Synthesis of nano magnetic supported NHC-palladium and investigation of its applications as a catalyst in the Mizoroki-Heck cross-coupling reaction in H₂O

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ABSTRACT

The unique properties of N-heterocyclic carbenes (NHCs) as an effective ligand for palladium catalytic centers have recently found much attention. In this work, Fe₃O₄ nanoparticle supported palladium(II)-N-heterocyclic carbene catalyst was successfully designed, synthesized and characterized by various methods. The activity of the catalyst was evaluated in the Mizoroki-Heck cross-coupling reaction in which the desired products were obtained in high yield in H₂O as a green solvent. The reaction was carried out in short reaction times using low amounts of the catalyst. Moreover, the catalyst was easily separated from the reaction media and reused for 5 cycles.

1. Introduction

The use of heterogeneous catalysts can be effective in reducing environmental problems [1]. In recent years, various supports such as polymers [2a,b], carbon nanotubes [3], silica [4], and metal oxides [5] have been used as a support to promote the catalytic properties. Therefore, by immobilization of Pd on a suitable support, they could be separated from the product and reused for several times [6]. Among the different supports, magnetic nanoparticles (MNPs) have recently emerged as robust alternatives for immobilization of homogeneous catalysts, in which this behavior is due to their high surface area to volume ratio, low porosity, nano scale dimension and high dispersion in the reaction media [7]. Despite the NPs benefits, they can easily be coagulated due to their colloidal nature. As a result, the magnetic form of NPs have been applied to resolve the problem, in which the catalyst can simply be coagulated due to their colloidal nature. In the case of silica and NPs supported catalysts, usually 3-halopropyltriethoxysilanes were used as linker [17]. Recently, in order to obtain more stable linker, the 1,2,3-triazole moiety has also been added to it [11]. In 2014, Khosropour’s group designed and prepared SPIONs-bis(NHC)-palladium(II) catalyst and used it as an efficient catalyst in C–C coupling reactions under heating or microwave irradiation [18]. In 2016, Hajipour and co-workers also reported the immobilization of a Pd–NHC complex on MNPs by anchoring phenyl-1H-imidazole onto the modified Fe₃O₄ NPs and the recyclable catalyst was used in the Heck and Suzuki–Miyaura cross-coupling reactions [19]. Therefore, as observed, various

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MNP-supported NHC–Pd catalysts have been applied in C–C coupling reactions. Hence, in continuation of our interest in preparing heterogeneous Pd containing catalysts [20], in order to achieve better stability and a minor quantity of palladium leaching we are intending to design and synthesize green supported catalyst Fe3O4@Si–NHC–Pd by adding 1,2,3-triazole moiety to the linker via a click reaction. As a result, for the first time, we have developed a new MNPs-supported catalyst by adding 1,2,3-triazole to linker and NHC as ligand and present its outstanding catalytic efficiency in the Mizoroki-Heck cross-coupling reaction.

2. Experimental

2.1. General

All chemicals were purchased from Merck, Sigma-Aldrich, and Fluka. Melting points were determined using a Büchi B540 melting point apparatus. The IR spectra were recorded on a Fourier Transform Infrared spectroscopy (ABB Bomem model FTIR 2000 spectrophotometer) (KBr). 1H NMR (300 MHz) and 13C NMR (75 MHz) spectra were recorded with a commercial Bruker AQS-300 Avance spectrometer using DMSO-d6 or CDCl3 as solvent. Palladium content of the catalyst was determined by inductively coupled plasma (ICP) on a Varian Vista-MPX apparatus. The IR spectra were recorded on an Fourier Transform Infrared spectrophotometer. The IR spectra were recorded on an Fourier Transform IR spectrometer.

2.2. Catalyst synthesis

2.2.1. Preparation of Fe3O4@SiO2

Magnetic (Fe3O4) nanoparticles were synthesized through coprecipitation method by the reaction of ferric and ferrous ion (2/1 in mol/mol) by using the reported method [11]. In the next step, the obtained Fe3O4 (0.5 g, 2.1 mmol), ethanol (50 ml), deionized water (5 ml), tetraethoxysilane (TEOS) (0.2 ml), and 5.0 ml of NaOH (10 wt %) were mixed. Then the product, Fe3O4@SiO2 was separated by an external magnetic field, washed repeatedly with ethanol and deionized water and dried at 80 ̊C under vacuum for 10 h. FT-IR (KBr, cm–1): 3445, 2937, 1072, 821, 653.

