

Supported Gold Nanoparticle Catalyzed Cross-coupling of Alkoxysilanes and Aryl Halides

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Abstract: Gold nanoparticles, being highly recyclable and benign in nature, are nowadays emerging as an attractive choice in various catalytic reactions. Fluoride free coupling of organosilane reagents with aryl halides is an environment-friendly protocol for the formation of C-C bond. Here, we present the coupling of phenyltrimethoxysilane with various aryl halides in ethanol/water mixture, catalyzed by gold nanoparticles under microwave heating. The effect of various parameters, such as catalyst concentration, base, time, temperature etc. on the reaction was investigated. Excellent activity of catalyst is indicated in terms of TON (1,666) and TOF (10,036 h⁻¹). This new result will undoubtedly expand the application of gold nanoparticles in organic catalytic reactions.



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Keyword: Resin-AuNPs, Hiyama reaction, ethanol/water system, microwave heating.

1. INTRODUCTION

In 1988, Hiyama *et al.* reported a method for the synthesis of biaryls using cross-coupling reaction of aryl halides with organosilanes [1-6]. These organosilicon reagents were non-toxic and cheaper in comparison to the tin reagents used in Stille coupling [7] and the boronic reagents [8] used in Suzuki reactions. However, the weak C-Si bond required fluoride ions for its activation and this made “the reaction protocol” unattractive to chemists. Lately, in the presence of metal nanoparticles, fluoride free reactions have been reported and the interest in this environmentally safe reaction has increased. Literature showed that the catalyst of choice for Hiyama cross coupling reaction is almost invariably palladium salts [9], palladium complexes [10] or supported palladium nanoparticles [11-15]. Rothenberg reported successful Hiyama coupling using Pd-Ni bimetallic nanoparticles [16] and tetrabutyl ammonium fluoride (TBAF) as activator.

Gold nanoparticles (AuNPs) as catalysts [17-19] are becoming an attractive choice in organic

reactions owing to their better selectivity, and longer stability in comparison to Pd and Pt catalysts. However, the overall performance of these gold nanoparticles is highly dependent on the size of nanoparticles and the nature of support. Several methods have been reported for controlling the size and shape of the gold nanoparticles [20-24]. In our lab we have successfully prepared AuNPs of size 5 – 8 nm on macroporous polystyrene resins, and used them for Suzuki coupling and reduction of nitroarenes. The micropores in these resins dictate the size and shape of the gold nanoparticles and the macropores assist in mass transfer. Here, we present for the first time the behavior of gold nanoparticles, supported on Amberlite XAD-4 resin for Hiyama cross-coupling reaction under microwave assisted closed vessel synthesis.

2. EXPERIMENTAL

All chemicals used were of analytical grade or of the highest purity available. All glassware was thoroughly cleaned with freshly prepared 3:1 HCl/HNO₃ (aqua regia) and rinsed thoroughly with Millipore-Q water. Phenyltrimethoxysilane was purchased from Aldrich. Aryl halides were obtained from BDH and Merck. All aryl halides standards were of 98–99% purity. Dichloromethane (DCM), diethyl ether (Et₂O), and NaOH were purchased from Finar chemicals. Water was

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purified by Millipore system and used in all experiments.

High resolution transmission electron microscopy (HR-TEM) pictures were taken using a JEOL, JEM 2100 instrument. The swollen resin beads were milled and a drop of alcoholic suspension was placed onto a 200 mesh carbon coated copper grid. It was then dried to evaporate the solvent and used for microscopy. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were carried out on a HJY Ultima-2 instrument: power 1000 W, nebulizer flow 1.29, nebulizer pressure 2.96, wave length 242.795 nm. GC-MS measurements were carried on Perkin Elmer USA Auto system XL. ^1H NMR spectra were recorded on a Bruker Advance II 400 NMR spectrometer. Reactions were carried out in CEM Microwave synthesizer (benchmate), in closed vessels with external cooling under aerobic conditions.

The resin supported gold nanoparticles were synthesized by a method developed in our lab [25] and characterized again by TEM. All compounds irrespective of their state were weighed for synthesis. 4 M solution of NaOH was prepared by dissolving 16 g NaOH in 100 mL double distilled water.

