

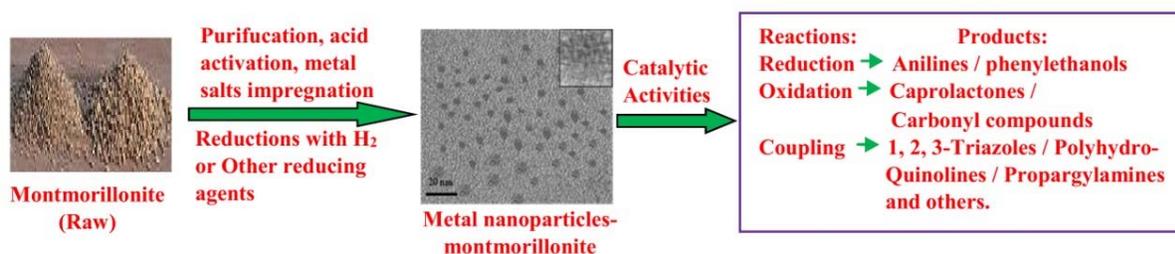
Recent advances in metal nanoparticles supported on Montmorillonite as catalysts for organic synthesis

Dipak Kumar Dutta*

CSIR-North East Institute of Science and Technology, Advanced Materials Group, Materials Sciences and Technology Division, Jorhat-785006, Assam, India

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ABSTRACT



Nanostructured materials has appealed considerable attention due to their characteristic properties and applications in different fields. Metal nanoparticles supported on modified montmorillonite composites have led to the generation of new and novel heterogeneous 'Nanocatalysts', which are much more efficient than other catalysts and thus pave the way for developing sustainable environmentally benign catalysis and chemical procedures. Such *nanocatalysts* are progressing towards their use in chemical industries. This review presents the recent trend of advances in the synthesis and catalytic reactions of supported metal nanoparticles on acid activated montmorillonite. Metals nanoparticles-montmorillonite composites show efficient catalytic activities with high conversions and selectivity for hydrogenation, transfer hydrogenation, oxidations and coupling reactions. Raw montmorillonite possesses no catalytic activity, however acid activated montmorillonite exhibits excellent acid catalytic activities.

Keywords: Metal-Nanoparticles, Supported Catalysts, Montmorillonite, Heterogeneous Catalysts, Nanocatalysts, Benign catalysts

INTRODUCTION

Nanostructure materials have attracted great attention in all fields of science.¹⁻³ The nano-catalytic processes show promising importance and interest in academic and chemical industries.⁴⁻⁷ The concept of nanoscience is related to the matrix of particles with less than 100 nm size, imparting innovative properties in

respect of electronic and structural modifications. Metal nanoparticles catalysts have obtained significance because of their high reactivity and selectivity. The newer type of catalysts i.e. 'Nanocatalysts' of metal nanoparticles, show enhanced activities. The catalysts are preferred due to: large surface area, greater activity, higher selectivity; higher recyclability and advantage in separation of the products. The activities are primarily based on size and shape of the crystals⁸⁻¹² and also on the chemical surroundings of the catalysts.^{1-3,13} Advantages of metal nanoparticles lead to the generation of promising efficient heterogeneous catalysts.¹⁴⁻¹⁷ As an example, Sn⁰-nanoparticles with size 20–30 nm promote allylation reactions of carbonyl compounds to produce the respective products showing higher yield 93% in 1.5 h than that of 13% yield exhibited by bulk Sn.¹⁴ Likewise, allylation reaction of benzaldehyde catalysed in presence of In nanoparticles of size < 100 nm showed yield 85% in 10 h, much higher than the yield of only 47% in 24 h mediated

*Corresponding Author: Dr. DK Dutta
CSIR-North East Institute of Science and Technology, Jorhat-785006, Assam, India
Email: dipakkrdutta@yahoo.com

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by 200 mesh In powder.¹⁴ The size and shape of the nanoparticles are of significant for efficient catalytic activities¹⁸⁻²¹ in hydrogenations,²²⁻²⁹ oxidations,^{30,31} and other coupling reactions.³²⁻³⁷ The properties of nanomaterials can be tuned by modifying their size, shape, and composition.^{11,38-40} By controlling shape of catalyst particles, higher selectivity could be maintained,⁴¹⁻⁴⁴ viz. hexagonal Pt(111) catalysts showed much higher activity compared to cubic Pt(100) for aromatization.⁴⁴⁻⁴⁶

Metal nanoparticles supported catalysts are generally synthesised on supports like, polymer, organic ligands, metal oxides, carbon, zeolites, clay etc.⁸⁻¹⁰ Montmorillonite is thoroughly studied for stabilizing nanoparticles of metals, as it shows several advantages like cheap, environmental friendly, flexible in nature etc.^{47,48} The synthesis and stabilization of nanoparticles of metals are performed by following any procedures: reduction of metal salts, thermal decomposition, vapour deposition, and electrochemical technique. Two mechanisms viz. electrostatic and steric stabilization⁹ explain the stabilization of nanoparticles of metals. There are several reports on the metal nanoparticles-montmorillonite composites which show the importance of the nanocatalysts.⁴⁸⁻⁵⁴ The surface activity of the montmorillonite and the catalytic sites of the metal nanoparticles lead to the development of a highly active nanocatalyst having both the characteristics i.e. metal and acid functions. In view of the tremendous opportunity for innovative research in respect of supporting metal nanoparticles; montmorillonite is selected for focused discussion.

This article presents the recent trend of the development of metal nanoparticles stabilized montmorillonite composites by several procedures and their catalytic applications.

RESULTS AND DISCUSSION

Preparation of support from montmorillonite:

Among the clay minerals, montmorillonite is thoroughly studied because of its novel and innovative surface characteristics,^{47,55-59} However, these inherent properties can be modified by activation through acid treatment of the clay mineral. The modified montmorillonite finds several applications in foodstuff, paper industry, detergents usage,⁶⁰ catalysts^{55,61,62} and catalyst supports.⁶³⁻⁶⁵ The acid activated montmorillonite serves as acidic catalysts for several organic synthesis, viz. isomerisation,⁶⁶ acylation,⁶⁷ alkylation^{63,64,68} reactions, etc. The structure and other characteristics of montmorillonite have been explored extensively for understating its novel core properties with focus on its innovative applications.

