September 2023

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.

Dr Thallada Bhaskar's Thermo-Chemical Conversion of Biomass Research Activities at CSIR-Indian Institute of Petroleum, Dehradun

❖ Background

As the world is moving towards the goal of decarbonization, the estimated requirement of biomass globally by 2050 stands at about 10 billion tonnes. India is no different and is committed to the increased utilization of its domestic carbon resources on high priority. Biomass is a renewable and sustainable source of different hydrocarbons and helps in meeting several SDG targets and national goals and missions as mentioned here. At CSIR-IIP, the biomasses that are considered for valorization are majorly the lignocellulosic biomass which do not cause the food vs. fuel issue. The agricultural residues, forestry wastes, defatted cakes etc. are used for all kinds of research. They are a rich source of renewable organic carbon that can be used to produce fuel, chemicals, materials or energy.
India is an agricultural economy, contributing nearly 20% to GDP and providing employment to around 50% population. The amount of crop residues generated in the country stand at around 600-700 MMTPA. In most places, these residues are used as fodder or for energy purposes and the rest is being burnt causing air pollution.

❖ Valorisation of spent aroma biomass

The National Aroma mission has been successful in providing livelihood to many farmers across the country. Due to this, around 6 MT of lignocellulosic biomass is available in the country by means of spent aromatic biomass (after the extraction of essential oil). Despite the removal of essential oils, there are large number of valuable compounds that can be produced from these

biomasses. We are developing thermochemical processes (pyrolysis and hydrothermal liquefaction) for the effective valorization of the residual aromatic biomass to produce solid bio-char and liquid bio-oils that have several applications.

❖ **Biomass Pelletisation**

The most feasible short-term application of biomass is for energy purpose either for heating applications or to generate electricity. As the world is moving towards the goal of decarbonization by 2050, it is estimated that solid bioenergy would contribute 60% of the energy requirement. The rest 30% would be in the form of liquid fuels and 10% by bio-gas. Considering that such a huge part would be in the form of solid bioenergy, we have developed a biomass pelletiser unit along with a pellet burner. The biomass would be crushed and pelletised for further use in biomass pellet burner which can be used for cooking applications. The Govt. of India is continuously looking at safer options for cooking applications and this can be one such option which eliminates the health hazards by traditional cooking using chulhas and wood. CSIR-IIP has developed a pelletisation unit (50 kg/hr capacity) which involves cutting the size of residues using a hammer mill, followed by pelletisation of biomass and also provides a pellet burner along with the unit. This burner can be used for domestic cooking applications or heating applications in small scale industries. These pellets when produced in larger quantities can also be supplied to heavy duty industries or even to thermal power plants to produce electricity by co-generation. The pellets can also be used in the chulha developed by CSIR-IIP as well.

❖ **Mobile pyrolyser**

As the biomass is available in large quantities, thermo-chemical conversion methods can be used to convert the biomass into useful products. Amongst the different thermochemical conversion methods available, pyrolysis process has the most potential for immediate deployment in decentralized locations. In this process, biomass/ biomass pellets are fed into a reactor unit in the absence of oxygen and heated up to the optimized temperature. Through this process, the domestic renewable organic carbon sources can be used for the production of energy/ functional or specialty chemicals/ fuels.

At CSIR-IIP, we have designed a mobile pyrolyser unit of capacity 50 kg/ hr has been designed and process demonstrated using biomass pellets to produce bio-oil and bio-char. The gas produced has also been demonstrated for use in heating/ cooking applications.

❖ **Bio-oil valorization**

The bio-oil is currently used to produce bio-bitumen/binder for flexible pavement applications with the collaboration of CSIR-CRRI, New Delhi, which would reduce the asphalt import into the country. The bio-oils produced can be used for supplementing furnace oil requirement and the testing of these oils for repellent properties etc are under progress.

❖ **Bio-char valorization**

The bio-char produced in the process can be used for soil amendment purpose as it helps in increasing the water retention, balances the soil pH and improves nutrient uptake. When bio-char is continuously applied in the long run, the requirement of fertilizers is reduced.
Some of the other high-end applications for bio-char are as follows

- **Biochar for supercapacitor application**

Biochar from carbonisation process was enhanced using facile activation in the CO_2 atmosphere. The extent of activation on the physicochemical and electrochemical properties was systematically studied on the activated biochar. Twofold increase in specific surface area, development of broader pores and increase in heteroatom content was observed. Specific capacitance was significantly enhanced to 493 F/g at 1 A/g current density. The capacitance retention was above 90 % for 10,000 charge-discharge cycles. The energy and power density of the aqueous symmetric supercapacitor prepared using activated biochar were 11.6 Wh kg^{-1} and 6000 W kg^{-1}, respectively.