2.2.2. Synthesis of compound 2

In a round-bottom flask, 1-methylimidazole (1 g, 12.18 mmol), propargyl bromide (1.9 ml, 25 mmol) and acetonitrile (50 ml) were mixed. The resulting mixture was refluxed for 24 h. Then the solvent was removed and product 2 was obtained as a red liquid [13].

2.2.3. Synthesis of 3-azidopropyltriethoxysilane (3)

In a round-bottom flask, a mixture of 3-Chloropropyltriethoxysilane (4.82 g, 20.0 mmol), sodium azide (1.95 g, 30.0 mmol), tetrabutylammonium bromide (TBAB, 1.29 g, 4.0 mmol) and dry acetonitrile (75 ml) was refluxed under nitrogen atmosphere for 24 h. The solvent was then removed under reduced pressure. To the resulting mixture Et2O (30 ml) was added and the suspension was filtered and subsequently washed with Et2O (2 × 10 ml). The combined solvent was evaporated and the colorless liquid as product 3 was formed (4.06 g, 82%) [10, 11].

2.2.4. Synthesis of azide-functionalized MNPs (4)

Fe3O4@SiO2 nanoparticles (1.5 g) were placed in a 100 ml round bottom flask and sonicated in dry toluene (75 ml) for 40 min. Then, 3-azidopropyltriethoxysilane (0.5 g, 2.02 mmol) was added and the mixture was stirred at reflux conditions under nitrogen for 24 h [10, 11].

The completion of the reaction was monitored by TLC (n–hexane-EtOAc: 4/1). Compound 4 was then collected by an external magnet, washed with acetone, and dried. FT-IR (KBr, cm–1): 3421, 2102, 1650, 1069, 800, 577,461.

2.2.5. Synthesis of compound (5) through click reaction

The mixture of compound 4 (0.5 g), compound 2 (0.3 g), CuI (0.5 g, 0.26 mmol), and K2CO3 (0.5 g, 3.62 mmol) in DMF/THF (100 ml) was placed in a 200 ml round bottom flask and stirred for 24 h at room temperature. The progress of the reaction was monitored by TLC (n–hexane-EtOAc: 4/2). After completion of the reaction the precipitated solids were filtered, washed and dried in air [10, 11, 13].

2.2.6. Preparation of Fe3O4@Si–NHC–Pd (6)

Synthesis of Compound 6 was carried out according to the method reported in the literature [16]. In a 25 ml round bottom flask, Pd(OAc)2 (17.0 mg, 0.076 mmol) in 10 ml MeOH was stirred at room temperature for 3 h. Then 0.3 g compound 5 and Na2CO3 (0.5 M, 30 ml) were added to the flask, and the temperature was raised to 60 ̊C for 24 h. To the end, the catalyst Fe3O4@Si–NHC–Pd was collected by an external magnetic field and washed with acetone, water and acetonitrile. Then it was dried under vacuum overnight. FT-IR (KBr, cm–1): 3494, 3085, 2123, 1656, 1569, 830, 619.

2.3. General procedure for the Heck cross-coupling reaction byFe3O4@Si–NHC–Pd

A mixture of the aryl halide (1.0 mmol), alkene (ethyl acrylate or styrene) (1.2 mmol), nanocatalyst (0.272 mol% Pd, 20 mg), base (2 mmol), and solvent (5.0 ml) was placed in 25 ml round bottom flask and was refluxed in an oil bath. The progress of the reaction was followed using TLC. After completion of the reaction, the mixture was cooled and the nanocatalyst separated by a magnet. The mixture was extracted with EtO2 (3 × 25 ml) and the solvent evaporated under reduced pressure. The resulting product was purified using thin layer chromatography to obtain pure coupling products in high yield and finally characterized using 1H and 13C-NMR spectroscopies (see supporting information).