Structure of montmorillonite:

The fundamental structure of montmorillonite is composed of silica and alumina as tetrahedral and octahedral layers which serve as the two basic building blocks of the montmorillonite.^{63,69} The tetrahedral layers is a continuous sheets of silica linked with three corners and the fourth corner is shared with alumina octahedra in adjacent layers (Figure 1). The flat layers of edge-sharing octahedral show cations at its centre and the apices are occupied by OH⁻ or O²⁻. Basically, montmorillonite possesses 2:1 layer silicates.^{47,70-72} The expandable nature of layered silicates leads to the most interesting group of natural catalysts which may have played a vital role in pre-biotic chemical evolution.⁷³⁻⁷⁵

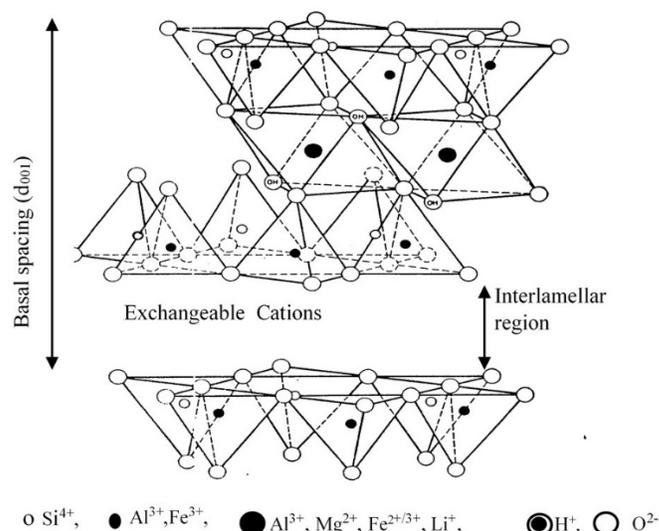


Figure 1. Layer structure (unit cell) of montmorillonite.

In the clay matrix, the partly replacement of Si⁴⁺ with Al³⁺ in tetrahedra and Al³⁺ or Fe³⁺ with Mg²⁺ or Fe²⁺ in the octahedra lead to generate negative charges which are normally neutralised by adsorbing interlayer cations such as alkali ions.⁷⁶ The amount of exchangeable cations adsorbed by the clay is called Cation-Exchange-Capacity (CEC) and is normally expressed as milli-equivalents per 100 g of dried clay. Montmorillonite can show both the Brønsted and Lewis acidic characters and Brønsted acidity develops from the dissociation of the coordinated water molecules in the interlayer region.^{57,77-82}

Acid activated montmorillonite:

Montmorillonite, upon acid activation, improves its characteristics in respect of porosity, surface area, acidity, and catalytic activities.⁸³ The activation of naturally occurring clay with acid treatment replaces the interlayer cations and thus results in leaching of Al³⁺, and leaving the SiO₄ group mostly intact. The activated montmorillonite is partially delaminated and show high surface area, high volume of pores, higher pore diameter^{55,63,84-86} and higher surface acidity⁶⁸ leading to their efficient catalytic activities. The acid activation of the clay results in several significant changes: (1) release of hydrated interlayer cations, (2) delamination of individual clay layers to disoriented aggregates; (3) dissolution of clay layers and (4) development of an amorphous silica. Montmorillonite with the aluminosilicate layered structures exhibits several applications as solid acid catalysts.^{87,88} The commercial clay catalysts K 10 montmorillonite and KSF montmorillonite are widely used as catalysts. K 10 montmorillonite shows much higher surface area (270 m²/g) than KSF montmorillonite (40 m²/g). The acid-activated montmorillonite (1 h acid activation)⁸⁹ showed micro- (<2 nm) and mesopores (2–8 nm), a surface area 580 m²/g and pore volume 0.7 cm³/g. As the acid activation time increases, the pore volume increases accordingly due to removal of some pores. Adsorption-desorption show type-IV isotherms along with an H3 hysteresis loop at P/Po 0.4-0.8, suggesting mesoporous matrix.

SYNTHESIS OF METAL NANOPARTICLES:

Chemical methods:

Metal nanoparticles are synthesized by several wet chemical techniques. The technique of reduction of metal salts aroused much interest because of several advantageous factors such as reproducibility, narrow size distribution, allow to prepare good quantities etc. Faraday, in 1857, first reported⁹⁰ the synthesis of zero-valent metal colloids from metal salts by chemical reduction in presence of stabilizers. The stabilizers such as ligands, polymers, etc. serve to control the growth nanoclusters and also to prevent agglomeration. Turkevich et.al.⁹¹⁻⁹³ reported first the synthesis of gold colloids of 20 nm by reduction of AuCl₄ with sodium citrate. The prominent stabilizing groups are, thioethers, polymers, phosphines, amines, propylene carbonate, long chain alcohols, organometallics and surfactants.

Metal nanoparticles supported montmorillonite composites:

The metal nanoparticles supported montmorillonite composites can be prepared conveniently through chemical reduction route. The technique involves the metal salts impregnated clay samples and their reduction by agents such as NaBH₄, ethylene glycol, H₂, etc.⁴⁹ The step wise synthesis of the metal nanoparticles stabilized on montmorillonite is presented in Figure 2.

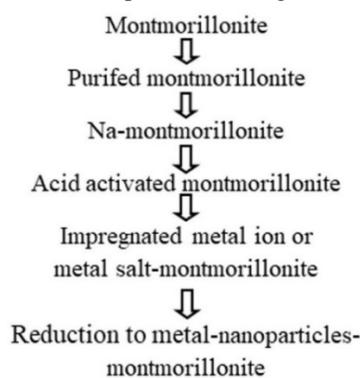


Figure 2. A general procedure for preparing metal nanoparticles stabilized montmorillonite composite.

