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Efficient one-pot synthesis of Propargylamines catalysed by Gold nanocrystals Stabilized on montmorillonite

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Abstract

The size selective Au^o-nanoparticles were generated *in situ* into the nanopores of modified montmorillonite. The modification of montmorillonite was carried out with HCl under controlled conditions for generating nanopores (less than 8 nm) into the matrix and these nanopores act as "host" for *in situ* generation of Au^o-nanoparticles. The synthesis consisted of impregnation of the acid-activated montmorillonite with $HAuCl_4$ aqueous solution followed by reduction with $NaBH_4$. The synthesised Au^o-nanoparticles crystallized in the face centred cubic (fcc) lattice were single crystals with a preferential growth direction along the (111) plane. The N_2 adsorption/desorption study revealed specific surface areas (BET) of 327-579 m^2/g, large specific pore volumes ~ 0.7 cm^3/g, pore diameters 0-10 nm of the support. TEM, FESEM and X-ray studies indicate Au^o-nanoparticles of 0-10 nm evenly distributed on the support and serve as an efficient green catalyst for one-pot, three-component (A^3) coupling of an aldehyde, an amine and an alkyne *via* C-H alkyne-activation to synthesize propargylamines with 82-94% yield and 100% selectivity under mild reaction condition. The nanocatalysts can be recycled and reused several times without significant loss of their catalytic activity.

Keywords: Au^o-nanoparticles; Montmorillonite; Face centred cubic; Propargylamines; C-H activation.

1. Introduction

The development of green chemistry is traced from the introduction of the concepts of atom economy and utilization of non-hazardous metals in catalysis [1]. In this connection, a large number of multicomponent reactions have been designed to synthesize different complex molecules through a combination of three or more starting materials in one-pot condition [2]. Among the different multicomponent reactions, the catalytic coupling reaction of aldehyde, amine and alkyne (so-called A^3 coupling) is one of the best examples, where propargylamines is produced as the main product [3]. Propargylamines have been attracting considerable attention over the last few years due to their wide applications in drug discovery. Propargylamines are versatile intermediates for the preparation of various nitrogen-containing compounds and are key components of biologically active pharmaceuticals and natural products and also for the synthesis of polyfunctional amino derivatives [4]. The importance of propargylamine motifs can be best understood from the discovery of rasagiline, which contains propargylamine moiety (trade name: Azilect), an FDA approved drug, that is prescribed for use as monotherapy in early Parkinson's disease [4]. Various methods typically involve C-H bond activation of terminal alkynes using a wide range of metals (e.g. Cu, Fe, Au, In, etc.) based catalysts have been well explored for the synthesis of propargylamines [5].

In the recent years, there has been increasing interest in gold for using as catalysts in organic transformations, though gold was traditionally considered to be chemically inert and regarded as a poor catalyst. The development of nanometer sized gold particles is intensively pursued because of their importance for both fundamental science and advanced technologies [6]. The main reasons for extensive use of gold are that it exhibits some unusual and unexpected properties in many organic transformations, highly stable in any form and more importantly the non-toxic nature [7]. The gold based compounds are well-known to exhibit high alkynophilicity for activating *sp* and even sp^2 and sp^3 C-H bonds and this property has been exploited for making it a promising catalyst in three-component A^3 coupling reactions of terminal alkynes with aldehydes and secondary amines [8]. In 2003, Li's group first reported the gold halides salts as a catalyst for alkynylation of iminium ions [9]. Wong and co-workers have reported Au(III)salen complex as a catalyst for A^3 coupling reaction [10]. Although, these catalytic systems showed good activity but the main disadvantages of these systems are that they are homogenous in nature