3. Results and discussion

The process of preparation of Fe3O4@Si–NHC–Pd catalyst has been shown in Scheme 1. At first the silica-coated Fe3O4 NPs were synthesized, and chosen as magnetic support (compound 1). In the next step, compound 2 was prepared from the reaction of 1-methylimidazole with propargyl bromide. In order to bring about the triazole moiety in the linker and prepare a more stable catalyst, in this step compound 3 was synthesized from the reaction of 3-Chloropropyltriethoxysilane, sodium azide and tetrabutylammonium bromide under nitrogen atmosphere. Subsequently in order to prepare compound 4, SiO2-coated Fe3O4 nanoparticles (compound 1) were sonicated in dry toluene (75 ml) for 40 min and 3-azidopropyltriethoxysilane (compound 3) was added to it. In this stage, the reaction of (compound 4) with compound 2 through the known click reaction resulted in the formation of triazole moiety to give (compound 5). In the final step compound 5, Pd(OAc)2 and Na2CO3 was heated at 60 °C for 24 h to obtain the desired catalyst Fe3O4@Si–NHC–Pd.

Modification of Fe3O4 NPs was confirmed by FT-IR spectroscopy (Figure 1a) All samples showed a peak at 653 which is related to (Fe–O). The adsorption bands at 1082 and 821 cm–1 are assigned to (Si–O–Si) bands, which are associated with Fe3O4 @SiO2. The broad adsorption at 3300 cm–1 is due to OH stretching of surface hydroxyl groups. Figure 1b showed a peak at 2104 cm–1, which is attributed to the stretching vibration of organic azide and confirmed incorporation of the azidopropyl group. The sharp peaks at 1569 cm–1 and 1659 cm–1 are related to C=N and C=C vibrations, respectively. Also a series of bands appeared around 531–619 cm–1 are related to Pd–C stretch mode (Figure 1c). The XRD pattern of the catalyst shows diffraction peaks, which is similar to the standard Fe3O4 sample (Figure 2). Also, the broad peak at the range of 20 to 30° is in accordance with an amorphous silica layer. Characteristic
peaks for Pd nanoparticles were not observed, which confirmed that the Pd nanoparticles were properly dispersed onto the MNPs. Figure 3 illustrated the SEM images of the support Fe3O4@SiO2 and the catalyst Fe3O4@Si–NHC–Pd. As is clear, the size of nano-Fe3O4 core shell was found to be about 43 nm (Figure 3a). Figure 3c and Figure 4 showed the elemental mapping data to confirm the presence of C, N, O, Si, Fe, Br, Pd in the catalyst. The content of palladium was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) and EDX, which was 1.45 wt%. The thermal stability of the Fe3O4@Si–NHC–Pd was evaluated by thermogravimetric (TG) analysis under nitrogen atmosphere. To estimate the amount of immobilized groups on the surface, elemental analysis and TGA were carried out. The TGA curve in Figure 5 indicated the first weight loss of 1.53% up to 120 °C, which was related to the removal of adsorbed water on the support. Furthermore, the weight loss below 500 °C which is 13.28% for the catalyst could be assigned to the organic part of the catalyst. Therefore, Fe3O4@Si–NHC–Pd was very stable and could be used at high temperatures. To evaluate the activity of the Fe3O4@Si–NHC–Pd catalyst, it was tested in the Mizoroki-Heck cross-coupling reaction. For optimization of the reaction conditions, the reaction of styrene and 4-iodotoluene was chosen as a model reaction. In order to show the role of solvent on the Mizoroki-Heck reaction, different protic solvent such as EtOH, EtOH/H2O, H2O (Table 1, Entry 4, 5, 6), and aprotic solvents such as DMF, DMSO, and CH3CN (Table 1, Entry 1, 2, 3) was evaluated. The reaction was significantly affected by the nature of the solvent and it was observed that H2O was appeared to be the best reaction medium in comparison to the others (Table 1, entry 6).

Catalyst: Fe3O4 @ Si-NHC-Pd

Scheme 1. Preparation of Fe3O4@Si–NHC–Pd; Reaction conditions: a) synthesis of silica-coated Fe3O4 nanoparticles; b) acetone, refluxed for 24 h; c) NaN3, CH3CN, TBAB, refluxed for 24 h; d) Silica-coated Fe3O4 Nanoparticles, toluene, reflux, 24 h; e) 4, 2, CuI, K2CO3, DMF/THF, 24 h; f) Pd(OAc)2, Na2CO3, MeOH, 24 h.
Figure 1. FT-IR spectra of Fe₃O₄@SiO₂ (a); azide-functionalized Fe₃O₄@SiO₂–N₃ (b); Fe₃O₄@Si–NHC–Pd sample (c).

