NANOMATERIALS: AN OVERVIEW ON THE RECENT APPLICATION IN CATALYSIS

Abstract

Nanoscience and nanotechnology attracts considerable attention in the recent time and has become one of the most important area of research because of their unique properties and applications as catalyst, sensors, electronics, medicine, bio-sciences, drug delivery, opto-electronics, abatement of pollution etc. It is highly multidisciplinary which deals with all branches of science. Nanomaterials are the chemical substances having the structure of at least one dimension within 1-100 nm range. They possess different important properties such as high surface area, surface energy, crystal structure, physical and chemical stability etc. Due to these properties, they have many applications in different field including catalysis. In this chapter, we have discussed only recent application of carbon based nanomaterials, metal-oxide based and clay/LDH based nanomaterials in the field of catalysis.

Keywords: Nanoparticles; Metal-oxide nanoparticle; Clay supported nanomaterials; LDH; Characterizations; Catalysis

Authors

Pinky Saikia
Joya Gogoi College, Khumtai,
Golaghat, Assam
pompipinkysaikia@gmail.com,

Subrat Jyoti Borah
Joya Gogoi College, Khumtai,
Golaghat, Assam
subratjb@gmail.com

I. INTRODUCTION

Nanomaterials are a set of substances with at least one dimension within nanometer range (1-100 nm). These includes nanoparticles, nanofibers and nanoplates [1]. Nanoparticles exhibits improved physical and chemical properties which are different from free atoms or molecules making up the nanoparticles and also from bulk solids with same chemical composition. Nanomaterials are used in various fields including chemical and textiles industries, sensors, catalysis, biotechnology, electronics, medicine to provide better and improved technologies in nanoscience [2-9]. Nanoparticles have large surface area due to distribution of large fraction of the atoms on the surface and are used as catalyst in different fields of research [8-9]. Due to the some unique properties including optical, magnetic, electrical, and other properties, they have greater impacts in the field of electronics, medicine, and catalysis [10]. These are also widely used in areas of medical diagnostics, material modification, abatement of environmental pollutants and biotechnology which requires further modification of nonmaterial into different structure with different features. The most important feature is the catalytic application [1].

The most commonly used approach for synthesis of Nanomaterials are -top down and bottom up approach respectively (Figure 1) [11]. Top down approach includes- mechanochemical processing, electroexplosion, sputtering, laser ablation, lithography, electrospining etc. [11] whereas bottom up approach includes- chemical vapour deposition, plasma arcing, wet chemical methods etc. [11]

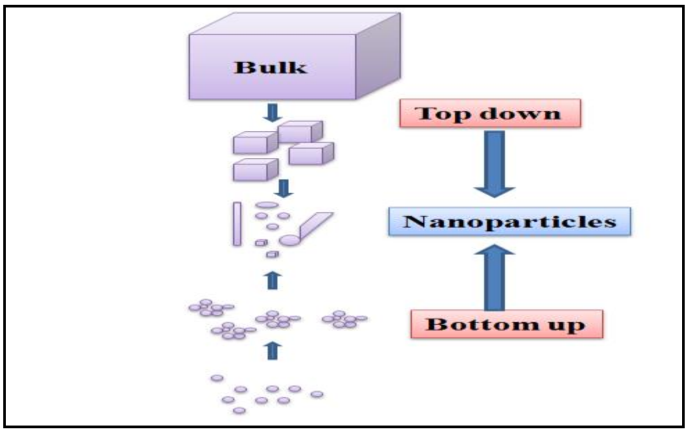


Figure 1: Schematic representation of synthesis of nanomaterials

In recent years, synthesis and application of Nanomaterials becomes one of the interesting field of research in Nanoscience and Nanotechnology due to their potential applications in science and industry [12].On the other hand, use of nanomaterials as heterogeneous catalysis is the another important field of research for the development of the chemical industry [13-16] due to their high catalytic activity and selectivity for specific reactions. Nanocatalysts have attracted more attention to researchers and are used for catalytic chemical reactions such as the oxidation reaction [13], the reduction reaction [14], coupling reaction [15,16] the electrochemical reaction [17-21]. In addition to this, they have some properties like the surface and interface effect, small size effect, quantum size effect and macroscopic quantum tunnel effect, potential applications like catalysis, biology, and medicine and so on.

Catalytic nanomaterials can be classified into the three types as described in Figure 2.