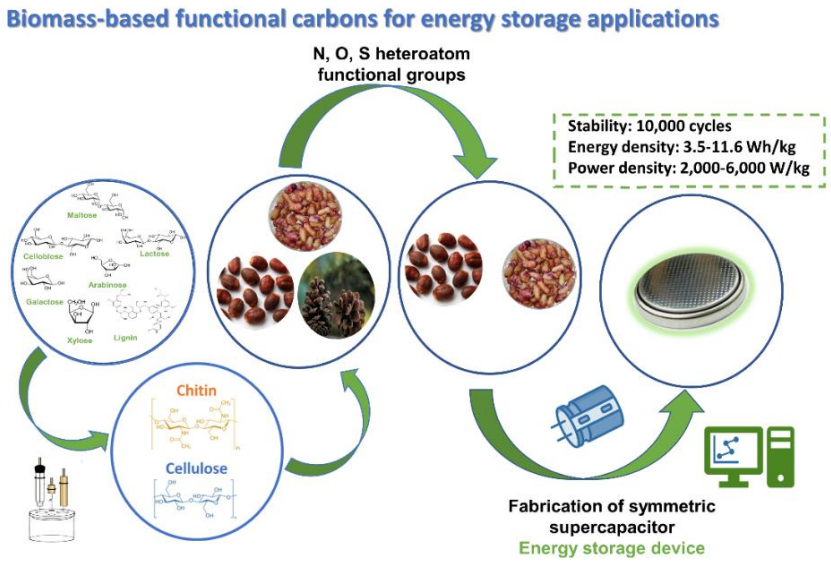


Figure 1: Biomass derived functional carbons

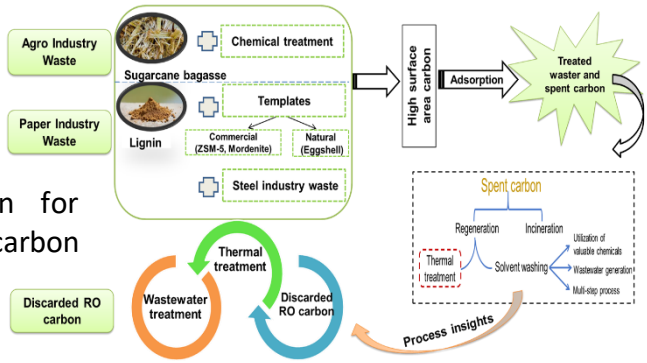
- **Biomass based carbon materials for wastewater treatment**

Access to clean drinkable water is a common right for all living beings and falls under SDG-06 of defined United Nation's Sustainable Development Goals. Improper monitoring and management in combination with exponential population and industrial growth has resulted in massive release and accumulation of anthropogenic contaminants in water bodies leading to depletion in availability of freshwater. Therefore, the research work at CSIR-IIP is targeted towards the achievement of aqueous sustainability via treatment of wastewater through adsorption. The adsorbent(s) preparation/activation involved the utilization of renewable, abundantly available, underutilized resources with less environmental load and adoption of low-cost activation

methods. In this regard, the study focused on utilizing low-cost resources i.e., agro and paper industry waste for preparation of adsorbents.

Notably, biomass-based carbon adsorbent(s) has aromatic carbon matrix and thus aromatic organic contaminants were targeted for removal. Some of the activities being pursued to achieve the objective are Fabrication and utilization of sugarcane derive biochar for phenol adsorption, Lignin derived hard templated carbon(s) for dye adsorption, Eggshell templated lignin carbon for wastewater treatment, Lignin derived magnetic carbon for dye adsorption, Effective utilization of discarded reverse osmosis post-carbon for adsorption of dyes from wastewater etc.

Biomass based carbon materials for wastewater treatment



❖ Hydrothermal liquefaction of biomass

Lignocellulosic biomasses are always not low in moisture content. In some cases, only wet biomass is present and it requires energy intensive drying steps. Invasive aquatic weeds lead to eutrophication and depletion of nutrients to the flora and fauna present leading to their death. For such feedstocks, hydrothermal liquefaction is the most suitable method of conversion where the moisture present take part and catalyzes the decomposition reactions. At CSIR-IIP, we have optimized the HTL process for several kinds of aquatic and wet lignocellulosic biomass.

❖ Lignin valorization

With increased emphasis on 2G ethanol production by the Govt. of India, lignin is a major by-product from them along with the pulp & paper industries. It is a very precious component of lignocellulosic biomass and can be used for the production of several functional chemicals/ petrochemical feedstocks which are now produced from fossil resources after several steps of functionalization. But, pre-treatment technique is the deciding factor to produce good quality lignin with bonds easily breakable during depolymerization.

