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Heterogeneous Metal-catalyzed C-H Functionalization Reactions: The Environmentally Benign Pathway for Industrial Applications

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Abstract

In the last few decades extensive attention has been given to the advancement of metal-catalysed C-H functionalization. Despite the steady progress in the process, atom economical techniques are being explored using varieties of metal catalysts. Many of these metal-based catalytic systems have the major drawback of limited catalyst recyclability. Contrary to the formerly mentioned catalytic system, heterogenous polymer and nanoparticle-based catalysts have shown promising results. These heterogenous catalysts are largely comprising of transition metal complexes and nanoparticles embedded within a polymer matrix. They provide a variety of advantages over homogeneous metal-based catalysts, such as easily available raw materials, ease of separation, thereby enhancing recyclability, etc. The focus on the heterogenous nanoparticle catalytic systems for C-H functionalization reactions is due to their unique size-dependent properties, which have a direct impact on the process selectivity. Herein, a comprehensive overview on the potential for greener and more sustainable C-H functionalization processes using heterogeneous polymer and nanoparticle catalysts is provided. In addition, selective functionalization, improving properties and sustainability in chemical processes of such heterogeneous catalytic systems are assessed. These lead to the conversion of the "unactivated" C(sp^2)-H and C(sp^3)-H bonds found in easily accessible hydrocarbons into useful compounds, thereby providing environmentally friendly methods for industrial applications in pharmaceuticals, agrochemicals, materials science, and in the formation of fine chemicals.

Keywords

Recyclable catalyst, Heterogeneous catalysis, Metal nanoparticles, Metal organic framework, C-H activation reaction, C-H functionalization

Introduction

Over the last few years, significant emphasis has been given to the direct functionalization of inactive C-H bonds, which tend to act as passive functional groups. The direct functionalization method has received significant interest when compared to the traditional cross coupling method due to use of pre-functionalized substrates, which ultimately offers a cost-effective and environment-friendly organic synthesis technique. Quite a few useful transition-metal catalysts have been developed for activation of C–H bond, [1-6] which have aided in streamlining organic synthesis. Despite the well-established stoichiometric and catalytic methods for synthesizing key molecules through the cross-coupling reactions [7-11], these classes of reactions require specific substrates and lead to subsequent unavoidable formation of halides, salts, borates, etc. which are undesirable by products. Consequently, C-H activation/functionalization reactions approach a more economical and effective alternative to cross-coupling reactions. Due to these benefits over the conventional organic transformation techniques, the C-H

functionalization reactions have found increasing number of applications in the field of pharmaceutical, agrochemicals, and industrial products as well as in the synthesis of naturally occurring compounds. In recent decades, homogenous catalysts have gained significant application in the manufacturing of fine chemicals and active pharmaceutical ingredients [12]. These synthetic methods involving homogenous catalysts ensure that the reactions proceed with high efficiency and good yield along with ensuring minimal production of unwanted by-products. However, the usage of transition metals as homogeneous catalysts or catalyst precursors is often associated with the limited availability of the specific transition metals. Thus, to mitigate all these disadvantages, a different strategy must be followed in which active complex is immobilized by grafting the ligand onto a solid support. This approach leads to the generation of recyclable heterogeneous catalysts as well as well-defined active sites. Since nanoparticle solid supports are beneficial, inorganic materials are utilized due to the various advantages like minimal swelling as well as high chemical, thermal and mechanical stability over organic matrices. This methodology would lead to high catalytic activity, stability & selectivity for C-H functionalization reactions. The interaction between the active catalysts and the supports can be either through chemical bonds or van der Waals forces. The lifespan and stability of the catalysts are enhanced by these bonds. For instance, metal alloys, metal oxides and metal nanoparticles that are dispersed over oxide support with high surface area, such as zirconia silica and alumina, form the common supports for the formation of heterogeneous catalysts. Unique properties of metal nanoparticles (MNPs) such as chemical properties and tunable electronic, specific shape, composition, size, and high surface-to-volume ratio were discovered. These MNPs effectively worked as efficient catalytic systems due to the above-mentioned properties and stimulate a variety of transformations including the C-H functionalization reaction [13] through the C-heteroatom or C-C coupling reactions via moderate reaction conditions. Other organic transformations like reduction [14], oxidation [15] and C-C coupling reactions [16] are also facilitated by MNPs. In this regard, it is noteworthy that the formation of porous organic polymers through a bottom-up approach provides a straightforward and direct synthetic route for heterogeneous catalysts. The bottom-up approach offers potentially high catalytic efficiency since it enables an extremely high catalyst loading onto high surface area. In addition, the porous organic polymers would have improved catalytic reusability which could ultimately address the economic issues allied with the solid catalysts in contrast to the reduced recyclability of homogenous catalysts. Since the bottom-up approach also allows the development of porous materials with surface chemistry and controlled porous structure, it offers the possibility to design desired polymer frameworks with different functionalities to the catalysts or ligands. Although there have been several excellent studies in literature addressing the general application and synthesis of porous organic polymers [17-19] and metal conjugates of nanoparticles, this review will discuss the recent advancements of MNPs and polymeric conjugates with MNPs in the catalytic approach of C-H functionalization using heterogeneous catalysts.

