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Ultrasound-assisted C–C coupling reactions catalyzed by unique SPION-A-Pd(EDTA) as a robust nanocatalyst

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A novel and highly stable Pd(EDTA)$^{2-}$ salt was synthesized as a catalyst, using a counter-cation of *N*-methylimidazolium bonded to 1,3,5-triazine-tethered SPIONs (superparamagnetic iron oxide nanoparticles). This well-defined complex efficiently catalyzed the Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions. The cross-coupled products were produced under conventional heating and ultrasound irradiation at an extremely low catalyst loading (as low as 0.032 mol% Pd). Results indicated that conventional synthesis took longer and gave moderate yields, while in the presence of ultrasound irradiation, the reaction occurred very fast in high to excellent yields. The catalyst could be quickly recovered by an external magnetic field and could be reused for several reaction cycles without any change in catalytic activity.

Introduction

With the increasing environmental consciousness in chemical research, the challenge of designing sustainable environmentally friendly procedures has become the fundamental aim of green chemistry. From the first report on using ultrasound in organic synthesis,[1] the motivation to use this technique in organic transformations increased tremendously. Ultrasonic-assisted organic synthesis (UAOS) is a promisingly useful approach to a green technique in organic synthesis.[2–4] The physical and chemical effects of ultrasound irradiation are based on acoustic cavitations resulting from the continuous formation, growth and implosive collapse of bubbles in a solution, which results in a high temperature and pressure pulse.[5–8] The advantages of ultrasound irradiation in organic synthesis are the formation of purer products in good yields, short reaction times, improved energy conservation, easier manipulation, mild conditions and waste minimization which is comparable to traditional methods.[9–15]

The palladium catalyzed cross-coupling reactions are the most powerful and selective tools for carbon–carbon bond formation.[16–18] These cross-coupling reactions have been abundantly used in organic synthesis, pharmaceuticals, and the synthetic methodologies of natural products, conducting polymers, and liquid crystals.[19,20] Among these reactions, the Mizoroki–Heck[21,22] and Suzuki–Miyaura[23] reactions have been recognized as important tools in modern organic synthesis.

The Heck reaction is a transformation between aryl halides and olefins that leads to the formation of disubstituted olefins.[24,25] The Suzuki reaction is the most powerful method for coupling aryl halides with phenylboronic acid, which provides an effective method for synthesizing biaryls.[26–30]

These reactions generally proceed in the presence of a homogeneous palladium catalyst. The difficulties in product separation and recycling of the catalyst have limited the applications of homogeneous palladium catalysts in recent years.[31,32] Therefore, in order to overcome these drawbacks, many investigations on developing effective methods for immobilization of Pd complexes on different solid supports, such as microporous polymers,[33] activated carbon,[34] clays,[35] and magnetic nanoparticles (MNPs) have been performed. Magnetic nanoparticle-supported catalysts are the better choice as they not only show excellent catalytic activities but the magnetic nature of these particles also allows for facile recovery and recycling of the catalyst without use of the traditional filtration method.[36,37] Moreover, surface modified superparamagnetic iron oxide nanoparticles (SPIONs) have received increasing interest in the past few years both in biomedical and organic transformations.[38] Very recently, we reported synthesis of SPION-ACl$_2$ as a green and powerful nano-catalyst for the efficient synthesis of Betti bases.[39] It was found that due to the high magnetization of the catalyst it could be satisfactory recovered by a simple external magnet. Moreover, the catalyst could be easily recycled and reused without a loss of its activity.

Now, encouraged by the previous results and our interest in developing efficient, sustainable and greener pathways for organic transformations,[40] particularly those under ultrasonic

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irradiation[41] and C–C coupling reactions,[42] we would like to report herein a new and powerful palladium-EDTA complex-tagged dicationic ionic liquid with a 1,3,5-triazine core anchored to superparamagnetic nanoparticles (SPION-ACl$_2$), and its application in cross-coupling reactions such as the Mizoroki–Heck and Suzuki–Miyaura reactions, under ultrasound irradiation.

