

1. Introduction

1.1. History of catalysis

The use of catalyst for a thermodynamically favorable reaction offers an alternative pathway to fasten the rate of the reaction. In addition, the required selectivity of product(s) can be achieved by the use of a suitable catalyst. Therefore, the use of catalysts significantly reduces production costs and promotes the development of environmentally friendly chemical techniques. In the 21st century, modern life largely depends on the catalytic process, including the production of petroleum, fine chemicals, water, food products, and pharmaceuticals. Growing environmental, health, and global warming issues present a new challenge to our society to use sustainable development. The field of catalysis is also facing these challenges, and new methods are emerging in response to the demand.^[1]

In the year 1794, Elizabeth Fulhame introduced the idea of catalysis.^[2] Later, in 1811, the application of a catalyst was shown to produce glucose from starch. The term "catalysis" was first used in the year 1835 by Jöns Jakob Berzelius.^[1] The "catalysis" word originates from two different Greek words: kata, which means "down," and lyein, which means "loosen". In 1894, Wilhelm Ostwald concurrently proposed the definition of a catalyst: "*A catalyst is a substance that accelerates the rate of chemical reactions by reducing its activation energy without affecting the end products.*"^[3] The term "catalyst" is defined by the IUPAC as "*A substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction; the process is called catalysis.*"^[4] Later, eminent scientists including the Nobel laureates Haber (1918), Natta and Ziegler (1963), Knowles, Noyori, and Sharpless (2001), and Ertl (2007), and Richard, Negishi and Suzuki (2010) and Benjamin and Macmillan (2021) provided a significant contribution to the field of catalysis.^{[5],[6]}

1.2. Factor related to catalysis

1.2.1. Thermodynamics and kinetics of catalytic reaction

In a catalytic reaction, reactant molecules and catalysts initially interact, forming an intermediate via a new pathway. This ultimately leads to the production of products while leaving the catalysts unchanged at the end of the reaction.^[7] Catalysts influence only the kinetics of the reaction, without altering its thermodynamics. The thermodynamics of a catalyzed reaction remain the same as in a non-catalyzed reaction, *i.e.*, a catalyst cannot make a thermodynamically infeasible reaction feasible.^{[8],[9]} The rate of a catalytic reaction can be described by the Arrhenius equation, where an increase in the temperature leads to the decrease in activation energy by improving the reaction rate (Figure 1.1). Catalyzed reactions follow an alternative pathway that has a lower energy profile compared to un-catalyzed reactions. This pathway involves adsorption, activation, reaction, desorption of products, and leaves the catalyst untouched.^[10] Catalyzed reactions often involve multiple transition states, leading to significantly lower activation energy and faster reaction rates.^{[11],[12],[13]}

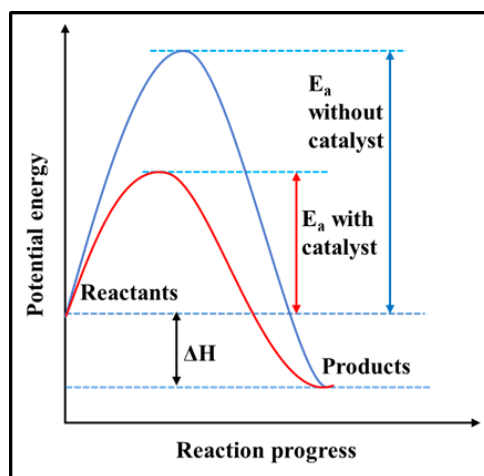


Figure 1.1. Potential energy diagram of a catalyzed and un-catalyzed reaction.

1.2.2. Turn over number and turn over frequency

The activity of a catalyst is measured by the turnover number (TON) and turn over frequency (TOF). The turnover number is defined by the number of moles of substrate molecules transforms into the product by one mole of the catalyst. The turnover frequency of the catalyst is measured by the turnover number of the catalytic cycle with respect to the time per active site.^[14]

$$\text{TON} = \frac{\text{Number of moles of product}}{\text{Number of moles of catalyst}}$$

$$\text{TOF} = \frac{\text{Number of moles of product}}{(\text{Number of moles of catalyst}) \times (\text{time})}$$

1.2.3. Selectivity in product formation

The selectivity of a catalyst refers to its ability to favor a specific reaction or product when multiple possible reactions or product formation are feasible. It reflects the degree to which a catalyst can control or direct a chemical reaction towards a desired outcome while minimizing the formation of unwanted byproducts. Selectivity is a crucial factor in catalysis, as it can significantly impact the efficiency, yield, and atom economy of a chemical process. In the chemical reaction different types of selectivity such as enantioselectivity, regioselectivity, chemoselectivity and stereoselectivity can be achieved to obtain the desired product.^{[15],[16]}

1.3. Classification of the catalysis process

Catalysts are frequently categorized based on their physical condition, structures, composition, application area, and the types of processes of reaction catalyzed by them. Homogeneous and heterogeneous catalysis are the two basic subcategories of catalysis.^{[17],[18]}

1.3.1. Homogeneous catalysts

In homogeneous catalysis, the catalysts and substrates are present in the same phase. The homogeneous catalysts not only improve the efficiency of the reaction, they also affect the regio-, chemo-, and stereoselectivity of the reaction.^[19] Another important feature of homogeneous catalysts is the ease of investigation by means of conventional spectroscopic techniques.^{[20],[21]}

Nonetheless, homogeneous catalysts have drawbacks, favoring heterogeneous systems in industrial applications. The primary limitation is the challenge of catalyst separation and recycling, especially with costly metals like rhodium or palladium.