Development and Applications of MNPs

In the year 2011, Huang and coworkers reported encapsulated palladium nanoparticles (Pd NPs) aiding the direct C_2 arylation of indoles (Figure 1). The synthesis of MIL-101 [MIL = Matrial Institut Lavoisier] involves hydrothermal reaction for 8 h at 220 °C involving H_2BDC (BDC = benzene-1,4-dicarboxylate) (1 mmol), $Cr(NO_3)_3.9H_2O$ (1 mmol), and H_2O (265 mmol) [20]. Based on chemical analysis, the former reaction produced chromium terephthalate with formula $Cr_3F(H_2O)_2OE(O_2C)\text{-}C_6H_4\text{-}(CO_2)_3.nH_2O$ (where n is 25). The effective yield is 50% based on chromium. Subsequently, the supported Pd NPs catalyst which is referred to as Pd/MIL-101(Cr)(M_1) was also formed. The catalyst system was made through infiltration of solution, prepared from $Pd(NO_3)_2$ as Pd metal precursor with MIL-101(Cr). It was followed by exposure of 200 °C for 4 h with H_2. Herein, reaction optimization condition screening was employed using N-methylindole and iodobenzene as the substrates. The direct C_2-H arylation could be carried out over M_1. The reaction takes place with the help of a base. Specifically, results showed that 85% yield was obtained when cesium acetate was used. The catalytic reaction was best achieved using CsOAc (2 mmol), aryl halide (1.2 mmol), N-methylindole (1 mmol), and the Pd catalyst were added in DMF at 120 °C for 24 h [20].

More recently, Van Velthoven et al. [21] described C-H activation reaction using heterogeneous Pd(II) single-site catalysts (Figure 2). The thioether based ligand L_1 and L_2 ligands were prepared by addition of 0.0529 mol of bromo-thiophenol in acetone. Further to the reaction mixture, 0.529 mol of sodium hydroxide was mixed and the resultant reaction mixture was cooled down until it reaches 35 °C followed by stirring for 1 h. Later, chloroform was added to the reactant, the reaction mixture was refluxed for an additional 24 h. 0.048 mol of 2[(4-bromophenyl) sulfanyl]-2-methylpropanoic acid was dissolved in sulfuric acid and methanol. The mixture was refluxed for 60 h and cooled down to room temperature. 2-[(4-bromophenyl)sulfanyl]-2-methylpropanoic acid (0.017 mol) in toluene, 0.02 mol of diethylphosphonate, 0.08 mol of triphenylphosphine and trimethylamine were added. The reaction mixture was there after continuously purged by N_2 for an additional half an hour. Furthermore, 0.001 mol of tetrakis (triphenylphosphine)palladium was added to the mixture and heated for 7 h at 110 °C. Consequently 0.008 mol of the obtained phosphonate derivative was dissolved in dry DCM and into that solution, 0.0274 mol of bromotrimethylsilane

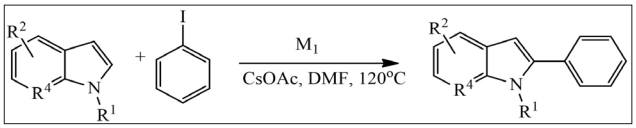

Figure 1: Reaction of N-methylindole and Iodobenzene.