Result and discussion

The synthetic pathway for the catalyst is depicted in Scheme 1.

SPION-A-Pd(EDTA) was characterized by means of Fourier transform infrared spectroscopy (FT-IR), inductively coupled plasma atomic emission spectroscopy (ICP) thermal gravimetric analysis (TGA), and high resolution transmission electron microscopy (HR-TEM).

Fig. 1 illustrates the FT-IR spectra of Fe_3O_4 (a), silica-encapsulated Fe_3O_4 (b), and the nanocatalyst **SPION-A-Pd(EDTA)** (c), respectively.

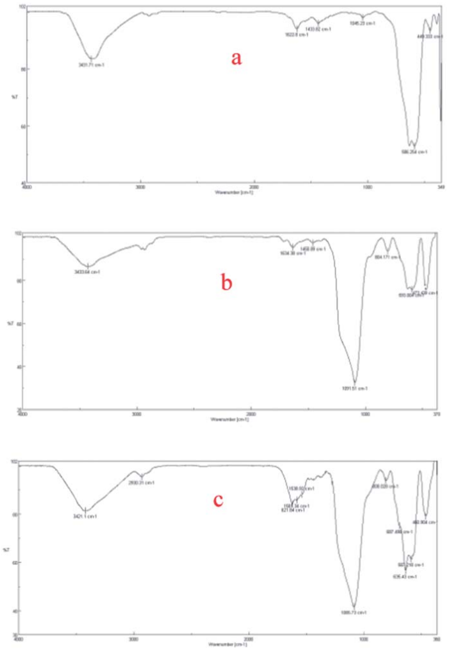


Fig. 1 Comparison of the FT-IR spectra of (a) Fe_3O_4; (b) silica-encapsulated Fe_3O_4; (c) **SPION-A-Pd(EDTA)**.

The FT-IR spectrum of **SPION-A-Pd(EDTA)** (Fig. 1c) showed absorption bands at 3421 cm^{-1} (N–H stretching vibration), 2930 cm^{-1} (C–H), 1622 cm^{-1} (C=N) and 635–587 cm^{-1} (Fe–O) SPIONs.

Inductively coupled plasma atomic emission spectroscopy (ICP) determined the amount of palladium in **SPION-A-Pd(EDTA)** as 3.41 wt%.

The thermal stability of **SPION-A-Pd(EDTA)** was also evaluated by thermal gravimetric analysis–differential thermal analysis (TGA-DTG). According to this curve, two weight loss steps were observed. In the first step (below 180 °C), the water molecules (4.59%) in the structure were omitted, while the organic part (11.28%) was lost between 180 and 480 °C (Fig. 2).

To study the morphology of **SPION-A-Pd(EDTA)**, an HR-TEM image was also investigated (Fig. 3).

HR-TEM images of **SPION-A-Pd(EDTA)** revealed that it appears to have an almost spherical structure with an average size of about 10–13 nm (Fig. 3b). Thus, the enormous active sites of this nanoparticle may display excellent activity levels in organic transformations.

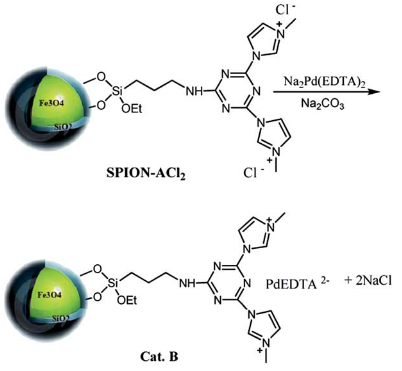
After the structure characterization of the catalyst, in order to evaluate the catalytic activity of **SPION-A-Pd(EDTA)**, we initially applied it in the Mizoroki–Heck reaction under ultrasound irradiation. To optimization the reaction conditions the reaction of iodobenzene (1.0 mmol) and styrene (1.0 mmol) was chosen as a model, and the role of various bases, solvents and the output power of the ultrasound apparatus were investigated. (Table 1, entries 1–14).

