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Engineering Graphene based heterogeneous nanocatalyst for efficient Carbon bond formation

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Abstract
An efficient heterogeneous catalytic protocol using GO supported was developed for amide synthesis from various carboxylic acids and N, N-dialkylformamides. GO supported catalysts were synthesized by a single-pot sol-gel method. The catalyst showed excellent activity, affording 98% conversion in the model reaction of benzoic acid with DMF. The enhanced activity is attributed to the uniform distribution of Cu and Co active sites on the high-surface-area graphene oxide support. The catalyst was characterized by XRD, FTIR, XPS, SEM, and TEM. Moreover, its magnetic recoverability and recyclability enabled reuse for up to five cycles with only a slight decrease in catalytic performance.
***Keyword**: GO, catalyst, magnetic recoverability.*

Introduction

Metal nanoparticles (MNPs) have become a focal point of research interest in the scientific community due to their exceptional catalytic capabilities and extensive surface area. This has spurred a surge in investigations aimed at unravelling their unique properties and potential applications. Precious metals like (Ag)gold, silver, platinum (Pt), and palladium (Pd) have found excellent application as catalysts across a broad spectrum of organic reactions. These metals exhibit distinct chemical characteristics that render them highly efficient in facilitating diverse chemical reactions. Apart from this, the adaptability of precious metal catalysts enables their utilization in a wide range of chemical transformations, spanning from fundamental bond formations to intricate rearrangements and manipulations of functional groups. Consequently, they serve as indispensable tools in advancing synthetic methodologies and facilitating the production of valuable organic compounds, serving varied industrial and academic objectives.

Palladium (Pd) metal stands out among precious metals as a favored catalyst for numerous chemical reactions due to its exceptional activity, selectivity, and stability across diverse reaction conditions. Its reliability and efficiency make it a preferred option for catalysing a wide range of transformations in organic synthesis and other chemical processes. Conversely, palladium (Pd) has become one of the most costly metal, priced at approximately 50 USD per gram, experiencing a rapid escalation in its value over recent years [1].Thus utilisation of Pd NPs as heterogeneous catalyst is very restricted. Now a day most of the drugs synthesising industries preferring utilization of carbonaceous supported Platinum (Pt@C) instead of Pd@C. Hence, the imperative task in the realm of catalysis, particularly within sustainable chemistry, is to design Pd based heterogeneous catalyst that require less palladium while maintaining or even improving catalytic efficiency.

In this context, there has been significant interest in utilizing supported palladium nanoparticles (PdNPs), characterized by particle sizes less than 10 nm, as supported heterogeneous catalysts for a range of reactions. This attention stems from their substantial surface-to-volume ratio and the presence of highly active surface atoms, which surpass those found in bulk catalysts [2].The choice of support material plays vitol role in achieving high-dispersed and monodisperse palladium nanoparticles (Pd NPs) with optimal catalytic efficiency and stability. In las few years the researchers has immobilised Pd nanoparticle over various support which includes alumina, carbon nanotubes, metal oxides, polymers,, graphene oxide (GO), zeolite, magnetic materials, and metal–organic frameworks [3].

Moreover different research groups have reported Metal organic framework as support for anchoring palladium nanoparticles (Pd NPs). Carson , F., and co-worker synthesised palladium nanoparticle supported on MOF denoted by Pd@MIL-101-NH_2 and investigated its catalytic efficiency in basic medium for Suzuki–Miyaura Coupling Reaction [4]**.**Similarly, *Pascanu, Vlad* and research group reported preparation and catalytic activity of MIL-101Cr-NH_2 over Suzuki–Miyaura [5]. *Shuixia Gao et.al.* have utilised MOF-5 as solid support for immobilisation of Pd Nanoparticle and reported Pd/MOF-5 catalyst for Sonogashira coupling reaction [6].Recently, *Chen, J., et. al*., reported synthesis palladium NPs supported on alumina [7]. *Aznárez, A.,* and co-worker revealed the preparation of Pd and Pt NPs immobilisation onto alumina clay-support and examined its catalytic efficiency over propene combustion [8].

