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Facile method for the synthesis of core/shell $Fe_3O_4@SiO_2@SiO_2-SH-Au$: a super magnetic nanocatalyst for water-medium and solvent-free alkyne hydration

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Abstract In a simple approach, gold was successfully anchored to the surface of thiol-functionalized super paramagnetic Fe₃O₄ nanoparticles as heterogeneous catalyst. The core/shell Fe₃O₄@SiO₂@SiO₂-SH-Au was prepared in a facile procedure, without using any reducing reagents by in situ reduction of Au³⁺. The catalyst was characterized by TEM, SEM, IR, XRD and EDX. The catalyst with loaded iron oxide nanoparticles can be recovered from the reaction mixture by an external magnet and reused without considerable decrease in activity even after four runs. As demonstrated experimentally, the catalyst shows remarkably high catalytic efficiencies in promoting water-medium and solvent-free alkyne hydration reaction.

Graphical abstract



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¹ Department of Chemistry, K. N. Toosi University of Technology, P.O. Box 15875-4416, Tehran, Iran **Keywords** Magnetic nanocatalyst \cdot Au nanoparticles \cdot Recyclable catalyst \cdot Alkyne hydration \cdot Heterogeneous catalysis

Introduction

The alkyne hydration reaction, leading to the creation of carbonyl derivatives, is of main interest considering the wide availability of alkynyl substrates and the fundamental importance of the carbonyl stile compounds in modern organic synthesis [1]. The alkyne hydration reaction possesses a long history. In 1881, Kucherov's observation has led to the development of a wide variety of metal-based catalytic systems [2]. This type of reaction is generally directed in organic solvents, and in most cases, presence of a Brønsted acid is essential.

The increasing environmental consciousness of the chemical community has led to the search for more efficient and environmentally friendly methods for chemical syntheses [3]. Because of the environmental acceptability, abundance, and low cost of water, organic reactions in water have received increased attention [4, 5]. Thus, the development of efficient procedures for alkyne hydration in water is highly appreciated.

Although, in recent years the heterogeneous and/or homogeneous gold catalysts were used for this reaction, but the utilization of a simple, efficient and reusable catalyst remains an unresolved challenge [6-12]. Therefore, the development of a magnetic catalytic system involving Au nanoparticles with superior recoverability would be of great advantage.

More recently, Au nanoparticles are widely used in a series of reactions due to their unique physical and chemical properties [13-15]. Au nanoparticle catalysts are



Fig. 1 The TEM (a) and SEM (b) images of Fe₃O₄@SiO₂@SiO₂-SH-Au

mainly employed for reactions including oxidation [16–18], cross-coupling [19–21] reactions, etc. Utilization of more environmentally friendly gold catalysts accompanied by practical and efficient processes for catalyst separation and recovery provide both economic and ecological benefits.

Recently, incorporation of a magnetic element (e.g., Fe_3O_4) to provide an additional functionality to the original material has been widely used in the field of catalysis.

Super magnetic nanoparticles work as an excellent framework for supporting various nanocatalysts as they allow easy separation of the catalyst from the reaction mixture using an external magnetic field [22–25]. Lately, many excellent studies about magnetic composite nanocatalysts have been reported [26–29].

The new prepared catalyst $Fe_3O_4@SiO_2@SiO_2-SH-$ Au with loaded iron oxide nanoparticles can be recovered from the reaction mixture by an external magnet and reused







Fig. 3 The EDX spectrum of Fe₃O₄@SiO₂@SiO₂-SH-Au

without considerable decrease in activity even after four runs.

However, so far only a few methods for the synthesis of Au nanoparticle functionalized magnetic silica spheres were reported in the literature, all of which used reducing reagents such as H₂ and NaBH₄ in the final stage for the conversion of Au³⁺ to Au⁰ [30, 31]. In the core/shell Fe₃O₄@SiO₂@SiO₂-SH-Au, in situ reduction of Au³⁺ with HS functionalized magnetic silica sphere resulted in the formation of some $-SO_3H$ functional groups. We have synthesized a catalyst (α -Fe₂O₃)-MCM-41-SH-Au with this method previously [29].

