

Abstract

The thesis entitled “*Engineering Nitrogen-Rich Porous Organic Polymer as Heterogeneous Catalyst for Organic Transformation Reactions*” consists of six chapters; viz. introduction, four experimental working chapters followed by conclusion and future scope.

Chapter 1 covers a brief background about the porous organic polymers (POPs), their classifications, strategic design synthesis process, and a few quoted applications related to their structural induced property. Chapter 2 to 5 cover the experimental and supported computational works exploring catalytic efficiency of POPs in various forefront organic transformation reactions. In chapter 2, a nitrogen-rich amide functionalized triazine based POP is designed, synthesized, and explored its catalytic activity in direct deamination reaction of benzamide. In chapter 3, the synthesized POP has been utilized as heterogeneous support catalyst for anaerobic oxidation of benzyl alcohol *via* hydride elimination. The study is further extended to multicomponent oxidative annulation reaction of alcohols to corresponding quinolines along with the evolution of H₂ and demonstrated in Chapter 4. Chapter 5 covers the utilization of eliminated H₂ from the anaerobic dehydrogenative oxidation reactions studied in Chapter 3 & 4 in *N*-alkylation reaction over Ni(II) embedded POP. Chapter 6 is the concluding chapter of the findings incorporated in the thesis with future perspectives.

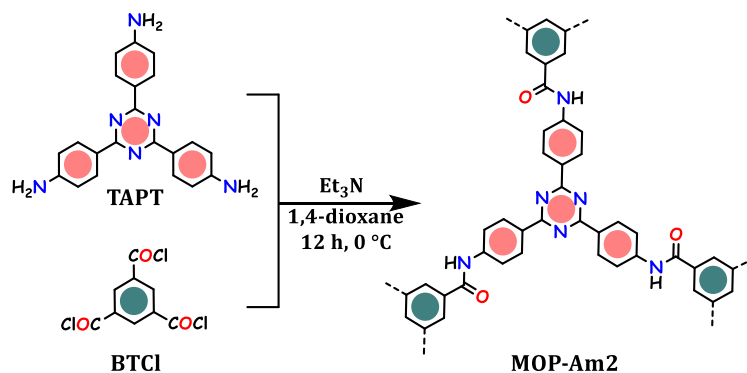
Chapter 1. Introduction

The existence of porous materials in nature is better realized for their unique chemical and physical properties since long. Their mimicable architecture encouraged the scientific community to discover various artificial hierarchical structures; marked by the synthesis of mordenite (a synthetic zeolite) in 1940 followed by other porous material such as porous organosilica, microporous aluminophosphate, metal organic framework (MOF), etc. A new addition to the domain, was the covalent organic framework (COF) that gained rapid attention of the scientific community with the synthesis of rigid porous solids from condensation reaction of phenyldiboronic acid and hexahydroxytriphenylene. Porous organic polymers (POPs) which is a more generalized term instead of COFs are the

combination of purely organic core unit and linker *via* strong covalent bond that follows the principle of reticular chemistry. It is defined as the chemistry of linking molecular building blocks by strong bonds to make crystalline extended networks. It permits to enlarge and enrich the discovery and synthesis of varied functional solid-state materials. The POP precursors are connected to each other generating permanent pores, voids, or channels in its extended ordered 1D, 2D or 3D lattice structure. The chemical composition of lighter elements such as B, C, N, O, Si, etc and the pores or the free space inside the structural skeleton affords less dense materials. IUPAC nomenclature classifies POPs as microporous, mesoporous, and macroporous based on the pore size while the degree of order of polymerization refers POP as crystalline or amorphous material. The presence of tunable pores, long channels, high surface area and continuous long range π -conjugation generates promising material for gas and energy storage, optoelectronic device, biomedical applications, and heterogeneous solid support for catalysis.