1.3.2. Heterogeneous catalysts

Heterogeneous catalysis has gained prominence due to its capacity for easy separation and recycling of materials from reaction products, thereby reducing production costs for the industrial applications.^[22] These systems involve catalysts and substrates in different phases, such as solid-liquid, solid-gas with reactions occurring on the catalyst surface.^{[23],[12]}

Heterogeneous catalysts are often designed to provide a large surface area, facilitating enhanced interaction between substrate molecules and the catalytic system. This leads to improved product yield, selectivity, and reaction time.^[24] Typically, heterogeneous catalysts comprise of metals, metal oxides, metal salts, metals integrated into supporting matrices (e.g., alumina, silica, N-doped carbon), and ion exchangers. Transition metals like Pt, Ni, Pd, Co, and Fe are particularly effective and find extensive use in the pharmaceutical and chemical industries.^{[25],[26]}

Materials like silica, alumina, carbon, and graphene-based substances are preferred for solid-supported catalysts due to their mechanical and thermal stability. These supported

catalysts offer more active sites and easier separation, promoting cost-effectiveness and environmental sustainability.^[27]

1.4. Nanocatalysis

Nanocatalysis have remarkable scientific and commercial significance due to their unique properties compared to bulk materials, featuring a higher surface-to-volume ratio that increases the number of active sites per unit area.^[28] Nanocatalysts have been applied for a wide range of selective organic transformation reactions delivering excellent product yield while reducing waste generation, making them environmentally friendly.^[29]

Transition metals, such as palladium, silver, gold, and ruthenium-based nanocatalysts find widespread use in reactions like C-C homo-coupling, C-C cross-coupling, carbon-heteroatom coupling, hydrogenation, oxidation, amination, reduction, and esterification.^{[30],[31],[32]} Meeting the demand for inexpensive transition metal-based nanocatalysts is crucial for organic transformation reactions.^{[33],[34]} Nanocatalysts derived from cobalt, nickel, iron, zinc, and copper offer cost-effective solutions for applications like oxidation, reduction, hydrogenation, and coupling reactions.^{[35],[36]}

1.5. Supported nanocatalyst

Supported nanocatalysts are a class of advanced materials that play a crucial role in catalyzing chemical reactions.^[37] They consist of nanoparticles of catalytically active centers dispersed on a solid support. The combination of nanoscale particles with a stable support structure provides several advantages over conventional catalysts (**Figure 1.2**).^{[38],[39]} The support ensures the stability and durability of the nanoparticles during the reaction, preventing aggregation or deactivation.^[40] The supported material offers distinct properties that can influence the catalytic behavior and efficiency of the heterogeneous nanocatalyst.^[41] The

choice of the support is crucial in designing supported catalyst as it can significantly influence the overall catalytic performance. Some common support materials include:^[42]

Metal oxides: Metal oxides like alumina (Al_2O_3),^[43] silica (SiO_2), and titania (TiO_2)^[25] are widely used as support materials due to their high surface area, thermal stability, and compatibility with many catalytic reactions (**Figure 1.2a**).^{[44],[45],[46]}

Zeolites: Zeolites are porous aluminosilicate materials with well-defined pore structures. They offer shape selectivity, allowing only specific reactants to access the active sites within the catalyst (**Figure 1.2b**).^[47]

Carbon-based materials: Carbon materials like activated carbon and carbon nanotubes can be used as the support for the loading of certain catalysts.^[48] They are particularly useful for catalytic reactions involving gaseous or volatile reactants (**Figure 1.2c**).^{[49],[42]}

N-doped carbon (NC): The carbon support can be further modified by the introduction of nitrogen into its lattices.^[50] Nitrogen doping enhances the catalytic activity by introducing new active sites and changing the electronic properties of the material. The introduction of nitrogen also facilitates better interaction between the catalyst and reactants (**Figure 1.2d**).^{[51],[52]}

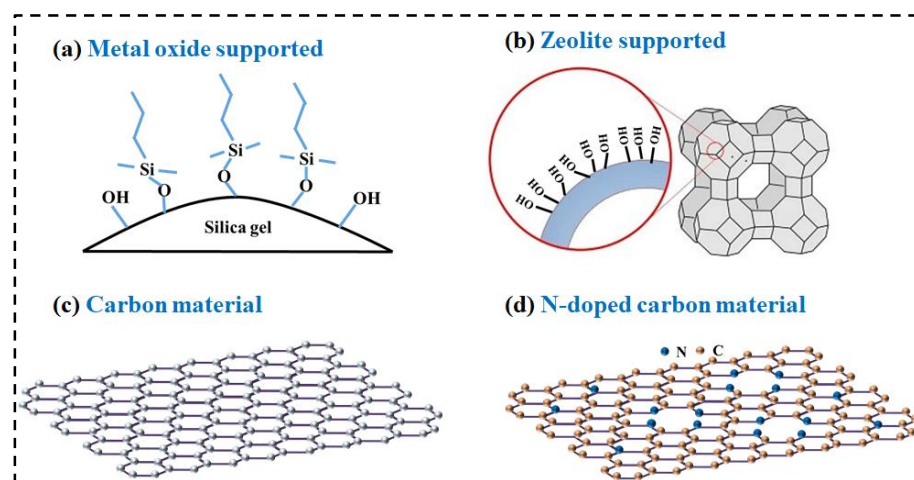


Figure 1.2. Different type of solid-supported materials.

