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Nano Ag-doped magnetic- Fe_3O_4 @mesoporous TiO₂ core-shell hollow spheres: synthesis and enhanced catalytic activity in A^3 and KA^2 coupling reactions

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Abstract Nano Ag-doped Fe₃O₄@mesoporous TiO₂ coreshell hollow spheres (h-Fe₃O₄@m-TiO₂/Ag) were efficiently prepared. They were fully characterized by FT-IR, FE-SEM, EDX, ICP, TGA, XRD, and BET methods. In addition, their magnetic properties were determined by means of the VSM method. Also, the ρ_{shell} of the prepared hollow Fe₃O₄ micro-particles was calculated, being found just slightly lighter than that of solid sphere-like Fe₃O₄. The catalytic activity of this novel catalyst system was successfully examined as a novel catalyst system in A³ coupling reactions (aldehyde + amine + acetylene). This highly active magnetic catalyst was easily separated using an external magnet and re-used in five consecutive runs in the model reaction without appreciable loss of its catalytic activity.

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Graphical abstract



Keywords Nanocatalyst · Hollow sphere · Silver catalyst · Three-component reaction · Heterogeneous catalyst

Introduction

In recent years, many attempts have been made on the synthesis of low or non-toxic nanomaterials, especially those of magnetic metals, alloys, and metal oxides. Among them, iron oxide-based magnetic materials have received much attention due to their low cost, high resistance to corrosion, and being relatively environmentally benign [1, 2]. In three recent decades, they have fruitfully been used in catalysis of a plethora of organic transformation, owing to their high specific surface areas as well as excellent stability, flexibility, simple recovery, and effective reusability [3–6]. Therefore, numerous methods for the preparation of iron oxide-based magnetic nanoparticles have been achieved and reported [7-14]. In this line, the preparation of various magnetite Fe-nanostructures with different morphologies including monodisperse nanoparticles, microspheres, nano-rods, nano-belts, nano-wires nano-tubes, and nano-flowers has been achieved [15-18]. Hollow structure nano-particles have particularly been

found enhancing several organic transformations [19–25]. Fe-nanoparticles have been found acting as highly effective hallow magnetic spheres [8, 26-30]. In particular, hollow magnetic iron oxide nanoparticles have stirred up the interest of organic synthetic chemists being examined as catalyst due to their low material density as well as strong magnetic response as well as simple recovery by an external magnet [31]. Recently, several strategies have been developed to prepare hollow magnetite spheres such as the nanoscale Kirkendall effect, Ostwald ripening, molten salt corrosion, reverse micelle transport, and layerby-layer assembly [32–36]. These approaches were mainly achieved, based on the use of well-established template method, such as hard template, soft template, and sacrificial template [37-39]. Thus, the template method has been the method of choice for the successful preparation of a wide array of hollow structures.

Hollow-structured porous spheres, featured with hollow cores and porous shells, exhibit low density, well-defined interior voids, high specific surface area [40–44].

Titanium dioxide has recently been employed as an essential shell, due to its unique surface properties, high photo catalytic activity, low cost, and non-toxicity [45]. In this regard, different nano TiO₂ structures have been designed, i.e., core-shell, mesoporous, and hollow sphere structures [46-48]. As could be expected, the inclusion of a magnetic Fe_3O_4 core into TiO_2 nano spheres gives them the advantage of simple recovery and thus recyclability as well avoiding their undesirable aggregation [49]. In the past few years, an increasing number of multicomponent reactions (MCRs) have been developed as a powerful tool for the synthesis of complex molecules through an assembly of several simple starting materials in a one-pot fashion. Nowadays, the advantages of MCRs are well established [50]. Among the different MCRs, the A^3 coupling reaction (aldehyde, alkyne, and amine) is a method of choice for the synthesis of high-value propargylamine derivatives [51]. Propargylamines are frequently used as synthetically flexible key intermediates [52–54] in the synthesis of natural products and biologically active compounds as well as nitrogen-containing biologically active molecules [55]. Propargylamines are conventionally synthesized by a catalyzed A³ coupling reaction using transition metals such as copper [56–58], iridium [59], nickel [60], and iron [61].

Due to its cost, silver has scarcely been used as catalyst in organic transformations. As a matter of fact its merits, such as high catalytic activity towards coupling reactions, cycloadditions, sigmatropic rearrangements, cycloisomerizations, and nitrene transfer reactions have largely been overlooked [62]. It might be mentioned that silver is absolutely non-toxic and easy to handle. Nowadays, the development of environmentally friendly catalyzed MCRs enjoying the easy recovery and effective recyclability of catalysts as well as improving atom economy is overgrowing, overshadowing and compensating the use of catalysts [58, 63–83]. Herein, we wish to report the preparation of novel, recoverable, and recyclable Ag nanoparticles supported on magnetic hollow-Fe₃O₄ cores with a mesoporous TiO₂ shell to efficiently catalyze A³ coupling reaction under mild reactions conditions to yield propargylamine derivatives in excellent yields.

Results and discussion

Synthesis of magnetic-Fe₃O₄@m-TiO₂/Ag hollow sphere

The route leading to magnetic-Fe₃O₄@m-TiO₂/Ag hollow spheres is illustrated in Scheme 1. The magnetized catalyst was prepared from relatively inexpensive commercially available materials and fully characterized by FT-IR, FE-SEM, TEM, XRD, TGA, BET, N₂ adsorbtion-desorbtion, and VSM techniques. A pathway to obtain the hollow microspheres was suggested as follows: the ethylene glycol used plays a dual role as a solvent and a reducer during the solvothermal process. It can also provide -OH groups which coordinate with Fe^{3+} . The Fe_3O_4 nuclei are generated by changing of pH (via the addition of NaAc) at elevated temperature; they quickly grow up to become small nanoparticles and aggregate to form the microspheres, owing to their high surface energy [84]. According to Scheme 1, a compact TiO₂ layer was directly immobilized on the generated hollow-Fe₃O₄ microspheres by a sol-gel method.

