

Review

The Use of Palladium on Magnetic Support as Catalyst for Suzuki–Miyaura Cross-Coupling Reactions

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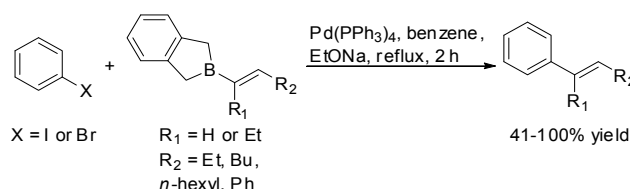
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Abstract: The development of new solid supports for palladium has received a lot of interest lately. These catalysts have been tested in a range of cross-coupling reactions, such as Suzuki–Miyaura, Mizoroki–Heck, and Sonogashira cross-coupling reactions, with good outcomes. Attaching the catalyst to a solid support simplifies the operations required in order to isolate and recycle the catalyst after a reaction has completed. Palladium on solid supports made of magnetic materials is particularly interesting since such catalysts can be removed very simply by utilizing an external magnet, which withholds the catalyst in the reaction vessel. This review will showcase some of the latest magnetic solid supports for palladium and highlight these catalysts' performance in Suzuki–Miyaura cross-coupling reactions.

Keywords: palladium; magnetic support; Suzuki–Miyaura cross-coupling; catalyst recycling

1. Introduction

Since the discovery of the Suzuki–Miyaura cross-coupling reaction in 1979 (Scheme 1) [1–3], it has become one of the most utilized cross-coupling reactions both in industrial and academic research laboratories [3–7]. For the development of this reaction Suzuki was awarded the 2010 Nobel prize in chemistry, together with Negishi and Heck, the chemists behind the Negishi coupling and Heck coupling, respectively [8–10]. Since the early reports by Suzuki and Miyaura on the cross-coupling reaction a tremendous development has taken place in terms of substrate flexibility and reaction conditions. A range of different catalysts and conditions are now available for the successful cross-coupling of halides, triflates, *O*-tosylates, and diazonium salts upon reaction with boronic acid, boronates, and trifluoroborates [3,7,11–15].



Scheme 1. Reaction conditions and substrates used in the first reported Suzuki–Miyaura cross-couplings [1].

Homogeneous palladium catalyst systems have, by far, been the most dominating catalysts utilized for this cross-coupling reaction [7]. In addition to the catalyst many reactions also require the addition of ligands in order to either promote a reaction that does not work or improve yields of sluggish reactions. However, lately there has been a growing interest for the use of heterogeneous catalysts for the Suzuki–Miyaura cross-coupling reaction, which can be seen by the increasing number

of publications on the topic [16–18]. The growing interest is due to the many possibilities that heterogeneous catalysts open up for recovery and recycling of the metal catalyst.

Palladium on charcoal (Pd/C) was used for the first time as a catalyst for the Suzuki–Miyaura cross-coupling in 1994 [19]. The work by Marck et al. marked the beginning of the use of heterogeneous catalysts systems in this particular cross-coupling reaction. Since then it has been applied to an increasing number of reactions making Pd/C one of the most utilized catalyst supports for heterogeneous Suzuki–Miyaura cross-coupling reactions. Several review articles have discussed their use in cross-coupling reactions and Suzuki–Miyaura cross-couplings in particular [20–23]. Lately graphene has also been taken into use as a catalyst support for palladium [24], in addition to graphite oxide [25]. Although graphene, similarly to charcoal, is pure carbon, it adds new properties to the catalyst that are not seen with charcoal as the catalyst support.

Other types of carbon-containing materials are also frequently used as support for palladium nanoparticles (NPs). A good overview of naturally-occurring biopolymers used as catalyst supports was presented by Kumbhar and Salunkhe in 2015 [26]. For example, palladium on various types of tea leaves [27], cellulose [28,29], chitosan [30,31], pyrolysed whole plants [32], cotton [33], and filter paper [33] have been used with success in Suzuki–Miyaura cross-coupling reactions. Palladium on synthetic polymer films has also been utilized with very promising results both in view of the conversion, but also in terms of recyclability [34–36]. Chalcogenide nanoparticles are a support material that has been used as a catalyst support [37]. In addition, metal-organic frameworks (MOF) have been used in order to support palladium used for cross-coupling reactions. A recent review by Dhakshinamoorthy et al. describes the current status of this type of support materials for palladium [38]. The use of MOF as a catalyst support is also briefly discussed in a review describing recent advances and applications in boron chemistry [39].

Although many of the catalyst supports mentioned briefly above are suitable for recycling there are very few of them that can be easily recycled. One very good example of a catalyst that is easy to recycle is palladium on a polymer film support, the so called dip catalyst [34,35]. The polymer film with the catalyst can be easily added to the reaction mixture and when the reaction has reached completion the film can simply be removed from the reaction flask. A quick washing procedure then makes the catalyst ready for the next reaction.

The preparation of palladium on magnetic supports, predominately Fe_3O_4 , with a range of different attachment strategies, has gained a lot of attention lately. The magnetic support makes it easy to isolate the catalyst by withholding it in the reaction flask by the use of an external magnet. The reaction mixture can then be removed and the catalyst can easily be washed preparing it for the next reaction. Naturally, catalysts that perform well over many runs with minimum loss of product yield are preferable. This review will discuss the developments made for the use of magnetic-supported catalysts for the Suzuki–Miyaura cross-coupling reaction since late 2013. For literature discussing the topic prior to 2013 the reader is referred to several reviews describing the topic [16,20,21].

