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Review

Fe_3O_4 supported Pd(0) nanoparticles catalyzed alkoxycarbonylation of aryl halides

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ABSTRACT

This paper describes the simple and efficient method for the alkoxycarbonylation of aryl iodides using magnetically recoverable Pd/Fe_3O_4 as the catalyst under atmospheric pressure of carbon monoxide. Various aryl iodides on alkoxycarbonylation with alcohols gave the corresponding products in good to excellent yields. The catalyst is completely recoverable with the simple application of an external magnetic field, and the efficiency of the catalyst remains unaltered even after five cycles.

Contents

1. Introduction

The introduction of carbonyl group into arenes using carbonylation reactions is an interesting method among the array of catalytic conversions of aryl halides performed by palladium complexes [1–4]. "Classic" syntheses of aromatic esters or amides generally require a carboxylic acid precursor. Alternatively, aryl carboxylic acid derivatives can be prepared through palladium-catalyzed carbonylation of the corresponding aryl halides in the presence of a suitable nucleophile [5–8,2]. Advantages of this method include the broad availability of substrates and the high tolerance of palladium catalysts against a variety of functional groups. Therefore, this route has become a useful tool for the preparation of substituted benzoic acid derivatives.

Despite its well-known toxicity, CO is a very valuable and convenient reagent for a variety of reasons: (i) it is thermally

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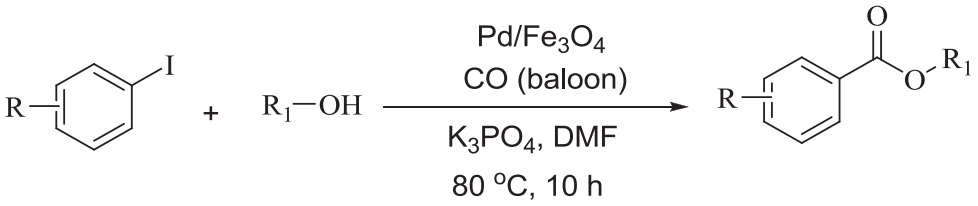


Scheme 1.

quite stable and yet chemically reactive and (ii) it is an inexpensive carbon source, which can be incorporated into a variety of organic compounds in its entirety without producing any undesirable byproduct. Since its toxicity problem can satisfactorily be dealt with in many instances, CO can be considered an environmentally friendly and convenient carbon source in an overall sense [9]. Consequently, considerable effort has been directed to the development of efficient and selective methods for the carbonylation using CO. Generally the phosphine ligands are used to complex and activate the palladium species, and excellent results have been reported for the palladium-catalyzed carbonylation reaction [10–13]. The use of such ligands is undesirable because of their toxicity and air as well as moisture sensitive with conversion to, for example, phosphine oxide species. However, few phosphine-free palladium catalysts have been used for the carbonylation of aryl halides under high pressure of carbon monoxide [14–17].

Despite the synthetic elegance the non-reusability of the precious palladium precludes wide synthetic applications in the industry. In view of the above, it is desirable to develop a ligand-free and reusable catalytic system for the carbonylation. Heterogeneous catalysis is particularly attractive as it allows the production and ready separation of large quantities of products with the use of a small amount of catalyst. However, heterogenized catalyst generally requires tedious preparation and/or separation procedures and there is a need to find new materials with speciality properties such as magnetic in order to overcome these limitations. Magnetic nanoparticles are a class of nanostructured materials of current interest, due largely to their advanced technological and medical applications, envisioned or realized [18–21]. Among the various magnetic nanoparticles under investigation, Fe_3O_4 nanoparticles are arguably the most extensively studied [22–24] and recently emerged as promising supports for immobilization metal nanoparticles. Fe_3O_4-supported metal catalysts can be separated from the reaction medium by an external permanent magnet [25–29]. Recently Palladium nanoparticles supported on Fe_3O_4 have been the subject of interest of several groups and widely used in a variety of organic reactions [30–33].