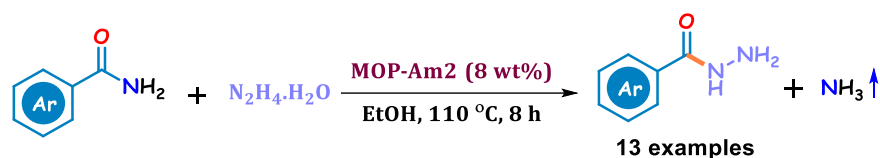
Chapter 2. Amide Functionalized Triazine Based 2D Porous Organic Polymer (MOP-Am2) to Promote Direct Deamination Reactions of Benzamides

This chapter covers the strategic design and synthesis of amide functionalized triazine based 2D porous organic polymer (MOP-Am2). The MOP-Am2 is synthesized from the room temperature [C₃+C₃] condensation of 2,4,6-tris-(4-aminophenyl)-1,3,5-triazine (TAPT) and 1,3,5-benzenetricarbonylchloride (BTCL) in 1,4-dioxane (Scheme 2.1). The release of corrosive and reactive HCl is neutralized with the addition of stoichiometric triethylamine (Et₃N) in the solution.



Scheme 2.1 Schematic representation of the synthesis of desired amide functionalized porous organic polymer (MOP-Am2)

The structural integrity of the obtained the MOP-Am2 is examined with various thermal, microscopic, and spectroscopic techniques. ^{13}C CP/MAS NMR analysis confirms the presence of triazine moiety and amide linkage. The amide moiety is a well-known synthon as for both H-bond donor and acceptor. The presence and the utility of the amide is reported as heterogeneous support catalyst for deamination reaction during hydrazide synthesis under solvent free condition (Scheme 2.2).



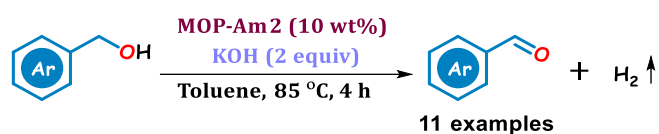
Scheme 2.2 Catalytic deamination of benzamide derivatives to corresponding benzhydrazide over MOP-Am2

The MOP-Am2 is found to be an excellent facilitator to convert $-\text{NH}_2$ to a good leaving group *via* weak H-bonding through amide moiety without using any external activating agent. Substrate scope is explored with excellent productivity under solvent free condition. The identification and quantitative product formation are characterized with LCMS analysis along with one crystal structure.

Chapter 3. Base Mediated Anaerobic Oxidation of Benzyl Alcohols Over Reusable MOP-Am2

Oxidation of benzyl alcohols is one of the most fundamental reactions gaining attention owing to its wide applications in the field of chemical and pharmaceutical industries; and is also considered as a benchmark reaction to evaluate the catalytic activity of the porous polymers. This chapter emphasizes the role of π -cloud of MOP-Am2 as mediator for the anaerobic oxidation of benzyl alcohols under basic medium (Scheme 3.1). As discussed in Chapter 2, the solid-state UV-Vis DR spectroscopic analyses reveal the presence of π -electron rich extended network in MOP-Am2. The extended π -cloud lowers the overall band gap that makes the benzylic carbon in benzyl alcohol more prone for weak interaction over MOP-Am2. The charge transfer from MOP-Am2 enhances the natural electronic charge on benzylic carbon and hence weakening the benzylic C–H bond. DFT study, taking M06-2X/6-311G* level of theory, supports the finding of the protocol where the weak interaction from MOP-Am2 behaves as the driving force for forming of the labile C–H bond. As a result,

hydride is eliminated in the form of H₂ confirmed by *in-situ* reduction of acetylene derivatives characterized *via* ¹H and ¹³C NMR spectroscopy.

