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Gold nanoparticles immobilized on lipoic acid functionalized SBA-15: Synthesis, characterization and catalytic applications



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ARTICLE INFO

Article history: Received 26 September 2012 Received in revised form 5 January 2013 Accepted 7 January 2013 Available online xxx

Keywords: SBA-15 Lipoic acid Gold nanoparticles Propargylamines Solvent-free system

ABSTRACT

Gold nanoparticles immobilized on lipoic acid functionalized SBA-15 (SBA-LAG) catalyst was synthesized via functionalization of SBA-15 with propylamine followed by tethering of lipoic acid and immobilization of gold nanoparticles. The structural and texctural characteristics of the catalyst have been determined by N₂ adsorption–desorption and low-angle XRD. The successive attachment of spacers has been characterized by ¹³C CP-MAS NMR, FT-IR and TG-DTA. The size, shape, surface composition and oxidation state of gold nanoparticles have been determined by XRD, TEM and XPS techniques. SBA-LAG catalyst is found to be an efficient solid catalyst for producing good to excellent yields of propargylamines by condensing three-components such as (i) amine, (ii) aldehyde and (iii) alkyne in one-pot under solvent-free conditions.

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1. Introduction

Gold, in its bulk form has been regarded to be chemically inert. Accordingly, bulk gold was considered to be uninteresting metal from the catalysis point of view. However, recently it is reported that gold catalysts are extremely active if deposited as nanoparticles on suitable supports [1–4]. Gold nanoparticles can be synthesized directly by adsorbing its salts on the supports followed by reduction with hydride source. In general, the deposition of nanoparticles on supports through conventional impregnation, deposition-precipitation, chemical vapor deposition and sonochemical methods are in practice, but the nanoparticles prepared in these methods are larger in size, easily undergo agglomeration and leaches under reaction conditions. Hence, in this context, novel nanoparticles deposition methods are highly desirable. It is realized that the bio-conjugate ligand molecules can significantly limits the aggregation and improves the stability of the gold nanoparticles [5-12]. Lipoic acid is a natural bio-molecule consisting of five membered cyclic disulphide and hydrocarbon tail ending with a carboxylic acid group. Lipoic acid has been the subject of numerous research studies and recently several authors have prepared lipoic acid capped gold nanoparticles for specific immobilization of histidine tagged proteins and electroluminescent luminol [13,14]. However, lipoic acid capped gold nanoparticles on SBA-15 have not yet been reported.

The advent of mesoporous SBA-15 silica in 1998 [15], has been emerging as a potential catalyst support, particularly for the stabilization of nanoparticles using a variety of organic spacers such as $-NH_2$, -SH, $-SO_3H$, -CN, -COOH [16,17]. The unique features like high surface area, hexagonal array of pores, large and uniform pore channels and good thermal stability makes SBA-15 a prominent support.

Propargylamines and its derivatives are versatile synthetic intermediates in organic synthesis and important structural skeletons of biologically active compounds [18-20]. Traditionally propargylamines are synthesized by nucleophilic attack of lithium acetylides or Grignard reagents on imines [21,22]. However, these reagents must be used in stoichiometric amounts, are highly moisture sensitive, and require strictly controlled reaction conditions. An alternate green and economic approach to synthesize propargylamines is accomplished by one-pot three-component condensation of an amine, an aldehyde and an alkyne via C-H alkyne-activation on various catalysts [23-25]. Compared to other transition-metal based catalysts gold complexes exhibited excellent affinity for alkynes. However these homogeneous systems are economically and environmentally not acceptable because of rapid reduction of cationic gold complexes into inactive metallic gold after C-H alkyne activation during the reaction [26-37]. In 2007 Kidwai et al. reported the use of unsupported Au⁽⁰⁾ nanoparticles in the preparation of propargylamines[38]. These unsupported Au