The immobilization of the catalyst on the support can be achieved through various techniques, including impregnation, precipitation, sol-gel, and deposition-precipitation. The choice of method depends on the nature of the catalyst and the desired properties of the supported catalyst.^[53] Supported catalysts find extensive applications in various industries, such as petrochemicals, environmental protection, pharmaceuticals, and fine chemicals manufacturing.^{[50],[54]} They are used in a wide range of reactions, including hydrogenation, oxidation, reduction, coupling, polymerization, and many others.^[55]

Ongoing research and development in this area aim to further optimize catalytic systems for enhanced performance and wider industrial applications. The N-doped carbon is one of the best heterogeneous catalysts used in various fields such as organic transformation, electrocatalyst, and other fields.^[56]

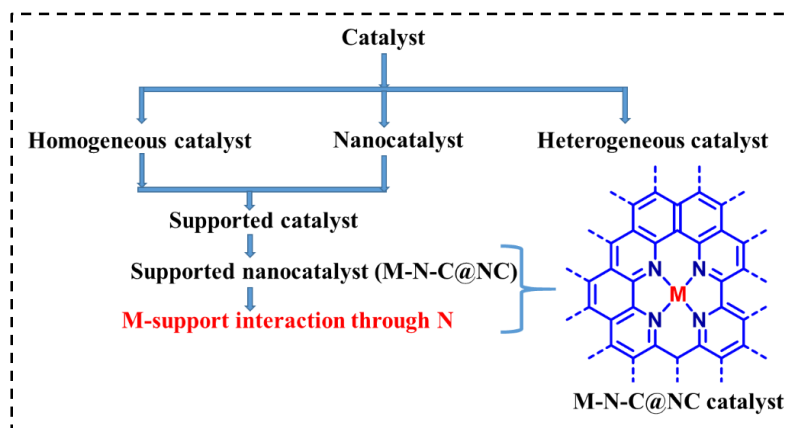


Figure 1.3. The graphical chart of the different type of catalyst.

1.6. M-N-C@NC type catalyst

Recently, the metal nanoparticles M-N-C@NC (M= Co, Ni, Fe, Cu, Zn, etc.) based catalytic systems have gained more attention because of their superior activity and stability compared to the other traditional ligated molecular catalysts.^[57] The M-N-C@NC type catalysts have

demonstrated successful applications in the field of electrocatalysis and organic reactions.^{[58],[59]} The designing of these catalysts require the choice of a suitable metal source, solid support, and solvent. Among the well-known solid supports (e.g., silica, graphene, porous carbon and carbon nanotubes), modified nitrogen-doped graphitic carbon (NC) materials have been considered as interesting supporting materials for heterogeneous catalyst.^[60] This preference is attributed to their improved chemical and electronic properties. Furthermore, the presence of electronegative nitrogen as a foundational site facilitates an efficient enrichment of protons/positive charges on the surface of NC materials.^[51]

The strong electronic interaction between the metal and support (N-doped carbon) enhances catalytic activity and stability.^{[61],[62]} However, achieving high activity and selectivity in these catalysts is a significant challenge. This stems from the need to carefully design the active catalyst sites and exert control over the coordination and electronic environments of these sites. The M-N coordination within the M-N-C@NC catalyst provides a ligand environment around the metal center, allowing for precise tuning of its electronic properties (**Figure 1.4a-b**).^{[60],[63][64]}

Electronic structure modulation: Nitrogen doping introduces new electronic states 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 (**Figure 1.4c-i**).^{[65],[66],[67]}

Types of nitrogen doping: In the M-N-C@NC catalyst different types of nitrogen doping, such as pyridinic, graphitic, and pyrrolic, lead to distinct electronic configurations (**Figure 1.4c-iv**). 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.^{[68],[69]}

Active sites for catalysis: Nitrogen atoms 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 nitrogen atoms 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 (**Figure 1.4c-ii, iii**).^[70]

Improved catalytic activity: The presence of a large number of available active sites, created through nitrogen doping, contributes to higher catalytic activity for organic transformation reactions. This means that the catalyst can efficiently promote the conversion of reactants into desired products, making it a valuable tool in various catalytic applications.^{[71],[67]}

