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RESEARCH PAPER

Stability of Palladium(II) beta-cyclodextrin nanocomposite in aqueous media and its catalytic activity in Homocoupling of Arylboronic acid

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A B S T R A C T:

Palladium(II) beta-Cyclodextrin (Pd(II)-β-CD) nanocomposites are water-soluble compounds which can be of great importance for performing palladium-catalyzed reactions in aqueous media. The stability of water-soluble Pd(II)-β-CD nanocomposites in water were examined and was found that this nanocomposit is losing its stability in water significantly with time in the time interval of 0 to 200 minutes. In addition, the Pd(II)-β-CD nanocomposite was used as a catalyst for Aerobic homocoupling of arylboronic acid (ArBA) in water. However, the results showed that the catalytic activity of same prepared Pd(II)-β-CD nanocomposite stock solution in water for homocoupling reaction of ArBA decreases with time significantly. The Stability of the Pd(II)-β-CD nanocomposite was monitored using Ultra Violet- Visible (UV-Vis) spectroscopy. used to monitor the catalyst stability

KEY WORDS: Palladium, Cyclodextrin, nanocomposites, Catalytic activity, Homocoupling, Arylboronic acid.
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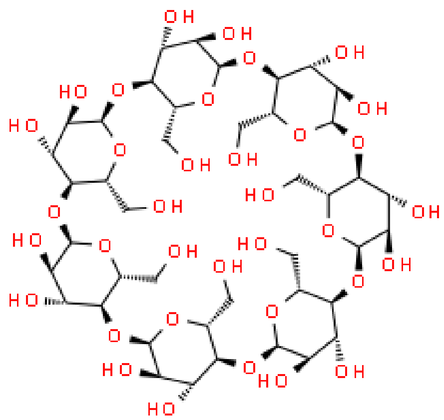
1.INTRODUCTION

Pd(II)-β-CD nanocomposites are water-soluble materials which consists of two palladium(II) metal linked inside a beta-cyclodextin (see scheme 1) (Wei et al, 2019 , Bahareh et al., 2019, Raihana, 2016 and Kenneth, 1997). The synthesis and characterization of Pd(II)-β-CD nanocomposite was first reported by Babak Kaboudin group (Babak. et al., 2016). Also, they have developed a new protocol for homogenous catalysis of Zuzuki-Miyaura coupling reaction in neat water using Pd(II)-β-CD as an efficient nanocatalyst with high turnover frequencies.



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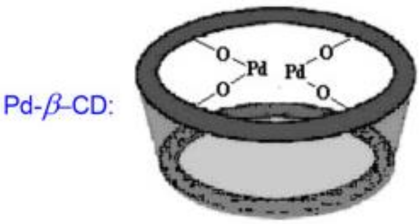

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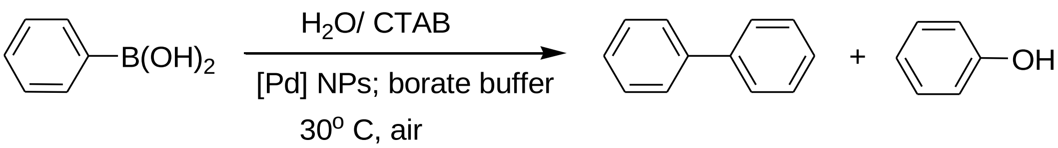
Scheme 1. a) Structure of Beta cyclodextrin. b) Structure of Pd(II)-*β*-CDs (Babak Kaboudin et al., 2016)