Reduction with hydrogen:

Metal nanoparticles are highly surface active and therefore, need stabilization on suitable support for practical applications. The development of heterogeneous metal-nanoparticles-montmorillonite catalysts involves intercalation of metal nanoparticles into the interlayer space of layered montmorillonite. Such process, generally involves intercalation of metal-complex into the layered space followed by reduction with suitable reducing agent like hydrogen. Transformation of metal ions to metal nanoparticles through reduction by hydrogen is considered as an efficient process. The tetraamine Pt-complex intercalated montmorillonite was reduced by hydrogen at 140°C⁹⁴ to produce Pt⁰-nanoparticles on montmorillonite surface. Kotkar et al. reported⁹⁵ the synthesis of Rh⁰-nanoparticles-montmorillonite composite by the oxidative degradation of tris(phenanthroline)-Rh(III) composite and reduction with H₂. The stabilization of Pt⁰-nanoparticle was performed⁹⁶ by the reduction of [Pt(NH₃)₄]²⁺ complex on Al-pillared-clay. RuCl₃ impregnated on Na-montmorillonite upon reduction with H₂ yields to Ru⁰-montmorillonite composite at

220°C.⁹⁷ Dutta et al.⁹⁸ reported recently, the synthesis of Pt⁰-nanoparticles of size 0 - 10 nm by reduction of H₂PtCl₆.6H₂O impregnated montmorillonite.

Reduction with hydrazine:

Montmorillonite supported metal nanoparticles composites are conveniently prepared by the reduction of impregnated metal ions with hydrazine. Such composites can be prepared by following surfactant-assisted technique and reduction by hydrazine.⁹⁹⁻¹⁰¹ Dhakshinamoorthy et al.⁵⁴ reported the synthesis of nickel-nanoparticles stabilized montmorillonite composites from Ni²⁺-impregnated K 10 montmorillonite by reduction with hydrazine.

The Pd⁰-nanoparticles supported on montmorillonite can be prepared from K₂PdCl₄ metal precursor by reduction with hydrazine hydrate.¹⁰² The catalytic activities of such Pd⁰-composite was also reported for Heck and Sonogashira reactions.

Reduction with borohydride:

Metal cations can be converted into metal nanoparticles supported on clay by reducing with sodium borohydride.^{52,53,89,103-105} Dutta et al.⁴⁹ reported recently, the methods for the synthesis of different metals nanoparticles. They showed that copper-nanoparticles upon loading on montmorillonite reduces the surface area to 307 m²/g from 680 m²/g suggesting occupancy of nanoparticles into the pores of montmorillonite. This observation was substantiated by lowering the pore volume from 0.69 to 0.40 cc/g. Ganguli et al.¹⁰³ prepared the Rh⁰-nanoparticles supported on K 10 montmorillonite by following reduction technique and the composite showed efficient catalysis. Borah et al.¹⁰⁴ prepared Cu⁰-nanoparticles < 10 nm (Figure 3) into the nanopores of activated montmorillonite which was carried out by the loading of Cu(CH₃COO)₂ following impregnation technique and reduction with NaBH₄ (Scheme 1). Zhou et al.¹⁰⁶ reported preparation of Fe(O)-nanoparticles of size 3–10 nm supported on montmorillonite from Fe³⁺-polycations. Kaneda et al.⁵³ prepared a stable Pd⁰-nanocluster into the interlayers of montmorillonite by reduction of a [Pd(dba)₂] (dba = trans,trans-dibenzylideneacetone) complex with KBH₄. Gold nanoparticles were prepared¹⁰⁷ from Au precursor in presence of N,N,N-trimethyl(11-mercapto-undecyl)-ammonium(HS(CH₂)₁₁NMe₃C)-stabilizing agent. Manikandan et al. reported^{108,109} the preparation of Pt⁰-nanoparticles into montmorillonite using hexadecyl trimethyl-ammoniumbromide as surfactant, hexachloroplatinic acid and NaBH₄. Pt⁰ and Ru⁰-nanoparticles in the interlayers of montmorillonite were synthesized by following a similar technique.¹¹⁰ Montmorillonite impregnated Rh⁰-nanoparticles were also reported.¹¹¹ Fan et al.¹¹² reported the synthesis of supported Fe(O)-nanoparticles from FeCl₃.6H₂O precursor and montmorillonite. By following the NaBH₄ reduction approach,¹¹³ Ag⁰-nanoparticles were synthesized on montmorillonite. Hexadecyl trimethyl ammonium bromide surfactant modified montmorillonite and NaBH₄ reduction technique were utilized to prepare supported Fe-nanoparticles.^{114,115} Gu et al.¹¹⁶ prepared Fe(O)-nanoparticles supporting on smectite clay layers. Zhang et al.¹¹⁷ also reported the preparation of Fe⁰-montmorillonite through chemical reduction route. Kadu et al. reported¹¹⁸ the preparation of bimetallic Fe,Ni-nanoparticles on a clay matrix. In the interlayers of surfactant modified montmorillonite, wormlike Ru⁰-

nanoparticles were prepared¹¹⁹ by following reduction with NaBH_4 .

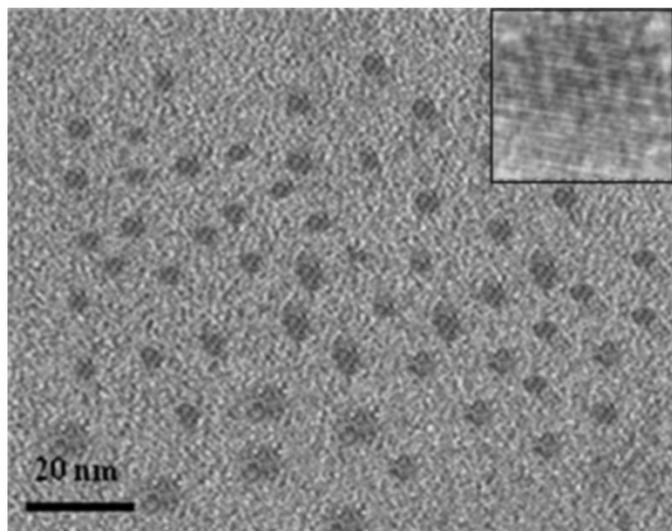
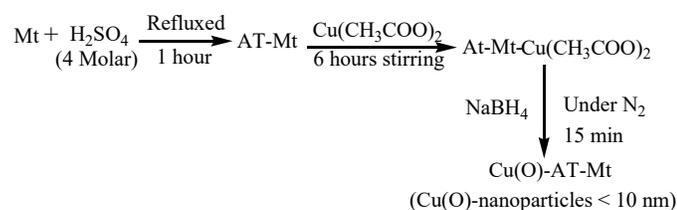


Figure 3. TEM and HRTEM (inset) images of Cu^0 -nanoparticles. (Reproduced from ref. 104 with due acknowledgement of the Royal Society of Chemistry)



Scheme 1 Synthesis of Cu(O)-AT-Mt .

