

RESEARCH PAPER

Preparation of Ag₂S Nanoparticles and using as Catalyst for the A³-coupling (Aldehyde-Amine-Alkyne) Reaction

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ARTICLE INFO

Article History:

Received 09 February 2019

Accepted 12 June 2019

Published 01 July 2019

Keywords:

A³-coupling

Nanocatalyst

Nanoparticles

Propargylamine

Silver Sulfide

ABSTRACT

Microwave assisted facile *one-step* approach was adopted to prepare mono-dispersed silver sulfide nanoparticles. The structures of the synthesized Ag₂S nanoparticles were confirmed by Fourier-transform infrared spectroscopy (FT-IR), diffuse reflectance UV-vis spectroscopy (DRS), X-ray diffractometer (XRD), energy dispersive X-ray analysis (EDX) and transmission electron microscope (TEM). The prepared Ag₂S nanoparticles (NPs) were successfully used as a heterogeneous catalyst in the one-pot three-component coupling reaction of aldehydes, amines and alkynes (A³-coupling) toward propargylamines. In this protocol, both aromatic and aliphatic aldehydes and secondary amines were reacted with terminal alkynes in the presence of Ag₂S NPs at low catalytic loading (0.5 mol %) that led to the rapid and efficient formation of propargylamines with good to excellent yields. The A³-coupling reaction occurred effectively at 80 °C under solvent-free conditions. The catalyst is easy to prepare and is perfectly stable under the reaction conditions. Also, the Ag₂S NPs catalyst can be easily recovered and reused several times and exhibited higher catalytic activity than other some commercially catalysts.

How to cite this article

Torabi P, Moradian M.. Preparation of Ag₂S Nanoparticles and using as Catalyst for the A³-coupling (Aldehyde-Amine-Alkyne) Reaction. J Nanostruct, 2019; 9(3): 478-488. DOI: 10.22052/JNS.2019.03.009

INTRODUCTION

Metal sulfides especially silver sulfide nanoparticles have exhibited good chemical stability and have attracted much attention due to their potential applications [1, 2] in photoconductors [3], light-emitting diodes (LED) [4, 5], near-infrared photo-detectors [6] and biological applications [7, 8]. The Ag₂S NPs is less toxic as compared to other sulfide nanoparticles such as cadmium, lead, and so on [9, 10]. There are different approaches for the preparation of silver sulfide nanoparticles such as the hydrothermal method, the solvothermal route and single-source precursor technique [11-16]. The homogeneous catalysts are unsuitable for separating from the reaction medium and making their reuse difficult and infecting the reaction

products. By using advanced solid materials as heterogeneous catalysts [17] in organic processes can mitigate these problems. Carbon-carbon bond-forming reactions are key transformations for synthesis of a wide variety of compounds that exhibit significance biological, pharmaceuticals and materials properties [18-20]. The discovery of metal oxide [21-24] and metal sulfide nanoparticles (NPs) as catalyst for the formation of C-C bonds was an important finding in organic synthesis. Furthermore, the using of NPs as a catalyst in the three-component coupling reaction of an alkyne, an aldehyde and an amine (briefly called A³-coupling), has been developed for the synthesis of propargylamines as biologically active compounds [25]. The nucleophilic addition of a metal acetylide to an imine through C-H

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activation of a terminal alkyne by a special catalyst is the general mechanism for the synthesis of propargylamines throughout the A³-coupling reaction. During the next decades, substantial progress has been made and new catalyst base on the copper salts as well as copper halides [26] such as CuCl [27], CuBr [28], CuCN, and CuI [29] or coordinated with organic donor ligands have been developed in this reaction [29-35]. However, some of these transition metals demonstrate noteworthy catalytic activity and selectivity but using the above mentioned protocols, reactions were carried out in both toxic catalyst and solvent.