2. Palladium on Magnetically Supports

Amongst the solid supports utilized for palladium, and other catalytic metals for that matter, magnetic particles have become quite popular. This is predominantly due to their easy removal from the reaction mixture after the reaction has reached completion [16]. Due to the magnetic beads, it is simple to apply an external magnetic field and decant the reaction mixture off (Figure 1). The catalyst can then be washed and used again in the next cross-coupling reaction. The ability for the various catalysts to tolerate many rounds of recycling then becomes an important parameter to consider.

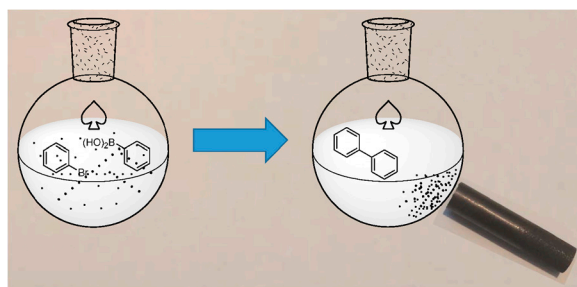


Figure 1. Application of an external magnetic field that collects the catalyst and withholds it in the reaction flask making it possible to decant the product mixture. The catalyst can then be washed and used in another cross-coupling reaction immediately afterwards.

2.1. The Magnetic Particle

A range of metals, Fe, Co, and Ni; alloys, FePt and CoPt; and ferrites, CoFe_2O_4 , MnFe_2O_4 , CuFe_2O_4 , CoFe_2O_4 , and ZnFe_2O_4 , can be formed into magnetic nanoparticles (NPs) [40]. However, the majority of magnetic retractable NP catalysts in use are metal oxides, such as iron(II) oxide (FeO), magnetite (Fe_3O_4), and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), due to their ease of formation. In the Suzuki–Miyaura cross-coupling the majority of catalyst systems on magnetic NPs are based on Fe_3O_4 . Another very interesting feature with iron oxides (Fe_xO_y) is that they have been found to facilitate the reduction of oxidized palladium species onto the iron oxide in Suzuki–Miyaura cross-couplings and by such means capture leached palladium [41]. Palladium can be deposited directly on the iron oxide NP surface [41], or a thin coating can be applied often in the form of SiO_2 (Figure 2a), which functions as a handle for attaching organic ligands that hold palladium in place (Figure 2b). Furthermore, polystyrene-coated iron nanoparticles have also been utilized with good outcome [42].

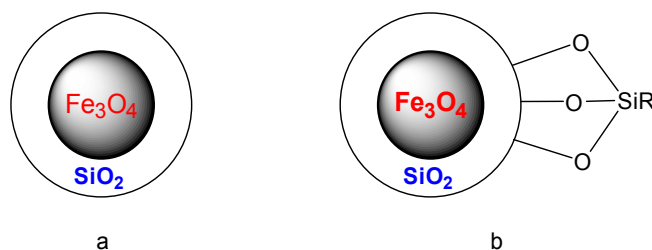
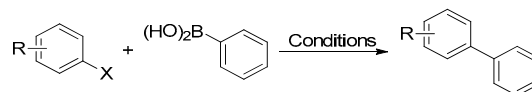


Figure 2. (a) Fe_3O_4 coated with SiO_2 is the predominant magnetic particle used in these catalyst systems; and (b) the finer details of how the ligand that holds palladium in place is attached to the magnetic particle.

2.2. Palladium Deposited Directly onto the Iron Oxide Nanoparticle

As just described in Section 2.1, one strategy for generating a magnetic retractable catalyst is to deposit the palladium directly onto the iron oxide nanoparticle. Several good examples of this strategy used for the Suzuki–Miyaura cross-coupling reaction have been reported over the last three years (Table 1).

In the work by Sun et al. $\text{Fe}_3\text{O}_4\text{-Pd@mSiO}_2$ was used in order to give the corresponding biaryls in good yield (Table 1, Entry 1) [43]. However, when 3-pyridyl boronic acid and 2-thiophenyl boronic acid was utilized the yields dropped to 19% and 38%, respectively. Park and co-workers obtained good, stable yields with $\text{Pd@Fe}_3\text{O}_4\text{-C}$ as a catalyst (Table 1, Entry 2) [44]. The catalyst gave stable yields >99% (for PhX with PhB(OH)_2) over four rounds of recycling. Li et al. obtained predominantly higher yields than 90% for X = Br and I (Table 1, Entry 3) [45]. However, when X = Cl the yields dropped dramatically to around 50%. The catalyst, namely $\text{Fe}_3\text{O}_4\text{-Pd@mCeO}_2$, was recycled 10 times, which resulted in the yields dropping from 99% to 90% for the cross-coupling of 4-iodoanisole with phenylboronic acid.

Table 1. Use of palladium directly deposited onto iron oxide nanoparticles as a catalyst for Suzuki–Miyaura cross-coupling.