Borah et al.⁸⁹ reported that different sized Au^0 -nanoparticles could be prepared depending on the various tailor made nanopores (1-10 nm) generated on the acid activated montmorillonite. Thus, size of the template or nanopores play a vital role in controlling the size of the metal-nanoparticles.

Reduction with polyol:

Polyol reduction process was reported by two groups; Fievet et al.¹²⁰ and Xia et al.^{121,122} wherein, polyol serves as solvent and reducing agent. Ravindranathan et al. reported¹²³ for the first time for the synthesis of Cu^0 -nanoparticles into the interlayers of montmorillonite involving polyol reduction method by refluxing a copper acetate impregnated clay in ethylene glycol. They also reported that by adopting the same reduction technique, improved copper metal nanoparticles of size 4–5 Å could be prepared.^{124,125} Pd^0 -nanoparticles of 2–3 nm size, could be synthesized¹²⁶ from Pd(II) -complexes intercalated montmorillonite. Ayyappan et al.¹²⁷ carried out preparation of metal clusters of 4–5 Å size by reduction of Ni^{2+} and Ag^+ in the interlayers of montmorillonite. A polyol process was reported by Dutta et al.¹²⁸ for the synthesis of Ni^0 and Zn^0 -montmorillonite nanocomposites from the intercalated / intersalated composites of metal acetate hydrates. They also reported¹²⁹ preparation of Ni^0 -K 10 montmorillonite and Co^0 -K 10 montmorillonite. Dutta et al.²⁹ also reported the preparation of Ni^0 -nanoparticles having 0–8 nm size from impregnated $\text{Ni(CH}_3\text{COO)}_2$ into montmorillonite. The composite

showed surface area of 296 to 548 m^2/g , pore volumes of 0.4 to 0.6 cm^3/g and pore diameter upto 6.8 nm. The XRD data of Ni^0 -nanoparticles reveal the formation of face centered cubic (fcc) lattice. The synthesis of Ru^0 -nanoparticles of about 5 nm size was reported by Sarmah et al.¹³⁰ wherein impregnated RuCl_3 into the nanopores of the modified montmorillonite was reduced by polyol (Scheme 2). The modified clay exhibited nanopores (below 10 nm), which served as support for stabilizing the metal nanoparticles (Figure 4A). Inter-planar lattice fringe spacing of about 0.21 nm of the FCC lattice was observed for the Ru^0 -nanoparticles (Figure 4B).

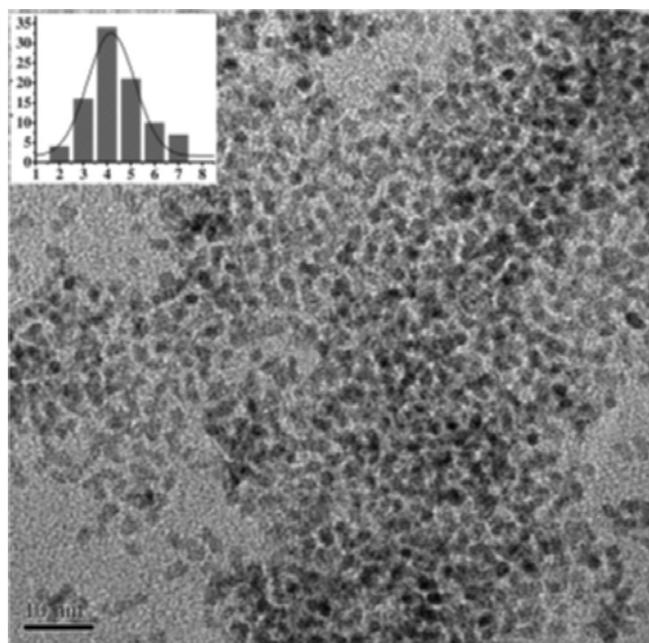


Figure 4 A. A TEM image and particle size histograms with a Gaussian curve fitting (inset) of Ru^0 -nanoparticles on AT-montmorillonite. (Reproduced from ref. 130 with due acknowledgement of the Royal Society of Chemistry).

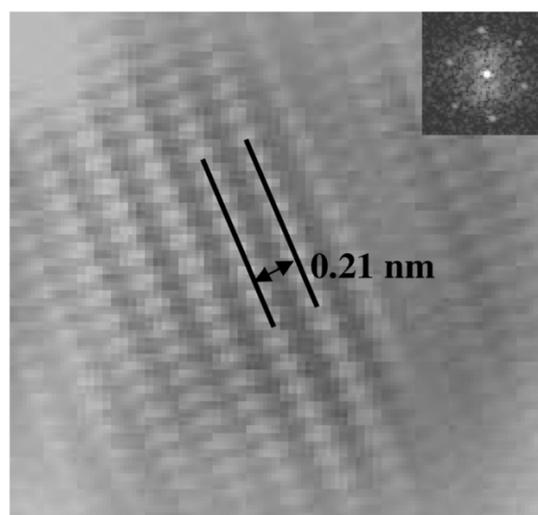
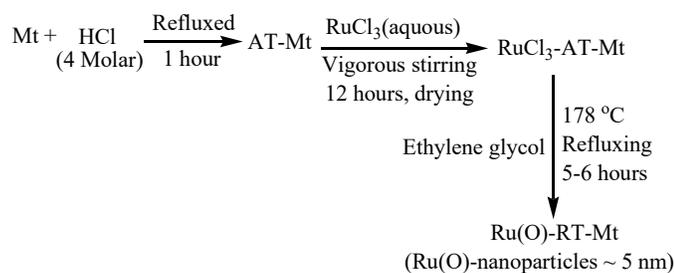


Figure 4 B. HRTEM image and corresponding SAED pattern (inset) of Ru^0 -nanoparticles on AT-montmorillonite (Reproduced from ref. 130 with due acknowledgement of the Royal Society of Chemistry).