Characterization of magnetic Fe₃O₄@m-TiO₂/Ag hollow spheres

FT-IR Spectra

The FT-IR spectra of the h-Fe₃O₄, h-Fe₃O₄@m-TiO₂, and h-Fe₃O₄@m-TiO₂ (h = hollow) doped with Ag nanoparticles in the range of 4000–500 cm⁻¹ were recorded and presented in Fig. 1. In all these spectra, two main absorption bands at around 450 and 560 cm⁻¹ are observed. These bands can be attributed to the intrinsic stretching vibrations of Fe–O and Ti–O in the sample. Other characteristic peaks at 1398 and 1633 cm⁻¹ are associated with the presence of stretching vibrations of Ti–O and Fe–O–Ti bonds [87].

X-Ray Diffraction Spectra

The X-ray diffraction (XRD) patterns of the as-synthesized microspheres are shown in Fig. 2a, b, showing the XRD patterns of the nano-Fe₃O₄ and hollow Fe₃O₄ microspheres. The strong diffraction peaks at $2\theta = 30.1^{\circ}$, 35.5°,





Fig. 1 The FT-IR spectra of a h-Fe₃O₄, b h-Fe₃O₄@m-TiO₂, and c h-Fe₃O₄@m-TiO₂/Ag

43.2°, 52.7°, 57.1°, and 62.7° can be indexed to the (220), (311), (400), (422), (511), and (440) reflections. They are typical in the structure of Fe₃O₄ (JCPDS no. 19-629). Compared with the nano-Fe₃O₄ particles, the peaks of h-Fe₃O₄ are narrower, indicating the formation of micro size particles. The h-Fe₃O₄@m-TiO₂ microspheres showed additional peaks, which can be assigned to anatase TiO₂ (JCPDS card No. 01-075-2545). The average crystal size of TiO₂ was measured being about 28 nm. In the XRD pattern of h-Fe₃O₄@m-TiO₂/Ag microspheres, Fig. 2d shows the characteristic peaks of h-Fe₃O₄ (labeled as F) and m-TiO₂ (labeled as M), indicating that the h-Fe₃O₄@m-TiO₂ structure remained unchanged. The characteristic peaks at 2θ of 37.9°, 44.1°, 64.3°, and 77.2° (labeled as A) could be attributed to XRD spectra of the face-centered-cubic structure of Ag (JCPDS card No. 04-0783) that confirmed the successful preparation of crystalline h-Fe₃O₄@m-TiO₂/Ag microspheres. The broadening of Ag diffraction peaks confirmed that the size of Ag particles is in the nano-meter range.

Thermo-gravimetric analysis (TGA)

The temperature-dependent changes can be verified by the determination of mass loss employing thermo-gravimetric analysis (TGA). The TGA of h-Fe₃O₄, h-Fe₃O₄@m-TiO₂, and h-Fe₃O₄@m-TiO₂/Ag microspheres are shown in Fig. 3. The initial loss region of samples (up to 150 °C) is due to the evaporation of the absorbed water and solvent. By increasing the temperature, a drastic weight loss for h-Fe₃O₄, h-Fe₃O₄@m-TiO₂ was observed, owing to the decomposition of adsorbed organic groups on their surfaces. The removal of organic components starts at around 200 °C and is virtually completed at 450 °C. Beyond this temperature, the mass loss stays constant. The h-Fe₃₋ O₄@m-TiO₂/Ag nano-composite shows lower weight lose (nearly 8%), because it doped with Ag nano-particles and has low porosity for absorbing solvent. Thus, it can be concluded that as-prepared magnetic composite is sufficiently stable under the reaction conditions including the reaction temperature.

Vibrating sample magnetometer (VSM)

The magnetic hysteresis loops of samples were conventionally studied by vibrating sample magnetometer (VSM). The magnetization curve for nano magnetic Fe_3O_4 hollow sphere, h-Fe_3O_4@m-TiO_2, and h-Fe_3O_4@m-TiO_2/Ag is





Fig. 3 TGA analysis of a

h-Fe₃O₄, b h-Fe₃O₄@m-TiO₂, and c h-Fe₃O₄@m-TiO₂/Ag



Field emission scanning electron microscopy (FE-SEM) For the full structural characterization of magnetic Fe₃O₄ hollow sphere products, FE-SEM and TEM images were measured at different stages during the course of its preparation. Figure 5a shows the SEM image of the h-Fe₃O₄ microspheres with diameters of 300–400 nm. The surface of the hollow spheres is rough and composed of closely packed Fe₃O₄ nano-particles with the well-distributed size ranging from 30 to 40 nm. The EDX characterization demonstrated that the hollow spheres were pure. Next, the Fe₃O₄ hollow spheres were coated with a layer of TiO₂ through a hydrothermal process. As it can be clearly seen, the TiO₂ layer formed via tiny particles is closely shelled on the surface of Fe₃O₄ hollow sphere. Moreover, the EDX pattern

Fig. 4 The magnetization *curves* of *a* h-Fe₃O₄, *b* h-Fe₃O₄@m-TiO₂, and *c* h-Fe₃O₄@m-TiO₂/Ag



of Fe₃O₄@m-TiO₂ hollow spheres confirmed the existence of Ti with 5.1% (by mass) in it (Fig. 5b). Finally, in order to prepare the h-Fe₃O₄@m-TiO₂/Ag core shell structure, Ag ions adsorbed on the Fe₃O₄@m-TiO₂ hollow spheres through an in situ wet chemistry. The FE-SEM images of the Agdoped Fe₃O₄@m-TiO₂ hollow spheres are shown in Fig. 5c. As it can be seen, the surfaces of the porous TiO₂ shell are covered with medial quantities of small particles. Furthermore, the corresponding EDX pattern confirmed that the prepared composite contains four elements (O, Fe, Ti, and Ag) and reveals the content of ~14.7 and 2.2 wt% for the TiO₂ shell and Ag nano-particles of the h-Fe₃O₄@m-TiO₂/ Ag. Inductively coupled plasma (ICP) results also indicated that the loading capacity of the Ag on the support is 2.1 wt%.

