various methodologies have been developed for converting CO_2 into useful chemicals such as methanol, methane, dimethyl ether, formic acid, urea, methanol, formamidine derivatives, benzimidazole derivatives, cyclic carbonates and polycarbonates as well as various niche pharmaceutical products. Three key processes are being currently explored: (i) **Cyclic carbonates (ii) Formic acid** (iii) **Methanol,** in addition hydroformylation reactions in the Division. The activities carried out in the catalysis division are categorized (i) CO_2 Utilization, (ii) CO_2 Capture through Porous Materials**.**

(i) CO_2 Utilization

CSIR CSMCRI has developed diverse catalytic systems for the chemical fixation of CO_2 with epoxide to cyclic carbonates. A Co-MOF, synthesized via simple method showed catalytic efficiency to convert mono-substituted epoxides to cyclic carbonate with high yields (>90%) under solvent-free conditions using 1 atm CO_2 [Patel et al, Appl. Cat. A, General, 2020]. A double-stranded Co-helicates, has been demonstrated as catalyst with good substrate scope covering terminal and, non-terminal epoxides and diols into their cyclic carbonates with excellent conversions and selectivities of TOF of 15,934h^{-1}/molecule[P.S.Subramanian & Coworkers, ACS Omega, 2020]. A heterogeneous catalyst was also developed by grafting a quaternary ammonium salts on a highly porous hydrocarbon framework recyclable with high conversion of epoxide without the use of any external additives or co-catalysts [Saravanan S, Catalysis Today, 2020]. Synthesis of new class of spiro-cyclic carbonates has been demonstrated recently [Kureshy & Coworkers, ACS Sustainable Chem. Eng. 2018]. Understanding the importance of fatty carbonates in oleochemical applications, a process for the direct oxidative carboxylation of fatty acid derivatives to corresponding cyclic carbonates with good conversions (WO2016006003A1.pdf) has been developed.

(ii) CO_2 Capture through Porous Materials

(a) Zeolites and Zeolite Based Membranes for CO_2 Capture from Flue gas and Bio-gas Mixture

CO_2 capture is a global concern, among the greenhouse gases, CO_2 contributes more than 60% to global warming. In the past, CSMCRI has developed different adsorbents for CO2 capture from flue gas mixture. Size and shape-selective Zeolite-A (R.V. Jasra and Coworkers WO2010052736A1), cation exchanged Zeolite ZSM-5 (WO/2010/113169), and KBa modified Zeolite-X (WO2010113173A2), for CO2 and N2 separation were undertaken significantly using different materials like Zeolite, Clay, MOF, and Carbon-based materials as witnessed in various publications by Govind et al, Applied Clay Science(2014), Bajaj & Coworkers Chem Engineering Journal (2012), Bajaj & Coworkers Environmental Progress and Sustainable Energy (2017), S Y Sawant et al separation Science and Technology (2014) were reported. Recently, a series of porous polymers with high CO_2 capacity and CO_2/N_2 selectivity with a surface area of up to 500-900 m^2/g were also developed. The modified zeolite in the mixed matrix membrane showing excellent separation performance, the associated experiments with a real flue gas mixture are in progress.

(b) MOF & COFs

Metal–organic frameworks (MOFs) are highly promising candidates for selective adsorption and catalytic fixation of CO_2. A chemically robust Ni(II)-framework (CSMCRI-3) from nitrogen-rich organic struts, extremely selective CO_2 adsorption over N_2 (292.5) and CH_4 (11.7). Prolonged water vapour exposure do not affect the surface area and/or multicyclic CO_2 uptake-release