Hajra and co-workers have reported an efficient and reusable heterogeneous nano indium oxide as a catalyst in the A³-coupling reaction [36]. Recently Kantam and his co-workers reported Zn dust as catalyst in this reaction [37]. Also some of nanocomposite materials such as imine-functionalized copper complex immobilized on silica (SiO₂-Py-CuI) [38], N-heterocyclic carben (NHC) silica supported CuI complex [39, 40], molecular sieves [41], magnetite [42], zeolites [43], Pybox complexes on polystyrene resin [44] and Cu(I)-MOF [45] as heterogeneous catalysts were as well reported for this reaction.

Silver salts and complexes mainly act as carbophilic and soft Lewis acids that extensively used in the homogeneous and heterogeneous catalysis of organic transformations [46]. Li and co-workers reported the first example of Ag(I) salts catalyzed A³-coupling reaction in 2003 and were found to be efficient catalyst for this reaction [47]. In this work the simple silver salt was used as homogeneous catalyst that AgI gave the best results. Since then, some other silver salts such as Ag₃PW₁₂O₄₀ [48], Ag(Ph₃P)Cl [49], Organonitrile ligated silver complexes [50], zeolite supported silver salts [51], silver nanoparticles [52, 53] and silver-NHC complexes [54, 55] have been explored to catalyze the A³-coupling reaction as valuable catalysts for this A³-MCR.

In this paper, a one-pot approach was adopted to prepare mono-dispersed Ag₂S nanoparticles via microwave irradiation. We would like to present use of Ag₂S as an efficient and green catalyst for the first time in the A³-coupling reaction of aldehyde, amine and alkyne toward propargylamine. Due to the high surface area of Ag₂S nanoparticles and high activity of solid NPs, the needing amounts of catalyst was negligible. The reaction was performed under solvent free conditions and does

not require any co-catalyst and after completion of the reaction, the catalyst was recovered by filtration and reused several times under the same reaction conditions.

MATERIALS AND METHODS

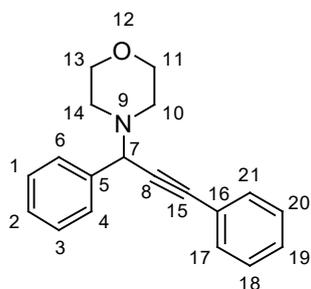
All commercially available reagents were used without further purification and purchased from the Merck Chemical Company in high purity. The used solvents were purified by standard procedure. The FT-IR spectra were recorded as KBr pellets on a Nicolet FT-IR spectrophotometer. The ¹H and ¹³C NMR spectra were recorded in CDCl₃ on a Bruker DRX-400 spectrometer. XRD patterns were recorded by an X'PertPro (Philips) instrument with 1.54 Ångström wavelengths of the X-ray beam and Cu anode material. The Microwave conditions were carried out in microwave oven specially designed for organic synthesis (Milestone LAVIS Basic Microwave). Transmission electron microscopy (TEM) was performed with a Jeol JEM-2100UHR, operated at 200 kV. Melting points obtained with a Yanagimoto micro melting point apparatus are uncorrected. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates (from Merck Company).

Synthesis of Ag₂S nanoparticles

In a general procedure, 0.01 mol of silver nitrate was carefully dissolved in 20 ml of ethylene glycol monomethyl ether under stirring at 80 °C. Then, 20 ml of thioacetamide solution (1 M in water) that was previously prepared was added to the main solution drop wise over 10 minutes. During this time, the solution was exposed to irradiation at microwave oven at working cycle of 30 seconds on and 100 seconds off and 350 watts of power; lastly for completion of the reaction, the irradiation was followed by 10 minutes excess at same conditions. After this time, the reaction mixture was slowly cooled to room temperature and the dark solid silver sulfide nanoparticles were precipitated and collected by centrifuge and consecutively washed with deionized water (5 × 50 ml) and absolute ethanol (3 × 10 ml). The Ag₂S NPs were dried in the vacuum desiccator at 50 °C temperature.

