Nanotechnology and Heterogeneous Catalysis.

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Introduction:

Worldwide in the recent years, Nano science and nanotechnology has become a popular field for research and development. As an example to explain its potential significance, heterogeneous catalysis was cite as a successful application that has great benefits for society. Thus, it is reasonable to expect that the increase in new developments in Nano science and nanotechnology would have a significant impact on the understanding, practice, and applications of catalysis. The nano definition of catalysts is the result of an interesting and expanding field of catalysts that are designed at the nanoscale level, especially for heterogeneous catalysis. The field of nanocatalysts (catalysts with a support or active sites in nanoscale dimensions) can assist researchers in the design of catalysts with good activity, stability and selectivity by simply manipulating their sizes, shapes and morphologies. It has been well established that the properties of the nonmaterial can be changed by their size, shape and composition, these properties of the nonmaterial are depends on their synthesis method.Nanocatalysts are often considered as quasi-homogeneous systems, because these material are fills the space between two classictypes of catalysts, that is, homogeneous and heterogeneouscatalysts.[1]

Nanocatalysis and Green Chemistry:

Catalysis is the very important part of green chemistry.Nano metal catalysis are used in smaller amounts which significant in cost reductions and utilisations in chemical processes.Nanocatalysis adds greener to chemical process through

a) Higher activity which avoids drastic reaction conditions and increases energy efficiency

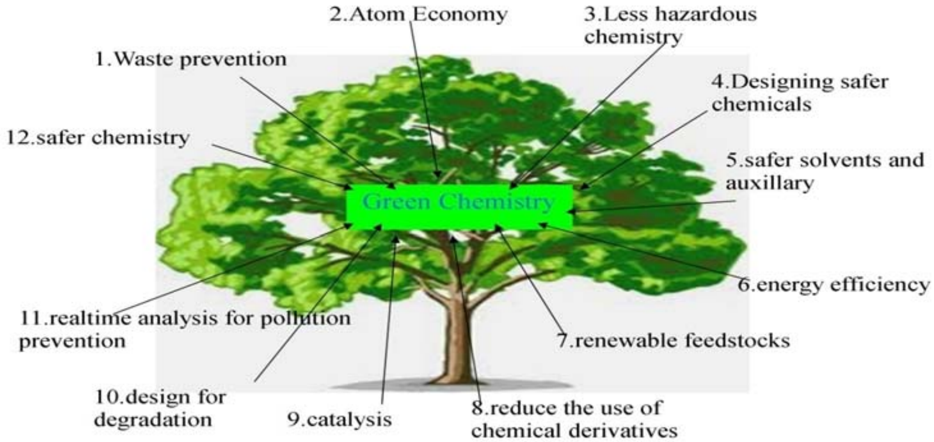
b) Higher selectivity which reduces the by-products and allows performing chemical reactions in a specific manner with the least possible consumption of substances. This, in turn, improves atom economy and waste prevention

c) Efficient recovery from reaction medium

d) Durability or recyclability

e) Cost-effectiveness.

Nanocatalysts are follows the mostly 12 basic principles of green chemistry which aredepicted in the following Diagram:



These nanocatalytic systems are active for several reasons:

1. It is well known that as an entity gets smaller, its surface area-to-volume ratio increases. Therefore, as nanocatalysts are very small in size, they have an enormous surface area to volume ratio.
2. The available surface area of the active component of nanocatalysts is significant, which therefore increases contact between the reactant molecules and catalyst appreciably. This enhanced interaction facilitates the heterogeneous catalytic system and helps to achieve a better reaction rate that is closer
to its homogeneous counterpart.
3. Effortless control of nanocatalysts size, shape and morphology makes it possible to rationally design the materials that are specifically needed for a particular catalytic application. Thus, tuning material properties is easily possible when working at the nanoscale, which would often be difficult in their macroscopic counterparts.
4. The use of magnetic nanoparticles as a catalyst support can also enable, in specific cases, easy and efficient separation of the catalysts from the reaction mixture with an external magnet.

There are various methods of synthesis of Nanocatalysis such as sol-gel method, micro emulsification, high energy ball milling, hydrothermal processing, micellar formation, chemical vapor depositionetc**.**[2]Some of the methods of synthesis are not useful because of its repeatability. In practical point of view sol-gel and micellar formation are the most efficient methods for the synthesis of nanocatalysts. In this paper we tried to discuss the Cu nanoparticles and their uses in organic transformations as a heterogeneous catalytic route.

