Application of $Cu_2(BDC)_2$DABCO Encapsulated Palladium Nanoparticle in Suzuki Coupling

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Abstract

In this paper palladium nanoparticle encapsulated in mesoporous metal-organic framework $Cu_2(BDC)_2$(DABCO) (BDC=1,4-benzenedicarboxylate, DABCO= 1,4-diazabicyclo[2.2.2]octane) and employed as a heterogeneous catalyst for the synthesis of biphenyl by Suzuki coupling. The Pd@MOFs offered higher catalytic activity than common Palladium salts such as $Pd(OAc)_2$, $PdCl_2$.

Keywords: Palladium nanoparticles, encapsulation, Metal organic framework, C-C coupling reaction, Suzuki reaction

1 Introduction

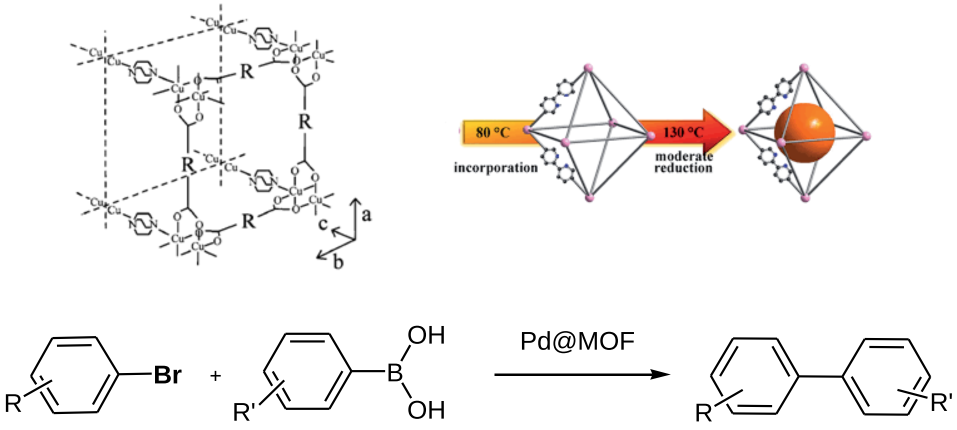
Formation of carbon-carbon bond is a fundamentally important subject in nature and the synthetic world [1-3]. At the center of the rapidly evolving green revolution in chemistry [4] catalysis plays an important role [5]. Without catalytic process, it would be unconceivable to aim for a sustainable chemical industry [6]. When it comes to organometallic catalysis, special attention is dedicated to the recycling of metallic species [7].

Palladium-catalyzed carbon–carbon bond formation via cross coupling plays an important role in modern organic chemistry for synthesize of complex organic molecules [8, 9]. In this area, application of palladium nanoparticles (Pd NPs) as green and efficient heterogeneous catalysts has attracted a considerable attention [10–12]. Palladium-catalyzed Suzuki–Miyaura coupling reaction is one of the most powerful methods to constructing biaryl units in organic synthesis [13,14]. Based on palladium, homogeneous catalytic system has played a significant role in organometallic catalysis [15]. However, homogeneous catalyst suffers from instability, non-reusability and difficulty to separate from the reaction system. Hence, to develop Pd catalyst with excellent recyclability and reusability has the great significance in sustainability development and protecting the environment. In order to achieve this task, heterogeneous catalytic system has been employed in recent years.

Recently, Metal–organic frameworks (MOFs), as a new class of organic inorganic hybrid porous materials, have attracted considerable attention for stabilization of metal nanoparticles as a novel class of functional materials due to their high surface areas, tunable pore sizes, and thermal stability. Owing to these outstanding properties, MOFs have been employed in gas storage [16, 17], catalysis [18, 19], adsorption [20], super-capacitor [21], and drug delivery [22]. In recent years, the employment of MOFs as the supports for Pd NPs has attracted considerable interest [24-26]. For catalytic applications, Pd NPs have been successfully deposited at the outer surface of the MOF supports (Pd/MOFs) [27–32] or loaded inside the cavities of the MOFs (Pd@MOFs) [35–41] via various methods such as impregnation [27–39] and chemical vapor deposition [40].