In the present work, we report our investigations on the application of Fe_3O_4 supported Pd(0) nanoparticles (Pd/Fe_3O_4) for the carbonylation of aryl halides with oxygen nucleophiles [34–36] using atmospheric pressure of carbon monoxide under ligand free conditions (Scheme 1).

2. Experimental

2.1. General

All chemicals were purchased from Sigma–Aldrich and S.D. Fine Chemicals, Pvt. Ltd. India and used as received. ACME silica gel (100–200 mesh) was used for column chromatography and TLC was performed on Merck precoated silica gel 60 F254 plates. All the other chemicals and solvents were obtained from commercial sources and purified using standard methods. The morphology, size and shape distribution of the Pd nanoparticles were recorded using TECNAI FE12 TEM instrument operating at 120 kV. The IR spectra of all compounds were recorded on a PerkinElmer, Spectrum GX FTIR spectrometer using KBr pellet method. The IR values are reported in reciprocal centimeters (cm^{-1}). The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. Chemical shifts (d) are reported in ppm, using TMS ($d = 0$) as an internal standard in $CDCl_3$. ESI mass spectra were recorded on a Finnigan LCQ Advantagemax spectrometer. EI mass spectra were recorded on a GC–MS QP2010 Plus (Shimadzu).

2.2. Preparation of the Pd/Fe_3O_4 catalyst [31]

1 g of dopamine-functionalized Fe_3O_4 nanoparticles were dispersed in water and $NaPdCl_4$ solution in water was added to the mixture to get 10 wt% of Pd. Diluted solution of hydrazine monohydrate was added drop wise to adjust the pH to 9. The reaction mixture was stirred overnight at room temperature and then allowed to settle. The product Pd/Fe_3O_4 was washed several times with water, centrifuged and dried at room temperature.

2.3. Typical experimental procedure for the alkoxycarbonylation of aryl iodides

A solution of the aryl iodide (1 mmol) and the alcohol (2 equiv.), K_3PO_4 (1.5 equiv.), Pd/Fe_3O_4 (1.5 mol% of Pd) in DMF (3 mL) was placed in a 10 mL reaction flask and fitted with condenser and carbon monoxide baloon. The resultant solution was stirred under carbon monoxide atmosphere at 80 °C temperature for 10 h. After completion of the reaction (monitored by TLC) the reaction flask was cooled to room temperature and carbon monoxide balloon was removed. The catalyst was easily separated from the reaction mixture with an external magnet. After removing the solvent from the reaction mixture, the crude material was chromatographed on silica gel using hexane–ethyl acetate mixture as eluent.

2.4. Reuse of catalyst

After completion of the reaction the catalyst was recovered by using external magnet and washed several times with ethyl acetate and then ether and dried for further reuse. The catalyst showed consistent activity for five cycles.

2.5. Spectroscopic data

All the products reported here are known compounds and the spectroscopic data was matched literature values. Data for the some of the compounds given below.

2.5.1. Butyl 4-methoxybenzoate (Table 2, entry 2)

IR (KBr): 2960, 1719, 1274, 1109 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.99 (t, 3H, $J = 7.4$ Hz), 1.45–1.54 (m, 2H), 1.69–1.79 (m, 2H), 3.85 (s, 3H), 4.27 (t, 2H, $J = 6.6$ Hz), 6.87 (d, 2H, $J = 8.8$ Hz), 7.95 (d, 1H, $J = 8.8$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 13.6, 19.1, 30.7, 55.2, 64.3, 113.4, 122.8, 131.3, 163.1, 166.2. ESI MS (m/z): 209 (M+H).