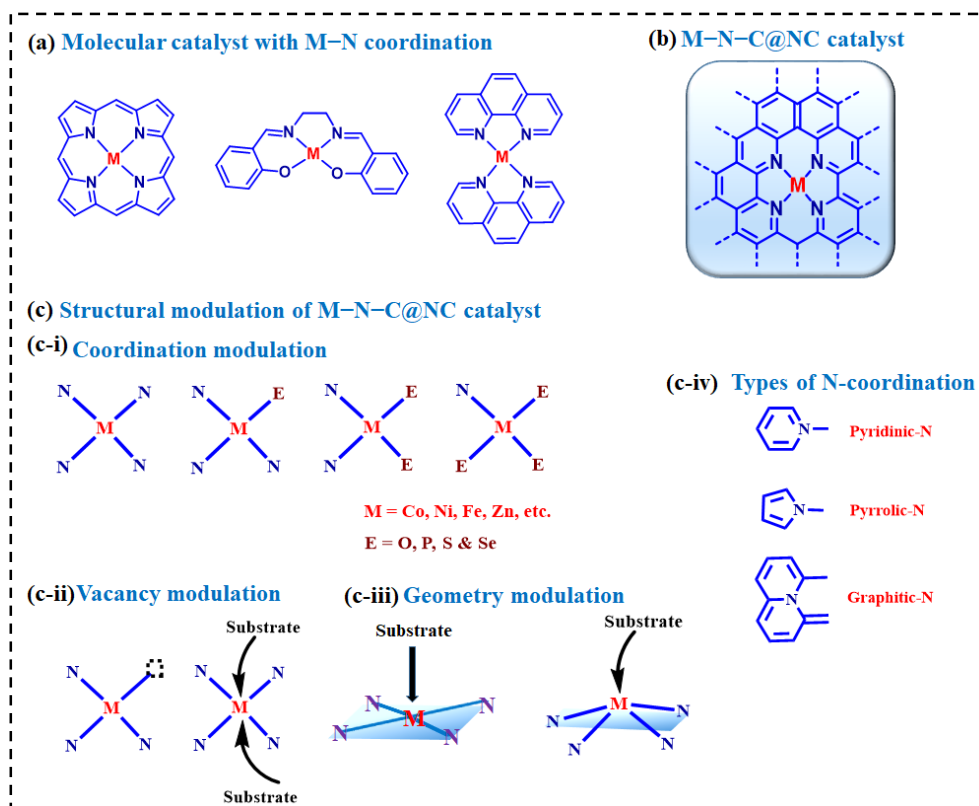


Figure 1.4. Structural modulation of M-N-C@NC catalyst.

As a result, the unique properties of M–N–C@NC catalyst have been explored for organic transformation reactions (Figure 1.5).^[72] The M–N–C@NC nanocatalysts have been produced by two methods: (i) Metal salt, nitrogen source, and solid support are pyrolyzed in the inert atmosphere to obtain M–N–C@NC nanocatalysts or (ii) molecular complexes (such as metal-porphyrin, salen, phenanthroline, or bipyridine complexes) have been pyrolyzed in the inert atmosphere to produce M–N–C@NC nanocatalysts.^[73] In the M–N–C@NC catalyst, the incorporated N atoms on the carbon matrix have been provided synergetic effects with non-noble metal (Co, Ni, Fe, and Cu) nanoparticles for catalytic applications.^{[59],[74]} As the M–N–C@NC were embedded in the porous NC framework; the corrosion and leaching of metal NPs can be avoided. More importantly, the strong interaction between the metal core and NC shell affected the electronic structures to improve the activity and selectivity of different organic reactions like transfer hydrogenation, oxidation, coupling and hydrogen borrowing reactions (Figure 1.5).^{[75],[76]}

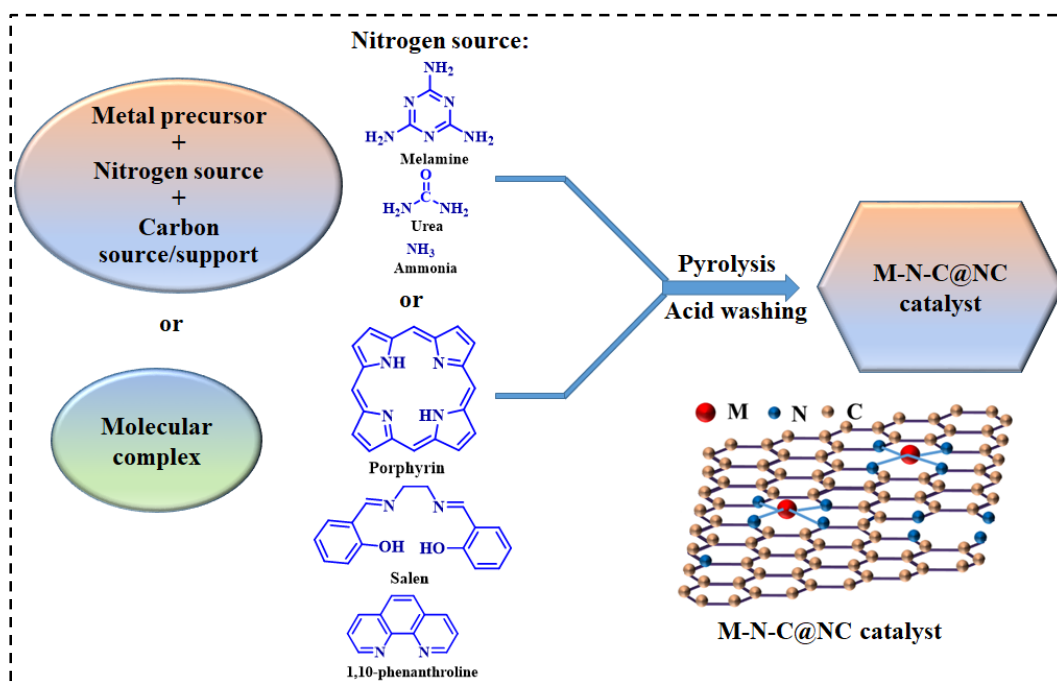


Figure 1.5. M–N–C@NC type catalyst with different N-containing ligands.