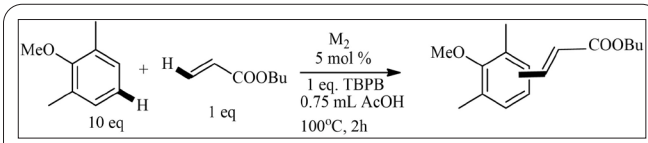

Figure 2: C-H activation reaction using heterogeneous M_2 catalyst.

was added dropwise. This reaction continued in ambient conditions for 4 h. In addition, a mixture of tetrahydrofurane and sodium hydroxide solution was used to dissolve crude oil by stirring for 6 h at room temperature. Preparation of L_2 ligand was like the procedure of L_1. The L_1 was activated by adding TiOP to deionized water for grafting of TiOP-L_1. The reaction mixture was stirred at 30 °C for 48 h. The Pd-complex was made using a similar amount of $Pd(OAc)_2$ (62.5 µmol) relative to L_1. The catalytic reaction was carried out for 2 h at 100 °C while stirring in presence of acetic acid, 2.50 mmol 2,6-dimethylanisole, 0.2 mmol n-butyl acrylate, 0.25 mmol tertbutyl peroxybenzoate and hexadecane along with 5 mol % of Pd-TiOP-L_1 (M_2). 80-90% yield of the product was obtained.

Konishi et al. [22] reported site selective C-H borylation in 2014. The C-H borylation of quinoline derivatives occurred at C_8 position through the utilization of heterogeneous Iridium (Ir) catalyst system (M_3) (Figure 3). Konishi and colleagues prepared silica-supported silicon-constrained monodentate trialkylphosphine, Silica-SMAP-Ir *in situ* by using silica-SMAP and $[Ir(OMe)(cod)]_2$, which exhibited high selectivity in achieving borylation of aromatic C-H bonds. At C_8 position the borylation of quinolines was accomplished by placing 2 mol% silica-SMAP, 0.33 mmol bis(pinacolato)diboron, and 0.5 ml anhydrous, degassed methyl tert-butyl ether in a glass tube. Consecutively, $[Ir(OMe)(cod)]_2$ dissolved in 1 ml methyl tert-butyl ether and 0.3 mmol of quinaldine was added. The reaction mixture was continued for 12 h at 50 °C and 86% isolated yield was observed.

Priorly, in 2014, another iridium based nanometal based catalyst was reported. Wu and co-worker have synthesized a mesoporous silica-based iridium bipyridine (M_5) complex for direct borylation in arenes [23]. The synthesis technique was initially reported to be analogous to Hartwig's 1/2 [{Ir(OMe)(cod)}$_2$]/dtbpy catalyst [24]. The catalyst bipyridine supported aiding silica was prepared by addition of EO-PO-EO, which is poly(ethyleneglycol)-block-poly(propyleneglycol)-block-poly-(ethyleneglycol) (24.0 g), aqueous HCl, and distilled water at 40 °C. Further, tetraethyl orthosilicate was added to the reaction mixture and stirred overnight. The resulting mixture was heated for 24 h at 100 °C.

Consequently, the formation of unsupported Ir catalyst (M_4) (Figure 4) was achieved by adding $[Ir(cod)(OMe)]_2$ (0.32 mmol) to 20 ml of cyclohexane. In the resulting mixture, cis-cyclooctene (4.2 mmol) was added. Subsequently the yellow-colored mixture was stirred for 10 min, after which pinacolborane (4.2 mmol) was added. The modified bipyridine 1 (0.64 mmol) was added for the formation of unsupported Ir catalyst (M_4). Besides M_4, preparation of the silica supported Ir catalyst (M_5) (Figure 4) was majorly like the procedure followed in synthesis of M_4. For M_5 silica-supported bipyridine

