

Silica Microparticles Supported Gold and Copper Ferrite Nanoparticles: A Magnetically Recyclable Bimetallic Catalyst for Sonogashira Reaction

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Abstract: Novel silica supported gold and copper ferrite nanoparticles (NPs) have been synthesized, characterized and used as a separable dual catalyst in Sonogashira type reaction. These Au-CuFe₂O₄@Silica NPs show a high efficiency as catalyst in the alkylation not only of aryl iodides but also aryl bromides. By using only 0.5 mol% loading and *t*-BuOK as base in *N,N*-dimethylacetamide as solvent, aryl iodides react at 115 °C in 1 d, whereas for aryl bromides the cross-coupling takes place at 130 °C in 2 d. The catalyst can be successfully recycled using an external magnet for four consecutive runs.

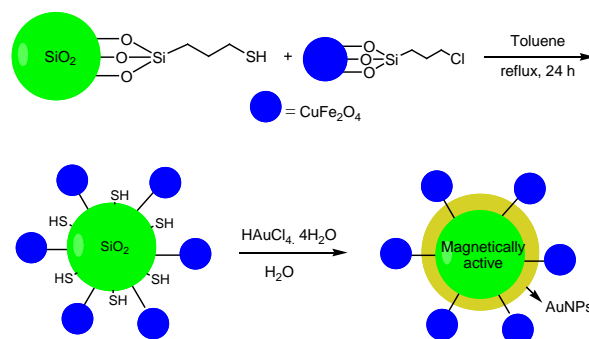
Introduction

Over the past few years, gold catalyzed organic transformations have attracted a great interest because of the well-recognized catalytic property of the gold. Oxidation of alcohols,¹ direct arene functionalization,² hydrogenation,³ oxycyclizations of alkynols and alkyndiols,⁴ cyclization of enynes,⁵ deoxygenation of epoxides to alkenes,⁶ and different coupling reactions such as Sonogashira,⁷ Suzuki⁸ and Ullmann⁹ are examples of gold catalyzed organic reactions. However, among the different gold catalyzed reactions, Sonogashira reaction¹⁰ which is the coupling reaction of vinyl or aryl halides or triflates with terminal alkynes, have been studied under precise conditions. Both heterogeneous and homogeneous gold catalysts have been employed for Sonogashira reaction. Lambert and co-workers showed metallic Au nanoparticles supported on silica, γ -alumina, BaO, lanthana, and ceria have high reactivity in Sonogashira coupling reaction of iodobenzene with phenylacetylene whereas Au^I and Au^{III} species were inert.^{7a} Despite that Echavarren and coworkers claim that trace quantities of palladium impurity is responsible in gold catalyzed Sonogashira reaction,^{7b} Corma and coworkers proved that gold is intrinsically active species to perform the Sonogashira coupling reaction.^{7e-g} Even with high efficiency and selectivity of reported gold catalyzed Sonogashira

coupling reaction, performing reactions at high temperatures (130-160 °C) and limitation of reaction to only few aryl iodides are the most drawbacks of the reported methods.⁷ Despite the many palladium catalyzed Sonogashira reaction in the presence of copper co-catalyst,¹⁰⁻¹¹ to the best of our knowledge there is no report on combination of copper and gold nanoparticles as a catalyst in Sonogashira coupling reaction. Now in this report, we introduce for the first time, immobilization of gold and CuFe₂O₄ nanoparticles on silica particles and its application as a magnetically separable dual catalyst in Sonogashira coupling reaction not only for aryl iodides but also for aryl bromides.

Results and Discussion

The stages of preparation of the catalyst are summarized in Scheme 1. The surface of silica particles was functionalized with thiol group using (3-mercaptopropyl)triethoxysilane (SH@SiO₂). The loading of organic group in SH@SiO₂ was determined using thermogravimetric analysis (TGA) to be 1.2 mmol·g⁻¹ (Figure 1, supporting information). In order to assemble CuFe₂O₄ nanoparticles, the prepared CuFe₂O₄ NPs were functionalized with chloro atom using (3-chloropropyl)triethoxysilane. TGA confirmed presence of organic group on CuFe₂O₄ NPs with loading of 0.4 mmol·g⁻¹ (Figure 2, supporting information). The chloro functionalized CuFe₂O₄ (Cl@CuFe₂O₄) were assemble on thiol functionalized silica particles under refluxing toluene. The resulting CuFe₂O₄@silica was reacted with HAuCl₄·4H₂O to produce final Au-CuFe₂O₄@Silica material. The loading of Au and Cu species in Au-CuFe₂O₄@Silica were determined using ICP to be 0.12 and 0.4 mmol·g⁻¹, respectively.