1.7. Metal-organic framework (MOF)-derived M–N–C@NC catalyst

1.7.1. Metal-organic framework (MOF) as the precursor

MOFs are porous crystalline materials that are formed through the combination of metal ions and organic connectors. The versatility in the building blocks has led to the formation of a wide range of MOFs with tunable properties.^{[77],[78]} MOFs like zeolitic imidazolate frameworks (ZIFs), and Prussian blue analogue (PBA), etc. have been successfully synthesized using various metal ions (**Figure 1.6**). The synthesis of MOF is facile and robust and it can be synthesized in large-scale by methods like solvothermal, hydrothermal, microwave heating, etc.^{[79],[80a-b],[81]}

1.7.2. Zeolitic imidazolate framework as the precursor of the M–N–C@NC catalyst

Zeolitic imidazolate frameworks (ZIFs) are a subclass of MOFs that have gained significant attention in recent years due to their unique properties and applications (**Figure 1.6**).^[82] ZIFs are composed of metal ions that are tetrahedrally coordinated with organic linker-imidazole.^{[83],[84]} These organic linkers play a crucial role in defining the structure of the framework and contribute to its porosity. The imidazole ligand in the ZIF provides the template for N-doped carbon during pyrolysis. In addition, their simple synthetic method, high nitrogen content, adjustable pore size, and morphology make them suitable precursors for the M–N–C@NC catalysts.^[85]

The ZIF-derived M–N–C@NC catalysts have found extensive use in electrocatalysis and energy storage.^[82] However, their application in organic transformations is still in its early stages. Only a limited number of studies have been reported for the organic transformations (oxidation, hydrogenation, and coupling reactions) using ZIF-derived M–N–C@NC as catalyst.^{[72],[52],[86]}

1.8. Catalytic reaction with M–N–C@NC

The MOFs-derived M–N–C@NC nanocatalysts have been used in the field of electrocatalysis, photocatalyst, sensor, adsorption, and dye degradation; due to their excellent catalytic properties (Figure 1.7).^{[87],[85],[88]} In addition, the M–N–C@NC catalysts have proceeded in different fields of organic transformation reactions.^{[89],[90]} The catalyst offered excellent stability, and activity and the catalyst can be easily separated from the reaction mixture and reused multiple times with a minimum loss of activity and selectivity.^{[91],[89]}

In the recent years, the 3d-transition metal MOF-derived (3d transition metal = Co, Ni, Cu, and Fe) M–N–C@NC -type catalysts have been used for oxidation, reduction, coupling reaction, etc.^{[89],[92],[93]} These M–N–C@NC-type catalysts produce high catalytic activity and selectivity for the organic transformation reactions (Figure 1.7).^{[56],[94a-b]}

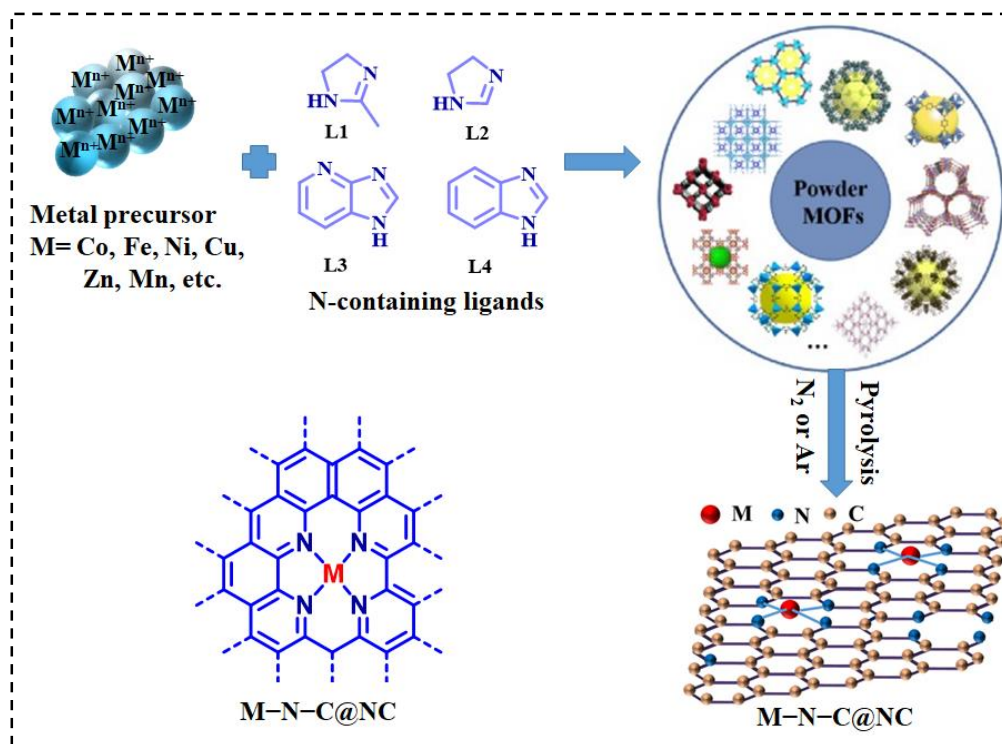


Figure 1.6. Synthetic strategy for the preparation of different types of MOF-derived M–N–C@NC catalysts.

