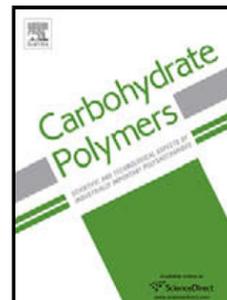


# Journal Pre-proof

Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads: A highly active, magnetically retrievable, and reusable nanocatalyst for cyanation of aryl halides

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**Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads: A highly active, magnetically retrievable, and reusable nanocatalyst for cyanation of aryl halides**

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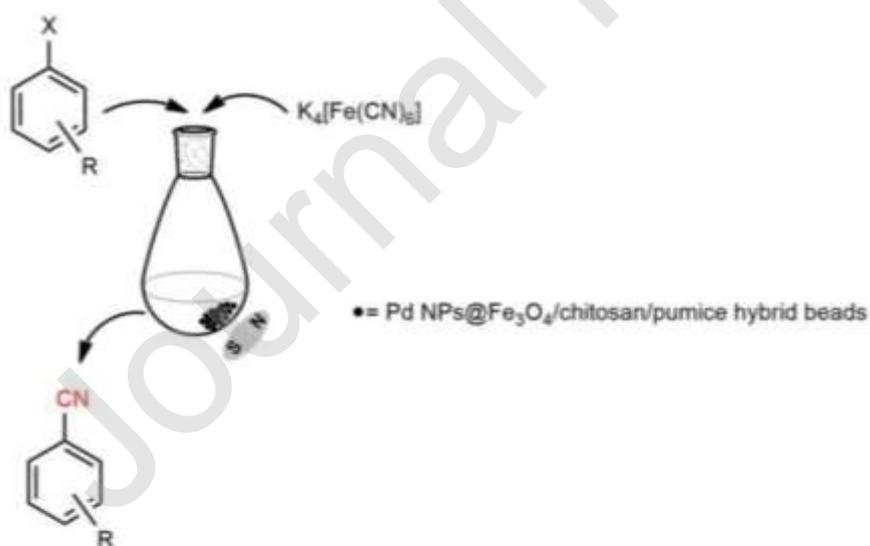
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**Graphical Abstract**



## Highlights

- Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads were characterized by different techniques
- The nanocatalyst showed good activity against synthesis of benzonitriles
- Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads reused several times

## Abstract

In this study, Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads were developed as a new stabilizer agent, and palladium nanoparticles (Pd NPs) were successfully decorated on the designed stabilizer without adding any toxic reducing resource. Then, the potential use of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads as a heterogeneous catalyst against different aryl halide cyanations was investigated with K<sub>4</sub>[Fe(CN)<sub>6</sub>]. In these reactions, Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads showed high catalytic activity by converting aryl halides to the desired benzonitriles with high product yields (80%-98%). Due to the magnetically separable nature of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads, they were reused several times, and 86% yield was obtained even after six successive runs. This paper reveals that Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads have a high potential to synthesis a broad range of nitriles due to their excellent catalytic and retrievable capability.

**Keywords:** chitosan; pumice; cyanation reaction; hybrid beads.

## 1. Introduction

Cyanation of aryl halides (Ar-X) play an important role in synthetic or industrial chemistry because aryl nitriles which are obtained after the cyanation reaction form the key components of agrochemicals, herbicides, pharmaceuticals, and dyes (Anbarasan, Schareina & Beller, 2011; Najam et al., 2018; Ren et al., 2011). Moreover, these compounds can be easily changed into various functional groups, and this property makes them valuable for different reactions (Chobanian, Fors & Lin, 2006; Veisi, 2019). Therefore, synthesis of nitriles has recently gained importance (Gazdag, Kunfi & London, 2018; Hemmati, Sedrpoushan, Soudalizadeh, Khosravi & Hekmati, 2019; Kandathil, Dateer, Sasidhar, Patil & Patil, 2018a). The most general method for this reaction is Rosenmund-von Braun and Sandmeyer reactions, but they require a high reaction temperature ( $>150^{\circ}\text{C}$ ) and CuCN (Anbarasan, Schareina & Beller, 2011; Rosenmund & Struck, 1919; Sandmeyer, 1884). Therefore, various synthesis methods have been developed for the construction of nitriles, and metal-catalyzed cyanation reactions with cyanation agents are the most effective and modern protocols among them (Guobing, Jian & Ling, 2012; Veisi, 2019). Recently, different transition metal catalysts have been designed and used in the cyanation reactions with varieties of cyanide resources such as CuSCN,  $\text{Zn}(\text{CN})_2$ , KCN, and NaCN (Cohen & Buchwald, 2015; Sundermeier, Zapf, Beller & Sans, 2001; Ushkov & Grushin, 2011; Zhang, Yu, Hu & Cheng, 2013). However, many of them are highly toxic and expensive, and their uses in the industrial scale applications are generally limited (Veisi, Hemmati & Safarimehr, 2018; Veisi, Tamoradi, Karmakar, Mohammadi & Hemmati, 2019). To overcome these drawbacks, different metal-catalyzed cyanations of aryl halides were carried out with  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , which is low-cost and nontoxic cyanide resource (Puthiaraj, Yu, Shim & Ahn, 2019; Schareina et al., 2009). Palladium catalysts have gained more attention compared to

other transition metal catalysts due to their high tolerance against different functional groups and high catalytic performance (Zhang, Yu, Hu & Cheng, 2013; Zheng, Yu & Shen, 2012).