Scheme 2. Synthesis of Ru(O)-AT-Mt.

Other chemical methods:

Reduction with ligand functional groups:

There are several ligands with suitable reducing functional groups which were utilized for synthesis of different metal nanoparticles supported into the interlayers of montmorillonite.¹³¹⁻¹³⁵

Impregnation method:

Many reports¹³⁶⁻¹³⁸ are there for the synthesis of supported metal nanoparticles by following ‘incipient wetness impregnation’ method involving solid matrix impregnation with metal precursors followed by drying and reduction. Rangarao and Mishra¹³⁹ synthesized a PdCu bimetallic catalyst on montmorillonite and Al-pillared montmorillonite following the impregnation technique. Zakarina et al.¹⁴⁰ followed the similar impregnation method for the synthesis of tri-metals, Pt, Pd and Ni supported on alumina pillared montmorillonite. Dutta et al.⁸⁹ reported the synthesis of Au⁰-nanoparticles-montmorillonite. The activation of montmorillonite was carried out by acid treatment for developing nanopores for stabilising the metal nanoparticles.^{53,102,130}

Reduction with ascorbic acid:

The Cu⁰-nanoparticles of < 2 nm size were synthesized by reducing with ascorbic acid which also served as capping agent.¹⁴¹ A mechanism was proposed for L-ascorbic acid reduction and stabilization for generation of copper nanoparticles. The structure of L-ascorbic acid gives adequate reducibility to convert Cu²⁺ ions into Cu(0) nanoparticles and the stabilization of the nanoparticles is affected through the formation of Cu-ascorbic acid complex nanoscopic template followed by reduction.

Citrate capped metal nanoparticles:

By following a seeding growth technique and in the presence of micellar template, Au-nanorods of aspect ratios, 4.6 ± 1.2 , 13 ± 2 , and 18 ± 2.5 nm (all with 16 ± 3 nm short axis) were synthesized¹⁴² The seed citrate-capped 3.5 nm diameter Au⁰-nanoparticles were synthesized from HAuCl₄ by reduction with borohydride.

Reduction with glucose:

Deposition-precipitation (DP) technique was followed for the preparation of Au⁰-nanoparticles stabilized on montmorillonite utilizing the precursor HAuCl₄.3H₂O by reducing with glucose in the presence of the stabilizer.¹⁴³

Different reduction techniques:

Szucs et al.¹⁴⁴ synthesized Pd⁰-nanoparticles (2.8–3.5 nm) supported on pillared montmorillonite through a process of reduction of Pd²⁺ of Pd(CH₃COO)₂ with the aid of an ethanol–toluene binary liquid mixture. The Ag/TiO₂ nanoparticles-montmorillonite composite was synthesized by a one-step, solvo-

thermal technique.¹⁴⁵ Reports^{146,147} are there for the synthesis of Ag⁰-nanoparticles-montmorillonite composite without using any reducing agents. A deposition technique was adopted by Gao et al.¹⁴⁸ for the synthesis of Ag⁰-nanoparticles-montmorillonite composite. Huang et al.¹⁴⁹ reported the synthesis of Ag⁰-nanoparticles-montmorillonite composite through an electrochemical procedure involving electrodes technique and methanol as reducing agent. Yao et al. reported¹⁵⁰ preparation of Au⁰-nanoparticles on the surface of chitosan functionalized-montmorillonite hybrid nanosheet in order to fabricate artificial nacre-like functional films. There are several reports¹⁵¹⁻¹⁵⁴ for *in-situ* development of nanometals clusters within the clay layers by a solid-state reaction technique. Ethanalamine was used as a reducing and stabilizer agent by Chen et al.¹⁵⁵ for the synthesis of Pd⁰-nanoparticles-montmorillonite composite.

PHYSICAL METHODS:

Ultrasonic intercalation:

There are several physico-chemical techniques to intercalate metal nanoparticles into the interlamellar region of layered montmorillonite clay mineral. The ultrasonication technique is one of the successful procedures for intercalation of metal nanoparticles into the layered materials. Irradiation of liquid by suitable ultrasonic waves results ‘Acoustic cavitation’ which involves formation, growth and collapse of bubbles. Such phenomena, generate *in-situ* high temperature and pressure along with a shock wave responsible for creating an environment which paves the way for affective intercalation of metal nanoparticles into the interlayer space of the layered clay. Belova et al.¹⁵⁶ in 2008, first reported a *green* method for the synthesis Au⁰-nanoparticles into the interlayers of montmorillonite involving ultrasonication. About 40 min. time was allowed for sonication for complete intercalation of Au⁰-nanoparticles into the clay layers. Belova et al.^{157,158} also reported that expansion of clay layers by neutral polyethelene glycol, negatively charged sodium dodecyl-sulfate and positively charged cetyltrimethyl-ammonium bromide occurred by ultrasonication, followed by replacement with Au⁰-nanoparticles. The Pt⁰-nanoparticles-montmorillonite composite was also prepared by ultrasonication¹⁵⁹

Supercritical fluids:

Supercritical fluids, having low viscosity, high diffusivity, very low surface tension etc. are suitable for several preparations.¹⁶⁰ Pan et al.¹⁶¹ introduced a new protocol based on supercritical technique for the synthesis of Pt⁰-nanoparticles-montmorillonite composite.