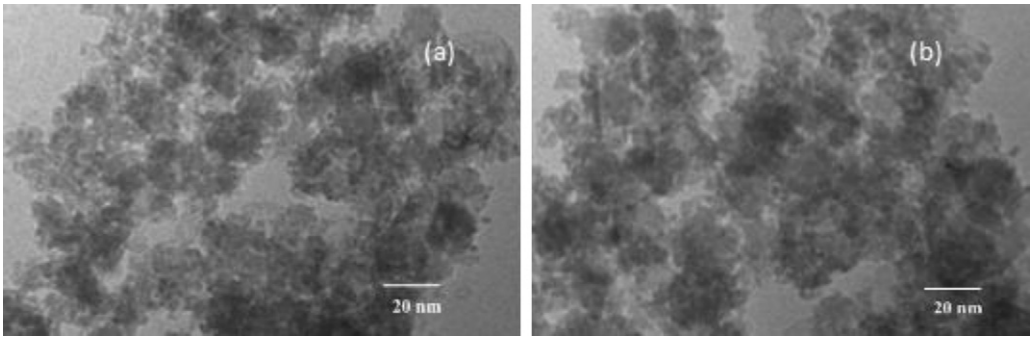


Fig. 1. TEM images of Pd/Fe_3O_4 nanoparticles: (a) fresh catalyst and (b) catalyst after five cycles.

2.5.2. Phenyl 4-methoxybenzoate (Table 2, entry 4)

IR (KBr): 2910, 1712, 1606, 1168, 1029, 770 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.89 (s, 3H), 6.94 (d, 2H, J = 9.1 Hz), 7.15–7.26 (m, 3H), 7.36–7.42 (m, 2H), 8.13 (d, 2H, J = 8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 55.5, 113.8, 121.7, 125.6, 129.4, 132.2, 151.0, 163.8, 164.8. ESI MS (m/z): 229 (M+H).

2.5.3. Butyl 2-methylbenzoate (Table 3, entry 3)

IR (KBr): 2985, 1722, 1259, 1085, 831 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.99 (t, 3H, J = 6.8 Hz), 1.48–1.56 (m, 2H), 1.72–1.78 (m, 2H), 2.59 (s, 3H), 4.28 (t, 3H, J = 6.4 Hz), 7.18–7.22 (m, 2H), 7.35 (t, 1H, J = 7.5 Hz), 7.88 (d, 1H, J = 7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 13.6, 19.2, 21.6, 30.6, 64.4, 125.5, 129.8, 130.3, 131.5, 131.6, 139.8, 167.6. EI MS (m/z): 198 (M^+).

2.5.4. Butyl 4-chlorobenzoate (Table 3, entry 6)

IR (KBr): 2943, 1712, 1606, 1261, 1023, 776 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.99 (t, 3H, J = 6.8 Hz), 1.46–1.55 (m, 2H), 1.71–1.81 (m, 2H), 4.33 (t, 2H, J = 6.0 Hz), 7.29 (ddd, J = 1.5 Hz, 7.5 Hz, 14.3 Hz), 7.36–7.45 (m, 2H), 7.79 (dd, 1H, J = 1.5 Hz, 7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 13.5, 19.1, 30.4, 65.2, 126.3, 130.3, 130.8, 131.1, 132.2, 133.3, 165.6. ESI MS (m/z): 213 (M+H).

2.5.5. Butyl 4-acetylbenzoate (Table 3, entry 9)

IR (KBr): 2973, 1703, 1689, 1278, 989 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.99 (t, 3H, J = 7.5 Hz), 1.43–1.56 (m, 2H), 1.73–1.82 (m, 2H), 2.62 (s, 3H), 4.35 (t, 2H, J = 6.8 Hz), 7.97 (d, 2H, J = 8.3 Hz), 8.10 (d, 2H, J = 8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 13.7, 19.2, 26.8, 30.6, 65.2, 128.1, 129.7, 134.2, 140.1, 165.7, 197.5. ESI MS (m/z): 221 (M+H).