Scheme 1. Preparation of Au-CuFe₂O₄@Silica.

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Silica microparticles were prepared by the Stober process using tetraethyl orthosilicate.¹² SEM image confirmed formation of microspherical particles in average size of 500 nm (Figure 1).

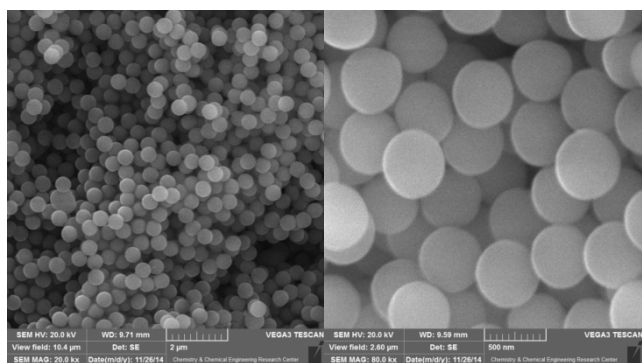


Figure 1. SEM images of prepared micro silica particles.

SEM image of prepared Au-CuFe₂O₄@Silica in different magnification showed attachment of CuFe₂O₄ nanoparticles on thiol functionalized silica particles (Figure 2). Also, EDS analysis obtained from SEM confirmed presence of Si, Fe, Cu and Au species in the structure of prepared material (Figure 3).

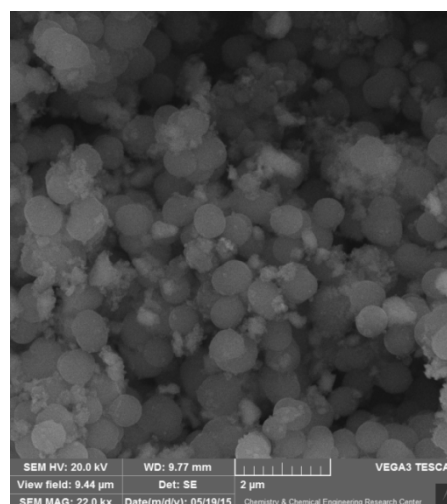
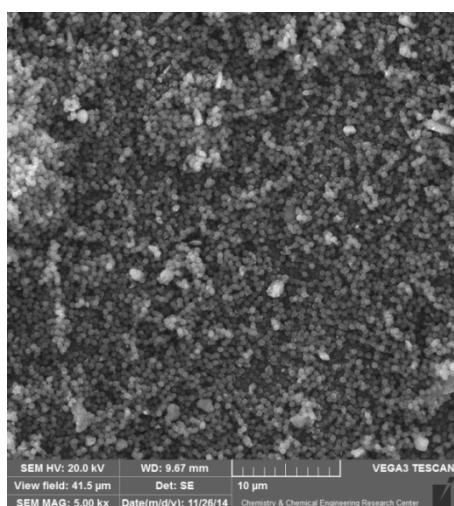


Figure 2. SEM images of the prepared Au-CuFe₂O₄@Silica.

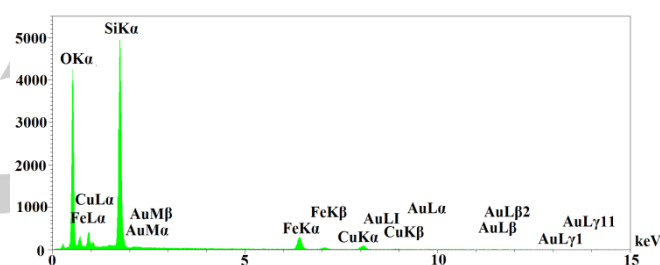
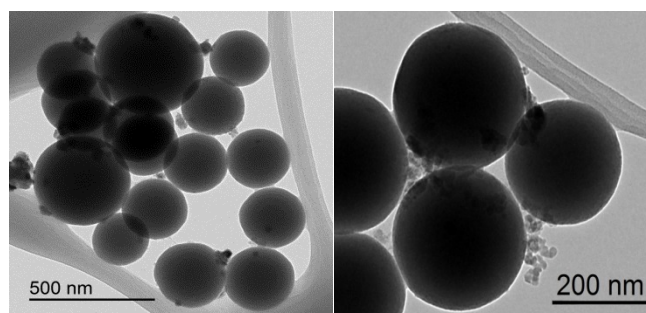