(Neogi & Coworkers *ACS Appl. Mater. Interfaces*, **2019**). With an aim to demonstrate CO_2 capture in humid condition, pillar-layer Zn(II) MOFs with varying linkers were constructed that displayed excellent CO_2/N_2 selectivity (>200) for larger pores (Neogi & Coworkers *ACS Sustainable Chem. Eng.*, **2017**). However, low pore aperture divulged minimum loss in CO_2 capture cycles upon extended water vapour exposure (Neogi & Coworkers *ACS Sustainable Chem. Eng.*, **2018**). A comparative study on N-functionalization actuated large improvement of CO_2 adsorption was demonstrated between a pair of isostructural diamondoid MOFs, where host-guest interactions are also validated (Neogi & Coworkers *J. Mater. Chem. C*, **2021**) and COF via solvent-assisted structural alteration (Neogi & Coworkers *ACS Appl. Mater. Interfaces*, **2020**). Effect of acid–base pairs for solvent-free CO_2 cycloaddition was studied in micro–mesoporous MOF, NH_2-MIL-101(Al) that yielded styrene carbonates with 99% conversion and selectivity (Neogi & Coworkers, *Dalton Transactions*, **2018**). Also, encapsulation of highly active and ultrasmall-sized Ni nanoparticles inside a robust metal–organic framework (MOF) results solvent-free and recyclable CO_2 cycloaddition in 98% yield and 99% selectivity under relatively mild conditions (Neogi & Coworkers, *Inorg. Chem.*, **2019**). Tandem cyclic carbonate synthesis is rarely accomplished in heterogeneous catalysis, yet highly demanding owing to its advantages like reduction in chemical usage, shortening of energy consumption and reaction time. Building on the presence of redox-active secondary building units (SBUs), oxidative tandem carboxylation of styrene and CO_2 is realized in acid-base stable, mixed-ligand Co(II)-MOF (CSMCRI-10) under mild condition (Neogi & Coworkers, *Chemical Engineering Journal*, **2022**).

In conclusion, this division with its strenuous efforts, able to provide know-hows for the process of making various adsorbents for gas separation and CO_2 based products such as cyclic carbonates, formic acid, in-addition to various catalytic fine and specialty products.

Source: Lakhya J. Konwar, Saravanan Subramanian, Govind Sethia, Ankush V. Biradar, Subhadip Neogi, P.S. Subramanian and Kannan Srinivasan, Inorganic Materials and Catalysis Division, CSIR-Central Salt and Marine Chemicals Research Institute, Bhavnagar – 364 002, Gujarat, India. ***Contact***: *E-mail: director@csmcri.res.in ;* Ph. No.+091-278-2569496

Commercial & Policies

- **Honeywell Announces New Technology for Green Hydrogen Production**

Honeywell announced that it has developed new catalyst-coated membrane (CCMs) technology for Green Hydrogen production and will further test the technology with electrolyzer manufacturers. The new Honeywell technology focuses on CCMs for Proton Exchange Membrane (PEM) electrolyzers and Anion Exchange Membrane (AEM) electrolyzers. Honeywell's latest CCMs have been shown in lab testing to enable higher electrolyzer efficiency and higher electric current density enabled by a breakthrough proprietary high ionic conductivity membrane and high activity catalyst. This is projected to provide a 25% reduction in electrolyzer stack cost. Source: Honeywell UOP, 3/2/2022.

- **Reliance seeking to be world's largest blue hydrogen maker**

Reliance will repurpose a $4 billion plant that converts petroleum coke into synthesis gas to produce blue hydrogen for between $1.2 and $1.5 a kilogram. Blue hydrogen is made using fossil fuels but captures the carbon dioxide formed during production, and Reliance regards the conversion as a temporary measure until the cost of green hydrogen, produced from the electrolysis of water using renewable energy, becomes competitive. "Subsequently, as hydrogen from syngas is replaced by green hydrogen, the entire syngas will be converted to chemicals." RIL Chairman has vowed to produce green hydrogen at $1 a kilo, a more than 60 per cent reduction from today's costs, by the turn of the decade.
Source: https://www.thenationalnews.com/business/energy/2022/02/13/indias-reliance-aims-to-be-worlds-top-blue-hydrogen-producer/

- **BPCL launches EV fast-charging corridor in South India**

India's leading oil marketing company Bharat Petroleum Corporation Ltd. (BPCL) has launched an electric-vehicle fast-charging corridor along the Chennai-Trichy-Madurai highway, deploying charging infrastructure at ten of its petrol pumps. The company has set up new charging stations along the 900-kilometre route. BPCL is developing a roadmap of sustainable solutions as the company looks to become a net-zero energy company by 2040. In 2021, the firm declared that it has a network of about 90,000 petrol pumps in the country and will deploy EV charging points on all of them soon.