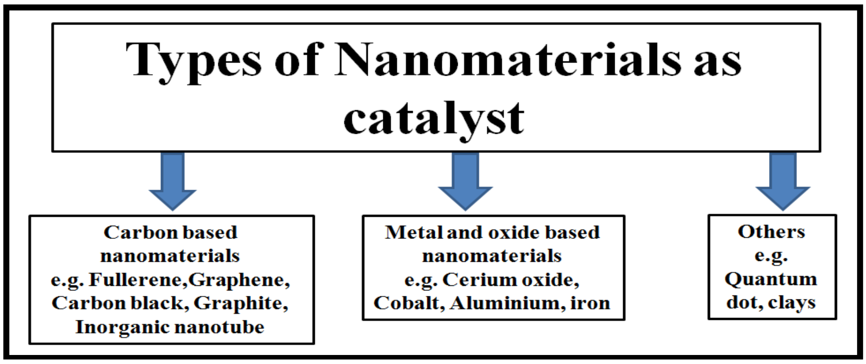


Figure 2: Different types of Nanomaterials used as catalyst

The catalytic nanomaterials can be characterized by different technique such as small-angle X-ray scattering, BET analysis, XRD, Temperature programmed oxidation (TPO) Temperature programmed reduction (TPR), SEM and TEM [22-24] etc. Table 1 shows different characterization techniques for nanomaterials.

Table 1: Different Characterization Techniques used for Nanomaterials

Techniques	Characterizations
Transmission electron microscopy (TEM)	It is used to determine the shape, size and crytallinity of nanomaterials
X ray diffraction (XRD)	To determine the crystal structure
UV-visible Spectroscopy	Used for light absorption and scattering
X ray photoelectron spectroscopy (XPS)	Used to determine the chemical composition
BET analysis	Determine the surface area of nanomaterials
Scanning electron microscopy (SEM)	Used to determine the shape and assembly structure
Energy dispersive X ray analysis (EDX)	It gives the chemical composition of different components present in the nanomaterials
Scanning tunneling microscopy(STM)	Used for the identification of size and shape of nanomaterials
Ultraviolet photoelectron spectroscopy (UPS)	It determines the electron valence band
X ray emission spectroscopy (XES)	It also determines the electron band gap

In this chapter we have discussed about the recent applications of some nanomaterials in the field of catalysis.

1. **Application of carbon based nanomaterials:** Carbon is one of the unique elements found in the universe and it becomes 6^{th} important common element in the universe and the 4^{th} most common element in the solar system and also 17^{th} most common element in

the Earth's crust [25]. Due to the ability of carbon to catenate the study of carbon science become one of the most important fields of nanoscience, materials science, engineering and biology also [26]. Different low dimensional allotropes of carbon are known such as graphite, activated carbon, carbon nanotube, Fullerene (C_{60}) family, polyaromatic molecules [27-30] and graphene [31-33] etc. And they have attracted substantial attention for researchers in the different fields such as in electronics and semiconductor industry, as data storage devices, as sensors and bioelectronics, composite materials, energy conversion, catalysis, biomedicine and theranostics [34] etc. The structure and application of some carbon based nanomaterials are discussed below:

- **Graphite:** The word Graphite was derived from the Greek word "graphein" [35]. In Graphite carbon atoms are arranged in a hexagonal ring like structure and are held together by strong covalent bond and the Graphite layers are held together by weak van der Waal forces which results the capability of layers to slide over each other and exhibiting soft and slippery physical properties[26]. It possesses the flaky like morphology as shown in Figure 3.

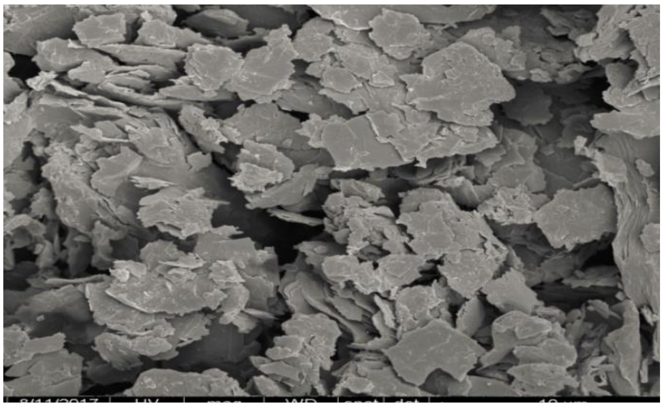


Figure 3: Field emission scanning electron micrographs of graphite [26].

