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Assemblies of Copper Ferrite and Palladium Nanoparticles on Silica Microparticles as a Magnetically Recoverable Catalyst for Sonogashira Reaction under Mild Conditions

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Dedicated to Dr. Diego A. Alonso

Copper ferrite and palladium nanoparticles assembled on silica microparticles are prepared successfully and characterized by scanning electron microscopy, transmission electron microscopy, electron-dispersive X-ray analysis, X-ray diffraction, thermogravimetric analysis, atomic absorption spectroscopy, and infrared studies. The catalyst is applied effectively for the Sonogashira coupling reaction of aryl iodides and bromides under heterogeneous and phosphine-free reaction conditions. The reactions proceed at 50 °C with a low loading of palladium catalyst. The magnetically recoverable catalyst is recycled successfully for five consecutive runs with very small drops in catalytic activity.

Introduction

Heterogeneous catalysts have been widely involved in different organic reactions, because the reuse of catalysts is highly desirable for economic and ecological reasons and to meet today's green chemistry objectives.[1] Thus, the choice of catalyst support plays an important role in the overall performance, catalytic activity, and reusability of heterogeneous catalysts.[1] However, despite the important achievements in this field, heterogeneous catalysts are difficult to separate from the reaction mixture by usual methods such as filtration and centrifugation.

In this regard, magnetic nanoparticles are increasingly engaged as excellent supports for catalytic systems in the design of new efficient and green processes.[2] In addition, because of their large ratio of surface area to volume, superparamagnetic behavior, and low toxicity, magnetic nanoparticles have attracted much attention in manifold technological fields such as biomedicine, biotechnology, and materials science.[3] However, despite the wide applications of magnetic nanoparticles as supports, less attention has been devoted to the catalytic performance of magnetic nanoparticles in organic reactions.[4] Among different magnetic compounds, $CuFe_2O_4$ nanoparticles are one of the most essential magnetic materials, and has recently been applied as a heterogeneous catalyst in different organic transformations.[5]

The palladium-catalyzed Sonogashira coupling reaction is one of the most potent approaches for the construction of aryl-alkynes and conjugated enynes through the coupling of vinyl or aryl halides or triflates with terminal alkynes in the presence of a copper(I) cocatalyst. The aryl-alkynes and conjugated enynes obtained by the Sonogashira reaction have wide applications in the chemistry of natural products and pharmaceuticals.[6]

The Sonogashira reaction usually requires a palladium catalyst in the presence of a copper cocatalyst.[6,7] Despite the different reported copper-free Sonogashira reactions, the addition of copper can increase the efficiency of the reaction under oxygen-free conditions to prevent the formation of alkyne homocoupling products.[6] A literature search revealed that some effort has been made to perform this reaction using copper[8] or other transition metal catalysts[9] in the absence of palladium. For example, we recently reported magnetite (Fe_3O_4) nanoparticles as a catalyst for Sonogashira coupling of aryl iodides in ethylene glycol.[4d] However, the reactions were performed at high temperatures and only aryl iodides were reacted efficiently. In addition, the Sonogashira reaction of aryl halides with alkynes catalyzed by copper ferrite ($CuFe_2O_4$) nanoparticles has been reported.[8m] However, with this catalyst, the reactions did not proceed efficiently and 70 % isolated yield was the best reaction yield obtained for the reaction of iodobenzene with phenyl acetylene at 110 °C. Furthermore, copper-catalyzed Sonogashira reactions have been performed at high temperatures using aryl iodides and active aryl bromides with the view that the presence of the palladium impurity is responsible for the reaction.[6,10] For example, a new study by Buchwald and Bolm revealed the fundamental role of metal contaminants in iron-catalyzed C–C bond-forming reactions.[11]

In recent years there has been growing interest in using bimetallic nanoparticles for heterogeneous catalysis.[12,13] The presence of two metal nanoparticles in the catalyst can enhance its activity and selectivity and reduce environmentally