▪ Reductive catalytic fractionation

During the pulping process, lignin undergoes significant structural changes to yield technical lignin. For a circular bio-economy, there is an urgent need to enhance the use of native lignin for generating more valuable products. Over the last few years, a new method called 'lignin-first', or 'reductive catalytic fractionation' (RCF), has been devised to achieve selective phenolic monomers under milder reaction conditions. This involves extraction and depolymerization of lignin and stabilization of obtained phenolic monomers before capitalizing on carbohydrates. Through reductive catalytic fractionation, the underutilized lignin component can find its potential for the production of bio-chemicals and the left-over pulp residue containing carbohydrates can be utilized for bioethanol production. In this way, the whole lignocellulosic biomass can be used efficiently without any wastage. In the RCF of sugarcane bagasse study, role of the catalyst in delignification and product yield was overviewed in which maximum LFDE

(Lignin-first delignification efficiency) of 81.2% was achieved with the production of bio-oil containing 55.7% alkyl substituted phenolic monomers. The upgradation of this bio-oil resulted in the production of alkylated cyclic alcohols with 90% selectivity. In the RCF study of cotton stalks, maximum delignification of 88% was achieved with 18.1 wt.% phenolic monomer yield and carbohydrate retention of 92%. These solid pulp residues containing these carbohydrates was then utilized for carbon synthesis for energy storage applications and for production of valuable chemicals including ethanol (2G). In this way, the whole lignocellulosic biomass is being utilized completely and efficiently to produce value-added products.

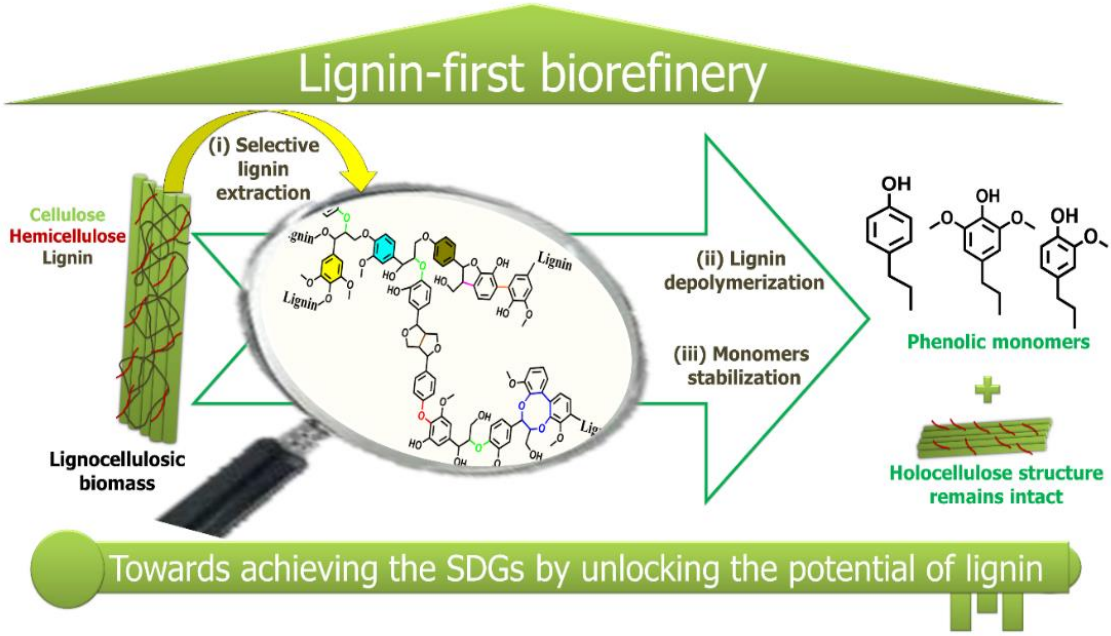


Figure 2: Reductive Catalytic Fractionation of biomass

At CSIR-Indian Institute of Petroleum, Dehradun we aim to develop strategic design of centralized/decentralized processes for effective utilization of domestic/renewable carbon resources. These processes will help in value addition and generating extra income to farmers since the residue to crop ratio is high and will also increase village level employment opportunities. The local requirement of energy can also be reduced when produced and utilized in a decentralized manner.

Overall, this will reduce the burden to import fossil fuels as it will be supplemented by the domestic carbon resources available within our borders and also lead the country on a path of self-reliance and decarbonization.

