

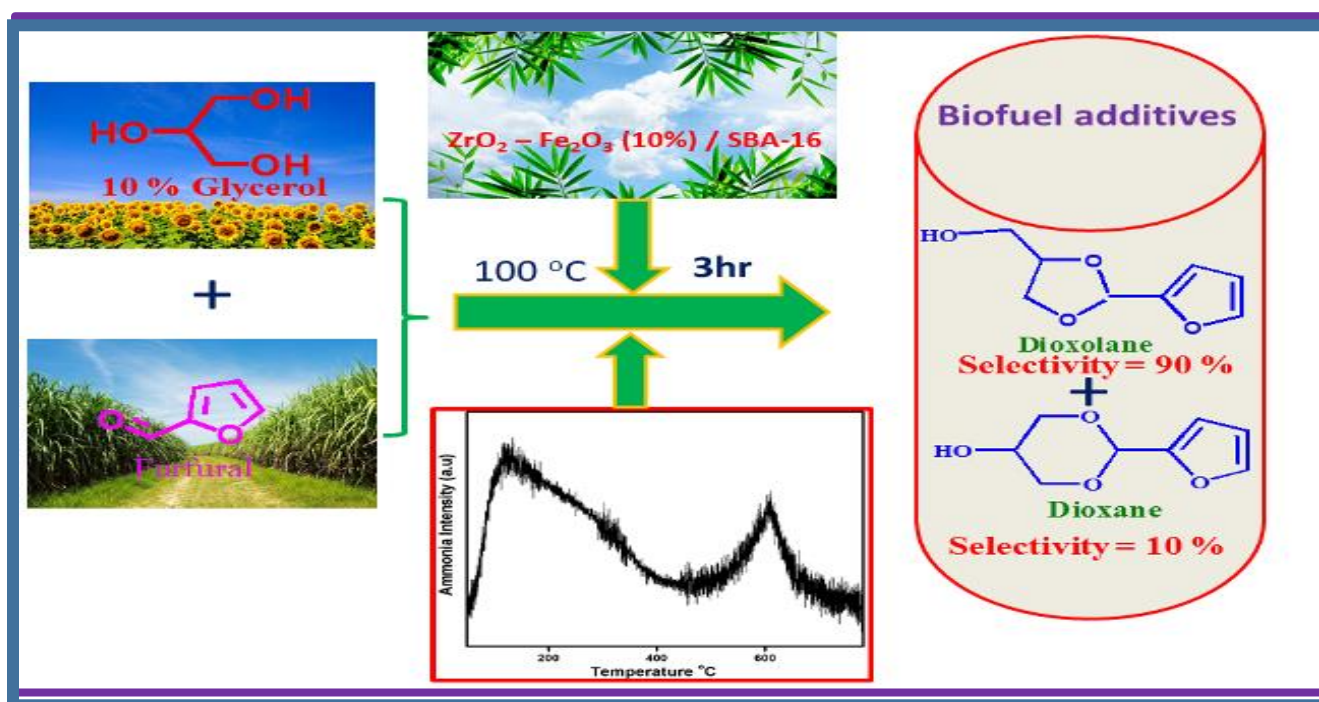
Graphical Abstract (Papers / Patents)

Name of Authors (UPES only) : Gopalakrishnan Govindasamy

Title of manuscript: Green synthesis of spherical mesoporous SBA-16 and its supported Fe_2O_3 - ZrO_2 catalyst for selective acetalization of glycerol to dioxolane as biofuel additive

Journal Name with impact factor: Journal of Environmental Chemical Engineering (IF:7.4)

Link (Doi): <https://doi.org/10.1016/j.jece.2023.109476>



Abstract (150-200 words): Acid catalyzed acetalization of glycerol to fuel additive is an important valorization for the available surplus glycerol arising due to ever increasing biodiesel production. For this reaction, mesoporous spherical SBA-16 was synthesized first time from bamboo leaf ash derived sodium silicate (BLASS) and impregnated with 10 wt.% each of Fe and Zr, characterized by XRD, N₂ adsorption-desorption, SEM-EDX, TEM, NH₃ TPD, XPS and evaluated for the acetalization of glycerol with furfural. The crystalline and pore structure of SBA-16 (BLASS) support were not altered by the impregnated Fe and Zr which formed α -Fe₂O₃ and monoclinic ZrO₂ respectively on its surface. Fe₂O₃ and ZrO₂ impregnated spherical SBA-16 (BLASS) gave higher glycerol conversion and dioxalane selectivity compared to the same impregnated on shapeless SBA-16, synthesized from tetraethyl orthosilicate (TEOS), confirmed the positive influence of spherical morphology. Further it retained the activity and selectivity for five