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nanoparticles exhibited excellent catalytic activity similar to those of homogeneous gold metal complexes. However, this protocol requires high loading of gold nanoparticles (10%) and the reactions needs to be conducted under inert conditions. Vinu and co-workers reported the gold nanoparticles embedded mesoporous carbon nitride functions as an efficient recyclable heterogeneous catalytic system for the synthesis of propargylamines [39] but this method requires carcinogenic organic solvents and limited to very few substrates. Recently Kantam et al. reported the synthesis of propargylamines using nanocrystalline magnesium oxide stabilized gold nanoparticles as a catalyst [40], it shows good activity but this protocol also requires organic solvents, long reaction times and loss of activity in its repeated use. Very recently Karimi et al. have developed gold nanoparticles supported periodic mesoporous silica with ionic liquid frame work catalyst for propargylamines but in this protocol reaction has conducted in harmful organic solvent [41]. Synthesis of propargylamines using eco-friendly and reusable catalyst under solvent-free conditions is still a thrust area in chemical field.

Here in, for the first time, using a new and facile strategy, SBA-LAG catalyst has been synthesized. Synthesis, characterization and catalytic activity towards the preparation of propargylamines through three-component one-pot synthesis under solvent-free conditions have been described.

2. Experimental

2.1. Preparation of SBA-15

A solution of $EO_{20}PO_{70}EO_{20}$:HCI:TEOS:H₂O=2:60:4.25:15 (mass ratio) was prepared, stirred for 12 h at 40 °C and then hydrothermally treated at 100 °C under static condition for 12 h, subsequently filtered, dried at 100 °C and calcined at 500 °C for 8 h to get the parent SBA-15 mesoporous silica support.

2.2. Preparation of SBA-NH₂

3 g of calcined SBA-15 was pre-treated for 3 h at 150 °C in vacuum and then refluxed with a solution containing 2.1 ml (9 mmol) of 3-(aminopropyl) triethoxysilane (APTES) in 50 ml of dry toluene for 24 h under anhydrous condition. The mixture was filtered, washed with 150 ml of toluene and dried in oven at 100 °C for 12 h, designated as SBA-NH₂.

2.3. Preparation of SBA-LA

To prepare lipoic acid functionalized SBA-15, lipoic acid was dissolved in dichloromethane (DCM). Then 1-hydroxy benzotriazole (HOBT) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) (molar ratio lipoic acid:HOBT:EDC at 1:1.1:1.5) was added to the above solution under N₂ atmosphere. After stirring for 30 min, the amine functionalized SBA-15 (SBA-NH₂) was added to the mixture and stirred at room temperature for 24 h under inert atmosphere and the material was filtered, washed with ethanol, dried under vacuum and the material was designated as SBA-LA.

2.4. Preparation of SBA-LAG

The vacuum dried SBA-LA was added to HAuCl₄ in methanol under stirring and reduced with NaBH₄ in inert atmosphere overnight, and then catalyst was filtered, washed with ethanol and water, dried under vacuum. Finally the sample was designated as SBA-LAG, wherein the loading of Au is 2.1 wt%. Following the similar method different loadings of Au was immobilized, which are designated as SBA-LAG 1, SBA-LAG 1.5, SBA-LAG 2.5, wherein the suffixed numerical value stands for the loading of Au by weight%.

2.5. Characterization of the catalyst

Solid-state ¹³C CP-MAS NMR spectra were obtained on a Bruker-Avance 500 MHz with 10 kHz of spinning rate. Low-angle XRD patterns were recorded on Ultima IV X-ray diffractometer at 40 kV and 40 mA using Cu K α radiation in the range 0.7–5° at room temperature. Wide-angle X-ray diffraction (XRD) patterns of catalysts was obtained on a Bruker D8 Advance X-ray powder diffractometer using Ni filtered Cu K α radiation at a scan speed of 2°/min. X-ray photoelectron spectroscopy (XPS) analysis of the catalyst was carried out by a Kratos analytical spectrophotometer, with Mg Ka monochromatic excited radiation (1253.6 eV). The residual pressure in the analysis chamber was around 10^{-9} mbar. The binding energy (BE) measurements were corrected for charging effects with reference to the C 1s peak of the adventitious carbon (284.6 eV). Infrared spectra were recorded on a Bruker Alpha-T, FT-IR system, in the scan range of 4000-400 cm⁻¹. A Philips Tecnai F12 FEI transmission electron microscope (TEM) operating at 80-100 kV was used to record TEM images. The TGA measurements were carried out using TGA/SDTA 851e thermal system (Mettler Toledo, Switzerland). The samples were heated in air from 27 to 1000 °C with a heating rate of 10°C/min. During the heating period, the weight loss and the temperature difference were recorded as a function of temperature.