Figure 2. XRD spectrum of Fe₃O₄@Si–NHC–Pd
Additionally, the influence of inorganic bases such as K₂CO₃, Cs₂CO₃, Na₂CO₃ and organic base Et₃N was explored (entries 8, 9, 10, and 6) and as indicated in Table 1, Et₃N was found to be the best base. To find out the effect of the temperature, the reaction was carried out at 90, 100, 110 °C in which no obvious improvement was observed at higher temperatures thus 90 °C was selected. (Entries 6, 11, 12). Next, we examined different amounts of the catalyst between 10, 15 and 20 mg (0.136, 0.204, 0.272 mol %) of Pd on the Heck reaction (Table 1, Entries 13, 14, 6). As can be seen in Table 1, 20 mg, (0.272 mol %) of the catalyst worked remarkably well with 95% yield of products. When 10 mg, (0.136 mol %) of the catalyst was used the yield dropped.

In Table 2, some electron-rich and electron-poor aryl halides as substrate were studied under the standard reaction conditions. As showed in Table 2, the reaction of aryl iodides and bromides containing electron-rich and electron-poor substituents were achieved with high yields. It is necessary to mention that aryl chloride generated a lower yield. When 10 mg, (0.136 mol %) of the catalyst was used the yield dropped.

In order to confirm the heterogeneity of the Fe₃O₄@Si–NHC–Pd and determine if palladium leaching occurs, the Mizoroki-Heck cross-coupling reaction under optimized conditions (according to Table 1, entry 6) and a hot filtration test were performed. After completion of the reaction, the catalyst was removed using an external magnetic field and the residual solution was then allowed to react for a further 2 h and the amount of the Pd species dissolved into solution was determined using ICP analysis. The results suggested a low amount of palladium is removed from the Fe₃O₄ support and is an evidence of heterogeneous nature of the catalyst. According to the results of ICP, 0.03 % Pd leaching can be found during the reaction, which indicated that the Fe₃O₄@Si–NHC–Pd catalyst is recoverable and stable up to five times (Figure 6).

4. Recyclability test

The easy recovery and reusability of the catalyst is key factor of a heterogeneous catalyst, mainly from the economic and ecological point of view. Therefore, we are intending to study reusability of our catalyst by running the reaction of styrene and 4-iodotoluene under the optimized reaction conditions. After completion of the reaction followed by TLC, the catalyst was separated from the mixture by an external magnet and washed with water and acetone (2 × 10). It was then dried in an oven at 80 °C for 1 h and was applied for the next run. It is worth noting that the catalyst was reused up to 5 cycles (Figure 6).

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Figure 4. Elemental maps of (a) C, (b) Fe (c) N, (d) Br, (e) O, (f) Si and (g) Pd obtained by EDX.

| Atom | Weight % |
|------|----------|
| C    | 12.50    |
| N    | 8.40     |
| O    | 27.21    |
| Si   | 13.41    |
| Fe   | 36.87    |
| Br   | 0.16     |
| Pd   | 1.45     |

Figure 5. Thermogravimetric curve of the Fe₃O₄@Si–NHC–Pd
Table 1. Optimization of the reaction conditions.