Nowadays, preparation of heterogeneous catalysts has attracted more attention than homogenous catalysts due to their advantages such as high activity and easy work-up. Therefore, different heterogeneous catalysts have been prepared using various supports by researchers (Das & Linert, 2016; Gholinejad & Aminianfar, 2015; Modak, Mondal & Bhaumik, 2012; Puthiaraj, Yu, Shim & Ahn, 2019). Although heterogeneous catalysts can be recovered from the reaction media via simple filtration, the loss of the catalyst is inevitable during these separation techniques in many cases (Baran, Sargin, Kaya, Mulerčikas, Kazlauskaitė & Menteş, 2018). It negatively effects both the reusability and recoverability of catalysts. Combination of prepared support or catalyst with magnetic components is the most effective way to solve this problem as catalysts can be easily recovered from reaction media via an external magnet due to their magnetic nature (Baran & Nasrollahzadeh, 2019; Chen et al., 2019). Another important issue in heterogeneous catalytic systems is metal leaching from catalyst support (Veisi, Ghadermazi & Naderi, 2016; Veisi, Pirhayati & Kakanejadifard, 2017). Therefore, the design of heterogeneous catalysts having a strong interaction with active metal species is required for catalytic reactions as these catalyst systems can supply some advantages such as high reusability, easy-work up, and separation of final product from reaction mixture.

Bio-polymers, which are extracted from natural sources, have outstanding properties such as being nontoxic, biodegradable, environment-friendly and cheap (Baran, 2019; Veisi, Ghadermazi & Naderi, 2016). Chitosan is one of the most important biopolymers, and it can easily be chemically modified as well as being water-compatible in reactions and very abundant in nature (Dhanavel, Manivannan, Mathivanan, Gupta, Narayanan & Stephen, 2018; Movassagh & Rezaei, 2015; Xiao, Li & Xia, 2005). Moreover, chitosan has free hydroxyl and

amine functional groups on the polymer chains which easily anchor on different transition metals (Doustkhah, Rostamnia, Gholipour, Zeynizadeh, Baghban & Luque, 2017; Lin, Yu & Yang, 2005; Molvinger, Quignard, Brunel, Boissière & Devoisselle, 2004). Due to these characteristics, chitosan and its derivatives serve as ideal stabilizers for production of metallic nanoparticles (Chen, Xu, Zheng, Guan & Liu, 2018; Jia, Liu, Chen, Guan, Zheng & Liu, 2017; Sin, Yi & Lee, 2010). As an alternative to other stabilizers, pumice is a highly porous, lightweight, and very low cost volcanic stone (Kitis & Kaplan, 2007; Panuccio, Sorgonà, Rizzo & Cacco, 2009). Moreover, pumice has a large surface area and microporous structure, and it is also rich in alumina and silica. These properties make it a good support material for catalytic reactions (Jonasi, Matina & Guyo, 2017). Thanks to their outstanding properties above-mentioned, chitosan/pumice composites with magnetic property can be prepared as a support, which can provide strong interaction with metals to prepare metal nanoparticles. Then, their catalytic and reusable performance can be evaluated in the different catalytic reactions. Therefore, this study proposes to prepare a highly active, magnetically retrievable, and reusable nano-catalyst derived from natural sources for the production of benzonitriles.

In light of our interest in the production of nano-catalysts from the natural sources, magnetic hybrid beads, which contain chitosan/pumice composites, were prepared as support ( $\text{Fe}_3\text{O}_4/\text{chitosan}/\text{pumice}$ ), and palladium nanoparticles were successfully immobilized on the  $\text{Fe}_3\text{O}_4/\text{chitosan}/\text{pumice}$  hybrid beads without the use of any reducing source in this study. Then, Pd NPs@ $\text{Fe}_3\text{O}_4/\text{chitosan}/\text{pumice}$  hybrid beads were utilized as heterogeneous nano-catalyst in the synthesis of benzonitriles with  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . Pd NPs@ $\text{Fe}_3\text{O}_4/\text{chitosan}/\text{pumice}$  hybrid beads displayed a good catalytic performance by transforming corresponding benzonitriles smoothly with 80%–98% yields. Moreover,  $\text{Fe}_3\text{O}_4/\text{chitosan}/\text{pumice}$  hybrid beads were easily recollected from the reaction media via external magnet, and they were reused six times in the cyanation of  $p\text{-CH}_3\text{C}_6\text{H}_4\text{I}$ .

## 2. Experimental

### 2.1. Experimental information

Aryl halides, chitosan,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{PdCl}_2$ , acetic acid, methanol, DMF,  $\text{K}_2\text{CO}_3$ , DMSO, NMP, toluene,  $\text{Na}_2\text{CO}_3$ , KOH, NaOH,  $\text{Cs}_2\text{CO}_3$ ,  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , and diethyl ether were purchased from Sigma-Aldrich. Pumice was obtained from Turkey. FT-IR spectra of  $\text{Fe}_3\text{O}_4$ /chitosan/pumice hybrid beads and Pd NPs@ $\text{Fe}_3\text{O}_4$ /chitosan/pumice hybrid beads were obtained on a Perkin Elmer Spectrum100 FT-IR spectrophotometer. TGA analyses of  $\text{Fe}_3\text{O}_4$ /chitosan/pumice hybrid beads and Pd NPs@ $\text{Fe}_3\text{O}_4$ /chitosan/pumice hybrid beads were studied by EXSTAR S11 7300 (nitrogen atmosphere; heating range: 30–650 °C). FE-SEM micrograms and EDS spectra of  $\text{Fe}_3\text{O}_4$ /chitosan/pumice hybrid beads and Pd NPs@ $\text{Fe}_3\text{O}_4$ /chitosan/pumice hybrid beads were obtained by QUANTA-FEG 250ESEM. XRD patterns of  $\text{Fe}_3\text{O}_4$ /chitosan/pumice hybrid beads and Pd NPs@ $\text{Fe}_3\text{O}_4$ /chitosan/pumice hybrid beads were recorded by Rigaku smart lab system (10–80°). TEM images of Pd NPs@ $\text{Fe}_3\text{O}_4$ /chitosan/pumice hybrid beads were recorded by TEM JEOL JEM-2100 (UHR). Benzonitriles were characterized by GC–MS AgilentGC-7890 A- MS 5975. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the benzonitriles were recorded on Agilent 600 MHz spectrometer.

