



DABCO-Triazole Modified Magnetic Nanoparticles Supported Gold as an Efficient Heterogeneous Catalyst for A³ Coupling Reaction

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Nowadays, a great sustainable and economic development to introduce efficient and easy magnetically recoverable and reusable gold catalysts for A³-coupling reaction in water, it is still pursued. In this work, a new heterogeneous catalyst, comprising gold supported on DABCO-Triazole modified magnetic nanoparticles (Fe₃O₄@DT-Au), is developed for A³-coupling reaction. This catalyst is characterized using different techniques such as TEM, SEM, SEM-elemental mapping, XRD, XPS, and TGA. Using a 0.05 mol% of this catalyst, the three-component reaction of amines, aldehydes and alkynes is efficiently performed at 40 °C in neat water. This catalyst is easily recovered and recycled for six times with a small decrease in the activity.

Introduction

The main drawback of homogeneous catalysts is the separation of the active catalytic species from the reaction mixture. The reusability and product contamination with particles of catalysts, especially in the case of toxic and expensive transition metal catalysts such as palladium and gold, are side effects of this disadvantage.¹ As alternative, different organic and inorganic materials such as polymers, magnetic compounds, silica-based compounds and clay minerals have been applied for the preparation of heterogeneous catalysts.¹

In spite of great achievement in this field, in most of the cases traditional methods such as filtration or centrifugation are time consuming and are not efficient for complete recovery and reusing of solid catalysts. Using magnetic nanoparticles (MNPs) based catalysts having excellent properties such as high surfaces area and distribution of active sites on outer surface, are easily and effectively separated by a magnetic field. It is worth mentioning that the surfaces of magnetic nanoparticles

can be modified with various organic ligands generating suitable sites for adsorption of catalytically active metal nanoparticles.² The construction of propargylamine functional moiety is one of the most important reactions, since the obtained products contain important structural motifs, which are attractive for the design of multifunctional drugs.³ For example, different anti-Parkinson and anti-Alzheimer drugs such as ASS234, Rasagiline, Deprenil and Ladostigil have propargylamine moieties in their structures.⁴ Propargylamines, are traditionally prepared via stoichiometric nucleophilic reaction of lithium acetylides or Grignard reagents to imines under inert atmosphere.⁵ However, in recent years, an efficient and simple method for the construction of propargylamines is based on a three component reaction of aldehyde, amine and alkynes using C-H bond activation of alkynes mediated by transition metals (A³-coupling reaction).⁶

Different transition metals such as Copper,⁷ Zinc,⁸ Silver,⁹ Iron,¹⁰ Nickel,¹¹ Cobalt,¹² Manganese,¹³ Iridium,¹⁴ Indium,¹⁵ Silver-Cobalt,¹⁶ and Copper-Zinc-Cobalt,¹⁷ have been reported as catalyst for A³-coupling reaction under homogeneous or heterogeneous reaction conditions. One of the most important developments in the field of A³-coupling reaction occurred when this reaction was efficiently performed by a homogeneous gold catalyst.¹⁸ In recent years many homogeneous or heterogeneous catalysts were used in A³-coupling reactions.^{19, 20} However, considering high price of the gold and problem of recovering and reusing of homogeneous gold catalysts, we envisaged that it would be a great challenge to design an efficient magnetically recyclable gold catalysts in A³-coupling reaction.^{7a, 20h, 21} So, we synthesize a new magnetic gold catalyst ligated to a DABCO-ionic liquid system derived

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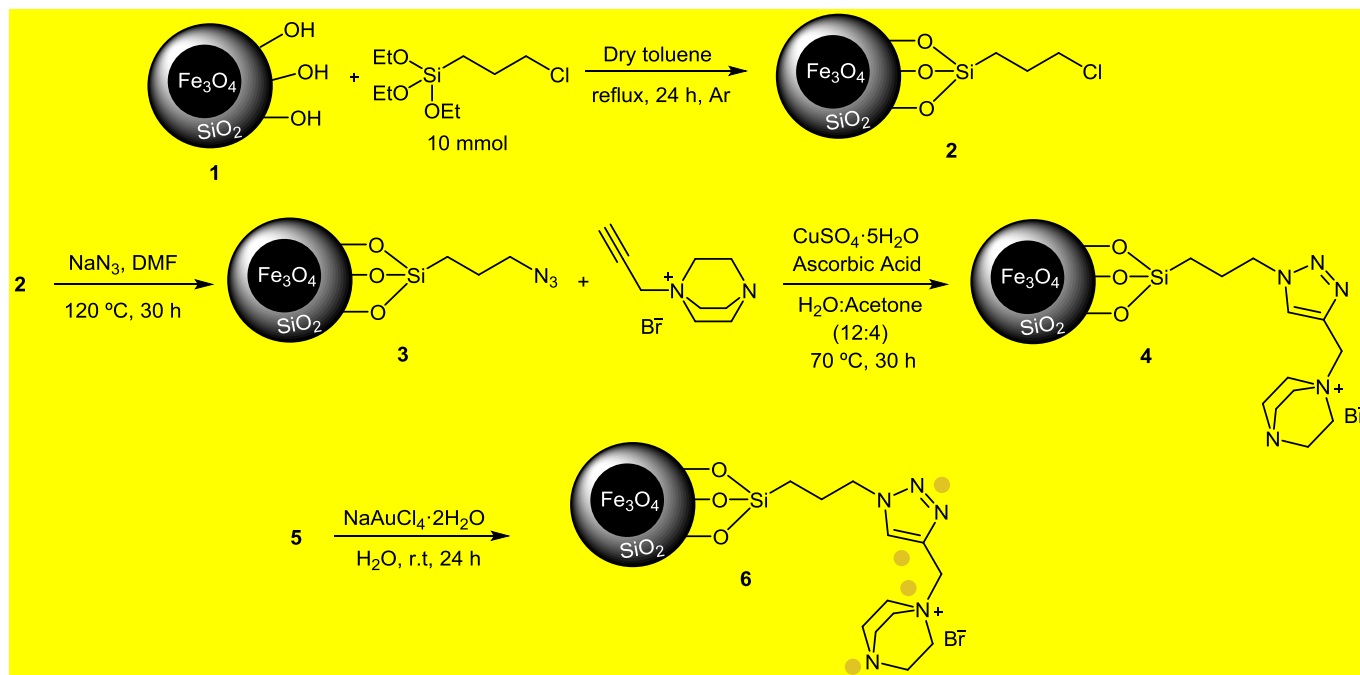
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from triazole and further applied to the synthesis of propargylamines under mild reaction conditions in water.