$Cu_2(BDC_2)$DABCO is a good example of highly stable MOFs. $Cu_2(BDC)_2$ DABCO is a copper based, metal–organic framework that connected through benzene fragment to produce a cubic closed pack structure.

In this study, $Cu_2(BDC_2)$DABCO has been shown to act as a proper support for deposition of Pd NPs. Using a simple and fast reduction method, Pd^{+2} cations are converted to Pd^o nanoparticles deposed on the surface of activated $Cu_2(BDC)_2$ DABCO carriers. The prepared Pd@$Cu_2(BDC)_2$DABCO nanocomposite show good catalytic activity and reusability in the Suzuki coupling reaction of aryl halides with benzeneboronic acid under mild reaction conditions in an ethanol–water green solvent mixture.



Scheme 1. Schematic representation of Pd@$Cu_2(BDC)_2$DABCO catalyst preperation

2 Experimental

2.1 Materials and instruments

All reagents including organic linker H_2BDC, metal salt $Cu(OAc)_2.H_2O$, 1,4 benzenedicarboxylate (BDC, 99%), 1,4-diazabicyclo[2.2.2]octane (DABCO), Palladium chloride ($PdCl_2$), aryl halides, arylbronic acids, potassium carbonate (K_2CO_3), anhydrous ethanol (EtOH) and N,N dimethyl formamides (DMF) were obtained from commercially available sources such as Sigma–Aldrich and Merck without any purification. X-ray powder diffraction (XRD) measurements were performed using an X'pert MPD. Philips diffractometer with Cu radiation source (λ = 1.54050˚A) at 40 Kv voltage and 40 mA current. BET (Brunauer-Emmett-Teller) surface area of the samples was determined from N_2 adsorption–desorption isotherms using a micromeritics ASAP 2020 analyzer. Gas chromatography (GC) analyses were performed to determine the reaction yields.

2.2 Preparation of catalyst (Pd@$Cu_2(BDC)_2$DABCO)

[$Cu_2(BDC)_2$DABCO] was synthesis by that are reported in litreture [41]. 0.1 g of the synthesized MOF was solved in 2cc of DMF and then 3 mg of $PdCl_2$ with purity of 99.9% were added to the mixture. The solution was sonicated for 20 min, then stirred at 80˚ C for 20 h and finally it was stirred at 130˚C with the purpose of Pd encapsulation in MOF. Finally, the product

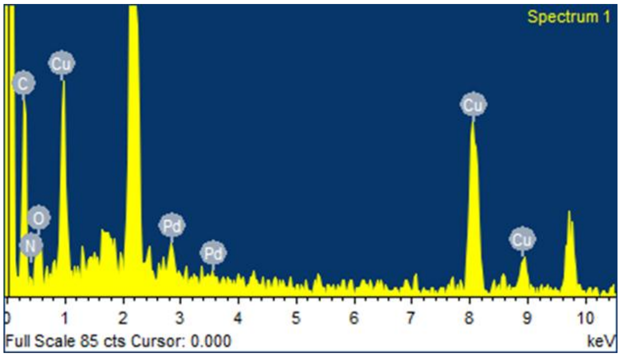
($Pd@Cu_2(BDC)_2DABCO$) was centrifuged, washed with DMF and dried in vacuum at 120 ^oC for 12 h.

2.3 Catalyst Usage for Suzuki–Miyaura Reaction

Typically, aryl halide (0.5 mmol), phenylboronic acid (0.6 mmol), alkali (1.5 mmol), EtOH H_2O (4 mL, 1:1, v/v) and $Pd@Cu_2$ $(BDC)_2DABCO$ (2 mg, 0.075 mol%) were added to a round-bottom flask. The mixture was stirred at room temperature for the appropriate time in air. After that, the reaction mixture was diluted with 10 mL of H_2O and extract with ethyl acetate (3 9 10 mL). Then, the organic layer was combined, dried over anhydrous $MgSO_4$ and filtered. Solvent was removed under vacuum. In the recyclability experiment, the reaction of bromobezene and phenylboronic acid was chosen as a model reaction. A mixture of bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), potassium carbonate (1.5 mmol), EtOH–H_2O (4 mL, 1;1, v/v) and $Pd@Cu_2(BDC)_2DABCO$ (2 mg, 0.075 mol%) was stirred at room temperature for 30 min, then the catalyst was separated by centrifugation and dried at room temperature. The conditions of the recycling reactions were same as describe above, except of using the recovered catalyst.