Catalysis using palladium nanoparticles (Pd-NPs) has been widely used in many types of chemical transformations, including C-C bond-forming reactions, and in particular the Suzuki-Miyaura and Heck reactions ((Wei et al, 2019, and Yafei et al., 2017, Moreno-Manas et.al., 2003, Sawoo et al., 2009, Karimi et al., 2010, Pérez-Lorenzo, 2012 and Dell'Anna et al., 2013). Yanru Yin et al. have studied the role of poly(vinylpyrrolidone) on the synthesis four types of Pd-nanoparticles from PdCl2 and Na2PdCl2 as precursors. They have found that the nanoparticles wich have synthesized without poly(vinylpyrrolidone) have smaller sizes and can reach maximum catalytic current transfer than the ones which are synthesized in the presence of poly(vinylpyrrolidone) (Yanru et al., 2019). Additionally, highly efficient and recyclable Palladium nanoparticles decorated olyethyleneimine/Polycaprolactone PEI/PCL@PdNPs) composite Fibers have been Constructed by Electrospinning reduction methods using elexctrospun. The prepared nanocomposite was used as an efficient , stable and reusable catalyst for the reduction reaction of 4-nitrophenol and 2-nitroanlinie (Cuiru, 2019). Moreover, Palladium nanoparticles immobilized on thio modified multi walled carbon nanotubes were used as heterogeneous and rescyclable nanocatalyst for Buchwald-Hartwig C-N cross coupling reactions. The catalyst was fully characterized using different spectroscopic techniques and showed reusability for Buchwaled-Hartwig reaction for six times without change in its catalytic activity (Veisi et al., 2019). Furthermore, palladium nanoparticles are widely used in C-C coupling reactions. It has been found that in most cases of C-C coupling Pd-NPs are not the only palladium present in the reaction system, but they might lead to the formation of other active species forming "cocktail of catalysts". The active species can be formed both from Pd-NPs and/or Pd(II) complexes (Trzeciak and Augustyniak, 2019).

The applications of Pd-NPs in catalysis have been motivated by the improvements in efficiency and selectivity of Pd-NP-catalysed reactions and also by the ease of recovery and recyclability of the catalysts (Astruc et al., 2005, Asturc, 2007, Taladriz-Blanco et al., 2013 and Daniel et al., 2004). However, Aerobic homocoupling of aryboronic acids (ArBA) using different palladium nanoparticles was studied in the literature (Mazin and Niklaas, 2011 and Azzedine et al., 2017).



Scheme 2. Aerobic homocoupling reaction of ArBA using Pd-nanoparticles as catalyst (Mazin and Niklaas, 2011).

In this work we have studied the stability of Pd(II)-*β*-CD catalyst and its catalytic activity for the aerobic homocoupling reaction of arylboronic acid. UV-Vis spectroscopy was used to monitor the catalyst stability and reactivity in aqueous media. The Absorbance of Biphenyl formation was followed for kinetic studies.

2. MATERIALS AND METHODS

2.1. Chemicals

Arylboronic acid is purchased from Acros, K_2CO_3 is purchased from Alfa Aesar) and used as purchased without further purifications. However, Pd(II)-*β*-CD nanocomposite was provided by the Babak Kaboudin group (Babak K. et al., 2016). Distilled water was the solvent for all stock solutions.

2.2. Pd(II)-β-CD nanocomposite stability procedure

Pd(II)-β-CD nanocomposite stability was studied using Jasco UV-Vis spectrophotometer by preparing a stock solution of Pd(II)-β-CD in distilled water and follow the time-resolved absorption peak every 20 minutes from 200-800 nm.