As illustrated in Table 1, DMF was the best solvent for this synthesis. Other solvents such as ethanol and toluene gave only moderate yields of the product (Table 1, entries 1–3).

Among the various bases screened, K_2CO_3 was found to be the most effective base for this transformation (Table 1, entry 4).

Other bases such as Na_2CO_3 and NEt_3 gave moderate yields of the product (Table 1, entries 5, 6).

No reaction occurred without the catalyst (Table 1, entry 7). More examination revealed that the yield reduced drastically with the replacement of Pd(OAc)2@nano-Fe3O4 or Pd(OAc)



Scheme 1 The synthetic pathway for **SPION-A-Pd(EDTA)**.

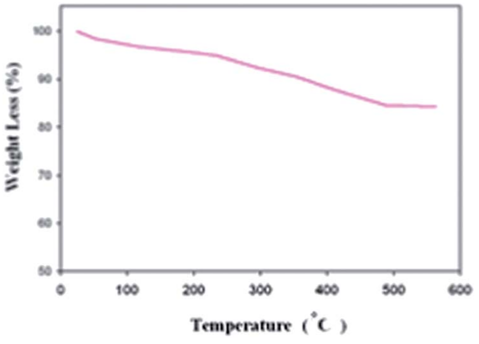


Fig. 2 TG-DTG analysis of **SPION-A-Pd(EDTA)**.

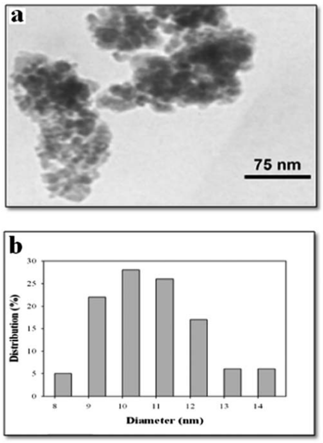
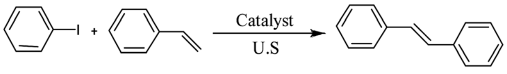


Fig. 3 (a) HR-TEM image of **SPION-A-Pd(EDTA)** and (b) **SPION-A-Pd(EDTA)** particle size distribution histogram.

Table 1 Optimization of the reaction of iodobenzene with styrene in the presence of **SPION-A-Pd(EDTA)**[a]



Entry		Yield[b] (%)
Solvent effect		
1	DMF	96
2	Toluene	60
3	Ethanol	55
Base effect		
4	K_2CO_3	96
5	Na_2CO_3	87
6	NEt_3	50
Catalyst effect		
7	—	—
8	$Pd(OAc)_2$@nanoFe_3O_4 nanoSiO_2	20
9	$Pd(OAc)_2$@nano-SiO_2	15
10	**SPION-A-Pd(EDTA)**	96
Power effect (watt)		
11	120	78
12	140	85
13	170	96
14	200	96

[a] Reaction conditions: Iodobenzene (1 mmol), styrene (1.5 mmol) and K_2CO_3 (1.5 mmol) in the presence of the catalyst containing 0.003 mol % Pd in 2 mL of DMF. [b] Isolated yield.

2@nano-SiO2 instead of **SPION-A-Pd(EDTA)** as the catalyst (Table 1, entries 8 and 9).

We also found that the output power of the ultrasound apparatus greatly affected this transformation. The obvious improvement in the conversion (96%) reached a plateau at 170 W of power. Higher acoustic power (200–400 W) made no obvious difference in the yield of the product (Table 1, entry 14) but using lower power (140 W) sharply decreased the conversion to approximately 85% even with more reaction time (Table 1, entry 12).