| Entry | Solvent | Base | Temp. (°C) | Catalyst (mol%) | Time (h) | Yield (%) |
|-------|---------|------|------------|-----------------|----------|-----------|
| 1     | DMF     | Et3N| 90         | 0.272           | 7        | 90%       |
| 2     | DMSO    | Et3N| 90         | 0.272           | 8        | 73%       |
| 3     | CH3CN   | Et3N| 90         | 0.272           | 7        | 61%       |
| 4     | EtOH    | Et3N| 90         | 0.272           | 9        | 80%       |
| 5     | EtOH/H2O| Et3N| 90         | 0.272           | 8        | 85%       |
| 6     | H2O     | Et3N| 90         | 0.272           | 8        | 95%       |
| 7     | DMF/H2O | Et3N| 90         | 0.272           | 9        | 95%       |
| 8     | H2O     | K2CO3| 90       | 0.272           | 9        | 78%       |
| 9     | H2O     | Cs2CO3| 90     | 0.272           | 8        | 85%       |
| 10    | H2O     | Na2CO3| 90    | 0.272           | 6        | 61%       |
| 11    | H2O     | Et2N | 100       | 0.272           | 7        | 95%       |
| 12    | H2O     | Et2N | 110       | 0.272           | 7        | 98%       |
| 13    | H2O     | Et2N | 90        | 0.136           | 10       | 80%       |
| 14    | H2O     | Et2N | 90        | 0.204           | 9        | 90%       |

Reactions conditions: styrene, 4-iodotoluene, base (2 mmol), Fe3O4@Si-NHC-Pd and solvent (2 ml).

Yields of isolated product.

Table 2. Heck reaction catalyst by Fe3O4@Si–NHC–Pd

| Entry | R1 | X    | R2  | Product | Time (h) | Yield (%) |
|-------|----|------|-----|---------|----------|-----------|
| 1     | 4-Me| I    | CO2Me | 8a      | 8        | 95        |
| 2     | H   | I    | CO2Et | 8b      | 8.5      | 95        |
| 3     | 4-Me| Br   | CO2Me | 8d      | 10.5     | 80        |
| 4     | 4-O-Me| Br | CO2Me | 8e      | 11       | 85        |
| 5     | 4-O-Me| Br | CO2Et | 8f      | 12       | 85        |
| 6     | 3-O-Me| Br | CO2Me | 8g      | 12.25    | 80        |
| 7     | 3-O-Me| Br | CO2Et | 8h      | 12.5     | 75        |
| 8     | 3-O-Me| Br | Ph    | 8i      | 15       | 80        |
| 9     | 3-O-Me| Br | Ph    | 8j      | 22       | 75        |
| 10    | 4-COMe| Cl | CO2Me | 8k      | 24       | 75        |
| 11    | 4-COMe| Cl | CO2Et | 8l      | 24       | 75        |
| 12    | 4-COMe| Cl | Ph    | 8m      | 10       | 85        |
| 13    | H   | Br   | CO2Me | 8n      | 12       | 90        |
| 14    | 4-CN| Br   | CO2Et | 8o      | 12       | 90        |
| 15    | 4-CN| Br   | Ph    | 8p      | 15       | 90        |
| 16    | 4-CHO| Br | CO2Me | 8q      | 16       | 90        |
| 17    | 4-CHO| Br | CO2Et | 8r      | 18       | 90        |
| 18    | H   | Br   | Ph    | 8s      | 8        | 98        |
| 19    | 4-Me| I    | CN   | 8t      | 8        | 90        |
| 20    | 4-COMe| Cl | CN   | 8t      | 8.5      | 80        |

Reactions conditions: styrene, 4-iodotoluene, Et3N, Fe3O4@Si–NHC–Pd catalyst, in H2O at 90 °C.

Yields of isolated product.

Table 3. Comparison of catalytic activity for the Heck cross coupling reaction using Fe3O4@Si–NHC–Pd catalyst with those obtained by reported catalysts.

| Entry | Catalyst | Pd (mol %) | Temp. (°C) | Time (h) | Solvent | Yield (%) | Ref. |
|-------|----------|------------|------------|----------|---------|-----------|------|
| 1     | Fe3O4@Si–NHC–Pd | 0.272     | 90         | 8        | H2O     | 98        | This work |
| 2     | NO2–NHC–Pd@Fe3O4 | 1.0       | 80         | 6        | MeCN    | 92        | [21] |
| 3     | Pd NPs@NHC@ZIF-8 | 0.08      | 110        | 2.5      | DMF–H2O | 90        | [22] |
| 4     | MnPs–NHC–Pd(II) | 0.036     | 70         | 0.23     | DMF     | 87        | [19] |
| 5     | Hydrazon-pd@ZnO | 0.26      | 130        | 1.5      | DMF     | 85        | [23] |
| 6     | PdCl2Kryptofix-5 | 0.9       | 130        | 24       | DMF     | 16        | [24] |

Reactions conditions: Bromobenzene (1 mmol), styrene (1.2 mmol), base, Catalyst and solvent.

