ABSTRACT

This work aims towards addressing the various challenges in sustainable catalysis such as use of expensive and hazardous metals, toxic organic solvents, harsh reaction conditions, catalyst stability, byproduct formation and recyclability. This was done by synthesis and characterization of polymer derived catalysts (metallopolymers and nanoreactors) for organic transformations (solitary and cascade) under ambient reaction conditions. They were rationally designed to possess the feature of stability and recyclability which is important for practical applications.

The work was executed in the following steps:

1. **Synthesis of some polymers (Crosslinked, covalent organic frameworks, amphiphilic) decorated with metal nanoparticles (Fe, Cu and Pd) to obtain metallopolymer and nanoreactors.**
2. **Characterization and structural evaluation of metallopolymers and nanoreactors**
3. **Assessment of the catalytic potential of metallopolymers and nanoreactors for synthesis of industrially important compounds by solitary and cascade routes.**
4. **Investigation of reaction parameters, kinetics, mechanism, substrate scope, and recycling efficiency of the catalytic process.**

Metallopolymers and nanoreactors were synthesized by various strategies, duly characterized and analyzed for their catalytic activities towards solitary and cascade organic transformations.

The synthesized crosslinked polymers and catalysts were characterized as follows:

Properties	**Technique/ Instruments**
Structural Elucidation	1H NMR, ^{13}C NMR, 2D NMR, FTIR, EDAX
Morphology and size	HR-TEM, FE-SEM, DLS
Optical	UV-Vis & Fluorescence Spectroscopy
Thermal	TGA
Magnetic	VSM
Metal loading	ICP-AES, EDAX
Oxidation state of metal	XPS

The synthesized covalent organic frameworks and catalyst were characterized as follows:

Properties	**Technique/ Instruments**
Structural Elucidation	^{1}H NMR, CP/MAS-NMR, FTIR, EDAX
Morphology and size	HR-TEM, FE-SEM
Confirm framework formation	PXRD
Thermal	TGA
Surface area and Porosity	BET
Metal loading	ICP-AES, EDAX
Oxidation state of metal	XPS
Product formation	GCMS

The synthesized polymer micelles and polymer vesicles and nanoreactors were characterized as follows

Properties	**Technique/ Instruments**
Structural Elucidation	^{1}H NMR, FTIR, EDAX
Morphology and size	HR-TEM, FE-SEM, DLS, AFM
Surface charge	Zeta potential
Thermal	TGA
Optical	UV-Vis & Fluorescence Spectroscopy
Self-assembly	**Vesicles:** FTIR, self-quenching, fluorescence spectroscopy & microscopy **Micelles:** CMC determination by pyrene encapsulation, self-quenching, fluorescence spectroscopy & microscopy
Metal loading	ICP-AES, AAS
Oxidation state of metal	XPS
Magnetic	VSM

The synthesized metallopolymers and nanoreactors were assessed for their ability to catalyze solitary (reduction of nitroaromatics and Suzuki Miyuara Cross Coupling reaction) and cascade (Benzimidazole synthesis and chemoenzymatic synthesis) reactions. p-Nitrophenol and 4-bromobenzene, p- Nitrophenylacetate were used as model reactants for different reactions. The reaction parameters such as temperature, solvent, base, etc., were investigated to optimize the reaction conditions. The kinetics of the reduction reaction was studied. The substrate scope was extended for each study. All the metallopolymers and nanoreactors were assessed for their recyclability and reusability. The morphology of polymer nanoreactors (vesicle and micelles) were thoroughly characterized to differentiate in their structures. The plausible mechanisms were proposed for all the catalytic systems.