Results and discussion

For the preparation of the catalyst, initially magnetite NPs were synthesized by a co-precipitation method. Afterwards, the obtained Fe_3O_4 -NPs were treated with tetraethylortosilicate to produce core-shell $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ NPs 1 (IS THERE ANY METHODOLOGY TO CITE?). Next, $\text{Fe}_3\text{O}_4@/\text{SiO}_2@/\text{N}_3$ 3 was obtained from the reaction of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ with 3-

chloropropyltriethoxysilane and sodium azide (Scheme 1.) The resulting $\text{Fe}_3\text{O}_4@/\text{SiO}_2@/\text{N}_3$ 3 was submitted to the 1,3-dipolar cycloaddition with the propargylic ionic liquid, which was prepared from the reaction DABCO and propargyl bromide. Finally, DABCO-triazole (DT) modified magnetic NPs 4 were treated with $\text{NaAuCl}_4\cdot 2\text{H}_2\text{O}$ to produce the new magnetic supported gold catalyst 6 ($\text{Fe}_3\text{O}_4@/\text{DT-Au}$) Using atomic absorption spectroscopy (AAS), the amount of Au in $\text{Fe}_3\text{O}_4@/\text{DT-Au}$ (6) was found to be $0.02 \text{ mmol}\cdot\text{g}^{-1}$.



Scheme 1. Preparation of the $\text{Fe}_3\text{O}_4@/\text{DT-Au}$

Thermogravimetric analysis (TGA) of $\text{Fe}_3\text{O}_4@/\text{DT-Au}$ (6) between 25 and 600 °C showed two main weight losses. The first one was detected between 25-100 and was associated to the loss of physically absorbed water and solvents. The second significant weight loss corresponded to the elimination of successful grafting organic groups (Figure 1).

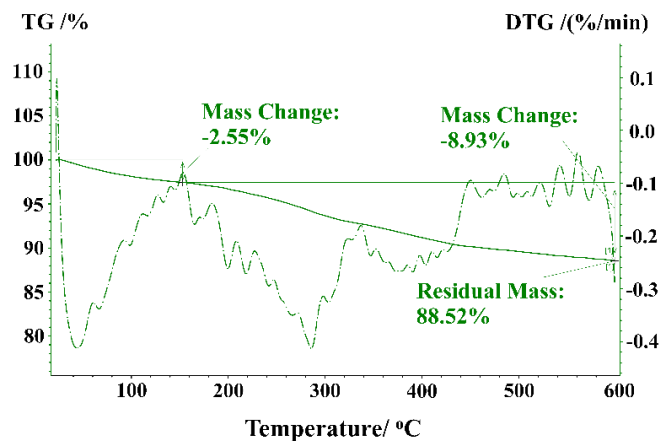


Figure 1. TGA curve of $\text{Fe}_3\text{O}_4@/\text{DT-Au}$ (6)

Transmission electron microscopy (TEM) images of $\text{Fe}_3\text{O}_4@/\text{DT-Au}$ nanoparticles are located under highly uniform conditions (Figure 2).

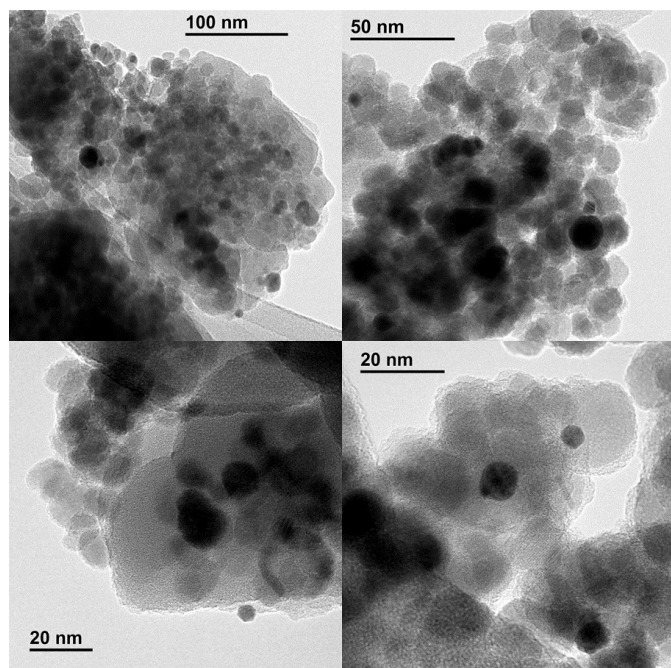


Figure 2. Transmission electron microscopy (TEM) images of $\text{Fe}_3\text{O}_4@DT\text{-Au}$ (6) at different magnifications