3. Results and Discussion

At the first we evaluated a simple and straightforward one-step protocol to encapsulate Pd NPs inside MOFs through temperature programming control from 80˚C to 130˚C for 20 h. $Cu_2(BDC)_2DABCO$ has been shown to act as a proper support for deposition of Pd NPs. Using temperature controlling method after sonication, Pd^{+2} cations are converted to Pd^o nanoparticles deposed on the surface of activated $Cu_2(BDC)_2DABCO$ carriers. The actual loading of Pd(0) was characterized by EDS analysis and found to be 0.32 % (Fig 1). Also EDS analysis confirmed the presence of zero-valent Pd in Pd^0-in- [$Cu_2(BDC)_2DABCO$].



Element	Weight%	Atomic%
C K	49.16	70.09
N K	4.94	6.03
O K	14.63	15.66
Cu K	29.31	7.90
Pd L	1.96	0.32
Totals	100.00	

Fig 1. EDX analysis of Pd@$Cu_2(BDC)_2$DABCO

The XRD pattern of Pd@Cu_2 $(BDC)_2$DABCO shows that the crystalline structure of $Cu_2(BDC)_2$DABCO is maintained after deposition of Pd NPs. The absence of a Pd diffraction pattern relates to the low Pd contents in the materials.

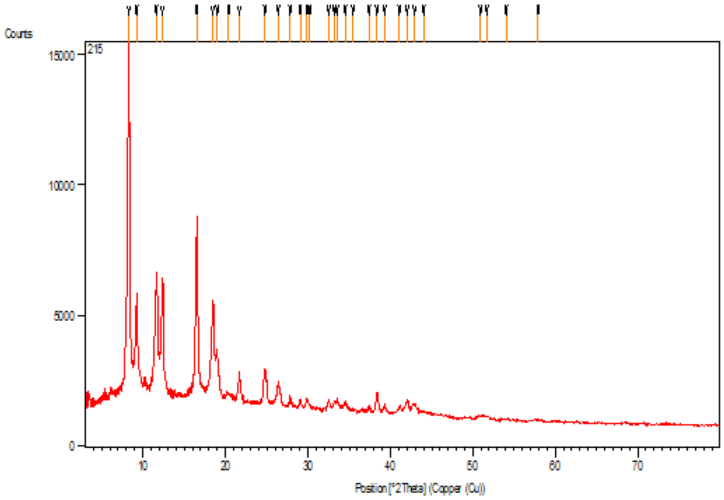


Fig 2. XRD pattern of prepared Pd NPs @$Cu_2(BDC)_2$(DABCO)

Specific surface areas of the samples were measured by N_2 adsorption at 77 K, with results presented in Table 1 nitrogen adsorption and surface areas of Pd^0-in-$Cu_2(BDC)_2$DABCO samples were noticeably reduced as compared to $Cu_2(BDC)_2$(DABCO) indicating that the cavities of indicating that the cavities of $Cu_2(BDC)_2(DABCO)$ may be occupied by highly dispersed Pd nanoparticles (fig 3).