Copper Nanoparticles:

Copper has gain considerable attention in among the transition metals in periodic table; metallic copper hardly shows any catalytic activity like other members of this transition metal family. Similar to other nonmaterial with the help of nanotechnology and nanosciencecopper received considerable interest because of their unique properties and applications in all branches of science such as medicine to material to catalyst.

To prepare Cu, Cu_2O, and CuOnanoparticles with well-defined morphology and chemical composition, both physical methods (chemical vapor deposition) and chemical methods (including sol–gel, hydrothermal, and electro-chemical deposition).Methods listed below used for the synthesis of Nano Cu, Cu_2O and CuI.

- ❖ Preparation of PEG-stabilized Cu Nanoparticles usingmicrowave irradiation.[3]

$CuSO_4$.5 H_2O, Ethylene glycol + N_2H_4.H_2O, NaOH, Ethylene glycol —(Microwave, 3.5Min)→ Copper Nanoparticles

- ❖ Preparation of polyvinylpyrrolidone-coated Cu_2O nanoparticles [4]

CuSO4 .5H2O + NaBH4, PVP → PVP coated Cu2O nanoparticles

- ❖ Solvothermal preparation of CuI nanoparticles [5]

Cu (OAC) $_2$. H_2O + DMG [Cu (dmg) $_2$] →
(Dimethylglyoxime)

[Cu (dmg) $_2$] + KI —(108° C.6h)→ CuINanoparticles
Autoclave

- ❖ SupportedNanoparticles

The small size of metal nanoclusters and its homogeneous nature, nanoparticles are supportedor anchored onto the solid surface to achieve an easy separation, and a few procedures are listed below.

I. Silica-supported Cu nanoparticles [6]
II. Mesoporous silica-supported Cu nanoparticles [7]
III. Deposition of Cu on activated carbon [8]
IV. Magnetically separable Cu catalysts [9]

Characterization of nanoparticles.

Several techniques are used for the characterization of nonmaterial.
TEM analysis is used to determine shape and size (diameter) of the nanoparticles.
EDX of the selected area of nanoparticles gives an indication of the composition.
Using XPS determined the oxidation state of the metal present in the material.
The phase purity of the bulk material of the nanoparticles can be determined by using XRD with comparison of those reported earlier.

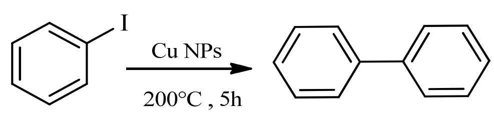
SEM (scanning electron microscopy) images gives information regarding to its morphology. UVspectroscopy also gives useful information of the nature of nanoparticles.

Copper Nanoparticles as Catalysts in organic reactions.

Copper has received more attention in organic synthesis due to its environmentally benign character, easy availability, and low cost. Copper has changed the total growth in organic transformations as a catalyst.A number of outstanding catalytic systems have been developed in recent years, many organic reactions, such as formation of C (aryl)-C (aryl), C (aryl)-N, C (aryl) - O andC (aryl)-S, bonds as well as many other useful transformations.

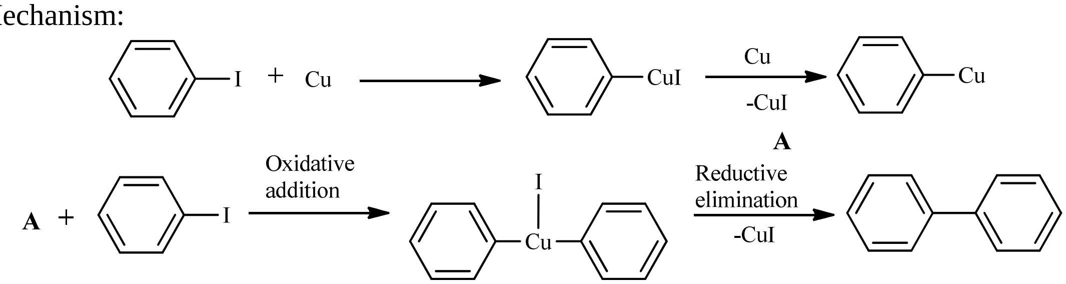
Carbon-Carbon bond formation.

I. Ullmann reaction:Ullmann coupling reactions of aryl iodide.[10]

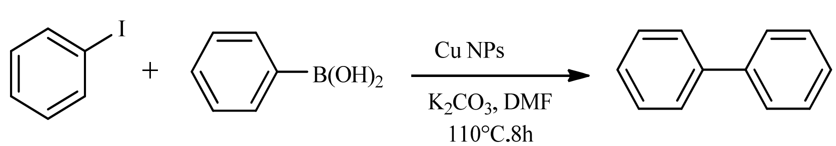


Reagents: Iodobenzene (0.5 mmol), Cu NPs (1.6 equiv.), DMSO (1 mL).