2.1. General Protocol For Coupling of Phenyltrimethoxysilane and Aryl Halide

Into a 10 mL vial phenyltrimethoxysilane (85 % purity, 1.5 mmol, 350 mg), resin-AuNPs (200 mg) and ethanol (2.0 mL) were taken. The reaction mixture was stirred vigorously and NaOH (4 M 1 mL, 4 mmol) was added drop wise. Then aryl halide 1 mmol [iodo benzene 204 mg; 4-iodobenzaldehyde 232 mg; 4-iodonitrobenzene 249 mg; 4-iodo acetophenone 246 mg; 4-methoxy iodobenzene 234 mg, 2-iodoacetophenone 246 mg; 3-methyl iodobenzene; 4-bromo iodobenzene 283 mg; bromobenzene 157 mg; chlorobenzene 112.6 mg] was added and the vial heated in CEM microwave (100 w, 110 °C) for different intervals of time. The hot reaction mixture was poured in 10 mL cold water. The resulting solution was extracted with Et₂O/DCM (2.5 mL). The combined organic extract was dried over anhydrous MgSO₄ and the solvent evaporated in a rotaevaporator. The crude products were recrystallized from appropriate solvents and identified by NMR.

The effect of base, solvent, temperature, catalyst concentration and time on the reaction yield were studied taking the coupling of 4-iodoacetophenone and phenyltrimethoxysilane as the standard reaction. The reaction mixtures after extraction in Et₂O/DCM were directly subjected to GC-MS analysis.

3. RESULT AND DISCUSSION

Amberlite XAD-4 is an inert resin, which makes it highly desirable as support in organic synthesis as it does not interfere in the reaction [26]. It is also thermally and mechanically stable under microwave conditions. It is a neutral resin as it is devoid of any functional group or ligand. The colourless resin beads turn pink on impregnation with AuNPs. HRTEM images (Fig. 1) revealed gold nanoparticles uniformly embedded in the matrix of resin with narrow distribution of particles size (3-8 nm in diameter) and HRTEM- lattice spacing $d = 0.2085$ nm. The concentration of gold in the solution was determined by ICP-AES was found to be 0.0032 mmol/g (0.630 mg/g) of the resin for resin-AuNPs.

The coupling of 4-iodoacetophenone and phenyltrimethoxysilane was selected as the standard reaction and the effect of solvent, catalyst quantity, time, nature of base etc. were studied to optimize reaction protocol. Nature of the base and its quantity had a great effect on the yield of the biphenyl. The C-Si is weak and requires activation. So, base is very important in coupling reactions. It not only neutralizes the acid eliminated in the reaction, but also helps in transmetalation by activating C-Si. Literature showed different in-organic bases [27, 28] can be used as activators but on the basis of our earlier studies, [29] only NaOH was tried as base which gave satisfactory results at 4 mmol concentration.

Hiyama reaction has been reported in a variety of organic solvents and water. Surfactants such as TBAF are used to enhance solubility of reactants in water and as activators. In our endeavor to utilize low boiling benign organic solvents, only alcohols and alcohol/water mixtures were tried as solvents. High $\tan \delta$ values of these solvents make them efficient absorbers of microwaves and thus, extremely suitable for microwave assisted organic synthesis, where they can be heated quickly above their boiling points in closed vessels. It was

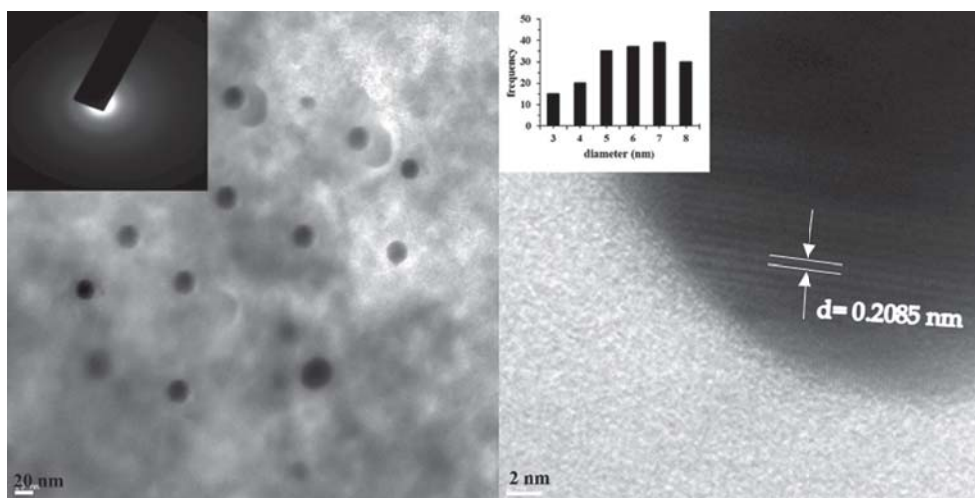


Fig. (1). HRTEM image and ED patterns of resin-AuNPs.

observed that water alone is not sufficient due to poor solubility of reactants. Even pure methanol and ethanol as solvent, resulted in low product yields. Best yields were obtained when EtOH:H₂O in 2:1 ratio was used as solvent.