Transmission electron microscopy (TEM)

Other detailed morphological and structural features of the nano magnetic hollow sphere were also examined by TEM. From the TEM image (Fig. 6), the magnetic cores as black spheres have average size of about 300 nm, and the titanium mesoporous shell in gray color has an average thickness of about 40 nm. These results disclosed that the spherical shape of the microspheres was retained even after etching with NH₃–H₂O. The Ag nano-particles could be observed with an average diameter of about 2 nm which are homogeneously immobilized on the surface of Fe₃. O₄@m-TiO₂ hollow spheres. Although a relatively high Ag loading of 2.1% was used, no evidence for Ag NPs agglomeration was observed.

 N_2 adsorption–desorption isotherms and BJH distribution To investigate the effect of Ag doped on the surface area and pore size distribution of the nano magnetic hollow sphere, the pore structures of the h-Fe₃O₄@m-TiO₂ and h-Fe₃O₄@m-TiO₂/Ag were measured by N₂ adsorptiondesorption analyses. As shown in Fig. 7a, the isotherms were identified as type IV according to the IUPAC classification, which is characteristic of mesopore structure. Measured by BET model, the h-Fe₃O₄@m-TiO₂ and h-Fe₃O₄@m-TiO₂/Ag had surface areas of 66.5 and $57.1 \text{ m}^2/\text{g}$ and pore volume of 0.142 and 0.139 m³/g. Moreover, their corresponding pore size distributions were evaluated using the Barrett-Joyner-Halenda (BJH) model and centered at 22 and 19.8 nm for h-Fe₃O₄@m-TiO₂ and h-Fe₃O₄@m-TiO₂/Ag (Fig. 7b). Considering the average pore size and the diameter of Ag NPs, the insertion of Ag into the pores is possible that can help to prevent the loss of Ag nano-particles in practical applications, especially when they are used as catalysts.

Determination of the physical property of the shell in hollow sphere

Determination of the physical property of shell in hollow sphere particles is important since it is a factor which directly affects functionality of the desired catalyst. Thus, we determined the shell density using specific surface area and shell thickness in accordance with our earlier report [88].

Evolution of the Catalytic activity of h-Fe₃O₄@ m-TiO₂/Ag

Having prepared and fully characterized h-Fe₃O₄@ m-TiO₂/Ag, its activity as a heterogeneous magnetically catalyst was evaluated in the A^3 and KA^2 coupling reactions. To find the optimized reaction conditions, the three-component reaction of benzaldehyde, piperidine, and



Fig. 5 The FEG-SEM-EDS analysis of a h-Fe₃O₄, b h-Fe₃O₄@m-TiO₂, and c h-Fe₃O₄@m-TiO₂/Ag

phenylacetylene as the model reaction was selected which gave the corresponding propargylamine 4a (Scheme 2). In this regard, various reaction parameters such as solvent, temperature, and the amount of catalyst were tested. In addition, with particular reference to the importance of green chemistry, the model reaction was also conducted under solvent-free conditions (Table 1).

As it can be seen in Table 1, in the absence of catalyst, a low yield of the products was obtained (entry 1). To illustrate the essential requirement of Ag for this reaction, the model reaction was conducted with h-Fe₃O₄ and h-Fe₃O₄@mTiO₂. The results showed that the reaction produced a lower yield in the specified time (entries 2 and 3). Delightfully, the best result was achieved when 1.0 equiv of benzaldehyde, 1.2 equiv of piperidine, 1.5 equiv of phenylacetylene were reacted in the presence of 0.01 g catalyst (2.1 mol % Ag) at 100 °C in solvent-free conditions (Table 1, entry 6).

Securing the optimal reaction conditions, the substrate scope of the reaction for the synthesis of propargylamine derivatives was investigated using differently substituted benzaldehydes, aliphatic aldehydes, and aryl acetylenes bearing electron-donating substituents as well as electron-withdrawing groups. The results are depicted in Table 2 (4a-4k). All the used arylaldehydes with either electron-donating or electron-withdrawing substituent afforded the corresponding products in good yields and short reaction



Fig. 7 a N_2 adsorption-desorption isotherms h-Fe₃O₄@m-TiO₂ and h-Fe₃O₄@m-TiO₂/Ag. b BJH pore size distribution curves for h-Fe₃O₄@m-TiO₂ and h-Fe₃O₄@m-TiO₂/Ag.



times. Moreover, as shown in Table 2, the synthesis of propargylamine derivatives also worked well with aliphatic aldehydes (Table 2, **4m–4p**). In addition, this strategy successfully worked in the coupling of various amines such as piperidine, morpholine and pyrrolidine.

Notably, the reaction failed to occur using aromatic amines. In addition, in order to envisage the scope of the catalytic activity of h-Fe₃O₄@m-TiO₂/Ag magnetic composite, the optimized reaction conditions were tested for the three-component coupling of ketones, secondary amines and arylacetylenes (KA² coupling, Table 3).

