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HETEROGENEOUS BIMETALLIC NANO ALLOYS CU-PD, NI-PD AND CU-NI ANCHORED ON GO CATALYZED SUZUKI AND SONOGASHIRA CROSS COUPLING REACTION

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ABSTRACT

Bimetallic nanoparticles are vital due to their high biocompatibility, stability and comparatively less toxicity. The synthesis method that includes physical, chemical and biological methods are explored and discussed in detail along with their advantages. Graphene Supported Pd-Cu bimetallic nanoparticles as a highly active catalyst. was prepared by a chemical reduction method and used for Coupling reaction. The Pd-Cu (1:1)/G exhibited the highest catalytic activity for the Sonogashira- types Coupling reactions and also exerted satisfied catalytic activity and recycle stability for Suzuki reaction cross coupling reaction. A study on the fabrication on diamino pyridine Pd (ll) Catalytic monolayer supported On Go describe how the Catalytic activity of the material can be influenced by the size of the Pd nanoparticle formed. The Suzuki reaction and the Sonogashira reaction are both types of organic reactions that use a metal catalyst to form carbon-carbon bonds. The Suzuki reaction uses a palladium complex catalyst to cross-couple an organohalide to a boronic acid while the Sonogashira reaction uses a palladium catalyst and a copper co-catalyst to form a carbon-carbon bond between an aryl or vinyl halide and a terminal alkyne.

Keywords: Metal Nanoparticles, Coupling Reactions, Catalysis, Multi Metallic Nanoparticles, Ligand Free Reactions, Nanocatalyst.

INTRODUCTION

Suzuki coupling: Suzuki coupling reaction is an organic coupling reaction where in the Coupling partners include a boronic acid and an organohalide. palladium complex is used to catalyze this reaction. This reaction is also called the Suzuki- Miyoura reaction or the Suzuki coupling. In the Suzuki couplings general scheme, the coupling of organoboron specimen with the halide over palladium results in the formation of a carbon-carbon single bond.

Sonogashira coupling: The Sonogashira reaction is a cross-coupling reaction used in organic synthesis to form carbon-carbon bonds. It employs Palladium catalyst as well as a copper co-catalyst to form a carbon-carbon bond between a terminal alkyne and an aryl or vinyl halide. The Sonogashira cross-coupling reaction has been employed in a wide variety of areas, due

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to its use in the formation of carbon-carbon bond [1,2].

Bimetallic nano particle Catalysts: Bimetallic nanoparticles (BNPs) are made of two different metals and are often used as catalysts because their catalytic properties are better than mono-metallic nano-particles. Bimetallic nanoparticle catalysts may show dramatic enhancement in terms of activity, selectivity and stability.

GO as a Supported for Nano particle catalysts: Graphene oxide (GO) is a material that can be used as a support for metal and metal oxide nanoparticles to catalyzed reaction. Green iron oxide (GIO) can be used to support bimetallic nanoparticle catalysts such as Pd-Cu which can be more active than supported catalysts. Reduced GO i.e. RGO is better supported for C-C Coupling reaction than graphene acid (GA) because it is a better charge doner and accepter.

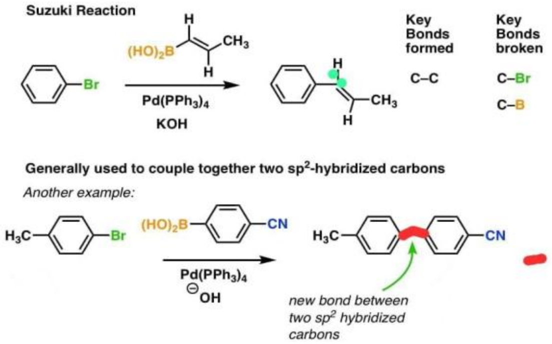
BNP IS CATALYSED IN SUZUKI COUPLING

Bimetallic nanoparticles are used as catalysts in Suzuki Coupling reaction to improve the catalytic properties of monometallic nanoparticles eg. Pd-Ni bimetallic catalyst. This catalyst was immobilized on dendrimer grafted magnetic graphene oxide. The catalyst was effective in promoting the Suzuki - Miyaura reaction of aryl bromide and chloride with arylboronic acid. The catalyst could be recycled in five times without a significant decrease in activity [3].

BNP CATALYSED SONOGASHIRA COUPLING

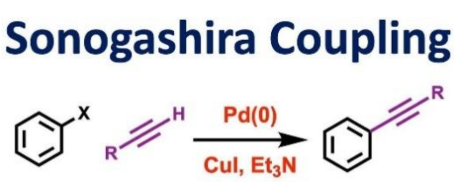
Bimetallic nano particles are used in the Sonogashira Coupling reaction to form carbon - carbon bond between aryl halides and terminal alkynes. Eg. Nickel- Palladium (Ni-Pd) bimetallic nanoparticles.

Mechanisms and role of Suzuki Coupling:



Palladium catalyst used to cross couple an organoboranic acid and an organohalide to form a carbon - carbon single bond.

Mechanisms and role of Sonogashira coupling:



The Sonogashira coupling employs Pd catalysts. In the presence of Cu-I and Et_3N it is used for base. The final product of Sonogashira is C-C single bond. It is a cross-coupling reaction [4].