General procedure for the synthesis of propargylamines by the Ag₂S nanoparticles as catalyst

In a typical procedure, to a mixture of the selected aldehyde (1.0 mmol), the selected secondary amine (1.1 mmol) and phenyl acetylene (1.2 mmol) in a 25 ml glass beaker equipped with a magnetic stirring bar, 1.5 mg Ag₂S NPs as catalyst was added. The final mixture was stirred at 80 °C and the progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction (from TLC), the resulting mixture was dissolved in CH₂Cl₂ and then filtered through a pad of celite to collect and recover the solid catalyst for next reactions. The filtered was evaporated under reduced pressure to give a crude product as viscous oil. The product was purified over silicagel by column chromatography (eluent: EtOAc / n-hexane) to give the desired extra pure propargylamine.



4-(1,3-diphenylprop-2-yn-1-yl)morpholine (4a)
Yield: 93%; Light red oil; ¹³C NMR (CDCl₃): δ 50.35 (C7), 57.21 (C10, C14), 68.54 (C11, C13), 84.08 (C8), 88.49 (C15), 115.17 (C16), 116.31 (C19), 121.96 (C21, C17), 123.67 (C2), 124.82 (C18, C20), 126.16 (C1, C3), 130.43 (C4), 131.87 (C6), 136.54 (C5); ¹H NMR (CDCl₃): δ 2.67-2.68 (m, 4H, C10H, C14H), 3.77-3.80 (m, 4H, C11H, C13H), 4.84 (s, 1H, C7H), 7.33-7.44 (m, 6H, ArH), 7.56-7.58 (m, 2H, ArH), 7.68-7.70 (m, 2H, ArH); FT-IR (KBr disk): ν cm⁻¹ 3059, 3014, 2984, 2957, 2950, 1598, 1489, 1449, 1318, 1280.

RESULTS AND DISCUSSIONS

Synthesis of the Ag₂S nanoparticles

The parameters of the reaction conditions for the synthesis of Ag₂S NPs were optimized via investigation of power and time of the reaction. The optimum power of the microwave irradiation was 350 watt. In this power, the temperature of the reaction media reach to 90 °C maximum; but, in lower powers (120 and 180 watts), the reaction was not completed and the NPs produced in below 50 % yield. In higher power of microwave instrument (580 and 720 watts), the reaction temperature reach to above 110 °C, and the nanoparticles agglomerate and the size of the nanoparticles was greater than 100 nm. The optimum time of the reaction was founded to be 20 minutes. If the reaction was continued over 20 minutes, the crystalline Ag₂S NPs is damaged and Ag₂O is dominant products. Also, at lower times, the reaction was not completed and the yield of the NPs was low.

Characterization of the Ag₂S nanoparticles

The structures of the synthesized Ag₂S nanoparticles were confirmed by Fourier-transform infrared spectroscopy (FT-IR), diffuse reflectance UV-vis spectroscopy (DRS), X-ray diffractometer (XRD), scanning electron microscope (SEM), energy dispersive X-ray analysis (EDX) and transmission electron microscope (TEM).

Fig. 1 shows the FT-IR spectra of Ag₂S NPs provided by KBr pellet method. In the present work, the FT-IR technique mainly used to recognize the presence of Ag-S bond around 600-700 cm⁻¹ and absence of some organic residues arisen from organic compounds that used during the process of nanoparticle synthesis. As can be seen, two peaks at 536 and 735 cm⁻¹ can be related to the Ag-S bond of the solid NPs. Moreover, the signals

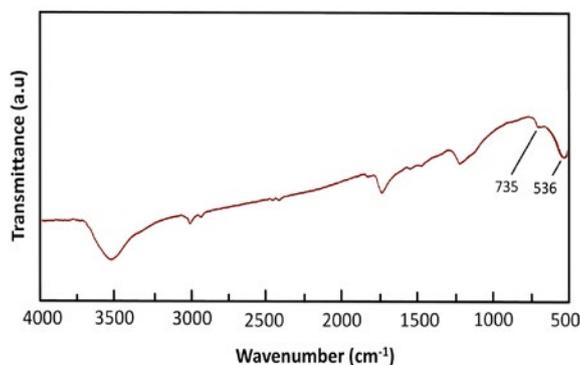


Fig. 1. FT-IR spectra of Ag₂S NPs

around the 1100 and 1700 cm^{-1} are very weak in the spectrum due to the presence of negligible organic residues in the Ag_2S solid nanomaterial.