Figure 3. EDS spectrum of the Au-CuFe₂O₄@Silica.

TEM images of Au.CuFe₂O₄@Silica in different magnification showed grafting of small size and mono-dispersed Au nanoparticle (2-3 nm) on silica surface. Also, CuFe₂O₄ with average size of 70 nm are observable in the surface of prepared material (Figure 4).



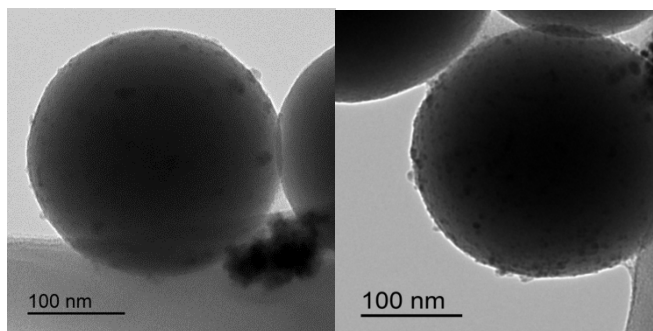


Figure 4. TEM images of the prepared Au-CuFe₂O₄@Silica in different magnification.

X-ray diffraction (XRD) analysis of prepared catalyst showed presence of CuFe₂O₄¹³ nanoparticles by screening Bragg's reflections related in $2\theta = 18.3^\circ, 30.3^\circ, 35.6^\circ, 57.1^\circ, 62.98^\circ$ and Bragg's reflections related to metal gold¹⁴ in $2\theta = 38.2^\circ, 44.5^\circ, 65.6^\circ$ and 78.6° as well as silica particles¹¹ $2\theta = 22^\circ$ (Figure 5).

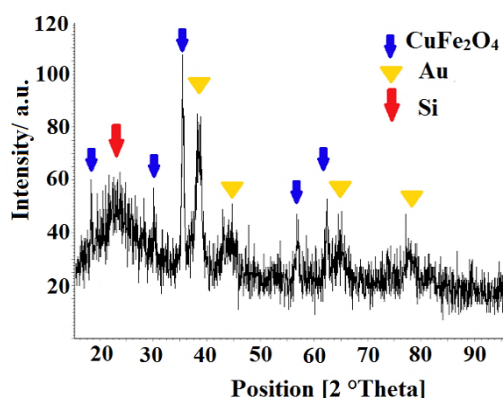


Figure 5. XRD pattern of the Au-CuFe₂O₄@Silica.

In order to get information of oxidation state of Au nanoparticles, X-ray photoelectron spectrum (XPS) of the material was studied (Figure 6). As seen in Fig. 6, the Au 4f_{7/2} and 4f_{5/2} bands with binding energies of 84.85 and 88.48 correspond to the Au(0) is only comprising Au species in the material.¹⁵

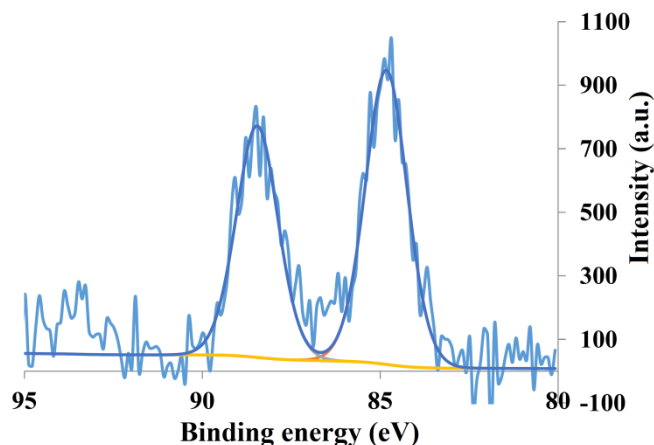


Figure 6. X-ray photoelectron spectroscopy (XPS) of the Au-CuFe₂O₄@Silica.

