Pd<sup>II</sup> Immobilized on Ferromagnetic Multi-Walled Carbon Nanotubes Functionalized by Aminated 2-Chloroethylphosphonic Acid with *S*-Methylisothiourea (FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs) Applied as a Highly Efficient and Recyclable Nanostructured Catalyst for Suzuki–Miyaura and Mizoroki–Heck Cross-Coupling Reactions in Solvent-Free Conditions

Maryam Sadat Ghasemzadeh<sup>A</sup> and Batool Akhlaghinia<sup>A,B</sup>

<sup>A</sup>Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad 9177948974, Iran.

<sup>B</sup>Corresponding author. Email: akhlaghinia@um.ac.ir

The new ferromagnetic nanostructured FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) as an eco-friendly heterogeneous nanocatalyst with a particle size of  $\sim$ 20–30 nm reported earlier by our group has been found to be very effective for Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions at ambient temperature. The procedure has been applied for a wide range of aryl halides, arylboronic acids, and alkenes. The magnetic separation by an external magnetic field, mild reaction conditions, and catalyst reusability up to four times without significant decrease in catalytic activity (reduced catalytic activity from 11 to 18% in the fifth, sixth, and seventh cycles) made the present method sustainable and economically viable for C–C cross-coupling reactions.

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# Introduction

In the last 30 years, the formation of C-C bonds which is well documented in the literature has gained increasing interest from both academic and industrial points of view.<sup>[1-3]</sup> Due to their versatility and efficiency, the C-C cross-coupling reactions via Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions are extremely useful tools in the preparation of natural products, organic synthesis, preparation of advanced materials, biologically active compounds, UV screens, herbicides, preparation of hydrocarbons, polymers, liquid crystal materials, and predominantly for pharmaceutical and agrochemical purposes.[4-6] Typically, the Suzuki-Miyaura and Mizoroki-Heck crosscoupling reactions are catalysed by palladium as a valuable transition-metal based on homogenous or heterogeneous systems.<sup>[7-12]</sup> With respect to global environmental concerns, every catalytic approach is critically examined in terms of activity, selectivity, and its environment friendly aspect as well.<sup>[13–17]</sup> The search for cleaner, simpler, and greener approaches has led to the advent of nanocatalysts which have fulfilled the need for developing sustainable and environmentally benign strategies.<sup>[14]</sup> The efficiency of nanocatalysts, which amalgamate the superior selectivity of homogeneous catalysts with the recyclability of heterogeneous catalysts, [15-17] depends on their nanostructure and composition. [18-20] A huge variety of these catalytic species with the anchorage of Pd nanoparticles on different kinds of supports, such as amorphous, or ordered silicates, clays, zeolites, or even carbon nanomaterials, i.e. carbon nanotubes and graphene, for C–C coupling reactions is reported each year.<sup>[21–28]</sup>

Carbon nanotubes (CNTs) including single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) have attracted a great deal of attention in fabricating advanced functional materials due to their excellent mechanical, structural, and electronic properties.<sup>[29-31]</sup> However, the main drawback of CNTs which has had a negative effect on their usage is their limited solubility. To tackle this issue, a kind of functionalization must be developed. This is achieved by introducing chemically active sites to the catalyst surface, which also function as anchoring sites for the deposition of metal nanoparticles (NPs). The two techniques used to recover heterogeneous metallic-based catalysts (i.e. filtration or centrifugation) are energy and time consuming and they also may lead to the loss of the catalyst during the separation process. In order to address these drawbacks, the designed nanocomposites (as catalyst supports) should contain both MWCNTs and magnetic materials. These nanocomposites lead to an increase in contact area, improve the separation of MWCNTs, and enhance thermal and chemical stability. The catalyst loss is



**Scheme 1.** Preparation of Pd<sup>II</sup> immobilized on ferromagnetic multi-walled carbon nanotubes functionalized by aminated 2-chloroethylphosphonic acid with *S*-methylisothiourea (FMMWCNTs@-CPA@SMTU@Pd<sup>II</sup> NPs) (**IV**).

prevented by the use of magnetic separation which in turn spares the researchers the difficulty of using traditional methods. This method of separation is both economical and practical. With this aim in view, we have recently been trying to develop new nanostructured magnetic catalysts.<sup>[32–42]</sup> Following these studies, the synthesis of Pd<sup>II</sup> immobilized on ferromagnetic multi-walled carbon nanotubes functionalized by

aminated 2-chloroethylphosphonic acid (CPA) with *S*-methylisothiourea (SMTU) (FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**)) was reported previously as a new heterogeneous nanocatalyst based on nanoparticles (see Scheme 1).<sup>[43]</sup> Subsequently, the nanostructured catalyst was used in the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions in solvent-free conditions at ambient temperature.



**Fig. 1.** UV-Vis DRS of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) in (a) Suzuki–Miyaura and (b) Mizoroki–Heck cross-coupling reactions.

## **Results and Discussion**

## Characterization of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**)

The nanocatalyst was characterized by the following techniques: FT-IR spectroscopy, X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDX), EDS mapping, thermogravimetric analysis (TGA), vibrating sample magnetometry (VSM), inductively coupled plasma–atomic emission spectroscopy (ICP-OES), X-ray photoelectron spectroscopy (XPS), and UV-vis diffuse reflectance spectroscopy (DRS).

FT-IR spectroscopy confirmed the presence of corresponding functional groups at different steps involved in the preparation of the catalyst (Scheme 1). Fig. 1 demonstrates the FT-IR spectra of MWCNTs, FMMWCNTs (I), FMMWCNTs@CPA (II), FMMWCNTs@CPA@SMTU (III), and FMMWCNTs@-CPA@SMTU@Pd<sup>II</sup> NPs (IV). Fig. S1a (Supplementary Material) shows the broad absorption band around  $3442 \text{ cm}^{-1}$  that can be ascribed to the hydroxy groups (vOH) of the raw MWCNTs. Meanwhile, the vibrational frequencies of C=C bonds due to graphite sheets appear around  $1612-1322 \text{ cm}^{-1}$ . The stretching vibration mode of the Fe-O bond appears in the region 600-400 cm<sup>-1</sup> (Fig. S1b, Supplementary Material). The presence of the strong band at  $1078 \text{ cm}^{-1}$  due to a P=O stretching vibration confirms the successful chemical attachment of CPA on the FMMWCNTs (I) surface (Fig. S1c, Supplementary Material). The absorption bands of N-H, C=NH, C-N, and C-S appear at 1649, 1551, 1404, and  $619 \text{ cm}^{-1}$  respectively, upon the amination of FMMWCNTs@CPA (II) with SMTU (Fig. S1d). The decrease in intensity of these bands then confirms the immobilization of Pd<sup>II</sup> on the surface of FMMWCNTs@CPA@SMTU (III) (Fig. S1e, Supplementary Material).<sup>[43]</sup>

The XRD technique was used to investigate the crystallographic structure of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**). As can be seen in Fig. S2 (Supplementary Material), the XRD pattern shows reflection peaks at  $2\theta = 31.2^{\circ}$ ,  $36.8^{\circ}$ ,  $38.5^{\circ}$ ,  $43.73^{\circ}$ ,  $55.6^{\circ}$ ,  $57.35^{\circ}$ , and  $65.1^{\circ}$  which can be related to the (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) reflections of the cubic structure of Fe<sub>3</sub>O<sub>4</sub>, respectively (ref. code: 04-014-9664). Moreover, the reflection peaks at  $2\theta = 41.04^{\circ}$ ,  $48.46^{\circ}$ , and 69.68° are indexed to the (1 1 1), (2 0 0), and (2 2 0) reflections of the cubic structure of Pd, respectively in the XRD pattern of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) (ref. code: 00-001-1201). Correspondingly, the diffraction peak at  $2\theta = 28^{\circ}$  demonstrates the (0 0 2) plane of the hexagonal graphite structure (ref. code: 41-1487). The Debye–Scherrer equation ( $d = K\lambda/(\beta \cos\theta)$ ) was used to calculate the average crystalline size of the FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) which was estimated to be 22 nm (Fig. S2, Supplementary Material).<sup>[43]</sup>