The prepared Ag_2S was analyzed by X-ray diffraction spectrometer. The resulted pattern was confirmed crystal phase of the Ag_2S NPs, which are shown in Fig. 1. It can be seen that all the diffraction peaks in the XRD pattern is well consistent with those of peaks in the library pattern of monoclinic Ag_2S (JCPDS Card no. 14-0072) and due to the nano-crystalline nature of the sample, several peaks are broadened. The pattern in Fig. 1 was shown very strong reflection peaks due to the Ag_2S NPs were well-crystallized. Moreover, there is no other peaks appear in the XRD patterns from Ag_2S , which confirm the pure phase of our samples and there was detected any peaks from other impurities such as Ag_2O .

The SEM and TEM image of the Ag_2S NPs was shown in Fig. 3a and 3b. According to the SEM image, the size of the nanoparticles are around 25-35 nm and are well-dispersed. Moreover, the size of nanoparticles was confirmed by the TEM image 3.

In accordance with the TEM image of the Ag_2S nanoparticles, the particle size distribution histogram was provided and shown in Fig. 4. As can be observed, the dispersed nanoparticles were formed with a uniform size and the mean value and standard deviation could be estimated 27 ± 5 nm from this size distribution histogram (Fig. 4).

The Energy Dispersive X-Ray analyzer (EDX) was also provided to prove the existence of silver and sulfur elements in the prepared NPs (Fig. 5). Also, quantitative compositional information was shown

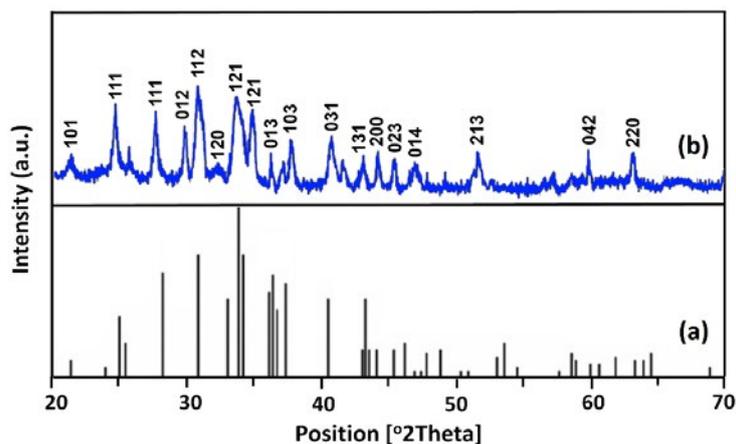


Fig. 2. The XRD pattern of silver sulfide nanoparticles; (a) the main peak from JCPDS Card no. 14-0072; (b) the resulted peaks from the prepared Ag_2S NPs