In the present work, the core/shell $Fe_3O_4@SiO_2$ was functionalized with (3-mercaptopropyl) trimethoxysilane (MPMS) and subsequently Au was anchored to $Fe_3O_4@SiO_2@SiO_2@SiO_2-SH$.

Due to soft-soft interaction between Au and S and the resulting semi-covalent bonds with approximately 45 kcal/ mol strength [32], we joined –SH on the surface of the magnetic nanoparticles for deposition of Au.

Then in a green approach, $Fe_3O_4@SiO_2@SiO_2-SH-Au$ has been used as a green and novel gold magnetic nanocatalyst for water-medium and solvent-free alkyne hydration.

Experimental

Chemicals and instruments

The reagents and solvents used in this work were obtained from Fluka or Merck and used without further purification. Melting points were recorded on a Buchi B-540 apparatus. IR spectra were recorded on an ABB Bomem Model FTLA200-100 instrument. ¹H and ¹³CNMR spectra were measured on a Bruker DRX-300 spectrometer, at 300 and 75 MHz, using TMS as an internal standard. Chemical shifts (δ) were reported relative to TMS, and coupling constants (J) were reported in hertz (Hz). X-ray powder diffraction (XRD) was carried out on a Philips X'Pert diffractometer with Co Ka radiation. The structure and morphology of the nanocatalysts were characterized by transmission electron microscope (TEM) and were recorded on a Philips CM-10 instrument on an accelerating voltage of 100 kV and scanning electron microscopy (SEM) analyses were performed by a VEGAIITESCAN electron microscope (Czech Republic) operating at an accelerating voltage of 15 kV. The chemical compositions of the samples are evaluated by scanning electron microscopy (SEM, SAMX) equipped with an energy-dispersive X-ray (EDX).

Catalyst preparation

Synthesis of thiol-modified silica-coated magnetic microspheres

The Fe₃O₄@SiO₂ microspheres were prepared using a published method [33]. Fe₃O₄@SiO₂ (0.1 g) microspheres were dispersed in 30 mL of toluene and ultrasonicated for 20 min. Then MPMS (0.35 mL) was added drop wise into the dispersion and ultrasonicated for another 10 min. Afterward, the mixture was refluxed for 8 h. The mixture was then separated by an external magnet and washed





Table 1 Optimization of reaction condition of phenylacetylene for 2 h



Reaction condition: phenylacetylene (0.3 mmol), solvent (4 ml) and 50 mg $Fe_3O_4@SiO_2@SiO_2-SH-Au$

with toluene and distilled deionized water to give $Fe_3O_4@$ SiO₂@SiO₂-SH as brown powder.

Loading of Au on thiol-modified silica-coated magnetic microspheres

In a typical synthesis, 0.1 g of above synthesized $Fe_3O_4@$ SiO₂@SiO₂-SH was dispersed in 10 mL of ethanol by sonication for 20 min and then 10 mL of 0.025 M ethanol solution of HAuCl₄ was added dropwise with vigorous stirring to this mixture at room temperature. After stirring for 24 h, the Fe₃O₄@SiO₂@SiO₂-SH-Au was collected by an external magnet and washed two times with deionized water and two times with ethanol (Scheme 1). The amount of gold in Fe₃O₄@SiO₂@SiO₂-SH which was determined by EDX was found to be (1.6 Au/g).