Scanning electron microscopy (SEM) map and overlay map images of $\text{Fe}_3\text{O}_4@DT\text{-Au}$ (6) showed highly uniform distribution of different elements such as Fe, Si, and Au (Figure 3).

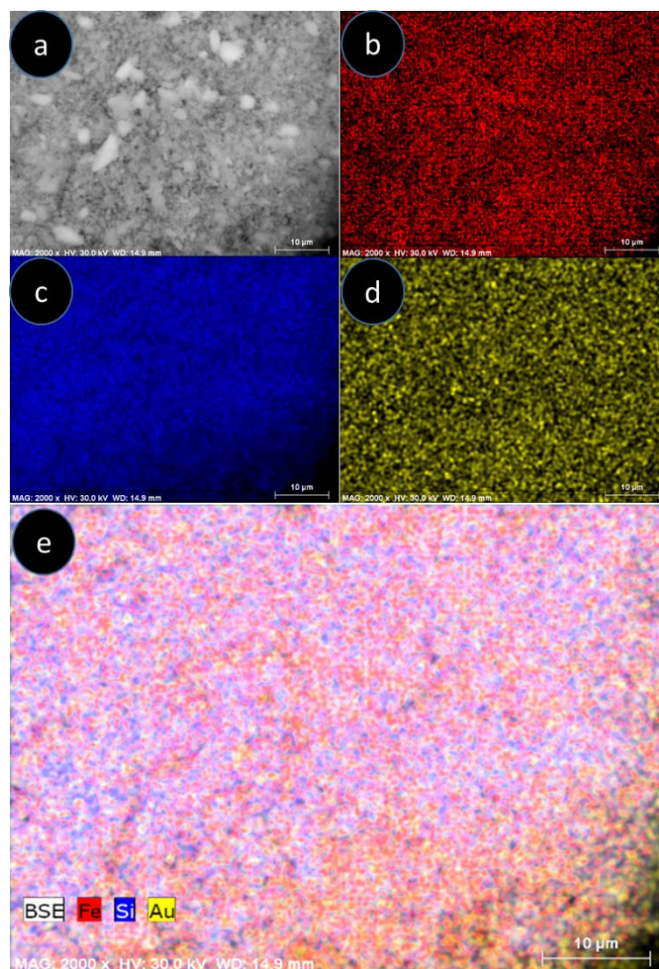


Figure 3. (a) Scanning electron microscopy (SEM) and map images of $\text{Fe}_3\text{O}_4@DT\text{-Au}$ (6), (b) Fe, (c) Si, and (d) Au, (e) overlay image

Structure of the $\text{Fe}_3\text{O}_4@DT\text{-Au}$ (6) was further studied by X-ray diffraction (XRD) and results showed Bragg's reflections at $2\theta = 30.18^\circ, 35.5^\circ, 43.4^\circ, 53.5^\circ, 57.2^\circ$ and 62.8° related to (210), (311), (400), (422), (511) and (440) planes of Fe_3O_4 NPs, respectively (Figure 4) ²².

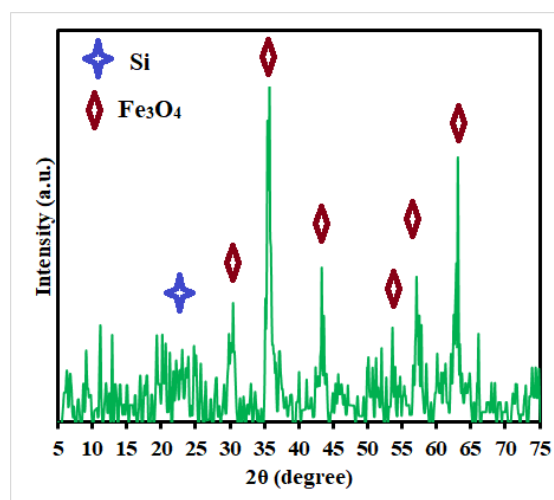


Figure 4. XRD pattern of $\text{Fe}_3\text{O}_4@DT\text{-Au}$ (6)

