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# HIGHLY ACTIVE AND ROBUST PALLADIUM NANOPARTICLES IMMOBILIZED ON BIODEGRADABLE MICROCAPSULES CONTAINING CHITOSAN-GUAR GUM COMPOSITE FOR SYNTHESIS OF BIARYL COMPOUNDS

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**ABSTRACT:** In this study, highly stable biodegradable microcapsules, which are composed of chitosan-guar gum composite (CS-GG), were prepared as catalyst support. Then, palladium nanoparticles were successfully decorated on the designed support without using any toxic reducing agent (Pd NPs@CS-GG). Structural characterizations of CS-GG and Pd NPs@CS-GG were carried out by different analytical techniques and it was detected that the size of palladium nanoparticles changed in the range of 23-48 nm. Then, the catalytic activity of Pd NPs@CS-GG was evaluated in the fabrication of various biaryl compounds under solventless media using microwave heating. Pd NPs@CS-GG showed high catalytic performance in the conversion of various aryl halides to desired biaryl compounds with good reaction yields. Moreover, it was found that Pd NPs@CS-GG was a catalyst having long life time because of its reuse at least seven times.

***Key Words:*** *Chitosan, Microcapsule, Catalyst, Palladium Nanoparticle*

## Biaril Bileşiklerinin Sentezi İçin Kitosan-Guar Sakizi Kompoziti İçeren Biyobozunur Mikrokapsüller Üzerine İmmobilize Edilmiş Oldukça Aktif ve Sağlam Paladyum Nanopartiküller

**ÖZ:** Bu çalışmada, kitosan-guar sakızı kompozitinden (CS-GG) oluşan son derece kararlı biyobozunur mikro kapsüller, katalizör desteği olarak hazırlandı. Daha sonra, paladyum partikülleri, herhangi bir toksik indirgeyici madde kullanmadan tasarlanan destek üzerine başarıyla dekore edildi (Pd NP@CS-GG). CS-GG ve Pd NP@CS-GG'lerin yapısal karakterizasyonu farklı analitik tekniklerle yapıldı ve paladyum nanopartiküllerinin boyutunun 23-48 nm aralığında değiştiği tespit edildi. Daha sonra, Pd NP @ CS-GG'nin katalitik aktivitesi, mikrodalga ısıtma kullanılarak çözücüsüz ortam altında çeşitli biaril bileşiklerin üretiminde değerlendirildi. Pd NPs@CS-GG, çeşitli aril halojenürlerin iyi reaksiyon verimleriyle istenilen biaril bileşiklerine dönüştürülmesinde yüksek katalitik performans gösterdi. Ayrıca, Pd NPs@CS-GG'nin, en az yedi kez tekrar kullanımı nedeniyle uzun yaşam süresine sahip bir katalizör olduğu bulundu.

***Anahtar Kelimeler:*** *Kitosan, Mikro Kapsül, Katalizör, Paladyum Nanopartikül*

## INTRODUCTION

Noble metal nanoparticles have recently attracted much attention due to their interesting chemical structure and electronic, mechanical, optical, and magnetic properties. Therefore, they have been widely used in different application areas such as photonics, electronics, biology and medicine (Daniel and

Astruc, 2004; Nasrollahzadeh et al., 2015; Rai et al., 2009). On the other hand, one of the most significant promising application area of metal nanoparticles is the use as catalyst in catalytic reactions (Gholinejad et al., 2017; Sudhakar and Soni, 2018). For these reasons, researchers have prepared different types of noble nanoparticles such as Cu, Ag, Au and Pt to use in catalytic applications (Naghdi et al., 2018; Nasrollahzadeh et al., 2015; Nasrollahzadeh et al., 2018; Rathi et al., 2016). Among noble metal nanoparticles, palladium nanoparticles are the most widely used as catalyst in the catalytic reactions due to their unique properties such as good thermal stability, high chemical stability and photo catalytic activity (Chen and Ostrom, 2015; Phan et al., 2019). On the other hand, one of the most important problem in the synthesis of nanoparticles is aggregation and it can be negatively affect catalytic activity of catalyst (Cui et al., 2017). The best way to overcome this problem is immobilization of nanoparticles on suitable solid supports (Nasrollahzadeh et al., 2019). Additionally, shape, size and stability of nanoparticles depend on support. Therefore, there is need ideal support for immobilization of nanoparticles. In recent years, researchers have used different inorganic materials such as zeolite (Xue et al., 2016), $TiO_2$ (Atarod et al., 2016), graphene oxide (Zahed and Hosseini-Monfared, 2015), perlit (Nasrollahzadeh et al., 2015), $Fe_3O_4$ (Veisi et al. 2015), and carbon nanotube (Xiang et al., 2003) as support for fabrication of metallic nanoparticles.