3. Results and discussion

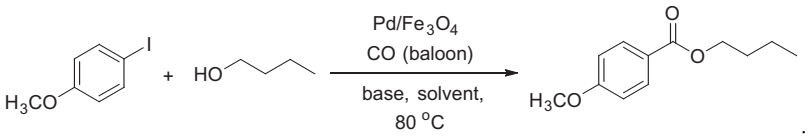
The amount of palladium in the prepared Pd/Fe_3O_4 catalyst was determined with an inductively coupled plasma, atomic emission spectroscopy (ICPAES) instrument and palladium content was measured as 0.14 mmol g^{-1}. The TEM images of both the fresh and used catalyst, it is seen that the average size of Fe_3O_4 nanoparticles is in the range of 20–25 nm in diameter and palladium nanoparticles of about 2–3 nm and are dispersed on Fe_3O_4 nanoparticles (Fig. 1). Furthermore, the TEM image (Fig 1(b)) clearly confirms no change in the morphology even after five cycles.

In an endeavor to identify the best catalytic system for the alkoxycarbonylation various bases in combination with different solvents were investigated using 4-iodoanisole as aryl halide and *n*-butanol as the nucleophile and the results are presented in Table 1. The bases used in this study include NEt_3, K_2CO_3, Na_2CO_3, K_3PO_4 and Cs_2CO_3, out of which K_3PO_4 and Cs_2CO_3 are equally effective and gave the product in good yield. Whereas, K_2CO_3, Na_2CO_3 gave the product in moderate yield (Table 1, entries 2–5). However, by maintaining carbon monoxide 0.5 kg/cm^2 (0.48 atm of CO) pressure in the presence triethylamine as the base gave the product in good yield (Table 1, entry 1). Among the different solvents used *N*,*N*-dimethylformamide (DMF) proved to be the good solvent and the reactions with other solvents such as DMA, DMSO and Toluene generate the desired product in moderate to low yields (Table 1, entries 6–8).

Proposed mechanism for the Pd/Fe_3O_4-catalyzed carbonylation of aryl halides under ambient pressure of CO (Fig. 2).

The best reaction conditions found on the model substrates were applied to different alcohols to obtain the corresponding ester derivatives as shown in Table 2. Isopropanol, *n*-butanol and *t*-butanol gave the product in moderate to good yields (Table 2,

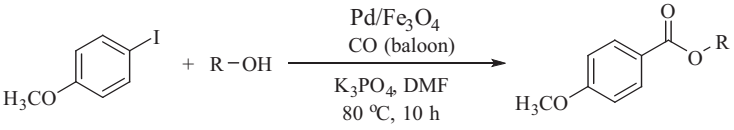
Table 1
Optimization of reaction conditions for the Pd/Fe_3O_4-catalyzed carbonylation of aryl halides under ambient pressure of CO.[a]

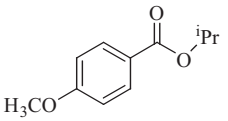
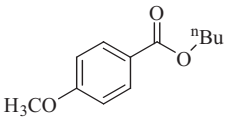
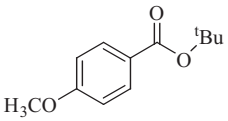
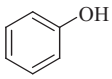
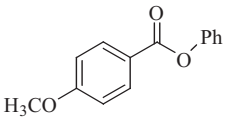
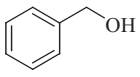
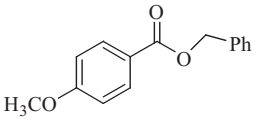


Entry	Base	Solvent	Yield (%)
1	NEt_3	DMF	82
2	K_2CO_3	DMF	60
3	Na_2CO_3	DMF	55
4	K_3PO_4	DMF	83
5	Cs_2CO_3	DMF	85
6	K_3PO_4	DMSO	68
7	K_3PO_4	DMA	75
8	K_3PO_4	Toluene	27

[a] Reaction conditions: 4-bromoanisole (1 mmol), *n*-butanol (2 equiv.), base (1.5 equiv.), Pd/Fe_3O_4 (1.5 mol%), solvent (3 mL) stirred at 80 °C, under CO atmosphere for 10 h.