We also characterized $\text{Fe}_3\text{O}_4\text{@DT-Au}$ (**6**) using XPS in Fe, Si, N and Au regions (Figure 5). XPS spectra in Fe region showed related peaks to Fe(II) at 711.1, 723.9 and peaks related to Fe(III) at 712.6 and 725.5 eV corresponding to the electronic states of Fe 2p_{3/2} and Fe 2p_{1/2}. Due to partial oxidation of Fe_3O_4 to Fe_2O_3 , satellite peaks at 718.9 eV and 727.7 eV, related to Fe^{3+} in the Fe_2O_3 phase, were observed (Figure 5a).^{21e, 22} The XPS spectra in Si region showed binding energy peaks at 103.3 eV and 103.9 eV corresponding to Si 2p and related to O-Si-C or O-Si-O bonds, respectively (Figure 5b).^{21e} Also, two peaks at 400.4 and 402.2 eV in N 1s region referred to the neutral and positively charged quaternary nitrogen of DABCO respectively (Figure 5c).²³ According to the different reports, the binding energies at 83.6–84.5 eV for electronic states 4f_{7/2} and 87.3–87.8 eV for the electronic states 4f_{5/2} were characteristic of the metallic gold.^{19e, 20s, 24} XPS results showed a doublet peak at 84.4 and 88 eV for Au 4f region which were in good agreement with Au(0) species. Reduction of cationic gold may be occurred during the course of irradiation by X-ray (Figure 5d).²⁵

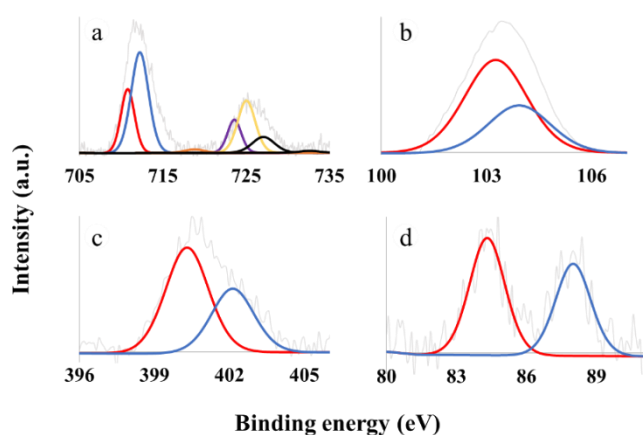
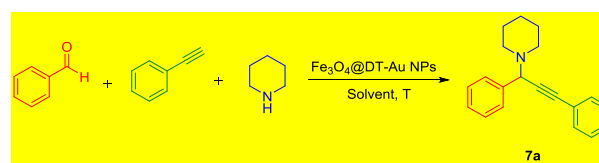


Figure 5. XPS spectra of $\text{Fe}_3\text{O}_4\text{@DT-Au}$ (**6**) in (a) Fe 2p, (b) Si 2p, (c) N 1s and (d) Au 4f regions

After characterization of the $\text{Fe}_3\text{O}_4\text{@DT-Au}$ (**6**), this material was employed as catalyst in the typical A^3 -coupling reaction. In order to find the optimized reaction conditions, reaction of benzaldehyde, piperidine and phenylacetylene was selected as a model reaction. The effect of the reaction solvent, temperature, time and catalyst amount were studied and the results are depicted in Table 1. Using 0.05 mol% catalyst in different solvents such as CHCl_3 , 1,4-dioxane, CH_3CN and toluene at 60 °C furnished low yield of the final compound **7a**, while using water as a solvent quantitative yield of **7a** was obtained (Table 1, entries 1-5). With decreasing reaction temperature to 40 °C reactivity of the catalyst was preserved and quantitative yield was achieved (Table 1, entry 6). However, with decreasing reaction temperature to 30 °C or catalysts amount to 0.03 or time to 12 h, lower yields were obtained (Table 1, entries 7-9). Therefore, using 0.05 mol%, water as solvent at 40 °C during 24 h was selected as an optimum reaction conditions.

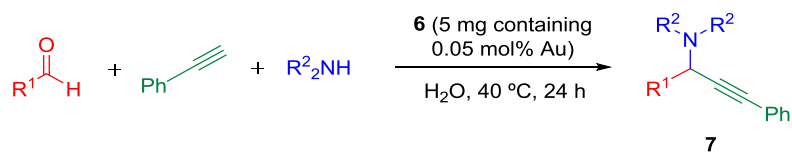
Table 1. Optimization of reaction conditions for the reaction of benzaldehyde, piperidine and phenylacetylene catalyzed by $\text{Fe}_3\text{O}_4\text{@DT-Au}$ (**6**)^[a]



| Entry | Temp. (°C) | Solvent | Time (h) | Catalyst (mol%) | Yield ^[b] (%) |
|-------|------------|------------------------|----------|-----------------|--------------------------|
| 1 | 60 | H_2O | 24 | 0.05 | 99> |
| 2 | 60 | CHCl_3 | 24 | 0.05 | 65 |
| 3 | 60 | 1,4-Dioxane | 24 | 0.05 | 35 |
| 4 | 60 | CH_3CN | 24 | 0.05 | 5 |
| 5 | 60 | Toluene | 24 | 0.05 | 10 |
| 6 | 40 | H_2O | 24 | 0.05 | 99> |
| 7 | 30 | H_2O | 24 | 0.05 | 48 |
| 8 | 40 | H_2O | 24 | 0.03 | 54 |
| 9 | 40 | H_2O | 12 | 0.05 | 75 |

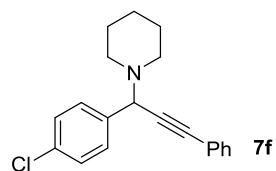
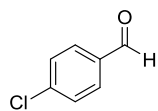
^a Reaction conditions: benzaldehyde (0.4 mmol), piperidine (0.8 mmol), phenylacetylene (0.8 mmol), solvent (1.5 mL) and catalyst (see column).
^b Yields were determined by ¹H NMR.