Natural biopolymers are important materials due to their low cost, large surface area, renewability, biocompatibility, high thermal stability, and environmentally friendly properties (Baran, 2017; Rajender Reddy et al., 2006). These outstanding properties make biopolymers or their composites an important candidate as stabilizer for immobilization of metallic nanoparticles. Chitosan and guar gum are the most important members of the polysaccharide family. Chitosan is a cationic carbohydrate polymer which is derived by deacetylation of chitin obtained from waste products of sea such as shrimp, crab, krill, and crayfish (Baskar and Kumar, 2009; Tajik et al., 2008). Guar gum is a biopolymer with high molecular weight that is commonly extracted from the seed of the leguminous shrub *Cyamopsis tetragonoloba* (Mudgil et al., 2014; Pal et al., 2011). Additionally, chitosan and guar gum versatile materials are very economical, easily available and abundant in nature (Thombare et al., 2016; Wan Ngah et al., 2011). Both chitosan and guar gum have also free active functional groups such as $-NH_2$ and OH, which can be strongly interacted with metal ions, on the polymer backbone (Sharma et al., 2018; Zhang et al., 2016). These significant characteristics make chitosan and guar gum a desirable support material for catalytic reactions.

In this study, a novel highly thermally durable support material (CS-GG), which was composed from chitosan-guar gum microspheres, was designed and then palladium nanoparticles were successfully decorated on the prepared CS-GG. Chemical structures of the fabricated CS-GG and Pd NPs@CS-GG were illuminated by different analytical techniques. Then, catalytic behavior of Pd NPs@CS-GG was evaluated in the synthesis of a series of biaryl compounds. These tests revealed that Pd NPs@CS-GG catalyzed fabrication of biaryl compounds with good reaction yields in the solvent-free media. Furthermore, it was found that Pd NPs@CS-GG was easily recovered from the reaction media and it could be reused at least for seven successive runs.

## EXPERIMENTAL

### Synthesis of support material (CS-GG)

1 g of chitosan was dissolved in 2% acetic acid solution (v:v) and then 1 g of guar gum was added in the reaction mixture and it was stirred at room temperature for overnight. Resulting chitosan-guar gum mixture was dropped into solution of water:methanol:NaOH (40mL:60mL:12g) to obtain gelatinous microspheres. Subsequently, gelatinous chitosan-guar gum microspheres were extensively washed with water to neutrality. Finally, microspheres were transferred into the solution of glutaraldehyde (5 mL) in methanol (50 mL) and the mixture was stirred under reflux for 24 h for cross-linking. After the cross-linking procedure, chitosan-guar gum microspheres were filtered, washed with methanol and dried.

**Preparation of palladium nanoparticles on CS-GG**

0. 5 g of CS-GG was added to the solution of $PdCl_2$ (0.2 g, 20 mL) in ethanol and the reaction mixture was stirred at 70°C for 4 h to provide completely reduction of Pd(+2) to Pd(0). It was observed that the color of the reaction solution also changed to dark gray after this period. Finally, palladium nanoparticles were collected by filtration, rinsed with water and dried.

**Typical procedure for synthesis of biaryl compounds in the presence of Pd NPs@CS-GG**

The mixture of aryl halides (1.0 mmol), phenylboronic acid (1.8 mmol), $K_2CO_3$ (3.5 mmol) and Pd NPs@CS-GG ($3x10^{-2}$ mmol) were placed in a Schlenk tube and then it was irradiated by microwave for 6 min. After the completion of the coupling reaction, 10 mL of water was added reaction mixture and then the resulting mixture was extracted with toluene. Subsequently, organic phase was dried over anhydrous $MgSO_4$, and the solvent was evaporated to obtain biaryl compounds. Finally, characterizations of biaryls were performed by GC/MS.