Accordingly, performing the reaction at 170 W in the presence of 0.094 g of **SPION-A-Pd(EDTA)** (0.003 mol % Pd), with K_2CO_3 as the base, and DMF as the solvent, at 50 °C, was optimal for the Mizoroki–Heck reaction. This optimized sonochemical reaction was applied to the synthesis of a variety of disubstituted olefins.

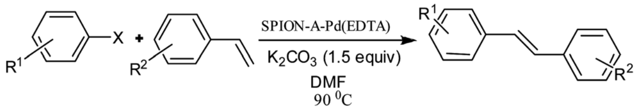
To assess the influence of ultrasonic irradiation on this transformation, we initially examined this reaction under thermal conditions (Table 2). As shown in Table 2, the reaction takes place efficiently in high TOF between 2 and 14 hours at 90 °C.

To demonstrate the effect of sonication, the synthesis of all the corresponding products was also investigated with ultrasonic irradiation (Table 3). It is apparent that the ultrasound accelerates this transformation under milder conditions.

For instance, at the optimal conditions, 1,2-diphenylethylene was produced almost quantitatively (96% isolated yield) with high TOF (5.6×10^5 h^{-1}) after 10 min sonication at 50 °C (Table 3, entry 1), while in silent conditions, a higher temperature (90 °C) was required to obtain the product in only 87% yield and with lower TOF after 2 h (Table 2, entry 1). This achievement could be extended to the other products.

We assume that the beneficial effect of ultrasound on this heterogeneous reaction may be attributed to a better mass

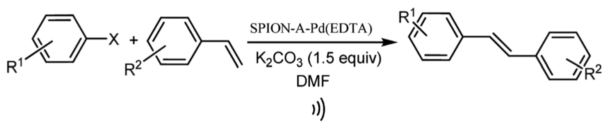
Table 2 Mizoroki–Heck cross-coupling of aryl halides and styrene derivatives in the presence of **SPION-A-Pd(EDTA)** under silent conditions[a]



Entry	R^1	R^2	X	Product	Time (h)	Yield[b] (%)	TOF[c]
1	H	H	I	**2a**	2	87	1.4×10^4
2	H	4-Me	I	**2b**	8	90	3.7×10^3
3	H	H	Br	**2a**	7	83	3.9×10^3
4	H	4-Me	Br	**2b**	9	85	3.1×10^3
5	4-MeO	4-Me	I	**2c**	6	84	4.7×10^3
6	4-Me	H	Br	**2b**	8	80	3.3×10^3
7	4-Me	4-Me	Br	**2d**	9	83	3.1×10^3
8	4-Me	H	I	**2b**	8	85	3.5×10^3
9	4-Me	4-Me	I	**2d**	10	87	2.9×10^3
10	4-Ac	H	I	**2e**	3	88	9.8×10^3
11	4-Ac	4-Me	Br	**2f**	5	86	5.7×10^3
12	4-Ac	H	Br	**2e**	7	84	4.0×10^3
13	4-Ac	4-Me	Br	**2f**	8	84	3.5×10^3
14	4-CHO	H	Br	**2g**	10	86	2.9×10^3
15	4 F	H	Br	**2h**	14	82	1.9×10^3
16	4 F	4-Me	Br	**2i**	12	87	2.4×10^3

[a] Reactions were carried out under aerobic conditions in 2 ml of mixture of DMF, 1 mmol aryl halide, 1.5 mmol styrene derivative, 1.5 mmol K_2CO_3 in the presence of **SPION-A-Pd(EDTA)** (0.003 mol% Pd) and 90 °C. [b] Isolated yield. [c] [mol product/mol palladium] h^{-1}.