Having optimized reaction conditions in hand, this catalyst **6** was used for A^3 -coupling reaction of different aldehydes, amines and alkynes (Table 2). Results indicated that benzaldehyde, 1-naphthaldehyde and aromatic aldehydes containing electron-donating (Table 2, entries 1-5) as well as aldehydes having electron-deficient groups reacted efficiently with piperidine and phenylacetylene and high to excellent yields of compounds **7** and high TOFs were achieved (Table 2, entries 6–9). Furthermore, reaction of heterocyclic 3-thiophenecarbaldehyde with piperidine and phenylacetylene proceeded well and corresponding propargylamine **7j** was obtained in 96% yield (Table 2, entry 10). Aromatic and aliphatic aldehydes were also appropriate when reacted with morpholine and phenylacetylene (Table 2, entries 11-16). In addition, reaction of pyrrolidine and dimethylamine were successful using aldehydes and phenylacetylene obtaining products **7q** and **7r** in 92 and 99 yields, respectively (Table 2, entries 17-18).

Table 2. Reactions of different aldehydes, amines and alkynes in the presence of Fe₃O₄@DT-Au (**6**)^[a]

| Entry | R ¹ CHO | R ² NH | Product | Yield (%) | TOF (h ⁻¹) |
|-------|--------------------|-------------------|---------|-----------|------------------------|
| 1 | PhCHO | | | >99 | 82.5 |
| 2 | | | | 95 | 79.1 |
| 3 | | | | 98 | 81.6 |
| 4 | | | | 97 | 80.8 |
| 5 | | | | 95 | 79.1 |

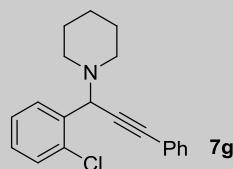
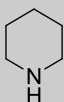
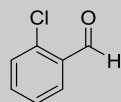
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>99

82.5

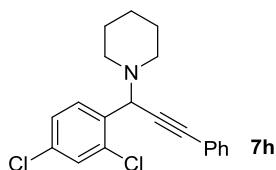
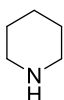
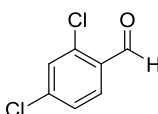
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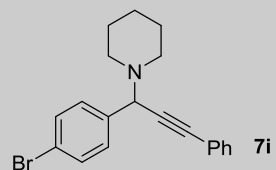
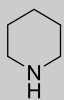
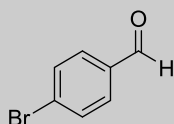
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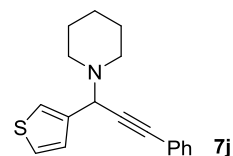
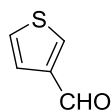
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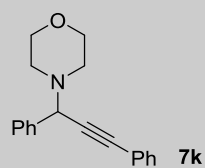
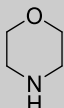
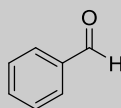
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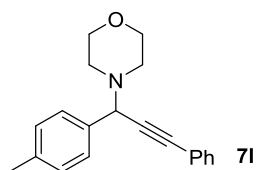
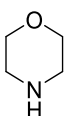
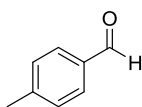
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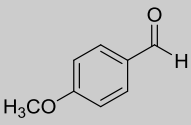
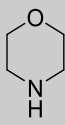
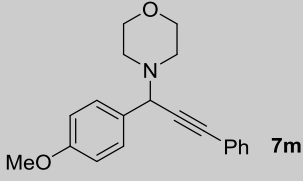
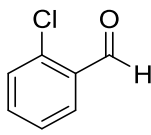
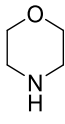
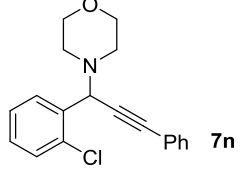
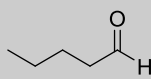
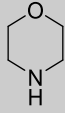
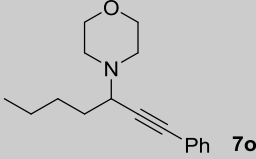
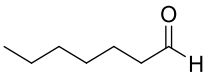
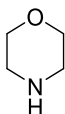
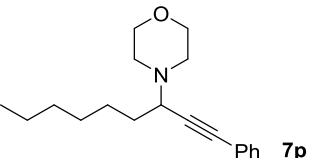
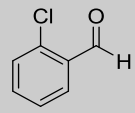
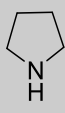
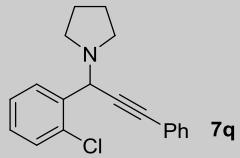
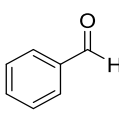
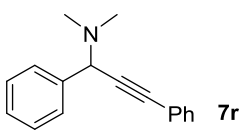
79.1

12



92

76.6

| | | | | | |
|----|---|---|--|-----|------|
| 13 |  |  |  | 95 | 79.1 |
| 14 |  |  |  | 90 | 75.0 |
| 15 |  |  |  | 98 | 81.6 |
| 16 |  |  |  | 95 | 79.1 |
| 17 |  |  |  | 92 | 76.6 |
| 18 |  | $\text{HN}(\text{CH}_3)_2$ |  | >99 | 82.5 |

^a Reaction conditions: aldehyde (0.4 mmol), amine (0.8 mmol), phenylacetylene (0.8 mmol), H₂O (1.5 mL) and catalyst (5 mg containing 0.05 mol% Au).