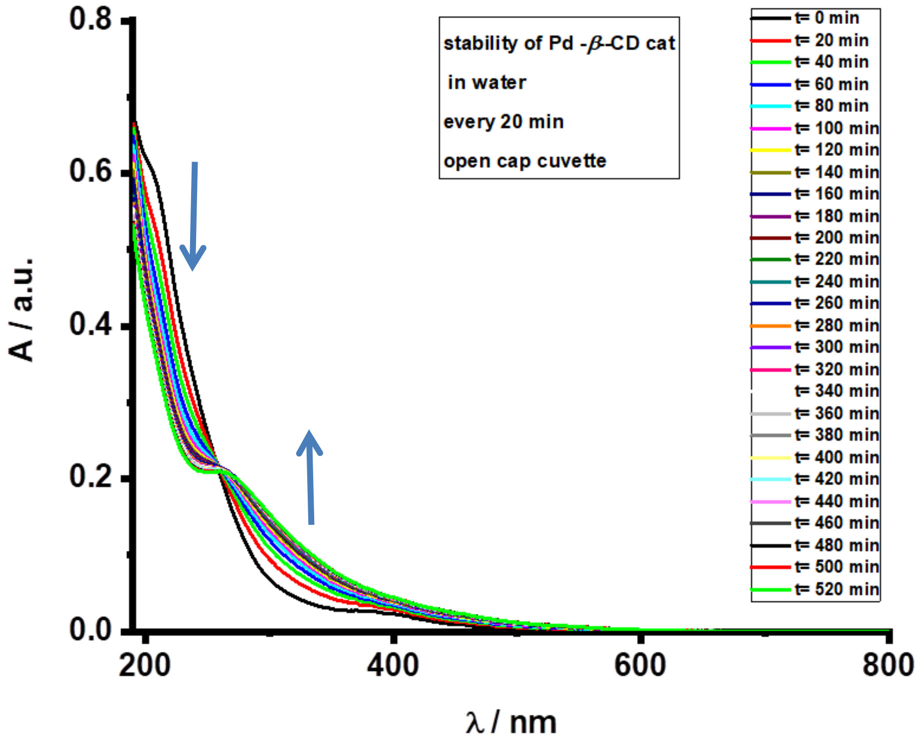
2.3. Pd(II)-β-CD nanocomposite activity for homocoupling reaction of ArBA

The catalytic activity of Pd(II)-β-CD nanocomposites for the homocoupling reaction of ArBA in aqueous media were studied using Jasco V-650 spectrophotometer with a PAC-743R Peltier thermostatted 6-cell changer (Jasco UK Ltd., Great Dunmow, UK) at fixed maximum wave length(λmax = 250 nm) by measuring the absorbance every 5 minutes for the reaction of 0.2 M ArBA using fixed concentration of the catalyst in a cuvette.

3. Results and Discussions

3.1. Pd(II)-β-CD nanocomposite stability in water

Figure 1 shows the UV-Vis spectra of 10.0 ppm Pd(II)-β-CD nanocomposite in distilled water. The spectrum of the color less solution was measured every 20 minutes at a wavelength range of 200-800 nm.



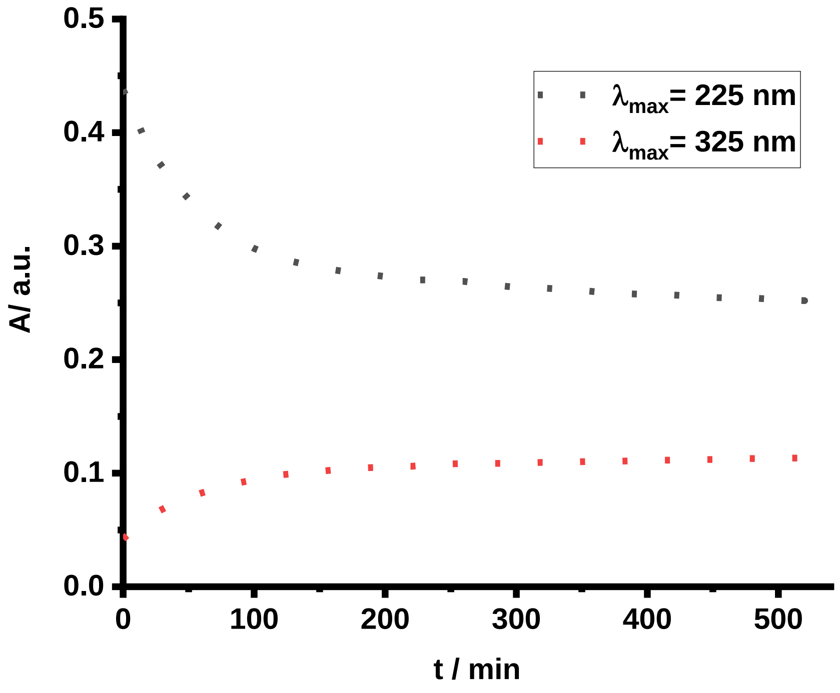


Fig. 1. a) UV-Vis Spectra of Pd(II)-β-CD nanocomposite in distilled water (20 min. is the time interval between each spectrum (see the time of each color)) b) the absorbance of Pd(II)-β-CD nanocomposite in distilled water at λmax 325 nm (red dots) and λmax 225 nm (black dots) with time.