and are, therefore, not economically and environmentally attractive. During the last decade, supported Au^o-nanocatalytic systems are explored as sustainable and competitive alternative to the gold complexes for A^3 coupling reaction. Supported Au^o-nanoparticles enhances the activity and selectivity of the reaction and more importantly satisfied the stringent criteria of becoming heterogeneous catalyst [2a,11]. In 2007, Kidwai and co-workers reported the first example of gold nanocluster (16-20 nm) derived from the reduction of $AuCl_3$ by hydrazine as a catalyst for the synthesis of propargylamine [11a]. Vinu and co-workers reported a new catalytic system for A^3 coupling reaction containing Au^o-nanoparticles embedded in mesoporous carbon nitride, however, they had restricted their experiments with only a few substrates [11c]. Kantam and co-workers reported the nanocrystalline MgO stabilized Au^o-nanoparticles based heterogeneous catalyst for propargylamine synthesis [11b]. Very recently, Karimi's group successfully synthesized Au^o-nanoparticles supported on periodic mesoporous organosilica with ionic liquid framework [2a]. Although, they have reported an efficient catalytic system for three-component coupling reaction, but their support preparation process is laborious and time consuming. Therefore, the development of new *greener,* efficient and recoverable Au-based catalytic system for A^3 coupling reaction is a challenge for researchers. Herein, we have reported a well-defined heterogeneous catalytic system i.e. crystalline Au^o-nanoparticles supported on modified montmorillonite for one-pot synthesis of propargylamines. These nanoparticles maintain their catalytic efficiency for several cycles and serve as potential reusable catalyst. The modified montmorillonite is considered as environmentally benign, cheap, easily available and robust support/stabilizer materials for the synthesis of different metal nanoparticles [12]. The virgin montmorillonite is collected from the indigenous source i.e. natural deposits of western part of India, which was purified and activated with mineral acid under controlled conditions to generate a matrix having high surface area and contain micro- and mesopores with diameter in the range 0-10 nm. These nano range pores act as "host" for *in situ* generation of Au^o-nanoparticles and thus limit the growth of the particles upto desired range.

2. Experimental

2.1 Support preparation

Purified bentonite (10 g) was dispersed in 200 ml 4 M hydrochloric acid and refluxed for various time intervals (1 and 2 h). After cooling, the supernatant liquid was discarded and the activated montmorillonite was repeatedly redispersed in deionised water until no Cl^- ions could be detected by the $AgNO_3$ test. The montmorillonite was recovered, dried in air oven at 50 ± 5 ^oC over night to obtain the solid product. These activated montmorillonites were designated as AT-Mont.-I and AT-Mont.-II indicating the activation time of 1 and 2 h.

2.2 Au^o-nanoparticles preparation

0.5 g of activated montmorillonite (AT-Mont.-I or -II) was impregnated by 15 ml (0.254 mmol) aqueous solution of $HAuCl_4$ under vigorous stirring condition. The stirring was continued for another 5-6 h before the mixture was evaporated to dryness in a rotavapour. 0.3 g of the dry composite was dispersed in 10 ml water and 134 mg $NaBH_4$ (3.54 mmol) in 10 ml distilled water were added slowly over 15 min under constant stirring. The colour changed immediately from yellow to dark violet. The mass was allowed to settle and washed with distilled water several times until the content was free of Cl^- ions. The Au^o-montmorillonite composite was collected and dried at 60 ^oC for 12 h and stored in airtight bottle. The samples thus prepared were designated as Au^o-Mont.-I and Au^o-Mont.-II.

2.3 General procedure for the one-pot synthesis of propargylamines

Aldehyde (1 mmol), amine (1 mmol), alkyne (1.2 mmol), 20 mg catalyst (Au^o-Mont.-I or Au^o-Mont.-II.) and 5 ml toluene were taken in a 25 ml round bottom flask and reaction mixture was refluxed at 110 ^oC for stipulated time period. The progress of the reactions was monitored by TLC. After completion of the reaction, solid catalyst was separated from the mixture by filtered through sintered funnel (G-3) and the solvent was removed under low pressure in a rotavapour. The recovered catalyst was washed with acetone (30 ml), dried in a desiccator and stored for another consecutive reaction run. The crude product obtained was then purified by silica gel column chromatography using ethyl acetate and hexane as eluents. The products were characterized by (^1H, ^{13}C) NMR and mass spectrometry and all gave satisfactory results [supporting information].