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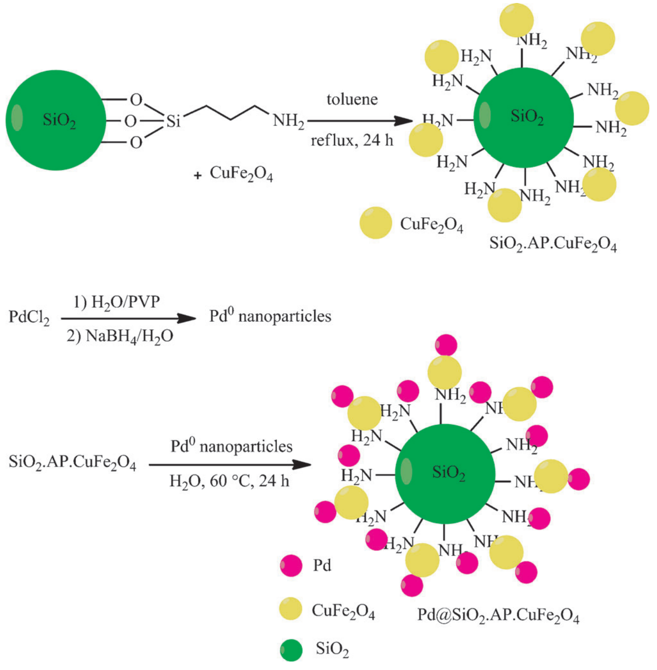
harmful side effects. Recently, the synthesis of composite particles with a gold surface, silica core, and magnetic inner layer for DNA interaction was reported.[14] In addition, silica spheres modified with (3-aminopropyl)trimethoxysilane were used as a template for the assembly of Fe_3O_4 nanoparticles and the subsequent assembly of nanoparticles of Au, CdSe/ZnS, or Pd on the magnetite-nanoparticle-bearing silica spheres.[15] The catalyst carrying palladium was tested in the Sonogashira coupling reaction in the presence CuI and PPh_3 additives. Recently, the combination of $CuFe_2O_4$ nanoparticles and palladium has been shown to exhibit high activity in the selective hydrogenation of arylacetylenes.[16] Moreover, very recently, we introduced copper-ferrite-supported palladium nanoparticles as an efficient catalyst for the cyanation of aryl halides.[17] The synergistic effect between palladium and copper nanoparticles played an important role in the catalytic activity of the catalyst. In this study, we have prepared $CuFe_2O_4$ nanoparticles supported on 500 nm spherical silica followed by the assembly of palladium nanoparticles (Scheme 1). The new magnetically recoverable catalyst is successfully applied in Sonogashira coupling reactions of aryl iodides and bromides with alkynes at 50 °C under phosphine-free reaction conditions.



Scheme 1. Preparation steps of the catalyst. PVP = polyvinylpyrrolidone.

Results and Discussion

Uniform and monodisperse spherical silica particles were prepared through the Stöber process using tetraethyl orthosilicate. Scanning electron microscopy (SEM) images of prepared silica particles showed the formation of monodisperse and uniform silica particles of 500 nm in size (Figure 1).

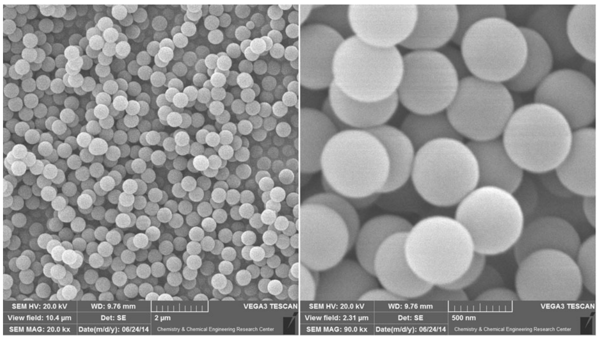


Figure 1. SEM images of silica particles prepared using the Stöber method.