Entry	Catalyst	Conditions	R	ArB(OH) ₂	X	Yield	Reference
1	Fe ₃ O ₄ @C-Pd@mSiO ₂	ArB(OH) ₂ (1.5 equiv.), ArX (1.0 equiv.), Cat. (1.5 mol% Pd), K ₂ CO ₃ , <i>i</i> PrOH, 70 °C, 6 h	H, 4-OMe, 4-NO ₂ , 4-COMe	Ph, 3-pyridyl, 2-thiophenyl, 1-naphthalene	I	73%–99% (for Ar = Ph) 19%–38% (for the heterocycles)	[43]
2	Pd@Fe ₃ O ₄ @C	ArB(OH) ₂ (1.2 equiv.), ArX (1.0 equiv.), Cat. (1.0 mol%), K ₂ CO ₃ , DMF/H ₂ O 4:1, 100 °C, 4 h	H, 4-F, 4-OMe, 2-Me, 4-COMe, 2-COMe	Ph (for all X), 4-Me-Ph, 4-CF ₃ -Ph	Cl, Br, OTf	>99% (for PhX with Ar = Ph) 45%–99%	[44]
3	Fe ₃ O ₄ @C-Pd@mCeO ₂	ArB(OH) ₂ (1.2 mmol), ArX (1.0 mmol), Cat. (Pd 3.05 wt%), K ₂ CO ₃ , EtOH/H ₂ O (1:1), 80 °C, 3 h	H, OMe, OEt, OCF ₃ , OH, NH ₂ , Me	Ph, 3-MePh, 4-MePh, 4-F, 4-OMe, 2-naphthyl	Cl, Br, I	68%–99% (X = Br and I) 50%–58% (X = Cl)	[45]
4	Fe ₃ O ₄ @Pd-OA ^a	ArB(OH) ₂ (1.5 equiv.), ArX (1 equiv.), K ₃ PO ₄ , DMF, 115 °C, 5 h	4-OMe	Ph, 4-FPh	I	80%–94% ^b	[46]
5	Pd@Fe ₃ O ₄ @ZnO	ArB(OH) ₂ (1 equiv.), ArX (1 equiv.), Cat. (Pd 0.1 mol%), K ₂ CO ₃ , H ₂ O, 100 °C, 1–3 h (for X = Br, I), 7–14 h (for X = Cl)	4-Me, 4-COMe, 4-Cl, 4-F, 4-NO ₂ , 4-NH ₂ , 4-CN, 4-pyridin	Ph, 2-FPh, 3-FPh, 4-FPh, 4-EtPh	Cl, Br, I	70%–95% (X = Br and I) 25%–53% (X = Cl)	[47]
6	Fe ₃ O ₄ @SiO ₂ -Pd@mCeO ₂	ArB(OH) ₂ (1.2 equiv.), ArX (1 equiv.), Cat. (Pd 0.5 mmol%), K ₂ CO ₃ , EtOH/H ₂ O (9:1) (for Br, I), 80 °C (for Br, I), DMF/H ₂ O (9:1), 100 °C (for Cl), 3 h	H, 3-Me, 4-OMe, 4-OCF ₃ , 4-COCH ₃	Ph, 3-MePh, 4-MePh, 4-OMePh, 4-FPh	Cl, Br, I	75%–99% (X = Br and I) 68%–88% (X = Cl)	[48]
7	Fe ₃ O ₄ @ <i>h</i> -Pd@mCeO ₂	ArB(OH) ₂ (1.2 equiv.), ArX (1 equiv.), Cat. (Pd 0.5 mmol%), K ₂ CO ₃ , EtOH/H ₂ O (9:1) (for Br, I), 80 °C (for Br, I), DMF/H ₂ O (9:1), 100 °C (for Cl), 3 h	H, 3-Me, 4-OMe, 4-OCF ₃ , 4-COCH ₃	Ph, 3-MePh, 4-MePh, 4-OMePh, 4-FPh	Cl, Br, I	82%–99% (X = Br and I) 72%–92% (X = Cl)	[48]
8	Pd@Ni@CB CB = carbon black	ArB(OH) ₂ (1.1 equiv.), ArX (1 equiv.), Cat. (Pd 0.1 mol%), K ₂ CO ₃ , EtOH/H ₂ O (1:1), 30 °C (for X = Br, I), 80 °C (for X = Cl), 45 min–1.5 h	H, 2-NO ₂ , 3-NO ₂ , 4-NO ₂ , 2-OMe, 3-OMe, 4-OMe, 4-Me, 4-OH, 4-CN, 4-CHO	Ph	Cl, Br, I	79%–95% (X = Br and I) 5%–60% (X = Cl)	[49]

^a OA = oleylamine; ^b Two examples were reported, Ar = Ph gave a yield of 80% and Ar = 4-FPh gave a yield of 94%.

The work by Strumia and co-workers predominantly focused on the development of the catalyst, however, the two examples of Suzuki–Miyaura cross-coupling reactions reported resulted in very good yields of the desired product (Table 1, Entry 4) [46]. Palladium on Fe₃O₄-ZnO nanoparticles were prepared by Hosseini-Sarvari et al. (Table 1, Entry 5) [47]. The catalyst system gave good yields for X = Br and I, but the yields with X = Cl was low (25%–53%) despite a prolonged reaction time. Ye and co-workers reported the use of two different magnetic palladium supports in their work (Table 1, Entries 6 and 7) [48]. Fe₃O₄@h-Pd@mCeO₂ was the preferable catalyst of choice, also giving good yields for the cross-coupling of aryl chlorides. Palladium on nickel and carbon black was used as a catalyst system by Wang and co-workers (Table 1, Entry 8) [49]. The catalyst gave good to excellent yields for X = Br and I, however, when the corresponding chloride was used, the yields dropped significantly. In their recycling experiments it was found that the product yield dropped by 18% over five runs.

Out of the catalysts presented in this section the work by Park and co-workers showed that the catalyst could be used four times, giving yields consistently at 99% [44], which is the most promising catalyst system in terms of recycling described in this section. However, in order to establish the full potential of the catalyst it should have been tested over several more cycles. There are several examples of catalysts that perform well over a few rounds of recycling before collapsing.