Table 2
Generalization of Pd/Fe_3O_4-catalyzed alkoxycarbonylation reaction using different alcohols under ambient pressure of CO.[a]



Entry	R-OH	Product	Yield (%)[b]
1	$(CH_3)_2CHOH$		75
2	C_4H_9OH		85
3	$(CH_3)_3COH$		70
4			91
5			95

[a] Reaction conditions: 4-iodoanisole (1 mmol), alcohol (isopropanol (10 equiv.), *n*-butanol, *t*-butanol (2 equiv.), phenol, *p*-methyl benzyl alcohol (1.2 equiv.)), Pd/Fe_3O_4 (1.5 mol% of Pd), base (1.5 equiv.), DMF (3 mL) and reaction stirred at 80 °C, under CO atmosphere for 10 h.
[b] Isolated yield.

entries 1–3). Whereas, phenol and benzyl alcohols gave esters in very good yield (Table 2, entries 4 and 5).

Encouraged by these results, we next investigated the scope of the reaction with respect to the aryl iodide substrate. We tested a variety of substituted aryl iodides under the optimized reaction conditions with *n*-butanol as a oxygen nucleophile. Various aryl iodides, including the deactivated aryl iodides, were readily converted to the corresponding coupled products in excellent yields as shown in Table 3. Unsubstituted as well as 4-methyl, 4-methoxy substituted iodobenzenes underwent smooth reaction with good yields when compared to 2-methyl-iodobenzene (Table 3, entries

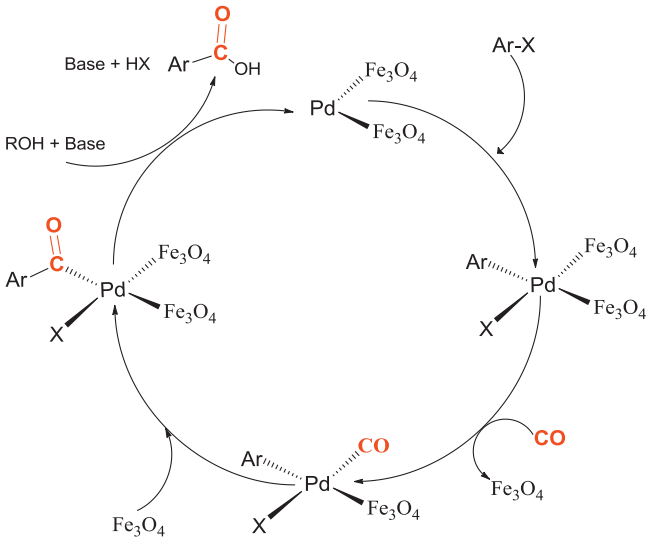


Fig. 2. Proposed mechanism for the Pd/Fe_3O_4-catalyzed carbonylation.