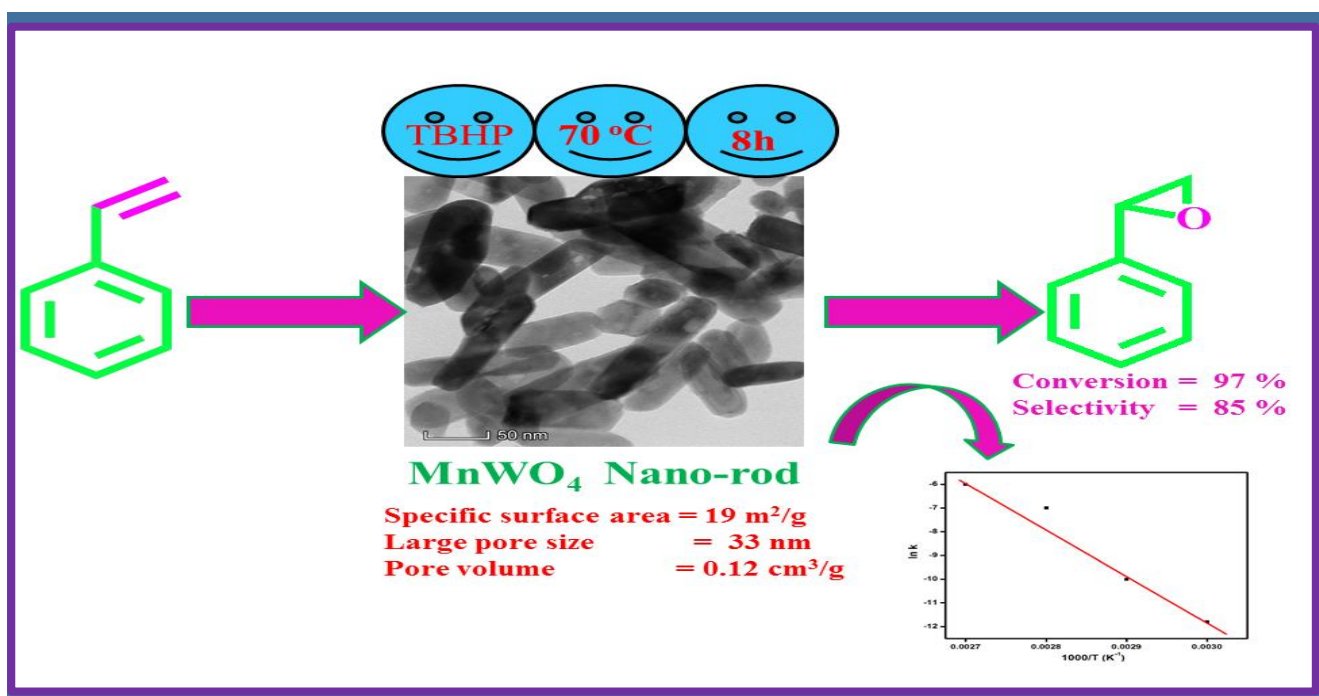
recycles. Prolonged reaction time transformed kinetically favored dioxolane to thermodynamically stable dioxane based on which plausible reaction mechanism was proposed. Optimum temperature, glycerol : furfural feed molar ratio, amount of catalyst and reaction time were found to be 100°C, 1:1, 3.6 wt.% of glycerol and 3 h respectively for the maximum glycerol conversion with the highest dioxolane selectivity. Glycerol conversion and dioxolane selectivity for acetalization of glycerol with para substituted benzaldehydes were less than benzaldehyde due to steric effect. Dioxalane selectivity decreased with increase in size of aldehydes due to inductive effect while the cyclic ketones were more reactive for the acetalization of glycerol.