2.3. Iron Oxide with Ligands Holding Palladium

Another strategy, which is more commonly used, is to attach an organic substrate to the magnetic nanoparticle. A range of chelating agents have been attached to magnetic nanoparticles in order to chelate to palladium and, by such means, keep the catalyst attached to the magnetic particle. Several of these catalysts are depicted in Figure 3. All but one catalyst is based on Fe₃O₄ nanoparticles with γ -Fe₂O₃ making up the last example. These catalysts have been utilized and put to the test in the Suzuki–Miyaura cross-coupling in addition to other cross-coupling reactions.

2.4. The Use of Palladium Chelated to Magnetic Nanoparticles

A general trend seen with all of the catalysts described in Figure 3, and further outlined in Table 2, is that the most reactive cross-coupling partners are the iodides, followed by bromides, with chlorides showing the lowest reactivity. The work by Zhang et al. utilized catalyst 1 for the formation of biaryls (Table 2, Entry 1) [50]. The catalyst gave constantly high yields for X = Br and I, however, when X = Cl the yields dropped dramatically. Somsook and co-workers utilized polyaniline attached to a magnetic nanoparticle in order to catalyze the Suzuki–Miyaura cross-coupling reaction between 1-bromo-4-methylbenzene and a range of aryl boronic acids (Table 2, Entry 2) [51]. The outcome of the reactions generally gave good yields with a few exceptions. Catalyst 2 showed high conversion and very good yields for aryl bromides, aryl iodides, and in the two examples that were performed with 1-chloro-4-nitrobenzene (Table 2, Entry 3) [52]. It would have been very interesting to see how this catalyst would perform in cross-coupling reactions between a broader range of aryl chlorides and more complex boronic acids. The catalyst also showed very good yields through 10 runs with only a 1% reduction in the isolated yield. Catalyst 3 gave good to excellent yields for aryl chlorides, bromides, and iodides (Table 2, Entry 4) [53]. The catalyst also maintained good catalytic activity over six runs both for cross-coupling of iodobenzene and 1-chloro-4-nitrobenzene with phenyl boronic acid.

Ma and co-workers prepared catalyst 4 and tested its performance in a range of Suzuki–Miyaura cross-coupling reactions (Table 2, Entry 5) [54]. The catalyst performed very well with aryl bromides and iodides in most cases, except for two examples, which contained a nitro group *ortho* to the halide. When aryl chlorides were tested under the same reaction conditions the yields dropped dramatically compared to the yields obtained with aryl bromides and iodides. In the work by Ghotbinejad et al. SPION-A-Pd(EDTA) (5) (EDTA = ethylenediaminetetraacetic acid) was used as catalyst under both conventional heating and ultrasound condition. The use of ultrasound reduced the reaction time

from hours to minutes and generally also resulted in slightly better yields compared with the yields obtained when conventional heating was used (Table 2, Entry 6) [55].

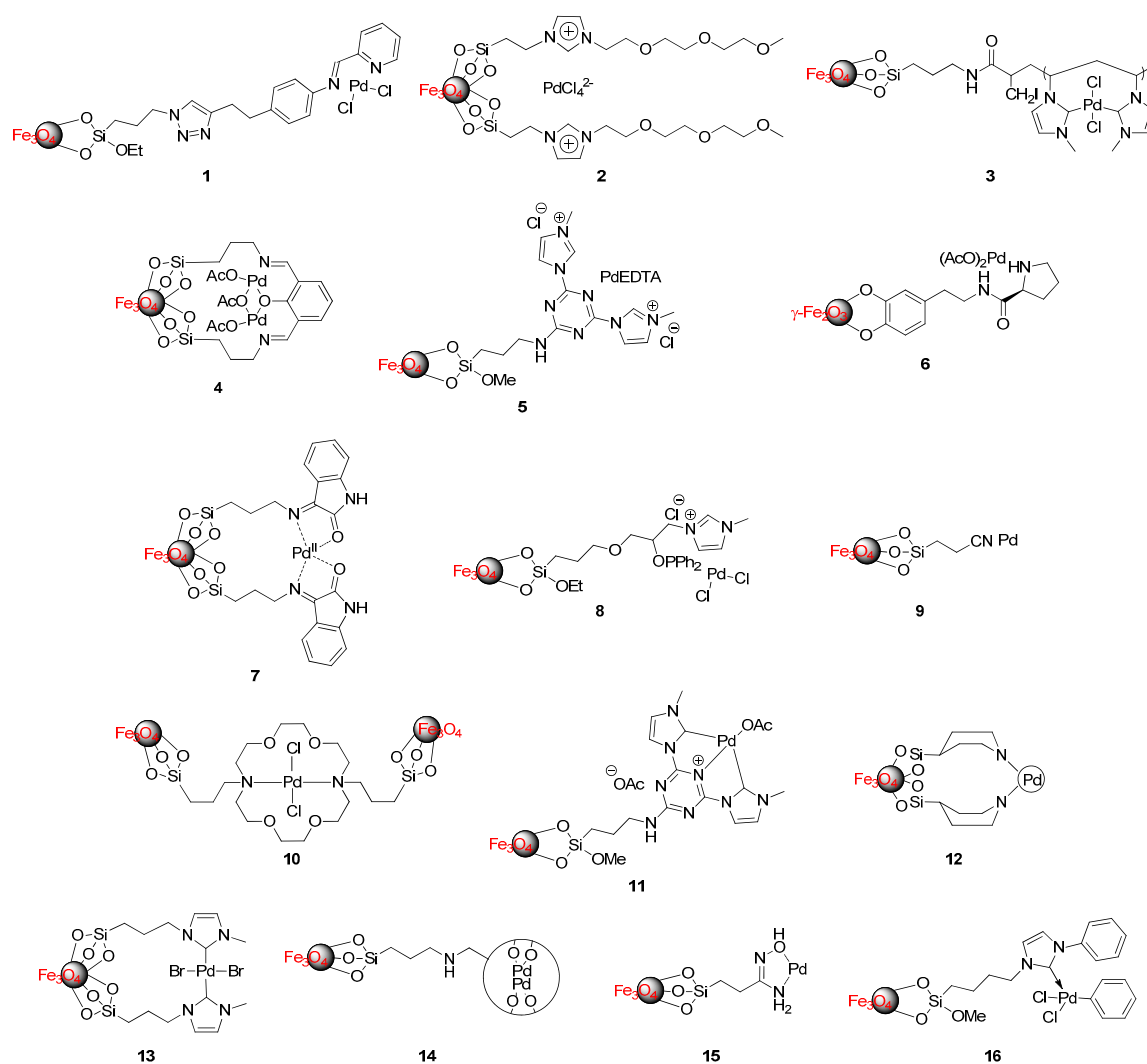
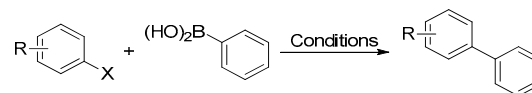