2.6. Catalytic activity

A mixture of aldehyde (1 mmol), piperdine (1.1 mmol), phenylacetylene (1.2 mmol) and SBA-LAG (35 mg) was taken in a 25 ml round bottomed flask, stirred at 100 °C for 8 h under solvent-free condition. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and diluted with ethyl acetate, the reaction mixture was centrifuged to separate the catalyst. The crude residue was washed with brine solution, dried over anhydrous Na₂SO₄, evaporated to get the crude product and purified by column chromatography to obtain the desired product.

3. Results and discussions

SBA-LAG was synthesized as shown in Scheme 1. Wherein, the first step is the functionalization of (3-aminopropyl) triethoxysilane (APTES) on the surface of SBA-15. The second step is the attachment of lipoic acid to SBA-NH₂ by amidation between the free amine groups and —COOH group of lipoic acid. The third step is the gold nanoparticles immobilization on SBA-LA by reducing with NaBH₄ (Scheme 2).

The loading of propylamine and lipoic acid functionalized on SBA-NH₂ and SBA-LA were determined from C, H, N and S elemental analysis and the loading of gold was determined by ICPMS. The details of the analysis data are presented in Table 1, which reveals that the propylamine loading is around 1.55 mmol/g and

Table 1

Elemental analysis of SBA-15, SBA-NH₂, SBA-LA, SBA-LAG samples.

Sample	Analysed by	C (%)	H (%)	N (%)	S (%)	Au (%)
SBA-15 SBA-NH ₂ SBA-LA SBA-LAG	CHNS CHNS CHNS ICPMS	NF 9.22 14.43	NF 1.73 2.25	NF 2.17 2.21	NF NF 3.75 -	- - 2.1
SBA-LAG	ICPMS	-	-	-	-	2.05 ^a

NF stands for not found.

^a Recycled catalyst.



Scheme 1. Schematic representation of SBA-LAG synthesis.



Scheme 2. Single-pot synthesis of propargylamines over SBA-LAG catalyst.

the lipoic acid loading is around 1.165 mmol/g. The loading of gold is approximately 2.1 wt%.

3.1. N₂ adsorption–desorption analysis

The textural characteristics of the catalyst right from parent SBA-15 are determined by N_2 adsorption–desorption technique. The BET surface area, pore volume, pore diameter and pore wall thickness are depicted in Table 2.

Table 2 Structural and textural characteristics of SBA-15, SBA-NH₂, SBA-LA and SBA-LAG.

Characteristics	SBA-15	SBA-NH ₂	SBA-LA	SBA-LAG
$S_{\text{BET}} (m^2/g)^{a}$	723	492	449	415
$V_{\rm p} (\rm cm^3/g)^b$	1.05	0.84	0.81	0.78
$D_{\rm p} ({\rm nm})^{\rm c}$	7.04	6.89	5.90	6.10
$d_{(100)} (nm)^{d}$	9.01	8.75	8.79	8.37
$a_{\rm o} ({\rm nm})^{\rm e}$	10.4	10.1	9.8	9.7
<i>t</i> (nm) ^f	5.30	5.00	4.70	4.56

^a BET surface area.

^b Total pore volume.

^c BJH pore diameter.

^d $d_{(100)}$ spacing.

^e Unit cell parameter $(a_0 = 2 \times d(100)/\sqrt{3})$.

^f Pore wall thickness ($t = a_0$ – pore size).