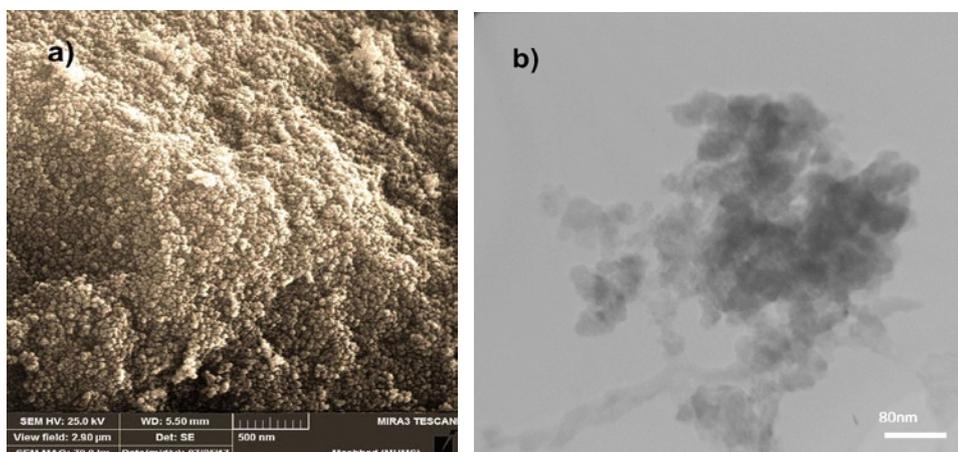


Fig. 3. SEM (a) and TEM (b) images of the Ag_2S NPs

an atomic ratio of 1.88:1 respectively for Ag and S, which is close to the appropriate stoichiometry of crystalline bulk silver sulfide. It is notable that, there are any other peaks in the spectrum from elements except Ag and S, which confirmed that the Ag₂S NPs are pure.

The specific surface area of the Ag₂S nanoparticles was determined by single point BET analysis. The surface area of NPs was found to be 25.8 m²/g and a mean particle size of 32.6 nanometers was calculated from the $d_{\text{BET}} = 6000/\bar{n}S$ equation (d is diameter in nanometer, S is specific surface area in m²g⁻¹ and \bar{n} is the theoretical density in g cm⁻³). This value is close to that obtained by TEM image and indicates that the powder consists of solid spheres and gas adsorption was able to access the whole surface area of the NPs, also agglomeration of nanoparticles does not occur.

The diffuse reflectance UV/Vis spectroscopy (DR UV/Vis) was used to confirm the optical property and subsequently crystallinity of the nanoparticles

(Fig. 6). Tang and co-workers reported a full account of synthesis and optical property of Ag₂S nanoparticles. It is notable that, the resulted DRS spectra of the prepared nanoparticles approved by the resulted ones in the aforesaid work [5].

Activity of the catalyst

After characterization of the Ag₂S nanoparticles, the prepared NPs were employed as a heterogeneous and reusable catalyst in the A³-coupling reaction of aldehydes, secondary amines and phenylacetylene toward related propargylamines. Initially, the parameters of the reaction were optimized using the reaction of benzaldehyde (1 mmol), morpholine (1.1 mmol) and phenyl acetylene (1.2 mmol) in the catalytic amount of Ag₂S NPs as a model reaction under solvent free conditions. In this model, all of the reactions were performed within 10 h and the effect of catalyst amount and reaction temperature was investigated and the results