Yields of isolated product.
In summary, a novel Fe3O4@Si–NHC–Pd has been successfully prepared with 1,2,3-triazole moiety using click reaction without any phosphine ligand. Furthermore, the heterogeneous catalyst was applied effectively in the Mizoroki-Heck cross-coupling. The high yield of products, performing the reaction in a green solvent (H2O), short reaction times, using low amounts of the catalyst are some advantages of this catalyst. Moreover, the recoverability of the catalyst was tested, which showed that it could be reused for 5 runs.

### Declarations

#### Author contribution statement
Razieh Ghavidel Kalishomi: Conceived and designed the experiments; Performed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.
Shahnaz Rostamizadeh: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.
Fatemeh Nouri: Contributed reagents, materials, analysis tools or data; Wrote the paper.
Ali Khazaei: Performed the experiments.

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#### Competing interest statement
The authors declare no conflict of interest.

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### References

[1] M. Doble, A.K. Kruthiventi, Green Chemistry and Engineering, Academic Press, London, 2007.

[2] a) B. Movassagh, F. Hajizadeh, E. Moammadi, Polystyrene-supported Pd(II)-N-heterocyclic carbene complex as a heterogeneous and recyclable precatalyst for cross-coupling of acyl chlorides with arylboronic acids, Appl. Organomet. Chem. 32 (2017) 1–4.

b) E. Moammadi, B. Movassagh, Synthesis of polystyrene-supported Pd(II)-NHC complex derived from theophylline as an efficient and reusable heterogeneous catalyst for the Heck-Matsuda cross-coupling reaction, J. Mol. Catal. A: Chem. 418 (2016) 158–167.

[3] L. Shao, B. Zhang, W. Zhang, S.Y. Hong, R. Schlögl, D.S. Su, The role of palladium dynamics in the surface catalysis of coupling reactions, Angew. Chem. Int. Ed. 52 (2013) 14–21.

[4] a) C.Y. Lai, Mesoporous silica nanomaterials applications in catalysis, Thermodyn. Catal. 5 (2013) 1–3.

b) T. Begum, M. Mondal, M.P. Borpuzari, R. Kar, G. Kalita, P.K. Gogoi, U. Bora, An immobilized symmetrical bis-(NHC) palladium complex as a highly efficient and recyclable Suzuki–Miyaura catalyst in aerobic aqueous media, Dalton Trans. 46 (2017) 539–546.

[5] a) D. Wang, C. Deraede, L. Salmon, C. Labrugere, L. Etienne, Efficient and magnetically recoverable “Click” PEGylated γ-Fe2O3-Pd nanoparticle catalysts for Suzuki–Miyaura, Sonogashira, and Heck reactions with positive dendritic effects, Chem. Eur. J. 20 (2014) 1–13.

b) M. Nasrollahzadeh, S.M. Sajadi, A. Rostami-Vartooni, A. Azarian, Palladium nanoparticles supported on copper oxide as an efficient and recyclable catalyst for carbon(sp2)–carbon(sp2) cross-coupling reaction, Mater. Res. Bull. 68 (2015) 150–154.

c) M. Nasrollahzadeh, S.M. Sajadi, A. Rostami-Vartooni, M. Bagherzadeh, Green synthesis of Pd/CuO nanoparticles by Theobroma cacao L. seeds extract and their catalytic performance for the reduction of 4-nitrophenol and phosphine-free Heck coupling reaction under aerobic conditions, J. Colloid. Interface Sci. 448 (2015) 105–112.

d) M. Nasrollahzadeh, S.M. Sajadi, A. Rostami-Vartooni, M. Khalaj, Green synthesis of Pd/Fe3O4 nanoparticles using Euphorbia cyparissias M. bieb root extract and their catalytic applications as magnetically recoverable and stable recyclable catalysts for the phosphine-free Sonogashira and Suzuki coupling reactions, J. Mol. Catal. A: Chem. 396 (2015) 31–39.

e) P.D. Stevens, J. Fan, H.M.R. Garimella, M. Yen, Y. Gao, Superparamagnetic nanoparticle-supported catalysis of Suzuki cross-coupling reactions, Org. Lett. 7 (2005) 2065–2068.