### 2.2. Synthesis of $\text{Fe}_3\text{O}_4$ /chitosan/pumice hybrid beads

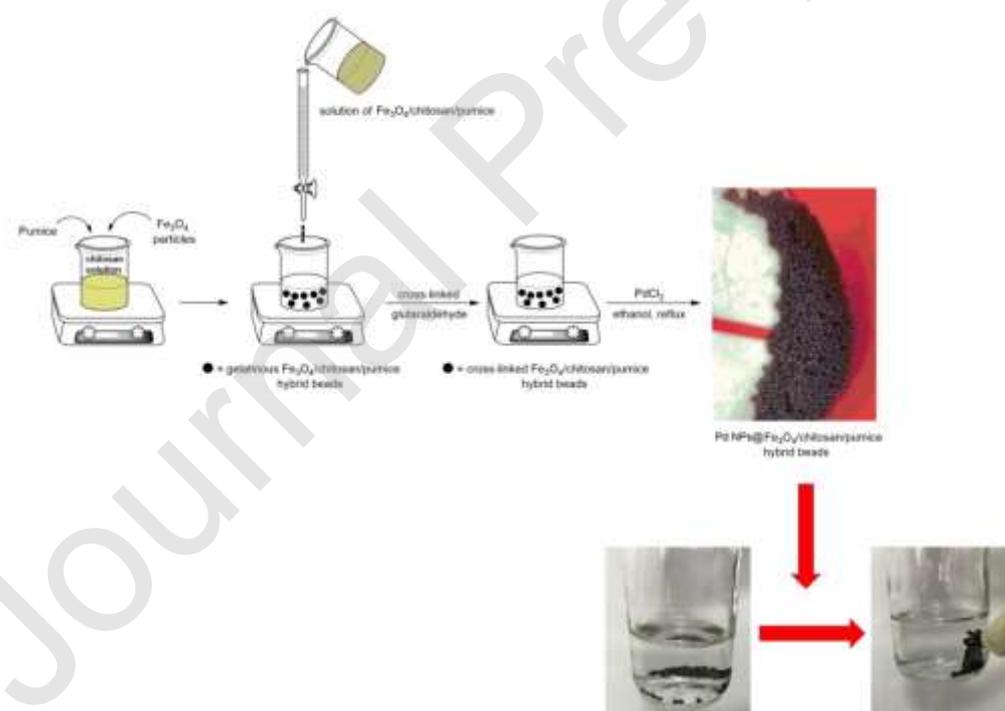
1 g of chitosan was added in acetic acid solution (100 mL, 2% by volume) and dissolved at room temperature. Then, 1 g of pumice was added in the chitosan solution and stirred until a homogeneous mixture was obtained. Afterwards, 1 g of  $\text{Fe}_3\text{O}_4$  particles, which are prepared in a way similar to our previous studies (Baran & Nasrollahzadeh, 2019), were introduced into the mixture, and this suspension was stirred overnight. Following this process, the resulting reaction mixture was dropped in alkaline solution containing water:methanol:NaOH (water-methanol-NaOH: 60 mL-40 mL-12 g) to acquire gelatinous

hybrid beads. Then, gelatinous hybrid beads were cross-linked by stirring with glutaraldehyde solution at 70 °C for 6h in ethanol. Finally, cross-linked  $\text{Fe}_3\text{O}_4$ /chitosan/pumice hybrid beads were collected with external magnet, washed with ethanol, and dried at room temperature.

### 2.3. Preparation of palladium nanoparticles on $\text{Fe}_3\text{O}_4$ /chitosan/pumice hybrid beads

The preparation of palladium nanoparticles without use of any reducing agent was carried out as follow:

1 g of  $\text{Fe}_3\text{O}_4$ /chitosan/pumice hybrid beads and 0.2 of  $\text{PdCl}_2$  were introduced into 30 mL of ethanol, and resulting mixture was refluxed for 4h. It was observed that color of reaction media turned to black after the reduction of  $\text{Pd}(+2)$  to  $\text{Pd}(0)$ . Finally, Pd NPs@ $\text{Fe}_3\text{O}_4$ /chitosan/pumice hybrid beads were easily collected due to their magnetic nature, rinsed with water, and dried.



.....Scheme 1.....