The morphology and mean diameter of the nanoparticles immobilized on the surface of FMMWCNTs (I) were investigated by TEM (Fig. S3, Supplementary Material). The TEM image of the FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (IV) proves that the nanocatalyst is decorated with well dispersed nanoparticles. In addition, TEM observation further indicates that the nanoparticles on the surface of the FMMWCNTs (I) are spherical in shape and the average size is found to be around 20–30 nm (Fig. S3, Supplementary Material).<sup>[43]</sup>

FE-SEM was carried out to show the surface morphology of the FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) (Fig. S4, Supplementary Material). The corresponding FE-SEM image illustrates a uniform rod-like morphology. In addition, the existence of Pd nanoparticles deposited on the nanostructured catalyst is clearly visible as bright spots in Fig. S4 (Supplementary Material).<sup>[43]</sup>

The EDX spectrum was obtained to record the type of elements in the FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) (Fig. S5, Supplementary Material). The presence of Fe, Pd, S, P, N, and O in the EDX spectrum confirms the composition of the FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) (Fig. S5, Supplementary Material).<sup>[43]</sup> The uniformly dispersed Fe, Pd, P, S, C, N, and O on the surface of the FMMWCNTs@CPA@-SMTU@Pd<sup>II</sup> NPs (**IV**) was recorded by an EDS map (Fig. S6, Supplementary Material).<sup>[43]</sup>

TGA was performed to determine the thermal stability and the amount of grafted organic moieties on the surface of the FMMWCNTs (I) (Fig. S7, Supplementary Material). The TGA curve of the MWCNTs indicates that the MWCNTs are decomposed in the temperature range of 500-600°C (Fig. S7a). The TGA curve of FMMWCNTs@CPA (II) shows three weight losses (Fig. S7b). In the first step, water evaporation occurs with a weight loss of 3 % from 105 to 200°C. During the second step, the decomposition of the CPA linker happens with a weight loss of 5% from 210 to 400°C. In addition, the amount of organic segments is calculated to be 0.35 mmol  $g^{-1}$  and this result is in good agreement with elemental analysis data (C = 14.49 %). The third step is related to the combustion of MWCNT fragments in the FMWCNTs (I) which happens from 410 to 500°C and gives an 8% weight loss. The TGA curve of FMMWCNTs@-CPA@SMTU (III) demonstrates three steps of weight loss from 25 to 900°C (Fig. S7c). The extrusion of physically absorbed water occurs at the first step (10% from 190 to 230°C). The removal of the organic moieties happens in the second step at a temperature range of 240-520°C (11%). Likewise, the grafted organic segments on the surface of the FMMWCNTs (I) is estimated to be 0.46 mmol  $g^{-1}$ . The elemental analysis data shows that the loading amount of organic segments supported on the FMMWCNTs (I) was  $0.4 \text{ mmol g}^{-1}$  based on carbon, nitrogen, and sulfur contents (C = 15.92, N = 3.20, and S = 3.57%). The third weight loss in Fig. S7c demonstrates the combustion of MWCNT fragments in the FMWCNTs (I) (9% from 520 to 650°C). In addition, the TGA curve of the



Scheme 2. (a) The Suzuki-Miyaura and (b) the Mizoroki-Heck cross-coupling reactions in the presence of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (IV).

FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) illustrates three steps of weight loss from 25 to 900°C (Fig. S7d). The first weight loss which happens from 120 to 200°C (11%) is indexed to the removal of adsorbed water molecules. The organic groups on the surface of the FMMWCNTs (**I**) decompose during the second step (16%) from 210 to 380°C. Thus, the amount of organic fragments is calculated to be 0.581 mmol g<sup>-1</sup>. In addition, the third weight loss which takes place at 400–700°C (15%), corresponds to the combustion of MWCNT fragments of FMWCNTs (**I**) (Fig. S7, Supplementary Material).<sup>[43]</sup>

The magnetization curves of FMMWCNTs (I) and FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (IV) are illustrated in Fig. S8a, b (Supplementary Material), respectively. Based on VSM analysis, an occurrence of a hysteresis loop at the magnetic hysteresis curves shows that all samples are ferromagnetic. The saturation magnetization values ( $M_s$ ) of the FMMWCNTs (I) and FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (IV) are 31.98 and 26.95. The decrease in the saturation magnetization value of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (IV) is related to the presence of non-magnetic materials on the surface of FMMWCNTs (I). Moreover, Table S1 (Supplementary Material) illustrates other magnetization ( $M_r$ )).<sup>[43]</sup>

The oxidation state of the palladium immobilized on the FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) was determined by XPS analysis (Fig. S9, Supplementary Material). Accordingly, in the Pd 3d XPS spectrum, the binding energy of the doublet peak at 339 eV (related to Pd  $3d_{5/2}$ ) and 343.7 eV (related to Pd  $3d_{3/2}$ ) can be indexed to the Pd<sup>II</sup> species (Fig. S9a). Furthermore, the peaks related to carbon (C 1s), nitrogen (N 1s), iron (Fe 2p), palladium (Pd 3d), sulfur (S 2p), and oxygen (O 1s) are demonstrated in the XPS elemental survey scan of the nanostructured catalyst (Fig. S9b).<sup>[43]</sup>

#### Catalytic Performance of the

# FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) in Suzuki– Miyaura and Mizoroki–Heck Cross-Coupling Reactions

Recently, FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) were presented as an efficient ferromagnetic nanostructured catalyst for the Sonogashira–Hagihara cross-coupling reaction under solvent-free conditions.<sup>[43]</sup> In order to show another application of the nanocatalyst, we applied it as a versatile nanocatalyst in C–C cross-coupling reactions, namely Suzuki–Miyaura and Mizoroki–Heck (see Scheme 2).

In order to investigate the catalytic activity of the prepared nanocatalyst in Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions, the reaction conditions were optimized and the results are illustrated in Tables 1 and 2. Initial studies were done on the reaction of iodobenzene with phenylboronic acid or methyl acrylate as model reactions of Suzuki– Miyaura or Mizoroki–Heck cross-coupling reactions, respectively. Initially, the effect of different parameters such as amount of catalyst loading, various molar ratios of iodobenzene/base, and type of base were studied on model reactions.

When a blank experiment in the absence of the nanocatalyst or base (in solvent-free conditions at ambient temperature) was conducted, only a trace amount of the products was acquired even after prolonged times (Tables 1 and 2, entries 1-3). To improve the yield of the coupled products, the cross-coupling reactions were examined by applying a 1/2 molar ratio of iodobenzene/base under the same reaction conditions. The optimum amount of nanocatalyst loading on the reaction rates was then obtained. Based on the results outlined in Tables 1 and 2, it is obvious that the best results were achieved by carrying out the reactions with 0.55 and 0.35 mol-% of the catalyst in the Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions, respectively (Tables 1 and 2, entry 5). It is worth mentioning that a higher amount of base did not increase the yields of products noticeably while decreasing the amount of base resulted in lower yields under the same conditions (Tables 1 and 2, entries 7–9). Afterwards, to further improve the yields of the desired products, the reactions were performed in  $H_2O$  (Tables 1 and 2, entry 10). As can be clearly seen, the same results were acquired in both solvent-free conditions and in aqueous media. The effect of base was also investigated using various bases, such as Et<sub>3</sub>N, N,Ndiisopropylethylamine (DIPEA), K2CO3, NaOAc, NaHCO3, KOH, n-butylamine, pyridine, and K<sub>3</sub>PO<sub>4</sub>. It was found that Et<sub>3</sub>N was the best base for these protocols. The unique catalytic behaviour of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (IV) in the Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions was revealed by examining the standard reactions individually in the presence of MWCNTs, FMMWCNTs (I), FMMWCNTs@CPA (II), FMMWCNTs@CPA@SMTU (III), and Pd(OAc)<sub>2</sub> (entries 19–23 both Tables 1 and 2). After continued reaction times, a considerable yield of desired coupling products was not obtained.