Fig. 1. $N_{\rm 2}$ adsorption–desorption isotherms of SBA-15, SBA-NH_2, SBA-LA and SBA-LAG.

The N₂ adsorption–desorption isotherms for SBA-15, SBA-NH₂, and SBA-LA and SBA-LAG catalyst are displayed in Fig. 1. It can be seen that all the four samples displays a type IV isotherm with an H1 hysteresis loop, characteristic of ordered mesoporous materials [42]. As shown in PSD curve (inset, Fig. 1), the pores are distributed in the range of 4.3–6.8 nm. The BET surface area of SBA-15 and SBA-NH₂ are 723 and 492 m²/g, the decrease in surface area indicates the functionalization of propylamine on the surface of parent SBA-15. Further decrease in surface area for SBA-LA (449 m²/g) is noticed. Further decrease in the surface area has been observed for SBA-LAG. Similar trend has been observed for pore volume and pore diameter with the introduction of amine, lipoic acid and Au nanoparticles respectively. This suggests the partial blockage of pore by the functionalizing agents and Au nanoparticles.

3.2. XRD analysis

The low angle XRD pattern of SBA-15, SBA-NH₂, SBA-LA, and SBA-LAG is shown in Fig. 2. Parent SBA-15 and its functionalized samples show three well resolved peaks at $0.95-1.1^{\circ}$, $1.63-1.7^{\circ}$ and $1.89-1.95^{\circ}$ respectively on the 2θ scale, which are assigned



Fig. 2. Low-angle XRD patterns of SBA-15, SBA-NH₂, SBA-LA and SBA-LAG.



Fig. 3. Wide-angle XRD patterns of SBA-15, SBA-NH₂, SBA-LA and SBA-LAG.

to (100), (110) and (200) reflections, these results suggest that the two-dimensional hexagonal mesoporous structure of parent SBA-15 with space group *p6mm* remain intact at all the stages of SBA-LAG catalyst preparation. But after anchoring of propylamine, lipoic acid followed by immobilization of gold nanoparticles, the reduction in intensity of (100) and (110), (200) reflections, which may be due to loss of some regularity in the 2D hexagonal structural ordering or due to reduction of the scattering contrast between the SBA-15 silica walls and filled pores with propylamine and lipoic acid moieties.

Wide angle XRD spectrum of SBA-LAG (Fig. 3) shows a broad peak with less intensity at 38.1° , which is attributed to $(1\,1\,1)$ plane of the Au nanoparticles [43]. However, the diffracted reflections that are supposed to appear at 44.2° , 64.7° and 77.5° associated with the $(2\,0\,0)(2\,2\,0)$ and $(3\,1\,1)$ planes are not observed, suggesting that the Au nanoparticles are well dispersed on the surface of SBA-15.

3.3. Solid state ¹³C CP-MAS NMR analysis

The functionalization of SBA-15 with propylamine followed by tethering of lipoic acid has been confirmed by solid state ¹³C NMR spectra. Fig. 4 shows the solid-state NMR spectra of SBA-NH₂ and SBA-LA. The ¹³C NMR spectrum of SBA-NH₂ shows three signals at 7.91, 20.42 and 41.3 ppm respectively, representing C¹, C² and C³ of the (3-aminopropyl) triethoxysilane (APTES), which confirms the APTES functionalization on the surface of SBA-15 [44]. The single peak that appears at 179.4 ppm for the pure lipoic acid corresponds to -C=0 of -COOH (Fig. 4, Inset). After lipoic acid treated with SBA-NH₂ the peak at 179.4 ppm shifted to 174 ppm, indicating the formation of amide bond. Additionally, the NMR spectrum of SBA-LA shows peaks at 174, 56, 40, 39, 36, 34, 29 and 25 ppm, which corresponds to the amidation of lipoic acid with SBA-NH₂ [14].