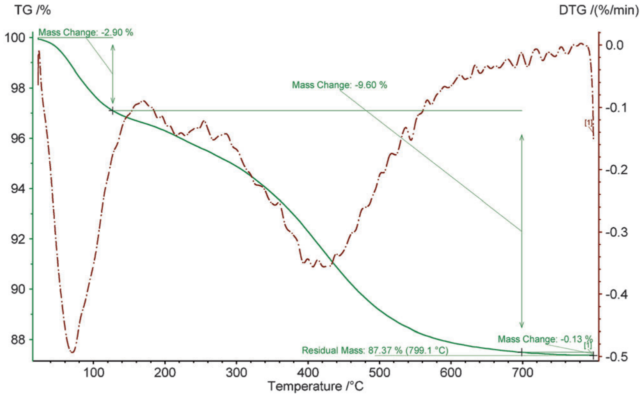


Figure 2. Thermogravimetric diagram of 3-aminopropyltriethoxysilane-functionalized silica particles.

The prepared silica particles were functionalized using 3-aminopropyltriethoxysilane in dry toluene. Thermal gravimetric analysis of 3-aminopropyltriethoxysilane-functionalized silica showed two weight-loss steps (Figure 2). The first weight loss is related to the removal of H_2O, and the second loss to the grafted organic group with a loading of 1.6 $mmol\,g^{-1}$.

$CuFe_2O_4$ nanoparticles were synthesized through the conventional coprecipitation method using $FeCl_3{\cdot}6H_2O$ and $CuCl_2$ $2H_2O$ in an argon atmosphere.[5i] A transmission electron microscopy (TEM) image of the prepared $CuFe_2O_4$ NPs confirmed the formation of nanoparticles of average size 30–40 nm (Figure 3).

The stabilization of $CuFe_2O_4$ on 3-aminopropyltriethoxysilane-modified silica particles was achieved by reflux of func-

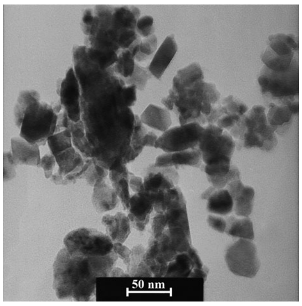


Figure 3. TEM image of prepared $CuFe_2O_4$ NPs.

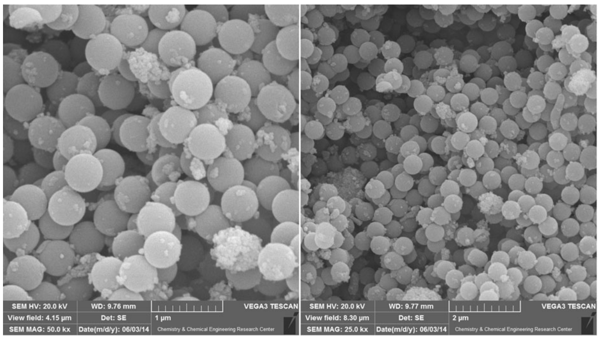


Figure 4. SEM images of prepared Pd@SiO_2·AP·$CuFe_2O_4$ catalyst.

tionalized silica particles and $CuFe_2O_4$ in toluene for 24 h. Finally, the catalyst was obtained by mixing the prepared palladium nanoparticles and silica-supported $CuFe_2O_4$ NPs. The presence of palladium in the final catalyst was confirmed by atomic absorption spectroscopy (AAS), which showed 0.3 mmol g^{-1} palladium. SEM images of the prepared catalyst showed the preservation of the size and monodispersity of the silica nanoparticles and the presence of $CuFe_2O_4$ and palladium nanoparticles in the catalyst (Figure 4). In addition, the electron-dispersive X-ray (EDX) spectrum of the catalyst exhibited the presence of Pd, Cu, Fe, and Si species in the structure of catalyst (Figure 5). Furthermore, the TEM image of the catalyst indicated the presence of $CuFe_2O_4$ and palladium nanoparticles on the surface of the silica particles (Figure 6).