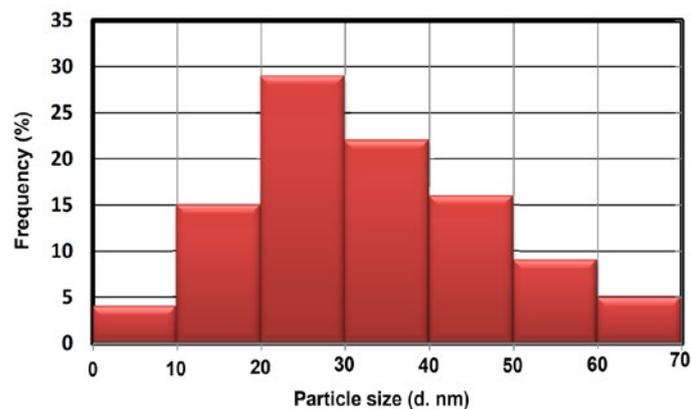


Fig. 4. Particle size distribution histogram of Ag₂S nanoparticles

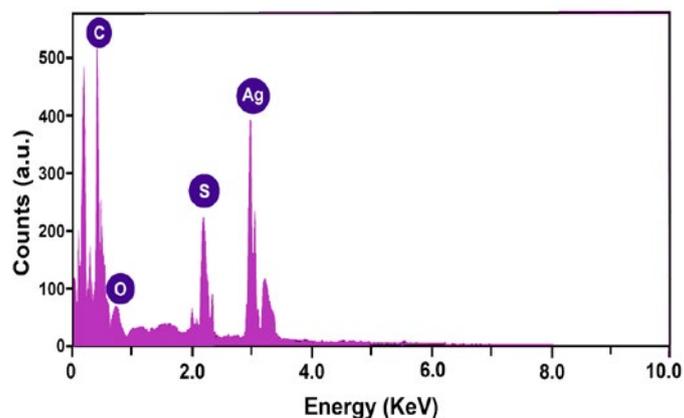


Fig. 5. The energy dispersive X-Ray analyzer of the Ag₂S NPs

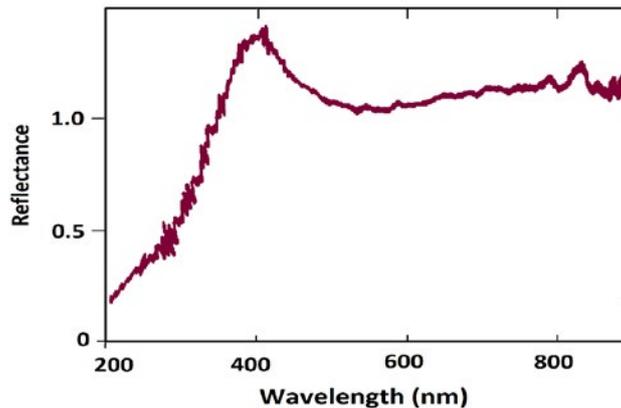
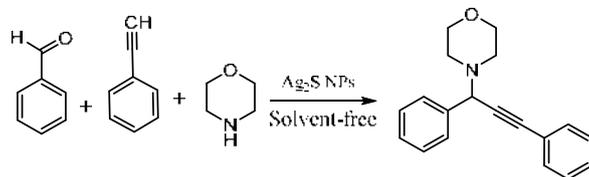


Fig. 6. The diffuse reflectance Uv/Vis spectroscopy of Ag₂S NPs

Table 1. Optimization of the reaction conditions^a



Entry	Catalyst mg (mol %)	Temp. (°C)	Yield (%) ^b
1 ^c	-	120	-
2	0.5 (0.2 mol %)	80	57
3	0.75 (0.3 mol %)	80	72
4	1.0 (0.4 mol %)	80	84
5	1.25 (0.5 mol %)	80	93
6	1.5 (0.6 mol %)	80	93
7	1.75 (0.7 mol %)	80	93
8	1.25 (0.5 mol %)	70	66
9	1.25 (0.5 mol %)	90	93
10	1.25 (0.5 mol %)	100	90
11	1.25 (0.5 mol %)	110	88

^a Benzaldehyde (1.0 mmol), Phenylacetylene (1.2 mmol), morpholine (1.1 mmol) reacted within 10 h

^b Based on isolated yields

^c The reaction was occurred within 24 h

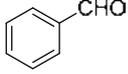
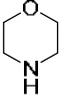
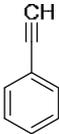
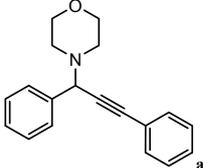
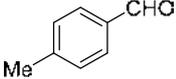
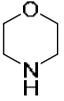
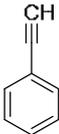
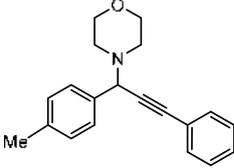
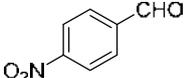
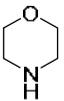
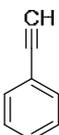
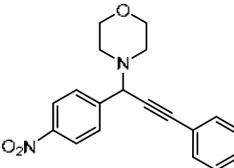
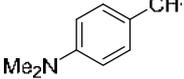
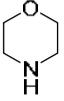
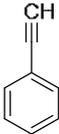
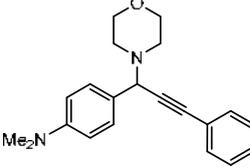
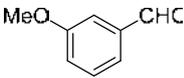
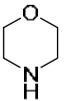
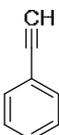
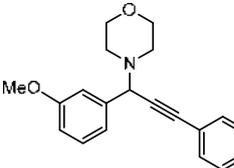
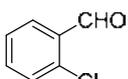
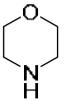
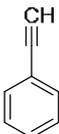
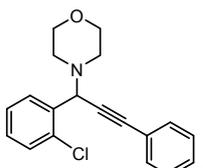
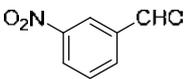
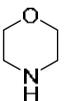
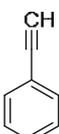
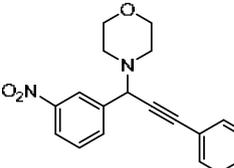
were provided in Table 1. As it can be seen in this Table, the best result was obtained when 0.5 mol % of the catalyst loaded into the reaction vessel and the reaction was performed at 80 °C under solvent-free conditions (Table 1, entry 5).