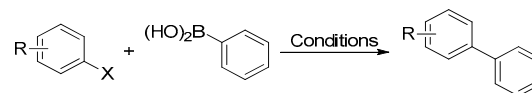
Figure 3. The structure of magnetically-supported palladium catalysts used in Suzuki–Miyaura cross-coupling reactions.

Catalyst 6 performed well in all the examples with aryl iodides take for the example where 1-iodo-4-nitrobenzene was cross-coupled with 2-thiophenyl boronic acid (Table 2, Entry 7) [56]. Out of the catalysts presented herein, catalyst 6 is the only one based on γ -Fe₂O₃ nanoparticles. Upon recycling of this catalyst the yields dropped from 99% to 90% over eight runs. Catalyst 7 prepared by Esmailpour and Javidi performed well for all three aryl halides with yields ranging from 70%–80% for the aryl chlorides tested (Table 2, Entry 8) [57]. The conditions reported by Biji and co-workers generally gave good yields for all three aryl halides when utilizing catalyst 8 (Table 2, Entry 9) [58]. Although the aryl chlorides only engaged in the cross-coupling reaction under quite forcing conditions (120 °C). Catalyst 9 worked excellently for aryl bromides and aryl iodides, however, the yields were disappointingly low in the examples with aryl chlorides (yields ranging from 20% to 25%) (Table 2, Entry 10) [59]. The catalyst prepared by Khakiani could be recycled seven times without significant loss in activity (the yield dropped by 1%–2%).

Table 2. Use of palladium catalyst chelated to magnetic nanoparticles as catalysts for Suzuki–Miyaura cross-coupling.