3. Results and discussion

3.1. Characterization of Support

The naturally occurring montmorillonite is considered as cheap, easily available and environmentally benign catalysts and catalyst supports [12a-f]. The raw virgin montmorillonite was first purified by dispersion-cum-sedimentation technique and then treated with 4 M HCl and refluxed for various time intervals (1 and 2 h) under controlled conditions in order to generate high surface area and nanoporous matrix. The characterization of the modified montmorillonite was thoroughly carried out with the help of different analytical instruments like Powder-XRD, FT-IR, N_2 adsorption-desorption and SEM-EDX. The parent montmorillonite (Parent Mont.) is 2:1 layered dioctahedral aluminosilicate and consists of two tetrahedral silicate sheets which are bonded to either side of an octahedral aluminate sheet having basal reflection at 7.06^o 2θ corresponding to a basal spacing of 12.5 Å. The powder XRD study reveals that, the intensity of basal reflection decreased with increasing activation time and after 2 h acid activation i.e. in AT-Mont.-II, the basal reflection is almost depleted which indicates that the layered structure of the clay mineral is disrupted. During acid activation, the surface area (upto 578.5 m^2/g) as well as pore volume (~ 0.7 cm^3/g) are increased in case of AT-Mont.-I (1 h treatment) due to the leaching of Al from the octahedral sites, which also introduced micro- (< 2 nm) and mesopores (> 2 nm) on the clay surface. The specific surface area of the clay matrix is decreased on prolonging the acid activation time upto 2 h (AT-Mont.-II) because of destruction of the pore walls without significantly changing the overall specific pore volume (Table 1). The pore size increased with increasing the activation time because of the elimination of smaller pores and formation of larger pores. The adsorption-desorption isotherms [Fig. 1] were of type-IV with a H3 hysteresis loop at P/P_o ~ 0.4-0.8, indicating mesoporous solids. The differential volumes versus pore diameter plots i.e. BJH plot indicated relatively narrow pore size distributions with a peak pore diameter 4.12 and 6.33 nm for AT-Mont.-I and AT-Mont.-II respectively and these nano range pores were advantageously utilized for the *in situ* synthesis of various metal nanoparticles as reported our group recently [12a-g]. The parent montmorillonite exhibited an intense IR absorption band at ~1034 cm^{-1} for Si-O stretching vibrations of tetrahedral sheet. The bands at 522 and 460 cm^{-1} were due to Si-O-Al and Si-O-Si bending vibrations. Upon acid activation, the band ~1034 cm^{-1} shifted to ~1083 cm^{-1}. The appearance of a pronounced band

near 800 cm^{-1} indicated amorphous silica. Montmorillonite also showed absorption bands at 3633 cm^{-1} due to stretching vibrations of OH groups of Al-OH. The bands at 917, 875 and 792 cm^{-1} were related to AlAl-OH, AlFe-OH and AlMg-OH vibrations. The gradual disappearance of these bands during acid-activation indicated the removal of Al, Fe and Mg ions from the clay mineral structure. The ^{29}Si and ^{27}Al MAS-NMR measurements and SEM-EDX studies also confirmed that during acid activation, nano range pores are formed on the surface of clay matrix due to Al leaching and predominant amounts of Si compared to Al were present on the surface [12a-f] [supporting information].

3.2. Au^o-nanoparticles characterization

The immediate evidence for the formation of Au^o-nanoparticles was provided by UV-visible spectroscopy. The appearance of surface plasmon resonance bands of different width at around ~ 520 nm of violet colour Au^o-Mont.-I and Au^o-Mont.-II substantiated its formation and also suggested that maximum particle sizes are below 10 nm [Fig. 2]. Therefore, the nanopores of clay matrix effectively controlled the size of the embedded Au^o-nanoparticles and isolated them from each other to avoid agglomeration.

The TEM images of nanoparticles composites showed that dispersed Au^o-nanoparticles were formed in the micro- and mesopores of AT-Mont.-I and AT-Mont.-II [supporting information]. The supported Au^o-nanoparticles were spherical in shape, well separated from each other and with sizes of 0-10 nm. The distribution of the particles was dependent on the pore diameter of the support. Some of the Au^o-nanoparticles were found to be larger than the pore size of the support. Typical HRTEM images of Au^o-Mont.-I showed the reticular lattice planes inside the nanoparticles [Fig. 3]. The lattice planes continuously extended to the whole particles without stacking faults or twins, indicating the single crystalline nature. The measured interplanar spacing for all lattice fringes was 2.35 Å, which agrees with the (111) plane of fcc gold crystals. The corresponding selected area electron diffraction (SAED) pattern of Au^o-nanoparticles obtained by focusing the electron beam on the nanoparticle lying flat on the TEM grid is shown in Fig. 3 (inset). The formation of hexagonal symmetrical diffraction spot patterns demonstrated that the Au^o-nanoparticles are single crystals with a preferential growth direction along the (111) plane.

The crystalline nature of the Au^o-nanoparticles was also confirmed by the powder XRD pattern [Fig. 4]. The four reflections were assigned to the (111), (200), (220) and (311) diffraction of a fcc lattice of gold. The intensity ratio of the (200) and (111) reflections was unusually lower than the conventional values (JCPDS file, 0.12 versus 0.33). These observations confirmed that the synthesised Au^o-nanoparticles were primarily dominated by (111) facets and thus their (111) planes tend to be preferentially oriented parallel to the surface of the support [13]. This result also substantiated the HRTEM and SAED observations.

The Au^o-Mont.-I was analyzed by XPS in order to determine the electronic state of the atom. The typical spectrum shows Au 4f doublet ($4f_{5/2}$, 88.3 ev and $4f_{7/2}$, 84.6 ev) and peak-to-peak distance (3.7 ev) [Fig. 5] which is in good agreement with the value due to Au(0) oxidation state [14]. This indicates that the alumino-silicate constituent of clay matrix efficiently stabilized Au^o-nanoparticles in their well developed nanopores and prevents from oxidation during the synthesis and stabilizing process.