The structure of Au-CuFe₂O₄@Silica was further studied using EDX-mapp images obtained from SEM. Elemental maps confirm that Au, Cu, Fe, and Si elements are presented in the structure (Figure 3, supporting information). Also, overlay EDX-mapp image showed that Au and Fe species are separately located in the surface of silica particles (Figure 7).

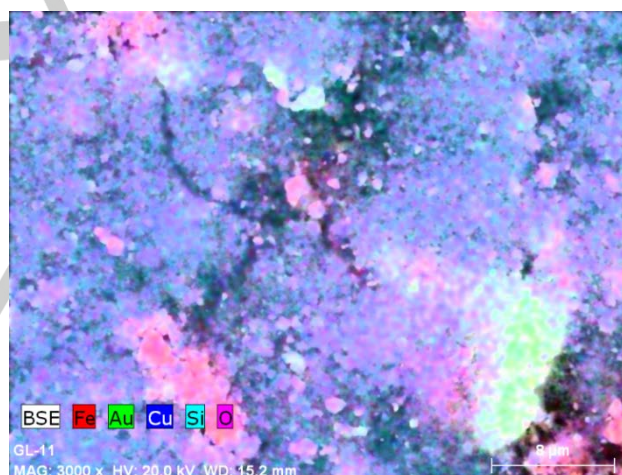
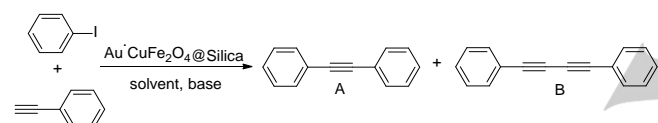


Figure 7. Overlay EDX-mapp image of Au-CuFe₂O₄@Silica

We have tested application of prepared material in Sonogashira coupling and reaction of iodobenzene with phenylacetylene was selected as a model reaction. Study of the reaction in *N,N*-dimethylacetamide (DMA) as solvent using different mol% of Au at 125 °C showed better results using *t*-BuOK as a base than K₂CO₃ in the presence of 0.9 mol% catalyst loading (Table 1, entries 1 and 2). When different bases such as K₃PO₄ and DABCO were assayed lower yields were obtained (Table 1, entries 3 and 4). The reaction was performed at 125 °C using *t*-BuOK 0.5 mol% of catalyst loading with similar yield (Table 1, compare entries 2 and 5). Lowering the temperature to 115 °C and

t-BuOK or K₂CO₃ as base in DMA a 95% or 6% yield were obtained, respectively (Table 1, entries 6 and 7). At this temperature a with 0.5 mol% catalyst loading the same 95% yield of tolane A was obtained and not formation of diyne B was detected (Table 1, entry 8). However, using 0.3 or 0.1 mol% catalyst loading the yield decreased to 46% or 19%, respectively (Table 1, entries 9 and 10). Study of reaction using *t*-BuOK at 115 °C in other solvents such as PEG, DMF, water and xylenes gave lower yields for the reaction even working with 0.9 mol% of catalyst (Table 1, entries 11-14). Further studies decreasing the reaction temperature to 105 °C and using *t*-BuOK as a base and 0.9 mol% Au loading cause decrease in reaction yields (Table 1, entry 15). Therefore *t*-BuOK as a base, DMA as a solvent and 0.5 mol% of Au at 115 °C was selected as optimized reaction conditions (Table 1, entry 8). It was worth mentioning that using 1.6 mol% of CuFe₂O₄@SiO₂ in the absence of Au for model reaction under found optimized condition showed only 28% conversion (determined by GC). Also, using Au@SiO₂ in the absence of CuFe₂O₄ showed 53% conversion to desired product.