Name of Authors (UPES only) : Gopalakrishnan Govindasamy

Title of manuscript: A novel manganese tungstate nanorod catalyst for the oxidation of styrene with tert-butyl hydroperoxide as oxidant

Journal Name with impact factor: Tungsten (IF: 5.6)

Link (Doi): <https://doi.org/10.1007/s42864-024-00278-w>



Abstract (150-200 words): Catalyst, solvent and process parameters are the key for the selective oxidation of styrene and other olefins to value added intermediates. Hence MnWO₄ was synthesized by the one-pot hydrothermal method using Pluronic F127 as a surfactant, characterized and evaluated for the oxidation of styrene and different olefins, using tert-butyl hydroperoxide (TBHP) as oxidant. X-ray diffractogram confirmed the phase purity of MnWO₄ which became further evident from the near surface equimolar proposition of Mn and W in +2 and +6 oxidation states, respectively, as inferred from X-

ray photoelectron spectra. N₂ sorption followed type IVa isotherm with H3 hysteresis loop, starting at P/P₀ of 0.9, typically of mesoporous materials containing macropores as further confirmed by pore-size distribution. Transmission electron microscope images of MnWO₄ revealed its nanorod morphology. In the absence of catalyst, styrene conversion was 35% with benzaldehyde as the sole product and addition of 75 g of MnWO₄ increased the styrene conversion to 97.3%, and the styrene oxide selectivity from 0 to 85% demonstrated its activity and selectivity. For the maximum conversion and styrene oxide selectivity optimum temperature, styrene: TBHP molar ratio, catalyst amount and solvent were found to be 70 °C, 1:2, 75 mg, and acetonitrile, respectively. MnWO₄ catalyst retained its activity and selectivity for five recycles, confirming its recoverability and reusability. From the kinetic studies, pre-exponential factor and apparent activation energy were found to be 0.206 s⁻¹ and 31.5 kJ·mol⁻¹, respectively, and a reaction mechanism was proposed. MnWO₄ catalyst was active for oxidation of alkenes, cycloolefins and alkenyl aromatics with high selectivity for epoxides

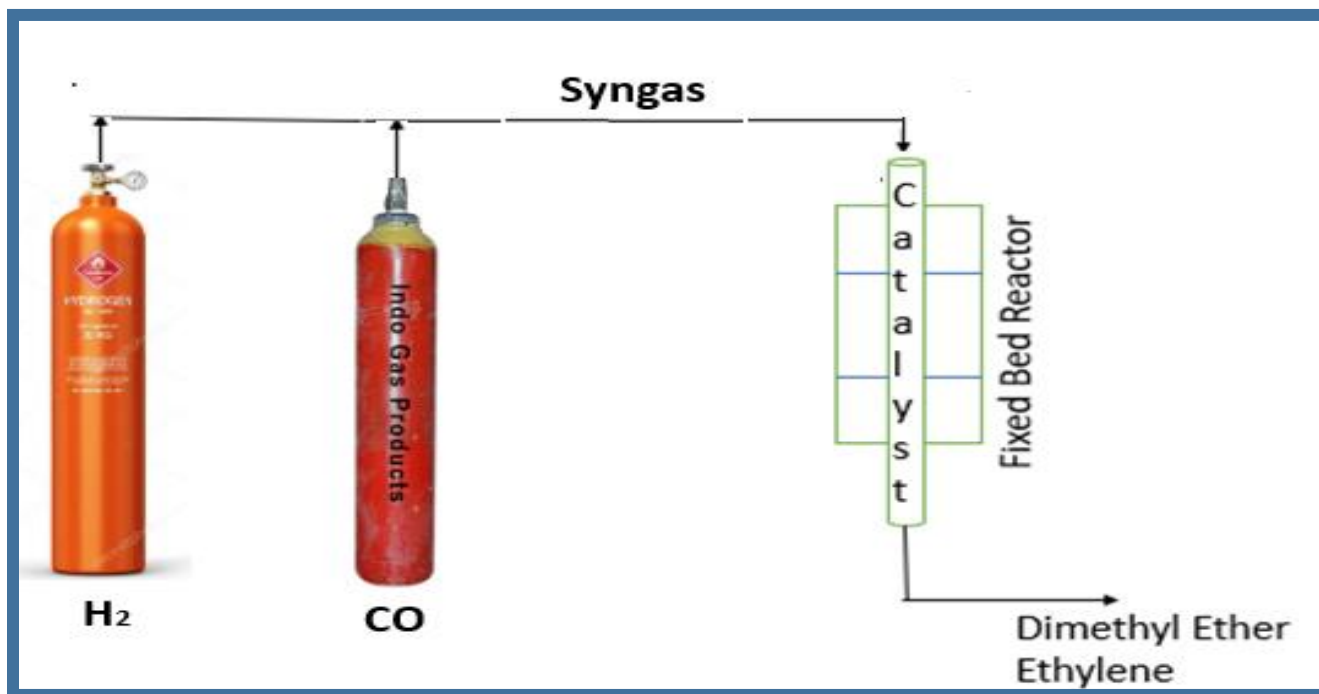
Graphical Abstract (Funded Projects / Consultancy)