For example, Li and co-workers conducted a series of investigations focused on employing MOF-derived catalysts for oxidation reactions. They reported the development of Co@NC for the esterification reaction using alcohol precursor in methanol.^[95] H. Jiang and coworkers explored the potential of the Co–CoO@N-doped carbon catalyst for the oxidation of alcohols into esters.^[96] Hui et al. reported the CoZn-ZIF-derived Co/CoO on N-doped carbon for the epoxidation of styrene.^[97] Further, Co@NC catalyst was demonstrated for the benzyl alcohol oxidation reaction and the catalyst showed exceptional reactivity for esterification reactions.^[98]

MOFs-derived M–N–C@NC catalysts were also found to be efficient for the reduction reactions. Li and co-workers reported MOF-derived Co@C–N for transfer hydrogenation reactions. They prepared the Co@C–N-900-15 h catalyst through the pyrolysis of a Co-containing MOF material known as [Co(bdc)(dabco)_{0.5}].2DMF.0.2H₂O.^{[93],[99]} Subsequently, Liu and coworkers developed MOF-derived Co@CN-900 for the chemoselective transfer hydrogenation of cinnamaldehyde.^[100]

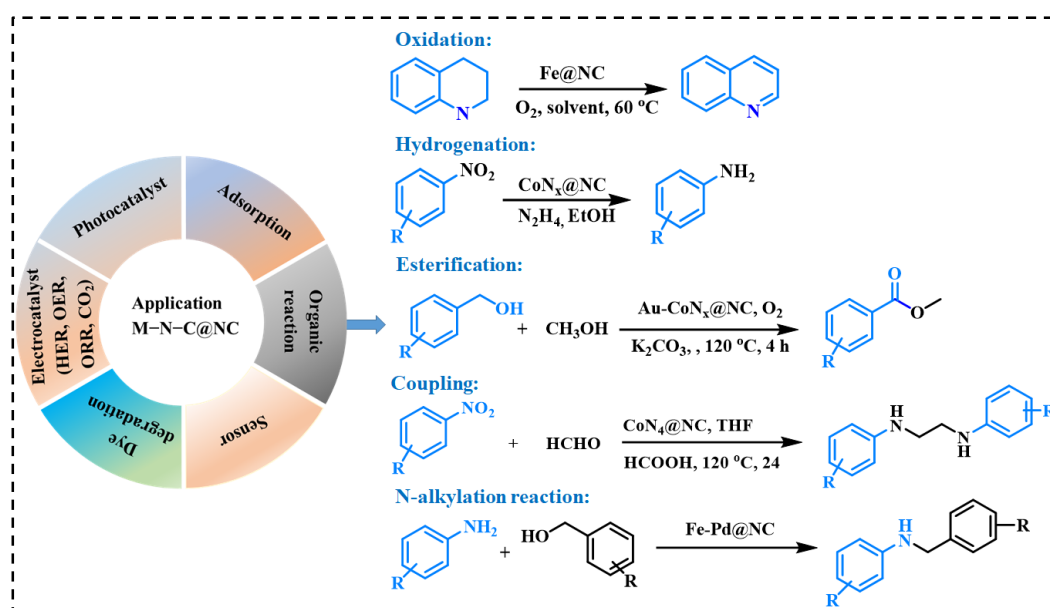


Figure 1.7. Different types of organic reactions are carried out using M–N–C@NC catalysts.

Beller, Jagadeesh, and coworkers reported Co_3O_4 - and Co-nanoparticles enclosed in a graphitic carbon shell and supported on carbon. This was achieved through a template synthesis approach using a cobalt-terephthalic acid MOF on carbon.^[101] The resulting catalyst demonstrated remarkable activity in hydrogenating various functionalized benzyl nitriles into their primary amines and it was also effective for the hydrogenation of heterocyclic nitriles and aliphatic nitriles into the primary amines.^[101] Yao and colleagues devolved MOF-derived Cu/SiO_2 for the hydrogenation of dimethyl oxalate to yield ethylene glycol.^[102]

Further, Wang and co-workers synthesized Pd-NPs supported with MOF-derived N-doped carbon for the Suzuki coupling reactions.^[103] Zheng and co-workers developed the $\text{Cu}/\text{Cu}_2\text{O}$ -rGO for cross-coupling of phenylacetylene with iodobenzene to obtain the 1,2-diphenylethyne product through the Sonogashira reaction.^[104] The transition metal (Pd) based heterogeneous catalyst mainly used in the C–C coupling and C–N coupling reactions.^{[105],[106]}

1.9. Importance of amines and amides

1.9.1. Importance of amines

Nitrogen-containing organic moieties, often referred to as "amines" or "amino groups," are crucial building blocks in various biologically active compounds and have significant applications across multiple fields of chemistry (**Figure 1.8a**).^[107] The primary or secondary amine bond formation reaction play a crucial role in the development of chemicals, pharmaceuticals, agrochemicals, and fine chemicals industries.^{[91],[108]} The amines were synthesized by different methods like hydroaminations, nucleophilic substitutions, Buchwald-Hartwig, Ullmann reactions, etc.^[109]

Further, biologically active N-containing heterocyclic benzimidazole compounds were produced by the C-N coupling reactions.^{[110],[111]} The benzimidazole compounds are used as

drugs for their anticancer, antibacterial, antitumor, anti-HIV and anthelmintic-related properties (**Figure 1.8b**).^{[112],[113]}