The effect of time on the reaction rate was analyzed by monitoring the concentration of 4-acetylbiphenyl by GC-MS (Fig. 2). It was observed that after 10 min, the peak for 4-iodoacetophenone disappeared completely and 4-acetylbiphenyl was identified as the sole coupling product by its mass spectrum.

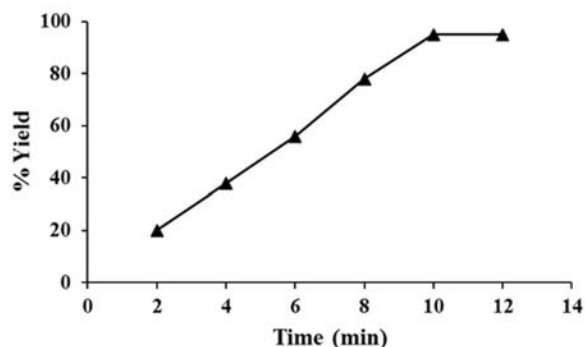


Fig. (2). Time course of Hiyama reaction between 4-iodoacetophenone and phenyltrimethoxysilane.

The catalytic activity of AuNPs was investigated by varying the amount of catalyst, while keeping the other parameters constant. It was observed that 200 mg resin (≈ 0.0006 mmol of Au, 0.06 mol % with respect to aryl halide) was sufficient for completing the reaction. Turnover number and Turnover frequency (h^{-1}) values indicate the efficiency of a catalyst and they were found to be 1,666 and 10,036 respectively. Optimization of the conditions is summarized in Table 1.

Table 1. Optimization of reaction condition on the Hiyama reaction.

Entry	Reaction Condition	Yield (%)
1	NaOH, EtOH: H ₂ O (2:1), Temp.= 110 °C	-
2	Catalyst 200 mg, NaOH, EtOH:H ₂ O (2:1), Temp.= 110 °C	92
3	Catalyst 150 mg, NaOH, EtOH:H ₂ O (2:1), Temp.= 110 °C	80
4	Catalyst 100 mg, NaOH, EtOH:H ₂ O (2:1), Temp.= 110 °C	60
5	Catalyst 50 mg, NaOH, EtOH:H ₂ O (2:1), Temp.= 110 °C	40
6	Catalyst 200 mg, NaOH, EtOH:H ₂ O (1:1), Temp.= 110 °C	75
7	Catalyst 200 mg, NaOH, EtOH, Temp.= 110 °C	55
8	Catalyst 200 mg, NaOH, H ₂ O, Temp.= 110 °C	40
9	Catalyst 200 mg, NaOH, EtOH:H ₂ O (2:1), Temp.= 100 °C	74
10	Catalyst 200 mg, NaOH, EtOH:H ₂ O (2:1), Temp.= 90 °C	64
11	Catalyst 200 mg, NaOH, MeOH:H ₂ O (2:1), Temp.= 110 °C	78
12	Catalyst 200 mg, NaOH, MeOH, Temp.= 110 °C	57

Standard Conditions: 4-iodoacetophenone (1.0 mmol), phenyltrimethoxysilane (1.5 mmol), NaOH (4.0 mmol, 4M 1 mL), EtOH (2.0 mL), and Resin-AuNPs catalyst

Recovery and recyclability of a catalyst enhances the working life of a catalyst and makes it economical for industrial applications. We have observed that Resin-AuNPs show better recyclability in comparison to palladium. The resin beads recovered after the completion of the reaction were washed with hot water, alcohol, DCM etc. to rid them of reaction products and were reused. The catalyst showed unchanged catalytic activity up to four reaction cycles and slight decrease was observed in the 5th cycle. The results are shown in Fig. (3).