Subsequently, to elucidate whether these protocols could be generalized, the Suzuki–Miyaura and Mizoroki–Heck products were synthesized using various aryl halides including those containing electron-donating or electron-withdrawing groups with different arylboronic acids or alkenes in the presence of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) at room

Table 1.	Optimization of reactio	on conditions for the	e Suzuki–Miyaura	cross-coupling	reaction of	iodobenzene	with phenyl	boronic acid	in the
		presence o	f FMMWCNTs@0	CPA@SMTU@	Pd <sup>II</sup> NPs (IV	7)			

FMMWCNTs@CPA@

			H) <sub>2</sub>	>	-		
Entry	Catalyst [mol-%]	Molar ratios of iodobenzene/base	Base	Solvent	Temperature [°C]	Time [min]	Isolated yield [%]
1	_	1:2			r.t.	15 h	_
2	—	1:2	Et <sub>3</sub> N	—	r.t.	15 h	Trace
3	0.6	1:2		—	r.t.	15 h	_
4	0.6	1:2	Et <sub>3</sub> N		r.t.	10	98
5	0.55	1:2	Et <sub>3</sub> N	_	r.t.	10	98
6	0.53	1:2	Et <sub>3</sub> N	_	r.t.	18	98
7	0.55	1:2.5	Et <sub>3</sub> N	_	r.t.	10	98
8	0.55	1:1.2	Et <sub>3</sub> N	—	r.t.	13	98
9	0.55	1:1	Et <sub>3</sub> N	_	r.t.	15	98
10	0.55	1:2	Et <sub>3</sub> N	$H_2O$	r.t.	10	98
11	0.55	1:2	DIPEA <sup>A</sup>		r.t.	20	98
12	0.55	1:2	$K_2CO_3$		r.t.	50	98
13	0.55	1:2	NaOAc		r.t.	56	90
14	0.55	1:2	NaHCO <sub>3</sub>		r.t.	68	98
15	0.55	1:2	KOH	_	r.t.	48	95
16	0.55	1:2	n-Butylamine		r.t.	80	90
17	0.55	1:2	Pyridine		r.t.	74	85
18	0.55	1:2	$K_3PO_4$		r.t.	52	90
19 <sup>B</sup>	0.005 g	1:2	Et <sub>3</sub> N		r.t.	10 h	Trace
$20^{\circ}$	0.005 g	1:2	Et <sub>3</sub> N	_	r.t.	10 h	Trace
21 <sup>D</sup>	0.005 g	1:2	Et <sub>3</sub> N		r.t.	10 h	15
$22^{E}$	0.005 g	1:2	Et <sub>3</sub> N		r.t.	10 h	25
23 <sup>F</sup>	0.005 g	1:2	Et <sub>3</sub> N	—	r.t.	10 h	15

<sup>A</sup>N,N-Diisopropylethylamine.

<sup>B</sup>The reaction was performed in the presence of MWCNTs.

<sup>C</sup>The reaction was performed in the presence of FMWCNTs (I).

<sup>D</sup>The reaction was performed in the presence of FMMWCNTs@CPA (II).

<sup>E</sup>The reaction was performed in the presence of FMMWCNTs@CPA@SMTU (III).

<sup>F</sup>The reaction was performed in the presence of Pd(OAc)<sub>2</sub>.

temperature. The results are summarized in Table 3. As revealed in Table 3, the use of aryl iodides led to higher yields compared with aryl chlorides and aryl bromides. The reaction of aryl iodides containing electron-releasing (such as -Me, -OMe) and electron-withdrawing substituents (such as -NO<sub>2</sub>, -CN, and -CHO) proceeded easily, and the desired products were obtained with excellent yields. The reactions of aryl bromides and aryl chlorides were also carried out with high yields. In our case, this could be evidenced by the parallel reactions of arylboronic acids bearing electron-accepting substituents in the Suzuki-Miyaura cross-coupling reaction. Electron-poor arylboronic acids furnished the corresponding biaryl products more efficiently (Table 3, entries 1, 2, 3, 6, 8 and 9 (c, d versus a)). More importantly, as shown in Table 3, we were pleased to observe that the Mizoroki-Heck cross-coupling reaction of different aryl halides with methyl acrylate, ethyl acrylate, and *n*-butyl acrylate produced the desired products rapidly with yields considered high. The present method was further used to study the coupling reactions of aryl halides with acrylonitrile. The results obviously disclosed that the Mizoroki-Heck cross-coupling reaction of aryl halides with acrylonitrile in the presence of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (IV) required longer reaction times to achieve reasonable yields of the desired products under the optimized reaction conditions (Table 3, entries 1, 2, 3, 6, and 8(g)). But as expected, the cross-coupling reaction of styrene leads to low

product yield even after a long period of time (Table 3, entries 1, 2, 3, 6, and 8(h)).

The synthesized compounds were known and identified in detail using physical and spectroscopic data (melting point, mass spectrometry, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy), and were consistent with those reported previously. The proposed structures of the products were established by molecular ion peaks in the gas chromatography mass spectrum. The coupled products were also detected by <sup>1</sup>H NMR spectroscopy, which showed that the products of the Mizoroki-Heck cross-coupling reaction were achieved purely in the E geometry of the double bonds. The coupling constant (J) of the olefinic hydrogens of products 1f, 2d, 2f, 3d, 4b, 4d, 5b, 5d, and 6d were estimated to be 16–16.1 Hz, which is a characteristic of E isomers (see Supplementary Material, Figs S17–S40). In the <sup>13</sup>C NMR spectra, resonating signals at 152.1-142.2 and 167.8-166.01 ppm matched to C=C and C=O of the products of the Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions (see Supplementary Material).

# Proposed Catalytic Mechanism for the Suzuki–Miyaura and Mizoroki–Heck Cross-Coupling Reactions

Through a comprehensive analogy of previous reports in the literature,<sup>[44–48]</sup> as well as our own research, the following mechanism can be proposed for the Suzuki–Miyaura and Mizoroki–Heck cross coupling reactions (see Scheme 3). In the first step, the mechanism proceeded through oxidative addition of

# Table 2. Optimization of reaction conditions for the Mizoroki–Heck cross-coupling reaction of iodobenzene with methyl acrylate in the presence of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (IV)