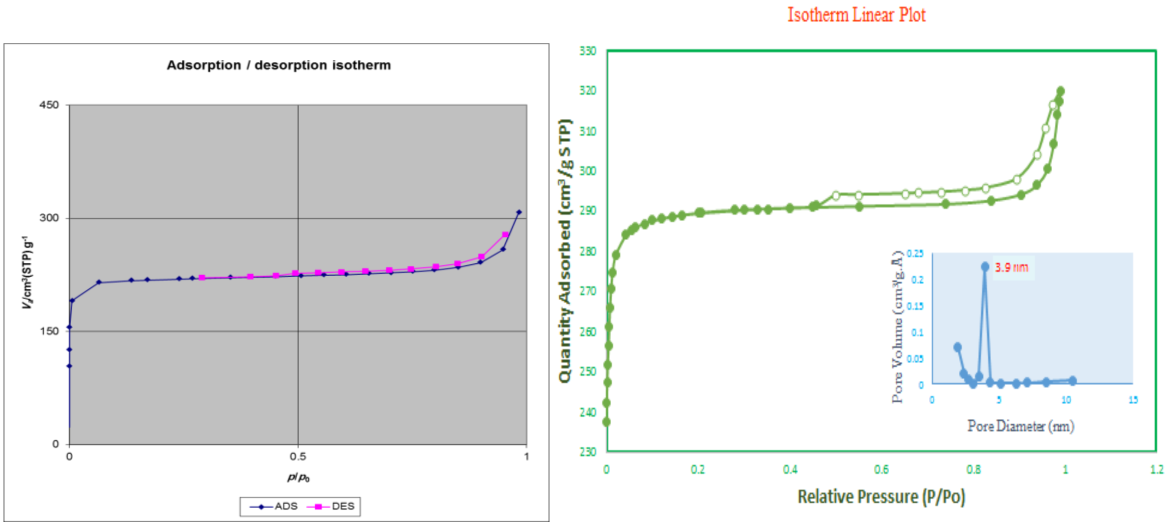


Figure 3. The N_2 adsorption–desorption isotherms of the mesoporous $[Cu_2(BDC)_2(DABCO)]$ (Right) and $Pd@[Cu_2(BDC)_2(DABCO)]$ (Left)

Table 1. Textural properties of $[Cu_2(BDC)_2(DABCO)]$ and $Pd@[Cu_2(BDC)_2(DABCO)]$ from N_2 adsorption–desorption experiments

Material	BET surface area (m^2/g)	Pore Volume (cm^3/g)
$[Cu_2(BDC)_2(DABCO)]$	1012	0.48
$Pd@[Cu_2(BDC)_2(DABCO)]$	873	0.475

The synthetic $Pd@Cu_2(BDC)_2DABCO$ was employed as a catalyst in the Suzuki coupling reaction. It is noticeable that the nature of base and solvent greatly affect the efficiency of the Suzuki coupling reaction (Table 2).

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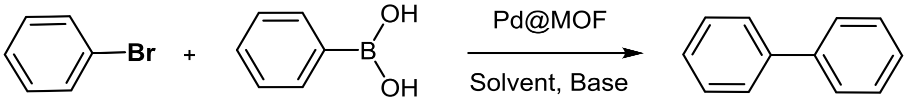
Table 2. Optimization of Reaction conditions



Entry	**Catalyst (Cu-MOF) (mg)**	**Base**	**Solvent**	**Time (h)**	**T (°C)**	**Yield (%)**
1	20	K_2CO_3	H_2O	2	r.t	35
2	20	Na_2CO_3	EtOH	2	r.t	40
3	20	K_2CO_3	H_2O/EtOH	2	r.t	78
4	20	Na_2CO_3	H_2O/EtOH	2	r.t	54
5	20	Cs_2CO_3	H_2O/EtOH	2	r.t	76

As a shown in table 2 the best result observed in entry 3. The yield of the Suzuki coupling reaction depends on the type of the aryl halide halogen and the positions electron-donating orwithdrawing nature of the substituents on the reactants [35]. Since the energy of the C–X bond increases as follows; C–Cl > C–Br > C–I, it is expected that longer reaction time is required for the activation of aryl chlorides compared with arylbromides or iodides. Results related to the optimized conditions for the Suzuki coupling reactions of different aryl halides with benzeneboronic acid catalyzed by MOF supported Pd NPs (Pd@MOFs or Pd/MOFs) and Pd (II) complexes incorporated into some MOFs. It is worthwhile to compare the results related to the catalytic activity of the synthesized Pd@$Cu_2(BDC)_2$DABCO nanocomposite with some results reported in the Suzuki coupling reaction catalyzed by different MOF supported Pd NPs. These results showed the good satiability of the catalyst during the catalytic reaction.

4. Conclusion

In conclusion, we have succeeded to prepare Pd NPs supported on $Cu_2(BDC)_2$DABCO Metal Organic Framework as an efficient heterogeneous catalyst for the Suzuki coupling reaction of different aryl halides especially bromo-arenes with benzeneboronic acid in environmentally green system of H_2O/EtOH mixture and in the presence of K_2CO_3 base. Moreover, the Pd@$Cu_2(BDC)_2$DABCO catalyst exhibits high stability during the catalytic reaction and can be reused several times without significant reduction of catalytic activity.

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