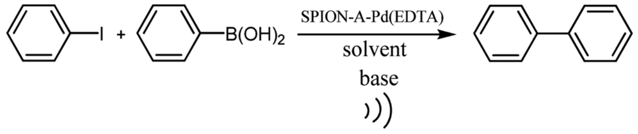
Table 3 Mizoroki–Heck cross-coupling of aryl halides and styrene derivatives in the presence of **SPION-A-Pd(EDTA)** by ultrasound irradiation[a]



Entry	R^1	R^2	X	Product	Time (min)	Yield[b] (%)	TOF[c]
1	H	H	I	**2a**	10	96	1.9×10^5
2	H	4-Me	I	**2b**	8	97	2.5×10^5
3	H	H	Br	**2a**	17	88	1.0×10^5
4	H	4-Me	Br	**2b**	15	91	1.2×10^5
5	4-MeO	4-Me	I	**2c**	20	91	9.2×10^4
6	4-Me	H	Br	**2b**	19	87	9.1×10^4
7	4-Me	4-Me	Br	**2d**	18	89	9.9×10^4
8	4-Me	H	I	**2b**	16	89	1.1×10^5
9	4-Me	4-Me	I	**2d**	15	91	1.2×10^5
10	4-Ac	H	I	**2e**	25	90	7.1×10^4
11	4-Ac	4-Me	Br	**2f**	22	90	8.1×10^4
12	4-Ac	H	Br	**2e**	26	88	6.8×10^4
13	4-Ac	4-Me	Br	**2f**	20	90	9.1×10^4
14	4-CHO	H	Br	**2g**	25	88	6.9×10^4
15	4 F	H	Br	**2h**	29	86	5.9×10^4
16	4 F	4-Me	Br	**2i**	35	89	5.1×10^4

[a] Reactions were carried out under aerobic conditions in 2 ml of mixture of DMF, 1 mmol aryl halide, 1.5 mmol styrene derivative, 1.5 mmol K_2CO_3 in the presence of **SPION-A-Pd(EDTA)** (0.003 mol% Pd) and power: 170 W at 50 °C. [b] Isolated yield. [c] [Mol product/mol palladium] h^{-1}.

Table 4 Optimization reaction for the synthesis of phenylbenzene as a model under ultrasonic irradiation in the presence of **SPION-A-Pd(EDTA)**



Entry	Solvent	Base	Pd (mol%)	Power	Yield[b] (%)
1	DMF	K_2CO_3	0.003	170	57
2	H_2O	K_2CO_3	0.003	170	54
3	H_2O/DMF[a]	K_2CO_3	0.003	160	95
4	H_2O/DMF[a]	K_2CO_3	0.003	160	95
5	H_2O/DMF[a]	Na_2CO_3	0.003	160	65
6	H_2O/DMF[a]	NEt_3	0.003	160	47
7	H_2O/DMF[a]	K_2CO_3	0.003	140	80
8	H_2O/DMF[a]	K_2CO_3	0.003	160	95
9	H_2O/DMF[a]	K_2CO_3	0.003	200	95

[a] H_2O/DMF (V/V) 2 : 1. [b] Isolated yield.

transfer and dispersion of the nanocatalyst in the medium in comparison with magnetically stirred reactions, which makes the catalyst more effective in this transformation.

To continue, for the investigation of the effect of the catalyst–sonication combination on the other C–C coupling reactions, we decided to study the Suzuki–Miyaura cross-coupling reaction of arylboronic acids with a variety of aryl halides in the presence of **SPION-A-Pd(EDTA)** under ultrasonic irradiation.

As shown in Table 4, the optimal conditions included the reaction of iodobenzene (1 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (1.5 mmol) and **SPION-A-Pd(EDTA)** (0.094 g, 0.003 mol% Pd) in DMF/H_2O (1 : 2) under ultrasound irradiation at 30 °C.

As with the aforementioned results, the generality of the reaction condition was also examined. The results revealed that the yields of the corresponding products were comparable under silent conditions and ultrasound irradiation, while the sonication was performed with a swift reaction under milder conditions in comparison to conventional heating (Table 5). The successful production of the biaryl derivatives indicated that this is a powerful procedure for the Suzuki–Miyaura reaction.

