# PREFACE

The supported metal nanocatalysts have garnered high attention in the field of organic transformation reactions. These nanocatalysts offer distinct advantages due to their high surface area, unique electronic properties, required geometry, and enhanced catalytic activity compared to bulk metals. The controlled synthesis of metal nanoparticles on suitable supports, such as metal oxides, polymers, carbon materials, and nitrogen-doped carbon (NC) has paved the way for precise control over particle size, uniform dispersion, and hence its catalytic performance.

In recent years, metal N-doped carbon nanocatalysts (M−N−C@NC), a class of new materials, have been explored for various catalytic applications due to their unique properties. The M−N bond shows a strong electronic interaction between metal and support to improve the catalytic activity and stability of the catalyst. Therefore, in the M−N−C@NC catalyst, the designing of the active catalyst sites and control over the coordination and electronic environments of the active sites are highly challenging to achieve high activity and selectivity for the organic reactions. In fact, the M−N coordination in the M−N−C@NC catalyst offers the ligand environment around the metal center to control its electronic properties.

In addition, the introduction of nitrogen atoms in the carbon lattice generates new electronic states within the band structure. The tunable electronic structure can improve charge transfer and electron mobility, which are critical for catalytic reactions. In the M−N−C@NC catalyst, different types of nitrogen doping (e.g., pyridinic, graphitic, pyrrolic, etc.) can result in distinct electronic configurations, affecting the catalyst's performance. Moreover, nitrogen atoms can act as active sites for catalytic reactions. Depending on their arrangement and the specific type of nitrogen doping, these atoms can serve as binding sites for reactants and intermediates. The presence of active sites enhances the adsorption of reactant molecules and their subsequent conversion to products. In addition, the large number of available active sites improves the catalytic activity for the organic transformation reaction.

In recent years, metal-organic framework (MOF)-derived N-doped carbon catalysts have been demonstrated in the field of organic transformation reactions. The MOF-derived (M−N−C@NC, M = Ni, Co, Fe, Cu, etc.) catalysts offer high catalytic activity and selectivity for the organic reactions. In the M−N−C@NC, the N-doped carbon (NC) plays an important role in the reaction's catalytic activity, because of the strong electronic interaction between the metal and nitrogen site with the carbon support.

In this thesis, we have employed MOF-derived M−N−C@NC catalysts for different types of C−N bond formation reactions. The C−N bond formation reactions are essential in the field of the chemical and pharmaceutical industries. In the literature, mostly noble metal catalysts have been used for the C−N bond formation to produce substituted amines, amides, quinolines, and benzimidazoles. These compounds are highly important in the field of pharmaceutical industries, peptide linkage, insecticide, and many other antibacterial, anticancer, and antimicrobial drug synthesis. However, for large-scale applications, the development of cheap and readily available transition metal-based catalysts is crucial.

In this context, herein, we have explored the use of M−N−C@NC type catalysts for the synthesis of functionalized amines, amides, and benzimidazoles by C−N cross-coupling reactions. In all the cases, the superiority of M−N−C@NC catalysts over the corresponding M@C and M has been established. Further, we have confirmed the improved performance of MOF-derived catalysts compared to the similar type of catalysts prepared from molecular precursors.

In the first chapter, we have discussed the details of the catalyst design for M−N−C@NC catalysts and their applications for different C−N coupling reactions on the basis of literature reports. The advantages of using MOF as the precursor of M−N−C@NC have also been thoroughly explained. The structural and electronic features of the catalysts have been explained by spectroscopic, microscopic, and analytical techniques.

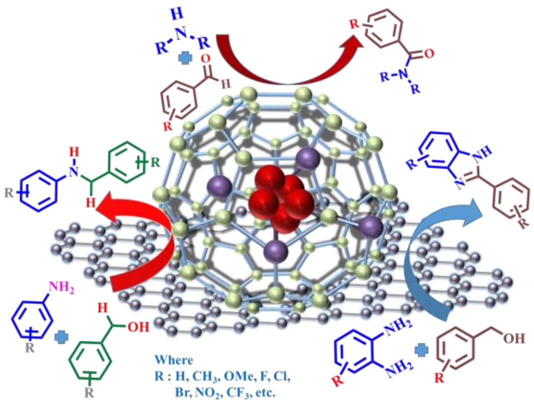

**Figure 1**

In the second chapter, we have reported MOF-derived Co−N−C@NC catalyst for the *N*-alkylation reaction of the secondary amine with the substituted alcohol and aniline (**Figure 1**). The pyrolysis of precursor ZIF-67@C produced Co−N−C@NC catalyst. The Co−N coordination helped to improve the catalyst-support interaction and, hence, enhanced the system's stability. The catalyst showed superior catalytic activity for the selective *N*-alkylation of amines. The catalyst was found to be recyclable five times without the loss of its initial activity.

In the third chapter, we have utilized MOF-derived Co−N−C@NC for the benzimidazole formation by reaction of o-phenylenediamine and substituted alcohols (**Figure 1**). The N-containing heterocyclic benzimidazole compounds are important in anticancer, antibacterial, antitumor, anti-HIV, and anthelmintic-related drugs. The catalyst is recyclable more than five times without loss of activity. The catalyst was synthesized from the precursor ZIF-67. In this chapter, we have improved the catalytic activity of the organic reactions. The doping of N in the carbon matrix and the formation of the Co−N bond manipulate the electron density on the catalytic sites during the reaction. Therefore, the catalytic activity of the Co−N−C@NC was improved.

The fourth chapter describes the MOF-derived Ni−N−C@NC catalyst for the amide bond formation reaction. The pyrolysis of the precursor Ni-ZIF-8 produced Ni−N−C@NC catalyst (**Figure 1**). The low loading of Ni (0.25 atomic %) in Ni−N−C@NC offered excellent turnover number for the amide bond formation reaction. The Ni−N coordination provides strong electronic structure modulation (single-atom catalyst, SAC) to improve the catalytic activity of the amide bond formation reactions.

In the fifth chapter, we have introduced another MOF-derived NiO@Ni Mott-Schottky catalyst for the amide bond formation reaction (**Figure 2**). The NiO@Ni Mott-Schottky catalyst was prepared by the calcination (in the presence of air) of precursor Ni-Ni CP (CP= Coordination polymer). NiO@Ni Mott-Schottky catalyst provided excellent catalytic activity for the amide reaction. This Mott-Schottky catalyst with a semi-metallic NiO core and metallic Ni shell was found to be beneficial in promoting catalytic activity. The NiO@Ni catalyst is recyclable more than five times for the reactions.

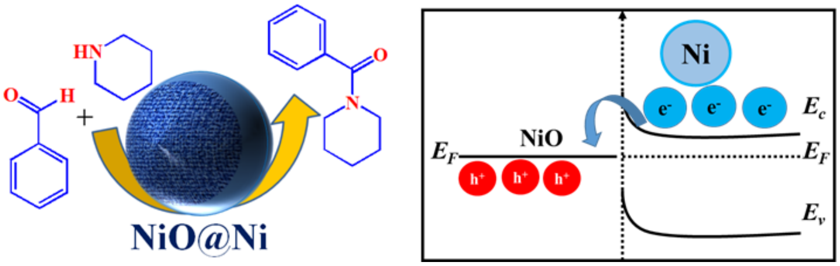

**Figure 2**