Solvent-free and water-medium alkyne hydration reactions

The solvent-free and water-medium alkyne hydrations were carried out in a 10 mL reaction vial for a specified temperature and time. For solvent-free alkyne hydration, alkyne (0.3 mmol), was added to 50 mg Fe₃O₄@SiO₂@SiO₂@SiO₂SH-Au (containing 0.004 mmol Au); it was then stirred at 70 °C for 2 h. For water-medium alkyne hydration, alkyne (0.3 mmol) and 50 mg Fe₃O₄@SiO₂@SiO₂-SH-Au (containing 0.004 mmol Au) were taken in water (4 ml) and the mixture was stirred at 80 °C for 2 h for the synthesis of different ketones. After completion of the reaction,

Table 2 Hydration reaction catalyzed by various catalysts

Entry	Catalyst	Time (h)	Yield %	
1	No catalyst	24	Trace	
2	Fe ₃ O ₄	24	<10	
3	Fe ₃ O ₄ @SiO ₂	24	<10	
4	Fe ₃ O ₄ @SiO ₂ @SiO ₂ -SH	24	<10	
5	Fe ₃ O ₄ @SiO ₂ @SiO ₂ -SH-Au	2	92	

Reaction condition: phenylacetylene (0.3 mmol), H_2O (4 ml), 50 mg catalyst and 80 $^{\circ}C$

the reaction mixture was filtered and purified by passing through a column of silica gel, eluting with 10 % EtOAc in hexane to afford the pure products.

Results and discussion

Characterization of Fe₃O₄@SiO₂@SiO₂-SH-Au

The newly prepared catalyst Fe₃O₄@SiO₂@SiO₂-SH-Au was characterized with TEM, SEM, XRD, EDX and IR. The morphologies and structural features of the synthesized

catalyst $Fe_3O_4@SiO_2@SiO_2-SH-Au$ could be observed directly through TEM images (Fig. 1a). The SEM images show that the diameter of resulting microspheres is ~50 nm (Fig. 1b).

The crystallinity and phase composition of the materials were characterized using wide-angle X-ray diffraction (WAXRD). Figure 2 displays the WAXRD pattern of the sample. The sample of Fe₃O₄@SiO₂@SiO₂-SH-Au showed a relatively well-defined XRD pattern, with peaks corresponding to Au and Fe₃O₄, and a broad diffraction band around 23° of 20 associated with amorphous silica phase. In contrast the XRD pattern of the composite material shows peaks at $2\theta = \sim 38.1^{\circ}$, ~44.2°, ~64.8°, and ~78° which correspond to Au (111), (200), (220), and (311) reflections indicating the formation of Au(0) nanoparticles with a face centered cubic (fcc) structure [34]. For Fe_3O_4 , all the diffraction peaks of (220), (311), (400), (422), (333), and (440) were in good agreement with the face centered cubic (fcc) structure of magnetite [35].

The elemental composition of the $Fe_3O_4@SiO_2@SiO_2$ -SH-Au samples was determined by EDX analysis. The result shown in Fig. 3 reveals that the as-prepared products contain Fe, Si, Au, S, C, and O.

Table 3 Solvent-free and water-medium alkyne hydrations over the Fe3O4@SiO2@SiO2-SH-Au catalyst



Entry	R ¹	\mathbb{R}^2	H ₂ O (ml)	Temperature (°C)	Time (h)	Yield %
1	Ph	Н	4.0	80	2	92
2	4-MePh	Н	4.0	80	2	90
3	4-ClPh	Н	4.0	80	2	92
4	4-MeOPh	Н	4.0	80	2	93
5	4-BrPh	Н	4.0	80	2	90
6	2-BrPh	Н	4.0	80	2	86
7	2-ClPh	Н	4.0	80	2	87
8	Ph	CH ₃	4.0	80	2	84
9	$n-C_6H_{13}$	Н	4.0	80	2	91
10	Ph	Н	0	70	2	95
11	4-MePh	Н	0	70	2	94
12	4-MeOPh	Н	0	70	2	95
13	Ph	CH ₃	0	70	2	88
14	$n-C_6H_{13}$	Н	0	70	2	95
15	2-BrPh	Н	0	70	2	93
16	2-ClPh	Н	0	70	2	91