The reaction mechanism of the amine and benzimidazole formation follows two pathways: (i) reductive route^[114] or (ii) hydrogen borrowing route.^[115] In the reductive amination process, reducing agent source such as sodium borohydride, hydrogen gas, ammonium formate, etc. has been added during the reaction. As a result, reductive amination produces high cost with the formation of side product or waste.^[116]

The *N*-alkylation of amines following the hydrogen borrowing mechanism is greener and reduces the cost of the products.^[117] The hydrogen borrowing reaction was discovered by Winans and Adkins (1932) using heterogeneous nickel catalyst.^[118] The first homogeneous catalyst was introduced in 1981 by Grigg, Watanabe, and co-workers. The *N*-alkylation of amine with alcohols has emerged as a sustainable protocol as the alcohols are inexpensive, have low toxicity, and produce only water as the by-product during the reaction.^[119]

The various MOF-derived catalysts have been used for the *N*-alkylation reaction of amines with alcohols. Shimizu and coworkers (2013) studied the production of amine with the nickel nanoparticles embedded on various supports.^[120] The heterogeneous Ni/ θ -Al₂O₃ catalyst was obtained by in situ H₂-reduction of NiO/ θ -Al₂O₃ and showed the excellent activity for the *N*-alkylation of amine under the given reaction conditions. Further, they extended the reaction for the formation of primary and secondary amines by the reaction of ammonia and alcohols.^[121]

In 2021, Ramon and co-workers used a heterogeneous catalyst to explore the iron-catalyzed *N*-alkylation of amine following the hydrogen borrowing mechanism.^[122] G. P. Lu and coworkers (2021) designed the Fe single atom catalyst (Fe-SAC) on N, S doped catalyst

via the pyrolysis of the Fe-ZIF precursor materials for the *N*-alkylation reaction of amine.^[107]

Chun and coworkers (2020) performed the *N*-alkylation of amine with Fe-Pd@NC bimetallic catalyst via a hydrogen borrowing process.^[123]

Beller and Jagadesh, and coworkers developed a Co@NC nanocatalyst and it used for the alkylation of amines via hydrogen borrowing methods.^[124] The Co/CeO₂-NC catalyst also showed excellent activity for the *N*-alkylation of amines.^[125]

1.9.2. Importance of amides

Amide bonds are crucial linkages in organic chemistry, and they play a fundamental role in various fields, including organic synthesis and medicinal chemistry. These bonds are essential components of proteins, peptides, and other biologically active molecules.^[126] As a result, developing efficient methods for forming amide bonds is of great importance to the researchers in academia and industry (**Figure 1.8c**).^{[127],[128]}

Advances in amide bond synthesis have led to the discovery of milder and more selective methods, allowing for the incorporation of amide bonds under a variety of reaction conditions. These advances have been critical in enabling the efficient synthesis of peptides, which are essential in fields such as drug development, biotechnology, and chemical biology.^{[129],[130]}

In recent years, researchers have also focused on the development of new catalytic methods for amide bond formation, including transition metal-catalyzed and organocatalytic reactions. These methods offer increased atom economy and selectivity, contributing to the advancement of greener and more sustainable synthetic strategies.^{[131],[132]} Metal-catalyzed approaches have indeed emerged as valuable alternatives to traditional methods for amide bond formation in recent years. These approaches offer several advantages that contribute to more efficient and sustainable synthesis processes.^[133]

In the past few decades, the transition metal-based (Pd, Ru, Ir, etc.) catalyst provide better yield and selectivity for the amide bond formation reaction.^{[134],[135]} These metal-catalyzed reaction faces some drawback such as high-cost, requirement of cocatalyst, and poor recyclability. In recent years, heterogeneous 3d transition metal catalysts play a crucial role in the amide bond formation reaction.^{[136],[128]}

Oxidative amidation has emerged as a powerful strategy for the direct conversion of alcohols into amides using an oxidizing agent and a nitrogen source. This approach can provide rapid access to amide derivatives from readily available starting materials.