Entry	Catalyst [mol-%]	Molar ratios of iodobenzene/base	Base	Solvent	Temperature [°C]	Time [min]	Isolated yield [%]
1		1:2		_	r.t.	12 h	
2	_	1:2	Et <sub>3</sub> N		r.t.	12 h	Trace
3	0.4	1:2	_		r.t.	12 h	
4	0.4	1:2	Et <sub>3</sub> N	—	r.t.	15	98
5	0.35	1:2	Et <sub>3</sub> N	_	r.t.	15	98
6	0.32	1:2	Et <sub>3</sub> N		r.t.	24	98
7	0.35	1:2.5	Et <sub>3</sub> N	_	r.t.	15	98
8	0.35	1:1.2	Et <sub>3</sub> N		r.t.	17	98
9	0.35	1:1	Et <sub>3</sub> N		r.t.	20	98
10	0.35	1:2	Et <sub>3</sub> N	$H_2O$	r.t.	15	98
11	0.35	1:2	DIPEA <sup>A</sup>	—	r.t.	28	98
12	0.35	1:2	$K_2CO_3$		r.t.	38	95
13	0.35	1:2	NaOAc		r.t.	53	95
14	0.35	1:2	NaHCO <sub>3</sub>		r.t.	45	98
15	0.35	1:2	KOH		r.t.	40	95
16	0.35	1:2	n-Butylamine		r.t.	65	95
17	0.35	1:2	pyridine		r.t.	70	95
18	0.35	1:2	K <sub>3</sub> PO <sub>4</sub>		r.t.	43	95
19 <sup>B</sup>	0.004 g	1:2	Et <sub>3</sub> N		r.t.	10 h	Trace
$20^{\circ}$	0.004 g	1:2	Et <sub>3</sub> N		r.t.	10 h	Trace
21 <sup>D</sup>	0.004 g	1:2	Et <sub>3</sub> N		r.t.	10 h	15
$22^{E}$	0.004 g	1:2	Et <sub>3</sub> N		r.t.	10 h	20
$23^{\mathrm{F}}$	0.004 g	1:2	Et <sub>3</sub> N	—	r.t.	10 h	20

<sup>A</sup>N,N-Diisopropylethylamine.

<sup>B</sup>The reaction was performed in the presence of MWCNTs.

<sup>C</sup>The reaction was performed in the presence of FMWCNTs (I).

<sup>D</sup>The reaction was performed in the presence of FMMWCNTs@CPA (II).

<sup>E</sup>The reaction was performed in the presence of FMMWCNTs@CPA@SMTU (III).

<sup>F</sup>The reaction was performed in the presence of  $Pd(OAc)_2$ .

an alkyl halide to FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs producing intermediate I through the oxidation of Pd<sup>II</sup> to Pd<sup>IV</sup>. (Based on the result of X-ray photoelectron spectroscopy (XPS) deduced from previous research,<sup>[43]</sup> the oxidation state of the palladium immobilized on the fresh FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) was Pd<sup>II</sup>.)

Transmetalation of intermediate I with arylboronic acid in basic media produced the intermediate II which upon reductive elimination led to the formation of desired coupling product III of the Suzuki–Miyaura cross-coupling reaction and the recovery of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs for the next catalytic trial. According to the suggested mechanism for the Mizoroki– Heck cross-coupling reaction, it was expected to gain intermediate V by adding an alkene to intermediate I via the formation of  $\pi$ -coordinated complex IV. Subsequently,  $\beta$ -hydride elimination produced the desired product VII and VIII. Finally, a reductive elimination in the presence of a base delivered the FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs to the next run.

DRS is a surface analytical technique. It uses UV, visible, or IR light as a probing medium. The interaction of light with strongly absorbing materials, such as metals, alloys, and semiconductors occurs in the first 10–20 nm. Thus the differential reflectometer probes 50–100 atomic layers into non-transparent solid surfaces.<sup>[49]</sup> In addition, to investigate the oxidation state of Pd, the model Suzuki–Miyaura and Mizoroki–Heck crosscoupling reactions were carried out in the presence of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) in two separate flasks. After the reactions were completed, the nanocatalyst was separated from the reaction mixture via a magnet. Next, UV-vis DRS of the nanocatalyst for the Suzuki–Miyaura and Mizoroki– Heck cross-coupling reactions were performed. As can be seen from Fig. 1, the presence of the peak at around 420 nm belongs to a Pd<sup>II</sup> species.<sup>[50–54]</sup>

The results of the XPS analysis demonstrated that the palladium immobilized on the 7th recovered FMMWCNTs@-CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) in the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions was Pd<sup>II</sup> (see the results of XPS analysis).

### Hot Filtration Test

To verify whether FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) was heterogeneous or not, the nanostructured catalyst was removed from the Suzuki–Miyaura and Mizoroki–Heck coupling reactions' media by a magnet after 5 and 7 min, respectively. The modal reactions were continued under the same conditions and monitored using TLC (Fig. 2). Both the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions stopped completely at 62 and 65% isolated yield, respectively. The

Table 3.	Suzuki–Miyaura/Mizoroki–Heck cross-coupling reactions of aryl halides with different phenylboronic acids/alkyl acrylates in the presence
	of FMMWCNTs@CPA@SMTU@Pd <sup>II</sup> NPs (IV)

Entry	Aryl halide		Coupling substrate	Product	Time [min]	Isolated yield [%]
1		а	B(OH) <sub>2</sub>		10	98
		b	CI-B(OH)2	ci —	8	98
		c	MeO — B(OH) <sub>2</sub>	MeO	22	90
		d	° V		15	98
		e	O Et	O Et	25	95
		f	O Bu <sup>n</sup>	O Bu"	35	95
		g	CN	CN	48	90
		h			2 h	70
2		а	B(OH)2		5	95
		b			12	98
	NO <sub>2</sub>	с	MeO — B(OH) <sub>2</sub>		20	90
		d		O <sub>2</sub> N O	10	95
		e	O Et	O_Et	15	95

Entry	Aryl halide		Coupling substrate	Product	Time [min]	Isolated yield [%]
		f	O Bu"	O Bu <sup>n</sup>	18	95
		g	CN	O <sub>2</sub> N CN	25	90
		h		NO <sub>2</sub>	1.80 h	75
3		a	B(OH)2		8	95
		b	CI B(OH)2		13	95
	N	с	MeO B(OH) <sub>2</sub>	MeO CN	15	90
		d		NC	14	95
		e	O Et	NC Et	22	90
		f	O Bu <sup>n</sup>	NC Bu"	25	90
		g	CN	NC CN	20	90
		h		CN CN	1.90 h	75
4		а	B(OH)2	Me	28	90
		b	° V	Me	20	85

Table 3. (Continued)

(continued)

Entry	Aryl halide		Coupling substrate	Product	Time [min]	Isolated yield [%]
		с	O Et	O Et	33	85
		d	O Bu <sup>n</sup>	O Bu <sup>n</sup>	48	85
5		a	B(OH)2		1.50 h	85
	OMe	b		° °	1.40 h	80
		с	O Et	MeO <sup>-</sup> C C Et	2 h	75
		d	O Bu"	MeO <sup>2</sup> O Bu <sup>n</sup>	2.30 h	75
6	Br	а	B(OH)2		22	90
		b	CIB(OH)2	ci	20	90
		с	MeO B(OH)2	MeO	32	85
		d			23	90
		e	O Et	O Et	30	85
		f	O Bu"	O Bu <sup>n</sup>	46	85
		g	CN	CN CN	65	90
		h			2.30 h	65

Table 3. (Continued)

Entry	Aryl halide		Coupling substrate	Product	Time [min]	Isolated yield [%]
7	Br	a	B(OH)2		15	90
	NO <sub>2</sub>	b		O <sub>2</sub> N O	17	90
		с	O Et	O <sub>2</sub> O <sub>2</sub> N	24	90
		d	O Bu"	O <sub>2</sub> N	38	85
8	CI	a	B(OH)2		30	80
		b			25	80
		с	MeO B(OH)2	MeO	42	75
		d	° V	° C	35	80
		e	O Et	O Et	45	70
		f	O Bu <sup>n</sup>	O Bu"	65	70
		g	CN	CN	1.45 h	65
		h			2.40 h	55

Table 3. (Continued)

(continued)

Entry	Aryl halide		Coupling substrate	Product	Time [min]	Isolated yield [%]
9	CI	a	B(OH)2	СНО	40	75
		b	CIB(OH)_2	СІСНО	25	70
	CHU	с	MeO B(OH)2	МеОСНО	35	70
		d		OHC	40	75
		e	O Et	OHC O Et	45	75
		f	O Bu"	O Bu"	1.20 h	65

Table 3. (Continued)

results indicated that the catalytic cross-coupling reactions were heterogeneous and occurred over the solid nanostructured catalyst rather than in the solution.