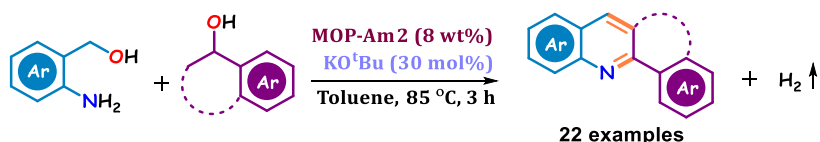


Scheme 3.1 Base mediated anaerobic oxidation of benzyl alcohol over MOP-Am2

Substrate scope study is performed with diverse benzyl alcohols recording prominent conversions. Their corresponding identifications and quantifications are confirmed with GCMS analysis. Carbon balance analysis using modified Walkley-Black method to record the carbon emission to the atmosphere during the protocol suggested it as affordable and environmentally benign.

Chapter 4. Morphologically modified MOP-Am2 as a Reusable Facilitator for Acceptorless Dehydrogenative Annulation of Alcohols

Quinoline, a widely known natural and artificial heterocycle with diverse medicinal and physical properties. Most of the quinoline derivatives are known for their antimalarial, anticancer, anti-Alzheimer's, anti-HIV, and agrochemical activities. But an environmentally benign and sustainable metal-free protocol is yet a challenge. The multicomponent oxidative annulation reaction is chosen to synthesize quinoline derivatives from alcohols (Scheme 4.1) using MOP-Am2. This chapter demonstrates the morphological modification on MOP-Am2 to access better surface interactions that promotes it as metal-free organocatalyst for base mediated multicomponent oxidative annulation reaction without indulging any external oxidant. The reaction is examined to be anaerobic in nature that consists of three reaction steps viz., oxidation of alcohols, imine condensation and cyclization.

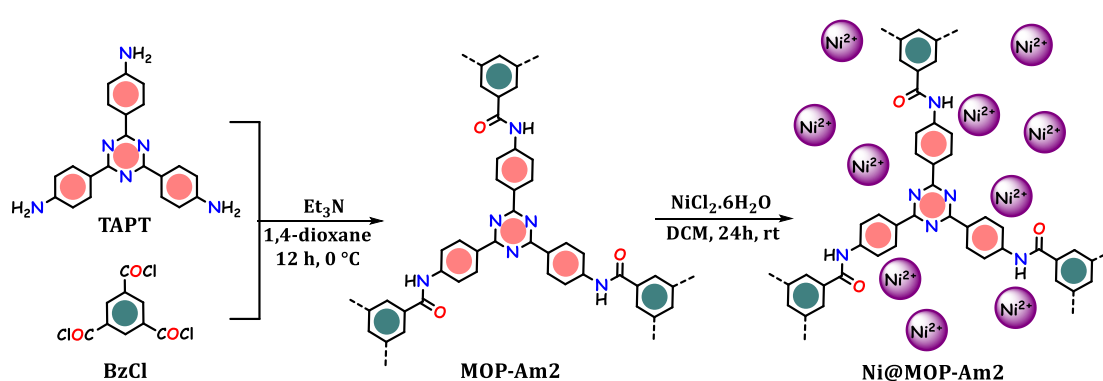


Scheme 4.1 MOP-Am2 promoted dehydrogenative annulations of alcohols to corresponding quinolines

Hydride elimination in the form of H₂ gas is also observed while performing this reaction with diverse substituted alcohols afford good to excellent conversion with excellent catalyst recovery. The product identification and quantification are confirmed through NMR and HRMS analyses. The mechanistic study is performed using ¹H NMR titration method. The green matrices for scale up synthesis are tested to check the industrial affordability.