The reaction was performed within 24 hours in the absence of catalyst under same reaction conditions. The reaction mixture was analyzed and any product was forming, this result noted that progress of the reaction needed a catalyst (Table 1, entry 1). Moreover, the amount of Ag₂S catalyst was optimized, and it was found that in the reaction condition, the desired product was obtained in 57, 72 and 84 % isolated yields in the presence of 0.2, 0.3 and 0.4 mol % catalyst respectively (Table 1, entries 2-4). Furthermore, when 0.5 mol % Ag₂S

NPs as heterogeneous catalyst was loaded in the reaction vessel, the reaction was generally completed and the desired product was obtained in 93 % isolated yield (Table 1, entry 5). Also, the reaction was performed in the presence of higher amounts of catalyst and the results were shown these reactions did not lead to the better product yield (Table 1, entries 6, 7).

For optimization of the reaction temperature, the reaction was separately performed at 70-110 °C and the results were provided and added in Table 1, entries 7-11. As can be seen, the lower temperature 70 °C, led to decreased yield of the desired propargylamine (Table 1, entry 8). Also, it was found that at 90 °C, the yield of the reaction was constant (Table 1, entry 9), however, at 100

Table 2. *Ag₂S* NPs catalyzed three-component synthesis of propargylamines^a

Entry	Aldehyde	Amine	alkyne	Product	Time (h)	Ref.	Yield (%)
1					10	[43, 48]	93
2					10	[56, 57]	91
3					8	[43]	93
4					14	[58]	88
5					12	[58]	90
6					11	[43]	87
7					10	[57]	91

°C and above it at 110 °C, the yield of the desired product was decreased due to the increased side reactions and by products (Table 1, entries 10, 11).

With the optimized conditions, the scope and

generality of the strategy with the *Ag₂S* NPs as heterogeneous solid catalyst was examined in the A³-coupling reaction. Some of the aromatic aldehydes with variety of functional groups were

applied to the reaction with phenyl acetylene and morpholine and the results were provided in Table 2, entries 1-10. It is notable that, benzaldehyde derivatives with an electron-withdrawing group afforded desired products in excellent yields (Table 2, entries 3, 8-10) in compare with an electron donating group that has a lower yield (Table 2, entries 4-6).

The piperidine as secondary amine substrate was also examined in this new strategy for the A³-coupling reaction, in optimized conditions (Table 2, entry 12). The coupling reaction was preceded readily and completely toward desired propargylamine in excellent yield 92 %. In entry 11 from this Table, the pentanal was used as aliphatic aldehyde and the result indicated that the desired propargylamine was produced in high yield at 16 hours in the optimized reaction conditions.

We also investigated the ability of recyclability and reusability of the nano-catalyst as well as catalyst leaching study in this strategy and, the

results were explained in this section. After the first step of the reaction, the solid Ag₂S nanocatalyst was separated by centrifuged and the solution phase was subjected as solvent to a new setup for propargylamine synthesis without any catalyst and under the same reaction conditions. The reaction was monitored after 10 h and the result was indicated that there was no further conversion of substrates to desired products. This means that any solid nanoparticles or active silver metal leached from solid nanocatalyst to remains in the filtrate.

Our proposed reaction mechanism for the catalytic reaction in the presence of Ag₂S NPs as catalyst is the same as the well-known mechanism for the A³-coupling reaction (Fig. 7). First step is the C-H activation of the alkyne group via adsorption on the surface of Ag₂S NPs and produces alkynyl-[Ag₂S] complex. Then, the complex reacts with the iminium ion formed from the reaction of aldehyde and amine to afford the desired propargylamine with regeneration of the catalyst.