**RESULTS AND DISCUSSION**

**Characterization of Pd NPs@CS-GG**

Chemical structures of CS-GG microcapsules and Pd NPs@CS-GG were investigated by FT-IR analysis and their spectra are illustrated in Fig. 1. FTIR spectrum of CS-GG microcapsules displayed characteristic bands at 3365$cm^{-1}$ (stretching of N-H and OH), 2931 and 2870$cm^{-1}$ (stretching of C-H), 1559$cm^{-1}$ (amide II band of chitosan), 1372$cm^{-1}$ (stretching of $NHCOCH_3$ group), 1444 and 1022$cm^{-1}$ (stretching of C–O–C and C-C) (Baran et al., 2015; Seeli and Prabaharan, 2017). Additionally, a strongly band was observed at 1658$cm^{-1}$ which was attributed to imine vibrations. These results showed the formation of chitosan-guar microcapsules. On the other hand, it was observed that these characteristic bands shifted to lower or higher wavenumbers in the spectrum of Pd NPs@CS-GG. These important changes can be attributed to strongly interaction of CS-GG microcapsules with palladium nanoparticles.

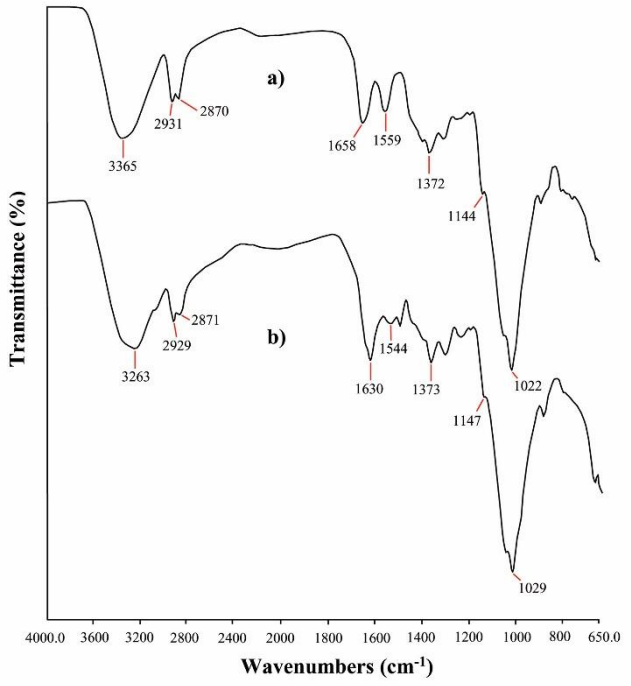



**Figure 1.** FT-IR spectra of a) CS-GG microcapsules and b) Pd NPs@CS-GG

Surface characteristics of CS-GG microcapsules and Pd NPs@CS-GG were studied by FE-SEM. As clearly shown in Fig. 2, CS-GG microcapsules and Pd NPs@CS-GG had spherical formation. While CS-GG microcapsules had nearly smooth surface (Fig. 2a), the surface of Pd NPs@CS-GG was covered with particles after the fabrication of palladium nanoparticles (Fig. 2b). Additionally, the surface morphology of Pd NPs@CS-GG was investigated at higher magnification to confirm the formation of nanoparticles (Fig. 2c). As seen in FE-SEM microgram of Pd NPs@CS-GG, palladium nanoparticles were successfully fabricated on the support and their average diameters were found to be between 23 and 48 nm.


**Figure 2.** FE-SEM images of a) CS-GG microcapsules and b) Pd NPs@CS-GG

Thermal durability of catalysts is one of the most important properties in catalytic systems to retain their catalytic performance. TG/DTG analysis was employed to determine thermal stability of Pd NPs@CS-GG and its curve is given in Fig. 3. When TG/DTG spectrum of Pd NPs@CS-GG was examined, it was found that Pd NPs@CS-GG had high thermal stability by protecting its chemical structure up to 250.4°C ($T_{max}$). This results show that Pd NPs@CS-GG is a suitable catalyst for catalytic systems which require high reaction temperature.