^a See reaction conditions in "Experimental" Section



Fig. 5 Catalyst recovery at the end of the reaction

Figure 4 shows the FT-IR spectra of the catalyst. The characteristic bands of Fe–O at 570.0 and 465.5 cm⁻¹ were attributed to the Fe–O stretch bands. The data were consistent with the values reported for Fe₃O₄ in the literature [36]. Two strong bands at about 1095.5 and 948.7 cm⁻¹ were assigned to ν_{as} (Si–O–Si) and ν_{s} (Si–O–Si), respectively [37]. Two strong bands at 3428.8 and 1626.9 cm⁻¹ were assigned to water stretches and bends [38]. MPMS displayed characteristic –CH₂ stretching bands at 2983 cm⁻¹ (Fig. 4a, b). The weak peak appearing at about 2502 cm⁻¹ is due to the vibration of the HS group (Fig. 4a). In comparison with the HS-, the Au-HS displayed no peak due to



Scheme 2 Plausible reaction mechanism of alkyne hydration reaction

the coordination of the HS-ligand with gold nanoparticles (Fig. 4b).

Reaction condition optimization

Various reaction conditions were investigated including routine solvents for this reaction [6–8] and temperature variation. To optimize the reaction conditions, the same reaction was carried out in each solvent at room temperature and at 80 °C. As can be seen the reactions using H₂O at 80 °C and solvent-free at 70° C gave the best results (Table 1, Entries 11 and 12). Water has been chosen because of being green and cost effective. Solvent-free conditions would be suitable for liquid alkynes, but would have dramatically reduced yields with solid alkynes. Use of water as solvent is suitable for all alkynes.

In continuation, to show the unique catalytic behavior of $Fe_3O_4@SiO_2@SiO_2-SH-Au$ and to show the role of gold in this catalyst, this reaction was performed in the presence of

Table 4 Comparison of phenylacetylene formation by Fe₃O₄@SiO₂@SiO₂-SH-Au Catalyst with literature reported methods

Entry	Catalyst	Reaction conditions	Time (h)/yield (%) [lit.]
1	AuCl ₃	MeOH, tetrachloroauric acid, reflux	24/60 [3]
2	(triphenylphosphine)gold(I)-p-tolylsulfonate	BF ₃ ·Et ₂ O, THF, 45 °C	4/98.8 [4]
3	(Ph ₃ P)AuCH ₃	H ₂ O, MeOH, CF ₃ SO ₃ H, 60 °C	1/98 [5]
4	$gold(I) - NHC$ complexes H_2O	KPF ₆ ; H ₂ O-MeOH, 80 °C	12/100 [8]
5	[(IPr)AuCl]AgSbF ₆	$1,4-Dioxane/H_2O(2:1)$	18/85 [7]
6	$t-NBu_4[Au(C_6F_5)_2Cl_2]$	H_2SO_4 , MeOH/ H_2O , reflux	1.5/100 [2]
7	Au-HS/SO ₃ H-PMO(Et)	H ₂ O, 80 ℃	1.5/99 [6]
8	(α-Fe ₂ O ₃)-MCM-41-SH-Au	H ₂ O, 80 ℃	2/98 [29]
9	Fe ₃ O ₄ @SiO ₂ @SiO ₂ -SH-Au	H ₂ O, 80 °C	2/92 ^a
8 9	$(\alpha$ -Fe ₂ O ₃)-MCM-41-SH-Au Fe ₃ O ₄ @SiO ₂ @SiO ₂ -SH-Au	H ₂ O, 80 °C H ₂ O, 80 °C	2/98 [29] 2/92 ^a

^a Present study

catalytic amounts of Fe_3O_4 , $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2@SiO_2=SH$ and in the absence of any catalyst (Table 2). It was observed that only $Fe_3O_4@SiO_2@SiO_2=SH$ -Au was able to catalyze this reaction (Table 2, entry 5). In addition, this table shows that the catalytic activity of Fe_3O_4 is very little (Table 2, entry 2–4), and only it's magnetic property facilitates the efficient recovery of the catalyst from the reaction mixture. So we can say Fe_3O_4 only helps in separation of the catalyst nanoparticles.