3.4. FT-IR analysis

FT-IR spectra of (a) SBA-15 (b) SBA-NH₂ (c) SBA-LA (d) SBA-LAG is shown in Fig. 5. A broad band observed in between 3437 and 3369 cm⁻¹ in all the samples, which indicates typically –OH stretching vibration, the band at 1629 cm⁻¹ in SBA-15 and SBA-NH₂ samples due to –OH deformation band, the sharp band around 967 cm⁻¹ is associated with Si–OH [45,46] and the band at



Fig. 4. ^{13}C CP-MAS NMR spectra of SBA-NH $_2$ and SBA-LA and ^{13}C NMR spectra of pure lipoic acid shown in inset.

3135 cm⁻¹ in SBA-NH₂ is due to $-NH_2$ stretching vibration, which is in hydrogen bonding with -OH groups. New bands were observed in the range of 2932–2864 cm⁻¹ and 1474–1384 cm⁻¹ for SBA-NH₂, SBA-LA and SBA-LAG are corresponding to $-CH_2$ stretching and bending vibrations. A sharp absorption band that appeared for the SBA-15 at 1629 cm⁻¹ is due to adsorbed water molecule has substantially reduced in intensity and generated a new infrared band at 1557 cm⁻¹, which corresponds to N–H (primary amine) bending vibrations [47–50]. After propylamine functionalization, significant decrease in the intensities of absorption bands that are responsible for -OH groups in the stretching (3437–3369 cm⁻¹) and bending (967 cm⁻¹) regions, implies the consumption of -OH groups due to anchoring of propylamine onto SBA-15 through chemical bonding. SBA-LA and SBA-LAG has two additional bands at 1651 and 1547 cm⁻¹, which can be assigned to -C=O amide (II) stretching



Fig. 5. FT-IR spectra of SBA-15, SBA-NH₂, SBA-LA and SBA-LAG.



Fig. 6. Au 4f X-ray photoelectron spectrum and catalyst. Inset shows the survey of XPS scan of SBA-LAG catalyst.

and —NH bending vibrations [13,51]. The results of IR spectra are in good agreement with the results obtained by NMR technique, confirming that propylamine and lipoic acid has been successfully grafted on the surface of SBA-15. 6. In General, the S–S stretching frequency to be observed in the range of 540–500 cm⁻¹ [52,53], but it might be masked by the silica SBA-15 peak and also the S–Au band supposed to be observed in the range of 240–210 cm⁻¹ [52], but the present IR spectrum was recorded in the range of 4000–400 cm⁻¹. So the S–S and S–Au stretching bands of SBA-LA and SBA-LAG are not observed.

3.5. XPS analysis

X-ray photoelectron spectra (XPS) analysis is a powerful technique used to provide information on the chemical oxidation state of elements present in the synthesized material. The XPS spectrum of SBA-LAG displayed in Fig. 6, which depicts the Au4f core level of the catalyst, showing the binding energies at 84 and 86.7 eV, which are assigned to the spin-orbit splitted components of Au ($4f_{7/2}$) and Au ($4f_{5/2}$) in the zero oxidation state of Au, which are in agreement with the reported values [14,51]. The binding energies at 85 and 89 eV are characteristic of cationic form of Au in +3 oxidation state, which are absent, suggesting the immobilization of Au nanoparticles on the surface of SBA-15.

3.6. TGA analysis

To know the amount of functionalized material and its stability on the surface of SBA-15, thermogravimetric analysis was made and the resultant thermograms of SBA-15, SBA-NH₂ and SBA-LA were shown in Fig. 7. Thermogram of parent SBA-15 shows a marginal loss of mass around 2.6%. This mass loss is due to the loss of adsorbed water on the surface of SBA-15 or the water that formed from the condensation of hydroxyl groups. The thermograms of all other samples show a significant mass loss between 348 °C and 668 °C. Beyond this temperature all the thermograms of samples are constant. The major mass loss is due to the decomposition of anchored organic moieties [54]. From the TGA results, it is found that the organic moieties are thermally stable when they are covalently anchored onto the surface of mesoporous SBA-15.