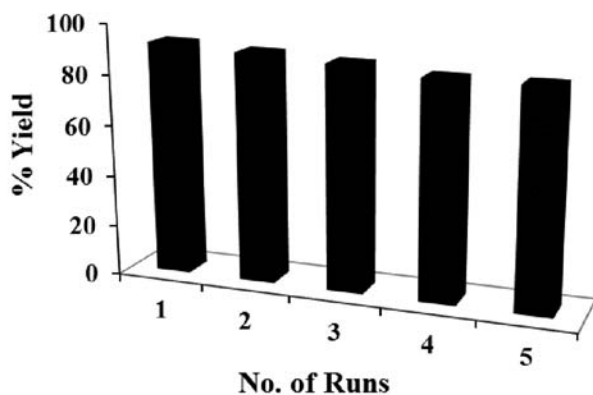


Fig. (3). Recycling efficiency of the resin-AuNPs in Hiyama coupling reaction.

Leaching of the catalyst under reaction conditions is generally studied as a probe to understand the reaction mechanism. Hot filtration test was performed to check the leaching of metal ions from the catalyst. The reaction between 4-iodoacetophenone and phenyltrimethoxysilane was stopped after 2 min and the resin was removed from the hot reaction mixture quickly. The filtrate was again heated in the microwave synthesizer and the concentration of product analyzed at different intervals of time. The results are given in Fig. (4). It was observed that the reaction did not proceed after removal of the catalyst. Additionally, the re-

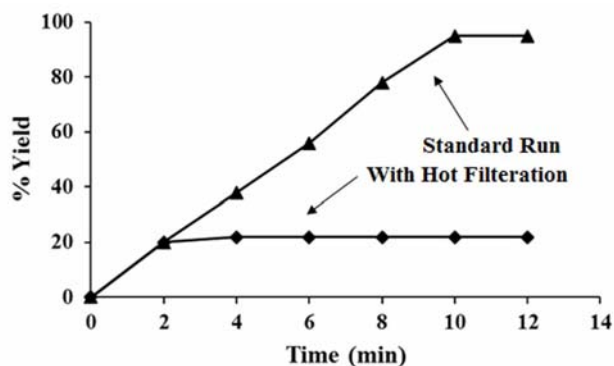
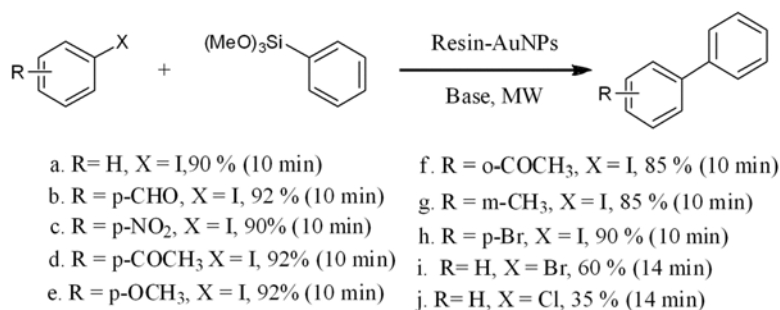


Fig. (4). Results of hot filtration test.

action mixture was analyzed for the presence of gold ions by ICP-AES. The concentration of gold could not be estimated in the solution. The absence of leaching points towards the heterogeneous nature of catalysis.

Hiyama reaction of aryl halides with phenyltrimethoxysilane, which is mostly catalyzed by palladium (Pd) catalysts, is a powerful and convenient synthetic method for the generation of biaryl in organic chemistry. We have for the first time reported AuNPs catalyzed Hiyama reaction. We carried out this reaction with other substituted iodobenzenes containing both electron withdrawing and electron releasing groups. The results are summarized in Scheme (1). A wide range of substituents, which include -CH₃, -CHO, -OCH₃, -NO₂, and -COCH₃, were compatible with this procedure. In all the cases, very high conversion of iodobenzenes was observed in short reaction times. Bromobenzene and chlorobenzene were also tried for coupling with phenyltrimethoxysilane but their reactivities were found to be lower than that of iodobenzene. This reaction confirms that order of reactivity for alkyl halides is I > Br > Cl. All the products formed were characterized by matching their ¹H NMR spectra with the reported data. The results are given in Appendix.



Scheme (1). Resin-AuNPs catalyst Hiyama cross-coupling reaction of various aryl halides with phenyltrimethoxysilane.

CONCLUSION

To the best of our knowledge, this is the first study of Hiyama cross-coupling reaction under microwave heating using resin supported gold nanoparticles. The reaction was completed in very short time in microwave (10-12 min), compared to conventional heating that required 6 to 12 hrs. Though, the reaction was slower compared to our earlier reported protocol with palladium nanoparticles, but we found that cleaning the gold nanoparticle impregnated resin was comparatively easy. The method can add to development of green and sustainable protocols for C-C coupling reactions.