#### Mercury Poisoning Test

The model Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions were conducted in the absence and in the presence of mercury (using an excess amount of  $Hg^0$  (Hg/Pd, 400 : 1)) under the optimum conditions catalyzed by FMMWCNTs@-CPA@SMTU@Pd<sup>II</sup> NPs (**IV**). The reaction progress was monitored by TLC. The yields of the corresponding products (1,1'-biphenyl and methyl cinnamate) were both 98 % after 1 h from the Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions. Time-dependent correlation of the product yields indicated that the improvement of the cross-coupling reactions has not been noticeably affected in the presence of mercury, and the reaction progress was exactly the same either in the absence or presence of the mercury (Fig. 3). This means that no leaching of Pd<sup>II</sup> (into the reaction media) took place during the course of the reactions which confirmed the truly heterogeneous nature of the nanostructured catalyst. As a result, the cross-coupling reactions were carried out on the surface of the nanostructured catalyst.

Recovery and catalyst reuse are important aspects for crosscoupling reactions. For this purpose, the reusability of the heterogeneous nanostructured catalyst in the model Suzuki– Miyaura and Heck–Mizoroki cross-coupling reactions was investigated (Fig. 4). At the end of each cycle, the nanostructured catalyst was separated by a magnet, rinsed with ethyl acetate ( $3 \times 20$  mL), and dried at ambient temperature for 24 h before being re-employed directly in another fresh reaction mixture of both catalytic systems. As can be seen in Fig. 4, a negligible drop in the nanocatalytic activity after following four runs was witnessed. In addition, in the fifth, sixth, and seventh cycles, between 11 and 18% of catalytic activity was lost. It is worth adding that the nanocatalyst was not only very active, but also very stable during the reaction runs.

This ferromagnetic nanostructured catalyst showed a good stability and reusability which was confirmed by FT-IR spectroscopy, XRD analysis, FE-SEM, TGA, VSM, XPS, and ICP-OES. FT-IR spectroscopy of the 7th recovered FMMWCNTs@-CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) from the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions clearly confirmed that there are insignificant changes in the frequencies, intensities, and shapes of absorption bands. The results also displayed that palladium ions were coordinated to the organic moieties on the surface of the FMMWCNTs@CPA@SMTU (**III**) NPs (Fig. 5b, c).<sup>[43]</sup>

XRD patterns of the 7th recovered nanocatalyst exhibited that the nanostructured catalyst underwent no changes during the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reaction processes (Fig. 6b, c). Moreover, the average crystalline size of the fresh and the 7th recovered FMMWCNTs@-CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) from the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions were estimated to be 22,<sup>[43]</sup> 26, and 24 nm, respectively, based on the Debye–Scherrer equation.

FE-SEM images showed the preservation of the uniform rod-like morphology in the recovered nanocatalyst after seven cycles of the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions (Fig. 7a, b).<sup>[43]</sup>

The thermal stability of FMMWCNTs@CPA@SMTU@-Pd<sup>II</sup> NPs (**IV**) after seven runs from the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions was studied by TGA.



**Scheme 3.** Plausible mechanism for the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions in the presence of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**).



Fig. 2. Hot filtration experiment in the model reaction of the (a) Suzuki–Miyaura and (b) Mizoroki–Heck cross-coupling reactions using  $FMMWCNTs@CPA@SMTU@Pd^{II} NPs$  (IV).



**Fig. 3.** Time-dependent correlation of the product yields of the model reactions of Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions catalyzed by FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) (a, c) in the presence and (b, d) in the absence of  $Hg^0$ .



**Fig. 4.** Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions of iodobenzene with phenylboronic acid and methyl acrylate under the optimized reaction conditions catalyzed by the recovered FMMWCNTs@-CPA@SMTU@Pd<sup>II</sup> NPs (**IV**).



**Fig. 5.** FT-IR spectra of (a) FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**), the 7th recovered FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) from the (b) Suzuki–Miyaura and (c) Mizoroki–Heck cross-coupling reactions.

The TGA curves of the 7th recovered nanostructured catalyst from the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions indicated a weight loss (10%) from 165 to 190°C for



**Fig. 6.** XRD patterns of (a) FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**), the 7th recovered FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) from the (b) Suzuki–Miyaura and (c) Mizoroki–Heck cross-coupling reactions.

the former and 160 to 195 °C for the latter, which was attributed to the release of water molecules. The second weight loss (14%) occurred in the temperature range of 195 to 385°C for the former and 202 to 393°C for the latter and was due to the decomposition of organic groups immobilized on the FMWCNTs (I) surface. The amount of organic segment was found to be 0.552 or  $0.565 \text{ mmol g}^{-1}$  (the organic segment of the fresh nanocatalyst was estimated to be  $0.581 \text{ mmol g}^{-1}$ ). Consequently, it means that 2.9 or 1.6% of the total amount of the organic linkers anchored on the FMMWCNTs (I) surface were lost during the seven cycles of the Suzuki-Miyaura and Mizoroki-Heck crosscoupling reactions, respectively. The combustion of MWCNTs happened during the third step of weight losses (13 or 14%) from 390 to 640°C for the former and 397 to 665°C for the latter. Based on the results, the thermal stability of the 7th recovered nanocatalyst is up to 700°C and the organic segments still existed (Fig. 8b, c).<sup>[43]</sup>



Fig. 7. The FE-SEM images of (a) the 7th recovered FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (IV) from the (a) Suzuki–Miyaura and (b) Mizoroki–Heck cross-coupling reactions.



**Fig. 8.** TGA curves of (a) FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**), the 7th recovered FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) from the (b) Suzuki–Miyaura and (c) Mizoroki–Heck cross-coupling reactions.

Fig. 9c, d reveal that the saturation magnetization values  $(M_s)$  of the 7th recovered FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) from the Suzuki–Miyaura and Mizoroki–Heck crosscoupling reactions are 9.5 and 8 emu g<sup>-1</sup>, which are lower than the fresh nanostructured catalyst (26.95 emu g<sup>-1</sup>).<sup>[43]</sup> As can be clearly seen, the magnetization decreased while the ferromagnetic properties of nanostructured catalysts were still present. Other magnetic properties (coercivity  $(H_{ci})$  and remnant magnetization  $(M_r)$ ) of the nanocatalysts are illustrated in Table 4.

The XPS study of the 7th reused nanostructured catalyst from the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions exhibited that the binding energies of the doublet peak at



**Fig. 9.** Magnetization curves of (a) FMMWCNTs (**I**), (b) FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**), the 7th recovered FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) from the (c) Suzuki–Miyaura and (d) Mizoroki–Heck cross-coupling reactions.

339 (assigned to Pd  $3d_{5/2}$ ) and 345 eV (assigned to Pd  $3d_{3/2}$ ) could be attributed to the Pd<sup>II</sup> species (Fig. 10a, b). Furthermore, the peaks related to carbon (C 1s), nitrogen (N 1s), iron (Fe 2p), palladium (Pd 3d), sulfur (S 2p), and oxygen (O 1s) were observed in the XPS elemental survey scans of the 7th recovered nanostructured catalyst from both the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions (Fig. 10c, d).