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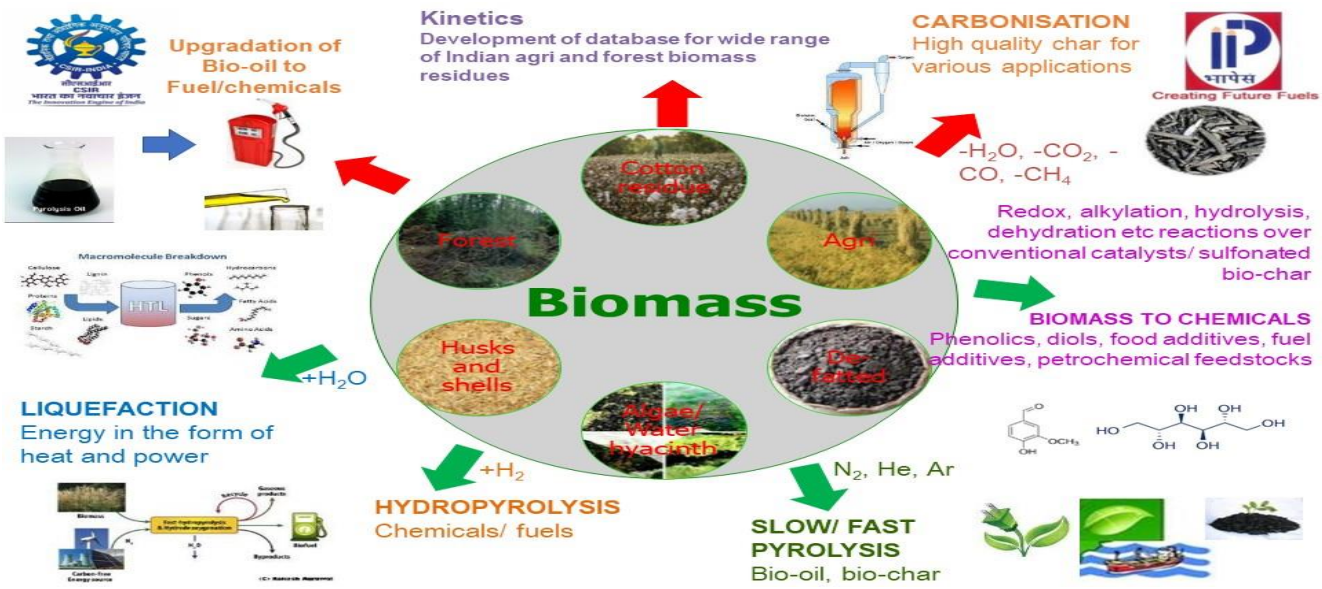

Figure 3: Snapshot of the research activities at CSIR-IIP

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Commercial & Policies

- **BHEL's Indigenous SCR Catalysts: A Game Changer in NOx Emission Control**

Bharat Heavy Electricals Ltd (BHEL) has achieved a significant milestone in the 'Make in India' initiative by successfully producing the first batch of domestic SCR Catalysts. This move is aimed at addressing NOx emissions in thermal power plants. The burning of coal in power plants results

in the conversion of nitrogen present in coal into various nitrogen oxide compounds, including nitric oxide (NO), nitrogen dioxide (NO_2), and nitrous oxide (N_2O). Collectively, these compounds are referred to as nitrogen oxides (NOx), which are a significant air pollutant. The technology has been indigenized by BHEL, building on expertise absorbed from the market leader, NANO, Republic of Korea.
Source: https://chemindigest.com/bhels-indigenous-scr-catalysts-a-game-changer-in-nox-emission-control/

- **Gulbrandsen Commissions its New Tin Catalyst Production Plant at its Site in Dahej**

Gulbrandsen, a specialty chemicals company, and one of the world's largest producers of tin catalysts for the polyurethane foaming industry, has completed the commissioning and safe start-up of its new Tin Catalyst production plant at its site in Dahej, India. The unit will produce Stannous Octoate and Stannous Neodecanoate. This facility will help us in meeting the growing demand for these products while also strengthening our commitment to delivering high-quality catalysts to the polyurethane foaming industry.
Source: https://chemindigest.com/gulbrandsen-commissions-its-new-tin-catalyst-production-plant-at-its-site-in-dahej/

- **An International Decade of Sciences for Sustainable Development**

Friday 25th August 2023, the United Nations General Assembly, during its 96th Plenary meeting of its 77th session adopted a resolution co-sponsored by many countrues. All stakeholders of the International Year of Basic Sciences for Sustainable Development fully support this resolution. Decides to proclaim the period 2024–2033 the International Decade of Sciences for Sustainable Development, within existing structures and available resources, to represent a unique opportunity for humanity to use the critical role that sciences play in the pursuit of sustainable development in its three dimensions as one of the key means of implementation as well as in responding to the complex challenges of our time to ensure a safe and prosperous future for all.
Source: https://www.iybssd2022.org/en/an-international-decade-of-sciences-for-sustainable-development/