Generally, ketoimines are considered to be less reactive towards nucleophilic additions than aldimines due to steric hindrance and electronic effects. Therefore, the in situ generation of ketoimines including the direct alkyne addition reaction still remains a significant challenge [89]. We optimized the reaction conditions for KA² coupling reaction of cyclohexanone, piperidine, and phenylacetylene. A

Entry	Catalyst (g)	Condition	Time/min	Yield/% ^a
1	None	Solvent free/100 °C	60	Trace
2	h-Fe ₃ O ₄	Solvent free/100 °C	60	Trace
3	h-Fe ₃ O ₄ @m-TiO ₂	Solvent free/100 °C	60	Trace
4	h-Fe ₃ O ₄ @m-TiO ₂ /Ag (0.01)	Solvent free/25 °C	300	Trace
5	h-Fe ₃ O ₄ @m-TiO ₂ /Ag (0.01)	Solvent free/60 °C	60	45
6	h-Fe ₃ O ₄ @m-TiO ₂ /Ag(0.01)	Solvent free/100 °C	60	97
7	h-Fe ₃ O ₄ @m-TiO ₂ /Ag (0.01)	Solvent free/120 °C	60	96
8	h-Fe ₃ O ₄ @m-TiO ₂ /Ag (0.015)	Solvent free/100 °C	50	84
9	h-Fe ₃ O ₄ @m-TiO ₂ /Ag (0.020)	Solvent free/100 °C	60	96
10 ^b	h-Fe ₃ O ₄ @m-TiO ₂ /Ag (0.01)	Toluene/100 °C	60	73
11 ^b	h-Fe ₃ O ₄ @m-TiO ₂ /Ag (0.01)	Water/100 °C	90	Trace
12 ^b	h-Fe ₃ O ₄ @m-TiO ₂ /Ag (0.01)	Ethanol/Reflux	90	43
13 ^b	h-Fe ₃ O ₄ @m-TiO ₂ /Ag (0.01)	DMSO/100 °C	90	50

Table 1 Optimization of the reaction of three-component reaction catalyzed by h-Fe $_3O_4$ @m-TiO $_2$ /Ag

Reaction conditions: benzaldehyde (1 mmol), piperidine (1.2 mmol), phenylacetylene (1.5 mmol)

^a Isolated yield

^b solvent (3 cm³)

Table 2 Three-component reaction of aldehydes, secondary amines, and terminal alkynes catalyzed by h-Fe₃O₄@m-TiO₂/Ag



Aldehyde	Amine	Alkyne	Product	Time/min	Yield/% ^a
C ₆ H ₅ –CHO	Piperidine	PhC≡CH	4 a	97	60
4-BrC ₆ H ₄ –CHO	Piperidine	$PhC \equiv CH$	4b	60	90
4-MeC ₆ H ₄ –CHO	Piperidine	$PhC \equiv CH$	4 c	65	91
Thiophene-2-carbaldehyde	Piperidine	$PhC \equiv CH$	4d	65	95
Terephthalaldehyde	Piperidine	$PhC \equiv CH$	4e	60	93
1-Naphthaldehyde	Piperidine	$PhC \equiv CH$	4f	50	90
C ₆ H ₅ –CHO	Piperidine	ρ -MeC ₆ H ₄ -C \equiv CH	4 g	75	85
C ₆ H ₅ –CHO	Piperidine	ρ -FC ₆ H ₄ –C \equiv CH	4h	90	91
C ₆ H ₅ –CHO	Morpholine	$PhC \equiv CH$	4i	55	90
C ₆ H ₅ –CHO	Pyrrolidine	$PhC \equiv CH$	4j	65	82
C ₆ H ₅ –CHO	Piperazine	$PhC \equiv CH$	4k	50	90
Cyclohexanecarbaldehyde	Pyrrolidine	$PhC \equiv CH$	41	50	86
Butyraldehyde	Morpholine	$PhC \equiv CH$	4m	45	90
НСНО	Piperidine	ρ -MeC ₆ H ₄ -C \equiv CH	4n	45	83
НСНО	Piperidine	ρ -FC ₆ H ₄ –C \equiv CH	40	50	92
НСНО	Morpholine	$PhC \equiv CH$	4p	40	90

Reaction conditions: aldehydes (1 mmol), amines (1.2 mmol), alkynes (1.5 mmol), h-Fe₃O₄@m-TiO₂/Ag (0.010 g) under solvent-free condition at 100 °C

^a Isolated yield

Table 3 Three-component reaction of aliphatic ketones, secondary amines, and terminal alkynes catalyzed by h-Fe₃O₄@m-TiO₂/Ag



Ketone	Amine	Alkyne	Product	Time/min	Yield/% ^a
Cyclopentanone	Piperidine	PhC=CH	5a	140	87
Cyclopentanone	Morpholine	$PhC \equiv CH$	5b	140	81
Cyclopentanone	Pyrrolidine	$PhC \equiv CH$	5c	150	80
Cyclohexanone	Piperidine	$PhC \equiv CH$	5d	160	85
Cyclohexanone	Piperidine	ρ -MeC ₆ H ₄ -C \equiv CH	5e	190	80
Cyclohexanone	Morpholine	$PhC \equiv CH$	5f	140	90
Cyclohexanone	Morpholine	$\rho\text{-FC}_6\text{H}_4\text{C}\equiv\text{CH}$	5g	160	80

Reaction conditions: ketones (1.5 mmol), amines (1 mmol), alkynes (1.5 mmol), h-Fe₃O₄@m-TiO₂/Ag (0.010 g), solvent-free at 100 °C ^a Isolated yield

1.5:1:1.5 mixture of the aforementioned compounds with 0.01 g magnetic composite was stirred under solvent-free condition at 100 °C. The desired quaternary carbon-containing propargylamine **5d** was obtained in 85% yield. The substrate scope of the KA² coupling reaction was evaluated using cyclic ketones (cyclohexanone and cyclopentanone), secondary amines, and alkynes under optimal conditions. The results are shown in Table 3. It might be noted that aromatic ketones are virtually unreactive which had been realized, previously [90, 91]. Table 4 shows clearly the merits of this protocol for the synthesis of propargylamine **4a** in comparison with other catalysts.