ICP-OES analysis revealed that the freshly prepared nanocatalyst contains 0.69 mmol of palladium per 1.000 g (7.31 wt-%) of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**),<sup>[43]</sup> while the 7th recovered catalyst from the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions contains 0.618 and 0.64 mmol of Pd per

Table 4.	Magnetic properties of MMWCNTs (I), MMWCNTs@CPA@SMTU@Pd <sup>II</sup> NPs (IV), and the 7th recovered MMWCNTs@CPA	<b>a</b> -
	SMTU@Pd <sup>II</sup> NPs (IV) from the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions	

Sample	Saturation magnetization $(M_s)$ [emu g <sup>-1</sup> ]	Coercivity (H <sub>ci</sub> ) [Oe]	Remnant magnetization $(M_r)$ [emu g <sup>-1</sup> ]
FMMWCNTs (I)	31.98	560	14.04
FMMWCNTs@CPA@SMTU@Pd <sup>II</sup> NPs (IV)	26.95	440	11.60
The 7th recovered catalyst from the Suzuki–Miyaura cross-coupling reaction	9.5	298	6.48
The 7th recovered catalyst from the Mizoroki–Heck cross-coupling reaction	8	276	6.08



Fig. 10. XPS spectra and XPS elemental survey scans of the 7th reused FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (IV) in (a, c) Suzuki–Miyaura and (b, d) Mizoroki–Heck cross-coupling reactions.

1.000 g (6.55 and 6.78 wt-%) of the nanostructured catalyst. The results indicate that 89.5 and 92 % of Pd<sup>II</sup> could be found in the structure of the catalyst after seven runs. According to the results, an insignificant leaching of palladium from the surface of the FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) was detected. The

above analysis revealed that the structure of FMMWCNTs@-CPA@SMTU@Pd<sup>II</sup> NPs (IV) had no changes even after seven following cycles.

With the purpose of examining the efficiency of the procedures presented, we compared the results of the Suzuki-Miyaura and

 Table 5.
 The comparison of the catalytic activity of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (IV) with some literature precedents for Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions

Entry	Catalyst [mol-%]	Reaction conditions	Time [h]	Yield [%]	Reference
1 <sup>A</sup>	$Fe_{3}O_{4}@SiO_{2}@C22-Pd^{II}(0.5)$	Et <sub>3</sub> N, DMF/H <sub>2</sub> O (1 : 1), 75°C	1	92	52
2 <sup>A</sup>	$Fe_3O_4$ ( $a$ EDTA-PdCl <sub>2</sub> (20 mg)	K <sub>2</sub> CO <sub>3</sub> , TBAB, H <sub>2</sub> O, 80°C	3	94	53
3 <sup>A</sup>	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /AEPH <sub>2</sub> -TC-Pd <sup>C</sup> (0.1)	K <sub>2</sub> CO <sub>3</sub> , TBAB, H <sub>2</sub> O, 40°C	10 min	98	54
$4^{\mathrm{A}}$	FMMWCNTs@CPA@SMTU@Pd <sup>II</sup> NPs (IV) (0.55)	Et <sub>3</sub> N, s.f., r.t.	10 min	98	Present study
5 <sup>B</sup>	$Pd-ZnFe_2O_4$ MNPs (4.62)	Et <sub>3</sub> N, DMF, 120°C	3	90	55
6 <sup>B</sup>	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /AEPH <sub>2</sub> -TC-Pd (0.1)	K <sub>2</sub> CO <sub>3</sub> , TBAB, H <sub>2</sub> O, 65°C	20 min	96	54
$7^{\mathrm{B}}$	$Fe_3O_4$ (a) $SiO_2$ -T/Pd <sup>D</sup> (20 mg)	Et <sub>3</sub> N, DMF, 120°C	2	94	56
$8^{\mathrm{B}}$	$MNPs@Cs-Ms-Co^{E}(1.1)$	K <sub>3</sub> PO <sub>4</sub> , PEG, 80°C	1	88	57
9 <sup>B</sup>	FMMWCNTs@CPA@SMTU@Pd <sup>II</sup> NPs (IV) (0.35)	Et <sub>3</sub> N, s.f., r.t.	15 min	98	Present study

<sup>A</sup>Suzuki–Miyaura cross-coupling reaction of iodobenzene with phenylboronic acid.

<sup>B</sup>Mizoroki-Heck cross-coupling reaction of iodobenzene with methyl acrylate.

<sup>C</sup>TC: thiophene-2-carbaldehyde.

<sup>D</sup>Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-T/Pd: Magnetic nanoparticle-supported tetrazole functionalized palladium catalyst.

<sup>E</sup>Cs: chitosan, Ms: methyl salicylate.

Mizoroki–Heck cross-coupling reactions here with previously reported results (Table 5). As can be seen, the present nanostructured catalyst is superior in terms of price, non-toxicity, and stability and also displays good to excellent yields of the coupled products with shorter reaction times than the other catalysts, while each of these catalytic systems has their own advantages.

### Conclusion

FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) has been found to show remarkable catalytic activity in the Suzuki–Miyaura and Heck–Mizoroki cross-coupling reactions under solvent-free conditions at room temperature. Factors such as simple separation of the nanocatalyst, easy recovery of final products, and milder reaction conditions than current catalytic systems illustrate that this procedure is proficient, economic, and environment friendly. In addition, it is found that the ferromagnetic nanostructured catalyst with uniform rod-like morphology and a particle size of  $\sim$ 20–30 nm does not change significantly even after seven recovery cycles.

### Experimental

### Materials and Instruments

All chemical reagents and solvents were purchased from Merck and Sigma-Aldrich chemical companies and were used as received without further purification. The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of the products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an Avatar 370 FT-IR Therma Nicolet spectrometer. Elemental analyses were performed using a Thermo Finnegan Flash EA 1112 Series instrument. The NMR spectra were obtained using Bruker Avance 300 and 400 MHz instruments in CDCl<sub>3</sub>. Mass spectra were recorded with a CH7A Varianmat Bremem instrument at 70 eV electron impact ionization. The crystal structure of the catalyst was analyzed by XRD using a Model Explorer Co.: GNR (Italy) diffractometer Dectvis operated at 40 kV and 30 mA utilising Cu K $\alpha$  radiation ( $\lambda$  0.154 A°). TEM was performed with a Leo 912 AB microscope (Zeiss, Germany) with an accelerating voltage of 120 kV. FE-SEM images, EDS, and EDS maps were recorded using a TESCAN, Model: MIRA3 scanning electron microscope operating at an acceleration voltage of 30.0 kV and a resolution of

~200 and 500 nm (manufactured in the Czech Republic). TGA analysis was carried out on a Shimadzu Thermogravimetric Analyzer (TG-50) in the temperature range of 25–920°C at a heating rate of 10°C min<sup>-1</sup> under air atmosphere. The magnetic properties of the catalyst were measured using a vibrating sample magnetometer (Magnetic Danesh Pajoh Inst.). XPS was performed using a Thermo Scientific, ESCALAB 250 Xi Mg X-ray resource and Bestec Al X-ray K $\alpha$ : 1486.6 (manufactured in Germany). UV-Vis DRS was measured using an Ava Spec 2048 TECH spectrometer. ICP-OES was carried out with a Varian VISTA-PRO, CCD (Australia). All yields refer to isolated products after purification by TLC and/or column chromatography.