The recovered **SPION-A-Pd(EDTA)** could also be reused easily using an applied magnetic field after the end of the reaction, without any significant loss of its high catalytic performance. The examination of the ultrasonic-assisted Mizoroki–Heck and Suzuki–Miyaura C–C coupling reactions using **SPION-A-Pd(EDTA)** was repeated six times to evaluate the catalyst's recyclability and stability (Fig. 4). The results illustrated the excellent stability of the catalyst under the reaction conditions.

Initially, the Suzuki–Miyaura cross-coupling of iodobenzene with phenylboronic acid in the presence of **SPION-A-Pd(EDTA)** was chosen as a template reaction for the optimization of parameters such as base type, solvent and ultrasonic irradiation power of the reaction. The results are summarized in Table 4.

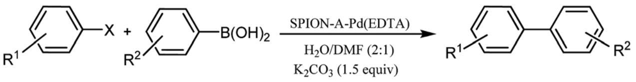
Finally, a comparison of this protocol with recent reports was performed with the Suzuki–Miyaura cross-coupling reaction of phenyl bromide and phenylboronic acid as a template. As shown in Table 6, the best TOF was obtained when utilizing **SPION-A-Pd(EDTA)**.

Experimental

All chemicals were purchased from the Merck chemical company. Fe_3O_4 nanocomposites and silica-coated magnetite nanoparticles (SiO_2@Fe_3O_4) were synthesised according to the literature.[43] The Na_2Pd(EDTA) complex was prepared by the dissolution of $Pd(OAc)_2$ (Aldrich), Na_2CO_3 and Na_2H_2EDTA (Merck) performed on UV-active aluminum-backed plates of silica gel (TLC Silica gel 60 F254). ^1H, and ^{13}C NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ with the chemical shift (δ) given in ppm. Coupling constants are given in Hz.

The FT-IR spectra were taken on a Nicolet-Impact 400D spectrophotometer with KBr pellets, and were reported in cm^{-1}. Melting points were determined using a Stuart Scientific SMP2 apparatus and are uncorrected. The sonication was performed in a UP 400S ultrasonic processor equipped with a 3 mm wide and 140 mm long probe, which was immersed directly into the reaction mixture. The operating frequency was 24 kHz and the output power was 0–400 Watts through manual adjustment.

Table 5 Suzuki–Miyaura cross-coupling of aryl halides and $ArB(OH)_2$ in the presence of **SPION-A-Pd(EDTA)**[a]



					Silent conditions[b]			Ultrasonic conditions[c]		
Entry	R^1	R^2	X	Product	Time (h)	Yield[d] (%)	TOF[e]	Time (min)	Yield[b] (%)	TOF[e]
1	H	H	I	**3a**	4	92	7.7×10^3	10	95	1.9×10^5
2	H	4-MeO	I	**3b**	2	93	$1 \times 5\ 10^4$	7	96	2.7×10^5
3	H	H	Br	**3a**	7	85	4.0×10^3	16	88	1.1×10^5
4	H	4-MeO	Br	**3b**	6	87	4.8×10^3	14	90	1.3×10^5
5	4-MeO	H	Br	**3b**	8	86	3.6×10^3	19	89	9.3×10^4
6	4-MeO	4-MeO	Br	**3c**	7	88	4.1×10^3	15	90	1.2×10^5
7	4-Me	H	Br	**3d**	8	86	3.6×10^3	16	90	1.1×10^5
8	4-Me	4-MeO	Br	**3e**	6	89	4.9×10^3	13	92	1.4×10^5
9	4 F	H	Br	**3f**	9	82	3.0×10^3	35	87	5.0×10^4
10	4-Ac	H	I	**3g**	6	83	4.6×10^3	25	88	6.9×10^4
11	4-Ac	4-MeO	I	**3h**	5	88	5.9×10^3	20	91	9.2×10^4
12	4-Me	H	I	**3d**	6	88	4.9×10^3	14	90	1.3×10^5
13	4-Me	4-MeO	I	**3e**	5	90	6.0×10^3	13	93	1.4×10^5
14	4-MeO	H	I	**3b**	3	89	9.9×10^3	17	91	1.1×10^5
15	4-MeO	4-MeO	I	**3c**	4	90	7.5×10^3	14	92	1.3×10^5
16	4-Ac	H	Br	**3g**	8	86	3.6×10^3	23	89	7.8×10^4
17	4-Ac	4-MeO	Br	**3h**	11	89	2.7×10^3	18	90	1.0×10^5
18	4-CHO	H	Br	**3i**	14	85	2.0×10^3	24	88	7.3 × 104