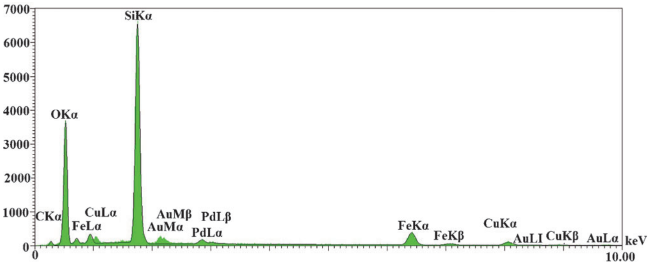


Figure 5. EDX spectrum of prepared Pd@SiO_2·AP·$CuFe_2O_4$ catalyst.

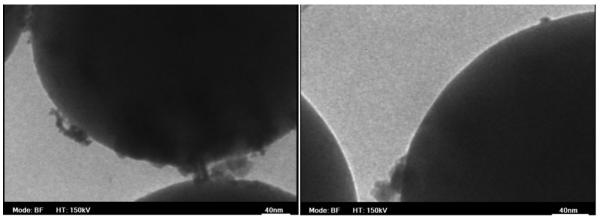


Figure 6. TEM images of prepared Pd@SiO_2·AP·$CuFe_2O_4$ catalyst.

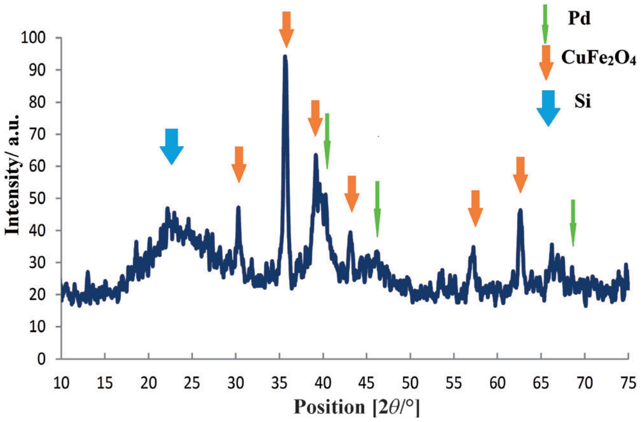


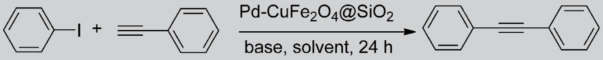
Figure 7. XRD pattern of the catalyst.

X-ray diffraction (XRD) analysis of the prepared catalyst showed the presence of $CuFe_2O_4$ nanoparticles by screening Bragg's reflections related in $2\theta = 18.3°$, $30.3°$, $35.6°$, $57.1°$, and $62.98°$[17] and Bragg's reflections related to palladium in $2\theta = 40.1°$, $46.7°$, and $68.1°$[19] and also related to silica particles $2\theta = 22°$[20] (Figure 7).

The catalytic activity of the prepared Pd-$CuFe_2O_4$@SiO_2 NPs was investigated in the Sonogashira coupling reaction. Initial experiments with iodobenzene and phenylacetylene were performed to optimize the reaction conditions such as the base, solvent, reaction temperature, and amount of catalyst used (Table 1).

The results showed that the use of dimethyl acetamide (DMA) as a solvent and 1,4-diazabicyclo[2.2.2]octane (DABCO) as a base at 50 °C provides the most suitable reaction conditions (Table 1, entry 22). Notably, the use of DMA and DABCO at 70 °C afforded 87 % yield (Table 1, entry 9); however, we preferred to select 50 °C as a milder reaction temperature. Having optimized the conditions, reactions of a variety of aryl halides with alkenes were studied in the presence of the catalyst. Under the optimized conditions, reactions of aryl iodides were

Table 1. Screening of different reaction conditions for the reaction of iodobenzene with phenylacetylene.