Mechanism:

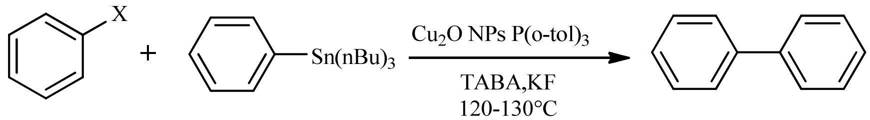


II.Suzuki reaction:Suzuki coupling reaction between aryl iodide and phenyl boronic acid.[11]



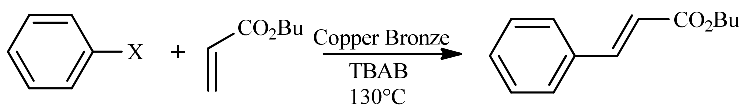
Reagents: Iodobenzene (0.50 mmol), phenyl boronic acid(0.75 mmol), K_2CO_3 (1.5 mmol), catalyst (2 mol%), DMF (12.5 mL).

III.Stille reaction:Cross coupling between aryl halides and organotin derivatives is known as Stille coupling.[12]



Reagents and reaction conditions: Aryl halide (0.3 mmol), tin reagent (0.4 mmol), Cu_2O NPs (10 mol %), P (o-tol)$_3$ (20 mol %), $KF·2H_2O$ (2 equiv.), TBAB (1.5 g); 125-130°C.

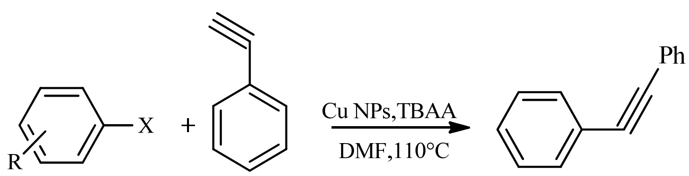
IV.Heck reaction:Coupling reaction between aryl halide and activated alkenes.[13]



X=I,Br

Reagents and reaction conditions: Aryl halide (1 mmol), butyl acrylate (1.2 mmol), TBAA (1.5 mmol), TBAB (3 g), copper bronze (3 mol %); 130°C, 16 h.

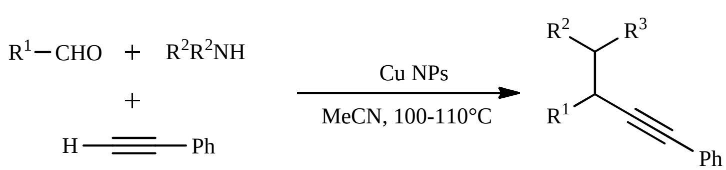
V. Sonogashira reaction:Sonogashira reaction of terminal alkynes with aryl halides.[14]



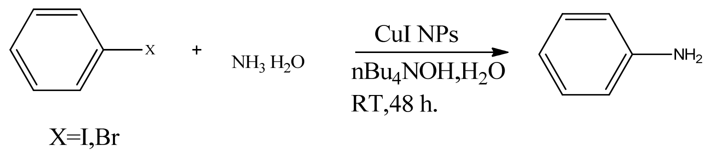
X=I,Br

Reagents and reaction conditions: Aryl halide (0.25 mmol), phenylacetylene (0.38 mmol), TBAA (0.40 mmol), Cu nanoclusters (1.2 mol %), DMF (2.5 mL); 110°C, 24 h.

VI. Three-component condensation: Coupling reaction between aldehyde, amine, and alkyne usingCuO nanoparticles [14]



VII. Aniline from aryl halides in aqueous solution.[15]



Reagents and reaction conditions Aryl bromide (1.0 mmol), CuI NPs (3.0 mol%, X=Br; 1.5 mol%, X=I), nBu4NOH (3 mmol), 28% aqueous NH3(5 equiv., X=I; 10 equiv., X=Br); (RT, X=I; 808C, X=Br), N2 atmosphere,
24–48 h for X=I and Br, respectively. 10 equiv. NH3. 48 h.

Conclusion:

Catalysis is amajor part of many chemical industrial processes and plays an important role in the conversion of several raw materials into useful products in under the laws of Green chemistry. This paper presents an account of the recent developments in C-C and C-heteroatom bond formation usingCu(0) Nanocatalysts and the scopes of Nanocatalysts.

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