Entry	Catalyst #	Conditions	R	ArB(OH) ₂	X	Yield	Reference
1	1	ArB(OH) ₂ (1.2 equiv.), ArX (1.0 equiv.), Cat. (0.2 mol% Pd), K ₂ CO ₃ , EtOH/H ₂ O (1:1), 60 °C, 3–12 h	H, 4-Me, 4-COCH ₃ , 4-NO ₂ , 4-CF ₃ , 4-CN, 4-NH ₂ , 4-OH, 3-OMe, 3-CHO, 2-OMe	Ph, 4-MePh, 4-OMePh, 4-ClPh	Cl, Br, I	80%–99% (X = Br and I) 5%–12% (X = Cl)	[50]
2	Pd/Poly(<i>m</i> -ferrocenyl-aniline)	ArB(OH) ₂ (1 equiv.), ArX (1 equiv.), Cat. (2.0 mol% Pd), KOH, toluene, reflux, 20 h	4-Me	Ph, 4-MePh, 3-MePh, 2-MePh, 4-CHOPh	Br	67%–98% 26% (for ArB(OH) ₂ = 4-CHOPh)	[51]
3	2	ArB(OH) ₂ (1.2 equiv.), ArX (1 equiv.), Cat. (0.025 mol% Pd), K ₂ CO ₃ , H ₂ O, 60–80 °C, 4–15 h (for Br, I), 24 h (for Cl) ^a	H, 4-NO ₂ , 4-OMe, 4-CHO, 4-OH, 4-NH ₂ , 3-OH, 2-CHO, 2-Me, 2-Et, 2,6-Me, 2-thiophenyl, 5-pyrimidinyl, 3-pyridyl, 2-pyridyl	Ph, 4-MePh, 2-MePh, 3-pyridyl	Cl, Br, I (three examples with Cl)	72%-quant. (X = Br and I) 85%–96% (X = Cl)	[52]
4	3	ArB(OH) ₂ (1.2 equiv.), ArX (1 equiv.), Cat. (0.0049 mol% Pd), K ₂ CO ₃ , NMP, 90 °C, 0.5–2.5 h (for X = Br or I), 2.5–9 h (for X = Cl)	H, 4-Me, 4-OMe, 4-CHO, 4-COCH ₃ , 4-CN, 4-NO ₂ , 4-Cl, 3-Me, 2-Me, 3-pyridyl, 5-pyrimidine, 3-thiophenyl	Ph,	Cl, Br, I	77%–95%	[53]
5	4	ArB(OH) ₂ (1.5 equiv.), ArX (1 equiv.), Cat. (0.5 mol%), K ₂ CO ₃ , EtOH, 80 °C, 3–10 h	H, 4-Me, 2-Me, 4-OH, 2-NO ₂	Ph, 4-ClPh (X = I)	Cl, Br, I	95%–99% (X = Br and I) 16%–64% (X = Cl)	[54]
6	5	ArB(OH) ₂ (1.1 equiv.), ArX (1 equiv.), Cat. (0.003 mol% Pd), K ₂ CO ₃ , DMF/H ₂ O (1:2), 70 °C, 2–14 h Ultrasound applied power 160 W, 30 °C, 7–35 min	H, 4-Me, 4-OMe, 4-CHO, 4-Ac, 4-F	Ph, 4-OMePh	Br, I	82%–93% (70 °C, conventional heating) 87%–96% (ultrasound conditions)	[55]
7	6	ArB(OH) ₂ (1.1 equiv.), ArX (1 equiv.), Cat. (0.1 mol%), Na ₂ CO ₃ , EtOH/H ₂ O (1:1), 80 °C, 30 min	H, 4-NO ₂	4-COMe, 4-COOEt, 4-CHO, 4-ethenyl, 4-tolyl, 4-ethenyl, 2-furanyl, 2-thiophenyl	Cl, Br, I (only one example with X = Cl and Br)	60%–99% (for X = I)	[56]
8	7	ArB(OH) ₂ (1.2 equiv.), ArX (1 equiv.), Cat. (0.3 mol%), K ₂ CO ₃ , NMP, 100 °C, 0.5–4.5 h (for Br, I), 4–12 h (for Cl)	H, 4-Me, 3-Me, 2-Me, 4-OMe, 4-NO ₂ , 2-Me-4-NO ₂ , 4-NH ₂ , 4-COMe, 4-CN, 1-naphthyl	Ph	Cl, Br, I	77%–96%	[57]
9	8	ArB(OH) ₂ (1.5 equiv.), ArX (1.0 equiv.), Cat. (0.3 mol%), K ₂ CO ₃ , EtOH/H ₂ O (1:1), 30 °C (for X = I), 60 °C (for X = Br), 120 °C (for X = Cl), 1–24 h (for X = Br or I), 48 h (for X = Cl)	H, 4-OH, 4-OMe, 4-CHO, 4-NO ₂ , 4-CN, 4-COMe, 4-biphenyl, 1-naphthalen, 5-pyrimidine	Ph, 4-ClPh, 4-MePh, 3,5-diFPh, 2-FPh, 2-NO ₂ Ph, 1-naphthalene	Cl, Br, I	74%–98%	[58]
10	9	ArB(OH) ₂ (1.1 equiv.), ArX (1 equiv.), Cat. (0.2 mol%), K ₂ CO ₃ , EtOH/H ₂ O, 20–25 °C, 0.2–6 h (for X = Br or I), 10–12 h (for X = Cl)	H, 4-Me, 4-COCH ₃ , 4-OMe, 4-Cl, 3-NO ₂ , 2-CHO, 1-naphthyl, 2-thienyl	Ph	Cl, Br, I	88%–98% (X = Br and I) 20%–25% (X = Cl)	[59]
11	Fe ₃ O ₄ @EDTA-PdCl ₂	ArB(OH) ₂ (1.1 equiv.), ArX (1 equiv.), K ₂ CO ₃ , TBAB ^a , H ₂ O, 80 °C, 2–6 h	H, 3-Me, 3-CF ₃ , 1-naphthyl, 2-thienyl, (for X = Br) H, 4-Me, 4-OMe, 4-NO ₂ , 4-CHO (for X = I)	Ph	Br, I	76%–95%	[60]

Table 2. Cont.