[6] a) S. Rostamnia, H. Golchin, E. Doustkhish, Homolateic chelating N-heterocyclic carbene complexes of palladium immobilized within the pores of SBA-15/IL (NHC–Pd@SBA-15/IL) as heterogeneous catalyst for Hiyama reaction, J. Organomet. Chem. 791 (2015) 18–23.

b) S. Rostamnia, E. Doustkhish, R. Bulgar, B. Zeynizadeh, Supported palladium ions inside periodic mesoporous organosilica with ionic liquid framework (Pd@IL-PMO) as an efficient green catalyst for S-arylation coupling, Micropor. Mesopor. Mater. 225 (2016) 272–279.

c) E. Doustkhish, M. Hassani, Y. Ide, M. Hoseini, N. Assadi, Pd nanomatrix for H2 generation from formic acid, ACS Appl. Nano Mater. 3 (2020) 22–43.

d) S. Rostamnia, E. Doustkhish, B. Zeynizadeh, Cationic modification of SBA-15 porous wall for Pd supporting Pd@SBA-15/ILDABCO as a catalyst for Suzuki coupling in water medium, Micropor. Mesopor. Mater. 222 (2016) 87–929.

e) P.D. Stevens, G. Li, J. Fan, M. Yen, Y. Gao, Recycling of homogenous Pd catalysts using superparamagnetic nanoparticles as novel soluble supports for Suzuki, Heck, and Sonogashira cross-coupling reactions, Chem. Commun. (2005) 4435–4437.

[7] a) B. Karimi, F. Mansouri, H. Mirzaei, Recent applications of magnetically recoverable nanocatalysts in C-C and C-X coupling reactions, Chem. Cat. Chem. 7 (2015) 1736–1789.

b) G. Mohammadi Ziarani, Z. Hassanzadeh, P. Gholamzadeh, S. Asadi, A. Badiei, Advances in click chemistry for silica-based material construction, RSC Adv. 6 (2016) 21979–22006.

c) H. Yang, Y. Wang, Y. Qin, Y. Chong, Q. Yang, G. Li, L. Zhang, W. Li, One-pot preparation of magnetic N-heterocyclic carbene-functionalized silica nanoparticles for the Suzuki-Miyaura coupling of aryl chlorides: improved activity and facile catalyst recovery, Green Chem. 13 (2011) 1352–1361.

d) Y. Zheng, P.D. Stevens, Y. Gao, Magnetic nanoparticles as an orthogonal support of polymer resins: applications to solid-phase Suzuki cross-coupling reactions, J. Org. Chem. 71 (2006) 537–542.

[8] L.P. Beletskaya, A.V. Cheprakov, The Heck reaction as a sharpening stone of palladium catalysis, Rev. Chem. 54 (2015) 3009–3066.

[9] F. Abmlard, J.H. Cho, R.F. Schinazi, Gal(-)-catalyzed Huisingen azide-alkyne 1,3-dipolar cycloaddition reaction in nucleoside, nucleotide, and oligonucleotide chemistry, Chem. Rev. 109 (2009) 4207–4220.

[10] G.F. Zhang, Y. Wang, X. Wen, R. Ding, Y. Li, Dual-functional click-triazole: a metal chelator and immobilization linker for the construction of a heterogeneous palladium catalyst and its application for the aerobic oxidation of alcohols, Chem. Commun. 48 (2012) 2979–2981.

[11] Q. Zhang, H. Su, J. Luo, Y. Wei, Click magnetic nanoparticle-supported palladium catalyst: a phosphine-free, highly efficient and magnetically recoverable catalyst for Suzuki–Miyaura coupling reactions, Catal. Sci. Technol. 3 (2013) 235–243.

[12] G. Lv, W. Mai, R. Jin, L. Gao, Immobilization of dipyrrolidyl complex to magnetic nanoparticle via click chemistry as a recyclable catalyst for Suzuki cross-coupling reactions, Synlett 9 (2008) 1418–1422.