The novel catalyst system has some advantages such as giving the selected three-component reaction in a short reaction time, providing excellent yields, and offering simple and almost quantitative recovery of the magnetized catalyst in pure form to be re-used in several further runs without appreciable loss in its catalytic activity (see below).

Recycling and leaching of the catalyst

The recovery and recyclability of the catalyst in catalytic reactions are important and vital issues. Most importantly, these aspects and qualities make the method economically feasible, thus, industrially profitable as well as environmentally sustainable. To study these important features and constancy of the activity of this novel used catalyst system, the catalyzed three-component reaction involving benzaldehyde, piperidine, and phenylacetylene was selected as

Table 4 Comparison of catalytic activity of h-Fe₃O₄@m-TiO₂/Ag with reported silver catalyst in the catalyzed synthesis of propargylamine 4a

Entry	Catalyst	Condition (solvent/temperature)	Time/h	Yield/ % ^b	References
1	PS-NHC-Ag(I) ^a	Solvent free/50 °C	5	92	[92]
2	ZnO-IL/Ag ^b	H ₂ O/reflux	3	92	[93]
3	Ag-CIN-1 ^c	H ₂ O/40 °C	12	98	[94]
4	$Ag-G^d$	CH ₂ Cl ₂ /60 °C	24	86	[95]
5	h-Fe ₃ O ₄ @m-TiO ₂ /Ag	Solvent free/100 °C	1	97	This work
6	Nano Ag	PEG/100 °C	20	86	[96]
7	Silver(I) complexes	CH ₂ Cl ₂ /60 °C	5	92	[97]
8	AgI	H ₂ O/reflux	14	70	[98]
9	Nano Ag ₂ O	CHCl ₃ /r.t.	10	80	[99]

^a Polystyrene-supported N-heterocyclic carbine-Ag(I)

^b IL: 1-(3-trimethoxysilylpropyl)-3-methylimidazolium

^c Silver grafted porous covalent imine network

^d Silver-graphene

a model reaction and conducted under optimal reaction conditions including the use of optimized quantity of the catalyst. The progress of this reaction was monitored by TLC (using *n*-hexane:ethyl acetate 80:20 as eluent). After completion the reaction, hot ethanol was added to the reaction mixture and the catalyst was easily separated using an external magnet. It was washed with ethanol and dried at 70 °C. There was no appreciable loss in weight of the used catalyst. We examined the model reaction to another important feature. The progress of the reaction was monitored as in initial model reaction. Before the completion of the reaction, the catalyst was excluded using an external magnet and allowed the reaction to proceed. After a while the reaction was stopped. No increase in the yield was observed showing the negligible amount of leaching. This experiment is referred to as hot method and is commonly used to prove that a minimum amount of leaching is involved in a certain catalyst system. Then, the recovered catalyst was reused in the selected model reaction under optimized reaction conditions using fresh substrates.

This reaction was conducted at least five times, performing the similar precautions which were taken for model reaction to check the possible leaching and to make sure the nature of heterogeneous catalysis involved in the reaction. The yields obtained when the recovered catalyst system was re-used were quite reasonable showing no significant loss of activity (Fig. 8). The tiny decrease observed in the yield, due to the gradual loss of the catalyst during washing up process, is well expected.

Conclusion

In conclusion, we designed and prepared Ag-doped Fe_3O_4 hollow spheres with mesoporous TiO_2 shells via a facile solvothermal method. The phase and structure of the catalyst were fully characterized by XRD, FT-IR, FE-SEM, EDX, TGA, and VSM measurements. The existence of porous shells was clearly and convincingly revealed by N_2 adsorbtion–desorbtion, BET, and TEM characterizations.

Run

30

Time/h

45

1st Run

2nd Run

3rd Run

-4th Run 5th Run

60



15

100

75

50

25

0

Yield/%

The magnetic Fe₃O₄@m-TiO₂/Ag hollow sphere catalyst exhibited high catalytic activity in the synthesis of propargylamine by A^3 and KA^2 coupling reactions. Furthermore, and most importantly, this catalyst could be easily separated and re-used up to five times without significant loss of activity and selectivity. Easy recoverability and reusability of the catalyst without any further purification nominate it as a potential candidate for being tried in different organic transformations and particularly worthwhile being tried in various catalyzed MCRs. We also believe that this facile preparative strategy can be extended, in particular applied to the preparation of super paramagnetic catalyst with hollow sphere structure having qualities expected for both.

Experimental

All chemicals, including $FeCl_3 \cdot 6H_2O$, NH_4Ac , ethylene glycol, ethanol, acetonitrile, NH₃ · H₂O, tetrabutyl orthotitanate (TBOT), and polyvinylpyrrolidone (PVP) in analytical grade, were purchased from Sigma-Aldrich, and used without further purification. The progress of the reaction was monitored by TLC on commercial aluminum-backed plates of silica gel 60 F254 and visualized using ultraviolet light. Melting points were determined in open capillaries using an Electrothermal 9100. ¹H NMR and ¹³C NMR spectra were recorded using Bruker spectrometer at 400, 300, and 100, 75 MHz. Magnetic h-Fe₃O₄@m-TiO₂/Ag characterized by FT-IR spectra which were obtained from KBr pellets in the range of 400-4000 cm⁻¹ using a Shimadzu 8400 s spectrometer. X-ray diffraction (XRD) was detected by Philips using Cu-Ka radiation of wavelength 1.54 Å; scanning electron microscopy, FE-SEM-EDX, analysis was performed using Tescanvega II XMU Digital Scanning Microscope. Samples were coated with gold at 10 mA for 2 min prior to analysis. Transmission Electron Microscope (TEM) images were taken with a CM30300Kv field emission transmission electron microscope. The magnetic properties of the catalyst were confirmed using a vibrating sample magnetometer (VSM, Lakeshore7407) at room temperature. BET surface areas were acquired on a Beckman Coulter SA3100 Surface Area Analyser. The elemental analysis of the catalyst was carried out on simultaneous ICP-Optical Emission spectrometer (Spectro Genesis-Metek, Germany). Thermogravimetric analysis (TGA) was obtained from a LINSEIS modele STS PT 16,000 thermal analyzer under air atmosphere at a heating rate of 5 °C min⁻¹.