- **L&T and Partners to invest $4 billion in green hydrogen projects**

Engineering major L&T and its renewable energy joint venture partners-Indian Oil Corporation and ReNew-will spend up to $4 billion (Rs 32,000 crores) in their green hydrogen businesses over three-five years, CEO & Managing Director S N Subrahmanyan said. L&T has partnered with state-run Indian Oil Corporation and clean energy company ReNew for its green hydrogen ventures. "We will invest around Rs 500 crore in making electrolyzers. Also, we have a JV with IOCL and Renew to put up green hydrogen plants.
Source: https://industry.siliconindia.com/news/lt-members-will-invest-4-billion-in-green-hydrogen-projects-nwid-40320.html

- **India's ONGC targets 8m tonnes/yr chemical capacity by '30; to build O2C plants**

India's state-owned Oil and Natural Gas Corp (ONGC) targets to nearly double its chemical and petrochemical capacity to 8m tonnes/year by 2030, with a plan to build two oil-to-chemicals

(O2C) plants amid strong domestic demand. “ONGC is collaborating with other entities to explore opportunities in the O2C, refining, and petrochemicals. ONGC also plans to spend around $12bn by 2030 on multiple green initiatives, including building a 1m tonne/year green ammonia plant at Mangalore in the southern Karnataka state, and scaling up its renewable energy portfolio to 10 gigawatts (GW) by 2030.

Source: https://www.offshore-technology.com/news/ongc-o2c-facilities-india/

- **IOC selects McDermott for Panipat naphtha cracker expansion project**

McDermott has been awarded a project management consultancy (PMC) and engineering, procurement, and construction management (EPCM) contract for the Naphtha Cracker Expansion (Phase II) polypropylene expansion and new ethylene derivative unit project from Indian Oil Corporation Limited (**IOCL)**. The project is located at the Panipat Refinery and Petrochemical Complex, located 62 miles (100 kilometers) from New Delhi, India. The project will increase the ethylene production capacity of the naphtha cracker unit (NCU) by approximately 20 percent.

Source: https://www.offshore-technology.com/news/mcdermott-iocl-indian-refinery/

- **India’s Dependency on Oil Imports Likely to Rise Above 80% By 2027**

India's reliance on oil imports is expected to increase from its present level of 78.6 percent to over 80 percent, the Union government informed Parliament.

Mr.Ameswar Teli, the minister of state for petroleum and natural gas informed that not only was India's reliance on oil imports expected to rise, but also that the country's expenditure on oil imports had nearly doubled over the previous three years despite a decline in domestic oil production over the previous five.

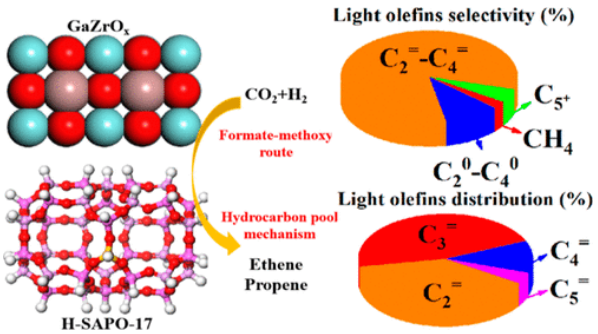
Minister informed, “Government has adopted a five-pronged strategy comprising increasing domestic production of oil and gas, promoting energy efficiency and conservation measures, giving thrust on demand substitution, promoting biofuels and other alternate fuels/renewables, EV charging facilities and refinery process improvements for reducing the county's oil dependence on imported crude oil."

Source: https://www.businessworld.in/article/India-s-Dependency-On-Oil-Imports-Likely-To-Rise-Above-80-By-2027-Informs-Centre-/05-08-2023-486716/

Scientific Updates

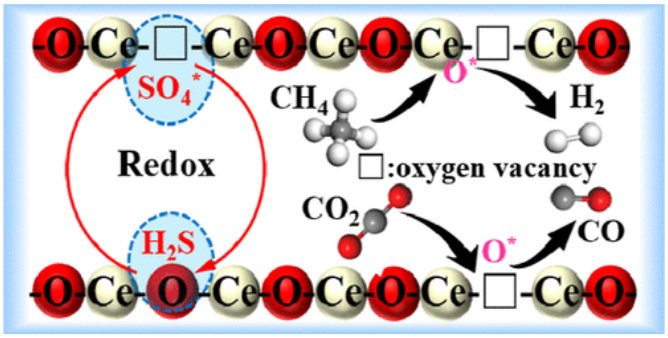
- **Selective Hydrogenation of CO_2 into Ethene and Propene over a GaZrOx/H-SAPO-17 Composite Catalyst**