Catalytic applications:

The supported metals nanoparticles-montmorillonite composites find applications as stable, efficient, benign heterogeneous catalysts for various organic synthesis.⁴⁸ The modified nanoporous montmorillonite support also serve as an acid catalyst.¹⁶² The different catalytic applications are exemplified below with examples:

Reduction:

Pan et al.¹⁶¹ reported the reduction of nitrobenzene by H₂ to produce aniline catalysed by Pt⁰-nanoparticles-montmorillonite composite. High selectivity, 82–99 % and 100% conversion with the turnover frequency, 1073, were attributed to Pt⁰-nanoparticles

having size 4–8 nm. Zhao et al.¹⁶³ showed that in hydrogenation of nitrobenzene, catalytic activities decrease with increase of size of Pt-particles. Recently, Dutta et al.⁹⁸ showed that stabilized Pt⁰-nanoparticles of < 10 nm size exhibited efficient catalytic reduction of chloronitrobenzenes, wherein, a very negligible C–Cl bond splitting was noticed. p-Chloroaniline(p-CAN) is an important intermediate for organic synthesis.^{164,165} The hydrogenation reactions were carried out by various precious metal catalysts.^{98,164–168} Hydrogenation of p-Chloronitrobenzene(p-CNB) is generally carried out with Pt-catalysts, and the selectivity to the undesired aniline was less than 1%.¹⁶⁹ Liu et al.¹⁷⁰ reported that Ni⁰-nanoparticles-bentonite composite showed efficient hydrogenation of p-CNB to produce p-CAN at 100°C and H₂ pressure of 15 bar leading to the conversion, 92% and selectivity, 98%.

Dutta et al.¹⁷¹ recently reported that the acid treated montmorillonite (AT-montmorillonite) supported Ni⁰-nanoparticles (size about 5 nm) (Figure 5) showed efficient heterogeneous catalysis for hydrogenation of p-CNB to produce p-CAN with a conversion, 97%, and selectivity, 99% under mild reaction conditions (Scheme 3). Among all the halonitrobenzene, chloronitrobenzene showed the highest conversion (Table 1). The high catalytic activities are attributed to the synergistic effects of high surface area (290 m²/g) of montmorillonite and highly exposed and stabilised Ni⁰-nanoparticle.

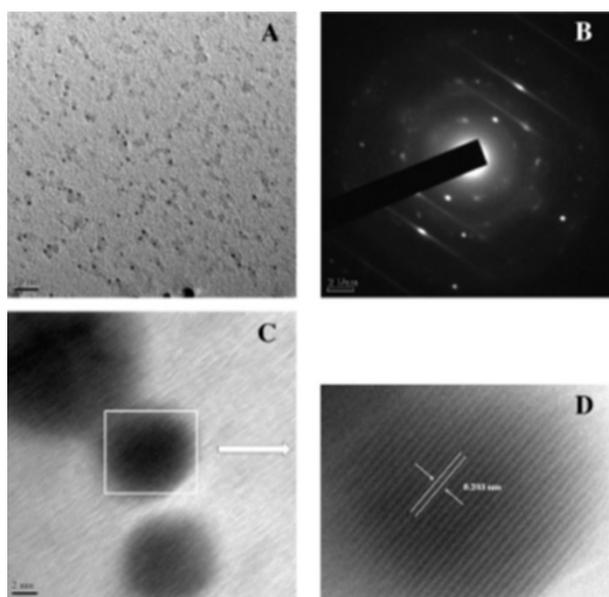


Figure 5. (A) TEM images of Ni⁰-AT-montmorillonite; (B) selected area electron diffraction (SEAD) pattern of Ni⁰-AT-montmorillonite; (C) HR-TEM images of Ni⁰-AT-montmorillonite; (D) enlarge image of HR-TEM with fringe spacing (Reproduced with permission from ref. 171. Copyright 2014 Elsevier B.V.).

Gu et al.¹¹⁶ reported that nitrobenzene could be converted to aniline by hydrogenation catalysed by zero-valent iron(ZVI) impregnated into the interlayers of montmorillonite. The catalyst ZVI exhibited higher reactivity involving Fe concentration of only 0.33 g/L. The high reduction activities of the catalyst is due to Fe(0) (< 0.5 nm) distributed on montmorillonite. The clay-templated ZVI showed very high reactivity.^{172,173}

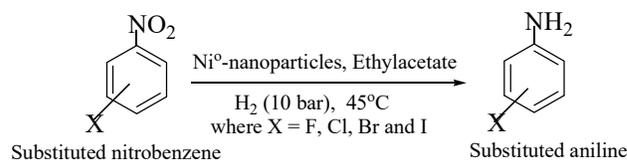
Sarma et al.¹³⁰ reported Ru⁰-nanoparticles (< 5 nm) stabilized on montmorillonite which showed high activity in transfer hydrogenation of substituted nitrobenzenes to anilines (Scheme 4) with conversion, 76–97% and selectivity, 91–100%. The catalysts were active for several catalytic runs.

Dutta et al.²⁹ reported the catalyst Ni⁰-nanoparticles (< 8 nm) which exhibited efficient catalytic activity for transfer hydrogenation of acetophenone to produce 1-phenylethanol showing about 98% conversion and about 100% selectivity (Scheme 5). The conversion gradually decreases upon subsequent runs. The well dispersed Ni⁰-nanoparticles are responsible for such high activity.

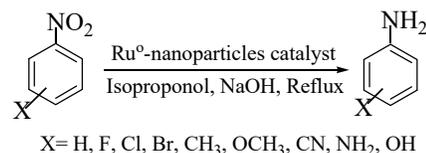
Table 1. Results of hydrogenation of halonitrobenzene over Ni⁰-AT- montmorillonite

Sl. No	Substrate	H ₂ Pr. (bar)	Time (h)	Conv. (%)	Selectivity (%)		
					HAN	AN	Other
1	p-CNB	5	1.0	43.0	99.4	0.6	-
2	p-CNB	10	1.0	97.0	99.1	0.3	0.6
3	p-CNB (2 nd run)	10	1.0	92.0	98.6	0.6	0.8
4	p-CNB (3 rd run)	10	1.0	88.4	97.9	0.8	1.3
5	p-CNB	10	0.8	100	96.0	1.6	2.4
6	o-CNB	10	1.0	96.5	98.3	0.7	1.0
7	m-CNB	10	1.0	98.2	98.2	0.6	1.2
8	p-BNB	10	1.0	92.3	97.9	2.0	0.1
9	p-INB	10	1.0	92.0	97.8	1.7	0.5
10	p-FNB	10	1.0	78.0	97.1	1.2	1.7

CNB = chloronitrobenzene, BNB = bromonitrobenzene, INB = iodonitrobenzene, FNB = fluonitrobenzene, HAN = haloaniline, AN = aniline (Reproduced with permission from ref. 171. Copyright 2014 Elsevier B.V.).