Synthesis of nano magnetic Fe₃O₄ hollow sphere

Hollow magnetic particles were synthesized through a solvothermal reaction [84]. Briefly, PVP (1.0 g) was

dissolved in 40 cm³ of ethylene glycol (EG), followed by the addition of 1.35 g FeCl₃·6H₂O (5 mmol) and 2.46 g CH₃COONa (30 mmol). The resulting mixture was stirred vigorously for 15 min, and was then transferred into a Teflon-lined stainless steel autoclave (100 cm³). Next, the autoclave was heated at 200 °C for 10 h. After this time, the autoclave was cooled to room temperature. Upon cooling, a black residue was formed which was washed several times with ethanol and deionized water and dried at 80 °C in a vacuum oven overnight.

Synthesis of h-Fe₃O₄@TiO₂ core shell

The Fe₃O₄@TiO₂ hollow spheres were synthesized by direct coating of a layer of TiO₂ on the Fe₃O₄ through solgel method, hydrolyzing tetrabutyl orthotitanate (TBOT) in a mixture of EtOH and CH₃CN [85]. Thus, 50 mg of the as-synthesized hollow Fe₃O₄ was dispersed in a mixed solvent containing 90 cm³ of ethanol and 30 cm³ of acetonitrile with the aid of ultrasound. Then, 0.5 cm³ of NH₃– H₂O was added into the mixture. After that, 1 cm³ of TBOT was added to the above suspension under stirring for 1.5 h. The above core shell was collected by an external magnet and washed three times with ethanol.

Preparation of $h-Fe_3O_4$ @mesopouros TiO₂ core shells via solvothermal treatment of $h-Fe_3O_4$ @TiO₂ core shell

The mesoporous TiO₂ shells were prepared by a solvothermal treatment of the already obtained Fe₃O₄@-TiO₂ hollow spheres in a mixed solvent of ethanol and deionized water, with NH₃·H₂O as a porosity modifier [85]. Briefly, 50 mg of the as-prepared Fe₃O₄@TiO₂ hollow spheres was dispersed in 40 cm³ of ethanol and 20 cm³ of deionized water, and later a certain amount of NH₃·H₂O (3 cm³) was added to the above suspension. The mixture was transferred to a Teflon-lined stainless steel autoclave which was then sealed (100 cm³ capacity). The sealed autoclave was kept at 160 °C for 20 h. Then, the autoclave was cooled to room temperature, and the desired product (h-Fe₃O₄@mesopouros TiO₂ core shell) was collected from the reaction medium with the help of an external magnet and washed with ethanol and water several times.

Loading Ag nanoparticles to obtain h-Fe₃O₄@m-TiO₂/Ag

The doping of Ag nanoparticles onto $h-Fe_3O_4@m-TiO_2$ was performed as follows [86]; initially, 0.06 g of $h-Fe_3$. $O_4@m-TiO_2$ was dispersed into 15 cm³ of 5 × 10⁻³ M Ag(NH₃)₂NO₃ solution under stirring at room temperature for 30 min. After that, the [Ag(NH₃)₂]⁺ ions were adsorbed onto the surfaces of h-Fe₃O₄@m-TiO₂ via the electrostatic attraction. This dispersion was added into 15 cm³ of ethanol contained PVP (0.1 g) and heated at 70 °C for 4 h. The precipitated solid was collected by the aid of an external magnet, washed several times with ethanol and deionized water, and dried at 50 °C for 12 h.

Synthesis of 1-(1,3-diphenylprop-2-ynyl)piperidine (4a): general procedure

To a mixture of an appropriate benzaldehyde (1.0 mmol), piperidine (1.2 mmol), and a suitable phenylacetylene (1.5 mmol), 100 mg magnetic h-Fe₃O₄@m-TiO₂/Ag was added. The mixture was heated at 100 °C for 1 h (the progress of reaction was monitored by TLC). After completion of the reaction, the mixture was cooled to room temperature and diluted with 10 cm³ hot ethanol. Then, the catalyst was separated by the aid of an external magnet from the cooled mixture, washed with acetone, dried in oven, and re-used for a consecutive run under the similar reaction conditions. After separation of catalyst, the mixture was purified by column chromatography on silica gel using a short column to afford the desired product in excellent yield (97%).