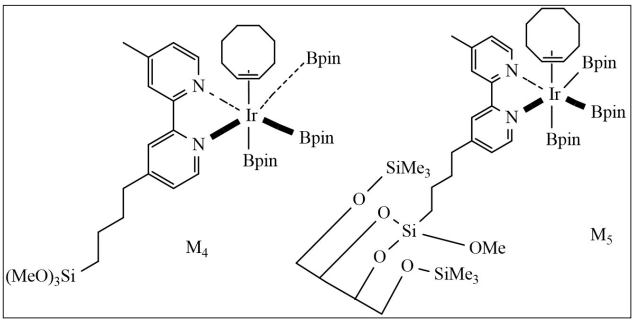

Figure 4: M_4 and M_5 metal complexes.

was added. The borylation was achieved when the Ir catalyst (0.0035 mmol), arene (1 mmol), (pinacolato)diboron (0.25 mmol) and anhydrous hexane was added (Figure 5). Both catalysts provided good to excellent (90 - 100%) yield.

In 2015, Gogoi et al. [25] described the formation of 2-(N-aryl) aminobenzo using gold nanoparticles (M_6) catalyzed oxidative C-H bond activation and the process involved functionalization of C-H bond which resulted in intramolecular establishment of C-S bond (Figure 6). The gold nanoparticles were prepared using $HAuCl_4$ and aqueous extract from *Kayea assamica* fruit. Initially, optimization studies were carried out by using model substrate, diphenyl thiourea with catalytic amount of M_6 which did not show any promising result as typically observed with Pd(0). Further, reaction conditions were standardized using different experiments which were performed by changing the parameters, such as solvent, time and temperature. The most optimized results were observed when a reaction mixture of M_6 in CH_2Cl_2 solvent was prepared in the presence of 10 mol% $KMnO_4$. The optimum reaction conditions for the above reactions were 80 °C temperature under O_2 atmosphere which gave 90% yield of the product.

Warratz et al. [26] in the year 2017 presented a method for the bromination of meta-carbon of purine bases via C-H functionalization (Figure 7). The remote C-H activation reaction was achieved using a heterogenous ruthenium catalyst (Ru-SiO_2) (M_7). The reaction was achieved under air by utilization of n-Bromosuccinimide and with solvent N, N-dimethylacetamide at 80 - 100 °C. The Ru-SiO_2 catalyst demonstrated better results in comparison to $RuCl_3$ as catalyst. Moreover, it also facilitated the meta-C-H halogenation with exceptional position selectivity and a remarkable catalytic

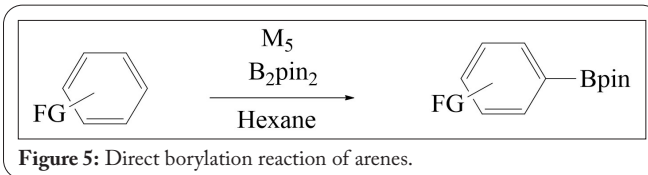

Figure 5: Direct borylation reaction of arenes.

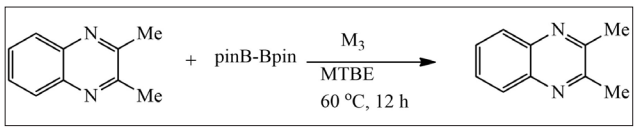

Figure 3: C-H borylation reaction of quinoline derivatives.

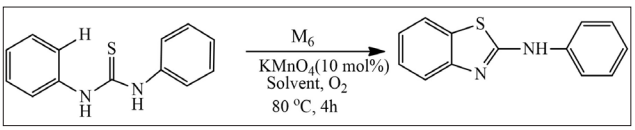

Figure 6: Oxidative C-H bond activation reaction.