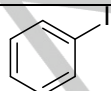
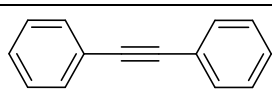
Table 1. Optimization of the reaction conditions for the reaction of iodobenzene with phenylacetylene^[a]



Entry	(Cat.mol%)	Base	Solvent	Temp (°C)	Yield A [%] ^[b]	Yield B [%] ^[b]
1	0.9	K ₂ CO ₃	DMA	125	81	6
2	0.9	<i>t</i> -BuOK	DMA	125	96	1
3	0.9	K ₃ PO ₄ ·3H ₂ O	DMA	125	66	9
4	0.9	DABC O	DMA	125	16	17
5	0.5	<i>t</i> -BuOK	DMA	125	93	2

Table 2. . The reactions of structurally different aryl iodides and bromides with alkynes in the presence of Au-CuFe₂O₄@SiO₂^[a]

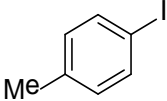
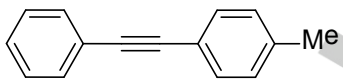
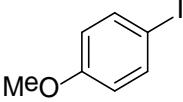
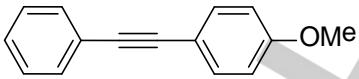
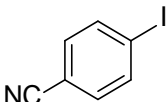
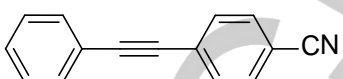
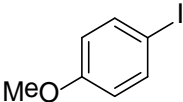

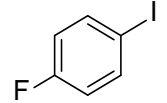
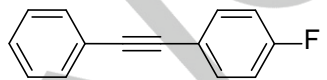
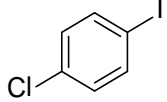
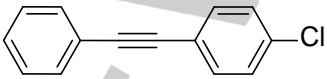
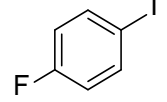
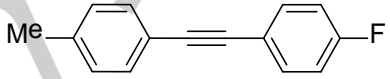
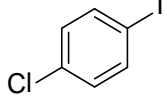
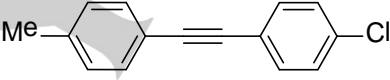
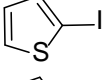
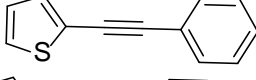
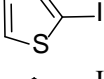
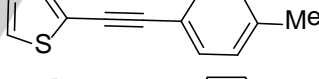
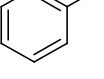
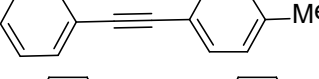
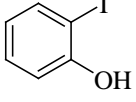
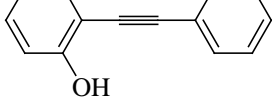
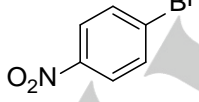
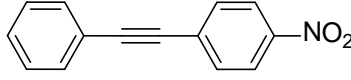
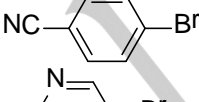
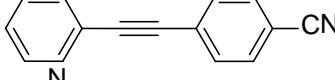
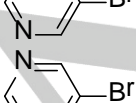
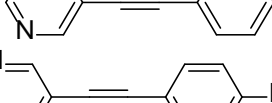
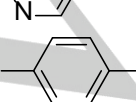
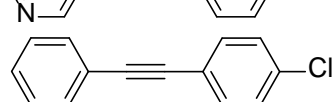


$$\text{Ar}^1\text{X} + \text{Ar}^2\text{C}\equiv\text{C} \xrightarrow[\text{115 } ^\circ\text{C}]{\text{Au-CuFe}_2\text{O}_4\text{@SiO}_2 \text{ (0.5 mol\%)}; \text{t-BuOK, DMA}} \text{Ar}^1\text{C}\equiv\text{C-Ar}^2$$

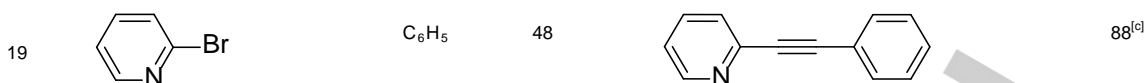
Entry	Ar ¹ X	Ar ²	Time [h]	Product	Yield [%] ^[b]
1		C ₆ H ₅	24		94