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- 1. Lu AH, Salabas EL, Schuth F (2007) Angew Chem Int Ed 46:1222
- Laurent S, Forge D, Port M, Roch A, Robic C, Elst LV, Muller RN (2008) Chem Rev 108:2064
- Arai T, Sato T, Kanoh H, Kaneko K, Oguma K, Yanagisawa A (2008) Chem Eur J 14:882
- 4. Yoon H, Ko S, Jang J (2007) Chem Commun:1468
- 5. Yi DK, Lee SS, Ying JY (2006) Chem Mater 18:2459
- Shokouhimehr M, Piao YZ, Kim JY, Jang YJ, Hyeon TW (2007) Angew Chem Int Ed 46:7039
- 7. Yan AG, Liu YJ, Liu Y, Li XH, Lei Z, Liu PT (2012) Mater Lett 68:402
- Deng H, Li XL, Peng Q, Wang X, Chen JP, Li YD (2005) Angew Chem Int Ed 44:2782
- Harris LA, Goff JD, Carmichael AY, Riffle JS, Harburn JJ, Pierre TGS, Saunders M (2003) Chem Mater 15:1367
- Pol VG, Motiei M, Gedanken A, Calderon-Moreno J, Mastai Y (2003) Chem Mater 15:1378

- Lyon JL, Fleming DA, Stone MB, Schiffer P, Williams ME (2004) Nano Lett 4:719
- 12. Dietz H, Douglas SM, Shih WM (2009) Science 325:725
- Douglas SM, Dietz H, Liedl T, Högberg B, Graf F, Shih WM (2009) Nature 459:414
- Sajjadi SH, Goharshadi EK (2017) J Environ Chem Eng 5:1096
- Cao SW, Zhu YJ, Ma MY, Li L, Zhang L (2008) J Phys Chem C 112:1851
- 16. Cao SW, Zhu YJ (2008) J Phys Chem C 112:12149
- 17. Gang Q, Wei L, Zhining B (2011) Chin J Chem 29:131
- Liu Y, Yu C, Dai W, Gao X, Qian H, Hu Y, Hu X (2013) J Alloys Compd 551:440
- Sun J, Dong Z, Sun X, Li P, Zhang F, Hu W, Yang H, Wang H, Li R (2013) J Mol Catal A Chem 367:46
- Shi ZQ, Jiao LX, Sun J, Chen ZB, Chen YZ, Zhu XH, Zhou JH, Zhou XC, Li XZ, Li R (2014) RSC Adv 4:47
- Gao J, Liu J, Bai S, Wang P, Zhong H, Yangand Q, Li C (2009) J Mater Chem 19:8580
- 22. Zhou J, Dong Z, Wang P, Shi Z, Zhou X, Li R (2014) J Mol Catal A Chem 382:15
- 23. Kang H, Lee HJ, Park JC, Song H, Park KH (2010) Top Catal 53:523
- 24. Liu H, Wang P, Yang H, Niu J, Ma J (2015) New J Chem 39:4343
- 25. Liu M, Zhu X, Wu L, Zhou X, Li J, Ma J (2015) RSC Adv 5:38264
- 26. Liang X, Wang X, Zhuang J, Chen YT, Wang DS, Li YD (2006) Adv Funct Mater 16:1805
- Shi Y, Shi MM, Qiao YQ, Tu JP, Chen HZ (2012) Nanotechnology 23:395601
- 28. Wang J, Chen QW, Zeng C, Hou BY (2004) Adv Mater 16:137
- 29. Geng BY, Zhan FM, Jiang H, Guo YJ, Xing ZJ (2008) Chem Commun:5773
- Zhong LS, Hu JS, Liang HP, Cao AM, Song WG, Wan LJ (2006) Adv Mater 18:2426
- Gawande MB, Monga Y, Zboril R, Sharma RK (2015) Coord Chem Rev 288:118
- 32. Cheng W, Tang KB, Qi YX, Sheng J, Liu ZP (2010) J Mater Chem 20:1799
- 33. Smigelskas AD, Kirkendall EO (1947) Trans AIME 171:130
- 34. Jia B, Gao L (2008) J Phys Chem C 112:666
- 35. Hu P, Yu L, Zuo A, Guo C, Yuan F (2009) J Phys Chem C 113:900
- Jaffari GH, Ceylan A, Bui HP, Beebe TP Jr, Ozcan S, Shah SI (2012) J Phys: Condens Matter 24:336004
- 37. Kim SW, Kim M, Lee WY, Hyeon T (2002) J Am Chem Soc 124:7642
- 38. Tan B, Rankin SE (2005) Langmuir 21:8180
- 39. Ding Y, Hu Y, Jiang X, Zhang L, Yang C (2004) Angew Chem Int Ed 43:6369
- 40. Deng CH, Ge XQ, Hu HM, Yao L, Han CL, Zhao DF (2014) CrystEngComm 16:2738
- Chen JC, Xue ZT, Feng SS, Tu B, Zhao DY (2014) J Colloid Interface Sci 429:62
- 42. Zhao Y, Jiang L (2009) Adv Mater 21:3621
- Liu C, Li JS, Qi JW, Wang J, Luo R, Shen JY, Sun XY, Han WQ, Wang LJ (2014) ACS Appl Mater Interfaces 6:13167
- 44. Tan LF, Liu TL, Li LL, Liu HY, Wu XL, Gao FP, He XL, Meng XW, Chen D, Tang FQ (2013) RSC Adv 3:5649
- 45. Ni M, Leung MKH, Leung DYC, Sumathy K (2007) Renew Sustain Energy Rev 11:401
- 46. Lee S, Lee J, Hwang SH, Yun J, Jang J (2015) ACS Nano 9:4939
- Elhamifar D, Nasr-Esfahani D, Karimi B, Moshkelgosha R, Shabani A (2014) ChemCatChem 6:2593
- 48. Chaudhuri RG, Paria S (2012) Chem Rev 112:2373