The encapsulation of Au^o-nanoparticles into the nanopores of the modified clay has changed some of the textural parameters of the materials as observed from the Fig. 1 that Au^o-Mont.-I and Au^o-Mont.-II exhibit similar type of isotherms and hysteresis loop with that of AT-Mont. This reveals that the highly ordered porous structure of clay is still maintained even after the encapsulation of Au^o-nanoparticles. The appreciable decrease of the specific surface area and the specific pore volume after supporting Au^o-nanoparticles (Table 1) might be due to clogging of some pores by Au^o-nanoparticles. In addition, the presence of Au^o-nanoparticles may influence the adsorption measurements. However, increase of pore diameter may be due to rupture of some smaller pores to generate bigger ones during the formation of Au^o-nanoparticles into the pores.

The Au contents in Au^o-Mont.-I and Au^o-Mont.-II as analyzed by ICP-AES, reveals the presence of 0.048 mol % of Au in each catalyst.

3.3. Catalytic activity

In order to determine the best reaction condition (i.e. solvent, reaction time, etc.) that are essential for the synthesis of propargylamines in an efficient way by our catalytic system, a series of three-component coupling reactions were carried out using benzaldehyde, piperidine and phenylacetylene as the model substrates in presence of Au^o-Mont.-I as catalyst. In the solvent screening study, initially different polar solvents like water, ethanol, methanol, acetonitrile were used for the reaction, but no encouraging results were obtained and in case of THF, DMF solvents, no products are formed even after 24 h of reaction time. Aromatic non-polar solvent such as toluene, surprisingly, yielded 94% of desired propargylamine product. The reaction required maximum 3 h for completion (as monitored by TLC) at the refluxing temparature of toluene. Therefore, it is found that, the present catalytic systems (Au^o-Mont.-I and Au^o-Mont.-II) proceed well in toluene at refluxing temperature. To understand the role of Au^o-nanoparticles, the model reaction was carried out in the optimized reaction condition using acid activated clays (AT-Mont.-I or AT-Mont.-II) alone as catalyst and only 5-10% yield of the product was formed (Table 2). A preliminary investigation was also carried out for the use of primary amines in the reaction, but no encouraging results were found and hence only secondary amines were used in the present study. Using optimized reaction conditions, we explored the versatility and limitations of various substrates as well as efficiency of our catalysts for the said one-pot three-components coupling reaction to synthesise propargylamines and the results are summarized in Table 2. In this study, we used phenylacetylene, 3-butyne-1-ol and 1,6-heptadiyne as alkynes, various electronically diverse aldehydes (e.g. benzaldehyde, 4-methoxybenzaldehyde, 4-chlorobenzaldehyde etc.) and secondary amines (e.g. piperidine, morpholine, diethylamine) and all the substrates produce the desired propargylamines with very good to excellent yields and about 100% selectivity irrespective of nature of the substrates. The model reaction, i.e. coupling between benzaldehyde, phenylacetylene and piperidine gives maximum 94% isolated yield when Au^o-Mont.-I is used as catalyst (entry 1). It is observed that the aromatic aldehydes containing electron withdrawing group gave slightly higher yield than that bearing electron donating group. The aliphatic alkyne i.e. 3-butyne-1-ol was allowed to react with two different iminium ions generated *in situ* from benzaldehyde and piperidine (entry 9) and benzaldehyde and morpholine (entry 10), it is found that desired propargylamines were formed with high yield. Again, the

aliphatic amine i.e. diethylamine (entry 7) showed lower conversion than the cyclic amine i.e. piperidine and morpholine (entry 1 and entry 8). It is observed that, the catalyst, Au^o-Mont.-I showed slightly higher activity than Au^o-Mont.-II. Therefore, Au^o-Mont.-I was exclusively used as catalyst for study with more substrates tolerance of the catalyst. Next, we explored our strategy for the synthesis of symmetrical bis-propargylamines derivatives by coupling of dialkyne, viz. 1,6-heptadiyne with benzaldehyde and piperidine (entry 11) and 4-methoxybenzaldehyde and diethyl amine (entry 12), as expected, the desired products were formed with good isolated yield (max. 85%) but the reactions needed a comparatively longer time i.e. 5 h for completion. We have also used aliphatic aldehyde i.e. pentanal (entry 13) and sterically hindered aldehyde i.e. 4-hydroxy-3-methoxybenzaldehyde (entry 14), the corresponding propargylamines are formed with good isolated yield and selectivity.