Hydrogenation of CO_2 into value-added light olefins is a promising route to achieve carbon recycling. Regulation of light olefins distribution and promotion of target olefins formation are highly important to improve



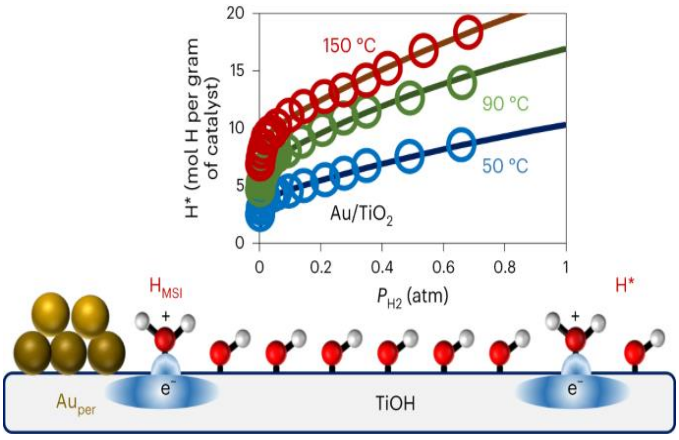
carbon utilization efficiency, but rather challenging. Herein, we designed a series of GaZrOx/H-SAPO-17 composite catalysts, which show the C2=–C4= selectivity of 82.5% (CO free), with those of CH4 and C20–C40 of only 2.5 and 10.2% in hydrocarbons, respectively, at a CO2 conversion of 9.0% at 375 °C and 1.5 MPa. In particular, ethene and propene accounted for >84% of C2=–C5= alkenes. Such a performance was well-maintained for at least 100 h.
Source: ACS Catalysis 2023, 13, XXX, 11919–11933, https://doi.org/10.1021/acscatal.3c01785

- **Sulfur-Accelerated Ceria Catalyst for Efficient CH_4/CO_2 Reforming: Unraveling the Special Role of Redox Functions and Its Reaction Mechanism**



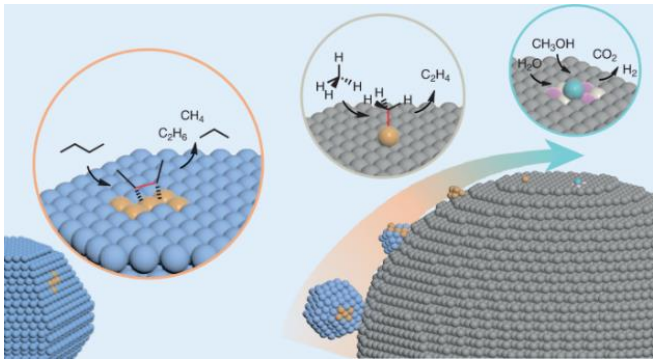
Sulfur poisoning remains a severe problem in industrial applications for CH_4 dry reforming, and developing a highly active and durable catalyst is of great environmental importance. Meanwhile, designing a Lewis acid catalyst of CeO_2 to replace traditional metal Ni for the challenging activation of CH_4 is interesting. Herein, valuable insights into the role of H_2S in promoting the catalytic activity of ceria catalysts for the dry reforming of methane are presented. Moreover, the special role of redox functions over the sulfur-accelerated CeO_2 catalyst and its reaction mechanism are unraveled by using quasi in situ XPS, in situ CH_4/CO_2-TPSR, and in situ DRIFTS and DFT calculations. This work gives a distinctive example of a sulfur-accelerated ceria catalyst for efficient CH_4/CO_2 reforming.
Source: ACS Catalysis 2023, 13, XXX, 12114–12124 https://doi.org/10.1021/acscatal.3c00752

- **The role of surface hydroxyls in the entropy-driven adsorption and spillover of H2 on Au/TiO_2 catalysts**



Hydrogen spillover involves the migration of H atom equivalents from metal nanoparticles to a support. While well documented, H spillover is poorly understood and largely unquantified. Here we measure weak, reversible H_2 adsorption on Au/TiO_2 catalysts, and extract the surface concentration of spilled-over hydrogen. The spillover species (H*) is best described as a loosely coupled proton/electron pair distributed across the titania surface hydroxyls. This study provides a quantitative assessment of how hydroxyl surface chemistry impacts spillover thermodynamics, and contributes to the general understanding of spillover phenomena.
Source: Nature Catalysis **6**, 710–719 (2023). https://doi.org/10.1038/s41929-023-00996-3