Source: https://www.saurenergy.com/ev-storage/bharat-petroleum-unveils-ev-fast-charging-corridor

- **L&T and Norway's HydrogenPro to Set up Electrolyzer Gigafab in India**

Larsen & Toubro (L&T), Indian multinational EPC solutions major, is venturing into electrolyzer production in India in partnership with HydrogenPro AS, a Norway-based alkaline electrolyzer specialist that aims for the green hydrogen production cost of US$ 1.2 per kg in 2022. Under this agreement, L&T and HydrogenPro will set up a joint venture in India for gigawatt-scale manufacturing of alkaline water electrolyzers based on HydrogenPro technology.
Source: https://www.pv-magazine-india.com/2022/01/27/lt-and-norways-hydrogenpro-to-set-up-electrolyzer-gigafab-in-india/

- **Slurry Alkylation Unit using solid catalyst without noble metal**

Alvega LLC, a subsidiary of Alvega Technologies Inc., completed the basic design of the world's first 3,500 bpd slurry alkylation unit. In November 2021, the company started developing a basic design engineering package for a 3,500-bpd alkylation unit based on a slurry reactor technology. The company has developed a solid catalyst without noble metals that allows processing any C2-C4 olefin feedstocks, and 100% isobutylene (which is important in connection with the rejection of MTBE) into a high-octane alkylate with RON up to 100. Estimated CAPEX will be approximately

1.5-3 times lower than existing processes on the market (acids, solids, ionic liquids). Source: Hydrocarbon Processing, 2/15/2022.

- **BASF and Heraeus form a joint venture to recover precious metals from spent automotive catalysts.**
  The new company is called BASF HERAEUS (China) Metal Resource Co., Ltd., is 50 % owned by both companies, and will be in Pinghu, China. The legal entity is scheduled to be established in the first quarter of 2022, following approval by the relevant authorities. Construction is scheduled to start in 2022 and operation in 2023.
  Source: BASF SE, Ludwigshafen, Germany

Scientific Updates

- **Electrocatalyst system to produce Energy-efficient Hydrogen from Urea**

Indian Scientists have designed an electrocatalyst system for energy-efficient hydrogen production with the help of electrolysis of urea. The urea electrolysis is helpful towards urea-based waste treatment with low-cost hydrogen production. The scientists have explored electrocatalysts and shown that surface defective NiO and Ni_2O_3 systems having more Ni^{3+} ions are more efficient electrocatalysts than conventional NiO. They have used high-energy electron beams to produce surface defective unsaturated Ni sites in NiO (e-NiO). Their study reveals that e-NiO prefers direct mechanism of urea electro-oxidation due to strong adsorption of urea molecule, whereas NiO favors indirect mechanism with low activity. Source: Energy Asia, 3/9/2022.

- **Customizing Alloy Catalysts for Hydrogenation**

The ethylene starting material typically contains trace amounts of acetylene, which must be removed because it can poison polymerization catalysts. Polymer suppliers generally remove the impurity using palladium catalysts to selectively convert acetylene to ethylene. But palladium’s high activity means the catalyst can over hydrogenate acetylene, forming unwanted ethane and generating dangerous levels of heat. To help tackle the problem, solid-state synthesis methods to precisely tailor the alloys, forming zinc-based metals with various types of catalytically active sites isolated palladium atoms, palladium trimers, and trimers in which two palladium atoms were bridged by a third metal. Catalysis tests and quantum calculations showed that small changes in the Pd–Zn ratio led to enormous differences four orders of magnitude in hydrogenation activity driven by the presence of overly active palladium trimers in some of the alloys. The study also showed that the high activity could be maintained but controlled by breaking up palladium trimers with an atom of copper or gold, providing clues for designing industrial catalysts. Source: Chemical & Engineering News (C&EN), 2/27/2022.