Due to the delocalization of π-electrons of carbon atom Graphite has an ability to conduct electricity [26]. Graphite possesses both metal and non-metallic properties, high thermal and electrical conductivity due to which it is used for the preparation of electrode and electrical arc lamp [36].

- **Buckminsterfullerene:** Harry Kroto and Richard Smalley from University of Sussex and Rice discovered Buckminster Fullerene [26] as one of the Allotrope of carbon. Due to the unique photo physical and photochemical properties they attracted significant attention in the field of research [26]. Fullerene consists of sp^2 bonded carbon atom of different size in the form of hollow sphere as shown in Figure 4 [37]. Fullerene has the ability to act as sensitizer and used for blood sterilization, cancer therapy [34] etc. It has diverse application in the field of nanomedicine such as antimicrobial, antiviral, and antioxidant agents [38, 39].On the other hand, Fullerene can also be used for the production of cosmetics in human skin care.

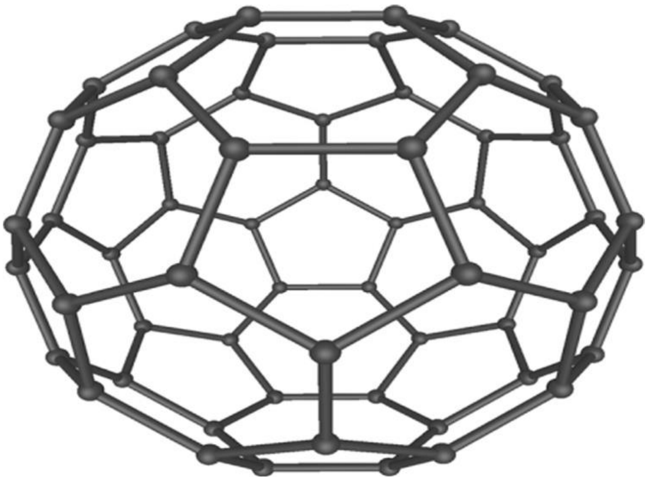


Figure 4: Structure of Fullerene [39]

- **Carbon nanotube:** Carbon nanotubes are the another type of allotrope of carbon having the hollow cylinder like structure consists of graphene sheets as shown in Figure 5[26,34,40]. Carbon nanotubes are classified into two types based upon the no of graphene sheet as single wall carbon nanotube (SWCNT) which can be formed by rolling of single graphitic sheet and multiwall carbon nanotube (MWCNT) which can be formed by the rolling of few graphitic sheet with an interlayer spacing of 3.4Å [40]. The diameter of CNT varies from 0.4 nm to 2.5 nm and sometimes also found to 100 nm [34]. The layers in MWCNT are held together by van der Waals force. Due to their unique mechanical, electrical and structural diversity, fast electron transfer rate, high surface area, it exhibits superior strength, flexibility, electrical conductivity and magical behaviour towards various application including biosensor, medical diagnosis and treatment of various diseases, catalysis [40,41] etc.

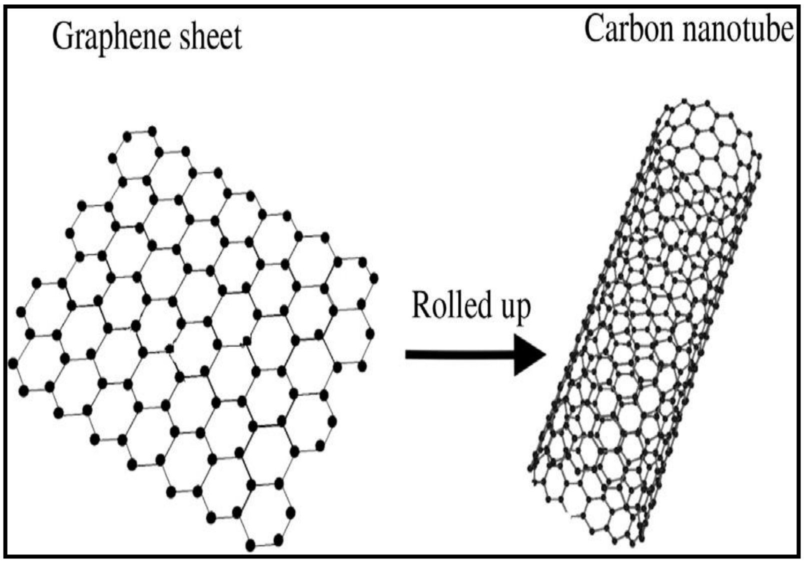


Figure 5: Structure of CNT [40]