Evaluation of the catalytic activity of $Fe_3O_4@SiO_2@SiO_2$. SiO₂-SH-Au trough the alkyne hydration reaction

After optimization of the reaction condition and with the above initial satisfactory catalytic results, the core–shell structured nanoparticles $Fe_3O_4@SiO_2@SiO_2-SH-Au$ were investigated for the alkyne hydration reaction in H₂O and under solvent-free conditions. To show the versatility of this reaction, a variety of alkynes, possessing aliphatic, internal and external alkynes were employed for the formation of corresponding ketones (Table 3).

This catalyst showed excellent catalytic activity in the hydration of different alkyne substrates with excellent vields (84–95 %). It can be noted that the presence of substituents on the *p*-position of benzene had very little influence on the catalytic efficiencies, showing 90-93 % yields for the corresponding products (Table 3, entries 2-5). Substituents on the o-position of benzene with more steric hindrance, showed 86 and 87 % yields for the corresponding products (Table 3, entries 6 and 7). The process was also applicable to aliphatic alkyne in excellent yield (91 %, entry 9). This table shows that steric hindrance played a certain role in the reaction efficiency. Excellent yields were also obtained in solvent-free alkyne hydration even at relatively lower temperature (70 °C). On one hand, this may be attributed to high polar character of nanostructures with high surface areas which could efficiently adsorb moisture (as the water source). On the other hand, the water molecules that coordinated with the acidic sites of the silica surface were sufficiently nucleophilic to react with the electrophilic species involved in the reaction [6].

The reusability and stability of the heterogeneous system is a critical requirement for its applications. The recyclability of the $Fe_3O_4@SiO_2@SiO_2-SH-Au$ catalyst was investigated in the alkyne hydration reaction using phenylacetylene as substrate. After each cycle of the reaction, the catalyst was recovered by simple magnetic separation, washed and then reused in the next reaction run. As shown in Fig. 5a, the results demonstrate that the catalyst can be reused for four runs without obvious loss of catalytic activity and selectivity. As shown in Fig. 5b, the composite $Fe_3O_4@SiO_2@SiO_2-SH-Au$ readily aggregated in a few seconds upon an external magnetic field, leaving

the solution transparent and redispersed quickly again via shaking or ultrasonication when the magnetic field was removed, demonstrating desired magnetic control of $Fe_3O_4@SiO_2@SiO_2-SH-Au$, which was particularly appropriate for its practical applications in catalysis.

To show the merit of this study, we compared the obtained results with the results reported. For this purpose, the reaction of phenylacetylene hydration was chosen as the model reaction and comparison was carried out on the basis of reaction conditions, reaction time and percentage yields obtained (Table 4). It is worth mentioning that this method is a greener than catalysts entry 1–6 and the recovery of catalyst is easier than entry 7. In addition, the preparation of this core/shell catalyst is simpler than entry 8 as a mesoporous catalyst.

The stereochemistry of water addition (syn vs. anti) with metal catalysts is not yet known; some researchers have discussed the necessity of an additional coordination site for water in the context of a proposed inner sphere (syn) addition mechanism [39, 40]. Therefore, we suggest for the gold (0) catalyzed addition of water to alkynes, a syn-addition mode involving activation of both water and the alkyne by Au which has been proposed (Scheme 2).

Conclusion

In summary, due to the high price of gold and the importance of the environment, we have developed a novel Core/ shell $Fe_3O_4@SiO_2@SiO_2-SH-Au$ nanocatalyst in a facile procedure, without using reducing reagents by in situ reduction of Au³⁺. The magnetically recyclable catalyst could be recovered in a facile manner from the reaction mixture with an external magnet, and used in subsequent runs without observation of significant decrease in activity even after 4 runs. These ligand-modified Au magnetic nanoparticles are highly efficient and stable heterogeneous catalysts for alkyne hydration reaction. In a green approach these reactions proceeded efficiently in aqueous media and solvent-free conditions without using any organic solvents and acids.

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