It is clear from figure 1(a and b)) that the spectra of the catalyst solution does not stay constant, there is an increase of the peak in the range of wave length 200-250 nm (λmax 325 nm) (which we believe is the peak of Pd(II)-β-CD nanocomposite without leaching of bound Pd to the CD) and a decrease in the range 300-350 nm (λmax 325 nm) (which we believe is the peak of Pd(II)-β-CD nanocomposite leaching of bound Pd to the CD) with time which gives an indication that the structure of the catalyst dose not stay constant in water. Figure 1 (b) shows that about 200 minutes are required to reach equilibrium between Pd(II)-β-CD nanocomposite and of Pd(II)-β-CD nanocomposite leaching of bound Pd to the CD.

To explore more ^{1}H nmr was measured for the catalyst in D_2O with time as shown in figure (2)

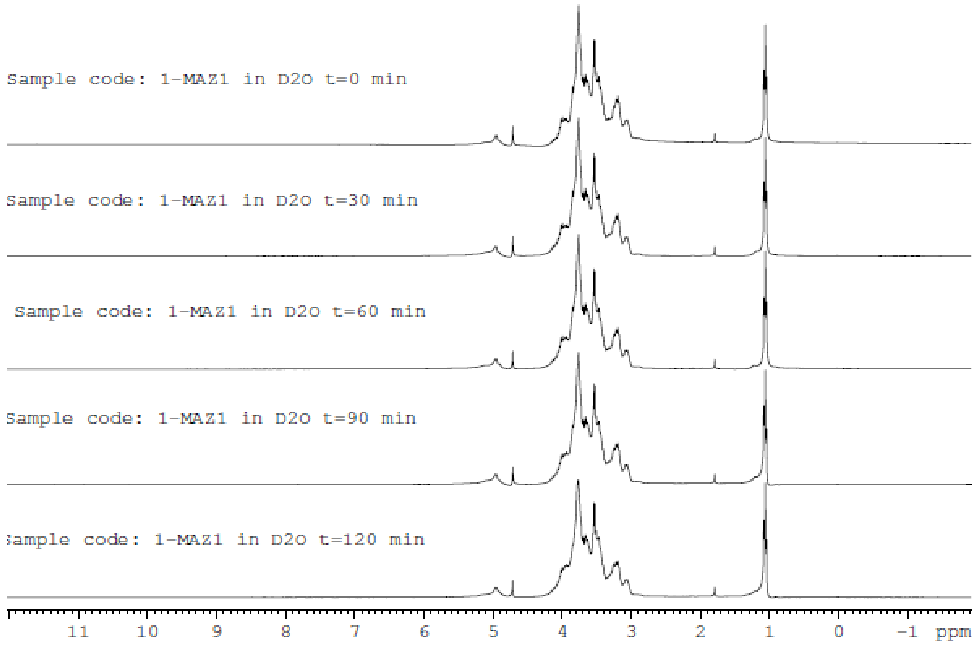
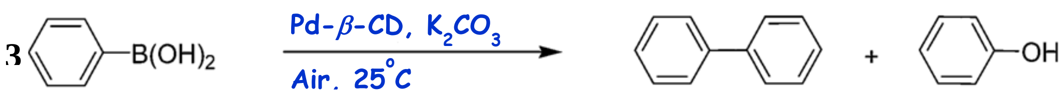


Fig. 2.Time-resolved ^{1}H nmr for Pd(II)-β-CD nanocomposite in D_2O

Figure 2 shows no changes in ^{1}H nmr peaks with time which indicates that the cyclodextrin structure does not change, this mean that Pd leach out to the solution and becomes unbound to catalyst the nanocomposite. Leaching out of some of Pd in to the solution is a common problem that some previous studies are referring to which leads to decreasing the catalytic activity of the catalyst (Azzedine et al., 2017). Also, according to Trzeciak and Augustyniak many Pd-NPs tend to form other unbound Pd species in the reaction solution which they called "Cocktail catalysts" which might be the case of changing the UV-Vis spectra of our Pd(II)-β-CD nanocomposite and no change in ^{1}H nmr spectra (Trzeciak and Augustyniak, 2019).

