Journal of Molecular Catalysis A: Chemical 398 (2015) 164–169

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Palladium supported on triphenylphosphine functionalized porous organic polymer: A highly active and recyclable catalyst for alkoxycarbonylation of aryl iodides

Yizhu Lei, Linjuan Wu, Xuefeng Zhang, Hui Mei, Yanlong Gu*, Guangxing Li*

Key Laboratory for Large-Format Battery Materials and System, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Luoyu Road 1037, Wuhan, Hubei 430074, PR China

ARTICLE INFO

Article history:
Received 11 July 2014
Received in revised form 2 December 2014
Accepted 6 December 2014
Available online 10 December 2014

Keywords:
Carbonylation
Palladium
Heterogeneous catalyst
Porous organic polymer

ABSTRACT

An efficient method for the alkoxycarbonylation of aryl iodides using palladium supported on triphenylphosphine functionalized porous organic polymer (Pd@KAPs(Ph-PPh_3)) as the catalyst is reported. Under balloon pressure of CO, various aryl iodides on carbonylation with alcohols and phenols give the corresponding products in moderate to excellent yields (74–96%). The catalyst can be easily separated by simple filtration process and recycled up to ten times without significant decrease in activity. The salient features of this protocol are the simplicity in handling of the catalyst, low CO pressure, negligible palladium leaching and good catalyst recyclability.

1. Introduction

Palladium catalyzed carbonylation reactions of aromatic halides in the presence of various nucleophiles represent a powerful method for the synthesis of a diverse array of benzoic acids and aryl ketone derivatives [1–3]. This field of research has attracted great interest because of its high compatibility to a wide variety of functional groups [4–9]. Nevertheless, there is still a constant strive dedicated to the developments of new carbonylative transformations, new catalysts, as well as to the improvement of existing Pd-catalyzed carbonylation reactions, including the heterogenization of homogeneous catalysts, the identification of milder reaction conditions, the use of lower carbon monoxide pressures and the development of carbon monoxide surrogates [4–9]. A number of research groups has been highly active in this field and has achieved great success including those of Beller and co-workers [10–18], Buchwald and co-workers [19–21], and Alper and co-workers [22–24]. Palladium catalyzed alkoxycarbonylation is an alternative route for ester synthesis, which has a number of advantages over the traditional methods that use carboxylic acid derivatives and alcohols or phenols. This new route is able to produce esters from inexpensive and easily available feedstock such as carbon monoxide and organic halides in the presence of suitable alcohols or phenols [25,26]. Although homogeneous catalysts have been extensively investigated, their practical applications on a large scale remain a big challenge because the catalysts are expensive and it is difficult to recover the metal and remove residual metal from the product, which is very important for pharmaceutical uses. In order to address these problems, heterogeneous Pd catalysis is a promising option [27,28]. Researchers have immobilized palladium complexes on various supports such as activated carbon [29–32], silica [33–36], MCM-41 [37], organic polymer [38,39], SBA-15 [40,41], ZIF-8 [42], Fe_3O_4 [43], and MOF-5 [44] to create heterogeneous catalysts for carbonylation of aryl halides. The latest and impressive heterogeneous catalyst example reported is the use of immobilized palladium metal-containing ionic liquid as a catalyst for the alkoxycarbonylation and aminocarbonylation of aryl iodides. Using this catalyst, high activities were achieved under 0.5–1.0 MPa CO pressure, and the catalyst could be recycled 4 times [45]. However, the main challenges remained in developing active and stable heterogeneous catalysts to carry out the reaction under mild reaction conditions and addressing the contamination of the leached metal impurities in the product.

The combination of the advantageous properties of molecular and solid catalysts was considered as the “Holy Grail” in catalysis research. Great potential was provided recently by porous polymers [46]. Porous organic polymers (POPs), emerged just in a few years ago, have attracted great attention due to their unique prop-

---

* Corresponding authors. Tel.: +86 27 87543032; fax: +86 27 87544532/3632.
E-mail addresses: klgyl@hust.edu.cn (Y. Gu), ligxabc@163.com (G. Li).

http://dx.doi.org/10.1016/j.molcata.2014.12.008

erties such as large surface area, low skeletal density, and high chemical stability [47]. One particular advantage of POPs is its ability to introduce a broad range of useful chemical functionalities into the porous framework. Porous organic polymers containing functional units such as phthalocyanine, bipyridine, porphyrins, and triazine rings have been reported, and these materials exhibited excellent catalytic activity in catalytic reactions [46]. Recently, palladium supported on triphenylphosphine-functionalized microporous knitting aryl network polymers (Pd@KAPs(Ph-PPh_3)) has been used in Suzuki reactions [47]. And it has displayed many advantages such as good reusability of the expensive metal and phosphine ligand, the abundant open micropore and macroporous structure that is favorable for catalysis process and the possibility to prevent the contamination of palladium and ligand residue in products. However, to the best of our knowledge, such porous polymer-supported palladium catalyst has not been used in carbonylation reactions.

In continuation of our interest on carbonylation reactions [48–50], herein we report a facile protocol for the atmospheric pressure carbonylation of aryl iodides with alcohols and phenols using Pd@KAPs(Ph-PPh_3) as an efficient, heterogeneous and recyclable catalyst.