6	0.9	<i>t</i> -BuOK	DMA	115	95	3
7	0.9	K ₂ CO ₃	DMA	115	6	33
8	0.5	<i>t</i> -BuOK	DMA	115	95	0
9	0.3	<i>t</i> -BuOK	DMA	115	46	0
10	0.1	<i>t</i> -BuOK	DMA	115	19	3
11	0.9	<i>t</i> -BuOK	PEG	115	12	0
12	0.9	<i>t</i> -BuOK	DMF	115	71	11
13	0.9	<i>t</i> -BuOK	H ₂ O	115	5	2
14	0.9	<i>t</i> -BuOK	Xylenes	115	1	2
15	0.9	<i>t</i> -BuOK	DMA	105	40	0

[a] Reaction conditions: iodobenzene (1 mmol), phenylacetylene (1.5 mmol), base (1.5 mmol), catalyst (see column) in 2 mL of solvent.

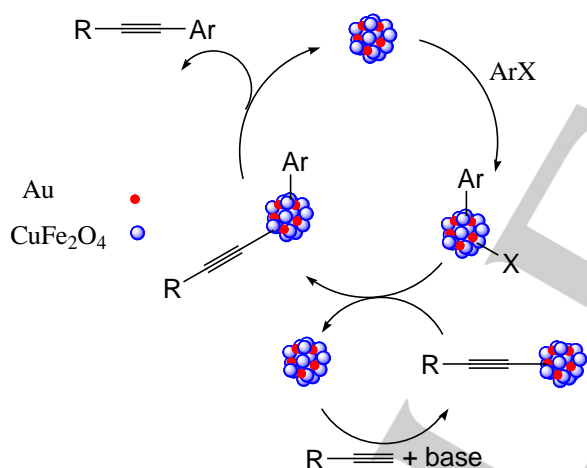
These reaction conditions were applied for the Sonogashira reactions of structurally different aryl halides. In the case of aryl iodides containing electron-donating groups such as 4-Me, 4-OMe as well as electron-withdrawing groups such as 4-NO₂, 4-Cl, 4-F, 4-CN reacted with phenylacetylene and 4-ethynyltoluene were proceeded efficiently and desired coupling products were obtained in 73-98 % isolated yields. Reactions of 2-iodothiophene as a heterocyclic aryl halide with both phenyl acetylene and 4-ethynyltoluene proceed very effectively and afford products in excellent yields (Table 2, entries 10,11). Furthermore reaction of less reactive and sterically hindered 2-iodophenol with phenylacetylene was proceed very well and disered coupling product was obtained without formation of any ring-closing 2-phenylbenzofuran product (Table 2, entry 13). However, study of reaction of 1-bromo-4-nitrobenzene with phenylacetylene under optimized reaction conditions showed formation of product with 67% yield. Therefore reaction temperature was increased to 130 °C and Sonogashira reaction of different tet aryl bromides were studied under efficient reaction conditions (Table 2, entries 14-19).

2		C_6H_5	48		96
3		C_6H_5	24		73
4		C_6H_5	24		98
5		4-MeC ₆ H ₄	24		93
6		C_6H_5	24		94
7		C_6H_5	24		97
8		4-MeC ₆ H ₄	24		96
9		4-MeC ₆ H ₄	24		95
10		C_6H_5	24		94
11		4-MeC ₆ H ₄	24		97
12		4-MeC ₆ H ₄	24		90
13		C_6H_5	24		84
14		C_6H_5	48		97 ^[c]
15		C_6H_5	48		100 ^[c]
16		C_6H_5	48		82 ^[c]
17		4-MeC ₆ H ₄	48		78 ^[c]
18		C_6H_5	48		84 ^[c]



[a] Reaction conditions: ArX (1 mmol), alkyne (1.5 mmol), *t*-BuOK (1.5 mmol), catalyst (40 mg catalyst containing 0.5 mol% Au) at 115 °C in DMA (2 mL). [b] Isolated product after column chromatography. [c] The reaction was performed at 130 °C.