3.2.Homocoupling of ArBA using Pd(II)-β-CD nanocomposite

Aerobic homocoupling of ArBA in basic aqueous media using Pd(II)-β-CD nanocomposite was studied using UV-Vis spectrophotometer in an open cap cuvette using K_2CO_3 as a base.



Scheme 3. Aerobic homocoupling reaction of ArBA using Pd(II)-β-CD nanocomposite in basic aqueous media. According to the literature the products of the reaction are biphenyl and phenol. (Mazin and Niklaas, 2011 and Azzedine et al., 2017)

The time-resolved absorption spectra were measured for the reaction see figure 3.

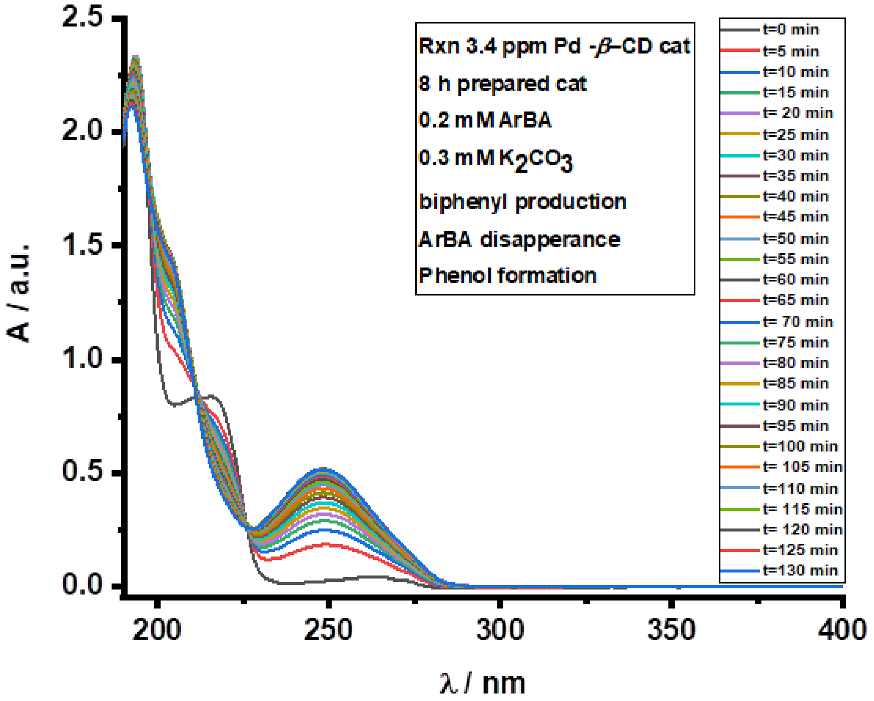


Figure 3. time-resolved absorption spectra for the aerobic homocoupling of 0.1 mM ArBA using 3 ppm Pd(II)-β-CD catalyst and 0.3 mM K_2CO_3 in distilled water. (the spec tra taken every 5 minutes).

From figure 3 we can follow the progress of the reaction with time from which we see decrease of ArBA peak (1) and an increase of biphenyl and phenol formation peaks 2 and 3 respectively. (Azzedine et al., 2017).

3.3. Pd(II)-β-CD nancomposite reactivity

The Pd(II)-β-CD nanocomposite reactivity was tested using aerobic homocoupling reaction of ArBA in aqueous media using K_2CO_3 as a base at room temperature. A 20.0 ppm of the Pd(II)-β-CD nanocomposite stock solution was prepared and used as a catalyst for the aerobic homocoupling reaction of ArBA at different time intervals of the stock solution in distilled water preparation. The reaction was monitored using UV-Vis spectroscopy and the absorbance of the biphenyl formation was measured with time at maximum wave length of 250 nm. The reaction was repeated after different period of the catalyst stock solution preparation using the same concentration of the catalyst see figure 4.