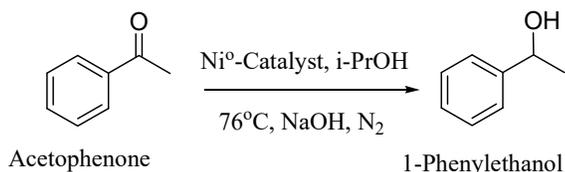


Scheme 3. Hydrogenation of halonitrobenzenes catalyzed by montmorillonite supported Ni⁰-nanoparticles.



Scheme 4. Ru⁰-nanoparticles catalysed transfer hydrogenation of substituted nitrobenzene.

Sarmah et al.⁵¹ reported that Rh⁰-nanoparticles (about 5 nm) montmorillonite composite showed catalytic reduction of aromatic carbonyl compounds to produce alcohols by the transfer hydrogenation with conversion of 56% and selectivity of 100%.



Scheme 5. Ni⁰-nanoparticles catalysed transfer hydrogenation of acetophenone.

Hydrogenation of aromatic molecules is an industrially important reaction. Ir⁰-nanoparticles-montmorillonite composite showed efficient catalysis.¹⁷⁴ The catalyst exhibited a maximum conversion up to 100%, and TOF up to 79 h⁻¹. Zhou et al.¹¹⁹ reported efficient hydrogenation of quinoline by worm-like Ru⁰-nanoparticles impregnated in montmorillonite.

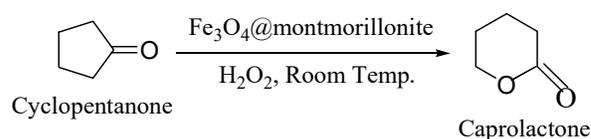
The Pt⁰-pillared-montmorillonite exhibited high catalytic activity in hydrogenation of benzene.⁹⁶ Jasra et al.¹¹¹ also reported the hydrogenation of benzene and other aromatic compounds using Rh⁰-nanoparticles-montmorillonite composite. Asymmetric hydrogenation of ethyl pyruvate to (R)-ethyl lactate was reported^{100,101} in the presence of Pt⁰-nanoparticles dispersed on the clays such as montmorillonite and hectorite. Manikandan et al. reported¹⁰⁹ that Pt⁰-nanoparticles-montmorillonite composite showed efficient hydrogenation of cinnamaldehyde to yield the cinnamyl alcohol. Kotkar et al.⁹⁵ reported the hydrogenation of cycloalkene using Rh⁰-nanoparticle-montmorillonite composite. Dhakshinamoorthy et al.⁵⁴ reported Ni⁰-nanoparticles immobilized K10-montmorillonite catalyst for hydrogenation of olefinic substrates and showed styrene hydrogenation with 100% yield within 8 hours of reaction time.

Oxidation:

Metal-nanoparticles-montmorillonite composites showed an important role for detoxication of organic pollutants. Iron nanoparticles supported on montmorillonite could be prepared^{50,106} by intercalation and reduction. The highly dispersed Fe(O)-nanoparticles (3-10 nm) on clay matrix showed the catalytic conversion, 49.5% of phenol oxidation with hydrogen peroxide.

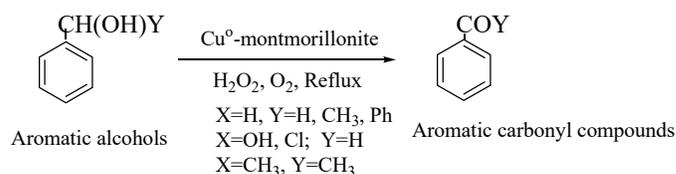
The magnetic Fe₃O₄ nanoparticles synthesized into the nanopores of acid activated montmorillonite showed high catalytic efficiency for the Baeyer–Villiger oxidation of various cyclic and aromatic ketones with a conversion upto 98% (Scheme 6). The catalyst can be recovered magnetically and recycled for several runs.¹⁷⁵

Dutta et al.¹⁷⁶ recently reported that Cu⁰-nanoparticles of size < 10 nm could be generated on montmorillonite which exhibited efficient catalytic activity for liquid phase oxidation of alcohols to carbonyl compounds. The Cu⁰-nanoparticles were synthesised by incipient wetness impregnation technique. The catalyst may serve for the broad range of the oxidation of alcohols with molecular O₂ to corresponding carbonyl compounds with excellent yields, up to 97% and selectivity, 100% (Scheme 7). The catalyst exhibited good reusability.



Scheme 6. Baeyer-Villiger oxidation of cyclic ketone catalysed by Fe₃O₄@montmorillonite under solvent-free condition at room temperature.

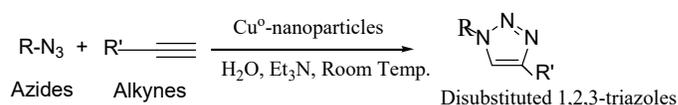
Gorobinskii et al.¹⁷⁷ reported Pt⁰- nanoparticles dispersed over activated pillared K 10 montmorillonite, synthesized by impregnation technique. The catalyst showed efficient CO oxidation in excess of hydrogen.



Scheme 7. Oxidation of aromatic alcohols to carbonyl compounds catalyzed by Cu⁰-montmorillonite.

Coupling and other reactions:

The metal-nanoparticles-based catalysis for clean synthesis is a big challenge for researchers.^{178,179} Recently, Dutta et al. reported^{139,102,104} different coupling reactions catalyzed by metal nanoparticles-montmorillonite composites. They also reported¹⁰⁴ Cu⁰-nanoparticles-montmorillonite catalyzed 1,3-dipolar cycloaddition reactions of terminal alkynes with azides to yield highly regioselective 1,4-disubstituted mono- and bis-1,2,3-triazoles (Scheme 8) in excellent yields (upto 95%). The nanocatalysts were reused for several runs.