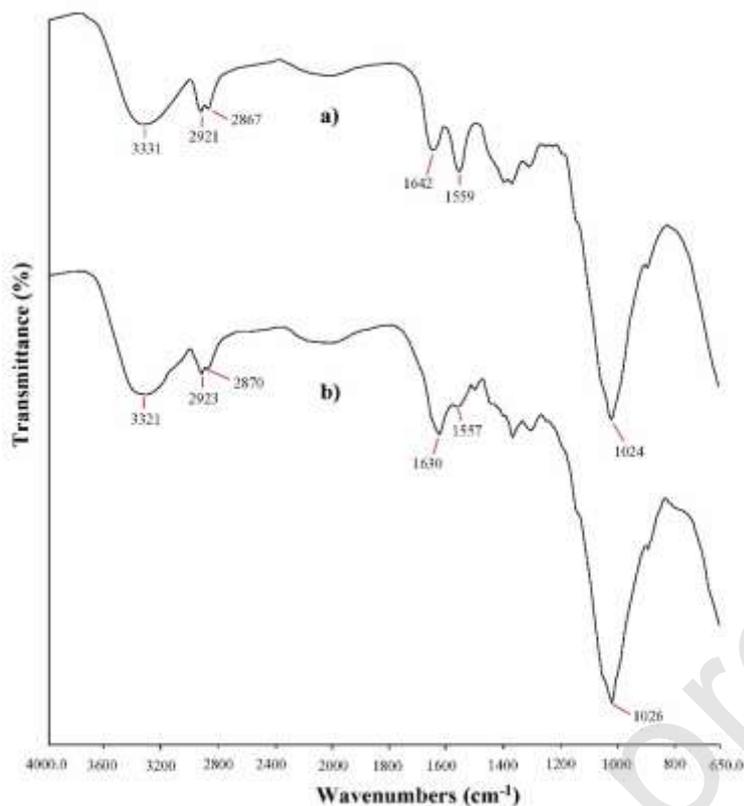
#### ***2.4. Typical method for aryl halide cyanation in the presence of catalyst***

Aryl halide (1.5 mmol), Na<sub>2</sub>CO<sub>3</sub> (1.8 mmol), K<sub>4</sub>[Fe(CN)<sub>6</sub>] (0.2 mmol), Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads (0.01 mol %), and DMF (5 mL) were put into a Schlenk tube and heated at 120 °C for 3h. After the cyanation reaction was completed, the resulting mixture was filtered. The filtrate was extracted with diethyl ether:water at three times, and the organic phase dried on MgSO<sub>4</sub>. Finally, the desired nitriles were obtained by evaporation of solvent, and they were sent to GC/MS, <sup>1</sup>H NMR and <sup>13</sup>C NMR analyses for characterization studies.

### **3. Results and discussion**

#### ***3.1. Characterization***

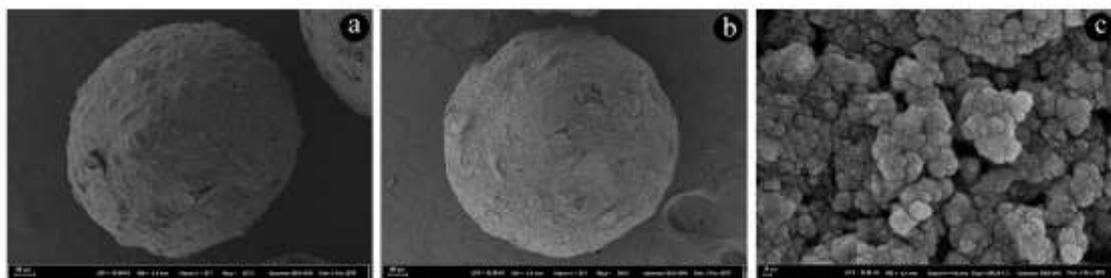
FTIR spectrum of Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads is shown in Figure 1a, and that of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads is shown in Figure 1b. FT-IR spectrum of Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads shows characteristic imine peaks at 1642cm<sup>-1</sup>. This peak shows that cross-linked procedure was successfully performed. The presence of a broad peak at 3331cm<sup>-1</sup> can be assigned to stretching of –OH groups of chitosan and pumice. The other important peaks which are seen in the spectrum of Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads are as follows: CH stretching: 2921 and 2867cm<sup>-1</sup>; NH<sub>2</sub> bending of chitosan: 1559cm<sup>-1</sup>; and C-O-C stretching of chitosan and Si–O–Si stretching of pumice: 1024cm<sup>-1</sup> (Sepehr, Amrane, Karimaian, Zarrabi & Ghaffari, 2014; Veisi, Najafi & Hemmati, 2018). On the other hand, it was noticed that the functional groups of Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads were shifted to lower wavenumbers following the production of Pd NPs (Fig. 1b). It can be explained by interactions between Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads and Pd NPs.



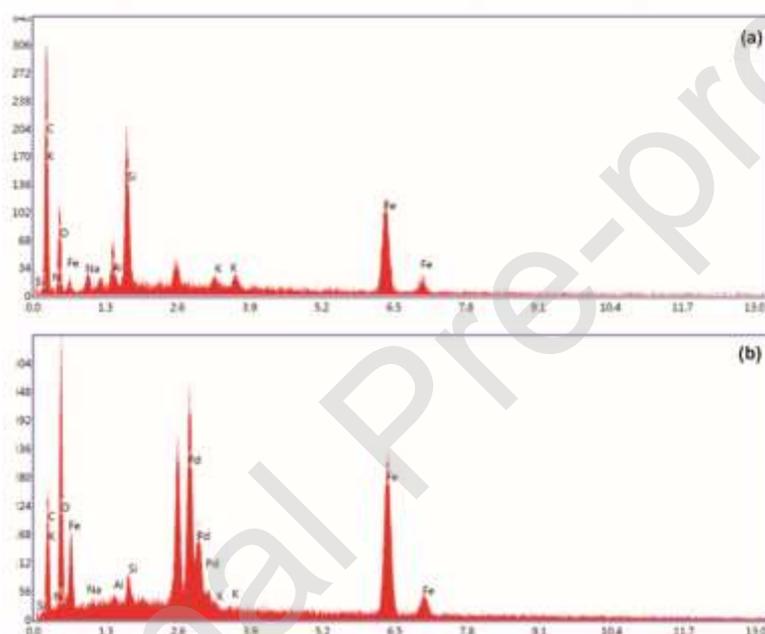
.....**Fig. 1**.....