Next, we investigated the ability of the catalyst to be recovered and reused in the reaction of benzaldehyde, piperidine and phenylacetylene. Results showed that, after completion of the reaction, catalyst could be easily separated by external magnet and, after washing with ethyl acetate, it was used in another batch of the reaction. Recycling process was repeated 6 times with small decrease in activity (Figure 6).

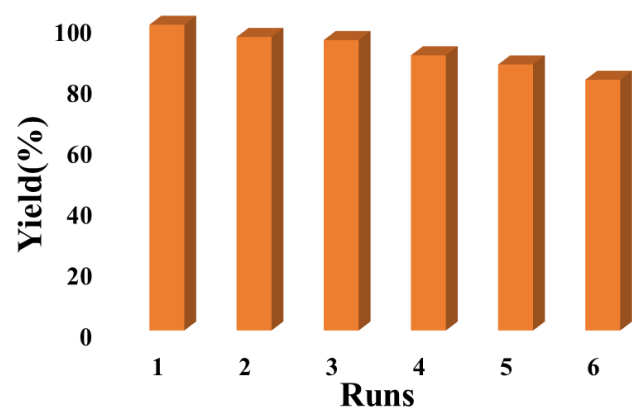


Figure 6. Recycling of catalyst for the reaction of benzaldehyde, piperidine and phenylacetylene.

TEM images of the reused catalyst after 6th run showed similar pattern to fresh catalyst and preserve its original core-shell structure (Figure 7).

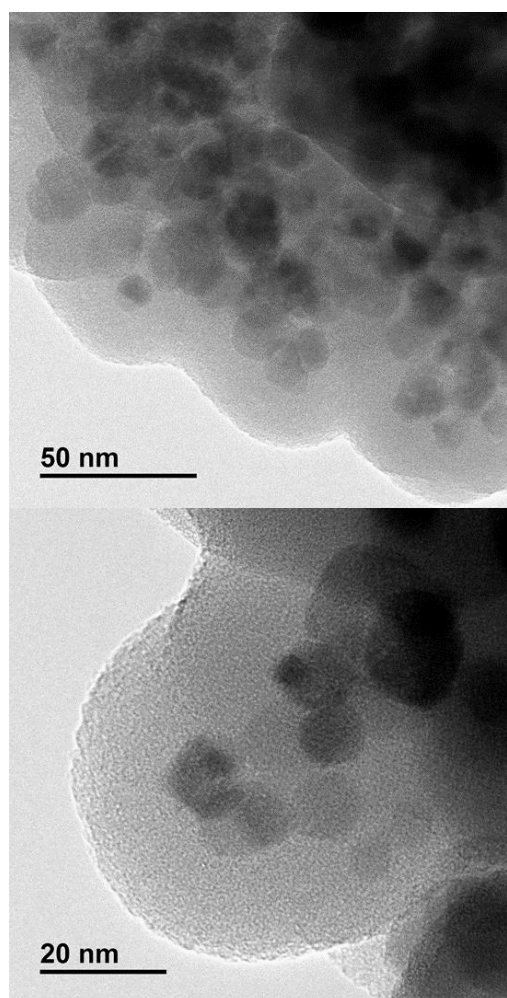
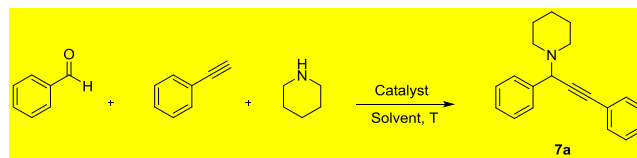


Figure 7. TEM images of catalyst after 6th run

Furthermore, SEM-map and overlay image of the reused catalyst showed uniform dispersion of the Au species (Figure 8).

Table 3. Comparative catalytic activity of Fe₃O₄@DT-Au with some reported Au catalysts in a A³-coupling reaction to obtain **7a**