The slightly higher conversion shown by catalyst Au^o-Mont.-I over Au^o-Mont.-II may be due to their higher surface area in the former catalyst (Table 1). The pore volume and pore size of the catalysts Au^o-Mont.-I and Au^o-Mont.-II, are adequate to carry out liquid phase catalytic reactions (Table 1). Each catalyst was recovered by simple filtration technique after experiment. The recovered catalyst was washed with acetone, dried in a desiccator and reused directly with fresh reaction mixture without further purification for the desired coupling products synthesis upto 3rd run. The results (Table 2, entries 15 and 16) showed that in each case, the catalyst remain active for several run without significantly loss in efficiency. All the reactions were carried out with 0.048 mol% of Au in Au^o-Mont.-I and Au^o-Mont.-II catalysts (Table 2).

The recovered catalyst was further investigated through N_2 adsorption-desorption and HRTEM analysis. The identical shape of the isotherms and the hysteresis loop reveal that the characteristics of the catalysts are retained even after successive reactions. The specific surface areas of the recovered catalysts decrease compared to freshly prepared catalyst (Table 1). The decrease of surface area of the recovered catalysts after each reaction may be due to the blockage of pores by the reactant molecules. In the HRTEM analysis of recovered Au^o-Mont.-I (after 3rd run), it is found that a few particles aggregate, but the sizes are still below 10 nm [supporting information]. These experimental results clearly suggest that the reactions undergo in a heterogeneous process as well as the robustness character of the catalyst.

A probable reaction mechanism for the one-pot, three components coupling of propargyl-amines catalyzed by Au^o-Mont.-I or Au^o-Mont.-II under heterogeneous conditions is proposed. The proposed mechanism is pictorially illustrated in Scheme 1. In the first step, Au^o-nanoparticles supported on AT-Mont. activate the C–H bond of the terminal alkyne to generate a gold-alkylidine complex on the surface of the AT-Mont. This is a very favourable step because Au^o is well known to exhibit high alkynophilicity for terminal alkynes [6]. The second step involves the reaction between the gold-alkylidine complex formed, and the iminium ion which is generated *in situ* from the reaction between aldehyde and secondary amine, to give the desired product and the catalyst is regenerated. The theoretical by-product obtained from the reaction is only water. The regenerated catalyst continues the catalytic cycles till the completion of the reaction.

4. Conclusion

The nanoporous modified montmorillonite was found to be excellent eco-friendly support for the *in situ* synthesis of Au^o-nanoparticles with different sizes. The Au^o-nanoparticles crystallized in the *fcc* lattice were single crystals with a preferential growth direction along the (111) plane. These nanoparticles demonstrated high catalytic activity in the one-pot three components coupling of aldehydes, amines and alkynes *via* C-H activation for the synthesis of propargylamine under mild reaction condition. Further, the nanocatalysts were reused for a new batch of reactions without significant loss of their activity under the same conditions. The operational simplicity and robustness of the catalyst, make it attractive not only for the large scale synthesis of this class of biologically active molecules, but also for the exploration in the synthesis of important drug intermediates.

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Table 1: Surface properties of montmorillonite based supports/catalysts

Samples		Surface properties		
		Specific surface area (m^2/g)	Average Pore diameter (nm)	Specific pore volume (cm^3/g)
AT-Mont.-I		578.5	4.12	0.596
AT-Mont.-II		400.5	6.33	0.604
Au^o-Mont.-I	**Fresh**	305.3	5.31	0.285
	After 1st run	265.6	6.12	0.253
	After 2nd run	230.5	7.44	0.231
	After 3rd run	210.3	8.01	0.206
Au^o-Mont.-II	**Fresh**	265.3	7.66	0.368
	After 1st run	234.8	8.22	0.315
	After 2nd run	216.3	9.01	0.277
	After 3rd run	201.2	9.23	0.249

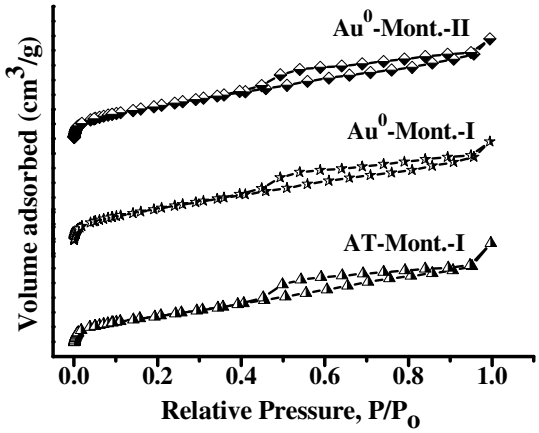


Fig. 1. N_2 adsorption-desorption isotherms of support and catalysts.