FE-SEM micrograms of Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads and Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads are shown in Fig. 2. As seen in the micrograms, both the designed support and the catalyst have spherical forms. These results confirmed that hybrid beads were successfully fabricated. Additionally, FE-SEM analyses was carried out at higher magnifications to detect formation of Pd NPs on Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads (Fig. 2c). It was found that the fabrication of palladium nanoparticles was successfully achieved. Fig. 3 displays EDS spectrum of Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads and Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads. As clearly seen in Fig. 3b, the presence of Pd peaks confirm the preparation of palladium nanoparticles. Additionally, TEM analyses of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads was performed and it was detected that the majority of

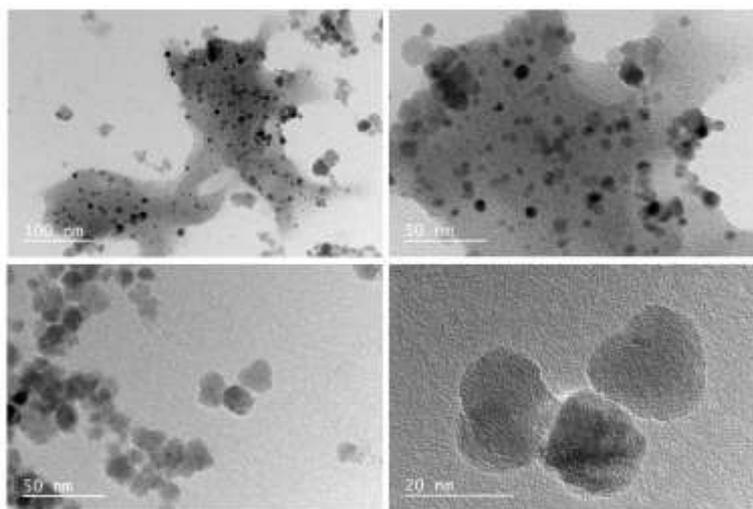
palladium nanoparticles, which are stabilized on the support, lie in the size range about 20 nm (Fig. 4).



.....Fig.2.....

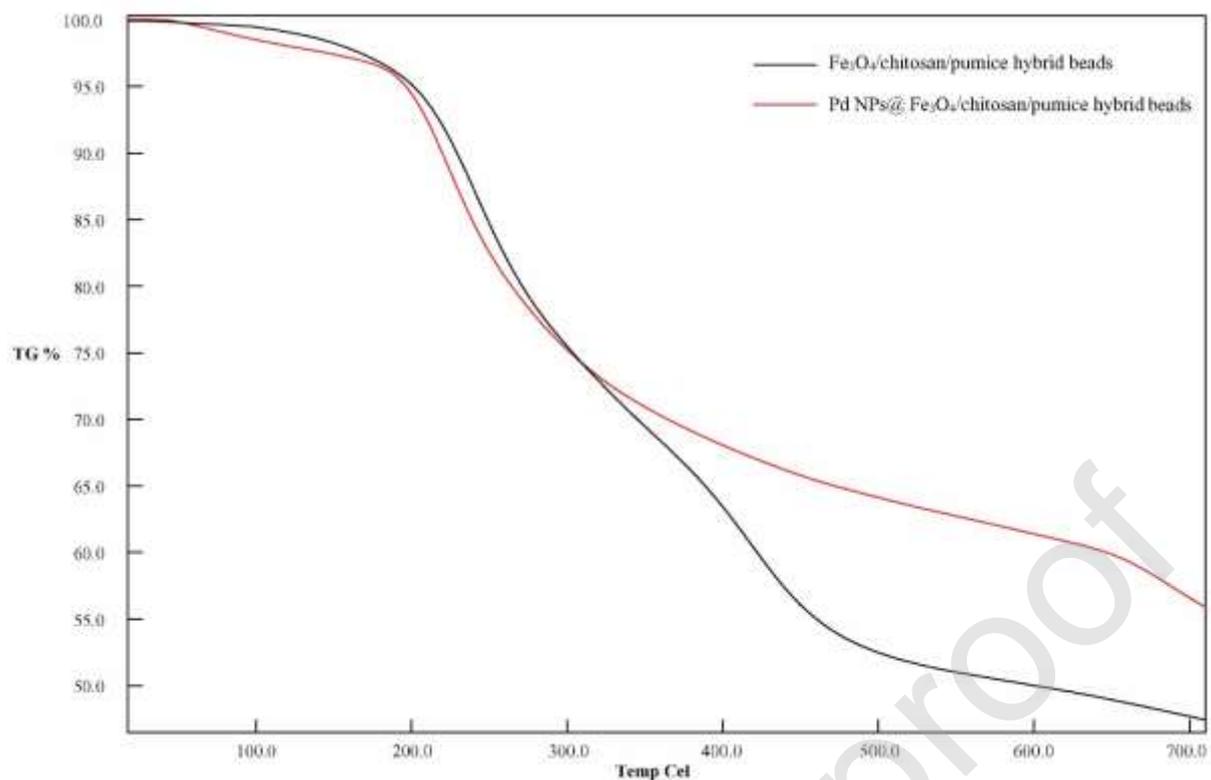


.....Fig. 3.....



.....**Fig. 4**.....