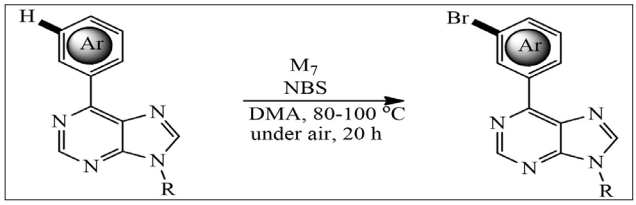

Figure 7: Bromination of purines.

efficiency in presence of varying substrate. Additionally, it was also detected that access to meta-halogenenation of purine derivatives can be done via Ru-based catalysis. This property illustrates the exceptional synthetic value of Ru-catalyzed C-H activation. The heterogeneous nanoparticle catalyst was continuously reused for over 7 cycles and was easily recovered. The yield was excellent for the initial five cycles. However, a drop from 62 % to 43% was noticed after the fifth cycle.

To perform C-H functionalization reaction on benzoxazole, Phan et al. [27] synthesized a crystalline $Ni_2(BDC)_2(DABCO)$ (M_8) porous metal organic framework (MOF). The MOF was formed by adding 2 mmol H_2BDC (H_2BDC = 1,4-benzenedicarboxylic acid) and 1 mmol 1,4-diazabicyclo[2.2.2]octane (DABCO) with 2 mmol $Ni(NO_3)_2.6H_2O$. This MOF was dissolved in 15 ml of N,N′-dimethylformamide (DMF). The obtained reaction solution was divided amongst two separate vials and these vials were heated for 48 h in an isothermal oven at 100 °C. 69% yield of green crystals having chemical formula $Ni_2(BDC)_2(DABCO)$ was obtained. Furthermore, $Ni_2(BDC)_2(DABCO)$ was added to a flask containing the mixture of 2 mmol phenylboronic acid, 1 mmol benzoxazole, 2 mmol of K_3PO_4 and 0.2 mmol of 2,2′-bipyridine as ligand. Also, as an internal standard 0.1 ml of n-hexadecane was also added in 5 ml of N,N'-dimethylacetamide (Figure 8). The concentration of the catalyst was determined based on the molar ratio of nickel/benzoxazole. The reaction condition involved constant stirring for 180 min at 100 °C and 61% and 75% of product yield was obtained.

Truong et al. [28] reported C-H bond functionalization reaction using $Cu_2(OBA)_2(BPY)$ (M_9) MOF (Figure 9). M_9 was produced by a solvothermal method. Three solutions of $Cu(NO_3)_2.3H_2O$ (1 mmol), 4,4′-oxybis(benzoic) acid (H_2OBA) (1 mmol) in DMF, and 4,4′-bipyridine (BPY) (0.5 mmol) in DMF were prepared. The solution of BPY and H_2OBA was added into the $Cu(NO_3)_2.3H_2O$ solution. The resultant solution was heated at 85 °C for 48 h. 71% yield of the MOF, involving $Cu_2(OBA)_2(BPY)$ was obtained. Benzothiazole (1 mmol) was taken as substrate for the catalytic activity and hexadecane (0.1 ml) and 1,4-dioxane (4 ml) were taken as solvent. A mixture of M_9 (3 mol%), as catalyst, iodobenzene (1.5 mmol), and 2 mmol of ^{t}BuOLi were rapidly added into the vial. This reaction mixture was refluxed at 120 °C for 6 h. On altering the reaction conditions, i.e., the temperature of 80 °C, 47% conversion was observed after 6 h. Increasing the temperature of the reaction provided 62% and 82% after 6 h at 100 °C and 120 °C, respectively.

In 2015, Korwar et al. [29] reported the formation of a nanoparticle catalyst Pd(II)/MWCNT (M_{10}) to support the C-H functionalization reaction (Figure 10). They observed that solid supported M_{10} can catalyze the functionalization reaction from C-H to C-O bonds. The required 10-chlorobenzo[h]-quinoline (10) was produced in 92% yield after reacting benzo[h]quinoline, N-chlorosuccinimide and M_{10} in acetonitrile at 100 °C for 5 h, which is equivalent to the formerly reported 95% yield in which a homogeneous catalyst was utilized [30]. It is noteworthy that the Pd(II)/MWCNT reaction proceeds significantly more quickly when compared to that of the homogeneous $Pd(OAc)_2$.