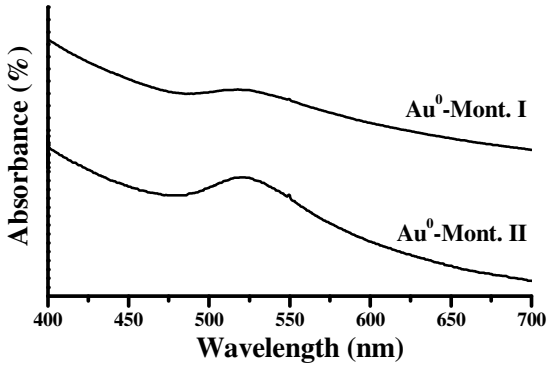


Fig. 2. UV-Visible spectra of Au^o-Mont.-I and Au^o-Mont.-II.

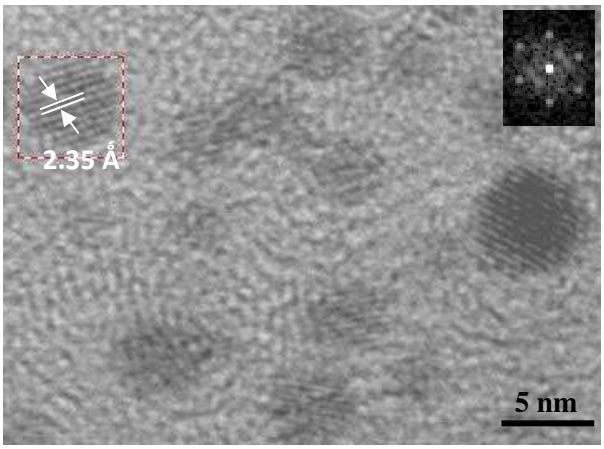


Fig. 3. HRTEM image and corresponding SAED pattern (inset) of Au^o-Mont.-I.

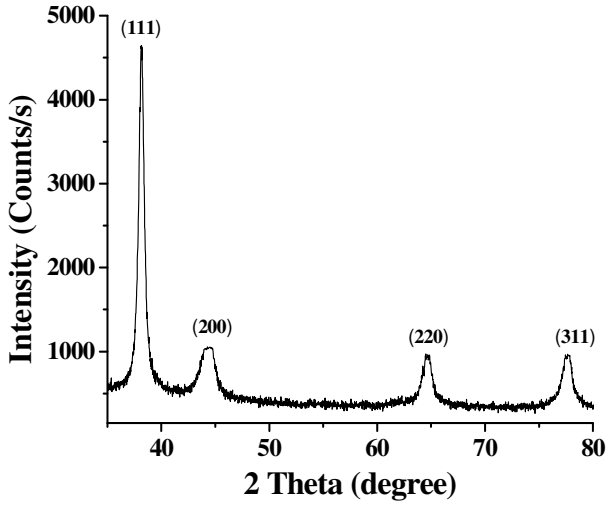


Fig. 4: Powder XRD pattern of Au^{o}-nanoparticles (Au^{o}-Mont.-I).