The proposed mechanism for the reaction is in accordance with Corma and col. DFT calculations.^{7g,h} In the case of Au NPS it can be formed an adsorption complex with iodobenzene in which the iodine atom is directly bonded to the Au atom, after transfer of the I atom to Au finally the Ph group is bonded to another Au atom. It means that the rupture of the C-I bond by Au NPs is feasible.^{7g} Moreover, phenylacetylene can be absorbed in activated Au^{δ+} species which helps in the C-H activation process.^{7h} In the case of Cu the most probably interaction is the formation of a copper acetylide with the participation of the base accelerating the reaction. In addition, in the Cu-catalyzed Sonogashira reaction aryl iodides can also react with acetylenes, it means that also Cu can cleave the C-I bond. We think that both Au and Cu species have positive effect in C-H bond activation of alkyne and C-X activation of aryl halides. Initial π -activation of the triple C-C bond by both Au and Cu can also participate in the reaction.



Scheme 2. Proposed reaction mechanism using Au-CuFe₂O₄@Silica

Finally we have studied the recyclable property of prepared Au.CuFe₂O₄@SiO₂ catalyst for the reaction of iodobenzene with phenylacetylene. For this purpose after 1 d reaction time, the resulting suspension was subjected to external magnet and after washing and drying was used for another reaction batch. Using this process, catalyst was successfully recycled for four consecutive runs with small decrease in activity (Figure 8). TEM image of recovered catalyst after fourth run showed that the catalyst structure was preserved during these processes (Figure 9).

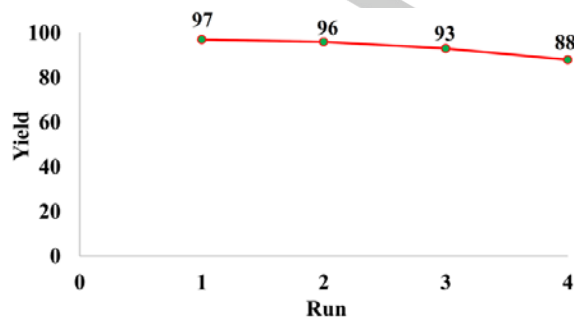


Figure 8. Recycling of catalyst for the reaction of iodobenzene with phenylacetylene.

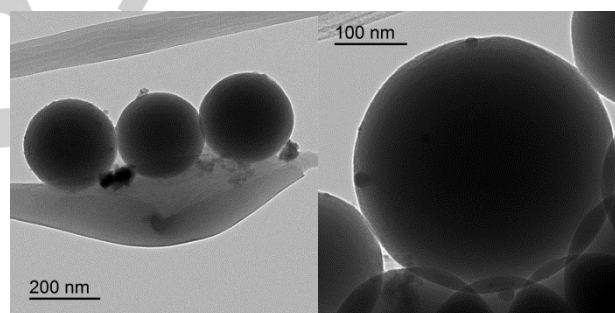


Figure 9. TEM images of recovered catalyst after fourth run.

Conclusions

The excellent catalytic activity of silica supported gold and copper ferrite nanoparticles (NPs) for the alkylation not only of aryl iodides but also of aryl bromides has been demonstrated. The cooperative effect of both metals, gold and copper *versus* only copper in the supported catalyst has been clearly demonstrated. The use of *t*-BuOK as base and DMA as solvent at 115 °C for iodides and 130 °C for bromides allowed the synthesis of internal alkynes in excellent yields with a very low Au-CuFe₂O₄@SiO₂ loading (0.5 mol%). The inorganic support facilitates the recyclability and reusability of this heterogeneous catalyst by a simple external magnet.

Experimental Section

Synthesis of 500 nm silica particles

The spherical silica particles were synthesized according a procedure reported in the literature, [12] which will briefly be explained as following. A mixture of deionized H₂O (3.4 mL), NH₃ (3.4 mL) and isopropanol (86.8 mL) was stirred for 10 min at room temperature. To the resulting mixture, Si(OEt)₄ (6.4 mL) were added dropwise. After 24 h, the silica particles were centrifugally separated from the suspension and washed with water and ethanol for four times, and then dried in oven at 60 °C.

Synthesis of (3-mercaptopropyl)triethoxysilane functionalized silica particles (SH@SiO₂)

The above described synthesized silica particles (1.2 g) were sonicated in dry toluene (40 mL) for 30 min. Then, 3-mercaptopropyltriethoxysilane (1.8 mL, 7.6 mmol) was added and the resulting mixture was refluxed for 24 h under argon atmosphere. Then, the (3-mercaptopropyl)triethoxysilane functionalized silica particles were separated using centrifugation and washed with EtOH (3x10 mL) and dried in oven at 60 °C for 24 h.