| Catalyst | Temp. (°C) | Time (h) | Au (mol%) | Yield (%) | TON | Refs. |
|---|------------|----------|-----------|-----------|------|----------------|
| This work | 40 | 24 | 0.05 | >99 | 1980 | |
| Dioxo(IMes)-Au(I)-MCM41 | 70 | 24 | 1 | 85 | 80 | ^{20g} |
| Fe ₃ O ₄ @C-NHCS ₂ H.Au _{NPs} | 60 | 12 | 0.8 | 93 | 116 | ^{19k} |
| Au@SH-CNC | 80 | 24 | 4.4 | 93 | 21 | ²⁶ |
| Au-NCs@Triazine COP | 60 | 6 | 0.8 | 87 | 108 | ²⁷ |
| Au ⁰ -Mont.-II | 100 | 3 | 0.84 | 91 | 108 | ^{20j} |
| Au ₃₈ (SC ₂ H ₄ Ph) ₂₄ | 80 | 5 | 0.01 | 95 | 9500 | ²⁸ |
| Au/CeO ₂ | 100 | 6 | 0.12 | >99 | 825 | ^{20c} |
| Au(III)@Salen Complex | 40 | 24 | 1 | 94 | 94 | ²⁹ |
| Au(0)@PMO-IL | 60 | 12 | 0.2 | 87 | 435 | ^{20h} |
| Au@CS ₂ -AP@Fe ₃ O ₄ | 90 | 24 | 1 | 85 | 85 | ^{19g} |
| NP@Au/NNN-pincer | 85 | 7 | 0.07 | 90 | 1285 | ^{20a} |

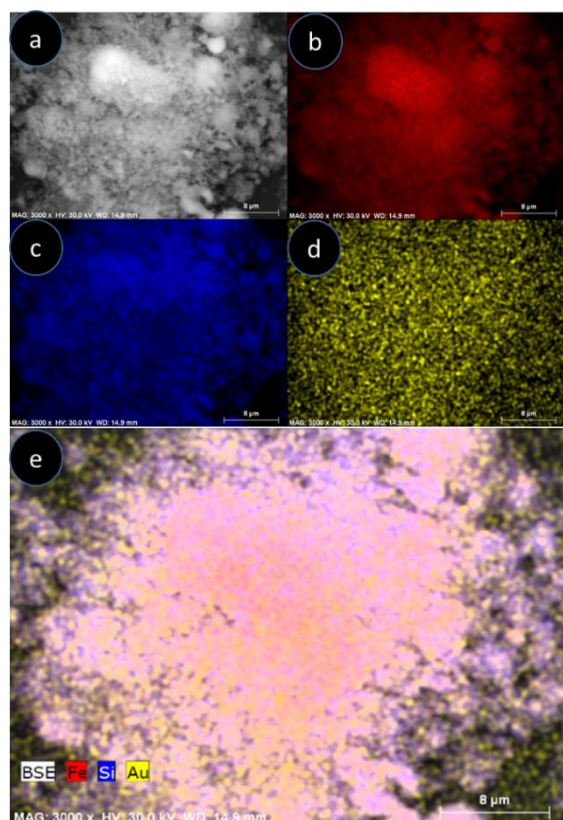


Figure 8. SEM map images of the catalyst 6 after 6th run

Also, stability of the catalyst was further confirmed by XPS in which Fe, Si, N, and Au regions in reused catalyst after 6th runs were in similar arrangement to those of the fresh catalyst (Fig. 9).

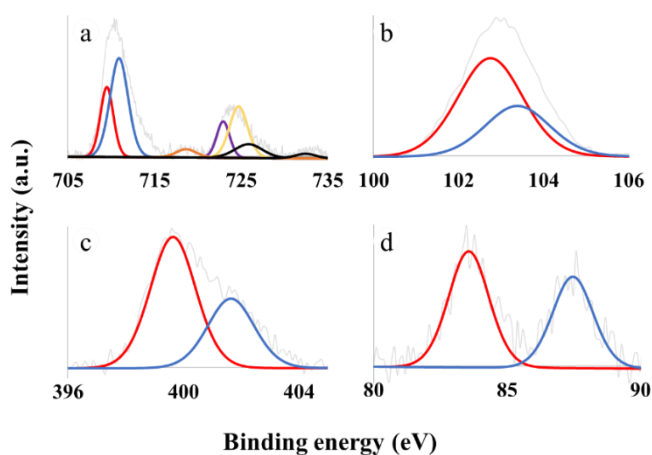


Figure 9. XPS spectra of reused catalyst 6 after 6th run in (a) Fe 2p, (b) Si 2p, (c) N 1s and (d) Au 4f regions.

Finally, we compared the catalytic activity of Fe₃O₄@DT-Au (6) with some other supported gold catalysts in the reaction of 4-benzaldehyde, piperidine and phenylacetylene (Table 3). These results showed similar high catalytic efficiency than the already published ones.

Conclusions

In conclusion, in this work we have prepared Fe₃O₄@DT-Au as highly water dispersible, efficient and magnetically separable heterogeneous catalyst for A3. Using this catalyst, various alkyl halides as well as arylboronic acids reacted efficiently with sodium azide and alkynes. This catalyst was recycled up to eleven times with small decrease in its activity and the fresh and recovered catalysts were adequately characterized by spectroscopic and microscopic techniques. PLEASE REWRITE THE CONCLUSIONS

Experimental

All materials were purchased from Sigma-Aldrich, across and Merck Millipore. Reactions were monitored by thin layer chromatography (TLC) using Merck silica gel 60F254 glass plate with 0.25 mm thickness. ¹H-NMR and ¹³C-NMR spectra were recorded at 250 MHz and 9.62 MHz, respectively on a Bruker Avance HD. Chemical shifts are given on the δ-scale in ppm and residual solvent peaks were used as internal standards. Thermogravimetric analysis was conducted from room temperature to 600 °C in an oxygen flow using a NETZSCH STA 409 PC/PG instrument. The transmission electron microscopy (TEM) and scanning electron microscopy (SEM) mapping images were captured with EOL JEM-2010 and Hitachi S3000 N. X-ray photoelectron spectroscopy (XPS) analyses were performed using a K-Alpha spectrometer. X-ray diffraction (XRD) patterns were recorded using Bruker-Germany D8-Advance instrument.