- **Graphene:** Mouras and co-workers first introduced Graphene as "graphitic intercalation compounds (GIC)" [40]. Graphene consists of planner graphitic sheet of sp^2 hybridized carbon network with carbon-carbon bond length of 1.42Å and an interlayer spacing of 3.4Å as shown in Figure 6 [40]. Due to the important optical, electrical, chemical properties, high surface area, chemical purity and free π electrons it attracts attention in the field of research [34]. It is used as biosensor, drug delivery, treatment of various diseases including cancer therapy etc [34,40-41]. Different researchers has developed various derivatives of graphene as graphene oxide, reduced graphene oxide, few layer graphene oxide, chemically changed graphene oxide [34]. Among these graphene oxide and reduced graphene oxide have attracted more attention in sol-gel chemistry. Graphene oxide is also used as biosensor, cellular imaging, nanoprobes, anticancer drug delivery [34] etc.

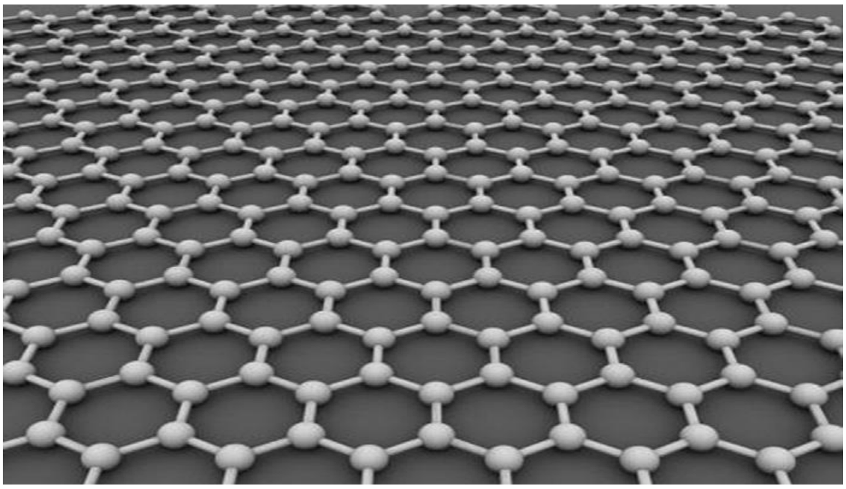


Figure 6: Structure of Graphene sheet [40]

Graphene and graphene based nanomaterials can be synthesized by different methods such as hydrothermal method, thermal annealing, chemical vapour deposition (CVD), photoreduction, graphene oxide exfoliation methods [40-43] etc. Different characterization techniques used for the of Graphene based nanomaterials are - XRD, Infrared spectroscopy, UV-Visible spectroscopy, Thermogravimetric analysis (TGA), SEM-EDXA, HRTEM, AFM, Raman spectroscopy, XPS, Atomic Force Microscopy (AFM) etc. Graphene based nanomaterials are also used as catalyst in different reaction like oxygen reduction reaction (ORR), water splitting, Fischer-Tropsch synthesis (FTS), CO_2 reduction, water treatment, air purification [43]. Different researchers have used graphene based nanomaterials as catalyst in different applications some of them are shown in Table 2.

Table 2: Different types of graphene based nanomaterials and their uses as catalyst [43]

Graphene based nanomaterials	Application as catalysts
Pt-M (M=Co,Ni) supported reduced Graphene Oxide nanocomposite	Used as electro catalyst in Oxygen Reduction Reaction
Pt/G-porous carbon nano fiber based nanomaterial, Ag/Nitrogen doped reduced graphene oxide	Used as electro catalyst in Oxygen Reduction Reaction
Nitrogen doped Graphene	As electrocatalyst in Oxygen Reduction Reaction
N−S/G, Pt/CNT-G	Hydrogen Evolution Reaction
N−P/G, Co−N/G, N-PC@G	Hydrogen Evolution Reaction, Oxygen Reduction Reaction
N-GQDs/g-C_3N_4	water splitting reaction
Cu_2O/FLG, Pt/TiO_2-rGO	water splitting
Fe/rGO, Ru/G	F-T synthesis
CZZA/rGO, Cu/p-NG, Pt-rGO, ZnO/G	CO_2 reduction
Mn-MGO, NRGO@Co, NG, CN/RGO/ZS, CN-G, TiO_2/G/Cu_2O	water treatment
MnO_2/G, ZnO/G, TiO_2/G	air purification
Pd/N-Rgo	Hydrogenation
Co/NG	Oxidation