Entry	Pd [mol %]	Base	Solvent	*T* [°C]	Yield [%][a]
1	0.3	K_2CO_3	DMF	60	10
2	0.3	K_2CO_3	DMF	50	7
3	0.3	K_2CO_3	DMF	60	8
4	0.3	K_2CO_3	H_2O	60	9
5	0.6	K_2CO_3	H_2O	25	7
6	0.3	K_2CO_3	H_2O	50	10
7	0.3	K_2CO_3	DMA	50	5
8	0.3	Cs_2CO_3	DMSO	50	7
9	0.3	DABCO	DMA	70	87
10	0.3	DABCO	DMSO	50	52
11	0.3	DABCO	DMSO	RT	19
12	0.3	DABCO	H_2O	50	67
13	0.3	DABCO	dioxane	50	20
14	0.3	DABCO	DMF	50	27
15	0.6	DABCO	DMSO	25	9
16	0.6	DABCO	H_2O	25	12
17	0.3	*t*BuOK	DMA	50	3
18	0.3	*t*BuOK	DMSO	50	7
19	0.3	DABCO	DMSO	70	78
20	0.3	DABCO	DMSO	60	76
21	0.3	DABCO	DMSO	50	35
22	0.3	DABCO	DMA	50	83
23	0.3	DABCO	DMSO	RT	6
24	0.3	DABCO	DMA	RT	25

[a] Yield determined by CG analysis.

performed efficiently and the desired alkyne products were obtained in good to excellent yields. In addition, the reactions of aryl bromides proceeded well and the desired aryl alkynes were obtained in 69–94% yields of isolated product. The results in Table 2 show that mostly the presence of electron-withdrawing groups at the *para*-position of the aryl halides affords high yields compared with electron-donating groups at the *para*-position. Reactions of 2-iodothiophene and 5-bromopyrimidine as heterocyclic aryl halides under optimized reaction conditions proceeded efficiently and afforded coupling products in 82–98% yields. We decided to examine the catalytic activity of Pd-$CuFe_2O_4$@SiO_2 for Sonogashira coupling reactions of aryl chlorides. However, the results indicated that under optimized reaction conditions, the reactions of chlorobenzene and 4-chlorobenzonitrile with phenylacetylene were sluggish, and the coupling products were obtained in 4–13% yields based on GC analysis. Notably, with a similar catalyst prepared from Fe_3O_4 NPs, the Sonogashira coupling reaction was performed in the presence of CuI and PPh_3 as additives, and a high reaction temperature was required.[15]

The stability and recovery of heterogeneous catalysts becomes an important factor owing to strict economic and ecological demands for sustainability. Therefore, we studied the possibility of recovery of the catalyst from the reaction mixture. For this purpose, the reaction of iodobenzene with phenylacetylene under optimized reaction conditions was selected. After 24 h, the catalyst was isolated from the reaction mixture by an external rod, and after washing with diethyl ether and drying, it was charged for another batch of the reaction.

Table 2. Sonogashira reactions of structurally different aryl iodides and bromides with alkynes in the presence of the catalyst.[a]

$$Ar^1X + R^2\!-\!\equiv \xrightarrow[\text{DMA, DABCO, 50 °C}]{\text{Pd-CuFe}_2\text{O}_4\text{@SiO}_2} Ar^1\!-\!\equiv\!-\!R^2$$