- **Ensemble effect for single-atom, small cluster and nanoparticle catalysts**

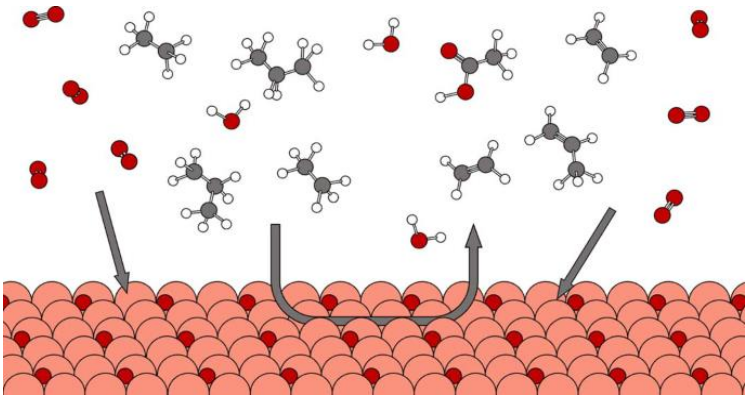


A large family of heterogeneous catalytic reactions require active sites with more than one metal atom, that is, an ensemble of metal atoms. The ensemble requirement, which refers to the minimum number of metal atoms that are needed to catalyse a reaction with optimal efficiency, is a useful metric to evaluate the effectiveness of catalysts for reactions with different site requirements. In this Review, we revisit the traditional ensemble effect and lay out the principles for its incorporation within efficient metal catalysts. Single-atom catalysts can also be described through the ensemble effect theory, as the co-ordination groups of single-atom catalysts constitute an ensemble that is vital for their reactivity.

The understanding of the ensemble requirement for metal catalysts provides insights into catalyst design with both optimized activity and atomic efficiency, and contributes to the development of sustainable heterogeneous catalytic transformations.

Source: Nature Catalysis **5**, 766–776 (2022). https://doi.org/10.1038/s41929-022-

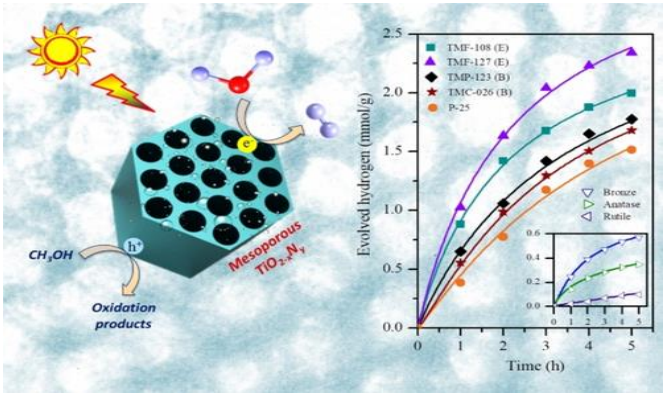
- **Activation of light alkanes at room temperature and ambient pressure**



Light alkane activation under mild conditions remains a substantial challenge. Here we report an aqueous reaction system capable of selectively converting light alkanes into corresponding olefins and oxygenates at room temperature and ambient pressure using Cu powder as the catalyst and O_2 as the oxidant. In ethane activation, we achieved a combined production of ethylene and acetic acid at a rate of 2.27 mmol g_{Cu}^{-1} h^{-1}, with a combined selectivity up to 97%. Propane is converted to propylene with a selectivity up to 94% and a production rate up to 1.83 mmol g_{Cu}^{-1} h^{-1}, while methane is converted mainly to carbon dioxide, methanol and acetic acid.

Source: Nature Catalysis 6, 666–675 (2023). https://doi.org/10.1038/s41929-023-00990-9

- **Defect-induced Ordered Mesoporous Titania Molecular Sieves: A Unique and Highly Efficient Hetero-phase Photocatalyst for Solar Hydrogen Generation**Photocatalysts made of N-doped TiO_2 are frequently utilized for breaking of water molecules in the process of generating hydrogen. To achieve this target, a unique defect-induced n itrogen-doped highly organized 2D-hexagonal periodic mesoporous titania, $TiO_{2-x}N_y$ with a well-crystallized framework is synthesized in a reproducible way using structure-directing agents, e. g., F108, F127, P123, and CTAB. or aqueous solution using solar irradiation are highly desired for the hydrogen economy. The nitrogen is incorporated into these samples through a facile method involving the calcination of templated materials in an air. Source: CHEMNANOMAT 2023 https://doi.org/10.1002/cnma.202300319