Fig. 7. Thermograms of SBA-15, SBA-NH₂ and SBA-LAG.

3.7. TEM analysis

The TEM images of SBA-15 and SBA-LAG are shown in Fig. 8. This reveals that the morphology of the SBA-LAG remains intact after deposition of Au nanoparticles onto SBA-LA. The TEM image also reveals the spherical nature of immobilized Au nanoparticles on SBA-15. The particles size distribution graph is shown in Fig. 8 as an inset, which shows that the mean diameter of Au nanoparticles is approximately 8–10 nm.

After realizing the potential applications of Au nanoparticles, much effort has been devoted to develop mesoporous material supported Au nanoparticles, particularly for preventing the agglomeration as well as maintaining the high dispersion. It is evidenced from the literature that the direct synthetic methodologies prevail over post-synthetic techniques particular to prepare smaller size and highly dispersed Au nanoparticles [55–61]. The structural and textural characteristics like BET surface area, pore diameter, pore volume and particle size of the most relevant publication are compared in Table 3. The variations in the structural and textural parameters are mainly depends on the method of preparation.

3.8. Catalytic activity studies

The catalytic activity of SBA-LAG was investigated for the synthesis of propargylamines by reacting benzaldehyde, piperdine and phenylacetylene as standard substrates. To optimize the reaction conditions, the reaction was carried out in different solvents and the results were shown in Table 4, which reveals that under solvent-free conditions the yields are better. Slightly lower yields are obtained, when the reaction was performed in CH₃CN, Toluene, and Benzene as solvents (Table 4, Entries 1, 2, 3). DMSO, DMF, CH₃OH and water gave low to moderate yields (Table 4, Entries 4, 5, 6, and 7). The optimized reaction conditions include 1 mmol of benzaldehyde, 1.1 mmol of piperdine, 1.2 mmol of phenylacetylene, 35 mg of catalyst, 100 °C temperature, and 8 h reaction time.

In order to elucidate the influence of core size on the activity on different SBA-LAG catalysts were studied, wherein same amount of Au is used by taking the different amounts of catalyst, i.e. 31–78 mg of catalyst (Table 5). It is found that there is a significant decrease in the conversion with increase core size.

To understand the nature of capping agents in the catalytic activity of Au nanoparticles same amount of Au was also immobilized on



Fig. 8. TEM image of SBA-LAG, inset Au nanoparticle size distribution of SBA-LAG.

Table 3

Comparison of structural and textural characteristics with reported literature.

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Particle size (nm)	Ref.
Au@MPTS-Al-	540	0.49	5.9	3.2-3.7	53
SBA-15					
0.5% GCM (F)	1048	>1.1	>6.2	-	54
Au/Ti-G-80	499	0.87	6.5	1.5	55
0.16Au11-SBA(20)	866	1.7	8	0.8-1.0	56
Au/10%CeOx/SBA-15	370	0.609	6.6	4.8	57
Au@APTS-SBA-15	885	1.27	6.79	2.1-19.4	58
Au/AF-MSTF	-	-	-	1-4	59
SBA-LAG	415	0.78	6.15	8-10	Present work

Table 4

Influence of solvent in the formation of propargylamines over SBA-LAG catalyst.

Entry	Solvent	Yield (%)
1	CH₃CN	75
2	Toluene	58
3	Benzene	45
4	DMSO	20
5	DMF	18
6	CH₃OH	25
7	H ₂ O	28
8	Neat	95

Reaction conditions: benzaldehyde (1 mmol), piperdine (1.1 mmol), phenylacety-lene (1.2 mmol), catalyst (35 mg), 100 $^\circ$ C, 8 h.

propyl amine functionalized SBA-15, which exhibited lower conversion (58%) compared to SBA-LAG (95%).

With the optimal reaction conditions in hand, various aldehydes and alkynes were used as substrates and

Table 5

Influence of Au loading, core size and dispersity on different SBA-LAG catalysts.