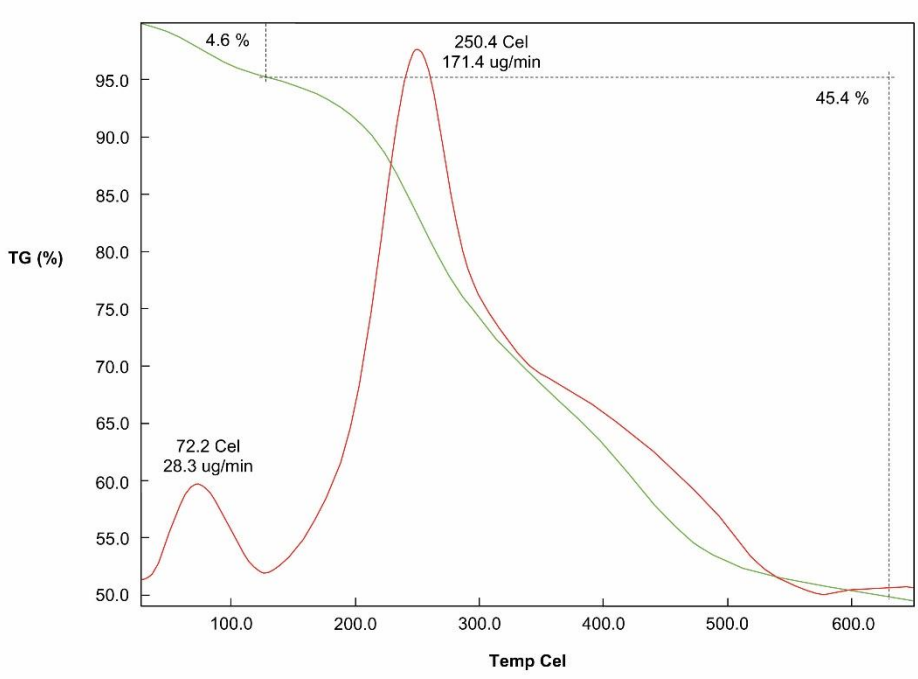



**Figure 3.** TG/DTG spectrum of Pd NPs@CS-GG

XRD analysis was performed to illuminate the crystalline nature of Pd NPs@CS-GG and its pattern is given in Fig 4. When XRD diagram of Pd NPs@CS-GG was examined, a weak and broad peak at 21.64° was observed which corresponded to characteristic peaks of chitosan and guar gum (Baran et al., 2015; Seeli and Prabaharan, 2016). Pd NPs@CS-GG also exhibited strong two peaks at 40.18° and 46.68° which corresponded to (111) and (200) crystalline planes of Pd, respectively (Nasrollahzadeh and Sajadi, 2016). These results showed the presence of palladium nanoparticles on the CS-GG.

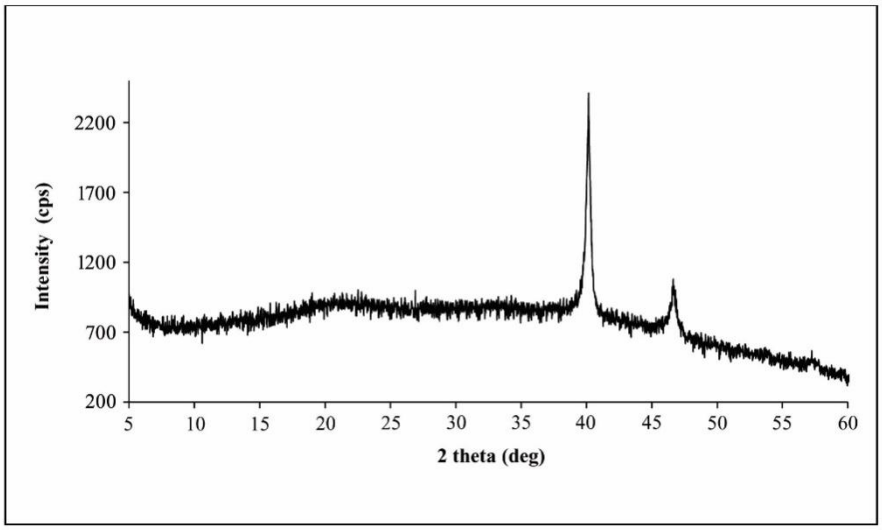
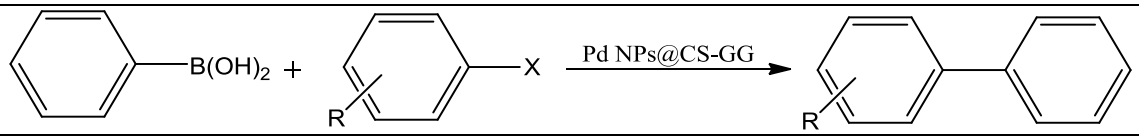