Entry	Catalyst #	Conditions	R	ArB(OH) ₂	X	Yield	Reference
12	10	ArB(OH) ₂ (1.2 equiv.), ArX (1 equiv.), Cat. (0.5 mol%), Et ₃ N, TBAB ^b , DMF/H ₂ O (1:1), 75 °C, 1–6 h (X = Br and I), 24 h (X = Cl)	H, 4-Br, 2-thiophenyl, 1-naphthyl, 4-CN, 4-NO ₂ , 4-Me	Ph, 4-OMePh	Cl, Br, I	47%–94% (X = Br and I) 35%–37% (X = Cl)	[61]
13	Pd/Fe ₃ O ₄ /r-GO ^c	ArB(OH) ₂ (1.5 equiv.), ArX (1.0 equiv.), Cat. (0.36 mol% Pd), K ₂ CO ₃ , H ₂ O, 80 °C, 15 min–2.5 h	H, 4-Me, 4-CN, 4-NO ₂	Ph	Cl, Br, I	78%–99%	[62]
14	Fe ₃ O ₄ -NHC-Pd	ArB(OH) ₂ (1.2 equiv.), ArX (1 equiv.), Cat. (0.02 mol%), K ₂ CO ₃ , EtOH/H ₂ O (3:1), 70 °C, 12 h	H, 4-Me, 4-OMe, 4-COMe, 4-CHO, 4-CO ₂ H, 4-CN, 4-NO ₂	Ph, 4-MePh, naphthyl, 2,6-diMePh	Br	87%–99% 61% for 2,6-diMePh	[63]
15	11	ArB(OH) ₂ (1.1 equiv.), ArX (1 equiv.), Cat. (0.002 mol%), K ₂ CO ₃ , DMF/H ₂ O (1:2), 70 °C, 4–14 h, microwave irradiation 200 W, 70 °C, 2–7 min	H, 4-Me, 4-OMe, 4-CHO	Ph, 4-OMePh	Br, I	81%–91% (conventional heating) 85%–95% (microwave irradiation)	[64]
16	Fe ₃ O ₄ @PEG-iminophosphine-Pd	ArB(OH) ₂ (1.2 equiv.), ArX (1 equiv.), Cat. (0.05 mol%), K ₂ CO ₃ , H ₂ O, 65 °C, 5–8 h (for Br, I) 24 h (for Cl)	4-Me, 3-Me, 2-Me, 4-OMe, 4-CH ₂ OH, 4-NO ₂ , 4-COMe, 4-F, 4-CN	Ph, 4-OMePh, 4-CF ₃ Ph	Cl (only one example), Br, I	89%–99% (X = Br and I) 88% (X = Cl, R = 4-NO ₂ , Ar = Ph)	[65]
17	12	ArB(OH) ₂ (1.0 equiv.), ArX (1.0 equiv.), Cat. (0.37 mol%), Na ₂ CO ₃ , PEG, 100 °C, 20–150 min	H, 4-Me, 4-OMe, 4-CN, 4-CN, 4-Cl, 4-NO ₂ , 3-CHO, 3-CF ₃ ,	Ph, 4-OMePh, 3,4-diFPh	Br, I	88%–98%	[66]
18	13	ArB(OH) ₂ (1.2 equiv.), ArX (1 equiv.), Cat. (0.024 mol%), K ₂ CO ₃ , Tx ^d /THF (9:1), 65 °C, 30 h (for Br) 80 °C, 90 h (for Cl)	4-Me	Ph	Cl, Br	100% conv. ^e	[67]
19	14	ArB(OH) ₂ (1.2 equiv.), ArX (1 equiv.), Cat. (0.03–0.30 mol%) ^f K ₂ CO ₃ , H ₂ O, reflux, 4–12 h (for X = Br or I), 24 h (for X = Cl)	H, 4-OMe, 4-CHO, 4-NO ₂ , 4-Cl, 2-Me, 5-pyrimidine,	Ph, 4-MePh, 4-OMePh, 3-NO ₂ Ph, 2,6-diMePh, 3,5-diFPh, 2-benzofuranyl, 2-naphthyl, 1-naphthyl	Cl, Br, I	75%–99% (X = Br and I) 36%–65% (X = Cl)	[68]
20	15	ArB(OH) ₂ (1.2 equiv.), ArX (1 equiv.), Cat. (0.1 mol%), K ₂ CO ₃ , EtOH/H ₂ O (1:1), 25 °C, 1–5 h (for Br, I), 15–24 h (for Cl)	H, 4-Me, 4-OMe, 2-OMe, 4-F, 4-NO ₂ , 4-COMe	Ph	Cl, Br, I	85%–96% (X = Br and I) 60%–70% (X = Cl)	[69]
21	16	ArB(OH) ₂ (1.1 equiv.), ArX (1 equiv.), Cat. (0.036 mol%), K ₂ CO ₃ , EtOH/H ₂ O (1:1), rt, 0.5–2 h	H, ^g 4-OMe, ^g 3-OMe, 2-OMe, 4-NO ₂ , ^g 4-CHO 4-Cl, <i>m</i> -Cl, <i>o</i> -Cl (X = Br)	Ph	Cl, Br, I	75%–98% (X = Br and I) 65%–74% (X = Cl)	[70]
22	Pd/Fe ₃ O ₄ @PDA ^h	ArB(OH) ₂ (1.1 equiv.), ArX (1 equiv.), Cat. (0.46 mol% for X = I and 0.27 for X = N ₂ ⁺ BF ₄ ⁻), K ₂ CO ₃ , EtOH/H ₂ O (1:1) (for X = Br and I), 100 °C (for X = Br), 80 °C (for X = I), rt (for X = N ₂ ⁺ BF ₄ ⁻), 10 h (for X = I) and 2–3.5 h (for X = N ₂ ⁺ BF ₄ ⁻)	H (for X = I) 4-OMePh, 4-BrPh, 4-NO ₂ Ph (for X = N ₂ ⁺ BF ₄ ⁻)		Br, I, N ₂ ⁺ BF ₄ ⁻	77%–98%	[71]

^a Reaction conducted at 120 °C with the addition of 0.5 equiv. of TBAB and DMF/H₂O (1:1) as solvent; ^b TBAB = tetrabutylammonium bromide; ^c Pd/Fe₃O₄/r-GO = Pd/Fe₃O₄/reduced-graphene oxide nanohybrid; ^d Tx = aqueous solution 0.21 wt% of Triton TM X-405; ^e Conversion determined by GC; ^f Highest catalyst loading only used for X = Cl; ^g Reactions conducted with X = Cl; ^h PDA = polydopamine.

Heydari and co-workers utilized EDTA attached to the magnetic nanoparticle in order to coordinate to the palladium catalyst (Table 2, Entry 11) [60]. The catalyst gave good to excellent yields for the aryl bromides and iodides they tested, however, the yields dropped significantly when the catalyst was recycled (the yield dropped from 90% in run 1 to 80% in run 5). Catalyst 10 gave a mix of results, with yields ranging from poor to very good when tested by the Mobaraki group (Table 2, Entry 12) [61]. In particular, the aryl chlorides tested gave very poor yields. Palladium/Fe₃O₄/reduced-graphene oxide was used by Nasrabadi and co-workers with good outcome to catalyze the Suzuki–Miyaura cross-coupling between a range of aryl chlorides, bromides, and iodides (Table 2, Entry 13) [62]. The catalyst system also maintained its catalytic activity over eight runs with the yield only dropping by 2% from 97% in the first run to 95% in the eighth run.