Name of PI / Co-PI: Dr. G. Gopalakrishnan/Ms. Pulla Rose Havilah

Title of the Project: Studies on the Syngas Conversion to Dimethyl Ether

Funding details (project number, funding body, duration, amount, etc.):

Dated July 7, 2021, UPES R&D SEED Grant, August 2021 – August 2022, INR 3,50,000.



Abstract (200-300 words): The aim of this project is to develop hybrid bi-functional catalyst for direct conversion of syngas to dimethyl ether (DME). Conventionally the syngas is converted to dimethyl ether by a two-step process involving production of methanol from syngas using Cu-ZnO-Al₂O₃ catalysts followed by dehydration of methanol over solid acid catalysts to DME which dehydrates further to ethylene over solid acid catalysts. However, the two-step process suffers from limiting thermodynamic equilibrium conversion of syngas to methanol not exceeding 20%. To overcome this constraint, direct conversion of syngas to DME and/or ethylene gained huge importance by developing a bi-functional catalyst, particularly with the emphasis on finding an effective dehydration catalyst as the room for further improvement of commercial methanol synthesis catalyst is not much. Hence hierarchical ZSM-5 of Si/Al ratio 40 and 80 were prepared by steam assisted crystallization method. Synthesized hierarchical ZSM-5 was modified by ammonium and magnesium by ion-exchange followed by calcination to get the mild solid acid catalyst of hierarchical HMgZSM-5. The same was made into hybrid bi-functional catalyst by physically mixing with commercial Cu/ZnO/Al₂O₃ (CZA) methanol synthesis catalyst sourced from Süd-Chemie India Pvt. Ltd in the weight ratio of 2:1 (CZA :

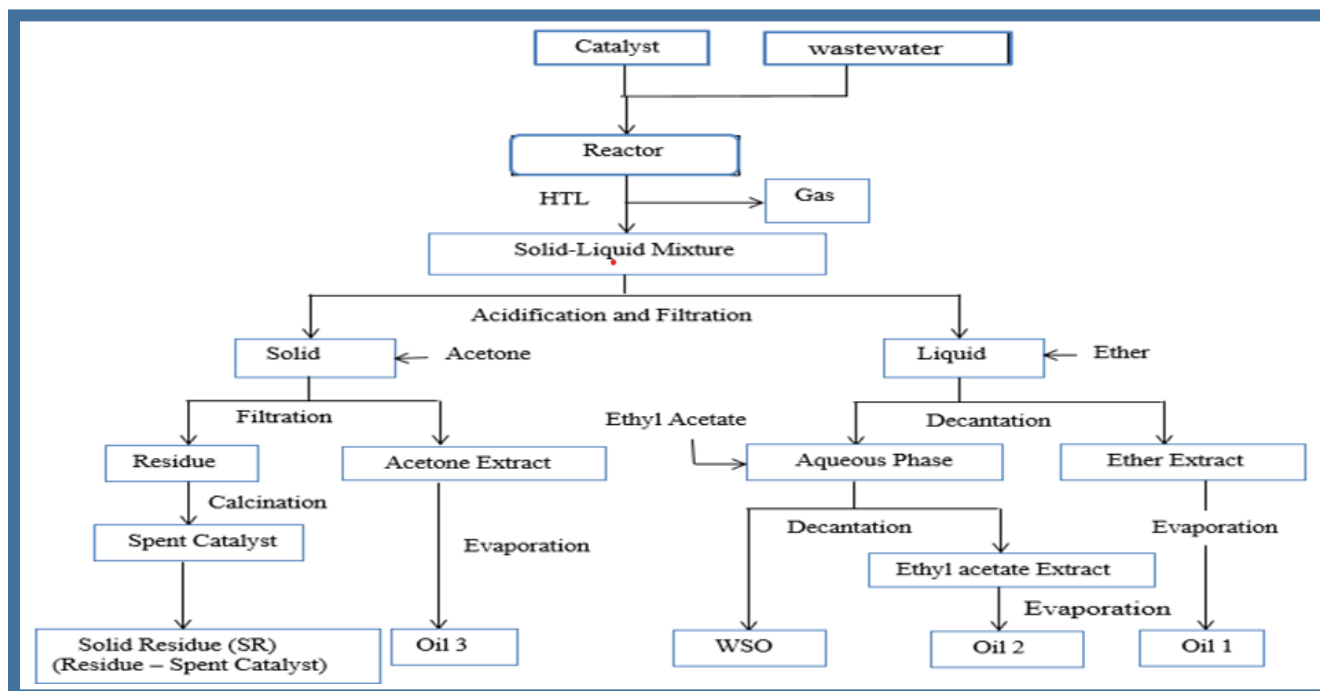
HMgZSM-5). Prepared catalysts were characterized by XRD, FTIR, SEM, BET and NH₃-TPD. The catalytic performance studies in a fixed bed plug flow reactor yielded ethylene as the sole product since the inhouse synthesized hierarchical HMgZSM-5 catalyst was highly active converting all the methanol formed from syngas by the CZA catalyst into DME then to ethylene.