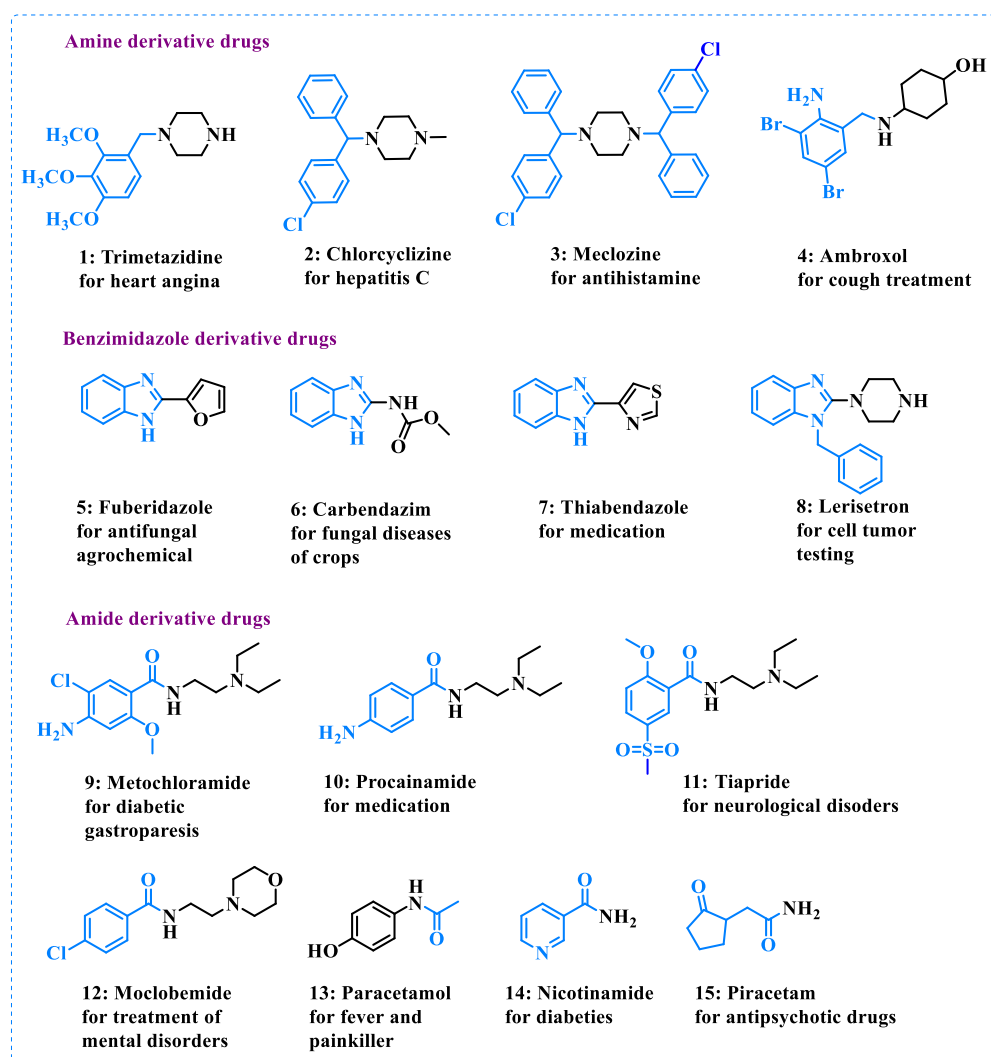


Figure 1.8. Examples of the different type drugs with amine and amide moieties.

1.10. Objectives of the thesis

The main objective of this thesis is to develop a facile method for the synthesis of M-N-C@NC catalysts using metal-organic frameworks (MOFs) as the precursors. In this respect, the catalyst design, understanding the electronic structure of the active catalyst, and the application of the catalysts for the organic transformation reaction have been studied. We have utilized M-N-C@NC catalysts for the reactions like *N*-alkylation of amine, formation of benzimidazoles and amide bonds (Figure 1.8). Optimization of the reaction conditions has been performed to achieve high yields and selectivity. In addition, the catalyst was recovered from the reaction mixture and recycled for multiple cycles.

This thesis contains six chapters. The brief description of the chapters is given below.

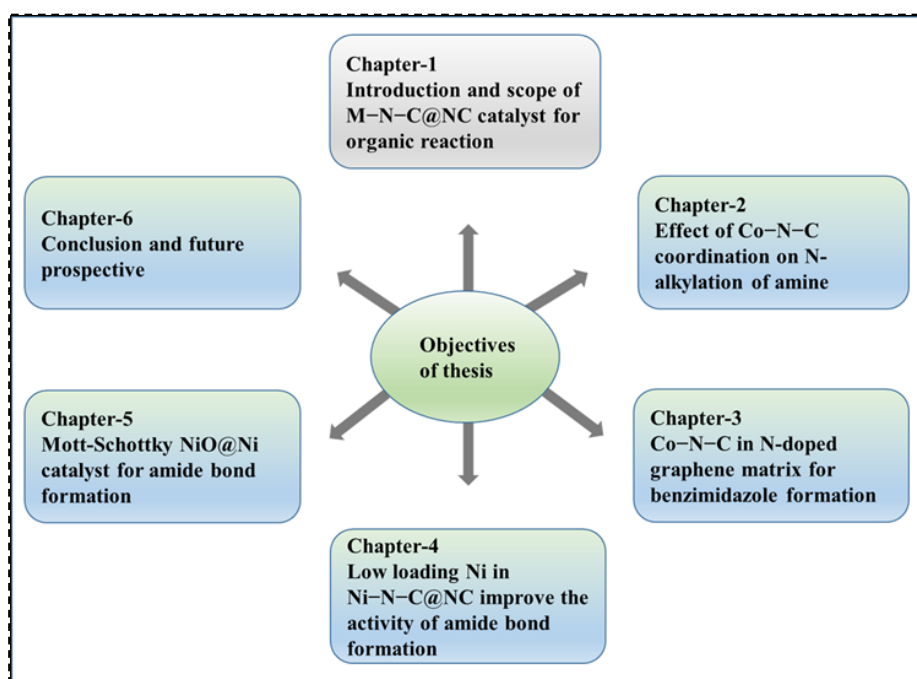


Figure 1.9. Diagram showing the chapter-wise specific objectives of the thesis.

Chapter-2: In the second chapter, 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 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 for five times without the loss of its initial activity.

Chapter-3: In the third chapter, we have shown the use of MOF-derived Co–N–C@NC catalyst for the benzimidazole formation by reaction *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, 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.

Chapter-4: 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. 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.

Chapter-5: In the fifth chapter, 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 PBA (PBA=

Prussian blue analogue). 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 to promote catalytic activity. The NiO@Ni catalyst are recyclable more than five times for the reactions.

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