**Figure 4.** XRD pattern of Pd NPs@CS-GG

**Microwave-assisted synthesis of biaryl compounds in the presence of Pd NPs@CS-GG**

Synthesis of biaryl compounds were carried out using microwave heating because it offers (i) higher reaction yields with short reaction time and, (ii) easy and safe operation when compared to traditional heating methods. Additionally, in terms of green chemistry, no solvent was used in the catalytic reactions. Before catalytic tests of Pd NPs@CS-GG, determination of reaction conditions such as base type, reaction time and amount of catalyst require because they affect reaction yield. To optimize the reaction conditions, 4-iodide anisole and phenylboronic acid were chosen as model substrates and then preliminary studies were carried out. The best reaction yield was reached with $K_2CO_3$ as base system, for 6 min reaction time and using $3x10^{-2}$ mmol amount of catalyst. Then, catalytic performance of Pd NPs@CS-GG was investigated against various Suzuki cross coupling reactions under the determined optimum conditions (Table 1). As seen in Table 1, catalytic activity of Pd NPs@CS-GG was studied in Suzuki cross coupling reactions of a range of aryl halides with phenylboronic acid. Firstly, coupling reactions of different substituted aryl iodides were performed in the presence of Pd NPs@CS-GG and the desired biaryl compounds were obtained with good reactions yields (Table 1, entries 1-4). For example, meta-$NO_2$ substituted aryl iodide afforded 94% yield (entry 2). At the next step, Pd NPs@CS-GG was also tested in the coupling reactions of a variety of aryl bromides and it was found that the yields of synthesized biaryl compounds were in the range from 70% to 98% (Table 1, entries 5-9). For example, the reaction of 4-bromobenzonitrile with phenylboronic acid produced the desired biaryl product with 98% yield. Finally, the substrates versatility of Pd NPs@CS-GG was also tested against aryl chlorides which are less reactive compared to aryl iodides and bromides in the coupling reactions (Table 1, entries 10-13). Pd NPs@CS-GG successfully catalyzed the conversion of aryl chloride to desired biaryl products. 76% and 82% reaction yields were reached for meta substituted–$NO_2$ and para substituted–CN aryl chlorides, respectively (Table 1, entries 11 and 12). The performed catalytic tests indicate that Pd NPs@CS-GG is a suitable catalyst for synthesis of biaryl compounds.

**Table 1.** Catalytic behavior of Pd NPs@CS-GG against synthesis of biaryls




| Entry | X | R | Yield |
|---|---|---|---|
| 1 | I | 4-$OCH_3$ | 98 |
| 2 | I | 3-$NO_2$ | 94 |
| 3 | I | 4-$NH_2$ | 80 |
| 4 | I | 4-$CH_3$ | 78 |
| 5 | Br | 4-$OCH_3$ | 92 |
| 6 | Br | 4-$NH_2$ | 77 |
| 7 | Br | 3-$NO_2$ | 92 |
| 8 | Br | 4-CN | 98 |
| 9 | Br | 4-$CH_3$ | 70 |
| 10 | Cl | 4-$OCH_3$ | 69 |
| 11 | Cl | 3-$NO_2$ | 76 |
| 12 | Cl | 4-CN | 82 |
| 13 | Cl | 4-$CH_3$ | 48 |

**Reaction conditions:** 1.8 mmol aryl halides, 1.2 mmol phenyl boronic acid, 3.5 mmol $K_2CO_3$, $3x10^{-2}$ mmol Pd NPs@CS-GG, 6 min, 400 W.

**Reusability of Pd NPs@CS-GG**

Highly reusable catalysts are desired for academic researches and industrial applications due to their economical and practical advantages (Baran et al., 2018). Therefore, in this study, reusability of Pd NPs@CS-GG was checked on the model reaction. After first cycle, Pd NPs@CS-GG was easily recovered with filtration from reaction media and it was rinsed with hot water, dried and then directly used for next runs. This process was repeated for each cycle. Reusability tests revealed that Pd NPs@CS-GG could be successfully reused seven times by giving 72% yield. This result shows that Pd NPs@CS-GG is a highly retrievable and reusable catalyst. FE-SEM analysis of the catalyst was performed after seven consecutive runs and it showed that the chemical structure of the catalyst was retained (Fig.5). Additionally, possible reaction mechanism of Suzuki coupling reaction using Pd NPs@CS-GG is given in Figure 6.