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Polymer supported heterogeneous catalysis proven to be an alternative route for homogeneous catalyst due to its excellent strength and easy recovery, and recyclability [9]. Recently, *Karami, Kazem; et.al* anchored Palladium nanoparticle (PdNPs) using Polymer of styrene divinyl benzene as support and carried out two different transformation successfully namely Suzuki coupling and oxidation of alcohol. The supported catalyst show good catalytic activity [10]**.** *Datta, Anupama*, demonstrated Palladium complex supported over phosphenated polymer catalyst for Sonogashira, Suzuki and Heck type of coupling reaction, and reported excellent catalytic activity with good yield using toluene as solvent at 60 ^{o}C [11]**.** Similarly *Targhan, Homa* and co-worker applied Nitrogen based polymer for immobilisation of palladium nanoparticle and investigated its catalytic efficiency for Suzuki and Heck type of coupling reaction. The prepared heterogeneous catalyst exhibited good to moderate catalytic efficiency and recorded product yield up to 98%. [12]

Carbonaceous material like graphene, graphene oxides possess remarkable mechanical as well as physical strength which is responsible for their wide utility Graphene possessed a sp2-hybridized carbon structure and is anticipated to make significant contributions to the field of catalysis. This expectation stems from their distinctive electronic properties and substantial surface area, distinguishing them from other carbon materials and thus enhancing their potential catalytic efficacy [13].GO is a derivative of graphene. The oxidation process applied to graphite material results in the introduction of oxygen functional groups onto the surface of graphene. This augmentation of oxygen functionalities contributes to an expansion in the inter-layer spacing, thereby facilitating the exfoliation of graphite into mono or a multiple-layers (2D) two-dimensional structure. The oxidation of graphene introduces various oxygen functionalities onto its surface, rendering it more conducive to catalytic activity. This augmentation of oxygen moieties enhances the catalytic potential of graphene, broadening its applicability in catalysis. Due to presence of pi-conjugated system in GO it felicitate greater interaction between the aromatic substrate with surface of graphene oxide and therefore it enhances adsorption of compound onto the surface of graphene oxide [14].The oxidised graphite associate with different oxygen functionality throughout the surface such as,-OH (hydroxyl groups),-COOH (carboxylic groups),-C=O (carbonyl groups),C-O-C (epoxy groups). These oxygenated functionality decorated over surface of graphene oxide offer distinct catalytic activity to graphene oxide, such as presence of carboxylic acid functionality make it acidic therefore GO could be used catalyst acid catalysed reactions. Moreover it behave like nucleophile and Nucleophilic nature enhances coupling reactions. Furthermore, presence of pi-conjugation creates defects over surface and it can felicitate various catalytic activity [15].

The Sonogashira reaction discovered by Sonogashira in 1975.Sonogashira cross coupling reaction catalysed by palladium is one of the most usful synthetic methodologies for formation of Sp2 C--Sp C between aryl halide and terminal alkynes. Hence it provides most promising approach for synthesis of wide range of functionalized organic molecules from laboratory to industrial scale5 The Conjugated acetylenic product obtained in Sonogashira reaction has wide synthetic application like synthesis of substituted alkynes, total synthesis of natural product, polymeric, pharmaceutical complex molecules and optic material, medical product.The Sonogashira reaction involves coupling of aromatic or aliphatic halide (aryl or alkenyl halide) with terminal aliphatic or aromatic or aliphatic alkyne form substituted product of alkyne. This reaction can be performed at room temperature in presence of palladium based catalyst like $PdCl_2(PPh_3)_2$ and Copper iodid (Cu-I) catalytic amount of co-catalyst[. Later on, *Heck* and *Dieck* and *Cassar* revealed that the reaction can be carried out even in presence of Palladium metal only but it require long reaction time and higher temperature. The utilisation catalytic amount of co-catalyst CuI for performing this coupling reaction though speedup the reaction but it faces certain challenge such as the precursor alkyne undergoes homocoupling and leads to formation of homocoupled unwanted product and utilization of very toxic phosphine ligand, nitrogen containing Ligands, and large excess amount of solvent like acetonitrile ,dimethyl sulphoxide (DMSO),tetra hydro furan(THF).This results into decline in the efficiency of Sonogashira cross coupling reaction for synthesis of C-C bond. Figure .3.1 shows Sonogashira coupling reaction.