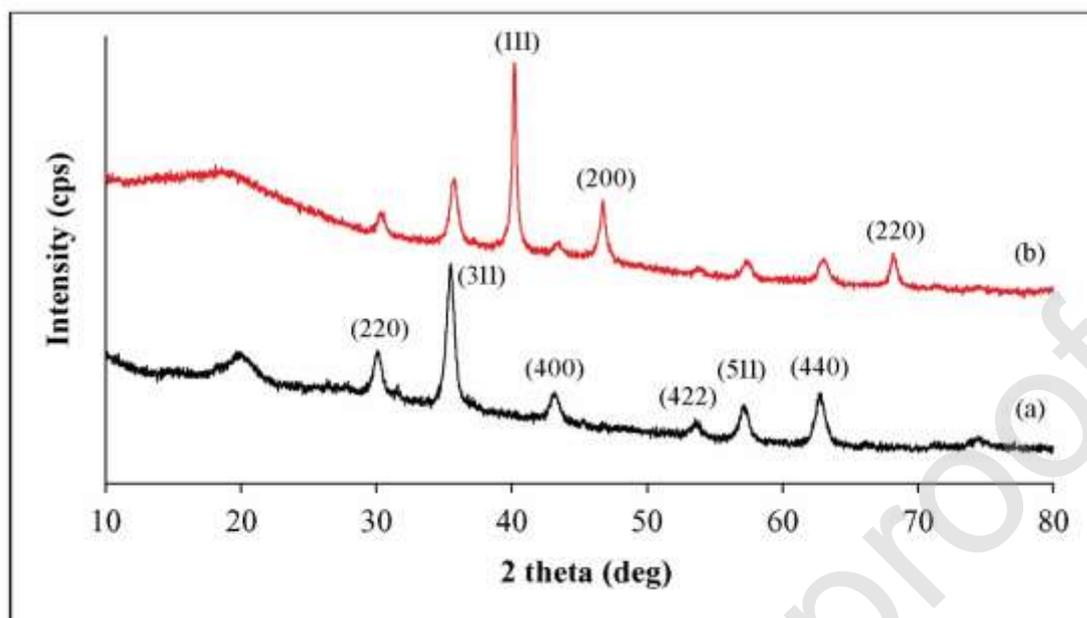
TGA was used to measure thermal durability of Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads and Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads (Fig. 5). The thermogram of Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads showed that the maximum decomposition temperature ( $T_{\max}$ ) was 240.7 °C. As depicted in Fig. 5, this value was recorded as 221.4 °C for Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads. These results showed that the thermal stability of Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads was found to be higher than those of the catalyst. This decrease in  $T_{\max}$  of the catalyst can be explained by the fact that the palladium nanoparticles catalyze the thermal decomposition of the chitosan/pumice matrix (Baran, Sargin, Kaya & Menteş, 2016; Ziegler-Borowska, Chełminiak & Kaczmarek, 2015).



.....**Fig. 5**.....

For further characterization of Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads and Pd NPs @Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads, powder XRD analyses were performed, and their diagrams are given in Fig. 6. Both Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads and its catalyst displayed broad peaks at ~20° which can be associated with characteristic peaks of chitosan and pumice (Baran & Menteş, 2017; Correcher, Gomez-Ros, Dogan, Garcia-Guinea & Topaksu, 2017). Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads displayed typical diffraction peaks at 30.16°, 35.44°, 43.29°, 53.61°, 57.28°, and 62.65°, which are assigned to (220), (311), (400), (422), (511), and (440) crystal planes of Fe<sub>3</sub>O<sub>4</sub>, respectively (Lotfi & Veisi, 2019) (Fig. 7a). In XRD pattern of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads, new peaks were observed at 40.16°, 46.75°, and 68.26° in addition to the characteristic peaks of Fe<sub>3</sub>O<sub>4</sub> (Fig. 6b). These important peaks are indexed to (111), (200), and (220) crystalline planes of face-centered Pd,

confirming the fabrication of palladium nanoparticles (Kora & Rastogi, 2018; Sadjadi, Malmir, Heravi & Ghoreyshi Kahangi, 2019).



.....Fig. 6.....

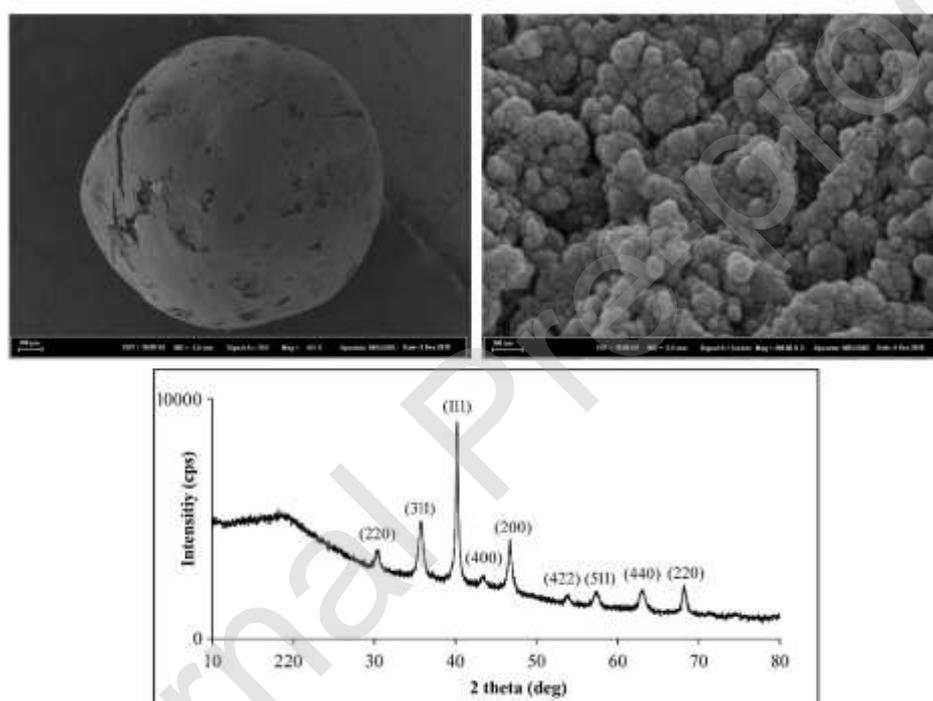
### 3.2. Investigation of catalytic role of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads

Before the catalytic efficacy of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads against synthesis of benzonitriles was investigated, preliminary studies were performed using *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>I, which is chosen as the test substrate, to detect optimal reaction conditions. The optimized reaction conditions were determined as follows: 0.01% mol catalyst, Na<sub>2</sub>CO<sub>3</sub> as base system, DMF as solvent, 120 °C as reaction temperature, and 3 hours as reaction time (please refer to Supplementary data). With the optimum reaction parameters at hand, the catalytic role of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads were tested in cyanation of various aryl iodides with K<sub>4</sub>[Fe(CN)<sub>6</sub>] (Table 1). The catalytic tests showed that aryl iodides, which bear different substituted groups, were transformed to corresponding benzonitriles by Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads in excellent yields. For example, Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads successfully cyanated *m*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>I with 97%

yield. *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>I furnished the desired benzonitrile product in 94% yield. Excellent benzonitriles yields were reached with *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>I, *m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>I, and *o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>I. To demonstrate universal adaptability of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads, their catalytic performance was also evaluated against aryl bromide cyanation using K<sub>4</sub>[Fe(CN)<sub>6</sub>]. Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads appeared to be highly efficient for cyanation of aryl bromides. *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Br and *m*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Br smoothly produced desired cyanides with good yields. Cyanation yield of *p*-CNC<sub>6</sub>H<sub>4</sub>Br to *p*-CNC<sub>6</sub>H<sub>4</sub>CN in the presence of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads was 97%. Additionally, the catalytic behavior of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads was also evaluated against cyanation of aryl chlorides, and good product yields were reached. The catalyst successfully cyanated *m*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl with 86% yield. These results show that the designed Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads are useful as a catalyst for aryl iodide, bromide, and chloride cyanations. In order to show the catalytic superiority of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads, their catalytic activity on the cyanation of *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Br was compared to that of the catalysts reported in literature, and the results are summarized in Table 2. These results show that Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads are more useful than the other catalysts in terms of reaction yield and reaction time.

Long-lasting catalysts provide a significant advantage for industrial applications. Therefore, the recoverability and reusability of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads were tested in the cyanation of *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>I using K<sub>4</sub>[Fe(CN)<sub>6</sub>]. After the typical cyanation reaction, Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads were recollected by external magnet, rinsed with water, and dried for next runs. The same procedure was followed for each cycle. Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid bead confirmed that it was durable catalyst since it gave a high reaction yield (84%) even after six successive runs. To show the constancy of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads, FE-SEM and XRD analyses were conducted after

the recycle test (Fig.7). The results of these analyses were found to be similar to fresh Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads. These findings show that the catalytic performance and constancy of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads were retained for a long time. Moreover, leaching of palladium ions from Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads was investigated by ICP analysis after the recycling test, and it was found to be insignificant (0.2%). This result display that the prepared Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads had good interaction against palladium nanoparticles. More importantly, this result proves that Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads have good catalytic stability.



.....**Fig. 7**.....

#### 4. Conclusion

In conclusion, a highly useful catalyst system was designed by immobilization of palladium nanoparticles on Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads. Then, Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads were evaluated as heterogeneous nanocatalyst against various aryl halide cyanations with K<sub>4</sub>[Fe(CN)<sub>6</sub>]. These tests show that Pd

NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads have good substrate tolerance by catalyzing the syntheses of various benzonitriles with high yields. Moreover, it was found that Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads could be easily collected via external magnet, and it could be reused at six successive runs without significant palladium leaching. This paper clearly shows that Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads are suitable as a catalyst for cyanation reactions in terms of their sustainability, high catalytic efficiency, easy separation, and high recyclability.

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**Scheme and Figure Captions**

**Fig. 1.** FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads (a) and Pd NPs @Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads (b)

**Fig. 2.** FE-SEM images of Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads (a) and Pd NPs @Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads (b and c)

**Fig. 3.** EDS spectra of Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads (a) and Pd NPs @Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads (b)