Appendices NMR data of the Compounds

- a. **Biphenyl**, Colorless solid; Reported mp 68.5-71 °C; Observed mp 69 °C; **Measured ¹H NMR**: (CDCl₃ 400 MHz) δ 7.6 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 6.8 Hz, 1H). **Reported ¹H NMR [30]**: (CDCl₃ 400 MHz) δ 7.58 (d, *J* = 8.0 Hz, 4H), 7.39 (t, *J* = 8.0 Hz, 4H), 7.32 (t, *J* = 8.0 Hz, 2H).
- b. **4-Biphenylcarboxaldehyde**, Light yellow solid; Reported mp 57-60 °C; Observed mp 60 °C; **Measured ¹H NMR**: (CDCl₃ 400 MHz) δ 10.01 (s, 1H), 7.94 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 6.8 Hz, 2H), 7.49-7.41 (m, 3H). **Reported ¹H NMR [31, 32]**: (CDCl₃ 400 MHz) δ 10.04 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 6.8 Hz, 2H), 7.49-7.40 (m, 3H).
- c. **4-Nitrobiphenyl**, Pale yellow solid; Reported mp 112-114 °C; Observed mp 114 °C; **Measured ¹H NMR**: (CDCl₃ 400 MHz) δ 8.26-8.32 (m, 2H), 7.70-7.74 (m, 2H), 7.60-7.65 (m, 2H), 7.42-7.56 (m, 3H). **Reported ¹H NMR [31, 32]**: (CDCl₃ 400 MHz) δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 6.8 Hz, 2H), 7.53-7.43 (m, 3H).
- d. **4-Acetylbiphenyl**, Colorless solid; Reported mp 118-123 °C; Observed mp 117 °C; **Measured ¹H NMR**: (CDCl₃ 400 MHz) δ 8.01-8.04 (d, 2H), 7.68 (d, 2H), 7.61-7.63 (d, 2H), 7.44 (t, 2H), 7.38-7.41 (tt, 1H), 2.64 (s, 3H). **m/z** 181, 152, 127, 91 and 76. **Reported ¹H NMR [30,32]**: δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J*

= 8.0 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 1H), 2.63 (s, 3 H).

- e. **4-Methoxybiphenyl**, Colorless solid; Reported mp 86-89 °C; Observed mp 89 °C; **Measured ¹H NMR**: (CDCl₃ 400 MHz) δ 7.51-7.56 (m, 4H), 7.39 - 7.43 (m, 2H), 7.28 - 7.31 (t, 1H), 6.96 - 6.99 (m, 2H), 3.84 (s, 3H). **Reported ¹H NMR [30-32]**: (CDCl₃ 400 MHz) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.36-7.32 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.12 (s, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H).
- f. **2-Acetylbiphenyl**, Yellow Liquid; Reported bp 337 °C; Observed bp 335 °C; **Measured ¹H NMR**: (CDCl₃ 400 MHz) δ 7.53-7.55 (d, 1H), 7.45-7.51 (m, 1H), 7.36-7.43 (m, 5H), 7.31-7.33 (m, 2H), 1.99 (s, 3H). **Reported ¹H NMR [33]**: (CDCl₃ 400 MHz) δ 7.82-7.70 (m, 4H), 7.59-7.46 (m, 5H), 2.39 (s, 3H).
- g. **3-Methylbiphenyl**, Colorless Liquid; Reported bp 272 °C; Observed bp 270 °C; **Measured ¹H NMR**: (CDCl₃ 400 MHz) δ 7.56-7.58 (d, 2H), 7.37-7.41 (m, 4H), 7.33 (m, 2H), 7.11 (d, 1H), 2.43 (s, 3H). **Reported ¹H NMR [32]**: (CDCl₃ 500 MHz) δ 7.55 (d, *J* = 7.84 Hz, 2H), 7.41-7.28 (m, 6H), 7.13 (d, *J* = 7.84 Hz, 1H), 2.44 (s, 3H).
- h. **4-Bromobiphenyl**, Colorless Solid; Reported mp 82-86 °C; Observed mp 84 °C; **Measured ¹H NMR**: (CDCl₃ 400 MHz) δ 7.47-7.43 (m, 4H), 7.15-7.19 (m, 5H). **Reported ¹H NMR [30]**: (CDCl₃ 400 MHz) δ 8.70 (d, *J* = 4.8 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.77-7.71 (m, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.24-7.21 (m, 1H).

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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