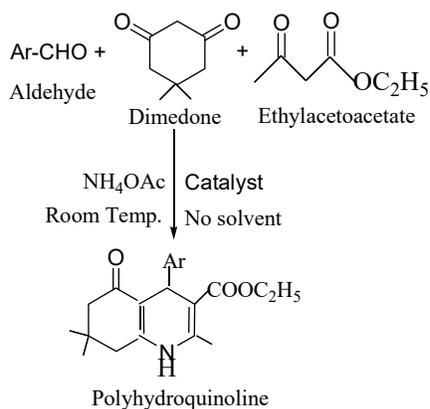


Scheme 8. 1,3-dipolar cycloaddition of azides and alkynes catalyzed by Cu⁰-nanoparticles supported on montmorillonite.

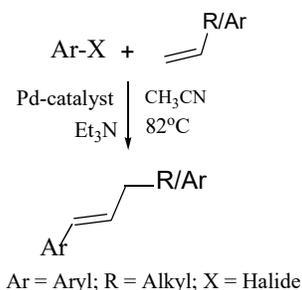
A multi-component one-pot synthesis of Hantzsch polyhydroquinoline was reported³⁹ by the condensation of aldehydes, dimedone, ethylacetoacetate, and ammonium acetate in the presence of Ni⁰-nanoparticles-montmorillonite catalyst (Scheme 9). The catalyst showed high yield, about 95%.

The cross-coupling reactions catalyzed by palladium is important for the formation of carbon-carbon bonds.¹⁸⁰⁻¹⁸⁵ There are tremendous interests to develop heterogeneous Pd-catalysts for increasing the efficiency of the Heck and Sonogashira reactions.¹⁸⁶⁻¹⁹⁰ Borah et al. reported¹⁰² the Pd⁰-nanoparticles-montmorillonite composite which showed efficient catalytic activities for efficient Heck and Sonogashira reactions. Aryl halides with olefins undergo cross-coupling reaction resulted in products of yield, 96% and about 99% trans selectivity (Scheme 10). The Sonogashira coupling reaction of aryl halides with

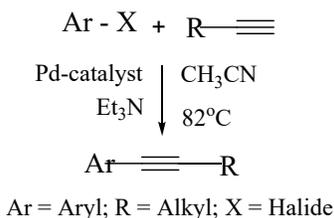
terminal alkynes, showed a yield, 94% along with 100% selectivity (Scheme 11).



Scheme 9. Ni⁰-nanoparticles supported montmorillonite catalyzed Hantzsch condensation reaction.



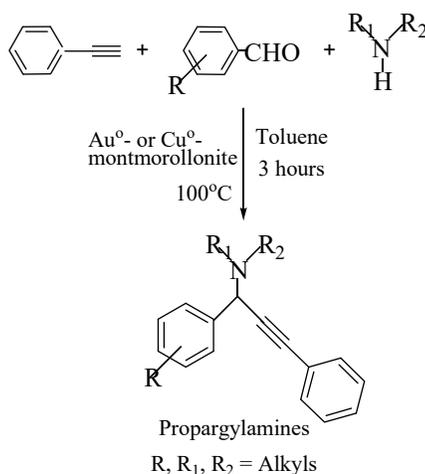
Scheme 10. Heck coupling reaction with aryl halides and alkenes catalyzed by Pd⁰-nanoparticles.



Scheme 11. Sonogashira coupling reaction with aryl halides and alkynes catalyzed by montmorillonite-supported Pd⁰-nanoparticles.

Multicomponent coupling reactions have aroused much interest in the recent time. The A³ coupling (aldehyde-amine-alkyne) reaction (Scheme 12) via C-H activation was carried out to prepare propargylamines.¹⁹¹ For the synthesis of different biologically important nitrogen containing compounds, propargylamines are used as intermediates.¹⁹² Propargylamines were produced by addition of metallated alkynes to an imine, but the process generates large amount of waste.¹⁹³ In recent years, various metal catalysts stabilized on different supports are used for A³ coupling reactions.¹⁹⁴ Borah et al.^{195,196} reported the Cu⁰ and Au⁰-montmorillonite composites for the synthesis of propargylamines with yields, 94% and selectivity, 100%. Recently, Ag⁰-nanoparticles-montmorillonite composite was reported for the three component (A³) coupling reactions of aldehyde, amine and

alkyne to produce propargylamines.¹⁹⁷ The catalyst showed high yields (82–94%) and 100% selectivity.



Scheme 12. Three-component coupling of aldehyde, alkyne, and amine catalyzed by Au⁰ or Cu⁰-montmorillonite for the synthesis of propargylamines.

CONCLUSION

Metal nanoparticles supported on modified montmorillonite composites have led to the generation of newer type of novel and sustainable environmentally benign heterogeneous 'Nanocatalysts', which are, in general, superior to the conventional catalysts. The supported metal nanoparticles catalysts exhibited high surface area and nanopores which contribute adequately in the fields of reduction, oxidation, coupling reactions etc. Such heterogeneous catalysts are useful for synthesis of fine and bulk chemicals and also find use in environmental catalysis. In addition, it may be possible that metal nanoparticles can be supported on other types of suitable nanoporous materials for developing robust and more efficient heterogeneous catalysts.

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AUTHOR BIOGRAPHY



Dr. Dipak Kumar Dutta, M.Sc, Ph.D. is a CSIR-Emeritus Scientist and prior to that he was a Chief Scientist in the Materials Science and Technology Division, CSIR-North-East Institute of Science and Technology (NEIST), Jorhat 785006, Assam, India. He has nearly 35 years of R & D experience in the area of chemical sciences relating to synthesis of metal complexes, homogeneous and heterogeneous catalysts and catalysis, nanoparticles of metals and their catalytic applications. He also worked on the development of high temperature stable materials. His current interest is in the field of *Green* and *Sustainable* Chemical Science. Dr. Dutta has published more than 100 scientific papers in sci journals, 8 Book Chapters, filed 45 patents (National and International), and supervised 17 Ph.D. works. He has developed several Know-how / Processes / Technologies. He has successfully completed several projects like: UK-India International projects; The Royal Society of Chemistry, UK - CSIR, India, Joint International Project, and DST (India) - RFBS (Russia) International project. He has been honoured with several awards like: (i) CRSI Bronze Medal 2015, (ii) CSIR Technology Award for Innovation 2010 and (iii) Durlabh Deka Memorial Award, by Assam Science Society, in Chemical Science, 2007, for his innovative R&D works.