Synthesis of (3-chloropropyl)trimethoxysilane functionalized CuFe₂O₄ particles Cl@CuFe₂O₄

Synthesized CuFe₂O₄NPs (500 mg) were dispersed in dry toluene (15 mL) for 30 min using ultrasound assistance. To the resulting solution, 3-chloropropyltrimethoxysilane (0.55 mL, 3 mmol) was added and mixture was refluxed for 24 h under argon atmosphere. The (3-chloropropyl)trimethoxysilane functionalized CuFe₂O₄NPs was subjected to magnetic separation, and was washed sequentially with EtOH (3x 20 mL) and dried under vacuum for 24 h.

Assemble of Cl@CuFe₂O₄ NPs on SH@SiO₂

Cl@CuFe₂O₄ (100 mg) and SH@SiO₂ particles (500 mg) were dispersed separately in toluene (15 mL) for 30 min and then mixed together. To the resulting mixture, Et₃N (0.28 mL, 2 mmol) was added and reaction mixture refluxed for 24 h under argon atmosphere. Then, the mixture was subjected to magnetic separation and the isolated CuFe₂O₄@SiO₂ NPs were washed sequentially with CH₂Cl₂ (2x 10 mL) and dried under vacuum for 24 h.

Preparation of Au-CuFe₂O₄@SiO₂

To mixture containing polyvinylpyrrolidone (40mg) and HAuCl₄.4H₂O (80 mg, 0.19 mmol) in H₂O (5 mL) a solution of NaBH₄ (75 mg, 2 mmol) in H₂O (3 mL) was added dropwise. The resulting mixture was added to the already sonicated CuFe₂O₄@SiO₂ (1gr in 10 mL of H₂O). The mixture was stirred for 24 h at room temperature under argon atmosphere. Then, the final Au-CuFe₂O₄@SiO₂ catalyst was separated magnetically and was washed sequentially using H₂O (20 mL) and CH₂Cl₂ (2x10 mL) and dried in oven at 60 °C for 24 h.

General procedure for Sonogashira coupling reaction of aryl halides

The catalyst (40 mg containing 0.5 mol% Au and 1.6 mol% Cu), aryl halides (1 mmol), alkyne (1.5 mmol), *t*-BuOK (2 mmol) and DMA (2 mL) were added to flask equipped with a stir bar under argon atmosphere. The reaction mixture was stirred for the appropriate reaction time at 115–130 °C. The progress of the reactions was monitored using gas chromatography. After completion of reaction, H₂O (2 mL) was added to reaction mixture and the crude product was extracted using ethyl acetate (3x5 mL). The combined organic extracts were dried over Na₂SO₄ and concentrated under reduced pressure. The resulting crude product was

further purified by column chromatography using n-hexane and ethyl acetate as eluents.

Typical procedure for the recycling of catalyst for the reaction of iodobenzene and phenylacetylene

After completion of reaction of iodobenzene with phenylacetylene, reaction mixture was subjected to magnetic separation and catalyst was separated. The catalyst can isolate from reaction mixture completely during 10 min (Figure 4, supporting information). Then, isolated catalyst was washed with diethyl ether and after drying was used for another batch of the reaction.

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Keywords: Nanoparticles • gold • copper ferrite • Sonogashira • Magnetic

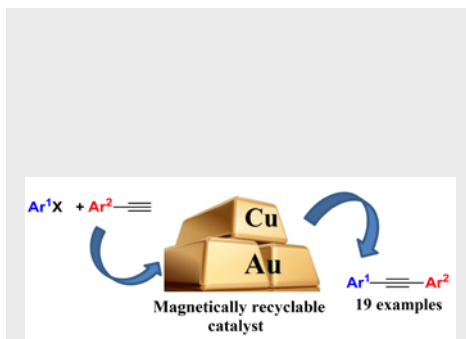
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Layout 1:

FULL PAPER

Au and CuFe₂O₄ NPs supported on silica as an efficient catalyst for Sonogashira reaction



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Silica Microparticles Supported Gold and Copper Ferrite Nanoparticles: A Magnetically Recyclable Bimetallic Catalyst for Sonogashira Reaction