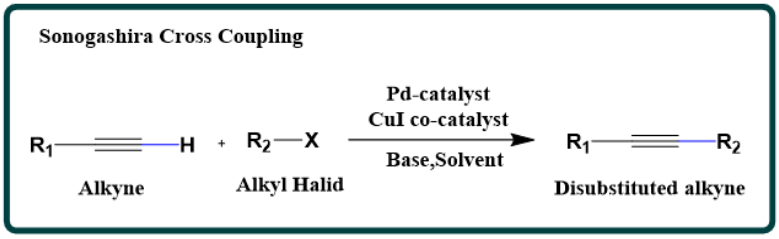


Figure. 1 shows Sonogashira coupling reaction

Here we have successfully synthesis Graphene oxide based Pd Nano particle which is magnetically separable by sol gel synthesis method. Catalyst have been employed for construction of C-C bond. The synthesised compound thoroughly characterised by using various spectroscopic techniques XPS, XRD, FT-IR, SEM,EDX and TEM. The catalyst employed for construction of C-C bond

Result and Discussion

IR

the spectra of GO, of catalyst shows , a prominent peak appears at 1714 cm^{-1}, alongside a broad absorption band spanning from 3100 cm^{-1} to 3700 cm^{-1}. These results are attributed to the stretching vibration of the O-H functional group. distinct bands at 1369 cm^{-1}, 1089 cm^{-1}, 1618 cm^{-1}, and 1220cm^{-1} corresponding to the stretching frequencies of various functional groups, namely, C-O-C, -C-OH, C=C (aromatic), and epoxy C-O functionality

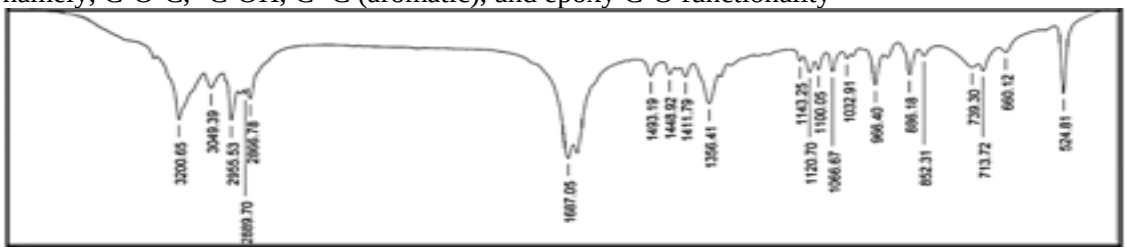


Fig.2 IR spectra of GO based catalyst

SEM and TEM

The surface morphology of the synthesised catalyst was examined using SEM at various magnifications (Figure 7). The structure of Fe_2O3-Pd @GO was found to be uneven, displaying some Pd-Fe_3O_4 nanoparticles agglomerated on the surface along with some semi-spherical-shaped particles. typical TEM image of the GO sheet, illustrating the structure and arrangement of Pd-Fe_3O_4 nanoparticles on the surface of the GO sheet. In the cross-sectional view of the HRTEM image of catalyst, the intersecting crystal fringes indicate the coexistence of Pd and Fe_3O_4 as a mixture, rather than individual metal entities Fig. 3. The combination of palladium nanoparticles with iron oxide nanoparticles has a synergistic impact in the form of palladium nanoparticle stability and dispersion, reducing agglomeration during the reaction and therefore increasing catalytic activity