Fe₃O₄-NHC-Pd was used by Wang et al. for a range of aryl bromides with a range of boronic acids (Table 2, Entry 14) [63]. The catalyst system was tested over 21 runs without loss of activity. The yields varied between 93% and 99% with 96% yield in the first run, and 97% yield in run number 21. Catalyst 11 gave very good yields for aryl bromides and iodides both under conventional heating and under microwave conditions (MW) (Table 2, Entry 15) [64]. The great advantage utilizing microwave conditions was that the reactions reached completion in a few minutes compared to hours under conventional conditions. In addition, the yields were slightly higher under MW conditions. The catalyst maintained most of its activity over seven rounds of recycling (yield dropped from 95% to 93%). Fe₃O₄@PEG-iminophosphine-Pd was used as catalyst by Lu and co-workers resulting in good to excellent yields of the desired biaryl system when utilizing all three aryl halides (Table 2, Entry 16) [65]. This catalyst system also showed good perseverance of activity over five runs with only a 2% drop in the isolated yield. Azadi and Ghorbani-Choghamarani developed catalyst 12, which was put to the test in the Suzuki–Miyaura cross-coupling reaction with good to very good yields for both aryl bromides and aryl iodides (Table 2, Entry 17) [66].

Andrés and co-workers prepared catalyst 13 and tested it in two reactions, namely the cross-coupling of phenyl boronic acid with 1-chloro-4-methylbenzene and 1-bromo-4-methylbenzene (Table 2, Entry 18) [67]. In both cases they reported 100% conversion as judged by GC analysis. The β-cyclodextrine-based catalyst system performed well in Suzuki–Miyaura cross-couplings with aryl bromides and aryl iodides, however, the yields dropped dramatically for the corresponding aryl chlorides (Table 2, Entry 19) [68]. Catalyst 14 also showed a dramatic drop in activity over five runs with the isolated yield going down 16% over the five runs. Catalyst 15 performed very well when utilizing aryl bromides and aryl iodides, however, the yields dropped roughly 30% when the corresponding aryl chlorides were used (Table 2, Entry 20) [69]. A similar drop in yields was also experienced by Hajipour et al. when they tested catalyst 16 with aryl chlorides (Table 2, Entry 21) [70]. However, with the more active aryl halides, viz. bromide and iodide, the catalyst performed well.

Dubey and Kumar, in addition to aryl bromide and aryl iodide, also tested the corresponding diazonium tetrafluoroborate (N₂⁺BF₄⁻) as the coupling partner with boronic acid (Table 2, Entry 22) [71]. This is the only example where this coupling partner has been utilized in combination with a magnetically retrievable catalyst. The reaction time when diazonium tetrafluoroborate was utilized was significantly quicker than the reaction time obtained when Br and I were utilized. The reaction time was as short as 2–3.5 h at room temperature. The yields in all examples were generally good ranging from 77% to 98%.

As mentioned, the trend that is usually seen for aryl chlorides when homogenous catalysts are used is also present in the examples brought forward herein. As just mentioned, the reactivity is significantly lower resulting, in most cases, to much longer reaction times when aryl chlorides are used. The yields are, in most cases, also dramatically lower for aryl chlorides compared to the corresponding iodide or bromide counterpart, although some very nice exceptions can be found in the work of Andrés and co-workers (Table 2, Entry 18) [67].

2.5. Recycling

As seen in the examples discussed in the forgoing the majority of the catalyst systems give good yields for aryl bromides and aryl iodides, and if the reaction time is prolonged compared to the reaction time used for the aryl bromides and aryl iodides, a number of the aryl chlorides also result in good conversion. However, when it comes to the ability of the various catalysts to perform at the same high level of conversion over multiple cycles, the differences between them becomes obvious. While some catalysts manage to maintain a high level of conversion over numerous rounds of recycling, other catalysts drastically deteriorate after just a few rounds of recycling. In particular, two catalyst systems by Karimi et al. [52] and Lin and co-workers [63] are singled out as better than the rest with the catalysts used by the Lin group being outstanding with its 21 runs without the catalyst losing its activity.

2.6. Catalyst Leaching

The active form of the catalyst in heterogeneous catalysis is a topic that has been much debated over the years [72]. Is the reaction catalyzed by the solid catalyst or is it catalyzed by palladium leached out from the heterogeneous catalyst. Very few reports deal with this issue, however, the work by Azadi and Ghorbani-Choghamarani tested this in a very clever way [66]. By removing the catalyst with a magnet when the reaction had proceeded to 50% conversion, they could evaluate if the reaction proceeded after that point. Their data clearly showed that the reaction stopped after the catalyst was removed, determining that the active catalyst was the heterogeneous palladium catalyst.

3. Concluding Remarks

The results presented in this article clearly show that catalysts on magnetic particles are fully able to catalyze the Suzuki–Miyaura cross-coupling reaction in good yields over a reasonable reaction time. However, the substrates demonstrated thus far are relatively simple compared with some of the starting materials used in Suzuki–Miyaura cross-coupling reactions conducted under homogenous conditions. For example, the substrates during such cross-coupling reactions conducted during synthesis of complex natural products or pharmaceuticals are far more complex than the ones utilized during the examples shown herein for heterogeneous catalysis. The use of palladium on magnetic retractable catalyst supports would be of interest in these settings, in particular the latter, where there are strict regulations regarding leftover palladium in the product. In addition, this type of catalyst would become more generally attractive if they were commercially available.

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