- 49. Xuan S, Jiang W, Gong X, Hu Y, Chen Z (2009) J Phys Chem C 113:553
- 50. Syamala M (2009) Org Prep Proc Int 41:1
- Peshkov VA, Pereshivko OP, Van der Eycken EV (2012) Chem Soc Rev 41:3790
- 52. Harada T, Fujiwara T, Iwazaki K, Oku LA (2000) Org Lett 2:1855
- 53. Ding CH, Chen DD, Luo ZB, Dai LX, Hou XL (2006) Synlett 1:272
- 54. Dyatkin AB, Rivero RA (1998) Tetrahedron Lett 39:3647
- 55. Wei CM, Mague JT, Li CJ (2004) Proc Natl Acad Sci 101:5749 56. Zeng T, Yang L, Hudson R, Song G, Moores AR, Li CJ (2011)
- Org Lett 13:442
- Sharghi H, Khalifeh R, Moeini F, Beyzavi MH, Salimi Beni A, Doroodmand MM (2011) J Iran Chem Soc 8:89
- 58. Nemati F, Elhampour A, Farrokhi H, Natanzi MB (2015) Catal Commun 66:15
- 59. Sakaguchi S, Kubo T, Ishii Y (2001) Angew Chem Int Ed 113:2602
- 60. Namitharan K, Pitchumani K (2010) Eur J Org Chem 2010:411
- 61. Zeng T, Chen WW, Cirtiu CM, Moores A, Songand G, Li CJ (2010) Green Chem 12:570
- 62. Harmata M (2010) Silver in organic chemistry. Wiley, Hoboken
- Nemati F, Elhampour A, Zulfaghari S (2015) Phosphorus. Sulfur Silicon Relat Elem 190:1692
- 64. Nemati F, Heravi M, Saeedirad R (2012) Chin J Catal 33:1825
- 65. Nemati F, Elhampour A (2016) Res Chem Intermed 42:7611
- 66. Elhampour A, Nemati F (2016) J Chin Chem Soc 63:653
- Osanlou F, Nemati F, Sabaqian S (2016) Res Chem Intermed. doi:10.1007/s11164-016-2752-z
- Nemati F, Nikkhah SH, Elhampour A (2015) Chin Chem Lett 26:1397
- 69. Nemati F, Heravi M, Elhampour A (2015) RSC Adv 5:45775
- Heravi M, Hashemi E, Beheshtiha YS, Ahmadi S, Hosseinnejad T (2014) J Mol Catal A Chem 394:74
- 71. Heravi M, Hashemi E, Nazari N (2014) Mol Divers 18:441
- 72. Heravi M, Hashemi E, Azimian F (2014) Tetrahedron 70:7
- 73. Heravi M, Fazeli A (2010) Heterocycles 81:1979
- 74. Sharafi T, Heravi M, Ghassemzadeh M, Neumuller B (2005) Z Anorg Allg Chem 631:2297
- Ayati A, Ahmadpour A, Bamoharram FF, Heravi M, Sillanpaa M (2012) Gold Bull 45:145
- 76. Mirsafaei R, Heravi M, Hosseinnejad T, Ahmadi S (2016) Appl Organomet Chem 30:823
- 77. Mirsafaei R, Heravi M, Ahmadi S, Moslemin MH, Hosseinnejad T (2015) J Mol Catal A Chem 402:100
- Heravi M, Hashemi E, Beheshtiha YS, Kamjou K, Toolabi M, Hosseintash N (2014) J Mol Catal A Chem 392:173
- 79. Hashemi E, Beheshtiha YS, Ahmadi S (2014) Transit Metal Chem 39:593
- Ghassemzadeh M, Fallahnedjad L, Heravi M, Neumuller B (2008) Polyhedron 27:1655
- Heravi M, Behbahani FK, Oskooie HA, Shoar RH (2005) Tetraheron Lett 46:2543
- Heravi M, Beheshtiha SY, Dehghani M, Hosseintash N (2015) J Iran Chem Soc 12:2075
- Heravi M, Bakhtiari K, Taheri S, Oskooie HA (2005) Green Chem 7:867
- Xiong QQ, Tu JP, Lu Y, Chen J, Yu YX, Qiao YQ, Wang XL, Gu CD (2012) J Phys Chem C 116:6495
- 85. Li C, Younesi R, Cai Y, Zhu Y, Ma M, Zhu J (2014) Appl Catal B Environ 156:314
- Chi Y, Yuan Q, Li Y, Zhao L, Li N, Li X, Yand W (2013) J Hazard Mater 262:404
- Xin T, Ma M, Zhang H, Gu J, Wang S, Liu M, Zhang Q (2014) Appl Surf Sci 288:51

- Elhampour A, Malmir M, Kowsari E, Boorboorajdari F, Nemati F (2016) RSC Adv 6:96623
- Aleem Ali MA, El-Remaily A, Hamad HA (2015) J Mol Catal A: Chem 404:148
- 90. Cheng M, Zhang Q, Hu XY, Li BG, Ji JX, Chan ASC (2011) Adv Synth Catal 353:1274
- 91. Kantam ML, Yadav J, Laha S, Jha S (2009) Syn Lett:1791
- 92. Li P, Wang L, Zhang Y, Wang M (2008) Tetrahedron Lett 49:6650
- 93. Movahedi F, Masrouri H, Kassaee MZ (2014) J Mol Catal A: Chem 395:52
- 94. Salam N, Kundu SK, Molla RA, Mondal P, Bhaumik A, Islam SM (2014) RSC Adv 4:47593
- 95. Salam S, Sinha A, Singha Roy A, Mondal P, Jana NR, Islam SM (2014) RSC Adv 4:10001
- 96. Yan W, Wang R, Xu Z, Xu J, Lin L, Shen Z, Zhou Y (2006) J Mol Catal A Chem 255:81
- 97. Prakash O, Joshi H, Kumar U, Sharma AK, Singh AK (2015) Dalton Trans 44:1962
- 98. Wei C, Li Z, Li CJ (2003) Org Lett 5:4473
- Zhou X, Lu Y, Zhai LL, Zhao Y, Liu Q, Sun WY (2031) RSC Adv 3:1732