Sciosci et al. [31] in 2020 reported C-H alkenylation by heterogeneous Pd catalyst of quinoline N-oxides (Figure 11). To investigate C-2 alkenylation of quinoline N-oxide at various reaction conditions, Sciosci et al. [31] prepared three distinct pincer-type ligands (L_3-L_5). Firstly, they synthesized the N-containing ligands built on derivatives of imidazolium (L_3), 1,2,4 triazolium (L_4), and 1,2,3 triazolium (L_5), which were subsequently immobilized on polystyrene resin. To optimize reaction conditions, for C-2 alkenylation of quinoline N-oxide, a diverse range of substrates of quinoline N-oxide derivatives were utilized. These effectively underwent alkenylation catalyzed by the POLITAG-Pd(II)-L_5 (M_{11}) catalyst. The catalytic reaction always preferred at the C-2 position and the products were isolated with remarkable yields.

Conclusion

In recent years a lot of progress in metal catalyzed C-H functionalization has been witnessed. However, many of the

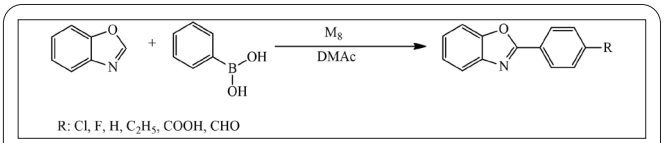

Figure 8: C-H functionalization reaction on benzoxazole.

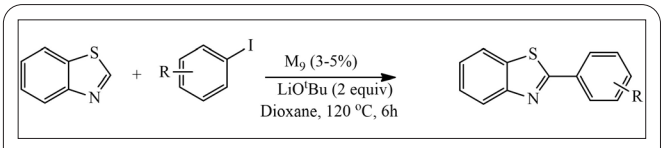

Figure 9: C-H bond functionalization reaction using M_9.

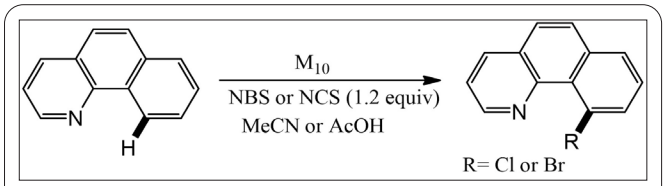

Figure 10: C-H functionalization reaction by using M_{10}.

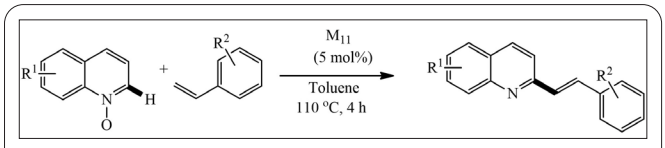

Figure 11: C-H alkenylation by heterogeneous Pd catalyst.

research efforts were on exploring various metal complexes in homogenous systems, which are fraught with numerous disadvantages. Hence, development of reusable and competent nanoparticle-based catalytic systems remains the foremost challenge. A key aspect linked to the modern metal-based catalysis is its recyclability and ultimately the separation of metal-based nano-catalysts from the products. There is an urgent need to address the fact that most of the catalytic protocols employ non-benign solvents as reaction medium. Regarding these concerns, one promising approach is the use of MNPs which offer advantages with respect to greener perspective and have potential applications in industries. By prudently selecting a good solid support, recyclability and catalytic activity can be enhanced. In addition, it can affect the stability, distribution, and size of nanoparticles used as catalyst. Utilization of flow technologies and/or alternative energy sources like ultrasound irradiation, microwave and light irradiation can also enhance the catalytic efficiency of MNPs, thereby opening exciting possibilities and applications. This review demonstrates rapid and varied advancements in the recent decade. A comprehensive understanding of reaction mechanism is a pertinent challenge for scientists and chemists of today. By improving and expanding the varieties of nanoparticle-based catalyst C-H functionalization methods, it will help to understand functional materials that are otherwise not accessible via synthetic routes used conventionally. It also creates prospects for adding value to nanoparticles, commodity polymers, and upcycling plastic waste.

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None.

Conflict of Interest

None.

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