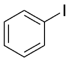
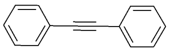
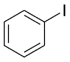
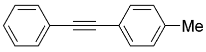
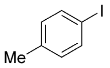
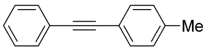
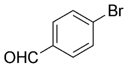
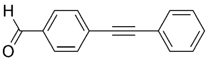
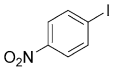
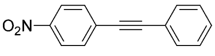
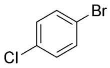
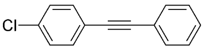
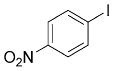
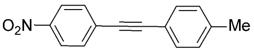
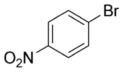
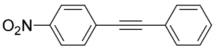
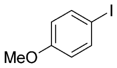
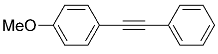
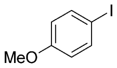
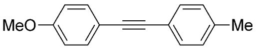
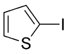
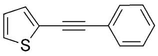
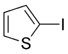
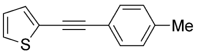
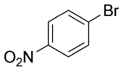
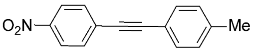
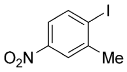
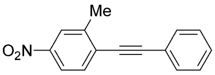
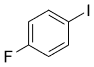
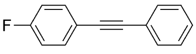
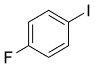
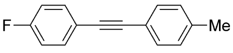
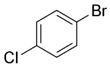
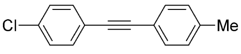
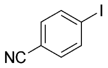
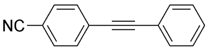
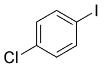
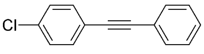
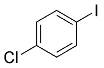
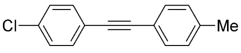
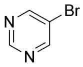
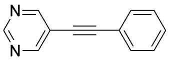
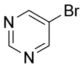
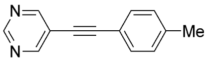
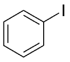
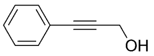
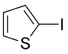
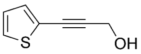
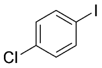
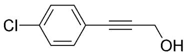
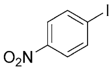
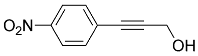
Entry	A^1X	R^2	*t* [h]	Product	Yield [%][b]
1		C_6H_5	24		80
2		4-$CH_3C_6H_4$	24		73
3		C_6H_5	24		82
4		C_6H_5	48		69
5		C_6H_5	7		95
6		C_6H_5	48		71
7		4-$CH_3C_6H_4$	7		97
8		C_6H_5	48		94
9		C_6H_5	24		68
10		4-$CH_3C_6H_4$	24		97
11		C_6H_5	24		95
12		4-$CH_3C_6H_4$	24		98
13		4-$CH_3C_6H_4$	48		95
14		C_6H_5	30		93
15		C_6H_5	24		98
16		4-$CH_3C_6H_4$	17		85
17		4-$CH_3C_6H_4$	48		74
18		C_6H_5	8		95
19		C_6H_5	24		97
20		4-$CH_3C_6H_4$	24		84
21		C_6H_5	48		94

Table 2. (Continued)

Entry	A^1X	R^2	*t* [h]	Product	Yield [%][b]
22		4-$CH_3C_6H_4$	48		82
23		CH_2OH	24		88
24		CH_2OH	24		98
25		CH_2OH	24		95
26		CH_2OH	8		98

[a] Reaction conditions: Ar^1X (1 mmol), alkyne (1.5 mmol), DABCO (2 mmol), DMA (2 mL), catalyst (10 mg, containing 0.3 mol% Pd) at 50 °C. [b] Yield of isolated product.

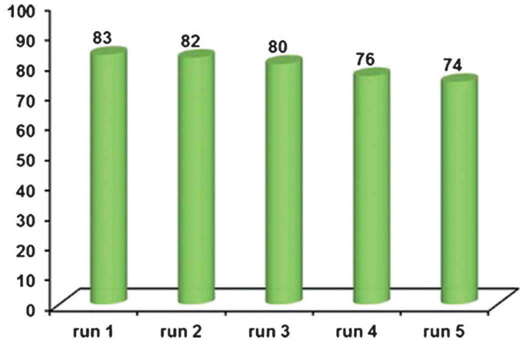


Figure 8. Recycling of catalyst for the reaction of iodobenzene with phenylacetylene.