2. **Application of metal oxide-based nanomaterials:** Due to some unique properties such as optical properties, higher ductility at elevated temperatures, cold welding properties, paramagnetic behaviour, catalytic and selective activity metal oxide nanoparticles are also widely used in the field of nanotechnology [43]. These are used for the development of functional nanomaterials and have lots of application from semiconductor to insulator [44]. Different types metal oxides such as CuO, ZnO, SnO_2, Al_2O_3, MgO, Fe_3O_4, ZrO_2, AgO, TiO_2, CeO_2 etc. are widely used in the materials chemistry research, medicine, agriculture, information technology, biomedical, optical, electronics, catalysis, environment, energy, and sensor based research [45]. The metal oxide nanomaterials are also used as gas sensing for different types of gases like carbon dioxide, CO, O_2, O_3, methane, nitric oxide, nitrogen dioxide, ammonia, hydrogen sulphide, hydrogen gas etc [45]

   In the recent years noble metal-based nanomaterials have attracted attention in the field of nanotechnology due to different unique chemical and physical properties [46]. Different types of noble metal such as Au, Ag, Pt, and Pd supported on TiO_2, CeO_2, ZrO_2 and Clay etc. The most common methods of preparation noble -metal based nanomaterials are such as impregnation, hydrothermal, photodeposition, chemical reduction, solvothermal, co-precipitation, deposition and precipitation method [46-47] etc. These are mainly used as a catalyst in abatement of pollutants, minimization of waste, conversion of energy, water splitting reaction and different types of organic reactions like Sonogashira, Heck, Miyaura-Suzuki-type reactions and other C-C bond formation reactions [47]. Different types of noble metal oxide nanomaterials and their application as catalyst reported by different researchers [47] are shown in Table 3.

Table 3: Different types of noble metal-metal oxidebased nanocomposite and their application as catalysts [47].

Noble-metal based nanomaterials	Applications as catalysts
TiO_2 supported Au^0-nano particle	As photocatalyst for oxidation of acetone and 2-propanol
Au @TiO_2	As photocatalyst for CO_2 reduction
Au/TiO_2	Water splitting reaction
Ag@Cu_2O	Photodegradation of methyl orange
Ag@ZnO	Photodegradation of rhodamine-B
TiO_2/Au	Photocatalytic H_2 generation
Pt/Cu_2O-TiO_2	Photocatalytic reduction of CO_2
Pt/rGO@TiO_2, Pt/C-Mn_xO_{1+x}, Pt/MnO_2/GS	Methanol oxidation
Pt/CeO_2-NBs	Formic acid oxidation
Pt/SnO_2, Pd-Mn_3O_4	Electrochemical H_2 evolution
Pd-Mn_3O_4/carbon black	Electrochemical O_2 evolution
ZnO/Au	water splitting
Pt/CeO_2, Pt/TiO_2	CO oxidation
Au-SnO_2, Fe_2O_3-Au	4-nitrophenol reduction
Ag@Cu_2O	Suzuki–Miyaura cross-coupling
Au/TiO_2	Photocatalytic activity
ZnO NP-Au	Degradation of methylene blue
Fe_3O_4@Montmorillonite	C-C bond formation reaction

3. **Application of clay based nanomaterials:** According to geologist clay is the geological materials with size greater than 4 μm [48]. Clays are aluminosilicate and arranged in layered structure which is composed of tetrahedral silica $[SiO_4]^{4-}$and octahedral alumina $[AlO_3(OH)_3]^{6-}$[48]. These tetrahedral and octahedral layers are combined to form each layer and the apex of tetrahedrons and octahedrons are occupied by oxygen and the interlayer is occupied by metal ion [48]. The layers are stacked together by van der Waals forces of interaction [48].

