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Biomass rice husk derived carbon supported Pd Nanocatalyst is an effective catalyst for carbonylative Suzuki-Miyaura cross coupling reaction

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Abstract
The catalytic performance of a Pd nanocatalyst derived from bio rice husk derived graphitic like carbon and palladium chloride has been investigated for the first time in the phosphine free carbonylative Suzuki- Miyaura cross coupling of iodobenzene and phenyl boronic acid in mild reaction conditions. The present catalytic system exhibited remarkable activity and selectivity in the synthesis of biaryl ketones. The high activity, selectivity and stability of this catalyst may be due to firm attachment of palladium nanoparticles to zigzag porous networked carbon support, confinement effect in porous system and nanoscale palladium particles.

Keywords: biomass, nanocatalyst, carbonylative, suzuki-miyaura

Introduction

As demand for sustainable materials with low price tag and concerning ecological issues, the innovations for novel materials have been grown. Utilization of waste or by-products from diverse industries, the crop growing sector has received increasing attention in the scientific, environmental and economic spheres in recent years [1]. Rice husk (RH) and Rice husk ash (RHA) are the by-products of manufacturing process of rice. Both RH and RHA are abundantly available in rice growing countries such as China, India, Brazil, the USA, and Southeast Asia. As it is reported that per annum around 150 metric tons of rice husk (RH) is produced globally, which is generating 28 metric tons of RHA through it burning according to 2017 metrics [2]. As a by-product obtained from the rice mill, RHA has very little or no industrial value and normally will finish up as a waste which generates disposal and health problems to the people. At this juncture, researchers are coming up with innovative thoughts to produce useful chemicals from RH. Production of valuable chemicals from sustainable biomass derived waste has significant importance. The useful chemicals like silica, carbon-silica and active carbon can be extracted from RH through different treatments. Porous silica materials synthesized from RH have numerous applications such as monoliths (ice-templating of RH ash) [3], low-toxic in vivo applications [4], high potential adsorbent for heavy metals like lead and copper from Industrial and domestic effluents [5]. In addition to the above applications, hierarchical porous carbon materials such as porous structured carbons with micro, meso and macro pores, which acquired massive attention as catalytic support materials. Similar to the ordered porous materials, RH derived carbons also possess high surface area and honey comb like morphology offer a best platform for the immobilization of metal nanoparticles. Porous graphitic like carbon materials possess abundant amounts of oxygen and C=C containing functional groups, which are responsible for tightly holding of the deposited nanoparticles in the carbon matrices, leading to increased stability of the catalysts. Aromatic ketones are essential structural components in biologically active natural products, pharmaceuticals and agrochemicals. In 1993 for the first time, Suzuki and his group reported the synthesis of biaryl ketones via carbon monoxide gas insertion, which reflected as a platform mode for many carbonylative coupling reactions [6-11].

In general, synthesis of bi-aryl ketones usually performed via Friedel-crafts acylation of arenes [12, 13]. This typical protocol needs stoichiometric amount of Lewis acid (anhydrous AlCl3) for acylation of benzoic acid derivatives in presence of organometallic reagents, leading to large amount of waste and result in poor regio-selectivity. Fries rearrangements, is also a known methodology, but is applicable to phenol derivatives, thus have limited the scope [14-23]. Among the alternative carbonylative coupling methods, transition metal catalyzed three components cross coupling between electrophilic aryl halide, aryl metal reagents and carbon monoxide is a convenient route for the synthesis of unsymmetrical biaryl ketones [24].

Of late, diverse CO substitute molecules like N-formyl saccharin, aryl formates, chloroform and par formaldehyde formic acid, and various techniques have been applied to generate CO sedentary instead of gaseous carbon monoxide intended for carbonylative coupling of iodo and bromo benzene [25-33]. Even though these in-situ CO generating precursors are harmless, selective carbonylative coupling product may not be accomplished with good yield and also the reaction may lead to direct coupling products. Even in Suzuki carbonylation reactions, the formation of a significant amount of biaryl product without carbon monoxide inclusion is the major limitation. The amount of ketone formation mainly depends on the nature of support, solvent and substrates including reaction temperature and pressure.

Since the past few decades various heterogeneous catalysts have been synthesized and used for carbonylative coupling reactions. Most of these catalysts contain Pd as an active metal component and supports are different varieties. Some important catalysts are listed as follows: Pd/AC [34], Pd(II)/MCM-41-2P(PdII) [35], Fe3O4@PANI(PdII) [36], Fe3O4@SiO2–SH–PdII [37], ImmPd-IL [38]. The materials used for the corresponding catalysts are highly expensive, difficult to prepare, non-ecological, involves time taking process and results low yields, less than 96% of benzophenone.

As a part of our ongoing interest in developing metal nanocatalysts using different silica materials as support for various organic transformations [39-45], herein, for the first time we have described the synthesis and characterization of Pd nanocatalyst scraped from rice husk derived graphitic like carbon and its catalytic application of phosphine free carbonylative Suzuki- Miyaura cross coupling of iodobenzene and phenyl boronic acid in mild reaction conditions.

Preparation of Catalysts

100 g of RH was weighed, washed thoroughly with distilled water to remove adhering soil, dried in an oven at 273 °C for 24 h. The dried RH was refluxed with 3N HCl solution at 100 °C for 1 h, subsequently filtered and washed repeatedly with warm distilled water to remove the acid completely. Dried it again at 100 °C for 24 h and calcined at 600 °C in an inert atmosphere for 3 h. The resulting RH grains were collected in a mortar and grinded into small particles using pestle. The obtained carbon-silica material was treated with 25% NaOH solution to get desired graphitic carbon.