Using this process, the catalyst was recycled for five consecutive runs with restoration of its catalytic activity (Figure 8). AAS analysis of the solution obtained after isolation of the catalyst in the first run showed 6% leaching of Pd.

To get information about stability of the catalyst, we performed TGA analysis of the recycled catalyst after the third run. The results showed that the catalyst is thermally stable up to 200 °C and organic functional groups were presented in the structure of the catalyst (Figure 9). In addition, the SEM images of the catalyst after the third run showed the preservation of catalyst structure and the presence of nanoparticles on silica cores (Figure 10). EDX analysis of the recycled catalyst after the third run confirmed the presence of Fe, Cu, and Pd species in the structure of the reused catalyst (Figure 11).

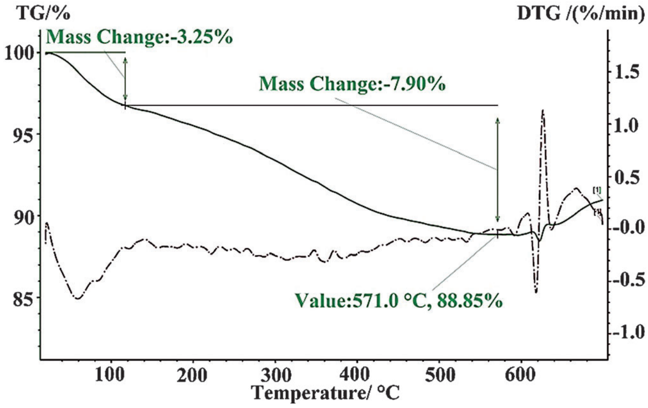


Figure 9. Thermogravimetric diagram of catalyst after third run.

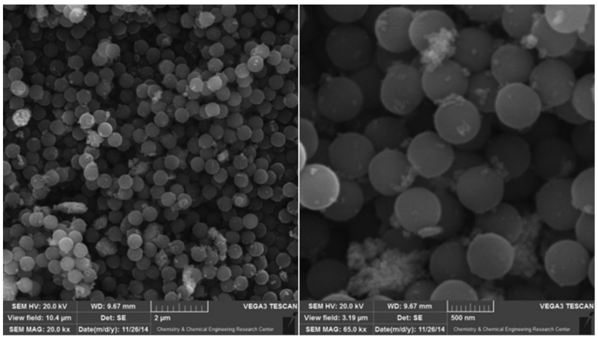


Figure 10. SEM images of recycled catalyst after third run.

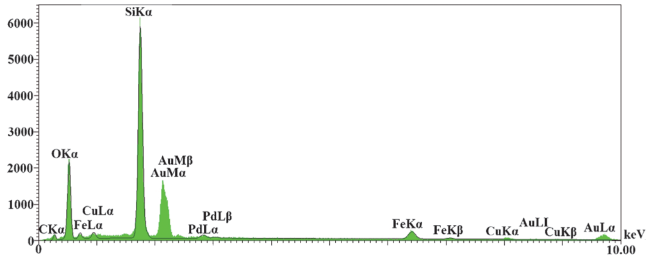


Figure 11. EDX spectrum of recycled catalyst after third run.

Conclusion

In conclusion, in this study we successfully prepared copper ferrite and palladium nanoparticles assembled on silica micro cores. The catalyst was characterized by SEM, TEM, EDX, XRD, TGA, AAS, and FTIR analysis. The catalytic activity of the catalyst was assessed in Sonogashira coupling reactions of aryl iodides and bromides under low Pd loading and mild, phosphine-free reaction conditions. The magnetically separable catalyst was recycled successfully for five consecutive runs with small drops in catalytic activity.