Table 4: Types of Clay Minerals [49]

Group	Layer Type	Group Members	Layer Charge	General Chemical Formula	Remarks
Smectite	2:1	montmorillonite, saponite, pyrophyllite, nontronite, talc, vermiculite	0.5-1.2	$(Na, Ca)_{x=0.33}$ $(Al, Mg)_2$ $(Si,Al)_4O_{10}(OH)_2 .xH_2O$	x indicate the variable amount of water molecules
Kaolinite	1:1	kaolinite, dickite, nacrite	~ 0	$Al_2Si_2O_5(OH)_4$	group members are polymorphs
Illite	2:1	Illite	1.4-2.0	$(K,H_3O)Al_2 (Si,Al)_4O_{10} (OH)_2 .xH_2O$	x indicate the variable amount of water molecules
Chlorite	2:1:1	amesite, cookeite, chamosite, daphnite	Variable	(Fe, Al, Li, Mg, Zn, $Cr)_{4-6}(Al, Si)_4$ $O_{10}(OH, O)_8$	sometimes placed as a separate group in phyllosillicate

Among the various clay minerals, Montmorillonite clay is the most widely used clay of the smectite group in different field [50-51]. It is one of the hydrated 2:1 layered aluminosilicate of the smectite group which composed of two tetrahedral silicate sheets, which are bonded to either side of an octahedral aluminate sheet. The isomorphous substitution of Si^{4+} and Al^{3+} by lower valence cations such as Mg^{2+} results in the imbalance of charge in the clay structure which is balanced by hydrated exchangeable cations and occupies the position between clay layers. The montmorillonite clay structure is pictorially is shown in Figure 7. The modified montmorillonite clay has attracted much attention of the chemists because of their large applications in various catalytic reactions [51]. Montmorillonite clay can be modified by treatment with mineral acid under controlled conditions to give partially delaminated clay with higher surface area and contains micro and mesopores with diameters 0-10 nm. This highly porous material can be efficiently used as a support for preparation of metal nanoparticles.

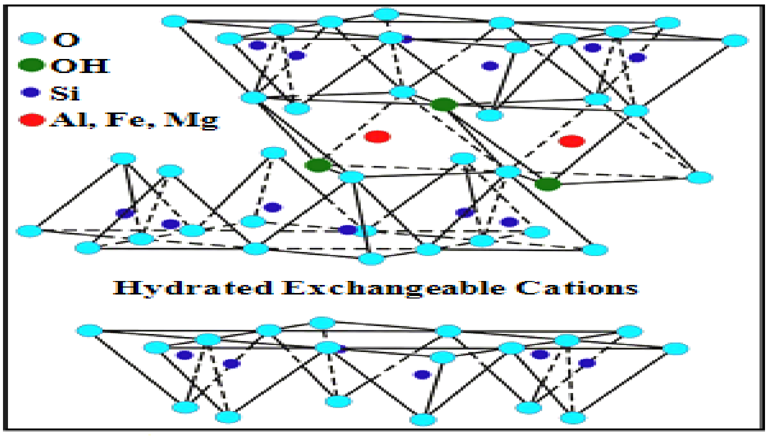


Figure 7: Structure of Montmorillonite clay [51]

Different characterization techniques used for Clay based nanomaterials are respectively X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), UV-Vis spectroscopy, Fourier Transform Infrared (FT-IR) spectroscopy, NMR spectroscopy, Thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC) etc [48].

Due to their interesting physical and chemical properties such as high surface area, swelling, ion exchange and active broken-edge $M\text{-}O^{-}$ bonds clay-based nanomaterials have many applications in the field of absorption, adsorption and catalysis etc [52]. The Bronsted and Lewis acid character and cation exchange capacity of clays leads them to use as catalyst for organic transformation reaction such as esterification of β-keto esters, Friedel-Crafts reactions, addition, oxidation, epoxidation, hydrogenation, allylation, alkylation, acylation, diazotization, rearrangement, isomerization, cyclization condensation, hydrogenation reaction[52]. Different types of clay-based nanomaterials such as TiO_2-pillared clay supported V_2O_5 catalyst can be used for the selective oxidation of H_2S containing water and ammonia [52]. Clay based catalyst are also useful for the conversion of biomass-based and biomass-derived feedstocks to some useful feedstocks [52]. Al/M pillared montmorillonite clays (where M= Fe, Cu, Mn) are employed for the degradation of organic pollutants [52].

In recent years anionic clay-based materials like Hydrotalcite type materials are more useful in many applications starting from adsorption to catalysis [53-55]. Layered double hydroxide (LDH) also known as anionic clays are 2D nanomaterial as shown in the following Figure 8 with structural formula of $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2](A^{n-})_{x/n}.mH_2O$ (where, M^{2+} and M^{3+} are divalent and trivalent metals, respectively; A^{n-} is the interlayer anion).