## Preparation of FMMWCNTs (I)

The raw MWCNTs (diameter 10–20 nm) (0.3 g) were dispersed in distilled water (50 mL) for 30 min under ultrasonication. Afterwards, a solution of FeSO<sub>4</sub>·7H<sub>2</sub>O (50 mL, 0.0179 mol L<sup>-1</sup>) and H<sub>2</sub>SO<sub>4</sub> (2 mL, 18 M) was added to the MWCNT suspension with ultrasonication for 30 min. NaBH<sub>4</sub> (100 mL, 0.135 mol L<sup>-1</sup>) was gradually added over 30 min to the transferred suspension in an open beaker under vigorous stirring. After cooling the reaction mixture to ambient temperature, the solid product was collected using filtration followed by washing with anhydrous ethanol and water to remove residual acid and dissociative Fe<sup>II</sup>. The prepared Fe/MWCNTs NPs were soaked in anhydrous ethanol for 60 min. Finally, the FMMWCNTs (I) were obtained after the separation of the solid residue using an external magnetic field and drying at 80°C overnight.<sup>[43]</sup>

### Preparation of FMMWCNTs@CPA (II)

FMMWCNTs (I) (1.5 g) in dry toluene (40 mL) was sonicated for 1 h. Next, CPA (5 mmol, 0.72 g) was added to the obtained suspension. The reaction mixture was refluxed and stirred for 20 h. The resulting FMMWCNTs@CPA (II) was separated by a magnet and rinsed in turn by diethyl ether ( $3 \times 15$  mL), CH<sub>2</sub>Cl<sub>2</sub> ( $3 \times 15$  mL), and dried under vacuum at ambient temperature. Elemental analysis and TGA revealed that the loading amount of Cl was 0.35 mmol per gram of catalyst.<sup>[43]</sup>

#### Preparation of FMMWCNTs@CPA@SMTU (III)

The obtained FMMWCNTs@CPA (II) (1g) was sonicated in ethanol (50 mL) for 30 min. Next, S-methylisothiourea

hemisulfate salt (2.5 mmol, 0.347 g) and potassium carbonate (2.5 mmol, 0.345 g) were added to the reaction mixture and refluxed for 24 h. Afterwards, the resulting FMMWCNTs@-CPA@SMTU NPs (III) were collected by an external magnet and washed with ethanol ( $4 \times 20$  mL) and dried at room temperature for 24 h. Elemental analysis and TGA revealed that the loading amount of S was 0.46 mmol per gram of catalyst.<sup>[43]</sup>

# Preparation of FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**)

FMMWCNTs@CPA@SMTU (**III**) (1 g) was added to a solution of palladium acetate (0.26 mmol, 0.06 g) in dry acetone (40 mL). The reaction mixture was stirred at ambient temperature overnight. The resulting product was separated via a magnet, washed three times with acetone (15 mL), and dried under vacuum to obtain FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**). ICP-OES analysis showed that the loading amount of Pd was 0.69 mmol per gram of catalyst.<sup>[43]</sup>

# *Typical Procedure for the Suzuki–Miyaura Cross-Coupling Reaction*

Triethylamine (NEt<sub>3</sub>) (2 mmol, 0.202 g) was added to a mixture of iodobenzene (1.0 mmol, 0.203 g) and phenylboronic acid (1.2 mmol, 0.146 g) in solvent-free conditions at ambient temperature. FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) (0.55 mol-%, 0.025 g) were then added to the resulting mixture under stirring. After the completion of the reaction (10 min) which was monitored by TLC, the nanocatalyst was separated by a magnetic field, washed with ethyl acetate, and dried at room temperature for 24 h to be used in the next run. The reaction mixture was then extracted with ethyl acetate (5 × 5 mL) and the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent, the crude product was purified by TLC (or column chromatography using *n*-hexane/ethyl acetate (50:1)) using *n*-hexane/ethyl acetate (8:2) to produce the pure 1,1'-biphenyl (0.144 g, 98 % yield).

# *Typical Procedure for the Mizoroki–Heck Cross-Coupling Reaction*

FMMWCNTs@CPA@SMTU@Pd<sup>II</sup> NPs (**IV**) (0.35 mol-%, 0.015 g) were added to a mixture of triethylamine (NEt<sub>3</sub>) (2 mmol, 0.202 g), methyl acrylate (1.2 mmol, 0.108 mL), and iodobenzene (1.0 mmol, 0.203 g) in solvent-free conditions at room temperature. After the completion of the reaction (15 min) which was monitored by TLC, the nanocatalyst was separated by a magnetic field, washed with ethyl acetate, and dried at room temperature for 24 h to be used in the next run. The reaction mixture was then extracted with ethyl acetate ( $5 \times 5$  mL) and the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent, the crude product was purified by TLC (or column chromatography using *n*-hexane/ethyl acetate (50:1)) using *n*-hexane/ethyl acetate (8:2) to produce the pure methyl cinnamate (0.153 g, 98 % yield).

1,1'-Biphenyl (1a) (0.279 g, 98 %): white solid; mp 70–71°C (Lit.<sup>[58,59]</sup> 70–72°C).  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 7.54 (d, *J* 8, 4H), 7.39 (t, *J* 8, 4H), 7.31–7.27 (m, 2H).  $\delta_{\rm C}$  (125 MHz, CDCl<sub>3</sub>) 141.2, 128.7, 127.2, 126.1. *m/z* 154 (M<sup>+</sup>, 80 %), 153 ([M – H]<sup>+</sup>, 102), 115 ([M – C<sub>3</sub>H<sub>3</sub>]<sup>+</sup>, 32), 102 ([M – C<sub>4</sub>H<sub>4</sub>]<sup>+</sup>, 28), 76 ([M – C<sub>6</sub>H<sub>6</sub>]<sup>+</sup>, 78).

4-Methoxy-1,1'-biphenyl (1c) (0.265 g, 90 %): white solid; mp 88–90°C (Lit.<sup>[59,60,61]</sup> 87–90°C).  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 7.45 (t, J 8.4, 4H), 7.34 (t, J 7.6, 2H), 7.21 (t, J 6.8, 1H), 6.89 (d, J 8.8, 2H), 3.75 (s, 3H).  $\delta_{\rm C}$  (125 MHz, CDCl<sub>3</sub>) 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 114.2, 55.3. m/z 184 (M<sup>+</sup>, 80%), 183 ([M - H]<sup>+</sup>, 102), 168 ([M - CH<sub>3</sub>]<sup>+</sup>, 84), 152 ([M - CH<sub>4</sub>O]<sup>+</sup>, 42), 140 ([M - C<sub>3</sub>H<sub>8</sub>]<sup>+</sup>, 82), 115 ([M - C<sub>4</sub>H<sub>5</sub>O]<sup>+</sup>, 80), 92 ([M - C<sub>6</sub>H<sub>5</sub>O]<sup>+</sup>, 44).

(*E*)-Butyl cinnamate (**1f**) (0.229 g, 95%): white solid; mp 141–142°C (Lit.<sup>[59,62,63]</sup> 140–142°C).  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 7.60 (d, *J* 16.4, 1H), 7.45–7.43 (m, 1H), 7.31–7.28 (m, 1H), 6.38 (d, *J* 16, 1H), 6.34 (d, *J* 16, 1H), 4.13 (t, *J* 6.8, 2H), 1.62–1.59 (m, 2H), 1.36–1.34 (m, 2H), 0.88 (t, *J* 7.6, 3H).  $\delta_{\rm C}$  (100 MHz, CDCl<sub>3</sub>) 166.8, 144.4, 134.4, 130.1, 128.8, 128.0, 118.2, 64.3, 30.8, 19.2, 13.7.

(*E*)-Methyl 3-(4-nitrophenyl) acrylate (**2d**) (0.277 g, 95%): white solid; mp 161–162°C (Lit.<sup>[59,64,65]</sup> 160–162°C).  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 8.25 (d, *J* 8.8, 2H), 7.72 (d, *J* 16.1, 1H), 7.67 (d, *J* 8.7, 2H), 6.56 (d, *J* 16.1, 1H), 3.84 (s, 3H).  $\delta_{\rm C}$  (75 MHz, CDCl<sub>3</sub>) 166.6, 148.7, 142.1, 140.7, 128.8, 124.4, 122.3, 52.3. *m/z* 207 (M<sup>+</sup>, 62%), 206 ([M – H]<sup>+</sup>, 92), 189 ([M – C<sub>2</sub>H<sub>6</sub>O]<sup>+</sup>, 38), 175 ([M – CH<sub>4</sub>O]<sup>+</sup>, 102), 148 ([M – C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>]<sup>+</sup>, 52), 129 ([M – C<sub>3</sub>H<sub>10</sub>O<sub>4</sub>]<sup>+</sup>, 80), 118 ([M – C<sub>4</sub>H<sub>9</sub>O<sub>2</sub>]<sup>+</sup>, 78), 102 ([M – C<sub>6</sub>H<sub>1</sub>O<sub>2</sub>]<sup>+</sup>, 88).