Name of PI / Co-PI: Dr. G. Gopalakrishnan

Title of the Project: Synthesis, modification, characterization and evaluation of Hierarchical ZSM-12 for hydrothermal liquefaction of wastewater into low-oxygen containing bio-oil

Funding details (project number, funding body, duration, amount, etc.):

Dated 12-10-2018, UPES R&D SEED Grant, November 2018 – November 2019, INR 2,30,000.



Abstract (200-300 words): Hydrothermal liquefaction (HTL) is a mimic of natural process of petroleum formation, taking only 30 min and converts 80% of organics in the wastewater. Thus, it has the potential to replace or compliment anaerobic digestion (AD) the only method currently available to treat the municipal wastewater into biogas as energy product which takes 30 days to bring 60% conversion of organics in the wastewater. HTL is carried out with hot compressed water which has 500 times of H⁺ and OH⁻ ions compared to ambient water bringing the acid–base hydrolysis of biopolymers presents in the wastewaters such as polysaccharides, proteins, fats to monosaccharides, amino acids and fatty acids respectively. Their further deoxygenation to bio-oil with high yield demands reusable heterogeneous catalysts with deep deoxygenation activity. The

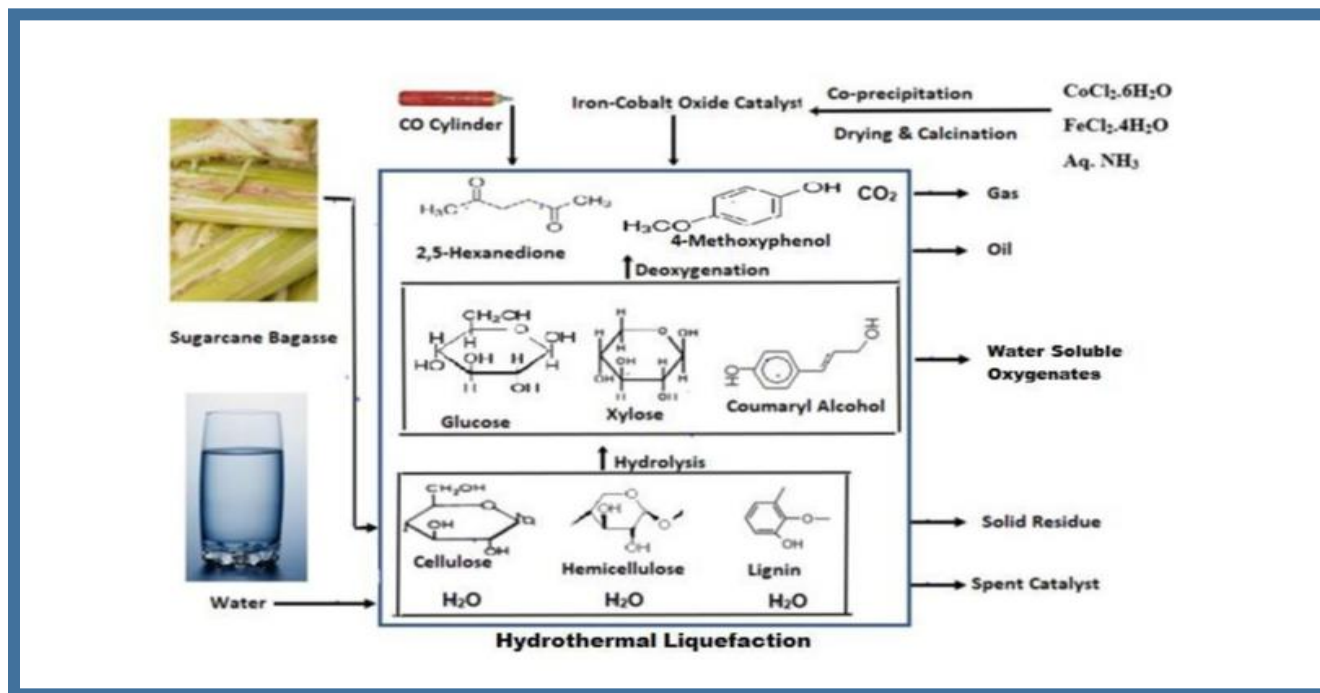
current project developed a procedure for synthesizing Fe and Co substituted hierarchical zeolites using steam assisted crystallization method (SAC) with tetraethyl ammonium hydroxide (TEAOH) as organic structure directing agent (OSDA) which does not demand secondary pore forming agents and thus efficient and green synthesis method. Hierarchical zeolites have conventional zeolite structures with micropores in addition to which contain mesopores allowing the diffusion of above-mentioned intermediates for their deoxygenation to bio-oil containing less oxygen to have higher calorific value and less acidity. Characterization of the synthesized catalysts by XRD, pore size distribution and chemical composition confirmed the formation