

6.1 Summary and Conclusions

In the conclusions, we have explored the use of MOF-derived 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. 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 drugs synthesis. However, for large-scale applications, the development of cheap and readily available transition metal-based catalysts is crucial.

In **chapter 2**, we have explored MOF-derived Co–N–C@NC catalyst for the N-alkylation reaction of the secondary amine with the substituted alcohol and aniline. The pyrolysis of precursor ZIF-67@C produced a 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 **chapter 3**, we have utilized MOF-derived Co–N–C@NC for the benzimidazole formation by reaction of o-phenylenediamine and substituted alcohols. 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, the Co-N-C@NC catalyst provided excellent catalytic activity for the benzimidazole formation. The N-doped carbon and N-doped CNTs support enhanced the catalytic stability and electron transfer in Co-N-C@NC catalyst and also improved the yield of benzimidazole formation. 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.

In **chapter 4**, we have described 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. 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 **chapter 5**, we have introduced another MOF-derived NiO@Ni Mott-Schottky catalyst for the amide bond formation reaction. 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. The concept of the semiconductor nature of metal oxide and metals to form Mott-Schottky heterojunctions has been proposed and demonstrated as a viable strategy to increase catalytic activity. This Mott-Schottky catalyst with a semi-metallic NiO core and metallic Ni shell was found to be beneficial to promote catalytic activity. The NiO@Ni catalyst is recyclable more than five times for the reactions.

6.2. Future scope and perspective

In this context, herein, we have explored the use of Co–N–C@NC, Ni–N–C@NC and NiO@Ni 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. The thesis work can be further extended to achieve the following points:

- (i) In the M–N–C@NC catalyst, we can change electronic modulation by introducing different heteroatoms (N, P, O, S, and Se) within the carbon lattice's band structure. These modifications enable the tuning of the electronic structure, which is essential for enhancing charge transfer and electron mobility in the catalytic reactions. Improved charge transfer and electron mobility of the catalyst contribute to the overall efficiency of the catalyst.
- (ii) In the M–N–C@NC catalyst different types of nitrogen doping, such as pyridinic, graphitic, and pyrrolic, lead to distinct electronic configurations. The M–N bond is central to their functionality and plays a crucial role in optimizing performance. These configurations have a direct impact on the catalyst performance, making it essential to carefully choose the type of nitrogen doping for specific applications.
- (iii) The heteroatoms introduced into the carbon lattice can also offer active sites for the catalytic reactions. Depending on their arrangement and the specific type of nitrogen doping, these heteroatoms can serve as binding sites for reactants and intermediates. This enhances the adsorption of reactant molecules onto the catalyst surface and facilitates their subsequent conversion into products.
- (iv) The presence of a large number of available active sites, created through nitrogen doping, contributes to higher catalytic activity for organic transformation reactions.