[13] A. Badiei, Y. Khantis, G. Mohammadi, Application of clickable nanoporous silica surface for immobilization of ionic liquids, J. Mater. Res. 27 (2012) 932–938.

[14] T. Weskamp, F.J. Kohl, W. Hieringer, D. Gleich, W.A. Herrmann, Highly active ruthenium catalysts for olefin metathesis: the synergy of N-heterocyclic carbens and coordinatively labile ligands, Angew. Chem. Int. Ed. 38 (16) (1999) 2416–2419.

[15] W.A. Herrmann, N-heterocyclic carbene: a new concept in organometallic chemistry, Angew. Chem. Int. Ed. 41 (2002) 1290–1309.

[16] a) N. Gurbas, E. Kara, Cross coupling reactions catalyzed by (NHC)Pd(II) complexes, Turk. J. Chem. 39 (2015) 1115–1127.

b) I. Ozdemir, M. Yigit, E. Cetinkaya, B. Cetinkaya, Synthesis of novel palladium N-
heterocyclic-carbene complexes as catalysts for Heck and Suzuki cross-coupling reactions, Appl. Organomet. Chem. 20 (2006) 187–192.

c) V. Kandathil, B. Kulkarni, A. Siddiqui, M. Komoniiddalah, B.S. Sasidhar, S.A. Patil, S.A. Patil, Immobilized N-heterocyclic carbene-palladium(II) complex on graphene oxide as efficient and recyclable catalyst for Suzuki–Miyaura cross-coupling and reduction of nitroarenes, Catal. Lett. 150 (2020) 484–503.

[17] a) K.V.S. Ranganath, S. Onitsuka, A.K. Kumar, J. Inanaga, Recent progress of N-heterocyclic carbenes in heterogeneous catalysis, Catal. Sci. Technol. 3 (2013) 2161–2181;

b) M. Nazrollahzadeh, Advances in magnetic nanoparticles-supported palladium complexes for coupling reactions, Molecules 23 (2018) 2532–2592.

[18] M. Ghotbinejad, A.R. Khoraspour, I. Mohammadpour-Baltork, M. Moghadam, S. Tangestaninejad, V. Mirkhani, SPIONs-bis(NHC)-palladium(II): a novel, catalyst powerful and efficient for Mizoroki–Heck and Suzuki–Miyaura reactions, J. Mol. Catal. Chem. 385 (2014) 78–84.

[19] A.R. Hajipour, N.S. Tadayoni, Z. Khorsandi, Magnetic iron oxide nanoparticles–N-heterocyclic carbene-palladium(II): a new, efficient and robust recyclable catalyst for Mizoroki–Heck and Suzuki–Miyaura coupling reactions, Appl. Organomet. Chem. 30 (2016) 590–595.

[20] F. Nouri, S. Rostamizadeh, M. Azad, Post-synthetic modification of IRMOF-3 complex with an imino-palladacycle and its application as an effective Suzuki–Miyaura heterogeneous catalyst in cross-coupling reaction temperature, Molecular Catalysis 443 (2017) 286–293.

[21] Shivaputra A. Patil, V. Kandathil, B. Fahlman, B.S. Sasidhar, Siddappa A. Patil, A convenient, efficient and reusable N-heterocyclic carbene-palladium(ii) based catalyst supported on magnetite for Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions, New J. Chem. 41 (2017) 9531–9545.

[22] M. Azad, S. Rostamizadeh, H. Estiri, F. Nouri, Ultrasmall and highly dispersed Pd nanoparticles inside the pores of ZIF8: sustainable approach to waste minimized Mizoroki Heck crosscoupling reaction based on reusable heterogeneous catalyst, Appl. Organomet. Chem. 33 (2019) 4952–4965.

[23] F. Nouri, S. Rostamizadeh, M. Azad, Synthesis of a novel ZnO nanoplates supported hydrazine-based palladacycle as an effective and recyclable heterogeneous catalyst for the Mizoroki-Heck cross-coupling reaction, Inorg. Chim. Acta. 471 (2018) 664–673.

[24] B. Movassagh, S. Ranjbari, Kryptofix 5 as an inexpensive and efficient ligand for the palladium catalyzed Mizoroki Heck reaction, Appl. Organomet. Chem. 32 (2018) 4224–4230.