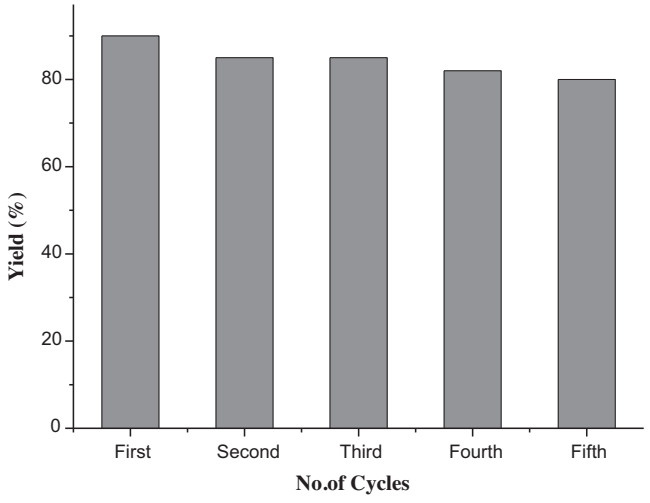
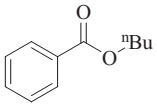
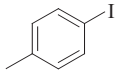
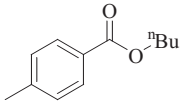
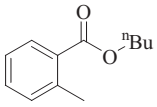
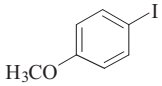
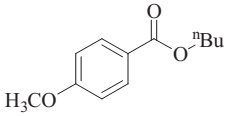
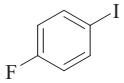
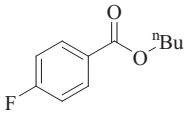
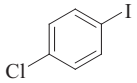
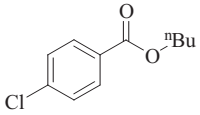
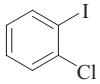
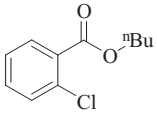
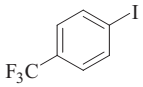
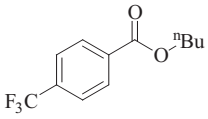
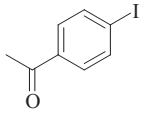
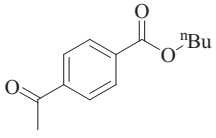


Fig. 3. Recovery and reuse of Pd/Fe_3O_4 catalyst for the alkoxycarbonylation of iodobenzene with *n*-butanol as nucleophile under ambient pressure of CO (reaction conditions: iodobenzene (1 mmol), *n*-butanol (2 equiv.), Pd/Fe_3O_4 (1.5 mol% of Pd), base (1.5 equiv.), DMF (3 mL) and reaction stirred at 80 °C, under CO atmosphere for 10 h. Isolated yield).

Table 3
Pd/Fe_3O_4-catalyzed alkoxycarbonylation of different aryl iodides with *n*-butanol as nucleophile under ambient pressure of CO.[a]

Entry	Aryl halide	Product	Yield (%)[b]
1			90
2			82
3			66
4			85
5			85
6			92
7			78
8			90
9			91

[a] Reaction conditions: aryliodide (1 mmol), *n*-butanol (2 equiv.), Pd/Fe_3O_4 (1.5 mol% of Pd), base (1.5 equiv.), DMF (3 mL) and reaction stirred at 80 °C, under CO atmosphere for 10 h.
[b] Isolated yield.

1–4). Among the different halogen substituted aryl iodides 4-chloro-iodobenzene gave the product in good yield (Table 3, entries 5–7). Furthermore, the reaction was extended to other aryl iodides having electron withdrawing groups such as trifluoromethyl and acetyl groups at para position to generate esters in good to excellent yields (Table 3, entries 8 and 9).

To check the reusability of the catalyst, as can be seen from Fig. 3, the reaction was performed with iodobenzene and *n*-butanol under the optimized reaction conditions. The catalyst was separated from the reaction mixture by applying external magnetic field and reused for five times without significant loss of catalytic activity. Inductively coupled plasma (ICP) mass-spectrometric analysis of the filtrate from the reaction mixture demonstrated that the palladium metal hardly leached into the solution within the limits of the detector (1 ppm), thus suggesting that the present alkoxycarbonylation reaction proceeded by heterogeneous catalysis.

4. Conclusion

In conclusion, we have developed a simple and efficient method for the alkoxycarbonylation of aryl iodides with different alcohols using magnetically recoverable Pd/Fe_3O_4 at atmospheric CO pressure under ligand free conditions. The catalyst is completely magnetically recoverable because of the superparamagnetic behavior of Fe_3O_4 and the efficiency of the catalyst remains unaltered even after 5 cycles. The operational simplicity and the mild reaction conditions add to the value of this method as a practical alternative to the alkoxycarbonylation.

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