[a] Reactions were carried out under aerobic conditions in 2 ml of mixture of DMF and water (1 : 2), 1 mmol aryl halide, 1.1 mmol arylboronic acid and 1.5 mmol K_2CO_3(1.5 mmol) with **SPION-A-Pd(EDTA)** (0.003 mol% Pd). [b] At 70 °C. [c] Applied power: 160 W at 30 °C. [d] Isolated yield. [e] [Mol product per mol palladium] h^{-1}.

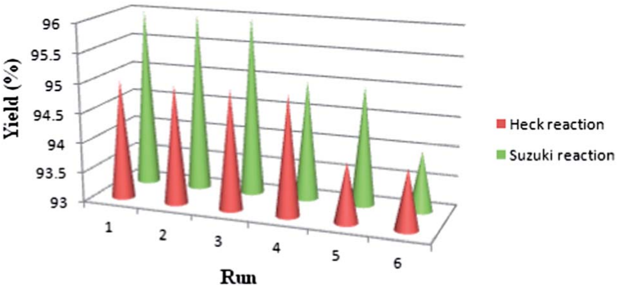


Fig. 4 Reuse of **SPION-A-Pd(EDTA)** examined on the model reactions of Mizoroki–Heck and Suzuki–Miyaura under ultrasonic irradiation.

The HRTEM images were taken with a Philips CM30 unit operated at 150 kV. The TGA curve was obtained with a heating rate of 10 °C min^{-1} on a TG 50 Mettler thermogravimetric analyzer from 30 °C to 600 °C. The Pd content of the catalyst was determined by Jarrell-Ash 1100 ICP analysis.

Preparation of SPION-A-Pd(EDTA)

Na_2CO_3 (0.2 mmol, 0.021 g) was added to a mixture of Na_2EDTA (0.1 mmol, 0.037 g) and $PdCl_2$ (0.1 mmol, 0.018 g) in water (5 ml) at 25 °C, and was stirred magnetically for 5 h. In an argon atmosphere, SPION-ACl_2 (0.53 g) in EtOH (5 ml) was added dropwise to the solution and the resulting mixture was stirred for a further 12 h at room temperature. Finally, the catalyst was

Table 6 Comparison of the present method with recent Suzuki–Miyaura cross-coupling procedures

Entry	Catalyst[a]	Time (min)	Yield[b] (%)	Pd amount (mol %)	TOF[c]	Ref.
1	**SPION-A-Pd(EDTA)**	16	88	0.003	1.1×10^5	This work
2	$Pd/IL\text{-}NH_2/SiO_2/Fe_3O_4$	300	87	0.5	34.8	45
3	SiO_2/BisILsR[PdEDTA]	600	99	1	99.0	44
4	Pd–NHC@Fe_3O_4-IL (3)	360	85	0.5	28.33	46
5	$Pd(OAc)_2$@Fe_3O_4-IL (3)	360	91	0.5	30.33	47
6	Fe_3O_4@SiO_2@$mSiO_2$–Pd(0)	360	97	0.075	215.56	48
7	SMNPs-Salen Pd(II)	180	100	0.5	6.67	49

[a] Reactions were carried out under aerobic conditions in 2 ml of mixture of DMF and water (1 : 2), 1 mmol phenyl bromide, 1.1 mmol phenylboronic acid and 1.5 mmol K_2CO_3. [b] Isolated yield. [c] [Mol product per mol palladium] h^{-1}.

collected by an external permanent magnet, washed with CH_2Cl_2 (3 × 10 ml) and H_2O, and dried under vacuum.