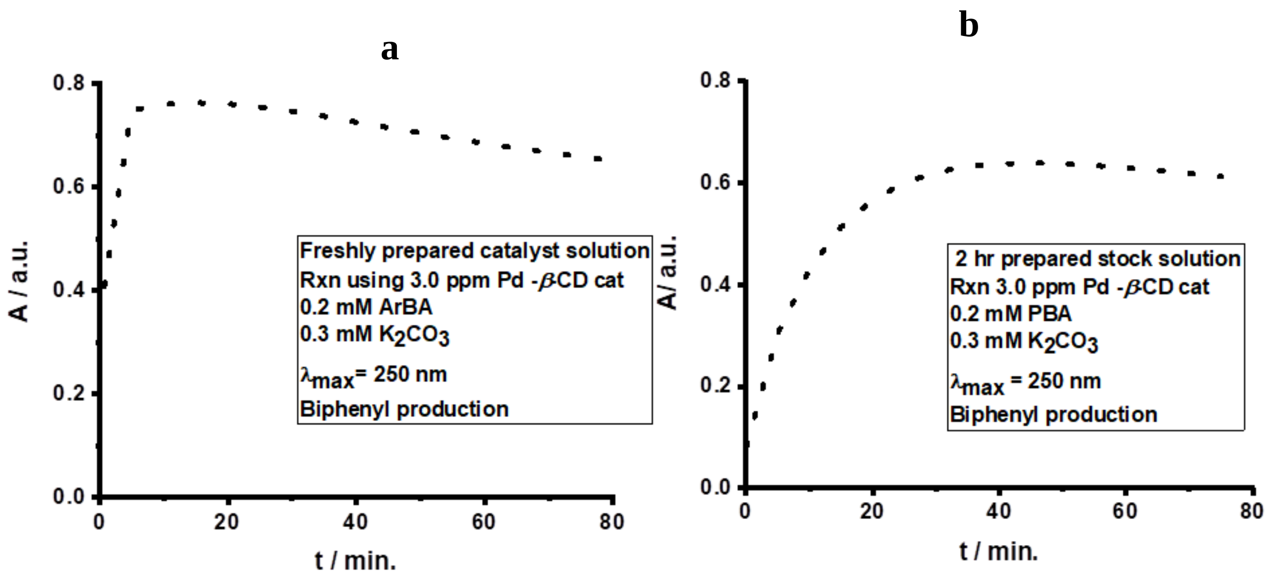


Figure 4. The absorbance of Biphenyl with time at λmax=250 nm for the aerobic homocoupling reaction of 0.2 mM ArBA using 0.3 mM K_2CO_3 and 3.0 ppm Pd(II)-β-CD nanocomposite a) fresh catalyst stock solution, b) catalyst stock solution after 2 hours preparation.

It is clear from figure 4 that the reaction rate decreases significantly when 2 hours is passing on after the catalyst stock solution preparation which indicates that the reactivity of the catalyst stock solution decreases with time. This goes in line with our result in figure 2 which shows the changing of the UV-Vis spectra of Pd(II)-β-CD nanocomposite in distilled water with time. According to our previous work on another palladium nanocomposite catalyst and other works in the literature (Azzedine et al., 2017 and Veisi et al., 2019) and our results in this work the Palladium will leach out of the catalyst solution which changes to unreactive palladium black and this will lead to the decrease of the catalyst reactivity with time.

Conclusions

In summary, the stability of Pd(II)-β-CD nanocomposites in aqueous media was followed using UV-Vis spectroscopy. The UV-Vis time-resolved absorption spectra of the Pd(II)-β-CD nanocomposite solution in distilled water showed a significant change with time which indicates that the structure of some of the Pd(II)-β-CD nanocomposite particles does not stay constant in aqueous solution due to the leach out of some of the cyclodextrin bound Pd in to the solution and becomes unbound to the cyclodextrin molecules and produce unreactive Pd black species and this process requires about 200 minutes. The reactivity of Pd(II)-β-CD nanocomposite as a catalyst for aerobic homocoupling reaction of ArBA in aqueous basic solution was decreasing with time of the catalyst stock solution preparation. These results led us to conclude that palladium will leach out of the catalyst stock solution which leads to the formation of unreactive palladium black which decreases the catalyst stock solution reactivity for the aerobic homocoupling reactions of ArBA with time.

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