(*E*)-Butyl 3-(4-nitrophenyl)acrylate (**2f**) (0.216 g, 95%): white solid; mp 68–69°C (Lit.<sup>[59,63,66,67]</sup> 67–69°C).  $\delta_{\rm H}$ (400 MHz, CDCl<sub>3</sub>) 8.20 (d, *J* 8, 2H), 7.66 (d, *J* 16.1, 1H), 7.44 (d, *J* 8.7, 2H), 6.53 (d, *J* 16, 1H), 4.20 (t, *J* 6.7, 2H), 1.69–1.62 (m, 2H), 1.44–1.35 (m, 2H), 0.92 (t, *J* 7.2, 3H).  $\delta_{\rm C}$  (100 MHz, CDCl<sub>3</sub>) 166.0, 148.3, 141.5, 140.5, 130.1, 128.6, 124.0, 122.5, 64.7, 30.6, 19.1, 13.6.

(*E*)-Methyl 3-(4-cyanophenyl)acrylate (**3d**) (0.243 g, 95 %): white solid; mp 124–126°C (Lit.<sup>[62]</sup> 122–126°C).  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>) 7.69–7.61 (m, 4H), 7.58 (d, *J* 16.1, 1H), 6.51 (d, *J* 16, 1H), 3.82 (s, 3H).  $\delta_{\rm C}$  (75 MHz, CDCl<sub>3</sub>) 166.6, 142.5, 138.8, 132.7, 128.5, 121.5, 118.4, 113.6, 52.0. *m/z* 187 (M<sup>+</sup>, 55 %), 186 ([M – H]<sup>+</sup>, 87), 155 ([M – CH<sub>6</sub>N]<sup>+</sup>, 103), 127 ([M – C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>]<sup>+</sup>, 90), 101 ([M – C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>]<sup>+</sup>, 78).

(*E*)-Methyl 3-(*p*-tolyl)acrylate (**4b**) (0.238 g, 85%): yellow solid; mp 56–57°C (Lit.<sup>[59,68,69]</sup> 55–57°C).  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 7.69 (d, *J* 16, 1H), 7.43 (d, *J* 8, 2H), 7.20 (d, *J* 8 2H), 6.41 (d, *J* 16, 1H), 3.81(s, 3H), 2.38 (s, 3H).  $\delta_{\rm C}$  (100 MHz, CDCl<sub>3</sub>) 167.6, 144.8, 140.7, 131.6, 129.6, 128.0, 116.7, 51.6, 21.4. *m/z* 177 (M<sup>+</sup>, 10%), 175 ([M – 2H]<sup>+</sup>, 94), 160 ([M – CH<sub>4</sub>]<sup>+</sup>, 40), 144 ([M – CH<sub>4</sub>O]<sup>+</sup>, 100), 130 ([M – C<sub>3</sub>H<sub>10</sub>]<sup>+</sup>, 38), 115 ([M – C<sub>2</sub>H<sub>5</sub>O]<sup>+</sup>, 90), 102 ([M – C<sub>3</sub>H<sub>6</sub>O<sub>2</sub>]<sup>+</sup>, 52), 91 ([M – C<sub>4</sub>H<sub>5</sub>O<sub>2</sub>]<sup>+</sup>, 82).

(*E*)-Butyl 3-(*p*-tolyl)acrylate (**4d**) (0.244 g, 85%): oil; (Lit. <sup>[59,63,67,69,70]</sup>).  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 7.52 (d, *J* 16.1, 1H), 7.32–7.28 (m, 2H), 7.07–7.04 (m, 2H), 6.30 (d, *J* 16, 1H), 4.09 (t, *J* 5, 2H), 2.24 (s, 3H), 1.32–1.40 (m, 2H), 1.23–1.31 (m, 2H), 0.85 (t, *J* 7.4, 3H).  $\delta_{\rm C}$  (100 MHz, CDCl<sub>3</sub>) 167.2, 144.5, 140.5, 131.7, 129.5, 128.0, 117.1, 64.2, 30.8, 21.4, 19.2, 13.7.

(*E*)-Methyl 3-(4-methoxyphenyl)acrylate (**5b**) (0.261 g, 80%): yellow solid; mp 89–91°C (Lit.<sup>[62,69]</sup> 88–91°C).  $\delta_{\rm H}$ (400 MHz, CDCl<sub>3</sub>) 7.67 (d, *J* 16, 1H), 7.50–7.47 (m, 2H), 6.94–6.90 (m, 2H), 6.33 (d, *J* 16, 1H), 3.85 (s, 3H), 3.81 (s, 3H).  $\delta_{\rm C}$  (100 MHz, CDCl<sub>3</sub>) 167.8, 161.4, 144.6, 129.8, 127.2, 115.3, 114.4, 55.4, 51.6. *m/z* 192 (M<sup>+</sup>, 95), 191 ([M – H]<sup>+</sup>, 100), 160 ([M – CH<sub>4</sub>O]<sup>+</sup>, 100), 133 ([M – C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>]<sup>+</sup>, 98), 118 ([M – C<sub>3</sub>H<sub>6</sub>O<sub>2</sub>]<sup>+</sup>, 37), 89 ([M – C<sub>7</sub>H<sub>3</sub>O]<sup>+</sup>, 49).

(*E*)-Butyl 3-(4-methoxyphenyl)acrylate (**5d**) (0.176 g, 75%): white solid; mp 90–92°C (Lit.<sup>[59,63,67,69,70]</sup> 90–92°C).  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 7.67 (d, *J* 16, 1H), 7.39 (d, *J* 4.2, 2H), 6.81 (d, *J* 4.8, 2H), 6.24 (d, *J* 16, 1H), 4.13 (t, *J* 7, 2H), 3.72 (s, 3H), 1.60–1.62 (m, 2H), 1.35–1.40 (m, 2H), 0.91 (t, *J* 7, 3H).  $\delta_{\rm C}$  (100 MHz, CDCl<sub>3</sub>) 167.8, 161.4, 144.6, 129.8, 127.2, 115.3,

(*E*)-Methyl cinnamate (**6d**) (0.254 g, 90 %): white solid; mp 36–37°C (Lit.<sup>[59,64,69]</sup> 35–37°C).  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 7.60 (d, *J* 16, 1H), 7.43–7.41 (m, 2H), 7.29–7.27 (m, 3H), 6.34 (d, *J* 16, 1H), 3.70 (s, 3H).  $\delta_{\rm C}$  (100 MHz, CDCl<sub>3</sub>) 166.9, 144.3, 133.9, 129.8, 128.4, 127.6, 117.3, 51.2. *m/z* 162 (M<sup>+</sup>, 62), 161 ([M–H]<sup>+</sup>, 89), 131 ([M–CH<sub>3</sub>O]<sup>+</sup>, 101), 117 ([M–C<sub>3</sub>H<sub>9</sub>]<sup>+</sup>, 34), 103 ([M–C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>]<sup>+</sup>, 92), 91 ([M–C<sub>3</sub>H<sub>3</sub>O<sub>2</sub>]<sup>+</sup>, 58).

#### **Supplementary Material**

Physicochemical characterization data of products (including colour, melting point, mass, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra) and the characterization data of the nanocatalyst are available on the Journal's website.

#### **Conflicts of Interest**

The authors declare no conflicts of interest.

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