PdNPs/C catalysts were prepared by dispersing graphitic like carbon in the solution of palladium chloride followed by reducing with hydrazine hydrate.

Catalytic Activity Test

The catalytic activity of PdNPs/C in C=O Coupling reaction has been carried out in the liquid phase at 120 °C. In a typical procedure 1mmol of reactant, 1.25mmol of phenyl boronic acid, 50mg of catalyst and 8ml solvent were added to a 50 ml flask and stirred at 3 bar CO pressure. After completion the products were extracted with ethyl acetate and the catalyst was removed by centrifugation. The product analysis was made by GC–MS (QP- 5050 model, M/s. Shimadzu Instruments, Japan) equipped with ZB-5 capillary column (0.32 mm dia. and 25 m long, supplied by M/s. J & W Scientific, USA).

Results and Discussion

Table 1: Textural and structural parameters of catalyst samples

				Pd Loadingd	
	SBETa m2/g	**Vtb cc/g**	**Dc nm**	**Theoritical**	**ICP-OES**
Carbon	517	0.4	3.3	-	-
0.5PdNPs/Carbon	504	0.4	4.0	0.5	0.43
1PdNPs/Carbon	477	0.3	4.18	1	0.89
2PdNPs/Carbon	232	0.1	3.28	2	1.86

Table 1 displays the textural parameters which include the BET surface area, average pore diameter and the total pore volumes of the carbon support and the synthesized PdNPs loaded carbon catalysts. The RH derived carbon support possesses a surface area of 517 m2/g, 0.4 cc/g pore volume and 3.3 nm pore diameter. A slight decrease in surface area and pore volume are observed with the addition of Pd loadings, probably due to surface blocking phenomenon by Pd nanoparticles over the surface of carbon support. The increase in pore diameter with the addition of PdNPs to the support suggests that the Pd metal nanoparticles are settling within the pore structure of the support, which will enhance the catalyst stability and minimize the leaching phenomenon. The ICP-AAS analysis results of PdNPs/Carbon catalysts suggest that the PdNPs loadings in synthesized catalysts are more or less equal to theoretically calculated loadings.

The TEM image of the as-prepared 1PdNPs/Carbon catalyst is shown in Figure 5. It clearly shows that Pd nanoparticles were homogenously distributed on the surface of the carbon materials, and no significant aggregation of Pd nanoparticles was observed. These results revealed that Pd nanoparticles would have a strong interaction with the carbon materials.

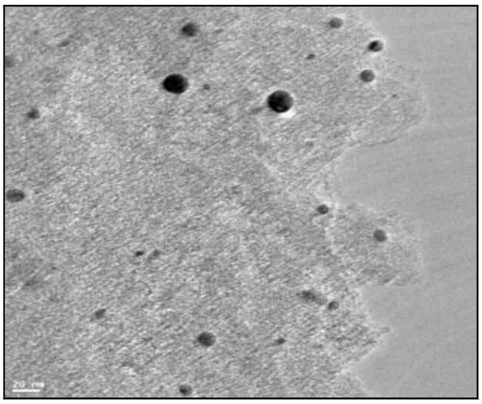


Fig 1: TEM images of 1PdNPs/Carbon catalyst

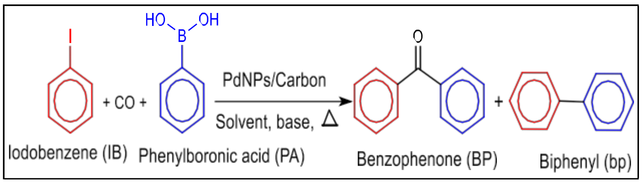
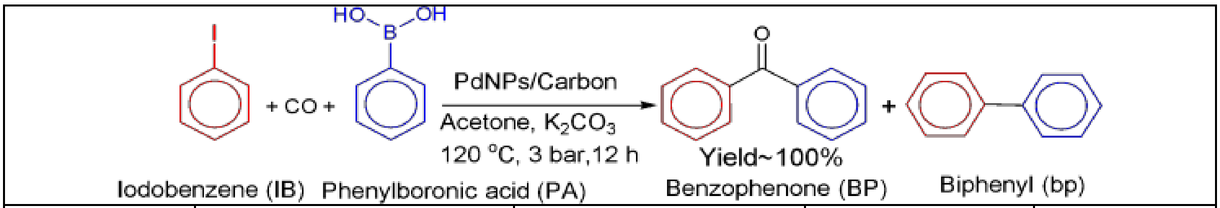


Fig 2: Carbonylative Suzuki- Miyaura cross coupling of iodobenzene and phenyl boronic acid

Table 2: Effect of reaction time and pressure of operation over1PdNPs/Carbon catalyst:



Time(h)	Pressure (bar)	Conv.IB (%)	Sel.BP (%)	Sel. Biph (%)
12	2	93	91	9
4	3	50	>99	<1
8	3	72	>99	<1
12	3	99	>99	<1

Conditions: IB = 1 mmol, PA = 1.25 mmol, K2CO3 = 2 mmol), acetone = 8 ml, Catalyst = 50 mg, temperature = 120 °C and pressure = 3 bar

Since reuse is one of the key components for the heterogeneous transition metal-catalyzed reaction from the view point of green chemistry and cost performance, reuse of the 1PdNPs/Carbon catalyst was attempted in similar reaction conditions. No significant loss of the catalytic activity was observed in four repeated cycles, indicating the versatility of the catalyst.

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