Catalysis Research out of India

1. VP Mahajan, YA Kolekar, BM Bhanage " Ni/Al_2O_3: Catalyzed Carbonylative Homocoupling of Aryl Iodides for the Synthesis of Symmetrical Diaryl Ketone Using Co2(CO)8 as CO Surrogate" **Catalysis Letters 2023**, https://doi.org/10.1007/s10562-023-04430-y
2. Manjunath S Lokolkar, Manoj K Pal, Sandip Dey, Bhalchandra M Bhanage, "POP-Pincer Xantphos Pd Complex of 4-Pyridylthiolate: Cyclocarbonylative Reaction for the Synthesis of Flavones Using Cobalt Carbonyl as a C1 Source" **Catalysis Letters,** 153 (8) 2359-2367 https://doi.org/10.1021/acs.iecr.3c00855
3. Komal Saini, Abhisek Sahoo, Thallada Bhaskar, "Graphene and its Derivatives Water/Wastewater Treatment and Other Environmental Applications" 2023, Vol 2, 1-18, Springer Nature Singapore
4. Aparna Deshpande, Shivam Rawat, Indrajit M Patil, Sunit Rane, T. Bhaskar, S. B Ogale, Srinivas Hotha, "Converting renewable saccharides to heteroatom doped porous carbons as supercapacitor electrodes", **Carbon,** 2023, Volume 214, 2023, 118368
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6. S. Sharma, R. Shanmugam, RB Harikrishna, U Prasad, G Ranga Rao, AM Kannan, "Y2O3 electrodeposited TiO_2 nanotube arrays as photoanode for enhanced photoelectrochemical water splitting" Int. **J. of Hydrogen Energy** 2023 https://doi.org/10.1016/j.ijhydene.2023.07.176
7. R. Jan, C. A. Biji, K Shakeela, Rafik R. Shaikh, G Ranag Rao, "Green Synthesis of Cyclic Carbonates from Epoxides and CO2 Using Transition Metal Substituted Polyoxometalate-

PDDA Hybrid Catalysts" **Catalysis Letters,** 2023, 1-11 https://doi.org/10.1007/s10562-023-04392-1

8. V. Mishra, B.D Mohapatra, Tapan Kr. Ghosh, G Ranga Rao, "Effect of MnO Content on the Oxygen Reduction Activity of MnO/C Nanostructures" **Electrocatalysis,** 2023, 14, 788–799
9. Komal P Tarade, Sanjay P Kamble, Chandrashekhar V Rode, Novel Sulfonic Acid Functionalized Silica Supported Isonicotinic Acid Catalyst for Conversion of 2-Methylfuran to Diesel Fuel Precursors**, Catalysis Letters 2023** (20 https://doi.org/10.1007/s10562-023-04383-2
10. Sanjeev Gupta, Surya Kr Vatti, Qinfen Gu, Dipti Wagh, Haresh Manyar, and P. Selvam, "Defect-induced Ordered Mesoporous Titania Molecular Sieves: A Unique and Highly Efficient Hetero-phase Photocatalyst for Solar Hydrogen Generation" CHEMNANOMAT 2023 https://doi.org/10.1002/cnma.202300319

▪ Upcoming Symposium/Conferences/Seminars/Workshop

1. Workshop on **Functional Materials & Heterogenous Catalysis** from 11th-15th, December, 2023 at IIT (ISM) Dhanbad. The details are available on https://gian.iitkgp.ac.in/GREGN/index
2. Indian Membrane Society is organizing an International Conference on "Membrane based Separations: Past, Present & Future" during **16th-18th October 2023** at MS University of Baroda along with CSIR-CSMCRI, Bhavnagar.
3. Catalysis for Energy, Environment and Sustainability (CEES-2023) & CO_2-India Network 2nd Annual Meet from September 25 to 27, 2023 at IIT Mandi.
4. International Conference on Organometallics and Catalysis from **30th – 2nd Nov 2023** at Goa, India https://www.icoc2023.com
5. 2nd International Conference on Catalysis and Chemical Engineering, November 09-10, 2023 Millennium Hotel Paris Charles De Gaulle, Paris, France https://scisynopsisconferences.com/catalysis/
6. International Catalysis Conference ICC 2023 from **15th-17th September 2023** at Miami USA https://www.catalysisworldconference.com/
7. 17th Edition of International Conference on Catalysis, Chemical Engineering and Technology" (Catalysis 2023) as Hybrid Event during **October 26th-28th, 2023,** at Boston, Massachusetts, USA.
8. International Conference on Green Chemistry Solutions for Sustainable Future 2023 **from 20th to 22nd September 2023,** Venue: GITAM University, Bengaluru Campus, India.

Quote of the Month

"Perfection is not attainable, but if we chase perfection we can catch excellence."

- Vince Lombardi

Editorial Team

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