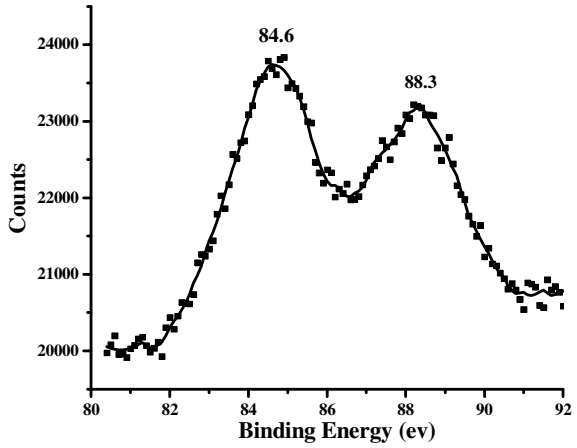
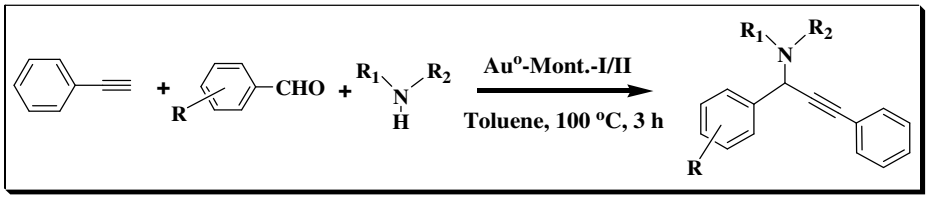
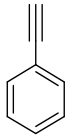
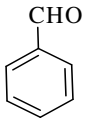
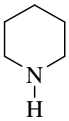
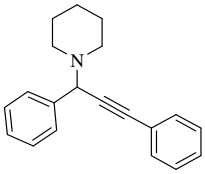
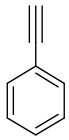
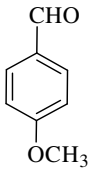
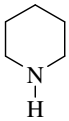
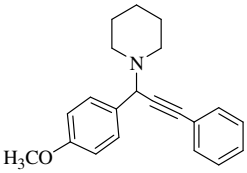
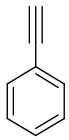
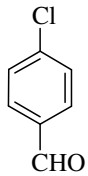
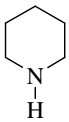
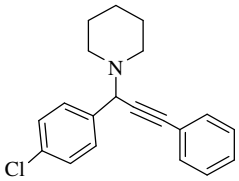
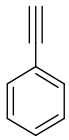
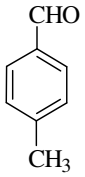
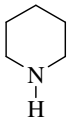
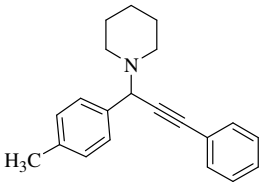
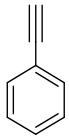
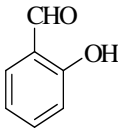
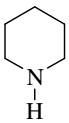
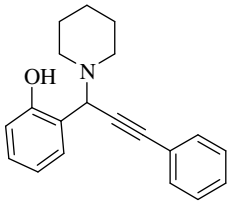
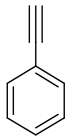
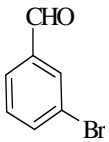
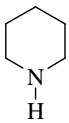
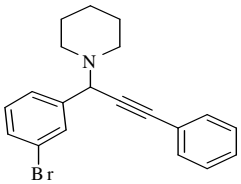
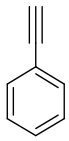
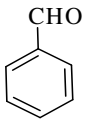
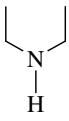
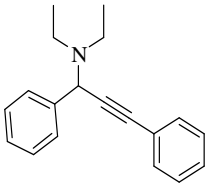
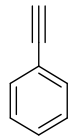
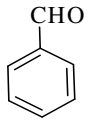
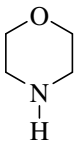
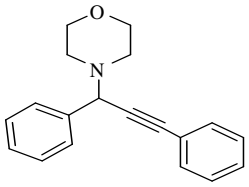
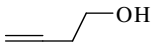
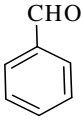
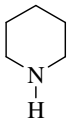
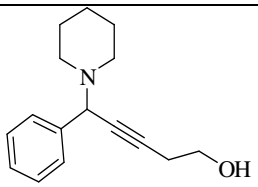
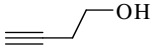
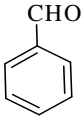
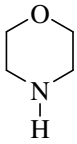
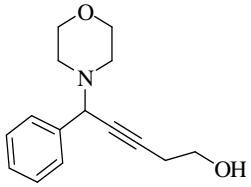
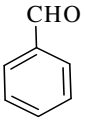
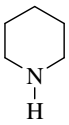
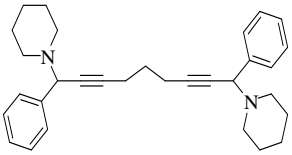
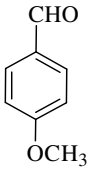
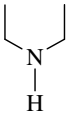
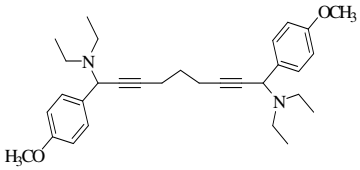
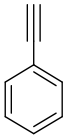
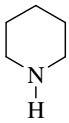
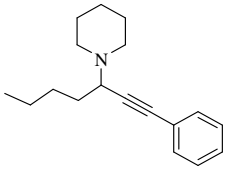
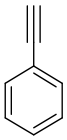
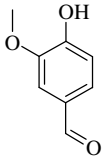
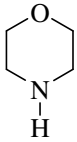
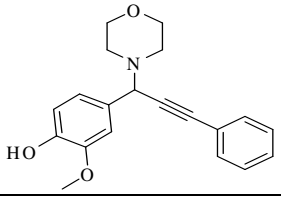
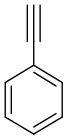
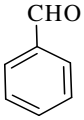
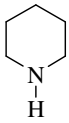
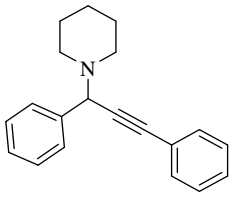


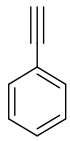
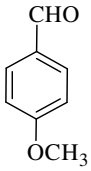
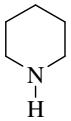
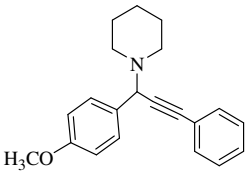
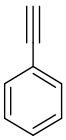
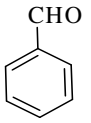
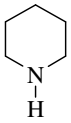
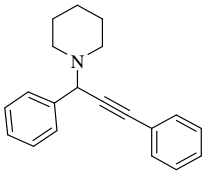
Fig. 5. XPS spectrum of Au^{o}-Mont.-I.