**Fig. 4.** TEM images of Pd NPs @Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads

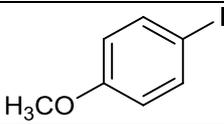
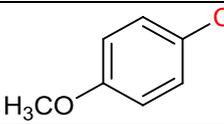
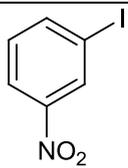
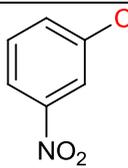
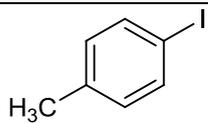
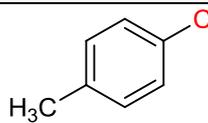
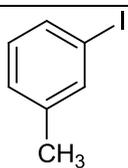
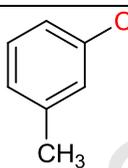
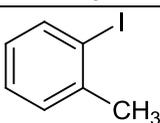
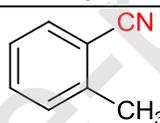
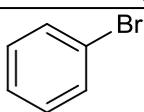
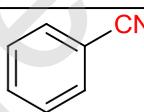
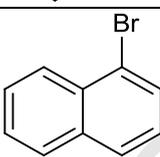
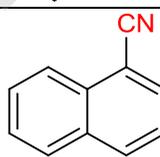
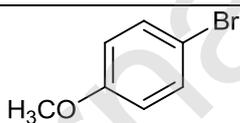
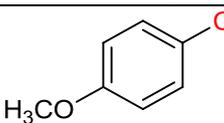
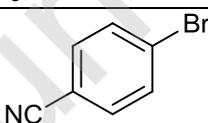
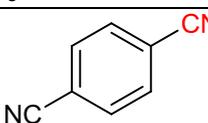
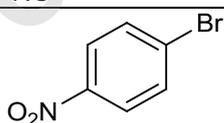
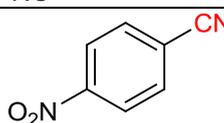
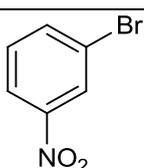
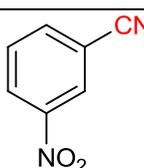
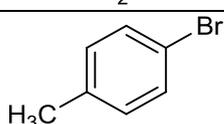
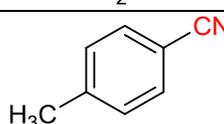
**Fig. 5.** TGA spectra of Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads and Pd NPs @Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads

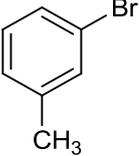
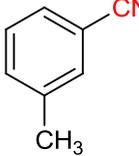
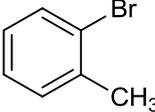
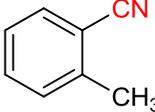
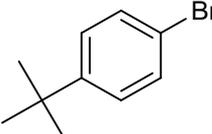
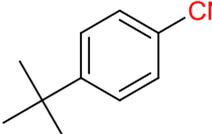
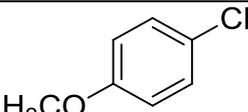
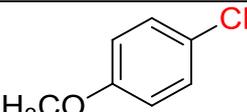
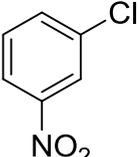
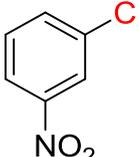
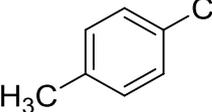
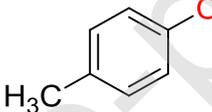
**Fig. 6.** XRD patterns of Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads (a) and Pd NPs @Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads (b)

**Fig. 7.** FE-SEM images and XRD pattern of Pd NPs @Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads after the reusability test

**Scheme 1.** Fabrication of Pd NPs @Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads

**Table 1.** Cyanation reaction of aryl halides with  $K_4[Fe(CN)_6]$  in the presence of Pd NPs@ $Fe_3O_4$ /chitosan/pumice hybrid beads

| Entry | Ar-X                                                                                | Product                                                                              | Yield (%) <sup>b</sup> |
|-------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|------------------------|
| 1     |    |    | 94                     |
| 2     |    |    | 97                     |
| 3     |    |    | 95                     |
| 4     |    |    | 93                     |
| 5     |   |   | 91                     |
| 6     |  |  | 92                     |
| 7     |  |  | 88                     |
| 8     |  |  | 91                     |
| 9     |  |  | 97                     |
| 10    |  |  | 98                     |
| 11    |  |  | 96                     |
| 12    |  |  | 91                     |

|    |                                                                                    |                                                                                     |    |
|----|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|----|
| 13 |   |   | 89 |
| 14 |   |   | 85 |
| 15 |   |   | 82 |
| 16 |   |   | 83 |
| 17 |   |   | 86 |
| 18 |  |  | 80 |

<sup>a</sup> **Reaction conditions:** Aryl halides (1.5 mmol),  $K_4Fe(CN)_6$  (0.2 mmol), base (1.8 mmol), 0.01% mol Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads, DMF (6.0 mL), 120°C.

<sup>b</sup>: isolated yield

**Table 2.** Comparison of Pd NPs@Fe<sub>3</sub>O<sub>4</sub>/chitosan/pumice hybrid beads with other reported catalysts in the cyanation of *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>Br

| Entry | Catalyst                                                            | Time | Yield (%) | Ref.                                                           |
|-------|---------------------------------------------------------------------|------|-----------|----------------------------------------------------------------|
| 1     | P–O bidentate chelate palladium complex                             | 16 h | 84        | (Fu, Li, Zhu, Chen, Kang & Guo, 2014)                          |
| 2     | Pd NPs/RGO-Rosa canina                                              | 6 h  | 90        | (Hemmati, Sedrpoushan, Soudalizadeh, Khosravi & Hekmati, 2019) |
| 3     | Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -BAT-Pd(II)        | 7h   | 90        | (Nasrollahzadeh, Maryami, Sajjadi & Mehdipour, 2019)           |
| 4     | Pd NPs                                                              | 9h   | 85        | (Kandathil, Dateer, Sasidhar, Patil & Patil, 2018b)            |
| 5     | Pd/CuO NP                                                           | 15 h | 88        | (Nasrollahzadeh, 2016)                                         |
| 6     | Pd/PPycatalyst                                                      | 8 h  | 66        | (Magdesieva, Nikitin, Zolotukhina & Vorotyntsev, 2014)         |
| 7     | PdLHMS-3 catalyst                                                   | 16 h | 75        | (Modak, Mondal & Bhaumik, 2012)                                |
| 8     | Pd NPs@Fe <sub>3</sub> O <sub>4</sub> /chitosan/pumice hybrid beads | 3 h  | 91        | Present study                                                  |