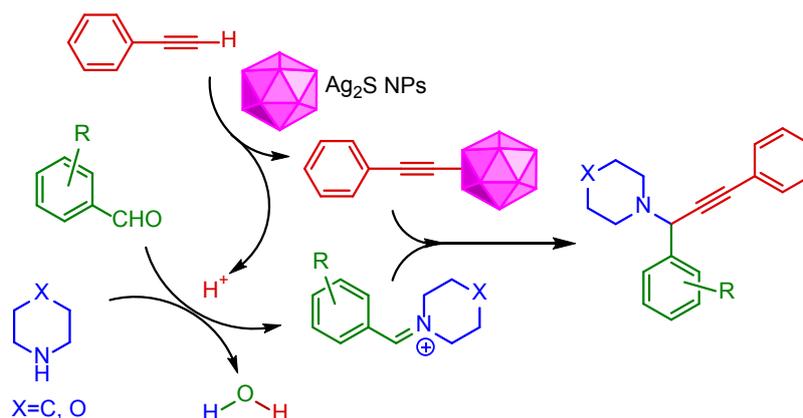


Fig. 7. Proposed reaction mechanism for the catalytic reaction

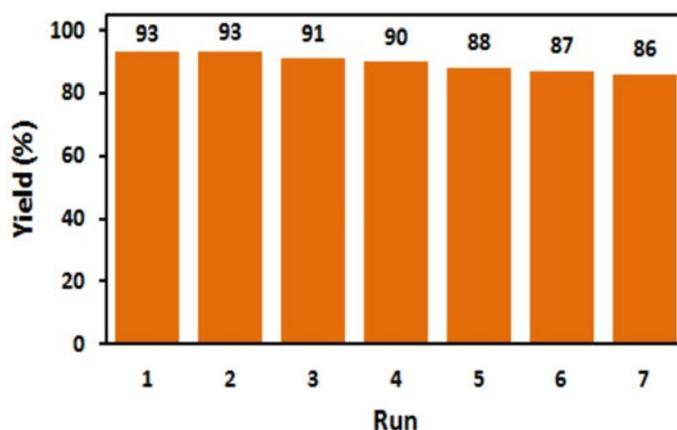


Fig. 8. The results of reusability of Ag₂S NPs catalyst in the A³-coupling reaction

After the first run of the reaction was completed, the reaction mixture was diluted with ethyl acetate and solid nanocatalyst was recovered by centrifugation. The recovered catalyst was thoroughly washed with CH₂Cl₂ (3×5 ml) and dried at 80 °C for 10 h. the recovered Ag₂S nanocatalyst was used for next run at optimized reaction conditions without any reactivation. This process was repeated for six runs and the yield of the propargylamine in each run was determined and the results were provided and plotted in Fig. 8. As can be seen in this Figure, in all of runs a negligible decrease in yields was observed and the solid catalyst can be reused for at least seven consecutive runs without major loss of activity.

CONCLUSION

The results show that the mono-dispersed Ag₂S nanoparticles can be readily prepared with a solventless thermolytic method assisted by microwave irradiation. The prepared Ag₂S NPs used as efficient heterogeneous and reusable catalyst for the synthesis of propargylamines. The Ag₂S nano-particles show high efficiency in the three-component coupling reaction of aldehydes, amines and alkynes named as A³-coupling strategy. By using these nanocatalysts, the reaction leading to the production of propargylamines in high yields, low reaction time in solvent free conditions. This reaction system has advantages as follow; 1) no metal waste was obtained, 2) the Glaser byproduct was not formed during the reaction, 3) the activity of catalyst over several cycles was maintained, 4) the catalyst could be readily recovered and reused several times, 5) no metal leaching was observed after utilization of the catalyst.

ACKNOWLEDGMENTS

The authors are grateful to Mahshahr Branch of Islamic Azad University and university of Kashan for supporting this work.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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