of hierarchical Fe-CoZSM-5 for the first time using SAC method. Their evaluation for HTL of synthetic wastewater containing 20% solids having 50 - 60% carbohydrate, 15 - 20% fat and 25-35% protein gave the highest bio-oil yield of 34.67% over hierarchical Fe-Co-ZSM-5 synthesized at 3 days of crystallization time due to its higher crystallinity compared to 4 days.

Name of PI / Co-PI: Dr. G. Gopalakrishnan

Title of the Project: Direct Conversion of Sugarcane Bagasse to Auto fuels by Catalytic Hydrous Pyrolysis in Presence of Carbon Monoxide

Funding details (project number, funding body, duration, amount, etc.):

7/184/2013-BF dated 20/03/2014, Ministry of New and Renewable Energy, 20-04-2014 to 20-01-201, INR 64,74,95.



Abstract (200-300 words): Development of suitable catalyst having deep deoxygenation activity is the key for the hydrothermal liquefaction (HTL) of biomass to auto fuels directly. In this study twelve catalysts namely Fe-MCM-41, Co-MCM-41, Mo-MCM-41, Ti-MCM-41, oxides of Fe, Co, Mo, Ti, Fe-Mo, Fe-Co, Co-Mo and Ti-Zr were synthesized, characterized by XRD, Textural analysis, FTIR and SEM. They were evaluated for HTL of sugarcane bagasse to bio-oil in the presence of hydrogen and carbon monoxide. For non-catalytic HTL, oil obtained in the presence of hydrogen contained less oxygen whereas for catalytic HTL, oil obtained in the presence of carbon monoxide contained less oxygen. Among the catalysts studied, iron-cobalt oxide was found to be the most selective as it gave the highest oil yield of 57.6 weight% containing the least oxygen of 10.8 weight% in the presence of CO. Co-MCM-41 and Cobalt oxide were yielding bio-oil with least oxygen among the metal substituted MCM-41 and metal oxides studied, indicating that Cobalt may be the most active catalytic species for strong deoxygenation activity. Metal substituted MCM-41 yielded oil with less oxygen compared to their oxides except Ti which may be due to very high surface area owing to their mesoporous structure.