- **Scientists Develop Catalytic Hydrocracking for Mixed Plastics to BTX**

A Johns Hopkins University team has developed a catalytic hydrocracking process that converts mixed plastics into the chemicals benzene, toluene, and xylene (BTX). CUPTech's catalytic hydrocracking process is carried out at pressures just above ambient and temperatures in the range of 700 to 1,000 degrees Fahrenheit. The output is a mix of the aromatic hydrocarbons benzene, toluene, and xylene (BTX), which could use in existing processes petrochemicals complexes. The CUPTech process is currently in the laboratory and will take time to scale up and demonstrate at a commercial scale. Lab-scale testing should be completed in the next few months and engineering of a pilot-scale system has already begun and is hoped to kick off a commercial demonstration project in 2023. Source: Plastics Recycling Update, 2/16/2022

- **Converting Methane Directly into Useful Chemicals**

A research team led by Cardiff University, UK, has demonstrated for the first time that methane can be directly converted into methanol and acetic acid using a gold catalyst. The catalyst was made from gold and supported on ZSM-5, and the team reacted methane with oxygen in the presence of the catalyst. The researchers expected the production of methanol using this catalyst but had not expected acetic acid to be produced. Upon inspection of the catalyst with electron microscopy, they found that the catalyst contained gold nanoparticles, which exhibit different properties to gold atoms or clusters that are typically found in gold catalysts. The new catalyst doesn't require the presence of a co-reductant, has a high selectivity to oxygenated products, and has low CO_2 production. Source: The Chemical Engineer, 2/23/2022.

- **Double-shelled Hollow Spheres for Use as Tandem Catalysts**

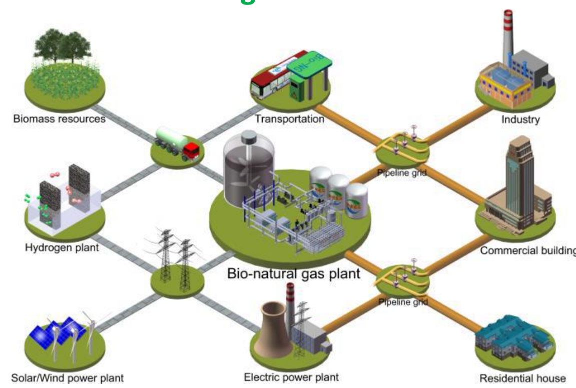
The double-shelled hollow spheres were created by starting with a ball-shaped carbon structure containing metallic ions, it served as the inner layer of the final sphere. The researchers then covered the ball with zeolite nanocrystals and then finished by applying a layer of calcinate. They noted that the thickness of the calcinate layer could be modified, allowing for different types of reactions. The resulting double shelled sphere could then be used as a tandem catalyst. A Fischer-Tropsch process by using a batch of their spheres to convert syngas (carbon monoxide mixed with hydrogen) into a waxy hydrocarbon and then to convert the hydrocarbon into a liquid fuel. The double-shelled approach works because it allows one layer of the sphere to interact with a chemical while the other layer interacts with another chemical. The researchers note that the process allows for producing a branched-type gasoline, which prevents knocking in engines. The researchers tested their spheres against several other more conventional catalysts and found that their double-shelled approach outperformed all of them. Source: Phys.Org, 2/16/2022.

- **Uses of CO_2 to Convert Propane into Propylene**

A Hokkaido University research group has developed a catalyst for the oxidative dehydrogenation (ODH) of propane that uses CO_2 to convert propane into propylene. Platinum activates propane and cobalt acts as an oxidant that activates the otherwise inefficient CO_2. At the same time, indium suppresses secondary reactions that produce non-propylene materials. Furthermore, cerium oxide fires the carbon to induce it to cover the surface of the catalyst, shortens its life, and remove it. With Hokkaido University's catalyst, catalytic activity is five times more intense than usual and sustains propylene selectivity for 20 hours. The team verified a reaction temperature of 550–600 degrees Celsius. Now development toward commercial viability is under way. In addition to propane, the catalyst holds promise for applications with lower alkanes like ethane and isobutane. Source: Japan Chemical Daily, 3/7/2022.