Table 2. Three-component coupling of aldehyde, alkyne and amine for the synthesis of propargylamine.



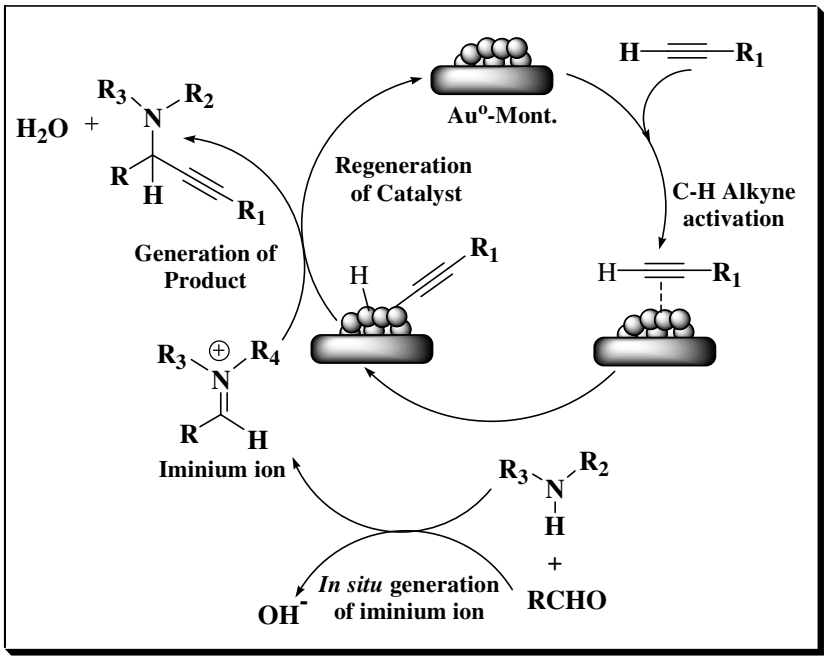
Entry	Alkyne	Aldehyde	Amine	Products	Catalyst	Yield* (%)
1					Au°-Mont.-I	94
					Au°-Mont.-II	91
2					Au°-Mont.-I	88
					Au°-Mont.-II	85
3					Au°-Mont.-I	86
					Au°-Mont.-II	84
4					Au°-Mont.-I	89
					Au°-Mont.-II	85
5					Au°-Mont.-I	86
					Au°-Mont.-II	82
6					Au°-Mont.-I	91
					Au°-Mont.-II	88
7					Au°-Mont.-I	86
					Au°-Mont.-II	83

8					Au^{o}-Mont.-I	91
					Au^{o}-Mont.-II	88
9					Au^{o}-Mont.-I	86
					Au^{o}-Mont.-II	82
10					Au^{o}-Mont.-I	84
11					Au^{o}-Mont.-I	85**
12					Au^{o}-Mont.-I	83**
13					Au^{o}-Mont.-I	88
14					Au^{o}-Mont.-I	83
15					Au^{o}-Mont.-I **(2nd run)**	91
					Au^{o}-Mont.-I **(3rd run)**	88

16					Au^{o}-Mont.-II **(2nd run)**	85
					Au^{o}-Mont.-II **(3rd run)**	82
17					AT-Mont.-I	10
					AT-Mont.-II	5

*__Yields__ are isolated products based on benzaldehyde after silica-gel column chromatography, **Reaction conditions:** Aldehyde (1 mmol), Amine (1 mmol), Alkyne (1.2 mmol), Catalyst (20 mg, contain 0.0084 mmol Au) and Toluene (5 ml); Refluxing temp. 100 ^{o}C, Time 3 h.

**Time required for completion of reactions is 5 h.



Scheme 1: Tentative reaction mechanism of A^3 coupling reaction

Efficient one-pot synthesis of Propargylamines catalysed by Gold nanocrystals Stabilized on montmorillonite

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Graphical Abstract

The size selective Au^{o}-nanoparticles were generated *in situ* into the nanopores of environmentally benign modified montmorillonite and their catalytic performance in three components (A^3) coupling reactions of Aldehyde, Amine and Alkyne in one-pot to synthesize propargylamines with excellent yield and selectivity.