General procedure for heterogeneous Heck reactions

A mixture of an aryl halide (1.0 mmol), an alkene (1.5 mmol), K_2CO_3 (207 mg, 1.5 mmol) and **SPION-A-Pd(EDTA)** (0.094 g, 0.003 mol % of Pd) in DMF (2 ml) was exposed to ultrasonic irradiation at 170 W at 50 °C for 8–35 min according to Table 3. The progress of the reaction was monitored by TLC (eluent: petroleum ether/ethyl acetate, 4 : 1). After the completion of the reaction, the catalyst was collected by an external permanent magnet, washed two times with absolute ethanol (2 × 1 ml), air-dried, and used directly for the next round of reactions without further purification. After separation of the catalyst, the collected solution was added to the residue of the reaction mixture and the volatile product was removed in vacuum. The organic residue was washed with water (3 × 10 ml) and dried over anhydrous $MgSO_4$. Purification by flash column chromatography (silica gel, ethyl acetate/petroleum ether) afforded the corresponding products in 86–96% yields.

All products are known in the literature and were identified by comparison of their FT-IR and NMR with literature data. As a sample, the characterization data for **2c** is given below.

(*E*)-1-Methoxy-4-(4-methylstyryl)benzene (2c). M.p.: 147–148 °C. IR (KBr) $\nu_{\max} = 2969, 1602, 1495, 1378, 1253, 860\ \text{cm}^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.37$ (d, $J = 8.8$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.08 (t, $J = 8.0$ Hz, 2H), 6.95 (A of ABq., $J = 16.4$ Hz, 1H), 6.84 (B of ABq, $J = 16.4$ Hz, 1H), 6.82 (d, $J = 8.8$ Hz, 2H), 3.76 (s, 3H), 2.28 (s, 3H).

General procedure for heterogeneous Suzuki reactions

A mixture of an aryl halide (1.0 mmol), an arylboronic acid (1.1 mmol), K_2CO_3 (207 mg, 1.5 mmol) and Cat. B (0.094 g, 0.003 mol % of Pd) in 2 ml DMF–H_2O (1 : 2 v/v) was exposed to ultrasonic irradiation at 160 W at 30 °C for 7–35 min according to Table 5. The progress of the reaction was monitored by TLC (eluent: petroleum ether–ethyl acetate, 4 : 1). After the completion of the reaction, the catalyst was collected by an external permanent magnet, washed two times with absolute ethanol (2 × 1 ml), air-dried, and used directly for the next round of the reaction without further purification. After separation of the catalyst, the collected solution was added to the residue of the reaction mixture and the volatile product was removed in vacuum. The organic residue was washed with water (3 × 10 ml) and dried over anhydrous $MgSO_4$. Purification by flash column chromatography (silica gel, ethyl acetate/petroleum ether) afforded the corresponding products in 87–96% yields.

All products are known in the literature and were identified by comparison of their FT-IR, ^{1}H, and ^{13}C NMR with literature data. As a sample, the characterization data for **3c** is given below.

4,4′-Dimethoxybiphenyl (3c). M.p.: 172–173 °C. IR (KBr)$\nu_{\max} = 2938, 1680, 1601, 1490, 1378, 1253, 852\ \text{cm}^{-1}$. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.50$ (d, $J = 8.8$ Hz, 4H), 7.50 (d, $J = 8.8$ Hz, 4H), 3.87 (s, 6H).

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