SYNTHETIC AND CHARACTERIZATION OF BIMETALLIC CU-PD, NI-PD AND CU-NI ON GO

The synthesis of bimetallic nano-alloys on graphene oxide (GO) involves combining the unique properties of GO as a support material with the catalytic advantages of bimetallic alloys. Graphene oxide provides a large surface area, good mechanical strength and abundant oxygen-containing functional groups (e.g., hydroxyl, epoxy, carboxyl), which allow strong interaction with metal nanoparticles, stabilizing them and enhancing their catalytic performance [5].

- TEM -Provides information about the size and morphology of the nanoparticles.
- XRD-Used to confirm the crystalline structure of the bimetallic nanoparticles.
- XPS-Provides information about the oxidation states of the metals in the catalyst.
- BET-Measures the surface area of the catalyst.

Advantages of Heterogeneous Go supported bimetallic nano catalyst:

1. Enhanced activity: Synergistic effects between metals
2. Improved selectivity: Tunable metal ratio and GO support
3. Increased stability: Resistance to sintering, leaching, and poisoning
4. Reduced precious metal loading: Efficient use of expensive metals

Synergistic effect in catalytic activity Selectivity:

1. Modified electronic structure: The presence of multiple metals alters the electronic properties, influencing the adsorption and reaction mechanisms
2. Geometric effects: The arrangement of metal atoms can create unique active sites, enhancing specificity.
3. Ensemble effects: The combination of metals can optimize the ensemble size, facilitating specific reaction pathways.

Stability:

1. Reduced sintering: Multi-metallic catalysts exhibit improved thermal stability, resisting particle agglomeration.
2. Enhanced corrosion resistance: The combination of metals can provide a protective layer, reducing degradation.
3. Poisoning resistance: Multi-metallic catalysts can better tolerate poisoning species, maintaining activity [6,7]

STRUCTURE AND ELECTRONICS PROPERTIES OF THE NI-PD ALLOY ON GO AND CU- PD ON GO AND CU-NI ON GO

Ni-Pd/GO	Cu-Pd/GO	Cu-Ni/GO
1. Structure: Ni and Pd atoms form a face-centered cubic (FCC) lattice on GO. 2. Electronic Properties: Density of States (DOS): Ni 3d and Pd 4d orbitals overlap, enhancing catalytic activity.	1. Structure: Cu and Pd form a CC lattice on GO, with Cu atoms segregating to the surface. 2. Electronic Properties: DOS: Cu 3d and Pd 4d orbitals interact, modifying the electronic structure.	1. Structure: Cu and Ni form a FCC lattice on GO, with Ni atom dispersed throughout. 2. Electronic Properties: DOS: Cu 3d and Ni 3d orbitals overlap, altering the electronic structure.

Unique properties of catalyzed support materials:

Electronic Properties:

1. High Electrical Conductivity: Graphene has exceptional electrical conductivity, surpassing copper and silver.
2. High Carrier Mobility: Graphene's charge carriers (electrons and holes) move quickly, enabling fast electronic devices.
3. Zero Bandgap: Graphene's electronic structure allows for efficient electron transport, making it suitable for high-speed electronics.
4. High Electron Density: Graphene's high electron density enables efficient charge transfer and storage [8,9].

Surface Properties:

1. High Surface Area: Graphene's 2D structure provides a large surface area, ideal for sensing, catalysis, and energy storage.
2. Chemical Stability: Graphene's inert surface resists chemical reactions, ensuring durability and stability. 3.Hydrophobicity: Graphene's surface is hydrophobic, repelling water and reducing corrosion [10,11]

BNP NI-PD, CU-PD ON GO CATALYSED SUZUKI COUPLING AND SYNTHETIC APPLICATION

BNP Ni-Pd/GO Catalyst [12,13]:

1. High catalytic activity: 99% yield, 100% selectivity
2. Low Pd loading: 0.1-1 mol%

BNP Cu-Pd/GO Catalyst:

1. Excellent yield: 95-99%
2. Low Cu loading: 0.5-2 mol%

Synthetic Applications

1. Pharmaceuticals: biphenyl-based drugs (e.g., valsartan)
2. Agrochemicals: aryl-substituted heterocycles (e.g., pyrimidines)
3. Materials Science: conjugated polymers (e.g., poly(aryleneethynylene)
4. Natural Product Synthesis: complex molecules, e.g., (-)-epibatidine.

BNP NI-PD, CU-PD ON GO CATALYSED SONOGASHIRA COUPLING AND SYNTHETIC APPLICATION

BNP Cu-Pd/GO Catalyst:

1. High catalytic activity: 95-99% yield
2. Low Pd loading: 0.1-1 mol%

BNP Cu-Ni/GO Catalyst:

1. Excellent yield: 90-95%
2. Low Ni loading: 0.5-2 mol%

Synthetic Applications:

1. Pharmaceuticals: alkynyl-substituted heterocycles (e.g., pyrimidines)
2. Agrochemicals: aryl-substituted alkynes (e.g., insecticides)
3. Materials Science: conjugated polymers (e.g., poly(arylene ethynylene)
4. Natural Product Synthesis: complex molecules (e.g., (-)-epibatidine)

CONCLUSION

Heterogeneous Bimetallic Nono-alloys, Cu-Pd and Cu-Ni, supported on graphene oxide (Go) have demonstrated exceptional catalytic. The use of go as a support material future enhance the performance of Cu-Ni catalysts, by preventing nanoparticles aggregation and increasing the surface area available for reaction. Enhanced catalytic activity and selectivity synergistic effects between cu and Pd- Ni improve electron transfer and stability.

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