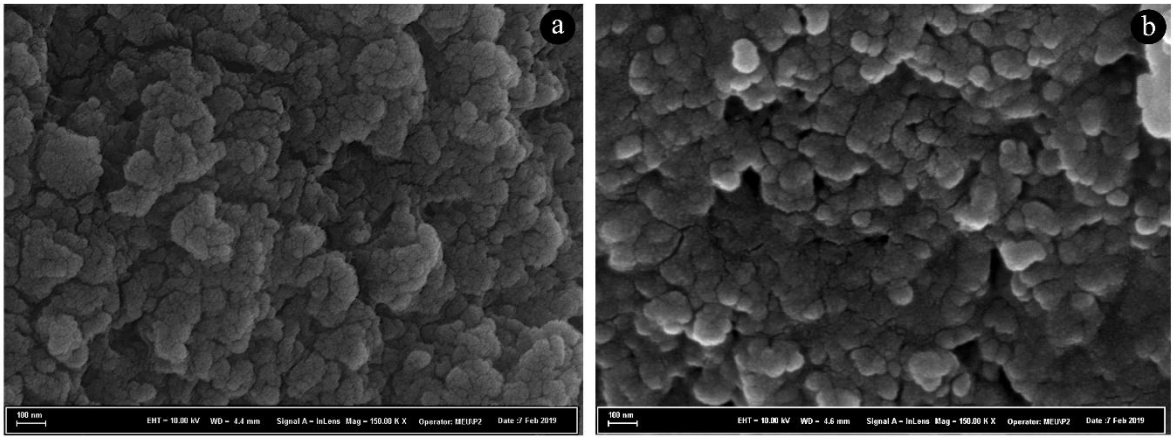



**Figure 5.** Surface morphologies of Pd NPs@CS-GG after a) 1th and b) 7th cycle

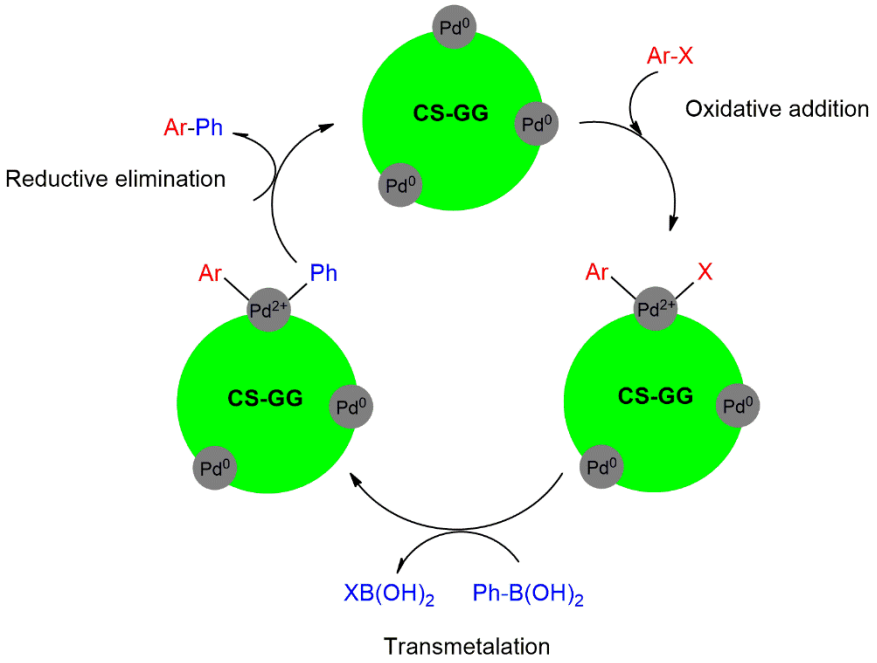



**Figure 6**. Possible mechanism of Suzuki coupling reaction using Pd NPs@CS-GG.

## CONCLUSIONS

In conclusion, Pd NPs@CS-GG was successfully designed, characterized and then it was used as heterogeneous catalyst for construction of several biaryl compounds. Catalytic studies showed that Pd NPs@CS-GG was a highly active catalyst which converted aryl iodides and bromides having variety of functionalized substrates to desired biaryl compounds with excellent yields. Pd NPs@CS-GG also served as a good catalyst for aryl chlorides. Furthermore, the prepared Pd NPs@CS-GG presented good recoverability and recyclability for at least seven runs. These findings indicate that Pd NPs@CS-GG is a useful catalyst for Suzuki cross coupling reactions.

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