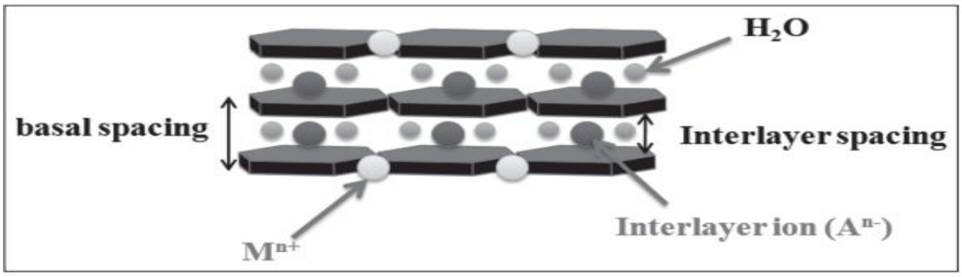
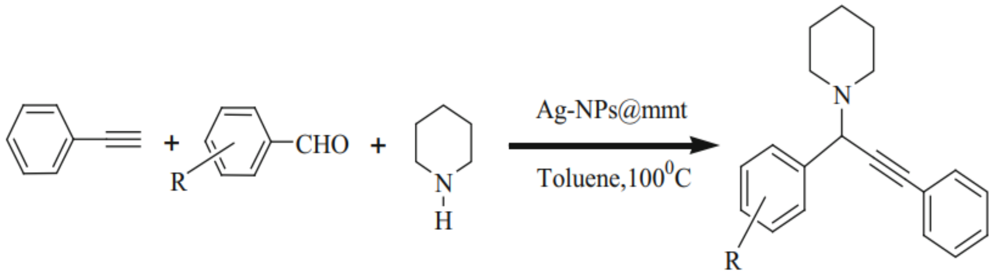


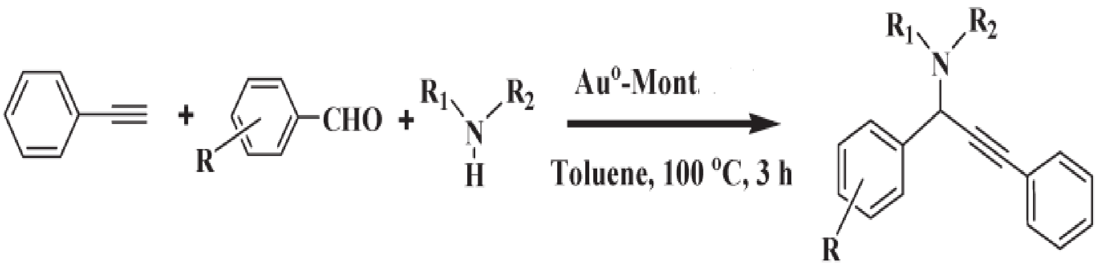
Figure 8: Schematic representation of Hydrotalcites

They play an important rule as catalyst in the field of research due to their unique properties like high surface area, uniform atomic level distribution, acid-base bifunctionality, high thermal stability, memory effect [53-55]. LDH or Hydrotalcite based nanomaterials are used as photocatalyst or photoelectrocatalyst for the conversion of solar energy to clean chemical reagent [54]. These are also used as efficient environmental catalyst for the treatment of green house gases such as N_2O, CO_2, CH_4 oxidation to useful feedstocks [54]. Now-a-days oxygen evolution reaction becomes one of the great challenges for researcher for example, Ni-Fe LDH, Ni-Co LDH, Co-Fe LDH and Ni/Co/Fe LDHs are used as electrocatalyst for water splitting reaction to hydrogen and oxygen evolution [55].