Synthesis of Fe₃O₄ NPs

Magnetic (Fe₃O₄) nanoparticles were prepared using known co-precipitation method. Briefly, FeCl₃·6H₂O (16 mmol, 4.3 g) and FeCl₂·4H₂O (8 mmol, 1.6 g) were dissolved in deionized water (100 mL) and stirred for 10 min at room temperature under an argon atmosphere. Then, aqueous ammonia (25%, 9 mL) was added slowly and the mixture was stirred at 80 °C for 4 h under an argon atmosphere. The black magnetic precipitates were separated using an external magnet and washed with deionized water (3 × 10 mL) and ethanol (3 × 20 mL) and dried in a vacuum oven at 60 °C for 24 h.

Synthesis of Fe₃O₄@SiO₂

Fe₃O₄ NPs (1.6 g) were sonicated in ethanol (200 mL) for 30 minutes under an argon atmosphere. Then, tetraethyl orthosilicate (13.5 mmol, 3 mL) and aqueous ammonia (12 mL) were added, and the resulting mixture was stirred for 24 h at room temperature. Produced Fe₃O₄@SiO₂ NPs were separated by an external magnet and washed with deionized water (2 × 20 mL) and dichloromethane (2 × 20 mL), and then dried under vacuum at 60 °C.

Synthesis of Fe₃O₄@SiO₂@Cl

Fe₃O₄@SiO₂ NPs (1.5 g) were sonicated in dried toluene (20 ml) for 30 minutes followed by dropwise addition of (3-Chloropropyl)triethoxysilane (10 mmol, 2.4 ml). The mixture was refluxed for 24 h at 110 °C under an argon atmosphere. Then, the resultant solids were collected using an external magnet, washed with deionized water (20 mL) and ethanol (3 × 20 ml), and dried under vacuum at 60 °C.

Synthesis of Fe₃O₄@SiO₂@N₃

Fe₃O₄@SiO₂@Cl (1.4 g) was sonicated in DMF (10 mL) for 10 minutes. Then sodium azide (30 mmol, 2 g) was added and the mixture was refluxed at 120 °C for 30 h. Finally, the obtained solid was subjected to magnetic separation and washed with deionized water (3 × 20 mL) and ethanol (2 × 20 mL), and then dried under vacuum at 60 °C.

Synthesis of [DABCO-Propargyl][Br]

To a flask containing a solution of propargyl bromide (8 mmol, 0.6 mL) in THF (5 mL) at 0 °C, solution of DABCO (30 mmol, 3.3 g in 15 mL THF) was added. Then, reaction temperature was allowed to reach room temperature and mixture was stirred for 24 h. The obtained white solid was crystallized in n-hexane and dried under vacuum at 40 °C. NMRs characterization verified the successful synthesis of [DABCO- Propargyl][Br]. (¹H NMR (250 MHz, Chloroform-d) δ (ppm): 4.92 (s, 2H), 3.88 (t, 6H), 3.25 (t, 6H), 2.99 (s, 1H)). ¹³C NMR (62.9 MHz, Chloroform-d) δ (ppm): 82.96, 70.95, 53.54, 52.01, 45.36.

Synthesis of Fe₃O₄@DT

Fe₃O₄@SiO₂@N₃ (0.8 g) was sonicated in solution of H₂O (15 mL) and acetone (5 mL) for 15 minutes. Then the [DABCO-Propargyl][Br] (3.5 mmol, 0.8 g), CuSO₄.5H₂O (0.06 mmol, 15 mg), and ascorbic acid (0.2 mmol, 45 mg) were added and mixture was stirred at 70 °C for 30 h. Finally, the obtained solids were separated using an external magnet and washed with deionized water (2 × 20 mL) and ethyl acetate (2 × 20 mL), and then dried under vacuum at 60 °C.

Synthesis of Fe₃O₄@DT-Au

Fe₃O₄@DT (500 mg) was sonicated in H₂O (6 ml) for 15 minutes and then the solution of NaAuCl₄.2H₂O (0.012 mmol, 5 mg in 2mL H₂O) was added dropwise and the mixture was stirred for 24 h at room temperature. Afterward, the solid was separated by using an external magnet, washed with water (3 × 10 mL) and ethanol (2 × 10 mL), and dried in an oven at 60°C.

General procedure for the synthesis of propargylamines

To a 5-mL flask, the catalyst (5 mg, 0.05 mol% Au), aldehyde (0.4 mmol), phenylacetylene (0.8 mmol), amine (0.8 mmol) and H₂O (1.5 mL) were added, and mixture was stirred at 40°C for 24 h. The progress of the reactions was monitored by thin-layer

chromatography or ¹H-NMR. After completion of the reaction, the crude products were extracted using ethyl acetate (3 × 5 mL). Further purification was performed by plate or column chromatography using hexane and ethyl acetate as eluents. All products were known and characterized by ¹H-NMR and ¹³C-NMR.

Please indicate they are in the supporting information

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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