Experimental Section

Synthesis of 500 nm silica particles: The spherical silica particles were synthesized following a procedure similar to that reported in the literature,[18] which will be explained briefly in the following. A mixture of deionized H_2O (3.4 mL), NH_3 (3.4 mL), and isopropanol (86.8 mL) was stirred for 10 min at room temperature. $Si(OEt)_4$ (6.4 mL) was added dropwise to the resulting mixture. After 24 h, the silica particles were separated centrifugally from the suspension and washed four times with water and ethanol, then dried in an oven at 60 °C.

Synthesis of (3-aminopropyl)triethoxysilane-functionalized silica particles: The synthesized silica particles (700 mg) were dispersed in dry toluene (40 mL) for 30 min using ultrasound assistance. 3-Aminopropyltriethoxysilane (4 mmol, 0.94 mL) was added to the resulting solution, and the mixture was heated at reflux for 24 h under an argon atmosphere. Then, the (3-aminopropyl)triethoxysilane-functionalized silica particles were separated by centrifugation and washed with EtOH (3×10 mL) and dried in oven at 60 °C for 24 h.

Assembly of $CuFe_2O_4$ NPs on (3-aminopropyl)triethoxysilane-functionalized silica: $CuFe_2O_4$ (80 mg) and (3-aminopropyl)triethoxysilane-functionalized silica particles (500 mg) were dispersed separately in toluene (15 mL) for 30 min, and then mixed together and heated at reflux for 24 h under an argon atmosphere. Then, the mixture was subjected to magnetic separation, and isolated SiO_2·AP·$CuFe_2O_4$ was washed sequentially with EtOH (3×10 mL) and dried under vacuum for 24 h.

Assembly of Pd NPs on prepared SiO_2·AP·$CuFe_2O_4$: Polyvinylpyrrolidone was added an acidic aqueous solution (5 mL) of $PdCl_2$ (0.14 mmol, 25 mg) under stirring. A solution of $NaBH_4$ (2 mmol in 5 mL H_2O) was added dropwise to the resulting mixture, and the obtained mixture was added to the sonicated SiO_2·AP·$CuFe_2O_4$ in 20 mL H_2O. The mixture was stirred for 24 h at 60 °C under an argon atmosphere. Then, the final Pd@SiO_2·AP·$CuFe_2O_4$ catalyst was separated magnetically, washed with H_2O (20 mL) and EtOH (3×10 mL), and dried in an oven at 60 °C.

General procedure for Sonogashira coupling reaction of aryl halides: The catalyst (10 mg containing 0.3 mol% Pd), aryl halides (1 mmol), alkyne (1.5 mmol), DABCO (2 mmol), and DMA (2 mL) were added to flasks equipped with a stirrer bar under argon protection. The reaction mixture was stirred for the appropriate reaction time at 50 °C under an argon atmosphere. The progress of the reactions was monitored by gas chromatography. After completion of the reaction, 2 mL H_2O was added to the reaction mixture and the crude product was extracted with ethyl acetate (3×5 mL). The crude product was further purified by column chromatography using *n*-hexane and ethyl acetate as eluents.

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Keywords: copper ferrite · heterogeneous catalysis · magnetic properties · palladium · Sonogashira coupling

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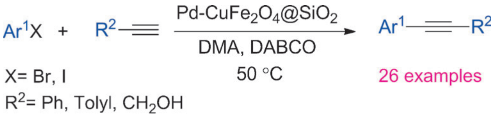
Assemblies of Copper Ferrite and Palladium Nanoparticles on Silica Microparticles as a Magnetically Recoverable Catalyst for Sonogashira Reaction under Mild Conditions



Heterogeneous catalysts: Copper ferrite and palladium nanoparticles on silica have been used to catalyze the Sonogashira reaction under mild reaction conditions (see scheme). The catalyst was recoverable and reusable, with only small drops in catalytic activity. DABCO = 1,4-diazabicyclo[2.2.2]octane, DMA = dimethyl acetamide.