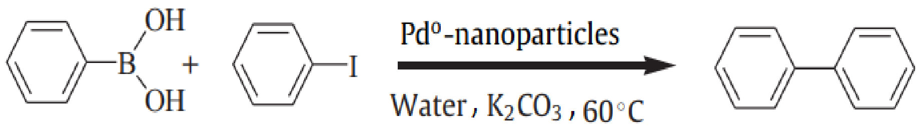
The clay supported metal nanoparticles have found wide range of applications in different field of research such as catalysis, biology, electrochemical sensor and electronics etc. Due to growing environmental concern, researchers have attracted for heterogeneous system of metals in catalysis. Clay supported silver nanoparticles can also be used as an active catalysts for various organic transformations like three component coupling reaction, rearrangement reaction, cycloaddition reaction, oxidation reaction etc [56-58]. Cu^0 -nanoparticles supported on montmorillonite clay used for different catalytic reactions such as alcohol oxidation, C-N cross coupling, coupling of alkyl azide and terminal alkyne to form 1,2,3-triazole and other C-C bond formation reaction [59, 60]. Gold nanocrystals stabilized on modified montmorillonite have been used as highly efficient catalyst for the three-component coupling reaction aldehyde, amine and alkyne to synthesize propargylamine which is a biologically active molecule. Clay supported Pd-nanoparticles have been used active catalyst for Suzuki–Miyaura coupling reaction in aqueous medium with recyclability of the catalyst [50]. Fe_3O_4 magnetic nanoparticles supported on modified montmorillonite have been used as active catalyst for BV Oxidation, synthesis of dihydropyrimidones [59-61]. Uses of clay-supported metal nanoparticles for some specific reactions [56-61] are listed below.



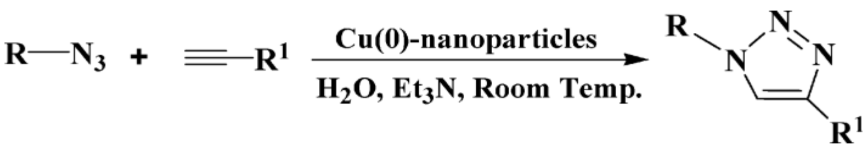
Scheme 1: Synthesis of propargylamine using Silver nanoparticles supported on modified montmorillonite clay



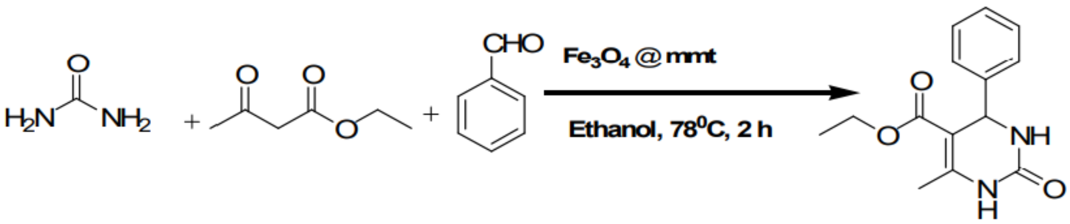
Scheme 2: Three-component coupling reaction of aldehyde, amine and alkyne catalysed by gold nanocrystals stabilized on montmorillonite.



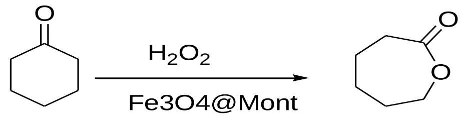
Scheme 3: Clay supported Pd⁰-nanoparticles catalyzed Suzuki–Miyaura reaction between iodobenzene and phenylboronic acid



Scheme 4: 1,3-dipolar cycloaddition of azide and terminal alkynes catalysed by clay supported Cu⁰- nanoparticles.



Scheme 5: Montmorillonite clay supported Fe_3O_4 nanoparticles catalysed three-component condensation reaction to synthesize DHPMs (Dihydropyrimidones)



Scheme 6: Baeyer-Villiger Oxidation catalysed by magnetic Fe_3O_4nanoparticles stabilized on montmorillonite using H_2O_2 as oxidant.

II. CONCLUSION

The carbon based nanomaterials like graphene, carbon nanotube has undoubtedly make attention towards nanoscience research due to their unique properties and has diverse used in optics, electronics, and energy storage as well as in catalysis.

Supported metal nanoparticles and other non-metal based nanocomposites are also become one of the new and novel sustainable catalyst for future research work and these nano catalysts are far better compared to conventional catalyst. Supported nano catalyst exhibited large surface area and are used for different organic and inorganic transformations like oxidation, reduction, coupling reaction and synthesis biologically important compounds etc. Due to their high efficiency, such nano catalysts may be useful large-scale synthesis of fine and bulk chemicals.

In addition to this clay-based nanomaterials have also many applications in catalysis due to their unique physicochemical properties such as high surface area, swelling, ion exchange and active broken-edge $M\text{-}O^-$ bonds. LDH based nanomaterials also act as an efficient environmental catalyst for the treatment of green house gas to useful feedstock and become another diverse field of research.

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