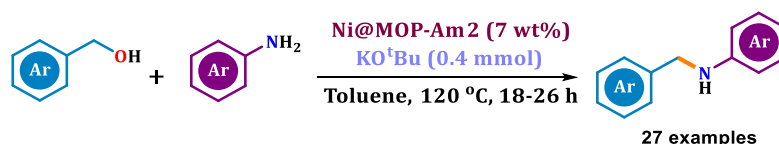
Chapter 5. One-Pot *N*-Alkylation Reaction Over Reusable Ni(II) Decorated MOP-Am2 via Borrowing Hydrogen Strategy

The C–N bond formation reaction is one of the most ubiquitous reactions in organic synthesis that provides direct access to all kinds of amines. Chapter 3 & 4 emphasized the release of H₂ at the end of the reactions. This chapter is an extended study of the previous two chapters where the evolved H₂ during benzyl alcohol oxidation and oxidative annulation is exploited *in-situ* reduction of imine C=N bond (condensed formed from its precursor amines and the *in-situ* oxidized benzyl alcohol) to afford C–N bond formation. NiCl₂.H₂O is intercalated on MOP-Am2 (Scheme 5.1) as capturing agent for the liberated H₂ formed during the alcohol oxidation. The Ni(II) supported polymer i.e., Ni@MOP-Am2 is characterized with various microscopic or spectroscopic analyses. The quantification and identification of the chemical compositions are determined from ICP-AAS, SEM-EDX and XPS analysis. Indeed the BET sorption experiment reveals the incorporation of Ni(II) into the pores leading to the expansion of pore diameter from microporous to mesoporous dimensions.



Scheme 5.1 Schematic representation of the synthesis of Ni(II) doped amide functionalized porous organic polymer (Ni@MOP-Am2)

The catalytic potency of Ni@MOP-Am2 is summarized with base mediated *N*-alkylation reaction from diverse alcohols and amines (Scheme 5.2). The protocol results good to excellent yield and easy recovery of the catalyst. Product quantification and identification are performed with ^1H and ^{13}C NMR and HRMS analyses. Control experiments suggest a three-step mechanism with the alcohol being first oxidized to its corresponding carbonyl compound under anaerobic condition leaving H_2 captured by Ni@MOP-Am2 in the reaction media; followed by the Schiff-base condensation of the carbonyl compound and amine to form $\text{C}=\text{N}$. The third step is the *in-situ* reduction of $\text{C}=\text{N}$ by the H_2 captured on the Ni-catalyst. This process of transferring H_2 is known as “hydrogen autotransfer” or “borrowing hydrogen”. This is one of its first kind where Ni@MOP-Am2 serves as both support catalyst for oxidation of alcohols as well as transporter of H_2 for *in-situ* reduction.



Scheme 5.2 Ni@MOP-Am2 promoted *N*-alkylation of benzyl alcohols with amines via borrowing hydrogenation strategy

Chapter 6. Conclusion and Future Scopes

This chapter represents a summary of all the significant findings from the series of experiments carried out to meet the objectives of the thesis. The presence of hydrogen bond donor and acceptor sites in the designed nitrogen-rich MOP-Am2 promotes it as an activating heterogeneous catalyst for benzhydrazide synthesis from benzamide. The surface electronic environment also accelerates the anaerobic oxidation of alcohols along with the evolution of H_2 . Further the utility of the catalyst is enhanced by incorporating a metal (Ni@MOP-Am2) to trap the liberated H_2 and bring about *N*-alkylation reaction of various amino alcohols. The possibility to trap the liberated H_2 opens a scope for numerous applications in catalytic transformation reactions. The material was exclusively explored for its potential in catalysis emphasizing the role of H-bonding motifs, electron rich units, and its ability to store H_2 . As a future scope, the prospect of exploring the material for photocatalysis, energy storage, conduction, drug delivery, toxic metal ion removal will be a worth; owing to its extensive electron conjugation, *N*-rich center, and amide bonding motifs.

Keywords

Porous organic polymer, Nitrogen enrichment, Morphology modification, Microporous, Mesoporous, Heterogeneous Catalysis, Transamidation, Hydrazides, Ammonia liberation, Anaerobic oxidation, Selective alcohol oxidation, Hydride elimination, Quinolines, Acceptorless dehydrogenation, Annulation, Ni(II) intercalation, Borrowing Hydrogen, N-alkylation, Monoalkylation.