S. no.	Catalyst	Core size (nm)	Poly dispersity (Pdi)	Conversion (%)
1	SBA-LAG 1 (78)	2-4	0.74	98
2	SBA-LAG 1.5 (52)	5-6	0.91	96
3	SBA-LAG 2.1 (35)	8-10	0.70	95
4	SBA-LAG 2.5 (31)	12-14	1.00	83

The value shown in parenthesis refers to the amount of catalyst (in mg) used in the experiment Reaction conditions: benzaldehyde (1 mmol), piperdine (1.1 mmol), phenylacetylene (1.2 mmol), catalyst (0.04 mol% Au), $100 \degree C$, 8 h.

the results are summarized in Table 6. Aromatic aldehydes with electron withdrawing as well as electron donating groups are investigated. The activity data demonstrate that the functional groups on the ring did not show any significant effect on the reaction. Both aromatic and aliphatic aldehydes smoothly reacted with piperdine and phenylacetylene. The yields of desired products are good to excellent (Table 6, Entries 1–8). Various terminal alkynes ($-CH_3$, $-OCH_3$) with piperdine and benzaldehyde are reacted smoothly and obtained good yields (Table 6, Entries 9, 10).

3.9. Reusability

To evaluate the reusability of the catalyst, the used catalyst was separated from the reaction mixture, washed with ethyl acetate,

Table 6	
SBA-LAG catalysed synthesis of propargylamines.	

Entry	<i>R</i> ₁	Amine	<i>R</i> ₂	Product	Yield (%)
1	Ph (1a)	Piperdine (2a)	-Ph (3a)	4a	95
2	$p-CH_{3}C_{6}H_{4}(1b)$	2a	3a	4b	83
3	p-OCH ₃ C ₆ H ₄ (1c)	2a	3a	4c	85
4	p-FC ₆ H ₄ (1d)	2a	3a	4d	90
5	p-ClC ₆ H ₄ (1e)	2a	3a	4e	88
6	p-BrC ₆ H ₄ (1f)	2a	3a	4f	87
7	H(1g)	2a	3a	4g	95
8	$C_{6}H_{11}(1h)$	2a	3a	4h	91
9	1a	2a	$p-CH_{3}C_{6}H_{4}$ (3b)	4i	86
10	1a	2a	p-OCH ₃ C ₆ H ₄ (3c)	4j	90

Reaction conditions: Benzaldehyde (1 mmol), piperdine (1.1 mmol), phenylacety-lene (1.2 mmol), catalyst (35 mg), temperature ($100 \,^{\circ}$ C) and time (8 h).



Fig. 9. The reusability of SBA-LAG catalyst.



Scheme 3. Proposed mechanism for one pot three component synthesis of propargylamines.

dried at room temperature and reused. The recyclability data was displayed in Fig. 9, which reveals that the catalytic activity is almost constant even after 5 repeated cycles.

3.10. Mechanism

Based on the literature reports [38,40] a mechanism is proposed for three-component one-pot synthesis of propargylamines over SBA-LAG catalyst (Scheme 3).

Initially, the immobilized Au nanoparticles on SBA-15 activate the C—H bond of alkynes to form the Au-Alkenyl intermediate, which is a key step, because Au has high alkynophilicity for terminal alkynes. Then the Au-alkenyl intermediate reacts with iminium ion which is formed in situ from aldehyde and *sec*-amine to give the corresponding propargylamine product and the immobilized Au nanoparticles on SBA-15 gets regenerated. The same catalytic cycle repeats till the completion of substrates.

4. Conclusions

In conclusion, the SBA-LAG is a versatile and useful eco-friendly catalyst. It shows high catalytic performance for the synthesis of propargylamines in one-pot synthesis under solvent-free conditions in good to excellent yields. It can be easily separated and reused at least 5 repeated cycles without loss in catalytic activity. Ease of separation, solvent-free operation and reusability are the advantages of this catalyst.

Acknowledgements

Narani Anand and Pochamoni Ramudu are thankful to Council of scientific and Industrial Research (CSIR) New Delhi, for awarding research fellowships.

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