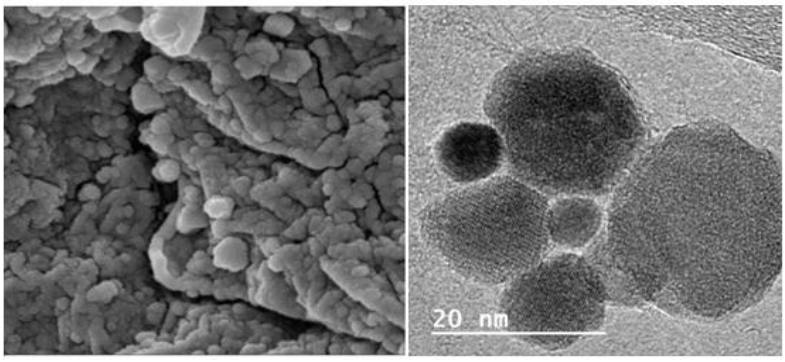
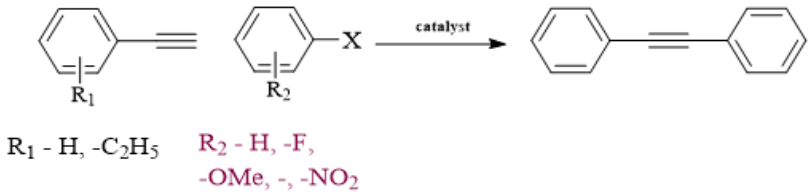


Fig. SEM and TEM image of catalyst

The catalytic activity of prepared heterogeneous catalyst GO has been assessed in Sonogashira cross coupling reaction by coupling various substituted aryl halides including electron donating and withdrawing substituents with substituted phenyl acetylene produced various substituted derivatives of biphenylacetylenes.as illustrated in fig scheme 3.1



Reaction Scheme

H[1]NMR

1,2-diphenylethyne:

Molecular formula: $C_{14}H_{10}$

[1]H NMR spectrum data :(500 MHz, Chloroform-*d*) δ 7.81 (m, 4H), 7.32 (6H).

Interpretation

The data represents the proton nuclear magnetic resonance (1H NMR) spectrum of a compound (1) measured at 500 MHz in chloroform-d (CDCl3) solvent. The spectrum displays signals at chemical shift δ 7.65, which corresponds to a multiplet (m) representing 4 hydrogen atoms, and chemical shift value at δ 7.44, represents a multiplet for 6 hydrogen atoms. These chemical shifts are consistent with aromatic protons typically observed in aromatic compounds.

Experimental

Catalyst were synthesised by Sol-gel method

Pd based nanocatalyst was synthesized through a sol–gel-assisted method. Graphene oxide (GO) was dispersed in deionized water by ultra-sonication, followed by the gradual addition of $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ under continuous stirring. The pH was adjusted to 9–10 using aqueous NH_4OH, promoting the formation of Fe_3O_4 nanoparticles on the GO surface. After stirring at 60–70 °C, an aqueous solution of $PdCl_2$ was introduced and the mixture was aged under stirring to facilitate interaction of Pd^{2+} ions with the oxygen-containing functional groups of GO. Subsequently, $NaBH_4$ was added slowly to reduce Pd^{2+} to Pd^0 nanoparticles. The resulting GO supported composite was aged, magnetically separated, washed repeatedly with deionized water and ethanol, and dried under vacuum at 50–60 °C to obtain the final magnetic nanocatalyst.

Conclusion

Here we have successfully synthesis Graphene oxide supported Pd Nano particle which is magnetically separable by solvothermal single pot synthesis method. The synthesised compound thoroughly characterised by using various spectroscopic techniques XRD,FT-IR, SEM, and TEM. The catalyst shows great efficiency in carbon coupling reaction.

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