- **Catalytic Production of low-carbon footprint sustainable Natural gas**

A catalyst with Ni_2Al_3 alloy phase enables nearly complete conversion of various agricultural and forestry residues, the total carbon yield of gas products reaches up to 93% after several hours at relative low temperature (300^{0}C). catalyst shows powerful processing capability to produce natural gas during thirty cycles. A low-carbon footprint is estimated by a preliminary life cycle assessment, especially for the low hydrogen pressure and non-fossil hydrogen, and technical economic analysis predicts that this process is an economically competitive production process.



Source: Nature Communications 2022, Volume 13, https://doi.org/10.1038/s41467-021-27919-9

Catalysis Research out of India

1. Subramanian Thiyagarajan, Raman Vijaya Sankar, Puthannur K. Anjalikrishna, Cherumuttathu H. Suresh, and Chidambaram Gunanathan, "Catalytic Formal Conjugate Addition: Direct Synthesis of δ-Hydroxynitriles from Nitriles and Allylic Alcohols" **ACS Catal.** 2022, 12, 2191−2204
2. Nitin B Mhamane, Sibo Chetry, Ravi Ranjan, Thirumalaiswamy Raja, Chinnakonda S Gopinath, "Sustainable CO_2 Reduction on In_2O_3 with Exclusive CO Selectivity: Catalysis and In Situ Valence Band Photoelectron Spectral Investigations, **ACS Sustainable Chemistry & Engineering,** 2022, https://doi.org/10.1021/acssuschemeng.1c07897
3. U. Mondal, G.D. Yadav, "Direct synthesis of dimethyl ether from CO_2 hydrogenation over highly active, selective and stable catalyst containing Cu-ZnO-Al_2O_3/Al-Zr (1:1)-SBA-15" **Reaction Chemistry & Engineering,** 2022, https://pubs.rsc.org/en/content/articlelanding/2022/re/d2re00025c/unauth
4. Chiranjit Santra, Sunil Bhoir, Sharad Lande, and Raksh Vir Jasra, "Process for Purification of Waste Terephthalic Acid Generated in Polyester Plant" **Catalysis in Green Chemistry and Engineering**, 2022, 10.1615/CatalGreenChemEng.2022040024 Web Published

5. Bharati Debnath, Saideep Singh, Sk Mujaffar Hossain, Shrreya Krishnamurthy, Vivek Polshettiwar, Satishchandra Ogale, "Visible Light-Driven Highly Selective CO_2 Reduction to CH_4 Using Potassium-Doped g-C_3N_5", **Langmuir** 2022, https://pubs.acs.org/doi/abs/10.1021/acs.langmuir.1c03127
6. Vivek Polshettiwar, Nisha Bayal, Baljeet Singh, Rustam Singh, Ayan Maity, "Synthesis of fibrous nano-silica spheres with controlled particle size, fibre density, and various textural properties, 2022, **US 11242257**
7. A Sreenavya, Shabas Ahammed, Arya Ramachandran, V Ganesh, A Sakthivel, Nickel–Ruthenium Bimetallic Species on Hydrotalcite Support: A Potential Hydrogenation Catalyst", **Catalysis Letters,** 2022, (152)848–862

Upcoming Symposium/ Conferences/Seminars

1. International Conference on Bio-catalysis & Green Chemistry Online 04-05, April 2022 https://crgconferences.com/green-chemistry/
2. International Conference on Environmental Materials and Catalysis (CEMC 2022) 22-24 April 2022, Suzhou, China.
3. 2022-4-22: ICCCSTNE 2022: International Conference on Carbon Capture, Storage Technologies, and Negative Emissions.
4. Alternate Energy Materials-2022, 6-8 April 2022, Imperial College London, England. https://www.aemlondon.com/
5. 2^{nd} Global Summit and Expo on Nanotechnology and Nanomaterials (GSENN2022) Copenhagen, Denmark on June 13-15, 2022. https://www.thescientistt.com/nanotechnology-nanomaterials/2022/speakers.php
6. International Conference on Green, Sustainable & Analytical Chemistry, 07-08 June 2022 Goa, India
7. International Conference on Environmental Materials and Catalysis (CEMC 2022) 22-24 April 2022 Suzhou, China

Quote of the Month

"To succeed in your mission, you must have a single-minded devotion to your goal." — **Dr. APJ Abdul Kalam**

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