2. Experimental

2.1. Reagents and characterization

Benzene, triphenylphosphine, $PdCl_2$, $FeCl_3$ (anhydrous) and 1,2-dichloroethane (DCE), acetonitrile were obtained from National Medicines Corporation Ltd., of China, all of which were of analytical grade and were used as received. Palladium on carbon (Pd/C, 5 wt%), aryl iodides, alcohols, phenols, and bases were of analytical reagent grade and commercially available. Formaldehyde dimethyl acetal (Alfa Aesar, 98%) was also used as received. All solvents were analytical grade and distilled prior to use. FT-IR spectra were recorded under ambient conditions in the wave number range of 4000–400 cm^{-1} using a Bruker Equinox 55 FTIR spectrophotometer. Pd content data were obtained on AAS using a PerkinElmer AA-300 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ on a Bruker AVANCE III 400 MHz spectrometer at room temperature using tetramethylsilane (TMS) as an internal reference.

2.2. Preparation of the catalysts

The Pd@KAPs(Ph-PPh_3) [47], Pd/Fe_3O_4 [43] were prepared according to the literature. $PdCl_2$(phen)@Y was prepared as we reported previously [48].

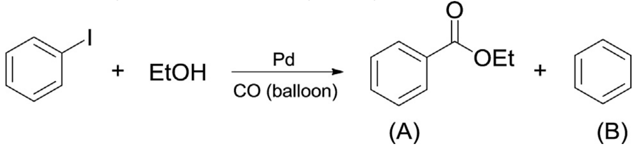
2.3. Typical procedure for carbonylation reactions

The catalytic reactions were carried out in a 10 mL reaction flask and fitted with condenser and carbon monoxide balloon. In a typical run, a catalyst containing 1.0 mol% Pd, aryl iodide (0.5 mmol) and DBU (1.5 mmol) were added to solvent and allowed to react under CO atmosphere at 80 °C temperature for 6–10 h. After the reaction, the flask was cooled to room temperature and carbon monoxide balloon was removed. The reaction mixture was then centrifuged and the clear supernatant was analyzed with GC by using *n*-butanol as an internal standard. For the study of substrate scope, after completion of the reaction, the catalyst was centrifuged and extracted with copious ethanol. The obtained liquid was concentrated. For phenoxycarbonylation, the obtained liquid was diluted with saturated NH_4Cl and extracted with diethyl ether. The organic layer was dried over anhydrous Na_2SO_4 and then concentrated. The product was obtained by preparative thin-layer chromatography (PTLC) using petroleum ether and ethyl acetate (30:1, v/v) as eluting solvent. The purity of products was checked by NMR and yields were based on aryl iodides.

3. Results and discussion

The Pd@KAPs(Ph-PPh_3) was characterized by Fourier transform infrared (FTIR) spectroscopy and atomic absorption spectrum (AAS). FTIR spectroscopy of KAPs(Ph-PPh_3) and Pd@KAPs(Ph-PPh_3) (Fig. S1 of Supplementary content) displays a series of bands around 1600–1450, 1250–950, and 900–650 cm^{-1} which can be attributed to benzene skeleton stretching, C—H out-of-plane bending and in-

Table 1
Effect of catalysts and bases on ethoxycarbonylation of iodobenzene.[a]



Entry	Catalyst	Pd [wt%]	Base	Yield A (%)[b]	Yield B (%)[b]
1	Pd@KAPs(Ph-PPh_3)	0.8	Et_3N	76	0
2	Pd/C	5	Et_3N	34	0
3	Pd/Fe_3O_4	10	Et_3N	19	0
4	$PdCl_2$(phen)@Y	2.1	Et_3N	17	0
5	Pd@KAPs(Ph-PPh_3)	0.8	K_2CO_3	45	55
6	Pd@KAPs(Ph-PPh_3)	0.8	$CsCO_3$	9	90
7	Pd@KAPs(Ph-PPh_3)	0.8	Na_2CO_3	49	49
8	Pd@KAPs(Ph-PPh_3)	0.8	$K_3PO_4 \cdot 3H_2O$	6	91
9	Pd@KAPs(Ph-PPh_3)	0.8	$NaHCO_3$	86	0
10	Pd@KAPs(Ph-PPh_3)	0.8	$KHCO_3$	91	0
11	Pd@KAPs(Ph-PPh_3)	0.8	Na_2HPO_4	5	0
12	Pd@KAPs(Ph-PPh_3)	0.8	K_2HPO_4	30	0
13	Pd@KAPs(Ph-PPh_3)	0.8	DBU	99	0
14[c]	Pd@KAPs(Ph-PPh_3)	0.8	DMAP	8	0
15	Pd@KAPs(Ph-PPh_3)	0.8	Pyridine	5	0
16[d]	Pd@KAPs(Ph-PPh_3)	0.8	DBU	85	0

[a] Reaction conditions: Pd catalyst (1.0 mol%), iodobenzene (0.5 mmol), base (1.5 mmol), EtOH (3 mL), 80 °C, 6 h, CO (1 atm).
[b] GC yield.
[c] DMAP = 4-dimethylaminopyridine.
[d] Pd catalyst was used in 0.5 mol%.